

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JANUARY, 1936.

### General, Physical, and Inorganic Chemistry.

Intensity of the hydrogen  $\alpha$ - and  $\beta$ -lines as determined by the frequency of the electrical field in electrodeless discharge. O. STUHLMAN, jun., and M. S. McCAY (Physical Rev., 1934, [ii], 45, 750—751; cf. A., 1935, 799). L. S. T.

Striation of the positive column in the glow discharge of hydrogen. H. H. PAUL (Z. Physik, 1935, 97, 330—354).—Probe measurements in the positive column suggest that striations are due to an electric double layer formed by positive and negative ions; this explains the increasing difficulty of obtaining striations with increasing purity of H<sub>2</sub>. A. B. D. C.

Reproducibility of the relative energy distribution of the continuous H<sub>2</sub> spectrum emitted by a hydrogen discharge tube. V. E. GONSALVES (Physica, 1935, 2, 1003—1015).—The H discharge tube may be used as an ultra-violet standard. The intensity of the total emission between 1850 and 3200 Å. is const. between 3.0 and 3.4 mm. if the current is const. The relative energy distribution is independent of the current between 150 and 250 m. amp. if the pressure is const., and does not change in the region 1—3.5 mm. for currents between 150 and 250 m. amp. T. G. P.

Nuclear moments of lithium, potassium, and sodium. M. FOX and I. I. RABl (Physical Rev., 1935, [ii], 48, 746—751).—The at. beam method of "zero moments" gave, for the hyperfine structure separations of the normal <sup>2</sup>S<sub>1/2</sub> state of Li, K, and Na, the vals.  $0.0268 \pm 0.0003$ ,  $0.0154 \pm 0.0002$ , and  $0.0596 \pm 0.0006$  cm.<sup>-1</sup>, respectively. The calc. nuclear magnetic moments are Li<sup>7</sup> 3.20, K<sup>39</sup> 0.397, and Na<sup>23</sup> 2.08 nuclear magnetons. The nuclear spin was 3/2 for Li; a higher resolution arrangement gave an upper limit of 5/2 for the spin of the K<sup>41</sup> nucleus, and 2/2, or greater, for Li<sup>6</sup>, the magnetic moment of the nucleus being of the order of that of the deuteron. N. M. B.

Vacuum arc spectra of rubidium and lithium. S. DATTA and P. C. BOSE (Z. Physik, 1935, 97, 321—329). A. B. D. C.

Rotation structure of the b'x band system of the nitrogen molecule in the Schumann region. V. M. TSCHULANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 155—156; cf. A., 1934, 575, 935).—A preliminary report of new data. J. W. S.

Ultra-violet absorption spectrum of oxygen. L. HERMAN and (MME.) R. HERMAN (Compt. rend., 1935, 201, 714—716; cf. A., 1934, 828).—Data for

the low- and high-pressure absorption bands of O<sub>2</sub> at  $\lambda\lambda$  2400—2800 Å. are compared and discussed.

H. J. E.

Far ultra-violet absorption spectrum of oxygen. W. C. PRICE and G. COLLINS (Physical Rev., 1935, [ii], 48, 714—719).—The spectrum was photographed under high dispersion in the region 1300—650 Å., and frequencies of the vibrational progressions are tabulated. The bands are explained as going to the various excited states of O<sub>2</sub><sup>+</sup> as limits. Results support Mulliken's assignment of the visible O<sub>2</sub><sup>+</sup> bands to the transition  $4\Sigma_g^- \rightarrow 4\Pi_u$ . The distances of these states of O<sub>2</sub><sup>+</sup> from the ground state of O<sub>2</sub> are 18.2 and 16.1 volts. N. M. B.

Influence of an electric field on the absorption spectrum of sodium. N. T. ZE and W. W. PO (Compt. rend., 1935, 201, 716—718).—The no. of members of the principal series observed decreases with increasing field strength. Certain of the forbidden S—D and S—S transitions were observed.

H. J. E.

Nuclear moment of aluminium. F. W. BROWN and R. K. COOK (Physical Rev., 1934, [ii], 45, 731).—A tentative val. of 4.8 for the  $g(I)$  factor has been calc. L. S. T.

New absorption spectrum of diatomic sulphur vapour in the Schumann region. K. WIELAND, W. MEHLI, and E. MIESCHER (Helv. phys. Acta, 1934, 7, 843—849; Chem. Zentr., 1935, i, 1978).—Data are given for two band systems between 1600 and 1870 Å., both originating from the S<sub>2</sub> mol. The heat of dissociation of S<sub>2</sub> in the <sup>3</sup> $\Sigma$  state is 1.68 volts. J. S. A.

Deep terms in the isoelectronic sequence VI to Cu VII. P. G. KRÜGER and (MISS) H. T. GILROY (Physical Rev., 1935, [ii], 48, 720—721; cf. A., 1932, 208).—The  $3d^3\ ^6S_{5/2}$  and  $3d^4 4p\ ^6P^0$  terms of this sequence have been identified by the use of const. second differences in the radiated frequencies from terms involving an electron transition to the ground state. N. M. B.

New terms in the spectrum of Fe II. J. C. DOBBIE (Proc. Roy. Soc., 1935, A, 151, 703—726).—An analysis of the spectrum of Fe II between 2327 and 9000 Å. has resulted in the discovery of numerous new terms, many of which belong to the doublet system; >900 lines, not previously classified, have been accounted for by the new terms. A fairly close approximation to Russell-Saunders coupling is found in the spectrum. The separations between the terms of higher and lower multiplicity derived

from the same parent terms are nearly all large compared with the intervals between the levels of these terms. L. L. B.

**Absolute intensity of the zinc resonance line 2139 Å. and life of  $2^1P_1$  state of zinc.** W. BILLER (Helv. phys. Acta, 1934, 7, 841—842; Chem. Zentr., 1935, i, 1979—1980).—The abs. intensity is calc. as  $f(2139)=1.17$ , and the life of the  $2^1P_1$  state as  $1.78 \times 10^{-9}$  sec. J. S. A.

**Ionisation potentials of Ge V, As VI, Se VII, Sb VI, and Te VII.** P. G. KRUGER and W. E. SHOUPP (Physical Rev., 1934, [ii], 45, 759).—Radiations represented by  $d^{10}1S_0$ — $3P_1^0$ ,  $1P_1^0$ ,  $3D_1^0$  have been found in the above. Term vals. of the  $d^{10}1S_0$  terms are given and ionisation potentials are 93, 127, 166, 107, and 137 volts, respectively. L. S. T.

**Influence of pressure on the discharge radiation of cadmium vapour.** V. A. FABRIKANT and A. S. KANEL (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 257—258).—Preliminary notice. W. R. A.

**Hyperfine structure and the gross structure analysis of the spectrum of doubly-ionised antimony.** J. S. BADAMI (Nature, 1935, 136, 836). L. S. T.

**Ultra-violet fluorescence spectra of iodine vapour.** F. DUSCHINSKY and P. PRINGSHEIM (Physica, 1935, 2, 923—932).—The fluorescence bands at 3400 Å. (Oldenberg, A., 1924, ii, 579) occurring in I vapour in presence of  $N_2$  have been studied. I in presence of He gives a different spectrum in the same region, which is also obtained with  $N_2$  at higher temp. The bands may also be obtained as a sensitised fluorescence in presence of Hg, accompanied by HgI bands. Modification of the usual energy level system of I is necessary if the bands are to be explained by transference. The 4400 Å. band of HgI has been investigated. T. G. P.

**Hyperfine structure and nuclear magnetic moment of Cs I.** L. P. GRANATH and R. K. STRANATHAN (Physical Rev., 1935, [ii], 48, 725—731).—The hyperfine structure of the lines  $\lambda\lambda$  8761, 4593, 4555, 3889, and 3877 of the arc spectrum of Cs was observed. The interval factors for the  $6^2S_{1/2}$ ,  $6^2P_{1/2}$ ,  $7^2P_{1/2}$ , and  $8^2P_{1/2}$  states were 0.0767, 0.00925, 0.00329, and 0.0017  $\text{cm}^{-1}$ , respectively. Assuming a nuclear spin of 7/2, the calc. nuclear magnetic moments are 2.66, 2.38, 2.62, and 3.01 nuclear magnetons for the respective states. N. M. B.

**Additional terms in the spectrum of La III.** R. C. GIBBS and G. K. SCHOEPFLE (Physical Rev., 1934, [ii], 45, 747).—The  $ns^2S$  and  $nd^2D$  series have been extended, one more pair of  $2P$  terms has been located, and certain of the  $2F$  and  $2G$  terms have been determined. L. S. T.

**Temperature classification of samarium lines.** A. S. KING (Astrophys. J., 1935, 82, 140—191).—A temp. classification for 4477 Sm lines between 2900 and 8700 Å. is given. L. S. T.

**Luminosity in the mercury discharge.** R. D. RUSK and A. L. PECKHAM (Physical Rev., 1934, [ii], 45, 751).—Recombination of slow electrons

and positive ions is a negligible factor in producing luminosity. L. S. T.

**Intensification by drying of Hg lines in a mercury-hydrogen discharge.** H. BECK (Z. Physik, 1935, 97, 382—389).—Protons are most likely the source of increased intensity of the Hg lines on drying of the Hg- $H_2$  mixture. A. B. D. C.

**Determination of the absorption coefficient,  $K(\lambda_0)$ , of the mercury resonance line, 2536.5 Å., by the resonance scattering method.** G. P. BALIN (Physikal. Z. Sovietunion, 1935, 8, 93—99).—The theory of the method of Goos and Meyer (A., 1926, 334) for determining absorption coeffs. by resonance scattering is discussed and extended. If the density of the saturated vapour used is not too great, the vals. of  $K(\lambda_0)$  are in good agreement with those obtained by other methods. A. J. M.

**Paschen-Back effect with Bellevue electromagnet supplied with supplementary coils.** P. JACQUINOT and T. BELLING (Compt. rend., 1935, 201, 778—779).—The effect has been studied with the Hg lines 5789—5790 and 5770 Å., and a field of 65,800 gauss. Displacements and doubling agree with theory. R. S. B.

**Line absorption of thallium doublet = 3519.29 Å. during thermal excitation of the metastable  $6^2P_{3/2}$  level.** F. MÜLLER (Helv. phys. Acta, 1934, 7, 813—840; Chem. Zentr., 1935, i, 1979).—Determination of the line absorption as a function of the TI pressure confirms the application of the Maxwell-Boltzmann partition law to metastable states. J. S. A.

**Term values in the spectrum of lead v.** G. K. SCHOEPFLE (Physical Rev., 1934, [ii], 45, 747).—65 terms, involving approx. 200 lines, have now been established. L. S. T.

**Absorption spectrum of lead vapour in the Schumann region.** N. V. KREMENEVSKI (Compt. rend. Acad. Sci., U.R.S.S., 1935, 3, 251—252).—The absorption spectrum of Pb vapour was examined between 2200 and 1350 Å. and between 420° and 1070°; the results are discussed. W. R. A.

**Determination of the temperatures of gases from the intensities of band spectra.** O. OLDENBERG (Physical Rev., 1934, [ii], 45, 738; cf. A., 1934, 1153).—Processes leading to normal and to abnormal rotation, i.e., rotation > the thermal val., are discussed. L. S. T.

**Intensity measurements in the ultra-violet with the aid of the photon counter.** I. L. ROICH (Physikal. Z. Sovietunion, 1935, 8, 223—226).—The Planck-Wien formula for black-body radiation has been confirmed in the ultra-violet using Schein's photon counter. T. G. P.

**Mechanism of high-frequency discharges.** H. BECK (Z. Physik, 1935, 97, 355—375).—Electrical and optical observations on high-frequency discharges have shown that spectral intensity, no. of excited levels, and electron temp. are very similar to those in the positive column of d.-c. discharges. A. B. D. C.

**Cathode head-like discharge.** H. BECK (Z. Physik, 1935, 97, 376—381).—This discharge, in



appearance similar to the symmetrical striations of anode columns, has been observed in Hg, Zn, and Cd; current-voltage characteristics are given together with conditions of its formation.

A. B. D. C.

**Nature of luminous streamers from the condensed spark *in vacuo*.** C. F. BAREFORD (Phil. Mag., 1935, [vii], 20, 825—834).—In the condensed spark in high vac. sharply defined luminous streamers, occurring in both the positive and negative phases of the oscillating current of the spark, pass through a hole bored in one of the electrodes and extend into the exhausted space beyond it. The spectra of the streamers show lines due to neutral and ionised atoms of the metal of the electrode opposite the hole. There is some evidence that aggregates rather than single atoms are concerned in the formation of the streamers.

N. M. B.

**Spectroscopic observation of recurrent phenomena in discharge tubes.** R. H. SLOANE and C. M. MINNIS (Proc. Physical Soc., 1935, 47, 1019—1028).—Irregular moving striations are photographed synchronously by forming an image of the positive column of a discharge tube along a spectrograph slit which is covered and uncovered by a mechanical shutter synchronised with the striations by a photo-electric device. The photographs for pure A show no appreciable recombination in the dark phase, and those for A-Hg mixtures show excitation of only the Hg lines in the dark phase; an explanation is proposed.

N. M. B.

**Pre-discharge currents and striking conditions in gas-filled hot-cathode tubes.** I. RUNGE (Z. tech. Phys., 1935, 16, 38—42; Chem. Zentr., 1935, i, 2140).

J. S. A.

**Air afterglow.** F. H. NEWMAN (Phil. Mag., 1935, [vii], 20, 777—781).—A detailed study of the spectra of air and O<sub>2</sub> afterglows shows that poisoning of the discharge-tube walls is necessary for glow formation; the effect persists after the discharge has ceased, but is eliminated by heating the tube. The bands in air are superposed on a continuous spectrum; band positions are given. Traces of H<sub>2</sub>O, COMe<sub>3</sub>, and C<sub>6</sub>H<sub>6</sub> vapour quenched the afterglows, but CS<sub>2</sub> gave the characteristic blue flame. The afterglows are attributed to the oxidation of NO by O<sub>3</sub>, both these gases being formed in the discharge tube.

N. M. B.

**Pressure effects of foreign gases on spectral lines.** H. MARGENAU (Physical Rev., 1935, [ii], 48, 755—765; cf. A., 1933, 201).—Mathematical. The effect of pressure on the shape and position of a spectral line is examined.

N. M. B.

**Spectro-photometric comparison of the zodiacal light and the light of the night sky.** J. CABANNES and J. DUFAY (Compt. rend., 1935, 201, 696—699).—The spectrum of the zodiacal light does not contain the line  $\lambda$  5577 or the bands  $\lambda\lambda$  4838, 4825 Å.

H. J. E.

**Fine structure of the *K* edges of magnesium and aluminium.** J. VELDKAMP (Physica, 1935, 2, 933—934).—Sandstrom's explanation (Diss., Upsala,

1935) of the fine structure of the *K* edges of Mg and Al is incorrect. Another interpretation is given.

T. G. P.

**Atomic scattering factors of nickel, copper, and zinc.** G. W. BRINDLEY and F. W. SPIERS (Phil. Mag., 1935, [vii], 20, 865—881; cf. A., 1935, 16).—At. scattering factors of Ni, Cu, and Zn for Cu *K* $\alpha$  radiation have been measured. Abs. vals. of the reflected intensities were obtained by comparison with reflexions from KCl. The results are compared with those of previous workers.

T. G. P.

**Width of *K* $\alpha$  lines of gaseous krypton and of elements in chemical compounds.** E. WILHELMY (Z. Physik, 1935, 97, 312—320).—Results are given for Kr, Rb in RbCl, Br in KBr, and Cu in CuO and CuF<sub>2</sub>; that for Kr shows state of aggregation to have no effect, whilst the others show effects due to chemical combination.

A. B. D. C.

***K*-Series spectrum of thorium.** J. C. HUDSON, H. G. VOGT, and A. H. ARMSTRONG (Physical Rev., 1934, [ii], 45, 755).

L. S. T.

***L*-Emission spectrum of argon.** M. BAČKOVSKY and V. DOLEJSEK (Nature, 1935, 136, 643).—Vals. for the *L*-series of A, measured directly by means of the ionic tube, agree with those calc. by interpolation of the data of Siegbahn and Magnusson (A., 1935, 909).

L. S. T.

**Relative energy of the *L* $\alpha$  satellites excited by cathode rays in the atomic number range 47—52.** F. R. HIRSH, jun. (Physical Rev., 1935, [ii], 48, 722—724; cf. A., 1934, 233).—Measurement of the integrated relative energy of the *L* $\alpha$  satellites with respect to their parent *L* $\alpha_1$  line have been extended photographically from Ag (47) to Te (52). In this range the satellites decrease rapidly in relative energy with increasing at. no., in agreement with the Coster-Kronig theory.

N. M. B.

***L* $\alpha$  [X-ray] emission of mercury, platinum, and tungsten.** (MLLE.) Y. CAUCHOIS (Compt. rend., 1935, 201, 721—722; cf. A., 1935, 800).—Data for the satellites to the *L* $\alpha$  radiation of Hg, Pt, and W are recorded.

H. J. E.

**Occurrence of the reversed absorption edges of the long wave-lengths of X-rays.** M. BAČKOVSKY and V. DOLEJSEK (Nature, 1935, 136, 836—837).

L. S. T.

**Enhancement of X-ray satellites by the Auger effect.** F. R. HIRSH, jun. (Physical Rev., 1935, [ii], 48, 776—777).

N. M. B.

**Soft X-ray spectra of aluminium and magnesium: wave-length measurements.** T. H. OSGOOD (Physical Rev., 1934, [ii], 45, 753).—Vals. are given for the  $\lambda$  of the sharp edge of the wide line in the *L* spectrum of Mg and Al.

L. S. T.

**Photo-electric emission and surface chemistry.** C. OUELLET (Natural. Canad., 1935, 62, 271—281; cf. A., 1935, 697).—A general survey of the relation of photo-electric emission to surface phenomena, and the use of the photo-electric counter.

N. M. B.

**Photo-electric properties of pure and gas-contaminated magnesium.** R. J. CASHMAN and W. S. HUXFORD (Physical Rev., 1935, [ii], 48, 734—741;

cf. A., 1933, 662).—The threshold characteristic of all gas-free surfaces obtained by successive distillations is at  $3430 \pm 20$  Å. The val. at 5100 Å., previously ascribed to pure Mg, is attributed to Mg contaminated with  $H_2$ . A trace of  $O_2$  causes a max. excursion of the long-wave limit to about 5700 Å. The formation of polar mols. on the Mg surface will account for the threshold shift observed when  $H_2$  or  $O_2$  is present. A method of purifying Mg by multiple distillations is described. N. M. B.

**Positive and negative thermionic emission from molybdenum.** H. B. WAHLIN and J. A. REYNOLDS (Physical Rev., 1935, [ii], 48, 751–754).—In view of discordant results reported, an investigation under rigorous outgassing gave the val. 4.17 volts for the electron work function and 8.35 volts for that of the positive ion. The positive ion emission agrees with the Saha theory of ion formation (cf. Moon, A., 1932, 1185). N. M. B.

**Potential drop and ionisation at mercury arc cathode.** E. S. LAMAR and K. T. COMPTON (Physical Rev., 1935, [ii], 48, 777; cf. A., 1931, 780).—A correction. N. M. B.

**Electron temperatures in the positive column in mixtures of neon and argon or mercury.** H. B. DORGELO, H. ALTING, and C. J. BOERS (Physica, 1935, 2, 959–967).—The electron temp. falls rapidly during the increase in partial pressure of A up to 15% in Ne-A mixtures at const. total pressure (5 mm.) and const. current (2 amp.). In Ne-Hg mixtures the electron temp. falls with increasing partial pressure of Hg. The results are explained on a development of Schottky's diffusion theory. T. G. P.

**Ion optical images with electrical lenses.** J. KOCH and W. WALCHER (Z. Physik, 1935, 97, 131–137).—Images have been obtained with K ion rays. A. B. D. C.

**Sudden losses of energy undergone by high-energy electrons.** L. LEPRINCE-RINGUET (Compt. rend., 1935, 201, 712–714; cf. A., 1935, 801).—Electrons of approx.  $2 \times 10^6$  e.v. suffer large energy losses in traversing A or Pb, 5–10 times as frequently as would be expected from theory. H. J. E.

**Quantum-like loss of velocity of slow electrons and effective cross-section in molecular gases.** H. LOHNER (Ann. Physik, 1935, [v], 24, 349–360).—Measurements of the loss of velocity of electrons by Lenard's counter-potential method indicate that inelastic collision begins at 4.25, 2.45, 2.45, 3.65, 7.2, and 7.1 volts for  $H_2$ ,  $N_2$ , NO, CO,  $N_2O$ , and  $CO_2$ , respectively. A relationship exists between the loss of velocity and the effective cross-section of the mol. J. W. S.

**Total ionisation produced by electron collisions in nitrogen.** G. A. ANSLOW (Physical Rev., 1934, [ii], 45, 750).—The total ionisation produced in  $N_2$  by electrons with energies up to 1500 volts has been measured. L. S. T.

**Double excitation of helium by electron impact.** H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1935, 31, 604–608).—The calc. probability of ex-

citation of helium by electron impact to doubly excited levels agrees qualitatively with experimental data. Reasons are given for the lack of quant. agreement. W. R. A.

**Velocity distribution of electrons moving in an electric field.** B. DAVIDOV (Physikal. Z. Sovietunion, 1935, 8, 59–70).—Theoretical. The velocity distribution of electrons moving in a gas under a const. electric field is calc. taking into account only elastic collisions between mols. and electrons. The distributions of velocities with regard to magnitude and direction, and formulæ for the mean energy and motion of the electrons are obtained. A. J. M.

**Paths of electrons in magnetons when space-charge effects are considered.** I. H. AVENDER, A. THOMA, and D. M. TOMBS (Z. Physik, 1935, 97, 202–210).—Theoretical. A. B. D. C.

**The positive electron.** A. T. WATERMAN (Amer. J. Sci., 1935, [v], 30, 541–548).—A review.

**Excitation function of mercury for atomic collision.** K. GAILER (Ann. Physik, 1935, [v], 24, 421–439).—The mutual excitation of H and Hg was investigated by the use of positive rays. In the case of H positive rays passed through Hg, only the Hg becomes excited. The excitation of the Hg at higher potentials is brought about almost entirely by neutral H atoms, excitation by  $H^+$  being at least 20 times smaller. The excitation function of Hg for collision with H is determined and compared with that for electron collision. The results are discussed from the viewpoint of "transferable energy." A. J. M.

**Electron collisions in mercury vapour: the 9.8 volt loss.** C. L. CROSS and J. A. ELDRIDGE (Proc. Iowa Acad. Sci., 1934, 41, 257).—Data for the magnetic analysis of electrons which have passed through Hg vapour are given. CH. ABS. (e)

**Homogeneous dissociation of hydrogen molecules by collision with positive ions.** A. SCHECHTER (J. Chem. Physics, 1935, 3, 433–434).—Special experimental conditions are given of work previously described (cf. A., 1934, 977) in view of reported failure of later investigators to obtain similar results (cf. Kunsman, A., 1935, 4). N. M. B.

**Disappearance of hydrogen in presence of positive ions.** C. H. KUNSMAN and R. A. NELSON (J. Chem. Physics, 1935, 3, 754).—A reply to Schechter (preceding abstract). F. L. U.

**Collisions of slow electrons with methane molecules.** H. L. BROSE and J. E. KEYSTON (Phil. Mag., 1935, [vii], 20, 902–912).—The effective cross-sections of  $CH_4$  mols. with respect to slow electrons of different velocities have been determined and are discussed. T. G. P.

**Effective cross-section and charging cross-section of helium with respect to  $He^+$ .** A. ROSTAGNI (Ann. Physik, 1935, [v], 24, 543–544).—The results of Wolf (A., 1935, 1294) give the charging cross-section > total effective cross-section. This may be due to inconstancy of field along the collector, and to the neglect of secondary electron emission. A. J. M.

**At. wt. of germanium. I. Analysis of germanium tetrabromide.** O. HONIGSCHMID, K. WINTERSBERGER, and F. WITTNER (*Z. anorg. Chem.*, 1935, 225, 81—89; cf. A., 1934, 1053).—The mean of 10 analyses of  $\text{GeBr}_4$  by nephelometric titration with  $\text{AgNO}_3$  gives  $\text{Ge } 72.588 \pm 0.008$ , and the mean of 10 gravimetric analyses  $72.586 \pm 0.012$ . The final val., 72.59, agrees with that of Baxter and Cooper (A., 1924, ii, 690; 1926, 5), but not with Aston's  $72.65 \pm 0.05$  (A., 1931, 1208). F. L. U.

**Rare earths. XLVI. At. wt. of gadolinium.** C. R. NAESER [with B. S. HOPKINS] (*J. Amer. Chem. Soc.*, 1935, 57, 2183—2184).—From the ratio  $\text{GdCl}_3 : \text{Ag}$  the at. wt. of Gd is  $156.85 \pm 0.011$ . E. S. H.

**At. wt. of tantalum. Analysis of tantalum pentachloride.** O. HONIGSCHMID and R. SCHLEE (*Z. anorg. Chem.*, 1935, 225, 64—68).—The prep. of pure  $\text{TaCl}_5$  from tantalite is described. The mean of 6 determinations of the Cl content of  $\text{TaCl}_5$  by nephelometric titration with  $\text{AgNO}_3$  gave  $\text{Ta } 180.88 \pm 0.01$ , agreeing with the val. previously obtained by analysis of  $\text{TaBr}_5$  (A., 1935, 140). F. L. U.

**Properties of the hydrogen isotopes as revealed by the mass-spectrograph.** W. BLEAKNEY (*Physical Rev.*, 1934, [ii], 45, 762).—A mass-spectrograph dealing with gases at very low pressure shows that no exchange takes place nor is equilibrium established when a non-equilibrium mixture is in contact with  $\text{H}_2\text{O}$ , Hg, soft glass, Pyrex glass, or stopcock grease. Certain catalysts, however, e.g., Ni and  $\text{Cr}_2\text{O}_3$ , established equilibrium at temp. as low as that of liquid air. L. S. T.

**Relative abundance of the silicon isotopes.** A. MCKELLAR (*Physical Rev.*, 1934, [ii], 45, 761).—Measurements of the violet bands of SiN indicate an approx. abundance ratio  $\text{Si}^{28} : \text{Si}^{29} : \text{Si}^{30} = 89.6 : 6.2 : 4.2$ . The abundance of  $\text{Si}^{29}$  and  $\text{Si}^{30}$  relative to  $\text{Si}^{28}$  is slightly > that estimated by Aston. An at. wt. > the accepted val. is obtained. L. S. T.

**Isotopes of nickel.** J. DE GIER and P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1935, 38, 810—813).— $\text{Ni}^{64}$  has been detected by the parabola method, but  $\text{Ni}^{61}$  (Aston, A., 1935, 802) was not found. The abundance figures are  $\text{Ni}^{58}$  68.1%,  $\text{Ni}^{60}$  27.2%,  $\text{Ni}^{62}$  3.8%, and  $\text{Ni}^{64}$  0.9%. R. S.

**Interference-spectroscopic examination of the gold hydride band spectrum in search of the isotope effect due to the suspected gold isotopes.** S. IMANISHI (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, 28, 129—134).—No evidence for the existence of  $\text{Au}^{199}$  could be obtained. This is in agreement with Dempster (A., 1935, 677). R. S.

**Periodic classification of the rare earths.** H. YAGODA (*J. Amer. Chem. Soc.*, 1935, 57, 2329—2330).—The tendency of the rare earths to form stable tervalent compounds is said to mask the fact that the properties of these elements in other valency states are a periodic function of at. no. Examples are given. E. S. H.

**New periodic table.** P. VAN RYSELBERGHE (*J. Chem. Educ.*, 1935, 12, 474—475).—The new table emphasises the importance of the azimuthal quantum

no. of the last electron added in the building up of the successive elements. L. S. T.

**Radioactive fluctuations.** A. E. RUARK and I. DEVOL (*Physical Rev.*, 1935, [ii], 48, 772).—Mathematical. Expressions are found for the fluctuations in the emission of sources which decay appreciably during the time of a single experiment, and for fluctuations in the counts recorded by a detector which receives only a fraction of the particles or rays emitted by a source. N. M. B.

**Renewed activity of radium bromide after heating.** C. T. KNIPP (*Trans. Illinois State Acad. Sci.*, 1934, 27, 128—129).—A minute amount of  $\text{RaBr}_2$  was sealed on the end of a rod by means of very thin Pyrex glass. The no. and length of the tracks in a Wilson chamber due to the specimen increased to a max. in 6—10 days. CH. ABS. (e)

**$^{43}\text{K}$  and the radioactivity of potassium.** H. J. WALKER (*Nature*, 1935, 136, 755).—Recent evidence supports the view (A., 1935, 275, 558) that  $^{40}\text{K}$  and not  $^{43}\text{K}$  (*ibid.*, 1185) is the source of the natural  $\beta$ -radioactivity of K. L. S. T.

**Temporal sequence of  $\alpha$ - and  $\gamma$ -radiation of radium.** W. JOHNER and E. STAHEL (*Helv. phys. Acta*, 1934, 7, 638—639; *Chem. Zentr.*, 1935, i, 2132—2133).—It is proposed to determine the relative order of  $\alpha$ - and  $\gamma$ -ray emission from Ra by examination of the absorption of the K lines, excited by inner absorption of the  $\gamma$ -radiation, in Tl, Au, and Hg filters. Absorption corresponding with the Ra spectrum would indicate emission of  $\gamma$ -radiation after loss of the  $\alpha$ -particle. Preliminary results indicate emission of Ra K radiation. J. S. A.

**Absorption of  $\gamma$ -rays by barium sulphate, gypsum, water, and flesh.** J. S. ROGERS (*Brit. J. Radiol.*, 1934, [ii], 7, 176—186; *Chem. Zentr.*, 1935, i, 2133).—The absorption has been determined photographically, and conclusions have been reached as to gypsum thicknesses for protection from  $\gamma$ -rays, and radiation intensities for penetration of varying flesh thicknesses. J. S. A.

**$\gamma$ -Ray emission of various targets under bombardment by deuterium ions.** L. R. HAFSTAD, M. A. TUVÉ, and C. F. BROWN (*Physical Rev.*, 1934, [ii], 45, 746—747).—Powerful  $\gamma$ -ray emission from Be, C, and  $\text{CaF}_2$  bombarded by deuterons is described. There is faint or doubtful emission from  $\text{SiO}_2$  and Al, but none from Ag. L. S. T.

**Experiments with neutrons slowed down at different temperatures.** C. H. WESTCOTT and H. NIEWODNICZANSKI (*Proc. Camb. Phil. Soc.*, 1935, 31, 617—624).—Neutrons were slowed down by paraffin wax at the temp. of liquid  $\text{N}_2$  and liquid  $\text{H}_2$ . The absorption produced by certain substances increased as the temp. was lowered. The no. of transformations also increased, the increase depending on the thickness of the paraffin layer. When liquid  $\text{H}_2$  was substituted for paraffin similar effects were produced. W. R. A.

**Disintegration by slow neutrons.** J. CHADWICK and M. GOLDBABER (*Proc. Camb. Phil. Soc.*, 1935, 31, 612—616).—Details of work (A., 1935, 277) are

given and a different interpretation of the results observed with B. The reaction between B and slow neutrons is  $B^{10} + n^1 \rightarrow Li^7 + He^4$ . The disintegration process with nitrogen is  $N^{14} + n^1 \rightarrow B^{11} + He^4$ . No increase was found for H, D, He, Be, C, O, F, Ne, Na, Mg, Al, Cl, A, Ca, Ni, Cu, Zn, In, and U. W. R. A.

**Excitation of secondary  $\gamma$ -rays by neutrons.** I. General; phenomena in paraffin. II. Measurements with iron, copper, cadmium, and lead. R. FLEISCHMANN (Z. Physik, 1935, 97, 242—264, 265—267).—Nuclear  $\gamma$ -rays have been excited by slow neutrons in H, Fe, Cu, Cd, and Pb, and absorption of the  $\gamma$ -rays by paraffin, Al, and Pb has been determined. The mass of the neutron is 1.0083. A. B. D. C.

**Absorption and detection of slow neutrons.** D. P. MITCHELL, J. R. DUNNING, E. SEGRÈ, and G. B. PEGRAM (Physical Rev., 1935, [ii], 48, 774—775; cf. A., 1935, 1441).—The disintegrations of B and Li were examined in terms of the absorption observed in B, Li, and Cd. Absorption-transmission curves show slight departure from the exponential.

N. M. B.

**Scattering of slow neutrons by iron and other substances.** D. BUDNITZKI and I. KURTSCHATOV (Physikal. Z. Sovietunion, 1935, 8, 170—178).—The free paths of slow neutrons in C, Fe, Cu, and Pb have been found by using their reflexion, and are compared with vals. obtained by Dunning *et al.* (Physical Rev., 1935, [ii], 47, 416) for fast and slow neutrons. In calculating paths the selective sensitivity of the indicator and the absorption of neutrons by  $H_2O$  must be considered. T. G. P.

**Absorption of slow neutrons by iron.** I. KARA, L. ROSENKEVITSCH, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 215—218).—Absorption in Fe and Cu is < recorded by Fermi (A., 1935, 910). T. G. P.

**Selective absorption of neutrons.** I. KARA, L. ROSENKEVITSCH, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 219—222; cf. preceding abstract).—Absorption of neutrons by Cu is independent of the change in concn. of  $B_2O_3$  in  $H_2O$  surrounding the indicator. This is explained by the selective absorption of B. The average vals. of sensitivity increase in the order B, Ag, Cu. The cross-section for absorption decreases rapidly with increased velocity of neutrons. T. G. P.

**Evaluation of the accuracy of Bethe and Peierls' formula concerning the decomposition of the deuteron with  $\gamma$ -radiation.** V. J. MAMASACHLISOV (Physikal. Z. Sovietunion, 1935, 8, 206—207; cf. A., 1935, 279). T. G. P.

**Disintegration of lithium by deuterons.** T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1935, [ii], 48, 742—746; cf. A., 1935, 1049).—The energy distribution of the neutrons from the disintegration of Li by 0.85 m.e.v. deuterons was determined by the method of recoil protons in a high-pressure cloud chamber. Results indicate that the neutrons come from the reactions  ${}_3Li^7 + {}_1H^2 \rightarrow {}_2He^4 + {}_0n^1$ , the neutrons (95% of the disintegrations) having a continuous energy distribution; and  ${}_3Li^7 + {}_1H^2 \rightarrow$

${}_4Be^8 + {}_0n^1$ , the neutrons (5% of the disintegrations) being nearly homogeneous, with a max. energy of  $13.3 \pm 0.5$  m.e.v. The calc. mass of  ${}_4Be^8$  is  $0.3 \pm 0.75$  m.e.v. > that of two  $\alpha$ -particles. N. M. B.

**Transmutation of deuterium by deuterons.** K. D. ALEXOPOULOUS (Naturwiss., 1935, 23, 817).—Experiments are described which indicate that no  $\gamma$ -radiation is emitted in the nuclear reaction between deuterons. A. J. M.

**Disintegration of lithium by lithium ions.** V. PETUHOV, C. SINELNIKOV, and A. WALTHER (Physikal. Z. Sovietunion, 1935, 8, 212—214).—The excitation function and abs. yield of the transmutation  ${}_3Li^6 + {}_3Li^6 \rightarrow {}_3Li^6 + {}_2He^4$  are > vals. predicted by Gamow's formula. The contrary result of Whitmer and Pool (Physical Rev., 1935, [ii], 47, 795) is probably due to protons in the ionic beam. T. G. P.

**Artificial radioactivity.** II. D. VAN DER VEEN (Chem. Weekblad, 1935, 32, 667—671).—A further review (see A., 1934, 826).

**Synthesis of radio-elements with deuterons accelerated by an impulse generator.** F. JOLIO, A. LAZARD, and P. SAVEL (Compt. rend., 1935, 201, 826—828).—Preliminary results for the conversion  ${}_6C^{12} + {}_1D^2 = {}_7N^{13} + {}_0n^1$  are recorded. Production of  ${}_7N^{13}$  becomes measurable with accelerating voltages >  $0.95 \times 10^6$  volts. H. J. E.

**Induced radioactivity by bombarding magnesium with  $\alpha$ -particles.** C. D. ELLIS and W. J. HENDERSON (Nature, 1935, 136, 755).—In addition to  $Al^{28}$  ( $\beta$ -ray period 137 sec.) two other radioactive bodies, probably  $Al^{29}$  and  $Si^{27}$ , emitting  $\beta$ -rays with a period of approx. 11 min. and positrons with a period of 5—7 min., respectively, are produced. Relative yields indicate that  $Mg^{25}$  has a strong resonance level for  $\alpha$ -particles of energy <  $5.4 \times 10^6$  volts, and that  $Mg^{24}$  and/or  $Mg^{26}$  have one for  $\alpha$ -particles of energies between 5.4 and  $6.1 \times 10^6$  volts. L. S. T.

**Radio-elements produced by neutrons.** P. PREISWERK and H. VON HALBAN (Compt. rend., 1935, 201, 722—724).—The induced activities of half-periods 97 and 4 min. observed on bombarding Tl with neutrons are attributed to  ${}_{81}Tl^{204}$  and  ${}_{81}Tl^{206}$ , respectively. No activity was observed on irradiating Bi with neutrons. P gave a product of half-period 15+1.5 days, attributed to  ${}_{15}P^{32}$ . H. J. E.

**Radioactivity of some rare-earths induced by neutron bombardment.** (SIR) J. C. McLENNAN and W. H. RANN (Nature, 1935, 136, 831—832; cf. A., 1935, 1049, 1050).—Bombardment of rare-earth oxides or oxalates by retarded neutrons from a Be+Ra source gave the following vals. for the half-periods: Nd  $35 \pm 5$  min., Gd  $6.4 \pm 0.3$  hr., Dy  $2.5 \pm 0.1$  hr., Er  $5.8 \pm 0.2$  min.,  $2.7 \pm 0.2$  hr., Ho 2.6 hr., and Lu  $3.6 \pm 0.4$  hr. L. S. T.

**Nature of the high-energy particles of penetrating radiation and the status of ionisation and radiation formulæ.** E. J. WILLIAMS (Physical Rev., 1934, [ii], 45, 729—730).—A discussion. L. S. T.

Alterations of intensity of cosmic radiation on the Hafelekar (2300 metres). V. F. HESS, H. T. GRAZLADEI, and R. STEINMAURER (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 313—338; *Helv. phys. Acta*, 1934, 7, 669—670; *Chem. Zentr.*, 1935, i, 2134). J. S. A.

Frequency and intensity of cosmic-ray bursts from lead. H. GEIGER and O. ZEILLER (*Z. Physik*, 1935, 97, 300—311). A. B. D. C.

Shower production in small thicknesses of lead and other elements. J. E. MORGAN and W. M. NIELSEN (*Physical Rev.*, 1935, [ii], 48, 773—774).—The increase in counting rate, for dual and triple coincident discharge of the counters, as a function of Pb thickness is examined. N. M. B.

System of masses of light atoms deduced from nuclear reactions alone. L. ISAKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 301—304).—19 equations of nuclear reactions of light nuclei have been collected, together with their uncertainties. Solution of these equations by the method of least squares, the individual equations being weighted according to their uncertainties, gives a system of at. mass vals. for  $H^1$  to  $Be^{11}$ . Vals. for  $H^1$ ,  $H^2$ ,  $He^4$ ,  $Li^6$ , and  $Li^7$  are in good agreement with mass-spectrograph vals. corr. for the error in the ratio  $He:O$  (1.8 parts in 10,000). It is shown that  $Be^8$  should be radioactive, although direct observation of its activity is difficult. A. J. M.

Nuclear theory. K. NAKABAYASI (*Z. Physik*, 1935, 97, 211—220).—Mass defects and nuclear radii are calc. A. B. D. C.

Pair production by magnetic multipole radiation. J. C. JAEGER (*Proc. Camb. Phil. Soc.*, 1935, 31, 609—611).—Pair production by magnetic multipole radiation has been calc. for dipoles, quadrupoles, and octopoles. The probability of pair production decreases with the order of the multipole. W. R. A.

Neutrino theory of light. III. R. DE L. KRONIG (*Physica*, 1935, 2, 968—980; cf. A., 1935, 1187).—Characteristics of neutrino-fields in relation to radiation-fields are deduced. T. G. P.

Properties of ultimate particles. G. WATAGHIN (*Ann. Acad. Brasil. Sci.*, 1935, 7, 273—276).—Modern views on the constitution of matter are discussed and the development of the conception of the electron, positron, photon, etc. is traced historically. D. R. D.

Evidence for a resonance level in the  $B^{10}$  nucleus. E. POLLARD (*Physical Rev.*, 1934, [ii] 45, 555—556). L. S. T.

Atomic frequencies in alkali metals. B. N. SEN (*Gazzetta*, 1935, 65, 907—908; cf. A., 1934, 719).—The calc. at. frequencies ( $\nu$ ) of the alkali metals (except Li) are in good agreement with experimental and other calc. vals. Since these elements have marked photo-electric properties, it seems likely that the discrepancy in the calc. val. of  $\nu$  for S and Se is due to the existence of allotropic forms and not to their photo-electric property, which in the case of S is very weak. O. J. W.

Permutation degeneration in vector models of atoms. M. MARKOV (*Compt. rend. Acad. Sci., U.R.S.S.*, 1935, 3, 103—104).—From the general permutation theory identities of the kind derived by Van Vleck for two equiv. *p* electrons arise for other kinds of electrons. W. R. A.

Calculation of the self-consistent field with exchange for lithium. V. A. FOOK and M. I. PETRASHEN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 295—296).—The difference between the observed and calc. term vals. for Li largely disappears when the self-consistent field method is used with quantum exchange instead of without it. The use of wave functions of the generalised self-consistent field gives the intensity of the principal line of each series with great precision. A. J. M.

Electromagnetic field theory. T. LEWIS (*Phil. Mag.*, 1935, [vii], 20, 1000—1025).—Theoretical. Pure field theory based on Maxwell's equations and the principle of least action leads to a satisfactory theory of the electron. T. G. P.

$\gamma$ -Transformation of electromagnetic fields. W. H. WATSON (*Physical Rev.*, 1935, [ii], 48, 776; cf. Schrödinger, A., 1935, 912).—Mathematical. N. M. B.

Elements of the quantum theory. V. B. The rigid rotator (concluded). S. DUSHMAN (*J. Chem. Educ.*, 1935, 12, 485—491; cf. A., 1935, 1298). L. S. T.

Collision problems and the conservation laws. (A) J. L. SYNGE. (B) B. HOFFMANN (*Physical Rev.*, 1934, [ii], 45, 500—501, 734—735).—Theoretical. L. S. T.

Ultra-violet radiation of chemical reactions. O. VIKTORIN (*Chem. Listy*, 1935, 29, 245—249).—Ultra-violet radiation is shown by means of an Al or CuI photocathode to accompany the reactions of oxidation of pyrogallol by atm.  $O_2$ , of  $K_2C_2O_4$  by Br, of EtOH by  $CrO_3$ , of glucose by  $KMnO_4$ , of  $Na_2S_2O_4$  in alkaline media, and of Al at the anode, and of neutralisation of  $HNO_3$  by NaOH. R. T.

Variation of spectra of detonations with the nature of the surrounding gas. A. MICHEL-LÉVY and H. MURAOUR (*Compt. rend.*, 1935, 201, 828—830).—With  $C(NO_2)_4 + PhMe$  in A, Kr,  $O_2$ ,  $CO_2$ , air, and  $Cl_2$  continuous emission predominated. In  $N_2$ , He, and  $H_2$  bands were observed. The luminosity is attributed to excitation of the surrounding gas by the shock wave. H. J. E.

Colour of smoky quartz. N. M. MOHLER (*Physical Rev.*, 1934, [ii], 45, 743).—Absorption spectra (200—700  $m\mu$ ) of smoky quartz before and after decoloration by heat and recoloration by exposure to Ra, and the spectra of irradiated clear crystal, and fused specimens, support the view that the colour of smoky quartz is due to radioactive action. L. S. T.

The 4502 Å. band of  $NH$ . R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (*Proc. Roy. Soc.*, 1935, A, 151, 602—609; cf. A., 1935, 679, 912).—A new band at 4502 Å., degraded to the red, has been observed in the spectrum of a hollow-cathode discharge in streaming  $NH_3$ . The band arises from a



$^1\Pi \rightarrow ^1\Sigma$  transition. The rotational consts. for the new level have been calc. L. L. B.

**Beryllium deuteride spectra.** P. G. KOONTZ (Physical Rev., 1935, [ii], 48, 707—713).—The spectra of the BeD green bands at 4990 Å. and the ultra-violet BeD<sup>+</sup> bands at 2200—3100 Å. were photographed. Rotational analyses of the former and rotational and vibrational analyses of the latter are tabulated. The electronic isotope shift in the ultra-violet is 0.8 cm.<sup>-1</sup> Rotational consts. are evaluated, and the slight discrepancy between the ratio of the  $B_e$  consts. for the deuterides and hydrides and the ratio of the reduced masses is discussed. N. M. B.

**Fine structure of the C bands of calcium deuteride.** B. GRUNDSTROM (Z. Physik, 1935, 97, 171—176). A. B. D. C.

**E Band system of calcium hydride.** W. W. WATSON and R. L. WEBER (Physical Rev., 1935, [ii], 48, 732—734).—The E band system of CaH at 4900 Å. is the  $\Delta v=0$  sequence of a  $^2\Pi \rightarrow ^2\Sigma$  transition, the lower state being the normal  $^2\Sigma^+$  state. Frequency assignments and calc. mol. consts. are tabulated. There is evidence of strong interaction between the E state and other near CaH states. N. M. B.

**Dissociation energy of carbon monoxide.** F. BRONS (Nature, 1935, 136, 796, and Physica, 1935, 11, 1108—1113).—The structure of the fourth positive group in the spectrum of CO confirms the val. 8.41 volts for dissociation energy (cf. A., 1934, 828).

L. S. T.

**Vibrational analysis of the hafnium oxide band spectrum.** R. W. SHAW and H. C. KETCHAM (Physical Rev., 1934, [ii], 45, 753).—Approx. 100 bands arising from the HfO mol. have been observed in the region 6350—3330 Å. in an arc flame. No rotational structure has been observed. L. S. T.

**Ultra-violet band spectrum of N<sub>2</sub>O<sub>3</sub>.** E. H. MELVIN and O. R. WULF (Physical Rev., 1934, [ii], 45, 751—752).—Mixtures of NO and small amounts of NO<sub>2</sub> give a group of bands in the near ultra-violet probably due to N<sub>2</sub>O<sub>3</sub>. A process of dissociation of the N<sub>2</sub>O<sub>3</sub> mol. in the region 2400—2200 Å. is indicated. L. S. T.

**Emission spectrum of the selenium oxide SeO.** I. BLOCH, E. BLOCH, and C. S. PIAT (Compt. rend., 1935, 201, 824—825; cf. A., 1935, 1443).—The spectrum of a high-frequency discharge in SeO<sub>2</sub> vapour has a no. of bands at  $\lambda$  3800—2880 Å., degraded to the red, attributed to SeO. The fundamental vibrational frequencies of SeO in the normal and excited state were 908.9 and 533.4 cm.<sup>-1</sup>, respectively; energy of dissociation 5.31 e.v. H. J. E.

**Spectra of SeO and SeO<sub>2</sub>.** R. K. ASUNDI, M. JAN-KHAN, and R. SAMUEL (Nature, 1935, 136, 642—643; cf. A., 1935, 1188).—The emission bands of SeO and the absorption bands of SeO<sub>2</sub> have been analysed. The energy of dissociation of unexcited SeO is 4.17 volts. L. S. T.

**Vibrational analysis of BaCl and BeCl bands.** A. E. PARKER (Physical Rev., 1934, [ii], 45, 752; cf. A., 1934, 1153).—A band system due to BeCl,

a  $^2\Pi \rightarrow ^2\Sigma$  transition degrading to the red, has been photographed. L. S. T.

**Photo-dissociation of polyatomic molecules in the Schumann ultra-violet.** A. TERENTIN and H. NEUMANN (J. Chem. Physics, 1935, 3, 436—437).—Threshold energies of dissociation were obtained for the vapours of H<sub>2</sub>O, MeOH, EtOH, HCO<sub>2</sub>H, AcOH, MeCN, NH<sub>3</sub>, and I. N. M. B.

**Spectrum, fluorescence, and photochemical decomposition of acetaldehyde.** H. W. THOMPSON and J. W. LINNETT (J.C.S., 1935, 1452—1459).—Absorption by the vapour was observed at  $\lambda$  3800—2900 and < 2320 Å. In the first region there were sharp bands, degraded to the red, and max. absorption was at approx. 3450 Å. The bands at < 2320 Å. were narrow and diffuse. No fluorescence was observed on irradiating with  $\lambda$  3800—3000 Å. The photochemical decomp. ( $\lambda$  3665, 3135 Å.) yielded polymerised C<sub>2</sub>H<sub>3</sub>·CHO, CO, and small amounts of C<sub>2</sub>H<sub>2</sub>. The quantum yield for the decomp. ( $\lambda$  3665 Å.) was approx. 10<sup>-2</sup>. That for the polymerisation was 2.3. Both vals. increased with decreasing  $\lambda$ .

H. J. E.

**Influence of temperature on methyl iodide absorption spectrum in [quartz] ultra-violet.** A. HENRICI and H. GRIENEISEN (Z. physikal. Chem., 1935, B, 30, 1—39; cf. A., 1933, 445).—Numerous new bands have been observed, particularly at higher temp. The electron transition responsible for the B bands is either in the C-I linking or in a non-linking I electron shell (cf. A., 1935, 562). Most of these bands may be accounted for by assuming vibrational frequencies of 525, 1 880, and 1237 cm.<sup>-1</sup> in the ground state and 508, 1 780, 1090, and 1 1250 cm.<sup>-1</sup> in the excited electronic state. A resolution of various bands, observed at higher temp., is interpreted as removal of a degeneracy. Several bands exhibit exceptional weakening with rise of temp. and apparently represent transitions to a new electron term, 49,220 cm.<sup>-1</sup>, the probability of transition to which varies with temp. In this term the frequencies have become 495, 1 805, and 985 cm.<sup>-1</sup> R. C.

**Optical absorption of substituted benzenes.** E. STEURER (Z. physikal. Chem., 1935, B, 30, 157—158).—The absorption curves of  $\psi$ -cumene, mesitylene, and  $p$ -xylene have been determined and the results compared with those of Conrad-Billroth (A., 1935, 913). R. C.

**Optical absorption of porphyrins. III.** A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1935, 174, 321—334; cf. A., 1935, 1444).—The absorption curves of two chloroporphyrin- $e_5$  Me<sub>2</sub> esters accord with the structure previously suggested (A., 1933, 402). The curve of 4-de-ethyldeoxy-phyloerythrin Me<sub>1</sub> ester exhibits only a small shift towards the blue compared with that of the corresponding porphyrin with Et substituted in the  $\beta$ -position. Absorption curves of derivatives of the chlorophyll- $b$  series reveal regularities similar to those observed in the  $a$  series. The effect on the light absorption of the hydrogenation of the vinyl group in methylphæophorbide- $a$  and - $b$  has been examined. R. C.



**Determination of ionisation by ultra-violet spectrophotometry: its validity and application to the measurement of the strength of very weak bases.** L. A. FLEXSER, L. P. HAMMETT, and A. DINGWALL (J. Amer. Chem. Soc., 1935, 57, 2103—2115).—Ultra-violet absorption spectra of  $\text{BzOH}$ ,  $2:4\text{-C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OH}$ ,  $\text{NH}_2\text{Ph}$ ,  $\text{COPh}_2$ , anthraquinone,  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ , and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in different solvents have been determined. The technique of ionisation determination by this method is described and discussed. The strengths of the very weak bases  $\text{COPh}_2$ ,  $\text{BzOH}$ , and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  have been measured.

E. S. H.

**Interpretation of vibration spectrum of organic molecules with the aid of the isotopy effect.** E. BARTHOLOME and H. SACHSSE (Z. physikal. Chem., 1935, B, 30, 40—52).—The magnitude of the change in a frequency when in a H compound D is substituted for H is a measure of the participation of the substituted atom in that particular mol. vibration. In numerous cases substitution reduces the symmetry of the original mol., resulting in a resolution of vibrations which are degenerate in the H compound; from the resolution the degree of degeneracy and hence the symmetry character of the original frequency may be deduced. Comparison of the infra-red absorption spectra of  $\text{MeOH}$  and  $\text{MeOD}$  has made it possible to identify the normal vibrations; in an appreciable proportion of the mols. there is no free rotation of the OH relative to the Me. The  $827\text{ cm}^{-1}$  band of  $\text{C}_2\text{H}_6$  is a degenerate  $\sigma$ -vibration, and  $1465$  and  $1495\text{ cm}^{-1}$  are  $\sigma$ -bands. The identification of the normal vibrations of  $\text{C}_2\text{H}_6$  is largely completed.

R. C.

**Infra-red spectrum of heavy water.** E. F. BARKER and W. W. SLEATOR (J. Chem. Physics, 1935, 3, 660—663).—The absorption bands  $\nu_2$  and  $\nu_3$  for  $\text{D}_2\text{O}$  and  $\nu_2$  and  $\nu_1$  for  $\text{HDO}$  have been located in water vapour containing 90 and 40% of D.  $\nu_3$  for  $\text{HDO}$  is masked by the corresponding band for  $\text{H}_2\text{O}$ . The fine structure of the  $\nu_2$  bands agrees approx. with that calc. from mol. dimensions.

F. L. U.

**Infra-red absorption spectrum of methyl deuteride.** N. GINSBURG and E. F. BARKER (J. Chem. Physics, 1935, 3, 668—674; cf. A., 1934, 716).—The six fundamental vibrational frequencies of  $\text{MeD}$  have been observed and the fine structure of the bands resolved. Moments of inertia and inter-nuclear distances are calc.

F. L. U.

**Infra-red absorption of cyanides and thiocyanates.** W. GORDY and D. WILLIAMS (J. Chem. Physics, 1935, 3, 664—667; cf. A., 1934, 1288).—The absorption of  $\text{MeCN}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CN}$ ,  $\text{MeCNS}$ , and aq. solutions of  $\text{HCN}$  and of some simple and complex metal cyanides shows in all cases a characteristic band in the region  $4.38\text{--}4.90\text{ }\mu$ . Slight variations in the position are attributed to changes in the vibrational energy of the bound CN groups. An additional band shown by highly ionised cyanide solutions is attributed to  $\text{CN}'$ .

F. L. U.

**Infra-red absorption spectra of plant and animal tissue and of various other substances.** R. STAIR and W. W. COBLENTZ (J. Res. Nat. Bur. Stand., 1935, 15, 295—316).—The infra-red absorption

spectra to  $15\text{ }\mu$  has been studied for pure rubber, gutta-percha hydrocarbon, balata hydrocarbon, polyindene, polystyrene, indene, styrene, Cellophane, pokeweed pith, onion skin, moonwort-seed septum, cotton-seed wing, chitin, pith of feathers, fish bladder, dragon-fly wing, bat-wing, ovalbumin, egg membrane, gelatin, polyvinyl acetate and chloroacetate, glyptal resin, shellac, paraffin oil, sperm oil, linseed oil,  $\text{CCl}_4$ ,  $(\text{CH}_2\text{Cl})_2$ ,  $\text{PhEt}$ ,  $\text{PhCl}$ ,  $o\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $\text{EtOAc}$ ,  $\text{Pr}^n\text{Br}$ ,  $\text{Bu}^n\text{Br}$ , and  $\text{C}_2\text{HCl}_5$ .

J. W. S.

**Origin of the wing accompanying the Rayleigh line in liquids.** S. C. SIRKAR (Nature, 1935, 136, 759—760).—The changes in intensity of the wings which accompany the dissolution of  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ , or  $\text{Ph}_2\text{O}$  in cyclohexane do not support the hypothesis of Gross and Vuks (A., 1935, 914).

L. S. T.

**Determination of degree of depolarisation of light scattered by molecules.** H. VOLKMANN (Ann. Physik, 1935, [v], 24, 457—484).—An apparatus is described by which the degree of depolarisation ( $\Delta$ ) of light scattered in  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  has been determined. The accuracy of former determinations is discussed.  $\Delta$  for  $\text{CH}_4$  is 0, indicating tetrahedral symmetry. The influence of the Raman effect on  $\Delta$  for  $\text{CH}_4$  is  $<0.001$ .  $\Delta$  for  $\text{CO}_2$  is  $0.0724 \pm 0.003$ ; for  $\text{H}_2$ ,  $0.009 \pm 0.001$ ; for  $\text{N}_2\text{O}$ ,  $0.102 \pm 0.004$ .

A. J. M.

**Rotational Raman spectrum of nitrous oxide.** D. BENDER (Physical Rev., 1934, [iii], 45, 732).—Comparison of the rotational Raman spectra of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  shows no resolution of  $\text{N}_2\text{O}$ , the mol. of which is asymmetric.

L. S. T.

**Raman effect in fuming sulphuric acid.** J. CHEDIN (Compt. rend., 1935, 201, 724—726).—Vals. are recorded for oleum with 10—68% of  $\text{SO}_3$ , and for  $\text{H}_2\text{SO}_4$ . Oleums rich in  $\text{SO}_3$  have no Raman lines in common with  $\text{H}_2\text{SO}_4$ . This is attributed to formation of  $\text{H}_2\text{S}_2\text{O}_7$ .

H. J. E.

**Raman spectrum of sodium nitrate, sodium acetate, and acetic acid.** E. R. LAIRD and D. A. FRANKLIN (Physical Rev., 1934, [ii], 45, 738).—The Raman one-line spectrum for  $\text{NaNO}_3$  solutions has been re-examined. The slight change in  $\lambda$  between dil. and conc. solutions and the marked change in  $\lambda$  for the crystals and the appearance of other lines in the solid have been confirmed. With solutions of  $\text{NaOAc}$ , there is no difference in appearance or position of the five lines found. The solid gives a strong continuous background with faint lines in approx. the same positions as solutions. All lines, except one, are different from those found for  $\text{AcOH}$ , in which the no. and position of the lines change markedly from the glacial acid to a 28% solution.

L. S. T.

**Raman spectrum of arsenic trichloride.** D. M. YOST and T. F. ANDERSON (J. Chem. Physics, 1935, 3, 754).—It is pointed out, with reference to a paper by Brodski and Sack (A., 1935, 1189), that central forces alone do not suffice for the treatment of mols. of the  $\text{AsCl}_3$  type.

F. L. U.

**Raman spectra of oxalic acid.** J. H. HIBBEN (J. Chem. Physics, 1935, 3, 675—679).—Raman spectra of  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , and of aq. and

EtOH solutions have been determined. The results indicate that in the anhyd. acid and aq. solutions the two  $\text{CO}_2\text{H}$  groups behave differently, whilst in EtOH they behave similarly. Shifts due to C:O oscillations are either absent or are far weaker in the dihydrate. Chemical interpretations are suggested.

F. L. U.

**Raman spectrum of the isomeric chloronitrobenzenes.** R. MANZONI-ANSIDEI (Gazzetta, 1935, 65, 871—877).—Raman lines are recorded for *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ . The vals. of the frequency characteristic of the  $\text{NO}_2$  group are: *o*- 1528, *m*- 1535, *p*- 1548  $\text{cm}^{-1}$ . Measurements of other workers are discussed.

O. J. W.

**Raman effect. XLV. Raman spectrum of organic substances. Poly-substituted benzenes. VII. K. W. F. KOHLRAUSCH and G. P. YPSILANTI. XLVI. Poly-substituted benzenes. VIII. A. W. REITZ and G. P. YPSILANTI. XLVII. Aromatic polycarboxylic acids. A. PONCRATZ and R. SEKA. XLVIII. Nuclear-substituted ethyl benzoates. K. W. F. KOHLRAUSCH and W. STOCKMAYER (Monatsh., 1935, 66, 285—298, 299—306, 307—315, 316—326).—XLV. The Raman spectra of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ , *o*- and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$ , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CN}$ , *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{F}$ , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Br}$ , *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{I}$ , *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{NH}_2$ , *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{I}$ , and *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{OH}$  have been determined. Three lines found in the Raman spectrum of these substances occur also in that of  $\text{C}_6\text{H}_6$ , and the degrees of depolarisation of these lines are almost identical with the corresponding ones for  $\text{C}_6\text{H}_6$ . Only the line 1156  $\text{cm}^{-1}$  occurs in *o*-, *m*-, and *p*-*di*-derivatives, in mono-derivatives, and in  $\text{C}_6\text{H}_6$  itself. The lines 615, 999, and 1020  $\text{cm}^{-1}$  occur independently of the substituent in mono-substituted derivatives, but in the di-derivatives 634 (corresponding with 615) occurs only in the spectrum of *p*-compounds, 994 only in that of *m*-compounds, and 1037 only in that of *o*-compounds. The special characteristics of the spectra of *p*-compounds are discussed.**

XLVI. The Raman spectra of compounds of the type  $\text{C}_6\text{H}_4\text{X}\cdot\text{OMe}$  [ $\text{X}=\text{NH}_2$  (*o*, *m*, and *p*),  $\text{OH}$  (*o*, *m*, and *p*),  $\text{Me}$  (*o*, *m*, and *p*),  $\text{F}$  (*p*),  $\text{Cl}$  (*o* and *p*),  $\text{Br}$  (*o* and *p*),  $\text{I}$  (*o*, and *p*),  $\text{CN}$  (*p*)] have been determined. All *p*-derivatives show lines at 634, 1169, and 1590  $\text{cm}^{-1}$ .

XLVII. The Raman spectra of *m*- and *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{X})_2$  ( $\text{X}=\text{Me}$ ,  $\text{Et}$ ), 1:2:3- and 1:3:5- $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_3$  have been determined. The positions of the double linkings in the nucleus with respect to the substituent groups cannot be found by a study of the constitutive effects of substituents on the frequencies of the nucleus.

XLVIII. The Raman spectra of compounds of the type  $\text{C}_6\text{H}_4\text{X}\cdot\text{CO}_2\text{Et}$  ( $\text{X}=\text{NH}_2$ ,  $\text{OH}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{NO}_2$ , *o*, *m*, and *p* in each case) have been determined. The effect of  $\text{X}$  on the inner vibrations of the  $\text{NO}_2$  and  $\text{CO}_2\text{R}$  groups is discussed. The effect is strongest in the *o*-position, and the characteristic frequencies of the  $\text{NO}_2$  and  $\text{CO}$  groups are increased by the introduction of further substituents, the increase being the greater the higher is the substituent in the series  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{Me}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{CO}_2\text{R}$ ,  $\text{NO}_2$ , *i.e.*, in the order in which

substituents tend to increase the dissociation const. of  $\text{BzOH}$ .

A. J. M.

**Raman effect and organic chemistry: isopropylacetylene, isopropylethylene, and some of their derivatives.** B. GREDY (Bull. Soc. chim., 1935, [v], 2, 1951—1958).—Raman lines are recorded for  $\text{CPr}^i\text{:CH}$ ,  $\text{CHPr}^i\text{:CH}_2$ , and some of their derivatives. Lines characteristic of the double and triple linkings are found in all the substances. The influence of substituted  $\text{Cl}$  or  $\text{Br}$  on the double linking frequency at about 1600  $\text{cm}^{-1}$  is confirmed.

O. J. W.

**Raman effect and organic chemistry. Raman spectra of the ethylenic compounds  $\text{CH}_2\text{:CHR}$ .** M. BOURGUEL and L. PIAUX (Bull. Soc. chim., 1935, [v], 2, 1958—1969).—Measurements are recorded for > 20 substances of the type  $\text{CH}_2\text{:CHR}$  ( $\text{R}=\text{a}$  variety of atoms and radicals). These all have five characteristic frequencies, each of which may vary within narrow limits. For butene the vals. are: 1295, 1417, 1642, 3004, and 3083  $\text{cm}^{-1}$ . The various radicals  $\text{R}$  are classified according to their influence on the 1600 frequency. In derivatives of the type  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{R'}$  this frequency is const. at 1642  $\text{cm}^{-1}$ .

O. J. W.

**Raman spectra of methyldiethylcarbinol, benzyldimethylcarbinol, and the corresponding olefines.** J. SAVARD (Compt. rend., 1935, 201, 833—835; cf. A., 1935, 681).—Data are recorded and compared.

H. J. E.

**Polarisation of Raman radiation.** F. HEIDENREICH (Z. Physik, 1935, 97, 277—299).—The method of circular polarisation (cf. Hanle, A., 1933, 114) has been applied to Raman displacements of  $\text{C}_2\text{H}_2\text{Cl}_2$  (*cis* and *trans*),  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_6\text{Cl}_6$ , cyclohexane (I), and  $\text{Ac}_2\text{O}$ . Pure rotation broadening should be shown by inverted circular polarisation, as do  $\text{PhMe}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{AcOH}$ , and  $\text{Ac}_2\text{O}$ ;  $\text{EtOH}$ ,  $\text{H}_2\text{O}$ , and (I) do not give inverted polarisation, and indicate that all broadening due to liquids is not rotation broadening. Sirkar's polarisation dispersion (cf. A., 1934, 942) could not be observed.

A. B. D. C.

**Depolarisation in the Raman spectra of halogenated derivatives of ethyl acetate.** H. C. CHENG (J. Chim. phys., 1935, 32, 541—548; cf. A., 1934, 1056).—Raman spectra of  $\text{AcOH}$ ,  $\text{EtOAc}$ ,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ ,  $\text{CHCl}_2\cdot\text{CO}_2\text{Et}$ , and  $\text{CCl}_3\cdot\text{CO}_2\text{Et}$  have been measured, and the fundamental frequencies of  $\text{C}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_2$ , and  $\text{CCl}_3$  ascertained. Various depolarised lines are fully discussed in relation to the groupings in the molecules.

T. G. P.

**Intensity and polarisation of Raman radiation from liquids.** A. V. RAO (Z. Physik, 1935, 97, 154—157).—The relative intensity and polarisation of  $Q$  branches of the different Raman lines of  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{AsCl}_3$  have been determined; the total depolarisation obtained from the Raman lines is an appreciable fraction of the depolarisation of the total scattered radiation.

A. B. D. C.

**Raman effect of organic molecules. Vibration spectra of acrylonitrile and ethylene oxide.** B. TRIM and R. MECKE (Z. Physik, 1935, 97, 221—224).—Frequencies are given for  $\text{C}_3\text{H}_3\cdot\text{CN}$  and

(CH<sub>2</sub>)<sub>2</sub>O, and are classed as valency frequencies of the vinyl groups, ring frequencies, and CH frequencies.

A. B. D. C.

**Relation between the ultra-violet absorption spectrum and the Raman spectrum of pyridine.** V. HENRI and P. ANGENOT (Compt. rend., 1935, 201, 895—896).—Fundamental frequencies of 600, 857, 993, 1031, and 1159 cm.<sup>-1</sup> have been observed in the ultra-violet absorption spectrum of the vapour of C<sub>5</sub>H<sub>5</sub>N (I) at various pressures. The frequencies correspond with those of the Raman spectrum of (I) and C<sub>6</sub>H<sub>6</sub>, since CH and N have nearly the same mass. For the higher electronic level the frequency 542 cm.<sup>-1</sup> has been observed. Ultra-violet light of  $\lambda < 2750$  Å. falling on (I) is photochemically active and causes predissociation.

R. S. B.

**Application of the Raman effect to the *cis-trans* isomerism of methylcyclohexanols.** J. TABUTEAU (Compt. rend., 1935, 201, 897—898).—The Raman spectra of *cis*- and *trans*-*o*-, *m*-, and *p*-methylcyclohexanol differ most for frequencies 300—900 cm.<sup>-1</sup> The spectra of the *cis*-alcohols and -acetates have many lines in common, but with the *trans*-compounds the no. of common lines is much less. The distinction between *cis*- and *trans*-isomerides decreases in the order *o*, *m*, *p*, and is  $<$  with the borneols and myrtanols owing to the relatively small mass of the Me.

R. S. B.

**Stability of the Lenard light centres in zinc sulphide.** N. RIEHL (Ann. Physik, 1935, [v], 24, 536—542).—An investigation has been made to discover whether the Lenard light centres change spontaneously in the course of time, depending on the history of the phosphor. ZnS phosphors which have been kept in the dark for some years show a decreased sensitivity to  $\alpha$ -ray phosphorescence and probably also to ordinary light phosphorescence, showing that spontaneous changes in the lattice or light centres have taken place. X-Ray analysis shows that the ageing is not due to a change of the wurtzite lattice into the Zn-blende lattice. The aged phosphor can be partly regenerated by prolonged heating at 500°. The thermodynamic instability of the light centres may be due to the rapid cooling of the phosphor when first prepared, the equilibrium being frozen, for minerals which have cooled comparatively slowly show but feeble phosphorescence. The existence of phosphorescent minerals indicates that the capacity to phosphoresce is not completely lost by ageing.

A. J. M.

**Luminescent properties of zinc sulphide in relation to X-rays.** L. LEVY and D. W. WEST (Brit. J. Radiol., 1935, 8, 184—185).—The afterglow and latent fluorescence of "Fluorazure" ZnS intensifying screens becomes very feeble if a trace of Ni is added before firing the powder. A screen made from ZnS and CdS is superior to one from CdWO<sub>4</sub>.

CH. ABS. (e)

**Polarised fluorescence of organic compounds.** S. M. MITRA (Z. Physik, 1935, 97, 138—153).—Variation in polarisation of fluorescence radiation from succinylfluorescein and eosin with temp., viscosity, and concn. of solution, and  $\lambda$  of the exciting radiation is given for the solvents glycerol, castor oil, sugar solutions, collodion, and gelatin.

A. B. D. C.

**Role of oxidation-reduction potential and acidity in quenching of fluorescence in solutions.** K. WEBER (Z. physikal. Chem., 1935, B, 30, 69—83).—For quinine sulphate and aesculin the logarithm of the concn.,  $k$ , of halogen ion which halves the fluorescence intensity increases linearly as the reduction-oxidation potential,  $E$ , of the halogen ion becomes increasingly negative, whilst for fluorescein and uranine the relation between  $k$  and  $E$  is more complex.  $k$  rises with [H<sup>+</sup>]. Following Schneider (A., 1935, 681) and assuming quenching by halogen ions to be a sensitised photo-oxidation, a reaction mechanism is postulated which leads to quenching formulae agreeing with experiment. These latter yield quantitatively the observed relation between  $k$  and  $E$ , so that from  $k$  the differences between the  $E$  vals. of the halogens may be derived. For the quenching of the fluorescence of the above substances by cations there is no connexion between  $k$  and  $E$ , suggesting that oxidation-reduction reactions play no part.

R. C.

**Photochemical reactions connected with the quenching of fluorescence of dyes by ferrous ions in solution.** J. WEISS (Nature, 1935, 136, 794—795; cf. A., 1935, 1211).—Irradiation of different dyes, e.g., methylene-blue, thionine, brilliant-cresyl-blue, etc., in acid FeSO<sub>4</sub> with the visible radiation of a strong C arc produces bleaching or a change in colour, due to the formation of leuco-dyes, which is irreversible when the Fe<sup>+++</sup> is pptd. by hydrolysis. With the above dyes the process is completely reversible in the dark, the Fe<sup>+++</sup> being reduced by the leuco-dye. The direct, unsensitised photochemical process is obtained by irradiating 0.5*M*-FeSO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> with light from a strong Hg arc, H<sub>2</sub> being formed when O<sub>2</sub> is excluded. The bearing of these results on biological problems is discussed.

L. S. T.

**Dependence of fluorescence spectra on the viscosity of the solvent.** A. JABLONSKI (Physikal. Z. Sovietunion, 1935, 8, 105—108).—The results of Tumermann (A., 1935, 807) are not inconsistent with those of Jablonski (A., 1932, 213).

A. J. M.

**Photoluminescence.** F. OBERHAUSER and R. CABRERA (Anal. Fac. Filos. Univ. Chile, 1934, 1, 28—44; cf. A., 1929, 793).—Org. acids containing a trace of fluorescein exhibit fluorescence and phosphorescence when exposed to light sources.

F. R. G.

**Diffusion in the bulb of a mercury rectifier.** D. R. KANASKOV (Physikal. Z. Sovietunion, 1935, 8, 119—135).—The dark space in a Hg rectifier has been examined with a Langmuir probe. Linear relations exist between (a) log random electron current or (b) log concn. of electrons, or (c) the potential, at a point along the axis of the tube and the distance of the point from the cathode.

T. G. P.

**Bulk and superficial conductivities of cuprous oxide.** L. DUBAR (Compt. rend., 1935, 201, 883—885).—Using conductors of different surface the bulk and superficial conductivities ( $\sigma$ ,  $\omega$ ) of Cu<sub>2</sub>O have been determined in dry air at 15.8°;  $\sigma = 1.61 \times 10^{-8}$  mho cm./cm.<sup>2</sup> and  $\omega = 21.7 \times 10^{-8}$  mho cm./cm.  $\sigma$  is unaffected by H<sub>2</sub>O vapour, but  $\omega$  decreases owing to

adsorption.  $\omega$  is greatly reduced by the action of dil.  $\text{H}_3\text{PO}_4$ . R. S. B.

**Investigations on electrets.** A. GEMANT (Phil. Mag., 1935, [vii], 20, 929—952).—The main results of Eguchi (A., 1925, ii, 462) have been verified. Electrets prepared by allowing substances to solidify in a field of 5—10 kv. per cm. are the electrical analogues of permanent magnets. The field on their free surface may be utilised provided they are nearly short-circuited and kept dry. The charge is acquired either by ionic space charges (heterocharge) or by the orientation of dipole mols. (homocharge) which may be accompanied by a secondary piezoelectric effect. Acidic substances yield ions producing heterocharge, whilst non-dissociating dipoles, chiefly esters, yield homocharge. For mixtures an additive law is valid. T. G. P.

**Elimination of peculiarities in the dielectric behaviour of water vapour.** J. D. STRANATHAN (Physical Rev., 1934, [ii], 45, 741).—The breaks in the pressure- $(K-1)$  curves for  $\text{H}_2\text{O}$  vapour have been eliminated by using a brass condenser, and quartz or Pyrex insulators, and by exercising a strict control on the rate at which the vapour enters the condenser. The electric moment of the  $\text{H}_2\text{O}$  mol. is  $1.83 \times 10^{-18}$ . L. S. T.

**Dipole moments and structure of quinoline derivatives.**—See A., 1935, 1506.

**Physical methods in chemistry. IV. Dipole measurement and its application to chemistry.** P. C. HENRIQUEZ and L. J. N. VAN DER HULST (Chem. Weekblad, 1935, 32, 636—645).—The calculation of at., electronic, and orientation polarisation and the relationships between dipole moment and structure are discussed. D. R. D.

**Configuration of the mercuric halides.** W. J. CURRAN and H. H. WENZKE (J. Amer. Chem. Soc., 1935, 57, 2162—2163).—Electric moments of  $\text{HgPh}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ , and  $\text{HgI}_2$  have been determined. The vals. are < those calc. from solubility data. The configuration of these compounds is not linear. E. S. H.

**Dipole measurements with isomeric platon-complexes.** K. A. JENSEN (Z. anorg. Chem., 1935, 225, 97—114).—Determinations of the dipole moments of compounds  $[\text{PtX}_2(\text{SR}_n)_2]$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NO}_2$ ,  $\text{NO}_3$ , and  $\text{R}=\text{Et}, \text{Pr}^n, \text{Pr}^s, \text{Bu}^n, \text{Bu}^s, \text{CHMeEt}, \text{CH}_2\text{Ph}$ ) give  $2.2\text{--}2.5 \times 10^{-18}$  e.s. unit for the  $\alpha$ -compounds and about  $9 \times 10^{-18}$  ( $\text{Cl}, \text{Br}$ ) or  $13 \times 10^{-18}$  ( $\text{NO}_2, \text{NO}_3$ ) for the  $\beta$ -compounds. The results indicate that the  $\alpha$ -compounds are *trans*- and the  $\beta$  *cis*-isomerides. Cryoscopic measurements in  $\text{C}_6\text{H}_6$  show both the  $\alpha$ - and  $\beta$ -chlorides to have simple mols., the latter being associated in conc. solutions. No interconversion of the  $\alpha$ - and  $\beta$ -forms occurs in  $\text{C}_6\text{H}_6$ , but it does in the case of  $[\text{PtCl}_2(\text{Et}_2\text{Sc})_2]$ . F. L. U.

**Dipole moments of ethyl and isoamyl borates and triphenyl phosphate.** E. G. COWLEY and J. R. PARTINGTON (Nature, 1935, 136, 643).—The vals. obtained in  $\text{C}_6\text{H}_6$  at  $20^\circ$  are 0.75, 0.81, and 2.79 *D*, respectively.  $P_\infty$  and  $P_E$  are 50.5 and 38.63, 94.3 and 80.20, 252.5 and 87.41 c.e., respectively. L. S. T.

**Dipole moments of certain organic compounds.** J. N. PEARCE and L. F. BERHENKE (Proc. Iowa Acad. Sci., 1934, 41, 141—142).—The dielectric consts. of  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CHO}$ ,  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ ,  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , and *p*-anisaldehyde in dioxan at  $25^\circ$  gave dipole moments 2.20, 3.27, 4.18, and  $3.70 \times 10^{-18}$ , respectively. The angle between the CHO moment and the line through the 1:4 C atoms of the  $\text{C}_6\text{H}_6$  nucleus was  $51^\circ$ . Those between the directions of the OH and CHO group moments were  $50^\circ, 49^\circ$ , respectively. CH. ABS. (e)

**Structure of antipyrine [and pyrimidone] in aqueous solution.** G. DEVOTO (Atti R. Accad. Lincei, 1935, 21, 819—820).—The dielectric consts. of aq. antipyrine (I) and pyrimidone (II) of various concns. have been determined at  $25^\circ$  ( $\lambda 90$  cm.).  $d\epsilon/dc=1.5$  for (I) and  $-6.7$  for (II), indicating that polar structures for these compounds are untenable. D. R. D.

**Transitions in camphor and chemically related compounds. I. Dipole rotation in crystalline solids.** W. A. YAGER and S. O. MORGAN. II. Vibration of atomic groups. A. H. WHITE and S. O. MORGAN (J. Amer. Chem. Soc., 1935, 57, 2071—2078, 2078—2086).—I. Determination of the dielectric properties of *d*- and *dl*-camphor, *d*-camphoric anhydride, borneol, *isoborneol*, and bornyl chloride shows that these compounds undergo transitions in the solid state. Above the transition temp. the dielectric const. of the solid is that normally expected of the polar substance in the liquid state; below the transition temp. the dielectric const. has a low val., approx. equal to  $n^2$ . This behaviour is explained by the rotation of dipoles in the solid.

II. An increase of about 18 g.-cal./ $^\circ\text{C.}/\text{mol.}$  in the sp. heat of *d*-camphor at the transition at  $-30^\circ$  has been observed; it is assumed that energetic intramol. vibration arises. The total polarisation behaviour of *d*-camphor in dil. solution is explained by assuming that at room temp. dipole moment is < and at. polarisation > was formerly supposed, and that at. polarisation begins to decline with falling temp. below  $-10^\circ$ , when the transition to the more rigid mols. begins. Similar transitions, observed in crystals of cyclohexane derivatives, appear to be due to transformations from the rigid to the pliable forms of the mols. forming the crystals. E. S. H.

**Calculation of dipole interaction.** R. P. BELL (Trans. Faraday Soc., 1935, 31, 1557—1560).—The method proposed by Martin (A., 1934, 1063) for calculating dipole interaction is shown to be valid for sufficiently small vals. of the dipole moment. F. L. U.

**Reactivity and dipole moment.** E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 30, 139—148; cf. A., 1935, 1232).—Measurement of the dipole moments of *p*-substituted derivatives of  $\text{NPhMe}_2$  and the corresponding substitution products of  $\text{C}_6\text{H}_6$  has shown that the effect of a substituent on the reactivity of a functional group ( $\text{NMe}_2$ ) runs parallel with its contribution to the dipole moment of the compound. It is suggested in explanation that the group moment of a substituent is the result chiefly of a considerable dissymmetry in the distribution

of charge about the point of attachment to the ring, and that the reactivity of a functional group is determined by the state of the nuclear C to which it is attached, this in its turn being a function of the states of the other C atoms of the ring. R. C.

**Index of refraction of HCl from 1 to 10  $\mu$ .** R. ROLLEFSON and A. H. ROLLEFSON (J. Chem. Physics, 1935, 3, 434).—Dispersion measurements over 1–10  $\mu$  show that the dispersion curve is matched best by using the vals.  $1.00 \times 10^{-10}$  and  $1.18 \times 10^{-18}$  e.s.u. for the effective charge of the rotator-vibrator and the electric moment of the rotator, respectively.

N. M. B.  
**Double refraction of chitin tendons.** J. M. DIEHL and G. VAN ITERSSEN, jun. (Kolloid-Z., 1935, 73, 142–146).—When chitin is immersed in glycerol-quinoline mixtures its double refraction changes from positive to negative as  $n$  of the liquid mixture increases.

E. S. H.  
**Maximum rotations of carboxylic acids containing a phenylethyl group.**—See this vol., 70.

**Optical rotatory power of solutions in an electric field.** J. KUNZ and A. McLEAN (Nature, 1935, 136, 795–796).—Changes in optical rotatory power are observed when solutions of 2-*l*-menthyl H 3-nitrophthalate in  $C_6H_6$  or PhMe are placed in an electric field. This behaviour is distinct from the Kerr effect and is attributed to the electric moment induced in the solvent mols. by the electric field. Anomalous effects are obtained with the 2-Et ester.

L. S. T.  
**Magnetic birefringence in solutions of paramagnetic salts of rare earths.** S. W. CHINCHALKAR (Phil. Mag., 1935, [vii], 20, 856–858; cf. A., 1932, 677).—The results of Haenny (cf. *ibid.*, 909) are reduced to the same equiv. concn., and the connexion between the birefringence and the orbital moment of the ion is discussed.

N. M. B.  
**Temperature variation of the electro-optical Kerr effect of nitrobenzene at its transition point.** W. HERZOG (Z. Physik, 1935, 97, 233–241).—No discontinuity was observed at the Wolfke-Mazur transition point (cf. A., 1932, 329).

A. B. D. C.  
**Magneto-optics.** C. G. DARWIN (Proc. Roy. Soc., 1935, A, 151, 512–539).—Theoretical. A formal method suitable for the discussion of magneto-optics, irrespective of the underlying at. theory, is developed. The magneto-optic effects of material of any at. character are discussed. The formulæ are applied to test the experimental results of the Kerr effect.

L. L. B.  
**Discussion of experiments on the time-lag in the magneto-optic effect.** G. F. HULL (Physical Rev., 1934, [ii], 45, 738).

L. S. T.  
**Affinity in Hume-Rothery phases.** U. DEHLINGER (Metallwirts., 1935, 14, 145–149; Chem. Zentr., 1935, i, 2130).—Theoretical. The affinity in Hume-Rothery phases is explained by the attribution of a definite lattice linking to each valency electron. The energy levels are calc. from Bloch's wave theory of metallic electrons, where  $\lambda$  must be an integral sub-multiple of the lattice spacing. Highly

symmetrical lattices, for which there are insufficient electrons for twofold occupation of each linking, can be formed only at high temp., when free rotation within the lattice is possible. J. S. A.

**Planar configuration of quadricovalent nickel, palladium, and platinum: dithio-oxalate derivatives.** E. G. COX, W. WARDLAW, and K. C. WEBSTER (J.C.S., 1935, 1475–1480).—The three salts  $K_2[M^H(COS)_4]$  ( $M^H=Ni, Pt, \text{ and } Pd$ ) have been prepared, and are shown to be isomorphous. The four valencies to the metal atom are co-planar in each case. The crystals are monoclinic; 4 mols. in unit cell; space-group  $A2/a$  ( $C_{2h}^0$ ). The principal interat. distances were Ni-S 2.30, Pd-S 2.44, Pt-S 2.44, C-S 1.83, K-O 2.57–3.0, K-S 3.73 (min.) Å. Crystallographic and X-ray data are given. H. J. E.

**Electronic structures of molecules. XIV. Linear triatomic molecules, especially carbon dioxide.** R. S. MULLIKEN (J. Chem. Physics, 1935, 3, 720–739; cf. A., 1935, 1188).—Electron configurations of a no. of triat. linear mols. are given, and ionisation potentials of  $CO_2$ ,  $CS_2$ ,  $N_2O$ , and  $HgCl_2$  are interpreted in relation to these. An explanation of the triangular form of  $NO_2$  is given. F. L. U.

**"Most probable" locations of the valency electrons in the carbon atom.** W. P. DAVEY (Physical Rev., 1934, [ii], 45, 763).—Theoretical.

L. S. T.  
**Deuterium. II. III.** D. MACGILLAVRY (Chem. Weekblad, 1935, 32, 650–655, 679–684; cf. A., 1935, 1185).—A further review.

**Deuterium and X-ray absorption.** D. K. FROMAN (Physical Rev., 1934, [ii], 45, 731).—The presence of  $D_2$  in ordinary  $H_2$  does not account for the peculiarity in its absorption of X-rays in the range 0.5–0.6 Å.

L. S. T.  
**Sputtering of metals by incidence of slow ions and measurement of sputtering swelling values.** H. LÜDER (Z. Physik, 1935, 97, 158–170).—Degree of sputtering by positive ions of energies of 40 volts and upwards was determined from the resistance of the sputtered wire. Swelling val. or min. energy of sputtering was determined for  $A^+$  ions incident on Ni, Cu, Fe, and W, for  $K^+$ ,  $Cs^+$ , and  $Li^+$  incident on W, and for  $Cs^+$  on Cu.

A. B. D. C.  
**Molecular ions from heated salts of some of the alkali metals.** L. L. BARNES (Physical Rev., 1934, [ii], 45, 751).—At temp. just < m.p., KCl give an ion of mass  $K_2Cl^+$ , and  $K_2SO_4$  one of mass  $K_3SO_4^+$ . Salts of other alkali metals give similar ions.

L. S. T.  
**Periodic system of energy coefficients.** A. E. FERSMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 173–176; cf. A., 1935, 1305).—The *VEK* vals. (energy of unit valency of an ion) for a large no. of ions are tabulated according to the periodic classification, and correlated. J. W. S.

**Solution of variation problems in quantum mechanics.** A. SCHUCHOVICKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 161–164).—Mathematical.

J. W. S.



**Temperatures and heat effects of genotypic transformation of alkali salts of long-chain fatty acids.** P. A. THIESSEN and J. VON KLENOK [with H. GOCKOWIAK and J. STAUFF] (*Z. physikal. Chem.*, 1935, 174, 335—358; cf. *A.*, 1933, 1004, 1011).—The temp. at which the heat effect,  $Q$ , corresponding with genotypic transformation sets in has been determined. The dielectric const.-temp. curve is discontinuous at the transformation point. For a single crystal of Na stearate on heating up through  $49^\circ$  the double refraction undergoes an abrupt irreversible change in sign.  $Q$  increases with the chain length and also runs parallel with the radius of the cation. Above the transformation temp. the sp. heat rises discontinuously. R. C.

**Kinetic interpretation of internal effects.** V. NJEGOVAN (*Z. Physik*, 1935, 97, 390—394).—Rotation and vibration of elastic mol. of an ideal gas effectively decrease the radius of the mol. and so liberate energy. This hypothesis is applied to thermal dissociation, ionisation, and gas degeneracy.

A. B. D. C.

**Movement of a heavy drop in the acoustic field.** S. V. GORBATSHEV and A. B. SEVERNY (*Kolloid-Z.*, 1935, 73, 146—154).—Theoretical.

E. S. H.

**Relation between internuclear distances and force constants of molecules and its application to polyatomic molecules.** R. M. BADGER (*J. Chem. Physics*, 1935, 3, 710—714; cf. *A.*, 1934, 477).—The relation between internuclear distances and force consts. found for diat. mols. persists in polyat. mols. This fact provides a method whereby internuclear distances in the latter can be calc. from vibrational data alone.

F. L. U.

**Mean free paths of molecules and wave mechanics.** J. A. EEDRIDGE (*Proc. Iowa Acad. Sci.*, 1934, 41, 257).—Direct determinations of the mean free path of  $H_2$ ,  $N_2$ , and  $O_2$  yield vals. for the effective cross-section of the mol. which are 4—5 times those based on viscosity data; theoretical factor should be  $\approx 2$ .

CH. ABS. (e)

**Electrostatic interaction in atoms.** R. F. BACHER and S. GOUDSMIT (*Physical Rev.*, 1934, [ii], 45, 767).

L. S. T.

**Vibrations and internal rotation of a chain of four atoms.** L. S. KASSEL and C. W. MONTGOMERY (*Physical Rev.*, 1934, [ii], 45, 766).—The dynamical behaviour of a chain of four equal atoms with tetrahedral bond angles has been studied in an attempt to classify the infra-red and Raman spectra of the higher hydrocarbons. Extra Raman lines observed by Kohlrausch and the tendency of long-chain hydrocarbons to exist in a linear form are explained.

L. S. T.

**Hydrocarbon linking additivity.** V. DEITZ (*J. Chem. Physics*, 1935, 3, 436).—Corrections previously proposed for obtaining linking additivity (cf. *A.*, 1935, 284) are tested with the help of experimental data (cf. Kistiakowsky, *ibid.*, 825) on the heats of hydrogenation of some olefines.

N. M. B.

**Fundamental frequencies of the cyanogen molecule.** S. C. WOO, T. K. LIU, and T. C. CHU

(*J. Chinese Chem. Soc.*, 1935, 3, 301—307).—The fundamental frequencies assigned by Kistiakowski *et al.* (*A.*, 1934, 30, 145) are criticised. The restoring force consts. of linkings in the mols. HCN, ClCN, BrCN,  $(CN)_2$ , and  $C_2H_2$  have been calc. from the fundamental frequencies of the valency vibrations. All the cyanides have the same type of CN linking. The frequencies have been re-assigned on the basis of the above calculations, the selection rule for infra-red and Raman spectra, and heats of formation of linkings.

A. J. M.

**Quantum-mechanical discussion of orientation of substituents in aromatic molecules.** G. W. WHELAND and L. PAULING (*J. Amer. Chem. Soc.*, 1935, 57, 2086—2095).—Using the method of mol. orbitals, the charge distribution in aromatic mols. undergoing substitution is discussed quantitatively, taking into consideration the inductive effect, the resonance effect, and the polarising effect of the attacking group. With reasonable vals. for the parameters involved, the calc. charge distributions for several aromatic compounds are in qual. agreement with experimental results regarding position and rate of substitution.

E. S. H.

**Effect of surface tension on flow from Poncelet apertures.** H. LAUFFER (*Forsch. Ing.*, 1934, 5, A, 266—274; *Chem. Zentr.*, 1935, i, 1987).—Theoretical. Contrary to accepted views, the flow from small apertures at low pressure is augmented by the influence of surface tension.

J. S. A.

**Aluminium alkoxides and their parachors.** R. A. ROBINSON and D. A. PEAK (*J. Physical Chem.*, 1935, 39, 1125—1133).—Surface tension and density data and parachor vals. are given for *Al acetylacetonate* (I), m.p.  $192^\circ$ , *aluminoethyl acetoacetate* (II), m.p.  $78-79^\circ$ , *Al diethylmalonate* (III), m.p.  $95-96^\circ$ , *Cr acetylacetonate*, m.p.  $212^\circ$ ,  $[Al(OEt)_3]_4$ , m.p.  $146-151^\circ$ ,  $[Al(OPr^a)_3]_4$ , m.p.  $106-108^\circ$ ,  $[Al(OPr^b)_3]_4$ , m.p.  $118^\circ$ ,  $[Al(OBu^a)_3]_4$ , m.p.  $102-106^\circ$ ,  $[Al(OBu^b)_3]_4$ , m.p.  $208-210^\circ$ , sec.- $[Al(OBu)_3]_4$ , b.p.  $174-176^\circ/5$  mm., *Sb(OEt)\_3*, b.p.  $99.5^\circ/13$  mm. Assuming singlet linkings in (I), (II), and (III), the mean parachor of Al is 39.5. The parachor deficiencies which occur in the alkoxides may be accounted for by an 8-membered ring in which the O are attached to Al by singlet linkings.

R. S.

**The parachor as a function of density and molecular volume of a substance in its different chemical states.** I. R. MOROZOV (*J. Gen. Chem. Russ.*, 1935, 5, 1020—1023).—The parachor is calc. from  $P = (V + V_1)(2dV_1/V)^{1/2}$ , where  $V$  is the sum of the vols. of the constituent atoms,  $V_1$  is the mol. vol. of the substance, and  $d$  is the density.

R. T.

**Investigations on diffusion of cathode rays by means of the cloud chamber.** I. GUNTHER (*Ann. Physik*, 1935, [v], 24, 377—392).—The directional distribution of cathode rays after passing various thickness of matter was particularly studied. The results suggest that the passage of rays through matter is a combination of absorption and diffusion processes.

J. W. S.

**Absorption of short-wave-length X-rays.** W. V. MAYNEORD and J. E. ROBERTS (*Nature*, 1935, 136,



793).—For elements up to Ca the mean absorption per electron for X-rays of  $\lambda$  59 X is in agreement with the Klein-Nishina formula. The photo-electric absorption coeff. per electron varies according to (at. no.)<sup>3</sup>.  
L. S. T.

Widths of X-ray bands in solids. J. REHNER, jun. (Physical Rev., 1934, [ii], 45, 735).—Theoretical (cf. A., 1934, 576).  
L. S. T.

X-Ray and magnetic measurements of KCl powders in relation to lattice distortion and photochemical coloration. G. W. BRINDLEY, F. W. SPIERS, and F. E. HOARE (Phil. Mag., 1935, [vii], 20, 1041—1054).—Comparisons of high-order spectra of finely-ground and pptd. KCl show that the greater photo-coloration of the former, which has been attributed to flaws and cracks (Smekal), is not due to lattice distortion. The question of extinction is considered in detail. Grinding reduces the diamagnetic susceptibility of KCl only from  $39.3 \times 10^{-6}$  to  $38.8 \times 10^{-6}$ , confirming the above conclusion.  
T. G. P.

Examination of electro-deposited nickel coatings by X-ray diffraction. W. A. WOOD (Phil. Mag., 1935, [vii], 20, 964—971).—Specimens of electro-deposited Ni differing in hardness and initial brightness have been examined. Brightness is associated with the selective orientation of the metal grains, and hardness with the degree of diffusion of the X-ray diffraction spectra. The grain size has been estimated from the broadening of the spectral lines for a series of deposits of known hardness.  
T. G. P.

X-Ray examination of lattice distortion in copper and nickel powders. G. W. BRINDLEY and F. W. SPIERS (Phil. Mag., 1935, [vii], 20, 882—893; cf. A., 1935, 150).—The scattering factors for Cu  $K\alpha$  radiation of finely filed Cu and Ni are < those of chemically prepared powders. The diminution increases with the order of the spectrum. The average displacements due to lattice distortion caused by filing are 0.106 Å. for Cu and 0.083 Å. for Ni, and are explicable if distortion is a random displacement of atoms from the points of the undistorted lattice. Scattering factors for the (200) reflexions indicate, however, that distortion is not entirely random.  
T. G. P.

Discontinuous variation in the diffusion of X-rays with the angle of diffusion. J. LAVAL (Compt. rend., 1935, 201, 889—891).—For a beam of X-rays of  $\lambda$  incident at an angle  $\phi$  on Al, Cr, Ni, In, Mo, Ag, Sb, Pt, and Au the diffusion of the rays varies discontinuously with  $\sin \phi/2$ . For similarly placed discontinuities  $\lambda \sin \phi/2$  is a linear function of at. no.  
R. S. B.

Effect of additions of cadmium on growth of zinc crystals. E. P. T. TYNDALL (Proc. Iowa Acad. Sci., 1934, 41, 252).—In Zn containing several tenths of 1% of Cd, mosaic formation was largely prevented (cf. Hoyem and Tyndall, A., 1929, 246).  
CH. ABS. (e)

Relation between the mechanical strain and the intensity of X-rays reflected by a quartz plate. I. E. FUKUSHIMA (Bull. Inst. Phys. Chem.

Res. Japan, 1935, 14, 1105—1112).—Intensities of X-rays reflected from a strained quartz plate have been measured. The distribution of intensity depends on the distribution of strain.  
R. S.

Relation between amorphous and crystalline scattering and its application to crystal analysis. N. S. GINGRICH and B. E. WARREN (Physical Rev., 1934, [ii], 45, 762—763).—An expression for the average radial distribution of atoms about any one atom, expressed as a series over the no. of lines in the powder pattern, is given. Interat. distances can be obtained directly without determining a complete structure.  
L. S. T.

Structure of layer lattices. W. LOTMAR (Z. Krist., 1935, 91, 187—191).—To explain the observed broadening of (*hkl*) reflexions in layer lattices as compared with the (*hko*) and (*ool*), a particular distortion is suggested which leaves the (*hko*) planes undisturbed.  
B. W. R.

Alternating axes and symmetry symbols in crystallography. J. D. H. DONNAY (J. Washington Acad. Sci., 1935, 25, 476—488).—A discussion of the use and nomenclature of the alternating axis, regarded as a single symmetry operation, in point- and space-group theory. The international point-group symbols are tabulated with the other notations in use.  
B. W. R.

Advantages of employing four-index notation for crystals of rhombohedral symmetry. H. UNGEMACH (Z. Krist., 1935, 91, 97—113).—The reasons for preferring the Bravais to the Miller system for crystallographic calculation and description are given.  
B. W. R.

Growth of metal crystals in metal vapour. IV. M. STRAUMANIS (Z. physikal. Chem., 1935, B, 30, 132—138; cf. A., 1934, 946).—Experiments have been made on the sublimation of Te and Se in H<sub>2</sub> and the equilibrium crystal forms determined. The results do not wholly agree with Stranski's theory of homopolar crystal growth.  
R. C.

X-Ray diffraction in solutions. J. A. PRINS and R. FONTEYNE (Physica, 1935, 2, 1016—1028; cf. A., 1935, 931).—"Superarrangement" of the cations is present with ThCl<sub>4</sub>, UO<sub>2</sub>Cl<sub>2</sub>, La(NO<sub>3</sub>)<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, ZnCl<sub>2</sub>, ZnI<sub>2</sub>, and NiCl<sub>2</sub>; it is probable with the multivalent anions of Na<sub>2</sub>WO<sub>4</sub>, Na<sub>2</sub>MoO<sub>4</sub>, H<sub>2</sub>PtCl<sub>6</sub>, HIO<sub>4</sub>, HClO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>. No such arrangement is found in univalent cations. HIO<sub>3</sub>; CdI<sub>2</sub> in H<sub>2</sub>O or EtOH; CdCl<sub>2</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, Na<sub>3</sub>(PW<sub>12</sub>O<sub>40</sub>), Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and Zr(NO<sub>3</sub>)<sub>4</sub> in H<sub>2</sub>O exhibit only gaseous distribution. Superarrangement is related to solvation. *d*<sup>18</sup> and have been determined for *M*/15 to *M*/85 aq. Th(NO<sub>3</sub>)<sub>4</sub>.  
T. G. P.

Cybotactic group structure of isopentane near the critical point. C. A. BENZ (Proc. Iowa Acad. Sci., 1934, 41, 249—250; cf. A., 1934, 1297).—X-Ray diffraction intensity curves were measured at various points on the isothermal diagram. There is no sharp transition as the gaseous state is approached. Cybotactic groups appear in regions commonly known as gas if the sp. vol. is kept near that of a liquid.  
CH. ABS. (e)

**Dimorphism of trinitroresorcinol, bromobenzhydrazine, and benzaldehyde-*p*-nitrophenylhydrazine.** R. FISCHER and A. KOFLER (Mikrochem., 1935, 19, 38—46).—The following stable (*s*) and metastable (*ms*) forms are obtained on vac. sublimation. Trinitroresorcinol: (*s*), m.p. 177°, monoclinic prisms of high optic axial angle; (*ms*), m.p. 165.5°, trigonal prisms, uniaxial and optically negative. "Bromobenzhydrazine": (*s*), m.p. 165°, rectangular monoclinic prisms with high double refraction; (*ms*) monoclinic plates, m.p. 159°. Benzaldehyde-*p*-nitrophenylhydrazine: (*s*), stout monoclinic rods, m.p. 261°; (*ms*), thin ill-formed monoclinic crystals, m.p. 234—236°. J. S. A.

**Silicon disulphide, a fibrous inorganic compound with chain molecules.** E. ZINTL and K. LOOSEN (Z. physikal. Chem., 1935, 174, 301—311).—In respect of the character of the constituent units of its lattice  $\text{SiS}_2$  is intermediate between the mols. of the mol. lattice of  $\text{CO}_2$  and the three-dimensional macromols. of  $\text{SiO}_2$  in quartz. It forms on sublimation flexible fibres, which consist of one-dimensional macromols. oriented parallel to each other. The crystals are rhombic and the probable space-group is  $V_{20}^a$ . R. C.

**Orthonitric acid,  $\text{H}_3\text{NO}_4$ .** E. ZINTL and W. HAUCKE (Z. physikal. Chem., 1935, 174, 312—316).—Comparison of the powder diagram of  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  with those of the five low-pressure modifications of  $\text{NH}_4\text{NO}_3$  and that of  $\text{H}_3\text{PO}_4$  makes it appear not improbable that  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  is orthonitric acid. R. C.

**Crystal growth of the alkali halides.** Z. GYULAI (Z. Krist., 1935, 91, 142—153).—Crystallisation from conc. solution, vapour, and melt of NaCl and KCl is studied microscopically, and the chief directions of growth from the nucleus are described. B. W. R.

**Crystal structure of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .** C. D. WEST (Z. Krist., 1935, 91, 181—186).—This typical member of the isomorphous orthorhombic pentammines  $[\text{R}(\text{NH}_3)_5\text{X}]\text{Y}_2$  has  $a_0$  13.32,  $b_0$  6.71,  $c_0$  10.42 Å., space-group  $V_{16}^b$ . The 16 necessary parameters are determined, and the structure is compared with that of the hexammines  $\text{R}(\text{NH}_3)_6\text{Y}_2$ . B. W. R.

**Structure of green basic cobalt bromide.** W. FEITKNECHT and W. LOTMAR (Z. Krist., 1935, 91, 136—141).—The three isomorphous basic compounds, basic Zn bromide III, green Co bromide and iodide, are investigated by X-rays. The existence of regular layers of pure hydroxide groups at intervals of 8.2 Å. is established; the intervening material is randomly arranged, and its origin and relations are discussed. B. W. R.

**Crystal structure of nickel sulphate heptahydrate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .** C. A. BEEVERS and C. M. SCHWARTZ (Z. Krist., 1935, 91, 157—169).—The at. parameters of the orthorhombic variety have been determined, using Patterson's method for the location of Ni and S and a double Fourier analysis for the remaining parameters. 6  $\text{H}_2\text{O}$  surround Ni forming an almost octahedral group. The structure is compared with that of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . B. W. R.

**Crystal structure of potassium persulphate,  $\text{K}_2\text{S}_2\text{O}_8$ .** R. C. KEEN (Z. Krist., 1935, 91, 129—135).—The cell is triclinic,  $a_0$  5.10,  $b_0$  6.83,  $c_0$  5.40 Å.,  $\alpha$  106° 54',  $\beta$  90° 10',  $\gamma$  102° 35', space-group  $C_1^1$ . At. parameters are found from intensity measurements. B. W. R.

**Crystallography of the copper-pyridine-saccharin complex.** J. BEINTEMA, P. TERPSTRA, and J. J. DE VRIEZE (Pharm. Weekblad, 1935, 72, 1287—1294).— $\text{Cu}(\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}, \text{C}_6\text{H}_5\text{O}_3\text{NS})_2$  (A., 1933, 732) forms rhombic bipyramidal crystals with 4 mols. in the unit cell of dimensions  $a$  9.50,  $b$  21.57,  $c$  13.16 Å., space-group  $V_{16}^a$ . Full crystallographic data are given and the orientation of the constituent mols. is discussed. D. R. D.

**Structure of natural wollastonite.** M. BARNICK (Naturwiss., 1935, 23, 770—771).—X-Ray methods give monoclinic symmetry for wollastonite ( $a$  15.33,  $b$  7.28,  $c$  7.07 Å.;  $\alpha=\gamma=90^\circ$ ,  $\beta$  95° 24' 30"). The unit cell contains 12  $(\text{CaO}, \text{SiO}_2)$ . It does not possess a chain structure, but has  $\text{Si}_3\text{O}_9$  rings. A. J. M.

**Crystal structure of hexagonal silver iodide.** L. HELMHOLTZ (J. Chem. Physics, 1935, 3, 740—747).—Hexagonal AgI has been examined by powder, Laue, and oscillation methods. At  $-180^\circ$  the structure is essentially that of wurtzite with the ideal parameter val., whilst at room temp. the Ag atoms appear to be distributed at random among four positions tetrahedrally surrounding the ideal position. On the basis of these structures an explanation of some of the peculiarities of AgI is offered. F. L. U.

**Crystal structure of silver azide.** M. BASSIERE (Compt. rend., 1935, 201, 735—737).—The crystals are orthorhombic ( $a$  5.58,  $b$  5.93,  $c$  6.04, all  $\pm 0.03$  Å.; 4 mols. in unit cell; space-group  $V_{20}^a$ ). The crystal is built up from Ag and  $\text{N}_3$  ions. The  $\text{N}_3$  group is linear, the N—N distance being  $1.18 \pm 0.04$  Å., as in other azides. H. J. E.

**Molecular structure of di-iodoethane. Iodine bond resonance and molecular structure of di-iodoethylene. Molecular packing in their crystal lattices.** H. P. KLUG (J. Chem. Physics, 1935, 3, 747—753).—Distances between the I atoms of  $(\text{CH}_2\text{I})_2$  and of *s-trans*- $\text{C}_2\text{H}_2\text{I}_2$  in mol. models predicted theoretically agree well with these distances within the crystal cells as given by X-ray data (A., 1935, 1195). These models, in conjunction with Mack's concept of the at. domain radius in crystals, lead to a picture of mol. packing which agrees with observed physical properties of the crystals. F. L. U.

**Molecular map of resorcinol.** J. M. ROBERTSON (Nature, 1935, 136, 755—756).—The electron density map obtained by a quant. X-ray analysis of resorcinol (I) is reproduced. The complete structure is described. OH belonging to adjacent (I) mols. approach to within 2.66 Å., indicating the existence of a strong (OH) linking or secondary valency force between mols. L. S. T.

**Crystal structure of pyrene.** J. DHAR and A. C. GUHA (Z. Krist., 1935, 91, 123—128).—Pyrene is monoclinic prismatic,  $a_0$  13.74,  $b_0$  9.22,  $c_0$  8.45 Å.,  $\beta$  102½°, 4 mols. in cell, space-group  $C_{2h}$ . Tentative mol. orientations are suggested. B. W. R.

**An orthorhombic crystalline modification of 1:2:5:6-dibenzanthracene.** K. S. KRISHNAN and S. BANERJEE (*Z. Krist.*, 1935, **91**, 170—172).—This substance is normally monoclinic; an orthorhombic bipyramidal form occurs occasionally when cryst. from EtOAc. M.p. and *d* are nearly the same as for the normal form. B. W. R.

**Magnetic anisotropy and crystal structure of 1:2:5:6-dibenzanthracene.** K. S. KRISHNAN and S. BANERJEE (*Z. Krist.*, 1935, **91**, 173—180).—Measurement of the anisotropy and the absolute susceptibility for very small crystals (0.02 mg.) is described. Measurements on both monoclinic and orthorhombic dibenzanthracene enable the directions of the lengths of the mols. and the angles of tilt of the mol. planes to be determined. B. W. R.

**Thread diagram for polyvinyl alcohol.** F. HALLE and W. HOFMANN (*Naturwiss.*, 1935, **23**, 770).—Polyvinyl alcohol gives a typical thread diagram similar to that of a natural fibre; identity period in the direction of the thread axis is  $2.57 \pm 0.02$  Å. It is composed of crystallites which readily arrange themselves parallel on stretching, especially when warmed. A. J. M.

**X-Ray structure investigations on elastic tissue with special reference to extension and shrinkage.** H. KOLPAK (*Kolloid-Z.*, 1935, **73**, 129—142).—The results previously reported (*A.*, 1934, 244) are confirmed and extended, and discussed in relation to current theories of valency chain structures. E. S. H.

**Electron diffraction by gases.** L. R. MAXWELL, S. B. HENDRICKS, and V. M. MOSLEY (*J. Chem. Physics*, 1935, **3**, 699—709; cf. *A.*, 1934, 17, 835).—The C—O—C valency angle in 4:4'-di-iododiphenyl ether has been found to be  $118 \pm 3^\circ$  by the electron diffraction method. This is  $>$  the O valency angle for simpler mols. such as  $F_2O$ ,  $Cl_2O$ , and  $Me_2O$ . By the same method P and As mols. have been shown to have regular tetrahedral structure, the at. separations being respectively 2.21 and 2.44 Å. F. L. U.

**Electron diffraction pattern from the natural (111) face of diamond.** R. BEECHING (*Phil. Mag.*, 1935, [vii], **20**, 841—855).—Intensity measurements on the pattern were made, relative intensities of the main spots were determined, and tolerances in the Bragg angles were compared with the widths of the corresponding Kikuchi lines (cf. *A.*, 1935, 570). The inner potential was measured, and various qual. observations were made. A case where a spot has been partly suppressed by Kikuchi lines is recorded. N. M. B.

**"Extra" electron diffraction rings.** (A) L. H. GERMER. (B) G. I. FINCH (*Nature*, 1935, **136**, 832).—(A) Calculations show that the exit face theory (*A.*, 1935, 287) of the origin of these rings is untenable.

(B) Germer's calculations agree with the view that the "extra" rings are due to surface contamination (*ibid.*, 1452). L. S. T.

**Electron diffraction in rubber films.** K. I. KRILOV (*Physikal. Z. Sovietunion*, 1935, **8**, 136—152).—The diffraction patterns from crepe rubber

films are rings. Stretched films gave points generally explicable on Susich's X-ray structure (*A.*, 1928, 1186), but certain modifications are necessary. Unstretched chloroprene gave spots of an orthorhombic unit: *a*, 10.93, *b* 8.23 Å. (for crepe *a* 12.23, *b* 8.3 Å.). No spots were obtained with Na-butadiene rubber. T. G. P.

**Permanent polarisation of Rochelle salt.** H. MÜLLER (*Physical Rev.*, 1934, [ii], **45**, 736; cf. *A.*, 1935, 288). L. S. T.

**Dielectric properties of Rochelle salt.** J. E. FORBES and H. MÜLLER (*Physical Rev.*, 1934, [ii], **45**, 736—737; cf. *A.*, 1935, 228). L. S. T.

**Magnetisation of imperfect crystals.** F. BRATER (*Physical Rev.*, 1934, [ii], **45**, 742; cf. *A.*, 1934, 945). L. S. T.

**Dependence of internal friction on magnetisation in iron.** W. T. COOKE (*Physical Rev.*, 1934, [ii], **45**, 742). L. S. T.

**Approach to the theoretical magnetisation curve.** T. D. YENSEN (*Physical Rev.*, 1934, [ii], **45**, 743).—The curves reproduced for Fe, Fe-Si and Fe-Ni alloys show that the approach to the theoretical curves, based on the Langevin-Weiss theory, depends not only on lattice orientation, but also on purity of material. L. S. T.

**Separation of magnetic viscosity and eddy-current lag.** A. V. MITKEVITSCH (*Compt. rend. Acad. Sci. U.S.S.R.*, 1935, **3**, 209—211).—Eddy-current lags can be detected through the sp. influence of previous changes in magnetic induction. C. W. G.

**Rotatory power of quartz for rays perpendicular to the optic axis and its dispersion between 2537 and 5780 Å.** G. BRUHAT and L. WEIL (*Compt. rend.*, 1935, **201**, 887—889).—The ratio of the rotatory powers of quartz for rays perpendicular and parallel to the optic axis is (mean)  $0.54 \pm 0.01$ . The dispersion is the same for both rays. R. S. B.

**Quantum mechanical investigation of the cohesive forces of metallic copper.** K. FUCHS (*Proc. Roy. Soc.*, 1935, **A**, 151, 585—602).—The wave functions and energies of the 4s electrons of Cu have been calc. by a method analogous to that used by Wigner and Seitz for Na (*A.*, 1933, 660). The right order of magnitude is obtained for the lattice const. and for the heat of vaporisation, but to obtain the correct compressibility, the interaction between the ions in the lattice due to the overlapping of the closed shells must be considered. For Cu, the face-centred structure will have lower energy than the body-centred, but for Na the two structures have almost equal energies. Thus the calculations show why Cu has a close-packed structure, but fail to show why Na should have one cubic structure rather than the other. L. L. B.

**Effect of photochemical colouring on the extension and strength limits of single crystals of rock-salt.** M. N. PODASCHEVSKI (*Physikal. Z. Sovietunion*, 1935, **8**, 81—92).—The extension and strength limits of single NaCl crystals are increased by photochemical coloration, the result being the

same whether the coloration is produced by X-rays or ultra-violet light. A. J. M.

**Plastic properties of silver chloride and sodium chloride single crystals.** A. V. STEPANOV (Physikal. Z. Sovietunion, 1935, 8, 25—40).—The plastic properties of single crystals of AgCl and NaCl are compared to show that they are connected with the polarisation effect of the lattice. Single crystals of AgCl show a high degree of plasticity and metallic properties in general. AgCl which has been exposed to light is not so plastic. The elastic limit along the cubic axis of a crystal tempered at 350° was 70 g. per sq. mm. Deformation on extension is similar to that of a metal belonging to the cubic system. The elastic limits for crystals of AgCl and NaCl are similar. The deformation work for NaCl is > for AgCl. At room temp. AgCl is more plastic than NaCl. A. J. M.

**Tension coefficient of [electrical] resistance of the single hexagonal crystals, zinc and cadmium.** M. ALLEN (Physical Rev., 1934, [ii], 45, 757). L. S. T.

**Allotropy of calcium.** M. C. NEUBERGER (Z. Elektrochem., 1935, 41, 790).—Published work is considered. E. S. H.

**Thermodynamics of stationary systems. I. The thermo-element. II. The diffusion element.** B. BRUZZ (Proc. Roy. Soc., 1935, A, 151, 640—651, 651—665).—I. A quant. application of the first and second laws of thermodynamics to stationary systems is connected with an introduction of certain arbitrary assumptions, of which two are distinguished. The first is the "non-interaction" assumption of Kelvin, leading to the well-known relations connecting the Seebeck, Peltier, and Thomson coeffs. The second postulates the existence of a const. ratio between the Joule and the polarisation effects, and leads to a new relationship between the Seebeck coeff. and the thermal and electrical conductivities of the material.

II. The above treatment of the thermo-element is extended to the problem of the diffusion element, and it is shown that a close correspondence exists between thermo- and diffusion element. The problem of the diffusion element reduces to a knowledge of the diffusion and electrical conductivities. L. L. B.

**Influence of a magnetic field on the high-frequency conductivity of an ionised medium.** E. V. APPLETON and D. B. BOOHARIWALLA (Proc. Physical Soc., 1935, 47, 1074—1084; cf. *ibid.*, 1932, 44, 246).—The relation between the transverse high-frequency conductivity and the pressure of ionised air under the influence of an imposed magnetic field was investigated. The pressure for max. conductivity varies with field intensity. The relation of results to ionospheric conductivity is discussed. N. M. B.

**Change in resistance of bismuth single crystals at the m.p.** J. H. SCHROEDER (Proc. Iowa Acad. Sci., 1934, 41, 254).—Measurements of resistance for various crystal orientations are recorded up to temp. > the m.p. The change from solid to liquid did not occur suddenly at the m.p., but began 1.5° < and continued 1.5° > m.p. CH. ABS. (e)

**Change in resistance of single crystals of bismuth in a magnetic field at low temperatures.** W. J. DE HAAS, J. W. BLOM, and L. SCHUBNIKOV (Physica, 1935, 2, 907—914; cf. A., 1930, 1102, 1353).—The influence of magnetic fields (4000—22,000 gauss) on the resistance of Bi single crystals is greater at 1.35° and 4.22° abs. than at 14.15° abs.

T. G. P.  
**Magneto-resistance of bismuth films at low temperature.** C. T. LANE (Physical Rev., 1934, [ii], 45, 733—744).—The magneto-resistance of films 0.1—4  $\mu$  thick has been measured at -180° and 20°. There is a change in direction of the  $[\Delta R_{-180^\circ}/\Delta R_{20^\circ}]$ -thickness curve at a thickness < 1  $\mu$ , and the magneto-resistance approaches temp. independence as the film thickness approaches zero. L. S. T.

**Resistance of single crystals of gallium in a magnetic field. III.** W. J. DE HAAS and J. W. BLOM (Physica, 1935, 2, 952—958; cf. A., 1934, 588).—Change of resistance of single crystals of Ga with the pseudo-tetragonal axis parallel to the length of the wire in a magnetic field perpendicular to the wire has been measured at liquid He temp. At 1.35° and 4.22° abs. the influence of the magnetic field is independent of temp., but > at liquid H<sub>2</sub> temp. T. G. P.

**Electrical resistance of tantalum wires charged with hydrogen.** A. SIEVERTS and H. BRUNING (Z. physikal. Chem., 1935, 174, 365—369).—For H. pressures,  $p$ , up to  $\sim 1$  atm., the amount sorbed by Ta at 500° and 600° is  $\propto \sqrt{p}$ ; at 400° there are deviations from this relation. The resulting increase in resistance is at 500° and 600°  $\propto \sqrt{p}$ , whilst at 400° this is approx. Comparison of these results with similar data for the system Pd-H<sub>2</sub> indicates that the sorption has not involved the formation of a new phase. R. C.

**Electrical conductance of colloidal solutions at high frequencies.** H. J. CURTIS and H. FRICKE (Physical Rev., 1935, [ii], 48, 775; cf. *ibid.*, 47, 974).—Suspensions of powdered glass and kaolin, and colloidal Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, starch, and gelatin showed a marked increase in conductance at frequencies  $\geq 16,000$  kc. per sec. The phenomenon is attributed to a form of Debye-Falkenhagen effect. N. M. B.

**Diamagnetism of the tervalent bismuth ion.** S. S. BHATNAGAR and B. S. BAHL (Current Sci., 1935, 4, 234).—The val. calc. for Bi<sup>+++</sup> is in agreement with the experimental val. (A., 1935, 1453). From Kido's work the predicted difference between the diamagnetism of Bi<sup>++++</sup> and Bi<sup>+++</sup> should be of the order of 12.87, as is obtained. W. R. A.

**Theory of dispersion of magnetic permeability in ferro-magnetic bodies.** L. LANDAU and E. LIFSCHITZ (Physikal. L. Sovietunion, 1935, 8, 153—169).—The distribution of magnetic moments in a ferromagnetic crystal is investigated. The crystal consists of elementary layers magnetised to saturation. T. G. P.

**Ionic diamagnetism in the solid state and in solution.** H. FAHLENBRACH (Ann. Physik, 1935, [v], 24, 485—488).—The results of Frivold *et al.* (A., 1935, 1197) on the susceptibility of solutions may

be explained by the work of Cabrera *et al.* (A., 1933, 766, 1002, 1233). The results of Flordahl *et al.* (A., 1935, 1197) are also discussed. A. J. M.

**Magnetic moment of the manganic ion.** L. C. JACKSON (Proc. Physical Soc., 1935, 47, 1029—1031).—The magnetic susceptibility of  $\text{Mn}^{\text{III}}$  acetylacetonate was measured for a powdered specimen in the range 292—16.9° abs. The law  $\chi(T+5.5)=\text{const.}$  is obeyed down to about 75° abs., below which the susceptibility increases more rapidly. The calc. magneton no. of the  $\text{Mn}^{+++}$  ion is 4.98, in agreement with the Bose-Stoner theory. N. M. B.

**Diamagnetic study of structure.** F. W. GRAY and J. H. CRUICKSHANK (Trans. Faraday Soc., 1935, 31, 1491—1510).—A new method of treating at. and mol. diamagnetic data is described, whereby deviations of the observed diamagnetism of mols. from that calc. from the diamagnetism of free atoms may be used to establish the modes of linking of atoms in mols. Details are worked out for  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ ,  $\cdot\text{CO}_2\text{H}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}_2$ . F. L. U.

**Effect of crystalline fields on the magnetic susceptibilities of  $\text{Sm}^{+++}$  and  $\text{Eu}^{+++}$ , and the heat capacity of  $\text{Sm}^{+++}$ .** (MISS) A. FRANK (Physical Rev., 1935, [ii], 48, 765—771; cf. A., 1932, 217).—Mathematical. The temp. variation of the paramagnetic susceptibility of  $\text{Sm}^{+++}$  is calc. on the assumption that the ion is subject to a cryst. field which can be represented by a potential expression. Eu behaves, in contrast, like the free ion even in presence of a cryst. field. The contribution to the heat capacity of  $\text{Sm}^{+++}$  at various temp. due to the excited levels is calc. Results are compared with available experimental data. N. M. B.

**Magnetic susceptibility of mixtures of oxides of the rare earths: mixtures of neodymium with praseodymium and of neodymium with samarium [oxides].** I. L. MAZZA (Atti R. Accad. Lincei, 1935, [vi], 21, 813—818).—The mixtures of the oxides were obtained by calcining the co-pptd. oxalates. In the system  $\text{Sm}_2\text{O}_3\text{--Nd}_2\text{O}_3$ , the magnetic susceptibility follows the simple additive law. In the system  $\text{Pr}_6\text{O}_{11}\text{--Nd}_2\text{O}_3$ , this could not be established, but the deviations are attributed to mutual reduction and oxidation of these oxides during the calcining. For  $\text{Nd}_2\text{O}_3$   $\kappa=3.10\times 10^{-7}$ ; for  $\text{Sm}_2\text{O}_3$ ,  $6.1\times 10^{-6}$ ; and for  $\text{Pr}_6\text{O}_{11}$ ,  $1.56\times 10^{-7}$ . D. R. D.

**Propagation of elastic waves in ice.** I. M. EWING, A. P. CRARY, and A. M. THORNE, jun. II. A. P. CRARY and M. EWING (Physical Rev., 1934, [ii], 45, 749). L. S. T.

**Propagation of sound and supersonic waves in gases.** H. L. SAXTON (Physical Rev., 1934, [ii], 45, 749).—The derivation of equations for velocity and the absorption const. is outlined. L. S. T.

**Vibrations of air and carbon dioxide in closed bulb resonators.** K. VOECKLER (Ann. Physik, 1935, [v], 24, 361—376).—The frequency of vibration is in accord with the theory of Rayleigh and Thiesen, and the damping is of the order of magnitude predicted by the theory. The damping is less in  $\text{CO}_2$

than in air and is diminished by addition of  $\text{H}_2\text{O}$  vapour. J. W. S.

**Collision excitation of intramolecular vibrations in gases and gas mixtures studied by sound dispersion measurements. III. Measurements with nitrous oxide.** A. EUCKEN and H. JAACKS (Z. physikal. Chem., 1935, B, 30, 85—112; cf. A., 1935, 155).—From determinations of the  $\lambda$  of ultrasonic waves in pure  $\text{N}_2\text{O}$  and mixtures of  $\text{N}_2\text{O}$  with foreign gases the variation of collision efficiency with temp. and pressure at  $-60^\circ$  to  $200^\circ$  and 0.3—1 atm. has been measured. The deactivation of  $\text{N}_2\text{O}$  mols. by either  $\text{N}_2\text{O}$  or  $\text{NH}_3$  mols. occurs by binary collisions. The difference between physical and chemical collision excitation of mol. vibration is discussed in relation to the collision efficiency in presence of  $\text{H}_2$ ,  $\text{D}_2$ , and He. Measurements have been made with  $\text{CO}_2$  mixed with a little  $\text{H}_2\text{O}$  to determine the effect of  $\text{H}_2\text{O}$  on the vibrational excitation of  $\text{CO}_2$ . The reported dispersion of the rotational heat of  $\text{H}_2$  in the ultrasonic region (A., 1934, 588) could not be confirmed (cf. *ibid.*, 950). R. C.

**Experiments at very low temperatures obtained by the magnetic method. II. New superconductors.** N. KURTI and F. SIMON (Proc. Roy. Soc., 1935, A, 151, 610—623; cf. A., 1935, 290).—The experimental technique of cooling down additional substances with the paramagnetic salts by applying the magnetic method (*loc. cit.*) is discussed. The measurement of the magnetic behaviour of a metal can be used to detect superconductivity, and to find the transition point and the threshold vals. Cd, Zr, and Hf become superconducting in the new temp. region, the normal transition points being  $0.54^\circ$ ,  $0.70^\circ$ , and  $0.35^\circ$  abs. Au, Cu, Bi, Mg, and Ge did not become superconducting down to  $0.05^\circ$  abs. L. L. B.

**Theory of anomalies in specific heats.** L. LANDAU (Physikal. Z. Sovietunion, 1935, 8, 113—118). T. G. P.

**Characteristic point of pure substances.** F. MICHAUD (J. Chim. phys., 1935, 32, 527—540).—The characteristic point of a solid body is defined as the point of contact of the tangent passing through the origin to the curve giving at. or mol. heat capacity as a function of abs. temp. The co-ordinates of this point define the characteristic temp. and characteristic heat capacity. The point with the same abscissa on the curve at. or mol. entropy/abs. temp. is the characteristic entropy. The characteristic point plays a part in comparisons of heat properties of solids analogous to that of the crit. point in comparisons of thermo-elastic properties of fluids. The curves  $S/\text{temp.}$  for certain substances are approx. superposable by a simple translation of the co-ordinates. The characteristic entropies of pure substances of the same atomicity are approx. equal amongst themselves, diat. and triat. mols. having twice and three times the characteristic entropy of a normal metal. A more rigorous comparison is effected by plotting log heat capacity/entropy. Such curves are a criterion of the existence of allotropic changes. Anomalies are discussed. T. G. P.



Specific heats of solid substances at higher temperatures. XX. Molecular heats of the alloys of palladium and antimony in comparison with the sum of the atomic heats of the free elements. XXI. Molecular heats of the compound  $\text{PtSb}_2$  in comparison with the sum of the atomic heats of the free composing elements. XXII. Molecular heats of the supposed binary compounds of copper and palladium. T. J. POPPEMA and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 822—833, 833—836, 836—841; cf. A., 1935, 924).—XX. The sp. heats of Sb measured under different conditions are not quite const., but no transformation point could be observed at  $414^\circ$ . At. heat data between  $100^\circ$  and  $600^\circ$  are tabulated and sp. heats of  $\text{PdSb}$ ,  $\text{PdSb}_2$ , and  $\text{Pd}_3\text{Sb}$  over a range of temp. are given. The difference between the mol. heats  $C_p$  and the sum of the at. heats  $\Sigma$  is small, but increases with rise of temp. and % of Pd. The change  $\beta\text{-Pd}_3\text{Sb} \rightarrow \alpha\text{-Pd}_3\text{Sb} - 4800 \text{ g.-cal. per g. occurs at } 950^\circ$ .

XXI. Sp. heat data are given for  $\text{PtSb}_2$  up to  $600^\circ$ .  $C_p - \Sigma$  increases from  $-8\%$  of  $C_p$  at  $200^\circ$  to  $-19\%$  at  $600^\circ$ .

XXII. Alloys of the composition  $\text{CuPd}$  and  $\text{Cu}_3\text{Pd}$  have been prepared and the sp. heats determined up to  $900^\circ$ .  $C_p - \Sigma$  is small, and it is concluded, in conjunction with X-ray measurements, that the alloys are chiefly composed of solid solutions.

R. S.

Specific heat of  $\text{Ag}_2\text{HgI}_4$  in relation to the crystal structure. J. A. A. KETELAAR (Z. physikal. Chem., 1935, B, 30, 53—60; cf. A., 1934, 1056).—The sp. heat has been measured at  $20\text{--}100^\circ$ . From  $37^\circ$  it rises anomalously, and immediately below the transition point at  $50^\circ$  reaches three times the normal val., to which it falls discontinuously at transition. The heat of transition is  $0.32$  for the homogeneous, and  $1.13 \text{ g.-cal. per g.}$  for the heterogeneous, part. The explanation of the sp. heat anomaly is that with rise in temp. even below the transition point there is increasing misplacing of the metal atoms (cf. *ibid.*, 947). An "averaged structure" may be interpreted either as a statistical distribution of the atoms over the available lattice points or as the result of repeated twinning (cf. *ibid.*, 16); X-ray examination affords no means of decision. With  $\alpha\text{-Ag}_2\text{HgI}_4$ , however, the high electrical conductivity and considerable heat of transition  $\beta \rightarrow \alpha$  decide for the former alternative.

R. C.

Specific heat of iron nitrides. S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 135—139; cf. A., 1933, 27).—The sp. heat of a series of Fe-N alloys is a max. at  $9.7\%$  N. This is discussed in relation to the Fe-N equilibrium diagram. R. S.

Evaporation as mechanical subdivision to molecules. P. V. ZOLOTAREV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 50—53).—Mathematical. The heat of evaporation of a given substance is shown to be  $\propto$  the work expended in breaking it down to its constituent mols. Formulae are derived for calculating Avogadro's const. for different types of mols., and for solids and liquids.

R. T.

Determination of fixed points at low temperatures with a hydrogen thermometer. S.

AOYAMA and E. KANDA (Bull. Chem. Soc. Japan, 1935, 10, 472—481).—Existing vals. for the b.p. of  $\text{O}_2$  and  $\text{N}_2$  and the sublimation point of  $\text{CO}_2$  are confirmed by means of the H thermometer described. Temp. are determined to within  $\pm 0.036^\circ$  at  $0^\circ$  and  $\pm 0.025^\circ$  at  $-200^\circ$ .

J. G. A. G.

Melting curve of oxygen to 170 kg. per sq. cm. J. H. C. LISMAN and W. H. KEESOM (Physica, 1935, 2, 901—906; cf. A., 1935, 1197).—Points on the melting curve of  $\text{O}_2$  have been determined up to  $167.7 \text{ kg. per sq. cm.}$  and  $56.25^\circ \text{ abs.}$  Extrapolation gives the triple point  $54.32(5)^\circ \text{ abs.}$  The density of solid  $\gamma\text{-O}_2$  at the triple point calc. from Clapeyron's equation is  $1.37(2)$ .

T. G. P.

Polarisation effects in thallous fluoride. E. HAYEK (Z. anorg. Chem., 1935, 225, 47—48).— $\text{TlF}$  has b.p.  $655^\circ \pm 10^\circ$ ,  $d_4^{20} 8.36$ . Attempts to prepare a subfluoride analogous to  $\text{Ag}_2\text{F}$  were unsuccessful.

F. L. U.

Transition points of hexachloroethane. E. H. WIEBENGA (Z. anorg. Chem., 1935, 225, 38—42).—Transition temp. of  $\text{C}_2\text{Cl}_6$ , determined both thermally and dilatometrically, are: rhombic—triclinic  $43.6^\circ$ , triclinic—cubic  $71.1^\circ$ . The transition reported at  $125^\circ$  does not occur. The rates of transformation, although slow, are finite except at the actual transition temp.

F. L. U.

New form of thermodynamic diagrams. K. PAVLOV and A. PIVOVAROVA (Chimstr., 1935, 7, 33—37).—A graphical method is described.

CH. ABS. (e)

Influence of the degree of dispersion on physico-chemical constants. IV. E. COHEN and J. J. A. BLEKKINGH (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 842—849).—Crystals of KCl of 0.1, 0.5, and 5 mm. mean cross-section have been prepared.  $d = 1.9891 \pm 0.0004$  in each case. R. S.

International Bureau of Physico-Chemical Standards. VII. Physical constants of twenty organic compounds. J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1935, 32, 501—526; cf. A., 1934, 480).—The following data for b.p./760 mm., f.p., and  $d_4^{25}$  have been determined:  $n\text{-C}_5\text{H}_{12}$   $36.10^\circ$ ,  $-129.1^\circ$ ,  $0.63114$ ;  $n\text{-C}_7\text{H}_{16}$   $98.35^\circ$ ,  $-90^\circ$ ,  $0.68785$ ;  $(\text{CH}_2\text{OH})_2$   $197.85^\circ$ ,  $-12.6^\circ$ ,  $1.11710$ ; glycerol —, —,  $1.26443$ ;  $\text{Et}_2\text{S}$   $92.10^\circ$ ,  $-103.3^\circ$ ,  $0.84102$ ;  $\text{HCO}\cdot\text{NH}_2$  —,  $2.55^\circ$ ,  $1.13756$ ;  $\text{PhF}$   $84.85^\circ$ ,  $-41.9^\circ$ ,  $1.03091$ ;  $\text{CH}_3\text{PhCl}$   $179.35^\circ$ ,  $-39.2^\circ$ ,  $1.10426$ ;  $\text{CH}_3\text{Ph}\cdot\text{OH}$   $205.45^\circ$ ,  $-15.3^\circ$ ,  $1.04927$ ; anisole  $153.80^\circ$ ,  $-37.5^\circ$ ,  $0.99858$ ;  $\text{COPhMe}$   $202.00^\circ$ ,  $19.6^\circ$ ,  $1.03236$ . The data include the relations between b.p. and pressure, coeffs. of dilatation, refractive indices, viscosity coeffs., and surface tensions. The crit. solution temp. of  $n\text{-C}_5\text{H}_{10}$  in  $\text{PhNO}_2$  is  $24.5^\circ$ . Earlier data are tabulated.

T. G. P.

Isotherms of methane between  $0^\circ$  and  $150^\circ$  and densities 19 and 53 Amagat (pressures between 20 and 80 atm.). A. MICHELS and G. W. NEDERBRAGT (Physica, 1935, 2, 1000—1002; cf. A., 1934, 837).—Isotherms of pure methane (b.p. const. to  $0.03^\circ$ ) have been determined at  $25^\circ$  intervals between  $0^\circ$  and  $150^\circ$ .

T. G. P.



**Acetylmethylcarbinol.** J. R. POUND and A. M. WILSON (J. Physical Chem., 1935, 39, 1135—1138).—The v.p. of acetoin between 0° and the b.p. (144°) has been determined and the polymerisation has been studied by measurement of *n* and *d*. Crystallographic and thermal data relating to the polymeride are given. R. S.

**Difference in vapour pressures of *ortho*- and *para*-deuterium.** F. G. BRICKWEDDE, R. B. SCOTT, and H. S. TAYLOR (J. Chem. Physics, 1935, 3, 653—660; cf. A., 1934, 1164).—The differences in v.p. of the mixture of *ortho*- and *para*-D<sub>2</sub> in equilibrium at 20.4° abs. and of the normal mixture have been determined between 15° and 20.4 abs. The speed of the uncatalysed change for normal liquid D<sub>2</sub> is about 0.001 of that for H<sub>2</sub>. F. L. U.

**Vapour pressures of neon of different isotopic compositions.** W. H. KEESOM and J. HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 810).—The differences in v.p. of Ne of five different isotopic compositions (at. wt. 20.043—21.157) have been determined. At const. temp., v.p. is a linear function of at. wt. The divergence between the theoretical and observed dependence on temp. of  $\log p_{20}/\log p_{22}$  for solid state is attributed to a difference between the potential energy of Ne<sup>20</sup> and Ne<sup>22</sup> and to variation in the zero-point energy. It is concluded, from data for the liquid state, that the sp. heat of Ne<sup>20</sup> is > that of Ne<sup>22</sup>. The triple point of Ne<sup>22</sup> is 0.134° > that of Ne<sup>20</sup> and the melting heat of Ne<sup>22</sup> is the greater by 1.18 g.-cal. per mol. R. S.

**Measurement of v.p. of mercury from absorption of resonance radiation.** H. VON HALBAN, jun. (Helv. Phys. Acta, 1934, 7, 856—875; Chem. Zentr., 1935, i, 1980).—The v.p. of Hg at -18° and -53.4° is calc. from abs. measurements of the absorption of the 2537 Å. resonance line by saturated Hg vapour at those temp. The accuracy is independent of the v.p. and unaffected by other gases at pressures below those causing broadening of the absorption line. J. S. A.

**Vapour pressure of metals and their velocity of vaporisation in a vacuum.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1935, 54, 847—852).—Formulae are derived relating the velocity of sublimation in a vac., v.p., and heat of sublimation with the at. wt., m.p., and at. vol. of the metal and the temp. The equations agree with experiment. J. W. S.

**Vapour pressure of zinc, lead, cadmium, cuprous, and silver chlorides.** D. N. TARASENKOV and P. A. KOSHMIJAKOV (J. Gen. Chem. Russ., 1935, 5, 830—835).—The v.p. have been determined at 516—728°/7.4—723 mm. for ZnCl<sub>2</sub>, at 650—942°/4.5—692 mm. for PbCl<sub>2</sub>, at 618—952°/3—722 mm. for CdCl<sub>2</sub>, at 632—1070°/3—216 mm. for Cu<sub>2</sub>Cl<sub>2</sub>, and at 882—1120°/3.7—59 mm. for AgCl. R. T.

**Variation of the volume of elements in the act of fusion.** I. L. LOSANA (Gazzetta, 1935, 65, 851—864).—The change in vol. in passing from the solid to the liquid state of the alkali metals is found to be (m.p. given in parentheses): Li (180.2°) 0.184, Na (97.7°) 0.512, K (62.1°) 1.072, Rb (38.8°) 1.472,

Cs (28.8°) 1.900 c.c. per g.-atom. These vals. were obtained by measuring the increased upthrust of a given wt. of metal at the m.p. in petroleum or vaseline oil by means of a hydrostatic balance. The vals. for Rb and Cs were confirmed by measurements of the m.p. at pressures from 1 to 135 atm. The change in vol. on fusion of elements in relation to their position in the periodic classification is discussed. O. J. W.

**Aggregative states. An empirical law.** E. I. ACHUMOV (J. Gen. Chem. Russ., 1935, 5, 843—847).—The empirical expression  $\beta(T_b - T_e) - C$ , where  $\beta$  is the coeff. of expansion of a liquid between the m.p.  $T_e$  and the b.p.  $T_b$ , and  $C$  is a const., is shown to hold for a no. of org. liquids. R. T.

**Thermal expansion of cast and rolled zinc.** H. G. JONES (Proc. Physical Soc., 1935, 47, 1117—1128).—Data tabulated and plotted for steady and continuously rising temp. show marked differences in the coeffs. for cast and rolled Zn. On rolling, the random orientation of crystals in the cast Zn is broken up, and most of the long axes are set perpendicular to the plane of rolling, but no change is produced in the vol. coeff. For small crystals the continuous expansion is small, but increases with the size of the crystals. Discontinuities in the continuous expansion are traced to the long axis. N. M. B.

**Linear thermal expansion of sodium tungstate between 20° and 600°.** J. B. AUSTIN and R. H. H. PIERCE, jun. (J. Chem. Physics, 1935, 3, 683—686; cf. A., 1933, 342).—The results, obtained by an interferometric method, show that at atm. pressure Na<sub>2</sub>WO<sub>4</sub> is trimorphous. The transition III—II occurs at 585°, and II—I at a slightly lower temp., II being stable over a very short range. F. L. U.

**Thermal stability of the lower atmosphere.** A. L. HALES (Proc. Roy. Soc., 1935, A, 151, 624—640).—Mathematical. Equations for the conduction of heat by turbulence, and for the stability of a compressible fluid when the hotter fluid is below, are deduced. Super-adiabatic lapse rates are possible in limited regions of the atm. L. L. B.

**Thermal conductivity law in moving media. Derivation of a molecular kinetic theory of thermal conductivity with an investigation of the limits of the Fourier method.** M. LANG (Ann. Physik, 1935, [v], 24, 393—408).—Theoretical. A. J. M.

**Viscosity of liquid phosphorus.** A. N. CAMPBELL and S. KATZ (J. Amer. Chem. Soc., 1935, 57, 2051—2055).—Viscosity has been determined between 20° and 140°. There is evidence of association in liquid P below 45°, but no evidence of a change of viscosity when heated P is suddenly chilled. E. S. H.

**Viscosity of liquid methane and ethylene in relation to temperature.** N. S. RUDENKO and L. V. SCHUBNIKOV (Physikal. Z. Sovietunion, 1935, 8, 179—184).—Measurements have been made between 90° and 111° abs. for CH<sub>4</sub> and between 110° and 169° abs. for C<sub>2</sub>H<sub>4</sub>. T. G. P.

**Complex viscosity.** A. GEMANT (Trans. Faraday Soc., 1935, 31, 1582—1590; cf. A., 1935, 1065).—

Maxwell's theory of the behaviour of materials exhibiting both viscosity and plasticity is generalised and developed so as to take account of mol. vibrations. The theory is applied to dielectric losses due to dipole rotation. F. L. Ü.

**Definition and correction of diffusion constants of gases.** J. KUUSINEN (Ann. Physik, 1935, [v], 24, 445—446).—The work of Trautz and Muller (A., 1935, 575) is criticised on the ground that a false interpretation of Fick's law was used. The Maxwell-Chapman method leads to results identical with those obtained by the correct use of Fick's law. A. J. M.

**Definitions of diffusion constants.** J. KUUSINEN (Ann. Physik, 1935, [v], 24, 447—456).—A general definition of the diffusion const. of a binary mixture is derived. A. J. M.

**Criticism of certain researches on the physico-chemical analysis of binary systems.** V. F. USTRKATSKINTZEV (J. Gen. Chem. Russ., 1935, 5, 892—898).—The experimental data given by Terpugov (A., 1933, 354; 1934, 1167) for the systems  $\text{Et}_2\text{O}-\text{AsCl}_3$  and  $-\text{H}_2\text{SO}_4$ , by Usanovitsch *et al.* (A., 1934, 1167) for  $\text{Et}_2\text{O}-\text{SbBr}_3$ , and by Pushin *et al.* (A., 1932, 1197) for  $\text{C}_5\text{H}_5\text{N}-\text{AcOH}$  do not confirm the conclusions reached by the authors relative to the existence of compounds. In general, systems which exhibit deviations from the additive rule for certain properties may follow it for others, and, in particular, max. and min. on curves which represent temp. coeffs. of various properties cannot be accepted as evidence of compound formation. R. T.

**Association and molecular polarisation.** V. Simultaneous formation of double and triple complexes in dipole association. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1120—1126; cf. A., 1935, 927).—The equilibrium consts. for double and triple dipole association can be calc. from dielectric data, and it is concluded that such complexes exist simultaneously in the mixtures  $\text{CCl}_4-\text{PhCl}$ ,  $\text{CCl}_4-\text{PhBr}$ ,  $\text{C}_6\text{H}_{14}-\text{PhNO}_2$ , and  $\text{C}_6\text{H}_6$ -quinoline. The heats of association have been calc. from the variation of the equilibrium consts. with temp. R. S.

**Simultaneous formation of double and triple complexes in dipole association.** E. HERTEL and E. DUMONT (Z. physikal. Chem., 1935, B, 30, 149—151).—Polemical against Sakurada (A., 1935, 927). R. C.

**Viscosity of sulphuric acid [solutions].** S. D. BESKOV and O. A. SLIZKOVSKAJA (Chimstr., 1935, 7, 32—33).—Vals. for  $\text{H}_2\text{SO}_4$  ( $d$  1.38—1.84) between  $5^\circ$  and  $90^\circ$  are recorded. The  $\eta$  of  $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$  mixtures does not follow the additive law.

CH. ABS. (e)

**Viscosity of solutions of salts in methyl alcohol.** G. JONES and H. J. FORNWALT (J. Amer. Chem. Soc., 1935, 57, 2041—2045).—Determinations of  $d$  and  $\eta$  at  $25^\circ$  have been carried out for solutions of KCl, KBr, KI, and  $\text{NH}_4\text{Cl}$  over a wide concn. range in MeOH. The results for  $d$  can be expressed by an equation of the form suggested by Root (A., 1933,

347). The data for  $\eta$  are used to test the validity of several equations connecting  $\eta$  with concn.

E. S. H.

**Viscosity of sugar and dextrin solutions containing salts.** J. H. C. MERCKEL (Kolloid-Z., 1935, 73, 171—174).—The influence of NaI, NaBr, NaCNS, NaCl,  $\text{NaBrO}_3$ ,  $\text{NaIO}_3$ , and NaF on the viscosity of sucrose or dextrin solutions is in the order of their lyotropic nos. E. S. H.

**S-Shaped viscosity curves.** M. USANOVITSCH (J. Gen. Chem. Russ., 1935, 5, 996—1001).—S-Shaped viscosity-composition curves are obtained in binary systems of which one component is associated when this forms an unassociated compound with the other component. The rule is exemplified by the systems  $\text{PhNO}_2-\text{H}_2\text{SO}_4$  and  $\text{AsCl}_3-\text{Et}_2\text{O}$ . R. T.

**Concentrated solutions. I. Conductivity, viscosity, and density of fused  $\text{NH}_4\text{Ag}(\text{NO}_3)_2$  and of its concentrated solutions.** M. S. SKANAVI-GRIGORIEVA and E. B. SCHTERNIN (J. Gen. Chem. Russ., 1935, 5, 799—806).—The conductivity  $\kappa$  of the fused salt rises abruptly at  $113^\circ$ , and then continues to increase at a slower rate with rising temp.;  $\eta$  falls linearly over the same range. Up to 10%  $\text{H}_2\text{O}$  has little effect on  $\kappa$  at  $100^\circ$ , but further addition of  $\text{H}_2\text{O}$  leads to a rapid rise in  $\kappa$  to a max. in 75% solutions. At  $25^\circ$  a well-defined max. val. of  $\kappa$  is found for 60% solutions. Composition- $d$  and  $-\eta$  curves are given for numerous aq. systems at  $25^\circ$ . R. T.

**Conductivity and viscosity in the systems (A) sulphuric acid-nitrobenzene, (B) nitrobenzene-acetic acid, (C) sulphuric acid-acetic acid.** M. USANOVITSCH (J. Gen. Chem. Russ., 1935, 5, 701—708, 709—711, 712—718).—(A) [with G. KOZMINA and V. TARTAKOVSKAJA]. The conductivity curves ( $0-30^\circ$ ) have a well-defined min., suggestive of the compound  $2\text{PhNO}_2\cdot\text{H}_2\text{SO}_4$ . The temp. coeff. of conductivity curves have 2 max. and a min., corresponding with 2:1, 1:1, and 1:2 compounds of  $\text{PhNO}_2$  and  $\text{H}_2\text{SO}_4$ . The  $\eta$ -composition curves do not possess max. or min.

(B) [with A. TENENBAUM]. The system ( $20-80^\circ$ ) is non-conducting, and the composition curves do not suggest compound formation. The formation of electrolytic solutions when two non-electrolytes are mixed is ascribed exclusively to compound formation.

(C) [with A. NAUMOVA]. The temp. coeff. of conductivity-composition curves ( $0-30^\circ$ ) suggest 1:1 and 1:2 compounds. R. T.

**Viscosity coefficients in the system fused  $\text{KCl}-\text{MgCl}_2$ .** S. KARPATSCHEV and A. STROMBERG (J. Gen. Chem. Russ., 1935, 5, 625—630).—The viscosity isotherms ( $550-650^\circ$ ) suggest the compound  $\text{MgCl}_2\cdot 2\text{KCl}$ . R. T.

**Chemical composition and optical properties of solutions. I. Quaternary system  $\text{KCl}-\text{NaCl}-\text{MgCl}_2-\text{H}_2\text{O}$  at  $15^\circ$ .** E. I. ACHUMOV and M. P. GOLOVKOV (J. Gen. Chem. Russ., 1935, 5, 500—509).—Composition- $n$  curves for the above system are of the same general shape as are those connecting composition with other physical properties. R. T.

**Equilibria in liquid mixtures and solutions.**  
**IV. B. p. and composition of vapour of solutions of carbonyl chloride in dichloroethane and xylene.** V. A. KIREEV, S. I. KAPLAN, and V. N. ZLOBIN (J. Appl. Chem. Russ., 1935, 8, 949—951).—B. p. and composition of the vapour phase at the b. p. have been determined for 0—35%  $\text{COCl}_2$  in xylene and in  $\text{C}_2\text{H}_4\text{Cl}_2$ . R. T.

**Fugacity of salts present in boiling solutions.**  
 P. ZOLOTAREV and J. ORUDOVSKAJA (Trans. Inst. Chem. Tech. Ivanovo, 1935, 54—55).—The salt content of river- $\text{H}_2\text{O}$  falls from 134.6 to 3.4 mg. per litre after one distillation; the same salts are present in the distillate as were originally present. The phenomenon is ascribed to sputtering at the heated walls of the vessel above the surface of the liquid, leading to the formation of an aerosol of the salts. R. T.

**Röntgen analysis of  $\beta$ -phases of Cu-Be and Al-Zn alloys at high temperatures.** G. F. KOSOLAPOV and A. K. TRAPESNIKOV (Metallwirt., 1935, 14, 45—46; Chem. Zentr., 1935, i, 2243).—The  $\beta$ -phase of a Cu-Be alloy (7.2% Be) exists above  $620^\circ$ , with a random-distributed body-centred lattice,  $a$  2.79 Å. The  $\alpha$ -phase has the Cu lattice, and the  $\gamma$ -phase at room temp. a CsCl structure,  $a$  ( $570^\circ$ ) 2.72 Å. Al-Zn alloy with 40% of Al exhibits the Zn and Al lattices at room temp., and a single face-centred  $\gamma$ -phase at  $410^\circ$ . J. S. A.

**X-Ray studies on the systems tin-antimony and tin-arsenic.** G. HÄGG and A. G. HYBINETTE (Phil. Mag., 1935, [vii], 20, 913—929).—The homogeneous phase extending from 45 to 55 at.-% Sb has a deformed NaCl structure. The unit cell at the Sn limit is a rhombohedron with  $r$  6.117 Å.,  $\alpha$   $89.70^\circ$ , and vol. 228.9 Å.<sup>3</sup> With increasing Sb content the vol. and deformation increase until  $r$  is 6.138 Å.,  $\alpha$   $89.18^\circ$ , and vol. 231.2 Å.<sup>3</sup> As is insol. in the Sn phase. Two intermediate phases of narrow range exist at  $\text{Sn}_3\text{As}_2$  and  $\text{SnS}$ . The Laue symmetry of the former is  $D_{3d}$ . The unit cell is a rhombohedron with  $r$  12.23 Å. and  $\alpha$   $19.22^\circ$ . The structure probably corresponds with the ideal formula  $\text{Sn}_4\text{As}_3$ , where some As is replaced by Sn. The probable space-group is  $D_{3d}^4$ . The phase at  $\text{SnAs}$  has the NaCl structure with lattice const. 5.716 Å. As dissolves 21 at.-% Sn, which increases the rhombohedral edge and diminishes the angle of the As phase. T. G. P.

**Alloys of rhodium with copper.** O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, No. 12, 37—66).—Cu-Rh alloys are easily oxidised in air. With 0—20 at.-% Rh they are homogeneous and have the structure of Cu. From 90—100 at.-% Rh they have the Rh structure. Between these limits there are two phases, except where the compounds  $\text{Cu}_2\text{Rh}_3$  and  $\text{CuRh}_3$  (both with a face-centred cubic structure) exist. There is also a partial change of structure at  $\text{Cu}_3\text{Rh}$ . CH. ABS. (e)

**Modulus of elasticity of copper-beryllium alloys.** L. GUILLET (Compt. rend., 1935, 201, 960—962).—The modulus of elasticity and Rockwell hardness increase linearly with [Be] up to approx. 18 and 12% Be, respectively. For [Be] > 12% the

hardness increase is less. The elasticity of the alloy with 15% of Be equals that of steel. H. J. E.

**Structure of zinc-cadmium eutectic.** M. STRAUMANIS and N. BRAKŠS (Z. physikal. Chem., 1935, B, 30, 117—131; cf. A., 1912, ii, 744).—The eutectic consists of comparatively coarse fibres which grow into the melt perpendicularly to the surface of cooling and are built up of alternating parallel crystal leaflets of Zn and Cd, running lengthwise. These leaflets, which are somewhat crumpled, are so arranged in the fibres that their wide basal faces are in contact and the digonal axes of the first position make an angle of  $0-5^\circ$  with the fibre axis. The leaflets are thinner the more rapid is the cooling. It is inferred that the structure of eutectics is determined primarily by the crystallophysical properties of the components, surface tension playing a part only in exceptional circumstances. R. C.

**Binary systems of alkali metals.** I. C. GORIA (Gazzetta, 1935, 65, 865—870).—The system Rb-K shows limited solubility in the solid state and a eutectic at  $34^\circ$  with 15 at.-% K. In the Rb-Na system there is a eutectic at  $-5.2^\circ$  with 92 at.-% Rb, but no solid solutions or compounds are formed. O. J. W.

**Electrical resistance of wires of palladium-silver and palladium-gold alloys charged with hydrogen.** A. SIEVERTS and H. HAGEN (Z. physikal. Chem., 1935, 174, 247—261).—The pressure-concn. ( $p$ - $c$ ) isotherms for alloys with 5 and 10% Ag are similar to those for pure Pd; at  $155^\circ$  there is a hysteresis loop and at  $200^\circ$  an approx. flat portion on the isotherm, but no hysteresis. The isotherms for alloys with 20—50% Ag are all parabolic. Up to 30 at.-% Ag the pressure-resistance ( $p$ - $R$ ) isotherms are similar to those of Pd, but for a given  $c$  and  $p$  the increase in  $R$  caused by the H is the smaller the larger is the proportion of Ag. For alloys with 30 and 40% Ag  $\Delta R$  is negative over a certain range of temp. and  $p$ , whilst for 50%  $\Delta R$  rises again. Pd-Au alloys behave similarly to Pd-Ag alloys of the same at. composition, but both the H absorption and  $\Delta R$  for the Ag alloys are for the Au alloys at the same temp. and  $p$ . R. C.

**Resistance thermometry below  $10^\circ$  abs.** J. D. BABBITT and K. MENDELSSOHN (Phil. Mag., 1935, [vii], 20, 1025—1041).—The resistances of phosphor-bronze wires have been measured at low temp. The superconductive component responsible for the temp. dependency below  $7^\circ$  abs. is Sn-P, transition point  $8.9^\circ$  abs. A binary alloy of definite composition properly treated is suitable for low-temp. thermometry, e.g., 5% Pb-Ag. T. G. P.

**Experiments on a superconductive alloy in a magnetic field.** J. M. C. JONKER and W. J. DE HAAS (Physica, 1935, 2, 935—942).—Resistance may be detected by studying the dying-out of the persisting current in a ring composed in part of Pb wire and in part of the alloy, when the latter is placed in a longitudinal magnetic field. The magnetic transition curve of a 64.8% Tl-Pb alloy has been studied. In a magnetic field slightly > the penetration val. there is no resistance >  $5 \times 10^{-11}$  ohm. The magnetic threshold depends on the measuring current. T. G. P.

**Intermetallic compounds.** W. KLEMM (Angew. Chem., 1935, 48, 713).—A review in which the general differences between intermetallic and salt-like compounds are discussed. R. S. B.

**New methods and results for the detection of intermetallic compounds.** G. GRUBE (Angew. Chem., 1935, 48, 714—719).—A review of experimental methods, including the study of magnetic susceptibility ( $\chi$ ). For Pd-Mn below 500°  $\chi$  rises rapidly with increasing % of Mn. The classification of compounds is discussed. R. S. B.

**Structure of intermetallic phases.** G. HAGG (Angew. Chem., 1935, 48, 720—723).—A review of structural relations from the viewpoint of the position of the constituents in the periodic table. R. S. B.

**Energy and space problems in the formation of intermetallic compounds.** W. BILTZ (Angew. Chem., 1935, 48, 729—734).—A lecture. E. S. H.

**Magnetism and chemical linking in intermetallic phases.** E. VOOT (Angew. Chem., 1935, 48, 734—740).—A crit. discussion of published work. E. S. H.

**Theory of transition of metallic mixed phases. III. Diagrams of state for partly ordered mixed phases.** G. BORELIUS (Ann. Physik, 1935, [v], 24, 489—506).—Theoretical. The theory previously put forward (A., 1934, 724, 1166) is applied to alloys in which the constituents are not in stoichiometrical proportions. The general thermodynamic theory underlying the equilibria in binary alloys is considered. The zero-point entropy and zero-point energy are discussed as measures of the at. ordering. A. J. M.

**Effect of thermal agitation on atomic arrangement in alloys. II.** W. L. BRAGG and E. J. WILLIAMS (Proc. Roy. Soc., 1935, A, 151, 540—566).—Theoretical. The treatment given previously (A., 1934, 954) for the order-disorder transformation in alloys, and a recent extension of it by Bethe (A., 1935, 1193), are compared with the formal methods of Borelius, Gorsky, and Dehlinger (A., 1928, 822, 1078; 1933, 896). The energy contents of the alloys CuZn and Cu<sub>3</sub>Au as deduced theoretically are compared with those found experimentally by Sykes (A., 1935, 576). Expressions are given for the dependence of temp. on composition. L. L. B.

**Solid solutions with a varying number of atoms in the unit cell.** G. HAGG (Z. Krist., 1935, 91, 114—122).—"Interstitial solution" is suggested to describe those solid solutions formed by adding or subtracting one kind of atom *A* in a given lattice *B*. For stability, a rigid skeleton lattice *B* and small substituent atoms *A* are desirable. The interstitial solutions can be classified according to the means whereby electrical neutrality is maintained. Valency change in one kind of atom may make an interstitial solution possible. The electrical conductivity of such lattices is discussed. B. W. R.

**Separation of binary liquid mixtures into two layers.** R. V. MERZLIN and V. F. UST-KATSCHKINTZEV (J. Gen. Chem. Russ., 1935, 5, 771—778).—Phase diagrams for KCl-H<sub>2</sub>O-NEt<sub>3</sub>, -C<sub>5</sub>H<sub>5</sub>N, and

-piperidine have been constructed at 0—80°. The systems H<sub>2</sub>O-C<sub>5</sub>H<sub>5</sub>N and -piperidine appear to have a high lower crit. miscibility temp. R. T.

**Physico-chemical properties of certain aqueous systems containing amines, and capable of stratification.** R. V. MERZLIN (J. Gen. Chem. Russ., 1935, 5, 886—891).—The composition- $d$  and -surface tension ( $\sigma$ ) and  $\sigma$ -temp. curves have been determined for the systems H<sub>2</sub>O- $\beta$ -collidine and -NEt<sub>3</sub>; the composition- $\eta$  curve for the latter suggests a 1:1 compound. The data suggest formation of thermolabile compounds in both systems. R. T.

**Viscosity of binary systems at critical zones.** R. V. MERZLIN (J. Gen. Chem. Russ., 1935, 5, 899—903).—Binary liquid systems exhibit irrational max. in the  $\eta$ -composition curves at the lower crit. temp. zone; at the upper crit. temp. two types of curve are possible, (a) in which the curves exhibit a negative deviation from additivity, due to dissociation of associated complexes, and (b) in which electrolytic dissociation of the complexes is superimposed on this effect. R. T.

**Mutual solubility and surface tension. II. Surface tension and dipole moment.** V. K. SEMENTSCHENKO and T. N. IVANOVA (J. Gen. Chem. Russ., 1935, 5, 807—813).—The surface tension,  $\sigma$ , of H<sub>2</sub>O, nicotine (I), and PhNO<sub>2</sub> (II) at 25° is depressed by PrCO-NH<sub>2</sub> (III), PrCl, PrCHO (IV), PrCN, PrOH, and PrCO<sub>2</sub>H (V), to an extent which increases with the concn. In the case of H<sub>2</sub>O no obvious connexion exists between surface activity and dipole moment,  $\mu$ ; in (I) and (II) it rises with increasing  $\mu$  for substances not containing N, and falls for those containing N. The crit. temp. of miscibility of (I) with H<sub>2</sub>O is raised by (III) and (V), is unaffected by PrOH, and lowered by the remaining substances, to an extent which increases linearly with the concn. The val. of  $\sigma$  at 70° at a H<sub>2</sub>O-(I) interface rises with increasing concn. of PrCl, (IV), and PrCN, but is practically unaffected by PrOH, and is lowered by (III) and (V). R. T.

**Homogenisation by means of amines of certain aqueous amine systems with an upper critical temperature of stratification.** R. V. MERZLIN and V. F. UST-KATSCHKINTZEV (J. Gen. Chem. Russ., 1935, 5, 904—919).—Phase diagrams have been constructed for the systems H<sub>2</sub>O-NHPh-NH<sub>2</sub> (I)-piperidine (II), -C<sub>5</sub>H<sub>5</sub>N, -NH<sub>2</sub>·CH<sub>2</sub>Ph (III), and -NH<sub>2</sub>Ph, and for H<sub>2</sub>O-NH<sub>2</sub>Ph-(II), -C<sub>5</sub>H<sub>5</sub>N, and -(III), at 0—50°. No connexion is apparent between the dipole moment, dissociation coeff., or dielectric const. of the amines and their homogenising action at any arbitrarily fixed temp. Within the temp. range studied the homogenising action rises in the series (I) < (III) < C<sub>5</sub>H<sub>5</sub>N < (II), but falls with rise of temp. for C<sub>5</sub>H<sub>5</sub>N and (III), and rises for (II); the principle of corresponding temp. should be taken into account in comparing the activity of a series of homogenisers. R. T.

**Solubility of ammonium oxalate in water.** A. E. HILL and E. F. DISTLER (J. Amer. Chem. Soc., 1935, 57, 2203—2204).—Data are recorded for the

range 0—100°. The solid phase throughout is the monohydrate. E. S. H.

**Solubility of sodium cyanide in water and in aqueous sodium hydroxide.** V. A. KIREEV and L. I. VAGRANSKAJA (J. Gen. Chem. Russ., 1935, 5, 963—966).—The solubility of NaCN at 0°, 25°, and 40° falls linearly with increasing [NaOH]. R. T.

**Solubility of cobaltous nitrate in aqueous nitric acid, and the transition point of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .** A. VALDMAN and L. L. KLATSCHKO-GURVITSCH (J. Gen. Chem. Russ., 1935, 5, 791—794).—Aq.  $\text{Co}(\text{NO}_3)_2$  saturated at 80° solidifies on cooling to 25°, to yield 39.5% of trihydrate (I) and 60.5% of hexahydrate (II). (I) alone can be prepared by cooling to 56°, and (II) alone by saturating at 56° and cooling. The transition point of (II) to (I) falls from 54° in absence of  $\text{HNO}_3$  to 42° in presence of 30% of  $\text{HNO}_3$ . R. T.

**Determination of solubility of the complex  $\text{K}_2\text{SiF}_6$  under various conditions.** A. A. VASSILIEV and N. N. MARTIANOV (Z. anal. Chem., 1935, 103, 103—106).—The solubility of  $\text{K}_2\text{SiF}_6$  in  $\text{H}_2\text{O}$  at 17° has been determined titrimetrically. The solubility is lower in 50% aq. EtOH, and is further decreased in presence of 2% of KCl. J. S. A.

**Solubility of phosphoric acid.** A. E. MAKOVETZKI and M. A. OSTROUMOV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 103—106).—The best solvents for separating  $\text{H}_3\text{PO}_4$  from its aq. solutions are isoamyl alcohol and fusel oil.  $\text{H}_3\text{PO}_4$  is almost insol. in  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , liquid  $\text{SO}_2$ , PhMe, xylene, benzene, kerosene, and turpentine. CH. ABS. (e)

**Solubility of 6-nitro-3-methylbenzoic acid in benzene, toluene, and water.** A. GIACALONE (Gazzetta, 1935, 65, 844—850).—The solubility of 6:3- $\text{NO}_2\text{-C}_6\text{H}_3\text{Me-CO}_2\text{H}$  (I) has been measured in  $\text{C}_6\text{H}_6$  and in PhMe between 10° and 80° and in  $\text{H}_2\text{O}$  between 10° and 100°. In the first two solvents the influence of temp. is given by  $S = K \times 2^{t/10}$ , where  $K$  is a const. (I) crystallises from  $\text{C}_6\text{H}_6$  in two forms, of which only one is stable at higher temp. The solubility in  $\text{H}_2\text{O}$  is very small up to 50°, but increases rapidly above 60° due to formation of hydrates. O. J. W.

**Solubility of several compounds of the mannose series in alcohols.** F. W. UPSON, E. A. FLUEVOG, and W. D. ALBERT (J. Physical Chem., 1935, 39, 1079—1094).—The solubilities of *l*-rhamnose (I),  $\alpha$ -*d*-mannose (II),  $\beta$ -*d*-mannose (III), *d*-mannono- $\gamma$ -lactone (IV), *d*-mannono- $\delta$ -lactone (V),  $\alpha$ -methyl-*d*-mannoside, and *d*-mannitol (VI) in MeOH, EtOH,  $\text{CH}_2\text{OH-CH}_2\text{OH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^i\text{OH}$ ,  $\text{Bu}^n\text{OH}$ ,  $\text{Bu}^i\text{OH}$ ,  $\text{Bu}^t\text{OH}$ , and *sec*-BuOH have been determined at different temp. (I) is the most sol. and (VI) the least sol. in all cases. (II) is more sol. than (III), whilst (IV) is almost twice as sol. as (V). R. S.

**Solute as liquid.** W. D. BANCROFT (Science, 1935, 82, 388—389).—A discussion. L. S. T.

**Equilibrium distribution of acetic acid between isopropyl ether and water.** A. A. SMITH and J. C. ELGIN (J. Physical Chem., 1935, 39, 1149—1153).—Distribution data are given for 20°. The

results, considered in relation to Almqvist's equation (A., 1934, 22), suggest that AcOH forms double mols. in  $\text{Pr}^i\text{O}$ . R. S.

**Equilibria and surface phenomena in the system water-formic acid-phenol.** V. I. NESTEROVA, N. N. PETIN, and K. V. TOPTSCHIEVA (J. Gen. Chem. Russ., 1935, 5, 848—861).—The partition coeff. of  $\text{HCO}_2\text{H}$  (I) between  $\text{H}_2\text{O}$  and PhOH at 20° rises with increasing concn. to 1.075*M*, and then falls to 1.507*M*-(I), at which concn. the system becomes homogeneous. The conductivity of the PhOH layer rises uninterruptedly to the crit. point, whilst that of the aq. layer rises to a max., and then falls with increasing  $[\text{HCO}_2\text{H}]$ . The dissociation coeff. of (I) rises with increasing  $[\text{HCO}_2\text{H}]$  in the PhOH, but remains const. in the aq. layer. The surface tension at the air- $\text{H}_2\text{O}$  interface remains const., but that at the  $\text{H}_2\text{O}$ -PhOH interface rises linearly with increasing  $[\text{HCO}_2\text{H}]$  to the crit. point. R. T.

**Solubility of deuterium and hydrogen in solid palladium.** A. SIEVERTS and G. ZAPF (Z. physikal. Chem., 1935, 174, 359—364).—The solubilities have been determined at 300—1100°. The ratio of the solubility of D to that of H is 0.67 at 300° and 0.91 at 1000° and approaches 1 at higher temp. The solubility of either at a given temp. is  $\propto \sqrt{\text{gas pressure}}$ . R. C.

**Colloid-chemical phenomena in metals. I. Gases in aluminium.** J. A. KLJATSCHKO (Kolloid-Z., 1935, 73, 226—236).—Mainly a discussion of published work. The vol. of gas liberated from Al and duralumin when heated at different temp. and the proportion of  $\text{H}_2$  contained therein have been measured. E. S. H.

**Accommodation coefficient of hydrogen on iron.** H. H. ROWLEY and W. V. EVANS (J. Amer. Chem. Soc., 1935, 57, 2059—2064).—The accommodation coeff. is 0.31 at 450—350° abs. and increases steadily with falling temp. to 0.55 at 120° abs. Comparison with other work suggests that the exchange of energy between  $\text{H}_2$  gas mols. and an adsorbed layer of  $\text{H}_2$  is measured in each case. An attempt to remove this adsorbed layer reduces the accommodation coeff. to 0.18 at 350° abs. E. S. H.

**Sorption of gases by minerals. V. [Extra-Japanese zeolites.] VI.** J. SAMESHIMA and N. MORITA (Bull. Chem. Soc. Japan, 1935, 10, 485—490, 490—494).—V. The rate of absorption of  $\text{NH}_3$  and  $\text{CO}_2$  at 1 atm. by the dehydrated minerals has been determined at 25°. Thomsonite, scolecite, epistilbite, and phillipsite absorb large vols. of  $\text{NH}_3$ , probably forming compounds, but only very small quantities of  $\text{CO}_2$  are absorbed; the absorption depends on the temp. of dehydration.

VI. Sepiolite absorbs large vols. of  $\text{NH}_3$  and  $\text{CO}_2$ , and belongs to the  $\text{SiO}_2$  gel class. Asbestos, acid clay, and bentonite absorb large vols. of  $\text{NH}_3$ , but only very small quantities of  $\text{CO}_2$ . Talc, serpentine, and vivianite absorb only very small quantities of  $\text{NH}_3$  and  $\text{CO}_2$ . J. G. A. G.

**Adsorption of alkali metals on metal surfaces. VI. Selective photo-electric effect.** J. H. DE BOER and C. F. VEENEMANS (Physica, 1935, 2, 915—



922; cf. A., 1935, 929).—The photo-electric emission of a cathode has been measured at increasing vals. of the covering fraction for  $\lambda\lambda > 3600 \text{ \AA.}$  and  $2537 \text{ \AA.}$  With the longer  $\lambda\lambda$  emission is due solely to the normal photo-electric effect, but at  $2537 \text{ \AA.}$  the selective effect contributes.

T. G. P.

**Mechanism of displacement adsorption of gases and vapours.** P. K. MIGAL (J. Gen. Chem. Russ., 1935, 5, 614—621).—The molar heat effect observed when an adsorbed gas is replaced by a vapour ( $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{MeOH}$ ,  $\text{CS}_2$ ,  $\text{EtI}$ ,  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ ) may be expressed by  $q = \lambda + [(C_2/\alpha_2) - (C_1/\alpha_1)]\beta P$ , where  $\lambda$  is the heat of condensation of 1 g.-mol. of vapour, and  $C_2$  are the sp. heats of the gas and vapour, respectively,  $\alpha_1$  and  $\alpha_2$  are the coeffs. of thermal compression,  $\beta$  is the compression coeff., and  $P$  is the deformative force due to the adsorbent. When the capillary activity of the second adsorbate is  $>$  that of the first, adsorption on the first adsorbate, but not displacement, occurs, but under converse conditions, adsorption takes place with replacement of the first adsorbate.

R. T.

**Velocity of adsorption of gases on porous adsorbents.** G. DAMKOHLER (Z. physikal. Chem., 1935, 174, 222—238).—Langmuir's theory of adsorption velocity is applicable only to pore-free adsorbents and leads to a val. of  $10^{-5}$ — $10^{-10}$  sec. for the time,  $\tau$ , required for the establishment of adsorption equilibrium. A theory of velocity of adsorption on porous adsorbents is developed, making various simplifying assumptions and taking the rate-determining process to be diffusion in the pores. This diffusion can be regarded as consisting of a Knudsen mol. streaming in a capillary and a surface diffusion in Volmer's sense on the pore walls. The two diffusion consts. and the pore size are estimated, and the theory indicates that if  $\tau$  is several min. the mean pore length is of the order of several mm. Langmuir's theory is not applicable to Berl and Weingaertner's experiments (A., 1935, 696), but these are reconcilable with the new theory.

R. C.

**Heats of adsorption of gases and vapours on crystallogenic adsorbents.** A. B. LAMB and E. N. OHL (J. Amer. Chem. Soc., 1935, 57, 2154—2161).—Heats of adsorption of several gases and vapours on dehydrated chabasite, thomsonite, and brucite have been determined at  $0^\circ$ . In cases where adsorption is considerable, the mol. heats are  $>$  those previously observed with C or  $\text{SiO}_2$ , but can be represented by the same empirical equation.

E. S. H.

**Liquid-side resistance against gas absorption by a liquid drop.** (A) Theoretical. (B) Experimental. S. HATTA and A. BABA (J. Soc. Chem. Ind. Japan, 1935, 38, 544—546B, 546—550B).—(A) The resistance to gas absorption due to turbulence on the liquid side of the interface has been calc. for falling drops with (i) no damping of the initial turbulence due to drop formation, (ii) gradual damping during fall, and (iii) immediate disappearance of turbulence, in which case absorption follows a diffusion law. The frictional resistance offered to a falling drop is discussed.

(B) The absorption of  $\text{CO}_2$  by falling drops of  $\text{H}_2\text{O}$

has been studied at  $20^\circ$ . Absorption during drop formation is negligible compared with that during time of fall.  $C/\bar{C}_\infty = 6q^{1/2} - 3q$  ( $C$  = mean concn. at time  $t$ ,  $\bar{C}_\infty$  = saturated concn.,  $q = Dt/a^2$ , where  $D$  = diffusion coeff. of dissolved gas,  $a$  = radius of drop), in agreement with (iii).  $D = 1.08 \times 10^{-3}$  sq. cm. per sec., which is 60—70 times the published val.

R. S. B.

**Surface tension of the system sulphuric acid-water.** L. E. SABININA and L. I. TERPUGOV (J. Gen. Chem. Russ., 1935, 5, 783—787).—The temp. coeff. of surface tension-composition curves ( $10$ — $50^\circ$ ) exhibits a min. corresponding with  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . The max. deviation from the additive rule for  $\sigma$  is found for the same concn.

R. T.

**Measurements of surface tension of solutions of potassium and lithium salts of higher fatty acids by the ring method with exclusion of atmospheric carbon dioxide and with special regard to other disturbing influences.** I. A. LOTTERMOSER and E. GIESE (Kolloid-Z., 1935, 73, 155—170).—The lack of reproducibility of surface tension measurements of soap solutions cannot be overcome entirely by exclusion of  $\text{CO}_2$ . Other sources of error are the enrichment of the solute by adsorption at the Pt ring and at other surfaces in the apparatus. Whilst these effects cannot be eliminated, means are considered whereby they may be reduced to a min. and kept const.

E. S. H.

**Cation exchange in permutites, especially hydrogen and heavy-metal permutites.** A. RENOLD (Kolloid-Beih., 1935, 43, 1—142).—A comprehensive investigation and discussion of the prep. and exchange reactions of permutites of H, alkali and alkaline-earth metals, Cd, Ni, Cu, Hg, and Ag.

E. S. H.

**Transmission of surface perturbations to within real crystals.** V. D. BALAREV [with V. CHRISTOFOROVA] (Z. physikal. Chem., 1935, B, 30, 152—156; cf. A., 1935, 1069).—Admixture with  $\text{NaCl}$ ,  $\text{KCl}$ , or  $\text{PbCl}_2$  causes the dehydration and rehydration curves for  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$   $\text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$  to approach; this can be due only to the transmission of surface energy from the points of contact of the two salts (cf. *ibid.*, 447).

R. C.

**Sorption phenomena and chemical processes. VII. Permutoid reactions.** I. PUTILOVA (J. Gen. Chem. Russ., 1935, 5, 934—937).—Experimental data for the heat effect of the reaction between nitroalizarin and aq.  $\text{Cu}(\text{OAc})_2$  agree with those calc. from the Le Chatelier theorem.

R. T.

**Surface potentials and force-area relations of unimolecular films. II. *d*-Pimaric acid and tetrahydro-*d*-pimaric acid.** W. D. HARKINS, H. E. RIES, jun., and E. F. CARMAN (J. Amer. Chem. Soc., 1935, 57, 2224—2227; cf. A., 1934, 141).—The max. thickness of the mono-layer is about  $12 \text{ \AA.}$  for both compounds. The coeffs. of compressibility have been calc. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions of the polar groups. The surface potential of tetrahydro-*d*-pimaric acid is about 200 mv., whilst that of



*d*-pimaric acid is about 100 mv. In the latter case an unprecedented decrease in surface potential on compression is observed. These facts may be related to an increasing intramol. dipole compensation on compression. E. S. H.

**Unimolecular films of molecules which lie flat on the surface of water. I. Surface pressures and potentials of films of long molecules: polymerides of  $\iota$ -hydroxydecoic acid.** W. D. HARKINS, E. F. CARMAN, and H. E. RIES, jun. (J. Chem. Physics, 1935, 3, 692—698).—Improvements in the apparatus of Harkins and Fischer (A., 1934, 141) are described. The relation between surface pressure and area per mol. (*A*) has been determined for a series of linear polymerides of  $\iota$ -hydroxydecoic acid with mol. wts. from 780 to 25,200. The films have high compressibilities and *A* is approx.  $\propto$  mol. wt. The mols. are oriented parallel to the surface. Their dimensions are calc. Differences between films with perpendicular and with parallel orientation are tabulated. Measurements of the surface potentials show that the contribution of each polar group is  $>$  that of the dipole of vertically oriented stearic acid. The films are not very sensitive to changes in  $[H^+]$ .

F. L. U.

**Theory of physico-chemical periodic processes. I.** A. A. VITT and F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1935, 5, 814—817).—Mathematical.

R. T.

**Emission wave theory of periodic reactions. VIII.** F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1935, 5, 943—949; cf. A., 1935, 453).—In general, the periodicity const. is given by  $K - \lambda V$ , where  $\lambda$  is the distance between two Liesegang rings, and  $V$  is the velocity of propagation, at limiting concns. of the substrates, whilst at optimal concns.  $K - V/4$ ; the latter relation also applies to micro-periodic phenomena. These findings are in accord with the theoretical considerations of Christiansen *et al.* (A., 1934, 955).

R. T.

**Relation between volumes of substances in the free state and in solution. I. I.** ZASLAVSKI, A. A. ASTASCHEVA, and I. A. SAKOV (Trans Inst. Chem. Tech. Ivanovo, 1935, 47—49).—The mol. wt.-equiv. vol. curves of chlorides of metals in the solid state and in solution exhibit parallel variations.

R. T.

**Viscosity of aqueous solutions of electrolytes. II. Comparison of specific ionic viscosities with other ionic properties of homologous elements.** H. TOLLERT (Z. physikal. Chem., 1935, 174, 239—246; cf. A., 1935, 443).—The lattice energies of the alkali chlorides and Na halides, the ionic radii in the lattice, the ionic hydration vals. and heats of hydration, and the mol. ionisation energies of the alkali chlorides all run parallel with the sp. ionic viscosities in 0.1*N* solution. It is inferred that the hydrated ions up to 0.1*N* are in a state of equilibrium with free  $H_2O$  which is a function of the at. no. in the same kind of way as are the above ionic properties.

R. C.

**Refractometric investigations of aqueous solutions of salt mixtures. System barium chloride-potassium chloride.** G. SPACU and E. POPPER

(Z. physikal. Chem., 1935, B, 30, 113—116; cf. A., 1934, 723).—The existence in solution of complex anions corresponding with the compounds  $[BaCl_4]K_2$  and  $[BaCl_5(H_2O)]BaK$  is said to have been established.

R. C.

**Structure of solutions of strong electrolytes in alcohols and water.** G. W. STEWART (Proc. Iowa Acad. Sci., 1934, 41, 250—251; cf. A., 1934, 591).—Aq. LiCl behaves as a submicroscopic emulsion, consisting of a  $LiCl-H_2O$  structure in  $H_2O$  as a solvent. Aq.  $MgCl_2$ ,  $(NH_4)_2SO_4$ ,  $NH_4Cl$ , and  $NaCl$  are similar. A solution of LiCl in EtOH shows a composite liquid structure, which behaves as if liquid alcoholate were thoroughly mixed with the EtOH, the two forming a single cybotactic structure.

CH. ABS. (e)

**Measurement of the size of colloidal particles from the intensity of light transmitted through the solutions.** N. N. ANDREEV (J. Gen. Chem. Russ., 1935, 5, 529—534).—The radius of suspended colourless particles (colophony) can be derived from the absorption of transmitted light by a modified Mie formula (Ann. Physik, 1908, [iv], 25, 377).

R. T.

**Donnan effect in ultrafiltration of colloidal solutions.** A. RABINOVITSCH, P. VASILEV, and T. GATOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 109—112).—In ultrafiltration the vol. of the initial sol is diminished by the same amount as the vol. of the ultrafiltrate is increased. By assuming complete dissociation of sols and ultrafiltrates new equations, based on those of Donnan, are derived; they yield theoretical vals. for  $Fe_2O_3$ ,  $WO_3$ ,  $TiO_2$ , and  $V_2O_5$  sols in good agreement with experimental data.

W. R. A.

**Uranium colloids. II.** S. I. DIJATSKHOVSKI and M. F. IVANOVA (J. Gen. Chem. Russ., 1935, 5, 638—642; cf. A., 1927, 1137).—Highly disperse, photosensitive sols of uranyl tartrate are described.

R. T.

**Formation of zirconate hydrosols and their disintegration by certain neutral salts.** A. W. THOMAS and H. S. OWENS (J. Amer. Chem. Soc., 1935, 57, 2131—2135).—The anions citrate, glycolate, lactate, malate, mucate, pyruvate, tartrate,  $H_2PO_4^-$ ,  $P_2O_7^{4-}$  reverse cationic basic Zr chloride micelles to anionic zirconate micelles. The conditions are: (1) ability of the salt anion to displace aquo-groups from the cationic micelle, (2) the formation of a sol. anionic complex, (3) the equilibrium const. of the anionic complex must be  $>$  the solubility product of  $ZrO(OH)_2$ . The basic Zr sols can be brought into crystalloidal solution by addition of K acetate, tartrate, or glycolate.

E. S. H.

**Distance between colloidal particles in the iridescent films of certain iron oxide sols.** W. HELLER (Compt. rend., 1935, 201, 831—833; cf. A., 1930, 439).—Vals. are recorded for the distances between layers at various concns. and for varying periods of ageing.

H. J. E.

**Magnetic study of sols of hydrated ferric oxide.** A. BOUTARIO and R. BONNEVIALE (Bull. Soc. chim., 1935, [v], 2, 1998—2008).—The measured sp. susceptibilities,  $\chi$ , of  $Fe_2O_3$  sols, containing up to

75 g. of  $\text{Fe}_2\text{O}_3$  per litre, obey the mixture law. The val. of  $\chi$  for  $\text{Fe}_2\text{O}_3$  does not vary appreciably with the length of dialysis, but decreases with increasing age of the sol, the decrease being faster at higher temp.

O. J. W.

**Osmotic pressure and mol. wt. of cellulose acetate.** A. DOBRY (Bull. Soc. chim., 1935, [v], 2, 1882—1884).—From the limiting val. of the osmotic pressure at zero concn. in various solvents the mol. wt. of cellulose acetate is found to be 66,500.

O. J. W.

**Viscosity of solutions of cellulose in cuprammonium.** O. KRATKY and G. SAITO (Cellulosechem., 1935, 16, 85—90).—Data are recorded for  $\eta$  of 0.1, 0.25, and 0.5% solutions of modified celluloses regenerated from alkali-cellulose aged in air, and these are approx. expressed by the equation  $\eta_{sp}/c = A + Bc$ , in which  $A$  and  $B$  are consts. The term  $Bc$  is regarded as due to mechanical interaction of the long chain mols. or micelles with each other. The ratio length/width of the particles calc. on this hypothesis agrees approx. with that calc. from Staudinger's equation.

A. G.

**Dissolution of cellulose nitrate. I—III.** T. TOMONARI (J. Soc. Chem. Ind. Japan, 1935, 38, 517—528B; cf. A., 1934, 637).—The solubility of various types of cellulose nitrate in org. solvents and in aq.  $\text{HNO}_3 + \text{H}_2\text{SO}_4$ , and the relative  $\eta$  for solutions, have been determined at 0—25°. Dissolution of di- and tri-nitrates in aq.  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  is hindered by the presence of an unknown constituent.

R. S. B.

**Action of alcohols on organosols (especially polystyrene, caoutchouc, and cellulose acetate).** H. ERBRING and K. SAKURADA (Kolloid-Z., 1935, 73, 191—201).—The pptg. effects of a homologous series of alcohols increases with increasing mol. polarisation, except for organosols of paraffin and caoutchouc, where the reverse effect is observed, and polystyrene in  $\text{COMeEt}$ , in which the pptg. val. is independent of mol. polarisation. In general the concn. of alcohol required for pptn. increases with increasing viscosity of the system. By addition of alcohols to polystyrene in  $\text{C}_6\text{H}_6$  a liquid-liquid system is formed at first.

E. S. H.

**Coagulation of organosols of cellulose nitrate by electrolytes. II.** S. PAPKOV and M. TSCHVEL-EVA (Kolloid-Z., 1935, 73, 202—203; cf. A., 1935, 1319).—The coagulation of sols of cellulose nitrate in  $\text{COMe}_2$  by  $\text{H}_2\text{O}$  in presence and in absence of electrolytes has been studied. The stability of the sols cannot be traced to the charge on the particles; the existence of such a charge is doubtful.

E. S. H.

**Variation of flocculation threshold in starch sols.** H. KOBER and F. DITTMAR (Kolloid-Z., 1935, 73, 219—226).—Capillary-active substances, such as sulphonated fatty acids, have very little influence on the coagulation of starch sols except in presence of salts, when small concns. cause turbidity or flocculation according to the concns. of electrolyte and sol. The effect also varies with the degree of hydrolysis of the starch which occurs during prep. of the sol.

E. S. H.

**Imbibition of organic solvents by Yamagata imbibing clay.** M. UTIDA (J. Soc. Chem. Ind. Japan, 1935, 38, 513—514B).—The quantity of org. solvent imbibed is  $<$  for  $\text{H}_2\text{O}$ , but no systematic relation applies. The relative  $\eta$  of the system clay sol- $\text{H}_2\text{O}$ - $\text{EtOH}$  is infinite near the max. point of the system  $\text{H}_2\text{O}$ - $\text{EtOH}$ .

R. S. B.

**Imbibition of electrolyte solution by Yamagata imbibing clay.** M. UTIDA (J. Soc. Chem. Ind. Japan, 1935, 38, 514B).—The swelling of clay in aq.  $\text{HCl}$ ,  $\text{NaOH}$ , and  $\text{NaCl}$  is compared with  $\eta$  for the systems clay sol-electrolyte. A base exchange occurs, as with zeolites, the reaction velocity increasing rapidly with concn. of electrolyte.

R. S. B.

**Structure viscosity of lyophilic sols. I. Gelatin sol.** N. PESKOV and S. AVERBUCH (Kolloid-Z., 1935, 73, 182—191).—A viscosimeter for use with lyophilic sols is described. The deviations from the Hagen-Poiseuille law shown by gelatin sols are traced to the inner structure and orientation of the particles. The influence of acids and alkalis on  $\eta$  is ascribed to the electro-viscous effect, the increase in dispersity, the possible increase in swelling power, and the change in the form of the micelles. Deviations from the law disappear at 34° in 2% electrodialysed gelatin, and at 30° when acids or bases are added to give  $p_H < 3.5$  or  $> 5.5$ .

E. S. H.

**Silicic acid gels. V. Determination of the hydrogen-ion concentration of gel mixtures.** C. B. HURD and R. L. GRIFFETH (J. Physical Chem., 1935, 39, 1155—1159; cf. A., 1934, 730).—The quinhydrone (I) method can be used for the determination of the  $p_H$  of  $\text{SiO}_2$  gels. The vals. obtained are  $< 7$  and const. during setting, whilst the time of setting is unaffected by the presence of (I).

R. S.

**Cryolysis, diffusion, and particle size. II. Investigations with myosin.** F. E. M. LANGE and F. F. NORB (Biochem. Z., 1935, 281, 444—446).—A table shows the diffusion coeffs. for myosin (unfrozen) at temp. down to  $-79^\circ$ . The decrease of these coeffs. with chilling points to an irreversible aggregating action.

P. W. C.

**Ideal and real protein solutions.** G. ETTISCH and R. HAVEMANN (Z. physikal. Chem., 1935, 174, 199—221).—If a homodisperse quartz suspension is allowed to sediment in presence of a protein the increase in the sedimented vol. compared with the val. in absence of the protein is a max. at the isoelectric  $p_H$  (I). This is a more precise method for the location of I than mere observation of the sedimented vol. alone. For ovalbumin and serum-albumin the val. of I so obtained falls with increasing protein concn.,  $c$ , when the latter is  $>$  a certain val. It follows therefore that at the higher  $c$  the mean valency of the protein mol. (cf. A., 1934, 36) is a function of  $c$ . Cataphoresis measurements show that at concns.  $> 0.5\%$  I of ovalbumin is not const. at  $p_H 4.93$ , but moves to lower  $p_H$  with rising  $c$ . These observations are attributed to electrical interaction between the isoelectric protein mols. in the more conc. (non-ideal) solutions. In such solutions the mols. behave as polypoles, and at I the  $\text{NH}_3^+$  and  $\text{CO}_2^-$  groups of

different mols. approach as close as possible. This theory accounts for the above phenomena and also for the effect of neutral salts on *I*. R. C.

**Diffusion of colouring matters in gelatin and morphology of their reactions with electrolytes.** S. VEIL (Bull. Soc. chim., 1935, [v], 2, 1830—1832).—The use of characteristic diffusion figures in gelatin (cf. A., 1934, 1172) for the purpose of qual. analysis is extended to the case of colouring matters.

O. J. W.

**Diffusion in gelatin and rhythmic precipitation of magnesium hydroxide.** G. AMMON and R. AMMON (Kolloid-Z., 1935, 73, 204—219).—The formation of periodic structures of  $Mg(OH)_2$  in gelatin by interaction of aq.  $NH_3$  and  $MgCl_2$  has been studied in relation to the diffusion coeffs. of the two reagents, the ratio of the distances between successive rings, and the viscosity of the gelatin. The results of other investigators are discussed in the light of these results.

E. S. H.

**Quinone-gelatin gels.** J. BUCHHOLZ (Kolloid-Z., 1935, 73, 237).—The phenomenon previously reported has been observed with tolu-, naphtha-, and anthra-quinone.

E. S. H.

**Lyophilic colloids. XXV. Coacervation. II. Complex coacervation of the system gum arabic-gelatin.** H. G. B. DE JONG and W. A. L. DEKKER (Kolloid-Beih., 1935, 43, 143—212; cf. A., 1935, 821).—Determinations of  $\eta$ , turbidity, and electrophoretic velocity have been carried out. Neutral salts inhibit coacervation; a valency influence, but not a lyotropic influence, is noted. Coacervation is still observed in very dil. solutions. The composition relations for optimum coacervation vary with  $pH$ . The behaviour of the coacervate droplets in the electric field is described.

E. S. H.

**Phenomena of electrofiltration in the electrolysis of gels.** J. SWYNGEDAuw (Compt. rend., 1935, 201, 821—823; cf. A., 1934, 961).—A discussion.

H. J. E.

**Generalised thermodynamic notation.** H. A. C. MCKAY (J. Chem. Physics, 1935, 3, 715—719)

F. L. U.

**Quantity parameter, intensity parameter, and stable equilibrium.** M. PLANCK (Physica, 1935, 2, 1029—1032).—Polemical. (cf. A., 1935, 1076).

T. G. P.

**Displacement of equilibrium and the laws of moderation [i.e., of Le Chatelier and van 't Hoff].** D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 109—118).—Mathematical.

D. R. D.

**Reversible thermo-elastic systems. Generalised coefficients.** D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 119—130).—Mathematical.

D. R. D.

**Osmotic equilibrium and real solutions.** D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 131—146).—Theoretical. A rigid thermodynamic treatment of equilibria across a semi-permeable membrane.

D. R. D.

**Partial molal quantities in an infinitely dilute solution.** I. R. KRITSCHESKI and J. S. KASARNOVSKI (J. Amer. Chem. Soc., 1935, 57, 2171—2172).—Theoretical.

E. S. H.

**Equilibrium studies on the exchange reaction between acetylene and heavy water.** L. H. REYERSON and B. GILLESPIE (J. Amer. Chem. Soc., 1935, 57, 2250—2251).—Average vals. of  $K_e$  for the reaction  $C_2H_2 + HDO = C_2HD + H_2O$  are 0.365, 0.45, and 0.51 at 0°, 25°, and 100°, respectively.

**Second dissociation constant of carbonic acid.** Y. KAUKO and V. MANTERE (Suomen Kem., 1935, 8, B, 34; cf. A., 1935, 823).—Extrapolation of measurements in dil. solution gives  $K_2 = 5.0 \times 10^{-11}$  at 18°.

R. S.

**Peculiar behaviour of aqueous carbonic acid.** Y. KAUKO (Suomen Kem., 1935, 8, B, 39—41).—Recorded vals. for the dissociation consts. of  $H_2CO_3$  are discussed. The author's val. for the second const. is  $5.3 \pm 0.3 \times 10^{-11}$  at 25°. A slow change occurs in the solution.

R. S. B.

**Relative strengths of acids in *n*-butyl alcohol.** L. A. WOOTEN and L. P. HAMMETT (J. Amer. Chem. Soc., 1935, 57, 2289—2296).—The relative strengths of 33 carboxylic and phenolic acids have been determined by the potentiometric method. The effect of a substituent on variation in relative strength with changing medium is that to be expected from the electric moment of the substituent and the dielectric const. of the medium, when the substituent is introduced into the mol. at some distance from  $CO_2H$ . Some other influence is preponderant when substitution is adjacent to  $CO_2H$ .

E. S. H.

**Existence of boric acid complexes with one and with two molecules of a diol in aqueous solutions.** J. BOESEKEN and N. VERMAAS, and (in part) W. H. ZAAYER, and J. L. LEEFERS (Rec. trav. chim., 1935, 54, 853—860).—From the equations representing the equilibria involved in the titration of diols with  $KBO_2$  (cf. A., 1932, 1204), and the evaluation of  $K_1$  ( $2.5 \times 10^{-6}$  at 18° for mannitol;  $3.7 \times 10^{-6}$  at 18.5° for sorbitol) and  $K_2$  ( $1.10$  and  $2.11 \times 10^{-4}$ , respectively), it is possible to calculate the concn. of all the components present in solution. Rotatory dispersions, in close agreement with the experimental vals., are calc. The rotatory dispersion curve for a solution containing an excess of borate is different from that containing an excess of mannitol. A preliminary analysis of the system  $NaBO_2$ -sorbitol indicates that the system is less simple.

J. W. B.

**Activity of chloride ions in some solutions of complex chlorides of cobalt and chromium (III).** M. CHATELET and F. KERTESZ (Compt. rend., 1935, 201, 817—819).—Electrode potential measurements with  $AgCl$  electrodes are recorded for aq.  $KCl$ ,  $BaCl_2$ ,  $[CoCl(NH_3)_5]Cl_2$ ,  $[CoH_2O(NH_3)_5]Cl_2$ , and  $[CrCl(NH_3)_5]Cl_2$  (0.0002—1 molar). For the two Co salts there is only one ionised Cl. For the Cr salt the ionisation of the second Cl increases with dilution.

H. J. E.

**Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their compounds of high mol. wt. XXX. Iso- and hetero-polytungstic acids, especially the mechanism of formation of arseno- and phospho-tungstic acids.** G. JANDER and H. BANTHIE (Z. anorg. Chem., 1935, 225, 162—172; cf. A., 1934, 1319).—In aq. solutions containing

$\text{WO}_4''$  and  $\text{PO}_4'''$  (or  $\text{AsO}_4'''$ ) increasing  $[\text{H}^+]$  leads to the successive formation of hexatungstic acids, and hetero-acids in which  $\text{P(As):W}=1:6, 1:12$ , or  $2:18$ . The systems have been studied by the diffusion method. F. L. U.

**Test of mass law on concentrated molten solutions by potential measurements.** L. HOLUB, F. NEUBERT, and F. SAUERWALD (Z. physikal. Chem., 1935, 174, 161—198).—Equilibrium consts. and activities have been determined by potentiometric measurements for the systems  $\text{Pb-Sn-Cl}_2$ ,  $\text{Pb-Cl}_2$ ,  $\text{Cd-Pb-Cl}_2$ ,  $\text{Cd-Cl}_2$ ,  $\text{Pb-Ag-Cl}_2$ ,  $\text{Pb-Ag-Br}_2$ ,  $\text{Pb-Ag-I}_2$ ,  $\text{Ti-Cd-Cl}_2$ ,  $\text{Ti-Pb-Cl}_2$ , and  $\text{Cd-Sn-Cl}_2$ . The equilibrium consts. determined directly with cells of the Daniell type differ from the vals. calc. from activities, indicating that activities cannot generally be determined electrochemically owing to irreversibility of the necessary electrodes. The Lorenz-van Laar mass law (A., 1926, 355) fails completely in almost every case. There are large deviations from the ideal mass law, and in some cases where the const. has approx. the correct val. this is due to the accidental compensation of opposed deviations from ideality on the part of the substances involved. It has not been possible to determine at what concns. there is ideality of behaviour of the mols. and ions. In attempting to determine the mol. state of reactants from the constancy of the appropriate mass law quotients it is found that quotients which are most nearly const. do not always correspond with the most probable reaction; both simple and associated mols. or ions may be present simultaneously. R. C.

**Physical chemistry of lipins. III.**—See A., 1935, 1523.

**Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures.** I. R. KRITSCHESKI and J. S. KASARNOVSKI (J. Amer. Chem. Soc., 1935, 57, 2168—2171).—A thermodynamic equation, which allows the calculation of the solubility of slightly sol. gases in solvents with small v.p., is given. The equation is verified for  $\text{N}_2$  and  $\text{H}_2$  in  $\text{H}_2\text{O}$  at 0—100° and pressures up to 1000 atm. Partial mol. vols. of  $\text{N}_2$  and  $\text{H}_2$  in aq. solution are calc. E. S. H.

**Deliquescence and efflorescence.** A. DAMIENS (Bull. Soc. chim., 1935, [v], 2, 1893—1901; cf. A., 1934, 490).—It is suggested that the terms "deliquescent" and "efflorescent" should be replaced by "critical hygrometric state" defined by  $100p/P$ , where  $p$  and  $P$  are the v.p. of the system and the v.p. of  $\text{H}_2\text{O}$ , respectively. Hygrometric data recorded in various parts of France during several years are discussed. O. J. W.

**Determination of critical hygrometric states.** M. DIENIS (Bull. Soc. chim., 1935, [v], 2, 1901—1907; cf. preceding abstract).—The aq. v.p. of various saturated salt solutions and solid salt hydrates has been measured at 20° and 25°. The "crit. hygrometric states" are recorded. O. J. W.

**Fusion curves of mixtures of water and deuterium oxide. Solution equilibrium in the system water-deuterium oxide.** M. DEZELIC (Z. anorg. Chem., 1935, 225, 173—174).— $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$

form an unbroken series of solid solutions, the f.p. of which is a linear function of the composition. Separation by means of fractional crystallisation is therefore impossible. F. L. U.

**Thermal analysis of the system  $\text{POCl}_3\text{-SO}_2\text{Cl}_2$ .** G. P. LUTSCHINSKI and A. I. LICHATSHEVA (Z. anorg. Chem., 1935, 225, 175—176).—The m.p.-composition diagram of  $\text{POCl}_3\text{-SO}_2\text{Cl}_2$  is of the simple eutectic type. The eutectic point is at  $-73.8^\circ$  and 25.1 mol.-% of  $\text{POCl}_3$ . F. L. U.

**Thermal analysis of the system argon-boron trifluoride. Compounds with the inert gases of the atmosphere.** H. S. BOOTH and K. S. WILLSON (J. Amer. Chem. Soc., 1935, 57, 2273—2280).—F.p.-composition curves show maxima at ratios of 1 atom of A to 1, 2, 3, 6, 8, and 16 mols. of  $\text{BF}_3$ , indicating that compounds are formed. The compounds are unstable and decompose above their m.p.;  $\text{A}_2\text{BF}_3$  appears to be the most stable. The influence of pressure on f.p. suggests the equilibrium  $\text{A} + x\text{BF}_3 \rightleftharpoons \text{A}_x\text{BF}_3$  or  $\text{A}_x\text{BF}_3 + y\text{BF}_3 \rightleftharpoons \text{A}_{(x+y)}\text{BF}_3$ . E. S. H.

**Critical phenomena of the system argon-boron trifluoride.** H. S. BOOTH and K. S. WILLSON (J. Amer. Chem. Soc., 1935, 57, 2280—2284).—Retrograde condensation and immiscibility are observed. The compounds formed in this system (cf. preceding abstract) are completely dissociated in the crit. temp. region and scarcely affect the results. E. S. H.

**Dissociation of ferrous carbonate.** J. KRUSTINSONS (Z. anorg. Chem., 1935, 225, 93—96).—Dissociation pressures of  $\text{FeCO}_3$  have been determined over the range 250—290°. The calc. heat of dissociation is 20.9 kg.-cal. F. L. U.

**Dissociation of NiS.** D. N. TARASENKOV and A. V. BOGOSLOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 836—838).—NiS gradually loses S when heated in  $\text{N}_2$  at 700°, and the v.p. gradually diminishes as the composition of the product approaches that of  $\text{Ni}_3\text{S}_2$ . This suggests that the NiS ordinarily prepared from Ni and S is a solid solution of S in some other sulphide. R. T.

**Direct determination of zinc vapour concentration in the thermal reduction of zinc oxide.** O. DONY-HÉNAULT and C. DECROLY (Compt. rend., 1935, 201, 726—728).—The  $[\text{Zn}]$  in the vapour phase has been determined by allowing the gas in the reduction vessel (at 920—1075°) to expand into a second evacuated vessel, cooling the latter, and determining its Zn content. H. J. E.

**Solubility product constant of calcium carbonate in sea-water.** R. REVELLE and R. H. FLEMING (Proc. 5th Pacific Sci. Cong., 1933, 3, 2089—2092).—The solubility product of  $\text{CaCO}_3$  in sea- $\text{H}_2\text{O}$  is  $2.37 \times 10^{-6}$ . The activity coeff. of  $\text{Ca}^{++}$  for normal salinity is 0.225. Sea- $\text{H}_2\text{O}$  is approx. saturated with  $\text{CaCO}_3$ . CH. ABS. (f)

**Equilibrium in the system  $\text{H}_2\text{O-MgBr}_2$ .** F. H. GETMAN (Rec. trav. chim., 1935, 54, 866—872).—Solubility data are recorded for  $-42.7^\circ$  to  $100^\circ$  and extrapolated to  $172.4^\circ$ , the m.p. of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ . F.p. data for  $\text{MgBr}_2$  solutions are also given. The only hydrates formed are  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  and

MgBr<sub>2</sub>·10H<sub>2</sub>O, the transition temp. being 0.83°. The eutectic temp. for MgBr<sub>2</sub>·10H<sub>2</sub>O, ice, and solution is -42.7°. Attempts to obtain MgBr<sub>2</sub>·4H<sub>2</sub>O by heating MgCl<sub>2</sub>·6H<sub>2</sub>O were unsuccessful. J. W. S.

**System alkali oxide-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CO<sub>2</sub>. V. Stable equilibria in the system Na<sub>2</sub>O-SiO<sub>2</sub>-CO<sub>2</sub> and pressures of CO<sub>2</sub> in the reaction between K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub>. C. KROGER and E. FINGAS (Z. anorg. Chem., 1935, 225, 1—23; cf. A., 1935, 935).—The reaction of Na<sub>2</sub>CO<sub>3</sub> with Na<sub>2</sub>SiO<sub>5</sub>, Na<sub>2</sub>SiO<sub>7</sub>, and Na<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> and mixtures of these has been studied by measuring the pressure (*p*) of CO<sub>2</sub> over the systems at various temp. (*t*). CO<sub>2</sub> is absorbed only when the ratio Na<sub>2</sub>O/SiO<sub>2</sub> > 0.5. *p-t* diagrams are given for this system and for the system K<sub>2</sub>O-SiO<sub>2</sub>-CO<sub>2</sub>. Thermal data relating to the formation of several Na silicates are calc. Dissociation pressures of cryst. and fused Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> have been determined. F. L. Ü.**

**Double decomposition in absence of a solvent. XXVIII. V. P. RADISCHTSHEV (J. Gen. Chem. Russ., 1935, 5, 455—490).—Equilibrium data are recorded for the system NaCl-NaBr-NaI-KCl-KBr-KI, which is treated as a combination of 9 binary, 2 ternary, and 4 quaternary systems. The solid phases are binary, ternary, and quaternary solid solutions. R. T.**

**Heat capacity and free energy of formation of naphthalene. J. N. PEARCE and W. B. TANNER (Proc. Iowa Acad. Sci., 1934, 41, 123—126).—The heat capacity of C<sub>10</sub>H<sub>8</sub> has been measured from liquid air temp. to 298.1° abs.; vals. for changes in heat content, entropy, and free energy accompanying its formation from its elements are calc. CH. ABS. (e)**

**Difference in the heats of formation of the two isomerides of butane. Estimate of the heat of formation of tetramethylmethane. F. D. ROSSINI (J. Chem. Physics, 1935, 3, 438; cf. A., 1934, 966, 1071).—Computed vals. (kg.-cal. per mol.) are: *n*-C<sub>4</sub>H<sub>10</sub> (gas) → *iso*-C<sub>4</sub>H<sub>10</sub> (gas), -1.63 ± 0.15; *n*-C<sub>5</sub>H<sub>12</sub> (gas) → CMe<sub>4</sub> (gas), -4.9 ± 1.0; 5C (graphite) + 6H<sub>2</sub> → CMe<sub>4</sub>, -40.7 ± 1.2; 5C (diamond) + 6H<sub>2</sub> → CMe<sub>4</sub>, -41.8 ± 1.2. N. M. B.**

**Ionic migration as a molecular-kinetic problem. A. MAGNUS (Z. physikal. Chem., 1935, 174, 262—268).—Regarding the solvent, not as a continuous medium, but as a system the mol. motions of which are controlled by the laws of the kinetic theory of gases, the steady mobility of ions is accounted for by supposing that between two collisions with solvent mols. the ion is accelerated in the direction of the electric field, then slowed down again by the next collision. From known ionic mobilities the mean free paths can be calc., and prove, especially for small and doubly-charged ions, to be the calc. mol.-kinetic vals. and independent of temp., a discrepancy which is attributed to attraction between the ions and the H<sub>2</sub>O dipoles. R. C.**

**Mobility of the hydrogen and hydroxyl ions in aqueous solution. I. G. WANNIER (Ann. Physik, 1935, [v], 24, 543—544).—The explanation of the high mobilities of H' and OH' on the basis of a proton transfer from one H<sub>2</sub>O mol. to the next is discussed.**

H' and OH' should approximate to Na' in mobility, and an interpretation of the proton transference is offered on the basis of the tetrahedral structure of H<sub>2</sub>O, H<sub>3</sub>O', and OH'. H<sub>2</sub>O has one potential "hole" and 3 protons, H<sub>3</sub>O' 2 holes and 2 protons, OH' 3 holes and one proton, so that in a sense OH' is the mirror image of H<sub>3</sub>O'. The effect of a field on the ions does not require further assumptions.

A. J. M.

**Electrolysis of copper in rock-salt. S. A. ARZIBISCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 157—160; cf. A., 1935, 39).—Data recorded previously are corr. and discussed. Cu diffuses readily in either NaCl or KCl, although the ionic radii of K' and Cu'' are very different. Au also diffuses readily in KCl or NaCl. J. W. S.**

**Thermodynamics of the electric cell in heterogeneous systems. D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 159—167).—Mathematical.**

D. R. D.

**The concentration cell and Nernst's formula. D. MATURO (Rev. Fac. Quim. Ind. Agric., 1934, 3, 168—176).—The equations already deduced (cf. preceding abstract) are applied to the study of the contact potential between a metal and a solution of one of its salts.**

D. R. D.

**Potentials of cells in liquid ammonia solutions. Thermodynamic constants of the amminocadmium chlorides and of cadmium chloride. C. S. GARNER, E. W. GREEN, and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 2055—2058).—E.m.f. of the cells Zn(amalgam, N<sub>2</sub>)|ZnCl<sub>2</sub>·6NH<sub>3</sub>(s), NH<sub>4</sub>Cl in NH<sub>3</sub>(l), CdCl<sub>2</sub>·6NH<sub>3</sub>(s)|Cd(amalgam, N<sub>2</sub>) have been determined at 25°. When Zn and Cd are present as pure metals *E*<sub>298.2</sub> = 0.3605 volt. The standard free energies, heat contents, and virtual entropies of CdCl<sub>2</sub> and CdCl<sub>2</sub>·*x*NH<sub>3</sub> (where *x* = 1, 2, 4, 6, 10) have been calc. E. S. H.**

**Becquerel cells. G. ATHANASIU (Ann. Physique, 1935, [xi], 4, 377—449; cf. A., 1925, ii, 1067).—For cells with Ag-AgI and Hg-Hg<sub>2</sub>I<sub>2</sub> electrodes the positive photo-voltaic effect is increased by the H ions of the electrolyte, and may be destroyed or reversed by the OH ions. This is explained by assuming that the electrolyte is a "receiver" of products liberated in the photo-chemical reaction. Lowering of temp. increases the photo-voltaic effect; this is explained by regarding the electrode as the seat of two opposing reactions, a photo-chemical, on which temp. has little effect, and a purely thermal inverse reaction. Ag-AgI electrodes show sensitivity max. at 0.4225 and 0.30 μ, coinciding with the absorption max. of AgI; 0.4225 μ coincides with the photo-conductivity max. of AgI. For Hg-Hg<sub>2</sub>I<sub>2</sub> electrodes the max. is at 0.400 μ, and the sensitivity threshold at 0.530—0.540 μ. The Cu-CuO electrode sensitivity ranges from 1 μ, in the infra-red, to a max. at 0.400 μ. Ag electrodes covered with a thick cryst. layer of Ag<sub>2</sub>S show a sensitivity max. at 1.35—1.4 μ, coinciding with the photo-conductivity max.; this is also the case for Cu electrodes covered with Cu<sub>2</sub>O by thermal and by electrical deposition. The sensitivity max. is at 0.480 μ, and the photo-voltaic and photo-cryst. effects are compared. Results, in general,**



support the theoretical explanations previously reported. N. M. B.

**Polarographic studies with the dropping mercury cathode. LV. Influence of air on solutions of salvarsan derivatives.** R. BRDIČKA (Coll. Czech. Chem. Comm., 1935, 7, 457—466; cf. A., 1934, 1241).—Traces of toxic oxidation products (I) present in neosalvarsan (II), syntharsan (III), and myosalvarsan (IV) may be determined electro-polarimetrically. (II) is most sensitive to oxidation and has been studied most fully. Using an atm. of  $H_2$  and a dropping Hg cathode it is shown that (II), (III), and (IV) are not electro-reduced in presence of NaCl, LiCl, and  $LiNO_3$ , but waves appear in the polarograms, due to electro-reducible (IV) (present even in the purest specimens). Solutions which have been oxidised by  $O_2$ , and from which dissolved  $O_2$  has been expelled by  $H_2$ , give more pronounced waves owing to increased concn. of (I); the latter may be determined from the height of the waves. (III) gives smaller waves than corresponding solutions of (II) owing to its greater purity, but is otherwise similar; (IV) is more slowly oxidised than (II). In presence of LiCl,  $Na^+$  gives a wave of the polarograms at  $-2.0$  volt, owing to the diffusion current associated with the deposition of Na, and the % of Na can be determined from the height of this wave.

R. S. B.

**Electrode polarisation in separation of metal from solutions of complex cyanides.** O. ESSIN and A. MATANZEV (Z. physikal. Chem., 1935, 174, 384—394).—Analysis of Glasstone's experimental data (A., 1929, 654; 1930, 864) has shown that the existence of concn. polarisation caused by accumulation of  $CN^-$  at the cathode leads in several cases to relations between polarisation and c.d. which are analogous to the equation for H overvoltage. For the discharge of Hg from cyanide solutions, this demonstrates the existence of chemical polarisation, supposedly due to delayed discharge in the sense of Volmer's theory of overvoltage. In the separation of Cu there is no chemical polarisation, but rather a depolarising action. For the separation of Ag and Cd the experimental data are indecisive. R. C.

**Organic depolarisers.** W. F. HUNTER and L. F. STONE (J. Physical Chem., 1935, 39, 1139—1147).—The single potentials of a no. of depolarisers have been measured against Pt, Au, Ag, Sn, and Ni cathodes. A general interpretation in terms of the electron affinity of depolarisers and the work function of electrodes is advanced. R. S.

**Acid-base titration in alcohol-water mixtures. III. Titration of alkaloids and alkaloid salts.**—See this vol., 91.

**Electrometric control of displacement reactions. (Mlle.) S. VEIL** (Compt. rend., 1935, 201, 885—887).—The e.m.f. produced by Pt and Zn when in contact and immersed in  $0.2N$ - $CuSO_4$  decreases rapidly from the Volta p.d. to a min., then rises to a max., and oscillates. R. S. B.

**Determination of activity of unsaturated organic compounds from the e.m.f. of their reaction with sodium.** B. V. TRONOV and L. P.

KULEV (J. Gen. Chem. Russ., 1935, 5, 1007—1015).—The e.m.f. between Na and Pt electrodes in  $C_6H_6$  solutions of ketones, keto-acids, aldehydes (except MeCHO), nitriles (except MeCN), amines,  $C_5H_5N$ , cyclohexanone, and mesitylene oxide is greatly increased in presence of NaI, whilst that of carboxylic acids, esters (including nitrates), alcohols, unsaturated hydrocarbons, pyrrole, and nitromethane is unaffected;  $PhNO_2$  and isoamyl nitrite occupy an intermediate position. R. T.

**Explosion regions. XXVI. Shape of explosion regions and their diameters.** W. P. JORISEN (Rec. trav. chim., 1935, 54, 888—892; cf. A., 1933, 469, 573, 790).—Theoretical. J. W. S.

**Heavy hydrogen. V. Elementary reactions of light and heavy hydrogen. Thermal conversion of ortho-deuterium and the interaction of hydrogen and deuterium. VI. Ratio of the magnetic moment of the proton to the magnetic moment of the deuteron.** A. FARKAS and L. FARKAS (Proc. Roy. Soc., 1935, A, 152, 124—151, 152—157).—V. In the temp. range  $850$ — $1000^\circ$  abs. and at pressures 3—74 mm. the reconversion of ortho- $D_2$  (i) and the interaction of  $H_2$  and  $D_2$  (ii) proceed in the homogeneous gas phase according to the mechanisms: (i)  $D + o\text{-}D_2 \rightleftharpoons p\text{-}D_2 + D$  and (ii)  $D + H_2$   $HD + H$ ,  $H + D_2$   $HD + D$ . Reaction (i) proceeds 2.4 times, and reaction (ii) 1.5 times, more slowly than the reconversion of para- $H_2$  at the same temp. and pressure. In (i) this is mainly due to the different collision frequency and concn. of D atoms. The difference in the energies of activation involved in the reactions  $D + D_2$ ,  $D_2 + D$  and  $H + H_2$   $H_2 - H$  is only 510 g.-cal., but in (ii), the different reaction rate is due to the fact that the energy of activation for the partial reaction  $H + D_2 \rightleftharpoons HD + D$  is about 1.7 kg.-cal. > that for  $D + H_2$   $HD + H$ . This behaviour is explained by assuming that the activated complexes HHH, DHH, HDD, and DDD possess zero-point energies similar to the mols.  $H_2$ , HD, and  $D_2$ . A scheme for the energy levels involved in these interchanges is worked out.

VI. From a comparison of the velocity coeffs. of the ortho-para  $H_2$  and  $D_2$  conversions, in the presence of  $O_2$ , using the theory of Kalckar and Teller (A., 1934, 940), the ratio of the magnetic moment of the proton to that of the deuteron is found to be 3.96—0.11. J. L. L. B.

**Mechanism of the chain reaction in oxygen-hydrogen mixtures.** M. PRETTE (Compt. rend., 1935, 201, 728—730; cf. A., 1935, 827).—The activation energy of the  $H_2$ - $O_2$  reaction in reaction vessels coated with KCl is  $95,000 \pm 6000$  g.-cal. The reaction kinetics under these conditions are consistent with the Haber chain mechanism. H. J. E.

**Explosion of mixtures of combustible gases with air by nuclear drops of water and other nuclei and by X-rays. V. Experimental conditions required for ignition of hydrogen-air mixtures and nuclei. VI. Nuclear drop-ignition temperatures of ethylene-air mixtures passing through a silica combustion tube; relation between wall and gas temperature and effect on**

ignition temperatures of the central thermocouple sheath. VII. Effect of a variety of nuclei, mainly mineral dusts, to ignite and explode a mixture of hydrogen and air; exceptional efficacy of  $\text{Ni}_2\text{O}_3$  dust to ignite mixtures of air with hydrogen, ethylene, or methane. R. O. KING and G. MOLE (J. Inst. Petroleum Tech., 1935, 21, 838—845, 845—853, 853—859; cf. A., 1934, 1074).—V. An apparatus for direct measurement of the steam-forming activities (from dry  $\text{H}_2$  and air) of various combustion-tube surfaces, *e.g.*, Cr-Ni steel, Ni steel, and  $\text{SiO}_2$ , is described. The over-all steam-forming effect varies in a particular tube with the variety, temp., and distribution of surface oxide, and steam is not formed at a const. rate until the oxide attains equilibrium with the  $\text{H}_2$  in the existing conditions. Self- ( $T_s$ ) and nuclear-ignition temp. ( $T_n$ ) were determined in the same apparatus.  $T_s$  varies with surface activity, and it is concluded that self-ignition occurs in the boundary layer adjacent to the hot surface.

VI. The wall temp. in the Ni-steel tube was  $16\text{--}30^\circ >$  the temp. indicated by a central thermocouple, and the differences were always  $2\text{--}5^\circ$  greater when the tube was coated with oxide. Experiments showed that the surface of the thermocouple sheath was without effect on  $T_s$  of  $\text{C}_2\text{H}_4$ -air mixtures. Ignition in this mixture may begin in the gaseous mixture apart from a free surface.  $T_s$  diminishes on changing from the active steel surface to the relatively inactive  $\text{SiO}_2$  surface and the range of inflammability increases to a remarkable extent. Nuclear ignition is obtainable when ignition from the surface is prevented by steam dilution of the adjacent layer of gaseous mixture, the effect then being obtained on the surface of the nuclei in the gaseous stream. The effect is obtained when oxidation nuclei reach a suitable concn., or it may be induced by providing nuclear centres, *e.g.*,  $\text{H}_2\text{O}$  or dust.

VII. Added nuclei such as compounds of Fe, Pb, Zn, Ni, and Cr all proved effective to explode a mixture of  $\text{H}_2$  and air,  $\text{Ni}_2\text{O}_3$  having an exceptional igniting effect;  $T_n$  was as low as  $430^\circ$  for  $\text{Ni}_2\text{O}_3$ , compared with  $640\text{--}690^\circ$  for other nuclei, for a 40%  $\text{H}_2$  mixture supplied to a Cr-Ni steel tube at 300 c.c. per min. In a  $\text{SiO}_2$  tube for  $\text{H}_2$ -air, the min.  $T_s$  under given conditions was  $566^\circ$  compared with  $T_n$   $395^\circ$ .  $\text{Ni}_2\text{O}_3$  has a smaller igniting effect on  $\text{C}_2\text{H}_4$ -air mixtures than on  $\text{H}_2$ -air, the max. igniting effect occurring when the  $[\text{C}_2\text{H}_4]$  is about 50% > is required for combining proportions. For  $\text{CH}_4$ -air, using  $\text{Ni}_2\text{O}_3$ ,  $T_n$  is about  $75^\circ < T_n$  and the min.  $T_n$  is obtained when the  $[\text{CH}_4]$  is 50% < is required for combining proportions. C. C.

Ignition of firedamp by compression.—See B., 1935, 1124.

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. IV. Decomposition of isopropyl nitrite. E. W. R. STEACIE and G. T. SHAW (Proc. Roy. Soc., 1935, A, 151, 685—693).—The thermal decomp. of  $\text{Pr}^i\text{NO}_2$  between  $170^\circ$  and  $210^\circ$  is homogeneous and of the first order. The main reaction is  $\text{Pr}^i\text{NO}_2 = \text{NO} + 0.5\text{COMe}_2 + 0.5\text{Pr}^i\text{OH}$ , analogous to those of the other alkyl nitrites investigated (cf. A., 1934, 847, 1312). The reaction rate is

given by  $k = 1.26 \times 10^{14} e^{-37,000/RT}$  sec.<sup>-1</sup> Comparison of the rates and activation energies of  $\text{Pr}^i\text{NO}_2$  and  $\text{Pr}^n\text{NO}_2$  shows that there is no appreciable variation due to chemical configuration. L. L. B.

Thermal decomposition of triethylamine. H. A. TAYLOR and E. E. JUTERBOCK (J. Physical Chem., 1935, 39, 1103—1110; cf. A., 1932, 1002).—The decomp. is unimol. at high pressures between  $450^\circ$  and  $500^\circ$  and tends to become bimol. at lower pressures. In the initial stages, the energy of activation is approx. 50,000 g.-cal. A sevenfold increase of surface and additions of  $\text{N}_2$  and  $\text{NH}_3$  are without effect, but marked differences occur when  $\text{H}_2$  is added. It is suggested that the intermediate products are  $\text{Et}_4\text{N}_2$  and  $\text{C}_4\text{H}_{10}$ , which ultimately yield  $\text{CH}_4$  and  $\text{N}_2$ . R. S.

Mechanism of slow oxidation of propane. R. N. PEASE (J. Amer. Chem. Soc., 1935, 57, 2296—2299).—At  $300^\circ$ , with mixtures containing 10—30% of  $\text{O}_2$ , the primary products are  $\text{MeOH}$ ,  $\text{MeCHO}$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ . The results are interpreted in terms of Rico's radical-chain theory, on the assumption that  $\text{OMe}$  and  $\text{Pr}$  are the chain carriers. Similar mechanisms may apply to the oxidation of  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$ . E. S. H.

Thermal decomposition of nitromethane. H. A. TAYLOR and V. V. VESSELOVSKY (J. Physical Chem., 1935, 39, 1095—1101; cf. A., 1931, 175).—The reaction is unimol. in its early stages and has an energy of activation of 61,000 g.-cal. The gaseous and solid products have been analysed and the intermediate formation of  $\text{MeNO}$  is postulated. Increase of surface affects the later stages of the reaction, additions of  $\text{He}$ ,  $\text{N}_2$ ,  $\text{NO}$ , and  $\text{CO}_2$  are without effect, whilst  $\text{O}_2$  reacts. H. S.

Induction period in gaseous thermal explosions. O. K. RICE, A. O. ALLEN, and H. C. CAMPBELL (J. Amer. Chem. Soc., 1935, 57, 2212—2222).—When the differential equation connecting temp. with time in an exothermic gas reaction is integrated, a sudden rise of temp., corresponding with an explosion, is indicated above a definite pressure. An approx. method for calculating the induction period in thermal explosions has been obtained from such curves, and applied to explosions of  $\text{Me}_2\text{N}_2$  and  $\text{EtN}_3$ . Approx. heats of decomp. of these compounds have been obtained. E. S. H.

Temperature coefficients in the acid hydration of sodium pyrophosphate. S. J. KIEHL and E. CLAUSSEN, jun. (J. Amer. Chem. Soc., 1935, 57, 2284—2289).—The rate of conversion of  $\text{Na}_4\text{P}_2\text{O}_7$  into  $\text{Na}_3\text{PO}_4$  in  $\text{HCl}$  solution has been determined at  $30\text{--}90^\circ$  and an empirical equation developed. Temp. coeffs. for  $15^\circ$  intervals have been calc. E. S. H.

Kinetics of the permanganate-oxalate reaction. I. Effect of various salts on the rate of reaction. R. W. FESSENDEN and B. C. REDMON (J. Amer. Chem. Soc., 1935, 57, 2246—2249).—A negative salt effect has been found in this reaction.  $\text{Zn}^{++}$ ,  $\text{Cd}^{++}$ , and  $\text{Al}^{+++}$ , which show apparent positive effects, form complex oxalates and thus decrease  $[\text{C}_2\text{O}_4^{--}]$ . E. S. H.

**Oxidation under pressure of ferrous sulphate in neutral and acid solution.** G. AGDE and F. SCHIMMEL (Z. anorg. Chem., 1935, 225, 29—32).—The influence of temp.,  $[\text{FeSO}_4]$ , and pressure of  $\text{O}_2$  on the oxidation of aq.  $\text{FeSO}_4$  has been determined. Under suitable conditions the oxidation is nearly complete. A part of the product is in the form of insol. basic salt, unless the required amount of free  $\text{H}_2\text{SO}_4$  is added. The presence of the latter does not affect the extent or the rate of oxidation. F. L. U.

**Kinetics of the reaction between permanganate and manganous ions.** M. J. POLISSAR (J. Physical Chem., 1935, 39, 1057—1066).—The reaction between  $\text{Mn}^{++}$  and  $\text{MnO}_4^-$  has been studied visually and by a semi-quant.  $\text{H}_2\text{C}_2\text{O}_4$ -I method. It is autocatalytic, catalysis being due to the  $\text{MnO}_2$  formed. The rate increases with the concn. of reactants, but diminishes with increasing acidity.  $\text{MnO}_2$  prepared in neutral solution is more effective than that prepared in acid solution, probably owing to its greater dispersion. Determinations of  $\text{MnO}_2$  by the  $\text{H}_2\text{C}_2\text{O}_4$  method may be carried out only at low  $[\text{Mn}^{++}]$ . The course of the reaction is altered by addition of  $\text{SO}_4^{--}$  or  $\text{F}^-$ , which form complex manganic ions, whilst sunlight has no appreciable effect. R. S.

**Hydrolysis velocity of ketimines: steric hindrance effect.** J. B. CULBERTSON, W. REYNOLDS, and C. MAIN (Proc. Iowa Acad. Sci., 1934, 41, 170—171).—Data are recorded for the rates of hydrolysis of 2:6-, 2:5-, 2:4-, and 3:5-dimethyldiphenyl ketimine hydrochlorides. CH. ABS. (c)

**Hydrolysis of phenyl furyl ketimine: relative negativity effect.** J. B. CULBERTSON and L. HINES (Proc. Iowa Acad. Sci., 1934, 41, 172).—Data for the rate of hydrolysis at  $0^\circ$  and  $25^\circ$  are recorded. The rule that the ketimine salts are more resistant to hydrolysis the more negative are the radicals attached to the C:NH is supported. CH. ABS. (c)

**Velocity of decomposition of diazo-compounds in water.** XVIII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1935, 38, 528—532B; cf. A., 1935, 1082).—The velocity coeffs. for the decomp. of 4:4'-tetrazo-, 2:2'-dimethyl-, 2:2'-dimethoxy-, and 2:2'-disulpho-4:4'-tetrazo-diphenyl chloride at  $30^\circ$  are respectively 1.31, 10.3, 0.0483 (extrapolated) and  $2.42 \times 10^{-4}$ . The temp. coeffs. have been determined. R. S. B.

**Reaction rate of acetic anhydride and water.** E. K. PLYLER and E. S. BARR (J. Chem. Physics, 1935, 3, 679—682; cf. A., 1934, 829).—By measuring the intensity of infra-red absorption bands characteristic of  $\text{AcOH}$  and  $\text{Ac}_2\text{O}$ , reaction velocities of  $\text{Ac}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{AcOH}$  have been determined. The reaction is approx. unimol. at all concns. studied, and the velocity coeff. decreases with time. An extended application of the method is suggested. F. L. U.

**Kinetics of addition of hypochlorous acid to double linkings. I. Crotonic acid.** E. A. SCHILOV and N. P. KANJAEV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 19—46).—The reaction of addition of  $\text{HOCl}$  (I) to crotonic acid (II), or its anion, is one of the first order with respect to (II), and of the second

with respect to (I); the reaction is retarded by  $\text{H}^+$ , and unaffected by neutral salts, whilst  $\text{Cl}^-$  acts catalytically in acid solutions only, so that in presence of  $\text{HCl}$  the velocity of reaction  $-d[\text{HOCl}]/dt = (k'[\text{H}^+] + k''n)[\text{HOCl}][\text{crotonic acid}][\text{Cl}^-]$ , where  $n$  is the dissociation const. of (II). The temp. coeff. of the reaction in presence of  $\text{HCl}$  is 1.62 per  $10^\circ$ . The order of the reaction varies greatly with changes in the concn. of the substrates and in the  $p_{\text{H}}$  of the medium. The reaction in acid media is supposed to consist of addition of the complex  $\text{HOCl} \cdot \text{HCl}$  to the  $\text{C}=\text{C}$ , followed by regrouping and elimination of  $\text{HCl}$ , whilst in alkaline media, in which  $\text{OCl}^-$  is the catalyst, the complex ion  $\text{HOCl} \cdot \text{OCl}^-$  is assumed to react directly with (II). R. T.

**Time course of the heat effects in rapid chemical changes.**—See this vol., 91.

**Oxidation of hæmoglobin to methæmoglobin by oxygen.** II.—See this vol., 92.

**Kinetics of displacement of silver from silver nitrate solutions by metallic lead.** S. KRZYŻAN-SKI (Z. anorg. Chem., 1935, 225, 151—161).—The reaction is of zero order for initial concns. within the limits 0.125—1N- $\text{AgNO}_3$ . The temp. coeff. of the velocity is of the same order as that of the diffusion coeff. F. L. U.

**Dust explosions.** A. A. VAN DER DUSSEN (Rec. trav. chim., 1935, 54, 873—884).—The quantities of Al-S mixture, coal, or anthracene dust required to be suspended in unit vol. of air to cause explosion on ignition have been measured. The effects of non-combustible powders in suppressing such explosions follow the order  $\text{K}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{stone dust} > \text{fuller's earth}$ . J. W. S.

**Corrosion of iron.**—See B., 1935, 1145.

**Sensitised explosions. I. Hydrogen-oxygen reaction catalysed by nitrogen peroxide.** S. G. FOORD and R. G. W. NORRISH (Proc. Roy. Soc., 1935, A, 152, 196—220; cf. A., 1933, 236).—The region of ignition, which occurs between narrow limits of concn. of catalyst, is bounded by regions of slow reaction, the velocity of which is increased by light which generates O atoms from the  $\text{NO}_2$ . There is no distinction in the mode of generation of the slow and explosive reactions; both intervene sharply at the end of an induction period, during which the no. of chains grows at first slowly and then rapidly to a crit. val. The induction periods are reduced by irradiation to  $< 1$  sec. over nearly the whole range of catalytic effect of  $\text{NO}_2$ . The data support the view that the branching initially exceeds the extinction of chains over the whole region of catalysis, and that an equilibrium concn. of chains is ultimately imposed on the slow reaction by the self-neutralisation of chains, and by an increase in their extinction due to products of reaction. The process becomes adiabatic when the no. of chains exceeds a crit. val.  $\text{NO}_2$  exercises a triple role in affecting the origin, branching, and extinction of chains. L. L. B.

**Oxidation of carbon monoxide catalysed by nitrogen dioxide.** R. H. CRIST and O. C. ROEHLING (J. Amer. Chem. Soc., 1935, 57, 2196—2203; cf. A.,

1934, 1314).—The rate is first order with respect to O, at high concns. of NO<sub>2</sub>, and at low concns. it is  $\propto$  [O<sub>2</sub>] and [CO]<sup>2</sup>. E. S. H.

**Aqueous solutions of stannic chloride. III. Autocatalytic character of the flocculation.** J. GUÉRON (Bull. Soc. chim., 1935, [v], 2, 1993—1998; cf. A., 1934, 960).—The curves previously given for the rate of hydrolysis of aq. SnCl<sub>4</sub> solutions can be represented satisfactorily by an equation of the autocatalytic type. The bearing of this on the structure of the colloidal particles formed during the flocculation is discussed. O. J. W.

**Thermal decomposition of sugars and its catalytic acceleration.**—See this vol., 56.

**Influence of pectin on inversion of sucrose.** S. BERLINGOZZI and M. TESTONI (Annali Chim. Appl., 1935, 25, 489—496).—The presence of pectin lowers the velocity of inversion of sucrose (I) in aq. citric acid, the effect being max. at 35° and tending to decrease with rise in temp. For the same temp., inhibition with high concns. of (I) is > that with low concns. F. O. H.

**Effect of salts on the velocity of inversion of sucrose at 25°.** J. N. PEARCE and M. THOMAS (Proc. Iowa Acad. Sci., 1934, 41, 139).—For equal molal concns. of different salts the velocity coeff. increased in the order KCl < NaCl < LiCl < BaCl<sub>2</sub> < Al(NO<sub>3</sub>)<sub>3</sub>. The salt effect is best explained on the basis of ionic hydration. CH. ABS. (c)

**Polar and non-polar effects in esterification.** C. N. HINSHELWOOD and A. R. LEGARD (J.C.S., 1935, 1588—1591; cf. A., 1935, 828).—The H<sup>+</sup>-catalysed rates of esterification by EtOH of Bu<sup>n</sup>CO<sub>2</sub>H and CCl<sub>3</sub>·CO<sub>2</sub>H are < of AcOH, and the energies of activation are raised. The influence of Cl is probably polar, but that of Me is of another kind. J. G. A. G.

**Titanium. Chlorination of titanium dioxide.** A. V. PAMFILOV, A. S. CHUDAKOV, and E. G. SHTANDEL (J. Gen. Chem. Russ., 1935, 5, 605—608).—Max. utilisation of Cl<sub>2</sub> is found at 400° in presence of birch C and MnO<sub>2</sub>; in absence of catalysts, velocity of reaction rises continuously with temp. Considerable quantities of COCl<sub>2</sub> are produced during the reaction. R. T.

**Displacement of noble metals from solutions of their salts by hydrogen at atmospheric or increased pressure. Displacement of (I) Pd from solutions of PdCl<sub>2</sub>, (II) Pt from solutions of H<sub>2</sub>PtCl<sub>6</sub>.** V. V. IPATIEV and V. G. TRONEV (J. Gen. Chem. Russ., 1935, 5, 643—652, 661—666).—I. The reaction PdCl<sub>2</sub> + H<sub>2</sub> → Pd + 2HCl is of an autocatalytic nature, and proceeds at considerable velocity at room temp. and atm. pressure; its velocity is determined by the rate of diffusion of H<sub>2</sub> into the solution. The reaction is retarded by increasing the [HCl] or by adding oxidising agents, but is unaffected by ions of less noble metals, which are displaced only after complete displacement of Pd.

II. The reaction consists of the steps H<sub>2</sub>PtCl<sub>6</sub> → H<sub>2</sub>PtCl<sub>4</sub> → Pt; the above considerations are also applicable to it. R. T.

**Active nitrogen of long duration, law of decay and of increased brightness on compression.** (LORD) RAYLEIGH (Proc. Roy. Soc., 1935, A, 151, 567—584).—The catalytic destruction of active N<sub>2</sub> caused by the walls of the vessel is reduced to a min. by coating the walls with H<sub>2</sub>SO<sub>4</sub> or HPO<sub>3</sub>. Using HPO<sub>3</sub> and a large bulb, the glow remains visible for > 6 hr. A photometric examination over a wide intensity range of the decay of the glow at const. vol., using (a) a bulb coated with Apiezon oil (considerable wall activity), and (b) a bulb coated with HPO<sub>3</sub>, shows that for (a) the decay proceeds according to an exponential law, being apparently a first order reaction, whilst for (b) the data indicate a reaction of the second, or possibly the third, order. The increase of luminosity under compression has been studied photometrically; the intrinsic brightness  $\propto$  (concn.)<sup>2</sup>. This indicates a bimol. reaction in which the excess of neutral N<sub>2</sub> mols. have no part. L. L. B.

**Chlorination of propane. II. The heterogeneous reaction.** L. H. REYERSON and S. YUSTER (J. Physical Chem., 1935, 39, 1111—1123; cf. A., 1935, 1082).—The reaction in presence of Al<sub>2</sub>O<sub>3</sub>, Cu, and CuCl<sub>2</sub> catalysts deposited on SiO<sub>2</sub> gel has been investigated and the energies of activation have been determined. Al<sub>2</sub>O<sub>3</sub> gave some H<sub>2</sub>O, but good results were obtained with CuCl<sub>2</sub>. The amount of Cl<sub>2</sub> reacting increased with rise of temp., but when 100% conversion was attained, the temp. could be considerably reduced without diminishing the % of reaction. This hysteresis effect is interpreted on the basis of the relation between the heat of reaction and the energy of activation. Production of the higher chlorinated products is favoured by high [Cl<sub>2</sub>], high temp., and greater rates of flow, whilst secondary chlorination of CHMe·CH<sub>3</sub>, arising from the pyrolysis of PrCl has been shown to occur. R. S.

**Hydrogenation catalysis. II. Technique of hydrogenation.** A. S. GINSBERG (J. Gen. Chem. Russ., 1935, 5, 795—798).—A simple method of hydrogenation consists in shaking a given wt. of unsaturated substance in EtOH with 1 g. of powdered Fe or Ni, and 0.1 g. of Pd (as PdCl<sub>2</sub>·2NaCl) in an atm. of H<sub>2</sub>. The decrease, *V*, in vol. of the gas is measured after 15 min., and the H no. (vol. of H<sub>2</sub> at n.t.p. absorbed by 1 g. of substance) is given by  $V(B-d)/760(1+\alpha)p-K$ , where *B* is the barometric pressure, *d* the v.p. of H<sub>2</sub>O at temp. *t*,  $\alpha=1/273$ , *p* the wt. of substance taken, and *K* the vol. of H<sub>2</sub> absorbed by the catalyst alone. Instructions for recovering Pd from the used catalyst are given. R. T.

**Conversion of fatty acids and their esters into higher alcohols by catalytic reduction under pressure.**—See B., 1935, 1149.

**Reduction of a catalyst for ammonia synthesis.**—See B., 1935, 1141.

**Catalytic oxidation of sulphur dioxide.**—See B., 1935, 1141.

**Methane formation in gas mixtures containing carbon monoxide and dioxide in contact with various nickel catalysts.**—See B., 1935, 1124.

**Electrolytic separation factor of hydrogen isotopes under various experimental conditions.** A. EUCKEN and K. BRATZLER (*Z. physikal. Chem.*, 1935, 174, 273—290).—Separation factors,  $S$ , varying from 2.7 to 17 have been observed. Using cathodes of Pt, Au, Ag, Cu, Pb, graphite, and Hg no relation between the material or overvoltage of the cathode and  $S$  could be detected. After anodic polarisation of the cathode, unless this is Hg,  $S$  is for some time abnormally high, which suggests that the max. separation will be obtained by electrolysis with a.c., or better, commutated d.c. This effect appears to be due not only to electrolytic liberation of O, but to sorption of O by the cathode from the solution or air, forming a surface oxide; probably the catalytic power of the surface for the union of H atoms to  $H_2$  mols. is in this way increased, so that very rapid removal of the H atoms liberated is achieved. Small amounts of  $\alpha$ -naphthoquinoline depress  $S$  considerably (cf. A., 1935, 309), possibly owing to the formation of intermediate reduction products the H and D atoms of which are able to equilibrate themselves with the solvent. For a given electrode metal  $S$ , if it is already large, rises with the c.d. There is no direct connexion between  $S$  and the slope of the logarithmic c.d.—potential curve. R. C.

**Efficiency of separation of hydrogen and deuterium by electrolysis.** T. H. ODDIE (*Proc. Physical Soc.*, 1935, 47, 1060—1067).—A method is described, taking account of evaporation and spraying losses, for determining the efficiency  $\alpha$  of concn. of  $D_2O$  by electrolysis of  $H_2O$ - $D_2O$  mixtures.  $\alpha$  is independent of the [H] of the electrolyte and the nature of the electrodes, but increases with rising c.d.  $\alpha = 4.0 \pm 0.2$  for c.d. 0.6, and  $4.6 \pm 0.1$  for c.d. 2 amp. per sq. cm., in agreement with theory.

N. M. B.

**Electrolytic separation of lithium isotopes.** A. EUCKEN and K. BRATZLER (*Z. physikal. Chem.*, 1935, 174, 269—272).—Experiments in which aq.  $Li_2SO_4$  was electrolysed with a flowing Hg cathode, and the Li set free reconverted into  $Li_2SO_4$ , and again electrolysed and so on five times gave finally a specimen of Li the at. wt. of which differed from that of ordinary Li by an amount within the limit of experimental error. The separation factor,  $S$ , was at most 1.070. Bell's calculation of  $S$  (A., 1934, 738) is criticised.

R. C.

**Kinetics of formation of anode films on metals.** II. Films of lead chloride on lead. L. J. KURTZ (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 305—308; cf. A., 1935, 1083).—When 0.5*N*-HCl saturated with  $PbCl_2$  is electrolysed with a Pb anode, the latter is first covered with "islands" of cryst.  $PbCl_2$ , which later spread over the whole surface and increase in thickness. The electrical conductivity of the  $PbCl_2$  film increases with increase of c.d., as for AgCl and AgBr films.  $PbCl_2$  films have very small porosity. The kinetics of the growth of  $PbCl_2$  films are studied in the same way as for AgCl films, but the polarisation curves show some differences owing to the greater porosity of the AgCl films. A. J. M.

**Reaction mechanism at a graphite anode.** V. SIHVONEN (*Suomen Kem.*, 1935, 8, B, 35; cf. A.,

1934, 1186).—The electrode processes occurring in presence of fused alkali and carbonate electrolytes are discussed. R. S.

**Electro-deposition of nickel from nickel chloride solutions.**—See B., 1935, 1147.

**Nickel-plating of aluminium.**—See B., 1935, 1147.

**Electric currents flowing over rusting iron.** U. R. EVANS (*Nature*, 1935, 136, 792—793).—An arrangement for investigating currents flowing over an Fe surface in contact with 0.01*N*- $NaHCO_3$  during rusting is described. Intense anodic action occurs immediately around a scratched line where rusting is rapid, while cathodic areas are free from attack.

L. S. T.

**Electrodeposition of tin alloys from alkaline stannate baths.**—See B., 1935, 1098.

**Chemical reactions in rarified gases under the influence of electric discharges.** P. JOLIBOIS (*Bull. Soc. chim.*, 1935, [v], 2, 2035—2052).—A lecture.

**Chemical reaction in the electric discharge.** I. Chemical effects of impulse discharges. E. J. B. WILLEY (*Proc. Roy. Soc.*, 1935, A, 152, 158—171).—Wrede's results for  $N_2$  (A., 1930, 394) may be confirmed by chemical means and by simpler apparatus. The controlled impulse discharge is far superior, as regards both abs. and power yields, to a.c. and d.c. discharges. Some probable consequences of the action of an impulse discharge on a gas are discussed. It is considered that, if the breakdown period is not too short compared with the total duration of the discharge, and if the development of the positive column does not lead to a destruction of products first formed in this induction period, the total effects may approximate to those found in cathodic reactions. L. L. B.

**Effect of light on periodic reactions.** V. K. NIKIFOROV (*J. Chim. phys.*, 1935, 32, 585—587).—Wave equations yield the correct order for the ratio between the distances apart of Liesegang rings in the presence and absence of light in the reaction  $2AgNO_3 + K_2Cr_2O_7 = Ag_2Cr_2O_7 + 2KNO_3$  (Kofman, A., 1934, 346).

T. G. P.

**Separation of the mercury isotopes by a photochemical method.** K. ZUBER (*Nature*, 1935, 136, 796).—A partial separation of  $Hg^{200}$  and  $Hg^{202}$  from ordinary Hg has been effected by irradiation of Hg vapour in a magnetic field with the Hg resonance line 2537 Å.

L. S. T.

**Question of further maxima of the density curves of photographic emulsions after the appearance of solarisation.** H. BORST (*Phot. Ind.*, 1935, 33, 1056, 1058).—With some plates (e.g., Agfa Normal), but not with others (e.g., Perutz Orthochromatic), second and third max. can be shown to occur in the density curve, after the first solarisation, on prolonged exposure (to Uviol or Nitrachrom lamp). Measurement of the densities of the direct blackening produced (not developed), by red light, shows similar variations, but these densities are always much <



those obtained by development, and cannot therefore be concerned with the causes of the recurring max.

J. L.

**Mechanism of the desensitisation of photographic plates.** II. M. BLAU and H. WAMBACHER (Z. wiss. Phot., 1935, 34, 253—266; cf. A., 1935, 177, 1331).—About 300 experiments were made to examine the relation of the density curves obtained from desensitised emulsions (Agfa Contrast) to the  $O_2$  content of the surrounding atm., and also to the concn. of the desensitiser. Graphs are given showing the relation between various factors, e.g., intensity of light against concn. of desensitiser, for const. density production. Previous results are substantiated, that desensitisation is dependent on the presence of  $O_2$ , without which there is no residual effect; the dye acts as  $O_2$  carrier for reoxidation of nascent Ag. Other theories are discussed in detail. Solarisation, unobtainable in desensitised plates at atm. pressure, appears on exposure in vac. Similarly, increased densities were obtainable in emulsions bathed in KBr or KI solutions, when exposed in vac.; bathing in  $NaNO_2$  or Na salicylate was, however, not affected by the presence or absence of  $O_2$ .

J. L.

**Law of blackening of the photographic plate.** H. KIENLE (Naturwiss., 1935, 23, 762—767).—The failure of the photographic reciprocity law is examined particularly in connexion with intermittent illumination. For each emulsion there is a lower-frequency limit of illumination, independent of intensity, above which the Talbot law holds. The curves expressing deviations from the reciprocity law are parallel for all  $\lambda$  at all temp. investigated.

A. J. M.

**Photographic photometry.** H. KIENLE (Naturwiss., 1935, 23, 759—762).—Theoretical discussion. The assignation of a scale to intensities of blackening produced on a photographic plate can be of val. only when the method of determining the intensities is stated. The different effect on the plate of intermittent and continuous illumination when the same total quantity of light falls on the plate is discussed.

A. J. M.

**Heterogeneous reaction kinetics. Effect of light exposure on the kinetics of thermal decomposition of silver oxalate.** A. F. BENTON and G. L. CUNNINGHAM (J. Amer. Chem. Soc., 1935, 57, 2227—2234).—Exposure to light, especially  $\lambda < 520$  m $\mu$ , accelerates the subsequent thermal reaction; the effect is relatively less at higher decomp. temp. Contact with  $O_2$  during exposure results in initial poisoning. In the earlier stages of thermal decomp., the extent of reaction at any time,  $t$ , approx.  $\propto t^m$ , where  $m$  is 3.5 for unexposed samples, but is progressively less with increasing exposure.

E. S. H.

**Change of sodium nitroprusside into Prussian-blue.** E. JUSTIN-MUELLER (Bull. Soc. chim., 1935, [v], 2, 1932—1936).—When exposed to sunlight in an open vessel an aq. solution of Na nitroprusside (I) is decomposed giving  $NaNO_2$ , HCN, and  $Na_2Fe_2(CN)_6$ . The last named, in presence of NaOH, is converted into Prussian-blue. When (I) is exposed to sunlight in a closed vessel NO is evolved. The structure of (I) is discussed.

O. J. W.

**Reaction between ethylene and chlorine in presence of chlorine acceptors. Photochlorination of ethylene.** T. D. STEWART and B. WEIDENBAUM (J. Amer. Chem. Soc., 1935, 57, 2036—2040).—The rate of photochlorination of  $C_2H_4 \propto [Cl_2]$  at const. light intensity and is independent of  $[C_2H_4]$ . In  $H_2-Cl_2-C_2H_4$  mixtures, illuminated or in the dark, practically no  $H_2$  reacts, although the  $C_2H_4-Cl_2$  reaction goes to completion. The reaction of  $C_2H_4$  with  $Cl_2$  in  $C_2H_4Cl_2$  solution is very rapid and involves  $< 10\%$  of the  $Cl_2$  in substitution; in pentane solution 37—73% of  $Cl_2$  is used for substitution, the amount increasing as the  $C_2H_4 : Cl_2$  ratio increases.

E. S. H.

**Photobromination of tetrachloroethylene and of chloroform with special reference to the effects of oxygen.** J. WILLARD and F. DANIELS (J. Amer. Chem. Soc., 1935, 57, 2240—2245).—Photobromination of  $C_2Cl_4$  is inhibited by the reaction product, and depends little on  $[C_2Cl_4]$ ; the temp. effect is small. Small amounts of  $O_2$  accelerate the reaction, but large amounts almost completely inhibit it, probably because of a competing Br-sensitised photo-oxidation.  $CHCl_3$  and Br react at  $25^\circ$  when illuminated with  $\lambda$  2650 Å. in presence, but not in absence, of  $O_2$ . The mechanism is discussed.

E. S. H.

**Catalysis of acetylene polymerisation in ultra-violet light by mercury vapour.** (A) F. TOUL. (B) W. KEMULA (Coll. Czech. Chem. Comm., 1935, 7, 491—492, 493—494).—(A) Polemical against Kemula (cf. A., 1935, 1208).

(B) A reply.

R. S. B.

**Primary process in the photochemical and thermal decomposition of azomethane.** F. PATAT (Naturwiss., 1935, 23, 801).—The photochemical decomp. of  $Me_2N_2$  under various pressures at temp. from  $20^\circ$  to  $266^\circ$  by light of  $\lambda$  366 m $\mu$  has a zero temp. coeff. in respect of the quantum yield. The primary process is  $Me_2N_2 \rightarrow 2Me + N_2$  and the existence of a chain reaction involving the interaction of Me with  $Me_2N_2$  is excluded.

W. O. K.

**Photochemical decomposition of methylamine and ethylamine.** H. J. ÉMELÉUS and L. J. JOLLEY (J.C.S., 1935, 1612—1617; cf. A., 1931, 1251).—The absorption spectra of  $NH_2Me$  and  $NH_2Et$  are on the short- $\lambda$  side of approx. 244 and 237 m $\mu$ , respectively, and the frequency differences between the bands lead to the frequencies 670 and 726 cm. $^{-1}$ , respectively, which are probably characteristic of the excited  $\cdot NH_2$ . The bands of long  $\lambda$  have fine structure. In the light of the Hg lamp and the Al spark, the chief products from  $NH_2Me$  are  $H_2$ ,  $NH_3$ , and a liquid, with small quantities of  $CH_4$  and  $N_2$ . Similarly,  $NH_2Et$  gives the same gaseous products and small quantities of  $C_2H_6$  and  $C_2H_4$ . Photo-oxidation of  $NH_2Me$  affords chiefly  $NH_3$  and a liquid, and smaller quantities of CO,  $N_2$ ,  $H_2$ , and  $CH_4$ . In each case,  $< 0.7$  mol. is decomposed per quantum absorbed.

J. G. A. G.

**Photochemical decomposition of nitrosoisopropylacetone and  $\beta$ -nitroso- $\beta$ -dimethylhexane.** K. D. ANDERSON, C. J. CRUMPLER, and D. L. HAMMICK (J.C.S., 1935, 1679—1684; cf. A., 1903, i, 322; 1935,

307).—The quantum efficiency of the decomp. of the monomeric forms of nitrosoisopropylacetone (I) and  $\beta$ -nitroso- $\beta$ -dimethylhexane (II) in  $C_6H_6$  solution is approx. unity in light of  $\lambda$  6400–7100 Å. (I) and (II) give  $H_2N_2O_2$  and its decomp. products; (I) also yields mesityl oxide and (II) affords, probably,  $\beta$ -dimethyl- $\Delta^8$ -hexene. The reaction probably proceeds by the primary elimination of  $HON^*$ .

J. G. A. G.

**Primary photochemical reactions.** VIII. Quantum yield of the photolysis of methyl *n*-butyl ketone. B. M. BLOCH and R. G. W. NORRISH (J.C.S., 1935, 1638–1642; cf. A., 1934, 852).—In light of  $\lambda$  2480–2770 Å., the quantum efficiency,  $\gamma$ , of the decomp. of COMeBu (I) at 760 mm. and 127° by the primary processes  $(I) \rightarrow CO + CH_3 + C_4H_9$  and  $(I) \rightarrow C_3H_6 + COMe_2$  is approx. 0.03 and 0.27, respectively.  $\gamma$  for condensation or polymerisation is approx. 0.04. The absorption spectrum is diffuse and fluorescence was not observed. It is probable that the energy of a considerable proportion of the excited mols. which do not decompose is degraded by an internal redistribution process. J. G. A. G.

**Products and processes of ionisation in methyl chloride as determined by a mass spectrometer.** S. H. BAUER and T. R. HOGNESS (J. Chem. Physics, 1935, 3, 687–692).—The following ions, in order of decreasing intensity, are generated as primary products in the decomp. of MeCl by electrons:  $MeCl^+$ ,  $Me^+$ ,  $CCl^+$ ,  $CH_3^+$ ,  $Cl^+$ ,  $HCl^+$ ,  $CH^+$ ,  $C^+$ ,  $H^+$ . Appearance potentials for  $MeCl^+$ ,  $Me^+$ , and  $Cl^+$  are respectively 11.0, 14.7, and 26 volts. Experimental details are given. F. L. U.

**Inversion of sucrose solutions in tropical sunlight.** N. A. YAJNIK, D. N. GOYLE, and M. L. WADIHERA (Z. anorg. Chem., 1935, 225, 24–28).—Aq. sucrose solutions contained in Jena glass vessels undergo inversion when exposed to tropical sunlight in the absence of acid. When acid (0.25*N*) is present the rate of inversion is increased by sunlight. These experiments confirm Dhar's observations (A., 1922, ii, 39). F. L. U.

**Photochemical oxidation of hæmoglobin.**—See this vol., 92.

**Action of radon on polymethylenes: cyclopentane and cyclopentene.** G. B. HEISIG (J. Physical Chem., 1935, 39, 1067–1073; cf. A., 1932, 918).—V.-p. data are given for cyclopentane and -pentene and the  $-M/N$  vals. for the Rn polymerisation are 1.7 and 4.5, respectively.  $-M/N$  is inversely  $\propto \Delta(H_2 + CH_4)/100 - \Delta H_C$  and increases above 2 with a negative heat of formation. R. S.

**Decomposition of ozone by the action of  $\alpha$ -particles.** P. C. CAPRON and R. CLOETENS (Bull. Soc. chim. Belg., 1935, 44, 441–466).— $M/I$  data for  $C_2H_2$  have been used to calculate  $M/I$  vals. in the decomp. of  $O_3$  (3–20 mm. in about 700 mm.  $O_2$ ). It is shown graphically that the velocity of decomp.  $\propto [O_3]$  and increases with the radiation intensity. Considering  $O_3$  ions alone, the ionic yield is approx. const. for a given intensity. R. S.

**Separation by rectification of neon into its isotopic components.** W. H. KESOM and J.

HAANTJES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 809).—Ne of at. wt. 21.157 has been prepared after 14 rectifications. R. S.

**Influence of hydrogen-ion concentration on oxidation and reduction reactions.** A. K. BABKO (Z. anal. Chem., 1935, 103, 98–103).—In oxidation-reduction reactions not directly involving  $H^+$ , but involving compounds of multivalent ions with O,  $H^+$  lowers the stability of the compounds, and raises the oxidation-reduction potential  $\epsilon$ . Expressions for the influence of  $[H^+]$  on  $\epsilon$  are derived. J. S. A.

**Change of isotopic composition of water by distillation.** J. HORIUTI and G. OKAMOTO (Bull. Chem. Soc. Japan, 1935, 10, 503–505).—The % of D in the distillate is < that in the original liquid when  $H_2O$  containing 2.6% of D is distilled between  $-7^\circ$  and  $22^\circ$ . J. G. A. G.

**Purification of water and its  $p_H$  value.** S. B. ELLIS and S. J. KIEHL (J. Amer. Chem. Soc., 1935, 57, 2145–2149).—Technique for purifying  $H_2O$  is critically discussed. The purest  $H_2O$ , collected in Ag vessels, had  $p_H$  7.01 at  $27.5^\circ$ , as determined by the glass electrode. E. S. H.

**Action of alkali hydroxide solutions on ultramarine-blue.** K. LESCHIEWSKI and E. PODSCHUS (Z. anorg. Chem., 1935, 225, 43–46; cf. A., 1934, 1318).—Aq. LiOH (1–2.5*N*) when boiled with ultramarine-blue (I) decolorises it and yields a cryst. product (II) containing no S. KOH is relatively inactive, but at a concn. of 7.5*N* removes all S on prolonged boiling, giving a cryst. product having a lattice different from that of (I) or (II). In both cases the Na of (I) is almost completely exchanged for Li or K. F. L. U.

**Hydrolysis of solutions of cupric sulphate.** O. BINDER (Compt. rend., 1935, 201, 893–894).—The slow hydrolysis of  $CuSO_4$  has been studied by boiling solutions for 0.25–12 hr., and determining the change in acidity by the glass electrode and the composition of the ppt. by X-rays and analysis. Hydrolysis increases with the time of boiling and the change in acidity increases with concn. (c). Insol. solid phases are  $4CuO, SO_3, 4H_2O$  ( $c < 0.06$  mol. per litre) and  $3CuO, SO_3, 2H_2O$  ( $c > 0.06$ ). R. S. B.

**Substitution of copper and silver by silver.** A. P. SERGEEV and A. A. KOSHUCHOVSKI (J. Appl. Chem. Russ., 1935, 8, 1073–1075).—A ppt. of Cu is obtained on the surface of Ag foil (I) when the latter is immersed in aq.  $CuSO_4$  containing excess of KCl or NaCl. When (I) is wrapped up in filter-paper moistened in  $H_2O$ , and the packet is placed on conc. aq.  $AgNO_3$ , crystals of Ag deposit on the filter-paper; the system acts as a concn. cell, in which Ag is dissolved from the foil, and pptd. at the boundary between conc. and dil.  $AgNO_3$ . R. T.

**Electrometric and analytical evidence for the composition of precipitated basic copper perchlorate.** R. A. BEEBE and S. GOLDWASSER (J. Physical Chem., 1935, 39, 1075–1078; cf. A., 1932, 243).—The composition of  $Cu(ClO_4)_2 \cdot 6CuO, xH_2O$  has been determined electrometrically and by direct analysis. R. S.

**Preparation of sulphur and magnesium sulphate from sulphur dioxide and magnesia.** II. H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1161—1176).—The velocity of absorption of dil.  $\text{SO}_2$  by aq.  $\text{Mg}(\text{OH})_2$  has been studied. When conc. aq.  $\text{Mg}(\text{HSO}_3)_2$  is heated with  $\text{MgO}$  (+S) in a sealed tube at 130—140°, the reaction  $3\text{Mg}(\text{HSO}_3)_2 + \text{MgO} = 4\text{MgSO}_4 + 3\text{H}_2\text{O} + 2\text{S}$  is complete. R. S.

**Preparation and properties of mono-, di-, and tri-calcium phosphates.** H. W. E. LARSON (Ind. Eng. Chem. [Anal.], 1935, 7, 401—406).— $\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  have been prepared. Their solubilities,  $p_{\text{H}}$  of the solutions,  $n$ , and behaviour on heating have been determined. E. S. H.

**Reactions of phosphates with soils.** II. **Action of lime on monocalcium phosphate in presence of anhydrous calcium sulphate.** J. CLARENS and H. MARGULIS (Bull. Soc. chim., 1935, [v], 2, 1980—1985; cf. B., 1934, 642).—When solutions of  $\text{H}_3\text{PO}_4$  and  $\text{Ca}(\text{OH})_2$  are mixed in presence of anhyd.  $\text{CaSO}_4$  pptn. of  $\text{CaHPO}_4$  first takes place. With further addition of  $\text{Ca}(\text{OH})_2$  the  $\text{CaHPO}_4$  is converted into  $\text{Ca}_3(\text{PO}_4)_2$ . O. J. W.

**Decomposition of barium sulphate by chlorine.**—See B., 1935, 1141.

**Cadminitrites of univalent metals.** A. FERRARI, A. BARONI, and C. COLLA (Gazzetta, 1935, 65, 797—809; cf. following abstract).—The prep. of  $\text{K}[\text{Cd}(\text{NO}_2)_2]$  and of the compounds  $\text{M}[\text{Cd}(\text{NO}_2)_2]$  ( $\text{M} = \text{Rb}, \text{Cs}, \text{Tl}, \text{NH}_4$ ) is described. They crystallise in the monometric system, 1 mol. per unit cell, and have, in the order given,  $a$  5.325, 5.375, 5.390, 5.340, 5.355 Å., and  $d_{\text{calc.}}$  3.183, 3.509, 4.063, 4.958, 2.902, respectively. Arguments in favour of the structure  $\text{M}_2[\text{Cd}(\text{NO}_2)_6]$  are given, but, as with the Hg compounds, the cationic Cd cannot be replaced by other metals. O. J. W.

**Mercurinitrites of univalent metals.** A. FERRARI and C. COLLA (Gazzetta, 1935, 65, 789—797).—The prep. of the compounds  $\text{MHg}(\text{NO}_2)_3$  ( $\text{M} = \text{Rb}, \text{Cs}, \text{Tl}$ ) is described. The corresponding K and  $\text{NH}_4$  compounds could not be obtained. These double nitrites crystallise in the monometric system with 1 mol. per unit cell. For the Rb, Cs, and Tl compounds  $a = 5.540, 5.475, 5.385$  Å., and  $d_{\text{calc.}} = 4.35, 4.77, 5.77$ , respectively. The Hg and M are at the corners and centre of the cube, but the position of the  $\text{NO}_2$  is uncertain. It seems probable that the formulae of these substances should be doubled, viz.,  $\text{M}_2\text{Hg}[\text{Hg}(\text{NO}_2)_6]$ . The Hg outside the complex cannot, however, be replaced by any other metal. O. J. W.

**Mercury powder.** A. GALATZKY (Bull. Soc. chim., 1935, [v], 2, 1801—1807).—Very finely-divided Hg powder is prepared by reducing  $\text{HgO}$  suspended in  $\text{H}_2\text{O}$  with  $\text{N}_2\text{H}_4$  and other reducing agents. The grey powder has an appreciable v.p., forms an amalgam by simple contact with Au or Sn, and is readily dissolved by 25%  $\text{HNO}_3$ . It is probably a mixture of Hg with small amounts of  $\text{HgO}$ . O. J. W.

**Rare earths.** XLV. **Preparation of rare-earth amalgams by displacement.** D. H. WEST

[with B. S. HOPKINS] (J. Amer. Chem. Soc., 1935, 57, 2185—2186).—Amalgams of Ce, Nd, "didymium," and Yt have been prepared by the action of Na amalgam on conc. alcoholic solutions of their chlorides. The metals (except Yt) can be obtained free from Hg by heating the amalgams in vac. E. S. H.

**Production of rare-earth metals by thermal decomposition of their amalgams.** L. F. AUDRIETH (Metallwirts., 1935, 14, 3—5; Chem. Zentr., 1935, i, 2145—2146).—Amalgams of Ce, La, Nd, Sm, and Y are made by electrolysis of EtOH solutions of the anhyd. chlorides with an Hg cathode. The amalgam is conc. in vac. at 250°, and Hg is removed completely by heating the residue at >1000°. Crucibles lined with pure rare-earth oxides, grading outwards into  $\text{Al}_2\text{O}_3$ , must be used. Ce is cubic face-centred,  $a$  5.14 Å.; La and Nd are hexagonal with  $a$  3.75, 3.65,  $c$  6.06, 5.88 Å., respectively. J. S. A.

**Action of Clerici's solution on gypsum.** G. PEHRMANN (Zentr. Min., 1935, A, 54—55; Chem. Zentr., 1935, i, 2146—2147).—Clerici's solution attacks gypsum (I) and deposits  $\text{Ti}_2\text{SO}_4$ , thereby making the apparent  $d$  of (I) too high. J. S. A.

**Preparation of carbon suboxide.** A. KLEMENC, R. WECHSBERG, and G. WAGNER (Monatsh., 1935, 66, 337—344).—Pure  $\text{C}_3\text{O}_2$  may be obtained by the dehydration of  $\text{CH}_2(\text{CO}_2\text{H})_2$ , and from diacetyltartaric anhydride, and subsequent fractionation of the products. A. J. M.

**Preparation of pure carbon monoxide.** G. MEYER, R. A. HENKES, and A. SLOOFF (Rec. trav. chim., 1935, 54, 797—799).—CO cannot be freed completely from  $\text{H}_2$  by fractional distillation. Pure CO is obtained by decomp. of  $\text{Ni}(\text{CO})_4$  at 200°, and a laboratory apparatus for this purpose is described. J. W. S.

**Silicates.** III. **Behaviour of talc on heating with  $\text{MgO}$  and Mg, Co, and Mn chlorides.** E. THILO (Z. anorg. Chem., 1935, 225, 49—63; cf. A., 1933, 794).—Experiments are described showing that, although the chemical composition and cryst. structure of pyrophyllite and talc are closely analogous, the latter behaves quite differently towards  $\text{MgO}$  and anhyd.  $\text{MgCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{MnCl}_2$ , when heated with them. An explanation based on the respective lattice structures is offered. F. L. U.

**Formation of "persilicate."** H. DITZ (Z. anorg. Chem., 1935, 225, 90—92).—Comments on a paper by Krauss and Oettner (A., 1935, 833). F. L. U.

**Carbides of lead and silver.** E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 1807—1809).— $\text{PbC}_2$  is obtained by adding  $\text{CaC}_2$  to a solution of  $\text{Pb}(\text{OAc})_2$  in MeOH. It is stable at room temp., but is easily hydrolysed, and in acid solution evolves  $\text{C}_2\text{H}_2$ . Pb cyanide could not be prepared. Org. Ag salts do not give  $\text{Ag}_2\text{C}_2$  when strongly heated. O. J. W.

**Attempted concentration of the heavy nitrogen isotope.** M. H. WAHL, J. F. HUFFMAN, and J. A. HIPPLE, jun. (J. Chem. Physics, 1935, 3, 434—435).—A study of the isotopic reaction  $\text{N}^{15}\text{H}_3 + \text{N}^{14}\text{H}_4\text{OH} \rightarrow \text{N}^{14}\text{H}_3 + \text{N}^{15}\text{H}_4\text{OH}$  showed that the distribution of  $\text{N}^{15}$  was slightly favoured in the  $\text{NH}_4\text{OH}$  mol. The

ratio of the v.p. of  $N^{14}H_3$  and  $N^{15}H_3$ , determined by fractional distillation of anhyd.  $NH_3$ , was  $1.0052 \pm 0.0013$ . N. M. B.

**Corrosive action of solutions of ammonium nitrate in liquid ammonia on metals.**—See B., 1935, 1091.

**Action of hydrogen sulphide on hydrogen sulphite solutions.** J. JANICKIS (Z. anorg. Chem., 1935, 225, 177—203; cf. A., 1931, 1255).—The products of the action of  $H_2S$  on aq.  $KHSO_3$  at  $p_H$  5.1—2.3 are  $S_2O_3^{''}$ ,  $S_nO_6^{''}$  ( $n=2-5$ ),  $S$ , and  $H^+$ . At first  $S_2O_3^{''}$  and  $S_3O_6^{''}$  are chiefly formed. The production of higher polythionates is favoured by increase of  $[H^+]$  or of  $[S_2O_3^{''}]$ , but there is no evidence that  $S_3O_6^{''}$  takes part in it. The occurrence of the reaction  $H_2SO_3 + 2HS_2O_3 \rightarrow S_5O_6^{''} + 2H_2O$  is supported by the above observations and by the qual. detection of  $H_2SO_3$  in the reaction mixture.  $S_4O_6$  and  $S_3O_6$  are successive degradation products of  $S_5O_6^{''}$  according to:  $S_5O_6^{''} + HSO_3 \rightarrow S_4O_6^{''} + S_2O_3^{''} + H^+$ ;  $S_4O_6^{''} + HSO_3 \rightarrow S_3O_6^{''} + S_2O_3^{''} + H^+$ . F. L. U.

**Reaction of sulphur dioxide with water under pressure.**—See B., 1935, 1091.

**Hydrogen sulphites. III. Reduction of sodium hydrogen sulphite by zinc amalgam.** II. T. MUROOKA (Bull. Inst. Phys. Chem. Japan, 1935, 14, 1154—1160).—Reduction of  $HSO_3^+$  by the amalgam method can be carried out in the presence of  $H_2SO_3$  or  $H_2SO_4$ . The yield decreases as the temp. rises, and the best result is obtained when the quantity of amalgam is 1.2 times the theoretical. The solid remaining after reduction has the approx. composition  $3ZnSO_3 \cdot Na_2SO_3 + Zn(OH)_2$ . R. S.

**Thermal decomposition of  $CrO_4 \cdot 3NH_3$ .** W. F. EHRET and A. GREENSTONE (J. Amer. Chem. Soc., 1935, 57, 2330—2331).— $CrO_4 \cdot 3NH_3$  does not lose  $NH_3$  in vac. at room temp., but at  $120 \pm 10^\circ$  a vigorous reaction occurs and a solid residue,  $CrO_3 \cdot NH_3$ , is formed. The presence of small amounts of impurities has a marked influence on the rate of decomp.; the reaction does not occur in the dark.  $CrO_3 \cdot NH_3$  has  $d$  2.073; it is stable in air, but hydrolysed by  $H_2O$ . E. S. H.

**Formation of masked complexes in normal and basic solutions of chromium and aluminium salts.** A. KÜNTZEL, C. RIESS, and G. KONIGFELD (Collegium, 1935, 484—502; cf. B., 1935, 818).—Cr acido-complexes are formed with both sulphates and chlorides, but analogous Al complexes are not formed. Conductivity measurements show that Al sulphato-complexes are not present in aq.  $Al_2(SO_4)_3$  which has been boiled and cooled again, but are formed in aq.  $Cr_2(SO_4)_3$ . The hydrolysis of Cr salts occurs in three successive stages, but that of Al salts is in one stage. Masking occurs on adding a neutral salt containing an anion common to both aq. Cr and Al salts; the rate of masking is greater in Al salts, but the masked Cr salts are more stable. Both basic Al and Cr salts form complexes; the change is complete in Al salts, but in Cr salts the degree of formation diminishes as the Cr salt is more aged. D. W.

**Isotopic exchange reactions with iodine.** F. JULIUSBURGER, B. TOPLEY, and J. WEISS (J. Chem. Physics, 1935, 3, 437—438; cf. A., 1935, 1328).—The reaction  $RX + I^- = RI + X^-$  ( $R$ =alkyl,  $X=I$ ) was examined for two series of aliphatic I compounds by dissolving activated  $Na^+I^-$  in alcohol- $H_2O$ , thereby obtaining radio-I ions in solution, adding the alkyl iodide, removing the partly activated org. iodide by pptn. with  $H_2O$ , and, after conversion into AgI, making Geiger-Müller counter measurements. Exchanges  $>50\%$  were found. The upper limit of the activation energy for the interchange reaction  $MeI + I^-$  in EtOH is 16.5 kg.-cal. N. M. B.

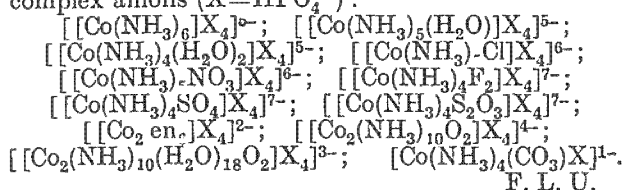
**X-Ray investigation of method of preparing spongy iron by reducing hæmatite with gases.** V. P. KASANZEV (Z. physikal. Chem., 1935, 174, 370—383).—X-Ray examination of the products of reduction with  $H_2$  shows them to consist of a mechanical mixture of  $\alpha$ -Fe, FeO,  $Fe_3O_4$ , and  $Fe_2O_3$ ; no solid solutions are present. The length of edge of the primary fine crystals of  $\alpha$ -Fe has been measured. At  $700^\circ$  the reduction of  $Fe_2O_3$  to  $Fe_3O_4$  is more rapid than the subsequent stages of reduction. After reduction is 82.5% complete the product is mainly  $\alpha$ -Fe with a small residue of  $Fe_3O_4$ . R. C.

**Ageing and stability towards light of ferrous oxide hydrates in presence and absence of alkali nitrates.** O. BAUDISCH (Ber., 1935, 68, [B], 2046—2049).—Colourless FeO hydrate is obtained by gradual addition of alkali to  $FeCl_2$  and allowing to age under  $H_2O$  during  $\frac{1}{2}$ —several hr. The suspension when agitated with  $O_2$  gives  $\alpha$ - $Fe_2O_3$  which probably contains  $\gamma$ - $Fe_2O_3$  on account of the magnetic properties. Ageing occurs very rapidly. Pptn. of  $Fe(OH)_2$  in presence of air and nitrates causes almost immediate reduction of the latter to nitrites. It is probable that  $H_2O$  eliminated from the primary  $Fe(OH)_2$  yields active H under the experimental conditions,  $H_2O \rightarrow H + OH(H_2O_2)$  and corresponding with production of the latter compounds the oxidation of suitable org. compounds (lactic acid, uracil, thymine) occurs concurrently in the system. Neither reduction nor oxidation is observed with aged  $Fe^{II}$  hydrates. Even after very long periods in the dark nitrates are not reduced by  $Fe^{II}$  salts in the complete absence of  $O_2$ . At. O, liberated from nitrates by light energy, has a powerful oxidising action and the nitrite thus produced reacts momentarily with excess of  $Fe^{II}$ ; according to the  $p_H$  of the medium, further and complete reduction of the O-N compounds ensues. H. W.

**Action of alkali sulphides on sodium nitroprusside.** E. JUSTIN-MUELLER (J. Pharm. Chim., 1935, [viii], 22, 496—503).—The violet colour is due to the formation of an intermediate compound,  $Na_2(CN)_3Fe(SNO)_2$ , which rapidly decomposes into  $Na(NO)S$  groups and  $Na_2Fe_2(CN)_6$ ; these partly recombine to give  $Fe_2S_4(NO)_2Na_6$  and the residual  $Na_2Fe_2(CN)_6$  is transformed into  $Fe[Fe_2(CN)_6]$  and finally into Prussian-blue. E. H. S.

**New group of complex compounds. Compounds with a complex anion, the central ion of which is a complex cation. III. Complex phos-**

phato-anions with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 33—37; cf. A., 1935, 1091).—Determination of the ionic wt. by measuring the rate of diffusion of complex Co cations in  $3N$ - $K_2HPO_4$  indicates the existence of the following complex anions ( $X=HPO_4''$ ):



F. L. U.

Mixed nickelnitrites of uni- and bi-valent metals. II. A. FERRARI and C. COLLA (Gazzetta, 1935, 65, 809—818; cf. A., 1935, 717).—The prep. of the triple nitrites  $M^iCd[Ni(NO_2)_6]$  ( $M^i=Ti, K$ ) is described. These are isomorphous with  $K_2Pb[Ni(NO_2)_6]$  and have  $a$  10.37 and 10.28 Å, respectively. When  $M^i$  is Rb, Cs, or  $NH_4$ , the triple nitrites with the general formula given above could not be obtained, as there is a great tendency to form solid solutions between nickelnitrites and cadmiumnitrites, with  $a$  10.58, 10.81, and 10.41 Å, respectively.

O. J. W.

Red and green forms of Magnus' salt. H. D. K. DREW and H. J. TRESS (J.C.S., 1935, 1586—1588).—When the red form of Magnus' salt,  $[Pt(NH_3)_4]PtCl_4$  (I), is treated with  $AgNO_3$  followed by  $K_2PdCl_4$ ,  $[Pt(NH_3)_4]PdCl_4$  is pptd., whereas the red triammine platino salt,  $[Pt(NH_3)_3]PtCl_4$  (II), of Peyrone and Cleve gives the quite different chlorotriamminoplatinous palladochloride,  $[Pt(NH_3)_3Cl]PdCl_4$ . Contrary to Cox *et al.* (A., 1933, 41), (II) could not be converted into a green form, and (I) and (II) are not identical. Earlier work (A., 1906, ii, 289) was confirmed, but some  $H_2PtCl_4$  solutions gave the red form of (I) even in the presence of much  $HCl$ , which usually favours the green isomeride. The red and green forms of (I) may be electro-isomerides. J. G. A. G.

Asymmetric platinum atom. VII.—See this vol., 84.

Microchemical spectral analysis in high-frequency spark. A. SCHLEICHER and N. BRECHT-BERGEN (Z. anal. Chem., 1935, 103, 198; cf. A., 1935, 947).—Supplemental details are recorded. J. S. A.

Quantitative analysis of solutions by spectrographic means. O. S. DUFFENDACK, F. H. WILEY, and J. S. OWENS (Ind. Eng. Chem. [Anal.], 1935, 7, 410—413).—An uncondensed spark in air between a suitable solid electrode and the solution is photographed and, from measurements of the relative intensities of chosen spectral lines, the analysis for metals is made by comparison with previously constructed reference curves. The method has been applied to the determination of Na, K, Mg, and Ca in dil., mixed solutions of their salts. The error is about 2%. E. S. H.

Solubility of precipitates in acids. A. K. BABKO (Z. anal. Chem., 1935, 103, 190—196).—A general expression is given for the solubility of ppts. with varying acid concn., with or without the presence of excess of precipitant. J. S. A.

Electro-capillary method of qualitative analysis. S. I. DIJATSKHOVSKI (J. Gen. Chem. Russ., 1935, 5, 728—730).—Theoretical aspects of electrolysis of solutions on filter-paper are discussed. R. T.

Analysis of anions. S. M. PUZEVSKAJA (J. Gen. Chem. Russ., 1935, 5, 498—499).—The procedure proposed by Birulia (A., 1933, 1260) is not feasible. R. T.

Application of the glass electrode to unbuffered systems. S. B. ELLIS and S. J. KIEHL (J. Amer. Chem. Soc., 1935, 57, 2139—2144).—General technique for  $p_H$  determination in unbuffered solutions is described. The method has been applied to very pure  $H_2O$  and to some very dil. salt solutions. E. S. H.

Application of bimetallic electrodes to titration of acids or alkalis. J. A. BOLTUNOV and M. A. VORSINA (J. Gen. Chem. Russ., 1935, 5, 519—528).—The bimetallic electrodes Pt-Ni, -Sb, -Co, -Pd, Pd-Ni, and Ni- $Hg_2Cl_2$  may be used repeatedly without inactivation for the titration of weak or strong acids ( $< 0.001N$ ), and of alkalis, Pt-W, -Mo, -Ta, W-Ni, and C-Sb are less suitable, as they have to be reactivated after each determination, whilst Pt-Fe, -Cu, -C, -Al, -Pb, and -Sn electrodes do not give trustworthy results under any conditions. R. T.

Determination of small quantities of water by Crismer's method. L. DE BROUCKERE and A. GILLET (Bull. Soc. chim. Belg., 1935, 44, 473—503).—Crit. solution temp. (c.s.t.) have been determined for the mixtures  $MeOH-CS_2$ ,  $MeOH-EtOH-CS_2$ ,  $MeOH-n-C_6H_{14}$ , and  $MeOH-cyclohexane$ . Interaction occurs between  $MeOH$  and  $CS_2$  at high temp., resulting in a progressive shift of the c.s.t., but this may be avoided by addition of  $EtOH$ , which lowers the c.s.t. Ac.s.t.  $\propto$  the concn. of  $H_2O$  added, and small quantities can be determined by this means. The combustion analysis of an org. compound is given as an example. R. S.

Titrimetric determination of water and alcohols by their acid-catalysed reactions with acetic anhydride in organic media. G. TOENNIES and M. ELLIOTT (J. Amer. Chem. Soc., 1935, 57, 2136—2139).—General technique and scope of the method are described. The error in concns. of about 1% is  $< \pm 1\%$ ; the lower limit of response is  $< 0.001\%$ . E. S. H.

Chromyl chloride test for chloride. L. MARTINI (Annali Chim. Appl., 1935, 25, 528—530).—A positive reaction with  $H_2SO_4-K_2Cr_2O_7$  may be due to either  $Cl'$  or  $F'$ . The vapour is absorbed in dil. alkali,  $CrO_4''$  confirmed as  $Pb$  salt, and  $Cl'$  or  $F'$  identified by the usual tests ( $CaCl_2$ ,  $AgNO_3$ , etc.) with due consideration to the presence of  $I$  or  $Br$ . F. O. H.

Determination of fluorine in soluble and insoluble fluorides by its separation as  $K_2SiF_6$  and subsequent titration of the complex. A. A. VASSILIEV [with N. N. MARTIANOV] (Z. anal. Chem., 1935, 103, 107—113).—Sol. fluorides are dissolved in  $H_2O$  and an equal vol. of aq.  $Na_2SiO_3$  (0.01 g. of  $SiO_2$  per c.c.) +  $KCl$  is added, and then acidified with 50%  $HCl$  (Me-orange). The solution is made 50%



with respect to EtOH. Pptd.  $K_2SiF_6$  is collected, dissolved in  $CO_2$ -free  $H_2O$ , and titrated with 0.1N-NaOH (phenolphthalein). The loss due to solubility of  $K_2SiF_6$  is calc. from the vol. of solution and wash liquid. Insol. fluorides are fused with  $SiO_2 + NaKCO_3$ , and extracted with about 10% aq.  $(NH_4)CO_3$ . F' in an aliquot part of the solution is determined as above.

J. S. A.

**Examination of therapeutic oxygen.**—See B., 1935, 1117.

**Determination of sulphur in soluble sulphides by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 598—601B).—The sol. sulphide is neutralised with HCl and titrated in presence of gum arabic with 0.01 and 0.001N-Pb( $NO_3$ )<sub>2</sub> and  $HgCl_2$ , the end-point being determined photometrically.  $BiCl_3$  may be similarly used in slightly acid solution. The method is trustworthy in presence of reducing agents (sulphite, thiosulphate) which preclude the use of the I method.

R. S. B.

**Determination of sulphuric acid in presence of ferric salts.** M. I. GARBER and I. V. SURIKOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 35—40).—Lunge's method (A., 1905, ii, 350) was superior to those of Allen and Bishop (A., 1913, ii, 722) and of Küster and Thiel (A., 1900, ii, 242).

CH. ABS. (e)

**Determination of carbon disulphide and hydrogen sulphide in air.**—See B., 1935, 1087.

**Potassium thiocyanate as a primary standard substance.** I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1935, 57, 2126—2131).—The side reactions occurring in the pptn. of  $Ag^+$  solutions with KCNS have been investigated. KCNS is a suitable standard for work of ordinary accuracy ( $\pm 0.1\%$ ). The solubility product of  $AgCNS$  at  $24^\circ$  in 0.05N- $KNO_3$  is  $3.2 \times 10^{-12}$ .

E. S. H.

**Stability of standard potassium thiocyanate solutions.** E. N. TARAN (J. Gen. Chem. Russ., 1935, 5, 602—604).—The titre of 0.1N-KCNS rises, during 8 months of storage, to a greater extent ( $+1.5\%$ ) in presence of air and diffused light than in their absence ( $+0.63\%$ ). The variations are ascribed to development of micro-organisms.

R. T.

**Kjeldahl method. IV. Metallic catalysts and metallic interferences.** R. A. OSBORNE and J. B. WILKIE (J. Assoc. Off. Agric. Chem., 1935, 18, 604—609; cf. A., 1934, 857).—Hg is the most satisfactory catalyst, but it must be pptd. as  $HgS$  before distillation of  $NH_3$ . Te, Ti, Fe, and Cu are also satisfactory. Se, Mo, V, W, and Ag are satisfactory in ordinary amounts ( $< 0.003$  g.-mol. per g. of material) or under less violent conditions of digestion. Pt and larger amounts of Se, V, and  $MnO_4'$  interfere. Mixed catalysts are not recommended for the digestion of samples of flour.

E. C. S.

**Micro-determination of phosphorus.** A. D. BRAUN (Trud. Vseso. Inst. Exp. Med., 1934, 1, No. 3, 171—174).—The Fiske-Subbarow method was modified by replacing the mixture of sulphite and H sulphite by 30%  $CH_2O$ .

CH. ABS. (e)

**Oxidative determination of hypophosphite.** L. MARTINI (Annali Chim. Appl., 1935, 25, 525—

528).—The sample (0.1 g. in 50 c.c.  $H_2O$ ) is boiled for 10 min. with 16%  $H_2SO_4$  (10 c.c.) and 0.1N- $KMnO_4$  (50 c.c.). The ppt. of Mn oxides is dissolved by addition of excess (25 c.c.) of 0.1N- $H_2C_2O_4$  and the solution is re-titrated with 0.1N- $KMnO_4$ . The difficulty of dehydrating  $NaH_2PO_2 \cdot H_2O$  is demonstrated.

F. O. H.

**Determination of small concentrations of arsine in air.** B. A. RASCHKOVAN (J. Gen. Chem. Russ., 1935, 5, 675—689).— $H_2SO_4$  and  $H_2MoO_4$  afford colourless sulphomolybdic acid (I), which is unstable when  $[H_2SO_4]/[MoO_3] < 30$ , and yields Mo-blue when  $SnCl_2$  is added. Addition of  $H_3AsO_3$  causes formation of arsenomolybdic acid (II), which is in equilibrium with (I) and  $H_2SO_4$ ; when  $[H_2SO_4]/[MoO_3] > 75$ , (II) is not formed, and no coloration results with  $SnCl_2$ . The following procedure, based on the above considerations, is proposed for determination of  $AsH_3$  ( $< 2 \times 10^{-8}$  g.) in air: the sample of air is shaken with 10—20 c.c. of 65%  $HNO_3$ , and a known vol. of the acid is evaporated to dryness after 24 hr. The residue is dissolved in a known vol. of  $H_2O$ , and 1 c.c. of the solution is shaken with 1 c.c. of a solution containing 3.4 g. of  $(NH_4)_2MoO_4$  and 3 c.c. of conc.  $H_2SO_4$  per 100 c.c. 15 min. later, the mixture is shaken with 0.05 c.c. of aq.  $SnCl_2$  (prepared by dissolving 25 g. of Sn in 30 c.c. of conc. HCl, adding a further 20 c.c. of HCl, and diluting to 1 litre), and the coloration is compared with that of a standard solution.

R. T.

**Determination of small amounts of boron by means of quinalizarin.** G. S. SMITH (Analyst, 1935, 60, 735—739).—A difference in colour produced by equal amounts of quinalizarin with 1 c.c. of test solution + 9 c.c. of  $H_2SO_4$ , and 10 c.c. of solution of 9 : 1  $H_2SO_4$ , indicates the presence of  $H_3BO_3$ , and may be matched against a standard solution of  $H_3BO_3$ . The method is suitable for determining  $1-40 \times 10^{-6}$  g. of B. Al-Si alloys may be dissolved in 10% NaOH, the solution after acidification being examined for B as above.

J. S. A.

**Determination of carbon monoxide in admixture with hydrogen and methane.** G. MEYER and A. SLOOFF (Rec. trav. chim., 1935, 54, 800—803).—CO in a mixture of CO,  $H_2$ , and  $CH_4$  may be oxidised to  $CO_2$  by passage over  $I_2O_5$  at  $120-130^\circ$ , the  $CO_2$  being retained by a liquid-air trap during measurement of the decrease of vol. Combustion of a second sample with CuO completes the analysis.

J. W. S.

**Dependence of the detection of carbon monoxide with palladium salt solutions on various additions.** W. DALLER (Z. anal. Chem., 1935, 103, 83—88).—The presence of excess of acid or of chlorides hinders the deposition of Pd; salts of weak acids, e.g., NaOAc, favour the action. Solutions of  $Na_2PdCl_4$  containing excess of  $Na_2SO_3$  are somewhat slowly reduced by CO but not by  $H_2$ , and may be used for the analysis of CO- $H_2$  mixtures.  $CH_4$  reduces Pd solutions at  $100^\circ$ , or at  $50^\circ$  in presence of NaOAc.

J. S. A.

**Determination of the  $CO_2$  pressure of natural waters.** A. PEKKARINEN (Suomen Kem., 1935, 8, B, 34—35).—If a stream of air containing a known % of  $CO_2$  is passed through dil.  $NaHCO_3$  and the solu-

tion is then shaken with a known vol. of air, the % of  $\text{CO}_2$  taken up is equal to that of the first air. This principle has been applied to the determination of free  $\text{CO}_2$  in natural  $\text{H}_2\text{O}$ . R. S.

**Electro-analytical determination of alkalis.** K. ABRESCH (*Angew. Chem.*, 1935, **48**, 683—685; cf. B., 1935, 1059).—K and Na are separated by the perchlorate or platinichloride method, and are then each determined by the polarographic method (cf. B., 1933, 944; A., 1933, 1024). K and Na can be determined in this manner conveniently and rapidly in solutions containing also Fe, Al, Ca, Mg, etc.

A. B. M.

**Application of spectrum analysis to determination of alkalis and alkaline earths. V. Direct photometric determination of alkali metals.** W. H. JANSEN, J. HEYES, and C. RICHTER (*Z. physikal. Chem.*, 1935, **174**, 291—300; cf. A., 1935, 185).—The liquid under examination is fed into a compressed air- $\text{C}_2\text{H}_2$  flame and the principal strong line of the element to be determined, picked out by a monochromator, falls on a photo-electric cell. The magnitude of the photo-electric current, which is measured by allowing it to charge a Lindemann electrometer, is within certain limits of concn. of the element in the flame a linear function of the concn., which is therefore determined by interpolation of data obtained with solutions of known concn. The experimental error is  $\pm 5\%$ . R. C.

**J. Lawrence Smith fusion [method].** M. O. LAMAR, W. M. HAZEL, and W. J. O'LEARY (*Ind. Eng. Chem. [Anal.]*, 1935, **7**, 429—431).—Modified procedure is recommended. E. S. H.

**Determination of calcium phosphates.** H. TRAPP (*J. pr. Chem.*, 1935, [ii], **144**, 93—105).—Ca in  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  can be determined (max. error,  $+0.17\%$  to  $-0.18\%$ ) by dissolving the sample (0.7—0.1 g.) in 30 c.c. of 30%  $\text{AcOH}$  + 1 c.c. of  $\text{HCl}$  ( $d$  1.19) at  $100^\circ$ , diluting to 400 c.c., and adding 4 g. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to the boiling solution. The ppt. is ignited, treated with  $(\text{NH}_4)_2\text{CO}_3$ , and weighed as  $\text{CaCO}_3$ . Similar results are obtained by dissolving  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{HCl}$ , diluting with  $\text{H}_2\text{O}$  to 250 c.c., adding  $\text{NH}_3$  until the solution is red to phenolphthalein, and then 25 c.c. of 10%  $\text{NH}_3$ . The mixture is heated for several hr. on the water-bath, kept overnight, and the pptd.  $\text{Ca}_3(\text{PO}_4)_2$  is washed with  $\text{H}_2\text{O}$  and weighed. Difficulties in the alkalimetric determination,  $3\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} = \text{Ca}_3(\text{PO}_4)_2 + \text{Na}_2\text{HPO}_4$ , by use of excess of 0.1N-NaOH and back-titration with acid are due to the tenacious occlusion of alkali by the ppt.; the optimum conditions are defined. Under suitable conditions, pptn. of  $\text{P}_2\text{O}_5$  by  $\text{MoO}_4^{4-}$  is quant. and the ratio  $\text{MoO}_3 : \text{P}_2\text{O}_5$  is const. Variations are due to the ignition, whereby reduction to ill-defined lower oxides readily occurs. Repeated alternate treatment with  $\text{NH}_3$  and ignition of the blue residues leads to its complete dissolution with the exception of a residue containing  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{P}_2\text{O}_5$ . The proportion of the blue matter in the residue varies with the conditions of ignition; it is richer in  $\text{P}_2\text{O}_5$  than the portion sol. in  $\text{NH}_3$ .

H. W.

**Spectrographic micro-determination of zinc [in plant material].** L. H. ROGERS (*Ind. Eng. Chem. [Anal.]*, 1935, **7**, 421—422).—The method is applicable when the concn. of Zn is 0.1—0.005%. Fe interferes in concns. of about 1%, but a procedure for making allowance is suggested. E. S. H.

**Quantitative separation of lead from other cations by the chromate method.** Z. KARAOGLANOV and M. MICHOV (*Z. anal. Chem.*, 1935, **103**, 113—119).—Pb is quantitatively pptd. as  $\text{PbCrO}_4$  by  $(\text{NH}_4)_2\text{CrO}_4$  in  $\text{HNO}_3$  solution, and may be so separated from Cu, Ni, Ag, Ca, Ba, Mn, Zn, Cd, Sr, Fe<sup>+++</sup>, or Al. J. S. A.

**Separation of lead from copper, cobalt, nickel, and cadmium by carbon dioxide in pyridine solution.** A. JÍLEK, J. KOT'Á, and J. VŘEŠT'AL (*Chem. Listy*, 1935, **29**, 299—304).—The solution of nitrates, containing alkali metals and  $> 0.2$  g. of Cu, is made alkaline with 10% aq.  $\text{C}_5\text{H}_5\text{N}$ , the vol. is made up to 100 c.c.,  $\text{CO}_2$  is passed for 5 min., 2 c.c. of aq.  $\text{NH}_3$  are added, and  $\text{CO}_2$  is passed for a further 40 min. The ppt. of  $\text{PbCO}_3$  is collected, washed with aq.-alcoholic  $\text{C}_5\text{H}_5\text{N}-\text{NH}_3$  mixture saturated with  $\text{CO}_2$ , ignited, and weighed as  $\text{PbO}$ ; Cu is determined electrolytically in the filtrate. Pb is separated from Ni and Co similarly, except that  $\text{NH}_3$  is omitted from the solutions. A similar method cannot be applied to separation of Pb from Cd. R. T.

**Use of ceric sulphate in determining cuprous oxide obtained by reducing sugars on Fehling's solution.** R. A. STEGEMAN and D. T. ENGLIS (*Trans. Illinois State Acad. Sci.*, 1934, **27**, 75—76).— $\text{Cu}_2\text{O}$  is treated with excess of  $\text{Ce}(\text{SO}_4)_2$  and the latter titrated back with standard  $\text{FeSO}_4$  (o-phenanthroline as internal indicator). The results are better than those by the  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  methods.

CH. ABS. (e)

**Determination of mercury in mercuric cyanide.** E. CATTELAINE (*J. Pharm. Chim.*, 1935, [viii], **22**, 454—456).— $\text{Hg}(\text{CN})_2$  acidified with  $\text{HCl}$  affords  $\text{HgS}$  quantitatively when boiled with  $\text{Na}_2\text{S}_2\text{O}_3$ . Traces of S are removed with  $\text{Na}_2\text{SO}_3$  and the residue is weighed. J. L. D.

**Volumetric determination of mercuric chloride by means of lead sulphide.** N. A. TANANAEV and V. D. PONOMAREV (*J. Appl. Chem. Russ.*, 1935, **8**, 1076—1078).—25 ml. of approx. 0.1N- $\text{HgCl}_2$  are boiled during 15 min. with 25 ml. of an aq. suspension of freshly pptd.  $\text{PbS}$ , the solution is filtered, the filtrate + washings are boiled, and titrated with 0.1N- $\text{Na}_2\text{CO}_3$  (phenolphthalein); the  $\text{HgCl}_2$  content is calc. according to the reaction  $\text{HgCl}_2 + \text{PbS} \rightarrow \text{HgS} + \text{PbCl}_2$ . The mean error is  $-0.4\%$ . R. T.

**Analytical reactions for detecting salts of cerium and other elements with methylene-blue.** L. PASSERINI and L. MICHELOTTI (*Gazzetta*, 1935, **65**, 824—832).—Complex compounds with characteristic colours are formed when an aq. solution of methylene-blue is added to solutions containing the following ions:  $\text{Ce}^{+++}$ ,  $\text{Hg}^{++}$ ,  $\text{PtCl}_6^{--}$ ,  $\text{Au}^{+++}$ ,  $\text{Ir}^{+++}$ ,  $\text{Pd}^{++}$ ,  $\text{MoO}_4^{--}$ ,  $\text{Fe}(\text{CN})_6^{--}$ ,  $\text{Fe}(\text{CN})_6^{--}$ ,  $\text{CNS}^+$ ,  $\text{Cr}_2\text{O}_7^{--}$ . With many other ions no characteristic colours are formed. The intense scarlet coloration formed with

Ce<sup>+++</sup> salts can be used for detecting this element in presence of all other elements of the third analytical group, including Fe and Cr. The composition of many of the coloured pptts. is given. O. J. W.

**Colour reactions of rare-earth metals with pyrogallol and gallic acid.** II. F. M. SOHEMJAKIN and T. V. VASCHEDTSCHENKO (J. Gen. Chem. Russ., 1935, 5, 667—674; cf. A., 1934, 621).—The phenomena observed when solutions of Ce(NO<sub>3</sub>)<sub>3</sub>, NH<sub>3</sub>, and pyrogallol or gallic acid (I) are mixed are represented on triaxial diagrams. A colorimetric method for Ce<sup>III</sup> determination, based on the diagrams, consists in placing 4 c.c. of 0.001*M*-(I) in a Nessler cylinder, adding 4 c.c. of 0.0001—0.0002*M*-Ce<sup>III</sup>, and 2 c.c. of 0.1*M*-NH<sub>3</sub> containing 1% of Na<sub>2</sub>SO<sub>3</sub>, filling the remaining space with Et<sub>2</sub>O, and comparing the intensity of coloration with that of a standard solution after < 2 min. R. T.

**Oxidation mechanisms in aqueous solution. [Manganic sulphate as a reagent.]** A. R. J. P. UBHELOHDE (J.C.S., 1935, 1605—1607).—A solution of Mn<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, stable when kept in the dark, is prepared by adding 3 c.c. of conc. H<sub>2</sub>SO<sub>4</sub> followed by six 2-c.c. portions of 0.5*N*-KMnO<sub>4</sub> at 3-min. intervals to 50 c.c. of MnSO<sub>4</sub> solution (15.1 g. of MnSO<sub>4</sub> in 1000 c.c. of 6*N*-H<sub>2</sub>SO<sub>4</sub>) with continuous cooling. 2 c.c. of conc. H<sub>2</sub>SO<sub>4</sub> are added after 8 c.c. and 12 c.c. of KMnO<sub>4</sub> have been added. The reagent rapidly oxidises nitrites, oxalates, VII to VV, H<sub>2</sub>O<sub>2</sub>, and Fe<sup>II</sup> in the presence of Cl<sup>-</sup>. The reactions are stoichiometric and the end-points are well defined, thus affording superior results to titrations with KMnO<sub>4</sub>. J. G. A. G.

**Bismuthate method for [determination of] manganese.** II. B. PARK (Ind. Eng. Chem. [Anal.], 1935, 7, 427; cf. A., 1926, 704).—Modified procedure is recommended. E. S. H.

**Absolute colorimetry. XII. Absolute colorimetric determination of iron.** A. THIEL and O. PETER (Z. anal. Chem., 1935, 103, 161—166; cf. A., 1934, 1324).—For the determination of Fe<sup>++</sup>, the sample is acidified with HCl (against Congo-red), and sulphosalicylic acid is added. The extinction of the red colour produced towards filtered blue or blue-green light is determined by comparison with the standard grey solution, Fe<sup>+++</sup> being calc. from the extinction coeff. For the determination of total Fe, the above solution is made alkaline with aq. NH<sub>3</sub>. Rapid atm. oxidation of Fe<sup>++</sup> occurs, and the yellow colour due to total Fe is colorimetric as before, using light of 462 mμ. Citrates and tartrates interfere. J. S. A.

**Simple reaction for cobalt ion.** A. V. VOLKOV (J. Appl. Chem. Russ., 1935, 8, 1095).—Crystals of MgCl<sub>2</sub>·6H<sub>2</sub>O acquire a bluish-green coloration when immersed in solutions containing Co. R. T.

**Thiocyanate-acetone reaction for detecting minimal quantities of cobalt in presence of iron.** H. DITZ and R. HELLEBRAND (Z. anorg. Chem., 1935, 225, 73—80; cf. A., 1934, 1085).—The sensitivity of the NH<sub>4</sub>CNS-COMe<sub>2</sub> test for Co is greatly reduced if accompanying Fe is removed

either by Na<sub>2</sub>CO<sub>3</sub> or by conversion into a complex fluoride. Removal of Fe by means of pptd. CaCO<sub>3</sub> leaves the sensitivity of the Co test unimpaired, so that 1.5 mg. of Co per litre can be detected in presence of 15 g. of Fe. F. L. U.

**Analysis of iron and nickel present together.** J. HANUS and J. VOŘÍŠEK (Chem. Listy, 1935, 29, 288—295).—When Ni : Fe < 1 : 40, a single pptn. of Fe suffices [acetate, succinate, and (CH<sub>3</sub>)<sub>4</sub>N<sub>4</sub> procedures], whilst when Ni : Fe > 1 : 40 a double pptn. is necessary for the first two methods, but does not give complete separation in the third method. The amount of Ni carried down with the Fe ppt. may be reduced by adding AcOH to 0.01*N* and NH<sub>4</sub>Cl to 1%. The fraction of the Ni pptg. together with Fe is const. for a given Ni : Fe, irrespective of the vols. of solutions taken. R. T.

**Determination of cobalt and nickel in zinc ores and electrolytic zinc.**—See B., 1935, 1146.

**Use of hydrogen peroxide and amyl acetate for micro-determination of chromium.** W. B. S. BISHOP and F. P. DWYER (J. Proc. Austral. Chem. Inst., 1935, 2, 278—280).—Amyl acetate is the best solvent for extraction of the blue colour given by CrO<sub>4</sub><sup>2-</sup>+H<sub>2</sub>O<sub>2</sub> in acid solution. 2×10<sup>-6</sup> g. of Cr may be so detected. J. S. A.

**Colorimetry of chromates at *p<sub>H</sub>* greater than 7.** V. N. SKVORTZOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 63—66).—A discussion. CH. ABS. (e)

**Determination of chromium in titanium oxide.** R. FLATT and X. VOOR (Bull. Soc. chim., 1935, [v], 2, 1985—1993).—The Cr is oxidised to chromate by fusing with a mixture of K<sub>2</sub>CO<sub>3</sub> and KClO<sub>3</sub>. After removal of most of the TiO<sub>2</sub> with HF the Cr is determined colorimetrically by means of the violet-red colour formed with diphenylcarbazide in acid solution. Using 10 g. of a commercial TiO<sub>2</sub> sample, 0.1—1.0 part of Cr in 10<sup>6</sup> can be determined with an accuracy of 15%. O. J. W.

**Colorimetric determination of molybdenum. Variables involved.** L. C. HURD and H. O. ALLEN (Ind. Eng. Chem. [Anal.], 1935, 7, 396—398).—Modified procedure in the KCNS-SnCl<sub>2</sub> method is recommended. E. S. H.

**Volumetric determination of tin with ceric sulphate.** N. A. RUDNEV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 51—62).—The titration of Sn<sup>++</sup> with Ce(SO<sub>4</sub>)<sub>2</sub>, with NHPh<sub>3</sub> as indicator, is described. CH. ABS. (e)

**Colorimetric determination of titanium by means of gallic acid, as compared with the hydrogen peroxide method.** F. M. SCHEMJAKIN and A. NEUMOLOTOVA (J. Gen. Chem. Russ., 1935, 5, 491—497).—4 c.c. of 5% NaOAc, 8 c.c. of 1% gallic acid, and a vol. of solution containing 3—800×10<sup>-7</sup> g. of Ti are placed in a 50-c.c. cylinder in the order given, H<sub>2</sub>O is added to the mark, and the coloration is compared with that given by a standard solution. Al does not interfere, but Fe, Mo, U, W, Th, Be, Mn, Zn, Ni, Co, and Ca should be removed. The order of accuracy is the same as for the H<sub>2</sub>O<sub>2</sub> method, which,

however, is applicable to the determination of  $\leq 6 \times 10^{-6}$  g. of Ti. R. T.

**Colorimetric determination of titanium in presence of bromine compounds.** G. P. LUTSCHINSKI and A. I. LICHATSHEVA (Z. anal. Chem., 1935, 103, 196—198).—A high  $[H_2SO_4]$  and a large excess of  $H_2O_2$  are added to the Ti solution, liberating Br quantitatively. Br is extracted with  $CHCl_3$ , and Ti in the aq. layer determined from the yellow coloration remaining. J. S. A.

**Detection of vanadium.** E. I. KRETSCH (J. Appl. Chem. Russ., 1935, 8, 1092—1094).—5—100 mg. of powdered salt or alloy are mixed with 0.05—0.1 g. of wood C and 0.2—0.5 g. of anhyd.  $AlCl_3$ , and the mixture is gently heated for 1—2 sec. in a test-tube having a plug of glass-wool moistened with 75%  $H_2SO_4$  inserted at about 7 cm. from the bottom, when an orange coloration indicates V ( $\leq 0.01$  mg. as  $V_2O_5$ ). Other elements not giving coloured chlorides volatile at  $< 150^\circ$  do not interfere. R. T.

**Persulphate method of determining vanadium.** L. N. MONJAKOVA (Rept. Cent. Inst. Met., 1934, No. 16, 197—199).—Factors affecting the method [e.g., the rate of reduction of V with Mohr's salt, and the time for oxidation of excess of Mohr's salt with  $(NH_4)_2S_2O_8$ ], and its application for determining V in high-V steel were studied. CH. ABS. (e)

**Possibility of determining bismuth as basic carbonate.** F. HECHT and R. REISSNER (Z. anal. Chem., 1935, 103, 186—189).—Bi, in solution as nitrate only, is treated at room temp. with the min. excess of aq.  $(NH_4)_2CO_3$ . The liquid is heated to boiling, and the ppt. of  $(BiO)_2CO_3$  is washed and dried at  $100^\circ$ . The method may be applied to micro-analytical determinations. J. S. A.

**Micro-electrolytic determination of bismuth and lead, and their separation by graded potential.** A. J. LINDSEY (Analyst, 1935, 60, 744—746).—Bi is deposited at  $60$ — $70^\circ$  from dil.  $HNO_3$  solution at a potential of 0.8 volt, in presence of  $N_2H_4 \cdot H_2O$  as depolariser. Pb is deposited anodically as  $PbO_2$  from dil.  $HNO_3$  at  $90$ — $100^\circ$ , at a potential of  $\leq 1$  volt. For the separation of Bi and Pb, Bi is first deposited as above. The solution and washings are treated with an excess of  $NaOH + Na_2O_2$ , and are finally acidified with  $HNO_3$ .  $PbO_2$  is deposited at a potential of 1.2 volts, and is preferably redissolved and re-deposited from 20%  $HNO_3$ . J. S. A.

**Determination of bismuth with  $[\alpha]$ -naphthoquinoline.** F. HECHT and R. REISSNER (Z. anal. Chem., 1935, 103, 88—98).—To a solution containing Bi as  $Bi_2(SO_4)_3$ , + 3% free  $H_2SO_4$ , 2.5% aq.  $\alpha$ -naphthoquinoline sulphate (I) and some  $H_2SO_3$  are added and then an excess of KI.  $C_{13}H_9N \cdot HBiI_4 \cdot H_2O$  is pptd., and is collected on a glass filter. The ppt. is washed twice with a solution of (I) + KI (3 c.c. for 10 mg. Bi), followed by  $\geq 6$  c.c. of  $H_2O$ . The ppt. is dried at room temp., and the Bi calc. as if from  $C_{13}H_9N \cdot HBiI_4$ . Vols. of solution and wash liquid must be rigidly adhered to, to ensure compensation between  $H_2O$  in the ppt. and loss of  $C_{13}H_9N \cdot HI$  during washing. J. S. A.

**Use of a [heated] bar in determining m.p.** R. DOLIQUE (J. Pharm. Chim., 1935, [viii], 22, 441—451).—The temp. gradients along bars of different metals heated at one end and with different cross-sectional areas are studied and the method is applied to the determination of m.p. J. L. D.

**Colour temperatures of the Hefner and acetylene flames.** A. R. PEARSON and B. PLEASANOE (Proc. Physical Soc., 1935, 47, 1032—1041).—The colour of the "cylindrical"  $C_2H_2$  flame depends on gas pressure, rate of consumption, and height of flame. In view of discordant data for photometric purposes, results for various burners and conditions are given. The colour temp. for  $C_2H_2$  flames is approx.  $2380$ — $2520^\circ$ , and for the Hefner flame  $1910^\circ$  abs. N. M. B.

**Simple thermo-regulator.** H. P. BLOXAM (J. Sci. Instr., 1935, 12, 361—363).—A bimetallic instrument with a general accuracy of  $\pm 2$ — $3^\circ$  is described. It is suitable for temp. up to  $300^\circ$ . C. W. G.

**Semi-automatic potentiometer for thermal analysis.** R. J. M. PAYNE (J. Sci. Instr., 1935, 12, 348—355).—A mechanically-driven potentiometer is combined with an inverse-rate recorder. C. W. G.

**Determination of the b.p. of small quantities of substances.** R. DOLIQUE (Bull. Soc. chim., 1935, [v], 2, 1832—1847).—A differential Hg manometer is described, which can be used for measuring v.p. and b.p. with only a few drops of liquid. The apparatus can be made suitable for the fractional distillation of small amounts of liquid, and can be used for distinguishing a pure liquid from an azeotropic mixture. O. J. W.

**Precision determination of lattice constants.** E. R. JETTE and F. FOOTE (J. Chem. Physics, 1935, 3, 605—616).—Theoretical and experimental conditions necessary for the precise determination of lattice consts. are discussed with reference to symmetrical focussing cameras. Methods for the evaluation of standard errors and fiduciary limits of results from one film and from a set of films are developed. X-Ray targets of alloys have been used to obtain a larger no. and better distribution of lines. The influence of the no. of Miller indices of diffraction lines on the vals. of lattice consts. in non-cubic systems is shown. The importance of the method of prep. of the samples is emphasised. Lattice consts. of pure Al, Ni, Ag, Au, Si, Fe, Mo, W, Mg, Zn, Cd, Sb, Bi, and Sn have been measured. T. G. P.

**New technique for obtaining X-ray powder patterns.** R. A. STEPHEN and R. J. BARNES (Nature, 1935, 136, 793—794).—In the method described a flat specimen such as is met with in metallurgical practice is used, the intensity of each line can be easily calc., and the sharpness controlled, and the time of exposure is lessened in certain cases. L. S. T.

**Variable-temperature X-ray powder camera.** W. H. BARNES and W. F. HAMPTON (Rev. Sci. Instr., 1935, [ii], 6, 342—344).—Temp. between  $-60^\circ$  and  $0^\circ$  are obtained in the camera by circulating through it a suitable liquid precooled in a separate bath. C. W. G.

**Two-crystal spectrometer for X-rays of wavelength  $0.030 < \lambda < 0.215 \text{ \AA}$ .** T. R. KUYKENDALL and M. T. JONES (Rev. Sci. Instr., 1935, [ii], 6, 356—361).—Transmission and reflexion through the body of the crystals are employed instead of reflexion from the surface. Specially designed induction coils and a cascade Coolidge tube for a source of short- $\lambda$  X-rays are described. C. W. G.

**Trichromatic colorimeter.** R. DONALDSON (Proc. Physical Soc., 1935, 47, 1068—1073).—A simplified instrument for use with a.c. or d.c. is described. The integrating properties of a diffusing sphere are employed to effect the mixture of the three instrumental stimuli; means are described for obtaining linearity of the scales. N. M. B.

**Universal colorimeter-nephelometer.** A. A. MALICIN (J. Appl. Chem. Russ., 1935, 8, 1110—1115).—A double-wedge colorimeter, also adapted to nephelometry, is described. R. T.

**Optical system of the disappearing-filament pyrometer.** F. A. CUNNOLD (Proc. Roy. Soc., 1935, A, 152, 64—80).—Reflexion at the round filament is negligible in the usual type of disappearing-filament pyrometer. Perfect disappearance of the filament is not essential for the attainment of max. accuracy. The aperture limits suggested by previous workers may be considerably widened, enabling pyrometers transmitting much more light to be constructed. L. L. B.

**Construction and use of a quartz quarter wave.** G. BRUHAT and L. WRIL (Compt. rend., 1935, 201, 719—721). H. J. E.

**Bismuth electrode.** D. N. MEHTA and S. K. K. JATKAR (J. Indian Inst. Sci., 1935, 18A, 109—113).—The Bi electrode can be used for  $p_{\text{H}}$  5.0—7.4. C. W. G.

**Glass electrodes.** P. L. VARNEY (Science, 1935, 82, 396—397).—A double-shank electrode is described. L. S. T.

**Micro-hydrogen electrode.** J. LOBERING (Z. anal. Chem., 1935, 103, 180—183).—An electrode for use with  $< 0.1$  c.c. of liquid is described. J. S. A.

**Unpolarisable electrodes to carry action currents.**—See A., 1935, 1552.

**Application of controlled potential to micro-chemical electrolytic analysis.** A. J. LINDSEY and H. J. S. SAND (Analyst, 1935, 60, 739—743).—Apparatus and procedure are described. J. S. A.

**Sound-proof box for electrically driven laboratory centrifuges.** N. POLLARD (Analyst, 1935, 60, 752—753). J. S. A.

**Image errors of the electron microscope.** W. GLASER (Z. Physik, 1935, 97, 177—201).—Comma and spherical aberration errors are discussed theoretically. A. B. D. C.

**[Mechanical] relay for spark counters of the Greinacher type.** H. TEICHMANN (Nature, 1935, 136, 871—872). L. S. T.

**Magnetic properties of natural and artificial iron-oxygen compounds. I. Magnetic measurements on powder samples.** W. LUYKEN and L. KRAEBER (Mitt. Kaiser-Willh. Inst. Eisenforsch.,

1934, 16, 169—178; Chem. Zentr., 1935, i, 2141).—A magnetic balance, especially suited for measurement on paramagnetic substances, is described. Conditions necessary for abs. measurements on ferromagnetic material have been investigated. J. S. A.

**Accurate measurement of volumes, and accurate titration.** R. GOLTZ (J. Gen. Chem. Russ., 1935, 5, 779—782).—A burette adapted for the accurate delivery of liquids is described, and conditions for prep., standardisation, and storage of standard solutions are specified. R. T.

**Absorber for titrimetric determination of traces of admixtures to gases.** V. G. GUREVITSCH (J. Appl. Chem. Russ., 1935, 8, 1107—1109).—A wash-bottle for the absorption of traces of admixtures to gases is described. R. T.

**Kjeldahl flasks and other apparatus of arsenic-free glass.** G. LOCKEMANN (Z. anal. Chem., 1935, 103, 81—82).—The use of apparatus of special Jena As-free glass (cf. A., 1935, 948) is discussed. J. S. A.

**Pyknometer.** G. A. FESTER (Rev. Fac. Quím. Ind. Agric., 1934, 3, 177).—The apparatus consists of a tap-funnel attached to a narrow U-tube with a bulb on the other limb and a graduation mark above the bulb. The liquid is run in through the tap until the meniscus reaches the mark, and the excess in the funnel is washed out before weighing. D. R. D.

**Absorption and titration flask for carbon dioxide determination.** R. GARDNER (Ind. Eng. Chem. [Anal.], 1935, 7, 437—438).—A modification of Thomas' absorption unit (B., 1933, 574) is proposed. E. S. H.

**Continuous distilling apparatus.** F. M. SCHERTZ (Ind. Eng. Chem. [Anal.], 1935, 7, 441).—The apparatus is suitable for liquids with b.p. 20—100°, and minimises risk of fire. E. S. H.

**Glass water-stills.** B. SIEDE (Chem.-Ztg., 1935, 59, 925).—Modern resistance glasses enable satisfactory stills to be constructed. The simple all-glass apparatus without rubber or ground joints illustrated compares favourably with metal stills for efficiency. G. H. C.

**Molecular still.** W. H. STRAIN and W. M. ALLEN (Ind. Eng. Chem. [Anal.], 1935, 7, 443).—Apparatus, accommodating 1—2 g. of substance, suitable for the purification of biological products is described. E. S. H.

**Automatic cut-off for electric stills.** M. R. A. RAO and B. S. RAO (Ind. Eng. Chem. [Anal.], 1935, 7, 377). E. S. H.

**Automatic still cut-off.** A. H. HALE and F. D. TUENMILER (Ind. Eng. Chem. [Anal.], 1935, 7, 441). E. S. H.

**All-glass valve.** J. WILLARD (J. Amer. Chem. Soc., 1935, 57, 2328—2329). E. S. H.

**Superiority of a Knudsen type vacuum gauge for large metal systems with organic vapour pumps, its design and operation.** J. W. M. DUMOND and W. M. PICKELS, jun. (Rev. Sci. Instr., 1935, [ii], 6, 362—370).—A discussion of the advantages and disadvantages of different types of gauge. C. W. G.



**Use of the Pirani gauge in finding vacuum leaks.** T. R. CUYKENDALL (Rev. Sci. Instr., 1935, [ii], 6, 371—372).—Gauges may be made from C-filament lamps. Leaks are shown by the gauge if a stream of illuminating gas is played over the surface of the apparatus. C. W. G.

**Precision oil gauge.** S. PALKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 434—435).—The gauge is suitable for measuring pressures  $< 40$  mm. with a precision of about 0.033 mm. Hg. E. S. H.

**Design of pressure control assembly.** S. PALKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 436).—The apparatus previously described (A., 1934, 1195) is modified. E. S. H.

**Sampling apparatus for chemical-climatological and technical investigations.** H. CAUER (Z. anal. Chem., 1935, 103, 166—180).—Portable and permanent installations of pump, flow meter, air filter, and absorption tubes for air sampling are described, and their uses indicated. J. S. A.

**Cataphoresis chamber for measurement of the cataphoretic migration velocity of microscopic particles.** R. HAVEMANN (Biochem. Z., 1935, 281, 402—407).—The usual methods for determination of  $\zeta$ -potential and the theoretical requirements for microscopic measurement of cataphoresis in suspensions with the help of a closed chamber are discussed. The setting up of a suitable chamber is described. P. W. C.

**Laboratory apparatus for ammonia synthesis.** V. F. POSTNIKOV (Trans. Inst. Chem. Tech. Ivanovo, 1935, 66—67).—Apparatus for the study of catalytic  $\text{NH}_3$  synthesis at  $500^\circ/100$  atm. is described. R. T.

**Precise method of measuring viscosity of solutions of organic substances.** A. VAN DER WYK and K. H. MEYER (J. Chim. phys., 1935, 32, 549—563).—With the object of determining viscosities of dil. solutions of org. substances the errors in Ubbelohde's method have been examined in detail, and necessary precautions and corrections ascertained so that  $\eta$  may be found in the range 0.015—0.050 with an accuracy of  $4 \times 10^{-4}$  g./cm. sec. T. G. P.

**Structure-capillary viscosimeter.** V. Z. DANES (Kolloid-Z., 1935, 73, 174—181).—An overflow capillary viscosimeter with a very wide range of working pressures is described. Results are given for  $\text{H}_2\text{O}$  and some aq. solutions. E. S. H.

**Durability of quartz glass ignition vessels.** M. A. BESBORODOV and T. A. LADE (J. Soc. Glass Tech., 1935, 19, 217—220).—Measurements of the loss in wt. of transparent fused  $\text{SiO}_2$  vessels when used for the ignition of various ppts. encountered in quant. analysis showed that, after three successive heatings, the corrosion was greatest with  $\text{PbSO}_4$  (especially marked),  $\text{ZnNH}_4\text{PO}_4$ ,  $\text{ZnCO}_3$ , and  $\text{SnO}_2$ . Little or no loss in wt. was caused by the following, for the ignition of which fused  $\text{SiO}_2$  vessels are recommended:  $\text{KNO}_3$ ,  $\text{K}_2\text{PtCl}_6$ ,  $\text{MgSO}_4$ ,  $\text{HCl}$  (conc.),  $\text{Ni}$  dimethyl-

glyoxime, mixtures of  $\text{Al}$  and  $\text{Fe}$  (or of  $\text{Al}$ ,  $\text{Fe}$ , and  $\text{Ti}$ ) hydroxides,  $\text{NaCl}$  and  $\text{KCl}$  (1:1),  $\text{MgNH}_4\text{PO}_4$ , graphite ash,  $\text{MgNH}_4\text{AsO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MnNH}_4\text{PO}_4$ ,  $\text{CaCO}_3$ , a mixture of  $\text{K}_2\text{S}_2\text{O}_7$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  (the loss in wt. was — that of a  $\text{Pt}$  vessel used under similar conditions),  $\text{CaC}_2\text{O}_4$ , and  $\text{BaSO}_4$ . A. L. R.

**Diacolation and filtration under pressure.** C. ROHMANN and J. H. EHLERS (Pharm. Ztg., 1935, 80, 1196—1197).—A laboratory apparatus for maintaining const. pressures  $\pm 1$  atm. for a const. delivery of 1 c.c. per min. from the diaculator or filter over a period of 80 hr. is described. E. H. S.

**Determination of the v.p. of compounds of metals.** D. N. TARASENKOV, A. N. GRIGOROVITSCH, and A. V. BOGOSLOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 924—933).—Jellinek's method (A., 1929, 1262) is preferred to that of Volmer (*ibid.*, 1226). The b.-p. method gives trustworthy results for salts of high v.p., on condition that no decomp. occurs. Johnston's static method (A., 1908, ii, 358) is in particular convenient for determination of dissociation pressure when one of the products is a gas. R. T.

**Stirring air within desiccators.** F. J. ZINK (Ind. Eng. Chem. [Anal.], 1935, 7, 442—443).—Small fans mounted on pivots inside the desiccator are caused to rotate by a series of mechanically moved permanent magnets passing near the outside. E. S. H.

**Reflux condenser for use with Erlenmeyer flasks.** J. W. OLSON and C. E. PLASS (Ind. Eng. Chem. [Anal.], 1935, 7, 444). E. S. H.

**Liquid absorption tube.** W. D. TURNER (Ind. Eng. Chem. [Anal.], 1935, 7, 444). E. S. H.

**Carbon dioxide from "dry ice."** W. S. LEE (Ind. Eng. Chem. [Anal.], 1935, 7, 442).—Solid  $\text{CO}_2$  is a convenient source of gaseous  $\text{CO}_2$  for use in the determination of  $\text{N}$  by the micro-Dumas method. A suitable apparatus is described. E. S. H.

**Continuous production of distilled water free from carbon dioxide and ammonia.** F. G. STRAUB (Ind. Eng. Chem. [Anal.], 1935, 7, 433—434).—The apparatus described gives a distillate having a conductivity of  $0.5\text{--}0.3 \times 10^{-6}$  mho and  $p_{\text{H}}$  6.8. E. S. H.

**Calculation of  $\Delta D$  in a crystal growth process.** M. GORDON (Ind. Eng. Chem. [Anal.], 1935, 7, 386—387).—Mathematical. E. S. H.

**Decantation of crystalline suspensions. I. General theory. II. Characteristic functions.** G. BOZZA (Atti R. Accad. Lincei, 1935, [vi], 21, 697—700, 752—755).—Mathematical. O. J. W.

**Decantation of suspensions of crystals. III. Continuous cylindrical decanting apparatus.** G. BOZZA (Atti R. Accad. Lincei, 1935, 21, 809—813).—Theoretical. Formule correlating rate of flow, efficiency, the dimensions of the apparatus, concn. of suspended matter, etc. are evolved. D. R. D.

## Geochemistry.

**Reduced thickness of the atmospheric ozone [layer] during Polar winter.** D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1935, 201, 787—789).—The quantity of  $O_3$  in the atm. has been studied spectroscopically at Abisko (Swedish Lapland) and compared with charts of air movements. Increased reduced thickness of  $O_3$  coincided with an invasion of Arctic air, which is richer in  $O_3$  than that of lower latitudes. The method permits the study of displacements of large masses of stratospheric air. Since air coming from regions to the north of the aurora zone is rich in  $O_3$  the origin of the latter is problematical.

R. S. B.

**Visual spectroscopic study of atmospheric ozone.** J. GAUZIT (Ann. Physique, 1935, [xi], 4, 450—532).—A simple spectrophotometer is described for the estimation of the abundance of atm.  $O_3$  by observation of the Chappuis bands when the sun is a few degrees below the horizon, by the study of the  $O_3$  absorption bands in the ultra-violet from observations of the blue sky, and by lunar spectrophotometry. Results of 156 measurements over 15 months show a max of  $O_3$  in March–April, and a min. in August–September. The distribution of  $O_3$  in a horizontal stratum was examined. Assuming the "thin layer" hypotheses, the estimated height of this layer is 20–50 km., with an average val. of 33 km.

N. M. B.

**Emanation content of air from the soil and underground tectonics.** (Foundation of geo-physical investigations on the basis of emanation measurements in air from soil.) H. ISRAEL-KOHLER and F. BECKER (Naturwiss., 1935, 23, 818).—It is assumed that Fick's law of diffusion governs the distribution of Rn in the air derived from the upper layers of soil. Three cases are possible: (a) the emanation originates completely in the surrounding earth, (b) an active layer at a certain depth is covered by weaker and inactive layers, (c) the sources of Rn are tectonic clefts covered with weakly active sedimentary layers. In the normal case the Rn content of the air increases rapidly with depth and reaches a const. concn. at a depth of about 5 m. In other cases the concn. varies exponentially with the depth.

A. J. M.

**Daruvar thermal spring.** S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1935, 6, 121—129).—The analytical data do not differ from those obtained in 1839.

R. T.

**Ansh-Bulat sulphate lake, and the possibilities of its exploitation.** A. B. ZDANOVSKI and D. I. RJABTSCHIKOV (J. Appl. Chem. Russ., 1935, 8, 981—993).—The  $H_2O$  contains 17.4% of solutes, chiefly  $Na_2SO_4$  6.9,  $MgSO_4$  2.5, and  $NaCl$  7.6%.  $Na_2SO_4 \cdot 10H_2O$  crystallises out over the range  $16^\circ$  to  $-5^\circ$ , and the mother-liquors yield 80 kg. of  $NaCl$  per ton when conc. at  $25^\circ$  and then cooled to  $-10^\circ$ . The final filtrates can be further conc. for the prep. of  $MgCl$ , and Br.

R. T.

**Distribution of nitrogen compounds in the sea near Southern California.** E. G. MOBERG and

R. H. FLEMING (Proc. 5th Pacific Sci. Cong., 1933, 3, 2085—2088).—The surface layer had 150 mg. of org. N and 30 mg. of  $NH_3$ -N per cu.m.,  $NO_2$  and  $NO_3$  being absent. The  $[NH_3]$  was const. to a depth of 70 m.  $NO_3$  was found at 40 m. and below.

CH. ABS. (e)

**Abnormal density of water from the deep portions of Lake Baikal.** J. MENDELEEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 105—108).—The  $d$  of samples of  $H_2O$  from different depths of the lake increase with increasing depth of the sample. Comparative vals. for the sample before and after distillation show an almost const. diminution of  $d$  on distillation.

W. R. A.

**Sulphur bacteria in the "pink" waters of the Surakhani oilfields and their significance in the geochemistry of water.** V. T. MALISCHEK and A. A. MALIANG (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 221—224).—Bacterial oxidation and reduction are discussed.

C. W. G.

**Occurrence of selenium in the Colorado River and some of its tributaries.** K. T. WILLIAMS and H. G. BYERS (Ind. Eng. Chem. [Anal.], 1935, 7, 431—432).—The Se content has been determined and its origins are traced.

E. S. H.

**Boron content of sea-water of the North Atlantic Coast.** N. W. RAKESTRAW and H. E. MAHNCKE (Ind. Eng. Chem. [Anal.], 1935, 7, 425).—The variation with locality and depth has been investigated.

E. S. H.

**Coastal ground water at Yumigahama, Tottori.** Y. TOYOHARA (Mem. Coll. Sci. Kyoto, 1935, A, 18, 295—309).—A theory based on hydrodynamical considerations holds good for the actual sea-shore as well as for models.

C. W. G.

**Geochemical characteristics of protocrystallisation.** A. E. FERSMAN (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 216—220).—Theoretical.

C. W. G.

**Granite of Schärding [Upper Austria].** G. HORNINGER (Tsch. Min. Petr. Mitt., 1935, 47, 26—79).—A description is given of the rock, with chemical analyses.

L. J. S.

**Baryte from Kitzbühel, Tyrol.** H. LEITMEIER (Tsch. Min. Petr. Mitt., 1935, 47, 1—25).—White sparry baryte occurring as veins in dolomite has long been mined at this locality. The dolomite-rock contains  $BaO$  0.15% (sol. in  $HCl$  and presumably as carbonate) near the veins and 0.08% at some distance from them, but there is no evidence that the baryte was accumulated by lateral secretion from the rock. At one place the mineral is violet-coloured, but this quickly fades on exposure to light, and is restored by exposure to Ra.

L. J. S.

**Wollastonite and parawollastonite.** M. A. PEACOCK (Amer. J. Sci., 1935, [v], 30, 495—529).—Measurements of wollastonite crystals from Crestmore, California, show them to be triclinic, whilst crystals from the limestone blocks of Monte Somma, Vesuvius, are mostly monoclinic, but some are triclinic and others

consist of an intergrowth of the two kinds. In both kinds the angles and cleavages in the prism-zone parallel to the *b*-axis are identical, and the optical characters are the same, except that in the triclinic crystals the extinction is  $2\frac{1}{2}^\circ$  to the *b*-axis. The name wollastonite is reserved for the more common triclinic form, and the monoclinic form is called parawollastonite. A third modification of  $\text{CaSiO}_3$  is pseudo-wollastonite. L. J. S.

**"Ferrosilite" as a natural mineral.** N. L. BOWEN (Amer. J. Sci., 1935, [v], 30, 481—494).—"Ferrosilite,"  $\text{FeSiO}_3$  (A., 1932, 926), has been asserted to have no real existence (A., 1932, 997; 1933, 1120; 1935, 447). Minute acicular crystals found in the lithophysæ of an obsidian from Lake Naivasha are monoclinic with a prism angle of  $90^\circ 50'$ ,  $\alpha$  1.763,  $\beta$  only slightly greater,  $\gamma$  1.794,  $c : \gamma = 34\frac{1}{2}$ ,  $2V$  very small, suggesting a monoclinic pyroxene. From these data it is further concluded (by extrapolation in the systems  $\text{CaSiO}_3\text{--FeSiO}_3$  and  $\text{MgSiO}_3\text{--FeSiO}_3$ ) that the crystals have the composition  $\text{FeSiO}_3$ , and the mineral is named clinoferrosilite. The systems  $\text{CaSiO}_3\text{--FeSiO}_3$  and  $\text{MgSiO}_3\text{--FeSiO}_3$  are now discussed afresh. Similar crystals were also found in lithophysal obsidians from Iceland, Wyoming, and California; analyses of the obsidians are given. L. J. S.

**Composition of tectites.** F. LOEWINSON-LESSING (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 181—185; cf. A., 1931, 60, 1028, 1146).—There are no eruptive rocks analogous to tectites, although many of the latter have acidity coeffs. and monobasic : dibasic oxide ratios similar to rocks of terrestrial origin. J. W. S.

**Synthesis of pyrophyllite.** R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1935, 225, 142—150).—In the synthesis of pyrophyllite (I) from orthoclase or anorthite (A., 1935, 1101) montmorillonite is not formed. The natural occurrence of kaolin or (I) arising from feldspars may serve as a geological thermometer, since (I) is not formed below  $400^\circ$ . F. L. U.

**Structural relationship of glauconite and mica.** J. W. GRUNER (Amer. Min., 1935, 20, 699—713).—X-Ray investigation (data given) of 8 glauconites subjected to various treatments shows that glauconite (I) is a mica in structure. The average vals. from 6 specimens for the consts. are  $a_0$  5.24,  $b_0$  9.07,  $c_0$  20.03 Å.,  $\beta$   $95^\circ 00'$ . (I) is as stable as biotite at temp. as high as  $750^\circ$ . It can absorb Tl ions, which probably replace  $\text{K}^+$  to  $\approx 25\%$ . The high  $\text{SiO}_2$  and  $\text{H}_2\text{O}$  content of (I) is apparently due to the environment in which it is formed. Excess of sol.  $\text{SiO}_2$  over sol.  $\text{Al}_2\text{O}_3$  gives rise to a Si : Al ratio in the  $(\text{Si}, \text{Al})_4\text{O}_{10}$  tetrahedral layer  $>$  in mica, and may even cause substitution of a few Si for  $\text{Fe}^{III}$  or Al in approx. the positions having a covalency of 6. In comparison with a muscovite (I) may occasionally have vacant positions in its structure, and a suitable formula is  $(\text{OH})_{6-10}\text{K}_{2-3}(\text{Mg}, \text{Fe}^{II} \text{Ca})_{1-3}(\text{Fe}^{III}, \text{Al}, \text{Si})_{3-6}$ . Probably one half of the  $\text{H}_2\text{O}$  given in analyses is adsorbed. L. S. T.

**Primary native silver ores at Batopilas, Mexico, and Bullard's Peak, New Mexico.** P. KRIEGER (Amer. Min., 1935, 20, 715—723).—At

Batopilas, native Ag is associated with safflorite, rammelsbergite, arsenopyrite (I), galena (II), and sphalerite (III). All the evidence indicates a primary origin for the Ag. The probable order of deposition is (i) sulphides, including pyrite, (II), and (III), (ii) Ni and Co arsenides and (I), and (iii) Ag minerals and Ag. At Bullard's Peak, native Ag is associated with a Ni-skutterudite in a manner similar to that of Ag and arsenides in the Cobalt district of Ontario. Primary origin of the Ag, and centrifugal replacement of the arsenide by Ag, are indicated. L. S. T.

**Monazite from West Portland Township, Quebec.** I. H. S. SPENOE. II. O. B. MUENCH (Amer. Min., 1935, 20, 724—732).—I. The waste dump of a felspar quarry at  $45^\circ 45' 30'' \text{N}$ ,  $75^\circ 36' 30'' \text{W}$  contained tourmaline, cuxenite, monazite, allanite (?), titanite-ilmenite, fergusonite (?), cyrtolite, muscovite, tenerite, and specularite.

II. Analysis of the monazite by Fenner's method gave Th 3.44, and Pb 0.068%; U, by emanation method, 0.054%. The Pb-U ratio is 0.053, giving a val. of 388—391  $\times 10^6$  years for the age of the mineral. The % of Pb obtained by a micro-analysis (A., 1935, 1216) is less (0.032—0.05%) than that obtained above by macro-methods. L. S. T.

**Piedmontite from Los Angeles County, California.** R. R. SIMONSON (Amer. Min., 1935, 20, 737—738).—Piedmontite occurs as small euhedral crystals in quartz-sericite-biotite schist and in quartzite from this locality. L. S. T.

**Radioactivity of ferro-manganese formations in seas and lakes of the U.S.S.R.** L. M. KURBATOV (Nature, 1935, 136, 871).—The Ra content of Fe-Mn bottom deposits of these lakes or seas varies from  $1.2 \times 10^{-10}\%$  (Caspian Sea) to  $31.8 \times 10^{-10}\%$  (Black Sea); it is much  $<$  in deep-water concretions of the Pacific Ocean ( $47.6\text{--}146.6 \times 10^{-10}\%$ ). Small concretions are more radioactive than large ones, and the surface layer is more active than the centre. The Th-X content is small. L. S. T.

**Crystallised melanterite from Pfaffenreuth, Bavaria.** F. MACHATSCHKI (Zentr. Min., 1935, A, 53—54; Chem. Zentr., 1935, i, 2148).—Native melanterite crystals, of octahedral habit, have been found;  $a : b : c = 1.180 : 1 : 1.534$ ,  $\beta = 104^\circ 23'$ . J. S. A.

**Maxixe beryl.** K. SCHLOSSMACHER and H. KLANG (Zentr. Min., 1935, A, 37—44; Chem. Zentr., 1935, i, 2147).—Structure and characteristics of the stone are discussed. The blue pleochroic colour is rapidly lost on exposure to light. J. S. A.

**Osmiridium.** III. X-Ray analysis. O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Ann. Inst. Platine, 1935, No. 12, 5—15; cf. A., 1932, 1107).—Natural osmiridium has a fibrous structure, probably due to partial recrystallisation. CH. ABS. (e)

**Gypsum crystals from Alfalfa County, Oklahoma.** C. A. MERRITT (Amer. Min., 1935, 20, 674). L. S. T.

**Method for removing iron oxide coatings from minerals.** M. DROSDOFF and E. TRUOG (Amer. Min., 1935, 20, 669—673).—The mineral is suspended in  $\text{H}_2\text{O}$ , treated with  $\text{H}_2\text{S}$ , and then with 0.05N-HCl.

Silicates and apatite are practically unaffected. The action of  $H_2S$  on haematite, limonite, goethite, biotite, basalt, granite, and certain Fe-coated minerals is also described. L. S. T.

**Augelite from Mono County, California.** D. M. LEMMON (Amer. Min., 1935, 20, 664—668).—Augelite, basic Al phosphate,  $d$  2.67, hardness 5, occurs as a hydrothermal mineral deposited from solutions which acted on the andalusite (I) deposit subsequent to the formation of (I), corundum, diaspore, topaz, etc. It is directly associated with lazulite, rutile, barite, pyrophyllite, muscovite, alunite, and quartz. Other occurrences are briefly described. L. S. T.

**Pseudo-brookite.** C. PALACHE (Amer. Min., 1935, 20, 660—663; cf. *ibid.*, 1934, 19, 16).—Pseudo-brookite from Thomas Mts., Utah, has [F. A. GONYER]  $Fe_2O_3$  60.57,  $TiO_2$  38.12, and  $MgO$  1.26, total 99.95%, indicating an excess of approx. 4% of  $TiO_2$  over that required by  $Fe_2TiO_5$ . L. S. T.

**Mineralogical classification of igneous rocks: comparison of recent proposals.** S. J. SHAND (J. Geol., 1935, 43, 609—617).—Various classifications based on texture, colour, degree of saturation with  $SiO_2$ , composition of the felspar developed in a rock, and the ratio of  $Al_2O_3$  to bases are compared and discussed. L. S. T.

**Mixing and unmixing of silicate rock magmas.** G. LINCK (Chem. Erde, 1935, 10, 126—128).—A criticism (cf. Grigoriov, Zentr. Min., 1935, 242). L. J. S.

**Lias clay from Dobbertin [Mecklenburg].** F. K. SCHLÜNZ (Chem. Erde, 1935, 10, 116—125).—Chemical analyses and microscopical examination were made of the fractions of the clay  $>1\mu$  and  $<1\mu$ . X-Ray patterns show the latter to be mainly halloysite. L. J. S.

**Minerals of lead slags.** W. FABER (Chem. Erde, 1935, 10, 67—115).—Chemical analyses and optical determinations are given of several fractions separated by heavy liquids from a Pb slag from the Harz. The minerals identified include  $\alpha$ -celsian, willemite, fayalite, magnetite, Zn-blende, and wurtzite. The diagrams of the systems  $CaO-FeO-SiO_2$  and  $\gamma-Ca_2SiO_4-Mg_2SiO_4-Zn_2SiO_4-Fe_2SiO_4$  are discussed. L. J. S.

**Recent and fossil red earth (terra rossa) formation.** E. BLANCK and E. VON OLDERSHAUSEN (Chem. Erde, 1935, 10, 1—66).—Analyses are given of soils and of the underlying limestone from which they are derived in the district of the southern Frankenalb in the Altmühl valley in Bavaria. L. J. S.

**Structure of dickite and other clay minerals.** C. J. KSANDA and T. F. W. BARTH (Amer. Min., 1935, 20, 631—637).—X-Ray measurements of dickite from Schuylkill Co., Pa., give  $a_0$  5.145,  $b_0$  8.882,  $c_0$  14.337,  $\beta$  96° 45',  $d_{calc}$  2.618, with four mols. of  $Al_2Si_2O_5(OH)_4$  per unit cell; space-group  $C4'$ . A test for piezo-electricity gave a negative result, making the latter improbable. Gruner's structure is, in the main, confirmed, but a certain difference renders proposed structures of kaolinite, nacrite, halloysite, and vermiculite uncertain. L. S. T.

**Combined water in clay substance.** O. KOERNER, K. PUKALL, and H. SALMANG (Z. anorg. Chem., 1935, 225, 69—72; cf. A., 1930, 720).—Isothermal dehydration of a very pure Zettlitz kaolin, extending over periods up to 1.5 years, shows that, contrary to the usual belief, the composition of the clay mol. is  $Al_2O_3 \cdot 2SiO_2 \cdot 1.5H_2O$ , the remaining  $H_2O$  being adsorbed. Dehydration proceeds by way of the mono- and hemi-hydrates. F. L. U.

**Minerals of Franklin and Sterling Hill, New Jersey.** C. PALACHE (U.S. Geol. Surv., 1935, Prof. Paper 180, 1—135).—Detailed descriptions are given of 148 minerals from this unique mineral locality; 30 of these minerals have not been found elsewhere. In addition to details from the lit., many new crystallographic and optical data and some new chemical analyses are given. Two new species are established: hydrohetaerolite,  $2ZnO \cdot 2Mn_2O_3 \cdot H_2O$ , tetragonal (?), as distinct from hetaerolite ( $ZnO \cdot Mn_2O_3$ ); and magnesium chlorophoenicite,  $(MgMn)_3As_2O_8 \cdot 7(Mg, Mn)(OH)_2$ , monoclinic, differing from chlorophoenicite in containing Mg in place of Zn. The primary ore is a granular mixture of franklinite (43%), willemite (26%), calcite (25%), zincite (1%), with tephroite and other silicates (5%). It is suggested that hydroxides of Mn and Fe and hemimorphite were first formed by the metasomatic replacement of limestone, and that this deposit was altered by regional metamorphism in pre-Cambrian times, and further alterations by later intrusions of pegmatites giving the complex variety of minerals. L. J. S.

**Heavy minerals of the "Erinpura" granite and microgranite of Danta state (N. Gujrat).** N. L. SHARMA and S. PURKAYASTHA (Proc. Indian Acad. Sci., 1935, 11, B, 369—376).—Comparative mineralogical data are recorded and discussed. A. G. P.

**Pre-Cambrian rocks of the Lake Superior Region.** C. K. LEITH, R. J. LUND, and A. LEITH (U.S. Geol. Surv., 1935, Prof. Paper 184, 1—34).—The correlation of the rocks in relation to their geological age is discussed. The extensive deposits of banded jaspery Fe ores were probably derived from the weathering of volcanic rocks with chemical (or organic-algal) pptn. from solution and subsequent concn. by oxidation and leaching of  $SiO_2$  by percolating surface waters. L. J. S.

**Dark inclusions in a tonalite of Southern California.** C. S. HURLBUT, jun. (Amer. Min., 1935, 20, 609—630).—Dark inclusions in a quartz diorite, known as the Bonsall tonalite (analysis given), are described. Plagioclase, hornblende, and biotite make up the bulk of the inclusions and are always present, whilst quartz, orthoclase, and pyroxene are sometimes found in small amounts. The inclusions and the tonalite are mineralogically similar, but the former are xenoliths of older rock (gabbro) and owe their present condition to reaction with the tonalite magma. L. S. T.

**Paragenesis of the mineral assemblage at Crestmore, Riverside County, California.** J. W. DALY (Amer. Min., 1935, 20, 638—659).—The geology of the district, the rocks, and the minerals are

described. The mode of formation of the latter is discussed, and the contact metamorphic minerals are grouped under the rocks to which they owe their origin. L. S. T.

**Radiometric prospecting of a [volcanic] flow of rhyolite.** E. ROTHE and (MME.) A. HÉE (Compt. rend., 1935, 201, 892—893).—The deposit at Welschbruch has been delimited radiometrically.

R. S. B.

**Occurrence of vanadium in fossil coals.** V. SILBERMINTZ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 117—120).—800 samples of coal of different types and origins were considered. Analyses for V were made on 500 samples. Most samples show very slight content of  $V_2O_5$  in the ash, but certain specimens contained up to 8.79%  $V_2O_5$ . Most coals high in  $V_2O_5$  are of the clarain-vitrain type and often have a lignite structure. The origin of V in coal appears to depend principally on local conditions. W. R. A.

**Conversion of plant substances into fossil coals.**—See B., 1935, 1122.

**Origin of petroleum.** G. A. FESTER and J. CRUELLES (Rev. Fac. Quím. Ind. Agríc., 1934, 3, 76—108).—The following theory is put forward, based on numerous analyses of relevant materials. Marine flora and fauna suffer decomp. in tropical climates, evolving gases (including  $H_2S$ ) and leaving mainly fatty material, which by further decomp. is converted into petroleum. In colder climates, the cellulose and lignin do not decompose completely and coal etc. are produced. This theory is supported by the geographical distribution of petroleum and coal. The presence of colloidal V sulphides in South American petroleum is explained by the presence of vanadates (derived from the local igneous rocks) in the  $H_2O$ , the  $H_2S$  causing pptn. of the V. Analyses and other data concerning South American raphaellites and petroleum are given. D. R. D.

## Organic Chemistry.

**Free radicals.** E. DARMOIS (Bull. Soc. chim., 1935, [v], 2, 2053—2067).—A lecture.

**Thermal decomposition of nitromethane.**—See this vol., 33.

**Thermal decomposition of hexane at high pressures.** J. N. PEARCE and J. W. NEWSOME (Proc. Iowa Acad. Sci., 1934, 41, 139—140).—Between 460° and 490°/14,000—15,000 lb. the gaseous product consists of 25%  $CH_4$ , 47%  $C_2H_6$ , 15%  $C_3H_8$ , and 7%  $C_4H_{10}$ ; at 460° it contains 2.1%  $H_2$ , 1.4%  $C_2H_4$ , 1.5%  $C_3H_6$ , and 2.1%  $C_4H_8$ . At 497° both  $H_2$  and  $C_2H_2$  have disappeared and the  $C_3H_8$ ,  $C_4H_{10}$ ,  $C_3H_6$ , and  $C_4H_8$  have fallen to 5.5%, 4.0%, 0.04%, and 0.16%, respectively. At this temp. abundant formation of C begins and the proportion of  $CH_4$  increases. The liquid product contained cycloparaffins,  $C_6H_6$ , substituted benzenes, and higher unsaturated compounds. CH. ABS. (r)

**Polymerisation of ethylene under high pressures and in presence of phosphoric acid.** V. N. IPATIEV and H. PINES (Ind. Eng. Chem., 1935, 27, 1364—1369).—The gaseous products of polymerisation of  $C_2H_4$  under pressure in presence of  $H_3PO_4$  at 250°, 280°, 300°, and 330° contain chiefly  $C_2H_4$  and iso- $C_4H_{10}$  (2.5% of the total product at 250° and 18.8% at 330°), produced by hydrogenation of  $\Delta^+$ - and  $\Delta^+$ - $C_4H_8$ . The liquid products b.p. < 60° are paraffins; olefines are present in all fractions, naphthenes occur in fractions b.p. > 110°, and fractions b.p. > 250° are mainly aromatic, the proportions of the lower paraffinoid and higher aromatic fractions increasing with rise of temp. of polymerisation. The thermal polymerisation of  $C_2H_4$  in absence of  $H_3PO_4$  gives rise almost exclusively to olefines and naphthenes and aromatic compounds are absent. At 180°  $C_2H_4$  and  $H_3PO_4$  give  $(OH)_2PO \cdot OEt$ , which decomposes at higher temp. with the formation of olefines and naphthenes. The latter are subsequently hydrogenated to paraffins and dehydrogenated to aromatics, respectively. There is no evidence of cracking. S. C.

**Hydrogenation catalysis. II. Technique.**—See this vol., 35.

**Oxidation of  $\gamma$ - and  $\beta$ -methyl- $\Delta^2$ -pentene by selenium dioxide.** A. GUILLEMONAT (Compt. rend., 1935, 201, 904—906; cf. A., 1935, 852).— $\gamma$ -Methyl- $\Delta^2$ -pentene with  $SeO_2$  in AcOH gives  $\gamma$ -methyl- $\Delta^2$ -penten- $\delta$ -ol (cf. A., 1910, i, 454) and  $\beta$ -methyl- $\Delta^2$ -pentene gives  $\beta$ -methyl- $\Delta^2$ -penten- $\alpha$ -ol, b.p. 61—63°/14 mm. (Ac derivative, b.p. 61—63°/12 mm.). J. L. D.

**Kinetics and mechanism of thermal transformations of unsaturated hydrocarbons. Polymerisation of  $\Delta^2$ -butadiene at atmospheric pressure.** V. G. MOOR, N. V. STRIGALEVA, and L. V. SCHILAEVA (J. Gen. Chem. Russ., 1935, 5, 818—829).— $C_4H_6$  yields chiefly  $C_8H_{12}$ , b.p. 130°, when heated at 400°, whilst at higher temp. (450—700°) fractions of higher and of lower b.p. are obtained. The velocity of the reaction  $2C_4H_6 \rightarrow C_8H_{12}$  varies with temp. according to  $\log K = -6400/T + 7.32 \pm 0.04$ ; the energy of activation is 28 kg.-cal. per mol. R. T.

**Oxidation with selenium dioxide.** Y. R. NAVES and (MME.) M. G. IGOLEN (Bull. Inst. Pin, 1935, 234—238).—A review of its various applications. J. L. D.

**Acetylene series. VI. Oxidation of acetylenic hydrocarbons with permanganate.** V. N. KRESTINSKI and M. K. KELBOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 871—876).— $C_2H_2$  and dil. aq.  $KMnO_4$  at 0° afford  $HCO_2H$  (I) and traces of  $H_2C_2O_4$ , CPh-CH gives  $BzOH$ ,  $CO_2$ , and traces of (I), CMe-CEt gives  $CO_2$ , AcOH, and  $EtCO_2H$ , and  $CBu^i$ :CH gives  $Bu^iCO_2H$ ,  $CO_2$ , and (I). Neutral intermediate oxidation products were not found in any case. R. T.

**Atomic equilibria in hydrocarbon molecules of the  $CH \cdot C \cdot CH_2 \cdot R$  series.** E. F. ZEBERG (J. Gen. Chem. Russ., 1935, 5, 1016—1019).— $\alpha\beta$ -Dibromo- $\gamma$ -phenylpropane and KOH at 100—120°, with or without EtOH, afford CPh:CMc and traces of  $CH_2Ph \cdot CH \cdot CH_2$ . R. T.



**Action of acetylene on acetyl chloride.** A. CORNILLON and R. ALQUIER (Compt. rend., 1935, 201, 857—838).—Condensation of  $\text{AcCl}$  with  $\text{C}_2\text{H}_2$  in presence of  $\text{AlCl}_3$  at  $15^\circ$  affords *Me*  $\beta$ -chlorovinyl ketone (I), b.p.  $40^\circ/20$  mm. [semicarbazone, m.p.  $180^\circ$  (decomp.)], which probably has a *cis*-configuration and rapidly decomposes, even in the dark, with evolution of  $\text{HCl}$  to an amorphous mass. With boiling  $\text{NaOH-EtOH}$  (I) gives a 20—25% yield of  $\text{C}_6\text{H}_5\text{Ac}_3$ . J. W. B.

**Use of copper to increase the yield of ethyl bromide.** P. HENDRIXSON (Proc. Iowa Acad. Sci., 1934, 41, 165).—Addition of  $\text{Cu}$  to the reaction mixture of  $\text{EtOH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{NaBr}$  increases the yield of  $\text{EtBr}$  from 57% to 80%. The effect is due to the liberation of  $\text{SO}_2$ , which reduces any free  $\text{Br}$  to  $\text{HBr}$ . CH. ABS. (r)

**Photochlorination of ethylene.**—See this vol., 37.

**Chlorination of propane.**—See this vol., 35.

**Mechanism of slow oxidation of propane.**—See this vol., 33.

**Photobromination of tetrachloroethylene and of chloroform.**—See this vol., 37.

**Isotopic exchange reactions with iodine.**—See this vol., 40.

**Aluminium alkoxides and their parachors.**—See this vol., 14.

**Synthesis of octadecyl alcohols with branched chain.** O. BRUNNER and G. WIEDEMANN (Monatsh., 1935, 66, 438—442).— $\text{CH}_3\text{Et}(\text{CO}_2\text{Et})_2$  is converted by myristyl iodide in presence of  $\text{Na}$  and  $\text{PhMe}$  into *Et*, ethyltetradecylmalonate, b.p.  $132\text{—}136^\circ/14$  mm., hydrolysed and decarboxylated to  $\alpha$ -ethylpalmitic acid, b.p.  $215\text{—}220^\circ/10$  mm. (amide, m.p.  $111\text{—}112^\circ$ ), the *Et* ester, b.p.  $198\text{—}203^\circ/12$  mm., of which is reduced by  $\text{Na}$  and  $\text{Bu}^\circ\text{OH}$  in light petroleum to  $\beta$ -ethylhexadecyl alcohol, m.p.  $15^\circ$  (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p.  $105\text{—}106^\circ$ ). Analogously, *Et*, *n*-butyldodecylmalonate, b.p.  $224\text{—}226^\circ/1$  mm., affords successively  $\alpha$ -butylmyristic acid, b.p.  $214\text{—}219^\circ/10$  mm. (*Et* ester, b.p.  $189\text{—}192^\circ/10$  mm.; amide, m.p.  $109\text{—}110^\circ$ ), and  $\beta$ -*n*-butyltetradecyl alcohol, b.p.  $125\text{—}130^\circ/\text{high vac.}$ , m.p.  $1^\circ$  (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p.  $102\text{—}103^\circ$ ). *Et*, hexyldodecylmalonate, b.p.  $222\text{—}225^\circ/12$  mm., yields successively  $\alpha$ -hexyl-lauric acid, b.p.  $218\text{—}222^\circ/12$  mm. (*Et* ester, b.p.  $195\text{—}198^\circ/12$  mm.; amide, m.p.  $110\text{—}111^\circ$ ), and  $\beta$ -hexyldodecyl alcohol, b.p.  $120^\circ/\text{high vac.}$ , f.p.  $-7.5^\circ$  (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p.  $77\text{—}78^\circ$ ). *Et*, dioctylmalonate, b.p.  $220\text{—}225^\circ/15$  mm., affords  $\alpha$ -octyldecoic acid, b.p.  $212\text{—}218^\circ/13$  mm. (*Et* ester, b.p.  $195\text{—}197^\circ/12$  mm.; amide, m.p.  $122.5\text{—}123.5^\circ$ ), and  $\beta$ -octyldecoyl alcohol, b.p.  $110\text{—}120^\circ/\text{high vac.}$ , f.p.  $-8^\circ$  (non-cryst. phenylurethane; 4'-chlorodiphenylcarbamate, m.p.  $96^\circ$ ).

H. W.

**Existence of boric acid complexes with one and two molecules of a diol in aqueous solution.**—See this vol., 29.

**Preparation of pure sorbitol and sorbose and the influence of this ketose on the conductivity of boric acid.** J. BOESEKEN and J. L. LEEFERS (Rec. trav. chim., 1935, 54, 861—865).—Details are given for the prep. of an efficient  $\text{Ni-Co-Cr}$  catalyst and its use in the reduction of glucose in 96%  $\text{EtOH}$  with  $\text{H}_2$  at  $150^\circ/150$  atm., to give cryst. sorbitol. An improved oxidation of sorbitol to sorbose using *Acetobacter suboxydans* is described, oxidation being complete in 3.5 days instead of 4—6 weeks, necessary with *B. xylinum*. Addition of  $0.1M\text{-H}_3\text{BO}_3$  to  $0.1M$ -sorbose causes a much greater increase in conductivity than does similar addition to fructose. J. W. B.

**Fluorination of halogenomethyl ethers. I. Fluorination of trichlorodimethyl ether.** H. S. BOOTH and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2069).—Treatment of  $\text{CCl}_3\text{-OME}$  with  $\text{SbF}_3$  without a catalyst yields *Me* chlorodifluoromethyl ether, b.p.  $55.3^\circ$ , m.p.  $-105.1^\circ$ , and *Me* trifluoromethyl ether, b.p.  $30.1^\circ$ , m.p.  $-96.2^\circ$ . These compounds are only slowly hydrolysed by  $\text{H}_2\text{O}$ . E. S. H.

$\alpha\delta$ - and  $\alpha\epsilon$ -Oxido-compounds. **Synthesis of  $\alpha\epsilon$ -oxidodecane.** A. FRANKE, A. KROUPA, and O. SCHMID (Monatsh., 1935, 66, 406—432).—*Et* hexoylacetate (improved prep. from technical *Me* heptinene-carboxylate) is converted by the successive action of  $\text{Na-EtOH}$  and  $\text{CH}_2(\text{CH}_2\text{Br})_2$  followed by heating of the product under diminished pressure into anhydrodecan- $\alpha$ -ol- $\epsilon$ -one (I), which readily adds  $\text{H}_2\text{O}$  giving decan- $\alpha$ -ol- $\epsilon$ -one (II), m.p.  $24.5\text{—}25.3^\circ$ , b.p.  $144\text{—}148^\circ/11$  mm. (distillable only in complete absence of acidic or halogenic impurities), which does not reduce Fehling's solution or  $\text{NH}_3\text{-Ag}_2\text{O}$ , is little changed when heated at  $100^\circ$ , and according to optical evidence has the open structure  $\text{C}_5\text{H}_{12}\text{CO}[\text{CH}_2]_3\text{CH}_2\text{OH}$ . Oxidation of (II) with  $\text{CrO}_3$  in  $\text{AcOH}$  affords  $\delta$ -ketodecoic acid, m.p.  $56.3^\circ$ , and  $\epsilon$ -keto-*n*-decyl  $\delta$ -ketodecoate, m.p.  $52^\circ$ , probably formed through the semiacetal, since the direct esterification of acid by alcohol is somewhat difficult. (II) is unchanged by  $\text{Al-Hg}$  or  $\text{Na-Hg}$  in  $\text{EtOH-H}_2\text{O}$ , but is reduced by  $\text{Na}$  in 96%  $\text{EtOH}$  to decane- $\alpha\epsilon$ -diol (III), m.p.  $23\text{—}24^\circ$ , b.p.  $155.5\text{—}157^\circ/11$  mm. Hydrogenation ( $\text{Pt}$  sponge in  $\text{Et}_2\text{O}$ ) of (I) leads to  $\alpha\epsilon$ -oxidodecane (IV), b.p.  $198.5\text{—}200.5^\circ/747$  mm., which is transformed successively into  $\alpha\epsilon$ -dibromo-*n*-decane, b.p.  $150\text{—}151.5^\circ/10$  mm.,  $\alpha\epsilon$ -dicyano-*n*-decane, b.p.  $187\text{—}193^\circ/9$  mm., and non-cryst.  $\alpha$ -*n*-amylpimelic acid (diamide, m.p.  $161.5^\circ$  after softening at  $160^\circ$ ); indications of the presence of isomeric diamides, and hence of  $\alpha\delta$ -oxide in the initial material, are not observed. Elimination of  $\text{H}_2\text{O}$  from (III) by  $\text{H}_2\text{SO}_4$  occurs at a noticeable rate with boiling 30% acid, and then leads mainly to an unsaturated alcohol,  $\text{C}_{10}\text{H}_{20}\text{O}$ , b.p.  $228\text{—}231^\circ/1$  atm., with smaller amounts of an oxide essentially (IV). Interaction of  $\text{Br}[\text{CH}_2]_6\text{Br}$  with  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  appears to lead mainly to the cryst. diketone  $\text{Ac}[\text{CH}_2]_3\text{Ac}$ . Treatment of dry  $\text{NaOBz}$  with  $\text{Br}[\text{CH}_2]_6\text{Br}$  at  $200^\circ$  affords  $\zeta$ -bromoheptyl benzoate (V), b.p.  $187\text{—}190^\circ/9$  mm., and  $\alpha\epsilon$ -dibenzoyloxy-*n*-hexane, m.p.  $55.5\text{—}56^\circ$  after softening at  $55^\circ$ . (V) and  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  in boiling  $\text{EtOH}$  containing  $\text{NaOEt}$  afford a product which

after successive acid and alkaline hydrolysis gives *nonan- $\alpha$ -ol-one*, m.p. 23—23.5°. When heated with  $\text{H}_3\text{PO}_4$  the ketol gives only complex substances of uncertain constitution, whereas (II) readily yields (VI).

H. W.

**Constitution of adenylypyrophosphoric and adenosinediphosphoric acid.** K. LOHMANN (Biochem. Z., 1935, 282, 120—123).—Examination of the electro-titration curve of adenosinediphosphoric acid (I) before and after hydrolysis indicates that it is adenylic acid (II) esterified with 1  $\text{H}_3\text{PO}_4$  and that adenylypyrophosphoric acid (III) is (II) esterified with 2  $\text{H}_3\text{PO}_4$ . Constitutional formulæ, based on these and other deductions, are given for (I) and (III). The  $\text{NH}_2$  of the adenine residue is free in (I) and (III).

W. McC.

**Introduction of chlorine into nitromethanedisulphonic acid.** H. J. BACKER (Rec. trav. chim., 1935, 54, 899—904).—The following salts of nitromethanedisulphonic acid (A., 1931, 64) are described, crystallographic data (by TERPSTRA) being given for some of these: *dibrucine*+10 $\text{H}_2\text{O}$ , *Ba*<sub>2</sub>+2 $\text{H}_2\text{O}$ , *K*<sub>3</sub>, *Tl*<sub>3</sub>, and *Ba*<sub>3</sub>. All salts of type  $\text{MO}_2\text{N}:\text{C}(\text{SO}_3\text{M})_2$  are explosive. The action of  $\text{Cl}_2$  on  $\text{KO}_2\text{N}:\text{C}(\text{SO}_3\text{K})_2$  in  $\text{H}_2\text{O}$  gives *K chloronitromethanedisulphonate* (I), whence the *strychnine*, *brucine*+4 $\text{H}_2\text{O}$ , *Ba*+3 $\text{H}_2\text{O}$ , decomp. 150°, *Tl*, *Ag*+2 $\text{H}_2\text{O}$ , and *Ca*+3 $\text{H}_2\text{O}$ , salts of *chloronitromethanedisulphonic acid*+4 $\text{H}_2\text{O}$  and +2 $\text{H}_2\text{O}$ , m.p. 95.5° (explosive decomp.) (prep. from *Ba* salt), are obtained. (I) and aq.  $\text{K}_2\text{SO}_3$  affords *K nitromethanedisulphonate* thus: (I)+ $\text{K}_2\text{SO}_3$ + $\text{H}_2\text{O}$   $\rightarrow$  ( $\text{SO}_3\text{K}$ )<sub>2</sub> $\text{CH}\cdot\text{NO}_2$ + $\text{KCl}$ + $\text{KHSO}_4$ . J. W. B.

**Influence of an element or of a negative group on the relative mobilities of alkyl radicals in their chloroformates.** P. CARRÉ and H. PASSEDOUET (Compt. rend., 1935, 201, 898—900).—The effect of introducing Cl or Ph into the alkyl of alkyl chloroformates is to diminish the temp. of thermal decomp. (cf. A., 1935, 1105), i.e., to increase the mobility of alkyl (cf. A., 1933, 806; 1934, 509). The *Pr*<sup>a</sup> ester has a lower mobility than the allyl ester, but the  $\beta$ -phenylpropyl ester has a higher mobility than the cinnamyl ester. The suggestion that the tendency to migration is the greater the more electropositive is the migrating group is abandoned. J. L. D.

**Condensation of carboxylic compounds with substances capable of forming organo-metallic compounds or tautomerides thereof under the influence of alkali metals and of their water-decomposable derivatives.** G. V. TSHELINCEV (J. Gen. Chem. Russ., 1935, 5, 562—569).—Theoretical. Ester condensation reactions consist of the steps:  $\text{EtOAc} + \text{CH}_2\text{Na}\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CO}_2\text{Et} \rightleftharpoons \text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et} + \text{NaOEt} \rightleftharpoons \text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} + \text{EtOH}$ .

R. T.

**Addition of hydrogen bromide to allylacetic acid.** M. S. KHARASCH and M. C. McNAB (Chem. and Ind., 1935, 989—990; cf. A., 1933, 805).—A criticism of the views of Linstead *et al.* (A., 1935, 195).

J. W. B.

**Addition of hydrogen bromide to olefinic acids.** R. P. Linstead and H. N. RYDON (Chem. and Ind., 1935, 1009).—A reply to the above. J. W. B.

**Addition of hydrogen bromide to triple and double linkings.** Undecynoic, undecenoic, and  $\kappa$ -epoxyundecenoic acids. P. L. HARRIS and J. C. SMITH (J.C.S., 1935, 1572—1576).—The reaction between  $\Delta^1$ -undecenoic acid and HBr is sensitive to "oxidants." In the presence of  $\text{BzO}_2\text{H}$  (I) (modified prep.) at 0° during 3 hr.  $\kappa$ -bromoundecenoic acid (II) is formed, whilst in the presence of  $\text{NHPh}_2$  the reaction is slower and the  $\gamma$ -Br-acid (III) results. Undecenoic acid (IV) and (I) (in ligroin at 30° during 24 hr.) yield  $\kappa$ -epoxyundecenoic acid (V), m.p. 45.5° (after 10 days m.p. 50°), which reacts with HBr in air, forming mixed bromohydrins, m.p. 49—53°. In ligroin solution (IV) and HBr in air yield (III); in presence of (I) (0° during 15 min.) or (V) the product is (II). None of the catalysts is effective in absence of mol.  $\text{O}_2$ . F. N. W.

***p*-Xenylamine as new reagent for the identification of fatty acids and fatty acid derivatives.** Synthesis of the *p*-xenylamides [*p*-phenylanilides] of oleic and elaidic acid and their bromoderivatives. W. KIMURA and M. NIHAYASHI (Ber., 1935, 68, [B], 2028—2034).—The *p*-phenylanilides are obtained by heating the requisite acid with  $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$  (prep. from  $\text{Ph}_2$  described) in a vac. or through the acid chlorides and their derivatives by bromination of the anilides or through the chlorides of the Br-acids. Their m.p. are 34—61° > those of the corresponding *p*-phenylphenacyl esters. The following are described: *ole*<sup>a</sup>, m.p. 120°, *elaid*<sup>a</sup>, m.p. 134—135°, *oleodibromostear*<sup>a</sup>, m.p. 87.5°, and *elaidodibromostear-p-phenylanilide*, m.p. 133.5°.

H. W.

**Preparation in a high state of purity of long-chain compounds. I. Oleic acid.** L. KEFFLER and J. H. McLEAN (J.S.C.I., 1935, 54, 362—367T).—The Pb salt method fails to remove the final 3—4% of saturated impurities in oleic acid, even when prepared from high-grade olive oil and a large excess of  $\text{Pb}(\text{OAc})_2$  is used. The higher unsaturated impurities can be completely removed by 10—12 recrystallisations of the Li salts from 5 vols. of 80% EtOH; the final 3—4% of saturated impurities can then be removed, within 0.2 or 0.3%, by repeated fractional distillation under much reduced pressure. Oleic esters which had "aged" by keeping for long periods have also been purified by repeated fractional distillation, but the pure products were highly susceptible to rancidity changes, as were also the samples known to contain highly saturated impurities. Improvements in fractional distillation of fatty esters are described.

**Oleic acid.** T. P. HILDRICH (Chem. and Ind., 1935, 1009).—A reply to Keffler *et al.* (see above).

J. W. B.

**Unsaturated acids of natural oils. IV. The highly unsaturated acid of *Telfairia occidentalis*.** E. H. FARMER and E. S. PAICE. V.  $\alpha$ - and  $\beta$ -Licanic acids. W. B. BROWN and E. H. FARMER (J.C.S., 1935, 1630—1632, 1632—1633).—IV. *T. occidentalis* oil (7 months old) on saponification gives a mixture of fatty acids from which  $\beta$ -elæostearic acid (10% yield) is obtained. Freshly extracted (light petroleum) kernels give an oil containing

$\alpha$ - but no  $\beta$ -elaeostearic acid, although after irradiation (12 hr. in presence of S) the  $\beta$ -acid only is found.

V. Technical oiticica fat (I) or the kernel fat of *Licana rigida* normally yields  $\alpha$ -licanic acid (*semicarbazone*, m.p. 110—111°; *Me* ester) on saponification, but after irradiation (8 hr. in presence of I or S) *isolicanic acid*, m.p. 99.5° (*semicarbazone*, m.p. 138°), is formed. The fatty acids from (I) contain stearic (1.4%) and palmitic acids (about 1%).

F. N. W.

Polymerisation of methyl esters of higher unsaturated fatty acids. XVI. Polymerisation of methyl stearolate. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 140—145).—*Me* stearolate heated in  $H_2$  at 280—290° slowly polymerises to a bimol. product, which is not depolymerised when catalytically hydrogenated.

E. W. W.

Oxidation products of the unsaturated acids of linseed oil. L. C. A. NUNN and I. S. MACLEAN (Biochem. J., 1935, 29, 2742—2745; cf. A., 1935, 998).—The unsaturated acids of saponified linseed oil are oxidised by alkaline  $KMnO_4$ , the OH-acids are separated, and the remainder is steam-distilled. From the OH-acid fraction *isolinusic*, *linusic*, di-, tetra-, and hexa-hydroxystearic acids are separated, and from the steam distillate *Zn* -*dihydroxy-decane- $\alpha$ -dicarboxylate* is identified. The  $\Delta^0$  and  $\Delta^8$  positions of the ethylenic linkings in linoleic acid are confirmed.

H. D.

Preparation of brassidic acid from colza oil. L. KEFFLER and A. M. MAIDEN (Bull. Soc. chim. Belg., 1935, 44, 467—472).—Brassidic acid obtained from colza oil by a variation of the method of Reimer *et al.* (A., 1887, 233) and purified by repeated crystallisation from EtOH solidifies at 59.9° and is 99% pure.

H. G. M.

Acid fraction of mean mol. wt. 354 from the seeds of *Butea frondosa*, Roxb.—See A., 1935, 1550.

Odour and constitution:  $\gamma$ -substituted  $\gamma$ -butyrolactones. B. ROTHSTEIN (Bull. Soc. chim., 1935, [v], 2, 1936—1944).— $\alpha\beta$ -Epoxy-saturated hydrocarbons condense with  $CHNa(CO_2Et)_2$ , the malonyl residue becoming attached to the  $\alpha$ -C (the less substituted). The products on hydrolysis and loss of  $CO_2$  yield  $\gamma$ -substituted  $\gamma$ -butyrolactones. The b.p.,  $n$ , and  $d$  of the following are given:

$CH_2<\overset{CH_2}{\underset{CO}{\text{C}}}>CHR$ ,  $R=Bu^a$ ; amyl;  $Me\cdot[CH_2]_6$ ;  $Me\cdot[CH_2]_7$ ;  $Me\cdot[CH_2]_8$ ;  $Me\cdot[CH_2]_9$ , b.p. 140°/0.30 mm.;  $Me\cdot[CH_2]_{10}$ , m.p. 32°, b.p. 159°/0.43 mm.;  $Pr^b\cdot[CH_2]_2$ , b.p. 135°/16 mm.; and  $Pr^b\cdot[CH_2]_3$ , b.p. 145°/14 mm., the last four compounds being new. The odour of these compounds is described. The following epoxy-hydrocarbons (prepared from the appropriate chlorohydrin or by  $BzO_2H$ -oxidation of the corresponding ethylene) appear new:  $CHR<\overset{O}{\underset{CH_2}{\text{C}}}$ ,  $R=Bu^a$ , b.p. 123—124°/763 mm.;  $Me\cdot[CH_2]_6$ , b.p. 75°/13 mm.;  $Me\cdot[CH_2]_7$ , b.p. 94°/15 mm.;  $Me\cdot[CH_2]_8$ , b.p. 124—125°/15 mm.;  $Me\cdot[CH_2]_{10}$ , b.p. 138—139°/15 mm.  $\alpha$ -Chloro- $\zeta$ -methylheptan- $\beta$ -ol has b.p. 99—100°/12 mm.

H. G. M.

Oxidation of *dl*- $\alpha$ -hydroxystearic acid and its significance as regards the structure of cerebronic acid. (A) E. KLENK and F. DITT. (B) P. A. LEVENE and P. S. YANG (J. Biol. Chem., 1935, 749—750, 751).—(A) *dl*- $\alpha$ -Hydroxystearic acid and  $KMnO_4$  in  $COMe_2$  give other acids as well as margaric. The conclusions of Levene *et al.* (A., 1933, 1276) concerning cerebronic acid are thus invalidated.

(B) The above result is admitted, but the conclusions are upheld.

R. S. C.

Condensation of  $\alpha$ -aldehydo- $\alpha\beta$ -dicarboxylic esters with esters of  $\alpha$ -halogeno-substituted acids. M. N. SHTSCHUKINA and N. A. PREOBRAZHENSKI (Ber., 1935, 68, [B], 1991—1998).—The condensation is considered to consist of an *O*-alkylation of the  $\cdot CH\cdot OH$  form of the aldehydosuccinic ester. Condensation of  $CH_2Cl\cdot CO_2Et$  with  $NaOEt$  and  $Et_2\alpha$ -aldehydo- $\beta$ -ethylsuccinate (I) or directly with the Na derivative of (I) obtained from  $CO_2Et\cdot CHEt\cdot CH_2\cdot CO_2Et$  and  $HCO_2Et$  gives *Et*,  $\alpha$ -carbethoxymethoxymethylene- $\beta$ -ethylsuccinate (II),  $CO_2Et\cdot CHEt\cdot C(CO_2Et)\cdot CH\cdot O\cdot CH_2\cdot CO_2Et$ , b.p. 207°/15 mm., 195°/4 mm., which does not colour fuchsin- $H_2SO_3$  or yield a semicarbazone, immediately adds Br, and reduces boiling  $Ag_2O\cdot NH_3$ . Hydrolysis of (II) with boiling 10%  $H_2C_2O_4$  affords an acid,  $C_8H_{12}O_5$ , m.p. 102.5—103° (also obtained amongst other products by use of boiling 10% HCl), slowly hydrolysed by boiling HCl to ethylsuccinaldehydic acid [*semicarbazone*, m.p. 161—162° (decomp.)] and  $OH\cdot CH_2\cdot CO_2H$ . *Et* aldehydosuccinate (III) and  $CH_2Br\cdot CO_2Et$  analogously yield *Et*,  $\alpha$ -carbethoxy-*n*-propoxymethylenesuccinate,  $CO_2Et\cdot CH_2\cdot C(CO_2Et)\cdot CH\cdot O\cdot CH_2\cdot CO_2Et$ , b.p. 187°/7 mm., 211.5°/22.5 mm., which gives the same reactions as (II). It is very slowly hydrolysed by boiling dil.  $H_2C_2O_4$  to an acid,  $C_8H_{12}O_5$ , b.p. 182—184°/8 mm., and by boiling 10% HCl to  $OH\cdot CH_2\cdot CO_2H$  and succinaldehydic acid (IV). The Na derivative of (III) and  $CH_2Cl\cdot CO_2Et$  in boiling EtOH give *Et*, carbethoxymethoxymethylenesuccinate,  $CO_2Et\cdot CH_2\cdot C(CO_2Et)\cdot CH\cdot O\cdot CH_2\cdot CO_2Et$ , b.p. 211—212°/20 mm., hydrolysed by 10% HCl to a non-aldehydic acid, m.p. 126—129°, and (IV). H. W.

Nature of oxidising graphite anode and comparative electrolysis of *d*- and *meso*-tartaric acid in sodium hydroxide. V. SIHVONEN and M. PYLKKANEN (Suomen Kem., 1935, 2, B, 37—39).—0.5*M*-Na tartrate has been anodically oxidised at 25° with Pt, Ni, Fe, and C anodes, using 3*N*-NaOH in the cathodic compartment. Quant. analysis has been made on the product for  $O_2$ ,  $CHO\cdot CO_2H$  (I),  $HCO_2H$ , and  $H_2CO_3$ , and qual. analysis for dihydroxymaleic (II) and -tartaric (III) acid. The % of  $HCO_2H$  is approx. the same as that of the  $CO_2$ , and hence there can be no decomp. at the anode of (I) into 2 mols. of  $HCO_2H$ .  $H_2C_2O_4$  is present only as a trace. The formation of (III) is greatest with Fe. There is no formation of  $OH\cdot CH(CO_2H)_2$  or  $CO(CO_2H)_2$ . The primary product is (II), and in agreement the oxidation yield of *d*- is slightly < that of *meso*-tartaric acid, since the formation of (II) is slightly easier with the latter. Occlusion of  $O_2$  by C in presence of NaOH is slow, and the anodic p.d. remains positive a longer

time than with the other electrodes. Otherwise oxidation with C resembles that with Ni. There is no marked difference between the isomerides.

R. S. B.

**Decomposition of citric acid by yeast.**—See A., 1935, 1538.

**Preparation of crystalline aldolactones.** R. WEIDENHAGEN (Z. Wirts. Zuckerind., 1935, 85, 689—691).—*d*-Gluconic (I) and *d*-arabonic (II) acids are converted into mixtures of the lactone and Et ester when heated with HCl-EtOH for 8—10 hr. at 150°. Dissolution of the mixture from (I) in COMe<sub>2</sub> and addition of light petroleum affords cryst. *d*-gluconolactone in 40% yield. Similarly, an 84% yield of *d*-arabonolactone is obtained from the Ca salt of (II).

P. G. C.

**alloMucic acid and a new tetrahydroxyadipic acid.** T. POSTERNAK (Helv. Chim. Acta, 1935, 18, 1283—1287; see A., 1935, 846, 1483).—The Ca salt (+6H<sub>2</sub>O) and *di*(phenylhydrazide), m.p. 227—230° (decomp.), of  $\alpha\beta\gamma\delta$ -tetrahydroxyadipic acid are also described. The m.p. of the lactone is now given as 200—201° (decomp.).

J. W. B.

**Combination of thiol acids with methyl- [and phenyl-]glyoxal.** M. P. SCHUBERT (J. Biol. Chem., 1935, 111, 671—678).—Aq. AcCHO gives additive compounds (1:1) with SH·CH<sub>2</sub>·CO<sub>2</sub>H (*Hg* salt, decomp. about 220°), and its anilide (II), m.p. 70°, and with glutathione, amorphous. BzCHO gives similar compounds with (I), m.p. 159°, thiosinamine, m.p. 108°, (II), m.p. 149°, *o*-SH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, m.p. 142°, and cysteine betaine (III), amorphous. Cysteine and CS(NH<sub>2</sub>)<sub>2</sub>, probably by virtue of the free NH<sub>2</sub> of the  $\psi$ -form, react with loss of H<sub>2</sub>O to give with AcCHO products, amorphous and m.p. 159°, and with BzCHO products, m.p. 141° and 222°, respectively. Cystine betaine, +H<sub>2</sub>O, cryst. (*Ag* and *Co* salts; *flavianate*, m.p. 230°), is prepared; it is readily reduced by Sn-HCl. The *flavianate* of (II) has m.p. 210°.

R. S. C.

**Optical rotation of configuratively related aldehydes.** P. A. LEVENE and A. ROTHEN (J. Biol. Chem., 1935, 111, 739—747).—*L*-C<sub>5</sub>H<sub>11</sub>·OH leads to  $\alpha$ -methylbutaldehyde, b.p. 90—92°, [*M*]<sub>D</sub><sup>20</sup> +20.3° (homogeneous), and  $\beta$ -methyl-*n*-valeraldehyde, b.p. 122°, [*M*]<sub>D</sub> -8.7° in heptane, CHMeEt·CH<sub>2</sub>·CH<sub>2</sub>Br, and thence  $\delta$ -methylhexan- $\alpha$ -al, b.p. 144°, [*M*]<sub>D</sub> +12.0° in heptane, and  $\epsilon$ -methylheptan- $\alpha$ -al, b.p. 72°/25 mm., [*M*]<sub>D</sub> +12.9° in heptane. [*M*] are max. vals. This series resembles the corresponding acids, azides, and iodides in changes of [*M*].

R. S. C.

**Action of alkyl halides on thio-aldehydes and -esters.** M. S. PLATONOV and S. B. ANISIMOV (J. Gen. Chem. Russ., 1935, 5, 622—624).—MeI or EtI and mono- or di-thioparaldehyde or Et thioacetate (110°; 20 hr.) yield SMe<sub>3</sub>I or SEt<sub>3</sub>I.

R. T.

**Mechanism and application of the Fries isomerisation.** V. C. SEKERA (Trans. Illinois State Acad. Sci., 1935, 27, 81—82; cf. A., 1928, 1010).—Anhyd. FeCl<sub>3</sub> and ZnCl<sub>2</sub> can replace AlCl<sub>3</sub> in this reaction, although they are not so effective.

CH. ABS. (r)

**Determination of diacetyl.** H. SCHMALFUSS and H. RETHORN (Z. Unters. Lebensm., 1935, 70, 233—240).—Ac<sub>2</sub> is heated at 100° with aq. NH<sub>2</sub>OH, HCl, NiCl<sub>2</sub>, and NH<sub>3</sub>. The Ni dioximine so formed is collected, washed at 0°, and weighed. The mean error of the determination of 0.05 g. of Ac<sub>2</sub> is -0.2%.

E. C. S.

**Properties and reactions of carbohydrates in liquid ammonia.** C. O. MILLER and A. E. SIEHRS (Proc. Soc. Exp. Biol. Med., 1931—1932, 29, 535—538; cf. A., 1934, 638).—Arabinose, glucose, fructose, galactose, sucrose, maltose, and  $\alpha$ -methylglucoside (I) are sol. in dry liquid NH<sub>3</sub> (II) at -33.5° and 25°. Glycogen (III) is dispersed to an opalescent solution. The presence of moisture causes caramel formation. Disaccharides and (I), but not monosaccharides, will crystallise from (II). Addition of a solution of KNH<sub>2</sub> causes pptn. of the K<sub>1</sub> salts of monosaccharides, the K<sub>2</sub> salts of disaccharides, and either, according to the proportions used, of (I); the salts are stable when dry. The K salt of (II) chars in air. Reducing sugars, but not sucrose, caramelize when sealed with KNH<sub>2</sub> at 20° for 24 hr.

CH. ABS. (r)

**Sugar determination by the ferricyanide electrode.**—See this vol., 126.

**Use of ceric sulphate in determining cuprous oxide obtained by reducing sugars on Fehling's solution.**—See this vol., 43.

**Action of phosphate on hexoses. II.** R. NODZU and K. MATSUI (Bull. Chem. Soc. Japan, 1935, 10, 467—471).—At  $p_H$  6.2—7 under the conditions previously defined (A., 1935, 734) Na<sub>2</sub>HPO<sub>4</sub>, K<sub>2</sub>HAsO<sub>4</sub>, and Na<sub>2</sub>SO<sub>3</sub> yield acetol (I) from glucose (II), but in smaller amounts than does K<sub>2</sub>HPO<sub>4</sub>. Alkali chlorides and sulphates are ineffective. Traces of Fe slightly increase, and of Zn or Cu decrease, the production of (I) by K<sub>2</sub>HPO<sub>4</sub>. Traces of Ca or Mg are without effect. (I) is obtained from pure (II) and K<sub>2</sub>HPO<sub>4</sub>.

R. S. C.

[2:3:6-Trimethylglucose anhydride.] K. HESS and F. NEUMANN (Ber., 1935, 68, [B], 2167; cf. A., 1933, 596, 1278).—A reply to Freudenberg *et al.* (A., 1935, 1484).

H. W.

**Colorimetric determination of glucose and fructose by their osazones.** V. S. BUTKEVITSCH and M. S. GAJEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 313—316).—A modification of Herzfeld's method (A., 1932, 416; 1933, 175) for the colorimetric determination of glucose and fructose is described. The accuracy is  $\pm 2.5\%$ .

P. G. C.

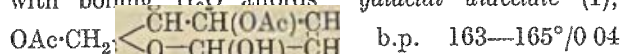
**Reduction products of aromatic amines and sugars [condensation products].** P. KARRER, H. SALOMON, R. KUNZ, and A. SEEBACH (Helv. Chim. Acta, 1935, 18, 1338—1342).—The following compounds, all of type NHR·CH<sub>2</sub>·[CH·OH]<sub>4</sub>·CH<sub>2</sub>·OH, are obtained by heating together *d*-glucose and the appropriate amine in MeOH or EtOH, and catalytic reduction of the product with H<sub>2</sub> (20—25 atm.) at 100° (Ni catalyst) or 30° (Pd-C): *N*-phenyl-, m.p. 134° (*benzylidene* derivative, m.p. 118—119°), *N*-*p*-tolyl-, m.p. 122°, *N*-*p*-ethoxyphenyl-, m.p. 123°, *N*-*p*-hydroxyphenyl-, m.p. 163°, *N*- $\beta$ -(*p*-hydroxyphenyl)ethyl- (only



as its *hydrochloride*, m.p. 208°, and *N*-ethyl- (as its *hydrochloride*, m.p. 134°) -*d*-glucosamine. These compounds are not febrifuges.

J. W. B.

*ψ*-Galactal. H. LOHAUS and O. WIDMAIER (Annalen, 1935, 520, 301—304).—Hydrolysis of galactal triacetate (Levene *et al.*, A., 1931, 1400) with boiling H<sub>2</sub>O affords galactal diacetate (I),



b.p. 163—165°/0.04 mm.,  $[\alpha]_D^{20}$  -26.9° [p-nitrophenylhydrazone, m.p. 176°; acetal (II), b.p. 136—138°/0.05 mm.,  $[\alpha]_D^{20}$  -39.70°], converted by Ba(OH)<sub>2</sub> into isogalactal (isolated as its p-nitrophenylhydrazone, m.p. 187°), which, when distilled, affords protoglucal (Bergmann *et al.*, A., 1934, 173). Reduction of (I) with Pd-H<sub>2</sub> gives its H<sub>2</sub>-derivative, b.p. 148—153°/0.04 mm.,  $[\alpha]_D^{20}$  +44.2° [p-nitrophenylhydrazone, m.p. 148°; acetal, b.p. 107—108°/0.04 mm.,  $[\alpha]_D^{20}$  +23.78°, by similar reduction of (II)]. Galactal is reduced to its H<sub>2</sub>-derivative, m.p. 128°,  $[\alpha]_D^{20}$  +48.1°.

J. W. B.

Interaction of fructose and dinitrobenzene. L. VON SZÉCSÉNYI-NAGY (Biochem. Z., 1935, 281, 175—177).—*o*- but not *m*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> yields a deep violet colour with fructose.

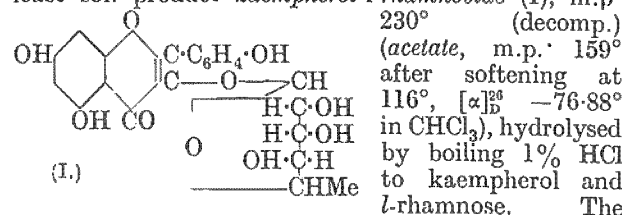
W. McC.

Inversion of sucrose solutions in tropical sunlight.—See this vol., 38.

Thermal decomposition of sugars and its catalytic acceleration. E. H. RIESENFELD and F. MÜLLER (Ber., 1935, 68, [B], 2052—2054).—Technical sugar and sucrose are heated at 150° alone and with NaCl containing varied proportions of FeCl<sub>3</sub>. Incipient caramelisation is observed in absence of catalyst, whereas addition of NaCl causes marked caramelisation and some carbonisation. The influence of > 0.005% of Fe (calc. on total mass) is inappreciable, but greater concns. cause more profound caramelisation and much greater separation of C. FeCl<sub>3</sub> alone induces carbonisation, but no caramelisation. K<sub>2</sub>CO<sub>3</sub> and other salts behave similarly to NaCl.

H. W.

Robinobiose and kaempferolrhamnoside. G. ZEMPLÉN and A. GERECs (Ber., 1935, 68, [B], 2054—2059).—Contrary to Charaux (A., 1926, 1183), enzymic fission of robinine (acetate, m.p. 175° after softening at 135°,  $[\alpha]_D^{25}$  -95.83° in CHCl<sub>3</sub>) gives as least sol. product kaempferol-*l*-rhamnoside (I), m.p.



(I.)

230° (decomp.) (acetate, m.p. 159° after softening at 116°,  $[\alpha]_D^{25}$  -76.88° in CHCl<sub>3</sub>), hydrolysed by boiling 1% HCl to kaempferol and *l*-rhamnose. The mother-liquors from (I) yield robinobiose,  $[\alpha]_D^{25}$  +2.72° to ±0° in H<sub>2</sub>O [acetate, m.p. 113° after softening at 70°,  $[\alpha]_D^{25}$  -19.23° in CHCl<sub>3</sub>; α-chloroacetate (II), decomp. 180°,  $[\alpha]_D^{25}$  -5.05° in CHCl<sub>3</sub>], very similar to Charaux' robinose (III) and shown by oxidation with OI' to be *l*-rhamnosido-*d*-galactose. (II), Ag<sub>2</sub>CO<sub>3</sub>, and MeOH give β-methylrobinoside acetate, m.p. 153.5—154.5°,  $[\alpha]_D^{24}$  -25.24° in CHCl<sub>3</sub>. The sequence of

monoses in the non-isolated (III) is therefore *l*-rhamnose-*d*-galactose-*l*-rhamnose.

H. W.

Cellotriose. L. ZECHMEISTER and G. TÓTH (Ber., 1935, 68, [B], 2134—2136).—In reply to Hess *et al.*, (A., 1935, 1226, 1308) the homogeneity of the author's cellotriose is maintained.

H. W.

Influence of substitution in the benzene nucleus on enzymic fission of phenol-β-*d*-glucosides.—See A., 1935, 1536.

Emulsin. XXIV. Glucoside syntheses with emulsin. B. HELFERICH and U. LAMPERT (Ber., 1935, 68, [B], 2050—2051).—The dependence of the synthesis on the temp., nature of aglucone, β-glucosidase val. of the emulsin, and solvent is fully discussed. The prep. of *n*-butyl-β-*d*-glucoside in good yield is described.

H. W.

Determination of cardio-active glucosides by the step-photometer.—See A., 1935, 1531.

Arabogalactan of Siberian larch.—See this vol., 123.

Starch nitrates. E. BERL and W. C. KUNZE (Annalen, 1935, 520, 279—289).—When potato-starch (I) is nitrated with 1:1 H<sub>3</sub>PO<sub>4</sub>-HNO<sub>3</sub> the P<sub>2</sub>O<sub>5</sub> content (approx. 0.3%) of the starch nitrate (II) is of the same order as the SO<sub>3</sub> content of (II) when H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> is used, but the N content (13.1%) never reaches the theoretical val. (14.14%) for the trinitrate. With H<sub>3</sub>PO<sub>4</sub>-HNO<sub>3</sub> the η of (II), which rises to a max. at 12 hr. nitration and then slowly falls, is 10 times > when H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> is used, and the stability of the product is higher (max. decomp. point 170°). X-Ray diagrams of (II) (3 interference rings) differ from those (9 rings) of (I), but hydrolysis of (II) gives a product different from (I). Microscopical examination of the grains of (II) shows a yellow outer section [amylopectin nitrate (III)] with a dark inner kernel [amylose nitrate (IV)], and by freezing moist in liquid air and subsequent flotation, separation into a lighter portion (smaller N content) and a heavier portion (higher N content) is effected. Addition of COMe<sub>2</sub> causes swelling, and the inner kernels split up into small granules, which, unlike (III), go into solution as the [COMe<sub>2</sub>] is increased. The η of (II) is dependent on the composition of the nitrating mixture, duration and temp. of nitration, and the nature of (I). The η of (II) from sol. starch is only 0.1 that of ordinary (I), but is not related to the mol. (micelle) wt. of (I) as determined by osmotic pressure measurements. Samples of high mol. wt. give a product of lower η. In agreement with the above, separate nitration of amylopectin gives (III) of lower N content (11.82—12.05%) and very high η, whereas amylose gives (IV) with higher N content (13.45%) and low η. Previous heating of (I) with H<sub>2</sub>O at 90—130°/0.715—2.7 atm. causes a 10<sup>3</sup> increase in η of (II), but at 150—180°/4.7—10 atm., a sudden and rapid fall in η of (II) occurs.

J. W. B.

Phosphorus of starches. T. POSTERNAK (Helv. Chim. Acta, 1935, 18, 1351—1369).—A more detailed account of work previously summarised (A., 1934, 59, 390; 1935, 1549).

J. W. B.



"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. I. Chemical structure of  $\beta$ -pachyman, the polysaccharide obtained from "Bukuryo," and its determination. K. TAKEDA (Mem. Tottori Agric. Coll., 1935, 3, 1—123).—Extraction of "Bukuryo" with EtOH-NaOH yielded  $\beta$ -pachyman (I),  $(C_6H_{10}O_5)_n$ , no m.p., but darkening at 230—235°,  $[\alpha]_D^{20} +24.78^\circ$  in 5% NaOH, mol. wt. probably < that of starch [*trinirate*, m.p. 195—199°,  $[\alpha]_D^{20} -63.63^\circ$  in  $C_5H_5N$ -EtOAc (3:2); *triacetate* (II), decomp. 255—258°,  $[\alpha]_D^{20} -68.75^\circ$  in  $CHCl_3$ ; Me<sub>2</sub> ether (III), m.p. 265—268°,  $[\alpha]_D^{20} -11.25^\circ$  in  $C_5H_5N$ - $C_6H_6$ ]. Hydrolysis of (I) with dil. or conc.  $H_2SO_4$  or dil. HCl yielded glucose (IV), whilst takadiastase gave (IV) and a disaccharide (*osazone*, m.p. 177°) similar to, but not identical with, gentiobiose. Hydrolysis with  $H_2C_2O_4$  or conc. HCl produced (IV) and an unstable *disaccharide*,  $C_{12}H_{22}O_{11}$ , m.p. 110°  $[\alpha]_D^{20} +76.7^\circ$  in  $H_2O$  (*osazone*, m.p. 167°), insol. in 95% EtOH, which on keeping decomposes to (IV). Neither fructose nor mannose was found in the hydrolytic products. Acetolysis of (I) using  $ZnCl_2$  yielded (II) and *biose octa-acetate*, m.p. 80—82°,  $[\alpha]_D^{20} +36.10^\circ$  in  $CHCl_3$ ,  $+25.3^\circ$  in  $C_6H_6$ ; hydrolysis of this yielded only (II). Acetolysis with  $HClO_4$  gave  $\beta$ -tetra-acetylglycuronic acid, and with  $H_2SO_4$  [using (II)], glucose  $\alpha$ -penta-acetate, m.p. 109—111°, was obtained. Hydrolysis of (III) with 5% HCl gave a 90% yield of 2:3:6-trimethylglucose, and with 1% MeOH-HCl, a 93% yield of 2:3:6-trimethylmethylglucoside. 2:3:4-Trimethylglucose was not detected. It is concluded that in the structure of (I), many  $\alpha$ - and  $\beta$ -glucofuranoses (1:4) are linked, commencing with the  $\alpha$ , at the first and fifth C. Two methods, the "alcohol" and the "enzyme," for the determination of (I) in "Bukuryo" are described. J. N. A.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. VII. Production of tetra-acetylglycuronic acid by acetolysis of  $\beta$ -pachyman in the presence of perchloric acid. K. TAKEDA (J. Agric. Chem. Soc. Japan, 1934, 10, 1010—1013).—Two *acetates* were obtained: (a), m.p. 83—86°,  $[\alpha]_D^{20} +9.56^\circ$  in  $CHCl_3$ ,  $+8.47^\circ$  in  $C_6H_6$ , (b)  $C_{14}H_{18}O_{11}$ , m.p. 103—107°,  $[\alpha]_D^{20} +65.6^\circ$  in  $C_6H_6$ ,  $+66.2^\circ$  in  $CHCl_3$ ,  $+60.9^\circ$  in MeOH. (b) is probably tetra-acetylglycuronic acid and hydrolysis gave a syrup which yielded an *osazone*,  $C_{18}H_{20}O_5N_4$ , m.p. 167—174°. J. N. A.

Hydrolysis of cellulose and its oligosaccharides. K. FREUDENBERG and G. BLONQUIST (Ber., 1935, 68, [B], 2070—2082).—New data are recorded for  $[M]$  for cellotriase (I) and cellotetraose (II) and the velocities of hydrolysis of cellobiose (III), (I), (II), and cellulose (IV) are measured in 51%  $H_2SO_4$ , the changes being followed polarimetrically and by iodometric determination of liberated  $\cdot CHO$ . The hypothesis that from (I) onwards each unit with a terminal union reacts according to  $k$ , with all other unions according to  $k_n$ , is a suitable basis for calculation, but is an approximation, and it appears probable that the hydrolysis of (IV) and its oligosaccharides (V) is precisely similar to the fission of the polypeptides of glycine and, in a measure, to the cracking of hydrocarbons. The evidence that the

(V) contain only one type of structure, that of (III), from which a straight chain leads to the polysaccharide, which is thus an extrapolation of (V), is as follows. Methylcellobiose (VI) is hydrolysed to 1 mol. of tri- (VII) and 1 mol. of tetra- (VIII) -methylglucose. Methylcellotriase (IX) yields 2 mols. of (VII) and 1 mol. of (VIII), whereas methylcelloetraose gives 3 mols. of (VII) and 1 mol. of (VIII), and methylcellulose many mols. of (VII) and one of (VIII). (VII), (VIII), (III), (VI), and (IX) have been completely synthesised and their structure has been elucidated.  $[M]$  from (III) onwards changes almost additively by the val. of one intermediate section for (I), of two sections for (II), and so on.  $[M]$  of this intermediate section is nearly  $[M]$  of the unit of (IV). The yield of (III) leads to the conclusion that the biose union alone is constitution-chemically and configuratively present in (IV). The course of the hydrolysis of (I), (II), and (IV) can be adequately explained by the hypothesis that all unions are of a single type, that of (III). Evaluation of the graphs obtained polarimetrically shows that all unions are sterically similar. H. W.

Action of ethylene oxide on cellulose. I. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1935, 8, 1023—1032).—Bleached cotton-wool (I) and  $(CH_2)_2O$  at 50° afford a product containing 1  $OH \cdot CH_2 \cdot CH_2 \cdot O \cdot$  (II) per 32  $C_6H_{10}O_5$  units; the proportion rises to 1:4—8 in presence of dil. alkalis, and attains a max. of 1:1.5 in presence of 18% NaOH or 35% KOH (50—60°; 15 min.). The products are much more readily hydrolysed and acetylated than is (I), but the velocity of benzoylation is not affected; they yield highly viscous solutions in NaOH, the viscosity rising with the no. of (II) introduced. R. T.

Celluloid formation. II. Effect of reaction medium on heterogeneous changes occurring in the fibrous state. M. WADANO, K. HESS, and C. TROGUS. III. Catalysed reactions in the fibrous state. Heterogeneous catalysis with a solid substrate and liquid catalyst. M. WADANO, C. TROGUS, and K. HESS. IV. Production of celluloid from cellulose nitrate and *l*- or *dl*-camphor. K. HESS, C. TROGUS, and M. WADANO (Z. physikal. Chem., 1935, B, 30, 159—182, 183—231, 232—235; cf. A., 1932, 568).—II. The reaction between cellulose nitrate (I) and camphor in presence of aliphatic alcohols as solvents is complete at such low camphor concns. that it can be effected at room temp. The X-ray diagrams and analysis of the solid phase show the existence of two new compounds, camphor-cellulose nitrate II (II) and camphor-cellulose nitrate III (III), in addition to the camphor-cellulose nitrate I (IV) previously observed. It seems probable that (III) corresponds with hydro-cellulose and (II) and (IV) correspond with natural cellulose. The camphor concn. at which reaction starts to proceed into the interior of the micelles increases with the size of the alkyl radical. The fact that the nature of the reaction product and the relation between the amount of camphor taken up and the camphor concn. vary with the solvent is possibly due to the first stage of the reaction being formation of

a double compound between the solvent and (I). Aromatic hydrocarbons promote the reaction of (I) with camphor in varying degrees.

III. The reaction of (I) with camphor in benzene solution in presence of ketones and alcohols has been studied. The effect of these substances on the concn. of camphor required for complete reaction is due to catalysis, and the varying fine structure of the product is determined by processes which are superimposed on the sorption of camphor.  $\text{COMe}_2$  and cyclohexanone are better catalysts than alcohols. For a camphor concn.,  $c$ , of 30% the amount taken up passes through a max. with increasing  $\text{COMe}_2$  concn.,  $C$ , whilst for const.  $C$  the amount of camphor taken up rises towards a limit with increase in  $c$ . When  $c$  is moderate and  $C$  small the product is (IV). (II) is obtained when  $C$  is  $\geq 1\%$ . If  $C$  is  $> 10\%$  and  $c = 5-20\%$ , the product is camphor-cellulose nitrate IV, which contains  $\text{COMe}_2$ . The formation of the various compounds of camphor and (I) is irreversible, and it is in general impossible to transform one into another. The catalytic action of  $\text{COMe}_2$  is attributed to its relatively rapid reaction with (I) to give a compound which reacts with camphor giving camphor-cellulose nitrate and re-forming  $\text{COMe}_2$ . With increasing  $C$  the swelling of the (I) fibres passes through a max., then through a min. EtOH and MeOH act similarly to  $\text{COMe}_2$  as catalysts. The presence of  $\text{H}_2\text{O}$  favours the formation of (II).

IV. The optical isomerides of camphor are identical in their behaviour towards (I). R. C.

**Reaction mechanism: action of fused sodium on mono-, di-, and tri-methylamines.** H. S. FRY and W. V. CULP (Rec. trav. chim., 1935, 54, 838—846).—Analogy with the reaction  $\text{RH}_n + n\text{NaOH}$

$\text{R(ONa)}_n + n\text{H}_2$  (A., 1928, 615) suggests the reaction  $\text{RH}_n + n\text{NaNH}_2 \rightarrow \text{R(NHNa)}_n + n\text{H}_2$ . Summation of the expected reaction stages leads to the equation  $\text{NH}_2\text{Me} + \text{NaNH}_2 \rightarrow \text{NaCN} + \text{NH}_3 + 2\text{H}_2$  for the interaction between  $\text{NH}_2\text{Me}$  and fused  $\text{NaNH}_2$  (in excess) at  $250^\circ$ . Determination of the  $\text{NH}_2\text{Me}$  used (liberated from  $\text{NH}_2\text{Me.HCl}$  by dropwise addition of  $10N\text{-NaOH}$ ),  $\text{NaCN}$  (Volhard),  $\text{NH}_3$  (absorbed in an excess of  $6N\text{-H}_2\text{SO}_4$ ), and  $\text{H}_2$  (no other gaseous products formed), gives 94% agreement with this equation. Similarly the mechanism  $\text{NHMe}_2 + 2\text{NaNH}_2 \rightarrow 2\text{NaCN} + \text{NH}_3 + 4\text{H}_2$  is verified to the extent of 97%, but the derived  $\text{NMe}_3 + 3\text{NaNH}_2 \rightarrow 3\text{NaCN} + \text{NH}_3 + 6\text{H}_2$  is invalid, since  $\text{NMe}_3$  does not react with fused  $\text{NaNH}_2$ . It is suggested that the initial stage  $\text{NMe}_2 + \text{NaNH}_2 \rightarrow [\text{NHMeR}_2 \cdot \text{NHNa}] \rightarrow \text{NHMeNa} + \text{NHR}_2$ , occurs with  $\text{NH}_2\text{Me}$  ( $\text{R}_2 = \text{H}_2$ ,  $K_b = 5.0 \times 10^{-4}$ ) and  $\text{NHMe}_2$  ( $\text{R}_2 = \text{MeH}$ ,  $K_b = 5.4 \times 10^{-4}$ ), but not with the more weakly basic  $\text{NMe}_3$  ( $\text{R}_2 = \text{Me}_2$ ,  $K_b = 5.9 \times 10^{-5}$ ). J. W. B.

**Thermal decomposition of triethylamine.**—See this vol., 33.

**Trichlorohydroxy-aliphatic amines.** F. D. CHATTAWAY and P. WITHERINGTON (J.C.S., 1935, 1623—1624).— $\gamma\gamma\gamma$ -Trichloro- $\alpha$ -amino- $\beta$ -hydroxypropane, m.p.  $123^\circ$  [oxalate, m.p.  $220^\circ$  (decomp.); sulphate, m.p.  $255^\circ$  (decomp)];  $\text{Ac}$  derivative, m.p.  $154^\circ$ ;  $\text{Ac}_2$  derivative, m.p.  $99^\circ$ ], is obtained from the hydrochloride (I), m.p.  $235^\circ$  (decomp.), which is pre-

pared by the reduction ( $\text{Sn-HCl}$ ) of  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -hydroxypropane. Similarly  $\gamma\gamma\delta$ -trichloro- $\alpha$ -amino- $\beta$ -hydroxy- $n$ -pentane, m.p.  $141^\circ$  (darkening) [hydrochloride (II), m.p. about  $231^\circ$  (decomp.); oxalate, m.p.  $232^\circ$  (decomp.); sulphate, m.p.  $235-240^\circ$  (decomp.);  $\text{Ac}$  derivative, m.p.  $109^\circ$ ;  $\text{Ac}_2$  derivative, m.p.  $136^\circ$ ], is obtained from the corresponding  $\text{NO}_2$ -compound. (I) with KCN yields  $\gamma\gamma\gamma$ -trichloro- $\beta$ -hydroxy- $n$ -propylcarbamide, m.p.  $175^\circ$ , and (II) similarly yields  $\gamma\gamma\delta$ -trichloro- $\beta$ -hydroxy- $n$ -amylcarbamide, m.p.  $175^\circ$ . F. N. W.

**Introduction of halogen or thiocyanate into organic compounds by means of dichloropentamethylenetetramine.** M. V. LICHOSCHERSTOV and T. D. ALDOSCHIN (J. Gen. Chem. Russ., 1935, 5, 981—985).—The reaction  $(\text{CH}_2)_5\text{N}_4\text{Cl}_2 + 2\text{MX} + 2\text{HR} \rightarrow 2\text{RX} + 2\text{MCl} + (\text{CH}_2)_5\text{N}_4\text{H}_2$  ( $\text{M} = \text{K}, \text{Na}$ ;  $\text{X} = \text{halogen or CNS}$ ;  $\text{R} = \text{aryl radical}$ ) is of general application, and affords high yields of relatively pure products in cases in which the ordinary methods do not do so (nitrophenols). R. T.

(A) Action of  $N$ -sulphuric acid and  $N$ -sodium hydroxide on glycine. (B) Interaction of glycine and glycyglycine with nicotine. I. S. JAIT-SCHNIKOV (J. Gen. Chem. Russ., 1935, 5, 967—969, 970—971).—(A) Formol-titratable  $N$  diminishes immediately after addition of glycine (I) to  $N\text{-H}_2\text{SO}_4$ , to attain a min. val. after 3 days, and then rises to a const. val. after 30 days at room temp.  $N\text{-NaOH}$  exerts a similar action, the min. val. being attained after 28 days. The phenomena are ascribed to transient formation of anhydride, peptide, or polymeride.

(B) (I) and glycyglycine combine with nicotine in presence of  $\text{CH}_2\text{O}$ . R. T.

**Determination of the sum of glycine and serine.** S. RAPOPORT (Biochem. Z., 1935, 281, 30—36).—The sum of the amounts of these acids (e.g., in protein hydrolysates) is determined, after removal of dicarboxylic  $\text{NH}_2$ -acids, by deamination with  $\text{NaNO}_2$  and oxidation (to  $\text{H}_2\text{C}_2\text{O}_4$ ) of the product with  $0.1N$  alkaline  $\text{KMnO}_4$ . The results are slightly  $>$  those obtained by other methods except with caseinogen, with which the vals. are much higher. At  $120^\circ$  in 5 hr. serine (I) is converted by  $\text{HI} + \text{P}$  into alanine (II), which is then determined by the method of Kendall *et al.* (A., 1931, 246), but this procedure gives inaccurate results when preformed (II) is present. Glycine is colorimetrically determined with the help of the blue colour produced on addition of conc.  $\text{H}_2\text{SO}_4$  and naphthoresorcinol, and hence (I) and glycine can be separately determined in sericin, the vals. being 8.71 and 1.69%, respectively. W. McC.

**Carbamido-acid and hydantoin of arginine.** W. R. BOON and W. ROBSON (Biochem. J., 1935, 29, 2573—2575).—Arginine on warming in aq. solution with  $\text{KCNO}$  gave carbamidoarginine, m.p.  $172^\circ$ , passing in warm acid solution into arginine-hydantoin, m.p.  $100^\circ$ . H. D.

**Conversion of arginine into citrulline.** K. DIRR and H. SPATH (Z. physiol. Chem., 1935, 237, 121—130; cf. A., 1934, 993).—The hydrochloride ( $\text{1H}_2\text{O}$ ), m.p.  $155^\circ$  (decomp.),  $[\alpha]_D^{25} + 13.0^\circ$ , of arginine-amide (I) [picrate, m.p.  $220^\circ$  (decomp.)] obtained from

the Me ester in MeOH and  $\text{NH}_3$ , and the *hydrochloride* ( $\text{1H}_2\text{O}$ ), decomp.  $260^\circ$ , of  $\alpha$ -monobenzoylarginine-amide (II) yield no citrulline (III) on hydrolysis and are not attacked by arginase (IV). Together with (I) *arginine-diketopiperazine*, decomp.  $316^\circ$ , is obtained. *Dibenzoylarginine Me ester hydrochloride* has m.p.  $171^\circ$ . (I) and (II) yield the  $\text{Bz}_3$  derivative of (I), m.p.  $245^\circ$ , which gives a 10% yield of the corresponding  $\text{Bz}_3$  derivative (V), m.p.  $220^\circ$ , of (II) on hydrolysis with conc.  $\text{HCl}$  at room temp., a substance, m.p.  $178^\circ$ , probably an inactive form of (V), being produced (sometimes) at the same time. Hot acid hydrolysis of (V) gives  $\text{BzOH}$ ,  $\text{NH}_3$ , ornithine, and proline, but no (III) or  $\text{CO}(\text{NH}_2)_2$ .  $\text{CH}_2\text{N}_2$  with  $\alpha$ -benzoylcitrulline gives the Me ester, decomp. about  $120^\circ$ , and  $\text{NH}_3$  converts the ester into the corresponding *amide* (VI), m.p. about  $140^\circ$ . Benzoylation of (VI) gives (V). It seems that in the biological conversion of arginine (VII) into (III) by deimidase and (IV) the attack on the guanidine residue must be preceded by blocking of the  $\text{CO}_2\text{H}$ . W. McC.

**Preparation of ornithine, ornithuric acid, and  $\alpha$ -benzoylornithine.** W. R. BOON and W. ROBSON (Biochem. J., 1935, 29, 2684—2688).—Improved methods (yields in brackets) for the prep. of the following are described: ornithuric acid (I) [68.5%] from arginine hydrochloride and [nearly theoretical] from carbamido-arginine (II); ornithine hydrochloride [nearly theoretical] from (II); and benzoylornithine [76%] from (I). J. N. A.

**Relationships between acidity and tautomerism.** IV. Effect of the cyano-group. F. ARNDT, H. SCHOLZ, and E. FROBEL (Annalen, 1935, 521, 95—121).—The behaviour of a series of CN-compounds towards  $\text{FeCl}_3$ , Br, and  $\text{CH}_2\text{N}_2$  shows that the acidifying action of CN exceeds that of any other simple C-containing substituent and approximates to that of  $\text{SO}_2$ . CN shows electromeric action in the form of "enotropic effect" and as conjugation partner; in both respects it is considerably inferior to keto-CO, but superior to ester CO.  $\text{CH}\cdot\text{CN}$  can therefore pass into  $\text{C}\equiv\text{C}\cdot\text{NH}$ , but a conjugation partner is necessary, which, as always, must not precede CN in the sequence of electromeric activity. A second CN, ester CO, or, in certain circumstances,  $\text{NO}$ , can function as conjugation partner for the eniminisation of CN. In addition, the prototropic expenditure of energy must be greatly decreased by strong acidification of the central CH to render eniminisation possible. Hence it does not occur with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  or  $\text{CH}_2(\text{CN})_2$ . In combination with keto-CO, CN behaves essentially as conjugation partner. The enimine group behaves towards  $\text{FeCl}_3$ , Br, and  $\text{CH}_2\text{N}_2$  similarly to the enol group and can, if it occurs, have a more or less considerable share of the empirical activity of the corresponding dissolved compound. With regard to acidifying action (inductive effort) and electromeric effect the sequences of substituents are, respectively,  $\text{NO}_2 > \text{SO}_2\text{OR} > \text{SO}_2\text{R} > \text{CN} > \text{CO}_2\text{R} > \text{CH}\cdot\text{O} > \text{CR}\cdot\text{O}$  and  $\text{CH}\cdot\text{O} > \text{CR}\cdot\text{O} > \text{ON} > \text{CO}_2\text{R} > \text{NO}_2$ .

Application of the Br titration method to the following compounds gives variable and non-reproducible results which frequently depend greatly on temp.

and solvent; the underlying reasons are fully discussed. Absorption of Br in some measure, however, invariably goes hand in hand with occurrence of a colour with  $\text{FeCl}_3$ .  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  gives a red colour with  $\text{FeCl}_3$  and immediately decolorises Br in MeOH, but not in  $\text{CHCl}_3$ . With  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  at  $-50^\circ$  it yields two substances, m.p.  $76^\circ$  and  $97-98^\circ$ ,



probably A and B, since the former passes into the latter when heated for some time at  $130^\circ$  and each forms the same compound with  $\text{NH}_3$ . The enimine or ester OH groups do not participate in the change. *p*-Toluenesulphonylacetonitrile (I), m.p.  $147-148^\circ$ , does not react with Br or  $\text{FeCl}_3$ ; in absence of catalyst it does not react with  $\text{CH}_2\text{N}_2$ , but after liberal addition of MeOH it slowly affords  $\alpha$ -*p*-toluenesulphonylpropionitrile, m.p.  $60^\circ$  (corresponding amide, m.p.  $168^\circ$ ), and the compound  $\text{N}\cdot\text{NMe} \text{---} \text{N}\cdot\text{CH} \text{---} \text{C}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , m.p.  $162^\circ$ .

Its acidity is therefore due solely to  $\text{CH}$ . *Me p*-toluenesulphonylcianoacetate, m.p.  $79-80^\circ$ , from the Na derivative of (I) and  $\text{ClCO}_2\text{Me}$ , shows marked reaction with  $\text{FeCl}_3$  and decolorisation of Br; with  $\text{CH}_2\text{N}_2$  it yields the substance  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}(\text{CN})\cdot\text{CNMe}$ , m.p.  $125-127^\circ$ , and *Me  $\alpha$ -cyano- $\alpha$ -p-toluenesulphonylpropionate*, m.p.  $101^\circ$ . The solid substance is therefore  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$ , and passes in solution completely or preponderatingly into the enimine form.  *$\alpha$ -Cyano- $\alpha$ -p-toluenesulphonylacetone*, m.p.  $122-123^\circ$ , from the Na derivative of (I) and  $\text{AcCl}$  in cold  $\text{Et}_2\text{O}$ , gives a moderate  $\text{FeCl}_3$  reaction, and immediately decolorises Br in  $\text{EtOH}$  or  $\text{CHCl}_3$ . In solution in  $\text{Et}_2\text{O}$  it is converted exclusively into the *enol ether*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{C}(\text{CN})\cdot\text{CMe}\cdot\text{OMe}$ , m.p.  $124^\circ$ , whereas the solid when treated with  $\text{CH}_2\text{N}_2\cdot\text{Et}_2\text{O}$  affords also  *$\alpha$ -acetyl- $\alpha$ -p-toluenesulphonylpropionitrile*, m.p.  $150-151^\circ$ . *N*-Methylation is not observed. The solid substance is  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CHAc}\cdot\text{CN}$  and is partly enolised but not eniminised in solution.  $\text{CH}_2(\text{CN})_2$  does not react with Br or  $\text{FeCl}_3$  or with  $\text{CH}_2\text{N}_2$  in presence of MeOH. *p*-Toluenesulphonylmalononitrile, m.p.  $101-102^\circ$  after softening at  $93^\circ$ , from the Na compound of (I) and  $\text{CNBr}$ , gives considerable  $\text{FeCl}_3$  reaction and immediately decolorises Br in  $\text{EtOH}$  or  $\text{CHCl}_3$ . With  $\text{CH}_2\text{N}_2$  at  $-50^\circ$  it yields small amounts of *p*-toluenesulphonylmethylmalononitrile, m.p.  $103^\circ$ , whereas under the customary conditions some *N*-methylation is observed. Hence the solid is  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}(\text{CN})_2$  and becomes eniminised in solution. *Me dicyanoacetate*, m.p.  $65^\circ$ , gives strong  $\text{FeCl}_3$  reaction and decolorises Br. With  $\text{CH}_2\text{N}_2$  at  $-50^\circ$  it gives a non-cryst. product with 6.3% NMe and 12.0% OMe (of which 10.9% is present as  $\text{CO}_2\text{Me}$ ).  *$\alpha\alpha$ -Dicyanoacetone*, m.p.  $141^\circ$ , from  $\text{CHNa}(\text{CN})_2$  and  $\text{AcCl}$  [*p*-nitrophenylhydrazones, m.p.  $144^\circ$  (decomp.)], gives a marked  $\text{FeCl}_3$  reaction and immediately decolorises a little Br. *O*-Methylation predominates with  $\text{CH}_2\text{N}_2$ , but some *N*-methylation is observed. An ethereal solution of  $\text{CH}(\text{CN})_3$  gives an intense  $\text{FeCl}_3$  reaction and absorbs much Br. The product formed with  $\text{CH}_2\text{N}_2$  gives about half the calc. NMe val., showing that NH is formed and resembles enolic OH in behaviour towards  $\text{FeCl}_3$ . H. W.

**Determination of thiol and disulphide compounds, with special reference to cysteine and cystine. III. Reaction between thiol compounds and mercuric chloride.** K. SHINOHARA (J. Biol. Chem., 1935, 111, 435—442).—Cysteine or  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  reacts rapidly with  $\text{HgCl}_2$  at  $p_H$  5, giving a mercaptide of the type  $\text{Hg}(\text{S}\cdot\text{R}\cdot\text{CO}_2\text{H})_2$ , followed by a slow reaction giving  $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{S}\cdot\text{Hg}\cdot\text{S}\cdot\text{R}\cdot\text{CO}_2\text{H}\cdot\text{HgCl}$ .

F. A. A.

**Optical rotatory dispersion in the carbohydraate group. VI. Amide rotation rule.** T. L. HARRIS, E. L. HIRST, and C. E. WOOD (J.C.S., 1935, 1658—1662; cf. A., 1935, 568).—The rotatory dispersion of *d*-dimethoxysuccinamide, *d*-dimethoxysuccinimethylamide, and 1:2:3:5-trimethylarabonamide (all obeying the amide rule) is controlled by the induced dissymmetry, and can be represented by a one-term Drude-Natanson equation. Similar examination of 4:6-dimethylmannonamide, which obeys the amide rule in EtOH but not in  $\text{H}_2\text{O}$ , shows that special stereochemical arrangements of the substituent groups may give rise to an induced activity opposite in sign to that of the normal amide. Data for various  $\lambda$  for the above compounds and for *Me d*-dimethoxysuccinate, b.p.  $120^\circ/12$  mm., with  $\text{H}_2\text{O}$  and EtOH as solvents are given.

F. N. W.

**Action of magnesium phenyl bromide on  $\alpha$ -bromobutyrdimethylamide.** S. P. TI (Bull. Soc. chim., 1935, [v], 2, 1799—1800; cf. A., 1931, 1279).—The reaction products of  $\text{MgPhBr}$  and  $\alpha$ -bromobutyrdimethylamide, b.p.  $123$ — $124^\circ/17$  mm., are butyrdimethylamide, *croton*dimethylamide (impure), b.p. about  $200^\circ$ , and a little  $\text{COPhPr}^+$  and  $\beta$ -dimethylamino- $\alpha$ -diphenylbutanol, m.p.  $58^\circ$  [picrate, m.p.  $155^\circ$ ; perchlorate, m.p.  $182^\circ$ ; *Ac* derivative (picrate, m.p.  $138^\circ$ )].

H. G. M.

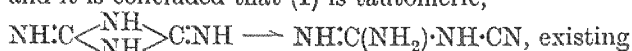
**Reactions of sulphuryl diamide (sulphamide).** F. C. WOOD (Nature, 1935, 136, 837).—*Dixanthyl sulphamide*, m.p.  $182$ — $184^\circ$ , is obtained by adding a solution of xanthhydrol (I) in EtOH to one of sulphamide in aq. AcOH. Condensation products have also been obtained with (I) and  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ , m.p.  $209^\circ$ ,  $m\text{-C}_6\text{H}_4(\text{SO}_2\cdot\text{NH}_2)_2$ , m.p.  $170^\circ$ , and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ , m.p.  $198^\circ$ . These general reactions can be used for the determination of sulphamides and sulphonamides.

L. S. T.

**Determination of glutamine in presence of asparagine.** H. B. VICKERY, G. W. PUCHER, H. E. CLARK, A. C. CHIBNALL, and R. G. WESTALL (Biochem. J., 1935, 29, 2710—2720).—The amide group is completely hydrolysed when glutamine (I) is heated at  $100^\circ$  for 2 hr. at  $p_H$  6.5. The increase in  $\text{NH}_2\cdot\text{N}$  that occurs gives the amount of (I)  $\text{NH}_2\cdot\text{N}$  in the extract of the plant tissue. The decrease in  $\text{NH}_2\cdot\text{N}$  of an extract on hydrolysis under these conditions is a valuable qual. criterion of the presence of (I). Interference from asparagine is negligible, for it requires heating for 3 hr. at  $100^\circ$  with  $\text{N}\cdot\text{H}_2\text{SO}_4$ , whilst the effect of  $\text{CO}(\text{NH}_2)_2$  and allantoin can be easily detected. Data on the stability of (I) with regard to temp. and  $p_H$  are given. The chief products hydrolysis of (I) at essentially neutral reaction are  $\text{NH}_3$  and pyrrolidonecarboxylic acid.

J. N. A.

**Dicyanodiamide.** F. CHASTELLAIN (Helv. Chim. Acta, 1935, 18, 1287—1302).—Hydrolysis of dicyanodiamide (I) with a slight excess of acid at  $50$ — $80^\circ$  gives a quant. yield of guanylcarbamide (II), but with insufficient acid further hydrolysis to  $\text{NH}_2\cdot\text{C}(\text{NH}_2)_2$  occurs. Hydrolysis of (I) with 1% NaOH at  $100^\circ$  has been quantitatively studied by determination of the  $\text{NH}_3$  evolved (cf. B., 1926, 505),  $\text{CO}(\text{NH}_2)_2$  (Fosse),  $\text{NH}_2\cdot\text{CN}$  (Perotti), and unchanged (I). The increase in the  $\text{NH}_3$  evolved is rapid during the first 2 hr. and thereafter becomes linear with time. The amount of  $\text{NH}_3$  evolved is equally dependent on the concn. of (I) and of NaOH, and is the same whether the mol. ratio (I)/NaOH ( $r$ ) is  $a$  or  $1/a$ . The  $\text{CO}(\text{NH}_2)_2$  formed [only slightly increased by excess of NaOH, but greatly increased by increasing the mol. proportion of (I)] increases to a max. at about 3 hr. and then decreases linearly with time. The sum  $\text{NH}_3\cdot\text{N} + \text{CO}(\text{NH}_2)_2\cdot\text{N}$  increases to a const. val. for any particular val. of  $r$ , and this const. val. itself increases from 16.5% of total N when  $r=5$  to 60% when  $r=0.5$ , and then remains approx. const. to  $r=0.2$ . The initial stage is the depolymerisation of (I) to  $\text{NH}_2\cdot\text{CN}$ , which reaches max. concn. after  $< 1$  hr., and disappears after 5 hr. ( $r=1$ ), and no (I) could be detected after 9 hr. During the first ten hr. only  $\text{CO}(\text{NH}_2)_2$  is hydrolysed, hydrolysis of melamine [formed from (I) and  $\text{NH}_2\cdot\text{CN}$ ] to (finally)  $(\text{HCNO})_3$ , requiring more drastic conditions. No (II),  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$ , or  $\text{NH}(\text{CO}\cdot\text{NH}_2)_2$  could be detected in the alkaline hydrolysis. These and earlier results are discussed and it is concluded that (I) is tautomeric,



solely as the former in alkaline and neutral solution and probably in the solid state, and as the latter in acid solution.

J. W. B.

**Photochemical and thermal decomposition of azomethane.**—See this vol., 37.

**Iron-cyanogen compounds. VI. Action of oxalates on the blue iron-cyanogen compounds.** M. KOHN (Monatsh., 1935, 66, 393—405; cf. A., 1924, i, 21).—Sol. and ordinary Prussian-blue (I) dissolve completely in  $\text{K}_2\text{C}_2\text{O}_4$  with formation of  $\text{K}_3\text{Fe}_2(\text{C}_2\text{O}_4)_3$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ ; Turnbull's blue (II) is mainly but not completely sol., leaving a residue of white  $\text{Fe}_3\text{Fe}(\text{CN})_6$ . The action of  $\text{H}_2\text{O}_2$  on a mixture of  $3\text{FeSO}_4 + 2\text{K}_3\text{Fe}(\text{CN})_6$  [(II)], whereby complete reaction should lead to  $\text{OH}\cdot\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}\text{Fe}(\text{CN})_6]_2$ , or on a mixture of  $2\text{FeSO}_4 + \text{K}_4\text{Fe}(\text{CN})_6$  which similarly should give  $(\text{OH})_2\text{Fe}^{\text{III}}_2[\text{Fe}(\text{CN})_6]$  gives in each case blue preps. of insol. basic (I), which are converted by  $\text{K}_2\text{C}_2\text{O}_4$  into  $\text{Fe}(\text{OH})_3$  in theoretical amount,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{K}_3\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$ . Oxidation of a mixture of  $\text{FeSO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  by  $\text{H}_2\text{O}_2$  affords a basic (I), colloidal sol. in  $\text{H}_2\text{O}$ , which when treated with  $\text{K}_2\text{C}_2\text{O}_4$  gives  $\text{K}_3\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and considerably more  $\text{Fe}(\text{OH})_3$  than is expected from theory, since the unused  $\text{K}_4\text{Fe}(\text{CN})_6$  is oxidised to  $\text{K}_3\text{Fe}(\text{CN})_6$  and the  $\text{OH}^+$  thus liberated is consumed by the blue ppt. For this reason basic (I) results from sol. (I) by the action of  $\text{H}_2\text{O}_2$  in presence of excess of  $\text{K}_4\text{Fe}(\text{CN})_6$ . Basic (I) is not formed in appreciable amount from sol. (I) under the influence of  $\text{H}_2\text{O}_2$ .

(I) is transformed by  $\text{KHC}_2\text{O}_4$  into a colloidal, blue solution and, if large amounts of  $\text{KHC}_2\text{O}_4$  are used, also converted into  $\text{H}_4\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ , whereby pale yellowish-green solutions which are sensitive to light result.

H. W.

**Dihydroxides of tertiary arsines, arsonium derivatives, and their salts.** G. A. RAZUVAEV, V. S. MALINOVSKI, and D. A. GODINA (J. Gen. Chem. Russ., 1935, 5, 721—727).— $\text{AsMe}_3$  in  $\text{Et}_2\text{O}$  and  $\text{HNO}_3$  yield the *mononitrate*, m.p.  $127^\circ$ , of  $\text{AsMe}_3(\text{OH})_2$ ; the free hydroxide readily eliminates  $\text{H}_2\text{O}$  to yield  $\text{AsMe}_3\text{O}$ .  $\text{AsMe}_4\text{I}$  affords  $\text{AsMe}_4\text{NO}_3$ , m.p.  $268-270^\circ$ , with  $\text{AgNO}_3$ , and  $\text{AsMe}_4\text{OH}$  with  $\text{AgOH}$ . The following compounds have been prepared analogously:  $\text{AsPhMe}_2\text{O}$ , m.p.  $157-161^\circ$ ,  $\text{OH}\cdot\text{AsPhMe}_2\text{NO}_3$ , m.p.  $149-150^\circ$ ,  $\text{AsPhMe}_3\text{OH}$ , m.p.  $106-116^\circ$  (*nitrate*, m.p.  $195-196^\circ$ ),  $\text{AsPh}_2\text{Me}(\text{OH})_2$  (*nitrate*, m.p.  $106-107^\circ$ ),  $\text{AsPh}_2\text{Me}_2\text{I}$ , m.p.  $211-213^\circ$ ,  $\text{AsPh}_2\text{Me}_2\text{OH}$ , m.p.  $120-135^\circ$  (*nitrate*, m.p.  $149-151^\circ$ ),  $\text{AsPh}_2\text{MeNO}_3$ , m.p.  $100^\circ$ ,  $(\text{AsPh}_2\text{OH})_2\text{SO}$ , m.p.  $195^\circ$ ,  $\text{AsR}_2\text{Me}$ , b.p.  $170^\circ/20\text{ mm.}$ ,  $\text{AsR}_2\text{Me}_2\text{I}$ , m.p.  $186-187^\circ$ ,  $\text{AsR}_2\text{MeOH}$  (*nitrate*, m.p.  $147^\circ$ ) ( $\text{R}=\text{cyclohexyl}$ ).

R. T.

**Preparation of germanium alkyl or phenyl trihalides,  $\text{RGeX}_3$ , and of germanium methylene hexachloride.** A. TCHAKIRIAN and M. LEWINSOHN (Compt. rend., 1935, 201, 835—837).—Good yields of  $\text{GeRX}_3$  are obtained by heating  $\text{Cs}[\text{GeCl}_3]$  (A., 1931, 322) with alkyl or aryl halides (iodides best). Thus at  $110^\circ$   $\text{EtI}$  affords  $\text{GeEtCl}_3$  (60% yield) and  $\text{PhI}$  at  $250^\circ$  gives  $\text{GePhCl}_3$  (80%). With  $\text{CH}_3\text{I}_2$  at  $200^\circ$  is obtained *germanium methylene hexachloride*, b.p.  $110^\circ/18\text{ mm.}$  (80%). Hydrolysis of these affords  $\text{McGeO}_2\text{H}$  and *germanomalonic acid*,  $\text{CH}_2(\text{GeO}_2\text{H})_2$ , reconverted into the chlorides by conc.  $\text{HCl}$ .

J. W. B.

**Preparation of lead diethyl dichloride.** A. J. JAKUBOVITSCH and I. PETROV (J. pr. Chem., 1935, [ii], 144, 67—68).—Passage of  $\text{HCl}$  into a solution of  $\text{PbEt}_4$  in  $\text{PhMe}$  at  $90^\circ$  leads to mixtures of  $\text{PbEt}_2\text{Cl}_2$  and  $\text{PbCl}_2$ , the composition of which varies with the duration of the action (cf. Gilman *et al.*, A., 1933, 900). Grüttner's method (A., 1916, i, 799) is trustworthy.

H. W.

**Dimethylcyclohexanes.** O. MILLER (Bull. Soc. chim. Belg., 1935, 44, 513—522; cf. A., 1933, 815).—Hydrogenation of *p*-xylene in  $\text{AcOH}$  with a Pt-black catalyst at room temp. gives mainly *cis*-, m.p.  $-91.6^\circ$ , b.p.  $124.59^\circ/760\text{ mm.}$ , and a little *trans*-1:4-dimethylcyclohexane, m.p.  $-37.2^\circ$ , b.p.  $119.63^\circ/760\text{ mm.}$ , separated by repeated fractional distillation. At  $200^\circ$  (and without  $\text{AcOH}$ ) the latter is the chief product. With a  $\text{Ni-Al}_2\text{O}_3$  catalyst at  $180^\circ$  the *trans*-isomeride is mainly formed together with some methylcyclohexane (I). Similarly hydrogenation of *m*-xylene yields *cis*-, m.p.  $-100^\circ$ , b.p.  $124.9^\circ/760\text{ mm.}$ , and *trans*-1:3-dimethylcyclohexane, m.p.  $-79.4^\circ$ , b.p.  $120.40^\circ/760\text{ mm.}$ , the latter being the chief product both at  $20^\circ$  and at  $180^\circ$ . With a  $\text{Ni-Al}_2\text{O}_3$  catalyst some (I) is also formed. In each case the *trans*-configuration has been assigned to the more volatile isomeride. 1:1-Dimethylcyclohexane, m.p.  $-34.1^\circ$ , b.p.  $119.8^\circ/760\text{ mm.}$  (A., 1932, 372), is most readily obtained by hydrogenation of dimethyl-

dihydroresorcinol in  $\text{EtOAc}$  with an active Pt catalyst. The *d*, *n*, and  $\eta$  of these compounds are recorded.

H. G. M.

**Constituents of the unsaponifiable fraction of wheat-germ oil. Vitamin-E.**—See A., 1935, 1551.

**The hydrocarbon  $\text{C}_6\text{D}_6$ .** H. ERLÉNMEYER and H. LONECK (Helv. Chim. Acta, 1935, 18, 1464—1466).—Distillation of dry  $\text{C}_6(\text{CO}_2)_6\text{Ca}_3$  with  $\text{Ca}(\text{OD})_2$  (from  $\text{Ca}$  and  $\text{D}_2\text{O}$ ) gives pure  $\text{C}_6\text{D}_6$ , b.p.  $79.4^\circ/760\text{ mm.}$ , m.p.  $6.8^\circ$  (cf. Wilson, A., 1935, 1198).

J. W. B.

**Fluorinated chlorobenzenes.** H. S. BOOTH, H. M. ELSEY, and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2064—2065).—The prep. of *m*-chlorofluorobenzene, b.p.  $127.6^\circ/760\text{ mm.}$ , m.p.  $<-78^\circ$ , and 2:4:6-trichlorofluorobenzene, b.p.  $208.4^\circ/760\text{ mm.}$ , m.p.  $11.2^\circ$ , is described. V.p. of these compounds at  $0-130^\circ$  have been measured.

E. S. II.

**Iodoxy-group and its relations.** I. MASSON, E. RACE, and (in part) F. E. POUNDER (J.C.S., 1935, 1669—1679).— $\text{PhIO}_2$  (I) (modified prep.) is not identical with *diphenyliodonium periodate*, m.p.  $129^\circ$  (decomp.); it is quantitatively nitrated (methods described) to *m*- $\text{IO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , m.p.  $37.9^\circ$ , is amphoteric, and yields the following salts: *sulphate*, m.p.  $127^\circ$  (decomp.), *perchlorate*, explosive decomp. at room temp., *nitrate*, and *phosphate*. With cold aq.  $\text{NaOH}$ , (I) first reacts as an acid of apparent  $K 10^{10}$ , forming a *phenyliodoxylate* (II) ( $\text{PhIO}_2+\text{OH}^- \rightleftharpoons \text{PhIO}_2\cdot\text{OH}^-$ ) which rapidly gives  $\text{NaIO}_3$  and  $\text{Ph}_2\text{IO}\cdot\text{OH}$  (III) or  $\text{Ph}_2\text{I}(\text{OH})_3$  [*Ac* derivative (IV), m.p.  $114^\circ$  (decomp.); *carbonate*, amorphous]; with aq. alkali at  $100^\circ$ , (I) or (III) yields the iodate and  $\text{C}_6\text{H}_6$ . This and other evidence shows the  $\cdot\text{IO}_2$  to be a *m*-directing, strongly cationoid dipole. Structures are suggested for (I), (II), and (IV).

F. N. W.

**Nitration of hydrocarbons by nitrogen peroxide in the gaseous phase, with and without the action of ultra-violet light.** P. P. SCHORIGIN and A. V. TOPTSCHEV (J. Gen. Chem. Russ., 1935, 5, 549—554).— $\text{PhMe}$  and  $\text{NO}_2$  at  $14^\circ$  afford  $\text{CH}_2\text{Ph}\cdot\text{NO}$  and  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ ; the yields of both are increased by ultra-violet light, and fall with rise in temp. The yields of  $\text{NO}_2$ -derivatives of  $\text{C}_6\text{H}_6$  and *cyclo*- and *n*-hexane are unaffected by ultra-violet light, whence it is concluded that this influences only those substrates capable of tautomeric change.

R. T.

**Benzotrifluoride and its halogenated derivatives.** H. S. BOOTH, H. M. ELSEY, and P. E. BURCHFIELD (J. Amer. Chem. Soc., 1935, 57, 2066—2069).—The prep. of  $\text{CPhF}_3$  from  $\text{CPhCl}_3$  and  $\text{SbF}_3$  is described. The following compounds have been prepared: *m*-, b.p.  $100.9^\circ$ , m.p.  $-81.5^\circ$ , and *p*- $\text{C}_6\text{H}_4\text{F}\cdot\text{CF}_3$ , b.p.  $102.8^\circ$ , m.p.  $-41.7^\circ$ ; *o*-, b.p.  $152.8^\circ$ , m.p.  $-7.4^\circ$  to  $-7.6^\circ$ , *m*-, b.p.  $138.4^\circ$ , m.p.  $-55.4^\circ$ , and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CF}_3$ , b.p.  $139.3^\circ$ , m.p.  $-34.0^\circ$ ; 3:4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CF}_3$ , b.p.  $173.5^\circ$ , m.p.  $-12.3^\circ$  to  $-12.5^\circ$ .

E. S. II.

**Condensations of alcohols with aromatic hydrocarbons in presence of aluminium chloride.**

**II. Condensation of secondary alcohols with benzene and toluene.** I. TZUKERVANIK and K. TOKAREVA (J. Gen. Chem. Russ., 1935, 5, 764—766).—



$C_6H_6$  and  $Pr^{\beta}OH$  in presence of  $AlCl_3$ , afford  $PhPr^{\beta}$  and  $C_6H_5Pr^{\beta}$ , b.p. 205–210°; with  $PhMe$  the product is  $p-C_6H_4MePr^{\beta}$ , and with  $Bu^{\beta}OH$ ,  $PhBu^{\beta}$  and  $C_6H_5MeBu^{\beta}$  are obtained. The reaction is  $ROH + AlCl_3 \rightarrow AlCl_2 \cdot OR$  (I) +  $HCl$ ; (I) +  $C_6H_6 \rightarrow PhR + AlCl_3 \cdot OH$ . R. T.

**Influence of structure on the polymerisation of substituted styrenes.** P. P. SOHORIGIN and N. V. SOHORIGINA (J. Gen. Chem. Russ., 1935, 5, 555–561).—The polymeride of *o*-tolylethylene is more elastic than is that of styrene, whilst those of *m*- and *p*-tolyl- and 1-naphthyl-ethylene are less so. R. T.

**Optical rotation of phenylethylmethyloctylmethane [ $\alpha$ -phenyl- $\gamma$ -methylundecane].** P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 111, 735–738).— $l-C_6H_5 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot MgBr$  and  $C_8H_{17} \cdot CHO$  give  $\alpha$ -phenyl- $\gamma$ -methylundecan- $\epsilon$ -ol, b.p. 183–184°/5 mm.,  $[\alpha]_D^{20} -2.64^\circ$ , converted by cold  $HI$  into the iodide, which, when hydrogenated (Raney Ni) in ligroin- $MeOH$ - $NaOH$ , affords  $\alpha$ -phenyl- $\gamma$ -methylundecane, b.p. 143–145°/2 mm.,  $[\alpha]_D^{20} -1.12^\circ$ , and thence ( $H_2$ - $PtO_2$ ;  $AcOH$ - $EtOAc$ )  $\alpha$ -cyclohexyl- $\gamma$ -methylundecane, b.p. 147°/3 mm.,  $[\alpha]_D^{20} -0.44^\circ$ . The contribution of  $C_6H_{11}$  to  $[M]$  is much < that of  $Pr^{\beta}$  in this series.  $[\alpha]$  are max. vals. for the homogeneous liquids. R. S. C.

**Laws of substitution in the sulphonation of naphthalene and its derivatives.** V. N. UMATZEV (J. Gen. Chem. Russ., 1935, 5, 653–660).—Substitution takes place according to the same laws as for  $C_6H_6$ , on the assumption that  $C_{10}H_8$  exists in three tautomeric forms, containing two aromatic nuclei, or one aromatic and one hydroaromatic nucleus. R. T.

**Nitration of 1-ethylnaphthalene.** G. LEVY (Compt. rend., 1935, 201, 900–902).— $1-C_{10}H_7Et$  when nitrated (cf. A., 1933, 57) gives an inseparable mixture of isomerides, reduced ( $Fe$ - $AcOH$ ) to 4-ethyl- $\alpha$ -naphthylamine, an oil ( $Ac$  derivative, m.p. 148.5°; hydrochloride), the sulphate of which with 1%  $H_2SO_4$  at 200° gives 4-ethyl- $\alpha$ -naphthol (cf. A., 1933, 1287). J. L. D.

**Methylethylnaphthalenes. III. Synthesis of 2-methyl-6-ethylnaphthalene.** O. BRUNNER and F. GROF (Monatsh., 1935, 66, 433–437).—Application of Reformatski's method to  $p-C_6H_4Et \cdot CHO$  and  $(HMeBr \cdot CO_2Et)$  leads to  $Et \alpha$ -methyl- $p$ -ethylcinnamate, b.p. 159–160°/11 mm., reduced by  $Na$  and  $EtOH$  to  $\gamma$ - $p$ -ethylphenyl- $\beta$ -methylpropanol (I), b.p. 140°/10 mm. (I) is transformed successively into  $\gamma$ - $p$ -ethylphenyl- $\beta$ -methyl- $n$ -propyl bromide, b.p. 141–142°/10 mm., and the corresponding nitrile, which is hydrolysed by boiling 10%  $KOH$ - $EtOH$  to  $\gamma$ - $p$ -ethylphenyl- $\beta$ -methyl- $n$ -butyric acid, b.p. 185–187°/10 mm. The acid and conc.  $H_2SO_4$  at 100° afford 4-keto-2-methyl-6-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 143–148°/11 mm., reduced (Clemmensen) to 2-methyl-6-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 140–145°/10 mm., dehydrogenated by  $S$  at 270–300° to 2-methyl-6-ethylnaphthalene, b.p. 145–150°/11 mm. (picrate, m.p. 100–101°; styphnate, m.p. 138–139°). H. W.

**Sulphonation of naphthalene. I. Determination of the relative proportions of naphthalene-**

**1- and 2-sulphonic acids.** R. LANTZ (Bull. Soc. chim., 1935, [v], 2, 1913–1932).—Under closely defined conditions  $1-C_{10}H_7 \cdot SO_3H$  (I) is brominated with loss of  $SO_3H$  to an insol. substance which is determined by  $CrO_3$ -oxidation (cf. B., 1932, 590), whilst  $2-C_{10}H_7 \cdot SO_3H$  (II) is brominated without loss of  $SO_3H$  and remains sol., thus permitting the determination of (I) and (II) in mixtures. H. G. M.

**Substitution in polycyclic systems. I. Nitration of fluorene and 9-bromofluorene.** S. V. ANANTAKRISHNAN and E. D. HUGHES (J.C.S., 1935, 1607–1609).—Nitration of fluorene (cf. A., 1930, 1425) yields 2:5- and 2:7-dinitrofluorene, m.p. 205–300° (decomp.) (lit. 269° and 334°). Mild nitration ( $HNO_3$  in  $Ac_2O$ ; 1 hr.; 0°) of 9-bromofluorene (I) gives 9-bromo-2-nitrofluorene (II); more vigorous treatment (2 hr. at 0°, followed by 15 hr. at room temp.) gives 9-bromo-2:5- (III), m.p. 199°, and -2:7-dinitrofluorene (IV), m.p. 255° (decomp.). Nitration of (I) in  $AcOH$  yields (IV) and 7-bromo-2-nitrofluorenone (?), whilst oxidation ( $Na_2Cr_2O_7$  in  $AcOH$ ) of (II), (III), and (IV) gives 2-nitro-, 2:5- and 2:7-dinitro-fluorenone, respectively. (III) and (IV) are also obtained by nitration ( $HNO_3$  in  $Ac_2O$ ) of (II). F. N. W.

**Influence of poles and polar linkings on the course pursued by elimination reactions. XXIII. Stable derivatives of the tervalent carbon compound of Ingold and Jessop.** E. D. HUGHES and K. I. KURIYAN (J.C.S., 1935, 1609–1611).—9-Bromo-2-nitrofluorene with  $Me_2S$  in  $MeNO_2$  yields 2-nitrofluorenyl-9-dimethylsulphonium bromide (I), m.p. 130° (decomp.). (I) or the corresponding picrate, m.p. 185° (decomp.), with alkali in  $H_2O$ ,  $EtOH$ , or  $COMe$ , yields dimethylsulphonium 9-2-nitrofluorenylidide, m.p. 300°, which decomposes in boiling  $MeNO_2$  solution forming 2:2'-dinitrobisdi-phenylene-ethylene (II), with liberation of  $Me_2S$ . (II) is oxidised ( $Na_2Cr_2O_7$ - $AcOH$ ) to 2-nitrofluorenone. Nitration [ $HNO_3$  (d 1.5) at -15°] of fluorenyl-9-dimethylsulphonium picrate yields 2:7-dinitrofluorenyl-9-dimethylsulphonium picrate (III), m.p. 180° (decomp.), converted by aq. alkali into dimethylsulphonium 9-2:7-dinitrofluorenylidide, which with  $HBr$ - $COMe$ , yields 2:7-dinitrofluorenyl-9-dimethylsulphonium bromide (IV), m.p. about 230°, and when boiled in  $MeNO_2$  gives 2:2':7:7'-tetranitrobisdi-phenylene-ethylene (V), m.p. >300°. (III) when refluxed with  $HBr$ - $AcOH$  (30 min.) gives 9-bromo-2:7-dinitrofluorene (VI), whilst (IV) with  $CrO_3$ - $AcOH$  yields 2:7-dinitrofluorenone and when heated alone forms (VI) with liberation of  $Me_2S$ . (V) is oxidised to 2:7-dinitrofluorenone.  $Me_2Se$  and 9-bromofluorene in  $MeNO_2$  give fluorenyl-9-dimethylselenonium bromide, m.p. 134–135° (corresponding picrate, m.p. 143°). F. N. W.

**Compounds related to the sterols, bile acids, and oestrus-producing hormones. VII. A.** COHEN, J. W. COOK, and C. L. HEWITT (J.C.S., 1935, 1633–1637).—2-Methyl-1-allyl-3:4-dihydrophenanthrene (I) (picrate, m.p. 75–76°) is obtained from  $CH_2=CH \cdot CH_2 \cdot MgBr$  and 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene (II) (modified prep.). 2-Methyl-1- $n$ -propylphenanthrene, m.p. 65° [picrate, m.p.

121.5—122°;  $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$  complex, m.p. 131°, is obtained from (I) either by heating with Se (320°, 15 hr.) or by heating in saturated HCl-AcOH solution (100°, 1 hr.). 2-Methyl-1- $\Delta^7$ -butenyl-3:4-dihydrophenanthrene, b.p. 155—160°/0.3 mm. (picrate, m.p. 77—78°), contaminated with 2-methyl-3:4-dihydrophenanthrene results from the interaction of (II) and  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr}$ , and when cyclised with  $\text{H}_2\text{SO}_4\text{-AcOH}$  (1:20) (100°, 2.25 hr.) yields principally methylhexahydrochrysene. 1-( $\beta$ -5-Tetralylethyl)cyclohexanol, b.p. 175—180°/0.4 mm. (3:5-dinitrobenzoate, m.p. 124—125°), obtained by the interaction of cyclohexanone and Mg  $\beta$ -5-tetralylethyl chloride, yields 1-( $\beta$ -5'-tetralylethyl)- $\Delta^1$ -cyclohexene (III), b.p. 140—150°/0.05 mm., when heated with  $\text{KHSO}_4$  (160—170°, 1 hr.). (III) when cyclised with  $\text{AlCl}_3$  (0°, 7.5 hr.) gives a mixture of dodecahydrochrysene, which is partly hydrogenated (300—310°, 14 hr., Se) to *s*-octahydrochrysene, m.p. 136—138° (picrate, m.p. 139—140°), and a hydrocarbon, b.p. 123—130°, which is dehydrogenated (Pt-black; 300—320°, 3 hr.) to 4:5-benzhydryndene-1-spirocyclohexane, m.p. 56—57° (picrate, m.p. 125—126°). F. N. W.

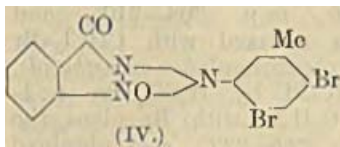
**The alleged dihydrophenylbenzamidine.** A. KIRSSANOV and I. IVASTCHENKO (Bull. Soc. chim., 1935, [v], 2, 1944—1950).—Contrary to the views of Bernthsen *et al.* (A., 1880, 639) no dihydrophenylbenzamidine (I) is obtained when phenylbenzamidine (II) (improved prep.) is reduced by Na-Hg, the only products being PhCHO,  $\text{NH}_2\text{Ph}$ ,  $\text{NHPh}\cdot\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ , and unchanged (II). The product regarded by Bernthsen as (I) is considered to be purified (II). (I) has therefore never been prepared.

H. G. M.

**Reactivity of halogen compounds. III, IV.**—See A., 1935, 1465.

**Derivatives of 6-bromo- and 4:6-dibromo-*m*-toluidine.** G. D. PARKES and E. D'A. BURNEY (J.C.S., 1935, 1619—1621).—The following *m*-toluidines, prepared by suitable modifications of ordinary methods, are described: *o*-, m.p. 146°, *m*-, m.p. 114°, and *p*-nitrobenz-, m.p. 148°; benz-6-bromo-, m.p. 123° (lit. 98°); *o*-, m.p. 163°, *m*-, m.p. 185.5°, and *p*-nitrobenz-6-bromo-, m.p. 258°; benz-4:6-dibromo-, m.p. 131°; *o*-, m.p. 203°, *m*-, m.p. 207°, and *p*-nitrobenz-4:6-dibromo-, m.p. 182.5°. 6-Bromo-, m.p. 191°, and 4:6-dibromo-*m*-tolylcarbamide, m.p. 218°, are obtained from the appropriate toluidine, KCNO, and warm 0.5*N*-HCl.  $\text{CO}(\text{NH}_2)_2$  when heated with excess of the appropriate base yields *s*-bis-6-bromo-, m.p. 276°, and 6-bis-4:6-dibromo-*m*-tolylcarbamide, m.p. 297°. 6-Bromo-, m.p. 143°, and 4:6-dibromo-*m*-tolueneazo- $\beta$ -naphthol, m.p. 193°, were prepared from the appropriate diazotised base and  $\beta\text{-C}_{10}\text{H}_7\text{OH}\cdot 2\text{N}\cdot\text{NaOH}$ . The following were prepared from the appropriate aldehyde and 6-bromo-*m*-tolylhydrazine hydrochloride obtained by reduction of diazotised 6-bromo-*m*-toluidine with  $\text{SnCl}_2\text{-HCl}$ : benzaldehyde-, m.p. 154°; *o*-, m.p. 175.5°, *m*- (I), m.p. 188°, and *p*-nitrobenzaldehyde-6-bromo-*m*-tolylhydrazone, m.p. 171.5°. The following were prepared by similar methods: benzaldehyde-, m.p. 109°; *o*-, m.p. 180°, *m*- (II), m.p. 204°, and *p*-nitrobenzaldehyde-4:6-dibromo-*m*-tolylhydrazone, m.p. 221°. *m*-

Nitrobenzaldehyde-*m*-tolylhydrazone with Br-AcOH affords  $\alpha$ -bromo-*m*-nitrobenzaldehyde-4:6-dibromo-*m*-tolylhydrazone, m.p. 191°, also obtained by bromination of (I) and (II).  $\alpha$ -Bromobenzaldehyde-, m.p. 122°, and  $\alpha$ -bromo-*o*-nitrobenzaldehyde-4:6-dibromo-*m*-tolylhydrazone (III), m.p. 151°, were similarly prepared.  $\alpha$ -Bromo-*p*-nitrobenzaldehyde-4:6-dibromo-*m*-tolylhydrazone when warmed with  $\text{EtOH-H}_2\text{O-NH}_3$  yields *p*-nitrobenzenyl-4:6-dibromo-*m*-tolylhydrazidine, m.p. 207°. The corresponding *m*- $\text{NO}_2$ -compound, similarly prepared, has m.p. 155°. (III) when warmed with just sufficient EtOH for dissolution yields 3-keto-1:3-endo-4':6'-dibromo-*m*-tolylimino-1:2-dihydro-1:2-benzisodiazole 1-oxide (IV), which explodes at 126°. H. G. M.



**Synthesis and chemical properties of  $\alpha$ -ethylenic carbimides,  $\text{R}\cdot\text{CH}:\text{CR}'\cdot\text{N}:\text{C}:\text{O}$ .** J. HOCH (Compt. rend., 1935, 201, 733—735).—*N*-Carbethoxyketimines (A., 1935, 1483) under reduced pressure in presence of kieselguhr at 400° afford carbimides. The following are prepared: 8- $\Delta^7$ -heptenyl-, b.p. 55—56°/17 mm.,  $\Delta^{1:2}$ -cyclohexenyl- (I), b.p. 61—63°/18 mm., 2-methyl- $\Delta^{1:2}$ -cyclohexenyl-, b.p. 73—74°/18 mm.,  $\alpha$ -phenylvinyl-, b.p. 99°/25 mm., and  $\alpha$ -phenyl- $\Delta^2$ -propenyl-carbimide, b.p. 110—112°/18 mm. They decolorise Br rapidly and with  $\text{NH}_2\text{Ph}$  in anhyd.  $\text{Et}_2\text{O}$  afford phenylcarbimides, m.p. 102°, 197°, 170°, 142°, and 185°, respectively, which are easily decomposed by dil. HCl into ketones and  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}_2$ . (I) with  $\text{NH}_3$  gives  $\Delta^{1:2}$ -cyclohexenylcarbamide, m.p. 144°, with  $\text{N}_2\text{H}_4$ , hydrazine- $\alpha\beta$ -dicarboxydicyclohexenylamide, m.p. 186°, and with  $\text{NHPhMe}$ , *N*-cyclohexenyl-*N*'-phenylmethylcarbamide, m.p. 88°. With EtOH,  $\text{Pr}^i\text{OH}$ , and PhOH, (I) affords Et, b.p. 148—149°/26 mm.,  $\text{Pr}^i$ , b.p. 147°/23 mm., and Ph  $\Delta^{1:2}$ -cyclohexenylcarbamate, m.p. 106—107°, respectively, and with  $\text{CPh}_2\cdot\text{NH}$ , *N*-cyclohexenyl-*N*'-diphenylmethylenecarbamide, m.p. 119°. J. L. D.

**Rearrangement of thiocyanates into thiocarbimides.** E. BERGMANN (J.C.S., 1935, 1361—1362). If the change  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{SCN} \rightarrow \text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{S}$  proceeds by attachment of N to terminal C and rupture between  $\text{CH}_2$  and S, cinnamyl thiocyanate (I), m.p. 68° (prepared from  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$  and KSCN), should when heated in vac. give  $\text{CHPh}(\text{NCS})\cdot\text{CH}:\text{CH}_2$ ; actually cinnamylthiocarbimide (II), b.p. 162°/12 mm., is formed. The structure of (I) is proved by hydrogenation to  $\gamma$ -phenylpropyl thiocyanate, b.p. 180°/30 mm., also obtained from  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{Br}$  (III) and  $\text{NH}_4\text{SCN}$ ; that of (II) by reaction with  $\text{NH}_2\text{Ph}$  to form *s*-phenylcinnamylthiocarbamide, m.p. 119°, also obtained from  $\text{NPh}:\text{C}:\text{S}$  and  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$  (IV); and that of (IV) confirmed by hydrogenating the phthalimide, from which it is prepared, to phthal- $\gamma$ -phenylpropylimide, m.p. 61°, also obtained from (III), and thus excluding the alternative structure  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}:\text{CH}_2$ .

E. W. W.

**Substitution in arylsulphon-1- and -2-naphthalides.** R. CONSDEN and J. KENYON (J.C.S., 1935,



1591—1596).—*m*-Nitrobenzenesulphon-1-naphthalide (I), m.p. 162—164° [obtained from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub> and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl (II)], is nitrated (a) by AcOH—conc. HNO<sub>3</sub> giving 2:4-dinitro-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 185—188° [hydrolysed by conc. H<sub>2</sub>SO<sub>4</sub> to 1:2:4-C<sub>10</sub>H<sub>5</sub>(NH<sub>2</sub>)(NO<sub>2</sub>)<sub>2</sub>], and (b) by ice-cold fuming HNO<sub>3</sub>, and (c) by AcOH—fuming HNO<sub>3</sub> on the water-bath giving the 2:4:5-(NO<sub>2</sub>)<sub>3</sub>-derivative, m.p. 215° (decomp.) (C<sub>5</sub>H<sub>5</sub>N salt, m.p. 170—175°), also obtained from 5-nitro-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 208—210°, and AcOH—HNO<sub>3</sub>. (I) when refluxed with CHCl<sub>3</sub>—Br gives 4-bromo-1-*m*-nitrobenzenesulphon-naphthalide, m.p. 174—176° (hydrolysed by H<sub>2</sub>SO<sub>4</sub> to 4:1-C<sub>10</sub>H<sub>6</sub>Br·NH<sub>2</sub>), and in C<sub>5</sub>H<sub>5</sub>N with Br gives the 2:4-Br<sub>2</sub>-derivative, m.p. 232—233°, also obtained from 2:4:1-C<sub>10</sub>H<sub>5</sub>Br<sub>2</sub>·NH<sub>2</sub> (improved prep.) and (II). 4-Nitro-1-*p*-toluenesulphon-naphthalide with Br in C<sub>5</sub>H<sub>5</sub>N (but not CHCl<sub>3</sub>) yields its 2-Br-derivative, m.p. 193—195°, hydrolysed to 2:4:1-C<sub>10</sub>H<sub>5</sub>Br(NO<sub>2</sub>)·NH<sub>2</sub>. *p*-Toluenesulphon-1-naphthalide with AcOH—conc. HNO<sub>3</sub> affords its 2:4-(NO<sub>2</sub>)<sub>2</sub>- and 2-NO<sub>2</sub>-derivative, m.p. 154°, hydrolysed to 1:2-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)·NO<sub>2</sub>. Nitration of 2:4-dinitro- $\alpha$ -naphthol with fuming HNO<sub>3</sub> (with or without AcOH) yields the 2:4:5- and 2:4:7-(NO<sub>2</sub>)<sub>3</sub>-derivatives in the ratio of about 5:2. *p*-Toluenesulphon-2-naphthalide (III) with Br—CHCl<sub>3</sub> yields its 1-Br-derivative. 1:3:2-C<sub>10</sub>H<sub>5</sub>Br<sub>2</sub>·NH<sub>2</sub> when refluxed (2 hr.) with EtOH—conc. HCl granulated Sn affords 3-bromo- $\beta$ -naphthylamine, m.p. 173° (*Ac* derivative, m.p. 177°), the *p*-toluenesulphonyl derivative, m.p. 127—129°, of which is nitrated in AcOH to 3-bromo-1-nitro-2-*p*-toluenesulphon-naphthalide, m.p. 237—239° (decomp.), also obtained from the appropriate nitro-compound with C<sub>5</sub>H<sub>5</sub>N—Br, reduced (Sn—HCl or Zn—AcOH) to 3-bromo-2-*p*-toluenesulphonyl-1:2-naphthylenediamine, m.p. 185°, and hydrolysed (ice-cold H<sub>2</sub>SO<sub>4</sub>) to 3-bromo-1-nitro- $\beta$ -naphthylamine (IV), m.p. 105° (*Ac* derivative, m.p. 136°). This with boiling *N*-NaOH affords 3-bromo-1-nitro- $\beta$ -naphthol, m.p. 131° (decomp.). (IV) is reduced with Sn—HCl to 3-bromo-1:2-naphthylenediamine, m.p. 85°, which with benzil in hot EtOH gives a quinoxaline derivative, m.p. 195—199°. 1:6-Dinitro-2-*p*-toluenesulphon-naphthalide with Br—C<sub>5</sub>H<sub>5</sub>N gives its 3-Br-derivative, m.p. 228—231° (decomp.), hydrolysed to 3-bromo-1:6-dinitro- $\beta$ -naphthylamine, m.p. 238—241° [*Ac* derivative, m.p. 273—277° (decomp.)]. (III) in C<sub>5</sub>H<sub>5</sub>N with I, ICl, or ICl<sub>3</sub> affords 1-iodo-2-*p*-toluenesulphon-naphthalide, m.p. 126—127°, from which the base could not be obtained owing to its instability (cf. J.C.S., 1885, 47, 520), and which when warmed with AcOH—NaNO<sub>2</sub> during 3 hr. affords the corresponding 1-NO<sub>2</sub>-derivative. The following were obtained by similar methods: 3-iodo-2-*p*-toluenesulphonamidodiphenyl, m.p. 114—115°; 3-iodo-4-*p*-toluenesulphonamidodiphenyl, m.p. 109—115°; 2-iodo-*p*-toluenesulphon-*p*-toluidide, m.p. 127—123°.

H. G. M.

**Ditolyl series. IV. Separation of *dl*-6-bromo-6'-amino-2:2'-dimethyldiphenyl into its optical antipodes.** A. ANGELETTI [in part with C. MIGLIARDI] (Gazzetta, 1935, 65, 819—823).—For the prep. of 6-bromo-6'-nitro-2:2'-dimethyldiphenyl (I),

the diazotisation of the 6-NH<sub>2</sub>-compound is best effected in HBr. (I) is reduced (SnCl<sub>2</sub>) to *dl*-6-bromo-6'-amino-2:2'-dimethyldiphenyl (II), m.p. 77—78°, which is resolved by *d*-tartaric acid into the *l*- (III), m.p. 77—78°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> —5.32°, and *d*-, m.p. 77—78°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +5.04°, forms. (II) is converted into *dl*-, m.p. 109—110°, and (III) into *l*-, m.p. 109—110°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> —6.2°, -6:6'-dibromo-2:2'-dimethyldiphenyl. E. W. W.

**Alkylated ethylenediamine derivatives. IV. Reaction between  $\alpha\beta$ -bis(benzylideneamino)-ethane, phenylcarbimide, and water.** J. VAN ALPHEN (Rec. trav. chim., 1935, 54, 885—887; cf. A., 1935, 1118).—Interaction of equimol. proportions of PhNCO and (·CH<sub>2</sub>·N·CHPh)<sub>2</sub> (I) in moist Et<sub>2</sub>O affords *s*-phenyl- $\beta$ -benzylideneaminoethylcarbamide (II), hydrolysed by dil. HCl to  $\beta$ -( $\gamma$ -phenylcarbamido)-ethylamine (*Bz* derivative, m.p. 210°), and reduced (Na—EtOH) to the hydrochloride of benzyl- $\beta$ -( $\gamma$ -phenylcarbamido)ethylamine (*Bz* derivative, m.p. 160°). With an excess of PhNCO (I) gives 2-keto-3:4-diphenyl-1- $\beta$ -( $\gamma$ -phenylcarbamido)ethyl-1:3-diazocyclobutane, NPh< $\begin{smallmatrix} \text{CHPh} \\ \text{CO} \end{smallmatrix}$ >N·C<sub>2</sub>H<sub>4</sub>·NH·CO·NHPh, m.p. 208° (decomp.) [also by action of PhNCO on (II)], hydrolysed by boiling dil. HCl to PhCHO and NHPh·CO·NHR, and reduced (Na—EtOH) to NHPh·CO·NHR·CH<sub>2</sub>Ph (R=C<sub>2</sub>H<sub>4</sub>·NH·CO·NHPh).

J. W. B.

**Preparation of *m*- and *p*-phenylenediethylamine and benzo-hexamethyleneimine from the three phenylenediacetonitriles.** P. RUGGLI, B. B. BUSSEMAKER, W. MÜLLER, and A. STAUB (Helv. Chim. Acta, 1935, 18, 1388—1395).—Reduction of *m*- and *p*-phenylenediacetonitrile, in EtOH saturated with NH<sub>3</sub>, with H<sub>2</sub>—Ni at 90—100°/70 atm. affords, respectively, *m*-[dihydrochloride + H<sub>2</sub>O, m.p. 300—302° (block)]; *platinichloride*, m.p. 242° (decomp.); *Bz*<sub>2</sub> derivative, m.p. 181°, and *p*-phenylene- $\beta\beta'$ -diethylamine, b.p. 130°/3 mm., m.p. 36° (*dihydrochloride*; *platinichloride*; *picrate*, decomp. 246°; *Ac*<sub>2</sub>, m.p. 210°, and *Bz*<sub>2</sub>, m.p. 225°, derivatives). Similar reduction of *o*-phenylenediacetonitrile gives *s*-homotetrahydroisoquinoline (von Braun *et al.*, A., 1926, 178) (*Bz*, m.p. 100°, and *Ac*, m.p. 70°, derivatives). A mechanism is suggested.

J. W. B.

**Interaction between aromatic diamines and ethyl acetoacetate.** O. G. BACKEBERG (J.C.S., 1935, 1568—1570).—Primary aromatic diamines with CH<sub>2</sub>Ac·CO<sub>2</sub>Et (I) yield  $\beta$ -phenylaminocrotonic esters and no acetoacetylides. *m*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> when heated with (I) on the water-bath (2 hr.), or when heated to 200° and rapidly poured into boiling (I), yields *Et m*-phenylenebis- $\beta$ -aminocrotonate. These reactants, however, when heated under seal gave 5- or 7-amino-2-hydroxylepidine (cf. A., 1898, i, 450). *m*-Aminoacetanilide and (I) when heated on the water-bath yield *Et*  $\beta$ -3-acetamidophenylaminocrotonate, m.p. 92°. *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> when heated to 200° and poured into boiling (I), or when heated with (I) on the water-bath (2 hr.) or at 150° (½ hr.) [but not at 170° (4 hr.)], yields *Et p*-phenylenebis- $\beta$ -aminocrotonate, m.p. 135° (cf. A., 1887, 247) (insol. in NaOH—H<sub>2</sub>O; gives dark red coloration with FeCl<sub>3</sub>—EtOH). By similar methods *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)·NHAc

and (I) yield *Et*  $\beta$ -4-acetamidophenylaminocrotonate, m.p. 185° (hydrolysed by boiling MeOH), but when heated under seal at 140° for 5 hr. affords some  $p$ -C<sub>6</sub>H<sub>4</sub>(NHAc)<sub>2</sub>. Dianisidine when refluxed with (I) in MeOH yields *Et* 3:3'-dimethoxydiphenylene-4:4'-bis- $\beta$ -aminocrotonate, m.p. 132—134°. Similarly tolidine and (I) afford *Et* 3:3'-dimethyldiphenylene-4:4'-bis- $\beta$ -aminocrotonate, m.p. 129—130°, whilst benzidine and (I) give a little *Et* diphenylene-4:4'-bis- $\beta$ -aminocrotonate, m.p. 99.5—100°, and mainly a double compound (NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·NHX)<sub>2</sub>·NHX·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·NHX (X = CMe·CH·CO<sub>2</sub>Et), m.p. 134° (cf. A., 1899, i, 366), which, although readily dissociated, could not be separated into its components, and with C<sub>6</sub>H<sub>5</sub>-Ac<sub>2</sub>O gave *Et* 4-acetamidodiphenyl-4'- $\beta$ -aminocrotonate, m.p. 201°, readily hydrolysed to monoacetylbenzidine.

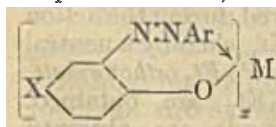
H. G. M.

**Reduction of azoxy-compounds in relation to that of diazonium derivatives.** D. BIGIARI and C. ALBANESE (Gazzetta, 1935, 65, 773—788).—NaHSnO<sub>2</sub> reacts at once with  $p$ -C<sub>6</sub>H<sub>4</sub>Me·N<sub>2</sub>·OH and  $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·OH, but KHSnO<sub>2</sub> only very slowly with the *o*-isomerides, or with 2:4:5-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·N<sub>2</sub>·OH. NaHSnO<sub>2</sub> reduces dimethylaminoazoxybenzene slowly to dimethylaminoazobenzene, and *pp'*-dihydroxyazoxybenzene to azophenol. Azoxybenzene, and the  $\alpha$ - and  $\beta$ -forms of its  $p$ -NH<sub>2</sub>-,  $p$ -Br-,  $p$ -OH-,  $p$ -CO<sub>2</sub>H-,  $p$ -Me,  $p$ -OEt-, and *oo'*-Me<sub>2</sub> derivatives, are reduced by NaHSnO<sub>2</sub> with varying ease to azo-compounds. Na<sub>3</sub>AsO<sub>3</sub> does not reduce  $\alpha$ - or  $\beta$ -benzeneazoxyphenol; these are, however, reduced by FeSO<sub>4</sub>, as is  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·Ph, which gives NH<sub>2</sub>Ph and  $p$ -NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH. A new test for small amounts of isodiazo-compounds in solution is to dip filter-paper into the latter, to which AcOH and  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH or *R*-salt are added; the paper removed and exposed to the air develops a red stain. This reaction is given only very slowly by phenylnitroamine; the last, and its NO-derivative, are reduced to isodiazo-compounds fairly rapidly by NaHSnO<sub>2</sub>, but only very slowly by Na<sub>3</sub>AsO<sub>3</sub>.

E. W. W.

### The azo-group as a chelating group. I. Metallic derivatives of *o*-hydroxyazo-compounds.

(MISS) M. ELKINS and L. HUNTER (J.C.S., 1935, 1598—1600).—The following Cu<sup>II</sup>, Ni, and Co<sup>III</sup> salts of some *o*-monohydroxyazo-compounds are described. They are insol. in H<sub>2</sub>O, sparingly sol. in polar solvents, readily sol. in non-polar solvents, and are chelated. They have the annexed structure, in which



the arrangement of the aryl groups about the azo-group is *trans*. Decomp. of the metallic

complexes by cold acid always regenerates the original azo-compound, and this supports the view that all stable azo-compounds are *trans*. *Cu*, m.p. 230°, *Ni*, m.p. 216°, and *Co* 3-benzeneazo-*p*-tolylloxide, m.p. 202°; *Cu*, m.p. 242°, *Ni*, m.p. 242—243°, and *Co* 3-*p'*-tolueneazo-*p*-tolylloxide, m.p. 200—201°; *Cu*, m.p. 221°, *Ni*, m.p. 214° (impure), and *Co* 3-*m'*-tolueneazo-*p*-tolylloxide, m.p. 187°; *Cu*, m.p. 243°, *Ni*, decomp. 295—310° (impure), and *Co* 2:4-bisbenzeneazophenoxide, m.p. 180—185°; *Cu*, m.p. 295°, *Ni*, m.p. 290° (dark green; gives brown solutions in C<sub>6</sub>H<sub>6</sub>, PhMe, and CHCl<sub>3</sub>), and

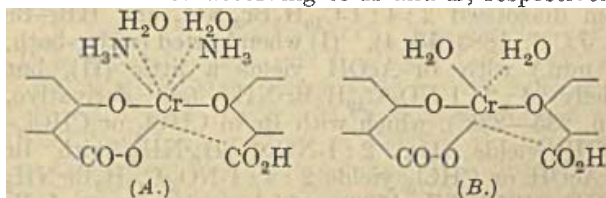
*Co* 1-benzeneazo- $\beta$ -naphthoxide, m.p. 221°; *Cu*, m.p. 237°, *Ni*, m.p. 293° (olive-green; gives brown solutions in C<sub>6</sub>H<sub>6</sub>, PhMe, and CHCl<sub>3</sub>), and *Co* 2-benzeneazo- $\alpha$ -naphthoxide, m.p. 199°. No metallic derivatives could be obtained from *p*-hydroxyazo-compounds, as chelation is impossible.

H. G. M.

**Azo-dyes and their intermediates. XVI. Reactions of tetrazo-compounds of the benzene and naphthalene series. *peri*-Disazo-dyes. III.** P. RUGGLI and E. CASPAR (Helv. Chim. Acta, 1935, 18, 1414—1420).—*m*-Xylylene-4:6-diamine hydrochloride (improved prep.) with NaNO<sub>2</sub>·HBF<sub>4</sub> at -10° gives the *bisdiazonium borofluoride*, which couples with 6:2-C<sub>10</sub>H<sub>6</sub>Br·OH in NaOAc-AcOH to give *m*-xylylene-4:6-bisazo-6'-bromo- $\beta$ -naphthol, is converted by CuSO<sub>4</sub>·KCN at 0° into 4:6-dimethylisophthalodinitrile, and by SH·CH<sub>2</sub>·CO<sub>2</sub>H into the unstable *bisazo-compound*, C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>(N=N·S·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, which decomposes in H<sub>2</sub>O to give *m*-xylylene-4:6-dithioglycolic acid. Similarly 1:8-C<sub>10</sub>H<sub>6</sub>(NH<sub>2</sub>)<sub>2</sub> affords its *bisdiazonium borofluoride*, which couples with (I) to give naphthylene-1:8-bisazo-6'-bromo- $\beta$ -naphthol.

J. W. B.

**Chromium compounds from salicylic acid-azo-dyes and from *o*-methoxybenzoic acid.** K. BRASS and W. WITTENBERGER (Ber., 1935, 68, [B], 1905—1912).—Introduction of Cr into salicylic acid-azo-dyes can be effected by Cr alum, but not by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> unless a reducing agent such as OH·CHMe·CO<sub>2</sub>H is present. The azo-dyes from *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> (I), NH<sub>2</sub>Ph, *o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>, and benzidine, respectively, are converted into the corresponding lakes by heating their solutions, after neutralisation with NaOH, with Cr alum (Cr:dye:Na::1:1:1). In the lakes, dye:Cr:H<sub>2</sub>O=2:1:2. They are stable at 130°, and Cr can be removed from them by boiling AcOH, leaving the homogeneous dye acid. H<sub>2</sub>O cannot be directly determined in them with accuracy, and attempts to displace it by NH<sub>3</sub> lead to adducts in which 2NH<sub>3</sub> is very firmly retained. These and the lakes are therefore formulated according to A and B, respectively:



Repetition of the work of Morgan *et al.* (A., 1924, i, 1359) shows that (I) prepared under their conditions contains unchanged dye, after removal of which the residue has the same composition as that obtained by the authors' method. Methylation of (I) is not effected with Me<sub>2</sub>SO<sub>4</sub> or ethylation with EtBr, and coupling of *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H with *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl does not lead to the methylated dye. In a simpler case the action of Cr alum on *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H affords the compound OH·Cr(O·CO·C<sub>6</sub>H<sub>4</sub>·OMe)<sub>2</sub>·H<sub>2</sub>O, suggesting the analogous structure OH·Cr(O·CO·C<sub>6</sub>H<sub>4</sub>·OH)<sub>2</sub>·H<sub>2</sub>O for Barbieri's chromisalicylic acid. Similar structures can be assigned to the lakes, but their difficult solubility in alkali is hard to explain.

H. W.



**Oxidation of hydrohalides of phenylhydrazine in presence of copper salts.** A. B. BRUKEV and L. S. SOBOROVSKI (J. Gen. Chem. Russ., 1935, 5, 1024—1028).— $\text{NHPh}\cdot\text{NH}_2$  in aq.  $\text{HCl}$  and  $\text{CuCl}_2$  form the compound  $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}\cdot\text{CuCl}_2$  decomp. at  $150^\circ$ , converted by excess of  $\text{Cu}^{\text{II}}$  or by atm.  $\text{O}_2$  into  $\text{PhCl}$  and  $\text{N}_2$ . When  $\text{F}$  is taken in place of  $\text{Cl}$  in the above reaction the sole products are  $\text{C}_6\text{H}_6$  and  $\text{N}_2$ . R. T.

**Aryldiazonium chloride-heavy metal chloride double salts and the preparation of organo-tin compounds through diazo-compounds.** A. N. NESMEJANOV, K. A. KOZESCHKOV, and V. A. KLIMOVA [with, in part, N. K. GRIP] (Ber., 1935, 68, [B], 1877—1883).—The synthesis of organo-mercury substances from diazonium compounds (A., 1929, 711) is an example of a general reaction,  $(\text{RN}_2\text{Cl})_m\text{XCl}_n + 2m/p\text{M}^{(p)} = \text{R}_m\text{X}^{(n)}\text{Cl}_{n-m} + m\text{N}_2 + 2m/p\text{M}^{(p)}\text{Cl}_p$ . Double salts are obtained by mixing cold solutions of the heavy metal chloride ( $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ ,  $\text{PtCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{AuCl}_3$ ) in  $\text{HCl}$  ( $d=1.19$ ) and the requisite aryldiazonium chloride ( $\text{Ph}$ ,  $o$ -,  $m$ -, and  $p$ - $\text{C}_6\text{H}_4\text{Me}$ ,  $p$ - $\text{OH}\cdot\text{C}_6\text{H}_4$ ,  $p$ - $\text{OMe}\cdot\text{C}_6\text{H}_4$ ,  $o$ -,  $m$ -, and  $p$ - $\text{C}_6\text{H}_4\text{Cl}$ ,  $p$ - $\text{C}_6\text{H}_4\text{Br}$ ,  $p$ - $\text{C}_6\text{H}_4\text{I}$ ,  $o$ -,  $m$ -, and  $p$ - $\text{NO}_2\cdot\text{C}_6\text{H}_4$ ) in about 5*N*- $\text{HCl}$ . For details the original must be consulted. Decomp. of  $(\text{RN}_2\text{Cl})_2\text{SnCl}_4$  is effected by its gradual addition to a well-stirred suspension of the metallic powder in the solvent heated at the requisite temp. The best solvent is usually  $\text{EtOAc}$  at its b.p.  $\text{Sn}$  powder is more effective than  $\text{Zn}$  dust or  $\text{Cu}$  powder. The sole organo-metallic product is  $\text{SnR}_2\text{Cl}_2$  except when  $\text{R} = o\text{-CO}_2\text{Me}\cdot\text{C}_6\text{H}_4$ . Small yields of  $\text{PbPh}_3\text{Cl}$  and  $\text{PbPh}_2\text{O}$  are obtained by decomp. of  $(\text{RN}_2\text{Cl})_2\text{PbCl}_4$ . H. W.

**Action of bromine on 2- and 4-nitro- $\alpha$ -naphthylamines.** R. CONSDEN and J. KENYON (J.C.S., 1935, 1596—1597).— $4:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$  (I) with  $\text{Br}$  in  $\text{CHCl}_3$  yields  $2:4$ -dibromo-1-naphthalenediazoperbromide (II), decomp.  $128\text{--}136^\circ$  according to rate of heating, but no  $\text{HBr}$ . (II) is converted into  $1:2:4\text{-C}_{10}\text{H}_5\text{Br}_3$  when heated, treated with  $\text{C}_2\text{H}_5\text{N}$ , or boiled with  $\text{Ac}_2\text{O}$  or  $\text{AcOH}$ , and was also obtained from diazotised  $2:4:1\text{-C}_{10}\text{H}_5\text{Br}_2\cdot\text{NH}_2$  and  $\text{HBr}\cdot\text{Br}$  (cf. J.C.S., 1883, 43, 4). (I) when heated (water-bath, 30 min.) with  $\text{Br}\cdot\text{AcOH}$  yields a little (II), but chiefly  $4:2:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{Br}\cdot\text{NH}_2$  (4c derivative, m.p.  $235\text{--}236^\circ$ ), which with  $\text{Br}$  in  $\text{CHCl}_3$  or  $\text{CHCl}_3\text{-AcOH}$  yields (II).  $2:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$  with  $\text{Br}$  in  $\text{AcOH}$  or  $\text{CHCl}_3$  yields  $2:4:1\text{-NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{Br}\cdot\text{NH}_2$  (J.C.S., 1910, 97, 1709), which with excess of  $\text{Br}$  yields (II).  $o$ - and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  with  $\text{Br}$  yield  $\text{Br}$ -derivatives and no diazo-perbromides. H. G. M.

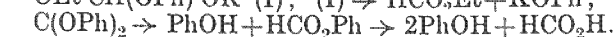
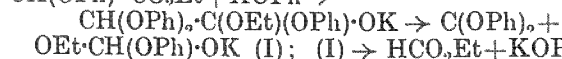
**Alkylation of phenols.** I. TZUKERVANIK and Z. NAZAROVA (J. Gen. Chem. Russ., 1935, 5, 767—770).—Amylene hydrate,  $\text{PhOH}$ , and  $\text{AlCl}_3$  in light petroleum yield a mixture of amylphenol and  $\text{C}_5\text{H}_{11}\text{Ph}$ .  $\text{PhOH}$  and  $\text{Bu}^n\text{OH}$  yield chiefly  $\text{C}_6\text{H}_4\text{Bu}^n\cdot\text{OH}$ , together with  $\text{PhBu}^n$  and  $\text{C}_6\text{H}_5\text{Bu}^n$ , in amounts increasing with the relative amount of  $\text{AlCl}_3$  present.  $\text{PhOH}$  and  $\text{Bu}^s\text{OH}$  under similar conditions yield chiefly  $\text{C}_6\text{H}_4\text{Bu}^s\cdot\text{OBu}^s$ , b.p.  $230^\circ$ , together with  $\text{C}_6\text{H}_4\text{Bu}^s\cdot\text{OH}$  and  $\text{PhBu}^s$ ;  $\text{PhOH}$  and  $\text{Pr}^s\text{OH}$  give similarly  $\text{C}_6\text{H}_4\text{Pr}^s\cdot\text{OPr}^s$ , b.p.  $232^\circ$ ,  $\text{C}_6\text{H}_4\text{Pr}^s\cdot\text{OH}$  (I), and  $\text{PhBr}^s$ , whilst  $\text{Pr}^s\text{OH}$

and  $\text{PhOMe}$  afford chiefly  $o$ - and  $p\text{-C}_6\text{H}_4\text{Pr}^s\cdot\text{OMe}$ , together with  $\text{C}_6\text{H}_3\text{Pr}^s\cdot\text{OMe}$  and (I). R. T.

**Action of isobutylene on phenyl methyl ethers, and the structure of *tert*-butylphenyl methyl ethers.** B. M. DUBININ (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 263—266).—The substance obtained from isobutylene and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OMe}$  (A., 1933, 60) is 3-*tert*-butyl-*p*-tolyl Me ether, since it is also obtained from  $\text{Bu}^n\text{Br}$  and  $1:4:3\text{-C}_6\text{H}_3\text{Me}(\text{OMe})\cdot\text{MgBr}$  (cf. A., 1894, i, 449). Nitration affords the 5- $\text{NO}_2$ -derivative, m.p.  $93.5^\circ$ , and then  $1:3:5:4\text{-C}_6\text{H}_2\text{Me}(\text{NO}_2)_2\cdot\text{OMe}$  by elimination of the  $\text{Bu}^n$ . The  $\text{Bu}^n$  groups in the  $\text{Bu}^n_1$  (I) and  $\text{Bu}^n_2$  (II) derivatives of  $1:3\text{-C}_6\text{H}_4(\text{OMe})_2$  are given the 4 and 4:6 positions, respectively, since nitration of (I) affords 4-nitro-6-*tert*-butylresorcinol Me<sub>2</sub> ether (III), m.p.  $99\text{--}100^\circ$ , and then  $4:6:1:3\text{-C}_6\text{H}_2(\text{NO}_2)_2(\text{OMe})_2$ ; (II) also affords (III). The blue colour produced in the prep. of (III) from (I), but not from (II), is due to the presence of a free position *p* to an  $\text{OMe}$  in (I) (cf. A., 1920, i, 37; 1921, i, 240; 1922, i, 135).

P. G. C.

**Compounds of bivalent carbon. XI. Carbon monoxide acetal fission of esters and amides of diphenoxycetic acid during chemical reactions. XII. Thermal carbon monoxide acetal fission of diphenoxycetic acid and its derivatives. XIII. Diphenoxymethylchloride (formyl chloride diphenyl acetal) and its transformation into tetraphenoxymethylene (dicarbon monoxide tetraphenyl acetal).** H. SCHEIBLER and M. DEPNER (Ber., 1935, 68, [B], 2136—2143, 2144—2151, 2151—2153).—XI. *Ph diphenoxycetate*, m.p.  $95^\circ$ , could not be obtained by heating  $\text{CH}(\text{OPh})_2\cdot\text{CO}\cdot\text{NH}_2$  with  $\text{PhOH}$  or  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et}$  with  $\text{PhOAc}$ , but is readily prepared by the successive action of  $\text{SOCl}_2$  and  $\text{PhOH}$  on the acid in  $\text{Et}_2\text{O}\text{-C}_6\text{H}_5\text{N}$ . It is converted by excess of  $\text{NaOEt}$  in boiling  $\text{C}_6\text{H}_6$  into  $\text{HCO}_2\text{Et}$ ,  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et}$ , and  $\text{C}(\text{OPh})_2\cdot\text{C}(\text{OEt})_2$ , whereas  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et}$  and  $\text{KOPh}$  in boiling  $\text{C}_6\text{H}_6$  afford  $\text{HCO}_2\text{Et}$  and (after treatment of the non-volatile portion with  $\text{H}_2\text{O}$ )  $\text{HCO}_2\text{H}$  and  $\text{PhOH}$ , whilst in boiling  $\text{EtOH}$  the products are  $\text{HCO}_2\text{H}$  and  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{H}$ . The change is therefore:  
 $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et} + \text{KOPh} \rightarrow$



The CO acetal fission is also observed during the action of  $\text{NEt}_3\cdot\text{MgBr}$  on  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et}$ , whereby a neutral product, b.p.  $85^\circ/15\text{ mm.}$ , possibly *Ph Et*<sub>2</sub> orthoformate, and, probably,  $\text{CH}(\text{OPh})_2\cdot\text{CO}\cdot\text{NEt}_3$  are obtained. Higher yields of these compounds are obtained when the reaction product is heated with  $\text{EtOH}$  at  $150^\circ$ , whereby  $\text{PhOEt}$  is also produced.

$\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Ph}$  is much more stable than the  $\text{Et}$  ester, but in  $\text{C}_6\text{H}_6$  at  $150^\circ$  gives  $\text{HCO}_2\text{H}$  and  $\text{PhOH}$  (?  $\text{HCO}_2\text{Ph}$ ). Only elimination of  $\text{PhOH}$  is observed by the action of  $\text{NEt}_3\cdot\text{MgBr}$  on *diphenoxycetdiethylamide*, m.p.  $137^\circ$  [from  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{Et}$  and  $\text{NHEt}$ , in  $\text{EtOH}$  at  $100^\circ$ ].

XII.  $\text{CH}(\text{OPh})_2\cdot\text{CO}_2\text{H}$  passes at  $120^\circ$  into  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCO}_2\text{Ph}$ ,  $\text{Ph}_2\text{CO}_3$ , and, probably, *diphenoxymaleic anhydride*, m.p.  $153^\circ$ ; CO acetal fission has only a



subordinate part in the change.  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Et}$  is comparatively thermostable, but the following thermolabile derivatives have been examined. *Diphenoxyacetyl chloride* (II), obtained by cautious treatment of the acid with  $\text{SOCl}_2$  in  $\text{C}_6\text{H}_6$ , passes at  $170\text{--}180^\circ$  into  $\text{CO}$  and  $\text{CHCl}(\text{OPh})_2$ , probably with intermediate production of  $\text{C}(\text{OPh})_2$  and  $\text{HCOCl}$ . *Acetic diphenoxyacetic anhydride* [attempted prep. from (II) and  $\text{AgOAc}$  or from  $\text{AcCl}$  and  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ag}$ ] is decomposed in  $\text{Et}_2\text{O}$  into  $\text{AcOH}$  and  $\text{C}(\text{OPh})_2 \cdot \text{CO}$ . (II) and  $\text{NaN}_3$  in  $\text{C}_6\text{H}_6$  give  $\text{NaCl}$ ,  $\text{C}(\text{OPh})_2 \cdot \text{CO}$ , and  $\text{N}_3\text{H}$ .  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ph}$  is produced by the action of  $\text{Ag}_2\text{O}$  (II) in  $\text{C}_6\text{H}_6$ ,  $\text{PhOH}$ , resulting from hydrolysis, reacting with  $\text{C}(\text{OPh})_2 \cdot \text{CO}$  or unchanged  $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$ .  $\text{C}(\text{OPh})_2 \cdot \text{CO}$  does not appear to be formed intermediately by the action of  $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$  on  $\text{PhOH}$  in presence of  $\text{C}_6\text{H}_5\text{N}$ . Elimination of  $\text{HCl}$  from  $\text{CH}(\text{OPh})_2 \cdot \text{COCl}$  occurs under the influence of  $p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NPh}$ , whereby the compound  $\text{C}_{12}\text{H}_{11}\text{ON}_2\text{Cl}$  separates and, on exposure to moisture,  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{H}$  is formed, presumably from  $\text{C}(\text{OPh})_2 \cdot \text{CO}$ . *Triphenylmethyl diphenoxyacetate*, m.p.  $112^\circ$ , from  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ag}$  and  $\text{CPh}_3\text{Cl}$  in anhyd.  $\text{Et}_2\text{O}$ , decomposes at  $160^\circ$ /high vac. into  $\text{CO}_2$ ,  $\text{CHPh}_3$ , and  $\text{C}(\text{OPh})_2$ .

XIII. Treatment of  $\text{CHCl}(\text{OPh})_2$  with  $\text{CNaPh}_3$  in  $\text{Et}_2\text{O}$  under  $\text{N}_2$  leads to  $\text{CHPh}_3$  and  $\alpha\beta\beta$ -tetraphenoxymethylene (dicarbon monoxide  $\text{Ph}_4$  acetal), m.p.  $168^\circ$ , which readily reduces alkaline  $\text{KMnO}_4$ , unites energetically with  $\text{Br}$  in  $\text{CHCl}_3$ , and is converted by 30%  $\text{HBr}$  in  $\text{AcOH}$  into  $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Ph}$ . H. W.

Ester enolates and ketal acetals. XIX. *Diphenylketendiphenylacetal*, and *phenyldiphenylvinyl ether*. H. SCHEIBLER and M. DEPNER (Ber., 1935, 68, [B], 2154—2157).— $\text{CH}(\text{OPh})_2 \cdot \text{CO}_2\text{Et}$  is transformed by  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  into  $\alpha$ -hydroxy- $\beta$ -diphenoxy- $\alpha$ -diphenylethane (hydroxydiphenylacetaldehyde  $\text{Ph}_2$  acetal) (I), m.p.  $103^\circ$ , converted by  $\text{SOCl}_2$  in  $\text{Et}_2\text{O}$ - $\text{C}_5\text{H}_5\text{N}$  into  $\alpha$ -chloro- $\beta$ -diphenoxy- $\alpha$ -diphenylethane (II), decomp.  $>100^\circ$ . (II) is transformed by  $\text{C}_6\text{H}_6$ -quinoline, less advantageously by  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgCN}$ , or  $\text{Hg}(\text{CN})_2$ , into  $\alpha\alpha$ -diphenoxy- $\beta\beta$ -diphenylethane (diphenylketen  $\text{Ph}_2$  acetal) (III), b.p.  $185^\circ/0.5$  mm., m.p.  $112^\circ$ , also obtained from (I),  $\text{P}_2\text{O}_5$ , and  $\text{NET}_3$  in  $\text{C}_6\text{H}_6$  at  $150^\circ$ . (III) is hydrolysed by  $\text{EtOH}$ - $\text{HCl}$  to  $\text{PhOH}$  and  $\text{CHPh}_2 \cdot \text{CO}_2\text{Et}$ , and by  $\text{HBr}$ - $\text{AcOH}$  to *Ph diphenylacetate*, m.p.  $65^\circ$ , also obtained with  $\text{C}_6\text{H}_5\text{Br}_3 \cdot \text{OH}$  from (III) and  $\text{Br}$  in  $\text{CCl}_4$ . (II) with  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  or with  $\text{Zn}$  dust and  $\text{C}_5\text{H}_5\text{N}$  affords  $\alpha\alpha$ -diphenylvinyl *Ph ether*, m.p.  $60^\circ$ . H. W.

Behaviour of bromine derivatives of guaiacol towards nitrating agents. L. C. RAIFORD and R. E. SILKER (Proc. Iowa Acad. Sci., 1934, 41, 171).—4 : 5 : 6-Tribromoguaiacol could not be nitrated, either with  $\text{HNO}_2$  (cf. Zincke, A., 1900, i, 545) or with  $\text{HNO}_3$ . The *Ac* and *Bz* derivatives, with fuming  $\text{HNO}_3$  at room temp., give 4 : 5 : 6-tribromo-3-nitro-2-methoxyphenyl acetate and *m*-nitrobenzoate, respectively. CH. ABS. (r)

Metallic derivatives of 2-nitroso-5-methoxy- and of 3-chloro-2-nitroso-5-methoxy-phenol. H. H. HODGSON and W. E. BATTY (J.C.S., 1935, 1617—1619).—2-Nitroso-5-methoxyphenol (I) exists in

the *NO*-form in  $\text{C}_6\text{H}_6$  and in the quinoneoxime form in  $\text{EtOH}$ , whereas its 3-*Cl*-derivative (II) is always in the *NO*-form and is highly chelated, being sparingly sol. in  $\text{H}_2\text{O}$  and readily sol. in  $\text{C}_6\text{H}_6$ . The following salts of (I) ( $\text{X}=\text{C}_7\text{H}_6\text{O}_3\text{N}$ ) and (II) ( $\text{Y}=\text{C}_7\text{H}_5\text{O}_3\text{NCl}$ ) are described; they are sol. in org. solvents ( $\text{C}_6\text{H}_6$  and  $\text{CHCl}_3$ ) and probably are co-ordination compounds:  $\text{HgX}_2$ , m.p.  $201^\circ$ ;  $\text{HgY}_2$ ;  $\text{AlXCl}_2$ ;  $\text{AlYCl}_2$ ;  $\text{SnXCl}_2$ , m.p.  $147^\circ$ ;  $\text{SnYCl}_2$ ;  $\text{Fe}(\text{OH})\text{X}_2$ ;  $\text{FeX}_3$ ;  $\text{Fe}(\text{OH})\text{Y}_2$ ;  $\text{FeY}_3$ ;  $\text{CoX}_3$ ;  $\text{CoY}_3$ ;  $\text{NiX}_2$ ;  $\text{NiY}_2$ ; and the following double compounds with salicylaldehyde ( $=\text{S}$ ):  $\text{NaX} \cdot \text{S}$ ;  $\text{NaY} \cdot \text{S}$ ;  $\text{KX} \cdot \text{S}$ ; and  $\text{KY} \cdot \text{S}$ . The following salts are insol. in org. solvents and probably are normal salts (non-co-ordinated):  $\text{NaX}$ ;  $\text{NaY}$ ;  $\text{KX}$ ;  $\text{KY}$ ;  $\text{AgX}$ ;  $\text{AgY}$ ;  $\text{ZnX}_2$ ;  $\text{ZnY}_2$ ;  $\text{CdX}_2$ ;  $\text{CdY}_2$ ;  $\text{PbX}_2$ ;  $\text{PbY}_2$ ;  $\text{MnX}_2$ ;  $\text{MnY}_2$ ;  $\text{UO}_2\text{X}_2$ ;  $\text{UO}_2\text{Y}_2$ . The *Ag* and *Hg* salts of 2-nitroso-3-ethoxyphenol described by Kietaihl (A., 1899, i, 343) are really those of 2-nitroso-5-ethoxyphenol. Wool mordanted with  $\text{Fe}^{II}$  salts is dyed bluish-green with nitrosophenol solutions: the colour lake is decolorised by acids, restored by  $\text{NH}_3$ , and destroyed by  $\text{SnCl}_2$ . H. G. M.

Dimorphism of trinitroresorcinol, bromobenzylhydrazine, and benzaldehyde-*p*-nitrophenylhydrazine.—See this vol., 16.

Diaryls and their derivatives. IV. Oxidation of  $\beta$ -naphthol-6-sulphonic acid and 2 : 6-dihydroxynaphthalene. V. Optical activity of 2 : 2'-dihydroxy-1 : 1'-dinaphthylsulphonic acids. I. S. JOFFE (J. Gen. Chem. Russ., 1935, 5, 877—885, 950—955).—IV [with S. G. KUZNETZOV]. 2 : 2'-Dihydroxy-1 : 1'-dinaphthyl-6 : 6'-disulphonic acid (I), obtained in 90% yield from  $\text{Na}\beta$ -naphthol-6-sulphonate and aq.  $\text{FeCl}_3$  ( $20\text{--}25^\circ$ ; 20 days), yields 2 : 2'-dihydroxy-1 : 1'-dinaphthyl when heated with  $\text{H}_2\text{SO}_4$  ( $170\text{--}180^\circ$ ; 12 hr.), and 2 : 6 : 2' : 6'-tetrahydroxy-1 : 1'-dinaphthyl (II), m.p.  $318\text{--}320^\circ$ , when heated with  $\text{KOH}$  ( $320\text{--}330^\circ$ ; 15 min.). (II) may also be obtained from dil. aq. 2 : 6- $\text{C}_{10}\text{H}_6(\text{OH})_2$  and  $\text{FeCl}_3$  at room temp.; excess of  $\text{FeCl}_3$  leads to the production of the corresponding octahydroxytetra-naphthyl. (II) in aq.  $\text{NaOAc}$  and  $p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl}$  yield the 5-*p*-nitrobenzeneazo-derivative, m.p.  $179\text{--}183^\circ$ .

V. [with I. V. GRATSCHEV]. The brucine salt of (I) is separable into two fractions,  $[\alpha]_D^{20} -43^\circ$  and  $-65^\circ$  in 50%  $\text{EtOH}$ , which yield two *Na* salts of (I),  $[\alpha]_D^{20} -154^\circ$  and  $+166^\circ$  in  $\text{H}_2\text{O}$ , when hydrolysed with 0.05*N*- $\text{NaOH}$  in presence of  $\text{CHCl}_3$ ; the analogous products from the corresponding 7 : 7'-disulphonate have  $[\alpha]_D^{20} -312^\circ$  and  $+259^\circ$ . The free acids do not exhibit optical activity, and both the acids and their salts readily racemise in aq. solution. R. T.

Application of the Raman effect to the *cis-trans* isomerism of methylcyclohexanols.—See this vol., 11.

Benzyl formate. R. HOLTZ (J. Appl. Chem. Russ., 1935, 8, 1014—1015).— $\text{CH}_2\text{Ph} \cdot \text{OH}$  and  $\text{HCO}_2\text{H}$  (21% excess) at the b.p. of the mixture, and in presence of sufficient  $\text{CaCl}_2$  to bind the  $\text{H}_2\text{O}$  produced, afford  $\text{HCO}_2 \cdot \text{CH}_2\text{Ph}$  in 91% yield, and of high purity.

R. T.

Synthesis of  $\beta$ -phenylbutyl alcohol. S. P. LAGEREV (J. Gen. Chem. Russ., 1935, 5, 515—516).—

Mg,  $\text{CH}_2\text{PhI}$ , and  $\text{EtCHO}$  afford  $\beta$ -phenylbutyl alcohol, b.p. 124—127°/25 mm. (benzoate, m.p. 115—116°), which with  $\text{HBr}$  in  $\text{Et}_2\text{O}$  yields the bromide, b.p. 112°/15 mm. R. T.

Semipinacolic deamination of  $\beta$ -amino- $p$ -tolyl- and  $\alpha$ -anisyl- $\alpha$ -phenylpropanol. Exclusive preferential migration of phenyl. M. TIFFENEAU, J. LEVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1871—1876).—Treatment of the  $\alpha$ - and  $\beta$ -forms of  $p$ - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NH}_2$  in  $\text{AcOH}$  with  $\text{NaNO}_2\text{--H}_2\text{O}$  yields  $p$ -tolyl  $\alpha$ -phenylethyl ketone, m.p. 43° (semicarbazone, m.p. 148°), also obtained by methylation of  $p$ - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ . Similarly the  $\alpha$ -form of  $p$ - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}(\text{OH})\cdot\text{CHMe}\cdot\text{NH}_2$  in  $\text{AcOH}$  and  $\text{NaNO}_2\text{--H}_2\text{O}$  yield  $p$ -anisyl  $\alpha$ -phenylethyl ketone, m.p. 55° (cf. lit.) also obtained by methylation of  $p$ - $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ . In each case only the Ph has migrated during deamination. H. G. M.

Formation of a single diastereoisomeride in the action of organo-magnesium derivatives on amino-ketones. M. TIFFENEAU, J. LEVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1848—1855; cf. A., 1930, 470).—The action of  $\text{MgRBr}$  on ketones  $\text{R}'\cdot\text{CO}\cdot\text{CHMe}\cdot\text{NH}_2$  (I) (R different from  $\text{R}'$ ) which have an asymmetric C adjacent to the CO gives rise to only one of the two possible diastereoisomeric products. The other is obtained by inverting the order in which the substituents are attached to the new asymmetric centre. A further example is given (cf. loc. cit.).  $p$ -Tolyl  $\alpha$ -aminoethyl ketone and  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  (II) yield solely  $\beta$ -amino- $\alpha$ - $p$ -tolyl- $\alpha$ -anisylpropanol, m.p. 90° (hydrochloride, m.p. 260°; picrate, m.p. 217°); the corresponding  $\beta$ -compound, m.p. 84° (hydrochloride, m.p. 242°; picrate, m.p. 197°), is obtained from anisyl  $\alpha$ -aminoethyl ketone and  $p$ - $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ . (II) and  $\omega$ -aminoacetophenone (which contains no asymmetric C) give the same  $\beta$ -amino- $\alpha$ -phenyl- $\alpha$ -anisylethanol, m.p. 100°, as do  $\omega$ -amino- $p$ -methoxyacetophenone and  $\text{MgPhBr}$ . An improved method is described for the prep. of the oximino-ketones which on reduction yield the ketones (I). These exist only as hydrochlorides, the free bases cyclising to the corresponding dihydropyrazines. H. G. M.

Deamination of  $\alpha$ -amino- $\beta$ -phenylpropan- $\beta$ -ol and  $\alpha$ -amino- $\beta$ -phenylbutan- $\beta$ -ol. Exclusive preferential migration of phenyl. M. TIFFENEAU and H. CAHNMANN (Bull. Soc. chim., 1935, [v], 2, 1876—1882).— $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{NH}_2$  [prepared from  $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}_2$  and  $\text{MgMeI}$ , and together with some  $\beta$ -phenylallylamine, b.p. 90—92°/14 mm. (hydrochloride, m.p. 143—144°; methiodide, m.p. 160°, also obtained from  $N$ -methyl- $\beta$ -phenylallylamine), by reduction with  $\text{Na}\text{--EtOH}$  of  $\text{OH}\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{N}\cdot\text{OH}$ , obtained from  $\text{COPh}\cdot\text{CH}_2\cdot\text{NOH}$ ] is deaminated by  $\text{AcOH}\text{--H}_2\text{O}\text{--NaNO}_2$  to  $\text{CH}_2\text{Ph}\cdot\text{COMe}$ . Similarly  $\text{OH}\cdot\text{CPhEt}\cdot\text{CH}_2\cdot\text{NH}_2$ , b.p. 137—146°/15 mm. (hydrochloride, m.p. 184.5—185°; prepared, together with some  $\beta$ -phenyl- $\Delta^8$ -butenylamine, b.p. 110—115°/15 mm. [hydrochloride, m.p. 166.5—167° (corr.)], by reduction of the product obtained from  $\text{COPh}\cdot\text{CH}_2\cdot\text{N}\cdot\text{OH}$  and  $\text{MgEtBr}$ ], is deaminated by  $\text{AcOH}\text{--H}_2\text{O}\text{--NaNO}_2$  to  $\text{CH}_2\text{Ph}\cdot\text{COEt}$  [semicarbazone,

m.p. 156.5—157° (cf. lit.)]. In each case only the Ph has migrated during the deamination. H. G. M.

Action of magnesium phenyl bromide on  $\alpha$ -dibenzoylglyceraldehyde. Formation of a single diastereoisomeride:  $\alpha$ - $d$ -dibenzoylphenylglycerol. M. TIFFENEAU, I. S. NEUBERG-RABINOVITCH, and H. CAHNMANN (Bull. Soc. chim., 1935, [v], 2, 1866—1871).— $\alpha$ -Dibenzoylglyceraldehyde and  $\text{MgPhBr}$  (1 mol.) give a single  $d$ -dibenzoylphenylglycerol (laevorotatory), which with  $\text{BzCl}$  and  $\text{C}_5\text{H}_5\text{N}$  gives solely laevorotatory  $\alpha$ - $d$ -tribenzoylphenylglycerol, m.p. 147°, converted into  $\alpha$ - $d$ -phenylglycerol, m.p. 105—106° (corr.),  $[\alpha]_{\text{D}}^{20} + 21.1^\circ$  and  $[\alpha]_{\text{D}}^{19.5} + 18.4^\circ$  in  $\text{H}_2\text{O}$ . H. G. M.

Cubebin. VII. [Criticism of] a new structural formula proposed for cubebin. VIII. Identity of cubebinolide with hinokinin. E. MAMELI (Gazzetta, 1935, 65, 877—885, 886—888).—VII. The objections of Ginzberg *et al.* (A., 1934, 302) to the formula proposed (A., 1913, i, 47; 1922, i, 347) for cubebin (I), and their new formula, are criticised and the earlier structure is upheld.

VIII. Cubebinolide (*loc. cit.*) is identical with the hinokinin (II) of Yoshiki and Ishiguro (J. Pharm. Soc. Japan, 1933, 53, 11); properties and derivatives are compared. The extraction of (II) from the conifer *Chamaecyparis obtusa*, Sieb. and Zucc., shows that the occurrence of (I) and its derivatives is not restricted to the angiosperms. E. W. W.

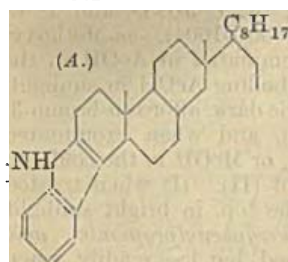
"Plane-radial" compounds. I. Hexahydroxymethylbenzene and its derivatives. II. Hexathiomethylbenzene and its thioethers. H. J. BACKER (Rec. trav. chim., 1935, 54, 833—837, 905—915).—I.  $\text{C}_6(\text{CH}_2\text{Br})_6$  (I) (A., 1935, 1487) is converted by boiling  $\text{KOAc}\text{--Ac}_2\text{O}$  into the  $\text{Ac}_6$  derivative, m.p. 163°, hydrolysed by  $\text{KOH}\text{--EtOH}$  to hexahydroxymethylbenzene, m.p. 310—311° (crystallographic data) {hexanitrate, m.p. 176.5° (decomp.); hexapropionate, m.p. 90—100° [from (I)– $\text{EtCO}_2\text{Na}\text{--}(\text{EtCO})_2\text{O}$ ];  $\text{Me}_6$ , m.p. 100°,  $\text{Et}_6$ , m.p. 93°, and  $\text{Ph}_6+2\text{PhMe}$ , and solvent-free, m.p. 223°, ethers [all from (I) by the action of  $\text{NaOR}\text{--ROH}$ ]}. II. Interaction of  $\text{C}_6(\text{CH}_2\text{Br})_6$  and  $\text{CS}(\text{NH}_2)_2$  in  $\text{EtOH}$  affords hexaisothiocarbamidomethylbenzene, decomp. 290°, as its hydrobromide, m.p. 250° (decomp.), hydrolysed by  $\text{NaOH}$  to hexathiomethylbenzene, m.p. 225—226° [ $\text{Na}+36\text{H}_2\text{O}$ , and  $\text{Pb}+3\text{H}_2\text{O}$ , salts:  $\text{Me}_6$ , m.p. 220—222°;  $\text{Et}_6$ , m.p. 131°;  $\text{Pr}_6$ , m.p. 55.5°;  $\text{Pr}^i_6$ , m.p. 232—232.5°;  $\text{Bu}^n_6$ , m.p. 34—34.5°; m.p. 94°; sec.- $\text{Bu}_6$ , m.p. 172°;  $\text{Bu}^i_6$ , m.p. 304° (decomp.)]; ( $n\text{-C}_5\text{H}_{11}$ ) $_6$ , m.p. 25.5—26°; ( $\text{CMe}_2\text{Et}$ ) $_6$ , m.p. 295°; ( $n\text{-C}_6\text{H}_{13}$ ) $_6$ , m.p. 11.5—12°;  $\text{Ph}_6+\text{PhMe}$  and solvent-free, m.p. 191—192°; ( $p\text{-C}_6\text{H}_4\text{Me}$ ) $_6$ , m.p. 183—184°; ( $p\text{-C}_6\text{H}_4\text{Cl}$ ) $_6$ , m.p. 179—180°; ( $p\text{-C}_6\text{H}_4\text{Bu}^i$ ) $_6$ , m.p. 182—183°, and ( $\text{CH}_2\text{Ph}$ ) $_6+\text{PhMe}$ , m.p. 148°, thioether, all formed by the action of  $\text{NaOEt}\text{--RSH}$  on  $\text{C}_6(\text{CH}_2\text{Br})_6$ ]. The close packing of branched-chain alkyl groups greatly raises the m.p., and with the  $n$ -alkyl thioethers, the m.p. is lower the longer is the normal C chain. Crystallographic data (TERPSTRA) are given for some of the above compounds. J B

Action of carbonyl chloride, chloromethyl chloroformates and carbonates on cholesterol.

A. KLING and M. ROUILLY (Compt. rend., 1935, 201, 782—784; cf. A., 1934, 216).—Cholesterol in warm  $\text{CHCl}_3$  reacts with  $\text{COCl}_2$  to give a *chlorocarbonate* (I), m.p.  $114^\circ$ .  $\text{ClCO}_2\text{Me}$  does not react;  $\text{ClCO}_2\text{CH}_2\text{Cl}$ ,  $\text{ClCO}_2\text{CHCl}_2$ , and  $\text{ClCO}_2\text{CCl}_3$  give a highly unstable product, *cholesteryl dichloromethyl carbonate*, m.p.  $85^\circ$ , and *cholesteryl  $\text{CCl}_3$  carbonate*, m.p.  $107^\circ$ , respectively.  $\text{CO}(\text{O}-\text{CCl}_3)_2$  similarly affords (I) (cf. A., 1920, i, 805). This reaction may account for the toxicity of these substances when inhaled.

J. L. D.

**Hydrogenation under the action of selenium.**  
I. Action of selenium on cholesterol at  $230^\circ$ .



C. DORÉE and V. A. PETROV (J.C.S., 1935, 1391—1393).—After 10 hr., cholesterol is partly converted by Se at  $230^\circ$  into *cholestanone* (I) (*semicarbazone*, m.p.  $234$ — $238^\circ$ ), with small quantities of *cholestanol* and *cholestenone*; after 25 hr., 10% of (I) is formed. With  $\text{NHPh}\cdot\text{NH}_2$  in  $\text{AcOH}$ ,

(I) forms a *tetrahydrocarbazole* derivative, m.p.  $180$ — $181^\circ$  (*picrate*, m.p.  $209$ — $210^\circ$ ), which from ease of formation and surface film area probably has the angular structure (A).

E. W. W.

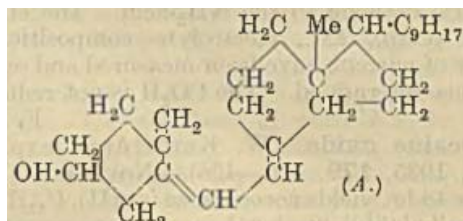
**Sitostanol and stigmastanol.** B. E. BENGTSSON (Z. physiol. Chem., 1935, 237, 46—51).—The probability of the identity of ordinary dihydrositosterol with tetrahydrostigmastanol is advanced. "Ordinary" and  $\gamma$ -sitostane can be differentiated by their mixed m.p. with stigmastane. Fucostanol is not identical with stigmastanol (cf. A., 1934, 1347).

F. O. H.

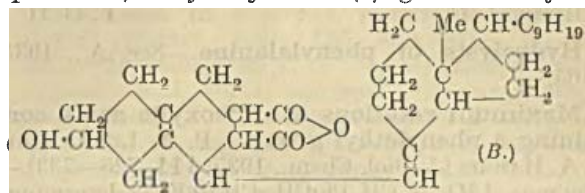
**Phytosterol of wheat-germ oil.**—See A., 1935, 1551.

**Constitution of vitamin- $\text{D}_2$ .** A. WINDAUS and W. THIELE (Annalen, 1935, 521, 160—175).—Treatment of calciferyl acetate with maleic anhydride in boiling  $\text{C}_6\text{H}_6$  affords an *adduct*, m.p. (indef.)  $189$ — $196^\circ$ , hydrolysed and then converted by  $\text{CH}_2\text{N}_2$  into  $\alpha$ -*calciferyl acetate  $\text{Me}_2$  maleate* (I), m.p.  $141^\circ$ ,  $[\alpha]_D^{20} +170.8^\circ$  in  $\text{CHCl}_3$ , which absorbs 2 O when titrated with  $\text{BzO}_2\text{H}$ . The filtrates from (I) when treated with  $\text{KOH}$ - $\text{MeOH}$  give a sparingly sol. *K* salt, from which  $\text{AcOH}$  liberates  $\beta$ -*calciferol-maleic acid* (II), m.p.  $196^\circ$  (decomp.), the *Me* ester, m.p.  $67$ — $68^\circ$ , of which is converted by  $\text{Ac}_2\text{O}$  into  $\beta$ -*calciferyl acetate  $\text{Me}_2$  maleate*, m.p.  $94$ — $95^\circ$ ,  $[\alpha]_D^{20} -158.3^\circ$  in  $\text{CHCl}_3$ , which absorbs 3 O from  $\text{BzO}_2\text{H}$ . The adducts can be distilled in a vac. without decomp. Hydrogenation (Pd in  $\text{COMe}_2$ ) of (I) gives the  $\text{H}_2$ -derivative (III), m.p.  $112^\circ$ ,  $[\alpha]_D^{20} +167.8^\circ$  in  $\text{CHCl}_3$ , which absorbs 1.16—1.33 O and is further reduced (Pt in  $\text{AcOH}$ ) to the  $\text{H}_4$ -compound. Similarly (II) gives a  $\text{H}_2$ -derivative, m.p.  $193^\circ$  (decomp.) [ $\beta$ -*dihydrocalciferyl acetate  $\text{Me}_2$  maleate* (IV), m.p.  $86$ — $86.5^\circ$ ,  $[\alpha]_D^{20} -144.7^\circ$  in  $\text{CHCl}_3$ , which absorbs 2 O from  $\text{BzO}_2\text{H}$ ], and a non-cryst.  $\text{H}_4$ -derivative, converted by acetylation and methylation into  $\beta$ -*tetrahydrocalciferyl acetate  $\text{Me}_2$  maleate*, m.p.  $122^\circ$ ,  $[\alpha]_D^{20} -51.5^\circ$  in  $\text{CHCl}_3$ , which absorbs Br but is only slowly attacked by  $\text{O}_3$ .

Ozonisation of (III) or (IV) in  $\text{CHCl}_3$  followed by reductive or oxidative fission of the ozonide yields a



ketone,  $\text{C}_{19}\text{H}_{34}\text{O}$  (*semicarbazone*, m.p.  $225^\circ$ ; *oxime*, m.p.  $129.5^\circ$ ). Hydrolysis of (I) gives  $\alpha$ -*calciferol*-



*maleic acid*, m.p.  $146$ — $147^\circ$  (decomp.), dehydrogenated by Pd-C at  $330$ — $340^\circ$  to  $\text{C}_{10}\text{H}_8$ , and  $\beta$ - $\text{C}_{10}\text{H}_7\text{CO}_2\text{H}$ , and by Se at  $280$ — $325^\circ$  to 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ . The structures A and B are therefore assigned to *calciferol* and the  $\text{H}_2$ -adduct, respectively.

H. W.

**Reaction of carboxylic acid chlorides with metallic hydrides.** O. NEUNHOEFFER and F. NERDEL (J. pr. Chem., 1935, [ii], 144, 63—66; cf. Wohl *et al.*, A., 1912, i, 161).—Freshly prepared  $\text{CuH}$  is red to chocolate-brown, and even when moist with  $\text{Et}_2\text{O}$  cannot be handled without some danger, whereas the aged product is black and almost non-dangerous. Its complete purification from compounds of P is extremely difficult. Interaction of  $\text{CuH}$  and  $\text{BzCl}$  in presence of  $\text{Et}_2\text{O}$  in an inert atm. affords  $\text{EtOBz}$  in widely varying yield, but no  $\text{PhCHO}$ . Since in presence of  $\text{C}_6\text{H}_6$  or *cyclohexane* in place of  $\text{Et}_2\text{O}$  there is no formation of  $\text{EtOBz}$ , its production must be ascribed to fission of  $\text{Et}_2\text{O}$ . Reaction between  $\text{CuH}$  and acid chloride is accompanied by evolution of  $\text{H}_2$ . Since the amount thus liberated + that evolved on subsequent addition of  $\text{HCl}$  equals the total H present, it follows that none is expended in reduction. Since  $\text{CuH}$  is very sensitive to  $\text{Cl}^+$ , the  $\text{BzCl}$  used is first shaken with  $\text{CaCO}_3$  and a trace of  $\text{C}_2\text{H}_5\text{N}$  is added to accelerate the change; under these conditions  $\text{CuH}$  is almost completely stable to  $\text{BzCl}$ , and evolution of  $\text{H}_2$  does not occur until  $\text{HCl}$  is added.  $\text{CaH}_2$  and  $\text{LiH}$  are more stable than  $\text{CuH}$ .  $\text{AcCl}$ ,  $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ , and adipyl chloride behave similarly to  $\text{BzCl}$ .

H. W.

**Nitration of benzoic and toluic acids.** A. GIACALONE (Gazzetta, 1935, 65, 840—844).—Nitration at  $0$ — $5^\circ$  of *m*-toluic acid (20 g.) with  $\text{KNO}_3$  in  $\text{H}_2\text{SO}_4$  gives 4-nitro- (12 g.) and 2-nitro- (6 g.) without 6-nitro-*m*-toluic acid. Similar nitration of  $\text{BzOH}$  and of *o*- and *p*-toluic acid gives products more readily purified than those obtained in the usual manner.

E. W. W.

**Effect of substituents on organic reactions.**—See A., 1935, 1465.

**Electrolytic preparation of anthranilic acid.** J. W. SHIPLEY and J. M. CALHOUN (Canad. J. Res.,



1935, 13, B, 123—132).— $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  is reduced electrolytically (92% yield) in  $\text{EtOH-H}_2\text{SO}_4$  with a Pb cathode to the  $\text{NH}_2$ -acid. The effects of varying temp., c.d., electrolyte composition, and quantity of current have been measured and optimum conditions determined. The  $\text{CO}_2\text{H}$  is not reduced.

F. R. S.

**Novocaine oxide.** W. KEIL (Arch. exp. Path. Pharm., 1935, 179, 425—426).—Novocaine (I) with  $\text{H}_2\text{O}_2$  for 48 hr. yields *novocaine oxide* (II),  $\text{C}_{12}\text{H}_{22}\text{O}_5\text{N}_2$ , a "genalkaloid" (isolated as *picrate*, m.p.  $172^\circ$ ). In its anaesthetic actions on the rabbit's cornea and human skin, (II) has respectively 50 and 25% of the activity of (I).

F. O. H.

**Hydrolysis of phenylalanine.**—See A., 1935, 1465.

**Maximum rotations of carboxylic acids containing a phenylethyl group.** P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 111, 725—733).—The max.  $[\alpha]_D$  of  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMeEt}$  is determined and that of related compounds calc. In the series,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_n\cdot\text{CO}_2\text{H}$ , there is periodic fluctuation of  $[\alpha]$  as  $n$  increases from 0 to 3.  $\gamma$ -Phenyl- $\alpha$ -methylbutyric acid, resolved by the cinchonidine salt in  $\text{COMe}_2$ , has  $[\alpha]^{20} = -28.75^\circ$ .  $\alpha$ -Phenyl- $\gamma$ -methylpentane, from (a) the alcohol and cold HI, followed by  $\text{H}_2$ -Raney Ni in 10%  $\text{NaOH-MeOH}$ , or (b)  $\text{l-C}_5\text{H}_{11}\cdot\text{MgBr}$  and  $\text{PhCHO}$ , has  $[\alpha]^{25} = -5.52^\circ$ .  $\zeta$ -Phenyl- $\delta$ -methylhexoic acid, b.p.  $152\text{—}154^\circ$  (or  $162^\circ$ )/1 mm.,  $[\alpha]_D^{15} = -1.60^\circ$ , is obtained from (a)  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{MgBr}$  and  $\text{CO}_2$ , or (b)  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$  and  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and leads to the *Et* ester, b.p.  $122^\circ/5$  mm.,  $[\alpha]^{25} = -3.71^\circ$ , and  $\zeta$ -phenyl- $\delta$ -methylhexan-2-ol, b.p.  $155^\circ/10$  mm.,  $[\alpha]^{25} = -5.27^\circ$ .  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot[\text{CH}_2]_3\cdot\text{MgBr}$  and  $\text{CO}_2$  give  $\zeta$ -phenyl- $\delta$ -methylheptoic acid, b.p.  $172^\circ/2.5$  mm.,  $[\alpha]^{25} = -3.27^\circ$ . Hydrogenation ( $\text{PtO}_2$ ) in  $\text{AcOH}$  affords  $\epsilon$ -cyclohexyl- $\gamma$ -methylhexoic acid, b.p.  $180^\circ/10$  mm.,  $[\alpha]_D = -1.18^\circ$ , and  $\zeta$ -cyclohexyl- $\delta$ -methylheptoic acid, b.p.  $136\text{—}140^\circ/0.3$  mm.,  $[\alpha]^{25} = -1.41^\circ$ .  $[\alpha]$  are max. vals. for the homogeneous liquids.

R. S. C.

**Catalytic hydrogenation of ethyl cinnamate under pressure.** S. P. LAGEREV (J. Gen. Chem. Russ., 1935, 5, 517—518).—*Et* cinnamate yields  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , but not  $\delta$ -phenylbutyl alcohol, when heated with  $\text{H}_2$  (12 hr.;  $250^\circ/220$  atm.) in presence of Cr-Cu catalyst in an Fe autoclave.

R. T.

**Steric factor in organic chemical reactions.**

**I. Influence of esterification on mode of addition of bromine to  $\beta$ -phenylpropionic acid.** P. R. AYYAR (J. Indian Inst. Sci., 1935, 18, A, 123—127).—Addition of Br to  $\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (I) at  $0^\circ$  in the dark affords *cis*- and *trans*- $\text{CPhBr}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$  in the ratio 3 : 2, whereas at  $0\text{—}25^\circ$  in diffused daylight the ratio is 2 : 1. Using the *Me* ester of (I), the ratios under the above conditions are 1 : 2 and 1 : 3, respectively.

P. G. C.

**Synthesis of a methyloctahydrophenanthrene-carboxylic acid and of 4-methylphenanthrene.** G. DARZENS and A. LEVY (Compt. rend., 1935, 201, 730—733).— $\beta$ -Chloromethyltetrahydronaphthalene (cf. A., 1931, 208) with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  gives *Et*, tetrahydronaphthylmethylmalonate, b.p.  $179^\circ/1.5$

mm. (the acid, m.p.  $123^\circ$ , loses  $\text{CO}_2$  in vac. at  $170^\circ$  to give  $\beta$ -tetrahydronaphthylpropionic acid, m.p.  $127^\circ$ ), the Na derivative of which affords (cf. A., 1935, 975) an allyl derivative, b.p.  $189\text{—}190^\circ/2$  mm. [acid, an oil, which loses  $\text{CO}_2$  in vac. at  $170\text{—}180^\circ$  to give  $\beta$ -tetrahydronaphthyl- $\alpha$ -allylpropionic acid (I), an oil]. (I) with  $\text{AcOH-H}_2\text{SO}_4$  at  $50^\circ$  gives a lactone, b.p.  $187^\circ/2$  mm., and 4-methyloctahydrophenanthrene-2-carboxylic acid, m.p.  $148\text{—}149^\circ$ , which with Se at  $300\text{—}350^\circ$  gives 4-methylphenanthrene, m.p.  $116^\circ$  (cf. A., 1931, 1282; 1932, 608).

J. L. D.

**Addition of halogens to unsaturated acids and esters.** **V. Bromination of *m*-methoxycinnamic acid and its ethyl ester.** J. I. JONES and T. C. JAMES (J.C.S., 1935, 1600—1604).—*m*-Methoxycinnamic acid (I) when brominated in  $\text{AcOH}$  in the dark (cf. A., 1928, 519), in boiling  $\text{AcOH}$  in sunlight, or in  $\text{CCl}_4$  or  $\text{CHCl}_3$  at  $0^\circ$  in the dark, affords 6-bromo-3-methoxycinnamic acid (II), and when brominated in boiling  $\text{MeOH}$  in sunlight, or  $\text{MeOH}$  in the cold and dark, yields the *Me* ester of (II). (I) when treated with Br and dry  $\text{CCl}_4$  at the b.p. in bright sunlight yields  $\alpha\beta$ -dibromo- $\beta$ -3-methoxyphenylpropionic acid (III), m.p.  $167^\circ$ , also obtained, but less readily, when (I) is brominated in  $\text{CCl}_4$  in the cold in sunlight, or in boiling  $\text{CS}_2$ . Bromination of (I) in boiling  $\text{CHCl}_3$  in sunlight gives a mixture consisting mainly of (II). (III) is unaffected by boiling  $\text{EtOH}$ , and is oxidised by  $\text{KMnO}_4$  to *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (IV). Bromination of the *Et* ester of (I) in  $\text{AcOH}$  or  $\text{CHCl}_3$  in the cold and dark gives only the *Et* ester of (II), but in  $\text{CCl}_4$  in strong sunlight gives the *Et* ester, m.p.  $58^\circ$ , of (III). (II) in boiling  $\text{CCl}_4$  with Br in strong sunlight yields  $\alpha\beta$ -dibromo- $\beta$ -6-bromo-3-methoxyphenylpropionic acid, m.p.  $163^\circ$ , also obtained by bromination of (III). (III) with  $\text{KOH-EtOH}$  affords  $\alpha$ -bromo-*m*-methoxycinnamic acid (V), m.p.  $122^\circ$  (A., 1934, 72), and  $\alpha$ -bromo-*m*-methoxyallicinnamic acid, m.p.  $91^\circ$ , separated by means of their Ba salts and also obtained by removal of  $\text{HBr}$  from the ester of (III). The *allo*-acid, when kept in the solid state or in  $\text{CCl}_4$  solution, in strong sunlight, or when heated during several hr. at  $150^\circ$ , is converted into (V). (V) when boiled with  $\text{KOH-EtOH}$  during 4 hr. yields *m*-methoxyphenylpropionic acid, m.p.  $109^\circ$ , which with  $\text{K}_2\text{CO}_3\text{-I-KI-H}_2\text{O}$  affords  $\alpha\beta$ -di-iodo-*m*-methoxycinnamic acid, m.p.  $142^\circ$ , and is hydrogenated (colloidal Pd "protected" by Na protalbate) to *m*-methoxyallicinnamic acid (VI), m.p.  $109\text{—}110^\circ$ , converted on long exposure to sunlight into (I). (VI) with  $\text{CHCl}_3\text{-Br}$  in the cold and dark affords 6-bromo-3-methoxyallicinnamic acid, m.p.  $133^\circ$ , oxidised by  $\text{KMnO}_4$  to (IV).

H. G. M.

**Preparation of fluorinated arylamides [of 2 : 3-hydroxynaphthoic acid].**—See B., 1935, 1132.

**Reaction of Grignard reagents with some succinic anhydrides.** C. WEIZMANN, (MRS.) O. BLUM-BERGEMANN, and F. BERGMANN (J.C.S., 1935, 1370—1371).— $(\text{CH}_2\text{CO})_2\text{O}$  treated with the Mg derivative of 1- or 2- $\text{C}_{10}\text{H}_7\text{-Br}$  yields  $\beta$ -(1- or  $\beta$ -(2-naphthoyl)propionic acid. Phenylsuccinic anhydride with  $\text{MgPhBr}$  and with the Mg derivative of 1- $\text{C}_{10}\text{H}_7\text{-Br}$  gives  $\alpha\gamma\gamma$ -triphenyl-, m.p.  $162^\circ$ , and  $\alpha$ -phenyl- $\gamma\gamma$ -di-(1-naphthyl)-*n*-butyrolactone, m.p.  $211^\circ$ , the last being accompanied by an acid, reduced to a

substance, b.p. 265—270°/1.4 mm. 3-Phenyl- $\Delta^4$ -tetrahydrophthalic anhydride and MgPhBr form an acid product, and a triphenyltetrahydrophthalide, 2-(diphenylmethylol)-6-phenyl- $\Delta^4$ -tetrahydrobenzoic acid lactone, m.p. 227°.

E. W. W.

**Hydrolysis of cyclopentanedicarboxylic esters.**  
—See A., 1935, 1465.

**Configurations of the  $\Delta^2$ -tetrahydro- and hexahydro-terephthalic acids.** W. H. MILLS and G. H. KEATS (J.C.S., 1935, 1373—1375).—"Fumaroid"  $\Delta^2$ -tetrahydroterephthalic acid (I), m.p. 228° ( $Me_2$  ester, m.p. 11°, b.p. 152—154°/30 mm.), is resolved into optical antimerides, and is thus the *trans*-form. The *brucine* salt,  $[\alpha]_D^{25} -117^\circ$ , gives 1-*trans*- $\Delta^2$ -tetrahydroterephthalic acid, m.p. 222°,  $[\alpha]_D^{25} -279^\circ$ ; an impure *d*-acid,  $[\alpha]_D^{25} +132^\circ$ , is also obtained. The "maleinoid" form, m.p. 161°, is not resolvable, and must be the *cis*-acid (II) ( $Me_2$  ester, b.p. 148°/30 mm.). (I) and (II) are hydrogenated (Pt) to *trans*- and *cis*-hexahydroterephthalic acid, respectively, m.p. 309° and 167°; the conclusions of Malachowski *et al.* (A., 1934, 1350) are thus confirmed. The primary and secondary dissociation consts. of (I) and (II) at 22° are: (I),  $K_1 1.18 \times 10^{-4}$ ,  $K_2 1.19 \times 10^{-5}$ ; (II),  $K_1 0.82 \times 10^{-4}$ ,  $K_2 0.81 \times 10^{-5}$ . The vals. of  $K_1/K_2$  indicate that the distance between dissociating H atom and negative charge on  $CO_2H \cdot C_6H_4 \cdot CO_2-$  is approx. 8.2 Å. in both (I) and (II) (cf. A., 1931, 1126); this is in agreement with models.

E. W. W.

**Grignard reactions with phthalic anhydride.** C. WEIZMANN, E. BERGMANN, and F. BERGMANN (J.C.S., 1935, 1367—1370).— $o$ - $C_6H_4(CO_2O)$  and its derivatives, including 4-methoxyphthalic anhydride, m.p. 97°, b.p. 202°/25 mm. (obtained from 4-hydroxyphthalic anhydride, b.p. 250—255°/24 mm., prepared from the acid, and  $CH_3N_2$ ), react with MgRBr to form derivatives of  $o$ - $C_6H_4(COR) \cdot CO_2H$  and of  $o$ - $C_6H_4(CR_2OH) \cdot CO_2H$  or its lactone. The following are new.  $o$ - $\beta$ -Naphthoylbenzoic acid, m.p. 128° (decomp.) (as hydrate), 168° (anhyd.); *di*- $\beta$ -naphthoylphthalide; *o*-(6-methoxy-2-naphthoyl)-, m.p. 166°, *o*-9-phenanthroyl-, m.p. 174—175°, 4(5?)-methoxy-2-benzoyl-, m.p. 167°, 4(5?)-methoxy-2- $\alpha$ -naphthoyl-, m.p. 196°, and tetrachloro-*o*-4-anisoyl-, m.p. 186—187°, -benzoic acid; tetrachlorodi-4-bromophenylphthalide, m.p. 144—145° (decomp.); and 2- $\alpha$ - (I), m.p. 228—229°, and 2- $\beta$ -naphthoyl-, m.p. 240°, and 2-4'-methoxybenzoyl-, m.p. 234°, -3-naphthoic acid. With  $AlCl_3$  and NaCl, *o*- $\alpha$ -naphthoylbenzoic acid yields naphthacenequinone, new m.p. 276°. In  $H_2SO_4$ , (I) condenses to 1:2:6:7-dibenzanthraquinone, m.p. 227°.

E. W. W.

**Synthesis of rotenone and its derivatives.**  
**VII. Tetrahydrotubaic acid.** A. ROBERTSON and G. L. RUSBY (J.C.S., 1935, 1371—1373).—A new synthesis of tetrahydrotubaic acid (I), of which the *Ac*, derivative, new m.p. 140—141°, is obtained by oxidation ( $KMnO_4$ ) of the *Ac*, derivative, m.p. 47.5°, of tetrahydrotuba-aldehyde (2:4-dihydroxy-3-isoamylbenzaldehyde) (II), m.p. 112.5° (semicarbazone, m.p. 198°), (II) being prepared  $[Zn(CN)_2]$  from tetrahydrotubanol (A., 1933, 1169). The orientation of (I) is established by converting (II) ( $MeI$ - $K_2CO_3$  in  $Ac_2O$ )

into 2-hydroxy-4-methoxy-3-isoamylbenzaldehyde, b.p. 180°/15 mm. (semicarbazone, m.p. 193°), since this condenses with  $\omega$ -methoxyacetoveratrone to 3:7:3':4'-tetramethoxy-8-isoamylflavylum chloride (ferrichloride, m.p. 131—132°); (III) is acetylated, oxidised, and deacetylated to 2-hydroxy-4-methoxy-3-isoamylbenzoic acid. The azlactone of asaraldehyde (A., 1932, 860) is converted by NaOH,  $SO_2$ , and HCl into 2:4:5-trimethoxyphenylpyruvic acid, m.p. 198°, of which the oxime treated with  $Ac_2O$  yields 2:4:5-trimethoxyphenylacetone nitrile, m.p. 85°, hydrolysed to the -acetic acid, new m.p. (hydrate) 81°, (anhyd.) 106°.

E. W. W.

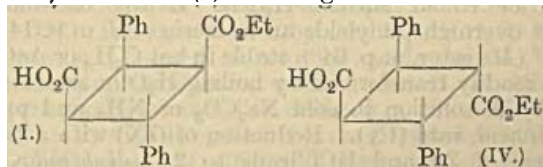
**Synthesis in the sex hormone group.** A. COHEN (Nature, 1935, 136, 869—870; A., 1935, 752).—At room temp., 1-vinylnaphthalene readily combines with maleic anhydride (I) giving dihydrophenanthrene-1:2-dicarboxylic anhydride (II), m.p. 186—189° (decomp.), dehydrogenated (Pt-black; 300°) to phenanthrene-1:2-dicarboxylic anhydride, m.p. 310° (corr.) (Fieser *et al.*, *ibid.*, 1495). Dehydration 6-methoxy-1-naphthylethyl alcohol yields 1-vinyl-6-methoxynaphthalene, m.p. 41—42° (picrate, m.p. 114.5°), which combines with (I) forming the OMe-derivative of (II), m.p. 171—175° (decomp.). This is dehydrogenated by Pt-black at 280—300° to 7-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p. 260° (corr.).

L. S. T.

**Diphenylmalonic acid.** H. J. MORSMAN (Helv. Chim. Acta, 1935, 18, 1466—1468).—Prolonged shaking with  $H_2O$  converts  $CPh_2(COCl)_2$  into cryst. diphenylmalonic acid, m.p. indefinite owing to rapid loss of  $CO_2$  to give  $CHPh_2 \cdot CO_2H$ .

J. W. B.

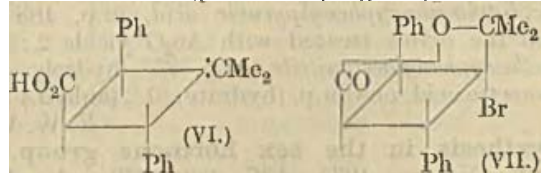
**Degradation of  $\gamma$ -truxillic acid to a diphenylcyclobutanemonocarboxylic acid.** XVIII. R. STOERMER and H. STROH [with, in part, H. ALBERT]. Unique position of  $\epsilon$ -truxillic acid; truxilketones. XIX. R. STOERMER and K. CRUSE. Semitruxonic acids of the truxillic acid series and the missing truxone, *peri*-truxone. XX. R. STOERMER and F. MÖLLER (Ber., 1935, 68, [B], 2102—2111, 2117—2124, 2125—2134).—XVIII. The degradation of  $\gamma$ -truxillic acid without contraction of the ring is effected through the stages:  $>CH \cdot CO_2H \rightarrow >CH \cdot CMe_2 \cdot OH \rightarrow >C \cdot CMe_2 \rightarrow >CO$ . Treatment of Et H  $\gamma$ -truxillate (I) with  $MgMeI$  affords 3 $\epsilon$ - $\alpha$ -hydr-



axisopropyl-2 $\epsilon$ -4'-diphenylcyclobutane-1 $\epsilon$ -carboxylic acid (II), m.p. 198° (*Me*, m.p. 102—103°, and *Et*, m.p. 77—78°, ester). Similar treatment of the *Et*, ester leads to 1 $\epsilon$ :3 $\epsilon$ -di- $\alpha$ -hydroxyisopropyl-2 $\epsilon$ :4'-diphenylcyclobutane (tetramethyl- $\gamma$ -truxilldiol), m.p. 127—128°, with the lactone (III), m.p. 148°, and ester of (II) into which they are converted by hydrolysis. Under similar conditions, Et H  $\alpha$ -truxillate (IV), m.p. 171°, best obtained by partial esterification of the corresponding acid, is transformed into 3 $\epsilon$ - $\alpha$ -hydroxyisopropyl-2 $\epsilon$ :4'-diphenylcyclobutane-1 $\epsilon$ -carboxylic acid (V), m.p. 174—175° (*Me* ester, m.p.



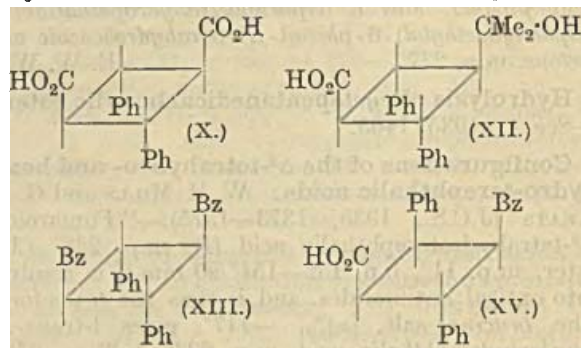
81—82°). (I), Mg, and EtBr give 3 $\epsilon$ - $\alpha$ -hydroxy- $\alpha$ -ethyl-*n*-propyl-2 $\epsilon$ : 4'-diphenylcyclobutane-1'-carboxylic acid, m.p. 216—217° (*Me* ester, m.p. 141°); 3 $\epsilon$ - $\alpha$ -hydroxy- $\alpha$ -ethyl-*n*-propyl-2 $\epsilon$ : 4'-diphenylcyclobutane-1'-carboxylic acid has m.p. 151° (*Me* ester, m.p. 97—98°). Treatment of (II), (III), or (V) with AcOH at 210° yields 3-isopropylidene-2 $\epsilon$ : 4'-diphenylcyclobutane-1'-carboxylic acid (VI), m.p. 143—144°



(sparingly sol. *Na* salt), best obtained by passing HCl rapidly through a solution of (II) in boiling conc. HCl. It is thus established that there is no alteration in the spatial distribution of the other groups around the cyclobutane ring. Bromination of (VI) in CHCl<sub>3</sub> affords a single, saturated bromolactone [probably (VII)], m.p. 157—158°, which is not debrominated in acid or neutral solution, but with Zn and AcOH or Al-Hg yields small amounts of (VI) and is converted by red P and HI (*d* 1.5) into a Br-free lactone, m.p. 161—162°, probably formed by ring fission, and an acid, C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>I, m.p. 210—211° (*Na* salt); treatment of it with alkali gives a CO-acid, an unsaturated acid, and a OH-lactone of unexplained structure. Treatment of the diol with AcOH at 210° yields 1:3-dusopropylidene-2 $\epsilon$ : 4'-diphenylcyclobutane, b.p. 202°/11 mm., ozonised to (?) isopropylidenediphenylcyclobutanone, m.p. 106—109°. Proof that the acid (VI) contains a semicyclic double linking is afforded by the production of CMe<sub>2</sub> after ozonisation. The ozonide decomposes very rapidly in CHCl<sub>3</sub>, AcOH, or EtOAc, and when treated with alkali gives phenylbenzylsuccinic acid (VIII), m.p. 183—184° (*Me* ester, m.p. 125°). If ozonisation is effected in EtOAc and the product is immediately catalytically hydrogenated, diphenylcyclobutanonecarboxylic acid (IX), m.p. 98° (*Me* ester, m.p. 72°; *p*-nitrophenylhydrazine, m.p. 184°), is almost quantitatively obtained; it appears unsaturated towards KMnO<sub>4</sub> and reduces ammoniacal Ag solution, but does not give the Angeli-Rimini test or colour fuchsin-H<sub>2</sub>SO<sub>3</sub>. If the ozonide is kept overnight, it yields an isomeric acid, m.p. 141—142° (*Me* ester, m.p. 64°), stable in hot C<sub>6</sub>H<sub>6</sub> or AcOH, but readily transformed by boiling H<sub>2</sub>O or aq. media, or by dissolution in cold Na<sub>2</sub>CO<sub>3</sub> or NH<sub>3</sub> and pptn. with acid, into (IX). Reduction of (IX) with a large excess of Zn and HCl leads to 2:4-diphenylcyclobutane-1-carboxylic acid, m.p. 111—112° (anilide, m.p. 165—166°).

XIX.  $\epsilon$ -Truxillic acid (X) is converted by boiling Ac<sub>2</sub>O into the polymeric  $\epsilon$ -anhydride, transformed by warm NH<sub>2</sub>Ph into a mixture of (X), its dianilide, and anilic acid. Repeated distillation of (X) under 0.4 mm. yields *peri*- and  $\gamma$ -truxillic anhydride, thus affording the first instance of a change of the  $\epsilon$ -configuration. *Me H*  $\epsilon$ -truxillate (XI), m.p. 131° (*Na* and *Ca* salts), obtained by the action of HNO<sub>3</sub> on *Me*  $\epsilon$ -truxillanilate or by half-hydrolysis of Me<sub>2</sub>  $\epsilon$ -truxillate, passes when heated into MeCl and CHPh:CH·CO<sub>2</sub>H.

It is considered therefore that monomeric  $\epsilon$ -truxillic anhydride cannot exist. Interaction of MgMeI and

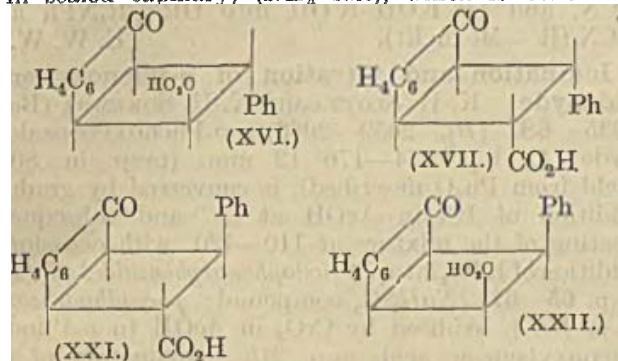


(XI) gives comparatively very large quantities of  $\epsilon$ -tetramethyltruxilldiol, m.p. 146°, and 3 $\epsilon$ - $\alpha$ -hydroxy-isopropyl-2 $\epsilon$ : 4'-diphenylcyclobutane-1'-carboxylic acid (XII), m.p. 145° (*Ca* salt), which gives CHPh:CH·CO<sub>2</sub>H and a non-cryst., non-hydrolysable substance of high b.p. when its dehydration is attempted by the methods used for the  $\gamma$ -acid (see above). Unexpectedly, treatment of (XI) with MgPhBr leads to (X) and 1 $\epsilon$ : 3 $\epsilon$ -dibenzoyl-2 $\epsilon$ : 4'-diphenylcyclobutane (XIII), m.p. 207—208°, which passes when heated with KOH-EtOH and NH<sub>2</sub>OH, but not with KOH-EtOH only, into an isomeric truxillketone, m.p. 222°; both ketones yield Ph styryl ketone when cautiously distilled under atm. pressure.

Treatment of  $\gamma$ -truxillic anhydride (XIV) with AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> at 100° gives 3 $\epsilon$ -benzoyl-2 $\epsilon$ : 4'-diphenylcyclobutane-1'-carboxylic acid (XV), m.p. 227° [sparingly sol. *Na* and NH<sub>4</sub> salts; phenylhydrazine, m.p. 100° (much decomp. with production of lactam); *Me*, m.p. 169°, and *Et*, m.p. 162°, ester], which is depolymerised when heated or treated with conc. H<sub>2</sub>SO<sub>4</sub> to CHPh:CH·CO<sub>2</sub>H and CHPh:CHBz. The corresponding chloride, m.p. 150—152°, is transformed by AlCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> into much non-cryst. matter and a substance, m.p. 92—93°. The behaviour of (XIV) towards AlCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> depends greatly on the quality of the AlCl<sub>3</sub>, temp., and duration of action. With somewhat weathered AlCl<sub>3</sub>, a truxillketone, m.p. 77—78°, and a substance (C<sub>11</sub>H<sub>6</sub>O<sub>2</sub>)<sub>n</sub>, m.p. 195° (possibly Stobbe's truxillketone D), are obtained in small yield.

XX. Treatment of  $\gamma$ -truxillic acid with HCl and cold MeOH gives the *Me H* ester (very sparingly sol. *Na* salt), converted by SOCl<sub>2</sub> in boiling C<sub>6</sub>H<sub>6</sub> into the corresponding chloride, m.p. about 86°, which is transformed by AlCl<sub>3</sub> in CS<sub>2</sub> into *Me*  $\gamma$ -truxonate. The latter is hydrolysed by KOH-EtOH to  $\gamma$ -truxonic acid (XVI), m.p. 152° (*Me* ester, m.p. 127—128°; oxime, m.p. 207°; amide, m.p. 236—237°; phenylhydrazine, m.p. 225°). *Me H*  $\alpha$ -truxillate, m.p. 195° (very sparingly sol. *Na* salt), is similarly transformed through the chloride into *Me*  $\alpha$ -truxonate, m.p. 186°, hydrolysed by alkali to (XVI), but by boiling AcOH containing a little H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O to  $\alpha$ -truxonic acid (XVII), m.p. 216° (sparingly sol. *Na*, *Ca*, and NH<sub>4</sub> salts; phenylhydrazine, m.p. 239°), converted by SOCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>, and thence by AlCl<sub>3</sub> in CS<sub>2</sub>, into  $\alpha$ -truxone. *peri*-Truxillic anhydride, m.p. 287°, is best obtained by heating the  $\gamma$ -anhydride under N<sub>2</sub> at about 280°, and converting the crude product by NH<sub>3</sub>-EtOH into

peri-truxillamic acid (XVIII), m.p. 256.5° (decomp. in sealed capillary) ( $\text{NH}_4$  salt), which is boiled in



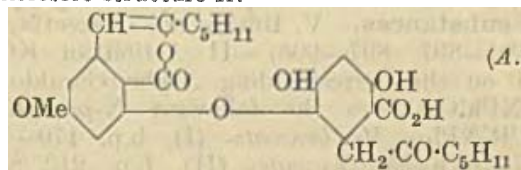
$\text{AcOH}$  or treated with  $\text{HNO}_2$  in  $\text{AcOH}$ . It is transformed by  $\text{CH}_2\text{N}_2$  in  $\text{C}_2\text{H}_4(\text{OH})_2$  into *Me H* peri-truxillamate, m.p. 197—198°, which with  $\text{HNO}_2$  in  $\text{AcOH}$  affords homogeneous *Me H* peri-truxillate. Treatment of (XVIII) with conc.  $\text{NH}_3$  at 110° gives unimol. peri-truxillimide, m.p. 237°, and epitruixill-b-amic acid (XIX), m.p. 263°, whereas with boiling 10%  $\text{NaOH}$  it yields epitruixillic acid, m.p. 286°. With  $\text{CH}_2\text{N}_2$  in  $\text{MeOH}$  (XIX) gives *Me* epitruixillamate, m.p. 228°, transformed by  $\text{HNO}_2$  in  $\text{AcOH}$  into *Me H* epitruixillate, m.p. 204.5°, identical with that obtained by half-hydrolysis of  $\text{Me}_2$  epitruixillate. The isomeric b-ester (XX), m.p. 141° (sparingly sol. *Na* salt), is obtained by saturating a suspension of the *epi*-acid in  $\text{MeOH}$  at 20° with  $\text{HCl}$ . (XX) is converted by  $\text{SOCl}_2$  and thence by the Friedel-Crafts reaction into *Me* epitruixonate, m.p. 106—107°, smoothly hydrolysed by  $\text{KOH-MeOH}$  to epitruixononic acid (XXI), m.p. 160° [oxime, m.p. 260° (decomp.)]. peri-Truxonic acid (XXII), m.p. 221—224° [phenylhydrazone, m.p. 189° (indef.)], is obtained among other products by the action of  $\text{AlCl}_3$  in  $\text{CS}_2$  on peri-truxillic anhydride and is converted through the chloride into peri-truxone, m.p. 194°, transformed by  $\text{NHPh-NH}_2$  in  $\text{AcOH}$  into the monophenylhydrazone, m.p. 217°, and by  $\text{NHPh-NH}_2$  in  $\text{N}_2$  at 150—160° into the diphenylhydrazone, m.p. about 280° (decomp.). Its isomerisation into  $\alpha$ -truxone by conc.  $\text{HCl}$  at 180° could not be established definitely. H. W.

**Phenylbenzylsuccinic acids.** R. STÖRMER and H. STROH (Ber., 1935, 68, [B], 2112—2116).— $\text{Et}_3\alpha$ -phenyl- $\beta$ -benzylethane- $\alpha\beta\beta$ -tricarboxylate, b.p. 232°/3 mm., m.p. 48°, from  $\text{CHPhBr}\cdot\text{CO}_2\text{Et}$  and  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , is hydrolysed by 18%  $\text{HCl}$  at 180—190° to phenylbenzylsuccinic acid (I), m.p. 176° (*Me* ester, m.p. 89—90°), whereas hydrolysis with  $\text{AcOH}$  and 50%  $\text{H}_2\text{SO}_4$  at 120° leads to the isomeric phenylbenzylsuccinic acid (II), m.p. 183—184° (*Me* ester, m.p. 125°, identical with that obtained by degradation of diphenylcyclobutanonecarboxylic acid obtained from  $\alpha$ - or  $\gamma$ -truxillic acid (preceding abstract). Short treatment of (II) with boiling  $\text{AcCl}$  leads to the corresponding anhydride, m.p. 92°, whereas (I) with warm  $\text{AcCl}$  affords a non-cryst. mixture of anhydrides converted by  $\text{H}_2\text{O}$  into a mixture of (I) and (II). Boiling  $\text{Ac}_2\text{O}$  containing  $\text{NaOAc}$  converts either acid into phenylbenzylangelic-lactone (III),  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO})\text{CPh}\cdot\text{CMe}>\text{O}$  m.p. 96° hydro-

lysed by  $\text{KOH-MeOH}$  to  $\beta$ -phenyl- $\alpha$ -benzyl-lævulic acid, m.p. 120—121° (*Me* ester, m.p. 81—82°), transformed by  $\text{NHPh-NH}_2$  in  $\text{AcOH}$  into 2:5-diphenyl-4-benzyl-6-methylpyridazin-3-one, m.p. 148—149°, and oxidised by  $\text{NaOBr}$  to (I). The change is therefore  $\text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CHPh}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CPhAc}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CHPhAc} \rightarrow$  (III). This view is supported by the observation that whereas  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is stable towards boiling  $\text{Ac}_2\text{O}$  containing  $\text{NaOAc}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  is converted into  $\text{CH}_2\text{Ph}\cdot\text{COMe}$  in very good yield. H. W.

**Oxidation of bisphenylpyruvic [ $\alpha$ -hydroxy- $\gamma$ -keto- $\beta$ -phenyl- $\alpha$ -benzylglutaric] acid.** J. JARROUSSE (Compt. rend., 1935, 201, 676—677).—Bisphenylpyruvic acid with  $\text{KMnO}_4$  in alkali at 0° affords  $\alpha\gamma$ -diketo- $\beta\delta$ -diphenylvaleric acid, which easily loses  $\text{CO}_2$  to give  $\beta$ -keto- $\alpha\gamma$ -diphenylbutaldehyde, m.p. 114° [semicarbazone, m.p. 200° (decomp.)], oxidised by I in presence of  $\text{Na}_2\text{CO}_3$  to a substance, m.p. 190° (decomp.). J. L. D.

**Lichen substances. LIX. Non-existence of  $\gamma$ -collatolic acid. LX. Microphylllic acid and its fission products. LXI. Olivetoric acid.** III. Y. ASAHINA and F. FUJIKAWA (Ber., 1935, 68, [B], 2020—2021, 2022—2025, 2026—2028).—LIX (cf. A., 1933, 713).— $\alpha$ -Collatolic acid (I) in moderately conc.  $\text{NaHCO}_3$  solution is slowly converted into  $\beta$ -collatolic acid (II). (II) is not a natural product, but is formed during the alkaline hydrolysis of *Me*  $\alpha$ -collatolate. *Me*  $\beta$ -collatolate, m.p. 75°, is formed by the restricted action of  $\text{CH}_2\text{N}_2$  on (II), whereas prolonged action gives the *Me* ester *Me*<sub>2</sub> ether (III), m.p. 114°, also obtained similarly from (I).  $\gamma$ -Collatolic acid is (II) more or less contaminated with (I), since homogeneous (II) can be isolated therefrom by crystallisation from  $\text{C}_6\text{H}_6$ , and treatment of it with an excess of  $\text{CH}_2\text{N}_2$  gives (III). (II) has therefore structure A.



LX (cf. A., 1935, 490). Microphylllic acid (IV), m.p. 116°, is transformed by boiling  $\text{HCO}_2\text{H}$  into olivetonide (V) and olivetonide *p*-Me ether (VI). (IV) and  $\text{Ac}_2\text{O}$  containing a little conc.  $\text{H}_2\text{SO}_4$  afford anhydrodiacetylmicrophylllic acid, m.p. 98°. Hydrolysis of (IV) with 11%  $\text{NaOH}$  gives (VI) and olivetonic acid (VII), m.p. 159—160° (*Me* ester, m.p. 85—86°), also obtained by the action of  $\text{KOH}$  on (V). (IV) is decomposed by excess of  $\text{CH}_2\text{N}_2$ , but treatment with  $\text{Ag}_2\text{O}$  and  $\text{MeI}$  gives *Me* microphyllate *Me*<sub>2</sub> ether (VIII), m.p. 89—90°, hydrolysed by boiling 95%  $\text{HCO}_2\text{H}$  to olivetonide *Me*<sub>2</sub> ether, m.p. 94° [also obtained by treatment of (VI) with  $\text{Ag}_2\text{O}$  and  $\text{MeI}$ ], and olivetonide *o*-Me ether, m.p. 146—147°, converted by  $\text{CH}_2\text{N}_2$  into (VIII). The following derivatives of (V) and (VII) are described: *p*-acetylolivetonic acid, m.p. 55°, and its *o*-Me ether, m.p. 84°, obtained by means of  $\text{Ag}_2\text{O}$  and  $\text{MeI}$ ; diacetylolivetonic acid, m.p. 59°; *o*-acetylolivetonic acid *p*-Me ether, m.p. 60—61°;



olivetononic acid *p*-, m.p. 94—95°, and *o*-Me ether, m.p. 119—120°; *Me olivetonate Me ether*, m.p. 80°.

LXI. Extraction of the thalli of *Parmelia olivetorum*, Nyl, with Et<sub>2</sub>O and treatment of the extract with NaHCO<sub>3</sub> yields (?) chloroatranorin and olivetoric acid, m.p. 150—151°. The latter is converted by cautious treatment with CH<sub>3</sub>N<sub>3</sub> into the *Me* ester, m.p. 134°, and by Ag<sub>2</sub>O and MeI into *Me olivetorate Me<sub>2</sub> ether*, m.p. 44—7.5°, alkaline hydrolysis of which affords olivetonic acid *Me<sub>2</sub> ether*, m.p. 92°, and olivetolcarboxylic acid *o*-Me ether, m.p. 105°. H. W.

Bile acids. XLVII. Preparation of the compound C<sub>24</sub>H<sub>30</sub>O<sub>10</sub>N<sub>2</sub> (bilianic acid series). M. SCHENCK (Z. physiol. Chem., 1935, 237, 105—112).—The ketolactamtricarboxylic acid, C<sub>24</sub>H<sub>35</sub>O<sub>8</sub>N (A., 1931, 841), purified by KMnO<sub>4</sub> in aq. Na<sub>2</sub>CO<sub>3</sub>, yields with 57% HNO<sub>3</sub> the compound C<sub>24</sub>H<sub>30</sub>O<sub>10</sub>N<sub>2</sub> (I), which with hot 90% H<sub>2</sub>SO<sub>4</sub> affords the "β-acid," (C<sub>24</sub>H<sub>30</sub>O<sub>10</sub>N<sub>2</sub>, decomp. 203° (A., 1930, 1435), and with hot HCl, the aminoamide, C<sub>24</sub>H<sub>38</sub>O<sub>11</sub>N<sub>2</sub>. The data support a lactamamide rather than the amino-nitrile structure for (I) (cf. A., 1932, 742).

F. O. H.

Cannizzaro reaction. C. D. NENITZESCU and I. GAVAT (Bul. Soc. Chim. Romania, 1934, 16, [A], 42—46).—The velocity of the Cannizzaro reaction with PhCHO in 80% MeOH at 20° is greatly increased by increase in the concn. of KOH from 0.5*N* to 1.6*N* and slightly (catalytically) by Cu at 50°. NMe<sub>4</sub>Et·OH effects the reaction, but Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>HPO<sub>4</sub> do not. Equimol. mixtures of PhCHO with CH<sub>3</sub>O or OMe·C<sub>6</sub>H<sub>4</sub>·CHO give both pairs of acids and alcohols. A large excess of CH<sub>3</sub>O gives almost exclusively HCO<sub>2</sub>H and the aromatic alcohol (CH<sub>3</sub>·Ph·OH, OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OH, or *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·OH).

R. S. C.

Nitrones. A new transposition reaction. II. III. Transformation [of oximes] into cyano-derivatives of anils. Simple method of preparing these substances. V. BELLAVITA (Gazzetta, 1935, 65, 889—897, 897—906).—II. Action of KCN in MeOH on the corresponding *N*-phenylaraldoximes, CH<sub>3</sub>R·NPh·O, gives the following *N*-phenylimides, OMe·CR·NPh. *Me benzoate*- (I), b.p. 170—175°/9 mm., *Me p-chlorobenzoate*- (II), b.p. 212°/8 mm. (obtained from *N*-phenyl-*p*-chlorobenzaldoxime, m.p. 153—154°), *Me anisate*- (III), b.p. 212°/8.5 mm.; *Me cinnamate*- (IV), m.p. 70°, *Me piperonylate*-, b.p. 224°/4 mm., and *Me piperonylacrylate*-, b.p. 242°/5 mm., *N*-phenylimides. These are hydrolysed to the ester (or acid), and aniline; (I) to (IV) also give the anilide.

III. *N*-Phenylbenzaldoxime triturated with KCN in MeOH at room temp. yields ω-cyanobenzaldanil, (N·CPh·NPh, m.p. 73.5°, an intermediate compound of the reaction described in the preceding abstract. The following are prepared similarly. ω-Cyano-*p*-chlorobenzaldanil, m.p. 108° (converted by KOH·EtOH into Et *p*-chlorobenzoate-*N*-phenylimide, b.p. 190—192°/10 mm.); ω-cyano-*o*-, -*m*-, and -*p*-nitrobenzaldanil, m.p. 105—106°, 101—102°, and 126.5°, respectively; ω-cyanosalicylaldanil, m.p. 96°; ω-cyanocinnamaldanil, m.p. 73—74°; ω-cyanoanisaldanil, m.p. 119°; ω-cyanopiperonaldanil, m.p. 139—140°;

and ω-cyanopiperonylacaldanil, m.p. 160—161°. These compounds are converted by acid into NH<sub>2</sub>Ph and RCN, and by KOH·R'OH into OR'·CR·NPh and KCN (R'=Me or Et).

E. W. W.

Iodination and nitration of *p*-phenoxybenzaldehyde. K. H. SLOTTA and K. H. SOREMB (Ber., 1935, 68, [B], 2059—2066).—*p*-Phenoxybenzaldehyde (I), b.p. 174—176°/12 mm. (prep. in 80% yield from Ph<sub>2</sub>O described), is converted by gradual addition of ICl in AcOH at 50° and subsequent heating of the mixture at 110—120° with occasional addition of *i*-iodophenoxybenzaldehyde (II), m.p. 65—67° (NaHSO<sub>3</sub> compound; phenylhydrazone, m.p. 150°), oxidised by CrO<sub>3</sub> in AcOH to *p*-4'-iodophenoxybenzoic acid, m.p. 215°. Iodination of (I) could not be effected with I+HIO<sub>3</sub> in aq. EtOH and (II) is not formed by treatment of *p*-C<sub>6</sub>H<sub>4</sub>I·OPh with AlCl<sub>3</sub>, HCl, and HCN. Nitration of (II) with conc. H<sub>2</sub>SO<sub>4</sub>·HNO<sub>3</sub> (*d* 1.41) gives a complex mixture of products, whereas addition of (II) to HNO<sub>3</sub> (*d* 1.410) at 15° affords *p*-4'-nitrophenoxybenzaldehyde, m.p. 107—108° (phenylhydrazone, m.p. 160°), also obtained with *p*-2'-nitrophenoxybenzaldehyde, m.p. 84—86°, from *p*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub> and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO. Under defined conditions (I) is transformed by H<sub>2</sub>SO<sub>4</sub>·HNO<sub>3</sub> into 3:2':4'-trinitro-4-phenoxybenzaldehyde (III), m.p. 169° (phenylhydrazone, m.p. 190—192°), also obtained by nitration of 2':4'-dinitro-4-phenoxybenzaldehyde; its constitution follows from its non-identity with 2':4':6'-trinitro-4-phenoxybenzaldehyde, m.p. 128° (phenylhydrazone, m.p. 225°), derived from picryl chloride and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO. Oxidation of (III) with CrO<sub>3</sub> in AcOH affords 3:2':4'-trinitro-4-phenoxybenzoic acid, m.p. 205—207°, converted by NaOH into 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·OH and 3-nitro-4-hydroxybenzoic acid.

H. W.

Synthesis of polyterpenoid compounds. II. J. W. COOK and C. A. LAWRENCE (J.C.S., 1935, 1637—1638; cf. A., 1935, 756).—β-Δ<sup>1</sup>-cyclohexenylethyl bromide (improved prep.) when heated (water-bath; 120 hr.) with CHK(CO<sub>2</sub>Et)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> affords Et β-(Δ<sup>1</sup>-cyclohexenylethyl)malonate, b.p. 148°/1—1.5 mm., hydrolysed to the acid, m.p. 123—124°, which when heated at 180° for ½ hr. and distilled in vac. yields γ-Δ<sup>1</sup>-cyclohexenylbutyric acid, b.p. 122—125°/0.8 mm. (*p*-phenylphenacyl ester, m.p. 79.5—81°). This was converted into the acid chloride which with CS<sub>2</sub>·SnCl<sub>4</sub> at -7° to -10° yields Δ<sup>9:10</sup>-α-octalone (A., 1933, 704).

H. G. M.

Nitro- and bromonitro-derivatives of *p*-aminoacetophenone. C. W. RAADSVELD (Rec. trav. chim., 1935, 54, 813—827).—With HNO<sub>3</sub> (*d* 1.52) at -15° to -20° *p*-C<sub>6</sub>H<sub>4</sub>Ac·NHAc affords its 3-NO<sub>2</sub> and 3:5-(NO<sub>2</sub>)<sub>2</sub>-derivatives, but with HNO<sub>3</sub>·Ac<sub>2</sub>O at 0° a 90% yield of the 3-NO<sub>2</sub>-compound (I) is obtained. With HNO<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub> at 100° picric acid is the only product isolated. *Me p*-acetylphenylcarbamate, m.p. 162° [obtained from *p*-C<sub>6</sub>H<sub>4</sub>Ac·NH<sub>2</sub> (II) and ClCO<sub>2</sub>Me·Na<sub>2</sub>CO<sub>3</sub> in boiling Et<sub>2</sub>O], with HNO<sub>3</sub> (*d* 1.45) gives its 2-NO<sub>2</sub>-derivative (III), m.p. 107°, but with HNO<sub>3</sub> (*d* 1.52) at 0° the 2:6-(NO<sub>2</sub>)<sub>2</sub>-derivative (IV), m.p. 213°, is obtained. Et *p*-acetylphenylcarbamate, m.p. 159°, and its 2-NO<sub>2</sub>- (V), m.p. 111°, and 2:6-(NO<sub>2</sub>)<sub>2</sub>-derivative (VI), m.p. 176°, are similarly obtained.

If the nitration products of these carbamates are heated to 50° before pouring on ice, *substances*, m.p. 200° and 135°, respectively (from the Me ester), and m.p. 153° and 113° (Et ester), are obtained. Nitration of *N*-4-acetylphenyl-*N'*-ethylcarbamide, m.p. 157° [from (II) and EtNCO in dry C<sub>6</sub>H<sub>6</sub> at 100°] with HNO<sub>3</sub> (*d* 1.45) at 0° affords *N*-(2-nitro-4-acetyl)-*N'*-nitro-*N'*-ethylcarbamide, C<sub>6</sub>H<sub>4</sub>Ac(NO<sub>2</sub>)·NH·CO·NEt·NO<sub>2</sub> (VII), m.p. 91°, whereas HNO<sub>3</sub> (*d* 1.52) gives the corresponding 2 : 6-*NO*<sub>2</sub>-nitroamine (VIII), m.p. 120° (decomp.), converted by the appropriate ROH, respectively, into carbamates. Hydrolysis of (VII) with boiling aq. COMe<sub>2</sub>, or (III) or (V) with conc. H<sub>2</sub>SO<sub>4</sub> at 100°, or of (I) with boiling 6*N*-HCl, affords 3-nitro-4-aminoacetophenone (VIII), the 3 : 5-(*NO*<sub>2</sub>)<sub>2</sub>-derivative, m.p. 176° (*Ac* derivative, m.p. 222°; cf. above), being obtained similarly from (IV) or (VI). Bromination of *p*-C<sub>6</sub>H<sub>4</sub>Ac·NHAc gives the 3-Br-compound, hydrolysed by 6*N*-HCl to the hydrochloride, decomp. <100° (Raiford *et al.*, A., 1928, 303, give m.p. 155—156°), of 3-bromo-4-aminoacetophenone, but with Br·AcOH at 100° the ω-Br-compound is obtained. *p*-C<sub>6</sub>H<sub>4</sub>Ac·NH<sub>2</sub> with CH<sub>2</sub>Br·COCl·AcOH·NaOAc at 0° gives *p*-bromoacetamidoacetophenone, m.p. 157°. With HNO<sub>3</sub> (*d* 1.52) at -10° to -15°, 3-bromo-4-acetamidoacetophenone gives its 5-*NO*<sub>2</sub>-derivative, m.p. 203°, hydrolysed (conc. H<sub>2</sub>SO<sub>4</sub> or 6*N*-HCl in presence of EtOH) to 3-bromo-5-nitro-4-aminoacetophenone, m.p. 181°, also obtained by the action of Br·AcOH on (VIII). The structures of these derivatives are confirmed by elimination of the NH<sub>2</sub> group after diazotisation, to give known COPhMe derivatives.

J. W. B.

**Derivatives of *p*-aminoacetophenone.** C. W. RAADSVELD (Rec. trav. chim., 1935, 54, 827—832).—Condensation of *p*-C<sub>6</sub>H<sub>4</sub>Ac·NH<sub>2</sub> (I) with the appropriate carbimide affords *p*-acetylphenylcarbamide, m.p. 183° (lit., m.p. 148°), *s*-*p*-acetylphenylphenyl-, m.p. 195°, and *s*-*p*-acetylphenyl- $\alpha$ -naphthylcarbamide, m.p. 209°. With PhNCS a *substance*, m.p. 195° (not the thiocarbamide), is obtained. Condensation of (I) with the appropriate aromatic compound containing reactive Cl affords *p*-(2 : 4-dinitroanilino)-, m.p. 192° (lit., m.p. 185°), *p*-(2 : 4 : 6-trinitroanilino)-, and *p*-(2 : 4-dinitro- $\alpha$ -naphthylamino)-, m.p. 162°, -acetophenone. With CO(NH<sub>2</sub>)<sub>2</sub> at 200—215° (I) gives a *substance*, decomp. 280° (block), and, with CS<sub>2</sub>·EtOH·KOH, a yellow *substance*, m.p. 230—235°. The following ketazines (with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub>) and phenylhydrazones are prepared: the *ketazine* of 3-nitro-4-amino-, m.p. 350° (*phenylhydrazone*, m.p. 135—138°); 3-nitro-4-acetamido-, m.p. 270° (*phenylhydrazone*, m.p. 160°); 3 : 5-dinitro-4-amino-, m.p. 345° (*phenylhydrazone*, m.p. 245°); 3-bromo-4-acetamido-, m.p. 80°; 5-bromo-3-nitro-4-amino-, m.p. 315° (*phenylhydrazone*, m.p. 80°); and 5-bromo-3-nitro-4-acetamido-, m.p. > 350°, -acetophenone.

J. W. B.

**Bromination of cholestanone and coprostanone;  $\Delta^{1:2}$ -cholesten-3-one.** A. BUTENANDT and A. WOLFF (Ber., 1935, 68, [B], 2091—2094).—The action of 1 mol. of Br on 3-keto-compounds of the sterol group results preferentially in substitution at C<sub>2</sub> or C<sub>4</sub> according as the initial ketone belongs to

the dihydrocholesterol (*allo* or *trans*) or the coprosterol (*cis*) series. Treatment of coprostanone with Br in AcOH containing traces of HBr gives 4-bromo-coprostanone, m.p. 110—111°, converted by boiling anhyd. C<sub>5</sub>H<sub>5</sub>N into cholestenone, m.p. 79—80° (yield 30%). Under similar conditions, cholestanone affords 2-bromocholestanone, m.p. 169—170° (apparently not homogeneous), largely resinified by boiling quinoline and transformed by boiling anhyd. C<sub>5</sub>H<sub>5</sub>N into a *compound*, m.p. > 300°. It is converted by AcOH·KOAc at 200° into  $\Delta^{1:2}$ -cholesten-2-one, m.p. 111—112°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -32.1° in EtOH (*oxime*, m.p. 146—147°).

H. W.

**Substituted unsaturated cyclic ketones.** A. COHEN and J. W. COOK (J.C.S., 1935, 1570—1572).—Unsaturated cyclic ketones are obtained by elimination of HCl from nitrosochlorides and hydrolysis of the resulting oximes. 1- $\beta$ -Phenylethyl- $\Delta^1$ -cyclohexene nitrosochloride, m.p. 139—140° (lit. 118—119°), when boiled with C<sub>5</sub>H<sub>5</sub>N for 2.5 hr. yields 2- $\beta$ -phenylethyl- $\Delta^2$ -cyclohexenoneoxime, m.p. 118—120°, hydrolysed by boiling 6*N*-H<sub>2</sub>SO<sub>4</sub> to the *ketone*, b.p. 125—130°/0.7 mm. (*semicarbazone*, m.p. 188—190°). Similarly 1-( $\beta$ -1'-naphthylethyl)- $\Delta^1$ -cyclopentene nitrosochloride, m.p. 108—110° (obtained from the cyclopentene, AcOH, Et<sub>2</sub>O, amyl nitrite, and HCl), when boiled with C<sub>5</sub>H<sub>5</sub>N for 5 min. affords 2-( $\beta$ -1'-naphthylethyl)- $\Delta^2$ -cyclopentenoneoxime, m.p. 106.5—107.5°, hydrolysed to the *ketone*, b.p. 165—167°/0.3 mm. (*semicarbazone*, m.p. 226—227°), which gave no oestrous response when injected into ovariectomised mice. All attempts to cyclise these ketones failed.

H. G. M.

**Benzanthrone derivatives. III. Autoxidisable dihydrobenzanthrone.** E. CLAR (Ber., 1935, 68, [B], 2066—2070; cf. A., 1932, 1134).—Benzanthrone (I) is reduced by Zn dust in boiling AcOH to dihydrobenzanthrone (II), m.p. 150—152° when rapidly heated under CO<sub>2</sub> in a sealed capillary, which is very sensitive to air, adds 2 O in xylene, immediately decolorises 2 Br, and becomes disproportioned by strong acids or weak bases or when heated at 150° to (I) and 9-hydroxy-1 : 10-trimethylenephenanthrene. Oxidation is accelerated by light and occurs most rapidly in AcOH, but then requires only 1.6 O. A peroxide could not be isolated, but the solutions retain peroxidic properties. Apparently in xylene the active O is imparted to the hydrocarbon and does not further affect unaltered (II), whereas in AcOH H<sub>2</sub>O<sub>2</sub> is formed which transforms (II) into (I). (II) gives an *acetate*, m.p. 159—161° in sealed capillary filled with CO<sub>2</sub>. The intermediate occurrence of an orange colour during the reduction of (I) indicates the possible formation of a H<sub>1</sub>-derivative similar to that, m.p. 120—125° in sealed tube under CO<sub>2</sub>, obtained by mixing equimol. amounts of (I) and (II) in hot AcOH under CO<sub>2</sub>. Bz-1-Bromodihydrobenzanthrone has m.p. 167° (decomp.).

H. W.

**Condensation of phthalic anhydride with *s*-octahydrophenanthrene.** E. DE B. BARNETT, N. F. GOODWAY, and C. A. LAWRENCE (J.C.S., 1935, 1684).—*s*-Octahydrophenanthrene and *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O with AlCl<sub>3</sub> in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> yield *o*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthroylbenzoic acid (I), m.p. 200°.

Similarly the corresponding 4':5'-dichloro-octahydro-phenanthrolylbenzoic acid, m.p. 276° (decomp.), is obtained from 4:5-dichlorophthalic anhydride, but the product from 3:6-dichlorophthalic anhydride could not be crystallised. (I) when heated (water-bath) during 15 hr. with activated Zn dust, NaOH, and  $\text{NH}_3\cdot\text{H}_2\text{O}$  yields  $\omega$ -1:2:3:4:5:6:7:8-octahydrophenanthryl-o-toluic acid, m.p. 192°, cyclised by cold, conc.  $\text{H}_2\text{SO}_4$  to octahydro-1:2:3:4-dibenzanthrone (II), m.p. 200°, converted by  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  into octahydro-1:2:3:4-dibenzanthranyl acetate, m.p. 214°. (II) is oxidised by boiling  $\text{CrO}_3\text{--AcOH}\cdot\text{H}_2\text{O}$  to octahydro-1:2:3:4-dibenzanthraquinone (III), m.p. 234°, and when boiled (3 hr.) with activated Zn dust,  $\text{EtOH}$ ,  $\text{H}_2\text{O}$ , and  $\text{KOH}$  is reduced to octahydro-1:2:3:4-dibenzanthracene, m.p. 129°. Attempts to dehydrogenate this with  $\text{Se}$ , and (III) with  $\text{Br}$ , failed to yield any pure products. H. G. M.

**Carvacrol. V. Benzyl ethers of acylated methylisopropylphenols.** H. JOHN and P. BEETZ (J. pr. Chem., 1935, 144, 49—53).—The following ethers are obtained in about 85% yield by the action of  $\text{CH}_3\text{PhCl}$  or  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$  on the K salt of the requisite phenol: *p*-acetothymyl  $\text{CH}_2\text{Ph}$ , m.p. 71°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p. 104°, ether; *p*-propiothymyl  $\text{CH}_2\text{Ph}$ , m.p. 64°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p. 110°, ether; *p*-butyrothymyl  $\text{CH}_2\text{Ph}$ , m.p. 47°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p. 91°, ether; *p*-isovalerothymyl  $\text{CH}_2\text{Ph}$ , m.p. 40°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p. 84°, ether; *p*-benzoylthymyl *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , ether, m.p. 91°; *p*-acetocarvacryl  $\text{CH}_2\text{Ph}$ , m.p. 64°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , m.p. 114°, ether; *p*-propiocarvacryl *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ , ether, m.p. 128°. Glyceryl  $\alpha$ -di-*p*-acetothymyl ether, m.p. 109°, from *p*-acetothymol,  $\text{OH}\cdot\text{CH}_2(\text{CH}_2\text{CH}_2)_2$ , and  $\text{KOH}\text{--EtOH}$ , and glyceryl  $\alpha$ -di-*o*-nitro-*p*-acetylthymyl ether, m.p. 95°, are described. H. W.

**Action of organo-magnesium compounds on adiponitrile.** A. COMPERE (Bull. Soc. chim. Belg., 1935, 44, 523—526).—Adiponitrile with  $\text{MgEtBr}$  and  $\text{Et}_2\text{O}$  yields  $\text{C}_8\text{H}_{10}$ , 1-imino-2-cyanocyclopentane, and decane- $\gamma$ -dione; with  $\text{MgPhBr}$  it gives  $\text{COPh}\cdot(\text{CH}_2)_4\cdot\text{COPh}$  and a little  $\text{Ph}_2$ , and with  $\text{CH}_2\text{Ph}\cdot\text{MgBr}$  it gives  $\alpha$ -diphenyloctane- $\beta$ -dione, m.p. 72° (disemicarbazone, m.p. 210°). H. G. M.

**7-Hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene.** A. BUTENANDT and G. SCHRAMM (Ber., 1935, 68, [B], 2083—2091).—Unlike 1-keto-1:2:3:4-tetrahydrophenanthrene, 7-hydroxy-1-keto-1:2:3:4-tetrahydrophenanthrene (I) is physiologically inactive according to the Allen-Doisy method. 1:6- $\text{NH}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$  is heated with  $\text{KOH}$  at 250—310° and the product is treated with cold  $\text{Ac}_2\text{O}$ , thus giving 1:6- $\text{NHAc}\cdot\text{C}_{10}\text{H}_7\cdot\text{OH}$ , m.p. 214°, in 36% yield. It is converted by  $\text{Me}_2\text{SO}\text{--NaOH}$  into 1:6- $\text{NHAc}\cdot\text{C}_{10}\text{H}_7\cdot\text{OMe}$ , m.p. 140°, hydrolysed by  $\text{HCl}\text{--EtOH}$  to 6-methoxy- $\alpha$ -naphthylamine (II), m.p. 74° [hydrochloride, m.p. 205—220° (decomp.)], whence 6-methoxy- $\alpha$ -naphthonitrile, m.p. 79°. Treatment of (II) in the usual manner but at the lowest possible temp. gives 1:6- $\text{C}_{10}\text{H}_7\cdot\text{I}\cdot\text{OMe}$  (in 55% yield), the Grignard compound from which is transformed by  $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  or  $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{MgI}$  into  $\gamma$ -6-methoxy-1-naphthylbutenoic acid, m.p. 156° [Me

ester (III), m.p. 60°].  $\gamma$ -Hydroxy- $\gamma$ -6-methoxy-1-naphthyl-*n*-butyric acid and the corresponding lactone, m.p. 114°, are obtained as by-products. Hydrogenation of (III) in  $\text{AcOH}$  ( $\text{Pt}$  or  $\text{Pd}$ ) and hydrolysis of the product gives  $\gamma$ -6-methoxy-1-naphthyl-*n*-butyric acid, m.p. 149°, cyclised by  $\text{SnCl}_4$  at 105° to 7-methoxy-1-keto-1:2:3:4-tetrahydrophenanthrene, m.p. 101°, which with  $\text{HBr}$  ( $d$  1.48) in boiling  $\text{AcOH}$  yields (I), m.p. 232° (slight decomp.) (*Bz* derivative, m.p. 212°). *Et succinaldehyde semicarbazone* has m.p. 133°. H. W.

**Manufacture of polynuclear cyclic ketones.**—See B., 1935, 1133.

**Sex hormone. VIII. Preparation of testosterone by use of mixed esters.** L. RUZICKA, A. WETTSTEIN, and H. KAGI. IX. *trans*- $\Delta^4$ -Dehydroandrosterone and the preparation of *trans*- $\Delta^5$ -dehydroandrosterone from stigmaterol. L. RUZICKA, W. FISCHER, and J. MEYER. X. Preparation of 17-methyltestosterone and other androstene and androstane derivatives. Relationship between chemical constitution and male hormone activity. L. RUZICKA, M. W. GOLDBERG, and H. R. ROSENBERG (Helv. Chim. Acta, 1935, 18, 1478—1482, 1483—1487, 1487—1498).—VIII. With  $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$  *trans*- $\Delta^5$ -androstene-3:17-diol 3-monoacetate (A., 1935, 1371) gives its 17-benzoate, m.p. 180—182°, hydrolysed by  $\text{KOH}\text{--MeOH}$  at room temp. to the 3:17-diol 17-mono-benzoate, m.p. 220.5—222°. Addition of  $\text{Br}\text{--AcOH}$ , followed by oxidation with  $\text{CrO}_3\text{--90\% AcOH}$ , and debromination of the product with  $\text{NaI}\text{--EtOH}\cdot\text{C}_6\text{H}_6$  and 2%  $\text{Na}_2\text{SO}_3$  gives the 17-monobenzoate, m.p. 194—196° (corr.), of 17-hydroxy- $\Delta^4$ -androstene-3-one (testosterone), which is obtained by hydrolysis with 2%  $\text{KOH}\text{--MeOH}$ .

IX. *trans*- $\Delta^5$ -Dehydroandrosterone (I) (A., 1935, 1125) in  $\text{Et}_2\text{O}$  with  $\text{EtOH}$  saturated with  $\text{HCl}$  at 0° gives its hydrochloride, m.p. 156—157°, converted by  $\text{KOAc}\text{--EtOH}$  into *trans*- $\Delta^4$ -dehydroandrosterone, m.p. 128.5—130° [rather less active than (I)]. Oxidation of stigmateryl acetate (hydrobromide, m.p. 160.5—161.5°) by bromination,  $\text{CrO}_3$ , and debromination (as for cholesteryl acetate) also gives (I). Stigmaterol with an excess of  $\text{HCl}\text{--Et}_2\text{O}$  gives its hydrochloride (*Ac* derivative, m.p. 183—183.5°).

X. (I) (semicarbazone, m.p. 267°) with  $\text{MgMeI}$  or  $\text{MgEtI}$  affords, respectively, *trans*- $\Delta^5$ -17-methyl- (II), m.p. 204°, and -17-ethyl-androstene-3:17-diol, m.p. 173°. (II) is converted by bromination, oxidation with  $\text{CrO}_3$ , and debromination with  $\text{Zn}$  into 17-hydroxy-17-methyl- $\Delta^4$ -androstene-3-one (17-methyl-testosterone), m.p. 163—164°. Oxidation of methyl-androstanediol (A., 1935, 1125) with  $\text{CrO}_3\text{--AcOH}$ , gives 17-hydroxy-17-methyl-androstan-3-one, m.p. 192—193° (semicarbazone, m.p. 235—236°). Reduction of *trans*-androstene-3-one (3-hydroxy- $\alpha$ -allocholan-17-one) (III) (semicarbazone, m.p. 282—283°) with  $\text{H}_2\text{--PtO}_2$  in  $\text{AcOH}$  and hydrolysis (some acetate formed) gives *trans*-androstane-3:17-diol, m.p. 168° (*Ac* derivative, m.p. 127—128°). With  $\text{MgMeI}$  or  $\text{MgEtI}$  (III) gives, respectively, *trans*-17-methyl-, m.p. 211—212°, and -17-ethyl-androstane-3:17-diol (IV), m.p. 204—205°. Oxidation of (IV) with  $\text{CrO}_3\text{--}$



AcOH affords 17-hydroxy-17-ethylandrostan-3-one, m.p. 137—138°. Androsterone and MgEtI afford cis-17-ethylandrostan-3:17-diol, m.p. 143—144°. The relationship between physiological activity (on the basis of both the cock's comb and rat tests) and (a) the *cis*- or *trans*-configuration, or the presence of a double linking at C<sub>5</sub>, or (b) the nature and configuration of substituents at C<sub>3</sub> and C<sub>17</sub>, for these and other known androstane derivatives, is summarised and discussed.

J. W. B.

**Sexual hormones and related substances. V. *epi*Dihydrocinchol and its oxidation to 3-*epi*-hydroxyætiolchohan-17-one (androsterone).** W. DIRSCHERL (Z. physiol. Chem., 1935, 237, 52—56).—Oxidation of dihydrocinchol (I) (from hydrolysis of acetyldihydrocinchol; A., 1935, 1242) by CrO<sub>3</sub> yields dihydrocinchone, m.p. 163° (all m.p. corr.), [α]<sub>D</sub><sup>20</sup> +42° in CHCl<sub>3</sub>, which on reduction (Pt-H<sub>2</sub>) affords *epidihydrocinchol* (II), m.p. 206°, [α]<sub>D</sub><sup>20</sup> +26° in CHCl<sub>3</sub> [obtained directly from (I) by reduction with NaOEt at 215° and subsequent isolation as digitonide]. Oxidation of the *Ac* derivative, m.p. 90°, [α]<sub>D</sub><sup>20</sup> +28.4° to +29.4° in CHCl<sub>3</sub>, of (II) with CrO<sub>3</sub> yields 3-*epi*acetoxyætiolchohan-17-one, the *semicarbazone*, m.p. 284—285°, of which is converted by AcOH-HCl followed by hydrolysis into 3-*epi*hydroxyætiolchohan-17-one (cf. *ibid.*; A., 1934, 1221).

F. O. H.

**Dehydroandrosterone.** A. BUTENANDT, H. DANNENBAUM, G. HANISCH, and H. KUDSZUS (Z. physiol. Chem., 1935, 237, 57—74).—Dehydroandrosterone (I) (A., 1935, 413, 1125) [benzoate, m.p. 250° (all m.p. uncorr.); *acetate*, m.p. 168—169°, [α]<sub>D</sub><sup>20</sup> +3.9° in EtOH; *oxime*, m.p. 188—191°; *semicarbazone*, decomp. 262—264°] exists in polymorphic modifications, e.g., m.p. 137—138° and 180°, the latter showing marked depression on irradiation by arc or sun-light. All forms have [α]<sub>D</sub><sup>20</sup> +10.9° ± 0.7° in EtOH. (I) is separated from the CHCl<sub>3</sub>-sol. unsaponifiable matter of men's urine by pptn. with digitonin; this yields a cryst. mixture from which cholesterol and, by means of the *semicarbazone*, (I) are isolated. Treatment of (I) with MeOH-HCl, pptn. by digitonin, etc. affords the chloroketone, C<sub>19</sub>H<sub>27</sub>OCl (A., 1935, 413), also prepared by treating (I) with SOCl<sub>2</sub> in presence of dry CaCO<sub>3</sub> and Et<sub>2</sub>O. Hydrogenation (Pd-CaCO<sub>3</sub>) of (I) in MeOH yields *iso*androsterone (A., 1935, 1033). Cholesteryl acetate in AcOH treated with Br followed by CrO<sub>3</sub> yields, on debromination etc., 2.78% of (I) and 3-hydroxy-Δ<sup>5:6</sup>-cholenic acid, m.p. 224° (cf. A., 1935, 1125) (3-OAc-acid, m.p. 181°, and its *Me* ester, m.p. 156—157°). Similarly 3-hydroxy-Δ<sup>5</sup>-bisorcholenic acid (A., 1933, 1290) was prepared from stigmasterol. Both (I) and its acetate have approx.  $\frac{1}{3}$  the activity of androsterone by the cock's-comb assay; the benzoate is much less active than (I).

F. O. H.

**Androstenedione. Genesis of reproductory hormones.** A. BUTENANDT and H. KUDSZUS (Z. physiol. Chem., 1935, 237, 75—88).—Dehydroandrosterone (I) (cf. preceding abstract) with Br and CrO<sub>3</sub> yields a product which on debromination (Zn) affords Δ<sup>4</sup>-androstene-3:17-dione (II), m.p. 173—174°, [α]<sub>D</sub><sup>20</sup> +185°, absorption max. at 235 mμ [*di-*

*oxime*, m.p. 143° (uncorr.)] (cf. A., 1935, 1125, 1242). (II) has no sp. progesterone activity, whilst the cock's-comb test indicates a ratio of activities for (I), (II), and androstanediol (A., 1935, 1033) of 1:3:9 (cf. A., 1935, 1285). (II), unlike related compounds, is more active by the "capon unit" than the "mouse unit." The physiological activity of (II) appears to be especially of a "male" character; its relation to other sex hormones and its possible conversion into testosterone (A., 1935, 1370) and, by loss of CH<sub>4</sub>, into æstrone are discussed.

F. O. H.

**Testosterone. Conversion of dehydroandrosterone into androstenediol and testosterone. Preparation of testosterone from cholesterol.** A. BUTENANDT and G. HANISCH (Z. physiol. Chem., 1935, 237, 89—97).—Testosterone (I) (A., 1935, 1033) is identical with Δ<sup>4</sup>-androsten-17-ol-3-one (*ibid.*, 1370), and hence can be synthesised from cholesterol. Growth of cocks' combs indicates that the ratio of activities of (I), androstanediol, and androsterone is approx. 6:2:1. (I) has also a much greater action on the genital organs of male rats.

F. O. H.

**Catalytic hydrogenation of progesterone.** A. BUTENANDT and G. FLEISCHER (Ber., 1935, 68, [B], 2094—2097).—Hydrogenation of progesterone (PtO<sub>2</sub> in AcOH) gives a mixture of diols (I) oxidised by CrO<sub>3</sub> in AcOH to *allopregnan*dione and *pregnan*-dione. Similar reduction of *pregnen*-3-ol-20-one affords (I) almost exclusively. In acid solution, therefore, the compounds behave as expected from their constitutions. Contrary to Slotta *et al.* (A., 1935, 128), there is no evidence of the production of a new diketone, m.p. 188°.

H. W.

**New members of the androsterone group.** A. BUTENANDT, K. TSCHERNING, and G. HANISCH (Ber., 1935, 68, [B], 2097—2102).—*iso*Androsterone (I) is reduced by Na and Pr<sup>o</sup>OH or by Al-Hg to *isoandrostanediol* (II) [*alloætiolchohan*-3:17-diol], m.p. 164°, [α]<sub>D</sub><sup>20</sup> +4.2° (*diacetate*, m.p. 123—124°), which does not yield a sparingly sol., additive compound with digitonin and which somewhat exceeds (I) in physiological activity. *iso*Androstanediol *diacetate* is partly hydrolysed and the monoacetate is oxidised by CrO<sub>3</sub> to androstan-17-ol-3-one acetate, the *semicarbazone* of which is hydrolysed to *androstan*-17-ol-3-one (III) [*alloætiolchohan*-17-ol-3-one], m.p. 178°, [α]<sub>D</sub><sup>20</sup> +32.4° in EtOH (*acetate*, m.p. 157°; *oxime*, m.p. 209°), also obtained, together with (II), by hydrogenation (Pd sponge in Et<sub>2</sub>O) of testosterone (IV). Physiologically (III) is more active than androsterone. Reduction of (IV) with Al(OPr<sup>o</sup>)<sub>3</sub> affords Δ<sup>4:5</sup>-*androstene*-3:17-diol, m.p. 155.5°, which gives a yellow colour with C(NO<sub>2</sub>)<sub>4</sub>, a violet colour with CCl<sub>3</sub>·CO<sub>2</sub>H, and an additive compound with digitonin; it has little physiological activity.

H. W.

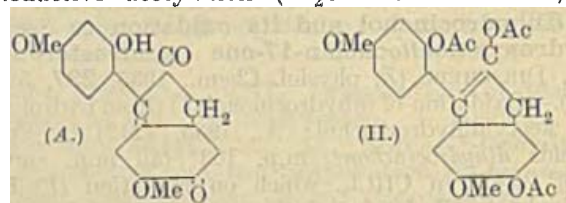
**Examination of products obtained in the preparation of ketones by the Friedel-Crafts reaction from acid chlorides and ethers of phenols. Synthesis of ketones of the naphthalene series.** P. E. POPOV (J. Gen. Chem. Russ., 1935, 5, 986—992).— $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OMe and AcCl in CS<sub>2</sub> with AlCl<sub>3</sub> afford chiefly 1-methoxy-4-acetylnaphthalene, to-

gether with 2:4-diacetyl- $\alpha$ -naphthol, m.p. 139—140°, also obtained from 4-acetyl- $\alpha$ -naphthol as above. Under analogous conditions,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OEt and BzCl yield chiefly 1-ethoxy-4-benzoylnaphthalene, together with 4-benzoyl-, m.p. 164—165°, and 2:4-dibenzoyl- $\alpha$ -naphthol, m.p. 138—139°. 2-Acetyl- $\alpha$ -naphthol and BzCl with AlCl<sub>3</sub> afford 4-benzoyl-2-acetyl- $\alpha$ -naphthol, m.p. 131—132°. R. T.

**2:6-Dibenzoylquinol.** O. DISCHENDORFER and A. VERDINO (Monatsh., 1935, 66, 255—285).—Doebner and Wolff's reaction product from  $p$ -C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> and BzCl (A., 1879, 638) is not, as regarded by Bogert and Howells (A., 1930, 477), 2:5-dibenzoylquinol (I) (cf. this vol., 82), but 2:6-dibenzoylquinol (II), as is shown by synthesis. The formation of (II) rather than (I) is in any case to be expected. (I) is prepared by Doebner's method. It is oxidised by alkaline KMnO<sub>4</sub> to BzOH, the absence of C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> showing the absence of condensed rings. It gives Ac<sub>2</sub>, m.p. 146°, and  $\alpha$ -Br-, m.p. 140—141°, derivatives, and a Me<sub>1</sub> ether (III), new m.p. 101° (Ac derivative, m.p. 105°), and is oxidised by the method of Bogert (*loc. cit.*) to 2:6-dibenzoylbenzoquinone (IV), new m.p. 162°. To establish that the second Bz in (II) is not attached to a C of the first Bz, C<sub>6</sub>H<sub>5</sub>, BzCl, and AlCl<sub>3</sub> were heated at 190—200°, and gave 1:3-C<sub>6</sub>H<sub>4</sub>Bz<sub>2</sub> and some 1:3:5-C<sub>6</sub>H<sub>3</sub>Bz<sub>3</sub>. Attempted synthesis from  $m$ -C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> failed. 5-Nitrosophthalic acid was converted into the chloride, and this by C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> in CS<sub>2</sub> into 5-nitro-1:3-dibenzoylbenzene, m.p. 130°. This is reduced by Na in MeOH to 3:5:3':5'-tetrabenzoylazoxybenzene, m.p. 202° to a cloudy liquid, clearing at 219°, and by SnCl<sub>2</sub> in AcOH to 3:5-dibenzoylaniline (V), m.p. 129—130° [hydrochloride, m.p. about 185°; sulphate; Ac, m.p. 147°, and Bz, m.p. 152—153°, derivatives; 2:4:6-Br<sub>3</sub>-derivative, m.p. 235° (Ac derivative, m.p. 215°)]. The benzylidene derivative, m.p. 124°, of (V) is converted by HNO<sub>3</sub> into 2:4(or 2:6)-dinitro-3:5-dibenzoylaniline, m.p. 197°. Diazotisation of (V) yields 3:5-dibenzoylphenol (VI), m.p. 135° (Ac derivative, m.p. 138—139°; 2:4:6-Br<sub>3</sub>-derivative, m.p. 216°). Attempts to isolate the 4-O<sub>2</sub>-derivative of (VI) having failed, (VI) was oxidised by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> [which converts *o*-cresotic acid into 2:5-dihydroxy-3-methylbenzoic acid (Ac<sub>2</sub> derivative, m.p. 150°)], and gave a very small quantity of (IV), identical with that obtained from (I). As additional evidence, 2-hydroxy-5-methoxybenzophenone was condensed with benzoin to 5-methoxy-7-benzoyl-2:3-diphenylcoumarone (VII), m.p. 155°, together with 2-hydroxy-5-methoxy-4(or 6)-desylbenzophenone, m.p. 232° (decomp.) (Ac derivative, m.p. 168°). Oxidation (CrO<sub>3</sub>) of (VII) gives (III), identical with that from (I). Thus the structure of (I) is established, and the other compounds described by Bogert (*loc. cit.*) are 2:6-dibenzoylquinol Me<sub>2</sub> ether, 2-anilino-3:5-dibenzoylquinol, and the triacetate of 2-hydroxy-3:5-dibenzoylquinol; the views of Bogert (*loc. cit.*) on the structure of Koznievski and Marchlevski's "Pechmann dye" now lose their foundation. E. W. W.

**Quinoid oxidation products in the brazilin series.** T. PFEIFFER and P. SCHNEIDER [with, in

part, H. KOBBS] (J. pr. Chem., 1935, [ii], 144, 54—62).—The main product of the oxidation of trimethyldeoxybrazilin is the colourless trimethylbrazilone, but small amounts of a red quinone (I), C<sub>17</sub>H<sub>14</sub>O<sub>5</sub>, m.p. 241° (yellow Ac derivative, m.p. 158—160°; violet monoxime), are also produced. The colour, solubility in KOH-EtOH with transient green colour, and degradation by H<sub>2</sub>O<sub>2</sub> to 2-hydroxy-4-methoxybenzoic acid establish the constitution A for it, thus supporting Robinson's formulation of brazilin. Reductive acetylation (Ac<sub>2</sub>O-NaOAc-Zn dust) of



(I) leads to the substance (II), m.p. 139°, the structure assigned to which is supported by the observation that 2-phenylindan-1-one is smoothly converted into an Ac derivative, C<sub>6</sub>H<sub>4</sub><CH<C(OAc)>CPh, m.p. 109—110°, into which it is readily re-converted by hydrolysis with 30% KOH-MeOH. Bromotrimethyldeoxybrazilin (Pfeiffer *et al.*, A., 1934, 780) is similarly oxidised to a Br-quinone, C<sub>17</sub>H<sub>13</sub>O<sub>5</sub>Br, m.p. 215° (Ac derivative, m.p. 208—210°). H. W.

**Reaction of glyoxal with dimethyldihydroresorcinol.** A. REZEK (Bull. Soc. Chim. Yougoslav., 1935, 6, 115—120).—Methone and glyoxal in EtOH-Et<sub>2</sub>O at the b.p. in presence of P<sub>2</sub>O<sub>5</sub> yield  $\alpha\alpha\beta\beta$ -tetra-(2-hydroxy-6-keto-4:4-dimethyl-3:4:5:6-tetrahydrophenyl)ethane, m.p. 235—236°. R. T.

**Diene synthesis.** B. A. ARBUZOV, E. P. SALMINA, and O. M. SCHAPSCHINSKAJA (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 2, 9—18).—Condensation could not be effected of maleic anhydride with 1-vinylnaphthalene (I) at 100° or with Ph<sub>2</sub> at 170—215°, or between benzoquinone and Ph<sub>2</sub>. Citraconic anhydride did not react with CPh<sub>2</sub>·CH<sub>2</sub> at 150°. During the prep. of (I) by the method of Tiffeneau and Daudel (A., 1908, i, 972),  $\alpha$ -1-naphthylethyl alcohol, m.p. 64°, b.p. 170—175°/35—40 mm., was obtained. CH. ABS. (r)

**Halochromism of 5-benzoyl-1:4-naphthaquinol.** R. SCHOLL, J. DONAT, and S. HASS (Ber., 1935, 68, [B], 2034—2039).—5-Benzoyl-1:4-naphthaquinol (I) does not resemble 1-benzoylanthraquinone and -anthraquinol in yielding halochromic salts of a furan derivative when treated with Al powder in conc. H<sub>2</sub>SO<sub>4</sub>, but nevertheless forms strongly halochromic salts. 5-Benzoyl-1:4-naphthaquinone, m.p. 152°, obtained in 25% yield by oxidation of 1-C<sub>10</sub>H<sub>7</sub>Bz in AcOH by CrO<sub>3</sub> at low temp., is reduced by SnCl<sub>2</sub> in EtOH to (I), m.p. 194—196°. With HClO<sub>4</sub> in COMe<sub>2</sub> (I) yields a violet-blue, lustrous perchlorate C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>·HClO<sub>4</sub>, from which it is regenerated in 90% yield by treatment with H<sub>2</sub>O and COMe<sub>2</sub> containing NaOAc. The less definite hydrochloride, sulphate, and mol. compound with SnCl<sub>4</sub> are described, all blue crystals with metallic lustre. Oxidation of 1-benzoyl-2-methylnaphthalene affords 5-benzoyl-6-

*methyl-1:4-naphthaquinone*, m.p. 146°, whilst *1-benzoyl-2:6-dimethylnaphthalene*, m.p. 83—84° (whence *5-benzoyl-2:6-dimethyl-1:4-naphthaquinone*, m.p. 169°), is obtained from 2:6-C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub>, BzCl, and AlCl<sub>3</sub> in CS<sub>2</sub>.

[With A. KELLER.] 1:1':4:4'-Tetrahydroxy-2:2'-dinaphthyl and the corresponding diquinone in AcOH give the *quinhydrone*, C<sub>20</sub>H<sub>12</sub>O<sub>4</sub>, decomp. about 200°. H. W.

**Constitution of alkannin, shikonin, and alkanan.** H. BROCKMANN (Annalen, 1935, 521, 1—47). Alkannin (I) is *l*-2- $\alpha$ -hydroxy-8-methyl- $\Delta^7$ -pentenylnaphthazarin; shikonin (II) is the *d*-form, mixed with 20% of the *dl*-form, which is named shikalkin. (I), m.p. 148°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -167° in C<sub>6</sub>H<sub>6</sub>, -226° in CHCl<sub>3</sub> (3 active H; Bz<sub>2</sub> derivative, m.p. 174—175°), best extracted from the roots of *Alkanna tinctoria* by ligroin, contains < 0.1% of *alkannan* (III) [2-*isohexylnaphthazarin*], m.p. 97—98°, [ $\alpha$ ] 0°, from which it is separated by adsorption from C<sub>6</sub>H<sub>6</sub> by kieselguhr. (I) is decomposed by long heating in Ac<sub>2</sub>O, but can be crystallised therefrom, and with Ac<sub>2</sub>O-NaOAc (short heating) or Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N gives the *Ac*<sub>3</sub> derivative (IV), m.p. 132°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -110° in C<sub>6</sub>H<sub>6</sub>. With Zn-Ac<sub>2</sub>O it gives a *substance*, C<sub>20</sub>H<sub>21</sub>O<sub>8</sub>, m.p. 147°, [ $\alpha$ ] 0°, probably a mixture. (I) sublimes unchanged at 140—150°/0.001 mm., but at 200°/760 mm. gives H<sub>2</sub>O and 5-methylquinizarin, m.p. 246—247°, which is readily obtained from diacetylnaphthazarin by condensation with piperylene in EtOH at 100° and aerial oxidation of the product in 2N-NaOH. When distilled with Zn dust, (I) gives 1- and 2-methylanthracene and C<sub>10</sub>H<sub>8</sub> [which last proves the two-ring structure of (I)]. With KMnO<sub>4</sub> in aq. alkali or COMe<sub>2</sub> (I) gives only AcOH and maleic acid, and with O<sub>3</sub> in AcOH a product oxidised by KMnO<sub>4</sub> to 0.8 mol. of COMe<sub>2</sub>, which is obtained to the same extent from (I) by the Kuhn-Roth method, proving the presence of CMe<sub>2</sub> in (I). (IV) and O<sub>3</sub> in CHCl<sub>3</sub> give a little 3:6-dihydroxyphthalic acid, establishing the naphthazarin grouping in (I). (I) and 10% HCl-MeOH at room temp. (15—18 hr.) yield 2- $\alpha$ -methoxy-8-methyl- $\Delta^7$ -pentenylnaphthazarin [*Me ether* of (I)] (V), m.p. 105°, sublimes at 140—150°/0.001 mm. (2 active H); complete racemisation occurs in this reaction, indicating the  $\alpha$ -position of the aliphatic OH, which is confirmed by the sparing solubility of (I) in aq. Na<sub>2</sub>CO<sub>3</sub>. The *dl*- $\alpha$ -*Et*, m.p. 83°, and *Pr*<sup>a</sup> *ether*, m.p. 57—58°, are similarly prepared. Hydrogenation of (I) is very rapid at first [1 mol.; formation of the quinol, which is very rapidly oxidised by air to (I)], then slower (further 2 mols.), and thereafter still slower. The second stage in the reduction (PtO<sub>2</sub>) in AcOH or other solvents gives (III) and other products. Intermediate reduction products could not be isolated. Hydrogenation of (V) is similar; absorption of 3 mols. gives (III), but at the 2 mol. stage some *dihydroalkannin Me ether* [2- $\alpha$ -methoxy-8-methyl-*n*-amylnaphthazarin], m.p. 50—51°, is obtained. This *ether* with KMnO<sub>4</sub> gives  $\alpha$ -methoxy- $\epsilon$ -methyl-*n*-hexoic acid (VI), the presence of which in the products is proved by formation of 8-methylvaleraldehyde (VII) (2:4-dinitrophenylhydrazones, m.p. 95°) therefrom by distillation with PbO<sub>2</sub> and dil. H<sub>3</sub>PO<sub>4</sub>.

The  $\alpha$ -position of the OH is thus proved. (VI), b.p. 123—124°/10 mm. (*p*-C<sub>6</sub>H<sub>4</sub>Br-CO-CH<sub>2</sub> ester, m.p. 74—75°), is synthesised from NaOMe and *Me*  $\alpha$ -bromo- $\epsilon$ -methyl-*n*-hexoate, b.p. 88—90°/10 mm., obtained by Br and red P at 100°; when mixed with other acids, it cannot be detected by conversion into (VII) by distillation with Cu, but the PbO<sub>2</sub>-H<sub>3</sub>PO<sub>4</sub> method is effective.

(III), m.p. 99°, sublimes at 120—140°/0.001 mm. (2 active H; *Ac*<sub>2</sub> derivative, m.p. 99—101°), gives only 0.23 mol. of COMe<sub>2</sub> (Kuhn-Roth), with Ac<sub>2</sub>O-Zn gives 1:4:5:8-tetra-acetoxy-2-8-methyl-*n*-amylnaphthalene, m.p. 170°, and with SnCl<sub>2</sub> the 1:4:5:8-(OH)<sub>4</sub>-compound, m.p. 65—66° [oxidised by air to (III) (only)]; with KMnO<sub>4</sub> it gives  $\epsilon$ -methyl-*n*-hexoic acid (*p*-C<sub>6</sub>H<sub>4</sub>Br-CO-CH<sub>2</sub> ester, m.p. 75°). With acids other than HCl or with 2N-NaOH at 100° (I) yields anhydroalkannin [2-8-methyl- $\Delta^7$ -pentadienylnaphthazarin], m.p. 155°, sublimes at 140—145°/0.001 mm. [gives 0.85 mol. of COMe<sub>2</sub> (Kuhn-Roth); 2 active H], which is hydrogenated (PtO<sub>2</sub>) in AcOH to (III). With SnCl<sub>4</sub> in C<sub>6</sub>H<sub>6</sub> or CHCl<sub>3</sub> (I) gives cycloalkannin [1:4:5-trihydroxy-8:8-dimethyl-5:6:7:8-tetrahydroanthraquinone] (VIII), m.p. 79—80°, sublimes at 140—145°/0.001 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -59.2° in C<sub>6</sub>H<sub>6</sub>.

(II), obtained by ligroin from the roots of *Lithospermum erythrorhizon*, has m.p. 143°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +135° in C<sub>6</sub>H<sub>6</sub>, gives a product, m.p. 146—147°, only after sublimation and repeated crystallisation, is identical with (I) in absorption spectrum, is hydrogenated as is (I), gives the inactive *Me ether*, and with SnCl<sub>2</sub> affords the impure *isomeride* [cycloshikonin], m.p. 79—80°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +51.2° in C<sub>6</sub>H<sub>6</sub>, of (VIII). The *racemate* of (VIII) has m.p. 86°. The relationship of (I) and (II) is proved by mixed m.p. determinations, which show a *racemate*, m.p. 148°, to be a stable compound. Absorption spectra and changes of colour with *pH* are recorded. (I) and (II) have lower oxidation potentials than naphthazarin, in spite of the  $\alpha$ -OH in the side chain, showing that they exist mainly in 5:8-dihydroxy-2-alkyl-1:4-quinone form with relatively little, if any, of the 6-alkyl form. M.p. are corr.

R. S. C.

**Some examples of substitution addition in the anthraquinone series.** C. MARSCHALK (Bull. Soc. chim., 1935, [v], 2, 1809—1830).—Na quinizarin-2-sulphonate (I), Na<sub>2</sub>CO<sub>3</sub>, KCN, and H<sub>2</sub>O at 90° (30 min.) yield a dicyano-leuco-compound oxidised by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to 1:4-dihydroxy-2:3-dicyanoanthraquinone (II), m.p. > 300°, also obtained, but less readily, from quinizarin and conc. KCN. (II) on hydrolysis with 90% H<sub>2</sub>SO<sub>4</sub> yields the anhydride of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic acid (+H<sub>2</sub>O) (III), readily obtained from the anhydride and by oxidation of 1:4-dihydroxy-2:3-dimethylanthraquinone with H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub>-NaNO<sub>2</sub> at 140—150° (8 hr.). This establishes the constitution of (III). (I) and NaOH-KCN at room temp. yield 1:4-dihydroxy-2-cyanoanthraquinone (IV), m.p. 228—229°, hydrolysed to the corresponding *amide*, m.p. > 300°, and acid (V). (IV) and Na<sub>2</sub>SO<sub>3</sub>-H<sub>2</sub>O at 80° yield 1:4-dihydroxy-3-cyanoanthraquinone-2-sulphonic acid (VI), also obtained from (I), Na<sub>2</sub>CO<sub>3</sub>-KCN-H<sub>2</sub>O, and air, and desulphonated to (IV) by



treatment with  $\text{Na}_2\text{S}_2\text{O}_4$  followed by oxidation. Both (IV) and (VI) with alkaline KCN give (II). (III) is decarboxylated to (V) (a) when heated with  $\text{H}_2\text{SO}_4\text{--H}_3\text{BO}_3$  at  $200^\circ$ , (b) when boiled with aq. NaOH, and (c) when treated below  $4^\circ$  during 1 hr. with  $\text{Na}_2\text{CO}_3\text{--Na}_2\text{S}_2\text{O}_4\text{--H}_2\text{O}$  followed by oxidation with NaOH-air. Prolonged boiling with NaOH and treatment with excess of  $\text{Na}_2\text{S}_2\text{O}_4$  at room temp. results in the loss of both  $\text{CO}_2\text{H}$ . (V), its amide and Et ester with KCN each yield products hydrolysed to (III), and Na quinizarin-2:6-disulphonate and KCN give a product which contains both S and N. Similarly 1-amino-4-hydroxyanthraquinone-2-sulphonic acid and the corresponding -3-sulphonic acid with KCN- $\text{Na}_2\text{CO}_3\text{--H}_2\text{O}$  at  $90\text{--}95^\circ$  afford 1-amino-4-hydroxy-2:3-dicyanoanthraquinone, m.p.  $< 300^\circ$ , oxidised by  $\text{H}_2\text{SO}_4\text{--MnO}_2$  to (II), and hydrolysed by  $\text{H}_2\text{SO}_4$  at  $140\text{--}150^\circ$  to 1-amino-4-hydroxyanthraquinone-2:3-dicarboxylic acid (anhydride). No reaction occurs with 1-amino-4-methoxyanthraquinone-2-sulphonic acid. cycloPontadiene reacts with (I) (with loss of  $\text{SO}_3\text{H}$ ), (IV), (V), quinizarin, and naphthazarin in aq. alkaline sol., but not in org. solvents. These are not considered to be normal "diene" reactions. The colours and colour reactions of the foregoing products are described.

H. G. M.

**Kinetics of sulphonation [of anthraquinone].**—See A., 1935, 1465.

**Turpentine oil. I. Laricinolic acid.** F. TROST (Annali Chim. Appl., 1935, 25, 496—504).—From laricinolic acid (I), m.p.  $146\text{--}147^\circ$  (block),  $[\alpha]_{\text{D}}^{20} -48.5^\circ$  in EtOH (from larch turpentine) (A., 1900, i, 680), were prepared: Me ester; retene, m.p.  $124^\circ$  (picrate, m.p.  $99^\circ$ ), by dehydrogenation by Se (A., 1928, 51); retenequinone, m.p.  $196\text{--}197^\circ$  (A., 1885, 905); the abietic acid, m.p.  $160\text{--}164^\circ$ , of Steele (A., 1922, i, 739); various isomerides formed during distillation and by treatment with AcOH and HCl; the additive compound, m.p.  $213.5\text{--}215^\circ$  of Me ester and maleic anhydride (A., 1932, 1254) and the derived anhydride-carboxylic acid, m.p.  $227\text{--}228^\circ$  (ibid.). The relation of (I) (for which the name "laricinic acid" is proposed) to abietic acids is discussed.

F. O. H.

**Synthesis of dl-piperitone (dl- $\Delta^1$ -p-menthen-3-one).** J. WALKER (J.C.S., 1935, 1585—1586).—Me  $\beta$ -chloroethyl ketone, Et  $\alpha$ -isopropylacetoacetate, and NaOEt give Et  $\Delta^1$ -p-menthen-3-one-4-carboxylate, b.p.  $155\text{--}165^\circ/16$  mm., hydrolysed (MeOH-KOH) to dl-piperitone, identical (oxime) with the racemised natural product.

F. R. S.

**Synthesis of dl-fenchone.** G. KOMPPA and A. KLAMI (Ber., 1935, 68, [B], 2001—2003).—dl-Camphenonic acid is converted by  $\text{SOCl}_2$  into dl-camphenonyl chloride, b.p.  $135\text{--}137^\circ/9$  mm., m.p.  $33^\circ$ , transformed by H, in xylene containing Pd- $\text{BaSO}_4$  at  $150^\circ$  into 1-ketofenchone (I), b.p.  $127\text{--}128^\circ/18$  mm. (monosemicarbazone, m.p.  $238^\circ$ ; monoxime, m.p.  $102\text{--}103^\circ$ ), which readily passes into a polymeride, m.p.  $240^\circ$ . Reduction of (I) in AcOH containing  $\text{PtO}_2\text{--FeSO}_4$  gives dl-fenchone (II) and  $\omega$ -hydroxyfenchone (III), b.p.  $134\text{--}135^\circ/17$  mm. (oxime, m.p.  $140^\circ$ ). (III) and  $\text{PCl}_5$  in  $\text{CHCl}_3$  afford  $\omega$ -chlorofenchone, b.p.  $121\text{--}123^\circ/18$  mm., from which

(II) is derived by treatment with Zn dust in boiling AcOH.

H. W.

**Snitter's camphenilene.** G. GRATTON and J. L. SIMONSEN (J.C.S., 1935, 1621—1623).—By elimination of HCl from camphenyl chloride, a hydrocarbon closely agreeing in physical properties with santene and Snitter's hydrocarbon (A., 1933, 1300) has been obtained. Oxidation ( $\text{O}_3$ ) shows it to be not homogeneous and to consist mainly of santene, giving acidic products,  $\text{CH}_2\text{O}$ , a ketone,  $\text{C}_8\text{H}_{12}\text{O}$  [2:4-dinitrophenylhydrazones (I), m.p.  $114\text{--}115^\circ$ ], and a hydrocarbon,  $\text{C}_9\text{H}_{14}$ , m.p.  $42^\circ$  (apocyclene). (I) differs from methylnorcamphor-2:4-dinitrophenylhydrazones, m.p.  $116\text{--}117^\circ$ . Snitter's hydrocarbon is probably mainly apocyclene.

F. R. S.

**Transition in camphor and chemically related compounds.**—See this vol., 12.

**Caryophyllenes. III.** G. R. RAMAGE and J. L. SIMONSEN (J.C.S., 1935, 1581—1584).—Ozonolysis of  $\beta$ -caryophyllene nitrosite in EtOAc- $\text{CCl}_4$  gives  $\text{CH}_2\text{O}$  and the  $\alpha$ -dinitro-ketone,  $\text{C}_{14}\text{H}_{22}\text{O}_5\text{N}_2$ , m.p.  $161.5^\circ$ ,  $[\alpha]_{\text{D}}^{25} -33.6^\circ$  in  $\text{CHCl}_3$  (phenylsemicarbazone, decomp.  $224^\circ$ ; 2:4-dinitrophenylhydrazones, decomp.  $225^\circ$ ), and in AcOH forms an isomeric  $\beta$ -dinitro-ketone, decomp.  $155^\circ$ , easily converted into the  $\alpha$ -form. The  $\alpha$ -ketone and  $\text{C}_2\text{H}_5\text{N}$  yield a nitro-ketone, m.p.  $69^\circ$ ,  $[\alpha]_{\text{D}}^{25} -114^\circ$  in  $\text{CHCl}_3$  (semicarbazone, m.p.  $186\text{--}187^\circ$ ), oxidised ( $\text{O}_3$ ) to a diketo-monocarboxylic acid,  $\text{C}_{14}\text{H}_{21}\text{O}_4$ , of which the Me ester, b.p.  $194\text{--}195^\circ/15$  mm. (bis-2:4-dinitrophenylhydrazones, decomp.  $108\text{--}110^\circ$ ), is identical with that obtained by Semmler and Mayer (A., 1912, i, 120). The constitution of the caryophyllenes is discussed.

F. R. S.

**Constituents of natural phenolic resins. III. Synthesis of dehydro-"sulphite-liquors lactone" dimethyl ether and some observations on the structure of podophyllotoxin.** R. D. HAWORTH, T. RICHARDSON, and G. SHELDRIK (J.C.S., 1935, 1576—1581).—Et  $\beta$ -(3:4-dimethoxybenzoyl)propionate, m.p.  $57\text{--}58^\circ$ , with  $\text{HCO}_2\text{Et}$  gives Et  $\beta$ -(3:4-dimethoxybenzoyl)- $\beta$ -hydroxymethylenepropionate, m.p.  $114\text{--}116^\circ$ , and with  $\text{Et}_2\text{C}_2\text{O}_4$  forms Et  $\beta$ -(3:4-dimethoxybenzoyl)- $\Delta^8$ -crotonolactone- $\gamma$ -carboxylate, m.p.  $154\text{--}156^\circ$ , neither ester giving well-defined reduction products.  $\beta$ -3:4-Dimethoxybenzoyl- $\alpha$ -(3':4'-dimethoxybenzylidene)- $\beta$ -methylenepropionic acid, m.p.  $157\text{--}158^\circ$ , obtained from the corresponding -propionic acid and aq.  $\text{CH}_2\text{O}$ , is converted (MeOH-HCl) into the lactone of the  $\beta$ -chloromethylpropionic acid, m.p.  $183\text{--}184^\circ$  (which with MeOH gives the lactone of the  $\beta$ -methoxymethylpropionic acid, m.p.  $145^\circ$ ), and Me 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-chloromethylnaphthalene-3-carboxylate, m.p.  $176\text{--}177^\circ$ , the corresponding acid (I), m.p.  $244\text{--}245^\circ$ , being cyclised to 4':5':6:7-tetramethoxybenzo-3:4-fluorene-1-carboxylic acid, m.p.  $303\text{--}305^\circ$  (Me ester, m.p.  $202\text{--}204^\circ$ ). (I) or its Me ester and NaOH give the lactone of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid (dehydro-sulphite-liquors lactone" Me, ether), m.p.  $215\text{--}216^\circ$ .

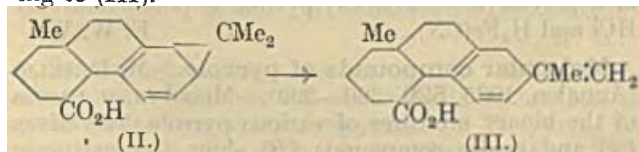
The Na salt of  $\beta$ -(3:4:5-trimethoxybenzoyl)propionic acid, m.p.  $121\text{--}122^\circ$ , obtained from Et 3:4:5-



trimethoxybenzoylacetate,  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ , and  $\text{NaOEt}$ , with piperonal and  $\text{Ac}_2\text{O}$  forms the  $\gamma$ -lactone of  $\beta$ -(3:4:5-trimethoxybenzoyl)- $\alpha$ -(3':4'-methylene-dioxybenzylidene)-propionic acid, m.p. 161—162°, hydrolysed to the acid, m.p. 183—184°, which is converted into the  $\beta$ -methylene-propionic acid, m.p. 169—170°. A similar series of reactions leads to 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)-2-chloromethylnaphthalene-3-carboxylic acid, m.p. > 300°, and the lactone of the 2-hydroxymethylnaphthalene-3-carboxylic acid (II), m.p. 288—289°. (II) differs from the lactone obtained from dehydroanhydro-piropodophyllin (III), and this is evidence in favour of the Borsche-Spath formula for podophyllotoxin. Oxidation ( $\text{KMnO}_4$ ) of (II) gives 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)naphthalene-2:3:dicarboxylic acid (anhydride, m.p. 299—300°;  $\text{Me}_2$  ester, m.p. 206—207°), identical with the oxidation product of (III). F. R. S.

**Complete deoxidation of resins by catalytic hydrogenation.** H. I. WATERMAN, J. F. CLAUSEN, and A. J. TULLENERS (Rec. trav. chim., 1935, 54, 701—710).—Brown colophony resin, consisting chiefly of abietic acid (I), is completely freed from O when heated to about 400° with  $\text{H}_2$  (initial pressure about 100 kg. per sq. cm.) in presence of a Mo or Ni catalyst. The temp. at which  $\text{H}_2$  is mainly absorbed depends on the nature of the catalyst. The products are stable, partly aromatic, and free from olefines even when a low initial  $\text{H}_2$  pressure (10 kg. per sq. cm.) is used. Two compounds,  $\text{C}_{19}\text{H}_{34}$  and  $\text{C}_{20}\text{H}_{36}$ , closely related to (I) ( $\text{C}_{20}\text{H}_{30}\text{O}_2$ ) in structure have been isolated. They were examined by the method of Waterman *et al.* (B., 1932, 536). H. G. M.

**Resinic acids of *Pinus sylvestris* resin.** I, II. P. S. PISCHTSCHIMUKA (J. Gen. Chem. Russ., 1935, 5, 738—751, 752—763).—I. The chief, if not only, acidic constituent of the fresh resin is  $\text{C}_{19}\text{H}_{29}\cdot\text{CO}_2\text{H}$  (I), m.p. 138°, the following salts of which are described:  $\text{MgR}_2$ ,  $\text{CaR}_2$ ,  $\text{BaR}_2$ ,  $\text{PbR}_2$ , m.p. 190°,  $\text{CuR}_2$ ,  $\text{HgR}_2$ ,  $\text{NaR}_2\cdot 3\text{HR}$ ,  $\text{CaR}_2\cdot 2\text{HR}$ , m.p. 160°,  $\text{BaR}_2\cdot 2\text{HR}$ , m.p. 158° ( $\text{R} = \text{C}_{19}\text{H}_{29}\cdot\text{CO}_2$ ). The acid from a 14-year-old sample of resin crystallised in hexagonal plates,  $[\alpha]_D^{25} = -30.36^\circ$  in EtOH, which passed at 118° into lentiform crystals, m.p. 157°.  $[\alpha]_D$  (in EtOH) of (I) changes from  $-61.7^\circ$  to  $+42.5^\circ$  when it is heated at 120° in  $\text{CO}_2$ , and again changes to  $-32.7^\circ$  at 145°. In xylene solution at 130°  $[\alpha]_D$  approaches zero after 5 hr., and attains a max. val. of  $+40^\circ$  after 24 hr., falling to  $+30.8^\circ$  after 48 hr., whilst at 200° and 250°  $[\alpha]_D$  tends to a const. val. of  $+10^\circ$ . The I val. of (I) corresponds with the presence of two ethylenic linkings. (I) is readily oxidised by atm.  $\text{O}_2$ , but not by  $\text{HNO}_3$ . It is suggested that abietic acid has the structure (II), readily changing to (III).



II. (I) and 33%  $\text{HNO}_3$  or (I) in ligroin and conc.  $\text{HNO}_3$  at 50—60° yield a dibasic acid (IV),

$\text{C}_{20}\text{H}_{22}\text{O}_9\text{N}_2$ , sintering at 128°, which readily adsorbs org. vapours. Attempts at elucidating the structure of (IV) were not successful. R. T.

**Sanguisorbigenin.** T. MATSUKAWA (J. Pharm. Soc. Japan, 1934, 54, 965—979; cf. Kodako and Abe, A., 1934, 175).—Pure sanguisorbigenin (I),  $\text{C}_{30}\text{H}_{46}\text{O}_2$  [monoacetate (II), m.p. 324°], has m.p. 275—276°, and contains one double linking. (I), with  $\text{AcOH-HCl}$ , yields acetylsanguisorbigenin lactone, decomp. 323°, which is hydrolysed to the parent lactone, m.p. 301°. (II) and  $\text{CrO}_3$  afford  $\beta$ - or  $\delta$ -hydroxy-acetylsanguisorbigenin lactone, decomp. 268° (acetate, m.p. 287°), which contains a *tert.*-OH. When heated, (I) yields sanguisorbigenol, m.p. 206° (acetate, m.p. 185—186°), a triterpene alcohol. When oxidised with  $\text{CrO}_3$ , (I) yields sanguisorbigenone, m.p. 159° and 229° (double m.p.) (monoxime, decomp. 281°). The *Me* ester (III), m.p. 207—209°, of (I) yields sanguisorbigenone *Me* ester, m.p. 216° (monoxime, decomp. 243°), on oxidation; hence the OH is *sec.* (I) is not hydrogenated with Pt-black. Methylation of (II) or acetylation of (III) affords acetylsanguisorbigenin *Me* ester, m.p. 243—245°. CH. ABS. (r)

**Toad poisons. I. Dehydrogenation of cinobufagin by selenium.** R. TSCHESCHE and H. A. OFFE (Ber., 1935, 68, [B], 1998—2000; cf. A., 1932, 397).—Dehydrogenation of cinobufagin (improved method of isolation from Ch'an Su) with Se at 270—330° gives very small amounts of methyleyclopentenophenanthrene, thus proving the poison to have the ring system of the sterols and bile acids. H. W.

**Constituents of red sandalwood. Homoptero-carpin.** H. LEONHARDT and E. OEOHLER (Arch. Pharm., 1935, 273, 447—452).—1-Dihydrohomoptero-carpin (modified prep.), m.p. 153—154°,  $[\alpha]_D^{20} = -5.8^\circ$  (2:4-dinitrophenylhydrazone, decomp. 292°), with  $\text{CrO}_3\text{-AcOH}$  or  $\text{BzO}_2\text{H}$  gives dihydrohomoptero-carpone (I),  $\text{C}_{17}\text{H}_{16}\text{O}_5$ , m.p. 178.5° [2:4-dinitro-, decomp. 258°, and *p*-nitro-phenylhydrazone, decomp. 148°; oxime, decomp. 225° (2:4-dinitrophenylhydrazone, decomp. 199°)]. (I) is a 1:4-quinone and with  $\text{Zn-Ac}_2\text{O-NaOAc}$  yields a quinol diacetate, m.p. 122—123°, sol. only in hot NaOH. R. S. C.

**Manchurian kaoliang.**—See this vol., 124.

**Acetylation of lignin.** F. KOMAROV and G. FILIMONOVA (J. Appl. Chem. Russ., 1935, 8, 1033—1042).— $\rightarrow$  5.6—6.6% of the OH-groups of sulphate lignin (I) are acetylated by treatment with  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$ , or with  $\text{Ac}_2\text{O}$  in  $\text{AcOH}$  in presence of catalysts ( $\text{H}_2\text{SO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ) (18—20°; 90 min.); in absence of catalysts the latter reaction takes place only at the b.p. of the mixture. Decomp. of (I), or elimination of Me groups, does not occur during the above reactions. The products are sparingly sol. in org. solvents. R. T.

**Hydrogenation of furfuraldehyde.** I. G. ROBERTI (Annali Chim. Appl., 1935, 25, 530—540).—Reduction of furfuraldehyde to furfuryl alcohol (I) at  $\rightarrow$  200° and under pressures of  $\text{H}_2$  of approx. 100 atm. with Ni, Cu, and Cu chromite (II) catalysts was investigated. With (II), an almost quant. formation of (I) occurs, but (II) rapidly loses its catalytic activity (cf. A., 1934, 1225). The influence of reagents

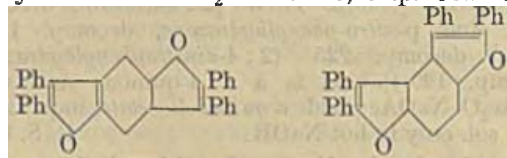
(e.g., CaO, AcOH) on the above hydrogenation catalysts is discussed. F. O. H.

**Hydrolysis of phenyl furyl ketimine.**—See this vol., 34.

**$\gamma$ -Tetrahydropyranaldehyde.** V. PRELOG and E. CERKOVNIKOV (Coll. Czech. Chem. Comm., 1935, 7, 430—435).—Catalytic reduction (poisoned Pd) of the chloride of  $\gamma$ -tetrahydropyran carboxylic acid (I) affords  $\gamma$ -tetrahydropyranaldehyde (II), b.p. 74—77°/11 mm. (phenylhydrazone, m.p. 93—94°; 2:4-dinitrophenylhydrazone, m.p. 163°; semicarbazone, m.p. 191°), also obtained by heating the mixed Ba salts of (I) and HCO<sub>2</sub>H. On keeping, (II) deposits a trimeride, m.p. 221°, depolymerised by heat. Condensation of (II) with rhodanine affords the substance, C<sub>9</sub>H<sub>11</sub>O<sub>6</sub>NS<sub>2</sub>, m.p. 254°, converted by aq. NaOH into  $\beta$ -4-tetrahydropyran- $\alpha$ -thionpropionic acid, O<CH<sub>2</sub>CH<sub>2</sub>>CH·CH<sub>2</sub>·CS·CO<sub>2</sub>H, m.p. 151—152°.

P. G. C.

**Condensation of benzoin with quinol.** O. DISCHENDORFER (Monatsh., 1935, 66, 201—217).—The alkali-sol. product obtained by Japp *et al.* (J.C.S., 1899, 75, 1035) by condensation of benzoin (I) with resorcinol (II) in H<sub>2</sub>SO<sub>4</sub> is proved to be 5-hydroxy-2:3-diphenylcoumarone, new m.p. 163°, since its Bz derivative, m.p. 122°, is oxidised (CrO<sub>3</sub>) to 2:5-dibenzoyloxybenzophenone, m.p. 118°, which is hydrolysed to 2-benzoylquinol. The alkali-insol. product, obtained by using excess of (I), is *s*-tetraphenyl-1:2:4:5-p-difuranobenzene (III) (cf. A., 1933, 1302), new m.p. 281° (cf. *loc. cit.*). (III) is oxidised (CrO<sub>3</sub>) to the Bz<sub>2</sub> derivative, m.p. 220—221°, of 2:5-dibenzoylquinol, m.p. 203° (Ac<sub>2</sub> derivative, m.p. 209°), different from the compound to which Bogert and Howells (A., 1930, 477) incorrectly ascribe this structure (cf. this vol., 78). With Br in C<sub>6</sub>H<sub>6</sub> at 100°, (III) yields a *meso*-Br<sub>2</sub>-derivative, m.p. 384—388°,



(III.)

(IV.)

which is also obtained from (I) and 2:5-dibromoquinol in H<sub>2</sub>SO<sub>4</sub>, and is oxidised (CrO<sub>3</sub> in PhNO<sub>2</sub>-AcOH) to the Bz<sub>2</sub> derivative, m.p. 317°, of 3:6-dibromo-2:5-dibenzoylquinol, m.p. 288° (decomp.). The position of Br is confirmed by oxidation (KMnO<sub>4</sub>-NaOH), which gives BzOH, without the Br-acids which would result from a bromophenyl compound. A third product from (I) and (II), recovered from the mother-liquors, is *as*-tetraphenyl-1:2:4:5-p-difuranobenzene (IV) (cf. A., 1933, 1302), m.p. 264—265°; this is oxidised (CrO<sub>3</sub>) to the Bz<sub>2</sub> derivative, m.p. 276°, of 2:3-dibenzoylquinol, m.p. 188°, which with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O yields 5:8-dihydroxy-1:4-diphenylphthalazine, m.p. 315° (decomp.). E. W. W.

**Configuration of dioxan and the *cis*- and *trans*-naphthadioxans.** J. BOESEKEN, F. TELLEGEN, and P. H. HENRIQUEZ (Rec. trav. chim., 1935, 54, 733—739).—The dipole moments, given in parentheses in Debye units, of the following compounds have been

measured with the apparatus previously described (cf. A., 1935, 598): dioxan (0.3); 2:3-dichloro- (I) (1.6), 2:3:5:6-tetrachloro-, m.p. 60° (0), m.p. 100° (1.85°), m.p. 144° (1.05), and 2:2:3:5:5:6-hexachloro-dioxan (0); thioxan (0.47); selenoxan (0.30); *cis*-, m.p. 111° (1.9), and *trans*-naphthadioxan, C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>, m.p. 136° (0.72). These last two isomerides were obtained from (I) and glycol (II), and from glyoxal and (II), and correspond with the *cis*- and *trans*-decalins. The configuration of these compounds is discussed (cf. A., 1935, 15). H. G. M.

**Unequal reactivity towards organometallic compounds of the carbonyl group in succinmethylimide and in *N*-methylpyrrolidone.** R. LUKES and K. SMOLEK (Coll. Czech. Chem. Comm., 1935, 7, 476—481; cf. A., 1929, 576, 935; 1930, 1296).—Succinmethylimide with CH<sub>3</sub>Ph·MgCl in cold dry C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O rapidly gives 2-benzyl-1-methyl-5-pyrrolone, whereas *N*-methylpyrrolidone with MgEtBr gives 1:2-dimethyl- $\Delta^2$ -pyrroline only after many hr. The difference is explained in terms of the polarities of the mol. groupings. J. L. D.

**Action of Grignard reagent on the amido-group. VIII. Action of organo-magnesium compounds on ethyl 1-methyl-2-pyrrolone-5-acetate.** R. LUKES and J. PREUCIL (Coll. Czech. Chem. Comm., 1935, 7, 482—490; cf. A., 1932, 521).—Et 1-methyl-2-pyrrolone-5-acetate (I) with MeMgI in C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O gives Et 1:2-dimethylpyrrole-5-acetate, b.p. 135—136°/20 mm. [the acid, m.p. 119.5° (decomp.), is decarboxylated to give 1:2:5-trimethylpyrrole]. Similarly, with Mg *n*-hexyl bromide and MgPhBr, (I) yields Et 1-methyl-2-hexylpyrrole-5-acetate, b.p. 184—185°/21 mm. (acid, m.p. 89—91°, which when heated gives 5-hexyl-1:2-dimethylpyrrole, b.p. 171—172°/71 mm.), and Et 2-phenyl-1-methylpyrrole-5-acetate, b.p. 208—210°/18 mm. [acid, m.p. 157° (decomp.), decarboxylated to 5-phenyl-1:2-dimethylpyrrole, m.p. 50—51°], respectively. In no case was a diketone isolated (cf. A., 1932, 621). MgRX does not attack the ·CO<sub>2</sub>Et because this is probably in close electronic association with N. J. L. D.

**Basic properties of pyrroles.** P. PRATESI (Gazzetta, 1935, 65, 658—668).—When pyrroles form salts, the using of the unshared N electrons converts the aromatic into a conjugated olefinic structure, the stability of which is increased by substituents. Thus 2:3:4-trimethylpyrrole forms a *hydrochloride* and a *ferrocyanide*; 2:4-dimethyl-3-ethylpyrrole can be recovered from HCl solution (as can 2:3:5-trimethyl-4-ethylpyrrole), and forms a *ferrocyanide*; these salts are monomeric. The *ferrocyanide* of 1-methyl-2:5-diethylpyrrole is contaminated with that of a polymeride. 2-Methylpyrrole is polymerised by HCl and H<sub>4</sub>Fe(CN)<sub>6</sub>. E. W. W.

**Molecular compounds of pyrrole.** M. DEZELIĆ (Annalen, 1935, 520, 290—300).—Mixed m.-p. curves of the binary mixtures of various pyrrole derivatives (A) and acidic compounds (B) show the existence of the following compounds. Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate gives compounds with



$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , m.p.  $85\cdot3^\circ$ ,  $\text{PhOH}$ , m.p.  $93^\circ$ , picric acid, m.p.  $97\cdot8^\circ$ , all of type  $AB$ , salicylic acid,  $AB$ , m.p.  $107^\circ$ , and  $AB_2$ , m.p.  $113^\circ$ ,  $o$ -, m.p.  $108\cdot5^\circ$ ,  $m$ -, m.p.  $139^\circ$ , and  $p\text{-C}_6\text{H}_4(\text{OH})_2$ , m.p.  $153^\circ$ , all of type  $AB_2$ . No compounds are formed with  $\text{AcOH}$ ,  $\text{BzOH}$ , or succinic acid. Et 2:4-dimethylpyrrole-5-carboxylate gives a compound  $AB_2$ , m.p.  $100^\circ$ , with picric acid (initial polymerisation to  $B_2$ ), but not with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ ,  $\text{BzOH}$ ,  $\text{PhOH}$ , salicylic acid, or  $o$ -,  $m$ -, or  $p\text{-C}_6\text{H}_4(\text{OH})_2$ . Et 3-aldehyde-2:4-dimethylpyrrole-5-carboxylate gives compounds with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , m.p.  $74\cdot5^\circ$ , salicylic acid, m.p.  $135^\circ$ , picric acid, m.p.  $97^\circ$ , and  $o$ -, m.p.  $114^\circ$ , and  $m\text{-C}_6\text{H}_4(\text{OH})_2$ , m.p.  $111^\circ$ , all of type  $AB$ , and of type  $AB_2$  with  $p\text{-C}_6\text{H}_4(\text{OH})_2$ , m.p.  $142^\circ$ : no compound with  $\text{BzOH}$ . Et 4-aldehyde-2:5-dimethylpyrrole-3-carboxylate gives compounds with salicylic acid,  $AB$ , m.p.  $111\cdot5^\circ$ , and  $AB_2$ , m.p.  $111^\circ$ , and  $m$ -, m.p.  $98^\circ$ , and  $p\text{-C}_6\text{H}_4(\text{OH})_2$ , m.p.  $117\cdot5^\circ$  (type  $AB$ ), but not with  $o\text{-C}_6\text{H}_4(\text{OH})_2$ . Constitutions are briefly discussed.

J. W. B.

Yellow coloration produced by ultra-violet light on mixtures of pyridine with sugars, monohydric alcohols, and acetone. R. CANTENI (Helv. Chim. Acta, 1935, 18, 1420—1427).—The relative effects of various concns. of the above-named substances on (a) the velocity of formation of the yellow colour, and (b) the fading of this yellow colour, produced by ultra-violet irradiation of  $\text{C}_5\text{H}_5\text{N}$  have been investigated quantitatively by colorimetric comparison with 1 vol.-% solutions of  $\text{C}_5\text{H}_5\text{N}$  in  $\text{H}_2\text{O}$ . The main conclusions are as follows: glucose, galactose, sucrose, and lactose accelerate colour formation and retard fading, but their effect is < that of fructose. Pure  $\text{MeOH}$  is almost without influence on colour formation, but has a greater retarding action on fading than has fructose. Pure  $\text{EtOH}$  retards colour formation, but the colour is more stable in  $\text{EtOH}$  than in  $\text{MeOH}$ .  $\text{COMe}_2$  has a powerful inhibiting effect on colour formation.

J. W. B.

**4-Bromopyridine.** J. P. WIBAUT, J. OVERHOFF, and H. GELDOF (Rec. trav. chim., 1935, 54, 807—812).—4-Hydroxypyridine with  $\text{POBr}_3$  and  $\text{PBr}_5$  at  $130\text{--}140^\circ$  affords (together with some 2:4:6-tribromopyridine) 4-bromopyridine (I), b.p.  $27\cdot5\text{--}30^\circ/0\cdot4\text{ mm.}$ , f.p.  $0\text{--}1^\circ$ , also obtained by the action of  $\text{NaNO}_2$ -conc.  $\text{HBr}$  on 4-nitroaminopyridine (Koenigs *et al.*, A., 1924, i, 989), and characterised as its picrate, sinters  $135\text{--}140^\circ$ , m.p.  $223^\circ$  (decomp.), mercurichloride, darkens  $130\text{--}140^\circ$ , decomp.  $> 270^\circ$ , and platinichloride. (I) is very unstable and is converted in the dark at  $0^\circ$ , and even in  $\text{Et}_2\text{O}$  solution, into a yellowish-brown substance which may be 4-bromo- $N$ -4'-pyridylpyridinium bromide (platinichloride, decomp.  $> 325^\circ$ ; platinibromide; mercurichloride, m.p. approx.  $221^\circ$ ). When heated with aq.  $\text{NH}_3$  (d 0.9) at  $200^\circ$ , (I) is converted into 4-aminopyridine.

J. W. B.

**2-Aminopyridine series.** III. 2-Salicylamidopyridine and its electrolytic reduction to 2-*o*-hydroxybenzylaminopyridine. K. FEIST, W. AWE, and W. VOLKSEN (Arch. Pharm., 1935, 273, 476—478; cf. A., 1935, 92).—Electrolytic reduction of 2-salicylamidopyridine in  $\text{EtOH}\text{--}\text{H}_2\text{SO}_4$  gives

2-*o*-hydroxybenzylaminopyridine, m.p.  $105^\circ$  (picrate, m.p.  $185\text{--}186^\circ$ ), thus proving the structure of the amide. Similar reduction of 2-pyridylphthalimide causes fission.

R. S. C.

**Hydroxyquinolines. I. Iodo-derivatives of 8-hydroxyquinoline.** F. PIRRONE and A. CHERUBINO (Gazzetta, 1935, 65, 743—754).—An extended account of work previously published (A., 1934, 418). 5-Iodo-8-hydroxyquinoline (I), new m.p.  $125\text{--}127^\circ$  (picrate, new m.p.  $170\text{--}172^\circ$ ; sulphate, new m.p.  $209\text{--}211^\circ$ ; 1-MeI derivative, new m.p.  $134\text{--}137^\circ$ ; chloroacetate, m.p.  $157\text{--}158^\circ$ ; Co salt), when prepared in aq.  $\text{EtOH}$ , using I and KI, is accompanied by 5:7-di-iodo-8-hydroxyquinoline, m.p.  $185\text{--}187^\circ$ . Using I in  $\text{EtOH}$  in presence of  $\text{NaOAc}$ , only (I) is formed.

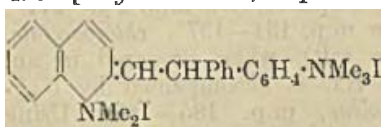
E. W. W.

**Absorption spectra in relation to the constitution of derivatives of isatin and carbostyryl.** R. G. AULT, E. L. HIRST, and R. A. MORTON (J.C.S., 1935, 1653—1657).—Absorption spectra of isatin (I) and derivatives have been measured under rigidly controlled conditions, and show that (I) and its *O*- and *N*-ethers all possess similar spectra. There is sufficient difference between the spectra of the lactam and lactim derivatives in the hydroxyquinoline series to permit the use of absorption spectra in structural determinations. (I) and  $\text{CH}_2\text{N}_2$  yield 3-hydroxy-, m.p.  $360^\circ$ , and 3-methoxy-quinoline, m.p.  $191^\circ$ . *N*-Methylisatin and  $\text{CH}_2\text{N}_2$  give 3-methoxy-1-methylquinoline, m.p.  $42^\circ$ , and *O*-methylisatin forms 3-hydroxy-2-methoxyquinoline, m.p.  $83\text{--}84^\circ$ .

F. R. S.

***p*-Dimethylaminobenzylidenequinaldine. Action of chromophoric and auxochrome groups.** H. RUPE, H. HAGENBACH, and A. COLLIN (Helv. Chim. Acta, 1935, 18, 1395—1413).—The following salts of 2-*p*-dimethylaminostyrylquinoline (I), m.p.  $183\cdot5\text{--}184\cdot5^\circ$  (Noelting *et al.*, A., 1906, i, 886; Pfeiffer *et al.*, A., 1925, i, 411, give m.p.  $177\text{--}179^\circ$ ), are prepared pure: colourless dihydrochloride; bluish-violet monohydrochloride, m.p.  $239\text{--}240^\circ$ ; almost colourless diperchlorate; reddish-violet monopерchlorate, m.p.  $229\text{--}230^\circ$  (decomp.), and monopicrate, m.p.  $167\text{--}168^\circ$ . With MeI in  $\text{MeOH}$  at  $100^\circ$  (I) gives a mixture of a pale yellow methiodide,  $\text{C}_9\text{H}_6\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I}$  (II), decomp.  $250\text{--}251^\circ$ , synthesised by condensation of *p*-aldehydophenyltrimethylammonium iodide, m.p.  $144^\circ$  (decomp.), and quinaldine in  $\text{EtOH}$ -piperidine, and a bluish-red methiodide,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_9\text{H}_6\text{NMeI}$  (III), m.p.  $253\text{--}254^\circ$  (decomp.), synthesised from quinaldine methiodide and *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (IV). With 1 mol. of  $\text{Me}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  (I) gives red 2-*p*-dimethylaminostyrylquinoline methosulphate, m.p.  $242\text{--}243^\circ$  (decomp.), of type (III), synthesised from 2-methylquinoline methosulphate, m.p.  $223\text{--}224^\circ$  (decomp.), and (IV), whereas condensation of *p*-dimethylaminobenzaldehyde methosulphate, m.p.  $154^\circ$ , and quinaldine give the colourless  $\beta$ -2-quinolylstyryltrimethylammonium methosulphate, m.p.  $201\cdot5\text{--}202\cdot5^\circ$  (decomp.), of type (II). With 2 mols. of  $\text{Me}_2\text{SO}_4$  (I) gives its colourless dimethosulphate, m.p.  $252\text{--}253^\circ$  (decomp.). Thus salts of type (II) and the bis-quaternary salts are colourless, and those of type (III) are coloured.

Reduction of (I) with  $H_2$ -Ni in EtOAc-EtOH first saturates the ethylenic linking and yields, finally, 2- $\beta$ -p-dimethylaminophenylethyl-1:2:3:4-tetrahydroquinoline, m.p. 68—68.5° (dihydrochloride, m.p. 210—211°; diperchlorate, m.p. 157—158°; dimethiodide, m.p. 158—159°; NO-, m.p. 90.5—91°, and Bz, m.p. 120.5—121.5°, derivatives). With MgPhBr in Et<sub>2</sub>O (I) affords a 1:4-adduct, 2-( $\beta$ -p-dimethylaminophenyl- $\beta$ -phenylethylidene)-1:2-dihydroquinoline (V), m.p. 125° [dihydrochloride; diperchlorate, m.p. 192—194°



(decomp.); methiodide, m.p. 125—126° (decomp.); NO-derivative, m.p. 195—196° (decomp.); N-methyl dimethiodide (annexed formula), m.p. 206—208° (decomp.); and N-methyl diperchlorate, m.p. 216—217° (decomp.), and a substance, m.p. 194.5° [perchlorate, m.p. 207—208°; dimethiodide, m.p. 196—197° (decomp.)], which is not isomeric with (V), and gives no NO- or Bz derivative. The relationship of colour to constitution is discussed. J. W. B.

**Reaction products of indoles with diazo-esters.** R. W. JACKSON and R. H. MANSKE (Canad. J. Res., 1935, 13, B, 170—174).—Addition of  $CHN_2 \cdot CO_2Et$  and indole gives, after hydrolysis, indolyl-3-acetic acid (I), and indylene-1:3-diacetic acid, m.p. 242°, hydrolysed to 3-methylindolyl-1-acetic acid, m.p. 178°. Indole and Et<sub>2</sub> diazosuccinate similarly form indolyl-3-succinic acid, m.p. 199°. No substitution occurs in position 2. Hydrolysis of Et<sub>2</sub>  $\beta$ -cyano-propionacetal to the acid, and further hydrolysis (HCl) to the semialdehyde of succinic acid, followed by condensation with  $NHPh \cdot NH_2$ , and treatment with  $H_2SO_4$ , leads by the Fischer synthesis to (I). F. R. S.

**Colour and constitution of indole derivatives.** C. TOFFOLI (Gazzetta, 1935, 65, 647—658).—Theoretical. The colour, and changes of colour on salt-formation, of various indoles, e.g., o-3-(2-methylindolyl)phenyl 3-(2-methylindolyl) ketone (A., 1934, 1110), and  $\alpha$ -3:3'-di-indolyl- and -3-indolyl-3'-indolidene-ethane (*ibid.*, 1113), are discussed on the basis of the Bonino model for pyrrole (A., 1933, 886), and of Burawoy's theories (A., 1931, 144, 544; 1932, 791). Salt-formation disturbs the aromatic character of indoles, and introduces chromophoric conjugated systems. E. W. W.

**Preparation and properties of mesochloroacridine and acridone, and their derivatives.** N. S. DROZDOV and N. S. LEZNOVA (J. Gen. Chem. Russ., 1935, 5, 690—700).—Mesochloroacridine (I) yields acridone (II), together with the hydrochloride (III) of a double salt of (I) and (II), when boiled with dil. HCl; (III) readily decomposes in aq.  $NH_3$  or boiling  $H_2O$  to yield (II). 4'-Methoxydiphenylamine-2-carboxylic acid and excess of  $POCl_3$  in xylene yield 5-chloro-3-methoxyacridine (IV), m.p. 154°, the hydrochloride of which is obtained by boiling with dil. HCl; with a limited amount of  $POCl_3$  the product is 3-methoxyacridone. 5-Chloro-1-nitro-7-methoxyacridine (V), m.p. 226°, and its hydrochloride are prepared analogously. o- $C_6H_4Cl \cdot CO_2H$ , 4-nitro-2-aminoanisole, KOH, and CuO in iso- $C_5H_{11} \cdot OH$  (140°; 10 hr.)

give 5'-nitro-2'-methoxydiphenylamine-2-carboxylic acid (VI), m.p. 234°, from which 4-nitro-1-methoxyacridone (VII), m.p. 281° (decomp.), may be prepared by heating with conc.  $H_2SO_4$  or with  $POCl_3$ . On chlorination, (VII) yields the corresponding 5-chloroacridine (VIII), m.p. 173° (hydrochloride), also obtained directly from (VI) and excess of  $POCl_3$ . 4-Chloro-4'-methoxydiphenylamine-2-carboxylic acid, m.p. 189°, prepared from 3:6-dichlorobenzoic acid, p-anisidine, KOH, and CuO in glycerol (140°; 10 hr.), affords similarly 1-chloro-7-methoxyacridone, m.p. > 300° and 1:5-dichloro-7-methoxyacridine (IX), m.p. 205—206° (hydrochloride). The hydrochlorides of (IV) and (IX) are hydrolysed when boiled with dil. HCl, under which conditions those of (V) and (VIII) are converted into the corresponding acridones. The above observations do not support the view that acridol is an intermediate stage in the conversion of mesochloroacridines into acridones. R. T.

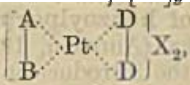
**Antimalarial drugs. Syntheses in the acridine series.** J. C. FELDMAN and E. L. KOPELOVITSCH (Arch. Pharm., 1935, 273, 488—495).—2:5- $C_6H_3Cl_2 \cdot CO_2H$  (prepared from o- $C_6H_4Me \cdot NO_2$  by way of 5-chloro-o-toluidine and 2:5- $C_6H_3MeCl_2$ ) with p-OMe- $C_6H_4 \cdot NH_2$ ,  $K_2CO_3$ , and a little Cu in iso- $C_5H_{11} \cdot OH$  at 130—135° gives 5-chloro-2-p-anisylaminobenzoic acid, m.p. 185—186°, converted by  $POCl_3$  at 100—123° into 5:7-dichloro-3-methoxyacridine, m.p. 203—204°, which with  $NH_2 \cdot CHMe \cdot [CH_2]_3 \cdot NEt_2$  yields 7-chloro-5- $\delta$ -diethylamino- $\alpha$ -methyl-n-butylamino-, m.p. 221—222°, and with  $NH_2 \cdot [CH_2]_3 \cdot NEt_2$  7-chloro-5- $\gamma$ -diethylaminopropyl-3-methoxyacridine dihydrochloride, m.p. 246—247°.  $C_6H_3MeCl_2$  with  $Cl_2 \cdot Fe$  gives a mixture, m.p. 80—81°,  $C_6H_3MeCl_2$ , converted by  $HNO_3$  into a mixture of 2:4:6- and 2:4:5- $C_6H_3Cl_3 \cdot CO_2H$  (I). (I) leads to 4:5-dichloro-2-p-anisylaminobenzoic acid, m.p. 233—234°, 5:7:8-trichloro-3-methoxyacridine, m.p. 192—193°, and 7:8-dichloro-5- $\delta$ -diethylamino- $\alpha$ -methylbutylaminoacridine dihydrochloride, m.p. 236—237°. The three acridine bases are less effective antimalarials than is acrichine (atebrine). R. S. C.

**3-Phenyl-1- $\beta$ -phenylethylpyrazol-5-one.** E. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1935, 7, 388—391).—3-Phenyl-1- $\beta$ -phenylethylpyrazol-5-one (I), m.p. 145.5° (methiodide, m.p. 174—175°), is obtained from  $CH_3Ph \cdot CH_2 \cdot NH \cdot NH_2$  and  $COPh \cdot CH_2 \cdot CO_2Et$ . (I) with  $NaNO_2 \cdot HCl$  affords a NO-derivative, m.p. 138—139°, converted by Zn-AcOH into the compound  $RH \cdot N \cdot R' \left( R = CH_2Ph \cdot CH_2 \cdot N \begin{array}{c} \text{N} = CPh \\ \text{CO} \cdot C \end{array} \right)$ , m.p. 165°, and an  $NH_2$ -derivative (not isolated) of (I). P. G. C.

**Asymmetric platinum atom. VII. A new type of optically active compound.** H. REIHLEN, G. SEIPEL, and E. WEINBRENNER (Annalen, 1935, 520, 256—269).—Dichloro-1-phenylethylenediamine-platinum (I) (A., 1935, 1132) boiled with 2:2'-dipyridyl affords dipyridyl-1-phenylethylenediamineplatinum chloride (II) +  $2H_2O$  and +  $3H_2O$ ,  $[M]_D + 90^\circ$  (platinohydrochloride), which is a racemate of the active Pt centre [denoted by ( $\pm$ )Pt]. With dil.  $HNO_3 \cdot NaNO_3$  it gives the ( $\pm$ )Pt nitrate, partly separated by shaking



with  $\text{H}_2\text{O}$  at  $10\text{--}15^\circ$  into the less sol., stable (+)Pt nitrate (III),  $[M]_D +115^\circ$ ,  $[\Delta\text{Pt}]_D +25^\circ$ , whereas the mother-liquor affords only the racemate from the readily racemised (–)Pt salt. With 1 mol. of Na *d*-bromocamphor- $\pi$ -sulphonate (IV) in  $\text{H}_2\text{O}$ , (II) gives the ( $\pm$ )Pt *d*-bromocamphor- $\pi$ -sulphonate chloride  $+3\text{H}_2\text{O}$ ,  $[M]_D +363^\circ$  ( $273^\circ +90^\circ$ ), but the gelatinous ( $\pm$ )Pt *di-d*-bromocamphor- $\pi$ -sulphonate,  $[M]_D +622^\circ$ , obtained by evaporation of (II) with 2 mols. of (IV), slowly affords crystals of the (+)Pt *d*-bromocamphor- $\pi$ -sulphonate chloride (V)  $+3\text{H}_2\text{O}$ ,  $[M]_D +392^\circ$ ,  $[\Delta\text{Pt}]_D +25^\circ$  to  $29^\circ$ , converted by dil.  $\text{HNO}_3\text{--NaNO}_3$  into (III). The mother-liquor of (V) with (IV) gives the (–)Pt *di-d*-bromocamphor- $\pi$ -sulphonate  $+2\text{H}_2\text{O}$ ,  $[M]_D +604^\circ$ ,  $[\Delta\text{Pt}]_D -32^\circ$ . *o*-Phenanthroline (VI) with  $\text{K}_2\text{PtCl}_4$  in hot  $\text{H}_2\text{O}$  affords dichloro-*o*-phenanthrolineplatinum, converted by  $\text{l-NH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$  into *o*-phenanthroline-1-phenylethylenediamineplatinum chloride  $+2\text{H}_2\text{O}$ ,  $[M]_D +121^\circ$  [also from (I) and (VI)] (nitrate,  $[M]_D +119^\circ$ ; platinochloride; *di-d*-bromocamphor- $\pi$ -sulphonate  $+2\text{H}_2\text{O}$ ,  $[M]_D +666^\circ \pm 10^\circ$ ). Similarly dichloroethylenediamineplatinum with (I) affords 1-phenylethylenediamine-ethylenediamineplatinum chloride, partly separated by crystallisation into fractions of  $[M]_D +134^\circ$  and  $+120^\circ$ , whence are obtained the iodide,  $[M]_D +139^\circ$  and  $+110.5^\circ$  (pure,  $[M]_D +125^\circ$ , the *d*-compound,  $[M]_D -125^\circ$ , also being obtained), perchlorate,  $[M]_D +110^\circ$  and  $+142^\circ$ , and iodide perchlorate,  $[M]_D +142^\circ$ . Thus

in the spirans of type  either the four

N are not in the same plane as the Pt, or the four Pt–N linkings are not equiv. All  $[M]_D$  vals. are in  $\text{H}_2\text{O}$ .

J. W. B.

**Preparation of 2:2'-diquinolyl by catalytic dehydrogenation of quinoline.** J. P. WIBAUT, H. D. T. WILLINK, jun., and W. E. NIEUWENHUIS (Rec. trav. chim., 1935, 54, 804–807).—Dehydrogenation of quinoline (I) by heating at  $325\text{--}335^\circ$  with a Ni– $\text{Al}_2\text{O}_3$  catalyst affords 2:2'-diquinolyl [15% yield, calc. on (I) consumed]. Very poor yields are also obtained using 0.5% of an I catalyst, but with 2.0% I complete decomp. results.

J. W. B.

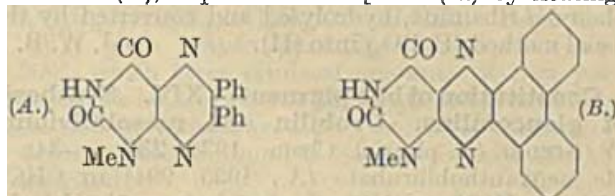
**Decolorisation of indigotin by alkyl- and aryl-sulphinic acids.** M. BAZLEN and F. SCHOLTZ (Ber., 1935, 68, [B], 2045).—Indigotin becomes decolorised when heated at  $180^\circ$  in glycerol with the Zn or Na salts of  $\text{MeSO}_2\text{H}$ ,  $\text{EtSO}_2\text{H}$ ,  $\text{PhSO}_2\text{H}$ , 1- or 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\text{H}$ ; the free acids cannot be used, since they become decomposed at temp. below that at which reducing action is developed. The colour returns when the solution is cooled and shaken with air. *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_2\text{H}$ , *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{H}$ , benzanthrone-*Bz*-1-sulphinic acid, and anthraquinone-2-sulphinic acid behave similarly.

H. W.

**Manufacture of conversion products of N-nitroamines etc. [benztriazoles].**—See B., 1935, 1132.

**Fluorescence of derivatives of pyrimidine, purine, and pyrimidine.** H. VON EULER, K. M. BRANDT, and G. NEUMULLER (Biochem. Z., 1935, 281, 206–214).—The fluorescence (substance and solution) of alloxazine (I), 6:7-dimethoxy- (I) and

4:5-diamino-3-methyluracil (II), diisobarbituric acid (III) and its oxidised form (IV), diuracilpyridazine, the azine (A), m.p.  $268\text{--}269^\circ$  [from (II) by heating



in  $\text{CO}_2$  at  $190\text{--}200^\circ$  for 45 min. with  $\text{Bz}_2$ ], the azine (B), m.p.  $> 330^\circ$  [from (II) by boiling in  $\text{AcOH}$  for 20–30 min. with phenanthraquinone], dioxindole (V), and acridine has been examined,  $\phi_{\text{H}}$ -fluorescence curves being given for (I)–(V).

W. McC.

**Crystalline hypoxanthine.** H. STEUDEL (Z. physiol. Chem., 1935, 236, 228–229).—Pure cryst. xanthine (I) (prisms) is obtained from the sulphate after conversion into the compound with  $\text{NH}_3$ , and pure cryst. hypoxanthine (II) (rhombic plates) from the hydrochloride, in both cases by treatment with  $\text{NaOAc}$ . The cryst. form attributed by Horbaczewski (A., 1898, i, 50) to (I) is that of (II).

W. McC.

**Flavin syntheses. VIII. Synthesis of 6-methyl-9-1-d-ribitylisoalloxazine and other synthetic investigations in the flavin series.** P. KARRER and F. M. STRONG (Helv. Chim. Acta, 1935, 18, 1343–1351).—4-Nitro-*m*-toluidine (improved prep.) with  $\text{ClCO}_2\text{Et}$  in  $\text{CHCl}_3$  gives its carbethoxy-derivative, m.p.  $51\text{--}52^\circ$ , reduced ( $\text{H}_2\text{--PtO}_2$ ) to 3-carbethoxyamino-*p*-toluidine, m.p.  $120^\circ$ , converted successively by usual methods (cf. A., 1934, 1134) into 2-carbethoxyamino-*p*-tolyl-*d*-ribamine, m.p.  $153^\circ$ , and 6-methyl-9-*d*-riboflavin (I), m.p.  $282^\circ$ ,  $[\alpha]_D -84.6^\circ$  in 0.05*N*- $\text{NaOH}$ . 6-Nitro-2:4-dimethylaniline (by hydrolysis of its Ac derivative, m.p.  $176.5^\circ$ ; lit., m.p.  $172^\circ$ ) with  $\text{ClCO}_2\text{Et}$  gives a poor yield of its carbethoxy-derivative, m.p.  $135^\circ$  (lit.,  $125\text{--}126^\circ$ ), which is best obtained by the action of conc.  $\text{H}_2\text{SO}_4\text{--HNO}_3$  (*d* 1.40) at  $100^\circ$  on Et 2:4-dimethylphenylcarbamate, and is reduced ( $\text{H}_2\text{--Pt}$ ) to the 6- $\text{NH}_2$ -compound, m.p.  $99.5^\circ$ , from which 2-carbethoxyamino-3:5-dimethylphenyl-*d*-ribamine, m.p.  $139^\circ$ , is obtained. Alkaline hydrolysis of this gives only 1-*d*-ribityl-2-hydroxy-4:6-dimethylbenzimidazole, m.p.  $248^\circ$ . (I) exhibits good growth-promoting efficiency in  $10\text{--}20 \times 10^{-6}$  g. daily doses.

J. W. B.

**Synthesis of lactoflavins.** P. KARRER, B. BECKER, F. BENZ, P. FREI, H. SALOMON, and K. SCHÖPP (Helv. Chim. Acta, 1935, 18, 1435–1448).—In part a historical résumé of flavin syntheses. Details are given for the prep. of *d*-ribose (I) (270 g.) from *d*-arabinose (3 kg.) by the method used by Austin *et al.* (A., 1934, 759) for *l*-ribose. The production of  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CH}_2\cdot\text{OH}$  by catalytic reduction of  $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{N}\cdot\text{CH}\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CH}_2\cdot\text{OH}$  (Kuhn *et al.*, A., 1935, 1382) is disputed, since these authors describe the condensation of 5-nitro-4-amino-*o*-xylene only with *l*-arabinose and not with *d*-ribose. The synthesis of 6:7-dimethyl-9-*d*-riboflavin (II), in good yield, by the following reaction sequence is detailed: *m*-xylene  $\rightarrow$  4- $\text{NO}_2$   $\rightarrow$  4- $\text{NH}_2$   $\rightarrow$  4- $\text{NH}\cdot\text{CO}_2\text{Et}$ -derivative  $\rightarrow$  4-carbethoxyamino-5-nitro-

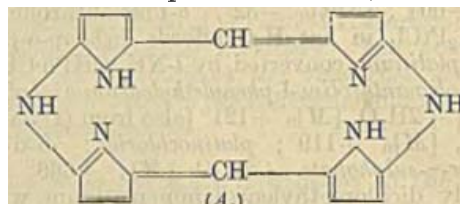
*o*-xylene, reduced to the 5-NH<sub>2</sub>-compound, which condenses with (I) to give, after catalytic reduction of the product, 2-carbethoxyamino-4:5-dimethylphenyl-*d*-ribamine, hydrolysed and converted by the usual method (H<sub>3</sub>BO<sub>3</sub>) into (II). J. W. B.

**Constitution of bile pigment. XIV. Synthesis of glaucobilins. Urobilin and mesobiliviolin.** W. SIEDEL (Z. physiol. Chem., 1935, 237, 8—34).—Me neoxanthobilirubate (A., 1935, 994) in CHCl<sub>3</sub> with dry HCN and HCl affords 5-hydroxy-5'-aldehyde-3':4'-dimethyl-3-ethyl-4'-β-carbomethoxyethylpyrromethene, m.p. 205.5° (all m.p. corr.), hydrolysed to the corresponding acid (I), m.p. 257°. Similarly Me isoneoxanthobilirubate (II) gives 5-methoxy-5'-aldehyde-3':3'-dimethyl-4-ethyl-4'-β-carbomethoxy-methylpyrromethene, m.p. 218—220° [corresponding acid (III), m.p. 273°]. 5-Bromo-3:3'-dimethyl-4-ethyl-4'-β-carbomethoxyethylpyrromethene hydrobromide (A., 1935, 632) yields (cf. A., 1933, 404) 5-methoxy-3:3'-dimethyl-4-ethyl-4'-β-carboxyethylpyrromethene, m.p. 160.5—161.5° [Me ester, m.p. 76°, from CH<sub>3</sub>N<sub>2</sub> and isoneoxanthobilirubic acid (IV) Me ether]. Ferrobilin IX α-Me<sub>2</sub> ester in CHCl<sub>3</sub> treated with 2*N*-NaOH affords "analytical" glaucobilin IX α-Me<sub>2</sub> ester (V), m.p. 232°, identical (by optical and physical characteristics) with the synthetic product, m.p. 232—234° [formed by refluxing (I)+(IV) in MeOH with HBr], and giving no depression of m.p. with isoglaucobilin IX α-Me<sub>2</sub> ester, m.p. 232° [from (III)+neoxanthobilirubic acid (VI)]. Similarly (I)+(IV) refluxed in MeOH with HCl affords glaucobilin IX α, m.p. 316.3° (decomp.), showing no depression with the analytical compound, m.p. 318° (decomp.). (I)+(IV) heated in AcOH with 2*N*-HCl in presence of FeCl<sub>3</sub> yields ferrobilin IX α, m.p. 265° (recryst. from COMe<sub>2</sub>-AcOH, m.p. 270°) showing no depression with the analytical compound, m.p. 265°; a similar identity holds for the Me<sub>2</sub> ester (VII), m.p. 264°. Glaucobilin XIII α-Me<sub>2</sub> ester (VIII), m.p. 246—247°, prepared by heating (I)+(VI) in MeOH with HBr, differs from (V) in solubility, but has similar optical properties, whilst depression of the mixed m.p. is small (approx. 1°). Treatment of mesobilirubin XIII in AcOH with FeCl<sub>3</sub> followed by dry HCl yields ferrobilin XIII α, m.p. 275° [Me<sub>2</sub> ester, m.p. 282.5°, showing no depression with (VII)]. (IV) heated with HCO<sub>2</sub>H and Ac<sub>2</sub>O followed by MeOH-HCl affords glaucobilin III α-Me<sub>2</sub> ester, m.p. 238.5°, showing small (approx. 2°) and marked (approx. 13°) depressions with (V) and (VIII), respectively. Equiv. amounts of (I) and (IV) Me ether heated in AcOH yield 1'-hydroxy-8'-methoxy-1:3:6:7-tetramethyl-2:8-diethyl-4:5-di-(β-carboxyethyl)bilin [Me ether of (V)]. Equiv. amounts of (I) and isoneobilirubic acid in MeOH heated with HBr give mesobiliviolin (IX), which yields a violet CHCl<sub>3</sub> solution (absorption max. at 575 mμ) turned blue by HCl (560, 607 mμ), and a blue solution fluorescing red (630 mμ) with EtOH-Zn(OAc)<sub>2</sub>. Condensation in presence of HBr of aldehydoneobilirubic acid and (IV) in MeOH yields mesobilirhodin (X), which gives a red CHCl<sub>3</sub> solution (575 mμ) turned violet by HCl (496, 557, 605 mμ) and a greenish-brown fluorescent (510 mμ) solution with EtOH-Zn(OAc)<sub>2</sub>. Chromatographic analysis of

(IX) prepared by oxidation (FeCl<sub>3</sub>) of mesobilirubinogen indicates the presence of (X). The bearing of the data on the structure of bile pigments is discussed.

F. O. H.

**Synthesis of di-iminoporphyrins. I. H. FISCHER, H. HABERLAND, and A. MÜLLER (Annalen, 1935, 521, 122—128).**—Prolonged contact of 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethene hydrobromide (I) with 25% NH<sub>3</sub> at room temp gives ββ-di-iminocoprophyrin II (cf. A.), m.p. 398—400° (ill-defined Cu salt; Me<sub>4</sub> ester, m.p. 250°, and its Cu salt, m.p. 312°). In spite of some doubt due to spectrochemical evidence, the structure A with 2 NH in place of 2 CH is preferred to a con-

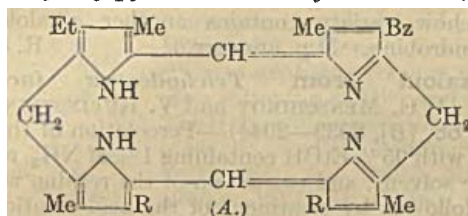


stitution with 2 N, since the substance has an enhanced acid no. in comparison with coproporphyrin and does not give a hydrobromide or hydrochloride. Also there is no evidence of dehydrogenation during or subsequent to the synthesis, and (I) with NH<sub>2</sub>Me or NH<sub>2</sub>Et gives substances spectroscopically similar to (II). H. W.

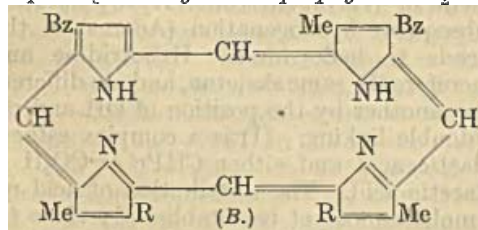
**Synthesis of benzoylporphyrins. H. FISCHER and K. HANSEN (Annalen, 1935, 521, 128—156).**—Attempts, by the introduction of heavy residue, are described to determine whether the stability of the chlorophyll mol., apart from the influence of the complex metal, is due to the involved isocyclic ring system. 2:3-Dimethylpyrrole is converted by CH<sub>2</sub>N<sub>2</sub>·CO<sub>2</sub>Et and Cu powder into Et 2:3-dimethylpyrrole-5-acetate, b.p. 142°/16 mm., hydrolysed and decarboxylated to 2:3:4-trimethylpyrrole. Et 2-methyl-3-ethylpyrrole-5-acetate, b.p. 143°/14 mm., is obtained similarly. Saturation of a solution of 2-methyl-3-ethylpyrrole and anhyd. HCN in Et<sub>2</sub>O with HCl and subsequent hydrolysis of the imine hydrochloride affords 2-methyl-3-ethylpyrrole-5-aldehyde (I), m.p. 109° (corresponding aldazine, m.p. 162°). Et 2:5-dimethylpyrrole-3-carboxylate, BzCl, and AlCl<sub>3</sub> in CS<sub>2</sub> give Et 4-benzoyl-2:5-dimethylpyrrole-3-carboxylate, m.p. 135°. Et 3-benzoyl-2:4-dimethylpyrrole-5-carboxylate is hydrolysed to 3-benzoyl-2:4-dimethylpyrrole-5-carboxylic acid, m.p. 194° (decomp.), which passes at 200° into 3-benzoyl-2:4-dimethylpyrrole (II), m.p. 130°. 2:3-Dimethylpyrrole-5-aldehyde and (II) condense in EtOH containing HBr to 4-benzoyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, m.p. 208° (decomp.), readily brominated in AcOH to 3-bromo-4'-benzoyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, decomp. 193°; under similar conditions 4'-acetyl-3':4:5:5'-tetramethylpyrromethene hydrobromide, decomp. 212°, gives ill-defined products. The wide applicability of the method of condensation is illustrated by the prep. of 4'-benzoyl-3':5:5'-trimethyl-4-ethylpyrromethene hydrobromide, m.p. 224° (decomp.) (3-Br-derivative, decomp. 202°), from 2-methyl-3-ethylpyrrole-5-aldehyde and (II), of 4'-acetyl-3':5:5'-



trimethyl-4-ethylpyrromethane hydrobromide, m.p. 214° (decomp.), from (I) and 3-acetyl-2:4-dimethylpyrrole, of 4'-benzoyl-3:3':4:5:5'-pentamethylpyrromethane hydrobromide, m.p. 224° (decomp.), from (II) and 2:3:4-trimethylpyrrole-5-aldehyde, of 4'-benzoyl-3:3':5:5'-tetramethyl-4-ethylpyrromethane hydrobromide (III), m.p. 211° (decomp.), from 2:4-dimethyl-3-ethylpyrrole-5-aldehyde and (II), of 4'-benzoyl-3:3':5:5'-tetramethylpyrromethane hydrobromide, m.p. 189° (decomp.) (corresponding 4-Br-derivative which becomes discoloured at about 210°), and of 4'-benzoyl-3:3':5:5'-trimethyl-4-β-carboxyethylpyrromethane hydrobromide, m.p. 204° (decomp.) (corresponding 5-Br-derivative, which has no defined m.p.). If (II) is heated with 95% HCO<sub>2</sub>H and 48% HBr is then added, 4:4'-dibenzoyl-3:3':5:5'-tetramethylpyrromethane hydrobromide (IV), decomp. 225°, is obtained, also prepared in AcOH or from Et 3-aldehydo-2:4-dimethylpyrrole-5-carboxylate and (II). 4:4'-Dibenzoyl-3:3':5:5'-tetramethylpyrromethane, m.p. 209°, is very stable. Addition of an intimate mixture of (III), 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethane hydrobromide, and



(·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> to boiling (·CH<sub>2</sub>·CO<sub>2</sub>H) gives, after treatment of the product with CH<sub>3</sub>N<sub>2</sub>, small amounts of 4-benzoyl-2:3:5:8-tetramethyl-1-ethyl-6:7-di-β-carbomethoxyethylporphin (cf. A; R=[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H), m.p. 263° (corr.), and mesoporphyrin 13, thus establishing the formation of cryptopyrrole-methene as intermediate product. Analogous treatment of (IV) and 5:5'-dibromo-4:4'-dimethyl-3:3'-di-β-carboxyethylpyrromethane hydrobromide leads to 1:4-dibenzoyl-2:3:5:8-tetramethyl-6:7-di-β-carbomethoxyethylporphin [dibenzoyldeuteroporphyrin Me<sub>2</sub> ether 13]



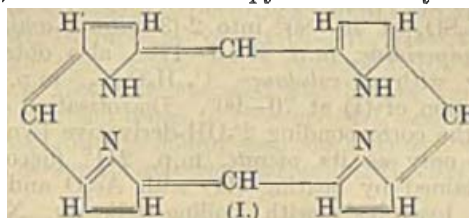
(cf. B: R=[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>Me), m.p. 252° (corr.), which with Fe(OAc)<sub>2</sub> and NaCl in boiling AcOH affords the compound C<sub>46</sub>H<sub>40</sub>O<sub>6</sub>N<sub>4</sub>FeCl, m.p. about 290°; products, m.p. 183.5° (corr.) and 257° (corr.), respectively, are also obtained in the synthesis, which gives poor yields. Dibenzoyldeuteroporphyrin 5 is described.

Treatment of pyrrohaemin ester with Bz<sub>2</sub>O and SnBr<sub>4</sub> at 70° leads to benzoylpyrrohaemin Me ester 5 (V), m.p. 313° (corr.), less readily obtained by use of SnCl<sub>4</sub>; the corresponding free acid (VI) has m.p. > 320°. Treatment of (V) with AcOH, Fe(OAc)<sub>2</sub>, and NaCl in boiling CHCl<sub>3</sub> affords benzoylpyrrohaemin Me ester, C<sub>39</sub>H<sub>38</sub>O<sub>3</sub>N<sub>4</sub>FeCl. (V) and Cu(OAc)<sub>2</sub> in

C<sub>5</sub>H<sub>5</sub>N·AcOH give the Cu salt, C<sub>39</sub>H<sub>38</sub>O<sub>3</sub>N<sub>4</sub>Cu. Benzoylpyrrohaemin oxime has m.p. 224°, but reaction is not observed with the acid and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> or NH<sub>2</sub>·CO·NH·NH<sub>2</sub>. Reduction of (VI) gives α-hydroxybenzylpyrrohaemin, m.p. > 300°, which gives minimal amounts of new porphyrins with boiling Ac<sub>2</sub>O or (EtCO)<sub>2</sub>O and pyrrohaemin when treated with conc. H<sub>2</sub>SO<sub>4</sub> at 100°. Reduction of benzoylpyrrohaemin with Na and isoamyl alcohol is described.

H. W.

**Porphyrins. XXXV. Synthesis of porphin.** H. FISCHER and W. GLEIM (Annalen, 1935, 521, 157—160).—Slow addition of pyrrole-2-aldehyde in EtOH



to boiling HCO<sub>2</sub>H followed by protracted ebullition of the mixture gives very small amount of porphin (I), which darkens above 360° and blackens at 400°, and, in dioxan, closely resembles spectroscopically deoxoetioporphyrin. The Cu and Fe salts have been examined spectroscopically.

H. W.

**Optical absorption of porphyrins. III.**—See this vol., 8.

**Fluorescence spectra of chlorophyll pigments.**—See this vol., 125.

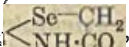
**Optical activity of hæmoglobin and its derivatives.**—See this vol., 92.

**Mechanism of oxidation of o-toluenesulphonamide to saccharin.** O. J. MAGIDSON and I. G. ZILBERG (J. Gen. Chem. Russ., 1935, 5, 920—923).—o-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NH<sub>2</sub> (I) in Ac<sub>2</sub>O and CrO<sub>3</sub> at -5° to 30° yield o-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NHAc, m.p. 132—134°, a substance (II), m.p. 174—176° (probably OAc·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·NHAc), and a substance (III), m.p. 103—105°; in presence of H<sub>2</sub>SO<sub>4</sub> acetsaccharin is obtained in addition to the above products. (II) and (III) yield saccharin (IV) when oxidised with KMnO<sub>4</sub>, and (II) is probably an intermediate in the oxidation of (I) to (IV).

R. T.

**Fission of ketosulphidocarboxylic acids. II.**

**Aryl selenohalides. VI.** O. BEHAGEL and W. MÜLLER (Ber., 1935, 68, [B], 2164—2166; cf. A., 1935, 1237, 1257).—3-Keto-2:3-dihydro-1:4-benzo-

selenazine (I), C<sub>6</sub>H<sub>4</sub>·, m.p. 182°, obtained by

reduction of o-nitrophenylselenolacetic acid, is converted by Br in CHCl<sub>3</sub> into 1:1-dibromo-3-keto-2:3-dihydro-1:4-benzoselenazine (II), m.p. 211°, which loses HBr in boiling PhMe giving 2-bromo-3-keto-2:3-dihydro-1:4-benzoselenazine (III), m.p. 213—214°. Analogously 1:1-dichloro-3-keto-2:3-dihydro-1:4-benzoselenazine (IV), m.p. 222°, affords 2-chloro-3-keto-2:3-dihydro-1:4-benzoselenazine, m.p. 228°. Boiling H<sub>2</sub>O transforms (II) or (IV) into the corresponding oxide, m.p. (indef.) 160°. (III) condenses

with  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  in feebly acid solution to the acid,  $\text{C}_9\text{H}_7\text{Sc}(\text{NH}\cdot\text{CO})\text{CH}_2\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m.p. 209—210°, hydrolysed by alkali to (I),  $\text{H}_2\text{S}$ , and  $\text{H}_2\text{C}_2\text{O}_4$ .

**Amidation with sodium and potassium amides on  $\alpha$ - and  $\alpha'$ -aminoanabasine. IV. Nitration of  $\alpha'$ -aminoanabasine.** M. M. KATZNELSON and M. I. KABATSHNIK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 169—172).—2-(2'-Amino-5'-pyridyl)piperidine (I), m.p. 109° ( $\alpha'$ -aminoanabasine; A., 1935, 223), with  $\text{HNO}_3$  (d 1.4)— $\text{H}_2\text{SO}_4$  at 0° affords the 2'-nitroamine isolated as its *sulphate* +  $\text{H}_2\text{O}$  and anhyd. (II), m.p. 233° (decomp.), converted by heating with conc.  $\text{H}_2\text{SO}_4$  at 70—80° into 2-(3'-nitro-2'-amino-5'-pyridyl)piperidine, m.p. 178.5—179°, also obtained, together with a substance,  $\text{C}_{10}\text{H}_9\text{O}_6\text{N}_3$ , m.p. 70°, by nitration of (I) at 70—90°. Diazotisation of (I) affords the corresponding 2'-OH-derivative (*Na* salt) isolated only as its *picrate*, m.p. 241° (decomp.), also obtained by heating (II) with  $\text{Ac}_2\text{O}$  and subsequent hydrolysis with boiling 5% aq.  $\text{NaOH}$ . [Note: the m.p. of the 3'- and 5'-pyridyl compounds (*loc. cit.*) should be interchanged; that of the former is 89.5—90°.] J. W. B.

**Cactus alkaloids. XV. Separation of the Anhalonium bases.** E. SPATH and F. BECKE (Monatsh., 1935, 66, 327—336).—Mescal buttons are extracted with pure  $\text{EtOH}$  at room temp. and, after removal of solvent, the extract is dissolved in  $\text{H}_2\text{O}$ , treated with excess of  $\text{KOH}$ , and exhaustively extracted with pure  $\text{Et}_2\text{O}$ . The extract is shaken with conc.  $\text{KOH}$ . The combined alkaline solutions are neutralised, rendered slightly alkaline with  $\text{K}_2\text{CO}_3$ , and extracted with  $\text{Et}_2\text{O}$ , thus giving all the phenolic alkaloids with small amounts of non-basic compounds. From them anhalamine is first separated as the hydrochloride. The free bases are isolated from the mother-liquors from this salt, distilled in a high vac., and pellotine is pptd. as the hydrochloride from their solution in  $\text{EtOH}$ - $\text{Et}_2\text{O}$ . The residual mixture of bases give a cryst. perchlorate which is not homogeneous. Treatment of the bases with  $\text{Et}_2\text{O}$  separates them into the sparingly sol. anhalonidine and anhalidine [*N*-methylanhalamine]. From the non-phenolic bases the bulk of the mescaline is first separated as the sulphate from  $\text{H}_2\text{O}$ ; from the mother-liquors anhalonine is isolated as the sparingly sol. hydrochloride. Anhalinine [*O*-methylanhalamine] is also isolated, whilst the final mother-liquors afford lophophorine, separated as the picrate. H. W.

**Alkaloids of *Papaver* types. I. Alkaloids of *P. armeniacum* and *P. orientale*.** R. KONOVALOVA, S. JUNUSOV, and A. OREKHOV (Ber., 1935, 68, [B], 2158—2163).—Percolation with  $\text{C}_2\text{H}_5\text{Cl}_2$  of the air-dried foliage of *P. orientale* which has been moistened with 10%  $\text{NH}_3$  leads to the isolation of thebaine and oripavine,  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$ , m.p. 200—201°,  $[\alpha]_D -211.8^\circ$  in  $\text{CHCl}_3$  (hydrochloride, m.p. 244—245°; methiodide, m.p. 207—208°), which dissolves in 10%  $\text{NaOH}$  giving a cryst. *Na* salt. It appears to be  $\text{C}_{18}\text{H}_{12}\text{O}(\text{NMe})(\text{OMe})\cdot\text{OH}$ . The presence of isothebaine could not be detected. Similar treatment of *P. armeniacum* yields armepavine (I),  $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}$ ,

m.p. 148—149° (or, + $\text{H}_2\text{O}$ , m.p. about 100°),  $[\alpha]_D -118.7^\circ$  in  $\text{CHCl}_3$  (hydrochloride, m.p. 151—152°; sparingly sol. oxalate, m.p. 211—212°; methiodide, m.p. 199—200°), which contains  $\text{NMe}$ , 2  $\text{OMe}$ , and  $\text{OH}$ . (I) is transformed by  $\text{MeI}$  and  $\text{NaOMe}$  in boiling  $\text{MeOH}$  into *O*-methylarmepavine methiodide, m.p. 120—122°. Treatment of (I) in  $\text{CHCl}_3$  with  $\text{ClCO}_2\text{Et}$  and  $\text{NaOH}$  gives an optically inactive oil, indicating that (I) may be a tetrahydroisoquinoline derivative. H. W.

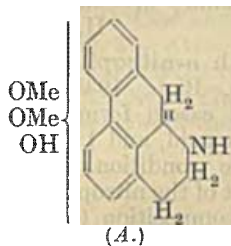
**Alkaloid of chin-shih-hu.** K. K. CHEN and H. L. CHEN (J. Biol. Chem., 1935, 111, 653—658).—Chin-shih-hu from Szechuan contains 0.52% of alkaloids, mainly dendrobine (modified isolation),  $\text{C}_{16}\text{H}_{25}\text{O}_2\text{N}$ , m.p. 135°,  $[\alpha]_D -52^\circ$  in  $\text{EtOH}$  [hydrochloride, m.p. 193°,  $[\alpha]_D -40.3^\circ$ ; hydrobromide, m.p. 259—259.5°,  $[\alpha]_D -34.3^\circ$ ; hydriodide, m.p. 284—284.5°,  $[\alpha]_D -29^\circ$ ; nitrate, m.p. 198.5—199°,  $[\alpha]_D -30.2^\circ$ ; sulphate, m.p. 178°,  $[\alpha]_D -36.7^\circ$ ; oxalate, m.p. 137—138°,  $[\alpha]_D -50.8^\circ$ ; picrate, m.p. 210° (decomp.); flavianate, decomp. 212°; methiodide, m.p. 246°,  $[\alpha]_D -28.8^\circ$  in  $\text{EtOH}$ ; aurichloride, m.p. 183—184°; platinichloride, m.p. 283°.  $[\alpha]$  are in  $\text{H}_2\text{O}$ ]. The Kweichow variety contains another alkaloid, but no dendrobine. M.p. are corr. R. S. C.

**Alkaloid from *Trichodesma incanum*** D.C. I. G. MENSCHIKOV and V. RUBINSTEIN (Ber., 1935, 68, [B], 2039—2044).—Percolation of the dried plant with 95%  $\text{EtOH}$  containing 1% of  $\text{NH}_3$ , removal of the solvent, and extraction of the residue with dil.  $\text{HCl}$  followed by treatment of the acid solution with  $\text{NH}_3$  and  $\text{CHCl}_3$  yields trichodesmine (I),  $\text{C}_{13}\text{H}_{27}\text{O}_6\text{N}$ , m.p. 160—161° (decomp.),  $[\alpha]_D +38^\circ$  in  $\text{EtOH}$  [methiodide, m.p. 202° (decomp.)], which does not react with cold  $\text{HNO}_3$ , and hence contains *tert*.-N. Hydrolysis of (I) with 10%  $\text{NaOH}$  at 100° affords  $\text{COMeBu}^s$ , *r*-lactic acid, and trichodesmidine (II),  $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$ , m.p. 117—118.5°,  $[\alpha]_D +50^\circ$  in  $\text{MeOH}$  (picrate, m.p. 142—143.5°), not identical with heliotridine. Hydrogenation of (II) readily affords the saturated hydroxytrichodesmidane (III),  $\text{C}_8\text{H}_{15}\text{ON}$ , m.p. 92—94° [picrate, m.p. 211.5—212.5° (decomp.)]. Treatment of (III) with conc.  $\text{H}_2\text{SO}_4$  at 165—170° and subsequent hydrogenation ( $\text{AdS}_4$ ) of the product leads to heliotridane. Heliotridine and (II) have therefore the same skeleton, and are differentiated from one another by the position of  $\text{OH}$  and possibly of the double linking. (I) is a complex ester of (II) and *r*-lactic acid and either  $\text{CHPr}^s\text{Ac}\cdot\text{CO}_2\text{H}$  or isovalerylacetic acid. The distribution of acid residues in the mol. cannot yet be established; since (I) does not give a colour with  $\text{FeCl}_3$ , it is probable that lactic acid esterifies the enolic  $\text{OH}$  of the tautomeric form of the  $\beta$ -CO-acid. H. W.

**Sinomenine. XLIV. Tuduranine, a new alkaloid from *Sinomenium acutum*.** K. GOTO (Annalen, 1935, 521, 175—184).—The mother-liquors from the extraction of sinomenine give the sparingly sol. tuduranine hydrochloride (I),  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}\cdot\text{HCl}$ , m.p. 286° (decomp.),  $[\alpha]_D -148^\circ$  in  $\text{H}_2\text{O}+\text{MeOH}$ , from which the poorly cryst. tuduranine (II), m.p. about 125° after softening at 105°, is isolated. (II) contains 2  $\text{OMe}$ , but no  $\text{CH}_2\text{O}$ ., is freely sol. in alkali, but gives a feeble  $\text{FeCl}_3$  or diazo-reaction. The presence of



1OH is established by the isolation of *diacetyltuduranine*, m.p. 170°,  $[\alpha]_D^{25}$   $-321.71^\circ$  in MeOH, which does not combine with MeI, and is hydrolysed to *N-acetyltuduranine*, m.p. 277°,  $[\alpha]_D^{25}$   $-395.24^\circ$  in MeOH-CHCl<sub>3</sub>, whence *N-acetyltuduranine Me ether*, m.p. 189°,  $[\alpha]_D^{25}$   $-400.17^\circ$  in CHCl<sub>3</sub>. (II) and MeI in MeOH afford *N-methyltuduranine methiodide* (III), m.p. 224°. (II) gives a characteristic, fuchsin-red colour with CH<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub>. Spectroscopically, (I) is closely similar to morphothebaine Me<sub>2</sub> ether (III). The Hofmann degradation of *N-methyltuduranine Me ether methiodide*, m.p. 219°, however, affords successively *de-N-dimethyltuduranine Me ether (methiodide)*, m.p. 279° and *trimethoxyvinylphenanthrene*, m.p. 93-5°, with NMe<sub>3</sub>; the positions of the 3 OMe in the ether do not therefore coincide with those in (III) or *isothebaine Me ether*. (I) is transformed by NaOH and Et<sub>2</sub>SO<sub>4</sub> followed by KI into *N-ethyltuduranine Et ether ethiodide*, m.p. 238°,  $[\alpha]_D^{25}$   $-112.47^\circ$  in CHCl<sub>3</sub> (with some *N-diethyltuduranine Et ether ethiodide*, m.p. 163-164°, converted by the successive action of NaOH and EtI into *de-N-diethyltuduranine Et ether ethiodide*, m.p. 164°,  $[\alpha]_D^{25}$   $\pm 0^\circ$  (corresponding *hydriodide*, m.p. 163-164°), whence *dimethoxyethoxyvinylphenanthrene*, m.p. 148° after softening at 110°, and NEt<sub>3</sub>. The Hofmann degradation of (III) gives *de-N-dimethyltuduranine (methiodide)*, m.p. 259°, whence a compound, C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>, m.p. 292-294°. Oxidation of (II) with



KMnO<sub>4</sub> gives very small amounts of an acid, m.p. about 263°, but no hemipinic or *metahemipinic* acid. The structure A is therefore assigned to (II). H. W.

**Sinomenine. XLII.** (+)- and (-)-**Bromothebenone.** K. GOTO, M. OGAWA, and J. SAITO (Bull. Chem. Soc. Japan, 1935, 10, 481-482; cf. A., 1935, 1138).—Dihydrode-*N*-methylmethoxydihydrosinomenine (I) and Br-AcOH give the (+)-1-*Br*-derivative (II), m.p. 192°,  $[\alpha]_D^{17}$   $+61.6^\circ$  in CHCl<sub>3</sub> [*hydrobromide*, m.p. 257° (decomp.); *methiodide*, m.p. 273°]. The methiodide of (I) and 25% KOH give (-)-1-*bromothebenone* (III), m.p. 70°,  $[\alpha]_D^{17}$   $-22.67^\circ$  in CHCl<sub>3</sub>. 1-Bromodimethoxydihydrosinomenine methiodide and 15% NaOH give 1-*bromode-N-methylmethoxydihydrosinomenine* (IV), m.p. 200-201°,  $[\alpha]_D^{17}$   $-8.67^\circ$  in CHCl<sub>3</sub>, the *methiodide*, decomp. 243°, of which with 11% NaOH affords (-)-1-*bromodehydrothebenone* (V), m.p. 145°,  $[\alpha]_D^{17}$   $-186.8^\circ$  in CHCl<sub>3</sub>. (-)-Dehydrosinomenine and Br-AcOH yield (-)-*iso*-9- or -10-*bromodehydrothebenone* (VI), m.p. 125-133°,  $[\alpha]_D^{17}$   $-113.3^\circ$  in CHCl<sub>3</sub>. The *stereoisomerides* are prepared from thebainone and admixture gives the *dl*-bases, (II), m.p. 175-177°, (III), m.p. 191-193°, (IV), m.p. 189-192°, (V), m.p. 159-162°, and (VI), m.p. 156-158°. R. S. C.

**Bitter principles of the Colombo root. III.** K. FEIST, E. KUNTZ, and R. BRACHVOGEL (Annalen, 1935, 521, 184-188; cf. A., 1935, 1245).—The discrepancies between the authors' observations and those of Wessely *et al.* (*ibid.*, 1432) are due to the use by the latter of insufficiently purified material. Columbin is very sensitive to alkali, and attempts to

methylate it by KOH-*p*-C<sub>6</sub>H<sub>4</sub>Me-SO<sub>3</sub>Me lead to *carboxyiso-V-columbin*, m.p. 194-195° (decomp.).

H. W.

**Alkaloids of *Duboisia Hopwoodii*.**—See this vol., 125.

**Alkaloids of European *Lycopodium* species.**—See this vol., 125.

**Influence of air on solutions of salvarsan derivatives.**—See this vol., 32.

**Arsenical derivatives of carbazole.** S. M. SOHERLIN and A. J. BERLIN (J. Gen. Chem. Russ., 1935, 5, 938-942).—Diazotised 3-aminocarbazole and Na<sub>3</sub>AsO<sub>3</sub> in presence of CuSO<sub>4</sub>-NH<sub>3</sub> yield *carbazyl-3-arsinic acid*, which yields *carbazyl-3-dichloroarsine* (I), m.p. 150°, when treated with SO<sub>2</sub> in conc. HCl-EtOH at room temp. in presence of I, and carbazole and AsCl<sub>3</sub> in the boiling solution. (I) and aq. NH<sub>3</sub> afford *carbazyl-3-arsinous acid*, m.p. 267-269°.

R. T.

**Action of alkyl iodides on heterocyclic organic arsenic compounds. I.** V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 510-514).—The Cl of 5-chloro- and 5-chloro-10-acetyl-5:10-dihydrophenarsazine, chlorophenoxarsine, and diphenylenechlorarsine in replaced by I when the compounds are heated with MeI, EtI, or *iso*-C<sub>5</sub>H<sub>11</sub>I in sealed tubes, products containing As<sup>V</sup> not being formed. 5:10-Dihydrophenarsazine oxide and MeI (6 hr.; 90°) afford an unidentified product, C<sub>14</sub>H<sub>15</sub>NAsI<sub>2</sub>, m.p. 138-142°, containing As<sup>V</sup>, whilst EtI and *iso*-C<sub>5</sub>H<sub>11</sub>I yield 5-iodo-5:10-dihydrophenarsazine. 5-Acetyl-5:10-dihydrophenarsazine and MeI give 5-methyl-5:10-dihydrophenarsazine methiodide.

R. T.

**Hydroxy-derivatives of 5-alkyl(aryl)-5:10-dihydrophenarsazine. II.** Synthesis and properties of monohydroxy-5-*R*-5-*R'*-5:10-dihydrophenarsazine. **III.** Synthesis of derivatives of the betaine type. G. A. RAZUVAEV and V. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 570-574, 575-579).—II [with A. F. SHIGATSKH and Z. I. AZARCH]. The methiodides of 5-alkyl(aryl)-dihydrophenarsazines yield the following hydroxides and nitrates with AgOH and AgNO<sub>3</sub>, respectively: *monohydroxide* of 5:5-dimethyl-, m.p. 242° [*nitrate* (I), m.p. 258°; NO<sub>2</sub>-derivative (II)], of 5-phenyl-5-methyl-, m.p. 202-204° [*nitrate*, m.p. 210°; NO<sub>2</sub>-derivative (III), m.p. 120-124°], and of 5-methyl-5-isoamyl-5:10-dihydrophenarsazine, m.p. not given (*nitrate*, m.p. 191-193°). Attempts to reduce the NO<sub>2</sub> of (II) and (III) resulted in its elimination.

III [with S. E. ARKINA]. 5-Methyl-5:10-dihydrophenarsazine and CH<sub>2</sub>Cl-CO<sub>2</sub>H in C<sub>6</sub>H<sub>6</sub> at 90° yield 5-chloro-5-methyl-5:10-dihydrophenarsazinoacetic acid (IV), m.p. 237-238° [*Et* ester (V), m.p. 198°; *nitrate*, m.p. 179°; *platinichloride*, m.p. 138-140°; *picrate*, m.p. 199°]; the analogous 5-*Et* derivative, m.p. 201-204° (*nitrate*, m.p. 170°), is obtained similarly. (IV) or (V) afford an *anhydride* (VI), m.p. 199-203°, of the betaine type, when heated with aq. NaOH. The *dinitro*-derivative of (VI), m.p. 163-165° obtained from (IV) and HNO<sub>3</sub>, yields (VI) when reduced with Fe(OH)<sub>2</sub> in aq. NaOH.

R. T.



**Behaviour of *o*-toluidine with mercuric acetate.** L. VECCHIOTTI and (SIENA) A. AJUTO (*Gazzetta*, 1935, 65, 832—836; cf. A., 1929, 1091, 1492).—*o*-Toluidine (1 mol.) and  $\text{Hg}(\text{OAc})_2$  (3 mol.) at 30° form 3 : 5 : 6-tri*aceto*mercuri-*o*-toluidine, m.p. 161°, of which the structure is determined by converting the *Ac* derivative, m.p. 211°, by  $\text{Cl}_2$  and  $\text{KCl}$  in  $\text{AcOH}$  into 3 : 5 : 6-tri*chloro*-*o*-*acet*-toluidide, m.p. 190—191°, hydrolysed to 3 : 5 : 6-tri*chloro*-*o*-toluidine.

E. W. W.

**Mercuric salicylate and dithiosalicylate.** V. PAOLINI (*Gazzetta*, 1935, 65, 836—839).—The product from  $\text{HgO}$  and salicylic acid in  $\text{H}_2\text{O}$ , or from  $(\text{o-HI} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2\text{Hg}$  at 170°, is sol. in  $\text{NaOH}$ , and therefore regarded as an *anhydride* of (3-hydroxymercuri)-salicylic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{Hg} \cdot \text{O}$ . Dithiosalicylic acid,  $[\text{C}_6\text{H}_4(\text{OH})(\text{CO}_2\text{S})]_2$ , reacts with  $\text{HgCl}_2$  to form compounds regarded as  $[\text{C}_6\text{H}_4(\text{OH})(\text{CO}_2\text{H})(\text{HgCl}) \cdot \text{S}]_2$  and  $\left[ \text{O} \cdot \text{CO} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4(\text{OH}) \cdot \text{S} \right]_2$ .

E. W. W.

[Preparation of] mercurated hydroxyaryl sulphides. See B., 1935, 1119.

**Synthesis of organoselenenic compounds.** VII. Selenium diphenol. S. KIMATSU and I. SATODA (*J. Pharm. Soc. Japan*, 1935, 55, 58—66).—Diazotised bis-(4-aminophenyl) diselenide when treated with  $\text{KSeCN}$  yields bis-(4-selenocyanophenyl) diselenide, m.p. 161°, reduced ( $\text{Zn}$  dust-dil.  $\text{H}_2\text{SO}_4$ ) to diselenoguaiacol, m.p. 120—121° (*Me\_2* ether, m.p. 81°), which undergoes aerial oxidation to a substance, m.p. 247—248°. Bis-(3-aminophenyl) diselenide (prep. described), diazotised and coupled with  $\text{KSeCN}$ , affords bis-(3-selenocyanophenyl) diselenide, m.p. 96° (*Me\_2* ether, b.p. 129—130°/2—2.5 mm.), reduced, as above, to diselenoresorcinol, which is very unstable, being oxidised in air to a product, m.p. 123—124°.

CH. ABS. (r)

**Vanado-organic compounds.** I. A. V. KIRSAKOV and T. V. SAZONOVA (*J. Gen. Chem. Russ.*, 1935, 5, 936—962).— $\text{R}_2\text{VO}_4$  ( $\text{R} = \text{iso-C}_3\text{H}_7$ ) and  $\text{MgPhBr}$  at  $-20^\circ$  yield chiefly  $\text{Ph}_2$  and  $\text{V}_2\text{O}_5$ , together with traces of an  $\text{Et}_2\text{O}$ -sol. product, readily oxidised by atm.  $\text{O}_2$  to yield  $\text{V}_2\text{O}_5$ , and probably  $\text{VPh}_2 \cdot \text{O} \cdot \text{MgBr}$ . The corresponding reaction with  $\text{MgMeI}$  gives chiefly  $\text{C}_2\text{H}_5$ , without formation of org. V derivatives. The following salts of V are described:  $\text{Et}_2\text{VOH}$  ( $\text{o-OH} \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$ ),  $\text{VOH}$ , ( $\text{o-NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$ ),  $\text{VOH}$ , and  $(\text{CH}_3\text{CO}_2)_2\text{VOH}$ .

R. T.

**Antoclave splitting of protein by means of absolute methyl alcohol.** V. S. SAMKOV and V. A. VANOVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 317—320).—Protein of blood serum, heated with 5 parts of  $\text{MeOH}$  at 180°/30—60 atm. for 3 hr., affords  $\text{NH}_3$  and a residue which is separated into  $\text{H}_2\text{O}$ -sol. and  $\text{H}_2\text{O}$ -insol. fractions.  $\text{Et}_2\text{O}$  extraction of the former gives unidentified cyclopeptides and a cycloleucyltriazine,  $\text{OH} \cdot \text{C} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \cdot \text{C} \cdot \text{OH}$ ; that of the latter affords a syrup (N, 8.35%; no  $\text{NH}_3$  or amide-N). Hydrolysis with 20%  $\text{H}_2\text{SO}_4$  is described; no chemical individuals are isolated. The results of the  $\text{MeOH}$  hydrolysis are compared with those obtained using  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ , or  $\text{EtOH}$ .

P. G. C.

**Chemical groups of proteins which possess affinity for polysaccharides.** VI. Role of lysine, leucine, phenylalanine, aspartic acid, glutamic acid, asparagine, cystine, and tryptophan. S. J. VON PRZYŁECKI, H. RAFAŁOWSKA, and J. CICHOCKA. VII. Nature of the polysaccharide-guanidine complex. W. GIEDROYĆ, J. CICHOCKA, and E. MYSTKOWSKI (*Biochem. Z.*, 1935, 281, 420—422, 422—430).—VI. None of the investigated acids shows any detectable affinity for P-free polysaccharides either at  $p_{\text{H}}$  3, 4, 6.5, or 7. The ppt. obtained with dextrin never contained > 3.5%.

VII. P-free polysaccharoproteins do not arise by use of primary valencies between the arginine residue and the free  $\cdot\text{CHO}$  groups, but much more probably through the presence of residual affinity of the  $(\text{NH}_2)_2\text{C} \cdot \text{NH}$  group and the alcohol group of the polysaccharides.

P. W. C.

**Structure of the simplest proteins.** E. WALDSCHMIDT-LEITZ (*Monatsh.*, 1935, 66, 357—366).—The structure  $[\text{M} \cdot \text{A} \cdot \text{A}]_3 \cdot \text{P} \cdot \text{A} \cdot \text{A} \cdot \text{M} \cdot \text{A} \cdot \text{A}$  is assigned to clupeine [ $\text{A}$ =arginine,  $\text{P}$ =proline,  $\text{M}$ =aliphatic  $(\text{NH}_2)_1$ -acid residue].

H. W.

**Compounds of proteins with *o*-nitrophenols.** A. BOELLIGER (*Austral. J. Exp. Biol.*, 1935, 13, 189—191).—Globin, cdestin, and casein form compounds with picric acid, picrolonic acid, and 1 : 2 : 4- $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ . Under suitable conditions these compounds are saturated in respect of the nitrophenols and are then of approx. const. composition (cf. A., 1935, 879).

W. O. K.

**Ultra-carbon determination.** W. LUTTGENS and W. CHRISTIAN (*Biochem. Z.*, 1935, 281, 310—313).—The material is combusted in the usual Pregl manner, the  $\text{CO}_2$  formed is absorbed in 0.1N- $\text{NaOH}$ , and is determined in an aliquot manometrically after re-liberation with  $\text{H}_2\text{SO}_4$ . An example gives details of calculation of results.

P. W. C.

**Organic analysis. Determination of (A) sulphur, (B) copper, in organic compounds.** N. N. MELNIKOV (*J. Gen. Chem. Russ.*, 1935, 5, 839—840, S41—S42).—(A) 0.2—0.5 g. of substance is heated at 70—140° with 10—15 c.c. of  $\text{H}_3\text{PO}_4$  ( $d$  1.7), and 1.5—4 g. of  $\text{KMnO}_4$  are gradually added. The melt is heated 15 min. longer, excess of  $\text{KMnO}_4$  is removed by  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$  is added to 300—400 c.c., and  $\text{SO}_4^{2-}$  is determined by pptn. as  $\text{BaSO}_4$ . The method is not applicable to volatile compounds.

(s) 0.1—0.5 g. of substance is heated at 70—80° with 10—15 c.c. of conc.  $\text{H}_2\text{SO}_4$  and 1—4 g. of  $\text{KMnO}_4$ , excess of  $\text{KMnO}_4$  is removed by  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{O}$  is added to 100—250 c.c., and  $\text{Cu}^{2+}$  is determined iodometrically.

R. T.

**Determination of small amounts of arsenic in organic materials.** K. WINTERFELD, E. DÖRFL, and C. RAUCH (*Arch. Pharm.*, 1935, 273, 457—467).—Org. matter is destroyed, the As distilled off as  $\text{AsCl}_3$ , collected and converted into  $\text{AsH}_3$ , which is collected in  $\text{HgCl}_2$  and determined by a modified I- $\text{Na}_2\text{S}_2\text{O}_3$  method.  $1.5 \times 10^{-4}$  g. of As can be thus determined.

R. S. C.

**Titrimetric determination of water and alcohols.**—See this vol., 41.

**Formaldehyde, alcohol, and acetone titrations.** Addendum. G. M. RICHARDSON (Proc. Roy. Soc., 1935, B, 119, 85—86; cf. A., 1934, 634).—In the titration of substances containing several acidic or basic groups the initial and end-points must be clearly defined. E. A. H. R.

**Determination of reducing sugars.**—See this vol., 126.

**Potentiometric determination of polypeptides and amino-acids.** E. W. BALSON, G. A. EARWICKER, and A. LAWSON (Biochem. J., 1935, 29, 2700—2704).—Titration of mixtures of  $\text{NH}_2$ -acids and polypeptides is carried out in 90% aq. EtOH: the degree of separation is discussed. As the  $p_H$  of the end-point for some mixtures varies over a range of 2 units depending on the proportions of the constituents, a potentiometric titration is used with a special method of differential plotting. J. N. A.

**Determination of benzene by the Pulfrich step-photometer.**—See this vol., 126.

**Determination of toluidines in aqueous solution.** D. CISMARU (Bul. Soc. Chim. Romania, 1934, 16, [A], 37—41).—Aq. *o*-, *m*-, or *p*-toluidine,  $\text{CuSO}_4$ , and 0.1N- $\text{NH}_4\text{CNS}$  give quantitatively salts,  $[\text{CuB}_t](\text{SCN})_2$ . The base is determined by filtration and titration of the excess of  $\text{NH}_4\text{CNS}$  in the filtrate. R. S. C.

**Spectrographic determination of phenol.**—See this vol., 126.

**Photo-electric determination of salicylic acid.** P. F. BECH (Dansk Tidsskr. Farm., 1935, 9, 289—302).—The depth of colour of the Fe-salicylic acid complex in aq. solution is measured photo-electrically with a previously calibrated apparatus. Improvements in the author's earlier method are described (Farm. Tidende, 1933, 446). The effects of excess of salicylic acid and EtOH and of varying  $p_H$  have been investigated. Reproducible results are obtainable so long as  $\text{Fe}^{+++}$  is in excess,  $[\text{EtOH}] \geq 8\%$ , and  $p_H < 2.2$ . M. H. M. A.

**Acid-base titration in alcohol-water mixtures.**

**III. Titration of alkaloids and alkaloid salts.** H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Dansk Tidsskr. Farm., 1935, 9, 253—288; cf. A., 1934, 160).—The acidity consts.  $P_K$  for narcotine, papaverine, strychnine, morphine, codeine, brucine, cocaine, procaine, quinine, emetine, cinchonine, atropine, and ephedrine in 50% and 75% aq. EtOH have been determined colorimetrically and electrometrically, and the variation of  $P_K$  with  $[\text{EtOH}]$  is compared with that of indicator end-points. Most alkaloids lie on the border of practicable titration in 50% EtOH, but titration of alkaloid salts with bases is more accurate in aq. EtOH than in  $\text{H}_2\text{O}$ . J. A. S.

## Biochemistry.

**Gravimetric method for determining oxygen consumption in man.** J. P. HETTVER (J. Lab. Clin. Med., 1935, 20, 499—506). CH. ABS. (p)

**Respiration apparatus for small animals.** S. BELAK and A. ILLENYI (Biochem. Z., 1935, 281, 27—29). W. McC.

**Oxygen saturation of human arterial blood.** K. MATTHES (Arch. exp. Path. Pharm., 1935, 179, 698—711).—Continuous photo-electric recording (cf. A., 1934, 1377) indicates variations in arterial  $\text{O}_2$  saturation during inspiration of  $\text{O}_2$ -rich air, hyperventilation, respiratory failure, speaking, singing, etc. During the respiratory pause there is a fall in  $\text{O}_2$  saturation, the rate of which is a function of alveolar vol. The exact respiratory vol. being known, determinations of this rate for resting men during a series of respiratory pauses give the vol. of residual air and total capacity of the lungs. Tension, consumption, and velocity of transport of  $\text{O}_2$  during relaxation after heavy work are discussed. F. O. H.

**Thermochemistry of the oxygen-haemoglobin reaction. I. Direct measurements of the heat of reaction under various conditions.** F. J. W. ROUGHTON (Biochem. J., 1935, 29, 2604—2621).—The heat of reaction ( $Q$ ) of haemoglobin (I) with  $\text{O}_2$  is measured by shaking the solution of (I) with  $\text{O}_2$  in one Thermos flask and determining the temp. difference between this and another flask containing the same amount of fluid.  $Q$  is independent of the degree of  $\text{O}_2$  saturation of the blood, and is practically

the same in whole and laked blood and in purified (I) solutions.  $Q$  increases with increasing  $p_H$ , due partly to the difference between the  $Q$  for ionised (I) and that for non-ionised (I), and partly to secondary ionic reactions. H. D.

**Time course of heat effects in rapid chemical changes. I. Apparatus and methods. II. Reactions of haemoglobin with oxygen and carbon monoxide.** J. B. BATEMAN and F. J. W. ROUGHTON (Biochem. J., 1935, 29, 2622—2638). The earlier apparatus for measuring the heat effects in rapid chemical changes (A., 1930, 426) is modified so that the method will follow to within 1—2% the time course of the heat effects over a period of 0—0.01 sec. in which the total temp. change is  $< 0.01^\circ$ . The method is applied to the reaction of haemoglobin (I) with  $\text{O}_2$  and CO. With  $\text{O}_2$  the liberation of heat is complete within 0.008 sec., and with CO in approx. 0.05 sec. The half-reaction times for (I) with  $\text{O}_2$  and CO were 0.002 and 0.010 sec., respectively, in ordinary solutions of (I); in the intact corpuscles the times were 0.007 and 0.016 sec., respectively. The reaction rates as determined in this way agree with those obtained by Millikan's optical technique (A., 1934, 383). It is concluded that the primary combination of (I) with  $\text{O}_2$  or CO is not followed by any secondary reactions of appreciable heat effect.

**Action of some guanidine derivatives on constituents of blood.** K. TACHIBANA (Folia Pharmacol. Japon., 1935, 19, 365—376).—Decamethylene-

pentamethylene-, and cyclohexyl-guanidine had no effect on red cells in rabbits, but increased pseudo-eosinophile and blood platelets when low concns. were used. Higher concns. hindered leucocyte formation. CH. ABS. (p)

**Normal hæmatological standards.** E. E. OSGOOD (Arch. Int. Med., 1935, 56, 849—863).—From examinations of > 500 healthy persons of both sexes and of ages between 4 and 30, average vals. have been obtained for the erythrocyte, reticulocyte, and leucocyte counts, the hæmoglobin content and coeff., cell vol., vol. coeff., the colour, vol., and saturation indices, and sedimentation rate. H. G. R.

**Oxidation of hæmoglobin to methæmoglobin by oxygen. II. Relation between rate of oxidation and partial pressure of oxygen.** J. BROOKS (Proc. Roy. Soc., 1935, B, 118, 560—577).—The rate of oxidation of hæmoglobin (I) to methæmoglobin at  $p_H$  5.69 and 30° is unimol. with respect to the (I) concn. With varying  $O_2$  partial pressures ( $p$ ) the rate is a max. at  $p=20$  mm., being  $\propto$  the reduced (I) concn. and to  $p/(1+bp)$ . The rate-determining step is not the selective action of  $O_2$  with any of the intermediate compounds of (I) and  $O_2$ , and the effect of  $O_2$  appears to be threefold: (i) the determination of the concn. of the other reactant, (ii) oxidation of compounds containing  $Fe^{++}$ , (iii) an inhibiting effect on the oxidation. There is evidence of the presence of another inhibitor. F. A. A.

**Photochemical oxidation of hæmoglobin.** F. G. LENNOX (Austral. J. Exp. Biol., 1935, 13, 193—196).—The photochemical conversion of hæmoglobin into methæmoglobin is accelerated by KI and  $NH_4I$ . Free I is without effect either in presence or absence of KI. W. O. K.

**Optical activity of hæmoglobin and of derivatives: sulphur content.** S. SIMONOVITS and G. BALASSA (Biochem. Z., 1935, 281, 186—197; cf. A., 1931, 857).—Horse-blood hæmoglobin (I) exists in two forms containing, respectively, 0.43 and 0.49% of S, the CO compounds of these having  $[\alpha]_{589}^{20} +11.6^\circ$  and  $+12.3^\circ$  in  $H_2O$ , respectively (in 0.1% aq.  $NaHCO_3$  the val. is independent of the concn.). Horse oxyhæmoglobin (II) once cryst. has  $[\alpha]_{589}^{20}$  about  $+14.4^\circ$  and  $[\alpha]_{570}^{20}$  about  $+12.4^\circ$  in  $H_2O$  (1%), the vals. decreasing as the dilution increases. Repeated recrystallisation causes these vals. to decrease and the max. absorption of the transmitted light to increase. CO-(I) from cattle has  $[\alpha]_{589}^{20} +7.9^\circ$  in  $H_2O$  (1%). Horse-(I) once cryst. and reduced with  $Na_2S_2O_4$  has  $[\alpha]_{589}^{20}$  about  $+28.3^\circ$  in  $H_2O$  (5%). The S content of (II) is not altered by recrystallisation. W. McC.

**Osmotic equilibria of hæmocyanin in a gravitational field.** J. ROCHE, A. ROCHE, G. S. ADAIR, and M. E. ADAIR (Biochem. J., 1935, 29, 2576—2587).—Hæmocyanin (I), prepared from the blood of *Helix pomatia*, *Carcinus moenas*, and *Octopus vulgaris*, is placed in  $M/15$ -phosphate buffer solution in a collodion sac, and the pressure attained at equilibrium with a similar buffer solution measured. Samples of the solution are withdrawn from different depths and protein is determined refractometrically.

The ratio of concns. at 1 cm. distance apart varied between 1.004 and 1.019. The osmotic pressures of the (I) solutions are calc., correcting for variation in concn. with height in the sac; estimates of the mol. wts. of the (I) obtained from the three sources are comparable with those obtained by Svedberg (A., 1933, 171). H. D.

**State of phenol added to blood.** G. BARAC (Compt. rend. Soc. Biol., 1935, 120, 522—523).—PhOH can be recovered completely from blood by deproteinisation with  $CCl_3CO_2H$ , and is therefore not destroyed by the red corpuscles. It is distributed equally between the plasma and the corpuscles. Plasma-PhOH is not partly bound to the lipins, since it is separated completely from these by ultra-filtration. R. N. C.

**Plasma-lipins of normal men at different ages.** I. H. PAGE, E. KIRK, W. H. LEWIS, jun., W. R. THOMPSON, and D. D. VAN SLYKE (J. Biol. Chem., 1935, 111, 613—639).—Free and ester cholesterol, neutral fat, and total lipins were determined in the plasma, and frequency distribution curves were plotted. The individual vals. and their relative magnitudes showed no dependence on the age of the subject. There is an approx. reciprocal relationship between the amounts of cholesteryl esters and neutral fats in the lipin mixtures. The vals. are compared with those obtained by other workers. H. D.

**Influence of harmine on blood-sugar picture in rabbits.** K. TACHIBANA (Folia Pharmacol. Japon., 1935, 19, 346—354).—Harmine (2—50 mg. per kg.) causes a marked hyperglycæmia. This action is inhibited by ergotamine, yohimbine, or by double splanchnicotomy, is increased by small doses of pilocarpine, and is opposed by insulin. CH. ABS. (p)

**Residual carbon of blood in relation to sensitisation and anaphylactic shock.** F. DIEHL (Arch. exp. Path. Pharm., 1935, 179, 670—677).—The total blood-residual C compounds (I) (i.e., not pptd. by, e.g., phosphotungstic acid) increase on sensitisation of dogs by injection of horse-serum. This increase is restricted to the "known" (I) [e.g., sugar (II), lactic acid (III), total phenols, and  $NH_2-N$ , urea-N, and glyoxaline derivatives], the "unknown" (I) remaining unchanged. The marked increase in (I) produced by subsequent anaphylactic shock is mainly restricted to unknown (I). The changes in (II), (III), and hydrolysable reducing substances indicate that carbohydrate metabolism is involved. F. O. H.

**Blood modifications provoked by subcutaneous injection of glucose.** G. DELRUE and P. HOLLEBEKE (Compt. rend. Soc. Biol., 1935, 120, 529—530).—Subcutaneous injection of glucose in the rabbit increases total proteins; the increase of globulins is > that of serines, and the serine-globulin ratio falls. Cl and total bases show decreases of the same order. Creatine and  $PO_4'''$  are increased. R. N. C.

**Precipitation of serum-proteins with chloroform.** A. GRÖNWALL (Biochem. Z., 1935, 282, 85—87).—The extent of pptn. of proteins from human serum by mixtures (3:1) of  $CHCl_3$  and  $C_3H_{11}OH$



varies greatly with  $[H^+]$ , max. being observed at  $p_H$  4.3, 6.5, 8.4—8.7, and 9.4. W. McC.

**Form of the micelles of the stroma-proteins.** G. BOEHM (Biochem. Z., 1935, 282, 32—46; cf. A., 1932, 121).—A method for separating the proteins of the stroma of red blood-corpuscles (calf) from the hæmoglobin is described. The product is sol. in salt solutions of  $p_H$  6.5—7.1. The solutions exhibit streaming double refraction and contain thread-like micelles (length-width ratio several thousand to 1). Since the space requirements of the micelles are very great, concns.  $> 3$ —4% cannot be obtained without production of gels. It follows that the stroma-protein of the erythrocytes is not conc. in a membrane, but extends throughout their interior. W. McC.

**Blood-amino-nitrogen in health and disease.** A. SIMON and B. ZEMPLÉN (Arch. exp. Path. Pharm., 1935, 179, 712—716).—The  $NH_2$ -N contents of whole blood, corpuscles, and plasma (before and after hæmolysis) of 21 normal and 44 diseased persons are tabulated and discussed. F. O. H.

**Significance of post-operative rises in blood-non-protein-nitrogen.** H. A. DEROW (New England J. Med., 1935, 212, 509—511).—In patients with normal renal function the increases may result from an oliguria, increased destruction of body-protein, or post-renal anuria. CH. ABS. (p)

**State of combination of residual nitrogen [in blood-serum] in experimental uranium poisoning.** M. JACOBY (Biochem. Z., 1935, 281, 198—199; cf. A., 1934, 558).—In rabbits the proportion of urea-N in the residual N of blood-serum increases following subcutaneous administration of  $UO_2(NO_3)_2$ . W. McC.

**True and apparent creatine and creatinine of blood and urine.** H. BOHN, A. FRIEDSAM, and F. HAHN (Zentr. inn. Med., 1935, No. 22, 465—473).—For determination of true creatine (I) alone, hydrolysis of the blood filtrate or urine must take place at a moderate temp. (60°) in presence of HCl. The true val. for blood-(I) in health is about 33% of the usually accepted val. In high blood pressure associated with paleness, the true blood-(I) is reduced. The results of Linneweh (Klin. Woch., 1934, 13, 589) indicate that preformed blood-creatinine is not entirely composed of pseudo-creatinine. NUTR. ABS. (m)

**Does creatinine occur in normal blood?** F. LINNEWEH (Klin. Woch., 1935, 14, 293—294).—Creatinine (I) can be detected in normal blood, extracted, and purified by adsorption on Lloyd's reagent. (I) excretion is therefore probably due to the removal of (I) from the blood by the kidneys, rather than to formation from creatine (II). The adsorbate from blood contains no substance that interferes with (I) determination, since  $Et_2O$  extraction does not reduce the (I) val., and supplementary (I) is not formed from (II) during the process. R. N. C.

**Occurrence of acetylcholine in blood.** R. AMMON (Klin. Woch., 1934, 13, 1472).—The acetylcholine-like effect of blood or urine, with or without eserine (I), on leech-muscle is not considered to be due to acetylcholine (II), since hæmolysed blood without

(I) contracts the uneserinised muscle, and this action is not inhibited by atropine or destroyed by treating the blood or urine with NaOH. Types of blood in which corpuscular  $K >$  serum-K show a (II)-like action when hæmolysed. R. N. C.

**Total and reduced glutathione compared with oxygen content and capacity in the blood of pregnant and non-pregnant women.** F. W. OBERST and E. B. WOODS (Proc. Iowa Acad. Sci., 1934, 41, 166—167).—No relationship was apparent between the  $O_2$  content and  $O_2$  capacity of blood and the concn. of total or reduced glutathione (I). Vals. were similar in pregnant and non-pregnant women. Added (I) disappeared more rapidly from blood than from  $H_2O$  at 38°. Disappearance from blood was accelerated by NaF. CH. ABS. (p)

**Azotæmia and chloræmia in vitro.** J. LOISELEUR (Compt. rend. Soc. Biol., 1935, 120, 605—608).—Addition of urea (I) to blood *in vitro* causes a movement of Cl from the corpuscles to the plasma  $\propto$  the (I) added. Glycylglycine causes a movement of Cl into the corpuscles. R. N. C.

**Azotæmia and chloræmia in course of histolysis.** J. LOISELEUR (Compt. rend. Soc. Biol., 1935, 120, 675—678).—The corpuscular/plasma-Cl ratio in the blood depends on  $p_H$ , and is also influenced by the release of N compounds into the blood-stream from cell histolysis. It is inversely  $\propto$  the urea-N/total residual N ratio, and consequently falls on injection of peptone. Total blood-Cl falls in azotæmia, the fall being  $\propto$  the no. of mols. of N compounds. R. N. C.

**Blood-iodine; a new chemical method.** D. R. McCULLAGH (Cleveland Clin. Quart., 1935, 2, No. 1, 15—37).—Variations in blood-I under varying conditions are examined by the author's method (A., 1934, 1397). CH. ABS. (p)

**Effect of age on the plasma-calcium content of men.** E. KIRK, W. H. LEWIS, jun., and W. R. THOMPSON (J. Biol. Chem., 1935, 111, 641—642).—The plasma-Ca of normal adult men was independent of their ages. H. D.

**Iron in the blood. Comparison of values for hæmoglobin determined by the Newcomer method and calculated from the iron content.** H. W. JOSEPHS (Bull. Johns Hopkins Hosp., 1934, 56, 50—56).—Calc. vals. were the higher in most cases. CH. ABS. (p)

**Spectrographic micro-method for detection of pathological lead in peripheral blood.** H. BLUMBERG and T. F. MCN. SCOTT (Bull. Johns Hopkins Hosp., 1935, 56, 32—36).—A pathological finding is indicated when the Pb line 2833 Å. is detectable on the plate without the use of a lens. 0.1 c.c. of blood is examined. CH. ABS. (p)

**Blood chemistry of swine. II. Blood changes following ingestion of glucose.** D. F. EVELETH and M. W. EVELETH (J. Biol. Chem., 1935, 111, 753—756; cf. A., 1934, 543).—Feeding of glucose to fasting swine increases the serum-Mg and  $H_2C_2O_4$ , and decreases the inorg.  $PO_4'''$  and Ca. Ingestion of  $H_2O$  alone decreases the serum-sugar, Ca, Mg,  $H_2C_2O_4$ , and inorg.  $PO_4'''$ . J. N. A.

**Sodium, potassium, calcium, and inorganic phosphate of blood during prolonged fasting.** D. TORRISI (Arch. Fisiol., 1935, 34, 259).—In the serum of dogs and rabbits, during prolonged fasting, there is a progressive decrease in Na to  $\leq 21\%$  of normal. The other elements show irregular and minor changes.

NUTR. ABS. (m)

**Distribution of different fractions of acid-soluble phosphorus in the blood of dogs during intermediary metabolism, as observed on an empty stomach after introduction of glucose and radon.** A. A. ARAPOVA (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 338—351).—Fractions of ortho- and pyro-phosphates and sol. and insol. phosphoric esters occur in blood-vessels. No creatininephosphoric acid is found in blood. The sol. ester fraction (I) is the most changed in its passage through organs, and also after introduction of glucose. Introduction of Rn increases (I) in arterial blood and in eliminations of the kidney.

CH. ABS. (p)

**Conductivity of blood in the wave-length region 6—25 m.** F. GRAUL (Ann. Physik, 1935, [v], 24, 326—348).—The conductivity of ox, pig, and human blood shows no change with frequency between  $\lambda\lambda$  6 and 20 m.; at 20—25 m. it decreases, but the effect is detectable only with centrifuged blood. Its variation at 13.6 m. with time of centrifuging and with the low-frequency conductivity is in accord with theory.

J. W. S.

**Effect of pressure on the hydrogen-ion concentration of blood: use of glass electrodes.** A. THIEL and H. GEMSA (Biochem. Z., 1935, 282, 146—156).—At 37°, no change in the  $p_H$  of cattle blood occurred when it was subjected to  $N_2$  pressures up to 100 atm.

W. McC.

**Amphibian metamorphosis. X. Hydrogen-ion concentration of the blood of anuran larvæ during involution.** O. M. HELFF (Biol. Bull., 1932, 63, 405—418).—Blood- $p_H$  shows a steady decline (7.50  $\rightarrow$  7.18) in progressive stages of metamorphosis.

CH. ABS. (p)

**Calcium salts and blood coagulation.** J. MATUSEVICH (Semana med., 1935, 1, 1021—1024).—Oral administration of  $CaCl_2$  has no action, but  $Ca$  lactate +  $NH_4Cl$  shows a considerable effect with a max. after 8 days. Injected  $CaCl_2$  +  $Ca$  gluconate is effective in 2—4 hr., with a return to normal after 24 hr.

CH. ABS. (p)

**Acceleration of blood coagulation by acidic substances, especially pectin.** O. RIESSER [with A. NAGEL] (Arch. exp. Path. Pharm., 1935, 179, 748—760).—Oral and parenteral administration of pectin (I) to rabbits accelerates the rate of coagulation, the effect persisting for 4—5 hr. Galacturonic and lactic acids,  $AcOH$ , and, in small intravenous doses,  $HCl$  have a similar action. Intramuscular injection of the neutral salts, *in-vitro* addition of the acids, or injection of (I)-activated blood [in which (I) is not detectable] into other animals has no effect. The mechanism of the phenomenon is discussed.

F. O. H.

**Determination of velocity of blood coagulation.** O. RIESSER and A. NAGEL (Arch. exp. Path. Pharm.,

1935, 179, 743—747).—The blood is introduced into a capillary tube, kept at const. temp., and the course of coagulation followed by its movements in response to unilateral pressure. Rabbits' blood (ear) gave vals. of 3—3.5 min. for the initiation and 4—5 min. for the completion of coagulation.

F. O. H.

**Absence of correlation between lacto-gelification and protein disequilibrium of blood-serum.** G. LEFFROU and L. AUFFRET (Compt. rend. Soc. Biol., 1935, 120, 614—616).—There is no evidence of correlation between the time of lacto-gelification and the degree of protein disequilibrium.

R. N. C.

**Hæmostatic effect of ascorbic acid in hæmaturia.** A. KORANYI and A. BENTSÁTH (Orvosi Hetilap, 1935, 79, 378—379).—In some, but not in all, cases the hæmostatic action was accompanied by changes in composition of protein fractions in blood-plasma.

CH. ABS. (p)

**Effect of Röntgen rays on the appearance of complement-fixing bodies in the blood.** I. P. MISCHTSCHENKO and M. M. FOMENKO (Ann. Roentgenol. Radiol. U.S.S.R., 1934, 13, 327—336).—Complement-fixing bodies appeared in blood following X-irradiation.

CH. ABS. (p)

**"Serum sickness" in rabbits following the intravenous injection of various foreign sera: relation to precipitins.** D. KHORAZO (J. Immunol., 1933, 25, 113—120).—No differences in the rate of precipitin formation or disappearance of injected antigen from the blood could be associated with "serum sickness."

CH. ABS. (p)

**Precipitin reaction between type III pneumococcus polysaccharide and homologous antibody. II. Conditions for quantitative precipitation of antibody in horse sera. III. Theory of the reaction mechanism.** M. HEIDELBERGER and F. E. KENDALL (J. Exp. Med., 1935, 61, 559—562; cf. A., 1930, 1608).—II. The customary immunological procedure (2 hr. at 37° and overnight in oil) does not permit establishment of equilibrium, or max. pptn. of antibody-N. Analysis should be carried out at 0° and materials kept cold for  $\leq 24$  hr. The chemical method for determining antibody is an accurate measure and does not include non-sp. protein.

III. Antibody solutions and sera probably contain  $> 1$  antibody reactive with S III. The reaction between the sp. polysaccharide and homologous antibody is represented as a bimol. reaction, followed by a series of competing bimol. reactions dependent on the relative proportions of the components.

CH. ABS. (p)

**Anaphylactogenic properties of milk. Immunochemistry of the purified proteins and antigenic changes resulting from heat and acidification.** B. RATNER and H. L. GRUEHL (Amer. J. Dis. Children, 1935, 49, 287—306).—Casein and lactalbumin fractions of milk-proteins retain antigenic characteristics after drying, acidification, superheating, or evaporation. The whey fraction shows a marked loss of antigenic properties after evaporation or superheating. Loss of antigenic

properties of heated milk is due to coagulation of whey proteins. CH. ABS. (p)

**Anaphylactogenic properties of malted sugars and maize-syrup.** B. RATNER and H. L. GRUEHL (Amer. J. Dis. Children, 1935, 49, 307—317).—Allergy to carbohydrate food is due to added protein constituents rather than to the carbohydrate itself. Malt extracts and the barley-malts from which they are derived are highly anaphylactogenic and react specifically with hordein. Maize-syrups and pure "dextrimaltose" sugars are not anaphylactogenic. Addition of wheat germ or dried milk to non-anaphylactogenic converts them into active substances.

CH. ABS. (p)

**Protein reaction for the more definite identification of blood-stains.** V. TUMA (Chem. Listy, 1935, 29, 313—316).—Agglutination and pptn. reactions serve to distinguish dried human from animal blood-stains, and to determine the serological group to which the blood belongs. R. T.

**Test for occult blood, especially in urine.** W. J. STONE and G. T. BURKE (J. Amer. Med. Assoc., 1934, 102, 1549—1550).—The sediment from 15 c.c. of centrifuged urine is treated with 2 drops of a 1% solution of toluidine in MeOH and 3 drops of a 1:1 mixture of AcOH and H<sub>2</sub>O<sub>2</sub>. A greenish-blue colour lasting 1 min. develops in the presence of 100 blood-cells per c.c. of sediment. CH. ABS. (p)

**Determination of calcium and phosphate content of bones.** C. K. DEISCHER and W. M. McNABB (Analyst, 1935, 60, 750—751).—Ca is pptd. as CaC<sub>2</sub>O<sub>4</sub>, which is titrated with KMnO<sub>4</sub>. P is pptd. as NH<sub>4</sub> phosphomolybdate, which is dissolved in excess of standard NaOH. The excess of NaOH is titrated with HCl. J. S. A.

**Fluorine content of bones and teeth.** R. KLEMENT (Ber., 1935, 68, [B], 2012—2019).—Examination of the bones and teeth of many animals leads to the following mean vals. for F in the inorg. matter: land mammals, 0.05%; sea mammals, 0.55%; land birds, 0.11%; sea birds, 0.32%; fresh-H<sub>2</sub>O fish, 0.03%; sea-H<sub>2</sub>O fish, 0.43%. The differences between land and sea animals are attributed to the F content of sea-H<sub>2</sub>O exceeding that of fresh H<sub>2</sub>O. F replaces OH in the hydroxyapatite (I) of bones and teeth with formation of mixed crystals to a greater extent with sea than with land animals; this is still more marked in fossil bones. The hardness of tooth enamel is explained by a small content of org. matter which causes a greater development of the crystallites of (I). F is probably without biological significance. H. W.

**Lipin content of the jelly of Wharton.** E. M. BORD (J. Biol. Chem., 1935, 111, 667—669).—The mean lipin content of the jelly is 0.209%, which is < that of any other body-tissue. This agrees with Bloor's hypothesis that tissues of low physiological activity have a low lipin content. E. A. H. R.

**Lipins.** I. Amounts of lecithin, total and free cholesterol, and cholesteryl ester in the organs of guinea-pigs fed on a vitamin-C-free diet and the ratio among these lipins. II. Relationship between oxidation in the animal body and the

lipin contents of various organs. S. HONGO (Sei-i-Kwai Med. J., 1934, 53, No. 5, 1—22, 23—28).—I. On a dry-wt. basis organs of scorbutic guinea-pigs contained more lecithin (I) (notably in testicles, muscle, and kidney, but not liver and lungs) and more free cholesterol (II) (especially lungs, intestine, and kidneys) than normal animals. Intestine and kidneys have more total (II). The ratio of (I):(II) in intestine, kidney, and muscle is smaller in scorbutic animals.

II. Increased oxidation in rabbits injected with thyroideum is generally associated with a decrease in fat acids (III) and other lipins in various organs. In muscle (III) increased. In liver there is an increase in unidentified unsaponifiable substance without change in other lipins. Removal of thyroid increases (III) (except in the spleen) and other lipins without affecting the ratios in the various organs.

CH. ABS. (p)

**Eel oil. I. Fatty acids.** T. ONO (J. Agric. Chem. Soc. Japan, 1935, 11, 773—780).—The oil contains myristic, palmitic, and stearic acid, a saturated acid, m.p. 57—58°, probably the unsaturated acids, C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>, C<sub>16</sub>H<sub>30</sub>O<sub>2</sub>, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, C<sub>18</sub>H<sub>32</sub>O<sub>2</sub> (iso-acid), C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>, C<sub>20</sub>H<sub>40</sub>O<sub>2</sub>, C<sub>22</sub>H<sub>44</sub>O<sub>2</sub>, and possibly C<sub>16</sub>H<sub>26</sub>O<sub>2</sub>, C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>, and C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>. The Carr-Price reaction is negative and is very weak even with the liver extract. W. McC.

**Renal threshold for glucose in man.** J. W. SHERRILL and E. M. MacKAY (Arch. Int. Med., 1935, 56, 877—883).—The average vals. found for diabetics and normal persons were 149 and 128 mg. per 100 c.c., respectively. It is suggested that the "normal val." is misleading and a normal average should not be given. H. G. R.

**Distribution of glycogen in the regions of the amphibian gastrula; micro-determination of glycogen.** N. G. HEATLEY (Biochem. J., 1935, 29, 2568—2572).—Tissue is fixed in EtOH and digested with KOH; glycogen (I) is pptd. with EtOH, hydrolysed with acid, and the sugars formed are determined by the Linderstrom-Lang method (A., 1931, 1455). During gastrulation of the embryo of *Triton alpestris* the quantities of (I) are in the order: dorsal ectoderm > ventral ectoderm > yolk endoderm. During invagination there is a loss of approx. 35% of (I) in the invaginating cells. H. D.

**Effects of repeated injections of glucose on the muscle-glycogen of the frog under normal conditions.** A. MOSCHINI (Compt. rend. Soc. Biol., 1935, 120, 531—533).—Repeated injections of glucose (I) increase muscle-glycogen (II), the increase depending on the total amount of (I) given when (II) is low, but when (II) reaches high vals. the increases produced by further doses of (I) are smaller, until a steady max. is attained. R. N. C.

**Effects of repeated injections of glucose on the muscle-glycogen of the frog, in different experimental states.** A. MOSCHINI (Compt. rend. Soc. Biol., 1935, 120, 533—535).—Glucose (I) increases muscle-glycogen (II) in frogs with muscles atrophied by prolonged fasting, to the same extent as in normal frogs. Section of the sciatic nerve has no

immediate effect, but when degeneration of the foot muscles sets in, the amount of glycogen taken up is decreased. (II) falls after pancreatectomy, but (I) injections still cause deposition and mask this effect.

R. N. C.

(A) Determination of fermentable carbohydrates in rabbit liver. (B) Isolation of a reducing dextrin. C. B. PURVES (Quart. J. Exp. Physiol., 1935, 24, 383—389, 391—395).—(A) The fermentable carbohydrate in liver could not be accounted for (by 25%) as glycogen and free sugar. The presence of a polysaccharide insol. in 90% EtOH, sol. in 32% EtOH, and destroyed during the glycogen determination, is postulated.

(B) The fermentable carbohydrate isolated was probably a mixture of dextrans containing free Cu-reducing groups.

CH. ABS. (p)

Colorimetric and iodometric determination of glutathione. K. UHLENBROOCK (Z. physiol. Chem., 1935, 236, 192—196; cf. A., 1935, 793; Fujita *et al.*, *ibid.*, 772).—For deproteinisation sulphosalicylic acid is much better than  $\text{HPO}_3$  and KCN should be replaced by  $\text{Na}_2\text{CO}_3$  in the method of Bierich *et al.* (A., 1933, 523), the apparatus of Lange (*ibid.*, 44) being used for measurement of the colour. Solutions should contain, per 100 c.c., 4.5—100 mg. of reduced glutathione (if < 4.5 mg. present larger vol. to be used). Results agree well with those obtained by titration with I for heart, muscle, lung, blood, brain, spinal cord, and spleen, but not for liver, kidney, and thymus. The last two contain substances which rapidly attack SH-compounds, and hence, with these organs, the colorimetric method cannot be applied. W. McC.

Bound water and phase equilibria in protein systems: ovalbumin and muscle. T. MORAN (Proc. Roy. Soc., 1935, B, 118, 548—559).—The bound  $\text{H}_2\text{O}$  of native (I) and denatured (II) ovalbumin at various temp. <  $0^\circ$  is dependent on the activity of  $\text{H}_2\text{O}$ . The chemically bound  $\text{H}_2\text{O}$  is approx. 0.26 g. per g. of protein for both (I) and (II), and for (I) the more loosely held  $\text{H}_2\text{O}$  is > for (II) at the higher activities. The bound  $\text{H}_2\text{O}$  of muscle at intermediate and high  $\text{H}_2\text{O}$  activities is approx. 0.40 g. per g. of dry solid. The eutectic temp. of muscle is about  $-37.5^\circ$ .

F. A. A.

Annelid muscle. I. Taurine in *Audouinia spirabanchus*, Moore. A. C. KURTZ and J. M. LUCK (J. Biol. Chem., 1935, 111, 577—584).—3% of taurine (I) was found in the muscle of *A. spirabanchus*, Moore, traces were found in *Nereis brandtii*, and none in *Glycera rugosa*, *Lumbricus* sp., *Urechis caupe*, and *Phoronopsis harmeri*. The possible function of (I) in maintaining the osmotic pressure of the muscle is discussed.

H. D.

Selenium in proteins from toxic foodstuffs. III. Removal of selenium from toxic protein hydrolysates. E. P. PAINTER and K. W. FRANKE (J. Biol. Chem., 1935, 111, 643—651).—The nature of the Se complex in toxic proteins is investigated. When the toxic proteins are hydrolysed, the Se may be extracted with BuOH. All the Se is completely pptd. by  $\text{HgCl}_2$ , but only partly by phosphotungstic acid and by Cu and Ag salts.

H. D.

Cryolysis, diffusion, and particle size. II. Investigations with myosin.—See this vol., 28.

Polysaccharoproteins. VI. State of glycogen in muscle. II. E. M. MISTKOVSKI, A. STILLER, and A. ZISMAN (Biochem. Z., 1935, 281, 231—237; cf. A., 1935, 1004).—Part of the glycogen (I) in the press-juice of rabbit, dog, and frog muscle exists irreversibly bound to myosin (II) and globulin-X (III). The amylase present degrades added (I) (at < the expected rate), but not the native bound (I), which also resists attack by ptyalin (IV). When the bound (I) is removed by alkaline hydrolysis it is attacked at the usual rate by amylase. The rate of hydrolysis of (I) by (IV) is reduced [extent of reduction  $\propto$  concn. of (II)] by adding (II), but appears to be increased by adding (III).

W. McC.

Protamines. VI. (i) Acid hydrolysis of salmine. M. YAMAGAWA and T. NISHIZAWA (J. Imp. Fisheries Inst. Japan, 1934, 30, 97—115).—Salmine prepared from *Oncorhynchus keta* is identical with that from Rhine salmon. All  $(\text{NH}_2)_1$ -acids are liberated by hydrolysis with  $4N\text{-H}_2\text{SO}_4$  for 8 hr., leaving a residue of di- and tri-arginide.

CH. ABS. (p)

Nature of the substance in fish meat which gives formaldehyde-like reactions. II. Squid (*Loligo bleekeri*, Keferstein) from Hokkaido. Y. HATTORI and T. HASELBE (J. Pharm. Soc. Japan, 1934, 54, 1081—1090).—The substance is identified as  $\text{NMe}_3\text{O}$ .

CH. ABS. (p)

Nuclein metabolism. VI. Constitution of the nucleic acids. K. MAKINO (Z. physiol. Chem., 1935, 236, 201—207; cf. A., 1935, 1003).—Samples of yeast-nucleic acid (I) differ greatly in regard to the ease with which they are degraded by alkali, there being no relation between age of sample and ease of hydrolysis. The reaction of purified nucleosides with  $\text{H}_3\text{BO}_3$  indicates that the deoxyribosides from thymus-nucleic acid (II) have the furan ring structure, and consequent changes are made in the proposed structural formulæ for (I) and (II). The criticisms of Klein *et al.* (*ibid.*, 510) are refuted.

W. McC.

Adenine nucleotide in tissues. II. In heart muscle. K. LOHMANN and P. SCHUSTER (Biochem. Z., 1935, 282, 104—108; cf. A., 1934, 1020).—Most of the adenine nucleotide (I) of rapidly removed calves' hearts occurs as adenylypyrophosphoric acid. A small amount of (I) is isolated as adenosinediphosphoric acid and adenylic acid.

W. McC.

Pigments of hair. H. ZWICKY and F. ALMASY (Biochem. Z., 1935, 281, 103—110).—Spectrophotometric examination of alkaline extracts of white, red, and black horse- and mule-hair indicate that, whilst two different pigments occur in the black hair (from different horses), one of them is indistinguishable from that which occurs in the red hair and in the hair from the darker parts of dappled horses.

W. McC.

Pigments of the bull-frog retina. G. WALD (Nature, 1935, 136, 832—833).—The substances and processes found in the retina and pigment epithelium of *Rana catesbiana* are identical with those in species of frogs previously examined (A., 1934, 913). The retina contains varying amounts of retinene (I) and



vitamin-A (II). With  $\text{SbCl}_3$ , (I) yields a sharp absorption band at 662–666  $\text{m}\mu$  and not at 655  $\text{m}\mu$ . Dark-adapted retinas contain only a trace of (II), which can be extracted in the dark by benzene without injury to the visual purple. Light bleaches the latter to visual yellow, after which benzene extracts a large amount of (I). Destruction of the visual purple in the dark with  $\text{CHCl}_3$  also liberates (I). Visual yellow thus appears to be simply free (I) (cf. *loc. cit.*). The (I) of bleached retinas is converted quantitatively into (II) by a thermal process in approx. 1 hr. in light or in darkness at 25°. In the isolated retina, (II) is the final product of the bleaching and fading reactions, but in the intact eye (II) is resynthesised to visual purple, thus completing the visual cycle.

L. S. T.

**Carotenoids of *Rana esculenta*.** O. BRUNNER and R. STEIN (Biochem. Z., 1935, 282, 47–50).—The liver, skin, fat glands, and ovaries contain  $\beta$ -carotene (I) and esterified lutein (II); the ovaries contain also free (II). About half of the total (I) and (II) occurs in the ovaries and about 25% in the liver. In liver, skin, and ovaries the contents of (I) and (II) are about equal, but the (II) content of the fat glands is much < the (I) content.

W. McC.

**Visual purple.** O. BRUNNER, E. BARONI, and W. KLEINAU (Z. physiol. Chem., 1935, 236, 257–262).— $\beta$ -Carotene, obtained from the retina by extraction with MeOH, is adsorbed by  $\text{Al}_2\text{O}_3$ . The light-absorption curve of the adsorbed material is similar, especially in the long-wave zone, to that of the visual purple. The retina contains no xanthophyll.

W. McC.

**Accumulation of acid dyes in the silkworm by different tissues according to the route of application.** P. P. GRASSE and L. LESPERON (Compt. rend., 1935, 201, 618–620).—Certain cells of the silkworm are stained by Congo-red, trypan-blue, trypan-red, and  $\text{NH}_4$  carminate, but the results depend on whether the dyes are injected or administered orally.

W. O. K.

**Progress of lactation in relation to the milk yield and the butter-fat percentage of milk produced by cows of the Shorthorn type.** C. D. OXLEY (J. Dairy Res., 1935, 6, 113–120).—The standard error of the mean of observations of milk yields and % of butter-fat in milking records is determined. The time lag between the period of max. yield and min. % of butter-fat is discussed.

A. G. P.

**Influence of diet on the antirachitic potency of cow's milk.** B. H. THOMAS and C. Y. CANNON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1934, 49).—Irradiated dried moulds may be used as a supplement to rations for increasing the vitamin-D content of milk. The response is most marked during the first few days of feeding and subsequently declines. The efficiency of transfer of -D from diet to milk is very low.

CH. ABS. (p)

**Effect of diet on the milk: chemical modification and sensitisation to the alcohol test.** L. ECHENIQUE and B. SUAREZ (Compt. rend. Soc. Biol., 1935, 120, 570–572).—*Xanthium cavanillense* is

non-toxic to cows, and when introduced into their diet provokes an increase in Ca in the milk; its withdrawal causes Ca to return to normal. The coagulation reaction with EtOH becomes positive when Ca is high. Milk that is coagulated by EtOH is not coagulated by boiling when the normal % of Ca in the ash is increased by 4.6.

R. N. C.

**Effect of electrolytes on the synthesis of lactose.** D. MICHLIN and T. FETISSOVA (Biochem. Z., 1935, 282, 26–31; cf. A., 1934, 1033).—The synthesis of lactose (I) in mammary gland is reversed when hydration of the tissue occurs. Added electrolytes ( $\text{CaCl}_2 > \text{LiCl}, \text{NaCl}$ ) check hydration and prevent shifting of the equilibrium, hence increasing the amount of (I) produced or preventing reversal of the reaction.  $\text{K}_2\text{SO}_4$  acts in the same way, but  $\text{NH}_4\text{CNS}$  and sometimes KCl check the synthesis. The synthesis is inhibited at  $p_{\text{H}}$  9.5, but not at 4.8.

W. McC.

**Mineral constituents in fresh and canned milk.** A. J. HERMANO and S. CLARAVALL (Philippine J. Sci., 1935, 57, 323–328).—Ca, P, Fe, fat, protein, and lactose have been determined in fresh and canned samples of carabao's, goat's, and cow's milk.

H. G. R.

**Cow's milk in Manchuria and Mongolia. IV. Non-protein nitrogenous substance.** M. SUGIURA (J. Orient. Med., 1935, 22, 60).—Total N, non-protein-N, and protein in the milk from Manchu Mongol cows were < in milk from Japan, America, and Europe. Free  $\text{NH}_3$  and urea showed considerable variations, but the uric acid and purine bases were const.

NUTR. ABS. (m)

**Methylene-blue reduction test: its efficiency and interpretation under Philippine conditions.** J. B. UICHANCO (Philippine J. Sci., 1935, 57, 295–319).—The test has been compared with the standard plate method on samples of carabao milk and is recommended for use with slight modification to suit local conditions.

H. G. R.

**Determination of amylase in milk.** M. MANICATIDE, BRATESCU, and M. POPA (Compt. rend. Soc. Biol., 1935, 120, 657–658).—Human colostrum contains 1024–2048 Wolgemuth units of amylase (I) per c.c., normal milk, 250 units (average). Cows' milk contains scarcely any (I). (I) is destroyed by boiling or pasteurisation.

R. N. C.

**Extractives of peripheral lymph.** S. ASAKUMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 136–137).— $\text{Et}_2\text{O}$ -sol. matter in lymph from the popliteal gland and of blood-serum from leg veins of rabbits averaged 285.8 and 244.6 mg. per 100 g. of fluid, respectively.

CH. ABS. (p)

**Hydrogen-ion concentration of peripheral lymph.** M. ARAKI and G. HŌJO (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 132–134).—The  $p_{\text{H}}$  of lymph from the popliteal gland of rabbits (7.90) was lowered by injection of strychnine and increased by that of veratrine.

CH. ABS. (p)

**Carbon dioxide content of lymph under different conditions.** G. HŌJO (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 140–144).—Lymph- $\text{CO}_2$  increased when rabbits were fastened

immovably. Vals. for efferent lymph from the popliteal gland were similar for both sides; those for thoracic duct and intestinal lymph were markedly < that in the legs. Intravenous injection of KCN and injection of pilocarpine hydrochloride by the ear vein lowered the  $\text{CO}_2$  content. Adrenaline had no action. CH. ABS. (p)

**Carbon dioxide content of peripheral lymph of rabbits.** K. TSUJI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 135).—Average vals. for efferent and afferent lymph were 44.33 and 46.64 c.c. per 100 parts (?), respectively. CH. ABS. (p)

**Sulphates in lymph.** I. II. Sulphates in peripheral lymph after intravenous injection of aqueous phenol solution. S. MASUDA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 22—24, 25—28).—I. Small amounts of  $\text{SO}_4$  occur in serous fluids, chyle, and blood. Only ethereal  $\text{SO}_4$  (I) occurs in lymph. The (I) content in peripheral lymph is > that of chyle, and, in turn, > in blood.

II. Injection causes an increase in (I) content of the lymph. CH. ABS. (p)

**Lactic acid in peripheral lymph.** Y. HŌJO (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 115—121).—Average vals. for efferent and afferent lymph were 0.795 and 0.673 mg. per 100 c.c., respectively. Vals. were decreased by injection of aq. NaF, NaI, or  $\text{CH}_3\text{I} \cdot \text{CO}_2\text{H}$ . CH. ABS. (p)

**Lipase of peripheral lymph.** K. ISHINO (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 48—52).—The lipase occurs in the inflowing and outflowing lymph of the popliteal gland, there being usually more in the outflow. It is not affected by neutral salts or by weakly acid or alkaline media. CH. ABS. (p)

**Total protein, globulin, and albumin fractions of peripheral lymph.** B. NAKADA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 112—114).—Vals. per 100 c.c. of lymph were: total protein, 2123 mg. in efferent and 1890 mg. in afferent lymph, globulin, 757 and 715, albumin, 1689 and 1599 mg., respectively. CH. ABS. (p)

**Autolysis of lymph.** I. Reducing power. M. FUKUOKA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 92—93).—The reducing power varied with the individual rabbit, reached a max. on the 2nd day of autolysis, and subsequently declined. CH. ABS. (p)

**Fibrin content of lymph.** B. NAKADA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 63—64).—Average vals. were 276.7 mg. of fibrin per 100 c.c. of efferent, and 261.1 mg. for afferent, lymph. CH. ABS. (p)

**Non-protein-nitrogen of vascular lymph.** S. ASAKUMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 46—47).—The average non-protein-N content of lymph was 0.504 and of blood-serum 0.513%. CH. ABS. (p)

**Resorption in the lymph passage.** I. Resorption of yatoconin by subcutaneous application. II. Resorption of colloidal silver. III. Resorption of starch. M. KOSAKA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 15—21

80—89, 152—160).—I. Injection is immediately followed by an increase in wt. and in Ca and P contents in the lymph gland.

II. The Ag content of the gland increased rapidly to a max. and subsequently declined. Ag is soon resorbed in the lymph passage, but part remains stored in the gland.

III. Injected starch was detected in the gland up to 4 hr. after treatment. Resorption was complete in 5.5—6.0 hr. Reducing substances in glands after hydrolysis reached a max. soon after injection. The max. for reducing substances before hydrolysis was reached somewhat later. CH. ABS. (p)

**Lymph obtained by the "Brunnenlymph" method of Watanabe.** Y. IWAKI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 7—14).—Physical and chemical properties of the lymph are examined. Incoming lymph has the same physical properties as that from lymph glands. CH. ABS. (p)

**Decomposition of atropine in the peripheral lymph of the rabbit.** S. KIRIYAMA (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 68—79).—Decomp. of atropine sulphate by lymph occurs at room temp. and at 37°, but not at low temp. Outflowing lymph was more active than inflowing lymph. CH. ABS. (p)

**Alteration of lymph after death of animal.** Y. IWAKI (Arb. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 99—111).—Physical and chemical changes during 2 hr. after death are recorded. CH. ABS. (p)

**Lymph in experimental pneumonia.** J. S. DAVIS, jun., and A. J. DELARIO (J. Lab. Clin. Med., 1935, 20, 460—467).—The increase in lactic acid (I) content of lymph and the decrease in  $\text{CO}_2$  content tend to compensate for the loss of  $\text{Cl}'$ . The increase in (I) is the more important factor. The  $\text{O}_2$  tension of lymph is > doubled by  $\text{O}_2$  therapy. CH. ABS. (p)

**Relationship between sugar and urea contents of the blood and spinal fluid.** J. N. CUMINGS and E. A. CARMICHAEL (Brain, 1934, 57, 338—347).—Levels of sugar and urea in lumbar fluid do not rise in association with the normal rise in the blood. Only in abnormal conditions does the ventricular fluid-sugar increase with a rise in blood-sugar. CH. ABS. (p)

**Proteolytic power of saliva.** I. Proteolysis in saliva. II. Action of human saliva on proteins. P. FANTL and J. WEINMANN (Biochem. Z., 1935, 281, 37—41, 42—48).—I. The portion of human saliva which does not pass through filters contains enzymes which degrade the proteins of the saliva. The amount of enzymes present varies greatly from person to person, but remains almost const. in the individual.

II. Proteins (hen's egg, fibrin from human and horse blood) denatured by boiling or by pptn. at room temp. are not attacked by the enzymes of the saliva. W. McC.

**Significance of iron and copper in human bile.** E. S. JUDD and T. J. DRY (J. Lab. Clin. Med., 1935, 20, 609—615).—The Fe content of liver

ranged from 0.031 to 1.68 and that of Cu from 0.063 to 1.07 mg. per 100 g. Cu is normally excreted by liver. Fe is secreted in bile and resorbed from the intestine. CH. ABS. (p)

**Microchemical study of human biliary calculi.** T. W. RAY (J. Biol. Chem., 1935, 111, 689—697).—There is no essential difference in chemical composition chole between cholesterol-pigment-Ca stones and sterol-pigment stones. E. A. H. R.

**Concentration function of the gall-bladder: biliary glutathione.** G. BALTACEANO and C. VASILIU (Compt. rend. Soc. Biol., 1935, 120, 666—668).—The concn. of the glutathione in the vesical bile is > in the hepatic bile. R. N. C.

**Bile acids. XLVII.**  $C_{24}H_{36}O_{10}N_2$ .—See this vol., 74.

**Constituent of bile pigment. XIV.**—See this vol., 86.

**Gastric secretion. VI. Action of pilocarpine on the secretion of a transplanted gastric pouch without Auerbach's plexus.** E. KLEIN (Arch. Surgery, 1935, 30, 277—283).—Pilocarpine hydrochloride (I) in 7-mg. doses stimulates secretion of free acid. Smaller doses stimulate pepsin secretion only. Atropine (1 mg.) inhibits secretion caused by (I) but not that produced by histamine. CH. ABS. (p)

**Copper content of urine of normal children.** A. ROSS and I. M. RABINOWITCH (J. Biol. Chem., 1935, 111, 803—805).—Cu is a const. constituent of urine and the amounts found ranged between 0.04 and 0.52 mg. per litre. J. N. A.

**Detection of dinitrophenol and its derivatives in urine.** A. MEYER and H. DRUTEL (Bull. Soc. Chim. biol., 1935, 17, 1455—1461).—Interference by skatole, which, like 2:4-dinitrophenol (I), gives a pink coloration in the Meyer test for (I), may be avoided by using  $Hg(NO_3)_2$  as defecating agent and extracting (I) with  $Et_2O$  before reducing with Zn in  $AcOH$ . A. L.

**Urinary diastase.** F. ECKARDT (Deut. Arch. klin. Med., 1935, 177, 517—526).—Diastase, expressed as g. of starch hydrolysed by 1000 c.c. of urine at 37° in 3 hr., ranged from < 8 to > 600 (in adolescents 10—40, in old age < 8 to 20); the mean val. for all ages is about 20. The val. was uninfluenced by sex, but varied inversely with food consumption. Vals. in many different types of disease are given.

NUTR. ABS. (m)

**Variations in urinary reducing substances of two normal dogs maintained on bread diets.** E. P. LAUG and T. P. NASH, jun. (J. Nutrition, 1935, 10, 81—92; cf. A., 1935, 513).—Significant variations in the total, fermentable, non-fermentable, and hydrolysable reducing substances of urine are correlated with particular bread diets. A. G. P.

**Lipuria in dogs experimentally deprived of their dorso-lumbosacral marrow.** H. HERMANN, J. DECHAUME, and J. VIAL (Compt. rend. Soc. Biol., 1935, 120, 648—649).—Removal of the dorso-lumbosacral marrow induces an immediate increase in fat excretion, which disappears after 3—5 weeks, reappears after 3 months, and then persists.  $Et_2O$  extracts are

yellow when fresh, but extracts from urines of the first period of lipuria are decolorised by light; those from the second period are unaffected. The fat is free from N and P, and the acid contained in it is chiefly oleic acid. R. N. C.

**Biochemistry of allantoin. I. Effect of leucolysis on allantoin excretion. II. Amounts of allantoin in urine of various animals. III. Effect of thyroxine ingestion on allantoin excretion.** T. MIYAHARA (Sci-i-Kwai Med. J., 1934, 53, No. 8, 9—27, 28—41, 43—48).—I. When a leucopenia is produced in rabbits by injection of a phagolytic serum of goat, excretion of allantoin (I), uric acid (II), and total N (III) is increased. The ratios of (II):(III) and of (I):(III) also increase, whilst the uricolytic index is unchanged. The chief end-product of purine metabolism is (I) with (II) as intermediary.

II. Data are given for rabbit, guinea-pig, dog, pig, ox, rat, sheep, goat, and horse.

III. Injection of thyroxine (IV) increases the excretion of (III) and (I) and decreases that of (II). The uricolytic index is increased. (IV) increases the oxidation of (II) to (I). CH. ABS. (p)

**Action of colloidal substances on crystallisation, with reference to the problem of stone formation.** S. VON KÜTHY (Magyar orvosi Arch., 1934, 35, 289—297; Chem. Zentr., 1935, i, 2209).—Urine and bile are to be considered as supersaturated solutions, in which normally crystallisation or concrement formation should begin, but the colloidal or surface-active substances of high mol. wt. exert a protective action. Model experiments with  $PbI_2$  indicate the mechanism of this action of the colloids to be by selective adsorption in stages. R. N. C.

**Determination of lead in excreta and tissues.** R. A. KEHOE (Amer. J. Clin. Path., 1935, 5, 13—20).—Methods of prep. and ashing of samples are discussed and analytical methods are compared. For Pb in tissues spectrographic methods are the most satisfactory. CH. ABS. (p)

**Effect of external factors on perspiratio insensibilis.** A. VAN HARREVELD, B. W. GRUTTERINK, and A. K. M. NOYONS (Biochem. Z., 1935, 281, 1—26).—In man the phenomenon is practically unaffected by a  $\pm 35\%$  change in the humidity and a change of temp. within the range 20—28.5° or by changes in the thickness of the clothing. Only after attainment of equilibrium are trustworthy results obtained. The val. varies greatly in the individual at different times with const. atm. conditions.

W. McC.

**Changes in hydration of serum-colloids as a general feature of a disease.** K. SCHULHOF (Trans. Illinois State Acad. Sci., 1934, 27, 80).—Measurements of  $n$  and  $\eta$  of serum are utilised to assess the vol. occupied per g. of protein.

CH. ABS. (p)

**Azotæmia and elevation of the alkaline reserve in course of anuria.** R. HUGUENIN, R. TRUHART, and C. SANNIÉ (Compt. rend. Soc. Biol., 1935, 120, 717—719).—Blood-urea (I) is increased and the alkaline reserve is lowered in anuria.  $NaHCO_3$  increases the

alkaline reserve without affecting (I). Total Cl and the corpuscular/plasma-Cl ratio fall. R. N. C.

**Influence of 3:5-di-iodotyrosine on experimental arteriosclerosis.** A. OGATA, S. SANO, and K. MITSUI (J. Pharm. Soc. Japan, 1934, 54, 248—272).—The lipin content of blood was increased by feeding lanoline (I). Substitution of 3:5-di-iodotyrosine (II) hastened the restoration to normal lipin levels. The ratio of Et<sub>2</sub>O extract to body-wt. for mice fed with (I) indicates the decrease in wt. following administration of (II) to result from a decline in lipin content. CH. ABS. (p)

**Proteins of cancerous cells.** C. ACHARD and M. PIETRIE (Compt. rend., 1935, 201, 751—753; cf. A., 1935, 376).—Renal sarcomas of the ox and horse contain lipins (1.38—2.95%, largely cholesterol), globulins (2.6—4.2%) from which amides (0.48—0.67%) are isolated, and albumins (0.5—0.7%), which, although exhibiting the general properties of serum-albumins, possess a much smaller mol. (cf. A., 1933, 730). The residue insol. in H<sub>2</sub>O affords myxoprotein. J. L. D.

**Heavy water and tumour growth.** W. H. WOGLON and L. A. WEBER (J. Amer. Med. Assoc., 1934, 102, 1289—1290).—D<sub>2</sub>O had no effect on mouse sarcoma. CH. ABS. (p)

**Phosphorus in the blood-plasma of hens suffering from sarcoma.** F. PENTIMALLI and G. SCHMIDT (Biochem. Z., 1935, 282, 62—73).—The amounts of total, lipid, and acid-sol. P in the plasma of hens suffering from Rous sarcoma are > those in healthy hen plasma (30% increase in total P). The plasma of the diseased (but not that of the healthy) hens contains protein-P possibly derived from the tumours, although plasma from the muscles, but not that from the tumours, loses acid-sol. P. W. McC.

**Anomalous crystallisation of sodium chloride in normal and in sarcomatous blood-serum.** V. KILIAN (Acta Cancerologica, 1934, 1, 22—28).—After dilution of serum with 0.9% NaCl and subsequent evaporation, the form of crystallisation of NaCl from samples from sarcomatous chicken differed from that from normal samples. CH. ABS. (p)

**Enzymes in uterine cancer.** II. Lipase and lecithinase. III. Esterase. IV. Invertase. V. Antitrypsin. K. NAKAHORI (Japan. J. Obstet. Gynecol., 1934, 17, 419—445; cf. A., 1935, 514).—The distribution of the enzymes in human uterine cancer tissues, lymphatic glands, mucosa, and muscular layers of the uterus is examined. CH. ABS. (p)

**Influence of magnesium on growth of carcinoma, sarcoma, and melanoma in animals.** K. SUIGURA and S. R. BENEDICT (Amer. J. Cancer, 1935, 23, 300—310).—Effects of varying levels of dietary Mg on the growths are examined. Neoplasms as well as normal tissue require definite amounts of Mg for growth. CH. ABS. (p)

**Effect of intravenous injections of complex soluble salts of iron and ascorbic acid on tumours.** F. ARLOING, A. MOREL, and A. JOSSE-AND (Compt. rend., 1935, 201, 745—747).—Clinical

results obtained in the treatment of cancers by injections of mixed complex Fe and Ca salts of ascorbic acid are better than when Fe-Na salts are used (cf. A., 1935, 1401). J. L. D.

**Experimental tumours produced by decreased doses of coal tar. General action of the carcinogenic agent.** L. M. SCHABAD (Acta Cancerologica, 1934, 1, 56—77).—The carcinogenicity of tar is due to a general rather than to a local action.

CH. ABS. (p)

**Effect of certain polycyclic hydrocarbons on the growth of the Jensen rat sarcoma.** A. HADDOW (Nature, 1935, 136, 868—869).—Intra-peritoneal injections of colloidal preps. of 1:2:5:6-dibenzanthracene, 1:2-benzpyrene, 5:6-cyclopenteno-1:2-benzanthracene, and 1:2-benzanthracene, but not anthracene and phenanthrene, produce marked inhibition of growth of the implanted tumour in rats. Carcinogenic substances, like X-rays, may thus act primarily by producing a certain type of inhibition in the activity of the normal cell. L. S. T.

**The Costa reaction (200 cases).** R. H. KAMPMEIER (J. Lab. Clin. Med., 1935, 20, 531—538).—The ppt. formed in blood-serum by addition of procaine, Na citrate, and CH<sub>2</sub>O occurred in 70% of cases with pulmonary tuberculosis and in 90% of cases with malignant tumour. None appeared in syphilis. CH. ABS. (p)

**Calcium and inorganic phosphorus of blood-serum in dental caries.** C. G. KERLEY, E. J. LORENZE, and E. R. GODFREY (J. Pediat., 1935, 6, 665—666).—Serum-Ca and -inorg. P were within normal limits. NUTR. ABS. (m)

**Secretion of urine in diabetic coma.** R. A. MCCANCE and R. D. LAWRENCE (Quart. J. Med., 1935, 4, 53—79).—In diabetic coma there may occur disorganisation of renal function involving retention of urea, creatinine, and probably uric acid, of ketones, if present, and of sugar, if above the threshold. Urine may become acid (p<sub>H</sub> 5); excretion of NH<sub>3</sub> and salt is normal. CH. ABS. (p)

**Hæmochromatosis. I. Iron and sulphur content of the tissues. II. Results of spectrographic examination with special reference to copper and calcium.** H. RAMAGE and J. H. SHELDON (Quart. J. Med., 1935, 4, 121—129).—I. In 5 patients with hæmochromatosis there was a uniform increase in the Fe content, distributed over all the tissues except the blood, brain, and colon. Organs such as the liver, pancreas, and salivary glands may have 50—100-fold increase. Enormous deposits occurred also in the lymph glands, thyroid, pituitary, choroid plexuses, and heart. The somatic muscles contain nearly as much Fe as the liver. The total Fe (calc.) of the body is 25—50 g. There was no general increase in S content. The moderate increase in S in the alimentary canal, omentum, pancreas, and adrenal glands is probably related to deposits of hæmofuscin.

II. Spectrographic examination showed a two- or three-fold increase in Cu in the liver and all tissues except the kidney, small intestine, and omentum.



An increase in Ca was general, but most evident in the liver, thyroid, striated muscles, and pancreas. Disturbance in the Na and K metabolism may have occurred, the concn. of these elements in the tissues usually deviating in reverse directions from the normal. The low Mn content of the liver is probably significant. No unusual elements were encountered.

NUTR. ABS. (*m*)

**Alkalosis, a clinical problem.** C. T. WAY and E. MUNTWYLER (*Ann. Intern. Med.*, 1935, 8, 818—824).—In cases of hypertension and renal disease with a slight or no increase in non-protein-N, the acid-base balance of blood may change with a tendency towards a lower Cl content. Administration of alkali should be controlled by blood acid-base analyses.

CH. ABS. (*p*)

**Role of pressor substances in arterial hypertension.** R. B. CAPPS, E. B. FERRIS, jun., F. H. L. TAYLOR, and S. WEISS (*Arch. Int. Med.*, 1935, 56, 864—876).—In hypertension the urinary pressor substance is  $\neq$  the normal, and appears to be a  $H_2O$ -sol. substance, acting centrally.  $COMe_2$  extraction does not completely separate the pressor and depressor substances, but this fraction contains more pressor and less depressor material than the  $EtOH$  fraction.

H. G. R.

**Calcium metabolism in idiopathic hypoparathyroidism.** A. GOERNER and G. SAMUELSEN (*J. Amer. Med. Assoc.*, 1934, 102, 1001—1002).—The positive Ca balance in hypoparathyroidism was reduced by parathyroid extract. The increased excretion was by the urine.

CH. ABS. (*p*)

**Goitre prophylaxis with iodised salt.** R. D. McCURE (*Science*, 1935, 82, 370—371). L. S. T.

**Malaria in Panama with reference to control with atebirin and plasmoquin.** W. H. W. KOMP and H. C. CLARK (*Amer. J. Trop. Med.*, 1935, 15, 131—154; cf. A., 1935, 1149).—Atebrin and plasmoquin administered simultaneously enhance the toxic action of the latter. When given separately the desired effect is obtained with less toxicity.

CH. ABS. (*p*)

**Muscle chemistry in myasthenia gravis, pseudohypertrophic muscular dystrophy, and myotonia.** S. NEVIN (*Brain*, 1934, 57, 239—254).—The  $PO_4^{'''}$  content of pathological muscle under various conditions is examined. A method for determining the partition of acid-sol. P between  $H_3PO_4$ , creatinephosphoric and adenosinetriphosphoric acids is described. Sol. carbohydrate phosphates are determined by difference. CH. ABS. (*p*)

**Calcium and inorganic phosphorus in the blood-serum of emotionally unbalanced children.** C. G. KERLEY, E. J. LORENZE, jun., and E. R. GODFREY (*N.Y. State J. Med.*, 1935, 35, 571—572).—Of 90 children 81 showed normal Ca vals. and 83 normal inorg. P vals. Exaggerated nervous symptoms were not more severe in children with low Ca vals. than in those with normal Ca and P vals.

NUTR. ABS. (*m*)

**Renal damage following ingestion of a diet containing an excess of inorganic phosphate.** E. N. MACKAY and J. OLIVER (*J. Exp. Med.*, 1935, 61, 319—333).—Permanent renal lesions were pro-

duced in rats by feedings an excess of K and Na phosphates or  $H_3PO_4$ . Removal of excess of  $PO_4^{'''}$  does not restore normal structure. CH. ABS. (*p*)

**Comparison of "yeast" milk and irradiated milk in the treatment of infantile rickets.** E. T. WYMAN, R. C. ELEY, J. W. M. BUNKER, and R. HARRIS (*New England J. Med.*, 1935, 212, 257—262).—The two milks are equally effective.

CH. ABS. (*p*)

**Nitrogen balance and oxidation process in experimental scurvy. II. Effect of reduced iron.** L. D. KASHEVNIK, S. A. EIDMANN, and J. B. FRIEDLAND (*Biochem. Z.*, 1935, 282, 56—61; cf. A., 1935, 888).—In guinea-pigs, daily oral administration of 10 mg. of reduced Fe prior to the onset of scurvy caused increase in N metabolism, stimulated subsequent urinary N excretion when scurvy had set in, and tended to decrease the O : N ratio. The Fe caused retention and deposition of fat during the course of the disease, but had no effect on the excretion of protein degradation products, there being retention of these when scurvy was developing and increased excretion when the disease was fully established. Subsequently, while the animals fasted, there was N retention.

W. McC.

**Correlation of mineral metabolism and the vegetative nervous system in thyroid disease.** J. KLEIN (*Ann. Int. Med.*, 1935, 8, 778—804).

CH. ABS. (*p*)

**Interpretation of abnormal glucose-tolerance curves occurring in toxæmia in terms of liver function.** S. SOSKIN, M. D. ALLWEISS, and I. A. MRSKY (*Arch. Int. Med.*, 1935, 56, 927—934).—Toxæmias cause abnormal glucose-tolerance curves through an interference with the homeostatic mechanism of the liver.

H. G. R.

**Amino-acid content of the blood of the rabbit in tuberculous infection of the Yersin type.** E. S. PANAYOTOPOULOU (*Compt. rend. Soc. Biol.*, 1935, 120, 604—605).— $NH_2$ -acids increase steadily until death. The increases are of the same order for avian and bovine infections.

R. N. C.

**Tyrosine index of serum-polypeptides in the rabbit in the course of tuberculous infection of the Yersin type.** E. S. PANAYOTOPOULOU (*Compt. rend. Soc. Biol.*, 1935, 120, 695—696).—The tyrosine index increases steadily from the time of inoculation until death.

R. N. C.

**Whooping-cough: diagnostic significance of blood counts.** N. D. BEGG and M. F. COVENEY (*Lancet*, 1935, 229, 1113—1114).

L. S. T.

**Mathematical physics in metabolising systems with reference to lung cells.** N. RASHEVSKY (*Physics*, 1935, 6, 117—119; cf. A., 1935, 1073).—Previous results are applied to glucose oxidation and glycolysis. The relative rates of the two reactions, when occurring simultaneously, determine whether the system will divide spontaneously or not. Rapidly-dividing cancer cells show abnormally high rates of glycolysis.

CH. ABS. (*p*)

**Metabolism in children doing muscular work. I. Effect of racing on urinary constituents in**

boys. I. NAKAGAWA and K. KAWAMO (Amer. J. Dis. Children, 1935, 49, 594—602).—Following a 1200-m. race some albuminuria and increased acidity occurred.  $\text{NH}_3$ , creatine, and creatinine concns. were practically unchanged. P increased and total N decreased temporarily. The ratios, total N:urine vol., total P:urine vol., creatine:total N, and  $\text{NH}_3$ :total N, were all increased. CH. ABS. (p)

Metabolism of injured tissue. H. DRUCKREY (Naturwiss., 1935, 23, 796—799).—Mechanical trauma, such as that sustained by cells in thin sections of tissue, produces a marked immediate rise in their metabolism followed by a slow fall. The role of tissue damage in producing the observed results of  $\text{O}_2$  deficiency and also its possible significance in tumour metabolism are discussed. W. O. K.

Insect metabolism at temperatures below  $0^\circ$ . I. V. KOSHANTSCHIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 373—376).—The R.Q. of larvae of *Pyrausta nubilalis*, Hb., and of *Loxostege sticticalis*, L., indicate that metabolism at  $0^\circ$  is mainly concerned with carbohydrate, but at  $-6^\circ$  and  $20^\circ$  fats and proteins become important. A. G. P.

Biological cell oxidation. A. BERTHO (Chem.-Ztg., 1935, 59, 953—957).—A review.

Metabolic oxidation and radiation. M. COPESAROW (Protoplasma, 1934, 21, 73—80).—Blood, urine, tissue extracts, and yeast exposed to atm.  $\text{O}_2$  in the dark at  $37^\circ$  emit ultra-violet radiations. The effect is abolished by heat; in the case of yeast it is also destroyed by  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , KCN, or CO, but not by  $\text{CO}_2$  or  $\text{N}_2$ . No radiation is given off by pure cholesterol, calciferol, ascorbic acid, alkaloids, or synthetic adrenaline. The radiation is associated with the chemical function of respiratory enzymes; metabolic products radiate only in presence of the enzymes. R. N. C.

Infant feeding and nutrition. S. FRIEDMAN (Amer. J. Dis. Children, 1935, 49, 152—190, 460—473).—A review. CH. ABS. (p)

Effect of low calorific diets and resultant loss in weight on plasma-cholesterol in the obese. C. A. POINDESTER and M. BRUGER (Arch. Int. Med., 1935, 56, 884—890).—Plasma-cholesterol (I) in complicated or uncomplicated obesity is not altered primarily by reduction in wt. on a low-calorific diet; but an increase is noted in some cases due to the "starvation effect." Some high vals. of (I) show a decrease due to secondary changes. H. G. R.

Growth, reproduction, lactation, longevity, and haemoglobin formation in albino rats on meat diets contrasted with their response on the Steenbock stock diet and on the Sherman milk diet. P. M. NELSON and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1933, 116; 1934, 144—145).—As a N source dried beef muscle was superior to cereal or milk proteins. Neither pork nor beef muscle at a level of 15% protein was adequate for maintenance of body-wt., reproduction, and lactation. Pork at 15 and 30% protein levels and beef at the 15% level fed to female rats allowed no reproduction beyond the second generation. Beef was

superior to pork. With 30% beef protein rats reproduced freely. CH. ABS. (p)

Supplementary values of animal protein concentrates in chick rations. H. J. ALMQUIST, E. L. R. STOKSTAD, and E. R. HALBROOK (J. Nutrition, 1935, 10, 193—211).—Vals. of various meat products as protein (I) supplements are determined. The cystine, tryptophan, and  $\text{H}_2\text{S}$  contents of (I) feeds do not afford a basis for predicting their nutrient vals. Determinations of intact (I) (Cu ppt.), (I) decomp. products (phosphotungstic acid ppt.), undigestible (I) (pepsin-HCl), and hot  $\text{H}_2\text{O}$ -sol. (I), to which are assigned the relative nutrient vals. 100, 40, 0, and 40, respectively, permit the determination of nutrient vals. of (I) concentrates which agree closely with biological trials. A. G. P.

Is linoleic acid essential in the nutrition of rats? E. BECKER (Z. Vitaminforsch., 1935, 4, 241—249).—Without small amounts of linoleic acid (I) rats fail to maintain normal growth and develop a deficiency disease, which can be cured by daily doses of 5 mg. of walnut oil containing 2—3 mg. of (I). The growth curves of rats run parallel with the amount of (I) in the oil. It is not known which isomeride of (I) is responsible for the action. J. N. A.

"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. V. Nutritive value of pachyman. K. TAKEDA (J. Agric. Chem. Soc. Japan, 1934, 10, 685—690).—Pachyman is not easily digested, and its nutritive val. resembles that of cellulose. Neither it nor "Bukuryo" can be used as a substitute for cereals. J. N. A.

Biochemistry of fermented soya-bean paste ("miso"). III. Effect of cystine on the nutritive value of miso-protein given as supplement to rice. I. IWAMURA (Bull. Agric. Chem. Soc. Japan, 1935, 11, 128—134).—The nutritive val. of the miso-protein, when used as a supplement to a rice diet for albino rats, is increased by addition of cystine (I). For young rats the optimum amount of (I) is about 0.1% ( $>0.5\%$  is harmful), but for adult rats 0.5% is favourable. W. McC.

Substitution of dithioethylamine (cystine-amine) for cystine in the diet of the white rat. H. H. MITCHELL (J. Biol. Chem., 1935, 111, 699—705).—Addition of cystine-amine (I) to a cystine-deficient diet depresses the growth of the animal and impairs appetite. There is therefore no evidence that (I) can replace cystine in a diet. E. A. H. R.

Protein requirements of chicks. J. D. MCCONACHIE, W. R. GRAHAM, jun., and H. D. BRANTON (Sci. Agric., 1935, 15, 754—764).—Optimum levels of protein feeding are determined for chicks of various ages. The efficiency of food utilisation declines with age. Mortality decreases as the proportion of protein fed approaches the optimum. High and low protein intakes tend to modify the contour and texture of feathers, although the optimum protein requirement for correct feather development is not necessarily the same as that for growth. Slipped tendons are not directly due to high-protein feeding. The occurrence of "crow heads" is a dietary rather than a genetic factor. A. G. P.

**Effect of protein and amino-acid metabolism on the urea and xylose clearance.** R. F. PITTS (J. Nutrition, 1935, 9, 657—666).—Post-absorptive clearances of urea and xylose on a basal diet are low and not greatly affected by feeding the diet. Introduction of meat into the diet produces a gradual and prolonged post-prandial rise in both clearances. When meat feeding is prolonged, post-absorptive clearances are raised without obliteration of the post-prandial effect. Similar effects are produced by feeding casein, by administration of thyroxine to dogs on a basal diet or of phloridzin to fasting dogs, or by replacement of part of the carbohydrate of the basal ration with glycine. The primary effect of protein on renal function results from the action of  $\text{NH}_2$ -acids or OH-acids produced in the course of their metabolism on glomerular activity. A. G. P.

**Effects of varying amounts of animal protein fed to white Leghorn pullets. I. Influence of low-, medium-, and high-protein diets on the weight and number of eggs.** C. C. RHODES, L. H. BARTEL, and P. E. F. JOOSTE (Empire J. Exp. Agric., 1935, 215—228).—Comparison is made of the food consumption with different rations and varying levels of protein content. Differences in the ratio of carbohydrate to protein consumed were apparent, but there was a definite tendency for birds to balance the ration to a common nutritive ratio. The amount of protein consumed produced little significant effect on the body-wt. of the birds or on egg size, but was directly related to the average no. of eggs per bird. A. G. P.

**Effect of feeding vegetable protein on copulation and fertilisation in the fowl.** T. HATANO (Bull. Agric. Chem. Soc. Japan, 1935, 11, 125—128).—Vegetable (soya-bean) is more effective than animal (fish-meal) protein. W. McC.

**Utilisation of meat by human subjects. II. Nitrogen and phosphorus of round and liver of beef.** Z. LONG and M. S. PITTMAN. **III. Nitrogen and phosphorus of beef heart.** B. L. KUNERTH, I. M. CHITWOOD, and M. S. PITTMAN (J. Nutrition, 1935, 9, 677—683, 685—690).—II. The N of round of beef was as effectively utilised as that of liver. A higher proportional utilisation of liver-P is indicated.

**III. Utilisation of the N and P of beef-heart was not appreciably different from that of round.**

A. G. P.

**"Continuing" metabolism of nitrogen in animals.** H. BORSOOK and G. L. KEIGHLEY (Proc. Roy. Soc., 1935, B, 118, 488—521).—The continuing N metabolism (I) is defined as the N already present in the tissues metabolised on any one day, and is distinct from "wear-and-tear" metabolism. For man in N equilibrium at a level of 10—11 g. of urinary N per day, (I) constitutes > 50% of total urinary N. S excretion is lowered, but only by about 50%, when a normal diet is interrupted either by a day of N starvation or a day on which N is ingested in the form of compounds low in S; the lowering persists for a short period after restoration of the original diet.  $\text{NH}_3$  may serve as precursor of urinary uric acid in man.  $\text{NH}_2$ -acids do not stimulate either (I) or endogenous N metabolism. F. A. A.

**Digestion of foods. V. Synthetic fats.** S. SUZUKI (J. Agric. Chem. Soc. Japan, 1935, 11, 1—10; cf. A., 1934, 920, 1027).—Comparison is made of triacetin (I), tributyrin (II), trioctoin, and tridecain fed at the rates of 2 and 12% with a fat-free polished rice ration. At the lower level differences between the real and apparent digestion coeffs. were considerable, but there was little influence on the digestion of other food constituents. At the 12% level fats retarded protein digestion. Except for (I) and (II), the lower acid compounds were the more digestible and had the higher nutrient vals. CH. ABS. (p)

**Fat metabolism. VII.  $\beta$ -Oxidation of normal saturated dicarboxylic acids administered *per os*.** P. E. VERKADE, J. VAN DER LEE, A. J. S. VAN ALPHEN, and M. ELZAS (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 943—948).—After administration to dogs of the Na salts of sebacic (I) or undecanedicarboxylic (II) acids, the urine was found to contain (I), suberic, and adipic acids or (II), azelaic, and pimelic acids, respectively. The ratios in which these acids are found varies, but (I) or (II) always occurs in a greater amount. H. G. R.

**Carbohydrate metabolism in the guinea-pig.** F. GOTTDENKER (Biochem. Z., 1935, 281, 128—139).—In autumn the blood-sugar is greatly (up to 250%) increased by fasting, but in the same animal, in winter, fasting causes only slight increase or even decrease, the difference not being due to the change in temp. of the surroundings. Oral administration of overdoses of glucose causes hyperglycaemia, which reaches its max. within 0.5—1.0 hr., then decreases in intensity, and finally attains a val. < that first reached. Overdoses of adrenaline cause increases of 250—300% in blood-sugar. Hypoglycaemic convulsions are produced by overdoses of insulin, but the blood-sugar level is only slightly lowered or even raised, there being no accompanying increase in the content of reducing substances other than sugar. W. McC.

**Nutritive value of lactose in man.** A. E. KOEHLER, I. RAPP, and E. HILL (J. Nutrition, 1935, 9, 715—723).—In normal adults ingestion of 1.5 g. of lactose per kg. had no appreciable effect on blood-sugar (I) levels. A similar ingestion of starch (II) produced an increase in (I) which was nearly as great as that produced by glucose (III). The total hyperglycaemia after (II) was > that after (III). In these individuals lactose produced a slight and in diabetics a marked rise in (I). A. G. P.

**Xylan.** H. IWATA (Bull. Imp. Coll. Agric. Morioka, 1935, No. 21, 120 pp.).—Xylanase was not present in the saliva, pancreas, or bile of higher animals, and only in small amounts in the intestines. Decomp. of xylan (I) in the intestines into xylose (II) and small quantities of org. acids by micro-organisms was very active and several new species were isolated; these also hydrolyse starch, dextrin, inulin, and several carbohydrates, but do not affect xylose. The digestion velocity of (I) was < that of starch, but was increased by mild treatment with alkali. On feeding (I) there was little change in the blood constituents and no increase in the urinary excretion of (II), but a protein-sparing action was observed. Both glycogen

and fat accumulation were nearly equiv. to that due to starch. The total calorific val. of (I) was 4167—4184 and the assimilation 61.6%. H. G. R.

**Influence of calcium on carbohydrate metabolism.** T. HARADA (Bull. Chem. Soc. Japan, 1935, 10, 494—503).—Injection of Ca lactate into albino rabbits decreases the hyperglycaemia and glycosuria caused by simultaneous injection of glucose, but does not alter the effect of adrenaline on the blood-sugar. R. S. C.

**Hydrolysis, oxidation, and energy exchanges in the dog. III. Absorption and assimilation of hexoses in the organs during intravenous administration of galactose, maltose, and glucose.** M. WIERZUCHOWSKI and H. FISZEL (Biochem. Z., 1935, 282, 124—145; cf. A., 1935, 522).—The absorption from and delivery to the blood of the carbohydrates by various organs are studied. As regards rate and extent of absorption of glucose (I) and galactose (II), the organs form the series liver > portal vein organs > organs of the head > motor system. The liver plays little part in absorption of maltose (III), the other groups of organs exhibiting absorptions equal to those shown with (I). As regards extent of absorption of (I) from the liver, the order is organs of the head > portal vein organs > motor system, the amounts of lactic acid (IV) simultaneously produced by those absorbing organs corresponding respectively with 14—17, 96—164, and 40—60% of the amount of (I) injected. 5—15% of the injected and absorbed (I) or (II) is given up by these organs as (IV) to the blood. Absorption of injected (I) by these organs is at first slight, whilst urinary (I) excretion increases but later becomes more pronounced. The (I) consumption of the organs during injection of (II) is about the same as it is during fasts. During (II) injection the liver ceases to give out (I), about 40% of the (II) absorbed by the organs being subsequently utilised or excreted in the urine. Amytal narcosis has no effect on the assimilation of carbohydrates. Loss of blood and laparotomy have no effect on assimilation of (II), but they interfere slightly with that of fructose (V) and considerably with that of (I) and (III). Of the intravenously injected carbohydrates tested (V) is the best utilised during the narcosis. W. McC.

**Effect of sulphur administration on carbohydrate metabolism.** T. YOSHIKAWA (Sei-i-kwai Med. J., 1934, 53, No. 6, 74—84).—Administration of S by rubbing S-ointment on rabbit's ears, by mouth, or intravenously produced no appreciable change in blood-sugar. CH. ABS. (p)

**Chief sulphur compounds in nutrition.** H. B. LEWIS (J. Nutrition, 1935, 10, 99—116).—A review. A. G. P.

**Calcium, phosphorus, and nitrogen retention of children. Effects of acid- and base-forming diets.** N. J. DAVIS (Amer. J. Dis. Children, 1935, 49, 611—624).—The total Ca output was similar on acid- and base-forming diets. Acid diet led to decreased faecal P and slightly increased urinary P. Basic diets induced greater N retention and higher  $\text{NH}_3$  excretion. CH. ABS. (p)

**Minerals for dairy cattle.** J. C. KNOTT (Proc. 7th Ann. State Coll. Washington Inst. Dairying, 1934, 120—124).—The occurrence and functions of Na, K, Mg, S, Cu, Fe, F, Zn, Mn, I, Ca, and P in dairy cows are discussed. CH. ABS. (p)

**Mineral requirements of milk production. Annual cycle of mineral and nitrogen metabolism of the milch cow as affected by lucerne hay, timothy hay, bone flour, and ground limestone.** E. B. FORBES [with A. BLACK, W. W. BRAMAN, D. E. H. FREAR, O. J. KAHLENBURG, F. J. McCLURE, R. W. SWIFT, and LE R. VORIS] (Penn. Agric. Exp. Sta. Bull., 1935, No. 319, 152 pp.).—Monthly determinations of balances of N, Ca, Mg, P, Na, K, and Cl resulting from the different rations are recorded and discussed. A. G. P.

**Chemical reactions in muscle. X.** P. OSTERN and T. BARANOWSKI (Biochem. Z., 1935, 281, 157—167; cf. A., 1935, 1150).—In dialysed and non-dialysed extracts of autolysed skeletal muscle [free from adenosinetriphosphoric acid (I) and adenylic acid (II)] phosphoglyceric acid and (II) successively added are converted into (I) [yield 40% calc. on (I)]. In heart extracts (horse) the products are diadenosine-pentaphosphoric acid and a substance (possibly a nucleotidephosphoric acid) yielding a Ba salt insol. in dil HCl. Extracts of rabbit heart contain free (II), very little phosphocreatine, and half as much adenosinepolyposphoric acid and total phosphate as does skeletal muscle. The direct transfer of phosphate [from phosphopyruvic acid to (II) and from (I) to creatine] is accelerated by  $\text{Mg}^{++}$ , which only slightly affects liberation of free phosphate. In heart the transfer of phosphate is the same as in skeletal muscle, but (II) is here more stable and more slowly deaminated by enzymes. W. McC.

**Fission of adenylypyrophosphoric and arginine-phosphoric acid in crab muscle.** K. LOHMANN (Biochem. Z., 1935, 282, 109—119; cf. A., 1934, 1033, 1034).—Only one of the readily eliminated  $\text{H}_3\text{PO}_4$  residues is removed from adenylypyrophosphoric acid (I) by washed crab muscle and dialysed extract of the muscle. On addition of  $\text{Mg}^{++}$  the adenosine-diphosphoric acid (II) produced is converted into adenylic acid (III). Hence dephosphorylation of (I) is a two-stage process (as in vertebrate muscle), different enzymes being involved. In the dialysed extract argininephosphoric acid (IV) is hydrolysed only if (I) or (II) is present because the extract, in presence of (IV), cannot convert (III) into (II) or (I), whilst (II) is easily rephosphorylated. Crab muscle contains no adenylic acid deaminase. W. McC.

**Production of kynurenic acid from tryptophan and indole derivatives.** L. C. BAUGUESS and C. P. BERG (Proc. Iowa Acad. Sci., 1934, 41, 174—175).—When administered to rabbits *l*-tryptophan-amides (free amide, mono- and di-ethyl-amides, amide, and ethylanilide) were as readily converted to kynurenic acid (I) as was *l*-tryptophan (II). Substituted carboxylic acid derivatives were not converted  $\beta$ -3-Indolylpyruvic and *dl*- $\beta$ -3-indolyl-lactic acids, but not  $\beta$ -3-indolylacrylic or  $\alpha$ -oximino- $\beta$ -3-indolylpropionic acids, were also converted into



(I), but in amounts < those from (II) derivatives. Indole derivatives are probably not intermediates in the conversion of (II) into (I). CH. ABS. (p)

**Transformation of urobilinogen in the liver.** K. FELIX and H. MOEBUS (Z. physiol. Chem., 1935, 236, 230—236).—Fresh liver pulp (pig) attacks urobilinogen ( $p_{H}$  optimum at 7.1) in presence of  $O_2$  causing cessation of power to react to the aldehyde test. Boiled liver pulp has no such effect.

W. McC.

**Absorption of salicylic acid after intramuscular injection. Absorption by the bladder.** W. BLUME and F. W. FISCHER (Arch. exp. Path. Pharm., 1935, 179, 646—654).—Following intramuscular injection of 10 c.c. of 2.5% Na salicylate into rabbits, salicylic acid (I) appears in the blood after 1—2 min. and in the urine after approx. 30 min. The rate of excretion is fairly const., 70% of the administered (I) being excreted within 24 hr. The blood-(I) attains a max. within 1 hr. and returns to zero in 6—7 hr. Absorption into the blood after intramuscular injection is > that after rectal or subcutaneous administration. (I) is absorbed by inflamed (EtOH), but not by normal, bladder mucosa.

F. O. H.

**Absorption of intrapleurally and intraperitoneally injected salicylic acid.** W. BLUME and K. PLUM (Arch. exp. Path. Pharm., 1935, 179, 655—661).—Following intrapleural and intraperitoneal injection of Na salicylate into rabbits, salicylic acid (I) appears in the blood after 3—10 and 1—2.5 min. (max. being attained after 1 and 0.5 hr.) and in the urine after 40 and 26 min., the total excretion being 77 and 59%, respectively. With both routes, max. excretion occurs after  $\frac{1}{2}$  hr. and falls to zero in approx. 7 hr. At max. excretion, the blood-(I) indicates a ratio of absorption by buccal mucosa, stomach-intestine, rectal mucosa, pleural cavity, muscle, and abdominal cavity of 3 : 6 : 8 : 10 : 12 : 14. F. O. H.

**Relationship between dielectric polarisation and pharmacological action.** K. W. ROSENEMUND (Angew. Chem., 1935, 48, 701—705; cf. A., 1934, 652).—The anthelmintic properties of different phenolic lactones are not related to surface activity, action on membrane permeability, or action on the swelling of proteins, but to the polarity of the mols., as varied by the relative positions of substituents in the  $C_6H_6$  ring.

F. A. A.

**Relation of cell types in leucæmia to sensitivity to radium.** R. ISAACS (Folia Hematol., 1934, 52, 414—425).—Within 24 hr. of application of X-rays or Ra, metabolic rates rise, showing increased  $O_2$  utilisation, and chemical changes associated with cell growth are accentuated. CH. ABS. (p)

**Action and hæmolytic dose of X-rays.** A. ROGOZINSKI and B. S. LEVIN (Compt. rend., 1935, 201, 798—799).—The dose required for complete hæmolysis is increased if irradiation is carried out in several stages, probably as a result of the formation of antilytic substances.

J. L. D.

**Ionisation in air and the biological effects of  $\gamma$ -rays.** G. FAILLA (Physical Rev., 1934, [ii], 45, 564).—Contrary to the conclusions of Packard,

equal ionisations in air produced by X- and  $\gamma$ -rays are not equally effective in killing fruit-fly eggs. The therapeutic efficacy of high-voltage X- and  $\gamma$ -rays cannot be predicted by the usual biological and physical tests.

L. S. T.

**Action of solar (ultra-violet) rays on the skin and the formation of cholesterol.** A. H. ROFFO (Compt. rend., 1935, 201, 566—568).—The ratio of the cholesterol (I) content of the skin of the cheek to that of the abdomen is in adults 3.42, in infants 1.4, and in the foetus 1.1. Skin exposed to sunlight or ultra-violet light *in vivo* or *in vitro* increases in (I) content.

J. L. D.

**Radio-hæmolysis and cholesterol.** B. S. LEVIN and C. PIFFAULT (Compt. rend. Soc. Biol., 1935, 120, 712—714).—The resistance of guinea-pigs' corpuscles to X-rays is increased by injection or ingestion of cholesterol.

R. N. C.

**Fats and a theory of pharmacodynamic actions of alkali and alkaline-earth ions.** J. WAJZER and L. LAPICQUE (Compt. rend. Soc. Biol., 1935, 120, 707—710).— $K^+$  and  $Na^+$  decrease, and  $Ca^{++}$  increases,  $\sigma$  between  $H_2O$  and oils, by the formation of a unimol. layer of soap at the interface. The effect is unaltered by aliphatic amines.

R. N. C.

**Salt requirements and space orientation of the littoral isopod *Ligia* in Bermuda.** T. C. BARNES (Biol. Bull., 1932, 63, 496—504).—Toxicity of cations in sea- $H_2O$  to *L. baudiniana* decreases in the order  $K$ ,  $Mg$ ,  $Ca$ ,  $Na$ .  $K$  exerts a sp. paralysing action on gill movements.

CH. ABS. (p)

**Difference in action of ter- and quinque-valent arsenic compounds on the explanted spleen from chick embryo.** H. OKADA (Folia Pharmacol. Japon., 1935, 19, 271—282).—The growth of spleen-tissue is increased by low concns. of  $Na_3AsO_3$  (I),  $Na_3AsO_4$  (II), atoxyl (III), and nearsphenamine (IV). Tissue is killed by high concns. Potency decreases in the order (I), (IV), (II), (III).

CH. ABS. (p)

**Influence of bromine on the growth and metamorphosis of the larvæ of *Bufo vulgaris*.** V. FAMIANI (Atti R. Accad. Lincei, 1935, [vi], 21, 821—824).—Toad tadpoles fed on egg-yolk to which a trace of  $Br-H_2O$  had been added grew more rapidly than controls fed on unbrominated yolk. Metamorphosis commenced earlier, but the tadpoles died during metamorphosis; the liver and intestines had developed to the adult state, the legs had appeared early, but were stunted, and the respiratory system had failed to develop.

D. R. D.

**Differential biological reaction of cobaltous compounds and of some cobaltic complexes (cobaltiammines).** J. M. LE GOFF (Compt. rend., 1935, 201, 531—532).—The human organism can differentiate between subcutaneously injected  $Co^{II}$  and  $Co^{III}$ , and between  $Co$  and  $N$  in complexes.

R. N. C.

**New toxicant occurring naturally in certain samples of plant foodstuffs. IX. Toxic effects of orally ingested selenium.** K. W. FRANKE and V. R. POTTER. **X. Effect of feeding toxic foodstuffs in varying amounts and for different time**

periods. K. W. FRANKE (J. Nutrition, 1935, 10, 213—221, 223—231).—IX. Symptoms of poisoning produced by  $\text{Na}_2\text{SeO}_3$  are practically identical with those shown by the natural toxicant.

X. Effects of feeding toxic grain are examined.

A. G. P.

Mechanism of the action of sulphur and mud baths. L. SCHMIDT (Orvosi Hetilap, 1935, 79, 318—319).—Absorption of chemical components of mineral waters is probable. The S of therapeutic muds is in steady circulation, but in dynamic equilibrium, part being oxidised and part reduced.

CH. ABS. (p)

Dietary depigmentation of young black and pied rats, promoted by rapid growth, prevented and cured by ingestion of copper. F. J. GORTER (Z. Vitaminforsch., 1935, 4, 277—293; cf. A., 1935, 1148).—The curative effect of yeast on depigmentation is due to its Cu content and not to its anti-pellagra property. Depigmentation in young growing rats is prevented by adding  $\text{CuSO}_4$  to the diet, the daily preventive dose of Cu being 0.02—0.12 mg., and the curative dose 0.07—0.24 mg. Other metals are ineffective. Cu in cereals appears to be more available than Cu in proteins.

J. N. A.

Feeding and thyroid function. I. Effect of cyanides on the function and histological picture of the rat thyroid. F. BRUMAN and L. BERMAN (Z. ges. exp. Med., 1935, 95, 724—728; Chem. Zentr., 1935, i, 2202—2203).—MeCN given daily does not alter basal metabolism in rats. The diminution of tissue oxidation due to MeCN is compensated by increased thyroxine secretion.

R. N. C.

Effect of iodoacetate on *post-mortem* glycogenolysis in liver. H. R. NOLTIE (Quart. J. Exp. Physiol., 1935, 24, 377—382).—Iodoacetate did not prevent glycogenolysis in rabbit liver incubated in  $\text{N}_2$  at 38°, or the accumulation of sugar (although exerting some inhibitory action), but caused the lactic acid content to remain stationary.

CH. ABS. (p)

Effect of dinitrophenol on calcium and phosphorus metabolism. C. L. ROBBINS (J. Nutrition, 1935, 10, 187—191).—Increased basal metabolism caused by administration of dinitrophenol was not accompanied by any change in the excretion of Ca, P, or N.

A. G. P.

Effects of moderate doses of dinitrophenol on the energy exchange and nitrogen metabolism of patients under conditions of restricted dietary. M. L. TAINTER, W. C. CUTTING, and E. HINES (J. Pharm. Exp. Ther., 1935, 55, 326—353).—0.3—0.4 g. of 2:4-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\cdot\text{OH}$  (I) was given daily for 1—2 weeks to normal human subjects maintained on a low-calorific diet with only sufficient protein to maintain N balance. (I) produced an increased loss in body-wt. associated with increased fat metabolism with the production of no ketones or acidosis. There was no extra metabolism of carbohydrates or proteins; (I) was not conjugated in the body as an org. sulphate and no extra secretion of Cl' in the urine, faeces, or sweat occurred.

H. D.

Antagonism of cryogenin and 2:4-dinitrophenol. A. LEULIER and G. BÉRUARD (Compt.

rend. Soc. Biol., 1935, 120, 650—651).—The temp. rise in pigeons given cryogenin and ( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\cdot\text{OH}$  (I) is < in those given (I) only.

R. N. C.

[Pharmacology of] phenanthrene derivatives. V. Homologous acids and aldehydes and some of their derivatives. N. B. EDDY (J. Pharm. Exp. Ther., 1935, 55, 354—364; cf. A., 1933, 858).—The action on cats of phenanthrenecarboxylic and  $\beta$ -(3-phenanthryl)propionic acids, their Me esters, amides, ketone and alcohol derivatives, and some position-isomerides of these compounds are compared. Effectiveness is greater in the higher homologues; that of the alcohols is > that of ketones. The amides and Me esters are less active than the acids. 3-derivatives are more active than the 2- or 9-derivatives. Of the compounds studied, Me phenanthrene-3-, m.p. 95°, and -9-carboxylate, m.p. 116°; phenanthrene-3-carboxydimethylamide, m.p. 120.5—121°, -2-carboxylamide, m.p. 242—243°, -3-, m.p. 79—80°, and -9-aldehyde, m.p. 100.5—101°;  $\beta$ -3-phenanthrylpropionic acid, m.p. 154.5—155° (Me ester, m.p. 61—62°; amide, m.p. 161—162°); 3-, m.p. 100—103.5, and 9-hydroxymethyl-, m.p. 149—149.5°; 3-, m.p. 72°, 2-, m.p. 143°, and 9-acetyl-, m.p. 74.5°, 3-propionyl-phenanthrene, m.p. 53—54°; phenanthryl-3-, m.p. 83—83.5°, and -2-methylcarbinol, m.p. 134.5—135.5°, are new.

Pharmacology of some hydroxyphenoxyethylalkylamines. D. BOVET, A. SIMON, and J. DRUEY (Compt. rend. Soc. Biol., 1935, 120, 690—691).—*sec*-Hydroxyphenoxyethylalkylamines exhibit adrenolytic action, whilst the *tert*-amines exhibit nicotine-like action and resemble hordenine in having a powerful ganglionic nicotine-like action which is abolished by methylation of the OH. Certain of the *tert*-amines exhibit both the above actions.

R. N. C.

Renal activity. VIII. Effect of xanthine and histidine fractions isolated from various organs of cows. IX. Effect of endocrine preparations on renal activity. Y. MIZUNO (Sci-i-Kwai Med. J., 1933, 52, No. 10, 50—70, 71—90; cf. A., 1935, 258).—VIII. Xanthine fractions (especially from adrenals) markedly accelerated renal activity in rabbits. The histidine fraction is less effective. Arginine and lysine fractions have no action.

IX. Injection of thyreoglandol caused marked acceleration. Pituitrin and adrenaline were non-effective.

CH. ABS. (p)

Effect of bile acids on sugar assimilation in depancreatized dogs. T. HASEGAWA (Arb. Med. Fak. Okayama, 1935, 4, 453—460).—Injection of Na cholate, with or without glucose, reduced hyperglycemia and glucosuria in depancreatized dogs.

CH. ABS. (p)

Influence of bile acids on calcium metabolism. VIII. Influence of bile acids and spleen extract on urinary calcium excretion. IX. Blood composition of normal and splenectomized rabbits under the influence of bile acids and spleen extract. M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 346—355, 356—364).—VIII. In normal or splenectomized rabbits subcutaneous injection of cholate (I) augments and spleen extract (II) decreases urinary Ca.

**IX. Splenectomy** is followed by hypercalcaemia, which gradually disappears. Blood-Ca is lowered by (II) in normal rabbits > in splenectomised rabbits. Post-operative hypercalcaemia is increased by (I) and lowered by (II). Spleen and liver are concerned in the regulation of blood-Ca. CH. ABS. (p)

**Influence of fractionated liver extract on blood composition of normal dogs.** M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 438—444).—The factor in aq. liver extracts which causes hypercalcaemia is sol. in EtOH and slightly less sol. in Et<sub>2</sub>O (cf. preceding abstract). CH. ABS. (p)

**Blood composition of normal and splenectomised rabbits under the influence of liver extracts from normal and splenectomised rabbits, spleen extracts, and bile salts.** M. IWADÔ (Arb. Med. Fak. Okayama, 1935, 4, 424—437).—Subcutaneous injection of Na cholate increases blood-Ca (I). Splenectomy removes a factor from the liver which is capable of increasing (I). CH. ABS. (p)

**Barbiturates. XI. Methods of barbital research.** C. R. LINEGAR, J. M. DILLE, and T. KOPANYI (J. Amer. Pharm. Assoc., 1935, 24, 847—852).—Prior to determination of barbiturates (I), highly pigmented urines are cleared by Na<sub>2</sub>MoO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> or CuSO<sub>4</sub>-Na<sub>2</sub>WO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>. Extraction of urines or cleared filtrates by CHCl<sub>3</sub> indicates that excreted (I) are present as acids even in alkaline urines. Following pptn. of blood with Na<sub>2</sub>WO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> (Folin-Wu), the CHCl<sub>3</sub> extract of the filtrate is free from substances interfering with the colorimetric determination. (I) are determined in brain by extraction of the powdered (liquid air) tissue with CHCl<sub>3</sub>, concn. of the extract, and removal of phospholipins by pptn. with COMe<sub>2</sub> (cf. A., 1935, 118). F. O. H.

**Barbiturate-picrotoxin antagonism.** C. R. LINEGAR, J. M. DILLE, and T. KOPANYI (Science, 1935, 82, 376—377). L. S. T.

**Use of coramine for combating poisoning from narcotics and hypnotics.** H. KILLIAN (Anesthesia and Analgesia, 1935, 14, 23—27). CH. ABS. (p)

**Effect of ultra-violet irradiation on the anaesthetising power of methyl and ethyl alcohols.** W. P. ELHART and O. S. ORTH (Anesthesia and Analgesia, 1935, 14, 15—19).—The anaesthetic action of MeOH and EtOH on goldfish was accelerated by irradiation as a result of formation of the aldehydes and acids. CH. ABS. (p)

**Rate of production of anaesthesia in mice by ether containing aldehyde and peroxide.** P. K. KNOEFEL and F. C. MURRELL (J. Pharm. Exp. Ther., 1935, 55, 235—241).—Et<sub>2</sub>O containing > 0.07% MeCHO and 0.02% H<sub>2</sub>O<sub>2</sub> is less effective anaesthetically than pure Et<sub>2</sub>O. EtOH acts merely as a diluent. H. D.

**cycloPropane anaesthesia: post-operative morbidity in 2200 cases.** E. R. SCHMIDT and R. M. WATERS (Anesthesia and Analgesia, 1935, 14, 1—3).—Respiratory, nausea, and emetic after-effects of cyclopropane and Et<sub>2</sub>O were < those of C<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>O (with CO<sub>2</sub> absorption), but circulatory complications were slightly greater. CH. ABS. (p)

**Novocaine oxide.**—See this vol., 70.

**Influence of morphine on local anaesthesia of the cornea through various local anaesthetics in rabbits.** K. ARIMA (Folia Pharmacol. Japon., 1935, 19, 283—286).—Small amounts of morphine which do not affect the sensitivity of the cornea increased and lengthened the action of cocaine, tutocaine, and pantocaine. CH. ABS. (p)

**Morphine and ether hyperglycaemia in hypophysectomised dogs.** E. DI B. DE SABELLI and E. J. DI BENEDETTO (Compt. rend. Soc. Biol., 1935, 120, 738—739).—Hyperglycaemia from morphine in hypophysectomised dogs is > in normal dogs, whilst that from Et<sub>2</sub>O is less. R. N. C.

[Pharmacology of] morphine, codeine, and their derivatives. X. Deoxymorphine-C, deoxycodine-C, and their hydrogenated derivatives. N. B. EDDY and H. A. HOWES (J. Pharm. Exp. Ther., 1935, 55, 257—267; cf. A., 1935, 780).—Reduction of the alcoholic OH in members of the morphine and codeine series increases the analgesic and depressor effects and decreases the emetic effect. Of the compounds formed, tetrahydrodeoxymorphine, m.p. 260°, [α]<sub>D</sub><sup>25</sup> -45.5° in EtOH, is new. H. D.

**Effects of morphine and its derivatives on intestinal movements. IV. Dihydro-ψ-codeine and dihydroallo-ψ-codeine.** H. KRUEGER, H. HOWES, and H. GAY (J. Pharm. Exp. Ther., 1935, 55, 288—318).—The quantities of morphine, ψ- and allo-ψ-codeine, dihydro-ψ-codeine and -allo-ψ-codeine required to reduce the frequency of rhythmic contractions of the dog's intestine were as 1:22:108:35:27, respectively; for producing peristalsis 1:45:65:31:54, and for equivalently maintained effects on tone 1:75:22:30:60. H. D.

**Emetic action of apomorphine in rabbit lymph.** S. TAKAHASHI (Arb. dritt. Abt. Anal. Inst. Univ. Kyoto, D, 1934, No. 4, 138—139).—The emetic effect is lost by incubation with blood-serum or lymph. CH. ABS. (p)

**Combined action of quinine and pituitrin, histamine, and barium on the excised uterus and isolated urine bladder of the rabbit.** K. KUNISHO (Folia Pharmacol. Japon., 1935, 19, 333—345).—Stimulative effects were obtained by use of half the min. active dose of one of the drugs with half the dose of any other. A potentiation was observed in all cases except with histamine and quinine on the pregnant uterus. CH. ABS. (p)

**Comparative toxicity of anabasine and nicotine sulphates to insects.** J. M. GINSBURG, J. B. SCHMITT, and P. GRANETT (J. Agric. Res., 1935, 51, 349—354).—Anabasine sulphate was more toxic to a no. of insects than was nicotine, but when used as a stomach poison for grasshoppers and silk-worm larvae was much inferior. A. G. P.

**Effect of nicotine in the albino rat.** C. S. SMITH, S. ROSENFELD, jun., and L. J. SACKS (J. Pharm. Exp. Ther., 1935, 55, 274—287).—Injection of 0.005—0.0075 mg. of nicotine per g. of body-wt. in rats decreased their voluntary muscular activity

and their fat contents; it had no influence on the growth curves or oestrus cycles. H. D.

**Balance of nicotine in the smoking of tobacco in cigarettes.** A. KOPERINA (Tabacn. Prom., 1934, No. 5, 37—40).—Of the nicotine (I) in tobacco, 60% is burned during smoking, 27% escapes on exhalation, and 12% is absorbed by the smoker. Absorption of (I) is through the lungs and not through the stomach or saliva. CH. ABS. (p)

**Use of rabbits in the assay of digitalis, strophanthus, and squill.** G. N. RAPSON and S. W. F. UNDERHILL (Quart. J. Pharm., 1935, 8, 409—423).—Application of the infusion method of assay (Gaddum, A., 1932, 964) indicates that rabbits are less sensitive than cats to ouabain (I), strophanthus (II), or squill, but more sensitive than dogs or guinea-pigs to (I) and (II); to digitalis, rabbits are the most resistant of the four species. With strict adherence to conditions characteristic for each drug, results from rabbits agree with those from cats. F. O. H.

**[Pharmacology of] samandarine and its derivatives and fission products.** O. GESSNER and W. ESSER (Arch. exp. Path. Pharm., 1935, 179, 639—645).—The pharmacological action and min. lethal dose of samandarine (I) and 9 derivatives (A., 1935, 97) were determined in mice. Samandarone approximates to (I) in its activity. No correlation between constitution and pharmacological (especially convulsive) action is apparent. F. O. H.

**Pharmacological action of dendrobine, the alkaloid of Chin-shih-hu.** K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1935, 55, 319—325).—Dendrobine produces moderate hyperglycæmia, diminishes cardiac activity in large doses, lowers blood pressure, suppresses respiration, inhibits isolated rabbit's intestine, and contracts the guinea-pig's uterus. H. D.

**Yolk-sac vessels of the chick embryo.** IV, V. T. NAKANO (Folia Pharmacol Japon., 1935, 19, 293—299, 300—305; cf. A., 1935, 893). CH. ABS. (p)

**Comparative actions of sympathomimetic compounds: bronchodilator actions in experimental bronchial spasm of parasymphathetic origin.** J. R. PEDDEN, M. L. TAINTER, and W. M. CAMERON (J. Pharm. Exp. Ther., 1935, 55, 242—256; cf. A., 1934, 1134).—Of fourteen amines tried, the most effective in producing bronchial dilation in dogs treated with arecoline were adrenaline, arterenol, and epininc; activity appeared to be associated with the pyrocatechol nucleus. H. D.

**Action on the gaseous metabolism of poisons for the vegetative nervous system.** F. PÉTER (Biochem. Z., 1935, 281, 111—120).—Subcutaneous administration of ergotamine increases the basal metabolic rate of fasting male rats at 28° (max. 42%) and its effects last 5—6 hr.; atropine (II) slightly reduces the rate, and Na luminal (III) does not affect it. (I)+(III) cause increase, (II)+(III) slight increase, and (I)+(II) and (I)+(II)+(III) have no effect. W. McC.

**Toxicity of optically active and inactive dihydrodeguelins.** W. A. GERSDORFF (J. Agric. Res., 1935, 51, 355—361).—The order of toxicity to goldfish was rotenone > active dihydrodeguelin (I) > deguelin > inactive (I), although the relative proportional toxicity varied somewhat with the concns. examined. A. G.

**Toxicity of methyl alcohol.** A. BENEDICENTI (Mem. R. Accad. Italia, 1935, 6, 601—633).—Injection of MeOH into rabbits and dogs lowers the alkaline reserve of the blood. The toxic action is not influenced by administration of cholesterol (I) or oils containing (I). Most animals tolerate 0.2—0.4 vol.-% in the inspired air, but considerable variations occur with different species and also with animals of the same species. MeOH in air is determined by conversion into  $\text{Me}_3\text{BO}_3$  and subsequent decomp. in 0.1N-NaOH. Severe poisoning is followed by accumulation of MeOH in blood, brain, etc. Normal combustion produces (non-toxic) traces of CO,  $\text{CH}_2\text{O}$ , and other reducing substances. Industrial hazards are discussed. F. O. H.

**Mechanism of mercury diuresis.** J. J. BERTERVIDE and C. RECHNIEWSKI (Prensa med. Argentina, 1934, 21, No. 50—51).—Novasural causes hydræmia only when  $\text{H}_2\text{O}$  is retained in the tissues. The globulin content of blood is reduced. CH. ABS. (p)

**Influence of mercury on cultivated tissues.** III. How will the action of mercury compounds on cultures of fibroblast *in vitro* be influenced by glucose? K. HIRASHIMA (Folia Pharmacol. Japon., 1935, 19, 323—332).—The toxic action of  $1 \times 10^{-6} M$ - $\text{HgCl}_2$  is decreased by raising the glucose concn. in fibroblast culture media 0.01M > that in normal media. Cultures in such media show normal resistance to  $\text{HgCl}_2$ . CH. ABS. (p)

**Repeated injections of a thio-derivative of gold: tolerance and localisation.** A. LEULIER and G. BERUARD (Compt. rend. Soc. Biol., 1935, 120, 651—654).—Sr aurothiopropansulphonate (I) is less toxic than the corresponding Na and Ca salts to guinea-pigs, and diffuses less readily through the organs on account of its low solubility; it is excreted less rapidly in the urine. The Au storage in the kidneys, spleen, liver, and other organs produced by repeated injections of (I) is not much > that produced by the more sol. salts. R. N. C.

**Has glucose any influence on the arsphenamine action on cultivated tissue?** H. OKADA (Folia Pharmacol. Japon., 1935, 19, 287—292).—Combination of glucose and neo- or myo-arsphenamine causes better growth in spleen-tissue cultures than arsenicals alone. CH. ABS. (p)

**Cyanide antidotes.** P. J. HANZLIK and A. P. RICHARDSON (J. Amer. Med. Assoc., 1934, 102, 1740—1745).—Intravenous injection of methylene blue is recommended. A mixture of  $\text{NaNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  is also effective. CH. ABS. (p)

**Antidote for acute mercury poisoning.** S. M. ROSENTHAL (J. Amer. Med. Assoc., 1934, 102, 1273—



1276).—Oral or intravenous administration of Na formaldehydesulphoxylate proved satisfactory.

CH. ABS.

**Influence of chronic fluorine toxicosis in laying hens on the fluorine content of the egg and its relation to the lipin content of the egg-yolk.** P. H. PHILLIPS, J. G. HALPIN, and E. B. HART (J. Nutrition, 1935, 10, 93—98).—Addition of F-containing rock phosphate to hen's rations increases the F content of egg-yolks. Within the yolk the additional F occurs mainly in the COMe<sub>2</sub>-insol. fraction of the fatty matter, possibly in combination with complex lipins. Ingestion of F by means of mineral phosphate did not reduce egg size.

A. G. P.

**Oxidation-reduction catalysis in the living cell.** P. JOYET-LAVERGNE (Protoplasma, 1935, 23, 50—69).—Published work is discussed in support of the concept that vitamin-A and glutathione act as complementary constituents of a catalytic system controlling intracellular oxidation-reduction processes located on the surface of the chondriome. A. G. P.

**Catalase in lymphocytes.** K. FUKUCHI (Arch. dritt. Abt. Anat. Inst. Univ. Kyoto, D, 1934, No. 4, 65—67).—The catalase activity of lymphocytes from the popliteal gland of rabbits is determined.

CH. ABS. (*p*)

**Iron. IX. Catalase and "readily eliminated" iron of blood.** G. BARKAN (Z. physiol. Chem., 1935, 236, 197—200).—Since the catalase (I) is not affected by CO under conditions in which elimination of Fe is greatly restricted, it follows that (I) is not identical with the "readily eliminated" blood-Fe.

W. McC.

**Cytochrome-c. IV.** K. ZEILE (Z. physiol. Chem., 1935, 236, 212—215; cf. A., 1934, 109; Theorell, A., 1935, 1277).—The mol. wt. (18,000) and hæmin content (3.5%) of the smallest unit of the cytochrome (I) are determined, taking advantage of the non-adsorption of reduced (I) on kaolin. The isoelectric point of (I) is at *p*<sub>H</sub> 8.2.

W. McC.

**Tyrosinase action on mono- and di-hydric substrates.** M. GRAUBARD and J. M. NELSON (J. Biol. Chem., 1935, 111, 757—770).—*p*<sub>H</sub>-activity curves for *p*-cresol (I) with various preps. of tyrosinase (II) are given. The system (I)–(II) proceeds differently from the system pyrocatechol (III)–(II), for in the former (II) is not inactivated, whilst in the latter it is inactivated very quickly and addition of NH<sub>2</sub>Ph produces very little change. With (I) the rate of reaction  $\propto$  concn. of (II), whilst with (III) the total O uptake depends on the *p*<sub>H</sub> and amount of (II). Neither NH<sub>2</sub>Ph nor NaHSO<sub>3</sub> inhibits the reaction, but there may be prolonged induction periods. It is concluded that (II) consists of only one enzyme and that it acts like a peroxidase.

J. N. A.

**Activation by glutathione of the enzymic dehydrogenation of alcohol.** T. WAGNER-JAUREGG and E. F. MÖLLER (Z. physiol. Chem., 1935, 236, 222—227).—Reduced (but not oxidised) glutathione (I), and also KCN [action > that of (I)], Na<sub>2</sub>S,  $\alpha$ -amino-3-naphthol-4-sulphonic acid, and thioglycollic acid (but not pyrophosphate) in presence of dialysed extract of washed yeast activate the enzymic dehydro-

genation of EtOH. The activation is due to the binding of heavy metals, since, when these are as completely removed as possible, the effects of reduced (I) and KCN are < usual and the inhibition caused by added CuSO<sub>4</sub> is counteracted by addition of reduced (I) or KCN [ $\leq$  about 10 mols. of reduced (I) or KCN per mol. of CuSO<sub>4</sub>]. Cysteine (II) does not accelerate the dehydrogenation and even counteracts the effect of reduced (I), probably because heavy-metal compounds of (II) catalyse oxidation of reduced (I).

W. McC.

**Dehydrogenase of lactic acid.** T. WAGNER-JAUREGG and E. F. MÖLLER (Z. physiol. Chem., 1935, 236, 216—221; cf. Adler *et al.*, A., 1935, 1276).—The yellow (flavin) enzyme of yeast plays no part in the aerobic enzymic conversion of lactic acid into AcCO<sub>2</sub>H.

W. McC.

**Enzymes of liver. III. Aldehydease. IV. Alcohol-dehydroase.** L. REICHEL and H. KOHLE (Z. physiol. Chem., 1935, 236, 145—157, 158—167; cf. A., 1934, 807; Battelli *et al.*, A., 1910, ii, 980).—III. Dry preps. of the aldehydease (I) (from pig liver), which retain their activity almost unchanged for > 1 year, have optimal effect at *p*<sub>H</sub> 7.5—7.8, are destroyed at 69°, and cease to act after 2 hr. The action is greatly (> 50%) diminished by KCN, probably because of cyanohydrin production, and decreases as the concn. of substrate increases. Benzoquinone (II) in high concn. inhibits anaerobic dismutation by (I), methylene-blue (III) in high concn. increases it, and the oxidation product (IV) of adrenaline has no effect. Cytochrome and indophenol-oxidase accompany (I), which acts only if they are present. In fresh liver, in presence or absence of O<sub>2</sub> the action of (I) is slight, most of the EtCHO being consumed in other ways.

IV. Alcohol-dehydroase (from frog-liver) does not act in absence of O<sub>2</sub>, converts PrOH (optimum at *p*<sub>H</sub> 6.7—7.3) into EtCHO, no EtCO<sub>2</sub>H being produced, retains its activity for 6—8 weeks in a vac., but loses it in a few days in air, is destroyed at 47.5° (*p*<sub>H</sub> 7.8), is not affected by KCN, and ceases to act after 80 min. The extent of action decreases as the concn. of substrate increases. (II), (III), and (IV) act as intermediate H acceptors in the process and increase the extent of dehydrogenation, but ascorbic acid diminishes it. The extent of dehydrogenation is also increased by preps. from spleen (calf).

W. McC.

**Cabbage-amylase.** B. A. RUBIN and V. E. TRUPP (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 229—232).—In addition to amylase (I) an enzyme cytase (II) exists, capable of hydrolysing cellulose to reducing sugar. In "Amager," a late variety, the leaves are richest in (II), whilst in "No. 1" the stalks have a higher (II) content. The (I) content is const. during storage for 6 months, whilst (II) gradually decreases.

**Reversible inhibition of  $\beta$ -malt-amylase by ascorbic acid and related compounds.** C. S. HANES (Biochem. J., 1935, 29, 2588—2603). The degree of inactivation of  $\beta$ -malt-amylase (I) by ascorbic acid (II), dihydroxymaleic acid (III), and reductone (IV) increases with the time of treatment. With low

conens. of (II) regeneration of activity occurs after 10 min. treatment; the regeneration is more rapid with (III) and (IV), and is correlated in all cases with decreases in the I vals. of the inhibitor-enzyme mixtures. (I) stabilises (II) against oxidation, whilst it accelerates the oxidation of (III) and (IV), thus explaining the difference in inhibiting powers of these three. Preliminary oxidation of the inhibitors, or the addition of a no. of reducing substances such as HCN, reverses the inhibition.  $\text{CuSO}_4$  causes increased inhibition. It is concluded that the sp. effect of (I) lies in its dienol group as opposed to its reducing powers.

H. D.

$\alpha$ - and  $\beta$ -Amylase in ripening wheat grain. P. S. UGRUMOV (Biochem. Z., 1935, 282, 74—78; cf. Purr, A., 1934, 934; Stenstam *et al.*, *ibid.*, 1258).—During the early stages of the ripening,  $\beta$ -amylase, which is predominantly a saccharifying agent, and  $\alpha$ -amylase (I), which produces dextrin, are present. (I) becomes inactive at the "milky" stage and cannot be detected during subsequent ripening or in resting wheat, but it reappears during germination.

W. McC.

Effect of potassium cyanide on amylase activity. J. O. PAGE and D. T. ENGLIS (Trans. Illinois State Acad. Sci., 1934, 27, 74).—The rate of saccharification by barley amylase is unaffected by KCN at  $p_H$  4.56. At  $p_H$  7.0 KCN increases the rate until it approximates to that at  $p_H$  4.56.

CH. ABS. (p)

Conversion of rutin into a brown pigment by tobacco enzymes. C. NEUBERG and M. KOBEL (Naturwiss., 1935, 23, 800—801).—The enzymes of the tobacco leaf convert rutin (quercetinrhamnogluco-side) into a dark brown  $\text{H}_2\text{O}$ -sol. product which on hydrolysis yields a  $\text{H}_2\text{O}$ -insol. aglucone. The reaction, which apparently consists in the oxidation of the rutin, is accelerated by the presence of 0.03%  $\text{H}_2\text{O}_2$ .

W. O. K.

Enzymes of pectin. III. Complete direct hydrolysis of pectolic acid to  $d$ -galacturonic acid by pectolase. F. EHRLICH, R. GUTTMANN, and R. HAENSEL (Biochem. Z., 1935, 281, 93—102; cf. A., 1933, 491).—Crude material obtained from pectin by heating with HCl and washing with  $\text{H}_2\text{O}$  and EtOH is rapidly (3—4 days) converted by pectolase into pure cryst.  $d$ - $\alpha$ -galacturonic acid in 87% yield. The conversion of purified material is much slower (2 months) and is incomplete except at  $p_H$  6—4.

W. McC.

Cellobiase activity of the bovine rumen. C. ANTONIANI (Biochim. Terap. sper., 1935, 22, 48).—Neither the mucosa of the rumen nor aq. extracts made by prolonged maceration in presence of PhMe at 37° hydrolyse cellobiose, although the presence of cellobiase (I) is readily demonstrated in expressed fluid. Possibly (I) is of alimentary origin.

NUTR. ABS. (m)

Retarding action of formaldehyde, acetaldehyde, and acetone on the enzymic hydrolysis of sucrose. A. CHAUDIN (Bull. Soc. Chim. biol., 1935, 17, 1346—1350).—The effect of  $\text{CH}_2\text{O}$ , MeCHO, and COMe<sub>2</sub> on the hydrolysis of sucrose by invertase, like that of alkalis, MeOH, and EtOH, is to retard the

reaction, and displace the curve of reaction rate against time so that the amount of enzyme present appears to be increased.

A. L.

Purification of choline-esterase. E. STEDMAN and (MRS.) E. STEDMAN (Biochem. J., 1935, 29, 2563—2567; cf. A., 1933, 1081).—Preps. of choline-esterase, 50 to 100 times as active as serum, may be prepared from the latter by fractional pptn. with  $(\text{NH}_4)_2\text{SO}_4$  and AcOH and adsorption on  $\text{Al}_2\text{O}_3$  or  $\text{Fe}(\text{OH})_3$  from acid solution using aq.  $\text{NH}_3$  and  $M/3$ -phosphate buffer at  $p_H$  8 as eluents. These preps. do not attack  $\text{PrCO}_2\text{Me}$ .

H. D.

Action of magnesium on the aspartase system. K. P. JACOBSON and F. B. PEREIRA (Compt. rend. Soc. Biol., 1935, 120, 551—554).—Addition of  $\text{Mg}^{++}$  to the aspartase system displaces the equilibrium in favour of fumaric acid formation,  $K_e^{37}$  showing a considerable decrease.

R. N. C.

Enzymes of snake venom. I. Activation of dipeptidase by the venom of the snake *Trimoresurus mucrosquamatus*. Y. TSUCHIYA (J. Agric. Chem. Soc. Japan, 1935, 11, 720—730).—The dipeptidases of extract of dried tortoise liver and of fresh or dried intestinal mucous membrane of the pig are activated by the venom, the effect being pronounced with respect to hydrolysis of leucylglycine, slight with respect to that of valylglycine, and absent with respect to that of glycyl- and alanyl-glycine when the tortoise liver extract is used. The  $p_H$ -activity curve exhibits max. within a certain  $[\text{H}^+]$  zone. The activating power decreases with time and the amount of venom required for max. activation  $\propto$  the amount of enzyme used.

W. McC.

Enzymic proteolysis. VI. Structure of protamines. II. Clupein. E. WALDSCHMIDT-LEITZ and E. KOFRANYI (Z. physiol. Chem., 1935, 236, 181—191; cf. A., 1931, 984).—Clupein is hydrolysed by activated trypsin, 4 peptide linkings being broken [no arginine (I) produced] and the product yields two fractions separated by pptn. with aq. EtOH. The less sol. (N :  $\text{NH}_2$  ratio 9) forms 73% of the product and is a mixture of tripeptides containing 2 (I) residues and 1  $(\text{NH}_2)_1$ -acid residue. The more sol. (N :  $\text{NH}_2$  5) forms 27% and is a mixture of dipeptides containing 1 (I) and 1  $(\text{NH}_2)_1$ -acid residue. The results of acid and enzymic (aminopolypeptidase, arginase, carboxypolypeptidase, dipeptidase) hydrolysis of these fractions indicate the structure of clupein (mol. wt. 2021), which is a chain of 10 (I), 4  $(\text{NH}_2)_1$ -acid, and 1 proline residues, the position of the latter alone being uncertain, although only 3 positions are possible.

W. McC.

Proteolytic enzymes. VIII. Proteolytic systems of papain. M. BERGMANN and W. F. ROSS (J. Biol. Chem., 1935, 111, 659—666).—The enzymic homogeneity and the activation processes of papain (I) are investigated. Substrates such as hippuryl-amide (II) and carbobenzyloxydiglycylglycine are acted on by (I) only after activation by HCN,  $\text{H}_2\text{S}$ , and thioglucose. (I) inactivated by oxidising agents ( $\text{H}_2\text{O}_2$ , I) has its proteinase but not its polypeptidase (III) action reactivated by the above activators,

so that (I) must contain two different proteolytic enzymes.  $\text{NHPh-NH}_2$  completely inhibits the splitting of (II) by HCN-activated (I), but the hydrolysis of gelatin is only slightly affected. Excess of I added to HCN-activated (I) destroys both enzymes, but small amounts inhibit (III) only. The results are in accord with the presence of a CHO group in (III).  
E. A. H. R.

**Enzymic amylolysis. V. Amylophosphatase of barley.** E. WALDSCHMIDT-LEITZ and K. MAYER (Z. physiol. Chem., 1935, 236, 168—180; cf. A., 1934, 449).—Barley and malt extracts contain an enzyme, amylophosphatase (I), which eliminates all bound  $\text{H}_3\text{PO}_4$  from starch paste, and the accompanying decrease in viscosity  $\propto$  the amount of  $\text{H}_3\text{PO}_4$  eliminated. The degradation (optimal at  $p_{\text{H}}$  5.6) results in the production of reducing substances apparently consisting of chains of about 36 glucose residues. (I), which is not activated by amylokinase from malt, is purified and freed from accompanying enzymes by selective adsorption on  $\text{Al}_2\text{O}_3$  and kaolin. Kidney-phosphatase behaves very similarly towards starch paste, but at  $p_{\text{H}}$  5.6 its action is very much slower.  
W. McC.

**Phosphatase of the prostate gland.** W. KUTSCHER and H. WOLBERGS (Z. physiol. Chem., 1935, 236, 237—240; cf. A., 1935, 1268).—The human prostate gland and seminal fluid contain large amounts of a phosphatase (I) not identical with urinary phosphatase. (I), which is destroyed in 5 min. at  $60^\circ$ , exhibits specificity as regards its action on phosphates,  $\alpha$ - and  $\beta$ -glycerophosphates being readily attacked, hexose diphosphate and pyrophosphate only slightly affected.  
W. McC.

**Glycerophosphatase activity of the tissue of animals in avitaminosis-A.** L. EMERIQUE (Bull. Soc. Chim. biol., 1935, 17, 1372—1377).—The phosphatase (I) content of the kidneys and liver of rats suffering from vitamin-A deficiency is the same as that in normal animals. In the lung, however, (I) is  $>$  normal.  
A. L.

**Combining power of taka-diastase towards glycerophosphates.** J. COURTOIS (Bull. Soc. Chim. biol., 1935, 17, 1340—1345).—The reaction coeffs. for the rates of hydrolysis of  $\alpha$ - and  $\beta$ -glycerophosphates by taka-diastase increase regularly with increasing amounts of enzyme up to a certain point and thereafter both remain const., the amount of diastase at this point being the same in both cases. This behaviour is explained by the affinities of the enzyme for both substrates being the same, but the rates of hydrolysis different.  
A. L.

**Comparative hydrolysis of  $\alpha$ - and  $\beta$ -glycerophosphoric acids by vegetable phosphatases. II. Taka-diastase.** J. COURTOIS (Bull. Soc. Chim. biol., 1935, 17, 1318—1339; cf. A., 1935, 122).—The vals. of the optimum  $p_{\text{H}}$  for the hydrolysis of  $\alpha$ - and  $\beta$ -glycerophosphoric acids increase with the substrate concn., the displacement being greater for the  $\beta$ - than the  $\alpha$ -compound. This behaviour is the result of two simultaneous reactions, one involving the affinity of the enzyme for the substrate which increases with acidity and on which depends the

optimum  $p_{\text{H}}$  val. for the reaction at low substrate concn., and the other the actual hydrolytic activity, which at high concn., when the enzyme surface is saturated, controls the  $p_{\text{H}}$  optimum. This interpretation is applied to corresponding observations made with laccase and urease.  
A. L.

**Inhibitory effect of phloridzin on an enzymic dismutation.** H. KALCKAR (Nature, 1935, 136, 872—873).—The dismutative conversion of triose-phosphoric acid into phosphoglyceric acid and glycero-phosphoric acid is prevented or markedly inhibited by approx. 0.01*N*-phloridzin (I). The velocity of conversion of hexose diphosphate into dihydroxy-acetone phosphate (II), and of (II) into glyceraldehyde phosphate, is not affected by this concn. of (I).  
L. S. T.

**Yeast zymin. I. Effect of some electrolytes on carbon dioxide production. II. Effect of ethanol on the production of carbon dioxide. III. Effect of some electrolytes, and of ethanol, on the phosphate content during fermentation.** H. E. STAVELEY, L. M. CHRISTENSEN, and E. I. FULMER (J. Biol. Chem., 1935, 111, 771—783, 785—790, 791—802).—I. The optimum  $p_{\text{H}}$  for the production of  $\text{CO}_2$  by zymin (I) is 5.8—6.2, and (I) is most active when prepared from yeast which has been kept for several days at refrigerator temp.  $\text{NH}_4\text{Cl}$ ,  $\text{MgSO}_4$ , NaCl, and KCl increase the initial max. rate of  $\text{CO}_2$  formation by (I), whilst  $\text{NH}_4\text{Cl}$  (most active),  $\text{MgSO}_4$ , NaCl, and  $\text{CaCl}_2$  increase the steady const. rate of  $\text{CO}_2$ .  $\text{NH}_4\text{Cl}$  and  $\text{MgSO}_4$  increase the rate of  $\text{CO}_2$  formation in presence of added inorg.  $\text{PO}_4'''$ , but the effect of the two salts is not additive.

II. Production of  $\text{CO}_2$  by dried yeast, yeast juice, living yeast, and (I) is increasingly lowered by EtOH in the order named. 1.86% of EtOH reduces the activity of (I) 50%, whereas 14% is necessary to reduce the activity of dried yeast 50%. Inorg.  $\text{PO}_4'''$  does not decrease the sensitivity of (I) towards EtOH.  $\text{NH}_4\text{Cl}$  in presence of EtOH increases the rate of  $\text{CO}_2$  production to  $>$  that observed in absence of EtOH.

III. The optimum  $p_{\text{H}}$  for disappearance of inorg.  $\text{PO}_4'''$  from a (I) fermentation mixture is 6.2—6.4. Electrolytes markedly decrease the time which elapses before  $\text{PO}_4'''$  attains a min. val., and the effects of the cations are in the order  $\text{NH}_4 > \text{Mg} > \text{Na} > \text{K} > \text{Ca}$ . EtOH in low concn. increases the time required for esterification and the min. steady state val. of  $\text{PO}_4'''$ , but the latter is decreased if  $\text{NH}_4\text{Cl}$ , KCl, or NaCl be present also. For compounds of the type  $\text{R-NH}_3\text{Cl}$ , the influence of R in decreasing the time necessary for inorg.  $\text{PO}_4'''$  to reach a min. val. is  $\text{C}_6\text{H}_{11}\text{O}_5 > \text{H} > \text{Me}$ .  
J. N. A.

**Fermentation of carbohydrates.** G. MALYOTH and E. SOMMERFELD (Biochem. Z., 1935, 281, 49—79).—The effect of changes in amount of enzyme, vol. of  $\text{H}_2\text{O}$ , and amount of sugar and of addition of  $\text{KH}_2\text{PO}_4$  with and without nutrient media on the rate and results of fermentation of glucose by yeast has been measured (error usually  $\pm 4\%$ ) in a modification of the micro-apparatus of Krogh. When cell-free press juice is used, 100% fermentation is recorded, the deficit with living yeast being due to sugar con-

sumption for building up the cells, to undetected gaseous exchanges, and to related causes. With living yeast, alone or in nutrient media, the fermentation is accelerated by  $\text{KH}_2\text{PO}_4$ , especially when the proportion of yeast is small. When the juice is used,  $\text{KH}_2\text{PO}_4$  with nutrient medium causes acceleration  $>$  that found with living yeast. The apparatus may also be used to measure the fermentation of polysaccharides (*e.g.*, hydrolysis of maltose by leucocytes from horse blood). W. McC.

**Chemical reactions during alcoholic fermentation.** I. Production and hydrolysis of adenosinetriphosphoric acid and their connexion with hydrolysis of sugar. C. LUTWAK-MANN and T. MANN. II. Theoretical considerations. J. K. PARNAS, C. LUTWAK-MANN, and T. MANN (Biochem. Z., 1935, 281, 140—156, 168—174).—I. Fresh bottom yeast contains appreciable amounts and Lebedev extract only small amounts of adenylic acid (I) and adenosinetriphosphoric acid (II). The extract contains an enzyme which converts (II) into (I), but no enzyme which produces  $\text{NH}_3$  and inorg. phosphate from (I). During alcoholic fermentation with yeast or extract (I) is converted into (II), phosphate being transferred to (I) from hexosediphosphoric acid (III) when the extract is used and otherwise from phosphoglyceric (IV) and phosphopyruvic acid (V) with accompanying production of  $\text{AcCO}_2\text{H}$ . In the first case the process is not affected by  $\text{NaF}$ , in the second it is completely inhibited. (II) added to the extract in presence of glucose yields (III) and (I), but no dephosphorylation of (II) occurs if (III) is present. It is concluded that when fermentable substances are added to (II) fructosediphosphoric acid is produced, and that the transformation of (IV) and (V) into  $\text{AcCO}_2\text{H}$  provides the occasion for a transformation of (II) additional to that which occurs during the first phase of fermentation by yeast.

II. The above (and other) results indicate that (I) and (II) act as phosphate carriers during alcoholic fermentation much in the same way as they do in muscle. W. McC.

**Effect of cholesterol and insulin on fermentation by yeast.** S. HERMANN [with R. NEIGER] (Biochem. Z., 1935, 281, 121—127).—The fermenting power of living yeast is specifically restricted by cholesterol (I) sols which, however, accelerate fermentation by autolysed yeast. Some samples of insulin (II) accelerate fermentation by living yeast, but this acceleration is checked by (I) sols. Fermentation by autolysed yeast is not accelerated by (II). The sensitivity of yeast to poisoning with  $\text{H}_2\text{SO}_4$  and salicylic acid is increased by washing with light petroleum. The acceleration of fermentation caused by cozymase (III) is checked by (I) sols. Apparently the samples of (II) contain a thermostable (not destroyed in 30 min. at  $100^\circ$ ) substance which is not (III). W. McC.

**Effect of vitamin-C on fermentation by yeast and on lactic acid production in *B. aerogenes* cultures and muscle pulp.** K. ZIFF and M. THURAU (Biochem. Z., 1935, 282, 51—55).—Alcoholic fermentation by yeast is not inhibited by ascorbic acid in concns. of 1 :  $10^6$ —1 : 125. Concns.  $<$  0.004M

inhibit production of lactic acid (I) by *B. aerogenes* and those  $<$  0.02M inhibit production of (I) in rabbit muscle pulp, but addition of glycogen to the pulp prevents the inhibition. W. McC.

**Determination of oxygen consumption of yeast.** G. NEUMANN (Biochem. Z., 1935, 281, 181—185).—Spectroscopic examination of a standard oxyhæmoglobin (I) solution (saturated with  $\text{O}_2$ ) to which a known amount of yeast has been added (with exclusion of  $\text{O}_2$ ) permits determination of the time required for the yeast to reduce (I) and hence of the  $\text{O}_2$  consumption of the yeast. If the time of reaction is suitably chosen, the vol. of  $\text{O}_2$  consumed by 1 mg. of yeast is about 17 c.c. with dil. and 22 c.c. with conc. (I) solutions. W. McC.

**Determination of phosphorus in yeast by the bomb calorimeter.** R. AIROLDI (Annali Chim. Appl., 1935, 25, 523—525).—Application of the method of Garelli and Carli (A., 1933, 621, 1179) to yeast is described. F. O. H.

**Influence of buffer on sugar consumption and acid production by *Aspergillus*.** V. BOLCATO (Annali Chim. Appl., 1935, 25, 515—523).—Production of acid by *Aspergillus* grown in aq. sucrose is increased by the presence of citrate buffer, due to both buffering action and diminished rate of carbohydrate consumption. Utilisation of the citric acid produced is unaffected. F. O. H.

**Chemistry of mould-tissue. VIII. Innate factors influencing growth and sterol production of *Aspergillus fischeri*.** P. R. WENCK, W. H. PETERSON, and H. C. GREENE. IX. Cultural factors influencing growth and sterol production of *A. fischeri*. P. R. WENCK, W. H. PETERSON, and E. B. FRED (Zentr. Bakt. Par., 1935, II, 92, 324—330, 330—338; cf. A., 1935, 535).—VIII. Growth and sterol (I) production varied with the strain used.

IX. With a no. of C sources the amount of mycelium produced and its (I) content were inversely related. Urea was the best N source in  $\text{CaCO}_3$ -free media, whereas  $\text{NH}_4\text{NO}_3$  was superior in the presence of  $\text{CaCO}_3$ . The % of (I) in mycelium increased with the glucose concn. in the medium, with the glucose : urea ratio (optimum 40 : 1), and with temp. (optimum  $37^\circ$ ). With prolonged incubation, production of (I) increased even after autolysis of mycelium set in. Aeration influenced the rate of fermentation, but not of (I) formation. The max. % of (I) was obtained in low-urea media at  $p_{\text{H}}$  2.0. A. G. P.

**Production of dimethylpyruvic and pyruvic acids by *Aspergillus niger*.** T. HIDA (J. Shanghai Sci. Inst., 1935, IV, 1, 201—214).—The mycelium of *A. niger*, when transferred to a medium of  $p_{\text{H}}$  7, containing glucose or sucrose 5%,  $\text{Na}_2\text{SO}_3$  5%,  $\text{NH}_4\text{Cl}$  1%,  $\text{KH}_2\text{PO}_4$  2%, produces  $\text{Pr}^2\text{CO}\cdot\text{CO}_2\text{H}$  (I) and  $\text{AcCO}_2\text{H}$  (II). (I) was synthesised by the interaction of  $\text{Et}_2\text{C}_2\text{O}_4$ ,  $\text{Pr}^2\text{Br}$ , and Mg in  $\text{Et}_2\text{O}$ . The Mg compound on decomp. with  $\text{H}_2\text{O}$  affords the Et ester of (I).  $\text{NH}_4^+$  favours the production of (I) and inhibits that of (II). J. H. B.

**Effect of thymol on progress of rabbit moniliasis.** W. D. STOVALL, S. B. PESSIN, and L. ALMON (J. Lab. Clin. Med., 1935, 20, 572—582).—Thymol



(I) inhibits growth of *Monilia* in cultures, but has no effect on the progress of infection in rabbits. (I) is completely absorbed and can be recovered from urine, blood, or liver, but not in appreciable amounts from faeces. CH. ABS. (p)

Effect of certain nitrogen compounds on growth of *Chlorogonium* and *Chilomonas*. J. B. LOEFER (Arch. Protistenk., 1935, 85, 74—86).—*Chilomonas* cannot utilise  $\text{NH}_2$ -acids, whereas *Chlorogonium* produces markedly increased growth, notably with aspartic acid. Neither species can use amide-N. A. G. P.

Alcohol- and carbohydrate-oxidising bacteria isolated from fruits, and a new classification of oxidising bacteria. II. T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 1124—1136; 1935, 10, 50—60; cf. A., 1934, 1036).—Organisms are grouped according to the optimum temp. for multiplication. The optimum  $p_{\text{H}}$  for production of gluconic acid is < that for multiplication. Peptone and glucose are the best sources of N and C, respectively. CH. ABS. (p)

Deamination of alanine by bacteria. E. AUBEL and F. EGAMI (Compt. rend. Soc. Biol., 1935, 120, 684—685).—"Resting" bacteria in aerobiosis convert alanine into  $\text{AcCO}_2\text{H}$  more readily in presence of  $\text{NO}_3^-$ , which is reduced, or of  $\text{NH}_2\text{OH}$ . The process is therefore probably a dehydrogenation; the action of catalase on the  $\text{H}_2\text{O}$  formed, which would otherwise destroy the  $\text{AcCO}_2\text{H}$ , is partly inhibited. R. N. C.

Mechanism of non-symbiotic fixation of atmospheric nitrogen. T. R. BHASKARAN and V. SUBRAHMANYAN (Current Sci., 1935, 4, 234—235).—In cultures of soil organisms glucose decomp. was rapid during the first 4 days. During this period  $\text{CO}_2$  and org. acids were produced and approx.  $\frac{1}{3}$  of the expected amount of N was fixed. Of this much was in a  $\text{H}_2\text{O}$ -sol. form. Subsequently (4—8 days) org. acids were destroyed, mucilage was formed, and N was fixed. Formation of mucilage and N fixation are related, but not proportional. A. G. P.

Occurrence of *Azotobacter* at high temperatures. J. SINGH and A. HUSSAIN (Current Sci., 1935, 4, 235—236).—*Azotobacter* survive in a vegetative condition at  $45^\circ$ . A. G. P.

Can *Azotobacter chroococcum* synthesise vitamin-D? J. E. GREAVES (J. Bact., 1935, 30, 143—148).—When grown on synthetic media *A. chroococcum* can synthesise ergosterol, which is transformed into vitamin-D by irradiation. A. G. P.

Occurrence of a strain of *Azotobacter chroococcum* which does not ferment mannitol. N. R. SMITH (J. Bact., 1935, 30, 323—328).—The organism is widely distributed in soils. A. G. P.

*Bacterium acidi lactici*, Hueppe, and its systematic classification on the basis of its properties. G. PRANGE (Zentr. Bakt. Par., 1935, II, 92, 305—324).—Comparison is made of the biochemical activities of various organisms of the *coli-aerogenes* group and of *B. acidi lactici*. The latter does not ferment sucrose, raffinose, dextrin, starch, inulin, dulcitol, or inositol, fails to grow in citrate-

$\text{NH}_4\text{Cl}$  media, and produces indole from tryptic-peptone- $\text{H}_2\text{O}$ . A. G.

Toxin formation by bacteria. I. Stimulatory and inhibitory substances in peptones. P. STADLER and I. MEISSNER (Zentr. Bakt. Par., 1935, I, 134, 102—109).—The influence of peptones on toxin production by *B. botulinus* varied with their source and method of prep., and was dependent on the presence of certain chemical substances. Decomp. products of animal proteins have an inhibitory action. A. G. P.

Metabolism of *Bact. coli*. Production of biogenic amines. P. STADLER and E. NEUS (Zentr. Bakt. Par., 1935, I, 134, 110—114).—Some strains of *B. coli* converted tyrosine into tyramine, others produced OH-acids by deamination. A. G. P.

Influence of lithium chloride on *Bact. coli*. II. K. RICHTER (Zentr. Bakt. Par., 1935, II, 92, 249—256).—Addition of  $\text{LiCl}_2$  to agar media lowered the dry-matter production, sugar fermentation, and respiration rates of cultures. A. G. P.

Acid and gas formation by members of the *coli-aerogenes* intermediate groups in the presence of certain sugar alcohols and their anhydrides. K. P. DOZOIS, F. HACHTEL, C. J. CARR, and J. C. KRANTZ, jun. (J. Bact., 1935, 30, 189—192).—Dulcitol and mannitol are fermented by many organisms of the group, but the anhydrides are not utilised. A. G. P.

Amino-acids necessary for growth of *Cl. sporogenes*. P. FILDES and G. M. RICHARDSON (Brit. J. Exp. Path., 1935, 16, 326—335).—Growth occurs in a medium containing  $\text{NH}_2$ -acids as N source, the indispensable  $\text{NH}_2$ -acids being tryptophan, tyrosine, phenylalanine, arginine, and leucine; histidine, cystine, methionine, and valine are also probably indispensable. R. N. C.

Gonococcal polysaccharides. S. MUTERMILCH and A. GRIMBERG (Compt. rend. Soc. Biol., 1935, 120, 587—589).—A polysaccharide with the properties of a hapten is isolated from *Gonococci* by dissolving in Na taurocholate, acidification with  $\text{AcOH}$ , filtration, neutralisation with  $\text{NaOH}$ , and evaporation in vac.; proteins are coagulated by heating to  $100^\circ$  and removed by filtration, and the polysaccharide is repeatedly pptd. with  $\text{EtOH}$  in alternately acid and alkaline solutions. The final product is protein-free, and yields a reducing sugar on hydrolysis. It fixes the antigenococcal antibody. R. N. C.

Interrelationship between the amount of V-factor and the amount of air necessary for growth of *Haemophilus influenza*, type b, in certain media. M. PITTMAN (J. Bact., 1935, 30, 148—161).—Growth of the organism in certain media containing small amounts of V-factor is initiated only if the culture is well aerated. With more V-factor less air is necessary. A. G. P.

Biochemistry of *Bacillus mesentericus hydrolyticus*. S. HERMANN and P. NEUSCHUL (Biochem. Z., 1935, 281, 219—230).—The bacillus, obtained from carrots, grows very poorly or not at all anaerobically, liquefies gelatin, and coagulates milk (clots

later liquefied). It grows best in media (*e.g.*, vegetables or suspensions containing them) containing org. N (no growth if no org. N) and cellulose or hemi-cellulose. Growth on bouillon or peptone solutions is not accompanied by production of  $H_2S$  or indole. Acid production is very small; no gas is evolved and no reducing substances (Fehling) are produced except from starch, which, like sugars (glucose, fructose, sucrose, galactose, maltose, lactose), is hydrolysed. The bacillus and enzymes obtained from it have powerful softening action on vegetables, the connective tissue being destroyed. W. McC.

**Relation of micro-organisms to carotenoids and vitamin-A. II. Production of carotenoids by *Mycobacterium phlei*.** M. A. INGRAHAM and H. STEENBOCK (Biochem. J., 1935, 29, 2553—2562).—On a medium containing asparagine (I), glucose (II),  $K_2HPO_4$ ,  $MgSO_4$ , and Na and  $Fe^{III}$  citrates *M. phlei* produced less pigment than when  $[K^+]$  and  $[HPO_4^{''}]$  were lowered, or when glycols and alcohols replaced (II); at normal  $p_H$  replacing (I) with  $NH_4^+$ ,  $CO(NH_2)_2$ , and peptones was without influence on pigmentation. Increasing the  $[Fe^{III}]$  prevents pigmentation; excess of (I) causes autolysis, and on media containing glycerol or low concn. of (II), (I) is attacked by the bacteria.  $C_2H_4$ ,  $Na^+$ ,  $Li^+$ ,  $Ca^{++}$ ,  $Mg^{++}$ , and Se, the redox potential, the light intensity, and temp. were without effect on pigmentation. By separating the pigments from light petroleum on an adsorption column the presence of  $\alpha$ - and  $\beta$ -carotene, kryptoxanthin, and esters of lutein, zeaxanthin, and azafrin was established. H. D.

**Solubility of *Pneumococcus* in saponin. III. Saponinlysis reaction as a means of differentiating *Pneumococcus* and *Streptococcus*.** S. J. KLEIN (J. Bact., 1935, 30, 43—48; cf. A., 1933, 1207). A. G. P.

**Kinetics of the attack on glucose and lactic acid by small concentrations of bacteria; concept of minimum active concentrations.** P. CHAIK (Compt. rend., 1935, 201, 626—628).—Of three species of propionic bacteria, one exhibited a threshold concn. below which it decomposed neither glucose nor lactic acid, the second a threshold for short but not for long periods of incubation, and the third a threshold for glucose, but for lactic acid only some retardation of decomp. W. O. K.

**Physiology of *Rhizobium*. III. Respiration and growth as influenced by the reaction of the medium.** D. W. THORNE and R. H. WALKER. IV. **Utilisation of carbonaceous materials.** O. R. NEAL and R. H. WALKER (J. Bact., 1935, 30, 33—42, 173—187; cf. A., 1933, 638, 752).—III. Growth of *R. meliloti* and *R. japonicum* reached max. at  $p_H$  7.0, 6.7—6.9, decreasing to zero at 4.6—4.9, 4.2 and 9.6, 9.5, respectively. The optimum  $p_H$  for respiration was  $>$  that for growth in both cases.

IV. No significant differences in the rate and extent of  $O_2$  consumption by *R. meliloti* were apparent in media containing glucose (I), mannitol (II), or sucrose (III). Galactose (IV) and arabinose (V) were more effectively utilised than (I) on  $NO_3^-$  and on  $NH_4^+$  media. Maltose (VI), lactose (VII), inositol, dulcitol,

and sorbitol with both forms of N and raffinose and erythritol (VIII) on  $NH_4^+$  media were inferior to (I). As measured by total  $O_2$  consumption  $NH_4^+$  was more readily utilised than  $NO_3^-$ . For *R. japonicum*, (V) was the best energy source, (I), (IV), and xylose were equally effective, whereas (II), (VI), (VII), (III), and (VIII) were utilised little or not at all.  $NO_3^-$  was more effective than  $NH_4^+$ . A. G. P.

**Factors influencing the respiration of *Rhizobium*.** D. W. THORNE and R. H. WALKER (Proc. Iowa Acad. Sci., 1934, 41, 63—70).—Stimulation of *R. meliloti* by certain substances (yeast and legume extracts) is attributable to their nutrient content. The assumption that there is a co-enzyme of respiration is not substantiated. CH. ABS. (p)

**Oxidation of glucose by *Rhizobium meliloti*.** O. R. NEAL and R. H. WALKER (Proc. Iowa Acad. Sci., 1934, 41, 167—168).—In media containing  $M/540$ — $M/180$  concns. of glucose the  $O_2$  consumption of *R. meliloti* increased rapidly for 4—8 hr. and subsequently declined to a low and fairly const. level, the total consumption being approx.  $\frac{1}{3}$  of that required for complete oxidation. The proportion of glucose-C converted into  $CO_2$  in the presence of  $NH_4^+$ -N was  $<$  that in the presence of  $NO_3^-$ -N. CH. ABS. (p)

**Inhibition of growth of *Bacillus subtilis* on a modified extract agar by X-irradiation of the medium.** I. H. BLANK and H. KERSTEN (J. Bact., 1935, 30, 21—32).—The action of soft X-rays on agar produces a diffusible, non-volatile substance which is toxic to *B. subtilis*. A. G. P.

**Metabolism of spirochaetes *in vitro*.** G. SCHEFF (Zentr. Bakt. Par., 1935, I, 134, 35—43).—In 4 species examined no  $O_2$  consumption was apparent. Production of  $CO_2$  occurs only in carbonate media and results from the action of lactic acid formed from sugars. A. G. P.

**Evolution of dehydrogenases of *Staphylococcus aureus* during growth.** D. BACH (Compt. rend. Soc. Biol., 1935, 120, 673—674).—The dehydrogenase content of the cultures falls as their age increases; the nature of the H donator does not affect the rate of decrease. R. N. C.

**Hydrogen donators for *Staphylococcus aureus*.** D. BACH (Compt. rend. Soc. Biol., 1935, 120, 608—610).—The active H donators include most carbohydrates and related substances and eight org. acids. EtOH and BuOH are the only active alcohols, and cysteine and glutamic acid the only active  $NH_2$ -acids; the activities of these are very feeble. Simple aldehydes, ketones, and natural bases are inactive. R. N. C.

***Staphylococcus* toxins and anti-toxins.** A. T. GLENNY and M. F. STEVENS (J. Path. Bact., 1935, 40, 201—210).—Certain strains produce two toxins for which there are corresponding antibodies. CH. ABS. (p)

**Differentiation of *Streptococcus pyogenes* from man and animals by the sorbitol-trehalose test.** F. C. MINETT (J. Path. Bact., 1935, 40, 357—364).—Trehalose is usually fermented by human, and sorbitol by bovine, strains. CH. ABS. (p)

**Toxic fraction of scarlatinal streptococci.** C. A. GREEN (Quart. J. Med., 1935, 4, 93—115).—All strains produced a heat-labile exotoxin. Broth filtrates also contained an acid-insol. toxic fraction similar to that from an alkaline extract of washed bacterial bodies. It was species-sp. CH. ABS. (*p*)

**Differences in effect of mercuric phenyl chloride on different races of bacteriophage and similarity in effect on a phage and its homologous organism.** N. R. GOLDSMITH (J. Bact., 1935, 30, 237—242).—Lysis by bacteriophages of *Staphylococcus* or of *Escherichia coli* was not affected by HgPhCl (1 : 20,000—80,000) in a contact period of 30 min. After 6 weeks' contact the *Staphylococcus* phage was destroyed, but that of *E. coli* remained unaffected. Toxicity of the antiseptic to the sp. phage is paralleled by that to the homologous organism.

A. G. P.

**Stimulation of bacterial growth rate by germanic methyl oxide.** P. L. CARPENTER, McD. FULTON, and C. A. STUART (J. Bact., 1935, 30, 137—142).—As compared with nutrient broth cultures those in germanic Me oxide broth are inhibited during the lag phase, stimulated during the early logarithmic phase, and show a premature period of decline.

A. G. P.

**Action of sulphurous acid on bactericidal power of blood.** H. CREMER (Z. Unters. Lebensm., 1935, 20, 315—317).—Prolonged administration of small amounts of H<sub>2</sub>SO<sub>3</sub> to rabbits markedly decreases the power of the blood to destroy staphylococci.

E. C. S.

**Bactericidal principle in excretions of surgical maggots, which destroys important etiological agents of pyogenic infections.** S. W. SIMMONS (J. Bact., 1935, 30, 253—267).—The active bactericidal principle (not a bacteriophage) isolated from excreta of surgical maggots is heat-stable and retains its activity longer in a desiccated condition than in solution.

A. G. P.

**Therapeutic application of phenylmercuric salts. Use of basic phenylmercuric nitrate in gynaecology.** L. H. BISKIND (Lancet, 1935, 229, 1049—1052).

L. S. T.

**Antiseptic action of certain metals.** V. JENSEN and A. JENSEN (Zentr. Bakt. Par., 1935, I, 134, 86—96).—The efficiency of Ag-Hg, Ag, Ag<sub>2</sub>O, and AgCl as urinary disinfectants is examined.

A. G. P.

**Microbiological basis of chemotherapeutic action. II. Microscopical detection of therapeutically applied gold in spirochaetes, trypanosomes, and bacteria by ultracrystallisation.** N. VON JANCsó and E. NOVAK (Zentr. Bakt. Par., 1935, I, 134, 76—86).—The method is based on the absorption of injected Au by spirochaetes in rats or mice. Spirochaetes are removed centrifugally from a blood sample. From a smear on a slide org. matter is removed by gentle ignition and the remaining minute Au crystals serve as nuclei for crystal formation from a "developing" solution of AuCl<sub>3</sub>-K<sub>3</sub>Fe(CN)<sub>6</sub>. The Au "picture" is examined microscopically.

A. G. P.

**Influence of various metallic compounds on the growth of bacteria.** W. HAASE (Med. Klin., 1934, 30, 1585—1587; Chem. Zentr., 1935, i, 2199).—The germicidal action of Cu, brass, Sn, Al, and Ag foil was relatively small compared with that of Simanit (Ag<sub>2</sub>O<sub>2</sub>, MnO<sub>2</sub>) or Euthagen (Ag salt of thiocellobiose).

A. G. P.

**Effect of hormones on alcohol metabolism.** E. M. P. WIDMARK (Biochem. Z., 1935, 282, 79—84; cf. A., 1934, 213; 1935, 655).—In dogs, administration of pituitrin, adrenaline, and thyroxine has no effect on the metabolism of EtOH, but that of insulin (I) greatly increases slow rates of EtOH metabolism until the max. attainable under normal conditions is reached; high rates are not affected. The naturally occurring differences in the rates are partly dependent on the (I) content of the organism. The effect of (I) is not counteracted by giving sucrose.

W. McC.

**Adrenaline content of adrenals of splenectomised dogs.** S. TSUJIOKA (Arb. Med. Fak. Okayama, 1935, 4, 445—452).—The abs. content of adrenaline and the amount per g. of gland increase until the 15th day after splenectomy and subsequently decline to normal (30th day).

CH. ABS. (*p*)

**Adrenal cortex. I. Fractionation of hormone concentrates.** J. J. PFIFFNER, O. WINTERSTEINER, and H. M. VARS. II. Isolation of several physiologically inactive crystalline compounds from active extracts. O. WINTERSTEINER and J. J. PFIFFNER (J. Biol. Chem., 1935, 111, 585—597, 599—612).—I. The cortical hormone preps. were assayed by an earlier method (A., 1934, 566). Preps. from ox glands (*ibid.*, 1267) were purified by alternate dissolution in H<sub>2</sub>O and Et<sub>2</sub>O and contained 100—200 dog units per mg.; these preps. gave phenylhydrazones in cold aq. AcOH. More active preps. which did not reduce alkaline AgNO<sub>3</sub> were obtained by using C<sub>6</sub>H<sub>6</sub> in place of Et<sub>2</sub>O in the alternate dissolution procedure. By fractionation of these preps. one containing 400 dog units per mg. was obtained; this absorbed at 236 mμ, was pptd. by NHPh-NH<sub>2</sub>, but no insol. NaHSO<sub>3</sub>, semicarbazide, oxime, or dimedon derivatives were obtained.

II. Four physiologically inactive compounds were separated from the most active preps.: C<sub>20</sub>H<sub>34</sub>O<sub>5</sub> or C<sub>21</sub>H<sub>36</sub>O<sub>5</sub>, m.p. 214°, C<sub>21</sub>H<sub>32</sub>O<sub>5</sub> (I), m.p. 210—214°, C<sub>24</sub>H<sub>40</sub>O<sub>7</sub>, m.p. 126—128°, and one with undetermined empirical formula, m.p. 236—239°. (I) reduces Benedict's solution and alkaline AgNO<sub>3</sub> and is possibly identical with the life maintenance hormone of Kendall, but the absence of physiological activity is stressed. Leucylproline anhydride was also separated.

H. D.

**Physico-chemical state of the adrenal hormone in the blood.** D. BROWN and H. SCHEINER (Compt. rend., 1935, 201, 794—795).—Minced adrenal capsules give up their adrenaline (I) to serum (II), distilled H<sub>2</sub>O (III), or H<sub>2</sub>O at *p*<sub>H</sub> 3.5—4.0 (IV). (III) and (IV) when injected into atropinised dogs under chloralose anaesthesia affect the blood pressure as does (I); (II) produces a much more prolonged, but less abrupt, rise in arterial pressure and there is no apnoea. The (I) in (III) and (IV) is completely

ultrafilterable, but in (II), practically not at all. Extraction of (II) with  $\text{Et}_2\text{O}$  or  $\text{C}_6\text{H}_6$ , or acidification to  $p_{\text{H}}$  3.5—4.0, or dilution with  $\text{H}_2\text{O}$ , or treatment with  $\text{Ca}^{++}$ , renders the (I) completely ultrafilterable. The hormone is probably bound to the protein-lipin complexes of the blood. J. L. D.

**Action of adrenaline on liver suspensions.** E. GEIGER (Biochem. Z., 1935, 281, 86—92; cf. A., 1932, 188).—The sedimentation of the material pptd. from colloidal liver preps. (frog) by  $\text{CCl}_3\text{-CO}_2\text{H}$  is specifically accelerated (thyroxine, insulin, histamine, ergotamine, ephedrine, morphine, and atropine in equiv. concns. have no effect) by added adrenaline (I) (concn.  $10^{-6}$ — $10^{-16}$ ), although degradation of glycogen (II) and sugar production are unaffected. The effect appears after  $\leq 5$  min., reaches its max. after about 20 min., and then becomes less pronounced. In the absence of (II) or at  $p_{\text{H}}$  outside the range 5.5—7.5, or if the diastatic activity of the preps. is destroyed by heating for 1 hr. at 48—50°, there is no effect, but sedimentation is more rapid when (II) is absent. Added (I) has no effect on the extent of degradation or on production of simplexes. Possibly (I) alters the physical state of (II), reducing its power as a protective colloid. W. McC.

**Influence of peripheral lymph on the blood-sugar fluctuation due to adrenaline.** H. ARAKI (Arb. dritt. Abt. Anat. Inst. Univ. Tokyo, D, 1934, No. 4, 145—151).—Blood-sugar fluctuations were greatly suppressed when adrenaline-lymph mixtures were stored (notably at 37° for 24 hr.) prior to injection. Lymph alone caused very little fluctuation.

CH. ABS. (p)

**[Slow] continuous injection of adrenaline: [absence of] effect on blood-urea, -cholesterol, and -calcium.** A. BAUDOUIN, H. BÉNARD, J. LEWIN, and J. SALLET (Compt. rend. Soc. Biol., 1935, 120, 629—631). R. N. C.

**Influence of oxidation-reduction system on adrenaline action.** III. K. TERAI and H. ICHITSUBO (Folia Pharmacol. Japon., 1935, 19, 306—322; cf. A., 1935, 1172).—Injection of  $\text{NaHSO}_4$  instead of quinol into rabbits produced the quinol-effect on adrenaline action.

CH. ABS. (p)

**Inactivation of adrenaline by acetaldehyde verified on several plain-muscle organs.** A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 547—550).—The inactivation of adrenaline by  $\text{MeCHO}$  is confirmed on the Löwen-Trendelenburg vascular prep., the isolated rabbit intestine, the enucleated frog's eye, and the bronchial muscle of the cat or dog. R. N. C.

**Inactivation of adrenaline by methylglyoxal, glyceraldehyde, and acetaldehyde.** J. T. RICO and A. M. BAPTISTA (Compt. rend. Soc. Biol., 1935, 120, 545—546).—Adrenaline is inactivated as regards its pressor effect in decerebrate dogs by  $\text{AcCHO}$ , glyceraldehyde, and  $\text{MeCHO}$ , but not by  $\text{AcCO}_2\text{H}$  or phosphoglyceric acid. The inactivation is not opposed by ascorbic acid. R. N. C.

**Hypocalcaemia of depancreatized dogs.** R. GERSCHMAN and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 737—738).—Total pancreatectomy

in normal and hypophysectomized dogs induces a fall of blood-Ca and an increase of plasma- $\text{PO}_4$ . Ca is restored to normal by parathormone, but depressed still further by anterior pituitary extract. The Ca depression is due to parathyroid lesions following pancreatectomy. R. N. C.

**Use of mice in the standardisation of parathyroid hormone.** Effect of parathyroid on rachitic rats examined by the "line" test. F. J. DYER (Quart. J. Pharm., 1935, 8, 513—524).—The Mg-Ca antagonism method of Simon (A., 1935, 539) is applied by using at least 20 mice in each group, administering 1.7—1.8 mg. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  per g. body-wt., and recording the max. no. of mice affected 20—60 min. after injection of Mg. The % obtained for parathyroid prep. and control are then referred to a standard curve. Parathyroid preps. supplement the calcification produced by vitamin-D as indicated by the "line" test (A., 1928, 1288), but the test when used for parathyroid alone is insensitive and non-sp. F. O. H.

**Influence of temperature on the secretion of thyrotropic hormone.** G. KUSCHINSKY (Arch. exp. Path. Pharm., 1935, 179, 726—737).—Exposure of rats to cold (4°) is accompanied by normal activity of the thyroid gland (indicated histologically) for 10 days, after which the activity markedly increases. At 38—40°, the gland is normal for the first few days, inactive at the 14th, and, in some cases, again active after 26—33 days. These changes are correlated with those in thyrotropic activity of the pituitary gland and the presence of an inhibitory factor.

F. O. H.

**Thyroid standardisation and dosage.** R. F. CORRAN, J. PRITCHARD, and F. E. RYMILL (Quart. J. Pharm., 1935, 8, 331—336).—Variations in total and thyroxine (I-I) contents of fresh and of dried defatted glands invalidate any correlation between "thyroid B.P. 1932" and preps. expressed as fresh or dried gland. The relative activities of U.S.P. X and B.P. 1932 thyroid preps. are approx.  $74 \pm 12 : 100$ . Following hydrolysis, direct determination of I on the acid-insol. [(I)-containing] ppt. affords a check for the B.P. 1932 method for (I) in thyroid preps.

F. O. H.

**Role of the thyroid in the process of plumage development in chicks.** I. N. LEKTORSKY and N. A. KUSMINA (Biol. Zentr., 1935, 55, 16—29).—The thyroid hormone shows no preferential effect on plumage development. R. N. C.

**Influence of thyroxine on the hypoglycaemic action of cholic acid.** H. KOSAKA (Arb. Med. Fak. Okayama, 1935, 4, 370—378).—Thyroxine does not alter the blood-sugar level of normal rabbits, but lowers the capacity of Na cholate to produce a hypoglycaemia when injected simultaneously.

CH. ABS. (p)

**Preparation of prolactin.** R. W. BATES and O. RIDDLE (J. Pharm. Exp. Ther., 1935, 55, 365—371).—Prolactin (I) free from follicle-stimulating (II) and thyrotropic hormone (III) is prepared by extraction of the anterior lobe with 60—70% aq.  $\text{EtOH}$  at  $p_{\text{H}}$  9—10 and pptn. of (I) at higher  $\text{EtOH}$  concns. (I) is separated from (II) and (III) by pptn. from aq.



solution with  $\text{H}_2\text{SO}_4$  and is further purified by dissolution in aq.  $\text{EtOH}$  and repeated pptn. with  $\text{NaCl}$  at  $p_{\text{H}}$  6. Preps. so obtained have a potency of 5–10 units per mg. and may be boiled at  $p_{\text{H}}$  8 for 1 hr. without loss of potency. H. D.

**Diabetogenic anterior pituitary action independent of the adrenals.** B. A. HOUSSAY and L. F. LELOIR (Compt. rend. Soc. Biol., 1935, 120, 670–672).—Adrenaline produces a transitory hyperglycæmia, but neither it nor cortin is diabetogenic. Anterior pituitary extract (I) produces diabetic hyperglycæmia in hypophysectomised, pancreatectomised, and adrenalectomised toads, and in adrenalectomised dogs, together with glycosuria; splanchnic section or sympathectomy does not inhibit the action. The hyperglycæmia produced in partly adrenalectomised dogs persists after complete adrenalectomy only if (I) administration is continued; the diabetogenic action of (I) is therefore independent of the adrenals. R. N. C.

**Effect of hypophysectomy on pregnancy and lacteal secretion in the bitch.** B. A. HOUSSAY (Compt. rend. Soc. Biol., 1935, 120, 496–497).—Hypophysectomy results in abortion in pregnant, and cessation of secretion in lactating, bitches. The anterior pituitary is the necessary part of the gland; the effects are not induced by removal of the posterior lobe only, and are abolished by anterior pituitary extract. R. N. C.

**Lacteal secretion provoked by anterior pituitary extract in the dog.** B. A. HOUSSAY (Compt. rend. Soc. Biol., 1935, 120, 502–503). R. N. C.

**Lacteal secretion through the action of anterior pituitary extract in male guinea-pigs.** J. L. SARDI (Compt. rend. Soc. Biol., 1935, 120, 503–504). R. N. C.

**Glutathione in the tissues of the hypophysectomised dog: evidence for a pituitary-thyroid and pituitary-testicular association.** L. BINET, L. KÉPINOV, and G. WELLER (Compt. rend. Soc. Biol., 1935, 120, 589–590).—Hypophysectomy produces a fall of total glutathione (I) of blood < that of reduced (I). The red cell count is only slightly reduced. (I) is normal in the adrenals, spleen, pancreas, and cardiac muscle, and only reduced (I) falls in skeletal muscle. Both total and reduced (I) fall considerably in the liver, thyroid, and testicle, the falls being similar to those noted by Marenzi in the toad. The results favour a biochemical association between the pituitary and the thyroid and testicle. R. N. C.

**Influence of extract of posterior lobe of pituitary gland on urine- and blood-inorganic phosphate.** G. DOBERO (Arch. Farm. sperim., 1935, 60, 422–429).—Subcutaneous or intravenous injection of posterior pituitary extracts into rabbits increases the serum-inorg.  $\text{PO}_4'''$ ; the urinary level tends to decrease. The phenomena are apparently independent of changes in renal function. F. O. H.

**Influence of luteinising substance on (a) function of the lipin-containing cells of ovaries, (b) testes.** G. KUSCHINSKY and TANG-SU (Arch.

exp. Path. Pharm., 1935, 179, 717–721, 722–725).—(a) Administration to rats of anterior pituitary-like prep. from pregnancy urine (prolan) (I) inhibits formation and ripening of follicles and promotes luteinisation in the ovaries. (b) (I) enlarges the lipin-containing cells of rats' testes. F. O. H.

**Estrogenic activity of cow's urine during pregnancy.** M. M. O. BARRIE, J. B. E. PATTERSON, and S. W. F. UNDERHILL (Quart. J. Pharm., 1935, 8, 424–428).—Only small amounts of œstrin (< 50 international units per litre) are excreted by cows during the first 23 weeks of pregnancy; after this period the level increases to 700 units per litre at the 30th week, 4000 at the 34th, and 17,000 at the 37th. During the final weeks, the content varies probably due to variations in the concn. of urine. F. O. H.

**Action of œstrin on mammary secretion.** J. W. ROBSON (Quart. J. Exp. Physiol., 1935, 24, 337–344).—In lactating mice cryst. ketohydroxy-œstrin temporarily inhibits mammary secretion according to the dosage and method of administration. CH. ABS. (*p*)

**Hormone of the corpus luteum.** E. FELS (Compt. rend. Soc. Biol., 1935, 120, 730–731).—A mixture of luteosterone-*C* and -*D*, or of either with pregnandione, is more potent than either separately. R. N. C.

**Dehydroandrosterone.**—See this vol., 77.

**Androstendione.**—See this vol., 77.

**Testosterone.**—See this vol., 77.

**Sexual hormones, and related substances.** V.—See this vol., 77.

**Sex hormones.** VIII–X. See this vol., 76.

**Recent progress in the study of vitamins.** P. KARRER (Chim. et Ind., 1935, 34, 1027–1035).—A review.

**International vitamin standards.** E. M. NELSON (J. Assoc. Off. Agric. Chem., 1935, 18, 610–611).—The standards adopted by the International Conference on Vitamin Standards (1935) are discussed. E. C. S.

**Aseptic culture of insects in vitamin research.** E. G. VAN'T HOOGE (Z. Vitaminforsch., 1935, 4, 300–324).—Symbiont-free, aseptic cultures of *Drosophila melanogaster* can be obtained from ova sterilised by  $\text{EtOH}$  and chloramine-*T*, provided that the synthetic food complies with certain requirements. *D. melanogaster* requires traces of vitamin- $B_1$  and - $B_2$  and other  $\text{H}_2\text{O}$ -sol. yeast factors together with a very small amount of fat or unsaponifiable fraction, and the absence of - $B_1$  or - $B_2$  can be determined easily with these cultures. The insect does not require vitamin-*A*, -*D*, or -*E*. J. N. A.

**Vitamin-*A*, -*C*, and  $B_2$ . Constitution and constitution specificity of action.** P. KARRER (Monatsh., 1935, 66, 367–392).—The development of the chemistry of these compounds and the connexion between constitution and physiological action are discussed. H. W.

**Sterol content and vitamin value of avocado oil.** R. C. ROBBINS and L. N. BILGER (Hawaii Agric. Exp. Sta. Rept. [1933], 1934, 23–24).—

Sterols are isolated from the expressed oil. The oil also contains vitamin-A and possesses strongly antirachitic properties. CH. ABS. (p)

**Influence of experimental technique during the preliminary period in vitamin-A determinations on the response of the test animal to supplementary feeding of the vitamin.** P. M. NELSON and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. on Agric. Res., 1933, 116—117; 1934, 145).—Vitamin-A supplements must be fed to the rats separately. The influence of the body-wt. at the end of the depletion period is shown. Females are more responsive to -A than are males. CH. ABS. (p)

**State of combination of vitamin-A in liver oils.** L. RETI (Compt. rend. Soc. Biol., 1935, 120, 577—580).—Extraction with MeOH of unsaponified liver oils dissolved in light petroleum removes none of the vitamin-A; if the unsaponifiable matter is extracted in the same way, the whole of the -A is removed. -A is therefore present in the oil as an ester of a higher fatty acid, and its formation in the liver from carotene is followed by esterification. R. N. C.

**Detection of vitamin-A by the Rosenthal-Erdélyi test.** H. WILLSTAEDT (Z. Vitaminforsch., 1935, 4, 272—276).—The test has no advantages over that of Carr and Price. Carotenoids do not give the rose-red to reddish-violet coloration, but interference can be caused by sterols. J. N. A.

**Vitamin-A and carotene content of human milk.** W. NEUWEILER (Z. Vitaminforsch., 1935, 4, 259—271).—The vitamin-A content of human milk varies from 25 to 300 rat units per 100 c.c. It is independent of the age of the mother, the no. of children, and daily vol. of milk, and is higher after suckling. Colostrum contains more -A than milk. Large doses of -A or of carotene (I) increase the -A content of milk. (I) is present to the extent of 0.005—0.400 mg. per 100 c.c. J. N. A.

**Vitamin-A and carotenoids in the frog.** C. RAND (Biochem. Z., 1935, 281, 200—205).—The liver and fat glands and to a smaller extent the other parts (skin, ovary, eggs, testicles, kidney, lung, fallopian tubes) of the frog (summer and winter) contain carotene accompanied by varying amounts of xanthophyll. The liver also contains vitamin-A. W. McC.

**Increase in length in rats receiving vitamin-A.** M. MALMBERG (Biochem. Z., 1935, 281, 215—218; cf. Orr *et al.*, A., 1934, 1040).—In young rats receiving a diet free from vitamin-A the length of the tail is increased by administration of 0.02 mg. of -A daily. Administration of thyroxine checks the increase. W. McC.

**Physiological action of substances used in treatment of flour.** II. Action on vitamin of flour and on the animal organism fed exclusively on bread. III. Effect of oxidising substances used in treatment of flour on vitamin of flour. S. VON VITÉZ (Z. Unters. Lebensm., 1935, 70, 258—265, 265—269; cf. A., 1935, 529).—I. The harmful effect of the oxidising substance is due to destruction of carotene and vitamin-A. NaBO<sub>3</sub> is more harmful than (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

III. The harmful effect of NaBO<sub>3</sub> and Bz<sub>2</sub>O<sub>2</sub> is counteracted by simultaneous administration of -A, but not by -B. E. C. S.

**Vitamin-A and -B of maize.** E. TAKAHASHI and G. MASUDA (J. Agric. Chem. Soc. Japan, 1935, 11, 741—749).—There is a close relationship between vitamin-A content and the yellow pigment of the endosperms, but the colour of the pericarp has no significance. As regards vitamin-B content, neither colour has any significance. One out of 5 kinds of Japanese maize had a high -A content, but the -B content was much the same in all the kinds. Pigeons required  $\leq 60\%$  of whole corn in the diet for normal growth. W. McC.

**Occurrence of vitamin-B in organs.** J. B. BRODIE and F. L. MACLEOD (J. Nutrition, 1935, 10, 179—186).—The -B content of organs decreased in the order liver, heart, brain, muscle. Only traces occur in blood, spleen, and lungs. The feeding of normal tissues to -B-deficient rats did not increase the survival period except in those receiving brain. The amount of -B in the body of the rat may be changed, within limits, by varying the dietary level of the vitamin. A. G. P.

**B-Avitaminosis in rats.** E. KODICEK and J. JOACHIM (Z. Vitaminforsch., 1935, 4, 250—255).—No hyperglycaemia could be observed in rats showing the typical nervous symptoms of B-avitaminosis, and the blood-cholesterol was normal. The hyperglycaemia in vitamin-B<sub>1</sub> deficiency in pigeons may be due to an increase in non-sugar reducing substances. J. N. A.

**Vitamin-B in relation to carbohydrates, proteins, and fats in food.** R. LECOQ (Bull. Soc. sci. Hyg. Aliment., 1934, 278—331; Chem. Zentr., 1935, i, 2205—2206).—The rate of assimilation of carbohydrate, protein, and fat is influenced by the supply of vitamin-B. The -B requirement is greatest with high-carbohydrate rations. Fats and proteins tend to lower the proportion of -B necessary. A. G. P.

**Crystalline vitamin-** IV. Injection method of assay. M. AMMERMAN and R. E. WATERMAN. V, VI. Effect of graduated doses on growing rats and on pigeons. R. E. WATERMAN and M. AMMERMAN (J. Nutrition, 1935, 10, 25—33, 35—44, 161—166).—IV. Appropriate technique is described.

V. The stimulative effect of the vitamin increases up to and probably beyond dosages of  $160 \times 10^{-6}$  g., an amount which is 80—160 times that necessary for maintenance of life.

VI. The min. dose of vitamin-B<sub>1</sub> hydrochloride to cure polyneuritis was  $4 \times 10^{-6}$  g. Larger amounts up to  $160 \times 10^{-6}$  g. increased the wt. of depleted pigeons, but failed to bring birds to normal wt. Results are discussed in relation to -B<sub>3</sub>. A. G. P.

**Physiological action of vitamin-B.** H. G. K. WESTENBRINK (Arch. Neerland. Physiol., 1935, 20, 481—484; cf. A., 1934, 568).—In pigeons on a diet free from carbohydrate and vitamin-B<sub>1</sub> onset of polyneuritis is not delayed by increasing the fat content of the diet. Probably the disease is caused by chronic poisoning with carbohydrate or with

a degradation product or products of carbohydrate resulting from the absence of  $-B_1$ . W. McC.

**Vitamin- $B_1$  in grapes and grape products.** C. VACCA (Quad. Nutrizione, 1934—1935, 1, 424—432). Tests on pigeons show that the berry of the grape, as opposed to the seed, is wholly or almost devoid of vitamin- $B_1$ . NUTR. ABS. (m)

**Vitamin content of beer.** A. SCHEUNERT and M. SCHIEBLICH (Z. Vitaminforsch, 1935, 4, 294—299).—Beer contains very small amounts of vitamins of the B group only. Dark beer contains 3 international units of  $-B_1$  and 7.4 biological units of  $-B_2$  per 100 c.c. If extracts of  $-B_1$  and  $-B_2$  are added to the beer after manufacture, no loss of vitamins occurs during storage. Possibly yeast withdraws the vitamins from beer during manufacture. J. N. A.

**Nutritive value of fungi. II. Vitamin- $B_1$ ,  $-B_2$ , and  $-B_4$  content of mycelium of *Aspergillus sydowi*. III. Growth of rats on supplemented and unsupplemented mould proteins.** H. J. GORCICA, W. H. PETERSON, and H. STEENBOCK (J. Nutrition, 1935, 9, 691—700, 701—714; cf. A., 1934, 220).—II. When fed at a 10% level in a vitamin- $B_1$ -deficient diet the mycelium protected chicks from polyneuritis and produced good growth. Pellagra was prevented by additions of 1% of mycelium to a  $-B_2$ -deficient ration, although 3% was necessary for good growth. At a 30% level in an otherwise  $-B_4$ -deficient ration the mould prevented the onset of paralysis.

III. Proteins of *A. sydowi* produced little growth in rats and failed to sustain life for > 7—9 weeks. Growth was resumed by supplementing mould-protein with casein, egg-white, or yeast-protein. Still better results were obtained with proteins of whole wheat or of maize-gluten feed. No improvement was obtained by use of gelatin, cystine (I), histidine, tyrosine (II), or a (I)–(II) mixture. A. G. P.

**Flavin syntheses. VIII.**—See this vol., 85.

**Preparation and nutritional value of hepatoflavin.** F. J. STARE (J. Biol. Chem., 1935, 111, 567—575).—Hepatoflavin (I) does not prevent dermatitis in vitamin- $B_2$ -deficient rats and chicks, whilst a fraction of the liver extract not adsorbed by fuller's earth does. Proper growth appears to depend on the presence of both these factors in the diet. The prep. of (I) is modified by pptn. from EtOH with hot  $\text{Ba}(\text{OH})_2$ ,  $p_H$  fractionation of the Ag ppt., and extraction of the Ag ppt. with hot  $\text{AcOH} + \text{H}_2\text{S}$ . H. D.

**Modification of the Sherman method of studying the multiple nature of vitamins, with an application to vitamin- $B_2$ .** T. S. HAMILTON and H. H. MITCHELL (J. Nutrition, 1935, 10, 117—128).—The precision of assay methods is much increased by careful control of the intake of the basal diet as well as of the vitamin supplement. The technique described disclosed no evidence of the multiple nature of vitamin- $B_2$ . A. G. P.

**Realisation of the normal ascorbic acid content in the organism responsive to deficiency.** A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935,

120, 633—635).—A guinea-pig requires 30 mg. of ascorbic acid (I) daily to maintain an adrenal (I) content > 1 mg. per g.-wt., and considerable quantities to maintain the normal (I) content. R. N. C.

**Ascorbic acid in lens and aqueous humour.** V. DEMOLE and H. K. MULLER (Biochem. Z., 1935, 281, 80—85).—Fresh aq. humour (from the eyes of cattle) exhibits pronounced antiscorbutic action (3 c.c. of humour equiv. to 5 mg. of ascorbic acid) when injected subcutaneously into guinea-pigs receiving a diet free from vitamin-C. A prep. from the lenses behaves similarly. In the humour the activity corresponds with 100%, in the lens with 50%, of the reducing power (dichlorophenol-indophenol). W. McC.

**Ascorbic acid content of blood and cerebrospinal fluid.** F. PLAUT and M. BULOW (Z. physiol. Chem., 1935, 236, 241—256; cf. A., 1935, 1036).—In human and rabbit cerebrospinal fluid the vitamin-C exists entirely in the reduced form, but in the blood most of the -C occurs in the oxidised form. The variations which occur in the amount of -C in blood (caused, e.g., by diet changes) concern the reduced part only and are not parallel to accompanying variations in the -C content of the fluid. Oral administration of moderate amounts of -C increases the -C content of the fluid and slightly increases that of blood. With large doses there are large increases in both. -C introduced into the blood is transported in reduced form, is not oxidised by blood *in vitro* or *in vivo*, and disappears rapidly. Oxidised -C is not reduced by the fluid *in vitro* or *in vivo* but is more rapidly absorbed than is reduced -C. In rabbits, injected -C can pass from blood into fluid and conversely but under physiological conditions the passage from fluid to blood is in some way controlled. In the fluid -C persists much longer than it does in blood. There is no evidence that the -C of the fluid is reduced in the nervous system or that this system produces reduced -C. W. McC.

**Comparison of the vitamin-C (ascorbic acid) content of the cerebrospinal fluid and of the urine in hypervitaminosis-C.** F. PLAUT and M. BULOW (Naturwiss., 1935, 23, 771).—The vitamin-C content of the cerebrospinal fluid can be used for diagnosis of vitamin-C-subnutrition in the same way as the urinary content (cf. A., 1935, 417), the results by the two methods giving close agreement. P. W. C.

**Ascorbic acid in glands. Isolation from the pituitary.** J. R. MENDIVE and V. DEULOFEU (Z. physiol. Chem., 1935, 236, 208—211).—As regards their content of the acid (I) organs of Argentinian cattle form the series: pituitary, corpus luteum, adrenals > thymus, spleen, > testicles, pancreas, thyroid gland > follicular fluid, the val. varying from 1.9 to < 0.2 g. per kg. (I) was isolated from the pituitary, but from the corpus luteum only 4-benzeneazo-3-l-threoglyceryl-1-phenylpyrazolone could be isolated. W. McC.

**Distribution of vitamin-C in lower organisms.** G. BOURNE and R. ALLEN (Austral. J. Exp. Biol., 1935, 13, 165—174).—Unicellular animals and plants, algae, and fungi contain granules which stain with

the  $\text{AcOH-AgNO}_3$  reagent and therefore presumably contain reduced vitamin-C. W. O. K.

**Vitamin-C in fresh apples and in apple powder.** M. POCHINO (La Pediat. med. prat., 1935, 10, 16).—Administration of fresh apples to guinea-pigs receiving Bezssonoff's scorbutic diet prevented appearance of symptoms of scurvy, but did not permit normal development, whilst administration of apple powder only delayed onset of the symptoms.

NUTR. ABS. (m)

(A) Effect of sulphitising on the preservation of vitamin-C. B. I. JANOVSKAJA. (B) Antiscorbutic activity of "marmelad" jelly, enriched, after four months' storage, with vitamin-C by addition of a concentrate of infusion of pine needles. N. JARUSOVA. (C) Antiscorbutic properties of pine needles. V. Effect produced on the vitamin-C content of pine needles when cut pine branches are kept for a short time. N. E. SHEPILEVSKAJA. (D) Antiscorbutic properties of sulphitised dried cabbage. Antiscorbutic turnip preparation. S. N. MATZKO (Problems of Nutrition, Moscow, 1935, 4, No. 2, 51—54, 54—55, 56—58, 59—60, 61—64).—(A) The process of sulphitising black-currant juice for storage seemed to preserve the vitamin-C (I) activity, which was lost in untreated, stored juice.

(B) Four months' storage at room temp. of a jam enriched with (I) concentrate from pine needles caused very little destruction of (I).

(C) Infusions in very dil.  $\text{HCl}$  of fresh pine needles and of needles from a bough that had been kept indoors for 10 days were almost equal in their antiscorbutic activity.

(D) The expressed juice from cooked, dried white cabbage, which had been sulphitised for storage, protected guinea-pigs from scurvy in a min. dose equiv. to 6 g. of original dry cabbage, so that in 1 kg. of dried cabbage there were about 160 "units" of (I). Juice of a damaged white "semi-table" turnip gave fairly good protection from scurvy in guinea-pigs.

NUTR. ABS. (m)

**Ascorbic acid in sprouted oats.** R. BOGART and J. S. HUGHES (J. Nutrition, 1935, 10, 157—160).—The vitamin-C content of sprouting oats increased to a max. at the tenth day. Vals. were similar whether sprouting was in light or in darkness.

A. G. P.

**Vitamin-C (ascorbic acid) content of the paprika product "Vitapric."** E. BECKER (Z. Vitaminforsch., 1935, 4, 255—259).—Vitapric contains about 0.45% of ascorbic acid (cf. B., 1935, 1116), and increases the resistance of animals not only to scurvy, but also to other diseases. J. N. A.

**Reducing power of vitamin-C in urine in health and disease.** (A) T. BAUMANN. (B) W. VON DRIGALSKI (Z. Vitaminforsch., 1935, 4, 354—356, 356—357).—(A) Von Drigalski's method of iodometric titration (A., 1935, 793) for the determination of ascorbic acid (I) in urine is untrustworthy.

(B) The method is upheld.

J. N. A.

**Chemical method for determining vitamin-C.** V. A. DEVIATNIN and V. M. DOROSCHENKO (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 177—180).—The

following modification of the method of Tillmans *et al.* (A., 1932, 310, 658) removes the reducing activity of most foreign substances in extracts of vitamin-C. The material is boiled with 5%  $\text{AcOH}$  ( $\text{CO}_2$  stream), cooled, neutralised ( $p_H$  5.0) with  $\text{CaCO}_3$ , and pptd. with  $\text{Pb(OAc)}_2$ . After filtration the extract is acidified with  $\text{AcOH}$  to  $p_H$  3.0 and titrated with 2 : 6-dichlorophenol-indophenol to a slight pink ( $\text{CO}_2$  stream). Good agreement with biological assays is obtained. J. W. B.

**Determination of ascorbic acid by titration.** B. AHMAD (Nature, 1935, 136, 797).—Boiling before extraction with  $\text{CCl}_3\text{-CO}_2\text{H}$  increases the ascorbic acid val. for Darjeeling cabbage. The results support the views of McHenry *et al.* (A., 1935, 903) as opposed to those of van Eekelen (*ibid.*, 1176). L. S. T.

**Value of the chemical titration method in determining the vitamin-C potency of certain foodstuffs.** N. B. GUERRANT, R. A. RASMUSSEN, and R. A. DUTCHER (J. Nutrition, 1935, 9, 667—675).—Titration of ascorbic acid with 2 : 6-dichlorophenol-indophenol gives approx. results suitable as preliminary data for biological assays of vitamin-C potency. The accuracy of the method varies with the nature of the test material. A. G. P.

**Influence of vitamin-C level on resistance to diphtheria toxin.** I. Changes in body-weight and duration of life. C. G. KING and M. L. MENTEN II. Production of diffuse hyperplastic arteriosclerosis and degeneration in various organs. M. L. MENTEN and C. G. KING (J. Nutrition, 1935, 10, 129—140, 141—153).—I. A wide zone of vitamin-C deficiency exists without the appearance of scurvy, but in which physiological processes are subnormal and sensitivity to bacterial toxins is increased. A. G. P.

**Reactions of animals susceptible to deficiency to increasing doses of ascorbic acid.** A. GIROUD, R. RATSIMAMANGA, A. BARATTE, and F. SYLVA (Compt. rend. Soc. Biol., 1935, 120, 701—703).—Vascular lesions and dental mobility decrease and haemoglobin increases steadily as the quantity of ascorbic acid administered increases. R. N. C.

**Fractionation studies on pro-vitamin-D.** E. M. KOCH and F. C. KOCH (Science, 1935, 82, 394—395).—"Cholesterol W" and heated purified cholesterol (I) are superior to viosterol or purified, unheated (I) in preventing leg weakness in rats and chicks. The pro-vitamin-D of heated (I) separates readily in crystallisation from  $\text{EtOH}$ . L. S. T.

**Antirachitic efficiency of irradiated milk, yeast milk, cod-liver oil, and irradiated cholesterol.** R. W. HAMAN and H. STEENBOCK (Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl. 7).—When fed to chicks on a rat unit basis, cod-liver oil, irradiated milk, and irradiated cholesterol showed 10—15 times the antirachitic potency of milk from cows fed on irradiated yeast.

NUTR. ABS. (m)

**Sensitivity of rachitic rats for vitamin-D.** J. VAN NIEKERK (Arch. Neerland. Physiol., 1935, 20, 477—480).—The sensitivity of the rat stock



fell to about 50% of the initial val. from 1929 to 1932, but no seasonal variations were noted. H. G. R.

**Relationship of the vitamin-D intake of the hen to the antirachitic potency of eggs produced.** N. B. GUERRANT, E. KOHLER, J. E. HUNTER, and R. R. MURPHY (J. Nutrition, 1935, 10, 167—178).—The antirachitic potency of eggs depends on the vitamin-D intake of the hen. The transfer of -D from diet to egg is of low efficiency, and is more complete from cod-liver oil than from viosterol.

A. G. P.

**Constitution of vitamin-D<sub>2</sub>.**—See this vol., 69.

**Sitostanol and stigmastanol.**—See this vol., 69.

**Differences in age of cells of some water plants in relation to their reducing powers.** M. LLIENSTERN (Protoplasma, 1935, 33, 86—92).—Differences in reducing power of laminae and midribs of leaves of varying age and under varying conditions of assimilation are examined by means of methylene-blue and thionine.

A. G. P.

**Permeability studies of *Valonia* osmometers. Behaviour with neutral salt solutions.** P. KORN-MANN (Protoplasma, 1935, 23, 34—49).—With a *Valonia* cell-membrane osmometer, K citrate, tartrate, phosphate, sulphate, and acetate solutions caused a withdrawal of fluid at rates which declined in the order of substances named. KNO<sub>3</sub> and KCl caused an intake of fluid. In isotonic solutions the order of intake of fluid was LiCl > NaCl > KCl. The phenomena are explained by differences in the degree of swelling of the internal and external sides of the membrane induced by the various salts.

A. G. P.

**Dry matter production [by plants] in nitrogen and potassium deficiency.** D. MÜLLER and P. LARSEN (Planta, 1935, 23, 501—517).—In H<sub>2</sub>O-cultures of *Sinapis alba* respiration losses were substantially the same for plants in normal and deficient media. Assimilation intensity was lower in deficient plants, the difference between these and normal plants declining with light intensity. The compensation point was the same in normal and deficient plants. Lowered assimilation is not due to reduced opening of stomata or smaller chlorophyll contents, but to "protoplasmic factors." The wt. of dry matter produced in stems and roots per unit leaf area was the same for completely manured and K-deficient plants, but was approx. doubled in N-deficient plants.

A. G. P.

**Heat-resistance of plants.** I. SAPPER (Planta, 1935, 23, 518—556).—Starved plants have a decreased heat-resistance, although small differences in C nutrition have only a slight effect. Deficiency of nutrient salts causing increased osmotic pressure may increase the resistance. Heavy excess of nutrients lowers resistance. The latter is controlled by sp. structural characteristics of the protoplasm and merely modified by the H<sub>2</sub>O content. A. G. P.

**Absorbing power of roots.** P. MAZE, P. J. MAZE, jun., and R. ANXIONNAZ (Compt. rend. Soc. Biol., 1935, 120, 693—695).—The absorbing power varies with the N compounds in the nutritive solution,

the concn. of the solution, and the nature of the inorg. N salts in solutions of which the roots are placed.

R. N. C.

**Root exudation and root types in sugar cane.** H. EVANS (Mauritius Dept. Agric. Sugar Cane Res. Sta. Bull., 1934, 5, 13).—Mineral analyses of exudates from cut roots of various parts of the rooting system are recorded.

CH. ABS. (p)

**Catadyn process for sterile cultures of higher plants.** F. C. GERRETSEN (Planta, 1935, 23, 593—603).—The root system of the plant is protected from infection by means of a cork layer containing a catadyn (Ag)-infusorial earth prep.

A. G. P.

**Regulation of protein exchange and the condition of proteolytic enzymes in plants.** K. PAECH (Planta, 1935, 24, 78—129).—Anaerobic decomp. of protein in plant cells does not depend on deprivation of O<sub>2</sub>, but is influenced by injury to the cell by prolonged anaerobiosis. In acid leaves death of cells in O<sub>2</sub> deficiency is not caused by increasing proteolysis. In wilting petals the "explosive" decomp. of protein is a post-mortal process resulting from destruction of protoplasts. Synthesis or hydrolysis of protein in intact cells is controlled by the relative amounts of active carbohydrate (monose) and sol. N (NH<sub>3</sub>) present.

A. G. P.

**Nitrogen fixation by germinating legume seeds without co-operation of nodule bacteria.** K. GIRTCHANOV (Zentr. Bakt. Par., 1935, II, 92, 349—363).—In the absence of nodule organisms germinating seeds of yellow lupin were unable to utilise atm. N<sub>2</sub> even under the influence of certain stimulants.

A. G. P.

**Apparent assimilation of nitrogen by germinating peas.** E. M. SMYTH and P. W. WILSON (Biochem. Z., 1935, 282, 1—25; cf. Vita, A., 1932, 436, 1180; Orcutt *et al.* A., 1934, 1273).—Apparent increases in the N content of peas germinating in presence of stimulants (salts, alkaloids) or H<sub>2</sub>O are due to inaccuracies in analytical methods. The Kjeldahl method and its modifications yield untrustworthy results, and the Dumas method is recommended. There is no evidence that direct assimilation of elementary N<sub>2</sub> occurs.

W. McC.

**Role of asparagine and glutamine in the higher plants.** G. SCHWAB (Planta, 1935, 24, 160—162).—Asparagine (I) and glutamine (II) are present simultaneously in plants. Increased "amide" in germinating seedlings or that induced by shading plants or supplying NH<sub>4</sub> salts involves increases in (I) and (II) in normal proportions. The (II) content of roots of *Aspidium filix* declines with the total sol. N during the summer months. Protein exchange in plants is discussed in relation to org. acid and carbohydrate contents. Plant extracts contain enzymes sp. for (I) and (II). Yeast extracts contain only (I) and can only effect the fission of (I).

A. G. P.

**Variation of saponins during germination and development in some species of grasses.** T. SOLACOLU and E. WELLES (Compt. rend. Soc. Biol., 1935, 120, 662—664).—Saponin accumulates in the seeds when they reach maturity; it is then used up partly in germination and partly in growth until the

appearance of the fifth leaf, after which it has disappeared entirely. R. N. C.

**Influence of partial pressure of carbon dioxide on photosynthetic efficiency.** B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 1, B, 909—927).—The rate of photosynthesis in radish leaves increases with rising  $[\text{CO}_2]$  to a stationary stage followed by a decline as the proportion of  $\text{CO}_2$  is further increased. With increasing light intensity the  $\text{CO}_2$ -photosynthesis curves show a steeper rising phase and earlier evidence of toxic effects. The curves are discussed in relation to those obtained by earlier observers. A. G. P.

**Oxygen intake of oily and starchy seeds.** E. REUHL (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 879—886).—In the early stages of germination *Brassica* seeds absorb  $\text{O}_2$  at a normal rate with decreasing  $\text{O}_2$  tension until it reaches 3%, whereas linseed shows a retarded rate almost immediately and buckwheat shows intermediate vals. During the later stages this behaviour is reversed. H. G. R.

**Energy of growth. XIV. Effect of zinc and manganese salts at toxic concentrations on the energy output during germination.** G. BOY (Bull. Soc. Chim. biol., 1935, 17, 1414—1426).—The energy output of rice seeds (heat of combustion of the cotyledon/difference between the heats of combustion of the original and the germinated seeds) grown in the dark in aq. solutions of Mn and Zn salts is < that of seeds grown in  $\text{H}_2\text{O}$ . With Mn the decrease  $\propto$  the concn.; with Zn the toxic action is not so marked, and is the same at a concn. of 2 as at 4 g. of Zn per litre. A. L.

**Possible association of vitamin-A with nutritional conditions in plants.** E. S. HABER, P. M. NELSON, and P. P. SWANSON (Iowa Agric. Exp. Sta. Rept. Agric. Res., 1933, 134—135; 1934, 163).—Poorly nourished plants were deficient in chlorophyll and in vitamin-A. The ability of plants to translocate -A is indicated. CH. ABS. (p)

**Effect of concentration of neutral salts on seedling growth.** J. PORT (Acta Comment. Univ. Tartu., 1932, A, 23, No. 1, 166 pp.).—Growth was influenced by salt solutions absorbed by paper on which seeds were sprouted. Concns. of  $< 0.1N$  inhibited the swelling of seed colloids and produced seedlings showing < normal growth and  $\text{H}_2\text{O}$  content. In wheat, diastatic activity was less in solutions of higher concn. The effect of salts on growth decreased in the order  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{++}$ , in  $0.1N$  concn. With concns. of  $0.01$ — $0.001N$  salt effects were sp. for different species. The favourable action of anions on root growth was in the reverse order of the lyotropic series.  $0.0001N$  solutions of  $\text{Li}^+$ ,  $\text{NH}_4^+$ , and  $\text{Ba}^{++}$  were particularly beneficial to growth, probably because of increased imbibition of  $\text{H}_2\text{O}$ . CH. ABS. (p)

**Elements indispensable for plant nutrition.** A. FREY-WYSSLING (Naturwiss., 1935, 23, 767—769).—For the higher plants C, N, P, S, O, H, K, Mg, Ca, and Fe appear to be essential. In addition, the absence of Mn, B, Cu, and Zn often leads to deficient and

diseased growth. Many elements, e.g., Al, Si, Na, Cl, are utilised by particular groups of plants in considerable amounts, but it is difficult to say that they are essential to the life of the plant. Other elements, although not essential to life, stimulate the growth of the plant. The functions of the various elements are discussed and it is pointed out that all the indispensable elements lie on a line drawn in the periodic table from A through C to A. P. W. C.

**Effect of humic acid on assimilation in plants.** A. V. BLAGOVESTSCHENSKI and A. A. PROSOROVSKAJA (Biochem. Z., 1935, 282, 99—103; cf. A., 1935, 265).—Humic acid (I) stimulates plant growth by increasing the permeability of the tissues and so facilitating osmosis.  $\text{NH}_4\text{NO}_3$  enabled to penetrate the cells by (I) has no effect on the synthesis of proteins there. W. McC.

**Vegetable growth-substances.** F. KOGL (Naturwiss., 1935, 23, 839—843).—A lecture.

**Physiological analysis of the growth substance.** A. J. HAAGEN SMIT and F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 852—857).—The cell-elongation and polar transport properties of a series of org. substances have been examined. Some, which have only growth-stimulating properties, do not exhibit polar transport and do not give the *Avena* bending test nor the bud-inhibition of the auxins. *allo*Cinnamic acid has the greatest cell-elongation power, comparable with that of 3-indolyl-acetic acid, whereas cinnamic acid has none. H. G. R.

**Analysis of the activity of two growth-promoting substances in plant tissues.** K. V. THIMMANN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 896—912).—Both indene-3-acetic acid and coumaryl-1-acetic acid show biological activity, although the latter does not produce any *Avena* curvature, but they lack the property of being readily transported in the plant. It appears that cell-elongation, root-formation, root-growth inhibition, and bud-inhibition arise from one primary reaction in the cell. H. G. R.

***Lambertella corni-maritima*, von Hohnel, a brown spotted parasitic discomycete.** T. H. HARRISON and A. F. EL-HELALY (Trans. Brit. Mycol. Soc., 1935, 19, 199—213).—Growth characteristics of the fungus are examined in relation to  $p_{\text{H}}$  of the medium. CH. ABS. (p)

**Xyloporosis—the new citrus disease.** I. REICHERT and J. PERLBERGER (Hadar, 1934, 163—167, 172, 193—202).—Fruit from diseased trees contained less total solids, higher total and reducing sugars and total acids than healthy fruit. CH. ABS. (p)

**Biochemical modifications and phytopathology.** Official oil of lavender from plants parasitised with *Septoria lavandulae*, Desm. R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 703—704). The infection reduces the quantity of oil and its terpene alcohol content, and increases  $d$  and the cineole content of the essence. R. N. C.

**Toxicity of magnesium towards higher plants.** D. RABINOVITZ-SERENI (Bull. Staz. Pat. veget.,

1933, 13, 346—366; Bied. Zentr., 1935, A, 5, 517).—Plants in solutions containing 1% of  $\text{MgSO}_4$  showed loss of chlorophyll, restricted growth, and browning. Enzyme processes are concerned. Low  $[\text{Mg}^{++}]$  stimulated and higher concns. retarded catalase activity. Oxidase activity was favoured at all concns. examined. Respiration was increased by 0.1% and retarded by 1% solution of  $\text{Mg}^{++}$ . A. G. P.

**Toxins of wilting [in plants].** O. K. ELPIDINA (Compt. rend. Acad. Sci. U.S.S.R., 1935, 3, 360—364).—The toxin produced by the *Fusarium* which causes wilting of potatoes is  $\text{NH}_3$ . A. G. P.

**Action of potassium oxalate on the living protoplasts of *Allium cepa*.** R. EICHBERGER (Planta, 1935, 23, 479—485).—Sections of *A. cepa*, after 10—15 min. treatment with aq.  $\text{K}_2\text{C}_2\text{O}_4$  (I), show normal urea-plasmolysis only in the central area. Injury to plasma by (I) is counteracted by treatment with  $\text{CaCl}_2$ , K citrate,  $\text{KNO}_3$ ,  $\text{NaCl}$ , or  $(\text{NH}_4)_2\text{SO}_4$ , or by prolonged washing with  $\text{H}_2\text{O}$ . No sp. action of  $\text{Ca}^{++}$  in this respect was apparent. A. G. P.

**Occurrence of lime in edible *Mormordica*.** H. L. CHAKRAVARTY (Current Sci., 1935, 4, 239—240).—Cystoliths in various Indian species are described. A. G. P.

**Iodine of seaweeds. III.** E. MASUDA and K. NISHIDA (J. Pharm. Soc. Japan, 1934, 54, 243—245; cf. A., 1934, 336).—Of the total I in *Laminaria japonica*, Aresch, an average of 48% occurs in org. forms. *L. ochotensis* contains 65% of sol. I as org. compounds. Warming causes a gradual transition to inorg. forms. In *Ecklonia cava* I is present as iodoammonium salts or I salts of amines and not as KI or NaI. CH. ABS. (p)

**Chemical composition of saltbushes from the Salmon Gums area.** L. J. H. TEAKLE (J. Dept. Agric. W. Austral., 1935, 12, 188—189).—Complete analyses of *Atriplex prostratum* and *A. halimoides* are given. Both specimens are high in  $\text{Na}_2\text{O}$  and Cl, but low in  $\text{P}_2\text{O}_5$ . NUTR. ABS. (m)

**Saltbush. Its mineral composition.** M. S. BENJAMIN (Agric. Gaz. N.S.W., 1935, 46, 309—310).—*Chenopodium triangulare* and *Atriplex semibaccatum* were analysed. < 54.06% of the sol. ash in the latter was NaCl. NUTR. ABS. (m)

**Phytin of seeds of *Eleusine coracana* (besna), *Sorghum verticillatum* (dura), *Eragrostis Teff* (teff), and *Pennisetum spicatum* (bultuc).** R. MONTUORI (Ateneo parmense, 1934, 6, 89).—The ash, P, and phytin contents of the seeds are recorded. NUTR. ABS. (m)

**Formation of acetic acid from ginkgo wood (*Ginkgo biloba*).** Y. C. TANG, Y. W. WANG, and H. L. WANG (Cellulosechem., 1935, 16, 90—92).—The Ac content of 4 samples of the wood (I) of different age and habitat is const. (mean 1.18%). The lignin-free portion (II) (68.74%) (ash content 0.58, 0.64, 0.41, and 0.38%) contains 1.70% Ac, in close agreement with the val. (1.72%) calc. from that of (I) and the loss resulting from isolation of (II). Thus no elimination of AcOH occurs during the process of

isolating (II), which must contain an Ac group and not a formyl group (semi-acetal). J. W. B.

**South American drugs. I. Bixol, a new alcohol from the oil of *Bixa Orellana*. II. Chemical composition of *Canavalia obtusifolia*.** M. BACHSTETZ and G. CAVALLINI (Chimica e l'Ind., 1935, 17, 650—651, 652).—I. The unsaponifiable matter (2.5%) of annatto-seed oil was submitted to chromatographic analysis, using  $\text{Al}_2\text{O}_3$ , which adsorbed ergosterol and vitamin-D (positive reactions in the Rosenheim and Brückner tests). The non-adsorbed portion was distilled in vac., yielding 0.58% (calc. on the seed) of *bixol*,  $\text{C}_{18}\text{H}_{30}\text{O}$ , b.p.  $176^\circ/2\text{ mm.}$ , a pale green oil, probably  $\text{CMe}_2[\text{CH}\cdot\text{CH}_2\cdot\text{CMe}]_3\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , oxidised to the corresponding aldehyde, b.p.  $175\text{—}180^\circ/6\text{ mm.}$  (semicarbazone, m.p.  $96\text{—}97^\circ$ ).

II. Ouari seeds contain 10.42%  $\text{H}_2\text{O}$ , 2.50% ash, 0.65% fatty matter, 4.25% N, 26.5% proteins (93.5% sol. in HCl+pepsin), 53.77% starch, 0.106% lecithin-phosphoric acid (calc. as  $\text{P}_2\text{O}_5$ ). They contain no HCN or alkaloids and are not toxic to rabbits.

D. R. D.

**"Bukuryo," sclerotia of *Pachyma Hoelen*, Rumph. III. Chemical constituents.** K. TAKEDA (Trans. Tottori Soc. Agric. Sci., 1934, 5, 62—73).—"Bukuryo" contains approx. 93% of a carbohydrate, pachyman (I), and also gum, chitin, protein, adenine, histidine, *d*-glucose, sterol, lecithin, and fat, Cl, S, P, Ca, Fe, Mg, Mn, K, Si, Na, enzymes which decompose fat and (I), and traces of pepsin and trypsin. J. N. A.

**Arabogalactan of Siberian larch.** N. I. NIKITIN and I. A. SOLOVIEV (J. Appl. Chem. Russ., 1935, 8, 1016—1022).—The arabogalactan (I) (1 mol.) with 12 mols. of NaOH and 13 of  $\text{Me}_2\text{SO}_4$  yields a product in which all the available OH-groups (20) are methylated. (I),  $\text{CH}_3\text{PhCl}$ , and NaOH ( $80^\circ$ ; 16 hr.) afford the *dibenzyl ether*, and (I),  $\text{BzCl}$ , and NaOH (with cooling) give the *Bz* ester. The mol. wt. of (I) cannot be determined cryoscopically, as the depression of f.p. is not  $\propto$  concn.; the I val. method gives a mol. wt. corresponding with  $[\text{C}_5\text{H}_8\text{O}_4(\text{C}_6\text{H}_{10}\text{O}_5)_6]_2$ . R. T.

**Lignin in straw and deciduous trees.** R. S. HILPERT [with E. LITTMANN, O. PETERS, H. HELLWAGE, and O. LISSNER] (Cellulosechem., 1935, 16, 92—96).—The action of 72%  $\text{H}_2\text{SO}_4$  at room temp. on various sugars produces insol. residues (I) which closely resemble lignin (II). Pentoses and fructose are especially sensitive, but aldohexoses (particularly glucose and galactose) are very stable. The amount of (I) formed decreases rapidly with fall in reaction temp. The amount of (II) similarly formed from straw also decreases from 41.66% at  $60^\circ$  to 2—3% at  $-10^\circ$ , and dilution of the filtrate affords a carbohydrate material of composition  $2\text{C}_6\text{H}_{10}\text{O}_5\text{—H}_2\text{O}$ . Thus the acid-sol. products are not (II) but carbohydrate. Treatment of straw with alkali effects dissolution of 20—30% (mainly hexoses) and dilution then ppt. a substance with the composition of a partly methylated cellulose anhydride (pentosan content increased from 24 to 29%; OMe reduced from 4 to 3.1%), which is acetylated in presence of 8%

H<sub>2</sub>SO<sub>4</sub> to a substance (83% yield) of composition [C, 49.5, H 6.0, OAc 61.6, OMe 1.3 (? 3.1), pentosans 13%] closely resembling that of cellulose triacetate. Since the OMe content is the same as that of the original straw, this group is present not in lignin but in the carbohydrate of which straw is composed. Treatment of the wood (III) of deciduous trees with HCl at -10° affords a residue (12%) of composition intermediate between that of (III) and (II). The H<sub>2</sub>O-pptd. material is also a cellulose anhydride. With HCl (*d* 1.19) at room temp. the C and H content of the residue is the same as that of (III), but the OMe content, and lignin formed, are higher. Hence the higher methylated portions are less readily attacked. The ground-substance is a cellulose anhydride which readily loses H<sub>2</sub>O intramolecularly to give (II).

J. W. B.

**New constituent of beechwood.** E. WEDEKIND and O. MÜLLER (Naturwiss., 1935, 23, 833—834).—MeOH extraction of beech, eucalyptus, alder, cherry, and, to a smaller extent, oak and hornbeam, but not of pine and ash, yields a substance (I) (C 57.1, H 4.3, OMe 4.8%) giving an intense red-violet colour with conc. acids. (I), which is separated admixed with a less sol. substance converted into (I) by hot aq. alkali, readily forms a Ac<sub>1</sub> derivative which does not give the colour reaction. F. O. H.

**Leaf starch: isolation and properties.** H. A. SPOEHR and H. W. MILNER (J. Biol. Chem., 1935, 111, 679—687).—Depletion of starch (I) in leaves does not occur on drying if the leaves have been frozen or treated with CHCl<sub>3</sub>. To prepare (I) the leaves are dried, ground, the pigments extracted with EtOH and light petroleum, polyuronides etc. are extracted with cold H<sub>2</sub>O, and (I) with hot H<sub>2</sub>O, from which, after cooling, it is separated by centrifuging. If a (I) solution is frozen for some time and then allowed to thaw, (I) is pptd. in a fibrous mass (retrogradation). Cooling for 3 days at -80° ppts. (I) completely, but 90—95% pptn. can be obtained if the solution is cooled only to -8°. Retrograded (I) dissolves in H<sub>2</sub>O, but if thoroughly dried, it is more sparingly sol. Determinations of the amounts of (I) were made on the basis of the reducing power of the solution after acid hydrolysis with an accuracy of ±1%. *d*-Glucose is the chief product of hydrolysis. The apparent lower reducing power of retrograded (I) is due to its slower rate of hydrolysis. The leaves of *Nicotiana tabacum* give the highest yield. E. A. H. R.

**Detection of hydroxylamine in autolysed green leaves.** M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Compt. rend., 1935, 201, 1067—1069).—By modification of Blom's reaction NH<sub>2</sub>OH has been detected in the juice of leaves allowed to autolyse for several days (1—3 mg. per kg. of original leaves), but is absent from the juice of fresh leaves. W. O. K.

**Determination of starch in plants with special reference to woody plants.** J. T. SULLIVAN (J. Assoc. Off. Agric. Chem., 1935, 18, 621—636).—The starch is extracted with slightly alkaline aq. CaCl<sub>2</sub>, pptd. with EtOH, redissolved in H<sub>2</sub>O, and pptd. with I in aq. KI in presence of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The starch is then hydrolysed and glucose determined by Cu reduction. A single extraction is sufficient if

the conditions specified with regard to [CaCl<sub>2</sub>], duration of boiling, and fineness of grinding are adhered to. The method is more trustworthy than that of enzymic hydrolysis. The applications of the method are discussed. E. C. S.

**Aromatic substances in maple sugar.** J. RISI and A. LABRIE (Canad. J. Res., 1935, B, 13, 175—184).—The aromatic substances in the syrup and sugar of the maple contain vanillin (I), vanillic acid (II), and a resinous part, which is hydrolysed to guaiacol (III) by emulsin. The bark contains an enzyme (acerase) which hydrolyses coniferin and amygdalin; the sap also contains an enzyme. The wood contains a little coniferin, which may be the parent substance of (I). The odour is due to presence of hadromal, which, during heating of the sap, is decomposed into (I), (II), and (III). Hadromal may be synthesised from (I), (III), and sucrose. F. R. S.

**Constituents of the sap of sugar maple (*Acer saccharum*, Marsh).** G. H. FINDLAY and J. F. SNELL (Canad. J. Res., 1935, 13, B, 269—275).—The development of the maple flavour from its precursor in sap, during boiling, is not due to oxidative changes. No individual constituent of various maple extracts examined was capable of imparting the flavour to sugar syrups. A. G. P.

**Biochemistry of amygdalin.** A. VIEHOEVER and H. MACK (Amer. J. Pharm., 1935, 107, 397—450).—The physiological properties of amygdalin (the commercial product contains 2H<sub>2</sub>O) and of its hydrolytic products are discussed. J. L. D.

**Manchurian kaoliang (*Andropogon sorghum*, Brot.).** S. HIRAO (J. Agric. Chem. Soc. Japan, 1935, 11, 921—924).—Three cryst. substances have been isolated from the hot aq. extract of kaoliang: (1) yellow, m.p. 249—250°, a quercetin monoglucoside, probably quercimeritrin; (2) long white needles, m.p. 240—242°, probably a new flavanonol; (3) short white crystals, m.p. 98—100°, similar to pyrocatechol. H. G. R.

**Action of *Nuphar luteum* on the heart.** M. BULAJEWSKI (Wiad. Farm., 1935, 62, 15—18, 29—32, 43—47, 57—62).—EtOH extracts of blossoms of *N. luteum* contain a cryst. glucoside, *nymphalin* (I), which exerts a toxic action on the animal heart. (I) has m.p. 40° (approx.) and gives a purple colour with α-C<sub>10</sub>H<sub>7</sub>OH and H<sub>2</sub>SO<sub>4</sub>. Hydrolysis yields Cu-reducing substances. (I) is present in flowers and seeds but not in roots. CH. ABS. (p)

**Ascorbic acid (vitamin-C) content of some Indian plant materials.** M. DANODARAN and M. SRINIVASAN (Proc. Indian Acad. Sci., 1935, 11, B, 377—386).—Data obtained by the Tillmans-Harris method are recorded. A. G. P.

**Constituents of red sandal wood.** Homoptero-carpin.—See this vol., 81.

**Pigments of cotton flowers.** I. Cambodia (*Gossypium hirsutum*). K. NEELAKANTAM, R. H. R. RAO, and T. R. SESHADRI (Proc. Indian Acad. Sci., 1935, 1, 887—890).—The presence is established of quercetin and quercimeritrin in proportions which varied with variety, locality, and season. A. G. P.



**Fluorescence spectra of chlorophyll pigments.** C. DHERE and A. RAFFY (Bull. Soc. Chim. biol., 1935, 17, 1385—1413).—The bands in the fluorescence spectra of  $\alpha$ -chlorophyll in hexane,  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ ,  $\text{EtOH}$ ,  $\text{MeOH}$ ,  $\text{C}_6\text{H}_6$ , cyclohexanol,  $\text{CHCl}_3$ , and  $\text{CS}_2$  have axes at 663, 663.5, 666, 666.5, 667, 666.5, 668, 670 and 676.5  $\text{m}\mu$ , respectively, the corresponding val. for  $\beta$ -chlorophyll in  $\text{Et}_2\text{O}$  being 646.2  $\text{m}\mu$ . The bands in the fluorescence spectrum of the leaves of *Pelargonium zonale* (in vivo) occur at 738 and 686, whilst with an  $\text{Et}_2\text{O}$  extract of the leaves the vals. are 732.5 and 672  $\text{m}\mu$ , respectively. The fluorescence bands of  $\alpha$ - and  $\beta$ -phytylphosphoribide in  $\text{CS}_2$  have axes at 679 and 663.5  $\text{m}\mu$ , respectively. A. L.

**Phlobaphen and durasantalin in the colouring matter of Manchurian kaoliang (*Andropogon sorghum*).** K. OKANO and I. OHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 767—772).—The  $\text{Et}_2\text{O}$ -insol. fraction of the colouring matter of the hulls contains phlobaphen (I) (43% of the whole colouring matter) and the  $\text{COMe}_2$ -insol. fraction contains durasantalin (II) (red dura) (35%). The colouring matter (2%) of the seed coats also contains (I) (82%) and (II) (15%). The coats contain 3% of  $\text{H}_2\text{O}$ -sol. tannin but no apigenin (cf. Perkin, J.C.S., 1910, 97, 220). W. McC.

**Carotenoids and some lipins of *Ipomaea reptans* (L.).** Pair. M. ISHII (J. Soc. Trop. Agric. [Nettai Nogoku Kwaishi], 1933, 5, No. 2, 192—197).—Analyses of the vegetable are given.  $\beta$ -Carotene, xanthophyll, and a trace of taraxanthin were separated. Lipins detected included *n*-hentriacontane, sitosterol and its glucoside, and a higher alcohol, m.p. 267°. CH. ABS. (p)

**Daturic acid.** R. W. CLARK (J. Amer. Pharm. Assoc., 1935, 24, 843—847).—Solid fatty acids were prepared from the oil of *Datura stramonium* seeds. Attempts to separate them by fractional crystallisation from  $\text{EtOH}$ , pptn. of Mg salts, and vac. distillation of the Me esters failed. The occurrence and identity of heptadecic acid are discussed. F. O. H.

**Apple- and pear-seed oils.** J. PRITZKER and R. JUNGKUNZ (Z. Unters. Lebensm., 1935, 70, 255—257).—Air-dried apple- and pear-seeds contained 19.23 and 21.44%, respectively, of their dry wt. of oil, which had refractometer val. (40°) 62.9 and 62.0, acidity 4.1° and 9.7°, acid val. 2.3 and 5.4, ester val. 185.4 and 184.1, sap. val. 187.7 and 189.5, I val. (Hanus) 122.4 and 124.1, Reichert-Meissl val. 0.22 and 0.33, Polenske val. 0.4 and 0.33, unsaponifiable matter 1.10 and 1.03%, phytosterol (min.) 0.36 and 0.28%, m.p. of phytosteryl acetate 122° and 119°, respectively. The fatty acids (95.8 and 95.7%) had refractometer val. 48.4 and 47.7, neutralisation val. 196.5 and 196.8, mean mol. wt. 285.5 and 285.1, solid fatty acids (Bertram) 7.2 and 10.3%, (Grossfeld) 4.9 and 6.0%, and isooleic acid 0.62 and 0.45%, respectively. Each oil gave positive Bellier, Bellier-Kreis, and  $\text{HNO}_3$  tests, and the apple-seed oil a positive Kreis test. The latter oil was clear yellow, and had a bitter almond flavour, the pear-seed oil egg-yellow, and had a slightly acid taste. E. C. S.

**Odorous substances of green tea. VI. Constituents of tea oil.** S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1262—1274).—From tea-leaf oil were isolated  $\text{CHMeEt-CHO}$ , *n*-hexyl, benzyl, and benzyl- and phenyl-ethyl alcohols,  $\text{PhOH}$ , cresol,  $\text{AcOH}$ , and hexoic acid. No ester with an odour characteristic of that of the oil was isolated (cf. A., 1934, 571).

F. O. H.

**Agar-agar of Black Sea phyllophora.** V. F. OPOTZKI and L. A. BORTNIK (Ukrain. Chem. J., 1935, 10, 331—335).—The washed dried agar-agar contains  $\text{H}_2\text{O}$  19, protein 5.5, Ac 9.8, org. and total S (as  $\text{SO}_3$ ) 10.7 and 14.6, galactosans 42.5, pentosans 0.64, methylpentosans 0.16, ash 11.73% ( $\text{SO}_3$  3.93,  $\text{SiO}_2$  1.81,  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  2.01,  $\text{CaO}$  2.52,  $\text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$  1.46%). Japanese agar differs chiefly in its lower protein (1.32%), org. S (4.35%), and ash content (3.98%). The hardness of the gels of Black Sea agar is considerably < that of Japanese agar, and the m.p. and setting points are lower. R. T.

**Bitter principles of the Colombo root. III.**—See this vol., 89.

**Alkaloid of Chin-shih-hu.**—See this vol., 88.

**Chemistry and pharmacology of the alkaloids of *Duboisia Hopwoodii*.** C. S. HICKS and H. L. MESSURIER (Austral. J. Exp. Biol., 1935, 13, 175—188).—The leaves contain an alkaloid,  $\text{C}_9\text{H}_{12}\text{N}_2$ , b.p. 266—268°,  $[\alpha]_D^{20} +38.6^\circ$  (picrate, m.p. 186—188°; picrolonate, m.p. 252—253°), which yields nicotinic acid on oxidation with  $\text{KMnO}_4$  and is probably *d*-nornicotine (cf. A., 1932, 177). W. O. K.

**Alkaloids of European *Lycopodium* species.** J. MUSZYŃSKI (Arch. Pharm., 1935, 273, 452—457).—*L. Selago*, *annotinum*, *inundatum*, *complanatum*, and *clavatum*, L., contain solid, non-volatile (amorphous salts) and volatile,  $\text{H}_2\text{O}$ -sol. alkaloids (cryst., hygroscopic salts). The latter, named *selagine*, *annotine*, *inundatine*, *complanatine*, and *clavatine*, respectively, confer poisonous properties on the plants. R. S. C.

**Distribution of alkaloids in *Ephedra sinica* (Ma-Huang).** M. TARLÉ (J. Chinese Chem. Soc., 1935, 3, 377—380).—In the young herb the total amount of ephedrine alkaloids (I) is almost evenly distributed between the pith and the rest of the stem, but in the ripe plant the former contains much > the latter. The percentage of *l*-ephedrine in (I) is nearly the same in early summer (56.45%) as in the autumn (57.7%). H. G. M.

**Histochemical detection of sodium in plants.** M. STEINER (Ber. deut. Bot. Ges., 1935, 53, 720—732).—An adaptation of the uranyl Zn acetate method is described. Other plant substances do not interfere. A. G. P.

**Spectrographic micro-determination of zinc [in plant material].**—See this vol., 43.

**Method of making latent finger-prints visible.** M. WAGENAAR (Pharm. Weekblad, 1935, 72, 1265—1271).—The latent finger-print is developed by treatment with I vapour and permanent impressions are taken from the developed stain on paper coated with a prep. consisting of 1 g. of rice starch, 2 g. of KI, and 0.3 g. of thymol in 20 c.c. of  $\text{H}_2\text{O}$ . S. C.

**Impregnation of the nervous system with silver.** J. SZEPESENWOL (Compt. rend. Soc. Biol., 1935, 120, 689—690).—Larvæ of batrachians are impregnated with Ag by means of a 10% solution of  $\text{CH}_2\text{O}$  in 4%  $\text{HCl}$  or  $\text{HCO}_2\text{H}$  as fixer, followed by  $\text{AgNO}_3$  solutions of gradually increasing concn.

R. N. C.

**Deproteinisation of blood and urine by copper ferrocyanide.** R. VLADESCO (Compt. rend. Soc. Biol., 1935, 120, 664—665; cf. A., 1935, 1044).—Deproteinisation of blood and urine by  $\text{Cu}_2\text{Fe}(\text{CN})_6$  removes uric acid and  $\text{NH}_2$ -acids in the ppt. Urea, creatine, and creatinine may be determined in the filtrate if excess of Cu is first removed with  $\text{H}_2\text{S}$ , as it interferes with the determination of the latter two substances with Na picrate. Deproteinisation by this method is preferable to the older methods in diabetic urines.

R. N. C.

**Determination of benzene by the Pulfrich step-photometer.** L. VON SZECSENYI-NAGY (Biochem. Z., 1935, 281, 178—180; cf. Janovsky, A., 1891, 685).—The  $\text{C}_6\text{H}_6$  is separated from the acidified material (biological) by distillation into a cooled nitration mixture. The  $\text{C}_6\text{H}_4(\text{NO}_2)_2$  obtained is dissolved in  $\text{COMe}_2$ , made alkaline with 33% aq.  $\text{NaOH}$ , and shaken. The intensity of the violet colour in the  $\text{COMe}_2$  is measured. About 70% of the  $\text{C}_6\text{H}_6$  is thus determined.

W. McC.

**Spectrographic determination of phenol in different media.** G. BARAC (Compt. rend. Soc. Biol., 1935, 120, 520—522).— $\text{PhOH}$  is determined in aq. solution, and in plasma and whole blood after deproteinisation with  $\text{H}_2\text{WO}_4$ , by extracting with  $\text{Et}_2\text{O}$  and spectroscopic examination of the extract in the Jobin-Yvon quartz spectrograph;  $\text{PhOH}$  shows three narrow bands at 267, 274, and 280.7  $\text{m}\mu$ , the mol. extinction coeff. in  $\text{Et}_2\text{O}$  for the third of these being 2400.

R. N. C.

**Sugar determination by the ferricyanide electrode.** P. A. SCHAEFFER and R. D. WILLIAMS (J. Biol. Chem., 1935, 111, 707—723).—Reducing sugars may be determined by the ferri-ferro-cyanide electrode. Vals. are unaffected by  $p_{\text{H}}$  change, by the products of the sugar oxidation, or by changes in the vol. of the solution about the electrode. The method can be adapted for determinations with 20 cu. mm. of blood. As no supplementary reagents are used, side reactions are avoided.

E. A. H. R.

**Rapid method for the determination of reducing sugars.** G. I. SOLOMOS (Bull. Soc. Chim. biol., 1935, 17, 1465—1469).—The solution containing the reducing sugar is added from a burette to a known amount of 0.4%  $\text{K}_3\text{Fe}(\text{CN})_6$  in  $N$ - $\text{NaOH}$  until the red colour disappears. The method is applied to blood, urine, and milk.

A. L.

**Determination of glutamine in presence of asparagine.**—See this vol., 60.

**Determination of carotenoids in blood, tissue, and fluids in clinical practice.** P. RATCHEVSKY (Bull. Soc. Chim. biol., 1935, 17, 1187—1193).—The method is based on the observation that  $0.03 \times 10^{-6}$

g. of carotene is the smallest amount detectable by the yellow residue obtained on evaporation of light petroleum solutions.

A. L.

**Infra-red absorption spectra of plant and animal tissue etc.**—See this vol., 9.

**Iodine value as a biological constant. Rapid micro-determination by means of bromine vapour.** H. WOLLSCHITT (Arch. exp. Path. Pharm., 1935, 179, 260—265).—The material (0.1—5.0 mg.) is exposed to  $\text{Br}$  vapour for 15—180 min. and then heated at  $100^\circ$  to const. wt. The increase in wt.  $\times 160/\text{wt. taken}$  is the I val. Vals. for common fats and fatty acids agree with theoretical vals., but the indicated nos. of double linkings of some carotenoids (crocin, methylbixin) and unsaturated esters are < the known vals. The method differentiates various body fats.

F. O. H.

**Determination of carbon in biological fluids.** F. LAVERSON and K. VOIT (Biochem. Z., 1935, 280, 276—285).—The fluid is burned in air or  $\text{O}_2$  in an electrically heated combustion furnace and the  $\text{CO}_2$  produced is passed into aq.  $\text{Ba}(\text{OH})_2$ . Excess of 0.01*N*- $\text{HCl}$  is added and the solution is titrated with 0.01*N*- $\text{NaOH}$  using Tashiro's mixed indicator (Amer. J. Physiol., 1920, 60, 519). 0.002 mg. of C can be determined.

W. McC.

**Calcium determination in biological material.** C. C. WANG (J. Biol. Chem., 1935, 111, 443—453).—Use of a washing solution, for  $\text{CaC}_2\text{O}_4$  ppts., consisting of 2% aq.  $\text{NH}_3$  in equal parts of  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{Et}_2\text{O}$  prevents loss by flotation and dissolution. Treatment with  $\text{CCl}_3\text{CO}_2\text{H}$  and C allows direct Ca determinations to be made on urines.

F. A. A.

**Determination of mercury in viscera.** C. NEWCOMB, S. R. NAIDU, and K. S. VARADACHAR (Analyst, 1935, 60, 732—735).—The org. matter is destroyed by heating with  $\text{HNO}_3 + \text{H}_2\text{SO}_4$ , and the solution is distilled in a current of air until  $\text{H}_2\text{SO}_4$  fumes appear. Distillation is continued in a stream of air charged with  $\text{HCl}$ ,  $\text{HgCl}_2$  distilling over.  $\text{Hg}$  in both distillates is pptd. as  $\text{HgS}$ , which is dissolved in  $\text{Br-H}_2\text{O}$  and repptd. Separation is quant. from other heavy metals, including  $\text{As}^{\text{III}}$ , which is oxidised to  $\text{As}^{\text{V}}$ .

J. S. A.

**Micro-determination of phosphoric acid in tissue.** L. THIVOLLE (Bull. Soc. Chim. biol., 1935, 17, 1427—1450).—Conc.  $\text{HNO}_3$  containing  $\text{Cu}(\text{NO}_3)_2$  is used for the mineralisation of the material. The aq. solution of the phosphomolybdate ppt. is reduced with Zn, added to aq. Na phosphomolybdate, and titrated with  $\text{KMnO}_4$  using benzidine as indicator.

A. L.

**Micro-determination of sulphur in biological material.** L. REVOL and M. FERRAND (Bull. Soc. Chim. biol., 1935, 17, 1451—1454).—Losses in the determination of S in org. compounds due to the escape of traces of  $\text{SO}_2$  are avoided by passing the vapour from the  $\text{HNO}_3\text{-H}_2\text{O}_2$  treatment of the material through aq.  $\text{Br}$  which is finally added to the main solution. The  $\text{SO}_4^{--}$  is pptd. with benzidine.

A. L.

# BRITISH CHEMICAL ABSTRACTS

## A—PURE CHEMISTRY

FEBRUARY, 1936.

### General, Physical, and Inorganic Chemistry.

**Spectral intensities for hydrogen.** P. RUDNICK (Physical Rev., 1935, [iii], 48, 807—811).—Mathematical. N. M. B.

**Extension of the Paschen series.** B. JOHANSEN (Naturwiss., 1935, 23, 866).—The infra-red spectrum of  $H_2$  has been photographed and the  $\lambda\lambda$  of the 6th—13th members of the Paschen series are determined. A. J. M.

**Fine structure of  $D_a$  with increased resolution.** R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1935, [ii], 48, 971; cf. A., 1934, 575).—The chief minor component resulting from the coincident transitions  $2p^2P_{1/2} - 3s^2S_{1/2}$  and  $2s^2S_{1/2} - 3p^2P_{1/2}$  has been resolved. The measured half-intensity breadth of the high-frequency main component is  $0.120\text{ cm}^{-1}$ , and the average interval between centres of components  $0.134\text{ cm}^{-1}$ . The deviation from theory may be due to a Stark effect. The val. of  $e/m$  calc. from the measured interval between components of the two isotopes is  $1.7577 \pm 0.0004 \times 10^7$  e.m.u. per g. N. M. B.

**Continuous spectrum of deuterium.** (MILLE.) A. TOURNAIRE and E. VASSY (Compt. rend., 1935, 201, 957—958).—The continuous spectrum of  $D_2$  is slightly more intense than that of  $H_2$  at  $\lambda\lambda < 4000\text{ \AA}$ . H. J. E.

**New investigations of helium and hydrogen lines with crossed electric and magnetic fields.** W. STEUBING (Physikal. Z., 1935, 36, 822—825).—The changes suffered by the Stark effect components of the first secondary series of He which have been magnetically split into duplets, when the strength of the electric field is varied, have been investigated. For  $H_2$  it was shown that the method could be applied in spite of the electrodynamic decomp. of the Balmer lines observed by Wien. Results for  $H_2$  are analogous to those for He. A. J. M.

**Doubly excited states of helium.** T. Y. WU and S. T. MA (Physical Rev., 1935, [ii], 48, 917; cf. *ibid.*, 1934, [ii], 46, 239).—A correction. N. M. B.

**Perturbations in the second positive nitrogen bands.** D. COSTER and F. BRONS (Z. Physik, 1935, 97, 570—572).—Perturbation of the 2nd and 3rd vibration states of the  $^3\pi C$  level of  $N_2$  is characterised by a weakening without displacement of only a few lines, and is not explained by Gero's analysis (A., 1935, 1437). A. B. D. C.

**New afterglow spectrum in nitrogen.** J. KAPLAN (Physical Rev., 1935, [ii], 48, 800—801).—A detailed account of results previously reported (cf. A., 1935, 907). N. M. B.

**Rotational structure of the Schumann-Runge bands of oxygen in the vacuum region.** H. P. KNAUSS and S. S. BALLARD (Physical Rev., 1935, [ii], 48, 796—799).—Data for the absorption bands photographed in the range  $1760\text{--}1925\text{ \AA}$ . and rotational analyses are tabulated. An expression for, and table of, band origins are given. The energy of dissociation is  $5.05$  volts. N. M. B.

**Absorption spectra of oxygen at high concentration.** B. J. EISEMAN, jun. (J. Math. Phys. Mass. Inst. Tech., 1935, 14, 260—261).—New data for the ultra-violet triple bands,  $2847\text{--}2434\text{ \AA}$ ., using highly purified  $O_2$  at  $440\text{--}55\text{ atm.}$ , are given. The bands at  $6280$ ,  $5765$ , and  $4775\text{ \AA}$ . at room temp. and  $>440\text{ atm.}$  degrade towards the short  $\lambda$ . The  $4470\text{ \AA}$ . band appeared only at low temp. at const. concn. N. M. B.

**Influence of foreign gases on the higher principal series lines of sodium.** C. FUCHTBAUER and P. SCHULZ (Z. Physik, 1935, 97, 699—707).—Ne, A, and  $N_2$  produced dissymmetry towards the red at the end of the series. A. B. D. C.

**Arc spectrum of alkali metals with high vapour density.** A. CARRELLI and M. BATTISTA (Nuovo Cim., 1934, [ii], 11, 685—689; Chem. Zentr., 1935, i, 2776).—The intensity of forbidden lines and of the continuum is explained by the formation of quasi-mols., the effect increasing with the polarisability of the atoms from Na to Cs. J. S. A.

**Absorption spectra of sulphur vapour.** L. D'OR (Compt. rend., 1935, 201, 1026—1028).—Changes in the absorption spectrum of S vapour with concn. and temp. indicate four species as well as S atoms. The band system between  $3600$  and  $4200\text{ \AA}$ . is due to  $S_4$  or  $S_3$ , and not  $S_8$  or  $S_2$ . The validity of Preuner's conclusions is questioned (A., 1912, ii, 1145). T. G. P.

**Predissociation in the sulphur bands.** B. ROSEN, M. DESIRANT, and J. DUCHESNE (Physical Rev., 1935, [ii], 48, 916).—The feature of predissociation is that the emission band system stops abruptly at  $v'=8$  and the last observed band (8,0) is shorter than the others. Spectroscopic examination showed abrupt termination of the rotational structure in the  $v'-8$  and  $v'=7$  progressions and in the (8,0) band. It is concluded that there is a predissociation in the  $v'-7$  level, and the derived heat of dissociation is  $4.41 \pm 0.02\text{ e.v.}$  N. M. B.

**Spectrum of Se II.** D. C. MARTIN (Physical Rev., 1935, [ii], 48, 938—944).— $\lambda$  measurements were made in the region  $500\text{--}2600\text{ \AA}$ . of the spectrum

excited by a hollow-cathode discharge in He. Identifications and  $J$  vals. of new terms are given, and data and classifications of all known Se II lines are tabulated.

N. M. B.

**Anomalous dispersion of silver vapour.** L. ALEGRETTI (Nuovo Cim., 1934, [ii], 11, 717—722; Chem. Zentr., 1935, i, 2776).—The intensity ratio of the first doublet of the Ag principal series was measured by means of anomalous dispersion. J. S. A.

**Spark spectrum of cadmium.** R. RICARD and A. SAUNIER (Compt. rend., 1935, 201, 1115—1116).—Lines of Cd III and Cd IV at  $\lambda\lambda$  3400—5000 Å. were measured.

H. J. E.

**Absorption spectrum of the iodine molecule in the vacuum ultra-violet.** H. CORDES (Z. Physik, 1935, 97, 603—624).

A. B. D. C.

**Arc spectrum of cerium.** K. HASPAS (Z. Physik, 1935, 96, 410—430).—430 lines are arranged in terms, the lowest being a  $^2D$  term. The first and second ionisation potentials are 6.9 and 14.8 volts, respectively.

A. B. D. C.

**Spectrum of polonium.** B. KARLIK and H. PETERSSON (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 379—383; Chem. Zentr., 1935, i, 2496).—2 (or 3 ?) strong Po lines are recorded from a Po deposit on Pt, enclosed in a heated SiO<sub>2</sub> tube and excited with radiation of short  $\lambda$ .

J. S. A.

**Ultra-violet spectrum of radium emanation.** H. PETERSSON (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 303—311; Chem. Zentr., 1935, i, 2647).— $\lambda\lambda$  and intensities are recorded for 169 lines, not due to other elements, between 3700 and 2280 Å. The lines found do not correspond with those reported by previous workers.

J. S. A.

**Energy transfer in collisions of excited thallium atoms with gas molecules.** N. PRILESHAEVA (Acta Physicochim. U.R.S.S., 1935, 2, 647—664).—Results on the quenching of the Tl fluorescence line 5351 Å. by various gases, previously published (A., 1934, 340), are discussed theoretically. F. L. U.

**Anomalous diffraction gratings.** R. W. WOOD (Physical Rev., 1935, [ii], 48, 928—936).—A Cr-plated echelette grating of 7200 lines per in. on Cu, and one of 15,000 lines on Al film on glass, showed narrow bright and dark bands in the continuous spectrum of a white source. The variation of the bands with incidence angle is studied, and the bands, unexplained by classical theory, are attributed to a type of destructive interference along the plane of the grating.

N. M. B.

**Initiation of electrical discharges by field emission.** J. W. FLOWERS (Physical Rev., 1935, [ii], 48, 954—959).—The initiation of highly over-voltage discharges in effectively ion-free gases by short-duration voltage impulses is independent of the gas between the electrodes, and of the pressure over the range 1 atm.—vac. spark stage. Oscillograms for discharges in asymmetrical fields are given and discussed.

N. M. B.

**Interpretation of the fine structure coefficient,  $\alpha$ .** S. A. DE MAYOLO (Compt. rend., 1935, 201, 1097—1099).

H. J. E.

**Behaviour of certain diatomic molecules in stellar atmospheres.** E. BODSON and F. E. NISOLI (Bull. Acad. roy. Belg., 1935, [v], 21, 922—926).—Russell's theory is applied to the stellar spectra of the oxides and hydrides of B, Al, Ca, and Mg in the dwarf and giant stars, and temp.—abundance curves are given and discussed in relation to influence of dissociation and ionisation.

N. M. B.

**Red-shift from nebulae.** F. ZWICKY (Physical Rev., 1935, [ii], 48, 802—806).—Mathematical. The expansion of the universe, the red-shift of light through intergalactic space, and the width of spectral lines from distant nebulae are examined.

N. M. B.

**Artificial crystal lattice for interference with optical light.** W. KRAMER (Physikal. Z., 1935, 36, 841—843).—A method for obtaining interference diagrams of a similar nature to X-ray interference patterns, with ordinary light, is described. The process depends on the use of stationary waves produced by a method similar to that employed in the Lippmann process for colour photography.

A. J. M.

**X-Ray determinations with the diamond.** M. RENNINGER (Physikal. Z., 1935, 36, 834—837).—Intensity determinations of the reflexions from the (222) plane have been made using Cu  $K\alpha$  rays. The structure factor,  $F_{222}$ , lies between 2.1 and 2.6.

A. J. M.

**K X-ray absorption of light elements.** E. DERSHEM (Physical Rev., 1934, [ii], 45, 768).—Absorption of the  $L\alpha_{12}$  lines of Cu, Ni, and Fe in CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Ne have been measured.

L. S. T.

**K-Absorption of X-rays at the K-edges.** H. NITKA (Naturwiss., 1935, 23, 866).—The determination of the absorption of X-rays by intensity measurements gives uncertain results for the heavier elements, but if the change of intensity coeff. on crossing an edge is considered, the effect of scattering is considerably reduced. There is a linear dependence of at. K-absorption at the K-edge on the  $\lambda$  of the edge.

A. J. M.

**Change in relative intensity of the satellites of  $L\alpha$  in the atomic number range 47—52.** F. R. HIRSH, jun., and F. K. RICHTMYER (Physical Rev., 1934, [ii], 45, 754).

L. S. T.

**Measurements of small light intensities with counter tubes. II.** K. H. KREUCHEN (Z. Physik, 1935, 97, 625—632; cf. A., 1935, 800).—Photo-electric sensitivity is given for Zn, Cd, and Cu in the region 400—185 m $\mu$ , both as solid and as deposited cathodes.

A. B. D. C.

**Neon lamps in counter circuits. I. Limits of region of photo-electric sensitivity.** G. VALLE and B. ROSSI (Nuovo Cim., 1934, [ii], 11, 708—716; Chem. Zentr., 1935, i, 2778).—The dependence of photo-electric sensitivity on  $\lambda$  has been investigated. The upper limit gives a max. rate of potential increase between two impulses.

J. S. A.

**Foreign ionisation and decrease of discharge potential in gases.** W. ROGOWSKI and A. WALL-RAEF (Z. Physik, 1935, 97, 758—764).

A. B. D. C.

**Role of space charge in the study of the Townsend ionisation coefficients and the mechanism**



of static spark breakdown. R. N. VARNEY, H. J. WHITE, L. B. LOEB, and D. Q. POSIN (Physical Rev., 1935, [ii], 48, 818—822).—The mechanism of spark breakdown is investigated by a study of the deviations of the pre-spark current from the simple electron ionisation law, on the basis of distortion of the field of the spark gap by space charge. N. M. B.

Electron affinity of iodine from space-charge effects. G. GLOCKLER and M. CALVIN (J. Chem. Physics, 1935, 3, 771—777; cf. A., 1934, 1054).—The electron affinity  $\Delta E_0$  of I atoms, determined directly by measuring the equilibrium of reaction  $I^- \rightarrow I + E^- - \Delta E_0$  at the surface of a hot W filament, was 74.6 kg.-cal., in good agreement with available data. The concn. of the several ions of different masses ( $I^-$  and  $E^-$ ) was calc. from their effect on space charge. I has no effect on the thermionic emission of W. N. M. B.

Charging potential and secondary emission of bodies irradiated with electrons. M. KNOLL (Physikal. Z., 1935, 36, 861—869).—The charging potential of a homogeneous metallic plate in a high vac. is discontinuous with respect to the velocity of the primary electrons over the range 0—5000 volts. For C, however, the charging potential  $\propto$  velocity of primary electrons. This behaviour is connected with the variation of emission of secondary electrons. A. J. M.

Energy distribution of electrons in the photo-electric effect. E. RUDBERG (Physical Rev., 1935, [ii], 48, 811—817).—Available expressions for the distribution of electron levels and the transition probabilities from these levels, characterising the photo-electric emission from a metal, are examined, and equations for the energy distribution are derived in each case. Results are compared with data for Mo (cf. Roehr, A., 1934, 130), and Mitchell's theory is supported (cf. *ibid.*, 1290). N. M. B.

Photo-ionisation in gases. R. N. VARNEY and L. B. LOEB (Physical Rev., 1935, [ii], 48, 822—824).—When the radiation emitted from a H discharge tube passed through a fluorite window into a balanced space-charge positive ion detector containing gas at 0.02 mm., it was proved that the ionisation, for discharge tube pressures  $> 5$  mm., was of electrostatic origin, and not caused by radiation. This may explain Lenard's observations on the ionisation of gases. For a given gas at each end of a tube, photo-ionisation of A and of Xe by its own radiation was found, but this disappeared when a fluorite window was inserted; no ionisation of  $N_2$  or air by its own radiation was observed with or without the window. Results indicate that in pure, clean, dry gases photo-ionisation by radiation of energy appreciably  $<$  the ionisation potential of the gas is improbable. N. M. B.

Surface ionisation of potassium on tungsten. A. L. REIMANN (Physical Rev., 1934, [ii], 45, 898).—The results of Copley and Phipps (cf. A., 1935, 1303) are discussed. L. S. T.

Surface ionisation of potassium on tungsten. M. J. COPLEY and T. E. PHIPPS (Physical Rev., 1935, [ii], 48, 960—968).—Work previously reported (cf.

A., 1935, 1303) is continued under improved conditions, and observations of degree of ionisation are made up to 2800° abs. The calc. work function for W is  $4.51 \pm 0.01$  volts. Difference between experiment and theory in the log ion-atom ratio- $1/T$  graph indicates a temp. coeff.  $\alpha$  of the work function; the calc. val. of  $\alpha$  is  $5.6 \times 10^{-5}$  volt per degree. N. M. B.

Monatomic films of alkali metals on platinum. H. MAYER (Physikal. Z., 1935, 36, 845—848).—The prep. of monat. films of alkali metals on Pt by means of at. rays is described. The thickness of the film can be calc. by assuming that to each four Pt atoms there is one K atom, since the lattice const. of Pt is approx. half that of K. The variation of the photo-electric sensitivity for both gas-containing and outgassed Pt on which were deposited at. films of K (gas-containing and outgassed, respectively) with thickness of K film was investigated. A. J. M.

Radiation characteristics of oxide cathodes. W. T. MILLIS and E. F. LOWRY (Physical Rev., 1934, [ii], 45, 764). L. S. T.

Thermionic emission and electronic conductivity of solids. A. GEHRTS (Physikal. Z., 1935, 36, 764—767).—The thermionic emission of cathodes consisting of a metal covered with a monat. adsorption layer is a pure surface phenomenon just as in the case of homogeneous cathodes. The electron emission work is smaller for a Th-covered W cathode (monat. layer) than for a homogeneous Th cathode. The thicker is the Th film the more nearly do the consts.  $A$  and  $b$  of the thermionic emission equation,  $I = AT^2 e^{-b/T}$  ( $I$ =saturation current), approach those for a homogeneous Th cathode. A. J. M.

Effect of temperature on electron field currents from thoriated tungsten. A. J. AHEARN (Physical Rev., 1934, [ii], 45, 764—765; cf. A., 1933, 993).—The measurements made agree with the view that the field currents are const. and independent of temp., and that thermionic emission accounts for the observed variations with temp. L. S. T.

Electron emission from thoriated tungsten. W. B. NOTTINGHAM (Physical Rev., 1934, [ii], 45, 765).—Variation with temp. and electric field of electron emission from C-free thoriated W has been measured for surface coverings from zero to approx. a single layer. L. S. T.

Potential of an insulated screening grid in an electron stream. H. STRUBIG (Z. Physik, 1935, 97, 538).—Preliminary. A. B. D. C.

Born theory of the electron. A. BRAMLEY (Science, 1935, 82, 438—439).—A discussion. L. S. T.

After-effect of aluminium bombarded by electrons. M. TANAKA (Physical Rev., 1935, [ii], 48, 916).—Livingood's experiments (cf. this vol., 131) were performed using 250—300 kv. tube voltage and bombarding Al foil in high vac. with high-speed electrons. The Al afterwards emitted an electron radiation decaying with half-val. periods of about 7 sec., 40 sec., and 10 min. A similar effect was observed for other elements, including Ni, Cu, and Ag. N. M. B.

**Inelastic scattering of electrons from metals.** E. RUDBERG (Physical Rev., 1934, [ii], 45, 764).

L. S. T.

**Saturation ionisation current from high-speed electrons in air.** L. S. TAYLOR (Physical Rev., 1935, [ii], 48, 970).—A method previously reported (cf. *ibid.*, 1934, [ii], 45, 762) of plotting results of ionisation produced in liquids is extended to determine the ionisation produced in air at normal pressure by a heterogeneous beam of electrons of max. energy 150 electron kv.

N. M. B.

**Acceleration of electrons to high energies.** J. W. BEAMS and H. TROTTER, jun. (Physical Rev., 1934, [ii], 45, 849—850).—A method of accelerating electrons by means of effectively moving electrical fields is described.

L. S. T.

**Energy losses of electrons in helium, neon, and argon.** R. WHIDDINGTON and E. G. WOODROOFE (Phil. Mag., 1935, [vii], 20, 1109—1120).—An extension of work previously reported (cf. A., 1934, 825). Energy losses, relative probabilities, and interpretations of the excitations are tabulated.

N. M. B.

**Limitations of the theory of the positron.** W. H. FURRY and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 45, 903—904; cf. A., 1934, 468; 1935, 278).

L. S. T.

**Proton-proton forces in anomalous scattering and in nuclear binding.** R. D. PRESENT (Physical Rev., 1935, [ii], 48, 919—920).—In view of anomalies reported by White (cf. *ibid.*, 47, 573) on the scattering of protons in  $H_2$ , the scattering cross-section is calc. for  $45^\circ$  scattering, using the Feenberg-Knipp nuclear model (cf. this vol., 134) and assuming an additional attractive proton interaction.

N. M. B.

**Scattering of molecular rays in gases.** R. G. J. FRASER, H. S. W. MASSEY, and C. B. O. MOHR (Z. Physik, 1935, 97, 740—744).—The geometry of the crossed mol.-ray method is worked out for a primary beam of rectangular cross-section, and used to obtain collision cross-sections for Na-H $\sigma$  and K-Hg.

A. B. D. C.

**High-current ion sources for nuclear investigations.** E. S. LAMAR, E. W. SAMSON, and K. T. COMPTON (Physical Rev., 1935, [ii], 48, 886—892).—Experiments are described with a capillary ion source designed by Tuve (cf. A., 1935, 1296), which has been modified by eliminating the auxiliary electrode for drawing ions out of the arc. The ion current for a 1.92 amp. arc was 4.2 milliamp.; currents up to 5 amp. have been used. The mass spectrograph, when the arc is operated in  $H_2$ , shows a preponderance of diat. and triat. ions with proton fractions 5—20% of the total ion current. There is evidence of the breaking up of the heavy ions into protons and neutral particles on collision at high speed with gas mols.

N. M. B.

**Positive rays. Application to the study of the Stark effect.** A. POIROT (Ann. Physique, 1935, [xi], 4, 533—645; cf. A., 1930, 657).—Morand's method (cf. A., 1927, 492) is extended to the emission of positive rays from Na, K, Ca, Ba, and Cr. The rays form a well-defined faintly luminous beam; the spectrum of the light emitted shows chiefly the lines of the

arc spectrum of the metal of the salt deposited on the anode. The phenomena observed can be explained by the electrolysis and partial volatilisation of the salt. The rays can be used for the study of the Stark effect, particularly in the case of metals which do not form stable volatile compounds for study by the discharge tube. The Stark effect for Li, the diffuse doublets of Na, and the singlets and triplets of Ba were observed.

N. M. B.

**At. wt. of neon.** A. VON ANTROPOFF [with R. JUNGBLUTH-FICHT and M. HOEPPENER] (Ber., 1935, 68, [B], 2389—2391).—Ne and He can be separated from one another by active C cooled in liquid air. The at. wt. of Ne, determined from its density, is 20.183.

H. W.

**Isotopic constitution of iron.** J. DE GIER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 959—961).—The isotope 58 of Fe has been detected in  $Fe(CO)_5$  by the mass spectrograph, its abundance being about 0.5%.

J. W. S.

**Isotopic structure of iridium.** A. J. DEMPSTER (Nature, 1935, 136, 909).—A mass analysis of the Ir ions formed by a high-frequency spark between Pt-Ir electrodes confirms the existence (cf. A., 1935, 1295) of  $Ir^{191}$  and  $Ir^{193}$ , the latter more abundant.

L. S. T.

**Production of  $H^3$  by a canal-ray discharge in deuterium.** G. P. HARNWELL, H. D. SMYTH, S. N. VAN VOORHIS, and J. B. H. KUPER (Physical Rev., 1934, [ii], 45, 655—656, 769).— $H^3$  has been accumulated by running a high-voltage discharge in  $D_2$  at low pressure and passing the resulting canal rays into  $D_2$  at a higher pressure. Circulation of the gas for 3 hr. increased the  $H^3$  content from 1 in  $2 \times 10^5$  to 1 in 5000 parts of  $D_2$ .

L. S. T.

**Prediction of isotopes.** J. H. BARTLETT, jun. (Physical Rev., 1934, [ii], 45, 847).—A list is given.

L. S. T.

**Inhomogeneous fields for mass spectrography.** S. H. BAUER (Physical Rev., 1935, [ii], 48, 917).—Mathematical.

N. M. B.

**Radioactivity of samarium and "columnar ionisation."** D. LYFORD and J. A. BEARDEN (Physical Rev., 1934, [ii], 45, 743—744).—3.9  $\alpha$ -particles, range 1.28 cm., are emitted per sq. cm. per min. from a  $Sm_2O_3$  surface.

L. S. T.

**Radioactivity of the rare-earths. I. Distribution of radioactivity in the fractionation of cerium earths.** L. MAZZA (Gazzetta, 1935, 65, 993—1008; cf. A., 1934, 578).—By means of an automatic Geiger counter the distribution of radioactivity in the various fractions resulting from the fractionation of rare-earth mixtures has been measured. La-Ce-Pr, Pr-Nd, and Nd-Sm mixtures, respectively, were used. Both La and Ce retain traces of radioactive elements very tenaciously and are themselves inactive. The Pr-Nd fractions are all feebly active, probably due to the radioactivity of Nd. In the Nd-Sm mixtures the radioactivity is due chiefly to Sm, although here also impurities of radioactive elements tend to become conc. in the more sol. fractions.

O. J. W.

**Interaction between  $\alpha$ -particles.** J. A. WHEELER (Physical Rev., 1934, [ii], 45, 746). L. S. T.

**Ionisation curves of single  $\alpha$ -particles.** H. ALFVEN (Z. Physik, 1935, 97, 718—724).—The current due to the ionic sheath surrounding an  $\alpha$ -particle track in a homogeneous electric field has the form of the Bragg curve (cf. A., 1935, 1048). A. B. D. C.

**Range of  $\alpha$ -rays from polonium and its dependence on intensity of the radiation, age of the preparation, and nature of the substrate.** B. KARLIK and E. RONA (Sitzungsber. Akad. Wiss. Wien, IIA, 1934, 143, 217—221; Chem. Zentr., 1935, i, 2773).—Strong preps. show inhomogeneity, which increases on ageing, and is  $>$  corresponds with self-absorption. The range decreases steadily on keeping in  $\text{CO}_2$ . Penetration of Ni or Pd substrates does not occur with weak sources. J. S. A.

**Excitation of  $K$ -radiation of nitrogen, oxygen, and neon by alpha-particles.** W. RIEZLER (Ann. Physik, 1935, [v], 24, 714—718).—The excitation function for  $K$ -radiation of  $\text{N}_2$ ,  $\text{O}_2$ , and Ne by  $\alpha$ -particles was investigated for  $\alpha$ -particles of range 13—35 mm. in air. The curve between range of  $\alpha$ -particle and excitation function is analogous to the Bragg curve for total ionisation by  $\alpha$ -particles, although the max. is much flatter. The Ne curve does not reach a max. in the range considered. A. J. M.

**Recoil by  $\beta$ -decay.** F. BLOCH and C. MÖLLER (Nature, 1935, 136, 911—912).—Theoretical. L. S. T.

**X-Ray levels of radioactive elements with applications to  $\beta$ - and  $\gamma$ -ray spectra.** F. A. MAXFIELD and A. E. RUARK (Physical Rev., 1934, [ii], 45, 744). L. S. T.

**Magnitude and composition of the absorption coefficients of hard  $\gamma$ -rays.** W. GENTNER (Physikal. Z., 1935, 36, 810—812).—The variation with  $\lambda$  of the absorption coeff. for  $\gamma$ -rays in Pb, and for  $\gamma$ -rays from Th-C'' ( $h\nu = 2.65 \times 10^6$  e.v.) the variation with at. no., have been determined. A. J. M.

**Magnetic moment of the neutron.** D. R. INGLIS and A. LANDE (Physical Rev., 1934, [ii], 45, 842; cf. A., 1935, 278).—Theoretical. L. S. T.

**Production of neutrons by annihilation of protons and electrons according to Fermi's theory.** F. BLOCH and C. MÖLLER (Nature, 1935, 136, 987).—Theoretical. L. S. T.

**Experiments with slow neutrons.** P. I. LUKIRSKI and T. V. ZAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 393—396).—A detailed account of work already noted (A., 1935, 1441).

**Production of secondary  $\gamma$ -rays by neutrons.** R. FLEISCHMANN (Physikal. Z., 1935, 36, 806—808).— $\gamma$ -Rays were produced by the action of slow neutrons on paraffin, Fe, Cu, Cd, and Pb. In the case of the metals the slow neutrons were produced by the preliminary passage of neutrons through paraffin. The efficiency is in all cases one quant per neutron. A. J. M.

**Absorption of residual neutrons.** L. SZILARD (Nature, 1935, 136, 950—951).—Slow neutrons

(paraffin) from a Rn-Be source filtered by thick Cd sheets are strongly absorbed by In and some other elements. Cd absorbs the bulk of the unfiltered beam more strongly than does In. The residual neutrons from the Cd filter are scarcely absorbed by Cd itself. They show marked selective absorption effects, and in some elements are more absorbable than the unfiltered beam. The results are contrary to the current theory of radiative capture. L. S. T.

**Scattering of neutrons by  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , paraffin, lithium, boron, and carbon, and the production of radioactive nuclei by neutrons found by Fermi.** J. R. DUNNING and G. B. PEGRAM (Physical Rev., 1934, [ii], 45, 768—769).—The scattering of Rn-Be neutrons by these substances shows that for light in contrast to heavy nuclei the cross-section for neutron-nucleus collision does not vary greatly with the nuclear charge or nuclear mass. Mg gives an induced radioactivity with a period of approx. 3 hr. L. S. T.

**Slowing down of neutrons by collisions with protons.** H. VON HALBAN, jun., and P. PREISWERK (Nature, 1935, 136, 951—952).—The degree of activation produced in a Ag plate by neutrons from a Rn-Be source slowed down by passage through various thicknesses of  $\text{H}_2\text{O}$ , EtOH,  $\text{C}_6\text{H}_6$ , and a liquid paraffin has been observed. The differences in the effect of these liquids on the intensity of slow neutrons cannot be ascribed to differences in the amounts of H, C, or O which the liquids contain. Mol. structure appears to be a factor. L. S. T.

**Energy distribution of neutrons from fluorine.** T. Y. WU (Physical Rev., 1934, [ii], 45, 846—847).—Theoretical. L. S. T.

**Geiger-counter characteristics with applied potentials reversed.** D. B. COWIE (Physical Rev., 1935, [ii], 48, 883—885).—Counters in which the cylinder potential is positive with respect to the wire operate with a reduced efficiency for which an explanation is discussed. N. M. B.

**Search for radioactivity induced by 800-kilovolt electrons.** J. J. LIVINGOOD and A. H. SNELL (Physical Rev., 1935, [ii], 48, 851—854).—About 50 elements were bombarded with 850-kv. electrons and examined with a Geiger counter for induced radioactivity. No positive results were obtained, indicating that the yield is  $< 1$  activation per  $10^{12}$  electrons. N. M. B.

**Radioactivity produced by artificially-accelerated particles.** H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 746). L. S. T.

**Disintegration of beryllium with fast protons.** B. ZIPPRICH (Z. Physik, 1935, 96, 337—341).—This disintegration produces  $\alpha$ -particles. A. B. D. C.

**Artificial radioactivity using carbon targets.** L. R. HAFSTAD and M. A. TUVE (Physical Rev., 1934, [ii], 45, 902—903).—The production from C bombarded with protons of a radio-element which has a decay period the same as that of C bombarded with deuterons (cf. A., 1935, 1442) is due to deuterons contaminating the proton beam. L. S. T.

**Induced radioactivity which follows bombardment of targets by deuterium ions.** L. R. HAFSTAD and M. A. TUVE (Physical Rev., 1934, [ii], 45, 767—768).—Delayed emission effects produced in a series of targets by deuteron bombardment are described. L. S. T.

**Protons from the disintegration of lithium by deuterons.** L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 48, 848; cf. *ibid.* 47, 971).—The range distribution of the  $\alpha$ -particles and protons emitted in the disintegration of Li by 700-kv. deuterons was determined. The calc. energy released in the disintegration is 4.3 m.e.v.; the calc. masses are  $\text{Li}^8$  8.0185, and  $\text{Be}^8$  8.0072 =  $2\text{He}^4 + 0.5 \pm 1.0$  m.e.v. N. M. B.

**Radioactivity induced in oxygen by deuteron bombardment.** H. W. NEWSON (Physical Rev., 1935, [ii], 48, 790—796).—An induced radioactivity of half-life 1.16 min. was observed after the bombardment of  $\text{O}_2$  or its compounds by 3-mv. deuterons. The disintegration particles were positrons, and the active substance an isotope of F. The probable reactions are:  $\text{O}^{16} + \text{D}^2 = \text{F}^{17} + n^1$ ;  $\text{F}^{17} = \text{O}^{17} + e^+$ . The activation function of O was measured, and the drop in the excitation curve at low deuteron energies is explained by assuming that the energy of reaction is the negative of the threshold energy; the estimated val. is -1.8 mv. This is approx. verified by measuring the max. angle between the direction of the deuteron beam and the paths of the radioactive recoil atoms when  $\text{SiO}_2$  and graphite were separately bombarded. N. M. B.

**Two radioactive substances from magnesium after deuteron bombardment.** M. C. HENDERSON (Physical Rev., 1935, [ii], 48, 855—861).—Mg bombarded by 3.3 m.e.v. deuterons became radioactive with emission of negative electrons and  $\gamma$ -rays, and with two decay periods,  $10.25 \pm 0.24$  min., and  $15.8 \pm 0.5$  hr., characteristic of  $\text{Mg}^{27}$  and  $\text{Na}^{24}$ . The reactions are:  ${}_{12}\text{Mg}^{26} + {}_1\text{H}^2 = {}_{12}\text{Mg}^{27} + {}_0\text{H}^1$ ;  ${}_{12}\text{Mg}^{26} + {}_1\text{H}^2 = {}_{11}\text{Na}^{24} + {}_2\text{He}^4$ ;  ${}_{12}\text{Mg}^{27} = {}_{13}\text{Al}^{27} + \beta + \gamma$ ;  ${}_{11}\text{Na}^{24} = {}_{12}\text{Mg}^{24} + \beta + \gamma$ . The measured voltage excitation functions of the two activities follow different laws. At 3 m.e.v. one atom becomes  $\text{Na}^{24}$  for each 9.6 atoms becoming  $\text{Mg}^{27}$ . The thick target yield of  $\text{Mg}^{27}$  atoms is about 5 per  $10^7$  deuterons. The nuclear cross-section ( $\text{Mg}^{26}$ ) at 3 m.e.v. is approx.  $2.4 \times 10^{-26}$  sq. cm. N. M. B.

**Collisions of  $\alpha$ -particles with neon nuclei.** W. W. EATON (Physical Rev., 1935, [ii], 48, 921—928).—Using a special projection method, collisions with nuclei were investigated from photographs of 700,000  $\alpha$ -particle tracks due to a source of Th active deposit. The Wilson chamber contained Ne 85%, air 10%, and  $\text{H}_2$  5%. Range-velocity curves for recoil atoms give no evidence of disintegrations of nuclei with emission of protons or neutrons. The probability of disintegrating  $\text{Ne}^{20}$  with  $\alpha$ -particles of  $< 6$  cm. range in air is small; from this the calc. lower limit for the mass of  $\text{Na}^{23}$  is 22.99945. N. M. B.

**Proton spectra of magnesium, silicon, and sulphur on bombardment with fast  $\alpha$ -particles.** O. HAXEL (Physikal. Z., 1935, 36, 804—806).—The

proton spectra of Mg, Si, and S when bombarded with  $\alpha$ -particles of 8.6 cm. range are very similar. This result is discussed on the basis of the nuclear structure of the three atoms. The spectra are those of the most abundant isotopes,  $\text{Mg}^{24}$ ,  $\text{Si}^{28}$ , and  $\text{S}^{32}$ . From the energies of the emitted proton groups, the energies of the excited nuclei of Al, P, and Cl can be obtained. These energies are identical for the three nuclei, and the excitation probabilities for all three elements are approx. equal. This can be explained if the nuclei differ from each other by only one  $\alpha$ -particle. A. J. M.

**Evidence for a resonance level in the nucleus of  $\text{B}^{10}$ .** E. POLLARD (Physical Rev., 1934, [ii], 45, 746).—The protons emitted by B under  $\alpha$ -particle bombardment consist of a group of 18 cm. range superposed on the 14-cm. group observed by Heidenreich. The new group is due to a broad resonance level through which  $\alpha$ -particles of 1.2—1.7 cm. range can enter the nucleus. L. S. T.

**Methods and types of artificial transformation of atoms.** W. BORNÉ (Physikal. Z., 1935, 36, 776—779).—A review of the types and products of nuclear reactions. The highest known stable isotope of any given at. no. must contain an even no. of neutrons. A. J. M.

**Artificial disintegration. III.** D. VAN DER VEEN (Chem. Weekblad, 1936, 33, 16—21).—A further review (see A., 1934, 826).

**Chemical detection of artificial transmutation of elements.** F. A. PANETH and H. LOEIT (Nature, 1935, 136, 950).—He produced by bombardment of Me borate with neutrons from a Rn-Be source has been observed spectroscopically and the vol. measured. One millicurie of Rn, mixed with Be, produces  $< 3 \times 10^3$  neutrons per sec. L. S. T.

**Excitation of nuclei by neutrons.** W. EHRENBURG (Nature, 1935, 136, 870; cf. A., 1935, 141).—Neutrons, apparently of medium velocity, from a Rn-Be source produce an increased activity in Ag and I and a decreased activity in Si and Al when the source is surrounded by a Ag shield. Collisions of neutrons with Ag nuclei lead either to excitation of the nucleus without capture or to capture with formation of a radioactive element. L. S. T.

**Radioactivity induced by neutron bombardment.** A. BRAMLEY (Physical Rev., 1934, [ii], 45, 901—902).—Nuclear reactions are discussed. L. S. T.

**Effect of substances containing hydrogen on artificial radioactivity excited by neutrons. II.** E. FERMI, B. PONTECORVO, and F. RASETTI (Ric. sci. Prog. tec., 1934, 5, II, 380—381; Chem. Zentr., 1935, i, 2492).—The collision area of the atoms of various elements is derived from the relative activity of Rh, embedded in paraffin wax, activated through a screen of the element in question. Elements of large collision area, except Li and B, show high activation by slow neutrons. Li and B probably form stable isotopes or emit very soft  $\beta$ -rays. J. S. A.

**Artificial radioactivity excited by neutron bombardment. VI.** E. AMALDI, O. D'AGOSTINO, and E. SEGRÉ (Ric. sci. Prog. tec., 5, 381—382;



Chem. Zentr., 1935, i, 2492—2493; cf. A., 1934, 1284).—In all cases (F, Na, Al, Cl, Ga, Ag, In, Cs, Pr, Pt, Re) where the radioactive species could be separated chemically from material activated with slowed-down neutrons, the active atom was isotopic with the starting material. New half-life periods are reported for F, Al, Cl, Pr, and Pt. J. S. A.

Problems of ultra-radiation. P. M. S. BLACKETT (Physikal. Z., 1935, 36, 773—776).—A review. A. J. M.

Transmission of ultra-radiation through matter. H. KULENKAMPF (Physikal. Z., 1935, 36, 785—787).—Coincidence determinations have been carried out using counter tubes placed horizontally above each other with absorbing layers above and between the tubes. A secondary corpuscular radiation with a range of about 35 cm. of Fe is found to be produced by  $\gamma$ -radiation of which the absorption coeff. in Fe is 0.009 cm.<sup>-1</sup> A. J. M.

Showers of rays which produce bursts of cosmic-ray ionisation. C. G. MONTGOMERY and D. D. MONTGOMERY (Physical Rev., 1935, [ii], 48, 786—789).—An expression for the probability that a shower of a given no. of rays will discharge a no. of Geiger-Müller counters is derived and verified experimentally. Results indicate that there is no marked discontinuity between small and large showers. N. M. B.

Compensation method for simultaneous measurement of ionisation collisions and intensity of cosmic rays. A. GASTELL (Z. Physik, 1935, 97, 403—413). A. B. D. C.

Ionisation collisions of cosmic rays. A. GASTELL (Z. Physik, 1935, 97, 414—435).—The gas in the ionisation chamber has little effect on collision measurements. The no. of collisions is sensitive to barometric pressure. A. B. D. C.

Investigation of ionisation by ultra-radiation with a double chamber. W. MESSERSCHMIDT (Physikal. Z., 1935, 36, 788—789).—A double ionisation chamber was used for the investigation of the absorption of Hoffmann "stösse" (A., 1934, 235). A half-val. thickness of 3.5 cm. Pb was obtained. The connexion between the shower groups observed by the cloud-chamber method and the "stösse" is discussed. A. J. M.

Solar components of ultra-radiation. J. BARNÓTHY and M. FORRÓ (Physikal. Z., 1935, 36, 789—791). A. J. M.

Analysis of corpuscular cosmic radiation under a screen of 28 m. of soil. P. AUGER and A. ROSENBERG (Compt. rend., 1935, 201, 1116—1118; cf. A., 1935, 560).—Soft cosmic radiation was almost completely eliminated at this depth. H. J. E.

Sign and nature of the ultra-penetrating particles of cosmic radiation. L. LEFRINCE-RINGUET (Compt. rend., 1935, 201, 1184—1187).—The most penetrating cosmic particles have been investigated in a large Wilson chamber working in a magnetic field. The majority have the paths of fast electrons. One third of the particles have such high energies that the sense of the deflexion of their paths

could not be ascertained. From the measurable paths, the ratio of positive to negative particles is 2:1, and their energies are >700 m.e.v. T. G. P.

What fraction of the primary cosmic radiation is positive? T. H. JOHNSON (Physical Rev., 1934, [ii], 45, 758). L. S. T.

Ionisation spurts resulting from cosmic-ray entities. W. F. G. SWANN and W. E. RAMSEY (Physical Rev., 1934, [ii], 45, 758). L. S. T.

Azimuthal effect of cosmic rays. R. GUNN (Physical Rev., 1934, [ii], 45, 900—901).—Theoretical. L. S. T.

Orbit of electric particles in field of a magnetic dipole, with application to the theory of cosmic radiation. C. STØRMER (Avh. Norske Vid. Akad. Oslo, 1933, No. 11; Chem. Zentr., 1935, i, 2774).—The author's auroral theory is applied to cosmic radiation. J. S. A.

Stellar theory. W. NERNST (Z. Physik, 1935, 97, 511—534).—A physical interpretation for the formation of stars is given. A. B. D. C.

Neutrino theory of light. O. SCHERZER (Z. Physik, 1935, 97, 725—739). A. B. D. C.

Decisive forces in the structure of the atomic nucleus. C. V. VON WEIZSACKER (Physikal. Z., 1935, 36, 779—785).—Theoretical discussion. A. J. M.

The Geiger counter and gas discharges as space-charge problems. A. VON HIPPEL (Z. Physik, 1935, 97, 455—481).—The conception of space charge is developed and applied to the region between initiation and continuous discharge; this gives an accurate definition of initiation potential. Extension to inhomogeneous fields gives a description of the properties of the Geiger counter. A. B. D. C.

Possibility of a metallic modification of hydrogen. E. WIGNER and H. B. HUNTINGTON (J. Chem. Physics, 1935, 3, 764—770).—The energy of a body-centred lattice of H<sub>2</sub>, calc. as a function of the lattice const., assumes its min. val. for a lattice const. which corresponds with a density many times > that of the ordinary mol. lattice of solid H<sub>2</sub>, and with a pressure of approx. 250,000 atm., beyond the range of present technique. N. M. B.

$\infty s$  orbits of the elements. E. FERMI and E. AMALDI (Mem. R. Accad. Italia, 1934, 6, 119—149).—Mathematical. The calculation of the proper functions of elements, using the Thomas-Fermi statistics, is described, and applied to the  $\infty s$  functions of 14 elements. O. J. W.

Tables for determining atomic wave functions and energies. P. M. MORSE, L. A. YOUNG, and (Miss) E. S. HAURWITZ (Physical Rev., 1935, [ii], 48, 948—954). N. M. B.

Value of the electronic charge. R. T. BIRGE (Physical Rev., 1935, [ii], 48, 918).—Kellstrom's result (cf. A., 1935, 1455) for the viscosity of air leads to the val.  $4.816 \pm 0.013 \times 10^{-10}$  for  $e$ , compared with  $4.8036 \pm 0.0005 \times 10^{-10}$  e.s.u. by abs. X-ray  $\lambda$  measurements. These results, however, still leave in doubt

any set of vals. of the interrelated consts.  $e$ ,  $e/m$ , and  $h$  that would satisfy all the experimental results.

N. M. B.

Quantised field theory and the mass of the proton. M. BORN (Nature, 1935, **136**, 952—953).

L. S. T.

Statistic perturbation theory. I. Perturbation calculations with the Thomas-Fermi theory excluding exchange. P. GOMBAS (Z. Physik, 1935, **97**, 633—654).

A. B. D. C.

Majorana's exchange energy. G. BREIT and E. WIGNER (Physical Rev., 1935, [ii], **48**, 918—919).—Mathematical. Anomalies arising from the differences in mass of the neutron and proton are corr.

N. M. B.

Absorption of high-energy particles by matter. J. SOLOMON (Compt. rend., 1935, **201**, 1110—1112).—Theoretical.

H. J. E.

Characteristic constants of the atomic sphere. L. LABOCETTA (Ric. sci. Prog. tec., 1934, **5**, II, 376—377; Chem. Zentr., 1935, i, 2491).—Theoretical.

J. S. A.

Intra-nuclear forces. E. FEENBERG and J. K. KNIPP (Physical Rev., 1935, [ii], **48**, 906—912).—Mathematical. The H and He isotopes are considered.

N. M. B.

Interaction of nuclear particles. L. A. YOUNG (Physical Rev., 1935, [ii], **48**, 913—915; cf. *ibid.*, **47**, 972).—Mathematical. Calculations of the ranges and strengths indicate that the interactions are of an exchange nature with approx. range  $2.8 \times 10^{-13}$  cm.; the neutron-neutron and proton-proton interactions are approx. equal, the former depending probably on spin orientation. A di-neutron or di-proton may be dynamically stable, but unstable with respect to  $\beta$ -decay.

N. M. B.

Application of the Dirac matrix method to the theory of metals. S. SCHUBIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, **3**, 15—18).—Theoretical. The Dirac matrix method is applied to the problem of the motion of electron gas under the influence of an alternating electric field.

A. J. M.

Elements of the quantum theory. VI. Hydrogen atom. S. DUSHMAN (J. Chem. Educ., 1935, **12**, 529—539; cf. this vol., 7).

L. S. T.

Electrostatic field and energy conditions in neighbourhood of a lattice edge. W. KLEBER (Zentr. Min., 1935, **A**, 45—52; Chem. Zentr., 1935, i, 2644—2645).—Theoretical.

J. S. A.

Quadratic Zeeman effect. G. RACAH (Nuovo Cim., 1934, [ii], **11**, 723—724; Chem. Zentr., 1935, i, 2775).—Relativistic treatment of the problem gives the same results as the use of Schrodinger's equation.

J. S. A.

Mass of the neutron from the nuclear reaction  $H^2 + H^2 \rightarrow He^3 + n^1$ . H. H. GOLDSMITH and V. W. COHEN (Physical Rev., 1934, [ii], **45**, 850).—A discussion.

L. S. T.

Extensive results of the classical simplest elastic hydrogen atom. L. ZEHNDER (Physikal. Z., 1935, **36**, 820—822).—The structure of the atom is

considered from the viewpoint of the "principle of greatest simplicity."

A. J. M.

Deviation of electrical charge distribution from spherical symmetry for some atomic nuclei. H. SCHÜLER (Physikal. Z., 1935, **36**, 812—814).—There is an asymmetry of the charge distribution in the nuclei of  $^{63}_{29}\text{Cu}$ ,  $^{65}_{29}\text{Cu}$ ,  $^{201}_{80}\text{Hg}$ ,  $^{209}_{83}\text{Bi}$ , the vals. of which are calc. The results are discussed with reference to nuclear structure (cf. A., 1935, 1051).

A. J. M.

Emission spectrum of the oxide of tellurium  $\text{TeO}$ . C. S. PLAW (Compt. rend., 1935, **201**, 1181—1183).— $\text{TeO}$  has a system of about 30 bands, degraded towards the red, between 3190 and 3820 Å., analogous to those of  $\text{SO}$  and  $\text{SeO}$ . The energy of dissociation of the normal mol. is 5.70 volts.

T. G. P.

Rotational structure of the  $D$  and  $E$  band systems of  $\text{CuCl}$ . J. TERRIEN (Compt. rend., 1935, **201**, 1029—1030).—The bands, produced in a discharge tube containing  $\text{CuCl}$ , are complex, since the frequencies of vibration and anharmonic factors of the two states are similar, and each atom has two isotopes. The  $E$  band,  $v'=0$ ,  $v''=0$ ,  $\lambda=4333.19$ , and the  $D$  band,  $v'=0$ ,  $v''=0$ ,  $\lambda=4353.86$ , have been investigated.

T. G. P.

Absorption spectrum of  $\text{SnI}_4$  vapour. A. V. BANOVA (Acta Physicochim. U.R.S.S., 1935, **2**, 733—736; cf. A., 1935, 807).—The continuous absorption of  $\text{SnI}_4$  between  $130^\circ$  and  $280^\circ$  shows max. at 3570, 2800, and 2450 Å. The first two are associated with the dissociation into  $\text{SnI}_3 + \text{I}$ , and  $\text{SnI}_3 + \text{I}^*$ , respectively. The dissociation energy of  $\text{SnI}_4$  into  $\text{SnI}_3 + \text{I}$  is 2.6 volts. The 2450 Å. max. is probably associated with  $\text{SnI}_4 \rightarrow \text{SnI}_2 + 2\text{I}$ .

T. G. P.

Absorption spectrum of tellurium dibromide vapour. J. LARIONOV (Acta Physicochim. U.R.S.S., 1935, **2**, 67—80).—The spectrum consists of diffuse bands without heads, grouped in triplets, of which the 8 most characteristic lie between 6255 and 5684 Å. Heats of dissociation of  $\text{TeBr}_2$  have been calc. from thermochemical data, and the possible dissociation processes are discussed in relation to the band spectrum.

R. S.

Absorption spectra of the vapours, and determination of the heats of sublimation of (I) the monoxides, (II) the monosulphides, of copper, iron, nickel, and cobalt. H. TRIVEDI (Proc. Acad. Sci. Agra and Oudh, 1935, **5**, 27—33, 34—40).—I. The spectrum of the vapours of  $\text{CuO}$  and  $\text{FeO}$  showed only one region, and of  $\text{NiO}$  and  $\text{CoO}$  two regions, of continuous absorption. The long- $\lambda$  limits are:  $\text{FeO}$  2500;  $\text{NiO}$  3270, 2380;  $\text{CoO}$  2750, 2100;  $\text{CuO}$  2410 Å. The difference between the limits of the two regions was approx. 32 kg.-cal. in each case; this may be due to dissociation into the metal atom and  $\text{O} (^3P)$  and  $\text{O} (^1D)$ . The calc. heats of vaporisation of  $\text{FeO}$ ,  $\text{CoO}$ , and  $\text{NiO}$  are 97.5, 101.5, and 111.5 kg.-cal., respectively.

II. The vapours of the sulphides showed continuous absorption from a long-wave limit, resulting in photo-dissociation into two normal atoms; after the first absorption there is a retransmitted patch and

a second absorption. The energy difference 1.31 volts is attributed to the difference  $^3P \rightarrow ^1D$  of S. The heats of vaporisation, determined indirectly, were FeS 93, NiS 101.6, CoS 89, and CuS 84 kg.-cal.

N. M. B.

**Continuous absorption spectrum of hydrogen bromide.** C. F. GOODEVE and A. W. C. TAYLOR (Proc. Roy. Soc., 1935, A, 152, 221—230).—The extinction coeffs. of HBr have been measured over a wide range of conditions, and the approx. upper potential energy curve has been calc. from the eigenfunction of the ground state and the observed extinctions. The results favour the dissociation into normal atoms.

L. L. B.

**Absorption spectrum of water in the ultra-violet.** E. HAAS (Biochem. Z., 1935, 282, 224—229).—A method for determination of the absorption of  $H_2O$  is described and tables summarise the results. The dissociation const. of  $H_2O$  is  $0.6 \times 10^{-14}$  at  $17^\circ$  and  $2.5 \times 10^{-14}$  at  $37^\circ$ . By raising the temp. to  $20^\circ$ , the  $[OH^-]$  increases from  $0.77 \times 10^{-7}$  to  $1.58 \times 10^{-7} N$ . Since  $10^{-7}$ — $10^{-6} N$ -NaOH absorbs as does  $H_2O$ , and since saturation with  $CO_2$  has little effect on the absorption, the effect of temp. on absorption cannot be explained in terms of dissociation.

P. W. C.

**Ultra-violet absorption of mixtures of  $NO$ ,  $NO_2$ , and  $H_2O$ .** E. H. MELVIN and O. R. WULF (J. Chem. Physics, 1935, 3, 755—759).—In the presence of a trace of  $O_2$  or  $NO_2$  in  $NO$ , a continuous absorption in the ultra-violet obscures the absorption of  $NO$  and part of that of  $NO_2$ ; the behaviour of this absorption relative to temp. and partial pressure of the constituents points to  $N_2O_3$ . When, in addition, traces of  $H_2O$  vapour are present, a group of bands appears in the region 4000—3000 Å., decreasing in intensity with rise of temp.; there is evidence of a predissociation process in the carrier, probably HONO.

N. M. B.

**Effect of heavy water of crystallisation on the line absorption spectrum of chrome alum.** G. JOOS and H. BOHM (Physikal. Z., 1935, 36, 826—827).—Replacement of  $H_2O$  in K Cr Se alum by  $D_2O$  causes considerable displacement of the absorption lines.

A. J. M.

**Influence of pressure and foreign gases on the optical absorption of chromyl chloride.** M. KANTZER (Compt. rend., 1935, 201, 1030—1031; cf. A., 1934, 472).—Absorption by the A series increases with pressure, whilst that of the B and C series diminishes. Addition of  $H_2$  up to 1 mol. proportion increases the general absorption, especially at longer  $\lambda$ . Similar effects observed with A,  $N_2$ ,  $CO_2$ ,  $SCl_2$ , and  $SF_6$  decrease regularly with increasing mol. wt.

T. G. P.

**Absorption, optical activity, and configuration of metal complexes.** J. P. MATHIEU (Compt. rend., 1935, 201, 1183—1184; cf. A., 1934, 944).—Examination of the visible absorption bands of 20 Co, Cr, and Ir complexes of the type  $[Co en_2 A A']$  shows that the  $\lambda$  of the max. increases with the mobility of the groups A or A' in the order I, Br, Cl, CNS,  $NO_2$ . Absorption shows a principal and a feeble subsidiary band, confirmed by measuring the circular dichroism,

which is also a means of comparing the configurations of active ions.

T. G. P.

**Paramagnetism. III. Light absorption in paramagnetic crystals and solutions.** S. DATTA and M. DEB (Phil. Mag., 1935, [vii], 20, 1121—1136; cf. A., 1934, 832).—Absorption spectra data are given for anhyd. and hydrated crystals of paramagnetic halides of the Fe group and their solutions at different temp. in  $H_2O$ , EtOH, or conc. HCl. The absorption max. for solutions of  $CrCl_3$ ,  $CoCl_2$ , and  $NiCl_2$  are shifted, relative to the max. in aq. solutions, to the longer- $\lambda$  side when the solvent has dielectric const.  $<$  that of  $H_2O$ , or when it contains excess of HCl; for the latter type of solutions, at low temp. the bands recede towards the shorter- $\lambda$  side and agree with those of the hydrated complexes, as in the aq. solutions. For powdered anhyd. chlorides the absorption max. lie in the longer- $\lambda$  side relative to those of the corresponding hydrated complexes, and agree fairly well with the positions for EtOH and HCl solutions at higher temp. Results are discussed relative to a theory of absorption by a transition group ion forming part of a complex ion or of an undissociated mol.

N. M. B.

**Absorption spectra of nitrophenylhydrazines.** A. K. MACBETH and J. R. PRICE (J.C.S., 1935, 1563—1567).—The absorption spectra of o-, m-, and p- $NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$  in EtOH and aq. EtOH (20%) have been compared with those of o-, m-, and p- $NO_2 \cdot C_6H_4 \cdot NH_2$  and  $-NO_2 \cdot C_6H_4 \cdot NMe_2$  (cf. A., 1934, 997). It is shown that the long-wave absorption is probably due to electronic excitation of the  $\cdot NO_2$  influenced by the nuclear  $\cdot NH_2$  or  $\cdot NH \cdot NH_2$ . This is supported by the fact that bands due to each influenced  $\cdot NO_2$  still persist in 4:6-dinitrotolyl- and 2:4-dinitrophenyl-hydrazine, although displaced by 2200  $cm^{-1}$ . The band max. for 1:2:4- $C_6H_3(NO_2)_3 \cdot NH_2$  can be calc. from the o- and p- $NO_2 \cdot C_6H_4 \cdot NH_2$  vals. using this figure. The band displacements due to the change from EtOH to 20% EtOH solution are similar to those for the nitroamines.

R. S.

**Spectroscopy of amino-acids and their derivatives. I. Ultra-violet absorption of l-tyrosine, dl-phenylalanine, and l-tryptophan.** (Miss) K. FERAUD, M. S. DUNN, and J. KAPLAN (J. Biol. Chem., 1935, 112, 323—328).—dl-Alanine, dl-leucine, l-hystidine dihydrochloride, l-proline, and l-hydroxyproline show general, but  $C_6H_6$ , PhOH, indole, l-tyrosine, dl-phenylalanine, and l-tryptophan show selective, absorption (band max. given) in the ultra-violet region.

R. S. C.

**Flame spectra of some aromatic compounds.** W. M. VAIDYA (Proc. Indian Acad. Sci., 1935, 2, A, 352—357; cf. A., 1935, 279).—Investigations with a Smithells flame separator are extended to  $C_6H_6$ , PhMe, PhOH, resorcinol, pyrogallol, PhCHO, BzOH,  $Ph_2O$ ,  $NH_2Ph$ ,  $PhNO_2$ , and  $C_5H_5N$ . The bands attributed to HCO were found in the spectra of the flames of  $C_6H_6$  and other aromatic compounds, and are attributed to the double linking of the  $C_6H_6$  ring and the breaking up of oxygenated mols. formed by direct incorporation of the  $O_2$  mol. There is a gradual variation in the spectra of the flames of aliphatic series, and more uniformity in the spectra of aromatics.

Light is thrown on the mechanism of combustion of  $C_6H_6$  by the spectra of  $C_5H_5N$ ,  $NH_2Ph$ , and  $PhNO_2$  flames in which the CN bands and the  $\gamma$ -bands of NO appear; the rupture of the ring seems to take place at the N atom. A tentative scheme for the combustion of  $C_6H_6$  is given. N. M. B.

**Barium hydride spectra in the infra-red.** P. G. KOONTZ and W. W. WATSON (Physical Rev., 1935, [ii], 48, 937—938; cf. A., 1935, 427).—Analyses and frequency assignments of the (1,0), (1,1), and (2,1) bands of the  $^2\Sigma \rightarrow ^2\Sigma$  system of BaH, and some details of the  $^2II \rightarrow ^2\Sigma$  band at 10,300 Å., are given. The spin doubling const. of the upper  $^2\Sigma$  state is  $-4.88$ , decreasing with increasing mol. rotation. N. M. B.

**Overtone absorption bands of gaseous HF.** D. E. KIRKPATRICK and E. O. SALANT (Physical Rev., 1935, [ii], 48, 945—948).—Measurements of the 3  $\leftarrow$  0 and 4  $\leftarrow$  0 vibration-rotation absorption bands are described and discussed, and mol. consts. are tabulated. N. M. B.

**Photography of the third harmonic of hydrogen chloride.** A. P. CLEAVES and C. W. EDWARDS (Physical Rev., 1935, [ii], 48, 850).—The wave-no. of the band origin of the third harmonic at 9153 Å. is 10,922.7  $cm^{-1}$ . Vals. and consts. calc. from previous available data are given. N. M. B.

**Infra-red absorption bands of methane.** A. H. NIELSEN and H. H. NIELSEN (Physical Rev., 1935, [ii], 48, 864—867; cf. following abstract).—The fundamental vibration-rotation bands at 3.3 and 7.7  $\mu$  have been remeasured, and, for the latter, additional complex rotational structure data are reported. The two combination bands at 4218 and 4315  $cm^{-1}$  have been partly resolved. N. M. B.

**Infra-red absorption spectrum of germane.** W. B. STEWARD and H. H. NIELSEN (Physical Rev., 1935, [ii], 48, 861—864; cf. A., 1935, 914).—Data and identifications in the range 1—13  $\mu$  of  $GeH_4$  are given for intense absorption regions, in order of intensity, at 4.74, 10.7, 3.4, and 2.3  $\mu$ ; there is a much weaker peak near 5.7  $\mu$ . Calc. vals. are: moment of inertia of the mol.  $7.0 \times 10^{-40}$  g.- $cm^2$ ; distances Ge—H  $1.37 \times 10^{-8}$ , H—H  $2.06 \times 10^{-8}$  cm. N. M. B.

**Symmetry considerations concerning the splitting of vibration-rotation levels in polyatomic molecules.** E. B. WILSON, jun. (J. Chem. Physics, 1935, 3, 818—821).—The max. no. of fine-structure components, their quantum wts. when nuclear spin is taken into account, and the selection rule for transitions are discussed in relation to the permutation symmetry of mols. containing several identical atoms. N. M. B.

**Raman spectra of the isotopic molecules  $H_2$ , HD, and  $D_2$ .** G. K. TEAL and G. E. MACWOOD (J. Chem. Physics, 1935, 3, 760—764).—Analyses are given for 42 lines excited at 3 atm. pressure by Hg  $\lambda$  2537. New vibrational consts. calc. from the Raman and emission spectrum data of  $H_2$  and HD give calc. vals. of the positions of the rotational-vibration Raman lines in good agreement with observation. Contrary to theory, the 0,0 line of the Q vibrational band of HD was observed. N. M. B.

**Raman effect and molecular structure.** B. SUSZ (Ann. Guebbard-Séverine, 1935, 11, 12—25).—A summary of the theory and technique.  $N_2O_5$  in  $HNO_3$  affords the Raman frequencies 1050 and 1399  $cm^{-1}$ , in addition to those due to  $HNO_3$ . J. G. A. G.

**Raman spectra. I. Raman spectra of sulphuric, nitric, and nitrosylsulphuric acids.** W. R. ANGUS and A. H. LECKIE (Proc. Roy. Soc., 1935, A, 149, 327—340).—Raman spectra are recorded for conc.  $H_2SO_4$  and  $HNO_3$ , for solutions of nitrosylsulphuric acid ( $HNSO_5$ ) in  $H_2SO_4$ , and for solid  $HNSO_5$ . From the spectra of  $HNSO_5$  in various concns. of  $H_2SO_4$  it is concluded that in solutions of  $HNSO_5$  in  $H_2SO_4$  containing  $> 60\%$   $H_2SO_4$  the hydrolysis of  $HNSO_5$  is incomplete. The spectra of  $HNSO_5$ , both in solution and in the solid state, are characterised by a prominent frequency of 1045  $cm^{-1}$  assignable to  $HSO_4'$ . Another prominent frequency of 2340  $cm^{-1}$  in solutions and 2311  $cm^{-1}$  in the solid is shown, by analogy with band spectral data for iso-electronic groups, to arise from  $NO^+$ . Of the different mol. structures reviewed, only  $[HOSO_3]'[NO]'$ , nitrosyl sulphate, is in agreement with observed data. W. R. A.

**Raman spectrum of crystalline selenious acid.** C. S. VENKATESWARAN (Current Sci., 1935, 4, 309—310).—Transparent crystals give an intense Raman spectrum consisting of a large no. of sharp lines, in some cases the anti-Stokes being present. As in the case of  $HIO_3$  (cf. A., 1935, 1301), the spectrum of the solid differs markedly from that of the aq. solution. N. M. B.

**Raman effect of fluosilicic acid.** J. K. SIRKIN and M. V. VOLKENSTEIN (Acta Physicochim. U.R.S.S., 1935, 2, 308—312).— $H_2SiF_6$  shows a strong Raman line at 649  $cm^{-1}$  (cf. 314 and 337 for  $SnCl_6''$  and  $SbCl_6'$ , respectively; A., 1933, 113), but no other. This indicates the symmetrical vibration of six F atoms at the corners of a regular octahedron, in accord with X-ray data. J. W. S.

**Raman effect. XLIX. Mixture of phosphorus trichloride and tribromide.** O. BURKARD. L. Vibrational spectrum of benzene. K. W. F. KOHLRAUSCH (Z. physikal. Chem., 1935, B, 30, 298—304, 305—315).—XLIX. In the Raman spectra of mixtures of  $PCl_3$  and  $PBr_3$  the valency frequencies of  $PCl_3$  rise and those of  $PBr_3$  fall with falling  $[PCl_3]$ , whereas judged from the dipole moments the reverse would be expected. The intensity of the lines due to  $PCl_3Br$  is a max. in the mixture  $2PCl_3 + PBr_3$  (cf. A., 1931, 785).

L. Regarding  $C_6H_6$  and  $C_6D_6$  as valency force systems with the symmetry  $D_{6h}$  and applying Wilson's theory (A., 1934, 829), five of the six force consts. necessary for stability have been calc. and have nearly the same vals. for each compound. From these have been deduced 16 of the 20 possible fundamental frequencies, and these and the selection rules are in almost quant. agreement with the observed vibrational spectrum (cf. A., 1935, 1301). For  $C_5H_5N$  the selection rules point to a ring system with "equalised" linkings and the symmetry  $C_{2v}$ . R. C.

**Raman spectra of solutions. II. Solutions of arsenic trichloride in methyl and ethyl alcohols.**



A. M. SACK and A. E. BRODSKI (*Acta Physicochim. U.R.S.S.*, 1935, 2, 215—220).—In the Raman spectra of  $\text{AsCl}_3$  in EtOH and MeOH, respectively, the frequencies of the alcohols are unchanged; those of  $\text{AsCl}_3$  at 372 and 410  $\text{cm}^{-1}$  are lowered. Denoting the four mol. frequencies of  $\text{AsCl}_3$  (which is a regular pyramid) by  $\omega_1, \omega_2, \omega_3$ , and  $\omega_4$ , the ratio  $\omega_1\omega_2/\omega_3\omega_4$  remains almost const. The  $\text{AsCl}_3$  mol. is thus only slightly deformed by the alcohol dipoles, but the elastic binding force between  $\text{As}^{+++}$  and  $\text{Cl}^-$  changes by about 10% in alcoholic solutions. A. J. M.

**Raman spectrum of tetraethylammonium iodide.** J. K. SIRKIN and M. V. VOLKENSTEIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 303—307).—The Raman spectrum of  $\text{NEt}_4\text{I}$  is compared with those of  $\text{NEt}_3$  and of EtI. None of the C-I or N-I frequencies are observed, indicating that the I of  $\text{NEt}_4\text{I}$  is ionically bound, and occurs outside the co-ordination sphere, in accord with the behaviour of  $\text{NEt}_4\text{I}$  as a binary electrolyte. The Raman spectrum observed is therefore that of  $\text{NEt}_4^+$ , and the strong lines of  $\text{NEt}_3$  occur, in some cases with modified frequency, with the exception of the 739  $\text{cm}^{-1}$  line. New strong frequencies are observed at 667 and 1231  $\text{cm}^{-1}$ . It is concluded that  $\text{NEt}_3$  is a pyramidal mol. with the N at the apex, whilst  $\text{NEt}_4^+$  is a regular tetrahedron with the N in the centre. J. W. S.

**Vibrations of benzene and Raman spectra of benzene- $d_1$  and benzene- $d_2$ .** O. REDLICH and W. STRICKS (*J. Chem. Physics*, 1935, 3, 834).—Raman data are reported. Experimental error cannot account for the increase from 2270 (PhD) to 2279 ( $\text{C}_6\text{H}_4\text{D}_2$ ). A test relation applied to these and the results of Wood for  $\text{C}_6\text{D}_6$  (cf. A., 1935, 1189) shows that Wilson's correlations of frequencies to vibrations (cf. *Physical Rev.*, 1934, [ii], 46, 146) cannot all be correct. N. M. B.

**Rotational Raman scattering in benzene.** S. BHAGAVANTAM (*Proc. Indian Acad. Sci.*, 1935, 2, A, 342—344).—Contrary to the results of Sirkar (cf. A., 1935, 914), the intensity distribution in the rotation wing accompanying the Rayleigh lines is in exact agreement, using a high-dispersion spectrograph, with results by instruments of lower dispersion. N. M. B.

**Raman effect. LI. Benzene derivatives. IX.** K. W. F. KOHLRAUSCH, W. STOCKMAIR, and (GROSS-PRINZ) YPSILANTI. **LII. Benzene derivatives. X.** A. W. REITZ and W. STOCKMAIR. **LIII. Nucleus-substituted benzoyl chlorides.** K. W. F. KOHLRAUSCH, A. PONGRATZ, and W. STOCKMAIR (*Monatsh.*, 1935, 67, 80—91, 92—103, 104—110; cf. A., 1935, 1190).—LI. Raman spectra of 1:3-dichloro-4-X-benzene ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{CN}, \text{Br}, \text{I}$ ), 1:4-dichloro-2-X-benzene ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{Br}, \text{I}$ ), and 4-chloro-2-X-toluene ( $X=\text{NH}_2, \text{OH}, \text{Br}, \text{I}$ ) have been measured.

LII. Raman spectra of the following are given:  $\text{CH}_2\text{PhX}$  ( $X=\text{NH}_2, \text{OH}, \text{Me}, \text{CN}, \text{SH}, \text{Cl}, \text{Br}$ ); *o*-, *m*-, and *p*- $\text{XC}_6\text{H}_4\text{NO}_2$  [ $X=\text{Cl}, \text{Br}, \text{OH}, \text{CN}$  (*m*-, *n*-), *F* (*p*-)];  $\text{PhNO}_2$ ;  $\text{PhSO}_2\text{Cl}$ .

LIII. Raman spectra of *o*-, *m*-, and *p*- $\text{XC}_6\text{H}_4\text{COCl}$  ( $X=\text{Me}, \text{Cl}, \text{Br}, \text{COCl}, p\text{-OMe}$ ) are given. The results are discussed theoretically. F. L. U.

**Raman spectra of hydroxy-acids and their esters and salts.** I. PEYCHES (*Bull. Soc. chim.*, 1935, [v], 2, 2195—2209; cf. A., 1935, 146).—Data are recorded for  $\text{AcOH}$ ,  $\text{KOAc}$ ,  $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{H}$ ,  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ ,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ , and lactic acid,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ ,  $[\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}]_2$ , their Et esters and Na salts. The results are discussed from the point of view of the structure of the  $\cdot\text{CO}_2\text{H}$  group and of the tartaric acid mol. and anion. F. L. U.

**Raman spectra of glasses.** T. G. KUJUMZELIS (*Z. Physik*, 1935, 97, 561—569).—Raman spectra of different Jena glasses show different characteristic features; a displacement of approx. 800  $\text{cm}^{-1}$  is present in all glasses examined independent of the presence or absence of the  $\text{SiO}_2$  group. A. B. D. C.

**Polarisation of scattered Raman light.** W. HANLE and F. HEIDENREICH (*Physikal. Z.*, 1935, 36, 851—853).—The edges of the Rayleigh lines are polarised in quite a different manner from the centres. The inversion factor (ratio of left to right circularly polarised light) is 6 if there is only rotational widening of the lines, whereas the experimental val. for PhMe is 1.7. There are, therefore, causes of widening of the lines other than rotation. The circular polarisation of the Raman lines of some substances has been determined, and from the inversion factor,  $U$ , the degree of depolarisation  $\rho_n$  has been calc. from Placzek's formula. The same vals. for  $\rho_n$  were found for right circularly polarised lines as for linearly polarised rays, but there were differences for left circularly polarised light. The rotational widenings of the Raman lines are always left circularly polarised, whilst the centres are right circularly polarised. The dispersion of polarisation of the scattered Raman light was investigated, the results disagreeing with those of Sirkar. The degree of polarisation is independent of  $\lambda$  outside the regions of absorption. Assuming that, in general, the polarisation of the line due to the same vibration in different substances is the same, the Raman lines of a no. of org. Cl-derivatives are assigned to their different mol. vibrations. A. J. M.

**$U$  Centres in alkali halide crystals.** P. TARTAKOVSKI and V. PODDUBNI (*Z. Physik*, 1935, 97, 765—773).—NaCl heated to 550—600° absorbs intensely near 1.2  $\mu$ , corresponding with electron transition from the ground to the  $U$  level. Electrons in this level can combine with  $\text{Cu}^+$  ions to colour the crystal red. A. B. D. C.

**Thermal formation of colour centres and their life-period.** R. HILSCH (*Physikal. Z.*, 1935, 36, 735—737).—The equilibrium between the  $U$  and  $F$  centres in KBr crystals with a stoichiometric excess of K is examined. The variation of the "degree of dissociation" of the  $U$  centres with temp. and concn. is determined by means of absorption experiments. The life-period of the  $F$  centres is also found. (Cf. this vol., 139.) A. J. M.

**Thermal diffusion of colour centres.** O. STASIW (*Physikal. Z.*, 1935, 36, 737—740).—The diffusion const. of  $F$  centres in KCl crystals in which the stoichiometric excess of K existed only in the form of these centres has been determined. From the

diffusion const. and the known mobility of the colour centres in an electric field, the mobility of the positive charges in the crystal is determined. The positive charges move more rapidly than electrons at temp.  $>700^\circ$ . Below this temp. retardation of electrons occurs owing to the positive charges. A. J. M.

**Photodissociation of stannous chloride vapour in the Schumann region.** H. NEUJMIN (Acta Physicochim. U.R.S.S., 1935, 2, 595—602; cf. A., 1934, 1286).—Fluorescence is excited in  $\text{SnCl}_2$  vapour in the visible region by  $\lambda$  1700—1800, and in the ultra-violet by  $\lambda$  1500—1700 Å. Analysis of the observed spectrum indicates photodissociation into Cl and excited  $\text{SnCl}$ . The energy required is calc. to be 90 kg.-cal. per mol. F. L. U.

**Correspondence between absorption and luminescence spectra of dilute solutions of dyes.** IV. Effect of temperature and solvents. V. L. LEVSHIN (Acta Physicochim. U.R.S.S., 1935, 2, 221—238; cf. A., 1935, 808).—Absorption and luminescence spectra of eosin B in  $\text{H}_2\text{O}$ , isoamyl alcohol, and  $\text{COMe}_2$ , and of erythrosin and rhodamine 6G in  $\text{H}_2\text{O}$  and  $\text{COMe}_2$ , have been investigated with respect to temp. and solvent. The symmetry of form of the two spectra is maintained in all cases. Change of solvent causes displacement of both absorption and luminescence spectra, the max. undergoing equal displacements. The direction of the displacement is not determined by the dielectric const. of the solvent. The area of the absorption spectrum is approx. the same for all solvents, although the luminescence efficiency,  $\eta$ , varies greatly. The variation of  $\eta$  with temp. is independent of dye concn. and of the properties of the solvent. A. J. M.

**Fluorescence spectra of chlorophyll pigments.**—See this vol., 125.

**Spectrographic investigation of the thermoluminescence of feldspar.** S. IMORI and E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 147—151).—The position of the thermoluminescence bands is unaffected by treatment with X-rays, but their intensity is increased. Data are given for 12 Japanese feldspars. The bands generally lie in the yellow and blue. R. S.

**Induced chemiluminescence of mercury in the carbon monoxide-oxygen flame.** V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1935, 2, 126—128).—Hg becomes chemiluminescent in  $\text{CO} + \text{O}_2$  at 650—700°. Since the line 2537 Å. is below the shortest  $\lambda$  of the CO flame spectrum, it is concluded that the activation must be due to collision with excited  $\text{CO}_2$ . A similar mechanism is proposed for the activation of  $\text{N}_2$  in the explosion of  $\text{CO} + \text{O}_2 + \text{N}_2$  at high pressures. R. S.

**Quantum equivalence of photo-electric conductivity in rock-salt crystals.** Z. GYULAI and P. TOMKA (Z. Physik, 1935, 96, 350—354).—Arsenjeva's results (A., 1926, 782) showing non-equivalence of absorbed light and conductivity are due to colloidal particles in the test-piece. A. B. D. C.

**Electronic conduction in silver and thallium halide crystals.** I. Electron yield on light

absorption in spectral regions of high absorption. II. Photo-electric secondary current. W. LEHFELDT (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 171—186; Chem. Zentr., 1935, i, 2322).—I. In electric fields giving saturation of the primary current in  $\text{TlBr}$  at  $-70^\circ$ , and in  $\text{AgCl}$  at  $-170^\circ$ , all photo-electrons move to the anode, the positive charge remaining stationary. In the ultra-violet absorption region the quantum yield is 0.1—0.5.

II. Crystals with long displacement paths for primary photo-electrons tend to give rise to secondary current, due to electrons drawn from the cathode. J. S. A.

**Electronic conduction of cuprous oxide.** W. SCHOTTKY and F. WAIBEL (Physikal. Z., 1935, 36, 912—914).—The sign of the Hall effect and the mechanism of conduction of specimens of  $\text{Cu}_2\text{O}$  with and without excess of  $\text{O}_2$  are discussed. A. J. M.

**Conductance of salt crystals.** W. H. RODEBUSH and T. G. COOKE (J. Chem. Physics, 1935, 3, 834).—Jost's expression (cf. A., 1934, 11) is inadequate to account for the conductance behaviour of various salts throughout the whole temp. range; it can be obtained by merely general considerations. N. M. B.

**Rate of migration of cations in alkali halide crystals.** O. STASIW (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 147—152; Chem. Zentr., 1935, i, 2318—2319).—The cation mobility increases exponentially with rise of temp., and equals that of electrons at 600—700°. H. J. E.

**Problems of ionic and electronic conduction in non-metallic solids.** B. GUDDEN and W. SCHOTTKY (Physikal. Z., 1935, 36, 717—721).—The different types of ionic conduction are discussed. The mechanism of electronic conduction on the basis of permitted and forbidden energy states is considered and applied to semi-conductors. The energy states may be determined by means of the photo-electric effect and the fine structure of X-ray absorption edges. A. J. M.

**Disorder phenomena in ionic lattices as a basis for ionic and electronic conduction.** C. WAGNER (Physikal. Z., 1935, 36, 721—725).—The types of disarrangement in the crystal lattice giving rise to the possibility of conduction are discussed. The conductivity ( $\kappa$ ) of oxides varies with the pressure ( $p$ ) of  $\text{O}_2$  above them. In this connexion, three classes of oxides may be considered: (1) those for which  $\kappa \propto p^{-1/4}$ , e.g.,  $\text{ZnO}$ ,  $\text{CdO}$ ; (2) those for which  $\kappa \propto p^{1/7}$ , e.g.,  $\text{Cu}_2\text{O}$ ,  $\text{FeO}$ ; (3) those for which  $\kappa$  is independent of  $p$ , e.g.,  $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ . The behaviour of oxides of class (1) is governed by dissociation of the oxide giving an excess of metal in solid solution in the oxide phase. With class (2), places with electron defect are formed in the lattice. Electron-defect conductivity is to be expected in those cases where the ions are in an intermediate valency state, whereas electron-excess conductivity is found where the ion is exerting its max. valency. The behaviour of  $\text{Co}_3\text{O}_4$  is explained on the basis of its lattice structure. A. J. M.

**Theory of electron motion in non-metallic crystal lattices.** F. HUND (Physikal. Z., 1935, 36, 725—729).—The description of the states of electrons

in solids is discussed from the viewpoint of quantum mechanics. The arrangement of energy bands in non-metallic ideal and distorted lattices is considered.

A. J. M.

**Electronic conduction in alkali halide crystals.** R. W. POHL (Physikal. Z., 1935, 36, 732—735).—The electronic conduction of a KBr crystal with a stoichiometric excess of K (part of the Br replaced by electrons) is considered. The excess of metal may exist as  $U$  (ultra-violet absorption) centres, or as  $F$  (visible absorption) centres. The production of, and thermal equilibrium between, these centres are discussed. The movements of electrons to the anode can be followed with the eye by means of the  $F$  centres. Crystals with  $U$  centres are semi-conductors. It is possible with the KBr crystal under consideration to determine the variation of both the no. and mobility of the electrons with temp. Crystals with  $U$  centres behave as photo-electric conductors for which the law of the quantum equiv. holds accurately.

A. J. M.

**Electrical conduction in melts of alkali salts with a stoichiometric excess of alkali metal.** E. MOLLWO (Physikal. Z., 1935, 36, 740—742).—The optical properties of alkali salts with a stoichiometric excess of metal indicate that the excess metal is dissolved in the form of neutral atoms. Electron conductivity was not found.

A. J. M.

**Formation of opposing potentials in solid ionic conductors.** A. SMEKAL (Physikal. Z., 1935, 36, 742—749).—Results previously obtained on the decrease with time of the d.c. conductivity of purely ionic conductors are summarised. The Maxwell-Wagner theory of dielectric anomalies, and the Jaffe theory of ions with retarding atm. (A., 1933, 338) fail to account for the facts. The most satisfactory explanation is based on the distortion conduction theory, according to which the formation of the opposing potential is due to retardation of the conducting ions in the structurally inhomogeneous crystal.

A. J. M.

**Electrical conduction in semi-conductors.** W. MEYER (Physikal. Z., 1935, 36, 749—755).—The nature of the consts.  $a$  and  $B$  in the equation  $\kappa = ae^{-B/T}$  connecting conductivity,  $\kappa$ , with abs. temp.,  $T$ , is discussed. No numerical val. can be assigned to  $a$  which will hold for all semi-conductors.  $\log \kappa = -kB$ , where  $k$  is const., is true as a first approximation. The connexion between  $a$  and  $\kappa$  was investigated for  $\text{TiO}_2$ .

A. J. M.

**Calculation of the magnitude and pressure dependence of ionic-disorder energy and mobilities in crystals.** W. JOST (Physikal. Z., 1935, 36, 757—760).—A rough calculation of the disorder energy of ions in crystals is possible from a consideration of the polarisation effect. The effect of pressure on the conductivity and degree of disorder is discussed. If the degree of disorder is affected by temp. it should be possible to arrive at disorder energies from consideration of sp. heats.

A. J. M.

**Electrical conductivity of cuprous oxide in equilibrium with its adjacent phase.** F. WAIBEL (Physikal. Z., 1935, 36, 760—764).—The cold con-

ductivity of  $\text{Cu}_2\text{O}$  plates in equilibrium with Cu after having been heated to temp. between  $10^\circ$  and  $1000^\circ$  was determined and plotted against temp. A max. occurs at a tempering temp. of  $400$ – $500^\circ$ , corresponding with a similar max. in the same curve for  $\text{Cu}_2\text{O}$  in equilibrium with  $\text{CuO}$ . The formation of the rectifying layer of  $\text{Cu}_2\text{O}$  rectifiers is discussed on the basis of this investigation. The amount of  $\text{O}_2$  dissolved in the  $\text{Cu}_2\text{O}$  was determined.

A. J. M.

**Specific resistance of cuprous oxide.** W. H. BRATTAIN (Physical Rev., 1934, [ii], 45, 745).—The sp. resistance of  $\text{Cu}_2\text{O}$  grown on Cu at  $1030^\circ$  in air is not uniform, but varies exponentially in the direction of growth of the oxide.

L. S. T.

**Determination of the metal-cuprous oxide contact resistance.** J. ROULLEAU (Compt. rend., 1935, 201, 947—948).—The factors controlling the Cu- $\text{Cu}_2\text{O}$  contact resistance were studied. High resistances occur only for cryst. surfaces.

H. J. E.

**Effect of cooling on the electrical properties of resistances which vary with temperature.** H. LUEDER and E. SPENKE (Physikal. Z., 1935, 36, 767—773).—The effects of cooling in various ways (e.g., at the edges, at the front of a plate, etc.) have been examined.

A. J. M.

**Conductivity of glasses.** R. L. MULLER (Acta Physicochim. U.R.S.S., 1935, 2, 103—125; cf. A., 1935, 567).—The Frenkel theory of electrical conductivity has been applied to glasses. Alkali-rich glasses approach the ion-lattice type, whilst alkali-poor glasses approx. to liquid salt solutions. The influence of the association of polar mols. on the conductivity has been studied in various glasses.

R. S.

**Dielectric coefficients of volatile compounds of fluorine and boron.**  $\text{CF}_4$ ,  $\text{NF}_3$ ,  $\text{CHF}_3$ ,  $(\text{CF}_3\text{N})_2$ ,  $\text{B}_2\text{H}_6$ , and  $\text{B}_3\text{N}_3\text{H}_6$ . K. L. RAMASWAMY (Proc. Indian Acad. Sci., 1935, 2, A, 364—377).—Data for dielectric coeffs. measured at different temp. are quoted, and give vals. of the electric moments 0, 0.21, 1.59, 0.46, 0, and  $0.67 \times 10^{-18}$ , respectively. Accurate vals. of compressibilities at room temp. by refractometric studies, and approx. vals. at low temp. by studying variations of dielectric coeffs. are given.

N. M. B.

**Discontinuity in the dielectric constant of liquids and their saturated vapours at the critical temperature.** J. MARSDEN and O. MAASS (Canad. J. Res., 1935, 13, B, 296—307).—A dielectric cell of small dimension for simultaneous liquid and gas measurements in the crit. temp. region is described. The electrodes were sealed in by frozen Hg capillary seals. Data are given for  $\text{Me}_2\text{O}$  and  $\text{C}_3\text{H}_8$  from room temp. to  $8^\circ$  above the crit. temp. The dielectric consts.,  $\epsilon$ , of liquid and gas were not identical at the crit. temp. Above the crit. temp. (for up to  $8^\circ$ ) a difference in  $\epsilon$  persisted between the medium above and below the position where the liquid meniscus was last seen, in spite of stirring of the medium.

H. J. E.

**Dependence of dielectric constants of anisotropic liquids on field strength and frequency.** W. KAST (Physikal. Z., 1935, 36, 869—873).—The

decrease of dielectric const.,  $\epsilon$ , of anisotropic liquids, e.g., *p*-azoxyanisole, with increase of field strength reaches a saturation val. at approx. 1000 volts per cm., and is regarded as a dipole saturation effect. Calculation shows that the saturation val. of  $\epsilon$  should be equal to the val. for the solid substance, but actually it is considerably greater, since not only does the mean moment of the mol. groups contribute to the orientation polarisation, but the single polar mols. within the groups are sufficiently movable to take part.

A. J. M.

**Electrical moments of *p*-benzoquinone and related compounds.** D. L. HAMMICK, G. C. HAMPSON, and G. I. JENKINS (Nature, 1935, 136, 990—991).—The following vals. of  $P_{A+O}$  (c.c.) have been obtained: *p*-benzoquinone 8.9 in  $C_6H_6$ , 9.6 in  $CCl_4$ , and 8.6 in  $n-C_6H_{14}$ ; and in  $C_6H_6$  2:5-dimethyl- 9.4, and 2:5-dichloro-1:4-benzoquinone 8.8, and tetramethylcyclobutane-1:3-dione 11.0. These vals. are apparently due either to a general effect of the solvent or to an abnormally large atom polarisation. L. S. T.

**Dipole moments of cyclohexa-1:4-dione, cyclopentadienebenzoquinone, benzoquinone, carbon suboxide, and carbonyl chloride.** C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 1696—1701).—The dielectric consts.,  $d$ , and  $n$ , of solutions of the above substances in  $C_6H_6$  and  $CCl_4$  have been determined, and the total polarisations, mol. refractivities, orientation polarisations, and dipole moments of the solutes have been calc. The dipole moment of cyclohexa-1:4-dione is 1.3 *D*, indicating a comparatively low *cis*-content. The mol. refractivity (27.8) shows that it is entirely ketonic. The dipole moment of cyclopentadienebenzoquinone is 1.39 *D*, and of *p*-benzoquinone 0.69 *D*. The orientation polarisation of the latter is approx. the same in  $C_6H_6$  and  $CCl_4$ , and does not vary with temp., results which may be due to the solute mols. not being completely rigid when bombarded by solvent mols. The orientation polarisation of  $C_3O_2$  is approx. 10 c.c., showing that in  $C_6H_6$  solution very little of the cyclic form can exist. The possible structures are reviewed. The dipole moment of  $COCl_2$  in  $CCl_4$  is 1.099 *D*. The size of the Cl—C—Cl angle is discussed.

A. J. M.

**Relation between molecular orientation polarisation of substances in the liquid, dissolved, and gaseous states.** C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1935, 1747—1751).—The relationship  ${}_oP_1/{}_oP_2 = K(\epsilon_2 + 2)/(\epsilon_1 + 2)$ , where  ${}_oP_1$  and  ${}_oP_2$  are the orientation polarisations developed by a mol. when surrounded by media of dielectric const.  $\epsilon_1$  and  $\epsilon_2$ , respectively, has been tested with a no. of pairs of solutions, solutions and solutes in the vapour state, solutions and liquid solutes in bulk, and substances in the pure liquid and gaseous state. It has no general applicability, since probably the mutual influences of mols. in conjunction with their shapes should be taken into account.  ${}_oP_{liq.}/{}_oP_{gas}$  should be given by  $1 - (\epsilon - 1)/(\epsilon + 2)f$ , where  $f$  depends on the shape and polarisability of the mols.

A. J. M.

**Optical dispersion of HCl in the infra-red.** R. ROLLEFSON and A. H. ROLLEFSON (Physical Rev.,

1935, [ii], 48, 779—785).—In view of the large discrepancy between the temp. invariant part of the dielectric const. of HCl and  $n_\infty^2$ , attributed to the contribution of infra-red vibration bands to  $n$ , the optical dispersion of HCl was measured over 1—10  $\mu$ . The val.  $1.00 \pm 0.05 \times 10^{-10}$  e.s.u. obtained for the effective charge of the rotator-vibrator shows that the contribution of the latter to  $n_\infty$  is too small to explain the discrepancy, which appears to be due to uncertainty in the dielectric const. measurements.

N. M. B.

**Refractivity of cellulose as function of the degree of swelling.** M. MEYER and A. FREY-WYSSLING (Helv. Chim. Acta, 1935, 18, 1428—1435).—Measurements of  $n_a$  by the immersion method show  $n$  to decrease regularly, although very slightly, with the H<sub>2</sub>O content of the fibre. Kanamaru's results (A., 1934, 1292) are attributed to displacement of H<sub>2</sub>O by the immersion medium. Reasons for the negligible influence of the adsorbed H<sub>2</sub>O on  $n$  are discussed.

J. S. A.

**Magnetic birefringence of nitric oxide.** H. BIZETTE and T. BELLING (Compt. rend., 1935, 201, 955—956).—Measurements are recorded at 16.5°/80—180 atm.

H. J. E.

**Quantum-mechanical calculation of polarisability and dispersive powers.** H. HELLMANN (Acta Physicochim. U.R.S.S., 1935, 2, 273—290).—Mathematical.

J. W. S.

**Constitution of diborane.** E. WIBURG (Z. anorg. Chem., 1935, 225, 262—269).—A crit. discussion of published work.

E. S. H.

**Constitution of complex metallic salts. III. Parachors of palladium and mercury in simple and complex compounds.** F. G. MANN and D. PURDIE (J.C.S., 1935, 1549—1563; cf. A., 1934, 640).—The parachor of Pd in homologous series of the type  $[(R_2S)_2PdCl_2]$ ,  $[(R_3P)_2PdCl_2]$ ,  $[(R_3As)_2PdCl_2]$  decreases and becomes negative with increasing length of alkyl chain.  $HgEt_2$  and  $Hg(n-C_5H_{11})_2$  do not exhibit this behaviour, whilst in the Hg mercaptides the parachor of Hg decreases to a const. at  $R=n$ -heptyl. Since the parachors of compounds of the type  $CRR'(SEt)_2$  show no abnormality, the above decrease cannot be due to the formation of a group  $\cdot S \cdot X \cdot S \cdot$ . It is shown that the parachors of the metal in ketonic derivatives of Tl, Be, and Al (cf. Sugden, "The Parachor and Valency," 1930) also decrease as the homologous series is ascended, and it is suggested that the effect is due to a diminution in the vol. of the mol. as a whole owing to increased compression resulting from the operation of "strain factors" (cf. A., 1929, 1219). Dipole moments of  $[(Et_3S)_2PdCl_2]$ ,  $[(Et_3P)_2PdCl_2]$ , and  $[(Et_3As)_2PdCl_2]$  have been determined, and it is concluded that these are stable *trans*-compounds, although  $[(Me_3As)_2PdCl_2]$  may have the *cis*-configuration. Densities, surface tensions, and parachors of the following compounds are given:  $Pr^a$ ,  $Bu^a$ , and *n*-amyl sulphides, *di-n*-amyl sulphoxide, m.p. 60°, *n*-hexyl, heptyl, and octyl sulphide, *Ph Bu^a*, b.p. 137—139°/12 mm., and *Bu^b* sulphide, b.p. 126—127°/12 mm.,  $\alpha$ -*bis*(phenylthiol)propane, b.p. 264°/12 mm. [from PhSH and



$\text{CH}_2(\text{CH}_2\text{Br})_2$ ];  $\alpha$ -bis(phenylthiol)acetone, m.p.  $43^\circ$ , similarly prepared from  $\text{CO}(\text{CH}_2\text{Cl})_2$ ; acetone bisethyl mercaptol, b.p.  $84.5\text{--}85^\circ/20$  mm.; *Me Et ketone bisethyl mercaptol*, b.p.  $99\text{--}100^\circ/18.5$  mm.;  $\text{Pr}^a$ ,  $\text{Bu}^a$ , *n*-amyl, hexyl, and heptyl thiols; *Et*,  $\text{Pr}^a$ ,  $\text{Bu}^a$ , and *n*-amyl phosphines, *tri-n-amylphosphine oxide*, m.p.  $59^\circ$ ;  $\text{Et}_3$  phosphite, b.p.  $55^\circ/19$  mm.;  $\text{AsMe}_3$ ,  $\text{AsEt}_3$ ,  $\text{AsPr}^a_3$ , and  $\text{AsBu}^a_3$ . *Bis(dialkylsulphide)palladium compounds* were prepared by addition of a sulphide to aq.  $(\text{NH}_4)_2\text{PdCl}_4$ . The *Me*, *Et*,  $\text{Bu}^a$ , and *isoamyl* dichlorides are described, also the *Me Et dichloride*, m.p.  $67^\circ$ , decomp. on heating,  $\text{Pr}^a_2$  dichloride, m.p.  $59^\circ$ ,  $\text{Pr}^a_2$  dichloride, m.p.  $163^\circ$ ,  $\text{Bu}^a_2$  dichloride, m.p.  $32^\circ$ , *diisoamyl dichloride*, m.p.  $41^\circ$ ; the *n*-heptyl and *octyl* derivatives obtained were impure; the *divinyl dichloride*, orange, decomposes at room temp., the *Ph Bu^a dichloride* has m.p.  $118^\circ$ , and the  $\text{Bu}^a_2$  compound melts at  $96^\circ$ ;  $\text{Ph}_2$  dichloride, orange, m.p.  $170^\circ$ , *dibenzyl dichloride*, orange, m.p.  $154^\circ$ , *bis(diethyl sulphide)palladium dibromide*, deep red, m.p.  $103^\circ$ , *di-iodide*, m.p.  $107\text{--}108^\circ$  (decomp.). Grinding the corresponding dichloride with aq.  $\text{NaNO}_2$  gave pale yellow dinitrites: *Me*, m.p.  $137\text{--}138^\circ$ , *Et*, m.p.  $161\text{--}163^\circ$  (slight decomp.),  $\text{Pr}^a_2$ , m.p.  $163\text{--}164^\circ$ ,  $\text{Bu}^a_2$ , m.p.  $165\text{--}166^\circ$ , *di-n-amyl*, m.p.  $163^\circ$ . The following *bis(trialkylphosphine)palladium compounds* were similarly prepared:  $\text{Et}_3$  dichloride, m.p.  $139^\circ$ , sublimes  $140^\circ$  in vac.,  $\text{Pr}^a_3$  dichloride, m.p.  $96^\circ$  (crystallographic data given);  $\text{Bu}^a_3$  dichloride, m.p.  $66^\circ$ , *dibromide*, m.p.  $73^\circ$ , and *di-iodide*, dark orange, m.p.  $64\text{--}65^\circ$ , *tri-n-amyl dichloride*, m.p.  $47^\circ$ . Alcoholic solutions of the dichlorides gave dinitrites with  $\text{NaNO}_2$ ;  $\text{Pr}^a_3$  dinitrite, m.p.  $167\text{--}168^\circ$  (decomp.). The following *bis(trialkylarsine)palladium salts* are described: *Me*, golden-yellow crystals, m.p.  $235^\circ$  (crystallographic data given),  $\text{Et}_3$ , m.p.  $116^\circ$ ,  $\text{Pr}^a_3$ , m.p.  $55^\circ$ ,  $\text{Bu}^a_3$ , m.p.  $54^\circ$ , and *tri-n-amyl dichloride*, m.p.  $10\text{--}11^\circ$ ;  $\text{Pr}^a_3$  *dibromide*, orange prisms, m.p.  $49^\circ$ ,  $\text{Et}_3$  *dinitrite*, m.p.  $176\text{--}177^\circ$ . Addition of a thiol in  $\text{CHCl}_3$  to  $(\text{NH}_4)_2\text{PdCl}_4$  gave deep reddish-orange *Pd mercaptides*; *Et* derivative, decomp.  $250^\circ$ ,  $\text{Pr}^a$ , m.p.  $209\text{--}210^\circ$  (crystallographic data given),  $\text{Bu}^a$ , m.p.  $142^\circ$ , *n-amyl*, m.p.  $83^\circ$ , whilst the amorphous vermilion  $\text{Ph}_2$  derivative is formed when  $\text{PhSH}$  is added to  $\text{EtOH}$  or  $\text{COMe}_2$  solutions containing  $[(\text{R}_2\text{S})_2\text{PdX}_2]$ , and gives *Pd* on heating. *Pd* can be determined in this way. Addition of a thiol to  $\text{HgO}$  gave the *Hg alkyl mercaptides*: *Et*, m.p.  $77^\circ$ ,  $\text{Pr}^a$ , m.p.  $67^\circ$ ,  $\text{Bu}^a$ , m.p.  $85^\circ$ , *n-amyl*, m.p.  $66^\circ$ , *n-hexyl*, m.p.  $58^\circ$ , *n-heptyl*, m.p.  $75^\circ$ , and *n-octyl*, m.p.  $71^\circ$ .  $[\text{Et}_2\text{S}, \text{HgCl}_2]$  has m.p.  $77.5\text{--}78.5^\circ$ .

R. S.

**Physical identity of enantiomerides. I. Rotatory dispersion of *l*-borneol, enantiomeric camphors, camphoric acids, sodium camphorates, camphoric anhydrides, and camphorimides.** B. K. SINGH and I. MAHANTI (Proc. Indian Acad. Sci., 1935, 2, A, 378—396).—In view of reported slight deviations in rotatory powers of *d*- and *l*-forms, suggested by wave mechanics, high-precision data for a no. of carefully purified compounds over a range of concns. in various solvents are tabulated. Results indicate that, within the limits of experimental error, Pasteur's principle is quantitatively strictly obeyed.

N. M. B.

**Maximum valency of elements and atomic structure. III, IV.** B. ORMONT (Acta Physicochim. U.R.S.S., 1935, 2, 533—546, 547—556; cf. A., 1935, 1058).—III. The dependence of the stability of the homopolar hydrides on the structure and valency of the central atoms (quantum states of the extranuclear electrons) is discussed.

IV. The stability of organo-metallic compounds containing homopolar linkings is discussed.

O. J. W.

**Maximum valency of elements and atomic structure. V. Maximum valency in the formation of hydrides, organometallic compounds, oxides, and halogen compounds.** B. ORMONT (Acta Physicochim. U.R.S.S., 1935, 2, 689—694; cf. preceding abstract).—Discussion. T. G. P.

**Natural classification of chemical compounds.**

II. F. M. SCHEMJAKIN (Acta Physicochim. U.R.S.S., 1935, 2, 421—426; cf. A., 1931, 287).—Analogies are observed between the physical properties of compounds of similar structural arrangement and between compounds in which the sums of the at. nos. of the constituent atoms are equal. J. W. S.

**Valency strength and the magnetism of complex salts.** J. H. VAN VLECK (J. Chem. Physics, 1935, 3, 807—813).—The anomalously low susceptibilities of ferro- and ferri-cyanides and certain other complex salts, compared with the predictions of the Bose-Stoner "spin only" formula, can be interpreted by Pauling's directed wave functions, or by the cryst. potential method (cf. Schlapp, A., 1933, 212), or by Mulliken's method of mol. orbitals (cf. A., 1932, 562).

N. M. B.

**Group relation between the Mulliken and Slater-Pauling theories of valency.** J. H. VAN VLECK (J. Chem. Physics, 1935, 3, 803—806).—By means of the group theory of characters, an intimate relation and transformation between Mulliken's mol. orbitals and the Slater-Pauling directed wave functions is shown.

N. M. B.

**Molecular structure of dielectrics.** (Sir) W. H. BRAGG (J. Inst. Electr. Eng., 1935, 77, 737—748).—Kelvin Lecture.

**New formulation of the Pauli principle for bond problems.** A. A. SCHUCHOVITSKI (Acta Physicochim. U.R.S.S., 1935, 2, 81—90).—Mathematical. R. S.

**Interaction between vibration and rotation for symmetrical molecules.** M. JOHNSTON and D. M. DENNISON (Physical Rev., 1935, [ii], 48, 868—883).—Mathematical. Teller's explanation of the anomalous fine structure of the infra-red bands of symmetrical mols. is developed. Expressions for the spacing const. of axially symmetrical and of tetrahedral mols. are derived, the internal angular momenta associated with the  $\perp$  frequencies of the axial mol.  $\text{YX}_3$  are calc., and results are applied to  $\text{NH}_3$  and  $\text{ND}_3$ . The axial mol.  $\text{ZXYX}_3$  is treated, and the moments of inertia of  $\text{MeF}$ ,  $\text{MeCl}$ ,  $\text{MeBr}$ , and  $\text{MeI}$  are calc. as  $5.61$ ,  $5.35$ ,  $5.44$ , and  $5.44 \times 10^{-40}$ , respectively. Results for overtones and combinations of two  $\perp$  frequencies are applied to  $\text{NH}_3$  and  $\text{MeCl}$ .

The calc. moment of inertia of  $\text{CH}_4$  is  $5.47 \times 10^{-40}$ . The overtones of  $\text{YX}_4$  are investigated. N. M. B.

Partial calculation of the potential energy function of the benzene molecule on the hypothesis of plane hexagonal symmetry. C. MANNEBACK (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 237—252; cf. A., 1935, 1057).—Coeffs. of the potential function of  $\text{C}_6\text{H}_6$  have been calc. with the aid of the Raman and infra-red spectra of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$ . It is shown that interaction occurs between non-adjacent C, giving a trellis-like elastic system. R. S.

Heat of dissociation of nitrogen. W. W. LOZIER (Physical Rev., 1934, [ii], **45**, 840).—A discussion. L. S. T.

Dissociation energy of carbon monoxide. P. GOLDFINGER, V. LASAREV, and B. ROSEN (Compt. rend., 1935, **201**, 958—960).—The dissociation energy of CO of 9.10 e.v. is consistent with related spectroscopic and thermochemical data. H. J. E.

Dissociation energy of CO. D. COSTER and F. BRONS (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 961—964; cf. A., 1934, 237).—The energy of predissociation in the fourth positive group of CO indicates that the energy of dissociation of the CO mol. is 8.41 volts (193.9 kg.-cal. per g.-mol.). From this the heat of sublimation of solid C is 107.6 kg.-cal. per mol. J. W. S.

Surface tension near the critical point. A. W. PORTER (Phil. Mag., 1935, [vii], **20**, 1163—1166).—A quant. discussion of surface flattening in a small tube near the crit. temp. N. M. B.

Surface tension of liquid metals. D. V. GOGATE and D. S. KOTHARI (Phil. Mag., 1935, [vii], **20**, 1136—1144).—Mathematical. An electron theory of surface tension is developed. Results agree with observed vals. N. M. B.

Surface tension of mercury and its alloys. M. LEMARCHANDS and L. CONVERS (J. Chim. phys., 1935, **32**, 657—669).—The drop-wt. method of determining the surface tension ( $\sigma$ ) of Hg in air leads to variable results owing to the adsorption of gases by the surface. The val. of  $\sigma$  determined by the same method in a vac. is 434 dynes per cm. This method applied to Ca amalgam was unsuccessful owing either to superficial oxidation or to the formation of a surface film of solid amalgam. J. W. S.

Contribution of X-ray analysis to the question of electron terms in ionic lattices. R. DE L. KRONIG (Physikal. Z., 1935, **36**, 729—732).—Two chief factors determine the fine structure of the X-ray absorption bands for ionic crystals: (1) the inability of electrons moving in a definite direction to take up certain quanta of energy on account of the zonal structure of the energy spectrum; this is a factor depending on the type of lattice, and (2) the effect of the modulation of the wave function on the probability of transition, depending on the variation of potential within the lattice cell. The various types of fine structure of the  $K$ -absorption edges encountered experimentally are discussed. A. J. M.

X-Ray interference for contact of the source of rays and the crystal. H. SEEMANN (Physikal. Z., 1935, **36**, 837—841).—Results obtained by the single-crystal anticathode method (cf. A., 1935, 1306) in which the crystal and X-ray source are one and the same are improved by separating the crystal from the source by a short distance. A. J. M.

Conditions determining the intensity of X-ray reflexions from microcrystalline layers. J. BRENTANO (Nature, 1935, **136**, 988).—A discussion (cf. A., 1935, 1306; this vol., 45). L. S. T.

Relation between the mechanical strain and the intensity of X-rays reflected by a quartz plate. II. E. FUKUSHIMA (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 1199—1204; cf. this vol., 15).—The intensity of the reflected X-rays approaches a max. as the applied force is increased. R. S.

Face-centred lattices with incompletely arranged cations. E. J. W. VERWEY (Chem. Weekblad, 1935, **32**, 721—726).—A discussion of crystals, the lattice structure of which is determined by the face-centred arrangement of the large anions, the cations being relatively very small. D. R. D.

State of electrons in crystal lattices. F. HUND (Physikal. Z., 1935, **36**, 888—890).—Theoretical. The position of the energy bands in some simple types of crystal lattice is calc. A. J. M.

Recrystallisation processes. I. Single particle recrystallisation of deformed single crystals. II. Recrystallisation of single crystals. III. Compressed powdered rock-salt. H. G. MÜLLER (Z. Physik, 1935, **96**, 279—306, 307—320, 321—327).—I. The speed of growth of visible particles and their rate of formation both follow a van 't Hoff law from 270° to 790°, and for pure NaCl are independent of time; as these both follow the one law there can be no special nuclei formation.

II. Recrystallisation of powdered NaCl to a single crystal gives this microscopic and amicroscopic defects.

III. The tensile strength of tempered compressed NaCl varies with temp. and time of tempering in the same manner as compressed metals. A. B. D. C.

Crystal growth and dissolution under local stress. G. A. RUSSELL (Amer. Min., 1935, **20**, 733—737).—Experiments with halite and alum show that stresses may be localised in crystals as well as in amorphous material, and that the solubility of a part of the crystal is related to local stress. Material dissolved from one part on account of local stress may be redeposited on a less strained part of the same crystal. L. S. T.

Lattice constants of beryllium. E. A. OWEN and L. PICKUP (Phil. Mag., 1935, [vii], **20**, 1155—1158).—In view of discrepancies between results previously obtained with a focussing camera (cf. A., 1934, 136) and those of other authors, determinations were made with a special type of spectrum camera, and data were analysed by a new method. Results for Be annealed in vac. were  $a$  2.2810,  $c$  1.5682 Å., in close agreement with the previous vals. N. M. B.

**Tetragonal martensite in carbon steels.** Z. NISHIYAMA (Sci. Rep. Tohoku, 1935, 24, 517—522).—The lattice const. of tetragonal or  $\alpha$ -martensite, calc. from the effective radii of Fe and C atoms, is in accord with vals. observed in quenched steel. This is interpreted as confirming that martensite is a solid solution of C in Fe. J. W. S.

**Metals and alloys. XVIII. Lattice structure of LiAl.** E. ZINTL and G. WOLTERS DORF (Z. Elektrochem., 1935, 41, 876—879; cf. A., 1934, 356).—LiAl has space-centred cubic lattice of the NaTl type with a 6.360 Å. The radius of both atoms is 1.38 Å. The lattice dimensions are determined solely by the Al atoms, the size of which remains unchanged, whilst the Li atoms undergo a large contraction. F. L. U.

**Structural type of aluminium boride (AlB<sub>2</sub>).** W. HOFMANN and W. JANICKE (Naturwiss., 1935, 23, 851).—The structure of AlB<sub>2</sub> (hexagonal leaflets) has been determined by the Laue, powder, and rotating-crystal methods. The unit cell has  $a$  3.00,  $c$  3.24 Å., and contains 1 mol. of AlB<sub>2</sub>. The Al atoms lie at the corners of the cell, and thus form planes parallel to the leaflet plane. The B form a lattice analogous to the C in graphite. A. J. M.

**Stabilised cubic iron sesquioxide.** A. MICHEL and G. CHAUDRON (Compt. rend., 1935, 201, 1191—1193).—Cubic Fe<sub>2</sub>O<sub>3</sub> is stable in presence of the ferrites of Na, Be, Ag, and K. Its virtual Curie point obtained by extrapolation of the system Na<sub>2</sub>O—Fe<sub>2</sub>O<sub>3</sub> is 675° ± 10°. T. G. P.

**Crystal structure of hydrogen peroxide.** F. FEHER and F. KLOTZER (Z. Elektrochem., 1935, 41, 850—851; cf. A., 1935, 806).—H<sub>2</sub>O<sub>2</sub> has tetragonal structure with  $a=b=4.02$ ,  $c$  8.02 Å. The unit cell contains 4 mols. F. L. U.

**Structure of ferric phosphate.** V. CAGLIOTI (Atti R. Accad. Lincei, 1935, [vi], 22, 146—149).—FePO<sub>4</sub>, prepared by the action of Na<sub>2</sub>HPO<sub>4</sub> on FeCl<sub>3</sub> in presence of NaOAc, crystallises in one phase isomorphous with quartz:  $a_0$  5.035,  $c_0$  5.588 Å.,  $d_{010}$  3.1. O. J. W.

**Crystal parameters of copper ammonium bromide.** A. SILBERSTEIN (Compt. rend., 1935, 201, 970—971).—CuBr<sub>2</sub>·2NH<sub>3</sub>·Br·2H<sub>2</sub>O is quadratic,  $a$  7.98,  $c$  8.41 Å.; 2 mols. in unit cell; space-group  $P4/mnm$  ( $D_{2h}^{14}$ ). H. J. E.

**Crystal structure of cerium tungstate.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1011—1015).—Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> is tetragonal-bipyramidal, possessing a scheelite-like structure with  $a_0$  5.336,  $c_0$  11.620 Å., and contains 4/3 Ce<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> in the unit cell. It is isomorphous with PbWO<sub>4</sub>, with which it forms a complete range of mixed crystals, but only 2/3 of the positions occupied by Pb in PbWO<sub>4</sub> are occupied by Ce, the remainder being void. J. W. S.

**Crystal structure and composition of sodium dihydropyrostibiate.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1015—1020).—Na<sub>2</sub>H<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>·5H<sub>2</sub>O crystallises in the tetragonal-bipyramidal form, the unit cell having  $a_0$  8.005,  $c_0$  7.868 Å. and containing 4 Na atoms. Cations and anions form a NaCl-like lattice, and in each anion Sb is surrounded by 6 O in almost octahedral configuration. The structure is in accord with the view that the composition is NaSb(OH)<sub>6</sub>. J. W. S.

$c_0$  7.868 Å. and containing 4 Na atoms. Cations and anions form a NaCl-like lattice, and in each anion Sb is surrounded by 6 O in almost octahedral configuration. The structure is in accord with the view that the composition is NaSb(OH)<sub>6</sub>. J. W. S.

**Structure and configuration of certain diamminopalladium compounds.** F. G. MANN, (MISS) D. CROWFOOT, D. C. GATTIKER, and (MRS.) N. WOOSTER (J.C.S., 1935, 1642—1652).—The deep red cryst. [(NH<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>] (I) which is produced when the rate of formation is slow is chemically identical with the usual yellow form, which is a *trans*-compound. (I) is twinned,  $a$  8.0,  $c$  7.8 Å., and has 4 mols. per unit cell. Both forms give the pale greenish-white *oxalate* (darkens 175—185°) on shaking with aq. K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and X-ray measurements indicate that this is a *cis*-compound having a planar configuration. The *trans*-dinitrite, pale yellow, m.p. 231—232° (decomp.), is formed in a similar manner and shows a planar coordination about the central Pd. Addition of [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub> to aq. NaNO<sub>2</sub> gives *cis*-diamminopalladium dinitrite, blackens at 234°, which is converted into the *trans*-dinitrite by slow recrystallisation. Since treatment of K palladonitrite with aq. NH<sub>3</sub> gives the *trans*-dinitrite, the production of the *cis*-form must be ascribed to the presence of NaCl or NaNO<sub>2</sub>. The *cis*-dinitrite gives an immediate brown ppt. with CS(NH<sub>2</sub>)<sub>2</sub>, whilst the *trans*-form does not. [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub> ppts. canary-yellow *tetramminopalladium palladonitrite* from aq. K palladonitrite, m.p. 224—225° (decomp.). Recrystallisation converts this into the *trans*-dinitrite, which gives yellow *diamminopalladium diiodide* with aq. KI. Treatment with COMe<sub>2</sub> yields a reddish-blue octahedral form which shows a new type of repeated polysynthetic twinning. X-Ray photographs indicate that it is internally highly heterogeneous and that the I are arranged irregularly along the  $c$ -axis. When the diiodide is dissolved in aq. NH<sub>3</sub>, [(NH<sub>3</sub>)<sub>4</sub>Pd]I<sub>2</sub> is formed, which dissociates on keeping and deposits red crystals identical with the yellow pptd. diiodide. The diiodide may also be formed by the action of aq. KI on the dichloride. Diamminopalladium oxalate, when treated with KI, does not give the expected *cis*-diiodide, but chocolate-brown *tetramminopalladium palladoiodide*, which may also be obtained from the palladochloride or from NH<sub>3</sub>, palladoiodide and [(NH<sub>3</sub>)<sub>4</sub>Pd]Cl<sub>2</sub>. Further crystallographic properties of the compounds are given in detail. R. S.

**X-Ray diagrams of sugar carbon submitted to various thermal treatments.** P. CORRIEZ (Compt. rend., 1935, 201, 1189—1191; cf. A., 1934, 1088).—X-Ray diagrams of sugar C heated for 2 hr. at 1200°, 1400°, 1600°, 1800°, and 2000° indicate that the structure approaches nearest to that of graphite in the specimen heated at the highest temp. T. G. P.

**Structure of cellulose.** F. WORSCHITZ (Magyar Chem. Fol., 1934, 40, 60—64; Chem. Zentr., 1935, i, 2825).—A series of fibre diagrams obtained from Canadian Pappel and Pe-mou (*Fokiana hodgensii*, A. Henry), and differing from the normal, are given. In one case the diagram points to orientation of the cellulose crystals along the  $a$ -axis. H. N. R.

**X-Ray analysis of the structure of iridescent shells. II. *Haliotide*.** S. RAMASWAMY (Proc. Indian Acad. Sci., 1935, 2, A, 345—351; cf. A., 1935, 1194).—X-Ray diffraction patterns were investigated, and orientations of the aragonite crystals obtained. Results are compared with those for *Turbo* and *Trochus* shells. N. M. B.

**Orientation of the CO<sub>3</sub> groups in the ammonium [and potassium] hydrogen carbonate crystal.** A. MOOKHERJEE (Physical Rev., 1934, [ii], 45, 844).—Magnetic anisotropy measurements confirm Mooney's conclusions (A., 1933, 1234) concerning NH<sub>4</sub>HCO<sub>3</sub>. KHCO<sub>3</sub> exhibits a much feebleness anisotropy, showing that the planes of the different CO<sub>3</sub> groups in the unit cell must be considerably inclined to each other. L. S. T.

**Anomalies in the diffraction of fast-moving electrons.** H. MARK and H. MOTZ (Monatsh., 1935, 67, 13—23).—Further experiments confirm the conclusion previously reached (A., 1935, 813, 820), that anomalous interference lines obtained with electrons of 20—30 kv. are due to the presence of traces of fatty material of high mol. wt. on the surface of the specimen. F. L. U.

**Deflexion of slow electrons by sublimed tungsten.** V. I. KASSATOTSHKIN (Acta Physicochim. U.R.S.S., 1935, 2, 317—336).—The deflexion of 40—400-volt electrons by a film of micro-cryst. sublimed W indicates that the inner potential of W is  $10.5 \pm 2$  e.v. A second group of deflexion max. correspond with electron diffraction at the surface of the W crystals. The results are in accord with measurements with single W crystals (cf. A., 1933, 549). J. W. S.

**Variation in the lattice constant of zinc oxide.** V. E. COSSLETT (Nature, 1935, 136, 988—989).—A ZnO film prepared from a granulated Zn melt had  $a\ 3.234 \pm 0.005$ ,  $c\ 1.615 \pm 0.005$  Å. when freshly prepared and  $a\ 3.279$ ,  $c\ 1.637$  Å. 18 and also 20 months later. Au films remained const. over this period. ZnO films prepared as described should not be used for high-voltage calibration or measurement. L. S. T.

**Diffraction of electrons by metal crystals and by mica.** J. A. DARBYSHIRE and E. R. COOPER (Proc. Roy. Soc., 1935, A, 152, 104—123).—An examination has been made of spot patterns produced when an electron beam of velocity  $\sim 30$  kv. is transmitted through thin cryst. films of Cd, Zn, and Bi, and through thin curved sheets of mica. The reciprocal lattice picture of electron diffraction is presented in a form suitable for discussing the results. The crystals of the metals were prepared by withdrawing the surface oxide film from the molten metals in air and in N<sub>2</sub>; these films produced Debye-Scherrer patterns due to the oxide and spot patterns due to occluded metal crystals. The spot patterns are caused chiefly by distortion of the metal crystals. This view is supported by the results obtained with mica. Forbidden spectra, probably due to successive reflexions by different crystallites in an aggregate, were observed. L. L. B.

**Molecular structures of sulphur dioxide, carbon disulphide, and carbonyl sulphide.** P. C. CROSS and L. O. BROCKWAY (J. Chem. Physics, 1935, 3, 821—824).—Mol. structure data obtained by the electron diffraction method are: SO<sub>2</sub>, S—O,  $1.46 \pm 0.02$ ; CS<sub>2</sub>, C—S,  $1.54 \pm 0.03$ ; COS, C—O,  $1.16 \pm 0.02$ , C—S,  $1.56 \pm 0.03$  Å. In SO<sub>2</sub> the mol. resonates between structures having single-double and double-single linkings between S and the two O, with a linking angle  $122^\circ \pm 5^\circ$ . CS<sub>2</sub> is a linear mol. having the two double linkings predominating over the single and triple linking structure. In COS the double-double linking arrangement and the structure having the triple C—O linking predominate. N. M. B.

**Molecular structure of nickel carbonyl.** L. O. BROCKWAY and P. C. CROSS (J. Chem. Physics, 1935, 3, 828—833).—Electron diffraction by Ni(CO)<sub>4</sub> vapour leads to a mol. model in which the four CO have a tetrahedral arrangement about the Ni with Ni—C,  $1.82 \pm 0.03$ , and C—O,  $1.15$  Å., corresponding with resonance between two electronic structures in which the C—O linking resonates between triple and double electron pair linkings, and the N—C linking between single and double electron pair linkings. N. M. B.

**Diffraction of electrons by chloroform and its molecular structure: the Urbain and tetrahedral models.** C. DEGARD (Compt. rend., 1935, 201, 951—952).—The Cl—Cl and C—Cl interat. distances in CHCl<sub>3</sub> were  $2.95 \pm 0.03$  and  $1.76$  Å., respectively. This is consistent with either the tetrahedral formulation or Urbain's co-ordinate formula CCl<sub>2</sub>HCl. H. J. E.

**Formation of molecular swarms in liquids.** R. GANS (Physikal. Z., 1936, 37, 19—22).—Theoretical. The calculation of the size and shape of mol. swarms in liquids by the determination of the degree of depolarisation of light scattered by the liquid is considered, the method of Krishnan (A., 1935, 11) being extended. A. J. M.

**Theory of influence of pressure on electrical resistance of metals.** M. H. LENSSEN and A. MICHELS (Physica, 1935, 11, 1091—1107). H. J. E.

**Resistance of very thin films of foreign substances in metallic contacts.** R. HOLM and B. KIRCHSTEIN (Physikal. Z., 1935, 36, 882—888).—Metallic surfaces become covered, in air, with a film of foreign matter of definite resistance. The resistance of very thin films may be calc. using the tunnel effect. Such calculation shows that the resistance is independent of temp. and obeys Ohm's law up to 0.5 volt, in agreement with experiment. A. J. M.

**Variation of electrical resistance and reflecting power of metallic mirrors condensed at low temperatures.** R. SUHRMANN and G. BARTH (Physikal. Z., 1935, 36, 843—845).—The resistance of mirrors of Cu, Ag, Au, Cd, Tl, and Pb deposited at 20—80° abs. decreases on warming to room temp. and there is a simultaneous increase in the reflecting power. The resistance of Bi mirrors deposited at 80° abs. increases with rise of temp. The results are analogous to the resistance changes which occur when the liquid metal solidifies, and therefore indicate that



rise of temp. from 80° abs. to room temp. involves an increase in the orderly arrangement of atoms in the lattice.

A. J. M.

**Longitudinal resistance changes in a magnetic field according to elementary theory.** A. SOMMERFELD and B. W. BARTLETT (Physikal. Z., 1935, 36, 894—899).—Mathematical. Previous calculations of the longitudinal resistance change in a magnetic field (current and magnetic field parallel) led to a zero val. If the electron orbits are quantised a finite result is obtained.

A. J. M.

**Dielectric investigations on crystals of Seignette's salt.** R. DAVID (Helv. phys. Acta, 1934, 7, 647—649; Chem. Zentr., 1935, i, 2779).—The dependence of the dielectric const. on elastic deformation of the crystal has been investigated. The charge-field strength curves exhibit hysteresis and saturation. Non-homogeneous deformation produces highly asymmetric hysteresis curves, which are attributed to internal stresses in the crystal.

J. S. A.

**Magnetisation of single crystals of nickel at various temperatures.** K. HONDA, H. MASUMOTO, and Y. SHIRAKAWA (Sci. Rep. Tohoku, 1935, 24, 391—410).—The magnetisation of single Ni crystals has been measured by the ballistic method between -252° and 370°. The magnetisation along the (111) axis at 20° increases rapidly at first and slowly later with increasing field strength to a saturation val. of about 503 gauss. At higher temp. magnetisation occurs more readily in weak fields, but the saturation val. is lower. The magnetisation along the (100) and (110) axes behaves similarly at higher temp., but at low temp. saturation is not reached with fields up to 1000 oersteds. The estimated val. of the magnetisation of Ni at 0° abs. is 533 gauss.

J. W. S.

**Cessation of spin in ferromagnetic crystals under the influence of mechanical strains.** R. GANS (Ann. Physik, 1935, [v], 24, 680—696).—Theoretical.

A. J. M.

**Directions of discontinuous changes of magnetisation in a rotating monocrystal of silicon-iron.** L. W. McKEEHAN and R. F. CLASH, jun. (Physical Rev., 1934, [ii], 45, 839—840; cf. A., 1935, 287).

L. S. T.

**Action of X- and  $\gamma$ -rays on piezo-electric crystals.** F. SEIDL and E. HUBER (Z. Physik, 1935, 97, 671—680).—Quartz and Rochelle salt show an increase in electrical conductivity when irradiated with X- or  $\gamma$ -rays, but the piezo-const. does not always change in one direction.  $\gamma$ -Rays colour Rochelle salt yellow.

A. B. D. C.

**Magnetostriction volume effect for nickel and magnetite.** M. KORNETZKI (Z. Physik, 1935, 97, 662—666).

A. B. D. C.

**Inversion of quartz to tridymite.** I. Natural tridymite. II. X-Ray distinction between tridymite and cristobalite. S. KONDO and T. YAMAUCHI (J. Soc. Chem. Inst. Japan, 1935, 38, 651—652B).—I. For natural tridymite (I)  $n_D$  varies from 1.477 to 1.479. Interplanar spacings and intensities have been calc. for 29 lines in the diffraction pattern.

II. Artificial (I), and natural and artificial cristobalite (II), have  $n_D$ , respectively, 1.469—1.474, 1.482, 1.484. (I) and (II) can be distinguished by the X-ray pattern.

T. W. P.

**Dynamic theory of crystal optics.** G. MOLIERE (Ann. Physik, 1935, [v], 24, 591—608).—Mathematical. Laue's method for X-rays is extended to longer  $\lambda$  and expressions for double refraction and optical activity are derived; the vals. calc. are in agreement with those obtained from the Born-Ewald lattice theory.

W. R. A.

**Negative cohesion pressure.** V. JACYNA, S. DEREJANKIN, and A. OBNORSKI (Z. Physik, 1935, 97, 774—776).—Weiss and Bridgman's revision of van der Waals' equation of state (cf. A., 1935, 1064) gives results that accord well with Jacyna's theory (A., 1934, 1070).

A. B. D. C.

**Lattice distortion and coercive force in single crystals of nickel-iron-aluminium.** W. G. BURGERS and J. L. SNOEK (Physica, 1935, 11, 1064—1074).—In the state of max. coercive force, the segregation of the supercooled metastable  $\alpha$ -phase into a stable  $\alpha$ - and a  $\gamma$ -phase has reached only a preliminary stage. The  $\gamma$ -phase is not in evidence in the X-ray diagrams. A highly stressed state occurs in the lattice.

H. J. E.

**Crystal plasticity.** IV. Dynamic plasticity law. E. OROWAN (Z. Physik, 1935, 97, 573—595).—Plastic flow of Zn crystals shows that the stress varies with the rate of slip and not with the actual displacement (cf. A., 1934, 949).

A. B. D. C.

**Plasticity of bismuth.** W. F. BERG and L. SANDLER (Nature, 1935, 136, 915).—Crystals of Bi grown in a vac. or under atm. pressure in  $N_2$ ,  $H_2$ , or  $CO_2$  by the Andrade-Rosecoe method are all soft, i.e., they slip in tensile tests at room temp. The hypothesis that the gas is responsible for the softness (A., 1934, 722) is untenable.

L. S. T.

**Strength of crystals towards pressure.** M. SCHULER and A. DIMPKER (Z. Instrument., 1935, 55, 63—70; Chem. Zentr., 1935, i, 2490).—Spheres and cones of materials (sapphire, ruby, diamond, quartz) used for construction of knife edges, pressed against the same material, crack readily, but require much higher loads for breakage. Steel spheres behave as required by the Hertz theory.

J. S. A.

**Elastic behaviour of tin single- and polycrystals.** W. BOAS (Helv. phys. Acta, 1934, 7, 878—883; Chem. Zentr., 1935, i, 2312).—Elastic moduli calc. from the Voigt formula for polycryst. Sn agree fairly well with published data. For single crystals, Bridgman's results are much > those calc.

J. S. A.

**Electrical evaluation of recovery in compressed rock-salt crystals.** J. BOROS and Z. GYULAI (Z. Physik, 1935, 96, 355—358).—Sudden changes in electric conductivity of NaCl under pressure are associated with recovery.

A. B. D. C.

**Explosive antimony.** II. Structure, electrical conductivity, and rate of crystallisation. C. C. COFFIN (Proc. Roy. Soc., 1935, A, 152, 47—63; cf. A., 1934, 1297).—A microscopical examination of

polished and etched surfaces shows that the explosive electrolytic deposit of Sb possesses a heterogeneous gel-like structure definitely oriented with respect to the cathode receiving surface. This oriented phase is probably an  $\text{SbCl}_3\text{-Sb}$  complex resulting from the deposition of a complex ion; the other phase is probably amorphous Sb. The electrical properties of the deposits are non-metallic in that the conductivity is very small and has a positive exponential temp. coeff. Ohm's law is obeyed, but Faraday's law is not involved, although a small polarisation is built up at the higher temp. At temp. too low to initiate explosion the deposits crystallise at a rate which is independent of the extent to which they have already crystallised. The rate of crystallisation increases exponentially with rise of temp. L. L. B.

**Two new phenomena [transitions produced in bismuth and phosphorus] at very high pressure.** P. W. BRIDGMAN (Physical Rev., 1934, [ii], 45, 844—845).—At approx. 25,000 kg. per sq. cm. and room temp., a new modification is produced reversibly from ordinary solid Bi with a vol. decrease of approx. 9%. At 35,000 kg. per sq. cm., black P is formed at room temp. from the modification of white P stable at atm. pressure only below  $-80^\circ$ . The transformation is not complete;  $d$  is 2.59, as compared with 2.69 for the usual form of black P.

L. S. T.

**Effects of high shearing stress combined with high hydrostatic pressure.** P. W. BRIDGMAN (Physical Rev., 1935, [ii], 48, 825—847).—With mean pressures up to 50,000 kg. per sq. cm., the effect of shearing stresses up to the plastic flow point was investigated for a no. of substances in the form of thin discs. Normally stable substances which detonated were: celluloid,  $\text{CHI}_3$ ,  $\text{PbO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Ag}_2\text{O}$ ,  $\text{MnO}_2$ ,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ,  $\text{AgNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{K}_2\text{SO}_4$  cryst. and anhyd.,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ . Rubber changed to a hard horn-like mass, paper, wood, and linen cloth changed to translucent horn-like substances, thymol-blue became insol., amorphous Se partly became metallic, cryst. S appeared to become amorphous,  $\text{PbO}$  decomposed to Pb without detonation, red  $\text{HgO}$  changed to black, and red P changed to the black form. Combinations of substances normally inert to each other which reacted explosively were  $\text{Cu}+\text{S}$ ,  $\text{Fe}_2\text{O}_3+\text{Al}$ ,  $\text{SiO}_2+\text{Mg}$ ,  $\text{K}_2\text{C}_2\text{O}_4+\text{Al}$ , and  $\text{Si}+\text{MgO}$ . Single substances giving negative results were: graphite, mica,  $\text{NH}_4\text{NO}_3$ , sugar, rosaniline,  $\text{CuS}$ ,  $\text{SiO}_2$ , tremolite,  $\text{NH}_4\text{F}$ ,  $\text{CuO}$ ,  $\text{MgO}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{LiF}$ ,  $\text{AgCl}$ ,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{NaBrO}_3$ ,  $\text{Si}$ ,  $\text{Na K tartrate}$ ,  $\text{HgNO}_3$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ . Polymorphic transitions under these stresses could be detected by a break in the shearing stress-pressure curve; out of 57 elements examined, breaks were found for Li, Sr, Ca, Ba, Cd, Zn, V, Mn, Sb, Te, I, La, Ce, Cr, Tl, Bi, Th, Sn, Yt, and Pr.

N. M. B.

**Polymorphism, principally of the elements, up to 50,000 kg.** P. W. BRIDGMAN (Physical Rev., 1935, [ii], 48, 893—906).—A new technique is described for applying to solids pressures up to 50,000 kg. per sq. cm. and measuring the parameters of transitions. Results of examination for polymorphism of a no. of elements are given; new modifications

were found for Bi, Hg, Tl, Te, Ga, and I, and transition parameters were measured. KCl, KBr, and KI at about 20,000 kg. per sq. cm. appear to assume the CsCl type of structure.

N. M. B.

**Coalescence in stages between two drops of a liquid.** M. KATALINIĆ (Nature, 1935, 136, 915—916; cf. A., 1935, 1062).

L. S. T.

**Recrystallisation accompanying an allotropic change.** C. F. ELAM (Nature, 1935, 136, 917; cf. A., 1935, 1452).—Such changes in  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$  can be followed under the microscope using crossed Nicols.

L. S. T.

**Softening of vitreous substances.** E. RENCKER (Ann. Chim., 1935, [xi], 4, 523—566; cf. A., 1934, 17, 480).—Determinations of the softening temp. and the transformation point of vitreous substances are discussed. A kinetic interpretation of the phenomena is advanced, and it is shown that the properties of "tempered" glasses cannot be ascribed to a persistence in the interior of the conditions which exist above the transformation temp.

R. S.

**Highly polymerised compounds. CXXV. Mol. wt. determinations with highly complex polyethylene oxides.** H. STAUDINGER and H. LOHMANN. CXXVI. Comparison of the osmotic and viscosimetric methods of determining mol. wt. in polymeric-homologous series. CXXVII. Osmotic determinations in solutions of rod-like and spherical particles. H. STAUDINGER and G. V. SCHULZ. CXXVIII. Abnormal mol. wts. of highly complex compounds. H. STAUDINGER, W. KERN, and J. J. HERRERA. CXXIX. Polymerisation as chain reaction. H. STAUDINGER and W. FROST. CXXX. Conception of mol. wt. of simple and complex compounds. H. STAUDINGER (Ber., 1935, 68, [B], 2313—2319, 2320 2335, 2336—2346, 2346—2350, 2351—2356, 2357 2362).—CXXV. Determination of the mol. wt. of hemicolloidal polyethylene oxides (concordant data for which are obtained by the cryoscopic, terminal group, and viscosimetric methods) shows that Brintzinger's process gives abnormal values; marked divergences are noted with relatively simple products the diffusion of which is not impeded by the too small diameter of the membrane pores. Diffusion of thread-like particles differs therefore from that of spherical particles, to which alone the expression  $K=\lambda\sqrt{M}$  can be applied. The osmotic and viscosimetric methods give approx. concordant results, proving that extrapolation of the viscosity equation is permissible and that the mol. wt. of complex materials with thread-like mols. can be determined viscosimetrically.

CXXVI. The relationship between mol. wt. and osmotic pressure is expressed by the equation  $M = RTc/p_c[1 - c(K/p_c)^{1/\nu}]$ , in which  $K$  and  $\nu$  are constants for all members of a given polymeric-homologous series and, if determined for mesocolloidal members, can be applied to eucolloids in solutions in which the van 't Hoff relationship does not hold good. The mol. wts. of cellulose acetates (I) and nitrates (II) and methylcelluloses (III) are thus determined and the results applied in the calculation of viscosimetric data.  $K_m$  has the same val. for (II) in COME

(III) in  $H_2O$ , and (I) in  $COMe_3$  or *m*-cresol, proving that  $\eta_{sp.}$  of solutions of thread mols. depends only on the length of the mol. and the concn. and is independent of particular structure. With balata and hydro-caoutchouc the differences between the mol. wt. determined osmotically and viscosimetrically are considerable. With approx. eucolloidal polyethylene oxides the agreement between the determinations by the two methods is scarcely so close as with the cellulose derivatives. Observations with polystyrenes are greatly influenced by the manner in which polymerisation has been effected; it is assumed that unknown complications, particularly at higher temp., cause branching of the thread mols. Similar results are obtained with other synthetic polymerides formed by chain reactions; these, therefore, differ from the natural products which are polymeric-uniform and permit the determination of mol. length and hence mol. wt. by measurement of viscosity.

CXXXVII. The cryoscopic and ebullioscopic methods are trustworthy for the determination of mol. wt. of relatively simple substances with thread-like mols., but their applicability to similarly constructed hemi-, meso-, and eu-colloids is difficult to assess, although the behaviour of cellulose derivatives suggests that they are trustworthy in very dil. solution. Determinations of osmotic pressure of polymeric-homologous caoutchoucs, polyethylene oxides, and cellulose nitrates show that in each series the additional pressure increases with increasing concn. more rapidly as the mol. wt. is greater. Additional pressure is not observed with spherical-colloidal ovalbumin and serum-albumin, whereas gelatin appears to have thread-like particles. In osmotic behaviour, spherocolloids conform approx. to van 't Hoff's law and  $p_c/c$  is const., whereas with linear colloids the  $p_c/c$  vals. increase with increasing concn.

CXXXVIII. The depression of the f.p. of  $C_{10}H_8$  by five fractions of complex polyanetholes, the mol. wt. of which is determined concordantly by the viscosimetric and ultra-centrifugal methods, increases more slowly than expected with increasing concn., and the mol. wts. calc. on the assumption that Raoult's laws are followed are much smaller in dil. than in conc. solution, in some cases being < that of the fundamental mol. The observations are similar to those of Hess with cellulose esters and ethers in  $AcOH$ .

CXXXIX. The view that polymerisation is a chain reaction and not a poly-condensation process is strengthened by the observation that intermediate products are not observed during the polymerisation of acrylic acid or styrene. The rate of polymerisation depends on the rates of activation, growth, and of "final" reaction leading to the formation of non-reactive positions at the end of the thread mols. The second process takes place very rapidly in comparison with the first and third. Catalysts accelerate the initial, but generally also the final, action, so that in general the products are less complex than those formed by slow polymerisation in absence of catalyst. Acceleration of the first change without affecting the third is achieved by polymerisation in soap emulsion, and the addition of a catalyst is here permissible, since it does not penetrate into the interior of the mol.

CXXX. The importance of discriminating between the physical mol. wt. (which does not involve the internal structure of the particles) and the chemical mol. wt. (sum of the wts. of all the atoms united by main valencies in a particle) in the case of highly polymerised compounds is stressed. H. W.

Conductivity of the Bunsen flame measured with direct and alternating current. H. ULLMANN (Z. Physik, 1935, 97, 496—510).—D.-c. and a.-c. conductivity has been determined for the pure Bunsen flame, and for one containing  $Na_2CO_3$ . Probe measurements show that the effect of electrodes is small for the pure flame, but high for the salt flame. The conductivities are 1 and  $14 \times 10^4$  for d.c. and a.c. in the pure flame, and 36 and  $173 \times 10^4$  sec.<sup>-1</sup> in the salt flame. A. B. D. C.

Electrical conductivity of compressed metal vapours. W. BRAUNBEK (Z. Physik, 1935, 97, 482—495).—Bloch's theory predicts a large pressure variation for the conductivity of metal vapours, but measurements on Hg and K vapours at 730° and 1200° and up to 35 and 10 atm., respectively, gave negative results. A. B. D. C.

Effect of ultra-violet light on the electrical conductivity of quartz. R. RADMANCHE (Compt. rend., 1935, 201, 1021—1022).—The conductivity of quartz increases with time of irradiation to a max., and falls gradually to the original val. after removing the light source. T. G. P.

Superconductivity and other low-temperature phenomena. A discussion (Proc. Roy. Soc., 1935, A, 152, 1—46).—J. C. MCLENNAN discussed new methods of liquefying He: (1) in which the cooling is produced by the adiabatic expansion of compressed He gas, (2) in which the gas is pre-cooled with liquid  $N_2$  and in expanding is made to do external work on an expansion engine which is included in the gas cycle. Discontinuities in certain physical properties of liquid He, the lowest temp. which has been reached with liquid He alone (0.71° abs.), and the temp. reached by the method of adiabatic demagnetisation (0.0044° abs.) were mentioned. Up to the present, the following elements have been shown to become superconducting: Nb, Pb, Ta, Hg, Sn, In, Tl, Ti, Th, Al, Ga, Zn, Mg, Zr, Cd, Hf. The magnetic fields around superconductors, superconductivity in thin films, the Hall effect in superconductors, thermal conductivity at low temp., the anomalous behaviour of certain alloys, low-temp. calorimetry applied to radioactive measurements, sp. heats, and the electric magnetic theory of superconductors were also considered.

J. D. COCKCROFT discussed Kapitza's method for the liquefaction of He.

D. SHOENBERG reviewed the magnetic properties of superconductors.

W. H. KEESOM discussed the lambda-phenomena in liquid He, the thermodynamic temp. scale below 0.9° abs., the heat capacity of electrons in metals, and the calorimetry of superconductors.

W. MEISSNER. The magnetic effects occurring on transition to the superconducting state.

R. DE L. KRONIG. The propagation of electro-

magnetic waves in metallic conductors, and its bearing on the problem of superconductivity.

L. BRILLOUIN. Superconductivity and the difficulties of its interpretation.

N. KURTI and F. SIMON. The sp. heat of  $\text{Fe NH}_4$  alum below  $1^\circ$  abs. and a preliminary determination of the thermodynamic temp. scale.

R. PEIERLS. The residual resistance of superconducting metals.

F. LONDON. The macroscopical interpretation of superconductivity.

K. MENDELSSOHN. The induction and energy content in various superconducting substances.

N. F. MOTT. The heat capacity of certain elements at low temp. L. L. B.

**Superconductivity.** M. VON LAUE, F. LONDON, and H. LONDON (Z. Physik, 1935, 96, 359—364).—Theoretical. A. B. D. C.

**Superconductivity of the elements. III. Origin and range of validity of a proposed criterion for superconductivity.** Z. A. ERSTEIN (Z. Physik, 1935, 96, 386—409).—Theoretical (cf. A., 1930, 1242). A. B. D. C.

**Electronic configuration of superconducting metals.** U. DEHLINGER (Physikal. Z., 1935, 36, 892—894).—The composition of the outermost electron shells in the lattices of superconducting metals is considered. Only those elements are superconducting which possess a lattice with high co-ordination no., not too small at. radius, and, in their outermost shells,  $>$  one electron per atom. This holds for all elements, including the transition metals, with the exception of Ti and its congeners, which are weakly superconducting. The superconductivity of alloys is probably governed by a similar law. Thus, although Bi has a lattice too distorted to be superconducting,  $\text{Au}_2\text{Bi}$  has a highly co-ordinated lattice and is superconducting. The superconductivity of the carbides and nitrides of the transition elements may be explained in a similar way. A. M.

**Effect of light on diamagnetic susceptibilities.** H. C. BHUYAN (Nature, 1935, 136, 872).—Exposure to visible light temporarily increases the susceptibilities of  $\text{Cl}_2$ , Br, and I. L. S. T.

**Magnetochemical investigations. XVIII. and  $\text{K}_2(\text{B}_2\text{H}_4[\text{OH}]_2)$ .** L. KLEMM and W. KLEMM. XIX. Magnetic behaviour of potassium polyoxides and polysulphides. W. KLEMM and H. SODOMANN (Z. anorg. Chem., 1935, 225, 258—261, 273—280; cf. A., 1935, 1312).—XVIII. Magnetochemical measurements support the above formulæ in preference to  $\text{KBH}_3$  and  $\text{KBH}_2\cdot\text{OH}$ .

XIX. Magnetochemical data do not suffice to differentiate between the formulæ  $\text{K}_2\text{O}_4$  and  $\text{KO}_2$ . The diamagnetic susceptibilities of  $\text{K}_2\text{S}$ ,  $\text{K}_2\text{S}_2$ ,  $\text{K}_2\text{S}_3$ ,  $\text{K}_2\text{S}_4$ , and  $\text{K}_2\text{S}_6$  have been determined at room temp. and  $-183^\circ$ .  $\text{K}_2\text{S}_3$  becomes ferromagnetic at  $-50^\circ$ . E. S. H.

**Principal magnetic susceptibilities of  $\text{K}_3\text{Fe}(\text{CN})_6$ .** J. B. HOWARD (J. Chem. Physics, 1935, 3, 813—817).—The calc. magnitudes, anisotropy, and temp. dependence of the principal magnetic susceptibilities are in good agreement with experiment.

The relation of susceptibility to electron spin is discussed. N. M. B.

**Magnetic susceptibilities of alkali and alkaline-earth halides.** U. VEIEL (Ann. Physik, 1935, [v], 24, 697—713).—The susceptibilities of alkali and alkaline-earth halides and the halogen acids in aq. solution have been determined as a function of concn. The relationship is linear, in agreement with the Wiedemann additive law. The susceptibilities of the individual halides are considered in relation to their total nuclear charges. The results do not agree with Pascal's rule (extension of the Wiedemann law to mol. constituents). The mol. susceptibilities are used to calculate ionic susceptibilities. The effect of temp. on the susceptibilities of NaCl and KI solutions was determined. The temp.-susceptibility curves show only a small deviation from the curve for  $\text{H}_2\text{O}$ . This may be explained by assuming that the susceptibility of the salt does not vary with temp., although it causes an increase in the susceptibility of  $\text{H}_2\text{O}$  owing to a displacement of the equilibrium between the mol. complexes in  $\text{H}_2\text{O}$ . A. J. M.

**Determination of paramagnetic susceptibilities of crystals of rare earths by measurement of the paramagnetic rotatory power.** J. BECQUEREL (Compt. rend., 1935, 201, 1112—1115).—Measurements with the Et sulphates of Pr, Nd, Dy, and Er verify Van Vleck's prediction that the relation between the magnetisation and the paramagnetic rotation should be independent of temp. H. J. E.

**Thermo-electric effect according to the new electron theory.** M. SATO (Sci. Rep. Tohoku, 1935, 24, 523—536).—Mathematical. J. W. S.

**Thermo-electric power, Peltier heat, and photo-potential of the element copper-cuprous oxide-copper.** G. MONCH (Physikal. Z., 1935, 36, 755—757).—The deductions which can be made from the thermo-electric power, Peltier effect, and photo-potential of an element including a semi-conductor concerning the mechanism of conduction are discussed. A. J. M.

**Diffraction of light by high-frequency sound waves. I, II.** C. V. RAMAN and N. S. N. NATH (Proc. Indian Acad. Sci., 1935, 2, A, 406—412, 413—420).—Mathematical. N. M. B.

**Propagation of ultrasonic waves in liquid media.** R. LUCAS (Compt. rend., 1935, 201, 1172—1174).—Diffusion may account for the rapid diminution in amplitude of ultrasonic waves in liquid media. T. G. P.

**Critical phenomena.** V. JACZYNA (Z. Physik, 1935, 97, 669—670).—The indistinct crit. state of He is not due to impurities, but to the crit. point being a fiction applicable only to an unattainable ideal physical substance. A. B. D. C.

**Entropy of deuterium.** K. CLUSIUS and E. BARTHOLOME (Z. physikal. Chem., 1935, B, 30, 258—264).—At  $298.1^\circ$  abs. the entropy calc. from thermal data is  $33.91_5$ , whilst the statistically calc. abs. val. is  $38.98_4$  g.-cal. per mol. per degree. The difference between these vals. may be accounted for by supposing that on cooling at  $10^\circ$  abs. the equilibrium between



*o*- and *p*-forms is "frozen in," but that down to 10° *p*-D<sub>2</sub> mols. rotate freely in the lattice with — the nuclear spin multiplicity of the *o*- and *p*-mols. being maintained. For practical thermodynamic calculations the abs. val. 34.62<sub>0</sub> should be used. At low temp. the chemical consts. of *o*-D<sub>2</sub> and normal D<sub>2</sub> and the v.-p. const. of normal D<sub>2</sub> are -0.68<sub>1</sub>, -0.522, and -0.67<sub>0</sub>, whilst above 200° abs. the chemical const. of *o*-D<sub>2</sub> and the v.-p. const. of normal D<sub>2</sub> are -2.61<sub>5</sub> and -2.76<sub>3</sub>, respectively. R. C.

**F.p. of organic compounds. XV. Esters of the fatty acids.** R. BILTERYS and J. GISSELEIRE (Bull. Soc. chim. Belg., 1935, 44, 567—586).—B.p., m.p., *d*, coeff. of expansion, viscosity, fluidity, surface tension, *n*, and mol. refractivity data are tabulated for *n*-heptioic acid, *n*-hexyl and *n*-heptyl alcohol, the Me, Pr<sup>a</sup>, Bu<sup>a</sup>, and *n*-C<sub>5</sub>H<sub>11</sub> esters of *n*-hexoic, *n*-heptioic, and *n*-octoic acids, and *n*-hexyl, *n*-heptyl, and *n*-octyl formate, acetate, propionate, *n*-butyrate, *n*-valerate, *n*-hexoate, *n*-heptate, and *n*-octoate. The variation of the m.p. with the no. of C in the alcohol and acid radicals respectively is discussed. R. S.

**Relation between b.p., m.p., and mol. wt.** V. K. NIKIFOROV, N. V. ISMAILOV, and S. S. SANDO-MIRSKI (J. Chim. phys., 1935, 32, 670—677).—Statistical formulæ are deduced relating the b.p. and m.p. of org. compounds of mol. wt. 100—300 with the mol. wt. The formula  $T^2/M = \text{const.}$  holds for the alcohol and paraffin series. J. W. S.

**Normal reduced b.p.** R. LAUTHÉ (Bull. Soc. chim., 1935, [v], 2, 2234—2235).—The formula  $4T_c/T_c + 10T_c/T_c = 12.69$  ( $T_c = \text{crit. temp. and } T_c = \text{b.p. abs.}$ ) has been verified for a large no. of compounds of different types, within 0.3%. Hg and He are exceptions. F. L. U.

**International Bureau of Physico-chemical Standards. VII. Physical constants of twenty organic compounds.** J. TIMMERMANS and (MME.) HENNAUT-ROLAND (J. Chim. phys., 1935, 32, 589—617; cf. A., 1934, 480).—The following data for b.p./760 mm., m.p., and *d*<sub>15</sub> have been determined: MeOBz 199.50°, -12.4°, 1.09334; EtOBz 212.45°, -34.7°, 1.05112; PhCN 191.10°, -13.8°, 1.00948; NH<sub>2</sub>Ph 184.40°, -6.1°, 1.02613; NHPHMe 196.25°, —, 0.99018; NPhMe<sub>2</sub> 194.15°, 2.45°, 0.96012; *o*-200.40°, -16.4°, 1.00279, and *m*-toluidine 203.40°, -31.25°, 0.99302; PhNO<sub>2</sub> 210.80°, 5.70°, 1.20824. Other data recorded include the variation of b.p. with pressure, coeffs. of dilatation, *r*<sup>15</sup>, viscosity coeffs., surface tensions, and crit. solution temp. in suitable solvents. Previous data are tabulated. J. W. S.

**B.p. of normal paraffin series.** E. R. COX (Ind. Eng. Chem., 1935, 27, 1423—1425).—From C<sub>3</sub>H<sub>8</sub> to C<sub>8</sub>H<sub>18</sub> (except C<sub>4</sub>H<sub>10</sub>) results calc. from  $\log_{10} B = 1.07575 + 0.949128 \log_{10} m - 0.101 \log_{10}^2 m$  ( $B = \text{b.p. abs.}$ ;  $m = \text{mol. wt.}$ ) agree with observation. Disagreement in the cases of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> is attributed to their not being true aliphatic compounds (cf. Rossini, A., 1934, 1071). J. W.

**Specific heat of iron carbide, Fe<sub>3</sub>C.** G. NAESER (Mitt. Kaiser-Willh. Inst. Eisenforsch., 1934, 16,

207—210; Chem. Zentr., 1935, i, 2325).—The mean sp. heat (*h*) of cementite, obtained electrolytically from Fe with 0.9% C, has been measured between -188° and 765°. *h* reaches a max., nearly const. val. at 250°. The heat of formation and of the magnetic transformation are calc. J. S. A.

**Heat capacity of gadolinium sulphate from 1.0° to 20.5° abs.** C. W. CLARK and W. H. KEESOM (Physica, 1935, 11, 1075—1079).—The anomalous thermal behaviour of Gd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O observed by Kurti (A., 1933, 449) was verified down to 1° abs. H. J. E.

**Phase equilibria in hydrocarbon systems. IX. Specific heats of *n*-butane and -propane.** B. H. SAGE and W. N. LACEY (Ind. Eng. Chem., 1935, 27, 1484—1488).—*c* was determined for both compounds in the gaseous and the condensed state; both *c<sub>g</sub>* and *c<sub>r</sub>* were determined. Apparatus is described. J. W.

**Calorimetric and thermal properties of condensed deuterium.** K. CLUSIUS and E. BARTHOLOME (Z. physikal. Chem., 1935, B, 30, 237—257).—The following data are recorded: latent heat of vaporisation at 194.5 mm., 302.3; heat of sublimation at 0° abs., 274.0; latent heat of fusion 47.0 g.-cal.; characteristic temp. of Debye function for *c<sub>p</sub>*, 89°; m.p., 18.65° abs.; slope of fusion curve at triple point, 40.5 kg. per sq. cm.; mol. vol. of liquid at triple point, 23.14; mol. vol. of solid at triple point, 20.48 c.c.; zero-point energy of lattice, ~215 g.-cal. The considerable differences between these vals. and the corresponding figures for H<sub>2</sub> are qualitatively accounted for if it is assumed that H<sub>2</sub> and D<sub>2</sub> have the same intermol. forces but different zero-point energies and anharmonicities of lattice vibration. R. C.

**Absolute zero, and the sub-zero region of temperatures and reactions.** P. N. PAVLOV (Ukrain. Chem. J., 1935, 10, 285—294).—Theoretical. The possibility of temp. < 0° abs. is envisaged, and the properties of matter in this region are discussed. R. T.

**Theory of the equation of state.** S. RAY (Kolloid-Z., 1935, 73, 269—272).—Ray's theory (A., 1931, 1117) is extended to saturated vapours and the liquid phase. E. S. H.

**Vapour pressures of some alkyl sulphides.** H. W. THOMPSON and J. W. LINNETT (Trans. Faraday Soc., 1935, 31, 1743—1747).—The v.p. of EtSH, Me<sub>2</sub>S, MeEtS, and Et<sub>2</sub>S have been determined at several temp. up to the b.p. The vals. of Trouton's const. deduced are normal, indicating non-association. J. W. S.

**Vapour pressure of drops.** S. V. GORBATSCHEV (Kolloid-Z., 1935, 73, 263—267).—Mathematical. E. S. H.

**Influence of degree of dispersion on physico-chemical constants.** V. E. COHEN and J. J. A. BLEKKINGH, jun. (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 978—982; cf. this vol., 20).—*d*<sub>15</sub> for *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H is 1.4340, independently of crystal size between 0.01 and 1 mm. J. W. S.

**Fluctuations in density at the critical point.** J. YVON (Compt. rend., 1935, 201, 1099—1102).—Theoretical. H. J. E.

**Röntgenographic thermal expansion of very pure sodium chloride.** W. RECK and A. SMEKAL (Helv. phys. Acta, 1934, 7, 876; Chem. Zentr., 1935, i, 2783).—Measurements between  $-175^{\circ}$  and  $725^{\circ}$  show uniform expansion. Saini's anomaly (A., 1935, 436) is illusory. J. S. A.

**Thermal expansion of rock-salt and of pure sodium chloride.** H. SAINI (Helv. phys. Acta, 1934, 7, 877; Chem. Zentr., 1935, i, 2783).—The conclusion of Reck and Smekal (cf. preceding abstract) is acknowledged. J. S. A.

**Joule-Thomson effect of methane, nitrogen, and their mixtures.** J. H. PERRY and C. V. HERRMANN (J. Physical Chem., 1935, 39, 1189—1195).—Joule-Thomson coeffs. of  $\text{CH}_4$ ,  $\text{N}_2$ , and of 25, 50, and 75% mixtures at five temp. are calc. from the Beattie-Bridgeman equation. F. L. U.

**Viscosity and constitution of organic liquids.** S. PAPKOV (Z. physikal. Chem., 1935, 174, 445—448).—For an org. compound the val. of  $S=M^{2/3}\eta/d$ , where  $M$  is the mol. wt. and  $d$  the viscosity,  $\eta$ , are for  $20^{\circ}$ , is additively made up of characteristic vals. for the constituent atoms. Degrees of association of various liquids have been calc.  $S$  varies with temp. R. C.

**Square root law of fluidity. I. Hydrocarbons.** R. LAUTIF (Bull. Soc. chim., 1935, [v], 2, 2187—2192; cf. A., 1935, 1064).—The law proposed is where  $\phi$  is the fluidity at  $t^{\circ}$ , and  $I_i$  denotes increments appropriate to the atoms, types of linking, etc. in the compound considered. Examples are given for saturated and unsaturated cyclic hydrocarbons, and for paraffins. For mixtures of normal liquids of not too low or too high viscosity ( $\eta$ ), which show little vol. change on mixing, the law  $100\sqrt{\eta}=\sum m_x\sqrt{\eta_x}$  (where  $m_x$ ,  $\eta_x$  indicate the mol.-% and viscosity coeff. of the several constituents) applies closely. F. L. U.

**Viscosity in the system chlorine-sulphur.** V. A. MAZEL (J. Gen. Chem. Russ., 1935, 5, 1066—1072).—The  $\eta$ -composition curves of the system  $\text{Cl}_2$ - $\text{SCl}_2$  have been studied at  $-15^{\circ}$ ,  $0^{\circ}$ , and  $25^{\circ}$ . R. T.

**Viscosity of the system  $\text{KAlSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$  and of perthite at high temperatures.** K. KANI (Proc. Imp. Acad. Tokyo, 1935, 11, 324—336).—The data refer to  $1300$ — $1450^{\circ}$  and the entire range of conens. of the system  $\text{KAlSi}_3\text{O}_8$  (I)- $\text{NaAlSi}_3\text{O}_8$ . Log  $\eta$  increases with concn. of (I), and the slope of the line connecting log  $\eta$  and temp. is the same for all mixtures. J. G. A. G.

**Thermal expansion of the binary system  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{B}_2\text{O}_3$  in the molten state.** M. P. VOLAROVITSCH (Acta Physicochim. U.R.S.S., 1935, 2, 695—710; cf. A., 1935, 24).—The sp. vols. of  $\text{Na}_2\text{B}_4\text{O}_7$ - $\text{B}_2\text{O}_3$  melts have been determined between  $500^{\circ}$  and  $1200^{\circ}$  in a Pt-Ir dilatometer. Fluidity varies linearly with temp. above  $820^{\circ}$ ; the large divergence at lower temp. is attributable to association. T. G. P.

**Dipole induction and the solvent effect in dipole moment measurements.** F. C. FRANK (Proc. Roy. Soc., 1935, A, 152, 171—196).—On the

basis of Weigle's formula (A., 1934, 12), a theory is developed to account for the effect of the solvent on the measured val. of the dipole moment of a solute. Examples of solvent effect are classified according to mol. geometry. The empirical laws advanced by Müller (A., 1932, 1077) and others apply only to a single class. The theory leads to important conclusions regarding dipole induction in radicals forming part of the polar mol.; in general, the more positive is the radical effect, the more negative is the solvent effect, and vice versa. The attraction of solvent mols. by dipole forces, the effect of anisotropic polar solvents, the bearing of the dielectric constants of aq. solutions on the structure of zwitterions, and the form of the dispersion curve in polar liquids are discussed in the light of the above theory. L. L. B.

**Dielectric polarisation and molecular-compound formation in solution. I. Structures of the compounds of ethers with halogeno-methanes and -ethanes. II. Structures of the compounds of acetone, quinoline, and dioxan with halogenomethanes.** D. P. EARP and S. GLASSTONE (J.C.S., 1935, 1709—1719, 1720—1723).—I. The dielectric polarisations of binary mixtures of  $\text{Et}_2\text{O}$ ,  $\text{Pr}^n_2\text{O}$ , and  $(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{O}$  with halogen derivatives of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  have been determined. The molecular polarisations of the constituents suggest that compound formation in such mixtures involves the introduction of a new co-ordinate linking, which contributes to the dipole moment. A method for calculating the proportion of compound present has been developed. In compounds of the type  $\text{R}_2\text{O}\cdot\text{CHX}_3$ , co-ordination occurs between O and H attached to X. When chemical interaction does not occur, polarisations are additive, even in mixtures of two polar substances, when allowance is made for variation of dielectric const.

II. Compound formation occurs which is analogous to that observed with ethers. The nature of the linking, which generally involves co-ordination with H, is discussed. E. S. H.

**Dipole theory of solutions.** N. BARBULES (J. Chim. phys., 1935, 32, 639—656).—The theory described leads to a formula for the osmotic pressure which corresponds with van der Waals' equation. Deviations of real from ideal solutions at high concentrations are explained by mol. polarisation, the existence of permanent electric moment causing deactivation of the solute in some cases and of the solvent in others. The formulæ are verified by experiment for mixtures of  $(\text{CH}_2\text{Cl})_n$  and  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ ,  $\text{O}_2$  and  $\text{N}_2$ ,  $\text{EtOAc}$  and  $\text{EtI}$ ,  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$  and  $\text{Et}_2\text{O}$ , and for  $\text{CHCl}_3$  and  $\text{COMe}_3$ . J. W. S.

**Surface tensions of binary liquid mixtures containing benzene.** J. W. BELTON (Trans. Faraday Soc., 1935, 31, 1642—1648).—The surface tensions of  $\text{C}_6\text{H}_6$ - $\text{AcOH}$  and  $\text{C}_6\text{H}_6$ - $\text{CS}_2$  mixtures have been measured at  $20^{\circ}$  and  $35^{\circ}$  and those of  $\text{C}_6\text{H}_6$ - $\text{CCl}_4$  mixtures at  $50^{\circ}$ , the surface adsorption being calc. from Gibbs' equation. The adsorbed layer is always < unimol. and varies with concn. Only with  $\text{C}_6\text{H}_6$ - $\text{AcOH}$  mixtures of low  $[\text{C}_6\text{H}_6]$  is  $\text{C}_6\text{H}_6$  adsorbed. J. W. S.

**Surface tensions of ternary solutions. III.** J. W. BELTON (Trans. Faraday Soc., 1935, **31**, 1648—1652; cf. A., 1935, 1316).—The surface tensions of solutions containing sucrose and NaCl, HCl and NaCl, and HCl and KCl have been measured and the surface adsorption of  $H_2O$  is calc. The adsorption for sucrose and NaCl is  $\ll$  the sum of the adsorptions which each solute produces separately, but a [HCl] which has inappreciable effect on the surface tension of  $H_2O$  greatly decreases the adsorption of  $H_2O$  on a salt solution. J. W. S.

**Calculation of various physical constants of heterogeneous substances. I. Dielectric constants and conductivities of mixtures of isotropic substances.** D. A. G. BRUGGEMAN (Ann. Physik, 1935, [v], **24**, 636—664).—Theoretical. Dielectric consts. and thermal and electrical conductivities are calc. by a unitary method from the consts. of the homogeneous constituents of the mixture. The accuracy of older formulæ is discussed and previously undetermined consts. in these formulæ are evaluated. W. R. A.

**Calculation of various physical constants of heterogeneous substances. I (cont.). Dielectric constants and conductivities of mixtures of isotropic substances.** D. A. G. BRUGGEMAN (Ann. Physik, 1935, [v], **24**, 665—679).—The above theory is applied to the conductivity of binary heterogeneous alloys. For Pt-Ag alloys the experimental results are in qual. agreement with theory. The dielectric consts. of compressed powdered KCl (KCl-air mixture) and of emulsions are considered in the light of the new theory. For salt-air mixtures experiment agrees with theory, but Piekara's results on emulsions of small concn. are best explained by the Rayleigh formula, although more conc. emulsions would probably be covered by the new theory. A. J. M.

**Vapour pressure of solutions of acids and salts in liquid ammonia at 15°.** A. I. SCHATTENSTEIN and L. S. USKOVA (Acta Physicochim. U.R.S.S., 1935, **2**, 337—344; cf. A., 1934, 838).—The v.p. and  $d$  of solutions of  $NH_4Cl$ ,  $NH_4Br$ ,  $NH_4I$ ,  $NH_4NO_3$ ,  $NH_4OAc$ , NaCl, and  $NaNO_3$  in liquid  $NH_3$  have been determined for wide ranges of concn. at 15°, and for the NaCl solutions also at 10°. The osmotic coeffs. of these solutes follow the order  $NH_4I > NH_4NO_3 > NaNO_3 > NH_4Br > NaCl > NH_4Cl > NH_4OAc$ . J. W. S.

**Numerical relationships in binary metallic systems.** D. STOOKDALE (Proc. Roy. Soc., 1935, **A**, **152**, 81—104).—The work of Hume-Rothery and others on the depression of the f.p. and m.p. of Cu and Ag by the addition of elements of the  $B$  subgroups, and the solubility limits in these alloys (A., 1934, 725), are discussed. It is shown that there are probably other simple integral relationships between the no. of atoms in a binary alloy, and the following empirical rules are adduced: (a) the solute and solvent atoms are present in a simple integral ratio in a saturated solid solution at the temp. of the eutectic or peritectic horizontal; (b) in a eutectic mixture the elements are present in a simple integral at. ratio; (c) in a eutectic mixture the ratio of the no. of atoms, irrespective of their kind, in the phases is

simple. It is improbable that rules (b) and (c) are both exact, but if either is true, then, in seven systems investigated, the other is true to within 1 part in 200. L. L. B.

**Effect of thermal agitation on atomic arrangement in alloys. III.** E. J. WILLIAMS (Proc. Roy. Soc., 1935, **A**, **152**, 231—252; cf. this vol, 24).—Mathematical. The equilibrium equations for a general case are derived from the Boltzmann distribution formula and from the principle of min. free energy. By comparing the dependence of the entropy of the at. arrangement on the order of nearest neighbours with its dependence on the superlattice order, the quant. relation of Bethe's treatment (A., 1935, 1193) to that of Bragg and Williams (*loc. cit.*) becomes evident. L. L. B.

**Methods of investigating the constitution [of alloys].** G. GRUBE (Z. Metallk., 1935, **27**, 194—195).—Dilatometric and magnetometric methods are briefly described and a detailed description is given of a delicate apparatus for measuring the magnetic susceptibility of metals at temp. up to 1400°; it consists of a micro-electric furnace in the middle of two inclined poles of a powerful electro-magnet, the specimen being suspended in the furnace by means of a lever system the movement of which is compensated for by a small coil, the current through which, measured by a milliammeter, is  $\propto$  the susceptibility. A. R. P.

**Relation between diffusion and structure in solid alloys.** W. SEITH and A. KEIL (Z. Metallk., 1935, **27**, 213—215).—In alloys which form homogeneous solid solutions  $\log D = A - Q/RT$ , where  $D$  is the rate of diffusion and  $A$  and  $Q$  are material consts.,  $Q$  being the equiv. of the heat of activation in chemical reactions. The diffusion of small amounts of one metal into another takes place the more readily the greater is the amount of distortion produced and less readily the greater the tendency to form solid solutions; the addition of metals which reduce the m.p. of the base metal increases the rate of diffusion in this metal. Transformation and recrystallisation, as well as the passage of a d.c. through the alloy, increase the rate of diffusion, the effect of the current being due to electrolytic transport. A. R. P.

**Electrical conductivity and equilibrium diagram for binary alloys. XVII. System lithium-aluminium.** G. GRUBE, L. MOHR, and W. BREUNING (Z. Elektrochem., 1935, **41**, 880—883; cf. A., 1935, 23).—The solid phases in the successive ranges are: 0—30 at.-% Li,  $\alpha$ -mixed crystals; 30—60%, LiAl; 60—78%,  $\beta$ -mixed crystals of LiAl with excess of Li; 78—100%, compound  $Li_2Al$ . Between 44.5 and 60.0 at.-% of Li at 698° there are two liquid phases. F. L. U.

**Constitution and properties of iron-carbon-beryllium alloys.** M. BALLAY (Compt. rend., 1935, **201**, 1124—1126).—The effect of Be (0—4%) on an alloy with C 3—4.45, Mn 0.25, Si 0.25, S 0.02, and P 0.05% is reviewed.  $Be_2C$  is almost insol. in austenite. The temp. of the  $\gamma$  transformation is only slightly affected by Be. Data for the hardness of a series of these alloys are given. H. J. E.

**X-Ray analysis of the homogeneous phase in the system Mg-Ni.** E. F. BACHMETEV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 567—570).—Preliminary. Two hexagonal homogeneous phases have been observed, one of which (I), probably  $\text{Mg}_3\text{Ni}$ , has  $a$  5.26,  $c$  about 13.3 Å., whilst the other (II) has  $a$  4.87,  $c$  about 16 Å. The unit cell of (I) contains 16, and of (II) 48, atoms. F. L. U.

**Is an intermetallic homogeneous phase formed in the system Mg-Mn?** E. F. BACHMETEV and J. M. GOLOVTSCHINER (*Acta Physicochim. U.R.S.S.*, 1935, 2, 571—574).—Preliminary. Crystals separating from a Mg-Mn alloy containing 36—51 at.-% Mn have cubic symmetry, and X-ray examination indicates that they consist of  $\beta$ -Mn. F. L. U.

**Modified aluminium-silicon alloys.** II. J. A. KLJATSCHKO (*J. Gen. Chem. Russ.*, 1935, 5, 1299—1301).—The silicide content of Si-Al alloys is reduced from 0.4 to 0.2% by treatment with Na. R. T.

**Physico-chemical investigation of the gold-manganese alloys.** V. A. NEMILOV and A. A. RUDNICKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 351—354).—The thermal properties, hardness, and electrical resistance of Au-Mn alloys have been investigated. AuMn exists in the molten alloy, whilst  $\text{AuMn}_3$  and  $\text{Au}_2\text{Mn}$  separate from the solid solutions formed on cooling. R. S.

**Nickel-manganese system.** II. S. VALENTINER (*Z. Physik*, 1935, 97, 745—757).—The electrical resistance in magnetic fields shows that alloys with 25—30% of Mn are abnormal (cf. A., 1935, 576). A. B. D. C.

**Mechanism of precipitation [in silver-copper alloys].** U. DEHLINGER (*Z. Metallk.*, 1935, 27, 209—212).—The particles of Ag which first separate during the decomp. of a quenched supersaturated solid solution of Ag in Cu do not act as nuclei for further pptn. The process of pptn. must therefore be propagated by lattice distortion probably at the boundaries of mosaic blocks. At these points thin films of Ag first separate and gradually coalesce into grains which are visible under the microscope. After deformation and recrystallisation decomp. of the solid solution is accelerated, probably owing to the concn. of an "active factor" at the boundaries of regions in which pptn. has already commenced. A. R. P.

**System copper-nickel-iron.** W. KOSTER and W. DANNOHL (*Z. Metallk.*, 1935, 27, 220—226).—The system has been investigated by thermal, magnetometric, and electrical resistance methods. The  $\alpha$ - $\gamma$  transformation occurs in all alloys the composition of which lies on the Fe side of a straight line joining the Cu corner of the ternary diagram to the 28% Ni point on the Fe-Ni side. The miscibility gap in the Fe-Cu system is gradually closed by addition of Ni and disappears entirely with 27% Ni at 1220° and with 82% Ni at 20°; alloys within this range are therefore amenable to pptn.-hardening, and such treatment gives rise to interesting magnetic properties. The equilibria in the system are showed in ternary diagrams and in numerous sectional diagrams for const. Ni contents and const. Fe : Cu ratio. A. R. P.

**X-Ray analysis of crystal formation in the ternary system Cu-Al-Ti.** E. F. BACHMETEV, N. G. SEVASTIANOV, and N. I. KOTOV (*Acta Physicochim. U.R.S.S.*, 1935, 2, 561—566).—In an alloy of composition Cu 40, Al 40, Ti 20 wt.-%, a preliminary examination has established the existence of two homogeneous phases, viz., cubic, with  $a$  3.94 (or 7.88) Å., and hexagonal, with  $a$  5.05,  $c$  8.06 Å. F. L. U.

**Magnetic investigations of precipitation-hardening.** H. AUER (*Physikal. Z.*, 1935, 36, 880—882).—The mechanism of the improvement of the mechanical properties of an alloy by suitable heat-treatment whereby a new phase is produced is discussed. The variation of susceptibility,  $\chi$ , of Cu-Al alloys during such a process is determined. There is a considerable decrease in  $\chi$  during the transition, and this fact can be used to follow the velocity of transition under different conditions of temp., concn., supersaturation, and previous heat-treatment. The mean transition velocity,  $u$ , is connected with abs. temp.,  $T$ , by  $\log u = A/T + B$  ( $A$  and  $B$  const.). The final val. of  $\chi$  depends in a discontinuous manner on the tempering temp. The points at which the discontinuities occur give points on the diagram of state. The val. of  $\chi$  shows that the separating phase is  $\text{CuAl}$ . An extended Curie law holds for the alloys when equilibrium is attained, but the considerable deviations found at the transition point are to be connected with supersaturation in the mixed crystal phase. A. J. M.

**Rate of diffusion in metallic crystals and atomic structure.** W. SEITH (*Z. Elektrochem.*, 1935, 41, 872—876; cf. A., 1935, 158, 1205).—The rates of diffusion of metals in solid Pb show the same dependence on their at. radius and no. of valency electrons as do their solubilities. F. L. U.

**Shape of critical temperature curves of binary systems.** R. V. MERZLIN (*J. Gen. Chem. Russ.*, 1935, 5, 1073—1076).—Stachorski's formula (A., 1928, 472) corresponds more closely with experimental surface tension data than do those of Pawlewski (A., 1882, 915; 1883, 176) or Strauss (Ber., 1881, 14, 510). R. T.

**Desaturation experiments on aqueous carbonic acid.** Y. KAUKO and H. KOMMUSAR (*Ann. Acad. Sci. fenn.*, 1934, A, 39, No. 8; *Chem. Zentr.*, 1935, i, 2767).—With good mixing of gas and liquid, the rates of saturation and desaturation of  $\text{CO}_2$  in  $\text{H}_2\text{O}$  are reproducible. J. S. A.

**Solubility of lime in water.** G. L. LAROCQUE and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 276—279; cf. A., 1933, 897).—Conductivity data at 0—30° are given for a series of  $\text{Ca}(\text{OH})_2$  solutions. Vals. for the solubility and degree of dissociation of  $\text{Ca}(\text{OH})_2$  are calc. Equilibrium between aq. solutions and solid  $\text{Ca}(\text{OH})_2$  is established very slowly. H. J. E.

**Solubilities of *l*-proline and *l*-hydroxyproline in water, the calculated heats of dissolution, and the partial molal volume of *l*-hydroxyproline.** T. TOMIYAMA and C. L. A. SCHMIDT (*J. Gen. Physiol.*, 1935, 19, 379—382). F. A. A.

**Solubilities of certain salts in liquefied ammonia.** III. Solubility of ammonium chloride,



and vapour pressure of the solution. S. ABE, K. WATANABE, and R. HARA (J. Soc. Chem. Ind. Japan, 1935, 38, 642—646B).—Solid phases in the  $\text{NH}_4\text{Cl}$ — $\text{NH}_3$  system are  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Cl}\cdot 3\text{NH}_3$ , which coexist at  $5.9^\circ$ . Solubilities between  $-20^\circ$  and  $25^\circ$  are recorded, and also v.p. of the saturated and unsaturated solutions. Heats of dissolution are calc.

J. S. A.

Absorption of hydrogen sulphide and sulphur dioxide from a current of air. V. A. PIANKOV (J. Gen. Chem. Russ., 1935, 5, 1112—1118).—The velocity of adsorption of  $\text{H}_2\text{S}$  by wood C is doubled at  $20^\circ$ , and quadrupled at  $40^\circ$ , by treatment with I, whilst for  $\text{SO}_2$  it is increased 1.8 times at  $20^\circ$  and  $40^\circ$ .

R. T.

Distribution of hydrogen sulphide between benzene and water. S. A. SCHTSCHUKAREV and I. B. CHACHAM (J. Gen. Chem. Russ., 1935, 5, 1056—1058).—The high vals. of the partition coeff. of  $\text{H}_2\text{S}$  between  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}$  are ascribed to anomalously low solubility in  $\text{H}_2\text{O}$ .

R. T.

Distribution of (A) saturated monocarboxylic fatty acids between glycerol and other organic solvents, (B) hexoic acid between two contiguous liquid phases. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 1041—1044, 1048—1055).—(A) [with F. S. KULIKOV]. Data are recorded for  $\text{EtCO}_2\text{H}$  with  $\text{CHCl}_3$  and for  $\text{Bu}^n\text{CO}_2\text{H}$  with  $\text{CHCl}_3$ ,  $\text{PhMe}$ , and  $\text{PhNO}_2$ , at  $25^\circ$ .

(B) [with M. O. LEVITAS]. Data are recorded for the systems  $\text{H}_2\text{O}$ — $\text{C}_6\text{H}_6$ , — $\text{PhMe}$ , —decahydronaphthalene, — $\text{CCl}_4$ , — $\text{MeI}$ , — $\text{PhBr}$ , — $\text{PhOMe}$ , and — $\text{PhNO}_2$ , at  $25^\circ$ . The val. of 1/partition coeff. approaches the same figure when the concn. of hexoic acid in the entire system approaches 7.8 g.-equiv. per litre.

R. T.

Points of intersection of curves representing distribution of solutes between two liquid phases. N. A. DE KOLOSOVSKI (J. Gen. Chem. Russ., 1935, 5, 1045—1047).—The curves connecting the total concn. of  $\text{Bu}^n\text{CO}_2\text{H}$  with the partition coeff. between a no. of org. solvents and  $\text{H}_2\text{O}$  intersect at the origin and at another point. The phenomenon is shown to be general when the solubility of the solute is unlimited in one, and limited in the other, solvent.

R. T.

A partition paradox. N. A. DE KOLOSOVSKI and F. S. KULIKOV (J. Gen. Chem. Russ., 1935, 5, 1037—1040).—It is shown mathematically that the concn. of a solute in each layer of a binary liquid mixture may increase as the result of the addition of a small amount of one of the solvents, owing to changes in the mutual solubility of the solvents themselves.

R. T.

Sorption of sulphur dioxide by active charcoal. VI. Rate of sorption. K. ARII (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1210—1232; cf. A., 1935, 577).—Rates of sorption and desorption determined between  $-20^\circ$  and  $-40^\circ$  are in agreement with Bangham's equation.

R. S.

Heterogeneous catalysis. II. Adsorption on graphite and diamond. E. STORFER (Z. Elektrochem., 1935, 41, 868—872; cf. A., 1935, 696).—Adsorption isotherms have been determined for  $\text{N}_2$ ,

$\text{CH}_4$ ,  $n\text{-C}_6\text{H}_{14}$ , cyclohexane, and  $\text{C}_6\text{H}_6$  on graphite and diamond at  $155^\circ$  and  $205^\circ$ . The first two exhibit stepped adsorption at low pressures, and are adsorbed in quantities approx.  $\propto$  the sp. surface. The three last are adsorbed by graphite more strongly than can be accounted for by its higher sp. surface. Heats of adsorption are calc.

F. L. U.

Van der Waals, activated, and atomic adsorption of hydrogen on copper and nickel, and their influence on the photo-effect. O. I. LEIPUNSKI (Acta Physicochim. U.R.S.S., 1935, 2, 737—760).—The adsorption of  $\text{H}_2$  on Cu and Ni has been investigated. The presence of a steric factor (Leipunski, A., 1935, 578) is generally characteristic of activated adsorption, which therefore involves a diffusion process, contrary to other views (cf. Taylor *et al.*, A., 1934, 1181). There is no activated adsorption on Cu which has been distilled in vac. or has been once oxidised and then reduced. Ni adsorbs  $\text{H}_2$  by two different processes according to the temp. The heats of adsorption are 4, 13, and 16—17 kg.-cal. per mol. at  $-183^\circ$ ,  $0^\circ$ , and  $100^\circ$ , respectively. At the higher temp. the activation energy is 3 kg.-cal. per mol. The surface of Ni is not homogeneous and only 10% of it is active. The activated adsorption at low temp. is a localised phenomenon, and each active area is heterogeneous. Neither adsorption process influences the photo-effect. At. H is adsorbed by Cu and Ni at  $-183^\circ$  to an extent corresponding with a layer 3 mols. thick. The kinetics of desorption of at. H from Ni at  $-106^\circ$  suggest that the process may be due to recombination of atoms in the surface followed by desorption of the mols. The energy of activation of the surface diffusion process is 23.8 kg.-cal. per mol.

T. G. P.

Adsorption of indium and thallium atoms on tungsten oxide. C. F. POWELL and R. L. MERCER (Phil. Trans., 1935, A, 235, 101—124).—The adsorption and desorption of In and Tl atoms have been studied thermionically on a film of  $\text{WO}_3$  on W,  $10^{-4}$  cm. thick, at  $656$ — $765^\circ$ . The condensation coeff. is independent of the fraction of surface covered ( $\theta$ ) and of the temp., and is probably 1. In contrast with the behaviour of Cs on W, the adsorbed phase is always uniform. From the ratio ( $r$ ) of positive ion to neutral atom emission the electronic work function ( $V$ ) of a bare surface is calc. to be 6.13 and 6.25 volts, using In and Tl, respectively. Surface migration and diffusion into the interior of the oxide film have been studied at approx.  $200^\circ$  below emission temp. The ratio  $r$  increases with  $\theta$ , and  $V$  for the partly covered surface decreases linearly with increasing  $\theta$ . The ratio of the dipole moments associated with adsorbed Tl and In is 0.80. Similar experiments with Ga are not possible, since this is too strongly adsorbed, and appreciable emission occurs only at temp. at which  $\text{WO}_3$  decomposes; Ga acts as a poison towards the adsorption of In and Tl. The oxides of Ni, U, Fe, and Mo have been studied as sources of positive ions,  $\text{Fe}_2\text{O}_3$  being most similar to  $\text{WO}_3$ .

R. S. B.

Sorption and diffusion of ammonia in analcime. A. TISELIUS (Z. physikal. Chem., 1935, 174, 401—423; cf. A., 1934, 726).—Langmuir's isotherm is

valid if the amount sorbed is not too great, and this equation yields a val. for the amount of  $\text{NH}_3$  sorbed at saturation which approximates to the val. calc. from the equiv. max.  $\text{H}_2\text{O}$  content; in the temp. range studied ( $302$ — $385^\circ$ ) this does not vary with temp. The const.  $b$  of the isotherm is  $\propto e^{Q/RT}$ , where  $Q$  is the heat of sorption. Each sorbing centre corresponds with a vol. which is of the order of magnitude of a mol. vibrating in the lattice rather than of a mol. able to move freely in the whole sorption space. The heat of sorption is  $16,640$  g.-cal. At  $302^\circ$  the diffusion coeff. in a single crystal is  $1.3 \times 10^{-8}$  (sq. cm., sec.). Diffusion apparently takes place by jumps along the canals in which the  $\text{H}_2\text{O}$  mols. are present (cf. *ibid.*, 947) and its rate determines that of the sorption as a whole; the energy of activation is  $14,480$  g.-cal., irrespective of the direction. R. C.

**Selective adsorption of heavy water.** A. KING, F. W. JAMES, C. G. LAWSON, and H. V. A. BRISCOE (J.C.S., 1935, 1545—1549; cf. A., 1934, 1062).—Steam from London tap- $\text{H}_2\text{O}$  was passed over  $\text{SiO}_2$  gel and various charcoals until equilibrium was attained, and the  $\text{H}_2\text{O}$  fractionally desorbed. The isotopic enrichment ratio, determined by measurement of  $d$ , is greatest (about 1.4) in the last fraction and is independent of the activity of the charcoal. An experiment with pure charcoal and  $\text{H}_2\text{O}$  containing 4% of  $\text{D}_2\text{O}$  gave a similar result, the % of  $\text{D}_2\text{O}$  being determined in this case from the f.p. It is suggested that the difference in the adsorption of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  is due to a difference in polarisability. R. S.

**Adsorption of anions by precipitated barium sulphate.** T. P. CHAO, K. H. HSIUNG, and Y. L. CHU (J. Chinese Chem. Soc., 1935, 3, 325—342).—The order of adsorption of anions by  $\text{BaSO}_4$  is  $\text{NO}_3' > \text{ClO}_3' > [\text{Fe}(\text{CN})_6]''' > [\text{Fe}(\text{CN})_6]''' > \text{NO}_2' > \text{CNS}' > \text{Cl}' > \text{Br}'$ . The Schulze-Hardy law is only qualitatively valid. The amount of adsorption is governed by the nature of the ion, its valency, and the solubility of its Ba compound. The less sol. are more strongly adsorbed.  $\text{NO}_3'$  and  $\text{ClO}_3'$  are particularly strongly adsorbed, and their presence in the quant. pptn. of  $\text{SO}_4'$  is to be avoided. A. J. M.

**Absorption of sodium hydroxide by cellulose.** S. M. NEALE (J. Physical Chem., 1935, 39, 1245; cf. A., 1930, 417, 1249).—The concn. of adsorbed aq.  $\text{NaOH}$  removed from cellulose by powerful centrifuging decreases as centrifuging proceeds. This effect is compatible with the assumption that  $[\text{OH}']$  in the adsorbed solution is determined by membrane equilibrium. F. L. U.

**Absorption of dyes by cellulose. VI. Effect of modification of the cellulose and a theory of the electrolyte effect.** J. HANSON, S. M. NEALE, and W. A. STRINGFELLOW (Trans. Faraday Soc., 1935, 31, 1718—1730; cf. A., 1934, 1169).—Increased motion of the absorbent relative to the dye-bath increases the rate of absorption of sky-blue FF considerably in the case of yarns and fabrics and slightly for Cellophane. Swollen cellulose takes up more dye than natural cellulose in a ratio which is independent of the concn. of added  $\text{NaCl}$ . Oxidation of cellulose reduces the absorption of dye, especially

at low  $[\text{NaCl}]$ . These effects are attributed to Donnan equilibria, and a theoretical equation is deduced which is in accord with the observed variation of the absorption with  $[\text{NaCl}]$  and dye concn. An extension of the theory embracing the ionisation of the  $\text{CO}_2\text{H}$  groups of oxycellulose is in qual. agreement with experiment. J. W. S.

**Adsorption of cyclopentanone by cellulose nitrate.** J. DESMAROUX, R. VANDONI, and (MLE.) T. PETITPAS (Compt. rend., 1935, 201, 1392—1393).—The adsorption of cyclopentanone by nitro-cotton (12.13 and 13.52% N) has been examined. It is independent of the N content. R. S. C.

**Adsorption problems. I.** TRAUBE (Trans. Faraday Soc., 1935, 31, 1730—1739).—Anthracene,  $\text{C}_{10}\text{H}_8$ ,  $\text{NHPh}$ , phthalic acid, and charcoal, added to aq. solutions of  $\text{C}_8\text{H}_{17}\cdot\text{OH}$  or  $\text{C}_7\text{H}_{15}\cdot\text{CO}_2\text{H}$  adsorb such small quantities of the solute that the Langmuir theory may be applicable, but if such adsorbents are added to  $\text{H}_2\text{O}$ -sol. or  $\text{H}_2\text{O}$ -insol. substances in an emulsified state, the emulsified substances are adsorbed to a very high degree and very firmly. This is attributed to the lower diminution of surface tension produced by colloid particles than by dissolved mols. The adsorption is generally accompanied by flocculation owing to linking of the adsorbent particles through the adsorbed substances, and this flocculation is compared with electrolytic flocculation of colloids by ions, coagulation by gelatinous colloids, and flocculation of ores by surface-active org. substances. J. W. S.

**Formation and constitution of crystals of lead salts containing water-soluble colloid.** F. D. MILES (Phil. Trans., 1935, A, 235, 125—164).—The adsorption of neutral dextrin, gum-arabic, and gelatin, and their influence on the crystal habit, have been studied with  $\text{PbCl}_2$ ,  $\text{PbBr}_2$ ,  $\text{PbI}_2$ ,  $\text{PbN}_6$ , and  $\text{PbSO}_4$  during slow and rapid crystallisation from aq. solution. At low concn. of colloid the crystal edges are curved, but the internal structure, as revealed by optical measurements, is almost unaffected up to 5% of adsorbed colloid. The max. adsorption is 10%. Colloids retard the formation of  $\beta$  crystals of  $\text{PbN}_6$  from the  $\alpha$  form, whereas dyes have the opposite effect. Adsorption occurs in the order  $\text{PbSO}_4$  and  $\text{PbN}_6 > \text{PbCl}_2 > \text{PbI}_2$  at  $20^\circ$ , i.e., in the order of increasing polarisability of the anion. Maltose is not adsorbed. From conductivity measurements on solutions of Pb salts in presence of dialysed dextrin it is inferred that no association occurs in solution. X-Ray studies on  $\text{PbSO}_4$  and  $\text{PbN}_6$  show that the lattice dimensions are unaffected, but that the particle size decreases with increasing content of colloid. With  $\text{PbN}_6$  the introduction of colloid causes the deposition of a colloidal Pb compound. It is inferred that at  $< 5\%$  adsorption the crystallites are approx. in the same crystallographic orientation and are separated by a layer of dextrin, the mols. being attached to the crystallites by some of their OH groups. At  $> 5\%$  adsorption the same orientation is not maintained throughout the crystal. R. S. B.

**Exchange adsorption on colloidal vanadium pentoxide.** V. A. KARGIN and H. B. KLEMOVITZKAJA

(Acta Physicochim. U.R.S.S., 1935, 2, 33—50; cf. A., 1935, 1069).—The pptn. of  $V_2O_5$  sol by  $BaCl_2$ ,  $CaCl_2$ , and  $MgCl_2$  has been studied and the changes in ionic concn. in the filtrate determined by gravimetric and potentiometric methods. The amounts of  $Ba^{++}$ ,  $Ca^{++}$ , and  $Mg^{++}$  adsorbed are not themselves equiv. nor are they equiv. to the total cations ( $H^+$  and  $NH_4^+$ ) released, whilst the amount of acid in the filtrate is approx. const. The intermicellar ionic concns. have been determined by analysis of the ultrafiltrate and the true adsorption calc., but the cation exchanges are again not equiv. Vanadic acids derived from the dissolution of the sol are present in the intermicellar liquid in approx. const. concn. The non-equivalence of the cation exchange and the fact that cation adsorption is also independent of sol concn. over a limited range are attributed to the formation of insol. Ba, Ca, or Mg salts of the intermicellar vanadic acids. R. S.

**Adsorption of grass and butter carotenes on alumina.** A. E. GILLAM and M. S. EL RIDI (Nature, 1935, 136, 914—915).—A double adsorption of pure  $\beta$ -carotene (I) from grass changes it partly into a substance resembling  $\alpha$ -carotene (II). This process is reversible, since re-adsorption changes this substance in part to (I).  $Ca(OH)_2$ , but not  $MgO$ , effects a similar change in (I), but less readily than does  $Al_2O_3$ . Pure (II) from palm oil is also changed by repeated adsorption on  $Al_2O_3$ . The possibility of changes brought about by chromatographic adsorption itself must thus be considered in work on the carotenes. L. S. T.

**Electrokinetics. XVII. Surface charge and ion antagonism.** L. S. MOYER and H. B. BULL (J. Gen. Physiol., 1935, 19, 239—247).—The surface charges of cellulose in contact with various salts are calc. from previously published data. The surface charge in contact with  $NaCl$  plotted as a function of temp. is discontinuous at  $39^\circ$ . Mixtures of Na, K, Mg, and Ca chlorides give lower surface charges at a given anion concn. than the single chlorides, thus showing ion antagonism. F. A. A.

**Affinities between proteins and fatty acids, fats, and lipins.** S. J. VON PRZYLECKI, E. HOFER, and S. FRAJBERGER-GRYNBERG (Biochem. Z., 1935, 282, 362—373).—Paraffins adsorb ovalbumin, serum-albumin, and edestin very readily, but caseinogen, gelatin, and peptone only slightly. Suspensions of cholesterol (I) behave similarly. Possibly the non-polar  $NH_2$ -acid residues (especially leucyl) are responsible for the adsorption, but the adsorption which occurs on acids and esters seems to be due to the polar groups of the proteins. The union with (I) may be partly strengthened by its  $CH:CH$  and  $OH$  groups. W. McC.

**Theory of adsorption.** H. BRADLEY (Trans. Faraday Soc., 1935, 31, 1652—1655).—The author's formula (A., 1927, 821), identical with that of Miyamoto (A., 1935, 578), is in accord with the observed adsorption of CO or A by coconut charcoal, of  $N_2$  by charcoal, of  $H_2O$  vapour by cotton, and of  $COMe.$  in  $H_2O$ , Br in  $H_2O$ ,  $iso-C_5H_{11}OH$  in  $H_2O$ , or  $BzOH$  in  $C_6H_6$  by blood charcoal. J. W. S.

**Formula for the rate of evaporation of adsorbed atoms and mols.** J. K. ROBERTS (Trans. Faraday Soc., 1935, 31, 1710—1713).—A formula derived from kinetic considerations is consistent with the behaviour of adsorbed films of O and H atoms on W, and with that of  $O_2$  mols. adsorbed on isolated W atoms left bare during formation of the at. O film. The theory is also applied to the case where the adsorbed atoms are the same as those in the surface, and an equation for v.p. is derived which is in good accord with experiment. J. W. S.

**Application of force-fields to the derivation of special thermodynamic relations, especially a general sorption equation and a new electrocapillary equation.** B. DERJAGUIN (Acta Physicochim. U.R.S.S., 1935, 2, 377—384).—Mathematical. J. W. S.

**Surface forces at the gas-liquid interface. VI. Method for determining the potential difference at still surfaces.** M. GEROVITSCH and A. FRUMKIN (Acta Physicochim. U.R.S.S., 1935, 2, 1—8).—The potential developed when a rapid stream of 0.01N-KCl is passed over a still surface of the same in air has been determined and compared with the result given by a radioactive probe. Good agreement is obtained, and it is shown that ionisation of the air does not affect the results for very dil. solutions. The potential and the sensitivity given by the stream method vary linearly with the height of the stream above the surface. R. S.

**Solid-liquid interface.** W. CLAYTON (J. Oil Col. Chem. Assoc., 1935, 18, 412—429).—A lecture on dielectric properties, polar groups, the electric double layer, adsorption, crystal growth, and surface films. E. S. H.

**Determinations of surface tension of solutions of potassium and lithium salts of higher fatty acids by the ring method with exclusion of atmospheric carbon dioxide and with special regard to other disturbing influences. II.** A. LOTTER-MOSER and E. GIESE (Kolloid-Z., 1935, 73, 276—288; cf. this vol., 26).—The surface tensions,  $\sigma$ , of several aq. K and Li soap solutions have been determined, using the precautions previously described. With rising temp.,  $\sigma$  decreases linearly as a rule; the causes of deviations have been traced. In certain soaps  $\sigma \propto \log$  concn. The cation has no influence on surface activity. At low concns. ( $10^{-5}$ — $10^{-4}$  g. per c.c.) Traube's rule holds qualitatively. E. S. H.

**Surface tension between aqueous and isopropyl ether solutions of acetic acid.** F. M. BROWNING and J. C. ELGIN (Ind. Eng. Chem. [Anal.], 1935, 7, 399—400).—Data for surface tension and  $d$  for dil. solutions at  $20^\circ$  are recorded. E. S. H.

**Graphical representation of the angle of wetting relations by the maximum bubble pressure method.** E. LANGE and K. NAGEL (Kolloid-Z., 1935, 73, 268—269).—Mathematical. E. S. H.

**Heat of wetting and the physical significance of the constants in Rodewald's equation.** P. J. ANDRIANOV (Kolloid-Z., 1935, 73, 328—334).—Theoretical. E. S. H.

**Constitution of the capillary layer in solutions of malachite-green.** (MLLE.) M. T. SALAZAR (Compt. rend., 1935, 201, 1120—1123).—The difference between the surface tension of  $H_2O$  ( $\sigma_w$ ) and that of the malachite-green solution ( $\sigma_s$ ) is const. for concns.  $> 6.5$  g. in 100 c.c. At lower concns. (c) the relation  $\sigma_w - \sigma_s = ac^b$  holds ( $a=15.14$ ,  $b=0.26$ ). The Gibbs equation is applied to these solutions. Above a certain concn. corresponding with the completion of a unimol. surface layer of solute, the quantity of solute absorbed in the surface is const. H. J. E.

**Investigation of unimolecular films.** I. LANGMUIR and K. B. BLODGETT (Kolloid-Z., 1935, 73, 257—263).—A discussion of technique. E. S. H.

**Semipermeability and neutral salts.** T. Y. CHANG and S. T. CH'IAO (J. Chinese Chem. Soc., 1935, 3, 308—320).—Experiments have been made to discover a possible relationship between semipermeability and the lyotropic series, due to the dehydration effect of the ions. Such an effect, leading to change of adsorption, provides an alternative theory to that of Zsigmondy on the variation of permeability with the nature of the solution. When increasing amounts of a neutral salt were added to an acid dye hydrosol, a collodion membrane became permeable at first, but later became impermeable. The effect of different salts was not in the order of the lyotropic series, and it appears that the effect is not simply a dehydration, but that discharge of the  $H_2O$  layer in the pore-wall and coagulation by the salts also intervene. Basic dye hydrosols were similarly examined. The membrane did not become permeable to the sol when neutral salt was added. The effect of tannin and EtOH was also studied.

A. J. M.

**Influence of a solid phase on the f.p. of water and of dilute aqueous solutions. I. Quartz sand-water.** A. V. RAKOVSKI, D. N. TARASENKOV, and A. V. KOMANDIN (J. Gen. Chem. Russ., 1935, 5, 1273—1278).—The f.p. of  $H_2O$  is depressed by  $SiO_2$  to an extent varying exponentially with the  $H_2O$  content of the mixture, and directly with the  $SiO_2$  surface. The phenomenon is not affected by the presence of  $0.1N-Na_2CO_3$  or  $-Ca(NO_3)_2$ . The results indicate that surface forces act at a distance of  $< 10,000$  mol. diameters.

R. T.

**Electrical investigation of solutions of stearanilide in paraffin wax.** W. JACKSON and F. C. FRANK (Trans. Faraday Soc., 1935, 31, 1700—1706).—The dielectric loss and d.c. conductivity of dil. solutions of stearanilide in molten and solid paraffin wax indicate the presence of polar groups containing  $< 10$  stearanilide mols. It is suggested that the mols. in the groups may approach a liquid crystalline formation, and that they adsorb ionic impurities.

J. W. S.

**Kinetic treatment of formation of nuclei in supersaturated vapours.** R. BECKER and W. DÖRING (Ann. Physik, 1935, [v], 24, 719—752).—Theoretical.

A. J. M.

**Theory of physico-chemical periodic processes.** F. M. SCHEMJAKIN and A. A. VITT (Acta Physicochim. U.R.S.S., 1935, 2, 171—176).—For certain periodic

reactions, the law of mass action and Fick's law of diffusion are together sufficient to explain the periodicity.

A. J. M.

**Formation of microscopic Liesegang rings.** E. C. BOTTI, O. W. LINK, and B. P. CALDWELL (J. Chem. Educ., 1935, 12, 540—541).—Details for the production of periodic ppts. of  $Ag_3AsO_4$  and  $Ag_2CrO_4$  in gelatin on a microscope slide are recorded; the advantages of the method are pointed out. L. S. T.

**Investigation of periodic reactions by application of physico-chemical analysis.** F. M. SCHEMJAKIN and P. F. MICHALEV (Acta Physicochim. U.R.S.S., 1935, 2, 427—432; cf. A., 1934, 363).—The product of the distance between successive bands and the velocity of diffusion for Liesegang ring type periodic structures produced with  $K_2Cr_2O_7$  and  $AgNO_3$  diffusing in gelatin varies with the concn. of the gel and of the electrolytes. Periodic ppts. have also been observed with  $K_2Cr_2O_7$  and neutral-red,  $K_4Fe(CN)_6$  and methylene-blue, and with  $K_2Cr_2O_7$  and Me-violet, all in gelatin. J. W. S.

**Physico-chemical analysis of periodic reactions. VI.** F. M. SCHEMJAKIN, E. A. FOKINA, and P. F. MICHALEV (J. Gen. Chem. Russ., 1935, 5, 1145—1157).—The val. of the periodicity const.  $K-\lambda v$  ( $\lambda$ =distance between rings,  $v$ =velocity of propagation) rises with increasing dilution of the internal electrolyte when aq.  $Pb(NO_3)_2$  diffuses into aq.  $KI$ ,  $Na_2CO_3$  into  $HgCl_2$  or  $BaCl_2$ ,  $AgNO_3$  into  $K_2CrO_4$ , and  $K_2CrO_4$  into  $CuSO_4$ . At the same time  $\lambda$  rises,  $v$  falls, whilst the no. of crystallites present in the ring falls, and the radius of the diffusion field increases. Periodic pptn. occurs in the reaction  $Na_2HPO_4 + CaCl_2 \rightarrow CaHPO_4 + 2NaCl$  at  $p_H$  0.5—12.9. In general,  $\lambda$  and  $K$  fall with increasing dilution of the  $Na_2HPO_4$  and with increasing deviation from  $p_H$  7.

R. T.

**Liesegang phenomenon in the precipitation of iodine in the absence of a gel.** B. N. SEN (Monatsh., 1935, 67, 10—12).—The rhythmic pptn. of I by the reduction of aq.  $KIO_3$  by  $As_2O_3$  in presence of  $CaCl_2$  is described.

F. L. U.

**Viscosity and plasticity of disperse systems. VIII. Application of Batschinski's formula to the viscosity of hydrogenated fats.** M. P. VOLAROVITSCH and G. B. RAVITSCH (Kolloid-Z., 1935, 73, 339—342; cf. A., 1935, 1318).—The viscosity of sunflower-seed oil and of two hydrogenated fats has been determined at 50—140°. The results are in accordance with Poiseuille's law. At high temp. there is a linear relation between fluidity and sp. vol.

E. S. H.

**Dispersion of multi-disperse solutions by Nistler's apparatus.** J. FAUTREZ (Bull. Acad. roy. Belg., 1935, [v], 21, 927—936).—Measurements of the variations of  $\lambda\lambda$  of the scattered light in colloidal suspensions of various colouring matters support the theory of multi-dispersion.

N. M. B.

**Light scattering in gold sols in relation to particle size and shape.** D. S. SUBBARAMAIYA (Proc. Indian Acad. Sci., 1935, 2, A, 358—363; cf. A., 1935, 821).—Measurements of the depolarisation obtained with unpolarised light and with per-



pendicular and parallel polarisation are reported. Results show that the particles in Faraday's sols are much  $<$  those in the other red sols prepared by using nuclear sols and  $\text{H}_2\text{O}_2$  as the reducing agent; those in the blue sols are relatively the largest. The size and anisotropy of the particles increase with increase in rate of growth caused by raising the temp. during prep. Addition of  $\text{K}_2\text{CO}_3$  to the mixture before reduction has the reverse effect. N. M. B.

**Cryolysis, diffusion, and particle size. III. Investigations with gum-arabic and polyacrylic acid.** C. ENDOH, F. E. M. LANGE, and F. F. NORD (Ber, 1935, 68, [B], 2004—2011; cf. A., 1935, 932).—Determinations of the conductivity of solutions of polyacrylic acid (I) show no difference between the frozen and unfrozen solutions. Proof that the purely chemical properties of (I) are not influenced by freezing is still more firmly established by conductometric titration of the acid with NaOH. The irreversible nature of the action of freezing lyophilic colloids is established, since a 2% solution of (I) diffuses more slowly after freezing than when unfrozen and the difference persists when the dilution is increased to 0.1%. A 0.1% solution after being frozen at  $-17^\circ$ , however, diffuses more rapidly than an unfrozen solution. Similar results are obtained with gum-arabic. H. W.

**Viscometric investigations of structure formation in  $\text{V}_2\text{O}_5$  sols. III. Action of anions.** G. SCHUMANN (Acta Physicochim. U.R.S.S., 1935, 2, 792—808; cf. A., 1935, 1073).—The viscosity-pressure curves of three  $\text{V}_2\text{O}_5$  sols in presence of Na salts have been determined. Structure formation is influenced in the order  $\text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-} > \text{CrO}_4^{2-}$ . All the salts depress the viscosity during the first day after addition. The results are discussed. T. G. P.

**Structure in hydrosols of aluminium oxide and the lyotropic effect of ions.** A. RABINERSON and Z. ARISTOVA (Acta Physicochim. U.R.S.S., 1935, 2, 585—594; cf. A., 1935, 700).—Undialysed hydrosols of  $\text{Al}(\text{OH})_3$  (from the acetate) show normal viscosity ( $\eta$ ), whilst dialysis causes to vary with the rate of shear owing to formation of structural elements. Comparison of the effects of various neutral salts in promoting structure-viscosity shows that the effect increases with hydration not only of the cation but also of the anion. It is inferred that sols of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  owe their stability in part to hydration, and that the action of electrolytes is not exclusively electrical. F. L. U.

**Mechanism of coagulation of sols by electrolytes. V. Sulphur sol.** H. B. WEISER and G. R. Y. Physical Chem., 1935, 39, 1163—1175; cf. A., 1933, 23).—Pptn. vals., adsorption, and capacity for displacing  $\text{H}^+$ , of  $\text{Th}^{4+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$ , have been measured for Raffa and Selmi S sols. Contrary to the results of Bassett and Durrant (A., 1932, 19) and of Bolam and Muir (A., 1933, 1011), neither the adsorption vals. of the several cations nor the quantities of  $\text{H}^+$  displaced by them are equiv. at the respective pptn. concns. Cationic adsorption and coagulating power vary in opposite senses at the pptn. concn., but in the same sense at higher concns.

The results are interpreted, and a mechanism is suggested, in terms of the theory of the diffuse double layer. F. L. U.

**Structure of colloid particles of artificial atacamite.** A. A. MOROZOV (Kolloid-Z., 1935, 73, 288—299).—Investigations of the kinetics of formation of the sol from  $\text{Cu}(\text{OAc})_2$  and NaCl, the behaviour on dilution, the conductivity, the charge on the particles, and the coagulation by electrolytes suggest the structure  $n\{[\text{Cu}(\text{OH})_2\text{Cu}]_3\text{Cl}_2\}_x\text{CuCl}_m, m\text{Cu}^{2+}, 2m\text{Cl}^-$ . E. S. H.

**Coagulation of ferrocyanide sols containing varying amounts of potassium ferrocyanide.** N. CHATTERJEE (J. Indian Chem. Soc., 1935, 12, 671—685).—The coagulating concn. (a) of various electrolytes on ferrocyanide sols freed as far as possible from intermicellar ions, and (b) of KCl on ferrocyanide sols in presence of (adsorbed)  $\text{K}_4\text{Fe}(\text{CN})_6$ , has been determined. With (b) if the concn. of added  $\text{K}_4\text{Fe}(\text{CN})_6$  ( $c_1$ ) is small the coagulating concn. of total K ions ( $c_2$ ) increases with  $c_1$ , and stability increases with dilution of sol. For greater vals. of  $c_1$ , max. and min. appear in the curves of  $c_1$  against  $c_2$  [Prussian-blue and  $\text{Cd}_2\text{Fe}(\text{CN})_6$ ] or the coagulating val. increases continuously (U, Cu, Al, and Zn ferrocyanides). These complicated results explain the disagreements between published observations. The sp. conductivity ( $\kappa$ ) of  $\text{Cu}_2\text{Fe}(\text{CN})_6$  sols and their ultrafiltrates and the  $p_H$  of the latter have been determined;  $\kappa$  increases with the dilution of the sol. The cataphoretic velocity for these Cu sols passes through a max. with increasing  $c_1$  and decreases with increasing dilution for low  $c_1$ . These results are correlated with the phenomena of coagulation. R. S. B.

**Effect of light on the flocculation of colloidal solutions in fluorescent media.** A. BOUTARIC (Ann. Guébbard-Séverine, 1935, 11, 25—34).—In general, fluorescent substances accelerate the flocculation of colloids only in the presence of visible or ultra-violet light and added electrolytes. The fall ( $\Delta t$ ) in the time of flocculation of colloidal  $\text{As}_2\text{S}_3$  which is associated with the addition of eosin, uranine, or erythrosin, diminishes as the fluorescing power of the dye is decreased by the added electrolyte. Oxidation inhibitors and dyes which diminish the fluorescing power have a similar influence on  $\Delta t$ . J. G. A. G.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity.** W. OSTWALD (Kolloid-Z., 1935, 73, 301—328).—A new theory of electrolyte coagulation of sols is put forward, in which attention is directed to the rôle of the dispersion medium. Coagulation is supposed to occur, not when the particles reach a certain state of charge, but when the intermicellar electrolyte reaches a certain physico-chemical state. The importance of the activity coeff. of the coagulating ions is emphasised and the interpretation of the valency rule and other regularities in coagulation is discussed. A large amount of published data is re-examined in the light of the theory. E. S. H.

**Variation of viscosity during the coagulation of colloid aluminium hydroxide by potassium chloride solutions.** S. S. JOSHI and K. P. N.

PANNIKAR (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 41—45; cf. A., 1935, 164).—The  $\eta$ -time curves for 0.5*N*—0.025*N*-KCl solutions show initial discontinuity in the progress of coagulation at low concns. The time corresponding with the viscosity at the first min. on the curve is independent of the concn., indicating that the min. may not denote a definite stage of coagulation. N. M. B.

**Gelatinised emulsions. I. Emulsifying power of different soaps. Thickness of [protective] layer. Role of water.** L. KREMNEV (Acta Physicochim. U.R.S.S., 1935, 2, 779—792).—Gelatinised emulsions are best prepared by manual shaking. The emulsification of  $C_6H_6$  by alkali oleates has been investigated. The emulsifying power decreases in the order  $Li > Na > K$ , and depends on the dispersion of the soap, being highest with 0.016*N* solutions, when an unsaturated monolayer covers the  $C_6H_6$  drops in the gelatinised emulsion. The influence of  $H_2O$  has been investigated, and the relationship between gelatinised and liquid emulsions is discussed. T. G. P.

**Thixotropy and allied phenomena, and their biological significance.** H. FREUNDLICH (Chem. Weekblad, 1935, 32, 739—745).—A lecture. E. S. H.

**Imbibition of hydrosols and of dye solutions through porous bodies.** A. BOUTARIC (J. Chim. phys., 1935, 32, 618—638, and Bull. Soc. Chim. biol., 1935, 17, 1522—1533).—The motion of the medium and of colloidal particles through filter-paper is in accord with the view that the particles are carried through the porous material mechanically by the medium unless adsorbed by the paper. The motion of the particles does not vary appreciably with the surface tension of the medium and has no direct relation with electric forces; the usual term "electro-capillary rise" is therefore a misnomer. J. W. S.

**X-Ray method for the study of "bound water" in hydrophilic colloids at low temperatures.** W. H. BARNES and W. F. HAMPTON (Canad. J. Res., 1935, 13, 218—227; cf. A., 1934, 597).—The X-ray camera (cf. this vol., 45) has been applied to the study of bound  $H_2O$  in gelatin between 0° and -50°. The presence of ice crystals due to free  $H_2O$  gives rise to randomly distributed diffraction spots on the photograph and causes a shift in the halo at 20°—19—24°. The amount of bound  $H_2O$  decreases with fall of temp. to 0.44 g. per g. of dry gelatin at some temp. between -11.5° and -25.4°, below which it remains const. R. S.

**Time of setting of gels.** M. PRASAD and M. U. PARMAR (Current Sci., 1935, 4, 310—311).—Divergent times obtained by optical and various mechanical methods, in the case of  $H_2SiO_3$  gel, suggest that a precise definition is required for the term "time of setting," the process involving at least three stages. N. M. B.

**Dielectric constant and conductivity of gelatin sols and gels.** A. PIEKARA and B. PIEKARA (Kolloid-Z., 1935, 73, 273—276).—The dielectric const. of gelatin sols is  $>$  that of  $H_2O$ , increases with concn., and decreases with rising temp. The conductivity of the sol is  $>$  that of the gel. E. S. H.

**Hydroxide and oxide hydrate gels, and their amphoteric properties.** R. FRICKE (Kolloid-Z., 1935, 73, 300).—A criticism (cf. A., 1935, 1075). E. S. H.

**Anomalous dispersion of metallised gelatin.** L. CAVALLARO (Boll. Soc. ital. Biol. speriment., 1935, 10, 198—200).—The metastability of gelatin (I) and ovalbumin increases progressively with their purity during electrodialysis, but reaches a max. before max. purity is attained, and falls considerably during the final stages of purification. The behaviour of  $\epsilon_{H_2O}^{20}$  with increase of  $\lambda$  in metallised (I) is qualitatively similar to that of non-metallised (I), but  $\epsilon$  is increased in all cases. R. N. C.

**Colloid chemistry of edestin. II.** K. HOLWERDA (Biochem. Z., 1935, 282, 317—344; cf. A., 1935, 1203; Hollemann *et al.*, A., 1934, 842).—The composition of the coacervates produced by adding  $H_2O$  to edestin sols indicates that the peptisation is not chiefly dependent on the amount of  $H_2O$  introduced with the salts, although the degree of adsorption of univalent ions accords with viscosimetric results. In the zone of peptisation the adsorption is positive, whilst in the zone of salting out it is negative. When the concn. of salt is insufficient to cause peptisation the adsorption is positive. The controlling factor in the peptisation is the lowering of the surface tension caused by the addition of the salts, but intermolecular cohesive forces are involved, and such forces probably play a part in the salting-out process also. W. McC.

**Physico-chemical researches on the proteins.** A. BOUTARIC and M. ROY (Acta Physicochim. U.R.S.S., 1935, 2, 51—66).—Proteins as ordinarily prepared contain salt impurities which modify their colloidal properties. Pure preps. obtained by  $COMe_2$  pptn. have now been investigated. The optical density and  $n$  of coagulating mixtures of resorcinol (I) with serum-albumin and myxoprotein have been determined. (I) is fixed by the pptd. protein, and the solubility decreases to zero as the amount fixed approaches a limiting val. Absorption data for a no. of proteins on charcoal standardised against Na oleate are given and the influence of different protein concns. on the time of pptn. of  $Fe(OH)_3$  sol has been determined. It has been shown by both methods that the degree of polymerisation of albumin and myxoprotein obtained from various physiological secretions is the same. R. S.

**Colloidal model for illustration of biological processes.** I.—See this vol., 232.

**M.-p. curve of mixtures of heavy water and water.** A. EUCKEN and K. SCHAFER (Z. anorg. Chem., 1935, 225, 319—320).—Contrary to Dezelic's results (this vol., 30), but in agreement with those of other investigators, the authors have shown that the solidus-liquidus curves do not coincide, the max. distance apart being 0.02° for mixtures containing 42%  $D_2O$ . The m.-p. curve is not a straight line, but concave towards the concn. axis. Measurements have been made in a special apparatus recording variations of temp. of 0.00001°. M. S. B.

**Exchange equilibria between deuterium and ammonia.** K. WIRTZ (Z. physikal. Chem., 1935, B, 30, 289—297; cf. A., 1935, 1460).—A method which may in principle be used to calculate the equilibrium consts. of all the exchange reactions possible in a mixture of  $\text{NH}_3$  and  $\text{D}_2$  is described. As yet, however, the experimental accuracy is not great enough for it to be possible fully to follow this procedure. From spectroscopic data the equilibrium consts. of  $\text{NH}_3 + \text{NHD}_2 = 2\text{NH}_2\text{D}$  and  $\text{ND}_3 + \text{NDH}_2 = 2\text{NHD}_2$  at  $573^\circ$  abs. have been calc. to be 2.30 and 2.89, respectively. The distribution ratio of D between  $\text{H}_2$  and  $\text{NH}_3$  has also been determined. R. C.

**Maximum concentration of endothermic compounds at high temperatures; application to ozone and nitric oxide.** E. BRINER and B. SUSZ [with E. ROD] (Helv. Chim. Acta, 1935, 18, 1468—1478).—The equilibrium concns. of  $\text{O}_3$  and of NO in gas mixtures at high temp. have been recalcd. using more exact thermochemical data and equilibrium consts. Vals. so calc. are < those found previously. J. S. A.

**Equilibrium constants of the reaction of formation of ethyl chloride from ethylene and hydrogen chloride.** D. M. RUDKOVSKI, A. G. TRIFEL, and A. V. FROST (Ukrain. Chem. J., 1935, 10, 277—282).—The equilibrium const. for  $\text{C}_2\text{H}_4 + \text{HCl} \rightleftharpoons \text{EtCl}$  over the range  $170\text{--}230^\circ$  is given by  $\log K = 4.96 - 2925/T$ , and the heat of the reaction is 13.4 kg.-cal. R. T.

**Law of displacement of equilibrium.** P. RENAUD and E. BAUMGARDT (Compt. rend., 1935, 201, 1129—1131).—Polemical against Planck (A., 1934, 837). H. J. E.

**Thermodynamic potentials and affinity.** P. VAN RYSSELBERGHE (Compt. rend., 1935, 201, 1126—1128).—Theoretical. H. J. E.

**Thermodynamic problem.** A. SKRABAL (Z. Elektrochem., 1935, 41, 883—884; cf. A., 1935, 301, 446, 1204).—Further discussion. F. L. U.

**Thermodynamic problem.** R. LUTHER (Z. Elektrochem., 1935, 41, 884—885; cf. preceding abstract).—Discussion concluded. F. L. U.

**First dissociation constant of carbonic acid equilibrium.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 3; Chem. Zentr., 1935, i, 2767).— $K = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$  is calc. at different temp. from published conductivity data, the uncertainty of  $K$  being principally dependent on the accuracy of the val. of the ionic conductivity of  $\text{H}^+$ . The heat of dissociation of  $\text{H}_2\text{CO}_3$  is calc. as 2500 g.-cal.  $K$  is determined independently by potentiometric measurements on aq.  $\text{CO}_2$  solutions. J. S. A.

**Dissociation constants of organic acids. XIII. Primary and secondary constants of some cyclic 1:1-dicarboxylic acids.** W. L. GERMAN, G. H. JEFFERY, and A. I. VOGEL (J.C.S., 1935, 1624—1630; cf. A., 1935, 1076).—Conductivity data are given for *cyclo*-propane-, -butane-, -pentane-, and -hexane-1:1-dicarboxylic acids and their Na salts, and the primary dissociation consts. calc. These have been confirmed by potentiometric titration of the acids using the quinhydrone electrode and the secondary dissociation consts. also obtained. The

distances between the  $\text{CO}_2\text{H}$  groups calc. from Bjerrum's expression are < those obtained by Gane and Ingold's method (A., 1931, 1126). R. S.

**Dissociation constants of monohalogenated anilines and phenols.** G. M. BENNETT, G. L. BROOKES, and S. GLASSSTONE (J.C.S., 1935, 1821—1826).—The dissociation consts. of *o*-, *m*-, and *p*-fluoro-, chloro-, bromo-, and iodo-aniline and -phenol at  $25.0^\circ$  in 30 vol.-% EtOH have been determined by observations of  $p_{\text{H}}$ , using the glass electrode. The results are discussed. E. S. H.

**Mathematical and graphical treatment of the equilibrium base-carbon dioxide-water in dilute solutions.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 1; Chem. Zentr., 1935, i, 2766—2767).— $\text{CO}_2$ - $\text{H}_2\text{O}$ -base equilibria are treated according to the classical and modern theories of solution, and a graphical method is described for the calculation of quantities involved in water-softening. The method is applicable also to quant. analysis of  $\text{H}_2\text{O}$ . J. S. A.

**Hydration of chromic chloride in heavy water.** G. CHAMPETIER (Compt. rend., 1935, 201, 1118—1120).—Measurements are recorded of the change in electrical conductivity with time of  $\text{CrCl}_3$  dissolved in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The rate of change is slower and the final val. is lower in  $\text{D}_2\text{O}$ . The absorption spectra for the  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  solutions appear to be the same. H. J. E.

**Ion hydration and aquo-complexes.** H. BRINTZINGER (Z. anorg. Chem., 1935, 225, 221—224).—The results of published work are discussed (cf. A., 1935, 1091, 1335). E. S. H.

**Complex ions [of ferro- and ferri-cyanides] and prussi- and prusso-compounds.** H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 217—220).—The ion wts. of  $[\text{Fe}^{\text{III}}\text{NO}_3(\text{CN})_5]^{4-}$ ,  $[\text{Fe}^{\text{III}}\text{NH}_3(\text{CN})_5]^{3-}$ ,  $[\text{Fe}^{\text{III}}\text{NO}_2(\text{CN})_5]^{3-}$ ,  $[\text{Fe}^{\text{II}}\text{NH}_3(\text{CN})_5]^{2+}$ ,  $[\text{Fe}^{\text{II}}\text{NO}_2(\text{CN})_5]^{2+}$ ,  $[\text{Fe}^{\text{II}}\text{H}_2\text{O}(\text{CN})_5]^{2+}$ , and  $[\text{Fe}^{\text{II}}\text{AsO}_2(\text{CN})_5]^{2+}$  have been determined by the dialysis method. E. S. H.

**Effect of temperature on borax solutions in the presence of polyhydric substances and organic acids.** S. M. MEHTA (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 46—49).—Preliminary results are given of an extension of Meldrum's investigations (Proc. Ind. Sci. Cong., 1923, 108) to the hydrolysis of borax in presence of mannitol and of salicylic acid, and the system  $\text{H}_3\text{BO}_3$ -NaOH, over a wide temp. range. N. M. B.

**Stability of sodium aluminate solutions.** V. D. DJATSCHKOV and O. S. KOSHUCHOVA (J. Gen. Chem. Russ., 1935, 5, 1139—1143).—The stability of Na aluminate (I) is unaffected by presence of < 1.4 mols. of  $\text{Na}_2\text{O}$  per mol. of  $\text{Al}_2\text{O}_3$ ; in higher concns. of NaOH it rises linearly, but is always least in solutions which contain 120—180 g. of (I) per litre. Agar-agar and Na silicate stabilise the solutions. R. T.

**Isotope exchange between water and some organic compounds.** M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 554—557).—Neglecting mols. of relatively low concn. the exchange of D between org. compounds and dil.  $\text{D}_2\text{O}$  proceeds

according to  $\text{RH}_n + \text{H}_2\text{O} \rightleftharpoons \text{RH}_{n-1}\text{D} + \text{H}_2\text{O}$ . The equilibrium consts.  $K = [\text{RH}_{n-1}\text{D}][\text{H}_2\text{O}]/[\text{RH}_n][\text{HDO}]$ , and the distribution coeffs.  $k = (\text{at. concn. of D in exchangeable H in compound})/(\text{at. concn. of D in H}_2\text{O})$  are:  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{PhCHO}$ , no exchange;  $\text{NH}_2\text{Ph}$   $k=K=1.11$ ;  $\text{PhOH}$   $k=1.07$ ,  $K=0.54$ ;  $\text{C}_6\text{H}_5\text{NH}_2$   $k=0.88$ ,  $K=0.44$ ;  $\text{BzOH}$   $k=1.04$ ,  $K=0.52$ ;  $(\text{CH}_2\text{Ph})_2\text{OH}$   $k=1.10$ ,  $K=0.55$ . R. S. B.

**Exchange reactions of hydrogen with deuterium. I. Exchange in carboxyl groups of succinic acid and in hydroxyl groups of quinol.** A. E. BRODSKI and O. C. SCARRE. **II. Exchange in sulphuric acid and in sodium hydroxide.** J. M. SCHERSCHEVER, A. E. BRODSKI, and M. M. SLUCKAJA (*Acta Physicochim. U.R.S.S.*, 1935, 2, 603—610, 611—614; cf. A., 1935, 44).—I. When  $(\text{CH}_2\text{CO}_2\text{H})_2$  or  $p\text{-C}_6\text{H}_4(\text{OH})_2$  is heated with  $\text{H}_2\text{O} + \text{D}_2\text{O}$  for 2—4 hr. in the absence of a catalyst, equilibrium is reached in which the coeff. of exchange between D and the H of the  $\text{CO}_2\text{H}$  or OH groups is approx. 1. The reverse change has been observed qualitatively.

II. The exchange coeff. of D between heavy water and dissolved  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$  has been found to be 1.0, thus affording direct evidence that in the production of  $\text{D}_2\text{O}$  by electrolysis acid or alkaline solutions the D content of the dissolved electrolyte changes *pari passu* with that of the water. F. L. U.

**Physicochemical studies of complex formation involving weak acids. XIV. Complex formation between malonates of the heavy metals and of sodium.** H. T. S. BRITTON and M. E. D. JARRETT (*J.C.S.*, 1935, 1728—1735; cf. A., 1935, 305, 449).—When Na malonate (I) is added to solutions of heavy-metal salts, the heavy metals remain in solution as feebly ionised basic hydromalonates; with excess of (I) complex anions are formed. Malonic acid solutions of heavy-metal bases do not contain definite complex acids. The prep. of  $\text{K}_2\text{CH}(\text{CO}_2\text{H})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Al}(\text{CH}(\text{CO}_2\text{H})_2)_3$ , and  $\text{Na}_2\text{Fe}(\text{CH}(\text{CO}_2\text{H})_2)_3$  is described. The solubility product of Ag malonate at  $18^\circ$  is  $1.41 \times 10^{-4}$ . E. S. H.

**Determination of weight of organic dye ions by the dialysis method.** H. BRINTZINGER and A. SCHALL (*Z. anorg. Chem.*, 1935, 225, 213—216).—Apparatus for use with small amounts of liquid is described. Results are given for 6 dyes. E. S. H.

**System lithium nitrite-water: the hydrate  $\text{LiNO}_2 \cdot 1.5\text{H}_2\text{O}$ .** J. BUREAU (*Compt. rend.* 1935, 201, 1193—1195).—Thermal analysis reveals the peritectic transformation of  $\text{LiNO}_2 \cdot 1.5\text{H}_2\text{O}$  into  $\text{LiNO}_2 \cdot \text{H}_2\text{O}$  at  $-7.95^\circ$ , of  $\text{LiNO}_2 \cdot \text{H}_2\text{O}$  into  $2\text{LiNO}_2 \cdot \text{H}_2\text{O}$  at  $30.9^\circ$ , and of  $2\text{LiNO}_2 \cdot \text{H}_2\text{O}$  into  $\text{LiNO}_2$  at  $94^\circ$ . T. G. P.

**Existence of two hydrates of potassium thiocyanate.** A. CHRISTEN and O. HOFFER (*Compt. rend.* 1935, 201, 1131—1133).—The  $\text{KCN} \cdot 0.5\text{H}_2\text{O}$  and  $\text{KCN} \cdot 0.5\text{H}_2\text{O}$  are formed. The former is the stable solid phase at  $-29.5^\circ$  to  $6.8^\circ$ , the latter is always metastable. It is formed at  $-30^\circ$  to  $-17.75^\circ$ . H. J. E.

**Vapour pressure of saturated solutions and hydrates of magnesium chloride.** N. V. KON-

DIREV and G. V. BEREZOVSKI (*J. Gen. Chem. Russ.*, 1935, 5, 1246—1251).—V.-p. data are recorded for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  over a wide temp. range. R. T.

**Dissociation pressures of nitrates and sulphates. IV. Sodium vanadates.** B. NEUMANN and A. SONNTAG (*Z. Elektrochem.*, 1935, 41, 860—868; cf. A., 1933, 1246).—O<sub>2</sub> pressures of Na vanadates with varying ratios of  $\text{Na}_2\text{O} : \text{V}_2\text{O}_5$ , with and without admixture of  $\text{SiO}_2$ , have been measured.  $\text{SO}_2$  is oxidised with appreciable rapidity only at temp. at which the vanadate is partly decomposed. The influence of  $\text{SiO}_2$  is purely physical, in preventing sintering and compaction of the products. The pressure measurements show that the catalytic activity of Na vanadates in promoting oxidation of  $\text{SO}_2$  depends on the formation of a definite, at present unidentified, sulphate which is more labile than  $\text{VOSO}_4$ . F. L. U.

**Thermodynamics of the liberation of oxygen from ferric oxide-ferrous oxide melts.** J. KIEHLAND (*Z. Elektrochem.*, 1935, 41, 834—838; cf. A., 1935, 1075).—An expression for the activity coeff. of the components is given. The calc. free energy change of the reaction  $\text{Fe}_2\text{O}_3 = 2\text{FeO} + 0.5\text{O}_2$  agrees with the observed val. (A., 1935, 1204). The standard entropy of  $\text{FeO}$  is calc. Mol. and partial mol. heats of mixing and free energies of liquid  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  are given. F. L. U.

**System calcium oxide-sulphur dioxide-water. I. Determination of vapour pressures and conductivities.** G. W. GURD, P. E. GISHLER, and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 209—217; cf. A., 1933, 897).—An apparatus is described in which pure  $\text{CaO}$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_2$  in accurately known amounts can be mixed at a const. temp. and the v.-p. and conductivity determined. V.-p. between  $25^\circ$  and  $130^\circ$  and conductivities between  $25^\circ$  and  $90^\circ$  are tabulated for  $[\text{SO}_2]$  up to 6% and  $[\text{CaO}]$  up to 2.5%. R. S.

**System calcium oxide-sulphur dioxide-water. II. Calculation of ionic concentrations.** P. E. GISHLER and O. MAASS (*Canad. J. Res.*, 1935, 13, B, 308—322; cf. preceding abstract).—Ionic concns. in the system  $\text{CaO}-\text{SO}_2-\text{H}_2\text{O}$  are calc. from earlier v.-p. and conductivity data. The existence of the compound  $\text{CaSO}_3 \cdot \text{Ca}(\text{HSO}_3)_2$  is deduced. Vals. of  $p_H$  up to  $90^\circ$  are extrapolated to  $140^\circ$ . H. J. E.

**Reciprocal solubility of aluminium, sodium, potassium, and ferric nitrate in water in presence of nitric acid. II.** A. J. SASLAVSKI, J. L. ETTINGER, and E. A. ESEROVA (*Z. anorg. Chem.*, 1935, 225, 305—311; cf. A., 1935, 928).—Data are given for the quaternary system  $\text{Al}(\text{NO}_3)_3-\text{NaNO}_3-\text{HNO}_3-\text{H}_2\text{O}$  at  $0^\circ$  and  $20^\circ$ . The only solid phases are  $\text{NaNO}_3$  and the hydrates  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $8\text{H}_2\text{O}$ , and  $6\text{H}_2\text{O}$ . The composition of the solution at the transition points has been determined. M. S. B.

**System  $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ . II.** R. NACKEN and R. MOSEBACH (*Z. anorg. Chem.*, 1935, 225, 285—288; A., 1933, 935).—Equilibrium data at  $23-1^\circ$  are given. E. S. H.



**System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ .** R. NAOKEN and R. MOSEBACH (Z. anorg. Chem., 1935, 225, 289-301).—Equilibrium data at  $23\pm 1^\circ$  are given. E. S. H.

**Binary additive compounds in tannary systems. IX. Phenacetin-sulphonal-resorcinol.** F. ADAMANIS (Rocz. Chem., 1935, 15, 383-390).—Equilibrium data are recorded for the system, which shows a 2:3 compound of phenacetin and resorcinol. R. T.

**Thermodynamic studies of silver and mercurous sulphate.** F. ISHIKAWA and H. HACHISAWA (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1205-1209).—The e.m.f. of the cell  $\text{Ag}|\text{Ag}_2\text{SO}_4(s), \text{aq. Ag}_2\text{SO}_4|0.0269M\text{-K}_2\text{SO}_4, \text{HgSO}_4(s)|\text{Hg}$  has been determined at  $20^\circ, 25^\circ$ , and  $30^\circ$  and various thermodynamic quantities are calc. R. S.

**Heats of dissolution and specific heats of rhombic sulphur in carbon disulphide. Surface energy of solid rhombic sulphur.** A. R. WILLIAMS, F. M. G. JOHNSON, and O. MAASS (Canad. J. Res., 1935, 13, B, 280-288).—The thermal data are recorded for  $20^\circ$  and  $25^\circ$  and for concns. of 6-17%. Modifications of the adiabatic rotating calorimeter are described (cf. A., 1928, 609). The surface energy of solid rhombic S, calc. from the heats of dissolution of coarse and finely-divided substance, is 1024 ergs per sq. cm. (accuracy approx. 30%). H. J. E.

**Thermodynamic properties of sulphur compounds. II. Sulphur dioxide, carbon disulphide, and carbonyl sulphide.** P. C. CROSS (J. Chem. Physics, 1935, 3, 825-827; cf. A., 1935, 569).—Vals. of free energy, entropy, and heat capacity are derived from the consts. obtained from electron diffraction and from Raman and infra-red spectra, and these are applied to several reactions involving the three compounds. The free energies of formation at  $298.1^\circ$  abs. are:  $\text{CS}_2$ , 15.24,  $\text{COS}$ , -40.48 kg.-cal. N. M. B.

**Thermal decomposition of iron carbide  $\text{Fe}_3\text{C}$ .** G. NAESER (Mitt. Kaiser-Wilh. Inst. Eisenforsch., 1934, 16, 211-212; Chem. Zentr., 1935, i, 2336). The decomp. of  $\text{Fe}_3\text{C}$ , studied by measurement of magnetic susceptibility, takes place at  $1050-1060^\circ$  with out-gassed material. Equilibrium in the system cementite-pearlite-ferrite-graphite are recorded. J. S. A.

**Heat of formation and free energy of formation of boron nitride.** S. SATOH (Bull. Inst. Phys. Chem. Res. Japan, 1935, 14, 1233-1240). The heat of formation and free energy of formation of BN calc. from the dissociation pressure and the sp. heats are 56,940 and 54,760 g.-cal., respectively. R. S.

**Heat of reaction between kaolin burnt at different temperatures and  $\text{Ca}(\text{OH})_2$ .** P. P. BUDNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 355-359).—The heat evolved when burnt kaolin is added to aq.  $\text{Ca}(\text{OH})_2$  is a max. when the burning temp. is  $800^\circ$  and becomes zero when this is  $>1000^\circ$ . It is suggested that meta-kaolinite formed below  $1000^\circ$  reacts with  $\text{Ca}(\text{OH})_2$  giving a Ca aluminosilicate.

**Nature of conductivity of non-aqueous solutions.** M. USSANOVITSCH (Acta Physicochim. U.R.S.S., 1935,

2, 239-271).—The conductivity and temp. coeff. of conductivity of solutions of  $\text{AsCl}_3$ ,  $\text{AsBr}_3$ ,  $\text{SbCl}_3$ , and  $\text{SbBr}_3$  in  $\text{Et}_2\text{O}$  have been determined. The conductivity is attributed to the formation of  $\text{Et}_2\text{O}\cdot\text{AsCl}_3$ ,  $\text{Et}_2\text{O}\cdot\text{AsBr}_3$ ,  $\text{Et}_2\text{O}\cdot 2\text{SbCl}_3$ , and  $\text{Et}_2\text{O}\cdot 2\text{SbBr}_3$ .  $\text{PCl}_3$  does not form a compound with  $\text{Et}_2\text{O}$ , and the solution is non-conducting. The conductivity of solutions of  $\text{AsCl}_3$  in  $\text{PhNO}_2$  and  $\text{C}_6\text{H}_5\text{N}$  also due to compound formation. Data for  $\text{AcOH}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  confirm the existence of  $2\text{H}_2\text{SO}_4\cdot\text{HNO}_3$  and  $\text{H}_2\text{SO}_4\cdot\text{HNO}_3$ . In the system  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , the  $\text{HNO}_3$  acts as a base. In the systems  $\text{H}_2\text{SO}_4$ ,  $\text{Me}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ ,  $\text{CO}_2\cdot\text{CO}_2\text{H}$ , in which there is no compound formation, a new type of dependence of conductivity on concn. is found. When corr. for viscosity, the conductivities of both systems are identical, although the dielectric consts. are widely different. A. J. M.

**Mobility of the hydrogen and hydroxyl ions in aqueous solution.** H. G. WANNIER (Ann. Physik, 1935, [v], 24, 509-590; cf. this vol., 31). An expression for the mean life of  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  is obtained by a combination of the theory of Debye and Hückel and quantum mechanics. An equation is derived for the effect of temp. on the mobility of the ions which is in agreement with experiment. Calculation of the electric moment of the ions, however, does not agree with the experimental val. The mobility of  $\text{D}_2\text{O}^\cdot$  is calc. A. J. M.

**Electrode potentials of sodium and potassium in liquid ammonia.** V. A. PLESKOV and A. M. MONOSSOV (Acta Physicochim. U.R.S.S., 1935, 2, 616-620; cf. A., 1935, 1077). Measurement of the e.m.f. of the cell  $\text{Hg}-\text{Na}|0.1N\text{-NaNO}_3(\text{sat. KNO}_3)|0.1N\text{-Ph}(\text{NO}_2)_3|\text{Ph}$  at  $35^\circ$ , the salts being dissolved in liquid  $\text{NH}_3$ , has been used to calculate the normal potential of Na. Results for K have been obtained in a similar manner. The potentials, referred to  $\text{H}^+ = 0$ , are: Na, -1.83 volt, K, -1.98 volt. These vals., which are nearly 1 volt  $\pm$  the corresponding potentials in  $\text{H}_2\text{O}$ , are considered partly responsible for the slowness of the reaction of the metals with liquid  $\text{NH}_3$ . P. L. U.

**Electrode potentials in water and in liquid ammonia.** V. A. PLESKOV and A. M. MONOSSOV (Acta Physicochim. U.R.S.S., 1935, 2, 621-632 cf. preceding abstract). A method of comparing electrode potentials in  $\text{H}_2\text{O}$  and liquid  $\text{NH}_3$  by means of a dropping electrode is described, and results of measurements for K, Na, Zn, Cd, Pb, H, Cu, Ag, and Hg, from which normal potentials in the two solvents are calc., are given. The ionic solvation energies calc. on purely electrostatic grounds are, with the exception of K and Na, greatly at variance with the energies of transfer given by the experiments. The discrepancies show that an important part is played by homopolar chemical forces. P. L. U.

**Electrode potentials of halides in liquid ammonia.** V. A. PLESKOV (Acta Physicochim. U.R.S.S., 1935, 2, 679-688). In calculating the normal potentials of halides in liquid  $\text{NH}_3$  the energy of formation of the crystal solvate must be considered. Homopolar forces play a part in the solvation. Calculations from previous data show that the normal potentials of

different halides differ less in liquid  $\text{NH}_3$  than in  $\text{H}_2\text{O}$  (cf. Fredenhagen, A., 1927, 936). T. G. P.

**Measurement of capacity of polarised mercury electrodes.** P. P. PORITROV (J. Gen. Chem. Russ., 1935, 5, 1077—1084).—The polarisation capacity  $P$  falls with increasing potential to a min. at about 1 volt, and then rises; with increasing c.d. the val. of  $P$  rises uninterruptedly, and the above min. becomes more abrupt. Using a.c. the val. of  $P$  is independent of the frequency, but  $\propto$  only to the p.d. R. T.

**Cathodic polarisation in the deposition of copper from solutions of its simple salts.** O. ESSIN and A. LEVIN (J. Gen. Chem. Russ., 1935, 5, 1302—1315).—Gordon's empirical equation (A., 1925, ii, 549),  $E = E_0 + b \log(1 - kD)$ , where  $E$  is the polarisation potential, and  $b$  and  $k$  are consts., is confirmed by the data for the electrolysis of 0.3—1.0N- $\text{CuSO}_4$  in 0.1—0.2N- $\text{H}_2\text{SO}_4$  at 25°, with a c.d.  $D$  of 1—110 m.amp. per sq. cm.;  $E_0$  cannot be considered to be the initial polarisation. The difference between the actual  $E$  and that calc. for the concn. potential is best represented by Erley-Gruz and Volmer's equation (A., 1930, 1376),  $E_x - 1/(a + k \log D)$ , indicating that  $E_x$  is ascribable to the retarded formation of crystal nuclei at the cathode. When the c.d. is increased gradually from 1 m.amp. per sq. cm., the potential becomes most negative at about 10 amp., but the potentials cannot be reproduced when the process is repeated or reversed. R. T.

**Hydrogen peroxide theory of electrolytic oxidation and the influence of the electrode surface on anodic polarisation.** S. GLASSTONE and A. HICKLING (Trans. Faraday Soc., 1935, 31, 1656—1660).—The anodic overpotentials at smooth Pt, platinised and otherwise prepared Pt, Au,  $\text{PbO}_2$ ,  $\text{MnO}_2$ , arc-gas C, and Ni electrodes cannot be simply correlated with their efficiencies in oxidation of  $\text{OAc}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SO}_3^{2-}$ . Difficulties in the discharged ion theory of anodic processes are pointed out, and it is shown that formation of  $\text{H}_2\text{O}_2$  from OH radicals is not improbable, since not only do catalysts for  $\text{H}_2\text{O}_2$  decomp. inhibit anodic oxidation, but the action of  $\text{H}_2\text{O}_2$  is in many cases qualitatively similar to that of electrolytic oxidation. Probably no one mechanism accounts for all types of anodic oxidation reactions. J. W. S.

**Significance of negative difference effect.** W. O. KROENIG and V. N. USPENSKAJA (Korros. u. Metallschutz, 1935, 11, 10—16; Chem. Zentr., 1935, i, 2781).—The negative difference effect is the increased H evolution from an Al electrode in acid (or a Mg electrode in salt solutions) on short-circuiting with a Pt cathode, and is associated with the oxide skin. Removal of the latter inhibits the negative and gives rise to a positive difference effect. The effect is due to destruction of the oxide skin by the augmented passage of ions into solution, the rate of dissolution of Al being thereby increased. J. S. A.

**Electrochemical behaviour of non-metallic inclusions in iron and its relation to corrosion.** E. CHYZEWSKI and A. SKAPSKI (Z. Elektrochem., 1935, 41, 843—849).—The e.m.f., current strength, and internal resistance of cells of the type: non-metal electrode|0.005N- $\text{FeSO}_4$ +0.005N- $\text{MnSO}_4$ |Fe

have been measured at room temp. The non-metal electrodes were of FeO,  $\text{Fe}_2\text{O}_3$ , magnetite, fayalite, haematite, FeS, MnS, and MnO, and the solutions were saturated with air or  $\text{O}_2$ . The results show that only MnS, and to some extent its solid solutions, can give rise to electrochemical corrosion. FeS can under certain conditions exert a protective action.

F. L. U.

**Application of the barium amalgam electrode to the determination of the activity of barium ions in aqueous solutions.** Z. J. BERESTNEVA and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1935, 2, 163—170).—The potential of a Ba-Hg electrode in  $N$ - to 0.001N- $\text{BaCl}$ , has been determined. Addition of  $\text{Na}^+$  up to 0.1N has no effect on the potential of the electrode. The Ba-Hg electrode may be used to determine the activity of  $\text{Ba}^{2+}$ , if its potential is first determined against a standard Ba solution.

A. J. M.

**Alkali amalgam electrodes and their application to the study of colloidal solutions.** Z. J. BERESTNEVA and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1935, 2, 151—162).—An attempt has been made to use alkali-metal amalgam electrodes to investigate the adsorption of ions in the coagulation of  $\text{As}_2\text{S}_3$  sols by NaCl and KCl. The electrodes are, however, poisoned by products of hydrolysis of  $\text{As}_2\text{S}_3$ , and trustworthy results cannot be obtained.

A. J. M.

**Activity of hydrogen in complexes of alcohols with unsaturated organic compounds.** B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1935, 5, 1233—1239).—The e.m.f. developed when Pt and Na electrodes are immersed in primary alcohols is unaffected by addition of  $\text{C}_5\text{H}_5\text{N}$  or  $\text{PhNO}_2$ ; the same applies to *sec.*-alcohols, with the exception of  $\text{Pr}^n\text{OH}$ , which appears to form a highly dissociated compound with  $\text{C}_5\text{H}_5\text{N}$ . *tert.*-Alcohols and the homologues of cyclohexyl alcohol give considerably higher e.m.f. in presence of  $\text{C}_5\text{H}_5\text{N}$  and  $\text{PhNO}_2$ .  $\text{NH}_4\text{Ph}$  and  $\text{NPhMe}$  do not affect the e.m.f. given by aliphatic alcohols, but slightly raise that given by aromatic alcohols.

R. T.

**Mechanism of explosive reactions.** C. C. ANDREEV (Bull. Soc. chim., 1935, [v], 2, 2128—2134).—See A., 1935, 708.

F. L. U.

**Absolute rate of homogeneous atomic reactions.** H. EYRING, H. GERSHINOWITZ, and C. E. SUN (J. Chem. Physics, 1935, 3, 786—796; cf. A., 1935, 1205).—The abs. rate of recombination of 3 H atoms is calc. theoretically. The manner in which rotation determines the dimensions of the activated complex in cases having little or no activation energy is discussed. A result of the theory (cf. *ibid.*, 586) is that energy transfer occurs most effectively among particles which can react with each other, free atoms being more efficient than mols. A qual. application of potential surfaces to the problem of energy transfer is made.

M B

**Reality of chains in gas explosions.** M. POLJAKOV and I. MALKIN (Acta Physicochim. U.R.S.S., 1935, 2, 211—214).—Apparatus is described by means of which the theory that OH is an intermediate in the chain reaction occurring when a mixture of  $\text{H}_2$

and  $O_2$  in the vol. ratio 2:1 is exploded may be proved. It is supposed that two OH combine to form  $H_2O_2$ , which may be frozen out. 25 explosions gave sufficient  $H_2O_2$  to be detected. The amount of  $H_2O_2$  formed decreases with distance from the heated Pt spiral by which the explosion is started. This result is due to the removal of OH by the walls of the vessel. A. J. M.

**Influence of gas adsorbed by the vessel walls on the chain reaction of hydrogen-oxygen mixtures.** M. PRETTE (Compt. rend., 1935, 201, 962—964).—The initial rate of reaction of  $H_2$  and  $O_2$  at  $540^\circ$  in a glass vessel increases progressively when the vessel walls are allowed to adsorb (at  $540^\circ$ ) increasing quantities of  $H_2O$  vapour (5—70 mm. pressure) before carrying out the reaction. Preliminary treatment of the vessel with  $H_2$  at  $550^\circ$  retards the reaction and eliminates the induction period. H. J. E.

**Ignition limits of oxygen-hydrogen mixtures.** F. I. DUBOVITSKI (Acta Physicochim. U.R.S.S., 1935, 2, 761—778).—The reaction between stoichiometric proportions of  $H_2$  and  $O_2$  irradiated by a  $H_2$  tube at pressures and temp. close to the ignition limits has been investigated. The limits of ignition are not determined by the surface. A decrease in reaction rate at high pressures in presence of A indicates that chain breaking grows in consequence of increased probability of the triple collision  $O+H_2+M=H_2O+M$ . The primary process in the reaction is  $O_2+h\nu=O^*+O$ . The results obtained are combined with earlier data and interpreted through Semenov's chain theory. T. G. P.

**Experimental activation energies of elementary reactions between hydrogen and the halogens.** J. C. MORRIS and R. N. PEASE (J. Chem. Physics, 1935, 3, 796—802).—Available experimental data on reactions of the type  $H+X_2 \rightarrow HX+X$ ,  $X+H_2 \rightarrow HX+H$ , and  $H+HX \rightarrow X+H_2$  are analysed to give vals. of the activation energies of the intermediate reactions involved, and these are compared with calc. vals. N. M. B.

**Kinetics of oxidation of hydrides in the gaseous phase. I. Oxidation of silane.** P. S. SCHANTAROVITSCH (Acta Physicochim. U.R.S.S., 1935, 2, 633—646).—The lower ( $p_1$ ) and upper ( $p_2$ ) pressure limits for the ignition of mixtures of  $SiH_4$  and  $O_2$  have been determined. With falling temp.  $p_1$  increases and  $p_2$  diminishes. Ignition occurs the more readily, the smaller is the proportion of  $O_2$  below the stoichiometric ratio. Reducing the diameter of the vessel increases  $p_1$ , but has little effect on  $p_2$ . Addition of 0.1% of  $NO_2$  displaces the ignition curves towards lower temp. The kinetics of the reaction resemble those of  $H_2$ , CO,  $PH_3$ , etc., whilst differing entirely from those of hydrocarbons. At lower temp. an induction period is observed which is absent when  $t > 120^\circ$ , whence it is inferred that a chain mechanism is involved. F. L. U.

**Non-adiabatic reactions: decomposition of  $N_2O$ .** A. E. STEARN and N. EYRING (J. Chem. Physics, 1935, 3, 778—785; cf. A., 1935, 586).—The experimental and calc. abs. rates for the non-adiabatic decomp. of  $N_2O$  are in good agreement.

The amount of chemical inertia present in other reactions involving the singlet-triplet transition of  $O_2$  is examined. A convenient method of constructing potential functions for polyat. mols. is indicated, and employed for the  $N_2O$  mol. N. M. B.

**Heterogeneous oxidation of nitric oxide at the temperature of liquid air.** M. TEMKIN and V. PISHOV (Acta Physicochim. U.R.S.S., 1935, 2, 473—486).—The oxidation of NO by  $O_2$  at  $5 \times 10^{-3}$  to  $8 \times 10^{-2}$  mm. Hg and  $83-88^\circ$  abs. is a heterogeneous reaction between  $O_2$  mols. of the gas phase and NO mols. adsorbed on the surface. The reaction velocity  $v$  is given by  $v=4.2 \times 10^{-9} e^{4300/RT} S \cdot p_{O_2} \cdot p_{NO}$ , where  $S$ =area of surface in sq. cm.,  $p$ =partial pressure in mm. The reaction product has the composition  $N_2O_5$ . O. J. W.

**Thermal reaction between gaseous iodine monochloride and hydrogen.** W. D. BONNER, W. L. GORE, and D. M. YOST (J. Amer. Chem. Soc., 1935, 57, 2723—2724).—The kinetics of the reaction  $2ICl+H_2 \rightarrow I_2+2HCl$  at  $205-240^\circ$  have been investigated. A mechanism involving a slow and a rapid reaction is suggested. The energy of activation of the slow reaction is 33,900 g.-cal. E. S. H.

**Flame speeds during the inflammation of moist carbon monoxide-oxygen mixtures.** W. PAYMAN and R. V. WHEELER (Nature, 1935, 136, 1028).—A discussion. L. S. T.

**Critical explosion limits in oxidation of carbonyl sulphide and monosilane.** H. GUTSCHMIDT and K. CLUSIUS (Z. physikal. Chem., 1935, B, 30, 265—279).—The lower crit. limit for the stoichiometric mixture of COS and  $O_2$  in quartz and glass at  $190-480^\circ$  has been determined. The results agree well with Bawn's (A., 1933, 355) but are incompatible with Semenov's equation,  $\log(p_1+p_2) A/T B$ , ( $p_1, p_2$ =inflammation pressures of components) except over a very narrow temp. range. The effect of the diameter of the vessel,  $d$ , can be represented by  $(p_1+p_2)d^{0.7}=C$ , where  $C$  rises rapidly as the temp. falls. For mixtures of  $SiH_4$  and  $O_2$  in varying proportions the lower crit. limit has been determined at several temp. Semenov's equation,  $p_1 p_2 d^2$  const., for the case where the chains break on the wall, does not hold. The probable cause of this discrepancy is that the course of the reaction varies with the composition of the mixture, for the form of the inflammation isotherms suggests the simultaneous occurrence of reactions yielding at least two different final products. No evidence of crit. limits could be obtained with mixtures of NO with  $CS_2$  vapour or  $PH_3$ . In all the examples of non-stationary chain reactions so far observed explosion involves no increase in the total no. of mols. present. R. C.

**Kinetics of the reaction between oxygen and sulphur. I. Reaction at  $240-280^\circ$ .** L. A. SAYCE (J.C.S., 1935, 1767—1774).— $SO_2$  is formed and chemiluminescence frequently occurs when a mixture of S vapour and 25—760 mm.  $O_2$  at  $200-280^\circ$  is cooled rapidly. The yield of  $SO_2$  is (i) greatest with air-cooling and least with very slow cooling, (ii) max. with 100—300 mm. of  $O_2$ , (iii) independent of  $[S]$  and initial temp. between  $240^\circ$  and  $280^\circ$ , but is very small at

< 220°. Effects due to this reaction were largely eliminated by a new static method for following the principal S-O<sub>2</sub> reaction. The latter is entirely heterogeneous at 240–280° and the velocity,  $k$ , on liquid S is 16-fold that on glass (cf. J.C.S., 1923, 123, 3203). The heat of activation on glass, and probably on liquid S, is 46,430 g.-cal., suggesting similar mechanisms on these surfaces. There is a linear relation between  $k$  and [O<sub>2</sub>], but with [O<sub>2</sub>] > 4 × 10<sup>-4</sup> g. per c.c. there is a marked acceleration probably owing to the development of a chain reaction. J. G. A. G.

**Esterification as a gas reaction.** C. A. WINKLER and C. N. HINSHELWOOD (Trans. Faraday Soc., 1935, 31, 1739–1743).—Reaction between MeOH and HCl vapours occurs readily at 450°, mainly on the surface of the reaction vessel. MeOH and AcOH do not react with appreciable velocity below the temp. at which decomp. of the MeOH becomes rapid. Reaction between MeOH, AcOH, and HCl to yield MeOAc occurs rapidly at 300°, probably in an adsorbed layer of MeOH where ionisation of the HCl can occur. Quant. results were irregular. The rate of esterification in a MeOH solution of AcOH and HCl decreases only slowly as the MeOH is replaced by CCl<sub>4</sub> until the [MeOH] reaches a small val., beyond which it  $\propto$  the [MeOH]. In this region the velocity of reaction  $\propto$  [AcOH]<sup>r</sup>. Some erratic behaviour is observed, related to the size of the liquid-vapour interface, so that adsorption at interfaces may play a part and thus the system becomes analogous to a gaseous system. J. W. S.

**Kinetics of ethylene polymerisation.** II. H. H. STORCH (J. Amer. Chem. Soc., 1935, 57, 2598–2601; cf. A., 1934, 369).—Addition of about 0.1% of EtSH to C<sub>2</sub>H<sub>4</sub> decreases the rate of polymerisation about 10-fold; the induction period is not eliminated, but its duration is markedly reduced. The induction period appears to be due to an intermediate compound, which survives cooling at -180° and subsequent reevaporation into the reaction chamber at 393°. The polymerisation of C<sub>2</sub>H<sub>4</sub> is probably not a simple bimol. reaction. The activation energy is 43,500 g.-cal. E. S. H.

**Thermal decomposition of methyl hydrogen peroxide.** S. MEDVEDEV and A. PODJAPOLSKAJA (Acta Physicochim. U.R.S.S., 1935, 2, 487–504).—Decomp. of MeO<sub>2</sub>H in an atm. of N<sub>2</sub> gave the following products: MeOH, Me<sub>2</sub>O, CH<sub>3</sub>O, HCO<sub>2</sub>H, O<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O, but no H<sub>2</sub> or CH<sub>4</sub>. Two primary decomp. reactions take place, viz. (1) MeO<sub>2</sub>H → CH<sub>3</sub>O + H<sub>2</sub>O, and (2) 2MeO<sub>2</sub>H → 2MeOH + O<sub>2</sub>. At low temp. (1), which is followed by MeO<sub>2</sub>H + CH<sub>3</sub>O → MeO<sub>2</sub>·CH<sub>2</sub>·OH predominates. The activation energies for (1) and (2) are 10,950 and 25,330 g.-cal., respectively. O. J. W.

**Abnormally small steric factors in chemical kinetics.** H. HELLMANN and J. K. SIRKIN (Acta Physicochim. U.R.S.S., 1935, 2, 433–466).—The wave-mechanical theory of collision processes presented is able to account for abnormally small steric factors (of the order of 10<sup>-5</sup>–10<sup>-8</sup>) in the velocity coeff. expression. The influence of tunnel effects on the steric factor is discussed. O. J. W.

**Polymorphism.** III. Linear velocity of the transformation of  $\alpha$ - into  $\beta$ -*o*-nitroaniline. N. H.

HARTSHORNE, G. S. WALTERS, and (in part) W. O. M. WILLIAMS (J.C.S., 1935, 1860–1873; cf. A., 1931, 1407).—Irregularities of the contour of the advancing interface between  $\alpha$ - and  $\beta$ -*o*-nitroaniline (I) are not due to local variations in the thickness of the film, although in very thin films the average velocity,  $v$ , is > in films 0.01–0.02 mm. thick. The decrease of  $v$  as the interface advances is not primarily due to impurities and is attributed to the progressive widening of the gap between the  $\alpha$ - and  $\beta$ -forms, since the  $d$  of  $\alpha$ - is < the  $d$  of  $\beta$ -(I). There were considerable variations in  $v$  with different specimens at the same temp., but there was no overlapping between the results at 0°, 20°, 30°, and 40°. No relation was found between  $v$  and the degree of purity of the specimens. The data are represented, in general, by the semi-empirical equation  $t = k_1 s^3 + k_2 s$ , where  $s$  is the linear displacement of the interface in time  $t$  from zero. The temp. coeff. between 20° and 40° leads to the activation energy 17–18 kg.-cal. per mol. This val. is in harmony with the view that  $v$  is controlled by the difference between the rates of evaporation of  $\alpha$ - and  $\beta$ -(I). J. G. A. G.

**Mechanism of polymerisation reactions.** I, II. H. DOSTAL (Monatsh., 1935, 67, 1–9, 63–79, 222).—I. Theoretical. The treatment previously developed (A., 1935, 1206) is extended to the stabilisation of growing chains, which is regarded as a unimol. process, the velocity coeff. of which may vary with the chain length.

II. The theory is applied to the dependence on time of the total quantity of polymeride, and to the influence of a steric factor, and of the combination of partly grown chains, on polymerisation. Stabilisation of chains, both spontaneously and in the presence of a foreign substance, is further considered. F. L. U.

**Activation energies of some reactions involving free radicals.** C. E. SUN (J. Chinese Chem. Soc., 1935, 3, 293–295).—The activation energy of reactions involving free radicals can be calc. by Eyring's method. The val. for a reaction in which there is a transfer of H from a C of the normal mol. to a free radical, the rest of the mol. remaining unaltered, is 17 kg.-cal. A. J. M.

**Kinetics of the reduction of (A) copper sulphate, (B) bismuth chloride, by hypophosphorous acid in aqueous solutions.** (A) G. S. VOZDVISHENSKI and A. F. GERASIMOV. (B) A. F. GERASIMOV and B. M. KOZUREV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 108–113, 126–133).—(A) The reaction was studied at 47°. The [Cu] at time  $t$  is given by  $\log [Cu] = 2.2932 - 0.48 \log t$ .

(B) The reaction was studied at 50°. The [Bi] at time  $t$  is given by  $\log [Bi] = -2.523 - 0.1 \log t$ .

CH. ABS. (e)  
**Velocity of decomposition of calcium carbonate solutions.** Y. KAUKO (Ann. Acad. Sci. fenn., 1934, A, 39, No. 9; Chem. Zentr., 1935, i, 2767).—The decomp. of Ca(HCO<sub>3</sub>)<sub>2</sub> at 0–15° by passage of CO<sub>2</sub>-free air follows the course HCO<sub>3</sub>' → OH' + CO<sub>2</sub>. At low [HCO<sub>3</sub>] the velocity is determined by the velocity of diffusion of CO<sub>2</sub>. J. S. A.



**Polar effects of the halogens in aromatic combination.** G. BADDELEY, G. M. BENNETT, S. GLASTONE, and B. JONES (J.C.S., 1935, 1827—1830; cf. A., 1933, 1151).—Data previously considered and new data (see below) are interpreted by means of the following factors: an electromeric effect (if any), a mesomeric polarisation, an inductive effect and field effects all varying in the order  $F > Cl > Br > I$ , and a polarisability effect varying in the order  $I > Br > Cl > F$ . The nature of these effects is discussed. J. G. A. G.

**Intermediate stages in aldehyde oxidation.**  
**III. Kinetics of the reaction between peracetic acid and aldehydes in aqueous solution.** G. D. LUBARSKI and M. J. KAGAN (Acta Physicochim. U.R.S.S., 1935, 2, 665—678; cf. A., 1935, 1084).—The reaction has been studied in various concns. of aq. AcOH. The velocity coeff. in presence of  $H_2O$  is  $>$  in non-aq. solution due to acceleration of the second stage  $OH\cdot CH_3CO\cdot OAc \rightarrow 2AcOH$ . In aq.  $MeCHO$  the velocity coeff. increases with  $H_2O$  content. The data do not support Wieland's hypothesis (A., 1932, 722). T. G. P.

**Kinetics of the bromination of benzaldehyde.** J. K. SIRKIN and A. T. GLADISHEV (Acta Physicochim. U.R.S.S., 1935, 2, 467—472).—The velocity of the bromination of  $PhCHO$  in  $CCl_4$  solution in the dark has been measured at 30°, 35°, and 40°. Assuming that the reaction is bimol. the activation energy is calc. to be 32,900 g.-cal. Quinol and I do not influence the velocity. As the reaction is very slow a unimol. equation is obeyed approx. O. J. W.

**Dilatometric method for following the hydrolysis of sucrose.** D. I. HITCHCOCK and R. B. DOUGAN (J. Physical Chem., 1935, 39, 1177—1188).—The vol. change of sucrose (I) solutions undergoing inversion by HCl follows strictly a unimol. formula, and the velocity coeffs. agree with those obtained polarimetrically. The total contraction per mol. of (I) at infinite dilution, for complete hydrolysis and with the products in mutarotation equilibrium, is by extrapolation 6.92 c.c. at 25°. Results obtained with invertase are similar but less simple. The dilatometric method may be used with confidence in studying the hydrolysis of (I) in acid solutions, and for comparing the activities under optimum conditions of preps. of yeast-invertase. F. L. U.

**Velocities of reaction of  $\beta$ -arylethyl chlorides with potassium iodide.** G. BADDELEY and G. M. BENNETT (J.C.S., 1935, 1819—1821).—The data refer to  $p\text{-}X\cdot C_6H_4\cdot C_2H_4Cl$ , where  $X=H, MeO, I, Br, Cl, F$ , and  $NO_2$ , in  $COMe_2$  solution at 55° and 75°. The velocity coeff. at 75° is  $halogens > MeO > H$ .

J. G. A. G.

**Velocities of reaction of substituted benzyl chlorides in two reactions of opposed polar types.** G. M. BENNETT and B. JONES (J.C.S., 1935, 1815—1819).—The data refer to the *o*-, *m*-, and *p*-monohalogen- and  $NO_2$ -, and *p*-Me-substituted benzyl chloride. The energy of activation,  $E$ , of the hydrolysis in 50% aq.  $COMe_2$  is approx. 20.9 kg.-cal. between 70° and 85°. The velocity coeff.,  $k$ , is approx. const. in the *m*-halogen series, but in the *o*- and *p*-halogen series  $F > Cl > Br > I$ . The  $k$  of the reaction

with KI in  $COMe_2$  at 0.1° and 20° has been determined.  $E$  is approx. 17.3 kg.-cal. for the *o*-compounds and 18.1 for the *m*- and *p*-derivatives. The anomalous vals. for  $k$  previously observed (A., 1925, i, 494) with *o*- and *p*- $C_6H_4Br\cdot CH_2Cl$  are due to the presence of *o*- and *p*- $C_6H_4Cl\cdot CH_2Br$ . The pure reagents were therefore prepared from the appropriate nuclear-substituted benzyl alcohol. J. G. A. G.

**Ester hydrolysis in pure water.** A. SKRABAL (Monatsh., 1935, 67, 118—128).—A discussion of papers by Kirmann (A., 1934, 847) and Poethke (A., 1935, 938). F. L. U.

**Energies and entropies of activation of the reaction between bromoacetate and thiosulphate ions.** V. K. LA MER and M. E. KAMNER (J. Amer. Chem. Soc., 1935, 57, 2662—2668).—The temp. coeffs. of the reaction have been studied over a range of temp. and concn. to obtain data for the effect of temp. and ionic environment on the energy of activation and the action const.  $B$ . The increase in  $\log k$  produced by the addition of  $Na^+$  is correlated with an increase of  $B$ . In presence of  $Ba^{++}$  and  $La^{+++}$  the energy of activation is increased, but is more than compensated by an increase in the entropy of activation. E. S. H.

**Influence of non-electrolytes on the kinetics of the reaction between bromoacetate and thiosulphate ions.** V. K. LA MER and M. E. KAMNER (J. Amer. Chem. Soc., 1935, 57, 2669—2673).—The velocity coeff. in  $H_2O$  is increased by adding  $CO(NH_2)_2$ , sucrose, glycerol, or dioxan, although  $CO(NH_2)_2$  raises the dielectric const. and the remainder lower it. The energy of activation is unchanged by  $CO(NH_2)_2$ , but decreased by the other non-electrolytes. In 32% sucrose solutions the positive salt catalysis arises from an increase in the entropy of activation, which more than compensates the retarding influence of an increase in the energy of activation. E. S. H.

**Temperature dependence of the energy of activation in the de-aldolisation of diacetone alcohol.** V. K. LA MER and M. L. MILLER (J. Amer. Chem. Soc., 1935, 57, 2674—2680).—The velocity coeff. in presence of dil. NaOH has been determined at 5° intervals between 0° and 50°; the proportionality between velocity coeff. and  $[NaOH]$  has been confirmed over a limited concn. range at 25°. The energy of activation is a function of temp., increasing from 15,850 g.-cal. at 5° to 17,250 g.-cal. at 32.5°, and then decreasing by about 400 g.-cal. at 45°. Addition of 18.5% MeOH causes an increase of  $>1700$  g.-cal. The corresponding vals. for the action const.  $B$  in  $H_2O$  and MeOH solutions are parallel. The data show the inadequacy of the collision theory and the importance of the entropy of activation. E. S. H.

**Kinetics of bimolecular reactions in solution.**  
**II. Formation of sulphonium salts.** J. K. SIRKIN and I. T. GLADISHEV (Acta Physicochim. U.R.S.S., 1935, 2, 291—302).—The kinetics of the reaction between  $MeI$  and  $Et_2S$  to yield  $SMeEt_2I$  has been studied at 17°, 27°, and 37° in MeOH, EtOH, PrOH, and  $COMe_2$  solutions. The calc. activation energies, corr. for the variation of frequency

of collision with viscosity, are 19,150, 20,760, 21,270, and 13,300 g.-cal. per mol., respectively. The velocities of reaction observed in alcohols are only about 0.01 of those calc. from the frequency of collision and activation energy, this being attributed to steric factors. In COMe, the velocity is only  $4 \times 10^{-7}$  of the calc. val. This reaction in these solvents is intermediate between a normal and a slow reaction. The mechanism of reaction in COMe<sub>2</sub> is discussed in detail.

J. W. S.

**Velocity of alkaline hydrolysis of crotonic esters.** E. SCHJANBERG (Z. physikal. Chem. 1935, 174, 465—471).—Branching of the C chain of the alkyl radical of the alcohol in the  $\alpha$ -position reduces the velocity coeff.,  $k$ , owing to fall in the action const.,  $\alpha$ . Comparison with the rates of hydrolysis of corresponding butyrates shows that an  $\alpha\beta$ -double linking in the acyl radical depresses  $k$ , whilst both the energy of activation,  $Q$ , and  $\alpha$  rise; the effect of the rise in  $Q$  outweighs that of the rise in  $\alpha$ , so that the net effect is a fall in  $k$ .

R. C.

**Coupled oxidation of alcohol.**—See this vol., 242.

**Relation between the apparent and true activation energy of heterogeneous reactions.** M. TEMKIN (Acta Physicochim. U.R.S.S., 1935, 2, 313—316).—Mathematical.

J. W. S.

**Reaction velocity in the system solid<sub>1</sub> gas  $\rightarrow$  solid<sub>2</sub>.** G. S. GARDNER (J. Math. Phys. Mass. Inst. Tech., 1935, 14, 241—259).—Based on Langmuir's treatment and Fourier's law for heat conduction, an equation is derived for the rate of a solid-gas reaction and is integrated for six special cases covering all types of available data. Results are illustrated by curves using available data for the reaction of anhyd. NH<sub>3</sub> with mixtures of powdered glass and  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>-OH, phthalic acid, tartaric acid, and quinol, and for NH<sub>3</sub>-anhyd. CuSO<sub>4</sub>, N<sub>2</sub>-CaC<sub>2</sub>, *p*-anisidine in HCl-air, and  $\psi$ -cumenol in NH<sub>3</sub>-air.

N. M. B.

**Stability of solid pharmaceutical hydrogen peroxide preparations.**—See B., 1936, 74.

**Influence of fluid velocity on heterogeneous reactions. IV. Absorption of ammonia in wetted-wall towers.** S. UCHIDA and S. MAEDA. **V. Model experiment of chemical change in packed towers.** S. UCHIDA and S. SHONOYA (J. Soc. Chem. Ind. Japan, 1935, 38, 625B, 626—629B).—**IV.** Uchida's theoretical relationship (A., 1934, 1312) is roughly confirmed by experiment.

**V.** The factors governing the velocity of solid-liquid reactions in dynamic systems, where the rate of diffusion is predominant, have been correlated from experiments on the dissolution of sugar in packed columns.

J. S. A.

**Application of A. N. Schtschukarev's method of determining densities to the study of the reaction of polymorphic transformation of  $\beta$ -into  $\alpha$ -silver iodide.** V. LINITZKI (Ukrain. Chem. J., 1935, 10, 283—284).—The rate of transformation is determined by measuring the apparent change in wt. of a sample immersed in paraffin heated at 148°.

R. T.

**Velocity of absorption of oxides of nitrogen.** V. I. ATROSCITSCHENKO (Ukrain. Chem. J., 1935, 10, 295—304).—The relative velocity,  $V$ , of absorption of NO<sub>2</sub> at 20° by various liquids is: H<sub>2</sub>O 1, 6 and 20% HNO<sub>3</sub> 0.84 and 0.79, 4.5 and 20% NaOH 0.57 and 0.526, 17% KOH 0.515, 90.2% H<sub>2</sub>SO<sub>4</sub> 0.42, 10.6% Na<sub>2</sub>CO<sub>3</sub> 0.375, and liquid paraffin 0.072. The corresponding figures for NO-NO<sub>2</sub> mixture are 1, 0.85 and 0.65, 0.83 and 1.02, 1.05, 14.0, 0.134, and 0.0, and the corresponding ratios  $V_{\text{NO}_2}/V_{\text{N}_2\text{O}_5}$  are 4.2, 4.2, 5.0, 2.9, 2.2, 2.1, and 0.13 (Na<sub>2</sub>CO<sub>3</sub> and paraffin not given).

R. T.

**Kinetics of dehydration of gypsum.** P. P. BUDNIKOV and L. A. SCHTSCHUKAREVA (Kolloid-Z., 1935, 73, 334—339).—Determinations of loss of wt. show that the dehydration of CaSO<sub>4</sub>·2H<sub>2</sub>O at 107° follows the course of a unimol. reaction. The presence of small amounts of NaCl or KCl has a strong retarding action.

E. S. H.

**Deflagration of explosive substances by ultrasonic radiation.** N. MARINESCO (Compt. rend., 1935, 201, 1187—1189).—Substances very sensitive to shock, e.g., NI<sub>3</sub>, have been deflagrated by ultrasonic radiation. Others must be suspended in non-wetting liquids, when deflagration is induced by heating of the adhering air.

T. G. P.

**Kinetics of solid-phase reactions of certain carbonates with mullite, silica, and alumina.**—See B., 1936, 20.

**Reduction of iron oxides by gaseous reducing agents. I. Velocity of reduction of ferric oxide by hydrogen.** G. I. TSCHUFAROV and A. P. LOCHVITZKAJA (J. Phys. Chem. U.S.S.R., 1934, 5, 1103—1113).—Reduction of Fe<sub>2</sub>O<sub>3</sub> is not autocatalytic. The remaining stages are autocatalytic intersurface reactions. Data for the rates of reduction at 300—900° under various conditions are given. The porosity of the product is the greater the lower is the reduction temp.

CH. Abs. (c)

**Comparison between the effect of hydrogen-ion concentration on the rate of corrosion of steel in pure oxygen and air at 25°.** J. M. BRYAN (Trans. Faraday Soc., 1935, 31, 1714—1718; cf. A., 1933, 1251; 1935, 43).—The effect of a high [O<sub>2</sub>] on the corrosion of Fe in citric acid containing varying amounts of Na citrate is to equalise the attack over most of the  $p_{\text{H}}$  range 2.4—5.5. Using fast-corroding steel the evolution of H<sub>2</sub> is inhibited by pure O<sub>2</sub> at high acidity, thus counterbalancing the increase in rate of corrosion through depolarisation. As the [Fe] in the solution increases its effect overshadows that of the direct action of O<sub>2</sub> at the metal surface.

J. W. S.

**Rate of dissolution of iron in molten zinc.**—See B., 1936, 23.

**Explosive decomposition of tetryl.** A. LUKIN and S. ROGINSKI (Acta Physicochim. U.R.S.S., 1935, 2, 385—396; cf. J.C.S., 1921, 119, 721).—The time required for the explosion of tetryl to occur in a sealed vessel has been studied as a function of temp. and at 156° as a function of the amount of picric acid added.

J. W. S.

**Kinetics of the oxidation of fats and oils.**—See B., 1936, 27.

**Structure theory of chemical change. Complete system of doublet reactions.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 177—202; cf. A., 1929, 519, 890).—A complete system of "doublet" reactions in org. chemistry is drawn up. All have not been experimentally realised. The theory of structure of reactions may also be applied to heterogeneous reactions. Hydrogenation reactions are more fully discussed. A. J. M.

**Directions of reactions of decomposition and condensation.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 345—362; cf. preceding abstract).—The author's theory is extended to the determination of the different possible directions in which a complicated mol. can react. J. W. S.

**Application of the structure theory of reactions to Lebedev's synthesis of butadiene from alcohol and to Rice's theory of pyrolysis.** A. A. BALANDIN (*Acta Physicochim. U.R.S.S.*, 1935, 2, 363—376).—The author's theory (cf. preceding abstracts) is applied to the catalytic decomp. of EtOH at 450°, with special reference to the formation of  $(\text{CH}_2\text{:CH})_2$ . Rice's theory of thermal decomp., which is in accord with the doublet mechanism of decomp., is developed and applied to cyclic hydrocarbons. The results are in qual. agreement with experiment. J. W. S.

**Inhibition of homogeneous reactions by small quantities of nitric oxide.** L. A. K. STAVELEY and C. N. HINSHELWOOD (*Nature*, 1936, 137, 29—30).—Small amounts of NO (0.1—1 mm.) reduce the rate of decomp. of  $\text{Et}_2\text{O}$ ,  $\text{EtOPr}$ ,  $\text{Pr}^t_2\text{O}$ , and  $\text{EtCHO}$  to a well-defined limit.  $\text{MeOH}$ ,  $\text{COMe}_3$ , and  $\text{MeCHO}$  give negative results. The effect is as though short reaction chains were broken up by the NO. L. S. T.

**Catalysis of hydrogen peroxide [decomposition] by iron salts.** N. JERMOLENKO and E. NOVIKOVA (*Z. anorg. Chem.*, 1935, 225, 333—336).—A study of the catalytic decomp. of  $\text{H}_2\text{O}_2$  by Fe salts of varying solubility and tendency to colloid formation indicates that catalysis is mainly due to colloidal  $\text{Fe}(\text{OH})_3$  containing adsorbed  $\text{Fe}^{+++}$ . M. S. B.

**Efficiency of stabilisers used in the preservation of hydrogen peroxide.**—See B., 1936, 18.

**Homogeneous catalysis: decomposition of acraldehyde catalysed by iodine.** H. W. THOMPSON and J. J. FREWING (*Trans. Faraday Soc.*, 1935, 13, 1660—1668).—The decomp. of  $\text{CH}_2\text{:CH}\cdot\text{CHO}$ , catalysed by I, occurs 100° lower than in the absence of catalyst. The velocity of reaction  $\propto [\text{I}]^{\frac{1}{2}}$ . The reaction is only slightly retarded by packing the vessel, but is appreciably retarded by increasing  $[\text{CH}_2\text{:CH}\cdot\text{CHO}]$ . Probably catalysis occurs through  $\text{I}_2$  mols. and the short chains are propagated and broken both by  $\text{CH}_2\text{:CH}\cdot\text{CHO}$  and  $\text{I}_2$  mols. J. W. S.

**Kinetics of the autoxidation of pyrocatechol in presence of several foreign substances.** G. E. K. BRANCH and M. A. JOSLYN (*J. Amer. Chem. Soc.*, 1935, 57, 2388—2394).—Cysteine,  $\text{K}_2\text{SO}_3$ , and  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  inhibit the  $\text{O}_2$  absorption of pyrocatechol (I), whilst quinol (II), resorcinol, pyrogallol (III), gallic acid, and  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  accelerate it.

In mixtures of (I) with (II) or (III) the rate increases almost to that for pure (II) or (III). A chain-exchanging mechanism is postulated. E. S. H.

**Behaviour of chromic oxide towards alkali halogenate solutions. II. Autocatalysis in the system chromic oxide-bromate and the influence of bromides in solution.** R. LYDEN (*Z. anorg. Chem.*, 1935, 226, 46—56).—Oxidation of  $\text{Cr}_2\text{O}_3$  by neutral aq.  $\text{KBrO}_3$  (cf. A., 1935, 834) is entirely prevented by the previous addition of alkali hydroxide or carbonate. The reaction is catalysed by  $\text{H}^+$ , and since these are formed in the course of the reaction the latter is autocatalytic. The effect of added  $\text{Br}^-$  is to depress the catalytic action of  $\text{H}^+$ . F. L. U.

**Theory of heterogeneous catalysis.** P. D. DANKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 253—256).—A theory which relates dispersion to catalytic activity renders possible the determination of the elementary catalysing area, indicates the connexion between the structure of the reacting mols. and the activity and structure of the catalyst, gives qualitatively new and quantitatively computable causes for the poisoning and promoting of catalysts, and points to new methods of interpreting and estimating chemical processes on the surface. W. R. A.

**Compact disperse materials. Action of hydrogen peroxide on ferric hydroxide.** H. W. KOHL-SCHUTTER and H. SIECKE (*Z. Elektrochem.*, 1935, 41, 851—860; cf. A., 1933, 1019).—The catalytic activity (in decomp.  $\text{H}_2\text{O}_2$ ) of pseudomorphic  $\text{Fe}(\text{OH})_3$  has been studied in relation to  $\text{H}_2\text{O}$  content, degree of dispersion, and chemical reactivity. The results are discussed from the point of view of its structure. F. L. U.

**Reality of the chains in heterogeneous-homogeneous catalysis.** M. POLJAKOV and A. ELKEN-BARD (*Acta Physicochim. U.R.S.S.*, 1935, 2, 397—400).—When a Pt spiral is heated to > about 250° in a 3 : 1  $\text{H}_2\text{-O}_2$  mixture contained in a vessel the walls of which are cooled in liquid air,  $\text{H}_2\text{O}_2$  is produced in a quantity which increases with rise of temp. of the Pt. If, however, a Pt gauze is interposed between the spiral and wall,  $\text{H}_2\text{O}_2$  formation is almost undetectable. The gauze therefore either eliminates the step in the reaction which gives rise to  $\text{H}_2\text{O}_2$  or causes stoppage of the chains. This observation proves the existence of a homogeneous process in this heterogeneous catalytic reaction, and also the chain mechanism of this process. J. W. S.

**Catalysis by fusions.** I. E. ADADUROV and P. D. DIDENKO (*J. Amer. Chem. Soc.*, 1935, 57, 2718—2722).—The catalytic activity of Sn in the oxidation of  $\text{NH}_3$  by air increases with rise of temp. beyond the m.p.; thus the crystal lattice of Sn is not involved, but it is shown that the catalysis is actually due to  $\text{SnO}_2$ . When Ag is used as the catalyst, no oxide is formed and the catalytic activity falls abruptly, with simultaneous change in the type of reaction, at the m.p. The bearing of these results on other catalytic reactions is discussed. E. S. H.

**Inflammability of ammonia in presence and absence of a catalyst.** H. ABESHAUS, N. TOKAREV, and N. NEKRASSOV (*Acta Physicochim. U.R.S.S.*,

1935, 2, 401—420).—The limiting pressures for the explosion of  $\text{NH}_3$ -air mixtures have been studied as a function of temp. and  $[\text{NH}_3]$  without a catalyst, and in presence of Pt gauze treated in various ways. The explosion region becomes narrower in presence of  $\text{H}_2\text{O}$  vapour, especially in decreasing the max.  $[\text{NH}_3]$  for explosion. The photochemical oxidation of  $\text{NH}_3$  has also been investigated, and the mechanism of the oxidation process is discussed.  
J. W. S.

**Velocity of decomposition of ammonia on thoriated tungsten.** I. MOTSCHAN, I. PEREVESSEV, and S. ROGINSKI (*Acta Physicochim. U.R.S.S.*, 1935, 2, 203—210).—The addition of Th to a W surface has no effect on the catalytic activity of W in the decomp. of  $\text{NH}_3$ .  
A. J. M.

**Dependence of the structure of an ammonia catalyst on the conditions of its reduction.** A. M. STEFANOVSKI, E. S. TATARSKI, and N. V. SELJAKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1935, 3, 21—24).—Higher temp. of prep. cause a diminution in activity associated with readjustment of the crystal lattice.  
C. W. G.

**Active oxides. LXXXVII. Active states of the systems cadmium oxide-iron oxide and beryllium oxide-iron oxide with regard to their catalytic activity in the decomposition of nitrous oxides.** G. F. HUTTIG, G. SIEBER, and H. KITTEL (*Acta Physicochim. U.R.S.S.*, 1935, 2, 129—150).—Equimol. mixtures of  $\text{CdO}$  and  $\text{Fe}_2\text{O}_3$ , and  $\text{BeO}$  and  $\text{Fe}_2\text{O}_3$ , respectively, were heated at various temp. and the catalytic effect on the decomp. of  $\text{N}_2\text{O}$ , colour, and magnetic susceptibility was determined with respect to the temp. at which the systems were heated. The results of the catalytic action are expressed by  $\log \alpha = (-q/RT) + \log n'$ , where  $\alpha$  is the % of  $\text{N}_2\text{O}$  decomposed,  $T$  is the abs. temp. of heating, and  $q$  and  $n'$  are consts. for each system.  $q$  may be regarded as a heat of activation, whereas  $n' \propto$  the no. of active spots. The higher is  $q$ , the smaller is the activity of individual active spots. For the system  $\text{CdO-Fe}_2\text{O}_3$  there is no perceptible change in properties at temp.  $< 450^\circ$ . At about this temp. there is a slight colour change, accompanied by the commencement of catalytic action, which reaches a max. at about  $550^\circ$ . The magnetic susceptibility shows a sudden increase at about  $550^\circ$ , and reaches a max. at  $750^\circ$ . Similar results are obtained for the system  $\text{BeO-Fe}_2\text{O}_3$ , but in this case, unlike the first, the decrease in activity after the max. cannot be ascribed to compound formation. The ageing of active  $\text{MgO}$  (decrease of activity with time) has also been investigated.  
A. J. M.

**Acceleration of the reaction  $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$  by the presence of some salts.** U. NISHIOKA (*Kin.-no-Ken.*, 1935, 12, 42—48).—Rates of formation of  $\text{CO}$  from  $\text{C}$  and  $\text{CO}_2$  at  $1000^\circ$  were measured with various carbonates and chlorides of alkali and alkaline-earth metals as catalysts. The catalytic activity increased with the at. wt. of the metal forming the salt.  
CH. ABS. (e)

**Catalytic oxidation of carbon.** J. E. DAY, R. F. ROBEY, and H. J. DAUBEN (*J. Amer. Chem. Soc.*, 1935, 57, 2725—2726).— $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,

$\text{BaCl}_2$ ,  $\text{Ca(OH)}_2$ ,  $\text{Ba(OH)}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4$  catalyse the oxidation of films of deposited  $\text{C}$ . E. S. H.

**Kinetics of the reaction between carbon dioxide and hydrogen on platinum from the viewpoint of the adsorption theory of catalysis.** M. TEMKIN and E. MICHALLOVA (*Acta Physicochim. U.R.S.S.*, 1935, 2, 9—32).—Previous results (A., 1925, ii, 564; 1930, 551) are in error owing to poisoning of the Pt wire. The reaction, which has been studied in vessels at  $-78^\circ$  with filament temp. of about  $800^\circ$  abs., yields a small amount of  $\text{C}$  besides the main products  $\text{CO} + \text{H}_2\text{O}$ . The rate is given by  $dp_{\text{CO}}/dt = k_1 p_{\text{H}_2} / (k_2 p_{\text{H}_2} + p_{\text{CO}})$ , which has been derived from the assumption that the reaction velocity depends on the rate of evaporation of  $\text{CO}$  from the surface. Rates of evaporation observed at different temp. are in agreement with Langmuir's results (A., 1921, ii, 629) and the activation energy of evaporation (22,000—25,000 g.-cal.) approximates to the heat of adsorption of  $\text{CO}$ . The application of adsorption equilibrium equations to heterogeneous reactions is not always valid.  
R. S.

**Dissociation of antimony trihydride: an autocatalytic heterogeneous reaction.** J. GUERON and A. LALANDE (*Bull. Soc. chim.*, 1935, [v], 2, 2240—2258).—An expression is derived for the velocity of an irreversible gaseous reaction catalysed by a solid, using Langmuir's adsorption equation. The expression is shown to represent the autocatalytic thermal decomp. (2—95%) of  $\text{SbH}_3$  if the reaction in the adsorbed phase is unimol.  
F. L. U.

**Nature of the surface of copper catalysts.** W. W. RUSSELL and L. G. GHERING (*J. Amer. Chem. Soc.*, 1935, 57, 2544—2552).—Determinations of the catalytic activity of poisoned (with  $\text{O}_2$  or  $\text{N}_2\text{O}$ ) and unpoisoned surfaces of  $\text{Cu}$  by means of the  $\text{C}_2\text{H}_4\text{-H}_2$  reaction at  $0^\circ$ , and of the heat of sorption of  $\text{O}_2$ , show that the  $\text{Cu}$  surface is non-uniform and that the above catalytic reaction proceeds almost exclusively on a relatively few surface types, probably of intermediate character.  
E. S. H.

**Promoter action of gases on hydrogenation catalysts.** K. ABLESOVA and S. ROGINSKI (*Z. physikal. Chem.*, 1935, 174, 449—464; cf. A., 1935, 830).—The catalytic activity in respect of the hydrogenation of  $\text{C}_2\text{H}_4$  of  $\text{Ni}$  films formed by evaporation in presence of  $\text{H}_2$  passes through a marked max. with increase in the amount of  $\text{H}_2$  sorbed in the prep. of the film; this corresponds with  $\sim 1 \text{ H}_2$  mol. per 100  $\text{Ni}$  atoms. Such activated films are not affected by poisons, but, except at very low temp., are irreversibly deactivated by exposure to high vac. The promoter action of the sorbed gas is possibly due to its influence on activated sorption; the prevention of recrystallisation may also be an accessory factor.  
R. C.

**Activation of specific bonds in complex molecules at catalytic surfaces.** H. S. TAYLOR, K. MORIKAWA, and W. S. BENEDICT (*J. Amer. Chem. Soc.*, 1935, 57, 2735).—By following the reactions (1)  $\text{C}_2\text{H}_6 + m\text{D}_2 \rightarrow \text{C}_2\text{H}_x\text{D}_y$  (where  $x+y=6$  and  $m$  may be varied arbitrarily) and (2)  $\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$ , which



involve, respectively, the C-H and C-C linkings, the specificity of catalyst surfaces may be studied.

E. S. H.

**Effect of adsorbed water on the catalytic decomposition of hydrocarbons (by a molecular beam method).** O. BEECK (Nature, 1935, 136, 1028—1029).—The catalytic decomp. of hydrocarbons at a hot Pt or C surface has been investigated by means of a mol. beam technique. No dehydrogenation of paraffins, olefines, or alcohols occurs unless traces of  $H_2O$  are present. It is probable that this  $H_2O$  is necessary to maintain a unimol. layer on the catalytic surface and that this layer is the true seat of dehydrogenation. Dehydrogenation is inhibited by an excess of  $H_2O$  on the Pt in the lower temp. region and the temp. at which the reaction falls off thus depends on the  $H_2O$  content of the gas investigated. Traces of air in presence of traces of  $H_2O$  do not affect the reactions. There is evidence that  $H_2O$  may be substituted by other mols. having H linkings with electronegative elements, *e.g.*,  $H_2S$ . The primary reaction appears to be the formation of free radicals by rupture of C-C, except in the case of  $CH_4$ , which may decompose into  $H_2$  and  $CH_2$ . The presence of  $H_2O$  is also necessary for the hydrogenation of unsaturated hydrocarbons. L. S. T.

**Decomposition of propane and *n*-butane at carbon filaments.** L. BELCHETZ and E. K. RIDEAL (J. Amer. Chem. Soc., 1935, 57, 2466—2469).—The gases were passed at high steaming velocity and low pressure (0.1 mm.) over a heated C filament placed 2—3 mm. from a Te mirror, kept at 100°, with which any radicals formed could react. The first step is the production of  $H_2$  and the complementary olefine. The latter can then dissociate to  $CH_2$  and the next lower olefine, except with  $\Delta^2$ -butene, which may be further dehydrogenated to butadiene.  $CH_2$  subsequently reacts with surrounding mols. The energies of activation for the two reactions are 94.2 and 93.2 kg.-cal., respectively. E. S. H.

**Reaction of hydrogen and deuterium with ethylene at a nickel surface.** T. TUCHOLSKI and E. K. RIDEAL (J.C.S., 1935, 1701—1704).—The combination of  $H_2$  and  $D_2$  with  $C_2H_4$  on a Ni filament at  $> 0^\circ$  is almost of zero order. At 0—140°, the velocity coeff.,  $k$ , for  $H_2$  is  $>$  for  $D_2$  and the difference between the energies of activation decreases from approx. 0.79 to approx. 0.5 kg.-cal. with rise of temp.  $k_H$  and  $k_D$  have max. vals. at approx. 140° and 160°, respectively, and at 165—168°,  $k_H$  and  $k_D$  are almost identical. The results negative zur Strassen's interpretation (A., 1934, 974) of the inversion of the temp. coeff., and a mechanism is suggested.

J. G. A. G.

**Hydrogenation of ethylene with nickel as a catalyst at low temperatures.** O. TOYAMA (Proc. Imp. Acad. Tokyo, 1935, 11, 319—321).—The velocity between  $-70^\circ$  and  $0^\circ$  increases with the pressure of  $H_2$  and decreases gradually with increasing pressure of  $C_2H_4$ .  $C_2H_6$  has little effect. The apparent heat of activation is approx. 6 kg.-cal. The rate of the initial reaction is increased by pretreating the catalyst with  $H_2$ , but  $C_2H_4$  has a retarding effect. The

reaction is probably a bimol. combination of  $H_2$  and  $C_2H_4$  at the Ni surface. J. G. A. G.

**Ferromagnetic transformation and catalytic activity. IV. Hydrogenation of carbon monoxide and ethylene over nickel, and formation of carbon dioxide from carbon monoxide over the Heusler alloy  $MnAlCu_2$ .** J. A. HEDVALL and R. HEDIN (Z. physikal. Chem., 1935, B, 30, 280—288; cf. A., 1935, 1467).—The course of each of these reactions changes abruptly when the ferromagnetic transformation of the catalyst occurs. R. C.

**Preparation of platinum oxide reduction catalysts.** W. F. SHORT (J.S.C.I., 1936, 55, 14T).—The  $H_2PtCl_6-NaNO_3$  fusion is conducted in a 50-c.c. Pyrex beaker resting in a cavity (47 mm. diameter, 25 mm. deep) in a Cu block (37—40 mm. high, 90 mm. diameter) provided with a thermometer pocket. By working at a definite temp. (usually 500—550°) catalysts of max. activity can be prepared with certainty.

**Catalytic properties of rhenium and of certain of its compounds.** S. B. ANISIMOV, V. M. KRASCHENNIKOVA, and M. S. PLATONOV (J. Gen. Chem. Russ., 1935, 5, 1059—1065).—The catalytic activity of Re (on kaolin) is small for reactions of hydrogenation, considerable for that of dehydrogenation of EtOH to MeCHO (max. yields at 300° and 600°, with a min. at 400°), and very small for those of oxidation, owing to formation of oxides of Re volatile at  $> 100^\circ$ . Re is readily recovered from the catalyst by heating the mass at 200° in an atm. of  $O_2$  in a sealed tube, when  $Re_2O_7$  condenses in the cooled upper part of the tube. R. T.

**Comparative action of mixed catalysts when used for the joint dehydration of ethyl alcohol and ammonia. I.** N. I. SCHUIKIN, A. A. BALANDIN, and Z. I. PLOTKIN. **Comparative action of mixed catalysts when used for the joint dehydration of ethyl alcohol and aniline. II.** N. I. SCHUIKIN, A. A. BALANDIN, and F. T. DIMOV (J. Physical Chem., 1935, 39, 1197—1205, 1207—1216; cf. A., 1932, 1232).—I. Mixtures of  $Al_2O_3$  with  $ZnO$  (10%),  $SnO$  (10%),  $Cr_2O_3$  (20%), and  $Fe_2O_3$  (10%) have been compared with pure  $Al_2O_3$  with regard to their activity in ethylating  $NH_3$ . All but the last-named decrease the reaction rate. The  $Al_2O_3-Fe_2O_3$  mixture is superior to  $Al_2O_3$  in causing less decomp. of EtOH. The results are discussed theoretically.

II. The activity of the above mixtures and of  $Al_2O_3+NiO$  (5%) in promoting the formation of  $NHPhEt$  and  $NPhEt_2$  from EtOH and  $NH_2Ph$  has been determined. All the mixtures studied are less active than  $Al_2O_3$ , but that with  $Fe_2O_3$  causes less decomp. of EtOH.  $NHPhEt$  is formed almost exclusively. F. L. U.

**Production of hydrocarbons from fatty acids by [catalytic] hydrogenation.**—See B., 1936, 10.

**Kinetics of catalytic oxidation of hydrocarbons and their derivatives.**—See B., 1936, 10.

**Activation of kaolin for catalytic processes.**—See B., 1936, 18.

[Asymmetric] catalysis with organic fibres. II. G. BREDIG, F. GERSTNER, and H. LANG (Biochem. Z., 1935, 282, 88—98; cf. A., 1932, 1062).—When PhCHO was replaced by MeCHO, cinnamaldehyde, anisaldehyde, and piperonal, part of the product was levorotatory in all cases. Bases other than  $\text{NH}_4\text{Et}_2$  (24 tested) combined with cotton fibres to produce substances which catalysed the production of mandelonitrile (I), levorotatory (I) being obtained in many cases. Catalysts from *tert.* bases produced no asymmetry; those from *sec.* produced asymmetry more often than those from primary bases. Catalyst from optically active bases other than coniine produced no asymmetry. *cis-d*-Diaminotrimethylcyclopentane (II) forms with the fibres a very active catalyst but this produces no asymmetry. (II) without fibres is less active but produces asymmetry. The decarboxylation of optically active and inactive camphorcarboxylic acid and bromocamphorcarboxylic acid by the catalysts (from optically active or inactive bases) yields no asymmetric products. Decarboxylation caused by (II) produces no asymmetry but the effect is greater with than without fixation on the fibres.

W. McC.

Influence of electrolyte on the concentration of heavy water. A. E. BRODSKI and N. P. SKRINNKOVA (Acta Physicochim. U.R.S.S., 1935, 2, 809—810; cf. this vol., 160).—The separation factors, determined by electrolysis 100 c.c. of 0.2*N*-salt solutions in 0.1%  $\text{D}_2\text{O}$  between Pt electrodes and measuring the concn. of  $\text{D}_2\text{O}$  in the residual liquid (12.5 c.c.), increase from 5.6 for KOH through  $\text{H}_2\text{SO}_4$ , KCl, NaCl, and  $\text{K}_2\text{CO}_3$  to 10.6 for  $\text{Li}_2\text{SO}_4$ .

T. G. P.

Electrolytic separation of the oxygen isotopes. G. OGDEN (Nature, 1935, 136, 912).—Using Ni electrodes and 1.25*N*-NaOH as electrolyte, the val. found for the electrolytic separation coeff.,  $\alpha$ , for the O isotopes is 0.87. Calc. vals. for  $\alpha$  lie between 0.86 and 1, depending on the width and height of the energy barrier, and allowing for the possibility of "tunnelling" of these barriers by complexes such as  $\text{O}^{16}\text{H}$  and  $\text{O}^{18}\text{H}$ . With the most favourable val. of  $\alpha$ , the  $[\text{O}^{18}]$  in pure  $\text{D}_2\text{O}$  prepared by electrolytic methods can never be > approx. 0.6%. L. S. T.

Theory of combustion of graphite. IV. V. SIHVONEN (Suomen Kem., 1935, 8, B, 47—49; cf. A., 1935, 1210).—Further experiments on the electrolytic oxidation of graphite (I) in fused  $\text{NaKCO}_3$  show  $\text{CO}$  and  $\text{CO}_2$  to be primary oxidation products in addition to electrolytically liberated  $\text{CO}_2$ . (I) with poorly developed crystal structure is more readily attacked by electrolytic oxidation than highly cryst. (I), but the lamellar structure of the latter favours formation of graphitic oxide.

J. S. A.

Electrolysis of bromides and iodides of zinc, nickel, and cobalt in mixtures of water and ethyl alcohol. C. CHARNETANT (Compt. rend., 1935, 201, 1174—1176; cf. A., 1935, 1086).—The nature of the products of electrolysis has been determined in relation to  $[\text{EtOH}]$ .

T. G. P.

Instantaneous action of certain colloids on the electrolytic deposition of copper. P. JACQUET

(Compt. rend., 1935, 201, 953—955; cf. A., 1935, 294).—Gelatin and serum-albumin influence the electro-deposition of Cu from aq.  $\text{CuSO}_4$  even during the first few secs. of the electrolysis. This is due to adsorption of the colloid on the metal surface. Other colloids which are not adsorbed (*e.g.*, gum arabic) must first be accumulated around the cathode by electrophoresis. Their action is not instantaneous.

H. J. E.

Electrolytic conduction of a solid insulator at high fields. Formation of anodic oxide film on aluminium. E. J. W. VERWEY (Physica, 1935, 11, 1059—1063; cf. A., 1935, 1307).—The formation of the  $\text{Al}_2\text{O}_3$  film is due to concn. of O ions at the Al anode.  $\text{Al}^{+++}$  ions liberated from the metal are then drawn into the O lattice. As soon as the field, which decreases with increasing thickness of the  $\text{Al}_2\text{O}_3$  layer, is insufficient for appreciable mobility of the cations, growth of the oxide coating stops.

H. J. E.

Electrolysis under the microscope. X. Crystallisation centres in cathodic deposition of gold. A. GLAZUNOV and B. HONZA (Chem. Obzor, 1934, 9, 124—126; Chem. Zentr., 1935, i, 2651).—The no. of crystallisation centres during electrolysis of  $\text{AuCl}_3$  increases with the c.d. Formation of complex Au ions leads to the deposition of colloidal Au. In acid solution or in presence of org. compounds, a higher c.d. is required for such colloidal deposition.  $\text{PdCl}_2$  behaves similarly.

J. S. A.

Action of silent electric discharge on nitric oxide. Production of active nitrogen. C. ZENGHELIS and K. EVANGELIDIS (Praktika, 1934, 9, 266—267; Chem. Zentr., 1935, i, 2770).—Reaction takes place in three stages: (i) decomp. into  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{O}_3$ , active N, which forms  $\text{NH}_3$  from  $\text{H}_2\text{O}$  present, and  $\text{NO}_x$ , (ii) oxidation of NO to  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ , (iii) reaction of NO with  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$ . Only stage (iii) is accelerated by the discharge.

J. S. A.

Influence of inert additions on the lower limit of the photochemical explosion of the  $\text{H}_2 + \text{Cl}_2$  mixture. F. A. LAVROV and T. PERELMAN (Acta Physicochim. U.R.S.S., 1935, 2, 91—102).—The influence of excess of  $\text{H}_2$  or  $\text{Cl}_2$  and additions of  $\text{N}_2$ , A,  $\text{CO}_2$ , and HCl on the lower explosion pressure  $P$  of stoichiometric  $\text{H}_2 + \text{Cl}_2$  mixtures has been studied.  $P$  is a min. at 70%  $\text{Cl}_2$  and then increases linearly with the pressure of added gas in accordance with a theoretical equation. Assuming equal deactivation probabilities  $\epsilon$  in each case, the ratio addition concn./ $[\text{N}_2]$  for a given  $P$  has been calc. and good agreement obtained with experimental ratios, except in the case of HCl, when  $\epsilon_{\text{N}_2} = 2.2\epsilon_{\text{HCl}}$ . It is supposed that HCl becomes excited and may then activate another  $\text{Cl}_2$ . The occurrence of  $P_{\text{min}}$  at 70%  $\text{Cl}_2$  is ascribed to excited  $\text{Cl}_2$  in the role of chain carrier.

R. S.

Photochemical decomposition of nitric oxide. P. J. FLORY and H. L. JOHNSTON (J. Amer. Chem. Soc., 1935, 57, 2641—2651).—Using radiation from the Hg arc or from sparks between electrodes of Al, Zn, Cd, Ni, Cu, or Sn over the range 0.02—7 mm., the final reaction products are  $\text{N}_2$  and  $\text{O}_2$ . The rate of decomp.  $\propto$  the rate of light absorption for light of the effective wave-length and, at very low pressures,

$\propto$  pressure. The rate is not influenced by dilution with  $N_2$ . Evidence of a primary process of pre-dissociation is adduced.

E. S. H.

**An error in photographic photometry.** J. LAGRULA (Compt. rend., 1935, 201, 1025—1026).

T. G. P.

[Photographic] image reversal in silver iodide and mercury iodide [emulsions]. LÜPPO-CRAMER (Z. wiss. Phot., 1935, 34, 292—304).—Similarly to AgI emulsions, HgI<sub>2</sub> emulsions (in gum arabic) give reversed images on development, if before or after the normal exposure to a 100-watt lamp they have been briefly exposed to diffuse daylight. Using either AgI or HgI<sub>2</sub> emulsions, prolonged exposure to sunlight produced lower densities than normal exposure to diffuse daylight. These and other similar data are compared with the usual types of solarisation (with AgBr emulsions), and the theory of solarisation is discussed at length; the regression theory (re-formation of Ag halide) is still supported, as it is claimed that no other hypothesis can explain the inhibition of solarisation by the presence of halogen acceptors (nitrites, sulphites).

J. L.

**Structure of the latent Röntgen [photographic] image.** W. HOFMANN (Z. wiss. Phot., 1935, 34, 267—275, 276—292).—An ordinary light image is formed mainly in the surface of a photographic layer, but an X-ray image is formed equally throughout the layer. Various experiments have been made on different aspects of the Villard effect (reduction of sensitivity to light by pre-exposure to X-rays). It is suggested that X-rays produce two kinds of latent image, one (R I) similar to an ordinary light image, and the other (R II) consisting of very small nuclei ("ultranuclei"). R II is not affected by physical or chemical development; the former produces a loose branching structure, not an image, and the latter, by dissolution of AgBr, causes assimilation of R II nuclei to R I nuclei, the R II image being therefore lost. Ordinary light converts R II into a new kind of image, L II, which is not physically developable, but after primary fixing gives nuclei more widespread and more developable than an ordinary light image, when subsequently chemically developed. The theory is applied to explain the Villard effect.

J. L.

**Effect of wave-length on the iodine-sensitised decomposition of ethylene iodide in carbon tetrachloride solution.** R. G. DICKINSON and N. P. NILES (J. Amer. Chem. Soc., 1935, 57, 2382—2386).—For  $\lambda$  4358, 5461, and 5770 with 5790 Å., the relative  $s$ . of the rate coeff. are 1 : 0.931 : 0.867. Light corresponding with continuous absorption in gaseous is slightly more effective in dissociating I in solution than is light corresponding with discontinuous absorption.

E. S. H.

**Photochemical investigations. II. Photochemical decomposition of ethylene iodide in solutions of carbon tetrachloride.** R. E. DEIGHT and E. O. WING (J. Amer. Chem. Soc., 1935, 57, 2411—2415; cf. A., 1930, 180).—The apparent quantum yield with  $\lambda$  303 and 313 m $\mu$  is 0.76, including the photo- and any subsequent thermal reactions. The

mechanism discussed involves primary dissociation into  $C_2H_4I$  and I atoms.

E. S. H.

**Photochemical reaction between sodium formate and iodine, and a relation between chemical reactivity and light absorption.** N. R. DHAR and P. N. BHARGAVA (J. Physical Chem., 1935, 39, 1231—1244).—The reaction between HCO<sub>2</sub>Na and aq. I in the absence of KI is unimol. in the dark and semimol. in the light. The velocity of the photochemical change  $\propto I^n$  ( $I$  intensity,  $n$  0.75—1.5). Einstein's law is not obeyed, the quantum yield increasing with temp. and with frequency of the incident radiation. More light is absorbed by the mixture than by the reactants separately owing, it is suggested, to weakening of the binding forces.

F. L. U.

**Photochemical reactions of SH-compounds in solution.** J. WEISS and H. FISCHGOLD (Nature, 1936, 137, 71—72).—When aq. neutral or alkaline solutions of NaSH, EtSH, thioglycollic acid, cysteine, etc. are exposed to the radiation of a strong Hg arc H<sub>2</sub> is produced with the simultaneous formation of the corresponding disulphide compound. The quantum efficiency with respect to H<sub>2</sub> formation is always much  $< 1$ , indicating that reverse reactions occur. Some decomp. of RSH into RH and S also takes place. Many SH compounds react with fluorescent dyes in the dark at a measurable rate, and by irradiating with light which is absorbed by the dye, this reduction reaction is accelerated. The possible bearing of these results on the assimilation of CO<sub>2</sub> by S bacteria is discussed.

L. S. T.

**Hydrolysis of glucosides and of certain organic compounds by ultra-violet rays.** A. GUILLAUME and G. TANRET (Compt. rend., 1935, 201, 1057—1060).—Various glucosides are hydrolysed by ultra-violet rays of  $\lambda$  1800—3100 Å., rise of temp. and acidity of the medium increasing the speed of hydrolysis. Certain esters and amides are also hydrolysed by ultra-violet rays but polypeptides and proteins are resistant.

W. O. K.

**Reduction of ferric chloride under the action of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays.** G. W. SPICER (Trans. Faraday Soc., 1935, 31, 1706—1710).—Complete reduction occurs when aq. or Et<sub>2</sub>O solutions of FeCl<sub>3</sub> are exposed to  $\alpha$ -rays, and when Et<sub>2</sub>O solutions are exposed to  $\beta$ - and  $\gamma$ -rays. Partial reduction only is observed when solid anhyd. FeCl<sub>3</sub> is exposed to  $\alpha$ -rays, but is probably complete in the thin layer penetrated by the radiation. No reduction is observed on exposing aq. FeCl<sub>3</sub> solutions to  $\beta$ - and  $\gamma$ -rays.

J. W. S.

**Ortho-para-hydrogen conversion under the action of  $\alpha$ -particles.** P. C. CAPRON (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 222—236).—The reaction has been studied at room temp. in presence of Hg, which exerts an inhibitory effect. The rate  $\propto [\text{para-H}][\text{Rn}]$ , whilst  $M/I \propto [\text{para-H}]$  and is independent of the radiation intensity. It is probable that 1—2 H are formed per ion-pair and that H disappears according to a unimol. law. The possibility of the conversion being due to H<sup>+</sup> has been considered, but the fact that no change occurs at  $-187^\circ$  suggests that H is the effective agent.

R. S.

**Chemical action caused by neutrons and  $\gamma$ -rays and the effects of these agents on colloids.** F. L. HOPWOOD and J. T. PHILLIPS (*Nature*, 1935, **136**, 1026).—The effect produced by a pure  $\gamma$ -ray source,  $\text{RaSO}_4$  in Pt or Rn in glass surrounded by Pb, on the oxidation of  $\text{K}_2\text{S}_2\text{O}_5$  or of  $\text{NaHSO}_3$  and on the decomp. of  $\text{H}_2\text{O}_2$  is increased by using a source of equal strength which also emits neutrons. With hydrosols of Ag, Au,  $\text{As}_2\text{S}_3$ ,  $\text{CdS}$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Fe}(\text{OH})_3$ , a source emitting  $\gamma$ -rays or  $\gamma$ -rays and neutrons increases the stability of the negatively charged sols and decreases that of the positively charged sols. Anomalous results are obtained when electrolytes are added to the sol before irradiation. The effect attributed to the neutrons alone is of the same order of magnitude as that due to the  $\gamma$ -rays, but the efficiency of the slow neutrons is much the greater. L. S. T.

**Sensitised decomposition of hydrogen with electrons of controlled energy.** G. GLOCKER and L. B. THOMAS (*J. Amer. Chem. Soc.*, 1935, **57**, 2352—2357).— $\text{H}_2$  mols. have been dissociated by electrons of known speed, using Hg atoms as a sensitising agent. The reactions are analogous to the photochemical decomp. of  $\text{H}_2$ , using  $\lambda$  2537 Å. and Hg. At low pressures ( $\text{H}_2$  at 0.02 mm. and Hg at 0.002 mm.) the short-lived radiative states of Hg (4.9 and 6.7 e.v.) and the well-known metastable states ( $6^3\text{P}_{0,2}$ ) are not efficient or are too short-lived to cause reaction, but electrons of 7.7 e.v. energy can dissociate  $\text{H}_2$  in presence of Hg. The mechanism is discussed. E. S. H.

**Decomposition of  $\text{SO}_2$  through electron impacts.** N. NEKRASSOV and A. SCHNEERSON (*Acta Physicochim. U.R.S.S.*, 1935, **2**, 711—732).—The crit. reaction potentials  $12.2 \pm 0.5$ ,  $15.7 \pm 0.5$ , and  $24.5$ — $26.5$  volts, corresponding with the changes  $\text{SO}_2 \rightarrow \text{SO}_2^+$ ,  $\text{SO}_2 \rightarrow \text{SO}^+ + \text{O}$  and double the potential of formation of  $\text{SO}_2^+$ , and the dependence of reaction velocity and electron yield on  $\text{SO}_2$  pressure and anode current, have been measured using a triode as a reaction chamber without freezing out the reaction products. The velocity of reaction is independent of temp. The conclusions of previous workers regarding reactions in electrical discharges are criticised as leaving out of account energetic relationships and ion recombination. T. G. P.

**Interaction of gases with solids.** H. W. MELVILLE (*Nature*, 1935, **136**, 899—900). L. S. T.

**Use of topology and invariants to describe chemical reactions.** F. M. SCHEMJAKIN (*Acta Physicochim. U.R.S.S.*, 1935, **2**, 557—558).—A preliminary note suggesting that chemical reactions may be classified according to geometric systems. O. J. W.

**Perchlorates. IV. Ammonia derivatives of alkali perchlorates.** C. SMEETS (*Natuurwetensch. Tijds.*, 1935, **17**, 213—217).—Isotherms for systems of the type  $\text{MClO}_4 \cdot \text{NH}_3$  indicate the existence of the compounds,  $\text{LiClO}_4 \cdot 2\text{NH}_3$  (I),  $\text{LiClO}_4 \cdot 3\text{NH}_3$  (II),  $\text{LiClO}_4 \cdot 5\text{NH}_3$ ,  $\text{NaClO}_4 \cdot 4\text{NH}_3$ , and  $\text{NH}_4\text{ClO}_4 \cdot 3\text{NH}_3$ . Only (I) and (II) are stable at room temp.  $\text{KClO}_4$  does not combine with  $\text{NH}_3$  even at  $-79^\circ$ . D. R. D.

**Formation and composition of lithium aluminate.** H. A. HORAN and J. B. DAMLANO (*J. Amer.*

*Chem. Soc.*, 1935, **57**, 2434—2436).—When  $\text{Al}^{+++}$  solutions, containing sufficient  $\text{Li}^+$ , are made alkaline with  $\text{NH}_3$ , a Li aluminate (at. ratio  $\text{Li} : \text{Al} = 1 : 2$ ) is pptd. almost quantitatively. After ignition to const. wt. the residue has the composition  $\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3$ . E. S. H.

**Chemical and mineralogical examination of the precipitate obtained from 50% NaOH and sodium sulphate.** D. BOBROVNIK (*Ukrain. Chem. J.*, 1935, **10**, 320—330).—The solid phases separating when  $\text{Na}_2\text{SO}_4$  is added to 50% aq. NaOH, and the solution is cooled, are triple salts of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and NaCl, in the ratios 1 : 2 : 2, 1 : 2 : 4, 1 : 2 : 5, and 1 : 3 : 13. R. T.

**Decomposition of copper sulphate pentahydrate by heat.** O. BINDER (*Compt. rend.*, 1935, **201**, 1035—1036; cf. this vol., 38).— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  heated at  $650^\circ$  yields  $\text{SO}_3 \cdot 2\text{CuO}$  (I), which gives  $\text{SO}_3 \cdot 4\text{CuO} \cdot 4\text{H}_2\text{O}$  (II) +  $2\text{CuSO}_4$  with cold  $\text{H}_2\text{O}$ , and  $\text{SO}_3 \cdot 3\text{CuO} \cdot 2\text{H}_2\text{O}$  (III) +  $\text{CuSO}_4$  with boiling  $\text{H}_2\text{O}$ . X-Ray photographs of (I), (II), and (III) are reproduced. T. G. P.

**Organic cupric tetrachlorides and tetrabromides.**—See this vol., 212.

**Reactions between aqueous solutions of silver nitrate, lead nitrate, and potassium permanganate.** F. JIRSA (*Z. anorg. Chem.*, 1935, **225**, 302—304).— $\text{AgNO}_3$  is oxidised by  $\text{KMnO}_4 + \text{KOH}$  to  $\text{Ag}_2\text{O}_2$ .  $\text{Pb}(\text{NO}_3)_2$  is oxidised by  $\text{KMnO}_4$  to  $\text{PbO}_2$ , and  $\text{Mn}_2\text{O}_3$  is formed. E. S. H.

**Hydrolysis of magnesium boride.** R. C. RAY and P. C. SINHA (*J.C.S.*, 1935, 1694—1695).—At  $>0^\circ$ , the hydrolysis of  $\text{Mg}_3\text{B}_2$  by  $\text{H}_2\text{O}$  or dil. aq.  $\text{EtOH} \cdot \text{HCl}$  is essentially  $\text{Mg}_3\text{B}_2 + 6\text{H}_2\text{O} \rightarrow \text{Mg}_3\text{B}_2(\text{OH})_6$  (I) +  $3\text{H}_2$ , but at  $<-10^\circ$  the product is  $\text{H}_3\text{B}_2(\text{MgOH})_3$ , which has reducing properties and is hydrolysed by  $\text{H}_2\text{O}$  to (I) and  $\text{H}_2$ . J. G. A. G.

**Mechanism of hydrolysis in solutions of salts of heavy metals.** (MLLE.) M. QUINTIN (*Compt. rend.*, 1935, **201**, 1176—1178).—In  $\text{CdCl}_2$  solutions  $< 0.05M$  the activity of the Cd ion  $\propto [\text{H}^+]$ . The first stage in the hydrolysis of this and similar salts (A., 1927, 729; 1928, 241) therefore involves complex formation. T. G. P.

**Chemical curiosity.** F. P. DWYER (*J. Proc. Austral. Chem. Inst.*, 1935, **2**, 318—320).—Vermiform growths are obtained by the action of Hg on  $\text{Hg}_2(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ , and  $\text{Ni}(\text{NO}_3)_2$  in 60—70%  $\text{HNO}_3$ . J. S. A.

**Boron hydrides. XX. Potassium diborane,  $\text{K}_2(\text{B}_2\text{H}_6)$ .** A. STOCK, W. SUTTERLIN, and F. KURZEN. **XXI. Potassium compounds of  $\text{B}_4\text{H}_{10}$  and  $\text{B}_5\text{H}_9$ .** A. STOCK, F. KURZEN, and H. LAUDENKLOS (*Z. anorg. Chem.*, 1935, **225**, 225—242, 243—253; cf. A., 1934, 497).—XX.  $\text{K}_2(\text{B}_2\text{H}_6)$  (I) is prepared by agitating K amalgam with excess of  $\text{B}_2\text{H}_6$  and separating from Hg by distillation. It is stable at  $300^\circ$ , but decomposes at  $400^\circ$  as follows: (I) =  $\text{KB}_2\text{H}_2 + \text{K} + 2\text{H}_2$ . (I) is insol. in the usual org. solvents, but is hydrolysed by  $\text{H}_2\text{O}$ . The mechanism of hydrolysis has been investigated. With  $\text{HBr}$  the reaction (I) +  $2\text{HBr} = 2\text{KBr} + \text{B}_2\text{H}_6 + \text{H}_2$  occurs.



XXI. (II) has been prepared from  $B_4H_{10}$  and K amalgam. Separation from Hg is complicated by the ready decomp. of (II); at  $170^\circ$   $K_2(B_4H_8)$  is formed. (II) appears to be an intermediate product in the thermal decomp. of (I). Evidence for the formation of  $K_2(B_5H_9)$  from  $B_5H_9$  and K amalgam is given. E. S. H.

X-Ray investigation of potassium diborane and its hydrolysis products, especially potassium dihydroxydiborane. E. S. VON BERGKAMPF (Z. anorg. Chem., 1935, 225, 254—257).—The mechanism of hydrolysis of  $K_2(B_2H_6)$  (cf. preceding abstract) is confirmed. E. S. H.

Boron halide additive compounds of anomalous composition. II. Action of phosphine on boron fluoride. E. WIBERG and V. HEUBAUM (Z. anorg. Chem., 1935, 225, 270—272; cf. A., 1933, 917).—PH, and BF<sub>3</sub> react at  $-145^\circ$  to form  $PH_3BF_3$ . E. S. H.

Conditions for the formation and existence of kernite,  $Na_2B_4O_7 \cdot 4H_2O$ . H. MENZEL, H. SCHULZ, and H. DECKERT (Naturwiss., 1935, 23, 832—833).—The chemical properties, artificial prep., and range of stability of kernite have been investigated. With  $H_2O$  it gives  $Na_2B_4O_7 \cdot 10H_2O$  or the metastable  $Na_2B_4O_7 \cdot 5H_2O$ . The formation of kernite starts from a dihydrate. It may be prepared artificially by heating  $Na_2B_4O_7$  with 4.5—6 mols. of  $H_2O$  at  $140^\circ$  for 20 hr. in a sealed tube. Its temp. range of existence is approx.  $58-152^\circ$ . A. J. M.

Somatoids. II. Influence of other dissolved constituents on the forms exhibited by monobasic aluminium sulphite. III. Topochemical reactions on aluminium sulphite somatoids. K. HUBER (Helv. Chim. Acta, 1935, 18, 1316—1326, 1327—1335; cf. A., 1935, 1072).—II. The influence of (a) mineral acids, and their hydrolysable heavy metal salts, (b) chromic sulphite, and (c) NaOAc,  $Na_2HPO_4$ , and  $UO_2(OAc)_2$  on the form of the somatoids of monobasic Al sulphite (I) has been investigated. From the absence of sp. effects, and the similarity of the effects to those produced by temp. and concn. changes in the absence of foreign salts, it is concluded that disturbances in the  $Al_2O_3-H_2O-SO_2$  equilibrium and in the intermediate formation of  $Al(OH)_3$  are involved.  $Cr^{+++}$  and  $UO_2^{++}$  are taken up by the (I) lattice without altering its structure or dimensions.

III. The effects of heat, hydrolysis by  $H_2O$  and alkali, and oxidation on somatoids of (I) show the presence of a lamellar structure, and a differentiation between the outer skin and the centre of the somatoids. By ignition at  $400-500^\circ$ , (I) is converted directly into  $\alpha-Al_2O_3$ . Evidence is advanced of inhomogeneities in the internal structure. J. S. A.

Preparation of aluminium carbide,  $Al_4C_3$ . O. RUFF (Chem.-Ztg., 1936, 60, 28).—Al and C are heated in  $H_2$  at  $2000^\circ$  for 30 min. E. S. H.

Compounds of aluminium bromide with lithium, copper, and silver bromides. V. A. PLOTNIKOV and E. J. GORENBEIN (J. Gen. Chem. Russ., 1935, 5, 1108—1111).—The compounds  $LiBr \cdot AlBr_3$ , m.p.  $192^\circ$ ,  $CuBr \cdot AlBr_3$ , m.p.  $241^\circ$ , and  $2AgBr \cdot 3AlBr_3$ ,

m.p.  $180-185^\circ$  (decomp.), are obtained by crystallising the mixed salts from EtBr. R. T.

Volatilisation of silicic acid and silicon as silicon sulphide. P. DOLCH (Chem. Fabr., 1935, 8, 512—514).—Published evidence of reactions involving the above is reviewed. E. S. H.

Reaction of titanium tetrachloride with phenol. G. P. LUTSCHINSKI [with E. S. ALTMANN] (Z. anorg. Chem., 1935, 225, 321—326).— $TiCl_4$  reacts vigorously with PhOH forming a dark red cryst. compound,  $TiCl_3 \cdot OPh$ . It fumes in moist air and reacts with  $H_2O$  giving PhOH and  $Ti(OH)_4 \cdot H_2O$ . Mixtures of  $TiCl_4$  and PhOH in  $CHCl_3$  solution show a max. light absorption for the equimol. mixture. The selective light absorption obeys the Lambert-Beer law and the reaction might be used for the colorimetric determination of either compound. M. S. B.

Reactions between solids. A. ALBERTO (Ann. Acad. brasil. Sci., 1934, 6, 49—52; Chem. Zentr., 1935, i, 2486).— $NH_4ClO_4$  is quoted as a very stable  $NH_4$  salt. J. S. A.

Slow action of fuming nitric acid vapour on metals. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], 2, 2260—2261).—At  $15^\circ$  the vapour of fuming  $HNO_3$  reacts only with Na, Ag, and Hg. F. L. U.

Action of heat on the ortho-, pyro-, and meta-arsenates of calcium and strontium. H. GUÉRIN (Compt. rend., 1935, 201, 1133—1135).—Neutral arsenates of Ca and Sr may be heated in vac. to  $1200^\circ$  without change. Products containing excess of  $As_2O_5$  lose  $As_2O_3$  and  $O_2$  at  $>1000^\circ$ , forming neutral orthoarsenate. The pyroarsenates form orthoarsenates at  $>800^\circ$ ,  $As_2O_3$  and  $O_2$  being liberated. The two meta-arsenates yield the pyroarsenates at  $500-800^\circ$ , and the orthoarsenates at higher temp. H. J. E.

Quantitative separation of protoactinium from pitchblende by means of titanium oxide. CHENG DA-CHANG (J. Chinese Chem. Soc., 1935, 3, 381—387).—Pa can be quantitatively pptd. with  $TiO_2$  from a solution of pitchblende in HCl to which  $TiCl_4$  is added. The  $TiO_2$  deposited on hydrolysis contains all the Pa present in the mineral. The  $\alpha$ -ray activity of the ppt. gives the quantity of Pa present. Pa salts are shown to be readily hydrolysed in acid solution, easily soluble in dil. HF, and completely pptd. by aq.  $NH_3$  in absence of HF. A. J. M.

Ductile chromium. W. KROLL (Z. anorg. Chem., 1935, 226, 23—32).—Cr powder, obtained by the action of twice distilled Ca on  $Cr_2O_3$  in molten  $CaCl_2 + BaCl_2$  and in an atm. of A, is degassed in a vac. at  $1300^\circ$  and sintered at  $1600-1700^\circ$ . The resulting mass can be rolled at  $1250^\circ$ . Rolled Cr is brittle at room temp., but deformable at  $180^\circ$ . F. L. U.

Action of hydrogen sulphide on chromates. Potassium dichromate. H. B. DUNNIELLE, G. S. KOTWANI, and M. A. HAMID (J. Physical Chem., 1935, 39, 1217—1229; cf. A., 1932, 133).—The brown solid formed during the action of  $H_2S$  on 5% aq.  $K_2Cr_2O_7$  consists of  $CrO_2$ ,  $Cr(OH)_3$ ,  $Cr_2(S_4O_6)_3$ , a Cr thiosulphate, and S, whilst the filtrate contains unchanged  $K_2Cr_2O_7$ ,  $K_2S_2O_3$ , and  $K_2S_4O_6$ . The final

products are a ppt. of  $\text{Cr}(\text{OH})_3$ , S, and a complex Cr thiosulphate, and a solution containing  $\text{K}_2\text{S}_2\text{O}_3$  and  $\text{K}_2\text{S}_x$ . The course of the reactions is discussed.

F. L. U.

**Preparation of potassium molybdo- and molybdi-cyanides.** H. H. WILLARD and R. C. THIELKE (J. Amer. Chem. Soc., 1935, 57, 2609—2611).— $\text{K}_3\text{Mo}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  (I) is prepared by pptg.  $\text{Mo}^{\text{IV}}$  pyridine thiocyanate in aq.  $\text{NH}_3$  and treating the ppt. with KCN. A quant. yield of  $\text{K}_3\text{Mo}(\text{CN})_6$  is obtained by oxidising (I) with  $\text{KMnO}_4$  in acid solution.

E. S. H.

**Lower oxides of tungsten.** F. EBERT and H. FLASCH (Z. anorg. Chem., 1935, 226, 65—81).— $\text{WO}_3$  treated with active H at room temp. for 13—30 hr., is completely converted into the compound  $\text{W}_4\text{O}_{10}(\text{OH})_2$ . By isobaric dehydration at 0.001 mm., the latter substance yields the compound  $\text{W}_{12}\text{O}_{32}(\text{OH})_2$  (I), which is stable between 150° and 500°, above which it passes into  $\text{W}_4\text{O}_{11}$  (A., 1934, 378). The identity of the compounds has been established by chemical and X-ray analysis. The following lattice consts. are given:  $\text{W}_4\text{O}_{10}(\text{OH})_2$ , tetragonal,  $a$  3.79,  $c$  3.74 Å.;  $\text{W}_{12}\text{O}_{32}(\text{OH})_2$ , tetragonal,  $a$  3.85,  $c$  3.65 Å.;  $\text{W}_4\text{O}_{11}$ , monoclinic,  $a$  3.85,  $b$  3.79,  $c$  3.85 Å.,  $\beta$  79.45°. (I) is also formed in the reduction of  $\text{WO}_3$  by mol. H., at 500—550°, and it is suggested that such addition of H is a general preliminary stage in the reduction of higher oxides by  $\text{H}_2$ .

F. L. U.

**Composition and properties of potassium phosphotungstate.** E. A. NIKITINA (J. Gen. Chem. Russ., 1935, 5, 1133—1138).—The salts pptd. by adding KOH or NaOH to aq. phosphotungstic acid have the composition  $\text{K}_3\text{H}_4[\text{P}(\text{W}_2\text{O}_7)_6]$  (I) or  $\text{Na}_3\text{H}_4[\text{P}(\text{W}_2\text{O}_7)_6]$  (II); their solubilities in  $\text{H}_2\text{O}$  and in aq. acids have been determined at 0—90°. That of (II) > that of (I); for both salts it falls with increasing acidity, but more so for (I), which is insol. in 18% HCl at 0—43°. At the same time, elimination of alkali metal from the solid phases takes place, to yield successively the  $\text{M}_6$  and  $\text{M}_1$  salt. The results obtained for the determination of K in presence of Na are high, owing to pptn. of some (II) from solutions of the acidity necessary to ensure complete pptn. of (I).

R. T.

**Reduction of 1-phospho-18-tungstic acid by ascorbic acid.**—See this vol., 255.

**Fluorine and its compounds.** A. DAMIENS (Bull. Soc. chim., 1936, [v], 3, 1—22).—A lecture.

**Bromine.** I. Preparation of bromine dipyridine perchlorate and bromine dipyridine nitrate. II. Preparation, properties, and constitution of an aquo-pyridine compound of bromine monoxide. H. CARLSOHN (Ber., 1935, 68, [B], 2209—2211, 2212—2214).—I (cf. Uschakov *et al.*, A., 1935, 857).—Addition of Br in  $\text{CHCl}_3$  to  $\text{AgNO}_3$  in  $\text{CHCl}_3\text{--C}_5\text{H}_5\text{N}$  at 15—20° followed by removal of AgBr and addition of the filtrate to  $\text{Et}_2\text{O}$  containing a little  $\text{C}_5\text{H}_5\text{N}$  gives the hygroscopic Br dipyridine nitrate (I) in 75—80% yield. Br dipyridine perchlorate is obtained by adding Br in  $\text{CHCl}_3$  to Ag dipyridine perchlorate (from  $\text{AgNO}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{NaClO}_4$  in  $\text{H}_2\text{O}$ ) in  $\text{CHCl}_3\text{--C}_5\text{H}_5\text{N}$ .

II. Treatment of (I) with 0.4N-NaOH gives a pale yellow ppt. which when rapidly dried on porous clay and then for 1 hr. in a vac. over KOH has the composition  $\text{Br}_2\text{O} \cdot \text{H}_2\text{O} \cdot \text{C}_5\text{H}_5\text{N}$ . The constitution  $[\text{BrC}_5\text{H}_5\text{N}(\text{OH}_2)]\text{OBr}$  is suggested.

H. W.

**Reaction of atomic iodine with quartz glass.** G. BRAUER (Z. physikal. Chem., 1935, 174, 435—440).—Thermally dissociated  $\text{I}_2$  vapour forms from quartz glass Si, but if the O formed is not removed a film of  $\text{SiO}_2$  results. Optically dissociated  $\text{I}_2$  behaves similarly.

R. C.

**Iron, even when impure, is not oxidised in salt solutions.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2171—2174; cf. A., 1935, 834).—Corrosion of impure Fe in NaCl solutions does not occur in the absence of foreign material in the surface.

F. L. U.

**Iron, when impure but rigorously freed from surface contamination, does not effervesce in dilute acids.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2174—2178; cf. preceding abstract).—Impure Fe effervesces in 1%  $\text{H}_2\text{SO}_4$  only when the surface of the Fe is contaminated with certain "extrinsic" materials. A reaction, however, still takes place. An antagonism between the effervescent and quiet reactions is observed.

F. L. U.

**Iron, even when impure, is not oxidised at the ordinary temperature in pure distilled and aerated water.** P. RONCERAY (Bull. Soc. chim., 1935, [v], 2, 2179—2182; cf. preceding abstract).—Impure Fe, if suitably cleaned, is not attacked by  $\text{H}_2\text{O}$  containing dissolved  $\text{O}_2$ . Localised rusting is due to extrinsic impurities, and the rust spreads from the primary corrosion centres thus formed.

F. L. U.

[Iron, even when impure, is not oxidised in air saturated with moisture.] L. GUITTON (Bull. Soc. chim., 1935, [v], 2, 2258—2260).—A criticism of experiments and conclusions published by Ronceray (A., 1935, 834).

F. L. U.

**Action of carbonic acid on ferrous sulphide.** Y. KAUKO and P. HAULIO (Suomen Kem., 1935, 8, B, 49—50).—From the relevant equilibrium consts., aq.  $\text{CO}_2$  should be able to convert FeS into sol.  $\text{Fe}(\text{HCO}_3)_2$ , from which  $\text{FeCO}_3$  is pptd.

J. S. A.

**Action of oxidising agents on sodium hypoferrite.** X. THIESSE (Compt. rend., 1935, 201, 1135—1137; cf. A., 1935, 314).—In 35% aq. NaOH solution,  $\text{Cl}_2$  causes pptn. of  $\text{Fe}(\text{OH})_3$ . In 40% NaOH a mixture of olive-green crystals and of hydrated  $\text{Fe}_2\text{O}_4$  is formed. The product from  $\text{Cl}_2$  and a 50% NaOH solution at 130—140°, when washed and dried, is  $\text{Fe}(\text{ONa})_3 \cdot 10\text{H}_2\text{O}$ ; at 170—180° with 60—70% NaOH it is  $\text{Na}_2\text{Fe}_2\text{O}_4$ .  $\text{Pb}(\text{OH})_2$  in presence of 50% NaOH yields  $\text{Fe}(\text{ONa})_3$ .

H. J. E.

**Dehydration of hydrated cobaltic oxide.** H. A. PAGEL, W. K. NOYCE, and M. T. KELLEY (J. Amer. Chem. Soc., 1935, 57, 2552—2553).—Dehydration occurs slowly at < 90°, but rapidly at 100—180°. The rate varies greatly with differences in the physical state of the oxide.

E. S. H.

**Topochemical reactions of compact-disperse materials.** IV. Mixed precipitation of nickel-zinc and cobalt-zinc hydroxides. W. FEITKNECHT and W. LOTMAR (Helv. Chim. Acta, 1935, 18, 1369—1388).—Pptn. of aq.  $\text{Co}(\text{NO}_3)_2$ – $\text{Zn}(\text{NO}_3)_2$  or  $\text{Ni}(\text{NO}_3)_2$ – $\text{Zn}(\text{NO}_3)_2$  mixtures with  $\text{NaOH}$  yields completely unordered, partly amorphous, ppts.  $(\text{Ni,Zn})(\text{OH})_2$  low in  $\text{Zn}$  passes on ageing at room temp. into cryst.  $\text{Ni}(\text{OH})_2$ , type C6, in which  $\approx 15\%$  of  $\text{Ni}$  atoms may be replaced by  $\text{Zn}$ , with some expansion of the lattice. From 15 to 65% of  $\text{Zn}(\text{OH})_2$ , a new hexagonal double hydroxide is formed, having  $a$  3.07,  $c$  8.2 Å., and consisting of sheets of  $\text{Ni}(\text{OH})_2$  in which  $\text{Ni}$  is partly replaced by  $\text{Zn}$ , intercalated with unordered  $\text{Zn}(\text{OH})_2$ . By heating freshly pptd.  $(\text{Ni,Zn})(\text{OH})_2$ , mixed crystals with up to 25% of  $\text{Zn}(\text{OH})_2$  may be obtained, which pass on prolonged heating into a new double hydroxide of type C6. Similar results are obtained by copptn. of  $\text{Zn}$  and  $\text{Co}$ ; an unstable double hydroxide of very imperfect structure is formed in presence of 40–60% of  $\text{Zn}(\text{OH})_2$ . J. S. A.

**Structure of complex compounds.** H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 312–318).—The anions  $\text{SO}_4^{4-}$ ,  $\text{C}_2\text{O}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{F}^-$ , etc. are capable of forming the complex anions containing a central complex cation, e.g.,  $[\{\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}\}(\text{SO}_4)_4]^{4-}$ , the existence of which is shown by dialysis (A., 1935, 1091, 1471; this vol., 40). Other anions, viz.,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CrO}_3^{3-}$ ,  $\text{MoO}_4^{2-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ , etc., do not form such complex anion. A necessary condition of formation appears to be the possession, by either the partaking cation or anions, of a large electrostatic potential, i.e., residual valencies, recognisable by the formation in aq. solution of aquo-complexes of the type  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_{18}]^{3+}$ ,  $[\text{C}_2\text{O}_4(\text{H}_2\text{O})_4]^{2-}$ ,  $[\text{HPO}_4(\text{H}_2\text{O})_6]^{2-}$ , etc., as demonstrated by dialytic methods. M. S. B.

**New group of complex compounds: complex compounds of which the central ion is a complex cation.** IV. Double-shelled arsenato-complex compounds with complex cobalt cations as central ions. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1935, 225, 365–368; cf. A., 1935, 1091, 1471; this vol., 40).—A no. of complex Co amines, slightly sol. in  $\text{H}_2\text{O}$ , are sol. in aq. arsenate, or, if decomposed by  $\text{H}_2\text{O}$ , are stable in aq. arsenate. Dialysis indicates that a complex anion is formed and consists of a central complex Co cation surrounded by a shell of arsenate anions; e.g.,  $[\{\text{Co}(\text{NH}_3)_6\}(\text{HAsO}_4)_4]^{4-}$  and  $[\{\text{Co}(\text{NH}_3)_5(\text{NO}_3)\}(\text{HAsO}_4)_4]^{4-}$  gives  $[\{\text{Co}(\text{NH}_3)_5(\text{NO}_3)\}(\text{HAsO}_4)_4]^{4-}$ . M. S. B.

**Nucleus formation on crystals of nickel sulphate heptahydrate.** W. E. GARNER and W. R. SOUTHOON (J.C.S., 1935, 1705–1709).—The nuclei formed by dehydrating  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  crystals in vac. consist of half-ellipses with one direction of growth on the crystal surface and the other into the interior at an angle of  $45^\circ$  to the surface. Before nuclei become visible, there is an induction period,  $t_i$ , which decreases with rise of temp. ( $1$ – $22^\circ$ ) and varies, within limits, from crystal to crystal, probably owing to variations in surface structure and the nature of the imperfections leading to nucleation. The rate of

growth of nuclei of diameter  $> 0.02$  mm. is linear, but is much smaller during  $t_i$ . After  $t_i$ , the no. of nuclei,  $N$ , increases with time,  $t$ , according to  $N = (t - t_i)^x$ , where  $x$  is 2, approx. The activation energy calc. from the temp. coeffs. of  $t_i$  and the linear rate of growth is 19.0 kg.-cal., approx. The interpretation of the results is discussed. J. G. A. G.

**Complex dipyridyl salts of nickel and copper.** F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 972–977).—Addition of 3 equivs. of dipyridyl (I) to  $\text{Ni}(\text{NO}_3)_2$  solution, followed by slow evaporation, yields red crystals of the compound  $[\text{Ni}(\text{dipy})_3](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  (II). With 2 equivs. of (I) some (II) is first obtained and then the violet compound  $[\text{Ni}(\text{dipy})_2](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (III). When only 1 equiv. of (I) is used, some (II) is deposited and then the compound  $[\text{Ni}(\text{dipy})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , in an impure state.  $\text{NiCl}_2$  similarly yields the compounds  $[\text{Ni}(\text{dipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  (IV) and  $[\text{Ni}(\text{dipy})(\text{H}_2\text{O})_2]\text{Cl}_2$ . The crystal structures of (II), (III), (IV), and  $[\text{Cu}(\text{dipy})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  are detailed. J. W. S.

**Affinity.** LXVI. Rhodium sulphides. R. JUZA, O. HULSMANN, K. MEISEL, and W. BILTZ (Z. anorg. Chem., 1935, 225, 369–385).—By direct combination of  $\text{Rh}$  with  $\text{S}$ , by v.p. measurements, and by X-ray analysis, the existence of  $\text{Rh}_2\text{S}_3$ ,  $d_4^{25}$  6.40, and  $\text{Rh}_2\text{S}_5$ ,  $d_4^{25}$  5.00, 4.92, has been confirmed, but not that of  $\text{RhS}$  and  $\text{RhS}_2$  as given by earlier investigators. The compounds  $\text{Rh}_3\text{S}_8$ ,  $d_4^{25}$  7.51, and  $\text{Rh}_3\text{S}_4$ ,  $d_4^{25}$  6.33, have also been obtained.  $\text{Rh}_2\text{S}_5$  has a pseudo-pyritic structure. M. S. B.

**Alkali bromo-salts and bromo-pyridine derivatives of rhodium.** P. POULENC (Ann. Chim., 1935, [xi], 4, 567–657).—The preparation of the following compounds is described:  $\text{RhBr}_3$ ;  $[\text{RhBr}_6]\text{Na}_3 \cdot 12\text{H}_2\text{O}$ , deep red crystals;  $[\text{RhBr}_5]\text{Li}_2 \cdot 6\text{H}_2\text{O}$ , a deep red hygroscopic powder;  $[\text{Rh}_2\text{Br}_9](\text{NH}_4)_3$ , green hexagonal micro-crystals;  $[\text{Rh}_2\text{Br}_9]\text{K}_3$ , green hexagonal micro-crystals;  $[\text{Rh}_2\text{Br}_{10}]\text{K}_4 \cdot 6\text{H}_2\text{O}$ , deep red octahedra, decomp.  $120^\circ$ ;  $[\text{Rh}_2\text{Br}_{11}]\text{K}_5 \cdot 6\text{H}_2\text{O}$ , deep red plates, unstable;  $[\text{Rh}_2\text{Br}_9]\text{Rb}_3$ , deep green micro-crystals, insol.;  $[\text{Rh}_2\text{Br}_{10}]\text{Rb}_4 \cdot 6\text{H}_2\text{O}$ ;  $[\text{Rh}_2\text{Br}_{11}]\text{Rb}_5 \cdot 6\text{H}_2\text{O}$ ;  $[\text{Rh}_2\text{Br}_9]\text{Cs}_3$ , deep green hexagonal micro-crystals, insol.;  $[\text{Rh}_2\text{Br}_{11}]\text{Cs}_5 \cdot 6\text{H}_2\text{O}$ ;  $[\text{RhCl}_{4.5}\text{Br}_{1.5}]\text{K}_3 \cdot \text{H}_2\text{O}$ , deep violet crystals; and  $[\text{Rh}_2\text{Cl}_{1.5}\text{Br}_{9.5}]\text{K}_5 \cdot 6\text{H}_2\text{O}$ . The structures of the compounds and the influence of the halogen and the metallic ion, respectively, on the type produced are discussed. Compounds described by previous authors (A., 1908, ii, 200; 1911, ii, 45) could not be obtained. The following pyridine (Pyr) compounds have been prepared:  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3 \cdot \text{H}_3 \cdot 3\text{H}_2\text{O}$ , dark prisms;  $[\text{Rh}_2\text{Br}_9]\text{Cs}_3$ ,  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3 \cdot \text{H}_3$ ;  $[\text{Rh}_2\text{Br}_{10}]\text{Pyr}_4 \cdot \text{H}_4 \cdot 9\text{H}_2\text{O}$ , insol. octahedra;  $[\text{RhPyBr}]\text{Pyr} \cdot \text{H}$ , deep red prisms;  $[\text{RhPyBr}_5]\text{CsPyrH}$ , red needles;  $[\text{RhPyBr}_5][\text{RhCl}(\text{NH}_3)_5][\text{RhBr}_6]\text{Pyr}_3 \cdot \text{H}_3$ , green powder decomp. in solution yielding  $[\text{Rh}_2\text{Br}_9]\text{Pyr}_3 \cdot \text{H}_3$ , and giving  $[\text{Rh}(\text{H}_2\text{O})\text{Br}_5]\text{Cs}_2$ , green prisms, with  $\text{CsOH}$  and wine-red  $[\text{Rh}(\text{H}_2\text{O})\text{Br}_5][\text{RhCl}(\text{NH}_3)_5]$  with  $[\text{RhCl}(\text{NH}_3)_5]\text{Cl}_2$ . Treatment of  $\text{RhBr}_3$  with  $\text{C}_5\text{H}_5\text{N}$  led to the following compounds and derivatives:  $[\text{RhPyr}_2\text{Br}_4]\text{PyrH}$ , red crystals, giving orange crystals of  $[\text{RhBr}_3\text{Pyr}_3]$  in  $\text{EtOH}$ ,  $[\text{RhPyr}_2\text{Br}_4]\text{K} \cdot \text{H}_2\text{O}$ , brick-

red crystals,  $[RhPyr_2Br_4]NH_4.H_2O$ , brick-red needles, and  $[RhPyr_2Br_4]Cs.H_2O$ , brick-red needles, all of which give buff-coloured needles of  $[RhBr_3(H_2O)Pyr_2].2H_2O$  in  $H_2O$ , and  $[RhBr_3Pyr_3]$  orange crystals, insol. The thermal and photodecomp. of aq. and alcoholic  $[RhBr_3Pyr_4]Br$  has been studied. Three forms of  $[RhBr_3Pyr_3]$  are produced, viz., orange prisms, buff crystals, and octahedra, characterised by different solubilities and X-ray diagrams. Addition of  $H_2O$  to their  $C_5H_5N$  solutions yields identical prisms. Similar forms of  $[RhCl_3Pyr_3]$  have been obtained and it is supposed that the octahedra and the buff crystals are the two possible isomerides whilst the prisms constitute a third cryst. form.  $[RhBr(C_5O_4)Pyr_3]$  forms orange prisms, insol., reddens on heating and decomposed by light. Addition of  $C_5H_5N$  to excess of  $RhBr_3$  yields orange-yellow prisms of  $[RhBr_2Pyr_4]Br.6H_2O$ , which gives the double salt  $[RhPyr_2Br_4]_2$ , and which is converted in presence of Br into isomeric orange prisms having a different solubility and a different X-ray diagram. Treatment of  $[RhBr_2Pyr_4]Br$  with  $AgNO_3$  yields  $[RhBr_2Pyr_4]NO_3.HNO_3$ , yellow prisms, which forms yellow crystals of  $[RhBr_2Pyr_4]NO_3$  in  $H_2O$  and  $[RhBr_2Pyr_4Ag](NO_3)_2$  (1), yellow crystals, giving insol. yellow needles of  $[RhBr_2Pyr_4Ag]Br_2$  with  $HBr$ . (1) is unstable, yielding chiefly  $[Rh(NO_3)BrPyr_4]NO_3$ , orange crystals, and on prolonged treatment with  $AgNO_3$   $[Rh(NO_3)_3Pyr_3]$ , lozenge-shaped orange crystals, very sol. in  $H_2O$ . R. S.

**Spectral analytical investigations of W. Kraemer.** (A) W. GERLACH. (B) W. KRAEMER (Z. anal. Chem., 1935, 103, 356; cf. A., 1934, 981).—(A) Polemical. Kraemer's identifications of spectral lines are largely erroneous.

(B) The cogency of Gerlach's criticism is admitted. J. S. A.

**Determination of the [metal] content of a mineral by measuring its density.** E. BORGHESEAN (Reso. assoc. min. sarda, 1935, 40, No. 2, 14—17).—If  $S_0$  is the  $d$  of the pure mineral ( $\rightarrow T_0\%$  of metal), and if  $S_x$  is the  $d$  of a mixture containing  $x$  vol.-% of pure mineral and  $(100-x)\%$  of rock of  $d-s$ , the average content of metal in the mixture is  $T_x = T_0(S_x - s)/S_0(S_0 - s)$ . CH. ABS. (e)

**Areometric analysis. Technique in determining small amounts of heavy precipitates.** V. R. DAMERELL and M. AXELROD (J. Amer. Chem. Soc., 1935, 57, 2724—2725).—Compact, circular piles of ppt. of reproducible dimensions are obtained in the centre of the flask bottom. The areas of these spots are measured and compared with areas produced by known amounts of ppt. E. S. H.

**Reaction rates and indicator acidities.** L. P. HAMMETT (Chem. Rev., 1935, 16, 67—79).—An argument for the expression of acidity in terms of measurement with a basic indicator. CH. ABS. (e)

**Colorimetric determination of hydrogen-ion concentration in aqueous solution.** M. KILPATRICK (Chem. Rev., 1935, 16, 57—66).—A summary and discussion. CH. ABS. (e)

**Simplification of optical bathmometry by application of "spectral mixed-colour colori-**

**metry" and other improvements.** A. THIEL and H. LOGEMANN (Angew. Chem., 1935, 48, 799—802).—A colorimetric method for  $p_H$  determination is described. E. S. H.

**Photometric determination of hydrogen-ion concentration.** A. G. DE ALMEIDA (Diss., Lisbon, 1935).—By plotting dominant hue, determined colorimetrically and expressed as a  $\lambda$ , against  $p_H$ , for a series of indicators, curves are obtained from which the  $p_H$  of an unknown solution can be determined more accurately than by electrometric methods. D. R. D.

**Determination of  $p_H$  by means of the glass electrode.** D. WOLFERS (Bull. Soc. Chim. biol., 1935, 17, 1559—1572).—The glass electrode may be used to determine the  $p_H$  of solutions of strong acids, e.g.,  $HNO_3$  or  $HCl$  from  $2N$  to  $0.0001N$ . Vals. for the  $p_H$  of urine are  $<$  those obtained using the quinhydrone electrode. A. L.

**Titration of a dibasic acid in stages.** S. KILPI (Z. physikal. Chem., 1935, 174, 441—444).—In the potentiometric titration of a weak or moderately strong acid the jump in potential is a max. or a min. at the first stoichiometrical equiv. point according as  $K_1/K_2$  is  $>$  or  $<$  13.93. If  $K_1/K_2$  is large the  $[H^+]$  at the point of max. potential jump is equal to that at the first equiv. point, independently of the strength of the acid. R. C.

**Application of organic redox systems to analysis. I, II.** L. KULBERG (J. Gen. Chem. Russ., 1935, 5, 1085—1090, 1240—1245).—The application of redox indicators to the detection and determination of inorg. oxidising and reducing substances is discussed, and formulæ determining their applicability are given. R. T.

**Step-photometric determination of free chlorine in chlorinated water.**—See B., 1936, 46.

**Determination of chlorate and perchlorate in presence of large amounts of nitrate.** E. S. TOMULA (Z. anal. Chem., 1935, 103, 427—430).— $ClO_3'$  is reduced by warming the material with 40% aq.  $CH_3O$  in presence of  $FeCl_3$  as catalyst. Na salts are pptd. with an excess of  $HCl$ , and the  $HCl$  solution is evaporated to dryness.  $Cl'$  is removed by treating the residue with the calc. quantity of  $Ag_2SO_4$ , and  $ClO_4'$  is reduced with a Zn-Cd couple in presence of  $Ti^{IV}$ .  $Ti^{III}$  is oxidised with  $KMnO_4$ , and  $Cl'$  in the resulting solution is finally titrated with  $AgNO_3$ .  $ClO_3'$  in a separate portion is reduced with Zn and  $H_2SO_4$ . J. S. A.

**Qualitative reaction for bromates.** I. M. KORENMAN (Z. anal. Chem., 1935, 103, 269—271).— $BrO_3'$  but not  $IO_3'$ ,  $ClO_3'$ ,  $NO_3'$ , or  $S_2O_8^{2-}$  in  $4N-HCl$  solution decolorises Me-orange rapidly. The reaction is very much faster than with  $Cr_2O_7^{2-}$ ,  $Fe(CN)_6^{3-}$ , or  $NO_2'$ .  $BrO_3'$  may be so detected in presence of a large excess of these ions. The reaction of  $ClO_3'$  with Me-orange is catalysed by  $BrO_3'$ :  $10^{-6}$  g. of  $BrO_3'$  per c.c. may be so detected. J. S. A.

**Detection of small amounts of bromide in sodium chloride.** R. C. LÓPEZ (Farm. moderna, 1935, 46, 55—57).—One drop of fuchsin solution



(0.2%) (I) in 10 c.c. of  $\text{H}_2\text{O}$  is decolorised by aq.  $\text{Cl}_2$ , added drop by drop. To 10 c.c. of the test solution are added 1 drop of (I) and twice the no. of drops of aq.  $\text{Cl}_2$  solution required above. Presence of  $\text{Br}^-$  is shown by a pink colour, which becomes purple, perhaps with pptn., if sufficient  $\text{Br}^-$  is present. 0.0001 g. of  $\text{KBr}$  in 10 c.c. of 20% aq.  $\text{NaCl}$  may be detected. The reaction is prevented by  $\text{I}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ , and  $\text{Fe}(\text{CN})_6^{4-}$ . Alkaline-reacting salts must be neutralised prior to the test.

CH. ABS. (p)

**Action of perchloric acid on iodine and iodine derivatives.** Determination of iodine in organic substances. E. KAHANE and T. TOMESCO (Compt. rend., 1935, 201, 1195—1198).— $\text{HClO}_4$  oxidises I compounds at 200—210° quantitatively to  $\text{HIO}_3$ . I may be determined in 2—10 mg. of substance by oxidation with  $\text{HNO}_3$ — $\text{H}_2\text{SO}_4$ — $\text{HClO}_4$ , followed by addition of  $\text{As}_2\text{O}_3$ , the whole of the I liberated in the processes being distilled into aq.  $\text{Br}$ , the excess of  $\text{Br}$  removed by boiling after acidification with  $\text{AcOH}$ , and the resulting  $\text{HIO}_3$  determined with  $\text{Na}_2\text{S}_2\text{O}_3$  after addition of  $\text{KI}$ .

T. G. P.

**Determination of fluorine in water by Sanchis' method.** E. H. DUCLOUX (Anal. Assoc. Quím. Argentina, 1935, 23, 63—66).—Modifications of the  $\text{Zr}(\text{NO}_3)_4$ —alizarin method (A., 1934, 500) are described.

F. R. G.

**Detection of small amounts of hydrogen peroxide.** J. PLANK (Magyar chem. Fol., 1934, 40, 105; Chem. Zentr., 1935, i, 2412).—Fresh  $\text{Ce}_2(\text{SO}_4)_3 + \text{K}_2\text{CO}_3$  detects 1 part of  $\text{H}_2\text{O}_2$  in 160,000 parts of solution.

J. S. A.

**Colour reaction between nitroprusside and sulphites (Bodeker's reaction).** G. SCAGLIARINI (Atti R. Accad. Lincei, 1935, [vi], 22, 155—159).—The formation of the complex ion  $[\text{Fe}(\text{CN})_5\text{NOSO}_3]^{4-}$  in the above reaction has been demonstrated by measurements of the oxidation-reduction potential of the process  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-} + \text{SO}_3 + 2e = [\text{Fe}(\text{CN})_5\text{NOSO}_3]^{4-}$ . The normal val. for 0.1M solutions at 21° is 0.468 volt.

O. J. W.

**Potentiometric titration of sulphite and sulphoxylate, etc.** E. MÜLLER (Z. anal. Chem., 1935, 103, 340—341).—Polemical against Lobering (A., 1935, 1092). Reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{II}$  by  $\text{SO}_3^{2-}$  or  $\text{HSO}_2^-$ , and consequently the analytical method based thereon, is impossible.

J. S. A.

**Potentiometric titration of sulphite and sulphoxylate alone and in presence of hyposulphite.** A. MUTSCHIN (Z. anal. Chem., 1935, 103, 342—348).—Polemical against Lobering (A., 1935, 1092; cf. also preceding abstract). The reaction between  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{SO}_3^{2-}$  or  $\text{HSO}_2^-$  is neither quant. nor stoichiometric, and cannot be used analytically.

J. S. A.

**Washing strontium sulphate precipitate with its saturated solution.** A. M. VASILIEV and O. S. TSCHEVIR-KORSUNSKA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 73—77).—The amount of  $\text{SO}_4^{2-}$  pptd. as  $\text{SrSO}_4$  by addition of excess of  $\text{SrCl}_2$  to approx. 0.05N- $\text{H}_2\text{SO}_4$  is equal to that pptd. by  $\text{BaCl}_2$ , if the excess of  $\text{SrCl}_2$  renders the solution

N in respect of Sr. The ppt. must be washed with saturated aq.  $\text{SrSO}_4$ .

CH. ABS. (p)

**Accuracy of the titration of thiocyanate with mercuric mercury.** I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1935, 57, 2377—2379).— $\text{KCNS}$  is a satisfactory standard when the accuracy required is  $\pm 0.05\%$ . The sources of errors are traced to side reactions; the formation of  $\text{NH}_4^+$  was detected.

E. S. H.

**Determination of traces of gases in air with Cauver's absorption tubes.** E. QUITMANN (Z. anal. Chem., 1935, 103, 258—261; cf. this vol., 47).—The quant. absorption of traces of  $\text{NH}_3$ ,  $\text{I}$ ,  $\text{HCl}$ , and  $\text{O}_3$  in air is described.

J. S. A.

**Determination of total oxidising power, nitrite, ozone, and total chlorine content of ordinary and foetid air. I. [Total oxidising power.]** H. CAUER (Z. anal. Chem., 1935, 103, 321—334).—For air low in total oxidants, 100—200 litres of air are sucked through a wash-tube containing 3 c.c. of aq.  $\text{KI}$ , at  $p_H < 2.8$ , containing  $3 \times 10^{-5}$  g. of  $\text{I}^-$ , using the apparatus described previously (this vol., 47).  $\text{I}$  is thereby liberated and volatilised away. Complete absorption of  $\text{HNO}_2$  is detected by a wash-bottle of Ilosvay's reagent following the  $\text{KI}$  tube. 0.3 c.c. of the  $\text{KI}$  solution is treated with  $\text{H}_2\text{SO}_4$  containing  $\text{NaNO}_2$ , and is then emulsified with 0.02 c.c. of  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  is separated centrifugally, and the amount of residual  $\text{I}$  determined colorimetrically by matching the  $\text{CHCl}_3$  drop against those from similarly treated solutions of known  $[\text{I}]$ . With air of higher oxidising power, larger initial amounts of  $\text{KI}$  and smaller vols. of air are used.

J. S. A.

**Determination of oxides of nitrogen in gaseous mixtures.** A. N. ZETTLIN (Ukrain. Chem. J., 1935, 10, 362—366).—The  $\text{NO} + \text{NO}_2$  is absorbed by 4%  $\text{KBrO}_3$  in  $\text{N-H}_2\text{SO}_4$  in an Orsat apparatus ( $< 10$  min.), and the difference in vol. of the sample is read.

R. T.

**Determination of phosphoric acid by precipitation as ammonium phosphomolybdate.** H. TERLET and A. BRIAU (Ann. Falsif., 1935, 28, 546—555; cf. B., 1935, 198).—Scheffer's method (J. Officiel, Aug. 30, 1934), which consists in the titration of the pptd.  $\text{NH}_4$  phosphomolybdate with aq.  $\text{NaOH}$  in presence of  $\text{CH}_3\text{O}$ , is trustworthy and accurate, provided steps are taken to remove  $\text{H}_2\text{MoO}_4$ , which is co-pptd. Procedures are outlined for the examination of natural  $\text{Ca}_3(\text{PO}_4)_2$ , fertilisers containing org. matter, superphosphates and the like, basic slag, and alkali phosphates.

E. C. S.

**Eliminating the effects of  $\text{PO}_4$  radical in qualitative analysis.** I—V. S. ISHIMARU (Sci. Rep. Tohoku, 1935, 24, 426—438, 439—447, 448—460, 461—472, 473—480).— $\text{I. PO}_4^{3-}$  can be removed completely from a solution rendered just acid to  $\text{Mc}$ -orange by addition of  $\text{Fe}(\text{NO}_3)_3$ . This method is more convenient in analysis than the  $\text{Pb}$  method, which can be applied satisfactorily only after removal of the  $\text{Al}$  group and  $\text{Mn}$ .

II. Pptn. with  $\text{Bi}^{III}$  leads to less occlusion and adsorption of other ions by the ppt. than the  $\text{Fe}$

method, but is unsatisfactory in presence of a high  $[\text{Fe}^{+++}]$ . The Zr method yields gelatinous ppts. and is of equal merit to the Fe method.

III. Pptn. with Sn leads to loss of Fe and Cr, but can be adopted after removal of the Al group and Mn. Reynoso's procedure (Ann. chim. phys., 1852, 34, 320) is the most satisfactory.

IV, V. Of analytical methods in which  $\text{PO}_4^{'''}$  or  $\text{C}_2\text{O}_4^{''}$  are added in excess to eliminate the effects of  $\text{PO}_4^{'''}$  already present Smith's phosphate method (A., 1933, 479) is the most satisfactory. J. W. S.

Rapid determination of assimilable phosphoric acid in freshly prepared superphosphates.—See B., 1936, 58.

Graphite formation. I. Determination of graphite. A. E. BALFOUR and H. L. RILEY (J.C.S., 1935, 1723—1728; cf. A., 1935, 453).—The  $\text{CO}_2$  evolved when a steady stream of air is bubbled through a suspension of 1 g. of C, graded between 60 and 100 I.M.M. sieves, in 50 c.c. of  $\text{CrO}_3\text{--H}_3\text{PO}_4$  (10 g. of  $\text{K}_2\text{Cr}_2\text{O}_7 + 50$  c.c. of  $\text{H}_3\text{PO}_4$ ,  $d$  1.75) at  $100^\circ$  is an approx. measure of the extent to which the sample is graphitised; e.g., electrode graphite, diamond, and sucrose carbonised at  $900^\circ$  gave 1600, 43, and 16 mg. of  $\text{CO}_2$ , respectively, under similar conditions. The differentiation disappears as the  $[\text{H}_3\text{PO}_4]$  is diminished and is small with conc.  $\text{H}_2\text{SO}_4$ .  $\text{H}_3\text{PO}_4$  probably reacts with graphitic C under sp. conditions. Coal carbonised at approx.  $650^\circ$  has a max. moisture absorption and a min. rate of wet oxidation, consistent with the view that graphitisation commences at approx.  $700^\circ$ . J. G. A. G.

Preservation of standard solutions of oxalic acid and sodium oxalate. II. S. ISHIMARU (Sci. Rep. Tohoku, 1935, 24, 411—425).—Either colourless or black bottles can be used safely for the storage of unacidified  $0.2N\text{--Na}_2\text{C}_2\text{O}_4$  or pure  $0.5N\text{--H}_2\text{C}_2\text{O}_4$  or of  $0.01N\text{--Na}_2\text{C}_2\text{O}_4$  and  $0.01N\text{--H}_2\text{C}_2\text{O}_4$  if 100 c.c. of conc.  $\text{H}_2\text{SO}_4$  are added per litre.  $0.01N\text{--Na}_2\text{C}_2\text{O}_4$  is also stable with 20 c.c. of  $\text{H}_2\text{SO}_4$  per litre in a black bottle. J. W. S.

Rapid determination of certain gases or vapours  $[\text{CO}_2, \text{HCN}]$  in air.—See B., 1936, 46.

Spectrophotometric determination of potassium chloride in sylvines. R. ROMANN and C. SPEITEL (Bull. Soc. chim., 1935, [v], 2, 2168—2170).—An aq. solution of a known wt. of the specimen is saturated with K. picrate, and the concn. of the latter, which is determined by the ratio K : Na in the specimen, is measured spectrophotometrically. The results agree with those obtained by the perchlorate method. F. L. U.

Determination of alkalis in silicates.—See B., 1936, 21.

Colorimetric determination of small amounts of silver with *p*-dimethylaminobenzylidenerhodanine. I. C. SCHOONOVER (J. Res. Nat. Bur. Stand., 1935, 15, 377—384).—Feigl's method (A., 1928, 1108) gives satisfactory results for Ag in concns. of 0.06—9 mg. per litre when  $\text{Cl}^-$ ,  $\text{Cu}^+$ , and  $\text{Hg}^+$  are absent and fused  $\text{SiO}_2$  vessels are used. Soft glass vessels adsorb appreciable amounts of Ag, but Pyrex adsorbs very little unless the solution is boiled. A. R. P.

Gravimetric determination of calcium and magnesium. A. M. VASILIEV and L. A. VASILIEVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 67—72).—Appreciable quantities of  $\text{CaC}_2\text{O}_4$  are dissolved by washing with  $\text{H}_2\text{O}$ .  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  should be substituted. Pptd.  $\text{MgNH}_4\text{PO}_4$  should be washed with a saturated solution of this salt, instead of with aq.  $\text{NH}_3$ , which causes losses. CH. ABS. (p)

Determination of barium silicofluoride in insecticidal powders.—See B., 1936, 36.

Determination of the [radium] content of substances containing radium. A. E. KORVEZEE (Chem. Weekblad, 1935, 32, 726—731).—A lecture. D. R. D.

Volumetric micro-determination of magnesium with methylene-blue following its precipitation as magnesium picrolonate. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1935, 69, 68—74).—Solutions ( $> 0.01N$ ) of Mg salts with Li picrolonate at  $100^\circ$  afford Mg picrolonate in which the picrolonic acid is determined; alternatively, the excess of the acid used is titrated (cf. A., 1934, 1017). Alkali picrolonates in concns.  $< 0.01N$  do not interfere; in larger concns., they are pptd. and the error involved is determined by a differential titration. A modification for determining Ca and Mg separately in the same sample is described. J. L. D.

Organic compounds as analytical reagents. IV. *p*-Nitrobenzeneazoresorcinol as a reagent for magnesium. L. NEWELL, N. R. PIKE, and J. B. FICKLEN (Z. anorg. Chem., 1935, 225, 281—284; cf. A., 1935, 951).—The reagent is sp. for Mg when the ions of groups I, II, and III, and  $\text{NH}_4^+$  are removed. The sensitivity is 1 in 500,000. E. S. H.

Determination of traces of heavy metals in mineral waters.—See B., 1936, 46.

Organic flocculating agents in the quantitative precipitation of zinc sulphide. J. R. CALDWELL and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 2372—2374).—Gelatin (0.5—2 mg.) or agar (2—5 mg.) produces immediate and complete flocculation of  $\text{ZnS}$  suspensions (0.3 g. in 300 c.c.). The solution may be filtered within 15 min. after pptn. Satisfactory separation from all metals but Co is obtained. E. S. H.

Separation of zinc from cobalt based on a new method for reducing post-precipitation. J. R. CALDWELL and H. V. MOYER (J. Amer. Chem. Soc., 1935, 57, 2375—2377).— $\text{ZnS}$  ppts., formed in presence of hydrophilic colloids (cf. preceding abstract), are not contaminated with Co when acetaldehyde is added. E. S. H.

Determination of small quantities of zinc. H. LUX (Z. anorg. Chem., 1935, 226, 1—20).—The method, which is intended for the examination of biological material, consists first in the incineration of the latter at a temp.  $> 550^\circ$ . The metal sulphides, pptd. from a  $\text{HNO}_3$  solution of the ash in presence of  $\text{CaCO}_3$ , are then oxidised in air at  $650\text{--}700^\circ$ , and the resulting oxides are heated in  $\text{H}_2$ . Zn volatilises and is condensed in a capillary, which is then drawn out to a conical end into which the whole of the Zn is driven. The Zn cone is measured microscopically. The method

is accurate to within  $\pm 2\%$  and can be used for quantities down to  $10^{-6}$  mg. Zn of biological origin obtained in this way is shown to contain  $< 0.1\%$  of Cd. F. L. U.

**Organic reagent for cadmium.** A. W. SCOTT and E. G. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2541—2542).—The prep. of N-2 : 6-dihydroxyphenyl-N'-allylthiocarbamide, decomp.  $230^\circ$ , N-2-hydroxy-5-nitrophenyl-N'-allylthiocarbamide, m.p.  $122^\circ$ , and 1-(2-quinolyl)-4-allylthiosemicarbazide (I), m.p.  $158^\circ$ , is described. A saturated solution of (I) in 50% EtOH, in presence of KI, gives a yellow ppt. with solutions containing 1 part of  $\text{Cd}^{++}$  in  $10^6$  parts. E. S. H.

**Determination of small amounts of lead by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 648—650B).—Pb is titrated photometrically with  $\text{Na}_2\text{S}$  (A., 1934, 856) in presence of AcOH and  $\text{NH}_4\text{OAc}$ . Pb may be first isolated as  $\text{PbSO}_4$ , which is dissolved in aq.  $\text{NH}_4\text{OAc}$  for titration. J. S. A.

**Separation of lead as sulphate.** A. M. VASILIEV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 61—65).—Washing  $\text{PbSO}_4$  ppts. with dil.  $\text{H}_2\text{SO}_4$  followed by 50% EtOH causes losses. Washing with saturated aq.  $\text{PbSO}_4$  gives accurate results.

CH. ABS. (p)

**Extraction of lead by means of diphenylthiocarbazone.** D. C. GARRATT (Analyst, 1935, 60, 817).—In the examination of org. substances for Pb by wet oxidation with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  followed by extraction of the Pb with diphenylthiocarbazone and  $\text{CHCl}_3$ , errors are caused by the dissolution of resistant  $\text{NO}_2$ -compounds in the  $\text{CHCl}_3$ ; these may be avoided by evaporating the first extract to dryness, heating with 2 c.c. of  $\text{H}_2\text{SO}_4$  and 10 c.c. of 6%  $\text{H}_2\text{O}_2$  until acid fumes are evolved, adding 2 g. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and continuing the heating for 30 min.; after cooling the Pb is extracted as before and comparison made with the standards. A. R. P.

**Determination of lead in official [B.P.] compounds and preparations.**—See B., 1936, 76.

**Determination of lead dioxide.** IV.—See B., 1936, 59.

**Volumetric determinations in strongly alkaline solutions.** III. Titration of thallium and cerium with hypobromite. O. TOMÍČEK and M. JAŠEK (J. Amer. Chem. Soc., 1935, 57, 2409—2411; cf. A., 1935, 838, 1094).—The titration of  $\text{Tl}^{\text{I}}$  salts with  $\text{NaOBr}$  is described.  $\text{NaOBr}$  solutions may be standardised by using  $\text{Ti}_2\text{CO}_3$  or  $\text{Ti}_2\text{SO}_4$  as standard.  $\text{Ce}^{\text{III}}$  salts can be titrated with  $\text{NaOBr}$  in 20—30%  $\text{K}_2\text{CO}_3$  solution, from which  $\text{O}_2$  has been removed, but the  $\text{K}_3\text{Fe}(\text{CN})_6$  method is preferred. E. S. H.

**Inorganic complex compounds in analytical chemistry.** III. Detection and determination of copper. C. MAHR (Z. anorg. Chem., 1935, 225, 386—392).— $\text{Cu}^{++}$ , freed from Hg, Ag, and Tl, is reduced to  $\text{Cu}^+$  by  $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  in aq. HCl. A drop of  $\text{NH}_4[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$  in HCl is added and a yellow ppt.,  $\text{Cu}[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2]$ , cryst. from warm solution, is formed. The method is very sensitive. One part of Cu in 15,000 of Bi, 10,000 of Cd, 20,000 of Zn, or 50,000 of Pb can be detected. The applic-

ation of the method to the determination of small quantities of Cu in the presence of a large no. of different metals is described. M. S. B.

**Determination of small amounts of mercury by photometric titration.** S. HIRANO (J. Soc. Chem. Ind. Japan, 1935, 38, 646—647B).—Hg, present in neutral solution as chloride or nitrate, is titrated photometrically (cf. A., 1934, 856) with 0.01N- or 0.001N- $\text{Na}_2\text{S}$ , using gum arabic as protective colloid. Cu and As do not interfere. J. S. A.

**Determination of small amounts of mercury with dithizone.** H. FISCHER and G. LEOPOLDI (Z. anal. Chem., 1935, 103, 241—257).—For the colorimetric determination of Hg, the Hg in dil.  $\text{HNO}_3$  solution, containing  $> 5 \times 10^{-6}$  g. of Hg per c.c., is extracted quantitatively with successive portions of a  $\text{CCl}_4$  solution of diphenylthiocarbazone (I). The excess of (I) is washed out of the united  $\text{CCl}_4$  extracts with very dil. aq.  $\text{NH}_3$ . The orange Hg-(I) compound is decomposed with slightly acid aq. KI, and the green colour of (I) remaining is either matched against that produced similarly with known amounts of Hg, or measured photometrically. Small amounts of Hg may be determined colorimetrically from the mixed orange-green colour of the original  $\text{CCl}_4$  extract. Volumetrically, Hg is extracted as before with a measured small excess of a solution of (I) previously standardised against Ag. The excess of (I) is bound by adding a standard solution of  $\text{Ag}^+$ , and the excess of  $\text{Ag}^+$  is titrated back with (I).  $\text{Cl}^-$  in large excess does not interfere. In presence of Zn, Cd, Pb, or Bi, Hg alone is extracted from acid solution. Any Zn etc. dissolved is removed by washing with 0.2N-acid. In presence of Cu, Hg is extracted preferentially, and may be determined volumetrically, but not colorimetrically. J. S. A.

**Electrocapillary method of detection of the cations of the first sub-group of group IV.** A. F. ORLENKO (J. Gen. Chem. Russ., 1935, 5, 1091—1092).—Al electrodes are placed on wet filter-paper, crystals of  $\text{K}_4\text{Fe}(\text{CN})_6$ , pyrogallol (I),  $\text{K}_2\text{Cr}_2\text{O}_7$ , and KI are placed at different points around the cathode, and drops of the solution, containing  $\text{Hg}^{++}$ ,  $\text{Cu}$ ,  $\text{Bi}^{+++}$ , and  $\text{Cd}^{++}$ , are placed around the anode, and a current is passed. A few min. later the  $\text{K}_4\text{Fe}(\text{CN})_6$  turns pink, and then brown, and the (I) red, pointing to the presence of  $\text{Cu}^{++}$ . A yellow stain due to formation of  $\text{BiO}_2 \cdot \text{Cr}_2\text{O}_7$  then forms around the  $\text{K}_2\text{Cr}_2\text{O}_7$ , and a pink coloration due to  $\text{HgI}_2$  around the KI crystal. The entire procedure requires 10—15 min. R. T.

**Spectral analysis of complex mixtures.** B. J. DAIN, I. V. GRANOVSKI, and E. S. PUZENKIN (J. Gen. Chem. Russ., 1935, 5, 1093—1097).—A system of standard Co-Mn mixtures giving invariant homologous pairs of spectral lines is proposed. The relative intensity of the lines is unaffected by Na, K, Ba, Al, and Ni, but the Mn lines are relatively more damped by Fe, and more so by Fe+Al, whence it follows that Fe must be eliminated from the mixtures for spectral analysis. R. T.

**Step-photometric determination of manganese in waters.**—See B., 1936, 46.

**Analytical applications of 8-hydroxy-5-methylquinoline.** C. E. GIETZ and A. SÁ (Anal. Asoc. Quím. Argentina, 1935, **23**, 45—57).—The detection of traces of the following is described:  $\text{Fe}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Pd}^{++}$ ,  $\text{Ti}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{VO}_3'$ ,  $\text{MoO}_4''$ ,  $\text{WO}_4''$ . F. R. G.

**Influence of silicic acid on the magnetic behaviour of dissociated mixtures with ferric oxide.** W. LEITGEBEL and K. BOCKEMUHL (Z. anorg. Chem., 1935, **225**, 209—212).—The amount of  $\text{Fe}_3\text{O}_4$  formed under different conditions has been determined by magnetic measurements. E. S. H.

**Detection of traces of iron in mercury salts.**—See B., 1936, 59.

**Determination of iron and aluminium by Crispo's method in natural phosphates.**—See B., 1936, 18.

**Determination of small amounts of nickel and cobalt in iron ores.**—See B., 1936, 63.

**Rapid determination of nickel in high-chromium steels and alloys.**—See B., 1936, 64.

**Importance of hydrogen-ion concentration in determination of molybdenum and vanadium by the 8-hydroxyquinoline method and solubility of 8-hydroxyquinoline in various solvents.** H. GOTO (J. Chem. Soc. Japan, 1935, **56**, 314—321).—Complete pptn. of Mo occurs in the  $p_{\text{H}}$  range 3.3—7.6 and that of V at  $p_{\text{H}}$  2.7—6.1. The solubility of 8-hydroxyquinoline in the  $\text{EtOH-COMe}_n$  mixture is small at  $p_{\text{H}}$  5.5—8.5. CH. ABS. (p)

**Iodometric titration of tin.** F. L. OKELL and J. LUMSDEN (Analyst, 1935, **60**, 803—810).—Low results in Sn titrations are shown to be due to  $\text{O}_2$  dissolved in the I solution and not to incomplete exclusion of air from the flask. In the analysis of Sn ores the presence of Ti gives erratic results; this is ascribed to its acting as a negative catalyst for the oxidation of  $\text{Sn}^{++}$  by dissolved  $\text{O}_2$ . No interference of Ti occurs if O-free I is used for titration. Reduction with Al turnings is recommended in ore analysis. A. R. P.

**Quantitative spectral analysis. IV.** R. BRECKTOR and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 266—292; cf. A., 1935, 719).—The spectral determination of Ti, V, Cr, Mn, Co, Ni, Mo, and In using a Cu base is discussed and tables of data are given. The Cu line previously described as 2480.13 Å. is actually 2479.8 Å., and coincident with an Fe line persistent at feeble amperages. R. S.

**Colorimetry of titanium. IV.** H. GINSBERG (Z. anorg. Chem., 1935, **226**, 57—64; cf. A., 1933, 566).—Errors in the colorimetric determination of  $\text{TiO}_2$  are discussed. By using a Pulfrich photometer 0.07 mg. of  $\text{TiO}_2$  per 100 c.c. can be determined within  $\pm 10\%$ . F. L. U.

**Determination of zirconium.** G. A. AMPT (J. Proc. Austral. Chem. Inst., 1935, **2**, 321—334).—A review of analytical methods for the determination of Zr and complete analysis of Zr minerals. J. S. A.

**Determination of the zirconium-hafnium ratio.** G. WERNIMONT and T. DE VRIES (J. Amer.

Chem. Soc., 1935, **57**, 2386—2387).—An equation for the calculation of the mol. ratio Hf : Zr in mixtures, when the effect of a known wt. of the mixed oxides on the rotation of certain reference tartrate solutions has been measured, is given. Results on two samples of mixed oxides are compared with those obtained by other methods. The procedure is not more accurate, but is rapid and convenient. E. S. H.

**Potentiometric determination of metavanadates with silver nitrate.** P. SPACU (Z. anal. Chem., 1935, **103**, 422—424).— $\text{VO}_3'$  is titrated potentiometrically with  $\text{AgNO}_3$  in 20% aq. EtOH solution. J. S. A.

**Electrometric determination of vanadium in (A) high-chromium steels, (B) slags.**—See B., 1936, 65.

**Determination of antimony in white metals.**—See B., 1936, 64.

**Determination of bismuth with 8-hydroxyquinoline.** F. HECHT and R. REISSNER (Z. anal. Chem., 1935, **103**, 261—269).—Determination of Bi as  $\text{C}_9\text{H}_6\text{N}\cdot\text{OH}\cdot\text{HBI}_4$  (cf. A., 1927, 847) is unsatisfactory, the ppt. undergoing partial decomp. during washing. Pptn. with 8-hydroxyquinoline from AcOH solution at 70° under the exact conditions described gives good macro- and micro-results. The ppt. is dried at 105° and weighed as  $\text{Bi}(\text{C}_9\text{H}_6\text{ON})_3\cdot\text{H}_2\text{O}$ . J. S. A.

**Colorimetric assay of bismuth pharmaceuticals.**—See B., 1936, 43.

**Potentiometric determination of quadrivalent osmium with chromous sulphate.** W. R. CROWELL and H. L. BAUMBACH (J. Amer. Chem. Soc., 1935, **57**, 2607—2609).—Apparatus and technique for (1) storing and titrating  $\text{CrSO}_4$  solutions, (2) standardising  $\text{CrSO}_4$  with  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , and (3) determining Os in  $\text{K}_2\text{OsBr}_6$  and  $\text{K}_2\text{OsCl}_6$  by potentiometric titration are described. E. S. H.

**Separation of the six platinum metals from one another and their gravimetric determination.** R. GILCHRIST and E. WICHES (J. Amer. Chem. Soc., 1935, **57**, 2565—2573).—Os is isolated by distilling  $\text{OsO}_4$  from  $\text{HNO}_3$  solution. Ru is next isolated by distilling  $\text{RuO}_4$  from a solution of the sulphates in dil.  $\text{H}_2\text{SO}_4$  containing  $\text{NaBrO}_3$ . A suitable reagent for absorption of  $\text{OsO}_4$  or  $\text{RuO}_4$  is 6N-HCl saturated with  $\text{SO}_2$ . The separation of Pt, Pd, Rh, and Ir is effected by controlled hydrolytic pptn. In the recovery and determination of these metals, Os, Ru, and Ir are pptd. as hydrated oxides, ignited, and weighed as metal; Rh and Pt are obtained as sulphides and ignited to metal; Pd is recovered as the glyoxime compound, which may be weighed directly or ignited and weighed as metal. The accuracy is equal to that of the best analytical procedures. E. S. H.

**Comparison of some platinum thermometers with the helium thermometer between 0° and -183°.** W. H. KEESOM and B. G. DAMMERS (Physica, 1935, **11**, 1080—1090).—A  $\text{C}_5\text{H}_{12}$  cryostat for use at 0° to -150° is described. H. J. E.

**Construction of platinum thermometers and determination of their basic points.** W. H. KEESOM and B. G. DAMMERS (Physica, 1935, **11**,



1051—1058).—The construction and calibration are described. The optimum annealing temp. was 840—850°.  
H. J. E.

**Micro-determination of m.p.** M. MEZENER and S. WEHRLI (Helv. Chim. Acta, 1935, 18, 1281—1283).—A sealed m.-p. tube is used, the specimen being observed through a low-power microscope.  
J. S. A.

**Calorimeter for measurement of continued heat effects.** W. SWIENTOSELAWSKI (Rocz. Chem., 1935, 15, 343—350).—A flow calorimeter is described in which heat effects of the order of 1—400 g.-cal. per hr. are determined by measuring the difference in temp. between a liquid entering and leaving the calorimeter at const. velocity. Efficient heat exchange is achieved by surrounding the reaction vessel and the thermometer with labyrinths through which the liquid circulates.  
R. T.

**Thermocouples from 2° to 90° abs.** J. E. AHLBERG and W. O. LUNDBERG (J. Amer. Chem. Soc., 1935, 57, 2722—2723).—Methods of calibration are discussed.  
E. S. H.

**Precision thermostat for use down to -20°.** G. A. BENFORD (J. Sci. Instr., 1936, 13, 4—6).—A commercial refrigerating element acts in opposition to a controlled heater.  
C. W. G.

**Thermal conductivity method for following the electrolytic separation of hydrogen isotopes.** W. C. NEWELL, R. H. PURCELL, H. S. GREGORY, and H. J. T. ELLINGHAM (Nature, 1936, 137, 69—70).—A method, accurate to approx. 0.1% of D<sub>2</sub>, using gas at 10 cm. pressure is described.  
L. S. T.

**Determination of transformation points [in alloy systems].** H. NIPPEN and E. LIPS (Z. Metallk., 1935, 27, 242—243).—An apparatus for the automatic registration of the torsion angle of wires at various temp. is described; a sharp change in the direction of the resulting curve indicates a change in the constitution of the alloy. The use of the apparatus in determining the solidus of Cu-Ag alloys is illustrated.  
A. R. P.

**Physical methods in the chemical laboratory. XXVII. Application of roentgenographic methods to chemical problems.** R. BRILL and H. HALLE (Angew. Chem., 1935, 48, 785—795).—X-Ray methods for the study of gases, liquids, crystals, fibres, etc. are reviewed.  
R. S.

**Accurate determination of glancing angles and lattice constants by the method of Debye and Scherrer.** M. STRAUMANIS and A. IEVINS (Naturwiss., 1935, 23, 833).—The usual method is improved by a different arrangement of the film in the camera.  
A. J. M.

**Subjective photometer.** W. D. WRIGHT and J. H. NELSON (J. Sci. Instr., 1935, 12, 373—377).—The intensity of a patch viewed by the left eye is compared with that of one viewed by the right, in order to measure the variation in sensitivity of the eye for different conditions of the visual mechanism.  
C. W. G.

**Use of a selenium photo-electric cell for the measurement of solar ultra-violet radiation near 3200 Å.** G. LIANDRAT (Compt. rend. Acad. Sci.

U.R.S.S., 1935, 3, 19—20).—A surface of 30 sq. cm. is used, behind a Ag filter.  
C. W. G.

**Cuprous oxide "sperrschicht" photo-electric cell as precision sunshine recorder.** H. MAYER (Meteorol. Z., 1935, 52, 15—18; Chem. Zentr., 1935, i, 2565).—The photo-electric cell has advantages over the glass-sphere instrument.  
J. S. A.

**X-Ray powder camera for specimens at various known temperatures.** W. H. BARNES and W. F. HAMPTON (Canad. J. Res., 1935, 13, 73—81).—The specimen is placed over a hole in a Cu block through which the X-rays are directed by a pinhole system. The temp. of the block is maintained const. by circulation of COMe<sub>2</sub> or other liquid, which passes through two coils at -78° and is then warmed to any desired temp. between 0° and -60° by an electric heater.  
R. S.

**Mapping ultra-violet absorption spectra, using a special hydrogen lamp and a microphotometer.** H. C. GULL and A. E. MARTIN (J. Sci. Instr., 1935, 12, 379—388).—The spectra are photographed with a H<sub>2</sub> lamp, of const. output. They are traversed in the microphotometer by a series of lines corresponding with known extinction coeffs.  
C. W. G.

**Square reagent glasses for comparators.** H. BAUSCH (Woch. Brau., 1935, 52, 397).—A reagent tube, part of which has a square cross-section, is described. The uniformity and enlargement of the field which are thus made possible facilitate colorimetric comparisons.  
I. A. P.

**Spectrograph with high illumination for Raman spectra.** G. DUPONT and J. TABUTEAU (Bull. Soc. chim., 1935, [v], 2, 2152—2156).—Apparatus and method of working are described.  
F. L. U.

**Sedimentometer.** J. MILBAUER (Z. anal. Chem., 1935, 103, 419—422).—A photo-electric cell is employed to measure velocity of sedimentation.  
J. S. A.

**Photo-electric half-shadow method for determination of rotational dispersion.** O. SCHONROCK and E. EINSPOHN (Physikal. Z., 1936, 37, 1—12).—The method employs a single photo-electric cell.  
A. J. M.

**Observing fluorescence.** D. W. DANA (Rev. Sci. Instr., 1935, [ii], 6, 417).—Corning glass No. 038, "Noviol A," may be used when the source of excitation extends into the visible violet.  
C. W. G.

**Resolving power of the two-crystal X-ray spectrometer.** L. G. PARRATT (Rev. Sci. Instr., 1935, [ii], 6, 387—399).—The physical meaning of resolving power when the shape of the diffraction pattern is unknown has been studied experimentally. New criteria of spectrometric perfection of calcite crystals are proposed.  
C. W. G.

**Illuminator for printing Laue photographs.** C. H. DWIGHT and H. KERSTEN (Rev. Sci. Instr., 1935, [ii], 6, 418; cf. A., 1935, 1340).—The priority of Trendelenburg and Franz (A., 1934, 504) is admitted.

**Double ionisation chamber for detection of corpuscular particles.** B. ZIPPRICH (Z. Physik, 1935, 96, 328—336).  
A. B. D. C.

**Mechanism of action of solid rectifiers.** V. P. SHUSÉ (Physikal. Z. Sovietunion, 1935, 7, 1—18).—A method for making rectifiers with blocking layers of  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{NaCl}$ ,  $\text{S}$ , glass, and bakelite, and with rectification coeffs. up to 100 is described.

CH. ABS. (e)

**Measurement of electromotive force and very weak direct current by means of electron tubes.** F. MÜLLER and W. DURICHEN (Z. Elektrochem., 1936, 42, 31—43).—A review.

**Magnification of currents of the order of  $10^{-13}$  amp.** H. ALFVEN (Z. Physik, 1935, 97, 708—717).—The valve circuit described automatically differentiates, with respect to time, the potential of the first grid, and so records the true form of the applied small current.

A. B. D. C.

**Hydraulic counter for elementary rays and photo-electrons.** H. GREINACHER (Helv. phys. Acta, 1934, 7, 514, 641; Chem. Zentr., 1934, ii, 2096; 1935, i, 2319).

J. S. A.

**Further hydroelectric counter for elementary rays and photo-electrons. III.** H. GREINACHER (Helv. phys. Acta, 1935, 8, 89—96; Chem. Zentr., 1935, i, 2852).—Elementary rays or photo-electrons initiate a discharge between a liquid surface and an Fe point electrode. The counter has advantages over the author's hydraulic counter (see above).

J. S. A.

**Further improvements in the Curie-Cheneveau magnetic balance.** F. W. GRAY, A. CLOW, and J. H. CRUIKSHANK (J. Sci. Instr., 1936, 13, 13—20).—Alterations in apparatus and technique are described (cf. Gray *et al.*, *ibid.*, 1932, 9, 1).

C. W. G.

**Routine gas analysis apparatus.** H. K. SEN, K. ROY, and P. ROY (J. Indian Chem. Soc., 1935, 12, 654—658).—The method of fractional combustion is employed.

R. S. B.

**Gas micro-analysis [apparatus] for following the course of oxidation of hydrocarbons.**—See B., 1936, 50.

**Container for analysing gases by combustion.** V. MATSCHKARIN (Novo. Tech., Seri. Gorn. Prom., 1935, No. 2, 13).—The sealed-in Pt wires of the explosion vessel are cooled by Hg, contained in glass tubes sealed to the outside of the vessel. Risk of cracking at the seals is thus eliminated.

CH. ABS. (e)

**Manometric device for gas analysis.**—See this vol., 259.

**Air analysis apparatus.**—See this vol., 259.

**Apparatus for determining the concentration of ammonium fluoride solutions.** M. SCRUTZA (Woch. Brau., 1935, 52, 405—406).—The described apparatus minimises the difficulties met with in titrating  $\text{NH}_4\text{HF}_2$  solution (I) with 0.1N-Ba(OH)<sub>2</sub> solution (litmus). The concn. of free HF varies in commercial samples of (I) from 29 to 33%, and a correction table is therefore supplied for the elimination of errors due to this variation.

I. A. P.

**Modified Rehberg burette for use with titrating solutions which react with mercury.** B. B. LONGWELL and R. M. HILL (J. Biol. Chem., 1936, 112, 319—321).—The Rehberg micro-burette (A.,

1925, i, 852) is modified so that Hg does not touch the titrating fluid.

H. D.

**Logarithmic head correction in viscometry.** G. BARR (J.C.S., 1935, 1793—1795).—The effects of several shapes of bulbs on the "head correction" for viscosimeters are evaluated. Bury's procedure (A., 1934, 1195) is modified.

J. G. A. G.

**Microscopical method for measuring the viscosity of a liquid.** F. HIRATA (Bull. Chem. Soc. Japan, 1935, 10, 507—524).—The velocity of flow of liquids under a known pressure through a capillary is observed under a microscope by using particles of C and SiC, 0.1—0.002 mm. in diameter, as indicators of flow. The particles have no effect on  $\eta$  within the experimental error.  $\eta$  has been measured for glycerol and for solutions of cellulose acetate in  $\text{COMe}_2$ , results agreeing with those obtained with the Oswald viscosimeter, and with theory.

R. S. B.

**Regulation of liquid flow by capillary tubes.** I. HVIDBERG (Kem. Maanedst., 1934, 15, 152; Chem. Zentr., 1935, i, 2409).—A simple device for fine flow regulation is described.

J. S. A.

**Sulphuric acid hygrometer.** A. BLACKIE (J. Sci. Instr., 1936, 13, 6—9).—The change of pressure of air at const. vol. on drying is measured.

C. W. G.

**Simple humidity chamber.** F. C. MEAD (J. Sci. Instr., 1935, 12, 394—395).—Suitable solutions are placed inside an air thermostat controlled by a bi-metallic regulator.

C. W. G.

**Obtaining and controlling high humidities at high temperatures.** W. LETHERSICH (J. Sci. Instr., 1935, 12, 388—391).—Separate heating is provided for a dish of  $\text{H}_2\text{O}$  inside a heated oven.

C. W. G.

**Chemical hygrometer.** T. M. CARPENTER (J. Biol. Chem., 1935, 112, 123—133).—An apparatus, on the principle of that used in gas analysis, for the determination of  $\text{H}_2\text{O}$  vapour by vol. in air is described. The vols. before and after removal of  $\text{H}_2\text{O}$  by  $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  are read against a const. vol. kept dry by  $\text{P}_2\text{O}_5$ . The agreement with results obtained by wt. of the absorbed  $\text{H}_2\text{O}$  is within 0.02%.

J. N. A.

**Development of air-driven spinning top as transparent centrifuge.** J. W. MCBAIN and C. M. O'SULLIVAN (J. Amer. Chem. Soc., 1935, 57, 2631—2641).—Apparatus and technique are described.

E. S. H.

**Mercury float-valves [taps] for high-vacuum work.** H. LUX (Z. anorg. Chem., 1935, 226, 21—22).—The greaseless taps devised by Stock (A., 1915, ii, 339; 1925, ii, 1195) have been modified by using floats provided with thin sintered glass plates, thus permitting rapid evacuation.

F. L. U.

**Rapid weighings with a Troemner solution balance.** E. T. BARTHOLOMEW and E. C. RABY (Science, 1935, 82, 468).—Modifications to ensure quicker and more convenient weighing with a 20-kg. capacity balance are described.

L. S. T.

**Modern developments in chemical balances.** J. L. BUCHAN (J. Sci. Instr., 1936, 13, 1—4).—Historical.

C. W. G.

**Determination of low gas pressures.** H. KLUMB and T. HAASE (Physikal. Z., 1936, 37, 27—32).—An apparatus for determining low gas pressures uses an electrically heated bimetal strip (invar-constantan), the loss of heat, varying with the pressure of the gas, being measured by the bending of the strip. The instrument is useful for pressures down to  $10^{-4}$  mm., and may also be used for determining the composition of a gas, since the effect is dependent on mol. wt. A. J. M.

**Laboratory apparatus.** A. OSTROGOVICH (Annali Chim. Appl., 1935, 25, 563—568).—Apparatus for drying substances in a vac., a reflux condenser, and a flask with neck adaptable to reflux condenser or distillation head are described and illustrated. F. O. H.

**Device for drilling oriented holes in spheres required in the construction of crystal structure models.** M. J. BUERGER (Rev. Sci. Instr., 1935, [ii], 6, 412—416).—Full constructional diagrams are given. C. W. G.

**Simple oil micromanometer.** O. BEECK (Rev. Sci. Instr., 1936, [ii], 6, 399—400).—Movement of Hg is magnified by transfer to movement of oil in a capillary. C. W. G.

**Apparatus for studying the elastic properties of filamentous materials.** I. J. SAXL (Rev. Sci. Instr., 1935, [ii], 6, 409—412).—Chainomatic wt. application is used. C. W. G.

**Making extremely thin films.** K. LARK-HOROVITZ, J. D. HOWE, and E. M. PURCELL (Rev. Sci. Instr., 1935, [ii], 6, 401—403).—The film is deposited on a layer of material such as camphor which is subsequently removed by vaporisation. C. W. G.

**Apparatus for the determination of colloid osmotic pressure in small amounts of fluid.** R. DUBACH and R. M. HILL (J. Biol. Chem., 1936, 112, 313—318).—The Krogh-Nakazawa osmometer (A., 1927, 1104) is modified by using brass parts, thus dispensing with washers around the membrane and allowing a view of the latter when in place. H. D.

## Geochemistry.

**Gases of the borate-carrying soffioni, with special reference to their content of helium and other noble gases.** U. SBORGI (Mem. R. Accad. Ital., Cl. Sci. fis. mat., 1934, 5, 667—713; Chem. Zentr., 1935, i, 2792).— $O_2$  is absent from soffioni gases, which vary little in composition from different sources. He and Ar are present, with little Ne. The Rn : He ratio is not const. J. S. A.

**Mineral composition of atmospheric dust collected at Baton Rouge, Louisiana.** R. D. RUSSELL (Amer. J. Sci., 1936, [v], 31, 50—66).—From dust storms of April, 1934 (and April, 1935) were compared. The vol. % size of particles 0—100, < 1 (1); 0.025—0.050, 4 (9); 0.005—0.0025, 20 (50); < 0.005 mm., 65 (40). The material was separated into lighter and heavier portions by centrifuging in  $CHBr_3$ , and particles > 0.01 mm. were identified and counted under the microscope. The lighter portion contained volcanic glass 42 (24), plant fragments etc. 18 (5), quartz 21 (53)%; and 11 other minerals were identified. In the heavier portion ( $d > 2.88$ ; 1% of the whole) 35 minerals were identified, including "black metallics" 25 (22), hematite with some limonite 18 (25), epidote 21 (27)%, etc. The relative abundance of volcanic glass is evidently due to its concn. by suspension in the air. The 1934 dust came from the northern plains, and that of 1935 from the south. L. J. S.

**Concentration of  $D_2O$  in natural ice.** II. E. BARONI and A. FINK (Monatsh., 1935, 67, 131—36; cf. A., 1935, 953).—Results of determinations of  $D_2O$  in samples of ice taken systematically from definite parts of glaciers (Caucasus) are given. Variations of 50 to +25% from the normal are recorded. F. L. U.

**Mineral waters of Harrogate.** A. WOODMANSEY (Analyst, 1936, 61, 23—26).—The composition,

pharmacology, transport, and storage of the waters are discussed. E. C. S.

**Analysis of water from Torrente Iungari, Calabria.** B. RICCA and P. MEDURI (Annali Chim. Appl., 1935, 25, 571—586).—Chemical, physico-chemical, and bacteriological data are given and the therapeutic val. of the  $H_2O$  is discussed. F. O. H.

**Chemical and biological aspects of Orbetello lagoon water.** I, II. C. M. MALDURA (Atti R. Accad. Lincei, 1935, [vi], 22, 64—68, 140—145).—I. Data for annual variations in temp., salinity, and oxygenation are given and discussed.

II. Data for variations in temp., salinity,  $pH$ , alkalinity, and content of  $Cl^-$ ,  $SO_4^{2-}$ ,  $O_2$ ,  $NH_3$ ,  $NO_2^-$ , and  $NO_3^-$ -N, P, and Si are tabulated. F. O. H.

**Hydrogen-ion concentration and temperature of surface waters of several seas.** R. C. MILLER (Proc. V Pacific Sci. Congr., 1934, 3, 2111—2113).—The  $pH$  varied from 8.23 to 8.03. CH. ABS. (e)

**Determination and quantity of boron in sea-water.** M. W. HARDING and E. G. MOBERG (Proc. V Pacific Sci. Congr., 1934, 3, 2093—2095).—The B in sea-water is titrated in presence of mannitol. The content was 4.3—4.8 mg. of B per kg. of sea-water. CH. ABS. (e)

**Probable role of boron in the buffer mechanism of sea-water.** R. REVELLE and E. G. MOBERG (Proc. V Pacific Sci. Congr., 1933, 3, 2147—2151).—The modification of the buffer relations of sea-water by borates is discussed. CH. ABS. (e)

**Simultaneous change in chemical composition of sea-water and *Mytilus crassitesta*, Lischke, influenced by season.** K. HAYASHI (Proc. V Pacific Sci. Congr., 1934, 3, 2069—2071).—The correlation between changes in the composition of sea-

for Cs 8521 and 8944 Å. The mineral is mixed with NaCl and evaporated in the C arc. Saturation of the arc with Na ions secures evaporation under comparable conditions. Comparison is made with known Cs and Rb contents, or with Ba and Li. In agreement with the authors' views and the large ionic radius of Cs and Rb, Cs and Rb are enriched relatively to Ca and Na in magmatic rocks and sedimentary rocks. J. S. A.

The pair chalcostibite-empлектite, and the agreement between dimensions of unit cells and the crystallographic parameters. M. H. UNGEMACH (Bull. Soc. franç. Min., 1934, 57, 186—207; Chem. Zentr., 1935, i, 2657).—Agreement with X-ray and crystallographic data for emplectite is obtained by a choice of new co-ordinate axes for chalcostibite. J. S. A.

Determination of the specific volume of fused masses at temperatures up to 1400°. M. P. VOLAROVITSCH and A. A. LEONTJEVA (Z. anorg. Chem., 1935, 225, 327—332).—By a dilatometric method, the sp. vol. of the rocks diorite, basalt, and diabase, and the salts  $K_2SiO_3$ ,  $NaBO_2$ , and  $K_2B_4O_7$ , in the fused state, has been determined at different temp. and the expansion coeff. calc. M. S. B.

Distribution of useful metals in the earth's crust. I. NODDACK and W. NODDACK (Angew. Chem., 1936, 49, 1—5).—A discussion. E. S. H.

Determination of activity of rocks with the tube counter. J. N. HUMMEL (Nach. Ges. Wiss. Göttingen, 1935, [ii], 1, 73—81; Chem. Zentr.,

1935, i, 2643—2644).—The Geiger counter is applied to the determination of the radioactivity of rocks. Separation of the effects of the Th and U families is possible only under (under-ground) conditions of screening from cosmic radiation. J. S. A.

Radioactivity of rocks in the Far East and its influence on forests. L. L. LAGUNOV (Bull. Far East. Branch Acad. Sci. U.S.S.R., 1934, No. 9, 105—109).—Increase in radioactivity of soil increases self-seeding, growth, and the no. of trees per unit area. CH. ABS. (e)

Enelectrite, a new mineral found in chemawinitite. T. L. WALKER (Univ. Toronto Studies, Geol. Ser., 1934, No. 36, 11—12).—The mineral (hydrocarbon?) forms colourless, lath-shaped monoclinic crystals. CH. ABS. (e)

Chemawinitite or Canadian amber. T. L. WALKER (Univ. Toronto Studies, Geol. Ser., 1934, No. 36, 5—10).—Cedarite and chemawinitite are identical. Physical properties are recorded. Analysis gave C 81.40, H, 10.70, O 7.23, N 0.02, ash 0.65%. CH. ABS. (e)

Distribution of sulphur in Illinois coals and its geological implications. G. H. CADY (Ill. State Geol. Survey, Rept. Invest., 1935, No. 35, 23—41).—Data are discussed. CH. ABS. (e)

Influence of structural irregularities on the chemical character of No. 6 coal in Franklin and Williamson counties, Illinois. E. T. BENSON and G. H. CADY (Ill. State Geol. Survey, Rept. Invest., 1935, No. 35, 5—22). CH. ABS. (e)

## Organic Chemistry.

Tautomerism. B. NILSEN (Tidsskr. Kjemi, 1935, 15, 145—150).—A review. M. H. M. A.

Hydrogenation of unsaturated compounds. N. K. JURASCHEVSKI (J. Gen. Chem. Russ., 1935, 5, 1098—1107).—Addition of  $H_2$  (Pd on Ni) to the second double linking of geraniol and linalyl acetate commences before complete saturation of the first, whilst in limonene (I) the two processes proceed simultaneously. The following pairs of substituted ethylenes behave similarly to (I): stilbene-benzoyl-eugenol (II), allyl alcohol (III)— $CHPh:CH \cdot CO_2Na$  (IV); in the pairs (IV)—pulegone (V), fumaric acid (VI)—(V), (V)— $CHMe:CM_e$ , (III)—(VI), (III)—(IV), (IV)—(I),  $CHPh:CH \cdot CO_2Me$  (VII)—(IV), and (VII)— $CHPh:CH \cdot CO_2H$  the second component is hydrogenated after complete or almost complete saturation of the first. The pair (II)—(IV) occupies an intermediate position. R. T.

Determination of butadiene by condensation with quinones. A. B. DOLGOPLOSK (Sintet. Kautschuk, 1934, No. 2, 29—31).—The rectified butadiene was bubbled through a solution of benzoquinone in PhOH at 120°. The condensation product is 1:4:5:8-tetrahydroanthraquinol. The method is applicable in presence of other olefines,  $Et_2O$ , and  $MeCHO$ . CH. ABS. (e)

Polymerisation products of normal ( $\Delta^2$ -) pentene at high temperature. H. I. WATERMAN, J. J. LEENDERTSE, and J. DE HULSTER (J. Inst. Petroleum Tech., 1935, 21, 952—958).—The polymerised product obtained from  $\Delta^2$ -pentene by treatment with  $AlCl_3$  at 0° did not undergo any appreciable change by heating at 200° (a) in presence of a Ni catalyst in  $N_2$ , or (b) in presence of  $H_2$  without a catalyst; hence with Ni and  $H_2$  it is probable that the mol. structure remains unaltered. At 300°, however, depolymerisation occurs under conditions (a) and (b). Rapid hydrogenation (high-pressure  $H_2$ ; Ni) protects the product from destruction, the product being similar to that obtained at 200° under the same conditions. At 435° an unsaturated and cyclic liquid product (with increased no. of rings) was obtained under conditions (a), whereas under (b) considerable destruction was also observed, but the total no. of rings had not appreciably changed. Under conditions (a) and (b) the higher-mol. fraction contained more rings per mol. than the raw material. C. C.

Reaction between sulphur dioxide and olefines. III. Higher olefines. Limitations of the reaction. L. L. RYDEN and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 2311—2314; cf. A., 1935, 1349).—*iso*- $C_4H_8$ ,  $\Delta^2$ - and  $\Delta^3$ -pentene,  $\Delta^2$ -nonene,  $\gamma$ -cyclohexylpropene, and 3-methylcyclohexene give



alcoholic polysulphones, m.p. (block) 340°, 290—300° (215—220° in a tube), 340°, >300°, 330°, and 270°, respectively, but further substitution on the ethylenic linking hinders addition. Mol. wt. determination by means of the Cl content of the  $\text{CH}_2\text{Cl}\cdot\text{CO}$  and  $\text{CCl}_3\cdot\text{CO}$  derivatives is inaccurate owing to difficulties of purification and low Cl content; mol. wts. are about 100,000—200,000. The N content of the anilide of propylenepolysulphone indicates a mol. wt. of about 50,000. Undecenyl alcohol and  $\Delta^8$ -heptenene give polysulphones, darkens at 330° ( $\text{CH}_2\text{Cl}\cdot\text{CO}$  derivative) and m.p. 160—169°, respectively. R. S. C.

$\alpha\gamma$ -Disubstituted allene.  $\Delta^{8\gamma}$ -Hexadiene. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1935, 44, 593—596).—Hexane- $\gamma\delta$ -diol with  $\text{PBr}_3$  affords the  $\gamma\delta$ -dibromide and  $\gamma$ -bromo- $\Delta^7$ -hexene, b.p. 49.0—49.2°/26 mm., which with KOH in  $\text{CH}_2\text{Ph}\cdot\text{OH}$  gives  $\Delta^{8\gamma}$ -hexadiene, b.p. 67.75—68.25°/760 mm.

J. L. D.

Chloroform-*d* (deuteriochloroform). F. W. BREUER (J. Amer. Chem. Soc., 1935, 57, 2236—2237).— $\text{CCl}_3\cdot\text{CHO}$  and  $\text{D}_2\text{O}$  give the deuterate (I), which with NaOD gives deuteriochloroform, m.p. —64.69° to —64.15°, b.p. 0.5° > that of  $\text{CHCl}_3$ . Physical data are given. (I) and NaOD are less sol. in  $\text{D}_2\text{O}$  than are  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$  and NaOH, respectively, in  $\text{H}_2\text{O}$ . R. S. C.

Synthesis of  $\alpha\beta$ -dichlorobutadiene, and its polymerisation. A. L. KLEBANSKI, A. S. VOLKENSCHTEIN, and A. P. ORLOVA (J. Gen. Chem. Russ., 1935, 5, 1255—1267).— $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$ , b.p. 55—57°, obtained in 57% yield by shaking  $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$  with aq. NaOCl for 10 hr. at room temp., yields  $\alpha\beta$ -dichloro- $\Delta^{\alpha\gamma}$ -butadiene (I), b.p. 60—65°/105 mm., when shaken with  $\text{CuCl}+\text{NH}_4\text{Cl}$  in 50% HCl (16 hr., room temp.); the structure of (I) is established by treating it with  $\text{O}_3$ , when  $\text{CHCl}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$  is obtained. (I) polymerises spontaneously at room temp., to yield a gelatinous product, sol. in org. solvents; the velocity of polymerisation is intermediate between that of chloroprene and chlorobutadiene, and increases with rising temp. and intensity of illumination. An ebonite-like product is obtained by hot-pressing the mixture (I) 5, MgO 1, ZnO 0.25, neozone 0.1, and colophony 0.25 pts.

R. T.

Initial formation of methyl alcohol in the oxidation of methane. W. A. BONE (Nature, 1935, 136, 910).—Small amounts of MeOH (0.13%) and  $\text{CH}_2\text{O}$  (0.03%) have been detected in the suddenly-cooled products of the explosion of a  $5\text{CH}_4+2\text{O}_2$  mixture at an initial pressure of approx. 50 atm. L. S. T.

Presence of active *sec*-butyl alcohol in fermentation propyl alcohols. Qualitative and quantitative analysis by Raman spectra. G. DUPONT and R. DULOU (Bull. Soc. chim., 1935, [v], 2, 2156—2163).—Samples of supposedly pure fermentation ProH are shown by Raman spectra to contain up to 19% of *l*-*sec*-BuOH. R. S. C.

South American drugs. I. Bixol. II. *Canavalia obtusifolia*.—See this vol., 123.

Application of the xanthic reaction to the dehydration of di-tertiary  $\alpha$ -glycols. V. A. FOMIN (J. Gen. Chem. Russ., 1935, 5, 1192—1194).— $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OK}$  in xylene and  $\text{CS}_2$  (100°; 4 hr.), followed by addition of MeI and further heating (100°; 6 hr.), yield the substance  $\begin{matrix} \text{CMe}\cdot\text{O} \\ | \\ \text{CMe}\cdot\text{O} \end{matrix} > \text{CS}$ , m.p. 156°, converted into pinacolin,  $\text{H}_2\text{S}$ , and  $\text{CO}_2$  by heating with  $\text{H}_2\text{SO}_4$ . R. T.

Reaction of ethylene oxide with acetylenic Grignard reagents. J. P. DANEHY, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1935, 57, 2327).—The Grignard reagent from 2 mols. of  $\Delta^8$ -heptenene (I) with  $(\text{CH}_2)_2\text{O}$  gives  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ , (I), and  $\Delta^7$ -heptenen- $\alpha$ -ol. The reagents from  $\Delta^8$ -hexinene and  $\text{CH}\cdot\text{CPh}$  react similarly. R. S. C.

Acetylene polymerides and their derivatives. XXIII. Preparation and polymerisation of oxy-prenes [ $\beta$ -alkoxybutadienes]. H. B. DYKSTRA (J. Amer. Chem. Soc., 1935, 57, 2255—2259; cf. A., 1935, 1480).—Me  $\beta$ -alkoxyethyl ketones and alkyl orthoformates give  $\alpha\gamma\gamma$ -trialkoxybutanes (I), which at >130° afford  $\beta$ -alkoxybutadienes (termed oxy-prenes). At lower temp. with acid catalysts unsaturated ketals (II),  $\text{CH}_2\text{:CH}\cdot\text{CMe}(\text{OR})_2$ , with basic catalysts  $\alpha\gamma$ -dialkoxy- $\Delta^8$ -butenes (III), are formed. Below the dissociation temp. (II) and (III) add alcohols, phenols, and thiophenols to give (I) and its S derivatives, mixed oxy-prenes being thus obtainable. Oxy-prenes alone polymerise very slightly in several months; in ultra-violet light at room temp. *ethoxy*prene ( $\beta$ -ethoxybutadiene) (IV) gives in 7 days 20% of rubbery polymeride (VI) only; at 100° (daylight) in 6 days 15% of polymerisation [1 part of liquid, largely dimeric polymeride and 3 of (VI)] occurs, at 130° 100% [equal parts of liquid and (VI)] in 2 weeks; certain catalysts, notably I and HCN, rapidly produce liquid polymerides of low mol. wt., metal halides and AcOH produce resins;  $\text{SnCl}_4$  acts explosively. (VI) is plastic and sol. in EtOAc and  $\text{C}_6\text{H}_6$ , but lacks the resilience of rubber; with hot dil. HCl it gives a polymeride,  $(\text{C}_4\text{H}_6\text{O})_x$ . Structures are established by reactions given below, but some doubt attaches to those of (III). The following are described.  $\alpha\gamma\gamma$ -*Tri-methoxy*-, b.p. 61—63°/20 mm., -*ethoxy*- (VII), b.p. 75°/9 mm., and -*n*-butoxy-*n*-butane, b.p. 120°/3 mm. *Me vinyl ketone*  $\text{Me}_2$ , b.p. 98—100°, *Et*, (VIII), b.p. 69°/100 mm.,  $\text{Bu}^{\alpha\alpha}_2$ , b.p. 79—80°/8 mm., and  $\text{Ph}_2$  ketal, b.p. 81°/2 mm.  $\alpha\gamma$ -*Di-ethoxy*- (IX), b.p. 101°/100 mm., and -*ethoxy*- $\Delta^8$ -butene, b.p. 91—93°/4 mm. *ethoxy*-, b.p. 75°, and -*n*-butoxy-*butadiene*, b.p. 65°/54 mm., and (IV), b.p. 96.5°, called *methoxy*prene etc. (IV) and EtOH at 100 or 130° give (VII), and with  $(\text{CH}_2\cdot\text{OH})_2$  at 110° gives a substance (—*hydroxyethoxybutadiene* or  $\text{CH}_2\text{:CH}\cdot\text{CMe}\begin{matrix} \text{O}\cdot\text{CH}_2 \\ | \\ \text{O}\cdot\text{CH} \end{matrix}$ ), b.p. 56°/100 mm.; PhOH and PhSH add on at room temp. (IV) and naphthaquinone give a product, oxidised to 2-ethoxyanthraquinone, m.p. 136° (lit. 135°). With  $\text{H}_2$ -PtO<sub>2</sub>-EtOH (IV) is only partly hydrogenated, yielding  $\beta$ -ethoxy- $\Delta^8$ - or - $\Delta^8$ -butene or a mixture thereof. With dil. HCl (IV) and (VIII) give  $\text{CH}_2\text{:CH}\cdot\text{COMe}$ . (VIII) and  $\text{H}_2$ -PtO<sub>2</sub> give 40% of  $\text{CMeEt}(\text{OEt})_2$ . (IX) with dil.

HCl gives  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$  and with  $\text{KMnO}_4$   $\text{AcOH}$  and  $\text{EtOAc}$ . Physical data are given.

R. S. C.

**Ester condensation and keten acetals.** F. ADICKES and M. MEISTER (Ber., 1935, 68, [B], 2191—2205).—Contrary to Scheibler (cf. A., 1926, 711; 1927, 338, 1051; 1929, 1296, etc.), no intermediate products are known between the ether enolates, which probably play a part in the reaction, and the enolates of the reaction products. A definite "primary reaction product" does not exist, and theories based thereon and on its fission to keten  $\text{Et}_2$  acetal are devoid of experimental foundation. The distillate from Scheibler's "primary product" consists of  $\text{EtOH}$ , the "acetal" reaction of which depends on the presence of small and varying amounts of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ . Treatment of the "primary product" in  $\text{Et}_2\text{O}$  with  $\text{CO}_2$  shows it to be mainly a mixture of  $\text{NaOEt}$  and  $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COEt}$ ; a substance  $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}+\text{EtOH}$  or  $\text{EtOAc}+\text{NaOEt}$  is not present. Similar observations apply to the condensation of  $\text{PhCHO}$  with  $\text{EtOAc}$ . Repetition of Scheibler's condensation of  $\text{CHPhK}\cdot\text{CO}_2\text{Et}$  with  $\text{BzCl}$  or  $\text{ClCO}_2\text{Et}$  shows that the supposed *o*-benzoylphenylketen acetal is *Et*  $\beta$ -benzoyloxy- $\alpha\beta$ -diphenylacrylate (I), m.p.  $103^\circ$ , the constitution of which is established by analysis, determination of  $\text{OEt}$ , hydrolysis by  $\text{KOH}\cdot\text{EtOH}$  to  $\text{BzOH}$  (2 mols.) and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  (1 mol.), and by conc.  $\text{H}_2\text{SO}_4$  alone or in presence of  $\text{AcOH}$  to  $\text{BzOH}$  (1 mol.) and  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$  (1 mol.). (I) is converted by  $\text{NHPh}\cdot\text{NH}_2$  into benzphenylhydrazide and 1:3:4-triphenylpyrazol-5-one, m.p.  $204\text{--}205^\circ$ . Hydrogenation ( $\text{PtO}_2$ ) of (I) leads to *Et*  $\beta$ -benzoyloxy- $\alpha\beta$ -diphenylpropionate (II), m.p.  $170^\circ$ , also obtained by use of  $\text{Al}\cdot\text{Hg}$  in moist  $\text{Et}_2\text{O}$  and hydrolysed by  $\text{KOH}\cdot\text{EtOH}$  to  $\text{BzOH}$  and phenylcinnamic acid, m.p.  $171^\circ$ . (I) is obtained synthetically by addition of  $\text{BzCl}$  to the enolate from  $\text{CHPhBz}\cdot\text{COEt}$  and powdered  $\text{K}$  or  $\text{NaNH}_2$  in  $\text{Et}_2\text{O}$ , whilst (II) is readily prepared from  $\text{BzCl}$  and  $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$  in  $\text{C}_5\text{H}_5\text{N}$ . When heated above its m.p., (I) is converted into a second (?) polymorphic variety, m.p.  $112^\circ$ . A third, obviously stereoisomeric form, m.p.  $105^\circ$ , which cannot be isomerised by heat, is not hydrogenated in presence of  $\text{Pt}$  and only incompletely reduced by  $\text{Al}$  in moist  $\text{Et}_2\text{O}$ , is obtained from  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$  and  $\text{BzCl}$  in  $\text{CHCl}_3\text{--C}_5\text{H}_5\text{N}$ ; it is almost quantitatively hydrolysed by conc.  $\text{H}_2\text{SO}_4$  to  $\text{BzOH}$  and  $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$ . *Et*  $\alpha\beta$ -dibromo- $\alpha\beta$ -diphenylpropionate, m.p.  $81\text{--}82^\circ$ , is incidentally described. Scheibler's pyrolytic product is identified as 4:6-diketo-5-benzoyl-2:3:5-triphenyl-5:6-dihydropyran (III), m.p.  $200\text{--}201^\circ$ , converted by conc.  $\text{H}_2\text{SO}_4$  into 4:6-diketo-2:3:5-triphenyl-5:6-dihydropyran, m.p.  $236^\circ$  (*K* salt), which gives (III) with  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  and is transformed by  $\text{AcCl}$  in  $\text{CHCl}_3\text{--C}_5\text{H}_5\text{N}$  into 4:6-diketo-5-acetyl-2:3:5-triphenyl-5:6-dihydropyran (IV), m.p.  $182^\circ$ . (III) or (IV) is transformed by conc.  $\text{NH}_3$  at  $160^\circ$  into 4:6-dihydroxy-2:3:5-triphenylpyridine, m.p.  $288\text{--}289^\circ$  (*K* salt;  $\text{Ac}_2$  derivative, m.p.  $143\text{--}144^\circ$ ). The product of the action of  $\text{ClCO}_2\text{Et}$  on  $\text{CHPhK}\cdot\text{CO}_2\text{Et}$  (Scheibler's *o*-carbethoxyphenylketen acetal) is identified as  $\text{CHPh}(\text{CO}_2\text{Et})_2$  mixed with  $\text{CPh}(\text{CO}_2\text{Et})_3$ ; the product decolorises

$\text{KMnO}_4\text{--Na}_2\text{CO}_3$ , which is not suitable for the identification of keten acetals.

H. W.

**Isotopic exchange reactions of organic compounds. I. Intermolecular nature of three-carbon tautomerism.** D. J. G. IVES and H. N. RYDON (J.C.S., 1935, 1735—1742).—The partition of D and H between butyric (I), crotonic (II), and vinylacetic (III) acids and dil.  $\text{D}_2\text{O}$  at  $100^\circ$  in presence of 1.05 mol. of  $\text{NaOH}$  is studied using a new method of isotopic analysis depending on *d* determinations accurate to 1 p.p.m. As (III) shows appreciable isotopic interchange with the solvent, whilst (I) and (II) do not, it is concluded that purely intramolecular mechanisms for this type of three-C tautomerism are unacceptable.

F. N. W.

**Configurative relationships of phenylmethyl- and methylhexyl-acetic acids. Correlation of the configurations of  $\alpha$ -hydroxy-acids with those of disubstituted acetic acids containing a methyl group.** P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 112, 195—208).—Correlation is established in the series,  $\text{CHMeRR'}$ , in which  $\text{R}=\text{Et}$  or  $\text{CO}_2\text{H}$  and  $\text{R'}=\text{Ph}$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2$ ,  $\text{C}_6\text{H}_{13}$ ,  $\text{C}_6\text{H}_{15}$ ,  $\text{C}_6\text{H}_{11}$ ,  $\text{C}_6\text{H}_{11}\cdot\text{CH}_2$ , or  $\text{C}_6\text{H}_{11}[\text{CH}_2]_2$ . Speculations are given concerning correlation of the series,  $\text{OH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  and  $\text{OH}\cdot\text{CHRR'}$ , with those,  $\text{CHMeR}\cdot\text{CO}_2\text{H}$  and  $\text{CHMeRR'}$ , respectively ( $\text{R}$  and  $\text{R'}=\text{alkyl}$ ,  $\text{aryl}$ , and  $\text{aralkyl}$ ).  $\text{CHMeEt}\cdot\text{CO}_2\text{Et}$ ,  $[\alpha]_D^{25} -7.11^\circ$ , and  $\text{MgBr}[\text{CH}_2]_5\cdot\text{MgBr}$  give 60% of  $\eta$ -methyl- $\Delta^8$ -nonen- $\zeta$ -ol (dibromide, b.p.  $161^\circ/4$  mm.) and 40% of 1-sec.-butylcyclohexan-1-ol, which on distillation gives  $\text{H}_2\text{O}$  and 1-1-sec.-butyl- $\Delta^1$ -cyclohexene, b.p.  $172\text{--}174^\circ$ ,  $[\alpha]_D^{25} -4.06^\circ$ , hydrogenated ( $\text{PtO}_2$ ) in abs.  $\text{EtOH}$  to d-sec.-butylcyclohexane, b.p.  $176\text{--}178^\circ$ ,  $[\alpha]_D^{25} +0.59^\circ$ .  $\text{C}_5\text{H}_{11}\cdot\text{MgBr}$  (from  $\text{C}_5\text{H}_{11}\text{Br}$ ,  $[\alpha]_D^{25} +2.40^\circ$ ) and  $\text{C}_6\text{H}_{13}\cdot\text{CHO}$  give  $\gamma$ -methylundecan- $\epsilon$ -ol, b.p.  $70\text{--}75^\circ/0.1$  mm.,  $[\alpha]_D^{25} +3.54^\circ$ , converted into the iodide, b.p.  $88^\circ/1$  mm.,  $[\alpha]_D^{25} +5.85^\circ$ , and thence (Raney  $\text{Ni}$ ) into  $\gamma$ -methylundecane, b.p.  $94^\circ/15$  mm.,  $[\alpha]_D^{25} +3.87^\circ$ .

R. S. C.

**Acetylenes. II. Pharmacological properties of the acetylenic linking.** G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2167—2168; cf. A., 1935, 193).— $\beta$ - $\text{NEt}_2\cdot\text{C}_2\text{H}_4$  octoate, b.p.  $162\text{--}164^\circ/20$  mm.,  $\Delta^8$ -octenoate, b.p.  $171\text{--}173^\circ/20$  mm., and  $\Delta^8$ -octinenate, b.p.  $150\text{--}152^\circ/7$  mm.,  $\text{NEt}_2[\text{CH}_2]_3$  octoate, b.p.  $178\text{--}181^\circ/20$  mm.,  $\Delta^8$ -octenoate, b.p.  $183\text{--}186^\circ/20$  mm., and  $\Delta^8$ -octinenate, b.p.  $164\text{--}166^\circ/7$  mm., and  $\text{NBu}_2[\text{CH}_2]_3$  octoate, b.p.  $212\text{--}215^\circ/20$  mm.,  $\Delta^8$ -octenoate, b.p.  $217\text{--}220^\circ/20$  mm., and  $\Delta^8$ -octinenate, b.p.  $193\text{--}195^\circ/7$  mm., are prepared.  $\Delta^8$ -Octenoyl chloride (prep. by  $\text{SOCl}_2$ ) has b.p.  $109\text{--}111^\circ/30$  mm. Physical data are given. The effectiveness of aliphatic novocaine analogues as local anaesthetics is, within limits,  $\propto$  the mol. wt. of the alcoholic component and inversely  $\propto$  the degree of unsaturation of the acid.

R. S. C.

**Direct esterification of higher fatty acids with glycerol and with ethylene glycol.** T. P. HILDITCH and J. G. RIGG (J.C.S., 1935, 1774—1778).—A mixture of mono- (I) and di-glycerides in which the latter predominate is obtained by the interaction of higher fatty acids and excess (10:1) of glycerol (II) at  $140\text{--}$



160° and reduced pressure. The yield of (I) [ $\alpha$ -monolaurin (100%), -palmitin (93%), -stearin (82%), -olein (95%)] is greatly increased by using an inert solvent (PhOH), and camphor- $\beta$ -sulphonic acid (III) (about 0.1%) as catalyst. Increase in the time or temp. of reaction or in the amount of (III) increases the total yield, but lowers the yield of (I), whilst a preponderance of (II) favours the formation of (I). Identical results, but higher yields, are obtained by using  $(\cdot\text{CH}_2\cdot\text{OH})_2$  in place of (II). F. N. W.

**Seeds of *Allanblackia klainei*.**—See this vol., 258.

**Crystalline substance from oil of *Lachnophyllum gossypinum*, Bge.**—See this vol., 259.

**Destructive distillation of calcium oleate and undecenoate.** G. BREUER and K. WEINMANN (Monatsh., 1935, 67, 42—50).—Ca oleate at 130—170°/15 mm. gives oleones, m.p. 58.5°, and liquid (*oxime* of the latter, an oil), and a little *hydroxyheptadecyl heptadecenyl ketone*, m.p. 60.5°, which with  $\text{H}_2\text{SO}_4$  give *di(hydroxyheptadecyl) ketones*, m.p. 89°, 90°, and 86°, respectively (possibly identical). Ca undecenoate at 90—120°/20 mm. gives *didecenyl ketone*, m.p. 51°.

R. S. C.

**Elaidinisation of oleic acid and *cis-trans* isomerism.** S. H. BERTRAM (Chem. Weekblad, 1936, 33, 3—5).—0.03—0.1% of Se at 150—200° is a most powerful catalyst for elaidinising unsaturated oils and fatty acids. Unlike other catalysts, it is very mild in its action and produces no by-products. Elaidinised castor oil is dimorphous, m.p. 47.5° and 55.4°, and has the same  $[\alpha]$  as the original oil. Elaidinisation of oleic acid is a balanced reaction irrespective of the catalyst used, the equilibrium mixture containing 2 mols. of elaidic and 1 mol. of oleic acid. The results are in accordance with the supposition that oleic acid has a *s*-configuration. S. C.

**Polymerisation of fatty oils. XI. Hydrogenation of polymerised ethyl linoleate.** A. STEGER and J. VAN LOON (Fettchem. Umschau, 1935, 42, 217—219; cf. A., 1935, 1482).—Vac.-distilled Et linoleate (I) (prepared from tetrabromolinoleic acid pptd. from the fatty acids of safflower oil) was polymerised by heating at 290° in an atm. of  $\text{CO}_2$  for 15 hr.; the product was saponified, the unsaponifiable matter removed, and the fatty acids were recovered and converted into Et esters, which were examined by fractional distillation and hydrogenation of the principal fractions over Pd-C at 170°/50 atm. and over colloidal Pd in EtOH solution at room temp. at 1 atm. The analyses of the hydrogenated fractions indicate that the polymerised ester contained [in addition to unchanged (I)] low-mol. decomp. products, small amounts ( $\approx 10\%$ ) of a cyclic ester which could not be reduced by  $\text{H}_2$ , high-mol. compounds formed by the combination of several mols. of linoleate and/or decomp. products (also unreducible to stearic acid or its ester), and  $\approx 5\%$  of a conjugated linoleic acid (II); the presence of (II) was confirmed quantitatively by a study (L. N. J. VAN DER HULST) of the ultra-violet absorption spectrum of the polymerised (I). E. L.

**Separation of physeteric acid from sardine and pilot-whale oils.** Y. TOYAMA and T. TSUCHIYA (J.

Soc. Chem. Ind. Japan, 1935, 38, 680—684B).—Physeteric acid has been isolated from sardine and pilot-whale (body) oils, and is shown by oxidation to be the  $\Delta^3$ -tetradecenoic acid.  $\Delta^6$ -Tetradecenoic acid was not isolated. H. G. M.

**Highly unsaturated acids in sardine oil. IX. Constitution of docosahexaenoic acid,  $\text{C}_{22}\text{H}_{32}\text{O}_2$ .**

**X. Separation of highly unsaturated  $\text{C}_{24}$  acids.**

**XI. Constitution of nisinic acid,  $\text{C}_{24}\text{H}_{36}\text{O}_2$ , in sardine oil.** Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 539—543, 543—547, 547—551).—IX. Ozonolysis of amyl docosahexaenoate (A., 1935, 1482) (containing a little amyl clupanodionate) affords  $\text{MeCHO}$ ,  $\text{AcOH}$ ,  $\text{CO}_2$ ,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , and its amyl H ester. Docosahexaenoic acid is therefore either  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{CH}\cdot\text{CH}_2]_4\cdot(\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_2)_3\cdot\text{CO}_2\text{H}$ , or  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2\cdot\text{CH}\cdot\text{CH}]_4\cdot[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ .

X. Separation of the  $\text{C}_{24}$  unsaturated acids (obtained by hydrolysis of the Me ester residues of high b.p.) by the Na salt-COME<sub>2</sub> method (*loc. cit.*), re-esterification and fractionation of the Me esters up to b.p. 215°/2 mm., and hydrolysis and refractionation as Na salts affords nisinic acid (I) (A., 1934, 1381) as the only pure product, but the presence of less saturated acids  $\text{C}_{24}\text{H}_{38}\text{O}_2$  and  $\text{C}_{24}\text{H}_{40}\text{O}_2$  was indicated.

XI. Ozonolysis of the amyl ester of (I) affords  $\text{EtCHO}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{MeCHO}$ , and  $\text{AcOH}$  [as secondary products from  $\text{CH}_2(\text{CO}_2\text{H})_2$ ],  $\text{CO}_2$ ,  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  and its amyl H ester. On the basis of these results the structure  $\text{CHEt}\cdot\text{CH}\cdot[\text{CH}_2\cdot\text{CH}\cdot\text{CH}]_3\cdot[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  is suggested for (I). J. W. B.

**Hydrogenation of fish oil. V. Formation of an unsaturated fatty acid of the linolenic series in the hydrogenation of methyl clupanodionate.** M. TAKANO (J. Soc. Chem. Ind. Japan, 1935, 38, 652—653B).—Me clupanodionate, b.p. 206—208°/0.8 mm., prepared from the acids obtained from sardine oil, when hydrogenated (Ni) affords a product which contains acids of the linoleic and linolenic series. The existence of two isomerides, one giving a tetra- and the other a hexa-thiocyanate, of the linolenic series is suggested. H. G. M.

**Catalytic hydrogenation of acetone compounds of  $\alpha$ -hydroxy-acids.** H. ŌEDA (Bull. Chem. Soc. Japan, 1935, 10, 531—539).—Reduction of the  $\text{CMe}_2\cdot$

derivatives of  $\alpha$ -OH-acids,  $\text{CMe}_2\cdot\begin{smallmatrix} \text{O}\cdot\text{CHR} \\ \text{O}\cdot\text{CO} \end{smallmatrix}$ , with  $\text{H}_2$  and a  $\text{CuO}\cdot\text{BaO}\cdot\text{Cr}_2\text{O}_3$  catalyst at 240—260°/100—120 atm. effects cleavage at both O linkings to give both alcohols and glycols. Thus the *isopropylidene* derivative of *dl*-lactic acid gives  $\text{Pr}^{\beta}\text{OH}$  (I) ( *$\alpha$ -naphthylurethane*, m.p. 104—105°) and  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$  (*bisphenylurethane*, m.p. 143—144°); that of *l*-leucic acid gives (I),  $\text{CH}_2\text{Bu}^{\beta}\cdot\text{CH}_2\cdot\text{OH}$ , and an active *isohexylene glycol*,  $\text{OH}\cdot\text{CHBu}^{\beta}\cdot\text{CH}_2\cdot\text{OH}$ , b.p. 111—113.5°/15 mm. (*bisphenylurethane*, m.p. 115—116°); that of *dl*-mandelic acid gives (I),  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$  (*phenylurethane*, m.p. 78—79°), and an aromatic hydrocarbon containing  $\text{PhEt}$ ; and that of *l*- $\alpha$ -hydroxy- $\beta$ -phenylpropionic acid affords (I),  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  (*phenylurethane*, m.p. 45—46°), active  $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{OH}$  (*phenylurethane*, m.p. 88—89°), and  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$  [*bisphenylurethane*,

obtained in two interconvertible forms *A*, m.p. 108—109° (cryst.), and *B*, m.p. 132—133° (amorphous)].

J. W. B.

**Action of hydrogen peroxide on simple carbon compounds. III. Glycollic acid.** H. S. FRY and K. L. MILSTEAD (J. Amer. Chem. Soc., 1935, 57, 2269—2272; cf. A., 1931, 819).—The  $\text{HCO}_2\text{H}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and unattacked  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I) formed when (I) reacts with acidified  $\text{H}_2\text{O}_2$  give the following percentages of the reactions occurring, the figures recorded being those obtained with 0.5 and 4 mols. of  $\text{H}_2\text{O}_2$ , respectively: (a) 6.3—37%:  $(\text{I}) \rightarrow \text{H}_2\text{O} + \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}_2\text{H} \rightarrow \text{H}_2\text{O} + \text{CHO}\cdot\text{CO}_2\text{H} \rightarrow \text{HCO}_2\text{H} + \text{CO}_2 + \text{H}_2\text{O}$ ; (b) 1.84—12.9%:  $(\text{I}) \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} + \text{CO}_2$ ;  $2\text{CH}_3\text{O} \rightarrow 2\text{HCO}_2\text{H} + \text{H}_2$ ; (c) 23.2—39.9%:  $\text{HCO}_2\text{H} \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$ .

R. S. C.

**Anhydrous glyoxylic acid.** A. TALVITIE (Suomen Kem., 1935, 8, B, 32).—Evaporation of a dil. aq. solution of  $\text{CHO}\cdot\text{CO}_2\text{H}$  over  $\text{H}_2\text{SO}_4$  at room temp./vac., extraction of the residual syrup with dry  $\text{Et}_2\text{O}$  (removes  $\text{CaC}_2\text{O}_4$ ), and re-evaporation of the  $\text{Et}_2\text{O}$  extract over  $\text{H}_2\text{SO}_4$  at room temp./< 1 mm. affords the anhyd. acid.

J. W. B.

**Application of the indophenine test to the detection of polycarboxylic acids.** J. V. SANCHEZ (Farm. moderna, 1935, 46, 58—63).—The aq. solution of the free acid is neutralised with  $\text{Na}_2\text{CO}_3$  (phenolphthalein), and a drop of the solution is evaporated to dryness in a small tube. The residue is heated (120°) and mixed with powdered  $\text{P}_2\text{S}_5$ . A solution of isatin in conc.  $\text{H}_2\text{SO}_4$  is added, and the mixture heated until fusion begins and S sublimes. A green or blue colour indicates the presence of succinic (I), pyrotartaric (II), tartaric, fumaric, maleic, or citric acid. Oxidation with acid  $\text{KMnO}_4$  oxidises all except (I) and (II), which may be detected separately. Glutaric, adipic, suberic, azelaic, and sebatic acids interfere and may be removed with  $\text{Pb}(\text{OAc})_2$ .

CH. ABS. (p)

**Detection of oxalate ions.** N. A. TANANAEV and A. A. BUDKEVITSCH (Z. anal. Chem., 1935, 103, 353—355).—To the test solution, acidified aq.  $\text{K}_2\text{Cr}_2\text{O}_7$  is added, followed by indigotin (I). In presence of  $\text{C}_2\text{O}_4^{2-}$  ( $\leq 10^{-4}N$ ), decolorisation occurs, due to the induced mutual oxidation of  $\text{C}_2\text{O}_4^{2-}$  and (I).  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$  must first be removed by boiling with  $\text{H}_2\text{SO}_4$ .  $\text{C}_2\text{O}_4^{2-}$  may alternatively be pptd. as  $\text{CaC}_2\text{O}_4$ , which is dissolved in  $\text{H}_2\text{SO}_4$  and detected by the decolorisation of 0.01*N*- $\text{KMnO}_4$ .

J. S. A.

**Potentiometric determination of oxalates with silver nitrate.** P. SPACU (Z. anal. Chem., 1935, 103, 272—274).— $\text{C}_2\text{O}_4^{2-}$  may be titrated potentiometrically with  $\text{AgNO}_3$  in 60% aq.  $\text{EtOH}$ .

J. S. A.

**Optical activity. IV. Racemisation of the optically active oxalates.** C. H. JOHNSON. V. Racemisation of the strychnine salts of *d*- and *l*-chromioxalate in the crystalline state. C. H. JOHNSON and A. MEAD. VI. Racemisation of potassium chromioxalate in aqueous solution. The accelerating influence of ions. N. W. D. BEESE and C. H. JOHNSON (Trans. Faraday Soc., 1935, 31, 1612—1621, 1621—1632, 1632—1642; cf. A., 1933, 114, 581, 585).—IV. The optical activity

and racemisation of compounds of the type  $\text{M}_3[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]$  are discussed. The experimental evidence accepted as supporting the theory of secondary ionisation in racemisation is untrustworthy and based on a misconception, since if ionisation were responsible for loss of rotatory power it could not be determined by ordinary chemical methods for compounds racemising at measurable rates. The racemisation of chromi- and cobalti-oxalates in the cryst. state suggests that intramol. rearrangement may occur in solution as well as in the crystals. The racemisation of these compounds is greatly accelerated by presence of  $\text{H}_2\text{O}$ .

V. The velocity of racemisation of tristrychnine *d*- and *l*-chromioxalates at 47.7—100° has been studied. The loss of rotatory power occurs principally after dehydration. The mechanism of the intramol. rearrangement is discussed.

VI.  $(\text{C}_2\text{O}_4)^{2-}$  does not affect the rate of racemisation of  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ , this being in accord either with the racemisation being a measure of the rate of ionisation, or with racemisation not involving ionisation. Loss of optical activity is accelerated by positive ions, the more so the higher is the valency of the ions. The results indicate that the  $\text{Hg}^{\text{I}}$  ion is  $\text{Hg}_2^{2+}$ . The effects of adding  $\text{CaCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{CuCl}_2$  have been studied in detail.

J. W. S.

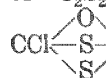
**Oxalates and formates in organic fluids.** M. PITTARELLI (Minerva Med., 1935, 1, 428—429).—Mg powder converts  $\text{H}_2\text{C}_2\text{O}_4$  into  $\text{CHO}\cdot\text{CO}_2\text{H}$ , and  $\text{HCO}_2\text{H}$  into  $\text{CH}_2\text{O}$ . On adding  $\text{NHPh}\cdot\text{NH}_2$  and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , and making alkaline with  $\text{NaOH}$ , the Pittarelli test is obtained. The red-violet colour is extractable with amyl alcohol. If Mg salts are present, a blue-violet lake is formed. CH. ABS. (e)

**Complex formation with malonates.**—See this vol., 160.

**Hydrogenation of aldonic  $\delta$ - and  $\gamma$ -lactones and of aldoses.** J. W. E. GLATTFIELD and G. W. SCHIMPF (J. Amer. Chem. Soc., 1935, 57, 2204—2208).—The best yields of aldoses by hydrogenation of aldonic lactones are obtained in 0.2*M* aq. solution with moderate amounts of catalyst and rapid agitation.  $\gamma$ -Lactones give more alcohol than do  $\delta$ -lactones. Aldoses give 63—80% of alcohols.

R. S. C.

**Dimeride of thiocarbonyl chloride and its derivatives, chloro-oxysulphide,  $\text{C}_2\text{S}_2\text{OCl}_2$ , and a new chlorosulphide,  $\text{C}_2\text{S}_3\text{Cl}_2$ .** M. DELÉPINE, L. LABRO, and F. LANGE (Bull. Soc. chim., 1935, [v], 2, 1969—1980).—The structure of  $\text{C}_2\text{S}_2\text{Cl}_4$  (I) is discussed (cf. A., 1933, 487). By the action of  $\text{EtOH}$  on (I) the compound, probably  $\text{S}(\text{CS}\cdot\text{Cl})_2$ , m.p. 58—59°, is obtained. The prep. and properties of  $\text{C}_2\text{S}_2\text{OCl}_2$  are described, and the structure



it affords the following thiuram oxides:  $\text{Me}_4$ , m.p. 79°;  $(\text{CH}_2\text{Ph})_4$ , m.p. 100—101°;  $\text{Ph}_2\text{Me}_2$ , m.p. 116°;  $\text{Ph}$ , *Et*, m.p. 147.5—148°; *di*-*o*-tolyl dimethyl-, m.p. 93—94°; diphenyl dibenzyl-, m.p. 128.5—129.5°; *di*-*o*-anisyl dimethyl-, m.p. 158°.

O. J. W.



Catalytic action of monoses on the form-aldehyde condensation. III. Intermediate products of the reaction. A. KUSIN (Ber., 1935, 68, [B], 2169—2173; cf. A., 1935, 733, 1224).—Attempts to isolate the intermediate products of the catalysis of the  $\text{CH}_2\text{O}$  condensation are unsuccessful when glucose or fructose is used as accelerator, but succeed if benzoin (I), which behaves analogously, is employed. The mechanism,  $\text{OH}\cdot\text{CR}\cdot\text{CR}\cdot\text{OH} + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CR}(\text{OH})\cdot\text{CH}(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}\cdot\text{CR}\cdot\text{CO}\cdot\text{R}$  (II);  $(\text{II}) + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CR}(\text{OH})\cdot\text{CO}\cdot\text{R} + \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{R} + \text{OH}\cdot\text{CH}\cdot\text{CH}(\text{OH})_2$  (III);  $(\text{III}) - \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$  (IV);  $(\text{IV}) + \text{CH}_2(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})_2$  etc., is suggested. (I) and  $\text{CH}_2\text{O}$  with  $\text{Ca}(\text{OH})_2$  in  $\text{H}_2\text{O}-\text{MeOH}-\text{EtOH}$  at  $37-40^\circ$  afford *benzoylphenylhydroxymethylcarbinol* (V), m.p.  $85.5^\circ$ , also obtained from (I),  $\text{CH}_2\text{O}$ , and  $\text{NaOH}$  in  $\text{EtOH}$ , which contains 2 OH (Zerevitinov) and with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  gives the compound  $\text{C}_{21}\text{H}_{18}\text{O}_4\text{N}_3$ , m.p.  $166.5^\circ$ . In 50%  $\text{EtOH}$  (V) gives a feeble fuchsin- $\text{H}_2\text{SO}_3$  reaction, and immediately reduces Fehling's solution (to Cu),  $\text{Ag}_2\text{O}-\text{NH}_3$ , and dichlorophenol-indophenol in alkaline but not in acid solution. (V) exactly resembles (I) in accelerating the  $\text{CH}_2\text{O}$  condensation with formation of sugar-like products; it is converted into (I) during the change.

H. W.

Thermal decomposition of certain gaseous organic compounds. M. W. TRAVERS (Nature, 1935, 136, 909—910).—Processes involved in the thermal decomp. of  $\text{MeCHO}$  and  $(\text{CH}_2)_2\text{O}$  are further discussed (cf. A., 1935, 708). Additional experiments support the view that the reactions depend on the surface of the system and involve a chain mechanism.

L. S. T.

Volumetric determination of carbonyl compounds. II. Determination of acetaldehyde by the hydrogen sulphite method. S. HAHNEL (Svensk Kem. Tidskr., 1935, 47, 275—285; cf. A., 1935, 1390).—The direct determination of  $\text{MeCHO}$  by  $\text{I}-\text{HSO}_3'$  gives more reproducible results than the indirect method. The formation of acetals in aq. alcoholic solutions has been studied, and methods for the determination of free and total  $\text{MeCHO}$  in such solutions are given. For the reaction  $\text{CHMe}(\text{OEt})_2 + \text{H}_2\text{O} \rightleftharpoons \text{CHMe}(\text{OH})\cdot\text{OEt} + \text{EtOH}$ ,  $K=0.94$ .

M. H. M. A.

$\beta$ -Chloropropaldehyde and its derivatives. A. KIRRMANN, M. GOUDARD, and M. CHAHIDZADEH (Bull. Soc. chim., 1935, [v], 2, 2143—2152).—The halogen of  $\beta$ -halogenopropaldehydes is very labile, but elimination of  $\text{HCl}$  often takes precedence over exchange reactions.  $\text{CH}_2\cdot\text{CH}\cdot\text{CHO}$  (I) and dry  $\text{HCl}$  at  $-10^\circ$  give  $\beta$ -chloropropaldehyde (II), b.p.  $130-131^\circ$  ( $\text{NaHSO}_3$  compound, from which it cannot be recovered), the  $\text{Me}_2$  acetal, b.p.  $51^\circ/19$  mm., of which with  $\text{HCl}$  gives  $\alpha\gamma$ -dichloro- $\alpha$ -methoxypropane (III), b.p.  $55^\circ/19$  mm.  $\beta$ -Bromopropaldehyde ( $\text{NaHSO}_3$  compound, from which it cannot be recovered) could not be obtained pure, but yielded a mixture of  $\beta$ -bromo- (IV), b.p.  $58-60^\circ/17$  mm., and  $\beta$ -methoxypropaldehyde  $\text{Me}_2$  acetal, b.p.  $45-46^\circ/17$  mm.,  $146^\circ/760$  mm., and  $\alpha\gamma$ -dibromo- $\alpha$ -methoxypropane, b.p.  $15^\circ/16$  mm. (II) with  $\text{NaOAc}$  or  $\text{NaOEt}$  loses  $\text{HCl}$  to re-form (I), but with  $\text{Ac}_2\text{O}$  gives the diacetate, m.p.  $43^\circ$ ,

$\alpha$ -chloroallyl acetate, and the trimeride, m.p.  $36^\circ$ . (IV) loses  $\text{HBr}$  with  $\text{NaOAc}$ ,  $\text{NaOMe}$ , or  $\text{Ag}_2\text{O}$ , but with  $\text{NHET}_2$  in hot  $\text{COMe}_2$  gives  $\beta$ -dimethylamino-propaldehyde  $\text{Me}_2$  acetal, b.p.  $85^\circ/16$  mm.  $\beta$ -Cyano-propaldehyde  $\text{Me}_2$  acetal, b.p.  $93^\circ/17$  mm., with  $\text{MgMeBr}$  gives laevulaldehyde  $\text{Me}_2$  acetal, b.p.  $85^\circ/16$  mm. (IV) does not react with  $\text{MgMeBr}$ , but (III) gives  $\alpha$ -chloro- $\gamma$ -methoxy- $n$ -butane, b.p.  $125^\circ$ , and with  $\text{MgPhBr}$  affords  $\alpha$ -chloro- $\gamma$ -methoxy- $\gamma$ -phenylpropane (V), b.p.  $113-114^\circ/16$  mm. (III) and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  give  $\alpha$ -methoxy- $\alpha\gamma$ -diphenylpropane, m.p.  $34^\circ$ , also obtained in traces similarly from (V). (III) does not react readily with  $\text{Mg}$  in hot  $\text{Et}_2\text{O}$  or  $\text{Bu}_2\text{O}$ . R. S. C.

Phytochemical reduction of lactaldehyde. E. OCHIAI and K. MIYAKI (Biochem. Z., 1935, 282, 293—296).—The production of optically inactive propylene glycol using a Japanese bottom yeast is described.

P. W. C.

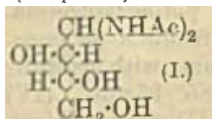
Constitution of dimeric keten. W. R. ANGUS, A. H. LECKIE, C. G. LE FÈVRE, R. J. W. LE FÈVRE, and A. WASSERMANN (J.C.S., 1935, 1751—1755).—The dipole moment ( $3.15$  at  $25^\circ$  in  $\text{C}_6\text{H}_6$ ;  $3.30$  in  $\text{CCl}_4$ ), mol. refraction, and heat of combustion ( $447.1$  kg.-cal. per mol. in the liquid and  $456 \pm 2$  kg.-cal. per mol. in the gaseous state) of dimeric keten favour the view that it exists predominately in the keto-enol form. Dissolution has little effect on the Raman spectrum, and therefore presumably on the constitution.

F. N. W.

Preparation of acyloins of high mol. wt. V. L. HANSLEY (J. Amer. Chem. Soc., 1935, 57, 2303—2305).—The appropriate ester and  $\text{Na}$  (2 atoms) in hot  $\text{PhMe}$  or xylene give 80—95% yields of the acyloins,  $\text{R}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$ , in which  $\text{R}=\text{C}_8\text{H}_{17}$ , m.p.  $45^\circ$ ,  $\text{C}_9\text{H}_{19}$ , m.p.  $51-62^\circ$  (osazone, m.p.  $79-80^\circ$ ),  $\text{C}_{11}\text{H}_{23}$  (I), m.p.  $61-62^\circ$  (osazone, m.p.  $61-63^\circ$ ),  $\text{C}_{13}\text{H}_{27}$ , m.p.  $71-72^\circ$  (osazone, m.p.  $44-46^\circ$ ),  $\text{C}_{15}\text{H}_{31}$ , m.p.  $77-78^\circ$ , and  $\text{C}_{17}\text{H}_{35}$ , m.p.  $82-83^\circ$ ; those in which  $\text{R}=\text{Me}$ ,  $\text{Pr}^a$ , m.p.  $-10^\circ$  (osazone, m.p.  $140-141^\circ$ ), and  $\text{C}_5\text{H}_{11}$ , m.p.  $9^\circ$  (osazone, m.p.  $119-120^\circ$ ), are best prepared in  $\text{Bu}^a_2\text{O}$  or  $\text{Bu}^n_2\text{O}$ . Oxidation of (I) gives *di-n-undecyl ketone*, m.p.  $71-72.5^\circ$ . Hydrogenation (Pt at room temp or Ni at  $125-150^\circ$ ) affords the glycols,  $(\text{OH}\cdot\text{CHR})_2$ , in which  $\text{R}=\text{C}_{17}\text{H}_{35}$ , m.p.  $123-124^\circ$  (diacetate),  $\text{C}_{13}\text{H}_{27}$ , m.p.  $124^\circ$  (diacetate),  $\text{C}_{11}\text{H}_{23}$ , m.p.  $125-126^\circ$  (diacetate),  $\text{C}_7\text{H}_{15}$ , m.p.  $129-130^\circ$  (diacetate),  $\text{C}_5\text{H}_{11}$ , m.p.  $135-136^\circ$ , and  $\text{Pr}$ , m.p.  $123-124^\circ$ . R. S. C.

Tetrose sugars. I. Crystalline triacetate of *d*-threose from the degradation of strontium xylonate with hydrogen peroxide. Nomenclature in the tetrose group. II. Degradation of *d*-xylose by Wohl's method. Rotation of *d*-threose. R. C. HOCKETT (J. Amer. Chem. Soc., 1935, 57, 2260—2264, 2265—2268).—I. By electrolytic oxidation xylose yields *Sr d*-xylonate,  $+5\text{H}_2\text{O}$ ,  $[\alpha]_D +13.2^\circ$  in  $\text{H}_2\text{O}$ , oxidised by  $\text{Fe}_2(\text{SO}_4)_3-\text{Ba}(\text{OAc})_2$  to *d*-threose triacetate, m.p.  $117-118^\circ$  (corr.),  $[\alpha]^{20} +35.55^\circ$  in  $\text{CHCl}_3$ , which by  $\text{NaOMe}$  at  $<0^\circ$  yields solutions of *d*-threose (I),  $[\alpha]^{20} -12.3^\circ$  in  $\text{H}_2\text{O}$ . Errors in nomenclature, due to overlooking Fischer's error in calling *d*-xylose *l*-xylose, are corr. The name erythritol should be confined to the inactive alcohol, the active tetrils being named *d*- and *l*-threitol.

II. *d*-Xylose oxime (syrupy mixture) with  $\text{Ac}_2\text{O}$  (dropwise) in dioxan gives tetra-acetyl-*d*-xylonitrile, m.p. 81–82° (corr.),  $[\alpha]_D^{20} +50.3^\circ$  in  $\text{CHCl}_3$ , which with conc. aq.  $\text{NH}_3$  yields diacetamido-*d*-threose (I), m.p. 165–167° (corr.),  $[\alpha]_D^{20} -10.86^\circ$  in  $\text{H}_2\text{O}$  (triacetate, m.p. 179–180°,  $[\alpha]_D^{20} +74.2^\circ$  in  $\text{CHCl}_3$ ), which gives (I) with  $[\alpha]$  as stated. R. S. C.

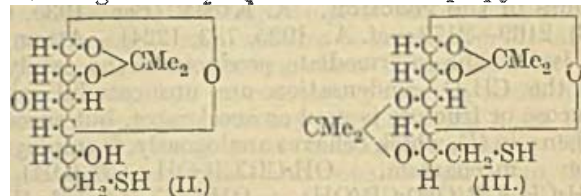


Detosylation [deacylation] of isopropylidene-*l*-methylrhamnoside-4- and -5-*p*-toluenesulphonates. P. A. LEVENE and J. COMPTON (J. Amer. Chem. Soc., 1935, 57, 2306–2316).—The high-boiling fraction obtained on alkaline hydrolysis of isopropylidene-*l*-methylrhamnoside 5-*p*-toluenesulphonate (I) is isopropylidene-*l*-methylrhamnopyranoside (II), derived from pyranoside present in (I) (cf. Muskat, A., 1935, 199). The following data appear new. (I), m.p. 82–83°,  $[\alpha]_D^{20} -13.6^\circ$  in MeOH. isopropylidene-*l*-methylpyranoside 4-*p*-toluenesulphonate, m.p. 61–62°,  $[\alpha]_D^{24} +21.94^\circ$  in MeOH. (II), b.p. 84–85°/0.3 mm.,  $[\alpha]_D^{25} -21.3^\circ$  in MeOH. The ring structure of the *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivatives is proved by their relative rates of hydrolysis. R. S. C.

Carbohydrates and furfuraldehyde. II. Reactions with  $\beta$ -methylglucoside and glucose; preparation of  $\beta$ -methylglucoside 2:3-diacetate. H. BREDERECK (Ber., 1935, 68, [B], 2299–2302; cf. A., 1935, 847).—Furfuraldehyde (I) containing a little  $\text{HNO}_3$  (*d* 1.20) and anhyd. glucose at 170–175° yield a non-cryst. product which when treated with  $\text{Ac}_2\text{O}$  and anhyd. NaOAc at 100° affords  $\beta$ -4:6-furfurylidene-glucose 1:2:3-triacetate (II), m.p. 203–204°,  $[\alpha]_D^{25} -46.6^\circ$  in  $\text{CHCl}_3$ , in modest yield. The constitution of (II) is established by elimination of (I) and transformation of the product into non-cryst.  $\beta$ -6-triphenylmethylglucose 1:2:3-triacetate, converted by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into  $\beta$ -6-triphenylmethylglucose 1:2:3:4-tetra-acetate, m.p. 165–166°,  $[\alpha]_D^{25} +48.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Similarly (I) and  $\beta$ -methylglucoside at 170–175° yield 4:6-furfurylidene- $\beta$ -methylglucoside, m.p. 160–162°,  $[\alpha]_D^{25} -97.2^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , transformed by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into 4:6-furfurylidene- $\beta$ -methylglucoside 2:3-diacetate, m.p. 205–207°,  $[\alpha]_D^{25} -85.1^\circ$  in  $\text{CHCl}_3$ , which is converted by  $\text{HCl}\cdot\text{EtOH}$  at 60° into  $\beta$ -methylglucoside 2:3-diacetate, m.p. 109–111°,  $[\alpha]_D^{25} -51.8^\circ$  in  $\text{CHCl}_3$ , whence  $\beta$ -methylglucoside 2:3-diacetate 4:6-dibenzoate, m.p. 167–168°,  $[\alpha]_D^{25} -11.8^\circ$  in  $\text{CHCl}_3$ . 4:6-Furfurylidene- $\alpha$ -methylmannoside and  $\text{PhCHO}$  do not react when heated in  $\text{CO}_2$ ; when shaken in presence of  $\text{ZnCl}_2$  they yield dibenzylidene- $\alpha$ -methylmannoside. H. W.

Syntheses with 5:6-anhydroisopropylidene-glucose. I. 6-Thiol-*d*-glucose, *d*-glucomethylglucose-6-sulphonic acid, and 6-acyl derivatives of isopropylideneglucose. H. OHLE and W. MERTENS [with, in part, M. ANDREE and E. EULER] (Ber., 1935, 68, [B], 2176–2187).—The action of  $\text{H}_2\text{S}$  on an aq. solution of  $\text{Ba}(\text{OH})_2$  and 5:6-anhydroisopropylideneglucose (I) at 0° rapidly affords isopropylidene-6-thiogluco-*d*-glucose (II), m.p. 96–97°, b.p. 200–220°/high vac.,  $[\alpha]_D^{21} -18.2^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{20} -14.35^\circ$  in  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{20} -11.87^\circ$  in  $\text{COMe}$ , (triacetate, m.p. 69°,  $[\alpha]_D^{20} +44.15^\circ$  in  $\text{CHCl}_3$ ). The position of SH in (II) is

established, since (I) is transformed by  $\text{COMe}$ , containing conc.  $\text{H}_2\text{SO}_4$  at 20° into diisopropylidene-6-



thiogluco-*d*-glucose (III), b.p. 120° (bath)/0.06 mm., m.p. 7.4°,  $[\alpha]_D^{20} +16.67^\circ$  in  $\text{CHCl}_3$ , which contains a free SH and with  $\text{HgCl}_2$  gives a white ppt. similar to but not identical with that yielded by (II). S is retained so firmly in (II) and (III) that it cannot be removed without fundamental alteration of the mol. The acidity of SH is slight; the alkali mercaptides are extensively hydrolysed in  $\text{H}_2\text{O}$ , and a marked tendency to autoxidation is absent. 6-Thiogluco-*d*-glucose could not be obtained cryst.; it gives ill-defined products with  $\text{NHPh}\cdot\text{NH}_2$ . Acetylation in  $\text{C}_5\text{H}_5\text{N}$  gives a mixture of penta-acetates from which 6-thio- $\beta$ -glucose penta-acetate, m.p. 123°,  $[\alpha]_D^{20} -14.5^\circ$  in  $\text{CHCl}_3$ , is isolated in small amount; the mixture does not give a cryst. product with  $\text{HBr}\cdot\text{AcOH}$  or  $\text{TiCl}_4$ . (II),  $\text{NaHCO}_3$ , and I afford 1:2-1':2'-diisopropylidenedi-*d*-glucosyl 6:6'-disulphide, m.p. 127°,  $[\alpha]_D^{20} -7.1^\circ$  in  $\text{CHCl}_3$  (tetra-acetate, m.p. 121°), which is hydrolysed to non-cryst. di-*d*-glucosyl 6:6'-disulphide, the non-homogeneous octa-acetate of which is transformed by  $\text{HBr}\cdot\text{AcOH}$  into  $\alpha\alpha'$ -hexa-acetyldi-*d*-glucosyl 6:6'-disulphide 1:1'-dibromohydrin, m.p. 160°,  $[\alpha]_D^{20} +193.2^\circ$  in  $\text{CHCl}_3$ . (I) condenses with (II) in boiling  $\text{C}_5\text{H}_5\text{N}$  containing  $\text{C}_5\text{H}_5\text{N}$  giving 1:2-1':2'-diisopropylidenedi-*d*-glucosyl 6:6'-sulphide, m.p. 125–126°,  $[\alpha]_D^{20} +9.3^\circ$  in  $\text{CHCl}_3$  (tetra-acetate, m.p. 122°); non-cryst. di-*d*-glucosyl 6:6'-sulphide, its non-homogeneous octa-acetate and  $\alpha\alpha'$ -hexa-acetyldi-*d*-glucosyl 6:6'-sulphide 1:1'-dibromohydrin, m.p. 175°,  $[\alpha]_D^{20} +231.1^\circ$  in  $\text{CHCl}_3$ , are described. Exhaustive oxidation of (II) with  $\text{Br}\cdot\text{NaHCO}_3$  or preferably with alkaline  $\text{KMnO}_4$  leads to *d*-glucomethylglucose-6-sulphonic acid (*K* salt,  $[\alpha]_D^{20} +59.5^\circ$  to  $+38.1^\circ$  in  $\text{H}_2\text{O}$ ; *K* salt of  $\text{Ac}_4$  derivative,  $[\alpha]_D^{20} +65.9^\circ$  in  $\text{H}_2\text{O}$ ) best characterised as the phenylhydrazine salt of the phenylosazone, m.p. 168–170°,  $[\alpha]_D^{20} -66.6^\circ$  to  $-39.2^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Addition of H halide to (I) is not possible in  $\text{H}_2\text{O}$  on account of the readier hydrolysis, and is complicated in  $\text{C}_5\text{H}_5\text{N}$  by the formation of quaternary salts. The adducts are, however, readily isolated in modest yield when acetylation occurs simultaneously, and thus are obtained diacetylisopropylidene-glucose 6-chlorohydrin, m.p. 129°,  $[\alpha]_D \pm 0^\circ$  in  $\text{CHCl}_3$ , the corresponding bromohydrin, m.p. 115°,  $[\alpha]_D^{20} -8.49^\circ$  in  $\text{CHCl}_3$ , and iodohydrin, m.p. 74–75°,  $[\alpha]_D^{20} -22^\circ$  in  $\text{CHCl}_3$ , in each of which the halogen is very firmly retained. Addition of carboxylic acid occurs when a few drops of  $\text{C}_5\text{H}_5\text{N}$  are added to a mixture of the components at 140°, the acid residue occupying position 6. Sulphonic acids are not added similarly. (I) and  $\text{MgMeI}$  could not be caused to react. H. W.

Improved preparation of diisopropylidene-glucose. D. J. BELL (J.C.S., 1935, 1874–1875).—Diisopropylideneglucose (72% yield) is obtained



by the interaction of glucose and  $\text{COMe}_2$  in presence of 4% of  $\text{H}_2\text{SO}_4$  during 5 hr. F. N. W.

**Fructose anhydride from the leaves of the barley plant.**—See this vol., 258.

**Advantageous preparation of isoglucosamine; catalytic hydrogenation of osazones.** K. MAURER and B. SCHLEDT (Ber., 1935, 68, [B], 2187—2191).—Hydrogenation of glucosazone in  $\text{AcOH-EtOH-H}_2\text{O}$  containing Pd acetate at room temp./3 atm. readily yields 1-aminofructose (isoglucosamine) acetate (I), m.p.  $137^\circ$ ,  $[\alpha]_D^{20} -63.7^\circ$  in  $\text{H}_2\text{O}$  (corresponding oxalate,  $[\alpha]_D^{20} -58.5^\circ$  in  $\text{H}_2\text{O}$ , and sparingly sol. *reineckate*). Treatment of (I) with  $\text{NH}_2\text{Et}$  in  $\text{MeOH}$  rapidly affords 2:5-ditetrahydroxybutylpyrazine, m.p.  $236^\circ$ ,  $[\alpha]_D^{20} -79.60^\circ$  in  $\text{H}_2\text{O}$  (identical with fructosepyrazine from fructose and  $\text{NH}_3$ ), which with  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  gives the *octa-acetate*, m.p.  $176^\circ$ ,  $[\alpha]_D^{20} -6.22^\circ$  in  $\text{CHCl}_3$ . Glucosazone *tetra-acetate* has m.p.  $116^\circ$ ,  $[\alpha]_D^{20} -57.22^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ . Similar hydrogenation of acetophenone-ketazine leads to *s-di- $\alpha$ -phenylethylhydrazine* (*hydrochloride*, m.p.  $174^\circ$ ; *sulphate*, m.p.  $236^\circ$ ; *reineckate*), transformed by  $\text{NPh:C:O}$  into 4-phenyl-1:2-di- $\alpha$ -phenylethylsemicarbazide. H. W.

**Crystalline *d*- $\alpha$ -galaheptose and its derivatives.** R. M. HANN, (Miss) A. T. MERRILL, and C. S. HUDSON (J. Amer. Chem. Soc., 1935, 57, 2100—2103).—*d*- $\alpha$ -Galaheptose (I) closely resembles the configuratively related mannose in chemical and physical properties. The prep. of *d*- $\alpha$ -galahepton-amide and -lactone, *d*- $\alpha$ -galaheptonic acid (optical behaviour recorded; Na salt,  $+\text{H}_2\text{O}$ ,  $[\alpha]_D^{20} +9.7^\circ$  in  $\text{H}_2\text{O}$ ), and (I) is improved. The following derivatives of (I) are prepared:  $\beta$ -*Me*, cryst.,  $[\alpha]_D^{20} -70.2^\circ$  in  $\text{H}_2\text{O}$  (*penta-acetate*, m.p.  $108^\circ$ ),  $[\alpha]_D^{20} -20.4^\circ$  in  $\text{CHCl}_3$ , and  $\beta$ -*Et d*- $\alpha$ -galaheptoside, m.p.  $138^\circ$ ,  $[\alpha]_D^{20} -65.4^\circ$  in  $\text{H}_2\text{O}$  (*penta-acetate*, m.p.  $92^\circ$ ,  $[\alpha]_D^{20} -24.9^\circ$  in  $\text{CHCl}_3$ ); *benzylthiol* derivative, m.p.  $191^\circ$ ,  $[\alpha]_D^{20} +30.3^\circ$  in  $\text{C}_6\text{H}_5\text{N}$  (*hexa-acetate*, m.p.  $120^\circ$ ,  $[\alpha]_D^{20} -10.6^\circ$  in  $\text{CHCl}_3$ , and *benzoate*, m.p.  $129^\circ$ ,  $[\alpha]_D^{20} -48.1^\circ$  in  $\text{CHCl}_3$ ). M.p. are corr. R. S. C.

**Caramelisation of sucrose.** A. JOSZT and S. MOLINSKI (Biochem. Z., 1935, 282, 269—276).—By heating sucrose in vac. (3—5 mm.) up to 10% wt. loss at a bath temp. just above the m.p. of sucrose ( $187.5-189.5^\circ$ ), no gaseous but only liquid substances separated, consisting largely of  $\text{H}_2\text{O}$  and 20% of dry substance which is chiefly  $\omega$ -hydroxymethylfurfuraldehyde. P. W. C.

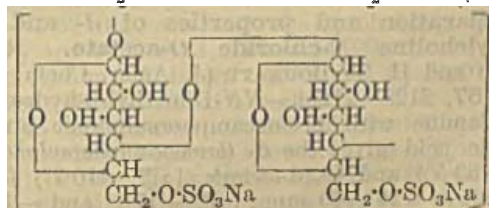
**Syntheses in the sugar series. II. Derivatives of cellobiose.** J. BRSKO and H. ZAK (Monatsh., 1935, 67, 111—117; cf. A., 1930, 583).—Hepta-acetylcellobiosidyl bromide with the appropriate Ag salt in dry xylene gives the *thiocyanate*, m.p.  $201^\circ$ ,  $[\alpha]_D^{19} -7.48^\circ$  in  $\text{EtOAc}$ , *phthalimide*, m.p.  $141-142^\circ$ , and *theophyllide*, m.p.  $174^\circ$  after sintering at  $165^\circ$ ,  $[\alpha]_D^{19} +14.1^\circ$  in  $\text{EtOAc}$ , all unstable in  $\text{H}_2\text{O}$ ; the cyanide and theobromide could not be obtained. 1-Menthylcellobioside *hepta-acetate*, m.p.  $163-165^\circ$ ,  $[\alpha]_D^{18} -11.2^\circ$  in  $\text{EtOAc}$ , was prepared, but the *d*-bornyl, vanillyl, and thymyl glucosides are unobtainable.  $[\alpha]$  are for white light. R. S. C.

**Polysaccharides synthesised by micro-organisms. II. Molecular structure of varianose produced from glucose by *Penicillium varians*,**

G. SMITH. W. N. HAWORTH, H. RAISTRICK, and M. STACEY (Biochem. J., 1935, 29, 2668—2678).—The mould grown in Czapek-Dox medium at  $24^\circ$  containing glucose yields a polysaccharide, *varianose* (I),  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ ,  $[\alpha]_D^{20} +15^\circ$  in  $\text{H}_2\text{O}$ , reducing Fehling's solution slightly and giving no colour with I. Hydrolysis with  $\text{HCl}$  affords galactose. The  $(1c_3)_n$  derivative,  $[\alpha]_D^{20} +30.0^\circ$  in  $\text{CHCl}_3$ ,  $+38.2^\circ$  in  $\text{COMe}_2$ , is homogeneous. Complete methylation of (I) or its acetate gives the  $(Me_3)_n$  derivative, m.p.  $90-100^\circ$ ,  $[\alpha]_D^{22} +20^\circ$  in  $\text{CHCl}_3$ ,  $+23^\circ$  in  $\text{C}_6\text{H}_6$ ,  $[\alpha]_D^{20} +15^\circ$  in  $\text{H}_2\text{O}$ , hydrolysed ( $\text{MeOH-HCl}$ ) to 2:3:4:6-tetramethylmethylglucopyranoside [14%; corresponding with a chain of 8 hexose members of mol. wt. 1300 for (I)] and trimethylmethylgalactoside (70%) which hydrolyses to a trimethylgalactose (II). (II) is oxidised by Br to a trimethyl- $\gamma$ -galactonolactone (III), m.p.  $99^\circ$  (amide, m.p.  $135^\circ$ ), and methylated by  $\text{MeI}$  to tetramethylmethylgalactoside, b.p.  $95/0.05$  mm., hydrolysed to a mixture of the pyranose (isolated as anilide, m.p.  $198^\circ$ ) and furanose forms of tetramethylgalactose. This indicates (III) to be the 2:3:6-isomeride (cf. A., 1932, 1113). Methylation of (I) also yields a trimethylmethylhexoside, hydrolysed to a trimethylhexose (IV), oxidised by Br to a trimethylhexono- $\gamma$ -lactone, b.p.  $110-115/0.04$  mm. (*Me* derivative; *phenylhydrazide*, m.p.  $175^\circ$ ), which on further oxidation ( $\text{HNO}_3$ ) and treatment with  $\text{NH}_3$  affords oxamide and *d*-dimethoxysuccinamide. Methylation of (IV) yields a tetramethylmethylhexoside, b.p.  $90-95/0.03$  mm., hydrolysis and subsequent oxidation of which affords a tetramethylhexonolactone (*phenylhydrazide*, m.p.  $172^\circ$ ). (IV) appears to be a derivative of either *d*-idose or *l*-altrose. Hence (I) is a chain of 6—8  $\beta$ -galactopyranose units with a glucopyranose unit at one end of the chain and a unit of either *l*-altrose or *d*-idose at the reducing end. F. O. H.

**Structure of deoxyriboside of thymus-nucleic acid.** K. MAKINO (Biochem. Z., 1935, 282, 263—264).—The author's earlier result (A., 1935, 772) according to which deoxyribosenucleoside from ox intestine must possess a pyran structure, since it gives a positive  $\text{H}_3\text{BO}_3$  test, is now negated in view of the fact that the pure nucleosides (hypoxanthine-, guanine-, and thymine-deoxyribosides) all give negative  $\text{H}_3\text{BO}_3$  reactions. P. W. C.

**Structure of [the mono]sodium sulphate ester of galactan from *Iridaea laminarioides* (Rhodophyceae).** W. Z. HASSID (J. Amer. Chem. Soc., 1935, 57, 2046—2050).—This ester (I) is probably as shown. It gives a  $Me_2$  derivative and  $Me_2$  ether (II),  $[\alpha]_D^{19}$



$+17.2^\circ$  in  $\text{CHCl}_3$ , is hydrolysed by hot 0.5N- $\text{H}_2\text{SO}_4$  or 5% aq.  $\text{Ba(OH)}_2$  to a galactan,  $[\alpha]_D^{19} +82.2^\circ$  in  $\text{H}_2\text{O}$ , the  $Me_2$  ether,  $[\alpha]_D^{19} +32.4^\circ$  in  $\text{H}_2\text{O}$ , of which with hot 2N- $\text{HCl}$  gives a trimethylgalactose (III), b.p.  $94/0.1$  mm. (III) does not give an osazone and,

when oxidised successively by Br and  $\text{HNO}_3$  and then esterified, gives *Me<sub>2</sub> arabodimethoxyglutarate*, b.p.  $115^\circ/0.1$  mm. Hydrolysis of (II) by 2%  $\text{H}_2\text{SO}_4$  affords a reducing monosaccharide, which with  $\text{HCl-MeOH}$  affords a *methylidimethylgalactoside*,  $[\alpha]_D^{20} +97.2^\circ$  in  $\text{H}_2\text{O}$ . When titrated, (I) behaves as the salt of a strong acid. Its mol. wt. is determined in  $\text{H}_2\text{O}$ .

R. S. C.

**Specific polysaccharide from the bacillus Calmette-Guerin (BCG).**—See this vol., 248.

**Constitution of starch and mode of action of starch-splitting enzymes.** W. ZIESE (Z. Spiritus-ind., 1936, 59, 3—4).— $\beta$ -Diasatase has no action on  $\text{PO}_4$ -free hydroxyethylstarch (I), whilst the action of  $\alpha$ -diasatases is restricted to the production of non-reducing derivatives of high mol. wt. The latter fact, together with viscosity measurements during the hydrolysis of (I) by  $\alpha$ -diasatases, indicates that other factors besides principal valency are concerned in the constitution of (I). Further, the distinctions between the dextrinising and saccharifying actions of diastase are thus emphasised.

I. A. P.

**Importance of Svedberg's ultracentrifuge for the determination of the mol. wt. of cellulose.** M. ULMANN (Cellulosechem., 1935, 16, 114—118).—A lecture.

R. S. C.

**Preparation and properties of double chlorides and bromides of bivalent nickel and of organic bases.** J. AMIEL (Compt. rend., 1935, 201, 1198—1200).—The following compounds, for which a co-ordination structure cannot yet be assigned, are prepared by evaporating conc. solutions of the mixed Ni and org. halides:  $\text{NiCl}_2 \cdot \text{NH}_3 \cdot \text{MeCl}$ ;  $\text{NiCl}_2 \cdot \text{NH}_3 \cdot \text{EtCl}$ ;  $\text{NiCl}_2 \cdot \text{NH}_3 \cdot \text{Pr}^i \text{Cl}$ ;  $2\text{NiCl}_2 \cdot (\text{C}_2\text{H}_5)_2\text{NH}_3 \cdot \text{Cl}_2$ , anhyd. or  $+6\text{H}_2\text{O}$ ;  $\text{NiCl}_2 \cdot \text{C}_3\text{H}_7\text{N} \cdot \text{HCl}$ ;  $\text{NiCl}_2 \cdot \text{C}_5\text{H}_{10}\text{N} \cdot \text{HCl}$ ;  $2\text{NiCl}_2 \cdot \text{C}_4\text{H}_8(\text{NH}_2)_2$ , anhyd. or  $+6\text{H}_2\text{O}$ ;  $\text{NiCl}_2 \cdot \text{C}_6\text{H}_7\text{N} \cdot \text{HCl}$ ;  $\text{NiBr}_2 \cdot \text{NH}_3 \cdot \text{MeBr}$ ;  $\text{NiBr}_2 \cdot \text{NH}_3 \cdot \text{EtBr}$ ;  $\text{NiBr}_2 \cdot \text{NH}_3 \cdot \text{Pr}^i \text{Br}$ ;  $2\text{NiBr}_2 \cdot (\text{CH}_3)_2\text{NH}_3 \cdot \text{Br}_2$ ;  $\text{NiBr}_2 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HBr}$ ;  $\text{NiBr}_2 \cdot \text{C}_6\text{H}_9\text{N} \cdot \text{HBr}$ ;  $2\text{NiBr}_2 \cdot \text{C}_4\text{H}_8(\text{NH}_2)_2$ , anhyd. or  $+6\text{H}_2\text{O}$ ;  $\text{NiBr}_2 \cdot \text{C}_6\text{H}_7\text{N} \cdot \text{HBr}$ . When heated the above decompose without melting. In solution the only Ni ions detected are  $\text{Ni}^{++}$ .

E. W. W.

**Preparation of ethyleneimine from ethanolamine.** H. WENKER (J. Amer. Chem. Soc., 1935, 57, 2328).— $(\text{CH}_2)_2\text{NH}$ , b.p.  $55-56.5^\circ$ , is readily prepared by heating  $\text{OH} \cdot \text{C}_2\text{H}_4 \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4$  at  $250^\circ$  and boiling the resulting  $\text{NH}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{SO}_3\text{H}$  with 40% aq. NaOH.

R. S. C.

**Preparation and properties of *d*- and *l*- $\beta$ -methylcholine *N*-chloride *O*-acetate.** R. T. MAJOR and H. T. BOUNATT (J. Amer. Chem. Soc., 1935, 57, 2125—2126).—*NN*-Dimethyl- $\beta$ -hydroxy-*n*-propylamine with bromocamphorsulphonic and *d*-tartaric acid gives the *d*- (bromocamphorsulphonate,  $[\alpha]_D^{20} +83.5^\circ$ ) and *l*- (*d*-tartrate,  $[\alpha]_D^{20} -10.7^\circ$ ) forms, b.p.  $124.5-126^\circ/770$  mm.,  $[\alpha]_D^{20} +17.1^\circ$  and  $-14.8^\circ$ , respectively, which lead to the *d*- and *l*-forms of  $\beta$ -methylcholine, m.p.  $165-167^\circ$ ,  $[\alpha]_D^{20} +38.8^\circ$ ,  $-38.2^\circ$  (iodide, m.p.  $176.5-177.5^\circ$ ,  $[\alpha]_D^{20} \pm 24.7^\circ$ ), and  $\beta$ -methylcholine *N*-chloride *O*-acetate, m.p.  $201-202^\circ$ ,  $[\alpha]_D^{20} +41.9^\circ$ ,  $-41.3^\circ$ .

R. S. C.

**Hydrogenation of carbon dioxide. Correction of the reported synthesis of urethanes.** M. W. FARLOW and H. ADKINS (J. Amer. Chem. Soc., 1935, 57, 2222—2223).— $\text{CO}_2$  and  $\text{H}_2$  in presence of amines and Raney Ni at  $80-150^\circ$  or brass at  $250^\circ$  gives  $\text{HCO}_2\text{H}$  (as amine formate) and  $\text{HCO}$ -derivatives (of primary bases). In presence of brass *s*-di-( $\beta$ -phenylethyl)- and *s*-di-*n*-amyl-carbamide, m.p.  $88^\circ$ , are also obtained. The following are incidentally described. *N*-Formyl-*n*-amylamine, b.p.  $124-125^\circ/10$  mm., and  $\beta$ -phenylethylamine, b.p.  $180-181^\circ/14$  mm.; formates of  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{NH}_2$ , m.p.  $128-129^\circ$  (decomp.), 4-hydroxy-2:2:6:6-tetramethylpiperidine, m.p.  $207^\circ$  (decomp.), and  $\alpha$ -phenylpropyl- $\beta$ -amine, m.p.  $160^\circ$  (decomp.). The so-called pentamethyleneurethanes previously recorded (cf. A., 1935, 70) are const.-boiling mixtures of formylpiperidine ( $\text{HgCl}_2$  compound, m.p.  $147-148^\circ$ ) and ROH.

R. S. C.

**Multivalent amino-acids and polypeptides.** V. Cystinecyamidene. J. P. GREENSTEIN (J. Biol. Chem., 1935, 112, 35—38; cf. A., 1935, 1203).—Di- $\alpha$ -guanidinopropionic acid  $\gamma$ -disulphide and conc. HCl give the dianhydride, decomp.  $>240^\circ$  (dihydrochloride, m.p.  $150^\circ$ ; monopicate, m.p.  $188^\circ$ ), readily hydrolysed by NaOH at both C-S and C-N linkings to give  $\text{AcCO}_2\text{H}$ .

R. S. C.

**Isolation of homocysteine. Its conversion into a thiolactone.** B. RIEGEL and V. DU VIGNEAUD (J. Biol. Chem., 1935, 112, 149—154).—*S*-Benzoyl-homocysteine and  $\text{Na-NH}_3$  give an 80% yield of homocysteine (I), m.p.  $232-233^\circ$  (corr.) (photomicrograph), converted by acid into the thiolactone [hydrochloride, m.p.  $200-201^\circ$  (corr.); hydriodide, also obtained similarly from methionine]. Lactonisation occurs as follows: with hot 0.1*N*-, 20%, and cold conc. HCl 50% in 3 hr., 100% in a few min., and 50% in 5 min. (100% in 1 hr.), respectively; with conc.  $\text{H}_2\text{SO}_4$  with much oxidation hot, but little cold; with *N*- or 6*N*- $\text{H}_2\text{SO}_4$  mainly ring-closure.

R. S. C.

**Carbon monoxide-ferroglutathione.** F. KUBOWITZ (Biochem. Z., 1935, 282, 277—281).—The ability of Fe to enable glutathione (I) to absorb CO as does ferrocytochrome depends on the concn. of (I). Ferroglutathione (II) itself dissociates. Using a const. concn. of  $\text{Fe}^{++}$  salt and increasing the amount of (I), the amount of (II) and of CO absorbed increase until finally the Fe becomes saturated with (I) and 2CO are fixed per atom of Fe. CO-(II) is split by visible light into (II)+CO.

P. W. C.

**Formation of amides from nitriles by the action of hydrogen peroxide.** L. McMASTER and C. R. NOLLER (J. Indian Chem. Soc., 1935, 12, 652—653).—Conditions are given for obtaining max. yields of amide from 13 nitriles by  $\text{H}_2\text{O}_2$ .

R. S. C.

**Micro-determination of carbamide in very dilute solutions.** K. W. HOU (Bull. Nat. Acad. Peiping, 1932, 3, No. 5, 7 pp.).—Pptn. with xanthlydrol gives results, of approx. 2% accuracy, with solutions containing 10—100 mg. of  $\text{CO}(\text{NH}_2)_2$  per litre.

CH. ABS. (p)

**Explosion in the preparation of guanidine nitrate from ammonium thiocyanate.** C. SCHOFF and H. KLAPPROTH (Angew. Chem., 1936, 49, 23).—



Gockel's method of prep. (A., 1935, 1111) may lead to an explosion, the cause of which has not been traced.

E. S. H.

[Explosion in the preparation of guanidine nitrate from ammonium thiocyanate.] H. GOCKEL (Angew. Chem., 1936, 49, 23; cf. preceding abstract).—The explosion is probably due to decomp. of  $\text{NH}_4\text{NO}_3$ .

E. S. H.

Separation of guanidine and methylguanidine by naphthalene-2-sulphonic acid. W. C. HESS and M. X. SULLIVAN (J. Amer. Chem. Soc., 1935, 57, 2331–2332).—2-Naphthalenesulphonyl guanidine, m.p. 204–206°, and -methylguanidine, m.p. 101–102°, are prepared. The bases can be separated by these derivatives, since the former is obtained preferentially with a limited amount of alkali.

R. S. C.

Second synthesis of *d*-glutamine. H. NIENBURG (Ber., 1935, 68, [B], 2232–2234).—*d*-Glutamic acid is converted into the Et  $\gamma$ -ester, the carbobenzyloxy-derivative of which is transformed by liquid  $\text{NH}_3$  at 15–20° into *N*-carbobenzyloxy-*d*-glutamine, hydrogenated (Pd–AcOH–EtOH) to *d*-glutamine, m.p. 184–185°,  $[\alpha]_D +8.3^\circ$  in  $\text{H}_2\text{O}$ .

H. W.

Formation of hydrocyanic acid from organic compounds in the presence of ammoniacal copper sulphite. J. PARRON (Compt. rend., 1935, 201, 993–995; cf. A., 1935, 1109).—Besides *d*-fructose, other sugars and allied compounds yield HCN at 58–62°. Lactose, maltose, and rhamnose give HCN only at higher temp. (80–85°). Yields of about 20 mols. of HCN per 100 C atoms in the compound have been obtained. CO and  $\text{CH}_2\text{O}$  do not yield HCN.

F. A. A.

Photolytic and thermal decomposition products of azomethane. Thermal reaction rates in quartz at 260–290°. L. J. HEIDT and G. S. FORBES (J. Amer. Chem. Soc., 1935, 57, 2331).—Pressure changes during the decomp. of azomethane at –183° to 30° and for the thermal reaction at 300° in  $\text{SiO}_2$  indicate decomp. to  $\text{N}_2$  and much  $\text{CH}_4$ . The 10° temp. coeff. for 260–290° is 2.9 and is but little affected by the presence of Hg.

R. S. C.

Compounds of the type  $\text{BCl}_{3-n}(\text{OR})_n$ . III. Preparation of  $\text{BCl}_2\cdot\text{OMe}$  and  $\text{BCl}(\text{OMe})_2$  from boron trichloride and methyl borate. E. WIBERG and H. SMEDSRUD (Z. anorg. Chem., 1935, 225, 204–208; cf. A., 1935, 459).—Improved methods of preparing  $\text{BCl}_2\cdot\text{OMe}$  and  $\text{BCl}(\text{OMe})_2$  are described.

F. L. U.

Preparation of magnesium dialkyl compounds from Grignard reagents. A. C. COPE (J. Amer. Chem. Soc., 1935, 57, 2238–2240).—The extent of disproportionation,  $2\text{MgRX} \rightarrow \text{MgR}_2 + \text{MgX}_2$ , in  $\text{Et}_2\text{O}$  is  $>$  in  $\text{Bu}_2\text{O}$ , and is raised by rise in temp. The mobility of the equilibrium is shown by gradual dissolution of the  $\text{MgPh}_2$  pptd. by dioxan. Dioxan ppts.  $\text{MgCl}_2$  etherate from  $\text{MgMeI}$  solutions.

R. S. C.

Constitution of platinum compounds with thioethers. K. A. JENSEN (Z. anorg. Chem., 1935, 225, 115–141).—Contrary to the inferences of Drew and others (cf. A., 1935, 100), there is no structural difference between the  $\alpha$ - (I) and  $\beta$ - (II) isomerides

of the type  $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$ . The marked difference in the electrical conductivities of (I) and (II) in  $\text{H}_2\text{O}$  or  $\text{MeOH}$  is due to the change  $[\text{PtCl}_2(\text{Et}_2\text{S})_2] + 2\text{H}_2\text{O} \rightarrow [\text{Pt}(\text{H}_2\text{O})_2(\text{Et}_2\text{S})_2]^{++} + 2\text{Cl}^-$  (or similarly with  $\text{MeOH}$ ) occurring rapidly with (II) and slowly with (I). Only two isomerides of this type exist, and "super-numerary isomerides" reported by various workers are shown to have been mixtures. Mol. wt. determinations show that compounds from equimol. proportions of  $\text{PtCl}_2$  and  $\text{R}_2\text{S}$  have the formula  $\text{Pt}_2(\text{R}_2\text{S})_4\text{Cl}_4$ .

F. L. U.

Complex metallic salts. III.—See this vol., 140.

1-Benzyl- $\Delta^1$ -cyclohexene and benzylidene-cyclohexane. K. VON AUWERS (Ber., 1935, 68, [B], 2174–2175; cf. A., 1915, i, 789).—A reply to Prevost *et al.*, (A., 1934, 649).

H. W.

Monodeutero benzene. N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 557–558).—PhD (97% pure) is obtained by distillation of  $\text{Ca}(\text{OBz})_2$  with  $\text{Ca}(\text{OD})_2$  at 300°.

J. W. B.

Preparation of partly deuterated benzenes. I. H. P. WELDON and C. L. WILSON (Nature, 1936, 137, 70).—1 : 3 : 5-Trideutero benzene, m.p. 6.1°, has been prepared [(?) from trimesic acid] by decarboxylation with  $\text{Ca}(\text{OD})_2$ .

L. S. T.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. IV. Mechanism of quaternary salt formation. V. Polar effects of alkyl groups. J. W. BAKER and W. S. NATHAN. VI. Effects of *p*-alkyl substituents on prototropy in the methyleneazomethine system. J. W. BAKER, W. S. NATHAN, and C. W. SHOPPEE (J.C.S., 1935, 1840–1844, 1844–1847, 1847–1849; cf. A., 1935, 710).—IV. Data for the velocity of interaction of the following benzyl bromides with  $\text{C}_5\text{H}_5\text{N}$  (I) in dry  $\text{COMe}_2$  show that the alkyl substituents increase the reaction velocity, and that with a single *p*-alkyl substituent, the velocity decreases in the order  $\text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^i$ : *p*-Me-, b.p. 84°/0.8 mm., m.p. 14.5–15.2°; *p*- $\text{Pr}^i$ -, b.p. 75°/0.4 mm., 2 : 4-*Me*-, b.p. 79°/1.2 mm., m.p. 15° [all obtained from the corresponding chlorides, prepared by Sommelet's method (A., 1914, i, 156), by refluxing with aq.- $\text{COMe}_2$  solution of  $\text{NaBr}$ ]; *p*- $\text{Bu}^i$ -, b.p. 99°/0.3 mm., m.p. 15.1° (prep. by direct bromination of *p*- $\text{C}_6\text{H}_4\text{MeBu}^i$ ), and 2 : 4-dinitrobenzyl bromide (II), m.p. 46.4° (modified prep.) [with (I) yields 2 : 4-dinitrobenzylpyridinium bromide, m.p. 196° (decomp.)]. The energy of activation of the reaction is 12.2–12.57 kg.-cal. and the probability factors ( $\times 10^6$ ) are 0.75–2.61. Data for the reaction between (I) and (II) in aq.  $\text{COMe}_2$  and aq.  $\text{EtOH}$ , and between (II) and  $\text{EtOH}$  are given.

V. An explanation of the unexpected order of electron release capacity shown by the alkyl groups studied in Part IV is given, based on the tentative supposition that when Me is attached to a conjugated system the duplet of electrons forming the C–H linking in this group are appreciably less localised (and hence more easily released) than those in a similarly placed C–C linking.

VI. In the azomethine system (*A*)  $p$ - $C_6H_4R\cdot CH=N\cdot CH_2Ph \rightleftharpoons$  (*B*)  $p$ - $C_6H_4R\cdot CH_2\cdot N\cdot CHPh$  the following order of mobility is obtained:  $p$ - $Bu^t > p$ - $Pr^i > p$ - $Me$ , whilst the % of form (*A*) at equilibrium are  $Me$  45.0,  $Pr^i$  56.0,  $Bu^t$  60.0. From these sequences it is inferred that the type of electron release by  $Me$  outlined in Part V is permanent (mesomeric). The Schiff's bases: *benzylidene-p*-*tert*-*butyl*-, b.p. 155—157°/0.4 mm.; *p*-*tert*-*butylbenzylidene*-, b.p. 161°/0.5 mm.; and *p*-*isopropylbenzylidene-benzylamine*-, b.p. 155°/0.5 mm., are obtained directly from the aldehyde and amine by Shoppee's method (A., 1931, 834). *p*-*tert*-*Butyl*- (*p*-*nitrophenylhydrazone*-, m.p. 214°) and *p*-*isopropylbenzaldehyde* (*p*-*nitrophenylhydrazone*-, m.p. 190°) are prepared by oxidation [boiling aq.  $Cu(NO_3)_2$  in  $CO_2$ ; 24 hr.] of the corresponding benzyl bromide and chloride, respectively. *p*-*tert*-*Butylbenzylamine*-, b.p. 124°/16 mm. [carbamido-derivative, m.p. 137°; *picrate*-, m.p. 270° (decomp.)], is obtained by the action of  $N_2H_4\cdot H_2O$  on *phthalop*-*tert*-*butylbenzylamine*-, m.p. 103°, which results from the interaction of  $K$  phthalimide and *tert*-*butylbenzyl bromide* (180°; 2–3 hr.). F. N. W.

**Derivatives of *p*-fluorobenzenesulphonic acid.** R. M. HANN (J. Amer. Chem. Soc., 1935, 57, 2166—2167).— $PhF$ ,  $HCl$ ,  $SO_2$ , and  $AlCl_3$  in  $CS_2$  give *Na p*-fluorobenzenesulphinate,  $+2H_2O$ , cryst., which leads to the *benzyl- $\psi$* -thiocarbamide salt, m.p. 161°, and the corresponding *sulphonate*-, m.p. 166°, *p*- $C_6H_4F\cdot CH_2Bz$ -, m.p. 151°, and *p*- $NO_2\cdot C_6H_4\cdot CH_2$  *sulphone*-, m.p. 185°, *p*-fluorophenylsulphonyl-*acetic acid*-, m.p. 110—111° [*benzyl- $\psi$* -thiocarbamide salt, m.p. 144° (decomp.)]; *p*- $C_6H_4Br\cdot CO\cdot CH_2$  ester-, m.p. 126°, and *-acelone*-, m.p. 66°, and *s*-*di-p*-fluorophenylsulphonylacetone-, m.p. 144°. All are ineffective against pneumococcal infections. M.p. are corr. R. S. C.

**Ullmann reaction.** H. C. YUAN and M. TSAO (J. Chinese Chem. Soc., 1935, 3, 358—364).—3-*Bromo-4*-*iodo-5*-*nitrotoluene* (I), m.p. 82—83° (prepared by boiling diazotised 3-bromo-5-nitro-*p*-toluidine with  $KI$ ), when heated with  $Cu$ -bronze at 230—250° in the absence of solvent yields 3-bromo-5-nitrotoluene (II), but when boiled in  $PhNO_2$  with  $Cu$ -bronze affords 2:2'-*dibromo-4*:4'-*dimethyl-6*:6'-*dinitrodiphenyl*-, m.p. 195—196°. The formation of (II) is considered to be due to the catalytic dehydrogenation by  $Cu$  of a part of (I) and the replacement of I in the remainder by the H thus formed. 3:5:6:1- $C_6H_2Cl_2I\cdot NO_2$  when heated with  $Cu$ -bronze, with or without  $PhNO_2$ , yields only 2:2':4:4'-*tetrachloro-6*:6'-*dinitrodiphenyl*-, m.p. 128—129°; no 3:5:1- $C_6H_3Cl_2\cdot NO_2$  was isolated. It is considered therefore that in (I) it is mainly the  $Me$  which is dehydrogenated. H. G. M.

**Butylcymenes and their nitro-derivatives.** H. BARBIER (Rev. Marques Parfum. Savonn., 1934, 12, 325—327; Chem. Zentr., 1935, i, 2350; cf. A., 1932, 729).—Condensation ( $AlCl_3$ ) of  $Pr^iCl$  and *p*-*tert*-*butyltoluene* (I) or (with  $H_2SO_4$ ) of  $Pr^iOH$  and (I) yields (?) *isopropyl-4*-*tert*-*butyltoluene*-, b.p. 230°, which on nitration affords a *dinitro-4*-*tert*-*butyltoluene*-, m.p. 90°. (?) *isoPropyl-3*-*tert*-*butyltoluene*-, b.p. 235°, and the corresponding  $(NO_2)_2$ -derivative, m.p. 172°, are obtained similarly. Condensation

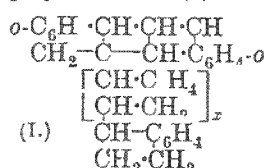
( $H_2SO_4$ ) of  $PhPr^i$  and  $Bu^tOH$  affords (?) *isopropyl*- (?) *tert*-*butylbenzene*-, b.p. 221°, which, with  $CH_3O$  and  $HCl$ , yields an *isopropyl-tert*-*butylbenzyl chloride*-, b.p. 98°/2 mm., converted, through the  $Mg$  compound, into a *tert*-*butylcymene*-, b.p. 236°, which yields a liquid  $(NO_2)_2$ -compound. H. N. R.

**s-Tetradiphenylvinylethane**, a tetra-substituted ethane hydrocarbon which decomposes into radicals. G. WITTIG and B. OBERMANN (Ber., 1935, 68, [B], 2214—2218).— $\alpha\alpha\epsilon\epsilon$ -Tetraphenylpentane- $\alpha\epsilon$ -diol is converted by boiling  $AcOH$  containing a little conc.  $H_2SO_4$  into  $\alpha\alpha\epsilon\epsilon$ -tetraphenyl- $\Delta^{\alpha\epsilon}$ -*penta*-*diene* (I), m.p. 76—77° (in absence of mineral acid the product is 2:2:6:6-tetraphenylpentamethylene oxide, m.p. 176—177°), transformed by successive treatment with  $LiPh$  and  $C_2Me_5Br$  into  $\alpha\alpha\beta\beta$ -tetra- $\beta'\beta'$ -*diphenylvinylethane* (II), m.p. 169—171.5° (slight decomp.), more conveniently obtained by dehydrogenating (I) with  $PhNO$ ,  $KMnO_4$ , or  $SeO_2$ . An unsymmetrical structure for (II) involving a conjugated system is excluded, since it does not react with maleic anhydride, behaves sluggishly towards  $KMnO_4$  and  $NaOH$  in  $COMe$ , and is converted by  $O_3$  or  $CrO_3$  in boiling  $AcOH$  mainly into  $COPH_2$ . When heated in boiling xylene or  $PhOMe$  (II) affords a yellowish-green solution the colour of which disappears on cooling. The instability of the ethane bridge is demonstrated by the reduction of (II) with  $P$  and  $HI$  in boiling  $AcOH$  to  $\alpha\alpha\epsilon\epsilon$ -tetraphenylethane. H. W.

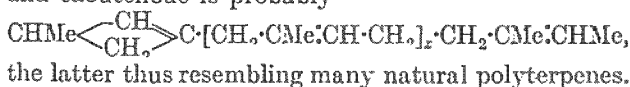
**Bromine derivatives of indene and indane.** H. D. PORTER and C. M. SUTER (J. Amer. Chem. Soc., 1935, 57, 2022—2026).—Many of Jacobi's results (A., 1931, 354) are incorrect. 2-Bromo-1-hydroxyindane (I) (prep. from crude indane-containing oil) at 155—160°, with  $PhBr$  at 156°, or best, with  $P_2O_5$  in hot  $CCl_4$ , gives 2-bromoindene (II), m.p. 38—39°, b.p. 125—127°/3 mm. This with hot  $NaOEt$  gives indan-2-one (III), but does not react with hot 2*N*- $NaOH$  or  $HCO_2K\cdot MeOH$ . (II) yields (Grignard) a little indene-2-carboxylic acid only. With  $HBr\cdot AcOH$  (II) gives an oil, hydrolysed to (I) by aq.  $COMe_2$ ; with  $Br$  in  $CCl_4$  it gives 1:2:3-tribromoindene (IV), an oil, oxidised by  $KMnO_4$  to  $\alpha$ - $C_6H_4(CO_2H)_2$ , and hydrolysed by  $CaCO_3$  in aq.  $COMe_2$  to an oily dibromoindanol. (I) and 47%  $HBr$  at 100° give indene dibromide (V), which at 200—210° alone or, better, in tetrahydronaphthalene gives (III). (V) with  $C_5H_5N$  in  $EtOH$  or  $CaCl_2$  and  $Na_2CO_3$  in aq.  $EtOH$  gives 38% of 2-bromo-1-ethoxyindane, b.p. 147—148°/19 mm., converted by  $NaNH_2$  in liquid  $NH_3$  or by hot 18%  $H_2SO_4$  into indan-1-one (VI), by  $Br\cdot CCl_4$  into (IV) and 2:2-dibromoindan-1-one. *trans*-1:2-Dihydroxyindane [improved prep. from (I); 60% yield; gives also a substance, m.p. >285°] with 10%  $H_2SO_4$  gives 71% of (III). (I) and 7%  $H_2SO_4$  give (VI) in 80.6% yield. R. S. C.

**Polymerisation. I. Formation, properties, and constitution of polyindenes, in particular of "tri-indene."** J. RISI and D. GAUVIN (Canad. J. Res., 1935, 13, 228—255).—"Tri-indene" (I) is shown to be a mixture of polymerides by fractional crystallisation. It is formed with a small amount of a substance (II),  $C_{27}H_{18}$ , m.p. 214°, by polymerisation of indene (III). Unsaturated di-indene (2-1'-hydrynd-

enylindene; modified prep. in 73% yield) at 215° gives 60% of truxene, m.p. 116°, and a mixture of polymerides. (I) is saturated (Br gives only substitution products) and unreactive. Pyrolysis of (I) at 325—340° gives (III) (30—40%), (II) (20%), and truxene (10%). HNO<sub>3</sub> (d 1.25) and the polymerised products give o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> and a NO<sub>2</sub>-acid,



m.p. 160—165°, the amount of the latter increasing with the degree of polymerisation of the substance oxidised. (I) is probably as annexed. Polystyrenes are probably  $\text{CHPh}\langle\text{CH}_2\rangle\text{CPh}\cdot[\text{CH}_2\cdot\text{CHPh}]_x\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$  and caoutchouc is probably



the latter thus resembling many natural polyterpenes.

R. S. C.

**Sulphonation of naphthalene. II. Mechanism of the monosulphonation.** R. LANTZ (Bull. Soc. chim., 1935, [v], 2, 2092—2108; cf. A., 1935, 1116).—The rates of sulphonation of C<sub>10</sub>H<sub>8</sub>, of hydrolysis of 1- and 2-C<sub>10</sub>H<sub>7</sub>·SO<sub>3</sub>H, and of transformation of one acid into the other are determined in sealed tubes at 60—180° in presence of 45—94% H<sub>2</sub>SO<sub>4</sub>. Hydrolysis of the 1-acid is about 50 times as fast as that of the 2-acid and is increased to a greater extent by rise in temp. and/or concn. of H<sub>2</sub>SO<sub>4</sub>. No 2-acid is formed from 1-acid by H<sub>2</sub>SO<sub>4</sub>, which, although strong enough to effect hydrolysis, is too weak to cause sulphonation. The relative amounts of 1- and 2-acid formed are independent of the concn. of the H<sub>2</sub>SO<sub>4</sub>. Only 2—4% of sulphones are formed at 140° with 45—70% H<sub>2</sub>SO<sub>4</sub> in 39 hr. and none in 2 hr. Increase in the amount of 2-acid at high temp. is due to the more rapid hydrolysis of the 1-acid.

R. S. C.

**Asymmetric syntheses. IV. Action of optically active nitrates on 2-bromofluorene.** J. T. THURSTON and R. L. SHRINER (J. Amer. Chem. Soc., 1935, 57, 2163—2166; cf. A., 1934, 76).—2-Bromofluorene (from fluorene, Br, and a trace of I in hot C<sub>6</sub>H<sub>6</sub>), m.p. 113°, *d*- or *l*-octan-β-ol nitrate, and KOEt in EtOH-Et<sub>2</sub>O give the *K* salts (I), [α]<sub>D</sub><sup>25</sup> +4.48°, -1.71° in dry EtOH, of 2-bromo-9-nitrofluorene (II), which with air give KNO<sub>2</sub> and 2-bromofluorenone, m.p. 196° (lit. 194—195°), with dil. AcOH give the acid-form (III), m.p. 132°, of (II) [converted in hot EtOH into the normal form (IV), m.p. 170°], with Br in EtOH yields 2:9-dibromo-9-nitrofluorene, m.p. 139°, [α]<sub>D</sub><sup>0</sup>, and leads by way of the *Ag* salt to 2-bromo-9-nitrofluorene *O*-Me ether (V), m.p. 72—80°, readily decomposed to CH<sub>3</sub>O and 2-bromofluorenone oxime (VI). (I), (III), (IV), (V), and (VI) absorb 0.9, 0.5, 0, 0.49—0.53, and 0.51 mol. of Br, respectively.

R. S. C.

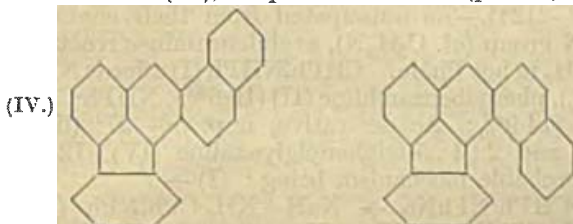
**Dissociable anthracene oxides: influence of mesonaphthyl groups.** A. WILLEMART (Compt. rend., 1935, 201, 1201—1202).—9:10-Dihydroxy-9:10-di-β-naphthylidihydroanthracene is converted by KI in AcOH into 9:10-di-β-naphthylanthracene, m.p. —379°. Both this and the di-α-naphthyl compound, in solutions exposed to sunlight in presence of

air, yield photo-oxides, which when heated at 180—200° lose O<sub>2</sub> and regenerate the hydrocarbons.

E. W. W.

**Dissociable organic oxides. Diphenyldi-*p*-bromophenyldibromorubene and its dissociable oxide.** C. DUFRAISSE and H. ROCHER (Bull. Soc. chim., 1935, [v], 2, 2235—2240).—(*p*-C<sub>6</sub>H<sub>4</sub>Br)<sub>2</sub>CO and CPh·C·MgBr give *γ*-phenyl-α-di-*p*-bromophenyl-Δ<sup>β</sup>-propinen-α-cl (I), m.p. 170—171°, which yields an unstable chloride, m.p. 122—123°, converted at 115°/vac. in quinoline into diphenyldi-*p*-bromophenyldibromorubene, m.p. 309—310°, yellow and garnet-red forms (absorption spectra given). In Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> in light this gives a cryst. oxide, which at 195—220° rapidly dissociates (45—58% of O<sub>2</sub> liberated). (I) (31c ether, m.p. 103°) with H<sub>2</sub>SO<sub>4</sub>-EtOH gives Ph ββ-di-*p*-bromophenylvinyl ketone, m.p. 112—113°. R. S. C.

**Cholanthrene and related hydrocarbons.** L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1935, 57, 2174—2176).—4-Bromohydrindone, m.p. 97°, prepared in 70% yield from β-*o*-bromophenylpropionic acid (best obtained from *o*-C<sub>6</sub>H<sub>4</sub>BrMe), gives (Clemmensen) a 77% yield of 4-bromohydrindene, b.p. 118°/18 mm., the Grignard reagent (I) of which with α-C<sub>10</sub>H<sub>7</sub>·COCl gives 4-α-naphthoylhydrindene, an oil (50% yield), pyrolysed at 400—405° to cholanthrene (34%), m.p. 173—173.5° (corr.) [picrate, m.p. 169—170° (corr.)]. (I) and β-C<sub>10</sub>H<sub>7</sub>·COCl give 4-β-naphthoylhydrindene, m.p. 68—69°, and thence 5:10-dimethylene-1:2-benzanthracene, m.p. 176.5—177° (corr.) [picrate, m.p. 158—159° (corr.)]. Fluorenone-1-carboxylic acid (modified prep. from 7:8-benzacenaphthene; 48% yield), m.p. 191—193°, and 4% Na-Hg and H<sub>2</sub>O give 83% of fluorene-1-carboxylic acid, m.p. 245°, the Grignard reagent (II) from the chloride of which with 1-C<sub>10</sub>H<sub>7</sub>Br in C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O gives 56% of 1-α-naphthoylfluorene (III), m.p. 113—114°, giving at 415° in N<sub>2</sub> 60% of 15:16-benzdehydrocholanthrene (IV), m.p. 181—181.3° (picrate, m.p.



174.5—175.5° (corr.)]. (II), C<sub>10</sub>H<sub>8</sub>, and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>Cl<sub>4</sub> give mainly 1-β-naphthoylfluorene, m.p. 159—162°, yielding 7:8-benz-1:2:1':2'-naphthacenaphthene (V), m.p. 178—179° (corr.) [picrate, m.p. 181—182° (corr.)]; in CS<sub>2</sub>, however, much (III) is formed.

R. S. C.

**Amides of benzene-sulphinic [and -sulphonic] acid.** L. C. RAIFORD and S. E. HAZLET (J. Amer. Chem. Soc., 1935, 57, 2172—2174).—The following are prepared, the yields varying greatly. Benzenesulphinic-*o*, m.p. 107—108°, -*m*-, m.p. 106°, and -*p*-chloroanilide, m.p. 155.5°, -*o*-, m.p. 108—110°, -*m*-, 112—114°, and -*p*-bromoanilide, m.p. 150.5°, -*o*-, m.p. 124—125°, -*m*-, m.p. 102—103°, and -*p*-toluidide, m.p. 100—101°, -*o*-, m.p. 108—113°, -*m*-, 133—134°, and -*p*-anisidide, m.p. 131°, -*p*-carbethoxyanilide, m.p. 114—115°, -4-nitro-*o*-toluidide, m.p. 133°, -β-naphth-

*alide*, m.p. 143—144°, *-benzylamide*, m.p. 100—104°, *-4'-diphenylamide*, m.p. 165.5°, *-4-chlorodiphenyl-2'*-, m.p. 206°, and *-4'-amide*, m.p. 165—166°; *benzenesulphon-o-*, m.p. 130—131°, and *-m-bromoanilide*, m.p. 117.5—118.5°, *-o-toluidide*, m.p. 122—123° (lit. 124—125°), *-m-anisidide*, m.p. 82.5—83.5°, *-p-carboethoxyanilide*, m.p. 183.5—184°, *-4-nitro-o-toluidide*, m.p. 175—176° (lit. 172°), *-4'-diphenylamide*, m.p. 147—148°, *-4-chlorodiphenyl-2'*-, m.p. 136—138°, and *-4'-amide*, m.p. 145—145.5°. R. S. C.

**Phenylthiocarbamides. Triad N·C·S. I. Aniline thiocyanate.** K. KRALL and R. D. GUPTA. **II. Action of hydrolytic agents on phenylthiocarbamide.** **III. Action of nitrous acid on phenylthiocarbamide.** S. MEHTA and H. KRALL (J. Indian Chem. Soc., 1935, 12, 629—634, 635—639, 640—646).—I. *NH<sub>2</sub>Ph.HCNS*, best obtained from *NH<sub>2</sub>Ph* and *HCNS* in *Et<sub>2</sub>O*, at above 85° rapidly gives *NHPh·CS·NH<sub>2</sub>* (I) with evolution of heat. Yields never exceed 80—83%, suggesting an equilibrium, but the reverse change cannot be realised. (I) is best obtained (80%) from dry *NH<sub>2</sub>Ph.HCl* and *KCNS* at 110° (1 hr.).

II. At high *p<sub>H</sub>* (I) hydrolyses in *H<sub>2</sub>O* mainly to *H<sub>2</sub>S* and *NHPh·CN*, at low *p<sub>H</sub>* mainly to *NH<sub>3</sub>* and *PhNCS*, with minor amounts of hydrolysis to *HCNS* and *NH<sub>2</sub>Ph*. The last reaction predominates at about *p<sub>H</sub>* 7. This indicates dynamic isomerism.

III. With aq. *NaNO<sub>2</sub>·HCl* (I) reacts mainly thus:  $2(I) + 4HNO_2 \rightarrow C_6H_5N_4S$  (A., 1889, 872) +  $4NO + 4H_2O + S$ , but with aq. *NaNO<sub>2</sub>·AcOH* mainly thus:  $(I) + HNO_2 \rightarrow PhNCS + N_2 + H_2O$ . Traces of *PhNC* are also formed. R. S. C.

**Organic reagent for cadmium.**—See this vol., 179.

**Mechanism of amination by sodamide. Preparation of substituted amidines.** A. KIRSSANOV and J. IVASTCHENKO (Bull. Soc. chim., 1935, [v], 2, 2109—2124).—As anticipated from their containing a C·N group (cf. *C<sub>2</sub>H<sub>5</sub>N*), arylideneamines react with *NaNH<sub>2</sub>* in hot *PhMe*. *CHPh·NHPh* (I) affords *NH<sub>2</sub>Ph* (12%), phenylbenzamidine (II) (19.6%), *NHPh·CH<sub>2</sub>Ph* (III) [14.9%; Ac derivative, m.p. 56—57° (lit. an oil)], and 2:4:5-triphenylglyoxaline (IV) (12.8%), the probable mechanism being:  $(I) \rightarrow NH_2·CHPh·NPhNa \rightarrow NaH + NH_2·CPh·NPh$  (V)  $\rightarrow NHNa·CPh·NPh$  (VI) +  $H_2$ ;  $(I) + H_2 \rightarrow (III)$ ;  $(V) + NaNH_2 \rightarrow (VI) + NH_3$ ;  $3(I) + 2NH_3 \rightarrow 3NH_2Ph + 2:4:5$ -triphenyl-4:5-dihydroglyoxaline  $\rightarrow$  (IV). *CHPh·N·C<sub>6</sub>H<sub>4</sub>Me·p* affords *p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>* (22.6%), *p-tolylbenzamidine* (22.6%), *p-C<sub>6</sub>H<sub>4</sub>Me·NH·CH<sub>2</sub>Ph* (20.6%), m.p. 19—20° (lit. an oil; NO-derivative, m.p. 45.5—48.5°), and the glyoxaline derivative (12.3%). Piperonylideneaniline gives 13% of the *amidine*, m.p. 138—139°, and a little piperonylaniline, m.p. 78—79°. This is the best way of preparing benzamidines. R. S. C.

**Preparation and geometrical isomerism of asymmetric quaternary ammonium salts and betaine hydrates derived therefrom.** (MME.) M. GUAINET-PILAUD (Ann. Chim., 1935, [xi], 4, 365—448).—The geometrical isomerism of the betaine hydrates previously described (A., 1930, 1563;

1933, 387, 948, 1004; 1934, 763) depends on the order of introduction of the hydrocarbon radicals. The quaternary iodide from *NPhEt·CH<sub>2</sub>·CO<sub>2</sub>Me* (*Et* ester, b.p. 149—150°/13 mm. and 150—151°/15 mm.) and *MeI* with *Ag<sub>2</sub>O* gives a new stable betaine monohydrate, m.p. 104° [*platinichloride*, m.p. 169°; *picrate*, 186° (decomp.) (not identical with the *picrate*, m.p. 158.5° [decomp.], of the betaine hydrates previously described), *d-camphorsulphonate*, m.p. 190—191° (decomp.); *oxalate*, m.p. 173° (decomp.) and 134.5°]. Similarly the quaternary iodide from *Et phenylpropylaminoacetate*, b.p. 161—162°/14 mm. (from *NHPhMe* with *CH<sub>2</sub>I·CO<sub>2</sub>Et* or *CH<sub>2</sub>Cl·CO<sub>2</sub>Et*), yields a stable betaine monohydrate, m.p. 108° [*picrate*, m.p. 189° (decomp.) [not identical with the *picrate*, m.p. 127° (decomp.)], of the betaine hydrates previously described, of which the following new derivatives are described: *platinichloride*, m.p. 198° (decomp.); *oxalate*, m.p. 208°; *d-camphorsulphonate*, m.p. 227—227.5° (decomp.)]. Similarly the quaternary iodide from *CH<sub>2</sub>I·CO<sub>2</sub>Et* and *p-C<sub>6</sub>H<sub>4</sub>Me·NEt<sub>2</sub>* gives a single betaine hydrate, *cryst.* (*oxalate*, m.p. 138—139°). The following were also prepared from the appropriate bases and iodides: *NPhMe<sub>2</sub>EtI*, m.p. 134° (decomp.); *p-C<sub>6</sub>H<sub>4</sub>Me·NEt<sub>2</sub>I*, m.p. 156.5°. *NHMePr picrate* has m.p. 105.5—106°. F. R. G.

**Decomposition of *p*-iodoaniline.** F. B. DAINS, R. Q. BREWSTER, and J. A. DAVIS (J. Amer. Chem. Soc., 1935, 57, 2326—2327).—Purified *p-C<sub>6</sub>H<sub>4</sub>I·NH<sub>2</sub>* in a glass-stoppered bottle in diffused light after 3 years had decomposed giving traces of *I* and *NH<sub>2</sub>Ph* and much 2:4-*C<sub>6</sub>H<sub>3</sub>I<sub>2</sub>·NH<sub>2</sub>*. R. S. C.

**Identification of carboxylic acids as salts of benzylamine and  $\alpha$ -phenylethylamine.** C. A. BUEHLER, L. CARSON, and R. EDDS (J. Amer. Chem. Soc., 1935, 57, 2181—2182).—The following *CH<sub>2</sub>Ph·NH<sub>2</sub>* and *CHMePh·NH<sub>2</sub>* salts, respectively, are prepared. Formate, m.p. 95—97°, 97.8—98.8°, acetate, m.p. 96.3—97.1°, 92.1—92.5°, propionate, m.p. 46.7—47.5°, b.p. 120—121°/42 mm., *n*-butyrate, b.p. 109—110°/15 mm., 125°/37 mm., *n*-valerate, m.p. 51.7—52.7°, —, chloro-, m.p. 119.9—120.9°, 94.7—95.5°, and trichloro-acetate, m.p. 120.3—121.3°, —, phenylacetate, m.p. 122—122.6°, 115.6—116.4°, *o*-toluate, m.p. 145.4—146.4°, 113.3—113.7°, cinnamate, m.p. 135.9—136.3°, 144.5—145.1°, benzoate, m.p. 127.2—128.4°, 140.6—141.2°, *o*-, m.p. 112—113.2°, 111—111.6°, *m*-, m.p. 135.9—136.5°, 168.9—169.4°, and *p*-amino-, m.p. 197.6—198.6°, 185.6—186.4°, *m*-bromo-, m.p. 160.6—161.2°, 148.9—149.7°, *o*-, m.p. 150.5—151.5°, 130.9—131.9°, *m*-, m.p. 149.2—149.8°, 144.7—145.3°, and *p*-chloro-, m.p. 160.3—161.3°, 152.3—153.3°, *m*-, m.p. 188.2—189.6°, 137.2—138.4°, and *p*-hydroxy-, m.p. 216.2—217.2°, 199.3—199.9°, *o*-, m.p. 121.5—122.3°, 158.7—159.1°, *m*-, m.p. 113.1—114.1°, 131.4—131.8°, and *p*-methoxy-, m.p. 144.8—145.6°, 132.8—133.4°, *o*-, m.p. 143.9—145.7°, 129.5—130.1°, *m*-, m.p. 174.9—175.5°, 170.7—171.1°, and *p*-nitro-benzoate, m.p. 197.3—198.9°, 195.8—196.8°, and salicylate, m.p. 94.3—95.5°, 102.1—102.9°. The low-melting salts can be distilled in vac. The aliphatic salts are hygroscopic. M.p. are corr. R. S. C.



**Organic sulphur-nitrogen linking. VIII.** E. RIESZ (Monatsh., 1935, 67, 51—62; cf. A., 1928, 748; 1931, 1295).—The product obtained from 4'-chloro-2'-nitrophenylthiol-*p*-dimethylaminoanilide (I) and  $K_2Cr_2O_7$  is 4'-chloro-2'-nitrophenyl-*p*-benzoquinonethioliminedimethyliminium dichromate. (I) and  $PbO_2$  in  $Et_2O$  or  $CHCl_3$  give a green solution, which slowly oxidises, contains 1 H less than (I) (quinol titration), and is fairly stable at  $-60^\circ$ . The green solution is considered to contain a free radical. Complete reduction of this green solution with quinol gives a mixture containing 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl disulphide, also obtained by I with a substance,  $C_8H_{10}N_2I_2$  (*p*-di-iodoaminodimethyl-aniline or *p*-benzoquinoneiodoiminedimethyliminium iodide). Formulae are discussed for the product, m.p.  $260-270^\circ$  (decomp.), about  $C_{48}H_{20-28}O_{12}N_{10}S_6Cl_6$ , obtained from *s*-di-4'-chloro-2'-nitrophenylthiol-*p*-phenylenediamine and  $CrO_3$ . R. S. C.

**Molecular compounds of benzidine with certain phenols and acids.** K. HRYNAKOWSKI, H. STASZEWSKI, and M. SZMYTOWNA (Rocz. Chem., 1935, 15, 391—399).—The m.p. diagrams suggest compounds of 1 mol. of benzidine with 2 of resorcinol, m.p.  $137^\circ$ , with 2 of salicylic acid, m.p.  $156^\circ$ , with 1 of quinol, m.p.  $130^\circ$ , with 3 of  $BzOH$ , m.p.  $108^\circ$ , and with 1 of  $\alpha$ -, m.p.  $97^\circ$ , and  $\beta$ -naphthol, m.p.  $178^\circ$ . The composition of the eutectic mixture can be predicted by Kordes' formula only when one of the components is present in large excess. R. T.

**as-Diphenylhydrazine (supercooling of the liquid and mol. form).** D. VORLANDER and C. BITTINS (Ber., 1935, 68, [B], 2269—2276).—The ease with which liquid  $NPh_2NH_2$  can be supercooled is not due to the presence of impurities, but is a consequence of its mol. dissymmetry. Examination of its derivatives shows that the relationships between supercooling and constitution are not simple. Treatment of  $NPh_2NH_2$  with  $CH_2BrCO_2Et$  in boiling  $EtOH$  or of  $NPh_2NH_2HCl$  and  $NaOEt$  with  $CH_2BrCO_2Na$  followed by hydrolysis of the ester with  $NaOH$  yields *Na as-diphenylhydrazinoacetate* (I),  $NPh_2NHCH_2CO_2Na$ , anhyd., decomp.  $180-185^\circ$  ( $+5H_2O$ ), m.p. about  $80^\circ$  (corresponding  $Pb$ ,  $Hg^{II}$ ,  $Mg$ ,  $Ca$ ,  $Sr$ ,  $Zn$ ,  $Cd$ ,  $Al$ , and  $K$  salts). The free acid (hydrochloride) gives a moss-green solution in conc.  $H_2SO_4$  at  $15-20^\circ$ , whereas non-oxidising acids ( $PhSO_3H$ ;  $p$ - $C_6H_4MeSO_3H$ ) give no colour.  $HClO_4$  gives a colourless salt. With  $PbO_2$  in  $AcOH$  it gives an immediate dark red and subsequently a comparatively stable reddish-violet colour. *N-Acetyl-as-diphenylhydrazinoacetic acid*, m.p.  $185^\circ$  (corr.  $+2^\circ$ ), from (I) and  $Ac_2O$  at about  $95^\circ$ , is converted by  $HNO_3$  (d 1.4) in  $AcOH$  at  $15-20^\circ$  into a  $(NO_2)_2$ -derivative, m.p. about  $210^\circ$  (decomp.). *as-Diphenylhydrazinoacet-as-diphenylhydrazide*, m.p.  $214^\circ$  (decomp.) after softening [hydrochloride; *Ac* derivative, m.p.  $229^\circ$  (corr.)], and non-cryst.  $\alpha$ -*diphenylhydrazino- $\beta$ - $\beta$ -diacetic acid* are obtained as by-products in the prep. of (I) under different conditions.  $NPh_2NHAc$  and sodio-*p*-nitrophenylnitrosoamine afford  $\alpha$ -acetyl- $\beta$ -phenyl- $\beta$ -*p*-nitrobenzeneazophenylhydrazine, m.p.  $246^\circ$  (corr.);  $\alpha$ -acetyl- $\beta$ -phenyl- $\beta$ -*p*-nitrobenzeneazophenylhydrazinoacetic acid is described. H. W.

**Ammonium character of tetra-arylhydrazines. II. Ammonium character of tetra(dimethylaminophenyl)hydrazine.** E. WEITZ and L. MÜLLER (Ber., 1935, 68, [B], 2306—2312; cf. A., 1927, 658).—The action of  $ClO_2$  on tetra-(*p*-dimethylaminophenyl)-hydrazine (I) gives a green product which is difficult to purify. (I) and tritolyllaminium perchlorate in  $PhBr$  afford the perchlorate of Bindschedler's green,  $NMe_2C_6H_4N:C_6H_4NMe_2ClO_4$  (obtained also from the chloride and  $NaClO_4$ ), and identified by its absorption spectrum and titration with di-*N*-ethylcollidinium (II)  $[C_5H_2Me_2N^+Et]_2$ , of which 2 equivs. are required, and the resulting yellow solution, when shaken with  $H_2O$  gives tetramethyldiaminodiphenylnitrosoamine, m.p.  $155^\circ$  (decomp.). The change is explained by dissociation of (I) into the free radicals and reaction of the latter in the valency-tautomeric form. By use of a deficiency of  $Cl$  or  $Br$ , (I) can be transformed into the chloride or bromide of Bindschedler's green, but the analogous use of  $I$  leads to a (?) periodide,  $RI + RI(I_2)$ , identical with the "hydriodide" of Drew *et al.* (A., 1933, 516), which has not the constitution assigned by the latter authors. Reduction of the salts with (II) leads to (I); the change can also be effected with  $Zn$  dust or  $Na-Hg$  in  $C_5H_5N$  or  $COMe$ , but the product has not yet been isolated in substance. During the reduction of the salts or of the more readily available  $ZnCl_2$  or  $ZnBr$  compounds, particularly with  $Zn$  dust in  $C_5H_5N$ , intermediate dark blue solutions are formed, from which by addition of  $Et_2O$  the substance  $[N(C_6H_4NMe_2)_2]Cl$ ,  $ZnCl_2$  and the analogous bromide are pptd. The corresponding iodide decomposed during its prep. 1 mol. of the blue salts requires 0.5 mol. of (II), and (I) is identified in the reddish-yellow solutions in the usual manner. H. W.

**Diazo-compounds. VI. Action of dilute solutions of alkalis on diazonium salts.** G. ODDO and INDOVINA (Gazzetta, 1935, 65, 939—993).—Earlier work is reviewed. Velocity of decomp. of diazo-compounds from chloro-, bromo-, iodo-, and nitroanilines, and aminophenols (*o*-, *m*-, and *p*- in each case), *o*- and *p*-anisidine, *m*-aminobenzaldehyde, *o*-, *m*-, and *p*-aminobenzoic acids, and their  $Et$  esters, in presence of 0.4, 0.8, and 1.6%  $NaOH$  at room temp. (from  $11^\circ$  to  $26^\circ$ ) is measured by  $N_2$  evolved, resin pptd., and stable diazotates and isodiazotates remaining; the results are tabulated and discussed. Increased  $[NaOH]$  normally increases stability, but accelerates decomp. of the esters. Diazotates derived from *o*- and *p*-nitroaniline are stable; those from *m*- and *p*-aminobenzoic acid are stable in presence of 1.2%  $NaOH$ ; those from *m*-iodo- and *m*-nitro-aniline decompose rapidly. Partial transformation into isodiazotates is normal, except where  $\cdot OH$  or  $\cdot CO_2H$  is the substituent. Decomp. graphs correspond approx. with unimol. reactions. The slow decomp. of isodiazotates is also studied. The industrial application of the decomp. tables is suggested. E. W. W.

**Reaction of titanium tetrachloride with phenol.**—See this vol., 173.

**Halogenation of phenolsulphonic acids in nitrobenzene.** R. C. HUSTON and A. H. NELEY (J. Amer. Chem. Soc., 1935, 57, 2176—2178).— $PhOH$  is

sulphonated and the product dissolved in  $\text{PhNO}_2$ , treated successively with oleum at  $< 10^\circ$  and Br in  $\text{PhNO}_2$ , and hydrolysed with steam at  $200^\circ$ . There are formed 10.4—46.5% of  $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$  (I), 72.7—9.5% of  $2:6\text{-C}_6\text{H}_3\text{Br}_2\cdot\text{OH}$  (II), and a little  $\text{C}_6\text{H}_5\text{Br}_3\cdot\text{OH}$ , the proportion of (I) and (II) depending on the amount of  $\text{H}_2\text{SO}_4$  used in the sulphonation. Similar procedure leads to 17—72% of  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ , and 70.3—24% of  $2:6\text{-C}_6\text{H}_3\text{Cl}_2\cdot\text{OH}$ , 3-bromo-*o*-cresol, b.p.  $206\text{--}207^\circ/740$  mm. (60%) and 3:5-dibromo-*o*-cresol (13%), 3-chloro- (30%), and 3:5-dichloro-*o*-cresol (12%), 2-bromo-*m*-cresol, m.p.  $61\text{--}62^\circ$  (7—40%), with ? some 4-Br- and 0—8% of 6-Br-compound, m.p.  $58\text{--}59.5^\circ$  (*p*-toluenesulphonate, m.p.  $112\text{--}113^\circ$ ), and 0—23% of 2:4-dibromo-*m*-cresol, m.p.  $36.5\text{--}37.5^\circ$  (*p*-toluenesulphonate, m.p.  $131\text{--}132^\circ$ ), and 2-chloro-, 2:6-, m.p.  $58\text{--}59^\circ$ , b.p.  $75\text{--}80^\circ/4$  mm.,  $235\text{--}236^\circ/745$  mm., and 2:4-dichloro-*m*-cresol, b.p.  $80\text{--}85^\circ/4$  mm.,  $239.5\text{--}240.5^\circ/745$  mm. The structures of the cresol derivatives are proved by their prep. also from nitrocresols and/or their chlorination to substances prepared from nitrocresols.

R. S. C.

**Pyrolysis of allyl-*p*-phenetidine.** F. L. CARNAHAN (J. Amer. Chem. Soc., 1935, 57, 2210—2211).—*N*-Allyl-*p*-phenetidine (prep. by  $\text{C}_3\text{H}_5\text{Br}$ , b.p.  $134.5^\circ/10$  mm.,  $265^\circ$  (decomp.)/ $745$  mm. ( $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivative, m.p.  $81^\circ$ , also obtained from *p*-toluenesulphon-*p*-phenetidine and  $\text{C}_3\text{H}_5\text{Br}$  in *N*-KOH), when refluxed, gives  $p\text{-OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (0.465 mol.),  $\text{C}_3\text{H}_6$  (0.4 mol.), and resin (equiv. to 0.447 mol.), but no  $\text{H}_2$  or quinoline derivative, probably by the following steps:  $\text{NHR}\cdot\text{C}_3\text{H}_5$  (I)  $\rightarrow$   $\text{NHR}\cdot + \text{C}_3\text{H}_5$ ; (I) +  $2\text{NHR}\cdot \rightarrow 2\text{NHLR} + \text{NR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$  (II); (I) +  $2\text{C}_3\text{H}_5 \rightarrow$  (II) +  $2\text{C}_3\text{H}_6$ ; (II)  $\rightarrow$  resin.

R. S. C.

**Acetylation of dulcin (*p*-phenetylcarbamide).** C. ALBERTI (Gazzetta, 1935, 65, 922—925).—*p*-Phenetylcarbamide (I) with  $\text{AcCl}\cdot\text{C}_5\text{H}_5\text{N}$  yields the Ac derivative (II);  $\text{Ac}_2\text{O}\cdot\text{NaOH}$  gives only a small quantity of (II), phenacetin (III) and  $\text{NH}_2\text{Ac}$  being formed.  $\text{AcOH}$  also decomposes (I), but yields, with (III), di-*p*-phenetylcarbamide and  $\text{NH}_4$  salts. Mechanisms are suggested (cf. A., 1928, 485).

E. W. W.

**Pyrolysis of *p*-phenetylcarbamide and of acetyl-*p*-phenetylcarbamide.** C. ALBERTI (Gazzetta, 1935, 65, 926—929).—*p*-Phenetylcarbamide (I) and its Ac derivative (II) are decomposed at about  $250^\circ$  to give di-*p*-phenetylcarbamide, with, from (I),  $\text{NH}_3$  and some  $\text{HNCO}$ , and, from (II),  $\text{CO}_2$ ,  $\text{NH}_2\text{Ac}$ ,  $\text{MeCN}$ , and some  $\text{NH}_3$ .

E. W. W.

**Derivatives of diphenyl ether.** L. C. RAIFORD and J. C. ZIMMERMANN (Amer. J. Pharm., 1935, 107, 472—475; cf. A., 1926, 1242; 1930, 767).—The product obtained by nitration of 2':4'-dibromo-4-nitrodiphenyl ether is 2':4'-dibromo-2:4:5'-trinitrodiphenyl ether, which, with piperidine (I), gives 2:4-dinitrophenylpiperidine and 2:4-dibromo-5-nitrophenol. (I) also reacts with other substituted diphenyl ethers giving substituted phenols.

W. McC.

**Preparation of [alkyl]aminoisopropylidene-pyrocatechols.** J. DRUEY (Bull. Soc. chim., 1935, [v], 2, 2261—2263).—Addition of  $\text{P}_2\text{O}_5$  to  $o\text{-C}_6\text{H}_4(\text{OH})_2$  in  $\text{CH}_2\text{Cl}\cdot\text{COMe}$  gives a 40—45% yield of the chloroiso-

propylidene derivative, b.p.  $104\text{--}105^\circ/13$  mm. ( $\text{NO}_2$ -derivative, m.p.  $80\text{--}81^\circ$ ), the Cl of which is inactive, but with the appropriate base in  $\text{C}_6\text{H}_6$  at  $180^\circ$  gives slowly poor yields of dimethylamino-, b.p.  $115\text{--}117^\circ/22$  mm. [hydrochloride, m.p.  $217\text{--}218^\circ$  (decomp.)], diethylamino-, b.p.  $123\text{--}125^\circ/20$  mm. (hydrochloride, an oil), and piperidino-isopropylidenepyrocatechol, b.p.  $150\text{--}151^\circ/17$  mm. [hydrochloride, m.p.  $224\text{--}225^\circ$  (decomp.)].

R. S. C.

**Syntheses of pharmacologically important amines. XI. Preparation of arylethylamines and arylethanolamines by catalytic reduction.** K. KINDLER, W. PESCHKE, and E. BRANDT (Ber., 1935, 68, [B], 2241—2245).—The interference of intermediate products in the smooth reduction of ketoximes and cyanohydrins to amines is avoided by the gradual addition of a solution of the substance to be reduced to the catalyst charged with H. In the prep. of primary amines, conc.  $\text{H}_2\text{SO}_4$  is added. The following examples are cited:  $\text{CPhMe}\cdot\text{N}\cdot\text{OH}$  to  $\text{CHPhMe}\cdot\text{NH}_2$  (yield 83%); *p*-methylacetophenone-oxime to  $\alpha$ -*p*-tolylethylamine (80% yield) [hydrochloride, m.p.  $167\text{--}168^\circ$ ]; *p*-methoxyacetophenone-oxime to  $\alpha$ -*p*-anisylethylamine (yield 70%); 3:4-dimethoxybenzaldehyde cyanohydrin to  $\beta$ -hydroxy- $\beta$ -3:4-dimethoxyphenylethylamine (yield 47%) and  $\beta$ -3:4-dimethoxyphenylethylamine (yield 18%); 3:4-diethoxybenzaldehyde cyanohydrin to  $\beta$ -hydroxy- $\beta$ -3:4-diethoxyphenylethylamine, m.p.  $93^\circ$  (picrate, m.p.  $171^\circ$ ), and  $\beta$ -3:4-diethoxyphenylethylamine; 3-methoxy-4-ethoxybenzaldehyde cyanohydrin to  $\beta$ -hydroxy- $\beta$ -3-ethoxy-4-ethoxyphenylethylamine, m.p.  $110^\circ$  (picrate, m.p.  $161^\circ$ ); hydrochloride, m.p.  $176^\circ$ ), and  $\beta$ -3-methoxy-4-ethoxyphenylethylamine, b.p.  $155^\circ/10$  mm. (picrate, m.p.  $182^\circ$ ).

H. W.

**Preparation of resorcinol methyl ether. Correction.** B. B. DEY (J. Indian Chem. Soc., 1935, 12, 685—686).—Details given for the prep. of this ether (A., 1935, 211) are corr.

R. S. C.

**M.p. of resorcinol.** N. A. VALJASCHKO and M. M. SCHTSCHERBAK (Ukrain. Chem. J., 1935, 10, 305—310).—The f.p. is  $109.8^\circ$  and the m.p.  $110.2^\circ$ .

R. T.

**Alkyl ethers of  $\beta\beta$ -di-*p*-hydroxyphenylpropane. I. Dialkyl ethers.** G. R. YONE and J. F. VITCHA (J. Amer. Chem. Soc., 1935, 57, 2259—2260).—An excess of  $\text{CMe}_2(\text{C}_6\text{H}_4\cdot\text{OH}\cdot p)_2$  with alkyl sulphates in aq. NaOH or KOH gives mono- and di-alkyl ethers; the  $\text{Me}_2$ , m.p.  $59\text{--}61.5^\circ$ , b.p.  $190^\circ/5$  mm.,  $\text{Et}_2$ , m.p.  $49\text{--}50^\circ$ ,  $\text{Pr}^n$ , b.p.  $200\text{--}202^\circ/3$  mm.,  $\text{Bu}^n$ , m.p.  $20^\circ$ , b.p.  $212\text{--}213^\circ/3$  mm., and di-*n*-amyl ether, m.p.  $34.5\text{--}35.5^\circ$ , b.p.  $225\text{--}230^\circ/3$  mm., are described.  $n\text{-C}_8\text{H}_{17}\cdot\text{OH}$  and  $\text{SOCl}_2$  are kept for 1 week and neutralised with NaOH, and the resulting mixture is then used for alkylation.

R. S. C.

**Production of dihydroxydihydroanthracene from anthracene.**—See this vol., 234.

**Molecular rearrangement of *N*-thiolanilides. II.** M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 2234—2236; cf. A., 1935, 1359).—With hot KOH-EtOH *N*-thiolanilides give *o*-thioldiphenylamines, possibly by way of *o*-aminodiphenyl sulphides. *N*-*o*-Nitrophenylthiol-anilide, -*o*-

and *p*-toluidide thus give *o*-nitro-*o*'-thiol-, -2'-thiol-5'-methyl-, and -2'-thiol-3'-methyl-diphenylamine (Na salts, which with MeI-EtOH give the *Me* ethers, m.p. 98°, 94°, and 84—85°), respectively. R. S. C.

**Spatial configurations of 1:2-dialkylcyclopentan-1-ols.** G. CHIURDOGLU (Bull. Soc. chim. Belg., 1935, 44, 527—550).—2-Methylcyclopentanone (cf. A., 1926, 1238) [phenylhydrazone, decomp. at 60°; Et 2-methylcyclopentanonecarboxylate (phenylhydrazone, decomp. at 68°)] is converted into 1:2-dimethylcyclopentan-1-ol, which when fractionally distilled yields *trans*- and *cis*-isomerides, m.p. 27.3° and 28.9°, respectively. The former is the more quickly converted into 1:2-dimethyl- $\Delta^1$ -cyclopentene by 85%  $\text{HCO}_2\text{H}$ , and is the more rapidly reduced ( $\text{H}_2$ -Pt), and has OH and H in *trans*-positions (cf. A., 1931, 954; 1932, 844). *trans*-Isomerides with different pairs of 1:2-substituents are reduced ( $\text{H}_2$ -Pt) at the same rate as are the *cis*-, and suffer no change in configuration prior to reduction. Reduction of either isomeride gives mainly a *trans*-product. A mechanism is suggested to explain these reactions. J. L. D.

**Addition of chloroform and bromoform to *p*-chlorobenzaldehyde.** J. W. HOWARD (J. Amer. Chem. Soc., 1935, 57, 2317—2318).—*p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ ,  $\text{CHCl}_3$ , and KOH give *p*-chlorophenyltrichloromethylcarbinol, b.p. 187—188°/26 mm. (acetate, m.p. 120—121°; propionate, m.p. 71—72°; benzoate, m.p. 128—129°). *p*-Chlorophenyltribromomethylcarbinol, m.p. 90—91°, is similarly obtained. R. S. C.

**Chemical study of the functions of ephedrine.** I. New method for its determination. J. A. SANCHEZ (J. Pharm. Chim., 1935, [viii], 22, 489—496).—The formation from ephedrine of BzOH by alkaline oxidation,  $\text{PhCHO}$  and an amine by the action of  $\text{KMnO}_4$  or  $\text{NaOCl}$ , and nitrosoephedrine by the action of  $\text{NaNO}_2$  and  $\text{HCl}$ , the reactions of the diazo-compound, and the products of pyrogenic decomp. are described. Ephedrine reacts with  $\text{NaOH}$  and  $\text{I}$  giving  $\text{CHI}_3$ , and a method of determination based on this sensitive reaction is proposed. E. H. S.

**Phenanthrene series. IX. Amino-alcohols derived from 1:2:3:4-tetrahydrophenanthrene.** E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1935, 57, 2189—2192; cf. A., 1935, 973).—Some phenanthrene derivatives carrying a basic and OH group in one reduced ring have analgesic action comparable with that of codeine. 2-Bromo-1-keto-1:2:3:4-tetrahydrophenanthrene (I), m.p. 84—85° [by bromination of the 1-CO-compound (II) in dry  $\text{Et}_2\text{O}$  containing a little  $\text{HCl}$ ], with the appropriate base affords 2-dimethylamino- [hydrochloride, m.p. 219—220 (decomp.)], 2-diethylamino- (III) (hydrochloride, m.p. 156° after sintering at 138°), 2-piperidino-, m.p. 138—140° [hydrochloride, m.p. 236—238° (decomp.)], and 2-1':2':3':4'-tetrahydroisoquinolino-1-keto-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 226—227° (decomp.)], hydrogenated ( $\text{PtO}_2$ ) in  $\text{MeOH}$  to 2-dimethylamino-, m.p. 105—108° after sintering at 95°, sublimes at 90°/high vac. [hydrochloride, m.p. 223—224° (decomp.)]; Bz derivative, m.p. 179—181° (decomp.)], 2-diethylamino-, m.p. 70—72° after softening at 60°, b.p. 90°/high vac. [hydro-

chloride, m.p. 221—223° (decomp.); 3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CO}$  derivative, m.p. 209—211° (decomp.)], 2-piperidino-, m.p. 121—126°, sublimes at 105°/high vac. [hydrochloride, m.p. 259° (decomp.)], and 2-1':2':3':4'-tetrahydroisoquinolino-1-hydroxy-1:2:3:4-tetrahydrophenanthrene, m.p. 155—156° [hydrochloride, m.p. 227° (decomp.)]. As by-products to (III) are obtained 1-hydroxyphenanthrene (IV), m.p. 153°, and an additive 1:1-compound (V), m.p. 119°, of (IV) and (I). (IV) is also obtained from (I) and  $\text{NPhEt}$ , or (II) and Se at 295°. (V) with hot  $\text{KOH}\cdot\text{EtOH}$  gives (I) and (IV), from which it is obtained by crystallisation of the 1:1 mixture, and with semicarbazide gives the semicarbazone of (I). 3-Bromo-4-keto-1:2:3:4-tetrahydrophenanthrene (VI), m.p. 104—105°, leads similarly to (a) 3-dimethylamino- [hydrochloride, m.p. 208—210° (decomp.)], 3-diethylamino- [hydrochloride, m.p. 184—185° (decomp.)]; picrate, m.p. 173—174° (decomp.)], 3-piperidino- [hydrochloride, m.p. 248—250° (decomp.)], and 3-1':2':3':4'-tetrahydroisoquinolino-4-keto-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 164—166° (decomp.)]; perchlorate, m.p. 210° (decomp.)], (b) 3-dimethylamino- [hydrochloride, m.p. 230° (decomp.)]; Bz derivative, m.p. 89—90° (hydrochloride, m.p. 177—178°)], 3-diethylamino- [hydrochloride, m.p. 239.5—240° (decomp.)]; picrate, m.p. 206—208° (decomp.)]; Bz derivative [picrate, m.p. 173—174° (decomp.)]; 3:5- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CO}$  derivative, m.p. 216—217.5°, 3-piperidino- [hydrochloride, m.p. 246—247° (decomp.)]; Bz derivative [hydrochloride, m.p. 181—182° (decomp.)], and 3-1':2':3':4'-tetrahydroisoquinolino-4-hydroxy-1:2:3:4-tetrahydrophenanthrene [hydrochloride, m.p. 230—231° (decomp.)], (c) 4-hydroxyphenanthrene, m.p. 113°, and the 1:1 additive compound thereof with (VI), m.p. 107°. M.p. are corr. R. S. C.

**Adrenal cortex. I. Fractionation of hormone concentrates. II. Isolation of physiologically inactive crystalline compounds from active extracts.**—See this vol., 115.

**Auxochromes and resonance.** C. R. BURY (J. Amer. Chem. Soc., 1935, 57, 2115—2117).—The theory that dyes owe their colour to resonance and that the function of auxochromes is to render resonance possible is applied to various classes of dyes.

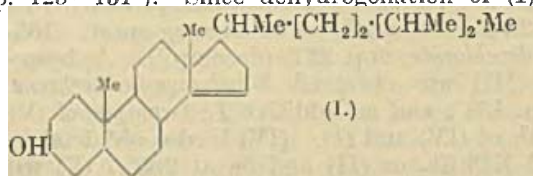
R. S. C.

**Carotenoid origin of cholesterol.** W. M. D. BRYANT (Chem. and Ind., 1935, 1082—1083).—Arguments are presented in favour of the carotenoid origin of sterols and related compounds. Sterols containing "extra" Me and Et groups may arise by degradation of more highly cyclised carotenoids.

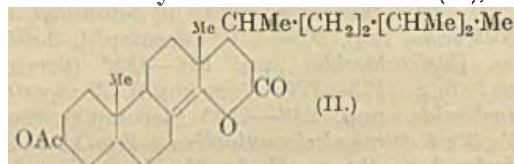
R. S. C.

**Constitution of  $\beta$ -ergosterol.** F. LAUCHT (Z. physiol. Chem., 1935, 237, 236—246).—Ozonisation of  $\alpha$ -ergosterenyl acetate suspended in  $\text{AcOH}$  and reductive fission of the ozonides yields at least two isomeric dehydroergosterols, m.p. (indef.) 132,  $[\alpha]_D^{25} -56.1^\circ$  in  $\text{CHCl}_3$ , and m.p. 114—116°,  $[\alpha]_D^{25} -81.0^\circ$  in  $\text{CHCl}_3$ , respectively.  $\text{O}_3$  functions therefore as a dehydrogenating agent, and its action affords no evidence of the position of the double linking in  $\alpha$ -ergosterol. Similar ozonisation of  $\beta$ -ergosterenyl acetate

affords the keto-alcohol,  $C_{16}H_{26}O_2$ , and its acetate (I) described by Achtermann (A., 1934, 1000) and an aldehyde containing 12 C (*semicarbazone*,  $C_{13}H_{25}ON_2$ , m.p. 125—131°). Since dehydrogenation of (I) by



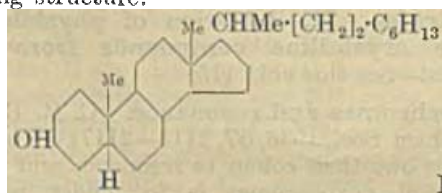
Se at 320° yields 2-methylphenanthrene, the above constitution is established for  $\beta$ -ergosterol. This view is confirmed by the isolation from the acidic products of ozonolysis of an *enol-lactone* (II), m.p.



144°,  $[\alpha]_D^{25} +92.5^\circ$  in  $CHCl_3$ , which is insol. in cold alkali and is transformed with some difficulty by boiling KOH-MeOH followed by acid into the corresponding non-cryst. acid, transformed by  $CH_2N_2$  into the Me ester,  $C_{29}H_{50}O_4$ , m.p. (indef.) 51°,  $[\alpha]_D^{25} -24.6^\circ$  in  $CHCl_3$  (acetate,  $C_{31}H_{52}O_5$ , m.p. 124°,  $[\alpha]_D^{25} +14.3^\circ$  in  $CHCl_3$ ). H. W.

Sexual hormones and related substances.

VI. Degradation of acetylepidihydrocincholinol to  $\beta$ -3-hydroxynorallocholanolic acid or to 3-hydroxynorallocholanolic acid. W. DIRSCHERL (Z. physiol. Chem., 1935, 237, 268—272).—Dihydrocincholinol acetate has been oxidised to  $\beta$ -3-hydroxynorallocholanolic acid and epidihydrocincholinol acetate to 3-hydroxynorallocholanolic acid. Dihydrocincholinol has therefore the following structure.

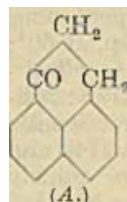


Action of hydrogen sulphide on acid chlorides.

VI. Hydrogen sulphide and 3:4-dimethylbenzoyl chloride. L. SZPERL and L. OZIEBŁO (Rocz. Chem., 1935, 15, 408—413).—1:2:4- $C_6H_3Me_2Br$  and Mg yield a Grignard compound, converted by  $CO_2$  into 3:4-dimethylbenzoic acid, the chloride of which, when treated with  $H_2S$  in boiling xylene, yields chiefly *di*-3:4-dimethylbenzoyl sulphide (I) m.p. 119—120°, together with some *disulphide*, m.p. 127—128°. (I) is converted by  $EtOH-NH_3$  into 3:4-dimethylbenzamide, m.p. 111—113.5°, and  $NH_4$  3:4-dimethylthiobenzoate. R. T.

Preparation of  $\beta$ -1-naphthylpropionic,  $\beta$ -2-naphthylpropionic, and  $\beta$ -2-tetrahydronaphthylpropionic acids. Synthesis of dihydrophenalene and 5:6-tetrahydrobenzindan-1-one. G. DARZENS and A. LEVY (Compt. rend., 1935, 201, 902—904).—1-Naphthylmethyl- and 2-tetrahydronaphthyl-

methyl-malonic esters (cf. A., 1935, 975) when hydrolysed and decarboxylated at 175—195° afford  $\beta$ -1-naphthylpropionic, m.p. 156° [amide, m.p. 133°; Me ester, b.p. 162°/2 mm.; chloride (I), m.p. 26°] (cf. A., 1922, i, 740), and  $\beta$ -2-tetrahydronaphthylpropionic acid, m.p. 127° [amide, m.p. 133°; Me ester, b.p. 183°/15 mm.; chloride (II), b.p. 162°/2 mm.], respectively; the Me ester of the latter with S or Se gives  $\beta$ -2-naphthylpropionic acid. (I) in  $PhNO_2$  containing  $AlCl_3$  gives 7:8-dihydrophenal-9-one (*perinaphthindanone*) (A, annexed). Similarly, (II) affords 5:6-tetrahydrobenzindan-1-one, m.p. 47° (oxime, m.p. 224°), which when oxidised ( $HNO_3$ ) gives 1:2:4:5- $C_6H_2(CO_2H)_4$ .



J. L. D.

Apparent cases of liquid-crystal formation in *p*-alkoxybenzoic acids. B. JONES (J.C.S., 1935, 1874).—The following acids, prepared by interaction of *p*-OH- $C_6H_4$ -CO $_2$ H (1 mol.) and the alkyl iodide (2 mol.) in presence of NaOH (1mol.; 1 hr.; 100°), show liquid crystal formation (the recorded temp. are the transition point and the true m.p.): *p*-n-amyloxy- (122°, 148°); *n*-hexyloxy- (105°, 150°); *n*-heptyloxy- (91°, 145°); *n*-octyloxy- (100°, 145°); *c*-tyloxy-benzoic acid (99°, 131°). The corresponding *m*-series does not show this formation. F. N. W.

Condensation of phenylglyoxyanilide with acetone, ethyl phenylacetate, and ethyl malonate. J. V. SCUDI and H. G. LINDWALL (J. Amer. Chem. Soc., 1935, 57, 2302—2303).—NHPh-COBz (I), COMe, and 5 drops of NH $Et_2$  at room temp. give  $\alpha$ -hydroxy- $\gamma$ -keto- $\alpha$ -phenyl-*n*-valerianilide, m.p. 137—138° [phenylhydrazone, m.p. 174—175° (decomp.); decomposed by hot aq. alkali into the starting products], which with more (I) gives  $\alpha\alpha'$ -dihydroxy- $\gamma$ -keto- $\alpha\alpha'$ -diphenylpimeldianilide, m.p. 171—172°.  $CH_2Ph$ -CO $_2$ Et, (I), and a little NH $Et_2$  give slowly diphenylmaleinanil, m.p. 178—179°, reduced by  $Na_2S_2O_4$  to  $\alpha\alpha'$ -diphenylsuccinanil.  $CH_2(CO_2Et)_2$  and (I) give *Et* $\beta$ -carbonanilido- $\beta$ -phenylpropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate, m.p. 107—108°, which, when distilled/25 mm., affords *Et*OH,  $CH_2(CO_2Et)_2$ , and  $\alpha$ -carbethoxyphenylmaleinanilide, m.p. 111°, reduced ( $Na_2S_2O_4$ ) to  $\alpha$ -carbethoxy- $\alpha'$ -phenylsuccinanil, m.p. 104—105°, which with conc. HCl gives phenylsuccinanil. R. S. C.

Walden inversion reactions of the *p*-toluenesulphinic and *p*-toluenesulphonic esters of ethyl *d*- $\beta$ -hydroxy- $\beta$ -phenylpropionate. J. KENYON, H. PHILLIPS, and G. R. SMUTT (J.C.S., 1935, 1663—1668).—*dl*- $\beta$ -Hydroxy- $\beta$ -phenylpropionic acid may be resolved through the brucine salt (cf. J.C.S., 1910, 97, 121). The *d*-acid with  $EtOH-HCl$  yields the *Et d*-(+)-ester (I), which with  $EtI$ ,  $Ag_2O$ , and anhyd.  $Et_2O$  yields *Et d*-(+)- $\beta$ -ethoxy- $\beta$ -phenylpropionate (II), b.p. 85—86°/0.1 mm.,  $\alpha_{441}^{25} +7.59^\circ$ , but with  $K-Et_2O$  gives chiefly  $CHPh:CH-CO_2Et$ . (I) when heated with  $Ac_2O$  or anhyd.  $HCO_2H$  affords, respectively, the corresponding *d*-(+)- $\beta$ -acetoxy- and *d*-(+)- $\beta$ -formoxy-derivatives, also obtained when *Et d*-(+)- $\beta$ -*p*-toluenesulphinoxy- $\beta$ -phenylpropionate (III),  $\alpha_{441}^{25} +3.77^\circ$  [an undistillable oil prepared from (I), *p*-toluenesulphonyl chloride, and  $C_5H_5N$ ], is heated respectively with  $AcOH-Ac_2O$  and anhyd.  $HCO_2H$ .



(III) when treated with  $\text{Cl}_2\text{-CHCl}_3$ ,  $\text{Cl}_2\text{-H}_2\text{O}$ ,  $\text{ICl}$ , or  $\text{HOCl}$  gives *Et l*-( $-$ )- $\beta$ -chloro- $\beta$ -phenylpropionate (IV); with  $\text{HOCl}$  some *Et l*-( $-$ )- $\beta$ -hydroxy- $\beta$ -phenylpropionate (V) was also formed. Similarly, (III) with  $\text{Br-CHCl}_3$  yields *Et l*-( $-$ )- $\beta$ -bromo- $\beta$ -phenylpropionate, b.p.  $82\text{--}84^\circ/\text{0.1 mm.}$ ,  $\alpha_{\text{D}}^{17} -1.43^\circ$ ; with  $\text{Br-H}_2\text{O}$  some (V) was also formed. (III) with  $\text{CNCl}$  in light petroleum yields *Et l*-( $-$ )- $\beta$ -cyano- $\beta$ -phenylpropionate, b.p.  $78\text{--}79^\circ/\text{0.1 mm.}$ ,  $\alpha_{\text{D}}^{17} -0.53^\circ$ . (III) when treated with  $\text{HNO}_2$  (in a freezing mixture) yields (V), and when refluxed in  $\text{EtOH}$  with  $\text{N}_2$  yields *Et l*-( $-$ )- $\beta$ -ethoxy- $\beta$ -phenylpropionate, but with  $\text{EtOH-K}_2\text{CO}_3\text{-N}_2$  yields mainly optically pure (I), no trace of the  $\text{OEt}$ -derivative being obtained. (III) when refluxed in  $\text{N}_2$  with  $\text{LiCl}$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{EtOH}$  yields (II). (III) is oxidised by  $\text{H}_2\text{O}_2$  to *Et d*-( $+$ )- $\beta$ -*p*-toluenesulphonoxy- $\beta$ -phenylpropionate (VI), which when refluxed with  $\text{K}_2\text{CO}_3\text{-EtOH}$  affords (V), but with  $\text{K}_2\text{CO}_3$ ,  $\text{LiCl}$ , and  $\text{EtOH}$  yields (II). (II) is also obtained when (IV) is refluxed with  $\text{K}_2\text{CO}_3\text{-EtOH}$ . (VI) with  $\text{AcOH}$  affords *Et l*-( $-$ )- $\beta$ -acetoxy- $\beta$ -phenylpropionate, also obtained together with some *Et*-( $-$ )- $\beta$ -chloro- $\beta$ -phenylpropionate (VII) from (VI),  $\text{Ac}_2\text{O}$ , and  $\text{LiCl}$ . (I) when treated in  $\text{Et}_2\text{O}$  with  $\text{PCl}_5$ ,  $\text{PCl}_5\text{-C}_6\text{H}_5\text{N}$ ,  $\text{PCl}_3$ ,  $\text{PCl}_3\text{-C}_6\text{H}_5\text{N}$ , or  $\text{SOCl}_2\text{-C}_6\text{H}_5\text{N}$  yields (VII), but with  $\text{SOCl}_2$  alone yields *Et*-( $+$ )- $\beta$ -chloro- $\beta$ -phenylpropionate (cf. A., 1930, 598; 1931, 480). (I) with  $\text{PBr}_3$  or  $\text{PBr}_3\text{-C}_6\text{H}_5\text{N}$  yields *Et*-( $-$ )- $\beta$ -bromo- $\beta$ -phenylpropionate. Reasons are given for the relative configurations ascribed to the various products obtained from (I). H. G. M.

**4-Hydroxy-3-phenylbenzoic acid.** K. H. SLOTTA and A. E. NOLD (Ber., 1935, 68, [B], 2226—2231).—Treatment of K 2-hydroxy-3-phenylbenzoate with  $\text{CO}_2$  under pressure at  $220\text{--}230^\circ$  does not cause migration of  $\text{CO}_2\text{K}$ . When similarly treated *o*- $\text{C}_6\text{H}_4\text{Ph-OH}$  acquires  $2\text{CO}_2\text{H}$ . Treatment of *o*- $\text{C}_6\text{H}_4\text{Ph-OH}$  with anhyd.  $\text{HCN}$  and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  gives an aldehyde, m.p.  $69\text{--}71.3^\circ$  (*p*-nitrophenylhydrazone, m.p.  $229^\circ$ ), scarcely oxidised by  $\text{KMnO}_4$ ,  $\text{KOB}$ , or  $\text{H}_2\text{O}_2$ , but converted by molten  $\text{KOH}$  into 2-hydroxy-3-phenylbenzoic acid. [ $3:4\text{-CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:CHO}$  is oxidised by  $\text{H}_2\text{O}_2$  in alkaline solution much more readily than  $3:4\text{-C}_6\text{H}_3(\text{OMe})_2\text{:CHO}$  or  $3:4\text{-C}_6\text{H}_3(\text{OEt})_2\text{:CHO}$ ]. Oxidation of 4-acetyl-2-phenylphenol with  $\text{CaOCl}_2$  gives amorphous, smeary products. *o*- $\text{C}_6\text{H}_4\text{Ph-OH}$  is transformed by  $\text{NaOH}$  and  $\text{Me}_2\text{SO}_4$  into *o*-phenylanisole, b.p.  $146\text{--}149^\circ/11\text{ mm.}$ , which with  $\text{AlCl}_3$  and  $\text{AcCl}$  in  $\text{CS}_2$  affords 4-acetyl-2-phenylanisole, m.p.  $91.5\text{--}92^\circ$ , in 92% yield. The latter compound is oxidised by  $\text{CaOCl}_2$  to 4-methoxy-3-phenylbenzoic acid, m.p.  $217.5\text{--}218^\circ$ , demethylated by  $\text{HBr}$  ( $d$  1.49) in boiling  $\text{AcOH}$  to 4-hydroxy-3-phenylbenzoic acid, m.p.  $148\text{--}149^\circ$  after softening at  $142^\circ$ . *Me*, m.p.  $91\text{--}92^\circ$ , and *Et*, m.p.  $62\text{--}63^\circ$ , 4-methoxy-3-phenylbenzoate and *E*, m.p.  $112\text{--}114^\circ$ , and *Pr*<sup>a</sup>, m.p.  $92\text{--}93^\circ$ , or m.p.  $104^\circ$ , 4-hydroxy-3-phenylbenzoate are described.

H. W.

**Diaryls and their derivatives. VI. Oxidation of  $\beta$ -naphthol-3-carboxylic acid. VII. Oxidation of 2-hydroxyanthracene.** I. S. JOFFE (J. Gen. Chem. Russ., 1935, 5, 1205—1209, 1210—1212).—[with I. Z. SMOLJANTSKAJA].  $\beta$ -Naphthol-3-carboxylic acid (I) in boiling  $\text{H}_2\text{O}$  or aq.  $\text{NaOH}$  and excess

of  $\text{FeCl}_3$  yield chiefly 2:2'-dihydroxy-1:1'-dinaphthyl-3:3'-dicarboxylic acid (II), together with some 1-chloro- $\beta$ -naphthol-3-carboxylic acid, which is the chief product when the reaction mixture is acid. (I) and  $\text{CuO}$  in  $\text{PhNO}_2$  ( $210\text{--}220^\circ$ ; 6 hr.) yield (II), which is converted into dinaphthylene dioxide by more prolonged treatment with  $\text{CuO}$  at  $300^\circ$ . (II) is not further oxidised by  $\text{FeCl}_3$ . The  $\text{Pb}$  salt of (II) undergoes a perylene condensation when heated with  $\text{AlCl}_3$  ( $160^\circ$ ; 1 hr.) to yield an acid orange dye, probably 1:12-dihydroxyperylene-2-carboxylic acid, m.p.  $> 330^\circ$ , converted into the quinone by  $\text{CrO}_3$ , and into perylene by distillation from  $\text{Zn}$  dust.

VII. 2-Hydroxyanthracene in boiling  $\text{AcOH}$  and conc. aq.  $\text{FeCl}_3$  yield 2-hydroxy-1:1':9:2'-dianthrillene oxide (*Ac* derivative, m.p.  $247\text{--}250^\circ$ ), converted at  $> 200^\circ$  into an unidentified product (probably the dioxide). R. T.

**Preparation of  $\beta$ -naphthol-3-carboxylic acid.** P. P. KARPUGHIN and I. E. CHUSIN (Ukrain. Chem. J., 1935, 10, 375—391).—At  $< 110^\circ$   $\beta\text{-C}_{10}\text{H}_7\text{ONa}$  and  $\text{CO}_2$  yield  $\text{C}_{10}\text{H}_7\text{O}\cdot\text{CO}_2\text{Na}$ , which at  $< 180^\circ$  is transformed into  $\beta$ -naphthol-1-carboxylic acid (I), converted into the 2:3-isomeride (II) at  $180\text{--}225^\circ$ . (II) can be obtained in good yield, and of high purity, by adding aq.  $\text{NaOH}$  to  $\beta\text{-C}_{10}\text{H}_7\text{OH}$  (III), drying at  $< \text{atm. pressure}$  at  $> 200^\circ$ , and treating the product with  $\text{CO}_2$  at  $225\text{--}260^\circ/2\text{--}50\text{ atm.}$  Methods involving esters of (I) as intermediates, or involving carboxylation in liquid media in presence of excess of (III), do not give as good results as the above. R. T.

**Condensation of aldehydes with malonic acid in presence of organic bases. IV. Piperonal.** T. A. VAHIDY and K. C. PANDYA (Proc. Indian Acad. Sci., 1935, 2, A, 402—405).—The condensation of piperonal (I) with  $\text{CH}_2(\text{CO}_2\text{H})_2$  (II) in presence of any of 19 different bases gives varying yields of piperonylacrylic acid, new m.p.  $242^\circ$ , also obtained from (I) and (II) alone, heated at  $100^\circ$  for 18 hr. E. W. W.

**Preparation of isovalerylsalicylic acid.** J. MILLOTIS (Bull. Soc. chim., 1935, [v], 2, 2134—2135).—This acid (prep. by  $\text{Bu}^t\text{COCl}$ ) has m.p.  $95^\circ$  (cf. A., 1911, i, 53; 1928, 1005). R. S. C.

**Action of selenium on acid anhydrides.** W. THIELE and G. TRAUTMANN (Ber., 1935, 68, [B], 2245—2247).—In connexion with the production of 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$  by dehydrogenation of vitamin-maleic anhydride adducts it is shown that 1- $\text{C}_{10}\text{H}_7\text{Me}$  is formed by the action of  $\text{Se}$  on 1:8- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$  at  $320\text{--}330^\circ$  in presence of cholesterol or from 1:8- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$  in absence of a  $\text{H}$  donor. Similarly, 2:3- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$  in presence of *p*-cyclohexylphenol yields 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ . H. W.

**Synthesis of phenanthrene and hydrophenanthrene derivatives. II. Hydrocarbon synthesis.** L. F. FIESER and E. B. HERSHBERG (J. Amer. Chem. Soc., 1935, 57, 2192—2196; cf. A., 1935, 1358).—3:4-Dihydronaphthalene-1:2-dicarboxylic anhydride (I), 1:2-dihydrophenanthrene-3:4-dicarboxylic anhydride, and the 3:4-dihydro-1:2-anhydride analogue of the latter add dienes slowly but smoothly; the acids derived from the product obtained from (I) have the expected properties; decarboxylation is

difficult and leads to mixed hydrophenanthrenes from which phenanthrene and its derivatives are readily obtained. (I) and  $(\text{CH}_2\cdot\text{CMe})_2$  at  $100^\circ$  (20–25 hr.) give 2:3-dimethyl-1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride (II), *forms*, m.p.  $75\text{--}76^\circ$  (unstable) and  $95\text{--}96^\circ$ , b.p.  $175\text{--}185^\circ/1\text{ mm.}$ , respectively, hydrolysed by hot 6*N*-KOH to the corresponding acid (III), m.p.  $176\text{--}177^\circ$  with loss of  $\text{H}_2\text{O}$ , or by hot KOH-MeOH to the *H Me* ester (IV), m.p.  $157\text{--}159^\circ$  with loss of MeOH; (III) or (IV) with  $\text{CH}_2\text{N}_2$  gives the  $\text{Me}_2$  ester, m.p.  $93\cdot5\text{--}94^\circ$ , which is resistant to hydrolysis and with 50% KOH gives (III). Hydrogenation ( $\text{PtO}_2$ ) of (II) in AcOH gives 2:3-dimethyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-11:12-dicarboxylic anhydride, m.p.  $117\text{--}118^\circ$ , hydrolysed to the acid (V),  $+0\cdot5\text{C}_6\text{H}_6$ , m.p.  $183\text{--}184^\circ$ . (III) or (V) with Se undergo reversal of the Diels-Alder reaction and S leads to a S-containing compound, m.p.  $73\text{--}74^\circ$ . (III) or (IV) with KOH at  $325\text{--}350^\circ$  and then at  $400\text{--}420^\circ$  gives much  $\text{H}_2$  and a mixture of (?)  $\text{H}_4$ - and  $\text{H}_8$ -hydrocarbons; the  $\text{K}_2$  salt of (III) gives CO and a similar mixture; these mixtures with Se give 2:3-dimethylphenanthrene, m.p.  $79\text{--}80^\circ$  [picrate, m.p.  $146\text{--}147^\circ$ ; styphnate, m.p.  $147\text{--}148^\circ$ ; quinone, m.p.  $237\cdot5\text{--}238\cdot5^\circ$  (quinoxaline derivative, m.p.  $208\text{--}209^\circ$ ); cf. lit.; oxidised to pyromellitic acid]. (I) and  $(\text{CH}_2\cdot\text{CH})_2$  give 1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, m.p.  $83\cdot5\text{--}84^\circ$ , b.p.  $160\text{--}170^\circ/1\text{ mm.}$ , converted by KOH into a hexahydrophenanthrene, b.p.  $179\text{--}180^\circ/23\text{ mm.}$  (no picrate), which with Se gives 86% of phenanthrene. Similarly are obtained in dioxan 4:5-dimethyl-1:2:3:6:15:16-hexahydrochrysene-15:16-dicarboxylic anhydride, m.p.  $196\text{--}196\cdot5^\circ$ , 1:4:9:10:11:12-hexahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride, m.p.  $161\cdot5\text{--}162^\circ$ , and 2:3-dimethyl-1:4:9:10:11:12-hexahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride, m.p.  $128\text{--}128\cdot5^\circ$ . R. S. C.

**Derivatives of diphenyl ether. II. Monoaldehydes.** G. LOCK and F. H. KEMPTER (Monatsh., 1935, **67**, 24–35; cf. A., 1930, 767).—*p*- $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (amide, m.p.  $130^\circ$ ) with  $\text{PCl}_5$  or  $\text{SOCl}_2$  gives, after distillation, xanthone, but the crude chloride, prep. by  $\text{SOCl}_2$ , when hydrogenated, affords *o*-phenoxybenzaldehyde (I), b.p.  $172\text{--}174^\circ$  (phenylhydrazone, m.p.  $147^\circ$ ; anil, m.p.  $66\text{--}67^\circ$ ), which is also obtained from *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  by reduction and diazotisation of the crude unstable  $\text{NH}_2$ -aldehyde; with  $\text{Ag}_2\text{O}$  (I) gives the acid and with 50% KOH at  $60^\circ$  also *o*-phenoxybenzyl alcohol, an oil. *m*-Phenoxybenzaldehyde, b.p.  $175\text{--}176^\circ/11\text{ mm.}$ , m.p.  $13\text{--}14^\circ$  (NaHSO<sub>3</sub> compound; phenylhydrazone, m.p.  $102^\circ$ ; oxime, m.p.  $45\text{--}46^\circ$ ; semicarbazone, m.p.  $217^\circ$ ; anil, m.p.  $58^\circ$ ), is obtained by  $\text{HCl}\text{--}\text{SnCl}_2\text{--}\text{Et}_2\text{O}$ -reduction of the nitrile, b.p.  $179\text{--}180^\circ/13\text{ mm.}$  (prep. from the  $\text{NO}_2$ -compound), and by hydrogenation of *m*-phenoxybenzoyl chloride, b.p.  $174\text{--}175^\circ/12\text{ mm.}$  (corresponding amide, m.p.  $127^\circ$ ), and is converted by boiling 50% aq. KOH into *m*-phenoxybenzyl alcohol, m.p.  $71^\circ$ , and *m*-phenoxy-cinnamic acid, m.p.  $115^\circ$ . *p*-Phenoxybenzaldehyde, m.p.  $24\cdot5\text{--}25^\circ$ , b.p.  $185^\circ/14\text{ mm.}$  (anil, m.p.  $48\text{--}49^\circ$ ),

is obtained by hydrogenation of the acid chloride and leads to *p*-phenoxybenzyl alcohol, m.p.  $53^\circ$ , and *p*-phenoxy-cinnamic acid, m.p.  $155^\circ$ . Temp. are corr. R. S. C.

**Pharmacology of phenanthrene derivatives.** V.—See this vol., 106.

**Action of oxidising agents on cyclobutylamine.** N. J. DEMJANOV and Z. I. SCHUJKINA (J. Gen. Chem. Russ., 1935, **5**, 1213–1225).—cyclobutylamine (I) is oxidised by  $\text{CrO}_3$ ,  $\text{CrO}_3\text{--H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ , and  $\text{O}_2\text{--O}_3$  to cyclobutanone (II), by the stages: (I)  $\rightarrow$  cyclobutylhydroxylamine  $\rightarrow$  (II) ketoxime  $\rightarrow$  (II)+ $\text{NH}_2\text{OH}$ ; (II)  $\rightarrow$  succinic acid (III);  $\text{NH}_2\text{OH} \rightarrow \text{HNO}_2$ . In presence of atm.  $\text{O}_2$  and Cu, or of  $\text{O}_2$  and osmic anhydride (IV) the process consists of (I)  $\rightarrow$  (II)+ $\text{NH}_3$ ; (II)  $\rightarrow$  (III). The highest yields of (II) (25%) are obtained using (IV) (12 hr. at room temp.). R. T.

**Multiplanar cyclohexane rings.** R. D. DESAI and R. F. HUNTER (Nature, 1935, **136**, 953–954; A., 1935, 1495).—In a further examination of the Sachse-Mohr hypothesis the condensation of the cyanohydrins of the methylcyclohexanones with arylamines has been investigated. The formation of two, but never  $>$  two, isomeric cyanoarylamino-methylcyclohexanes has been observed in certain cases. L. S. T.

**Reduction of oximes.** (MLLE.) A. WOHL (Bull. Soc. chim., 1935, [v], **2**, 2135–2140).—Hydrogenation ( $\text{PtO}_2$ ) of  $\text{CHPh}\cdot\text{NOH}$  in 95% EtOH gives  $\text{NH}(\text{CH}_3\text{Ph})$ , (absorption spectrum given), but ketoximes [ $\text{CPhMe}\cdot\text{N}\cdot\text{OH}$  (I) and  $\text{CMe}_2\text{Bu}\cdot\text{CPh}\cdot\text{N}\cdot\text{OH}$  (II)] are unaffected. (I) and (II) are not reduced by  $\text{CaCl}_2\text{--Zn}$  in hot EtOH. With Al-Hg in moist  $\text{Et}_2\text{O}$  (I) gives  $\text{CHPhMe}\cdot\text{OH}$ , but (II) is unaffected owing to its isooxime structure. R. S. C.

**Chemistry and spectroscopy of oxime acetates.** (MLLE.) A. WOHL (Bull. Soc. chim., 1935, [v], **2**, 2140–2143).—The absorption spectra of oximes and their acetates are very similar. With Al-Hg  $\text{CPhMe}\cdot\text{N}\cdot\text{OAc}$  gives  $\text{CHPhMe}\cdot\text{OH}$  and  $\text{CHPhMe}\cdot\text{OAc}$ , m.p.  $75^\circ$  (lit.  $65^\circ$ ), but *Ph*  $\alpha$ -dimethylbutyl ketoxime acetate, b.p.  $172\text{--}173^\circ/17\text{ mm.}$ , is not affected owing to its isooxime structure. R. S. C.

**Reaction of ketens with Grignard reagents.** C. D. HURD, R. N. JONES, and F. H. BLUNCK (J. Amer. Chem. Soc., 1935, **57**, 2033–2036).—The ester groups of  $\text{CO}_2\text{Et}\cdot\text{C}\cdot\text{CO}$  (I) and  $\text{CO}_2\text{Et}\cdot\text{C}\cdot\text{CO}$  (II) do not react with  $\text{MgEtBr}$  or  $\text{MgPhBr}$ .  $\text{CHEt}(\text{CO}_2\text{Et})_2$  (prep. in 62% yield by EtBr or 80–88% yield by  $\text{Et}_2\text{SO}_4$ ) with  $\text{P}_2\text{O}_5$  at  $180\text{--}200^\circ$  gives 23% of (I), b.p.  $45\text{--}55^\circ/11\text{--}12\text{ mm.}$ , stable at  $-78^\circ$ , and a little  $\text{Pr}^+\text{CO}_2\text{H}$ . (I) reacts with  $\text{NH}_3\text{Ph}$ , but not with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  in  $\text{C}_6\text{H}_6$ . (I) and  $\text{MgPhBr}$  (1 mol.) give, after hydrolysis,  $\text{CHBzEt}\cdot\text{CO}_2\text{Et}$  (III), but with 3 mols. of  $\text{MgPhBr}$  affords also some *Ph*  $\alpha$ -benzhydrylidene-propyl ketone (IV), m.p.  $126\text{--}127^\circ$  (with  $\text{O}_3$  gives  $\text{COPh}_2$ ,  $\text{BzOH}$ , and  $\text{EtCO}_2\text{H}$ ), probably arising thus: (I)  $\rightarrow \text{CO}_2\text{Et}\cdot\text{C}\cdot\text{CPh}\cdot\text{OMgBr} + \text{MgPhBr} \rightarrow \text{CBzEt}\cdot\text{CPh}\cdot\text{OMgBr} \rightarrow (+\text{MgPhBr} + \text{H}_2\text{O})$  (IV). (II) and  $\text{MgPhBr}$  lead to (III). (I) and  $\text{MgEtBr}$  (1 mol.) give a product, hydrolysed to  $\text{COEt}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$  (V)

and pyrolysed at 200—300° to EtBr and an unsaturated substance, b.p. 100—110°. (III) and MgEtBr give (V). R. S. C.

**Attempted resolution of oximes.** (MILLER) A. WOHL (Bull. Soc. chim., 1935, [v], 2, 2163—2168).—CPhEt·N·ONa, CH<sub>2</sub>Cl·CO<sub>2</sub>H, and NaOAc in EtOH give *propiofenoneoxime O-glycollic acid ether*, m.p. 58°, which resembles the parent oxime in absorption. CMe<sub>2</sub>Bu·CPh·N·OH (I) gives similarly *Ph α-dimethylbutyl ketoxime O-glycollic acid ether*, m.p. 70°, which, since it resembles (I) in absorption, has the *isoxime* structure, but could, nevertheless, not be resolved by alkaloids or moulds; the *brucine* salt has  $[\alpha]_D^{25} +15^\circ$ . (I) with NaOEt and CMe<sub>2</sub>Br·CO<sub>2</sub>Na in EtOH gives an ether, m.p. 135°, and in a second experiment an (?) isomeric ether, m.p. 79°. R. S. C.

**Ketones obtained by condensation of acetyl chloride with saturated hydrocarbons in presence of aluminium chloride.** C. D. NENTZESCU and G. G. VANTU (Bull. Soc. chim., 1935, [v], 2, 2209—2219).—cycloHexane (I), AlCl<sub>3</sub>, and excess of AlCl<sub>3</sub> give only 2-acetyl-1-methylcyclopentane (II), but with less AlCl<sub>3</sub> some 2-acetyl-1-methyl-Δ<sup>1</sup>-cyclopentene (III) is also formed by the following steps: (I) methylcyclopentane → 1-methyl-Δ<sup>1</sup>-cyclopentene → 1-chloro-2-acetyl-1-methylcyclopentane → HCl

+ (III) or — HCl + (II). 1-Methylcyclopentane-2-carboxyl chloride (IV) gives by the Br-azide method 2-methylcyclopentanone and a little 1-methyl-Δ<sup>1</sup>-cyclopentene-2-carboxylic acid. (II) gives (Clemmensen) a mixture of 78.7% of *trans*- and 21.3% of *cis*-1-methyl-2-ethylcyclopentane, b.p. 121°/753 mm. 1-Methyl-2-α-hydroxyethylcyclopentane is dehydrated by the xanthate method to 2-ethylidene-1-methylcyclopentane, b.p. 123—124°, but H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or KHSO<sub>4</sub> gives a mixture thereof with a little 1:3-dimethyl-Δ<sup>1</sup>-cyclohexene. (II) and PhCHO give 2-cinnamoyl-1-methylcyclopentane, b.p. 153°/4 mm. (*dibromide*, m.p. 107°). *Et* 1-methylcyclopentane-2-carboxylate, b.p. 179—180°, and Na·EtOH give 1-methylcyclopentyl-2-carbinol, b.p. 171—172°/758 mm., and thence the *bromide*, b.p. 65°/14 mm., 1:2-dimethylcyclopentane, b.p. 93—94°, and β-1-methylcyclopentyl-2-propionic acid, b.p. 147—148°/15 mm. (*chloride*, b.p. 98°/15 mm.; *amide*, m.p. 93°). Hydrogenation of (IV) gives 1-methylcyclopentane-2-aldehyde, b.p. 148—150° (*semicarbazone*, m.p. 121.5°). Physical data are given. R. S. C.

**Benzophenones from carboxylic acids.** H. P. NEWTON and P. H. GROGGINS (Ind. Eng. Chem., 1935, 27, 1397—1399; cf. A., 1935, 214).—Boiling PhCl (3—6 mols.) with *p*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H (1 mol.) and AlCl<sub>3</sub> gives 4:4'-dichlorobenzophenone (>80%) and the 2:4'-isomeride. 4-Chloro- (82%), 4-chloro-4'-methyl- (81%), and 3:4-dichloro-benzophenone (79%) are prepared similarly. *p*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub> with PhCl and AlCl<sub>3</sub> at 175—180° gives 3:4-dichloro-4':4''-dichlorobenzoylbenzophenone, m.p. 253° (*oxime*, m.p. 210°; *anilide*, m.p. 288°). Cu increases the yield of 4:4'-diaminobenzophenone (prepared from the Cl-compound and NH<sub>3</sub>) to a greater extent at 180° than at 200°; at the higher temp. the extent of non-catalytic amination increases greatly. KClO<sub>4</sub> sometimes exerts a beneficial effect. In the absence of

catalysts, 4'-chloro-4-aminobenzophenone is the main product. 4'-Amino-4-methylbenzophenone is prepared from the Cl-compound. J. L. D.

**Reversibility of the Friedel-Crafts condensation. Hydrogenation phenomena.** L. L. ALEXANDER, A. L. JACOBY, and R. C. FUSON (J. Amer. Chem. Soc., 1935, 57, 2208—2209).—In presence of AlCl<sub>3</sub> the reaction, C<sub>6</sub>H<sub>5</sub>X·CH·CHR (R=CO·R or Ph) + C<sub>6</sub>H<sub>6</sub> → (+2H) 2C<sub>6</sub>H<sub>5</sub>X + CH<sub>2</sub>Ph·CH<sub>2</sub>R, occurs, but the origin of the 2H is unknown. Thus Ph ββ-di-*p*-chlorophenylvinyl ketone and Ph ββ-diphenylvinyl ketone both give Ph ββ-diphenylethyl ketone, the latter perhaps by simple hydrogenation; similarly, ββ-diphenylvinyl Bu<sup>ν</sup> ketone adds H<sub>2</sub>. β-*p*-Chlorophenylcinnamic acid, m.p. 168°, with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> gives ββ-diphenylpropionic acid; *pp'*-dichlorostilbene, (CH<sub>2</sub>Ph)<sub>2</sub>; stilbene, (CH<sub>2</sub>Ph)<sub>2</sub>; *p*-bromostilbene, (CH<sub>2</sub>Ph)<sub>2</sub>. *p*-C<sub>6</sub>H<sub>4</sub>Cl·COPh gives (Reformatsky) *Et* β-hydroxy-β-phenyl-β-*p*-chlorophenylpropionate, m.p. 79—80.5°, hydrolysed to the acid, m.p. 188.5—189° (decomp.), which with Ac<sub>2</sub>O·NaOAc yields (II). R. S. C.

**Chemistry and physiology of the androsterone group.** K. TSCHERNING (Angew. Chem., 1936, 49, 11—16).—A summary.

**Oestrogenic activity of 1-keto-1:2:3:4-tetrahydrophenanthrene.** A. BUTENANDT and G. SCHRAMM (Ber., 1935, 68, [B], 2303; cf. this vol., 76).—The physiological activity of 1-keto-1:2:3:4-tetrahydrophenanthrene is confirmed (cf. Cook *et al.*, A., 1933, 323). H. W.

**Anhydrobismethone (bithon).** N. J. TOIVONEN, T. FJADER, and A. HEIKEL (Suomen Kem., 1935, 8, B, 32—33).—When boiled in aq. solution containing 0.2—0.5 mol. of NaOH and NH<sub>4</sub>Cl dimedon (I) (1:1-dimethylcyclohexane-3:5-dione) gives a condensation product, "*bithon*" (II), m.p. 155—157°, probably 4-(5'-keto-3':3'-dimethylcyclohexylidene)-1:1-dimethylcyclohexane-3:5-dione (*Ag* and *Cu* salts). (II) is also obtained by boiling a C<sub>6</sub>H<sub>6</sub> solution of (I) with K, or by heating (I) at 150—170°. Prolonged boiling of (II) in aq. solution partly reconverts it into (I). J. W. B.

**Self-condensation of acetylacetone.** A. HEIKEL (Suomen Kem., 1935, 8, B, 33—34).—When boiled with very dil. aq. NaOH, CH<sub>2</sub>Ac<sub>2</sub> affords 4-acetyl-*m*-5-xyleneol (von Auwers, A., 1915, i, 145; 1916, i, 34). A mechanism is suggested. J. W. B.

**Dimesityl diketones and their derivatives.** II. Isomerism of βε-dibromo-αζ-dimesityl-αζ-hexanedione. T. Y. KAO and Y. J. LO (J. Chinese Chem. Soc., 1935, 3, 355—357).—αζ-Dimesityl-αζ-hexanedione, m.p. 105—107° (lit. 102—103°), prepared from adipyl chloride and mesitylene, with Br affords two forms of βε-dibromo-αζ-dimesityl-αζ-hexanedione, m.p. 203—204° and 151—152°, respectively. The former is the chief product, and is also obtained when the latter is heated to 155°. H. G. M.

**Attempted preparation of vanilloylformic acid.** W. E. BARCH (J. Amer. Chem. Soc., 1935, 57, 2330).—Contrary to Mottern (A., 1934, 1354) this acid is not obtained from apocyanin (I), PhNO<sub>2</sub>, and alkali,

a result confirmed by other workers. (I) is best obtained by a low-temp. Fries isomerisation. R. S. C.

**Action of the Grignard reagent on fuchsones.** P. L. JULIAN and W. J. GIST (J. Amer. Chem. Soc., 1935, 57, 2030—2033).—1:6-Addition of  $\text{MgMeI}$  to fuchsones (I) is confirmed by methylation ( $\text{Me}_2\text{SO}_4\text{--NaOH}$ ) of the product to  $\alpha$ -diphenyl- $\alpha$ -p-anisylethane, m.p. 77°, also prepared from  $p\text{-OMe-C}_6\text{H}_4\text{-CPh}_2\text{Cl}$  and  $\text{MgMeI}$  (3 mols.). 4-Benzoyl-1-naphthyl Me ether and  $\text{MgPhBr}$  give diphenyl-4-methoxynaphthyl-1-carbinol, m.p. 162°, converted by  $\text{SOCl}_2$  (not  $\text{HCl}$  in  $\text{Et}_2\text{O}$ ) into the chloride, m.p. 151°, which at 180—200° yields naphthafuchsones (II), m.p. 83°. 1:6-Addition of  $\text{MgMeI}$  to (II) occurs, but only in small amount; the product,  $\alpha$ -diphenyl- $\alpha$ -4-methoxynaphthyl-1-ethane, b.p. 220—230° (bath)/0.1 mm., m.p. 144°, is also obtained from  $\text{OMe-C}_{10}\text{H}_6\text{-CPh}_2\text{Cl}$  and  $\text{MgMeI}$ . Anthrafuchsones (III) reacts with  $\text{MgMeI}$ , however, by 1:2-addition to give 10-benzhydrylidene-9-methyl-9:10-dihydroanthranol, m.p. 223°, oxidised by  $\text{CrO}_3$  to  $\text{COPh}$ , and anthraquinone. Little or no 1:6-addition occurs with  $\text{MgPhBr}$ , (I) and (II) giving gums, whilst (III) yields 9-phenyl-10-benzhydrylidene-9:10-dihydroanthranol (IV), converted by  $\text{HCl-Et}_2\text{O}$  into 9-chloro-9-phenyl-10-benzhydrylidene-9:10-dihydroanthracene, m.p. 220° (decomp. from 185°), reconverted into (IV) by moist  $\text{CaCO}_3$  in  $\text{COMe}_2$  and giving with  $\text{Ag}$  in  $\text{C}_6\text{H}_6$  followed by air an oily peroxide. The corresponding 9-Br-compound, m.p. 165°, differs from a Br-derivative (V), m.p. 143°, prepared from (?) 9-phenyl-10-benzhydrylanthracene (A., 1930, 903). Hydrolysis of (V) does not give (IV). R. S. C.

**Vat dyes of the benzanthrone series.** XIII. XIV. 6:6'- and 8:8'-Derivatives of isoviolanthrone. T. MAKI and Y. NAGAI (J. Soc. Chem. Ind. Japan, 1935, 38, 560—564B, 564—567B; cf. A., 1935, 1499).—XIII. 6:13-Dichlorobenzanthrone (I) when heated with  $\text{KOH-PhOH-EtOH}$  at 143° (1 hr.) yields chiefly 6:6'-dichloroisoviolanthrone (II) and a compound, insol. in alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  and converted by hot conc.  $\text{H}_2\text{SO}_4$  into a vat dye (cf. B., 1934, 752); provisional structures are proposed for the two last-mentioned compounds. Some alkali- and  $\text{AcOH-sol.}$  products are also formed. (II), when heated repeatedly with  $\text{KOH-MeOH}$  at 180° (7 hr.), is converted into 6:6'-dimethoxyisoviolanthrone, whilst with  $\text{KOH-PhOH}$  at 200° it yields 6:6'-dihydroxyisoviolanthrone (di-p-nitrobenzoyl derivative). These compounds form vats with  $\text{Na}_2\text{S}_2\text{O}_4\text{-EtOH-H}_2\text{O}$  at 80°, and dye cotton various shades of blue.

XIV. 8:13-Dichlorobenzanthrone (III) with  $\text{KOH-PhOH-EtOH}$  at 143° (1 hr.) yields 8:8'-dihydroxyisoviolanthrone (di-p-nitrobenzoyl derivative; converted into Me<sub>2</sub> ether when boiled with  $\text{PhNO}_2\text{-Me}_2\text{SO}_4\text{-NaOH}$ ) and a "B-dyestuff" (cf. loc. cit.), sol. in alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ , and converted by hot conc.  $\text{H}_2\text{SO}_4$  into a dark grey-violet vat dye. The Cl at position 8 is much more labile than at 6. The 8:8'-substitution has little bathochromic effect; the derivatives form vats more readily than the 6:6'-derivatives, and dye cotton violet. H. G. M.

**Grignard reagent of pinene hydrochloride.** Action of phthalic anhydride. R. BOUSSET (Bull.

Soc. chim., 1935, [v], 2, 2182—2187).—Pinene hydrochloride, m.p. 125—126°, under  $\text{H}_2$  gives a Grignard reagent, which with  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  (1 mol.) yields d-2-o-carboxybenzoylcamphane, m.p. 154°, with small amounts of another acid, m.p. 337° (rapid heating; sublimes if slowly heated), d-bornylene, and dl-camphane. R. S. C.

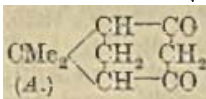
**Simultaneous formation of two diastereoisomeric alcohols in the action of organomagnesium derivatives on active camphenyl ketones.** M. TIFFENEAU, J. LEVY, and E. DITZ (Bull. Soc. chim., 1935, [v], 2, 1855—1866; cf. A., 1931, 848).—Campholenamide with  $\text{MgEtX}$  and  $\text{MgPhX}$  yields respectively camphenyl Et ketone (I), b.p. 77°/2 mm.,  $[\alpha]_{\text{D}}^{20} + 27.5^\circ$ ,  $[\alpha]_{\text{D}}^{19} + 30.6^\circ$  (semicarbazone, m.p. 162°; oxime, b.p. 145°/14 mm.), and Ph camphenyl ketone (II), b.p. 121°/2 mm.,  $[\alpha]_{\text{D}}^{20} + 34.1^\circ$ ,  $[\alpha]_{\text{D}}^{20} + 38.6^\circ$  (semicarbazone, m.p. 167°; oxido-derivative, m.p. 64—65°,  $[\alpha]_{\text{D}}^{19} + 27.8^\circ$ ,  $[\alpha]_{\text{D}}^{19} + 31.0^\circ$ ) (cf. loc. cit.). (I) and  $\text{MgPhX}$  gives an oil which with  $\text{BzO}_2\text{H}$  yields mainly  $\alpha$ -oxidocamphenylphenylethylcarbinol, m.p. 98°,  $[\alpha]_{\text{D}}^{19} - 42.7^\circ$ ,  $[\alpha]_{\text{D}}^{19} - 51.7^\circ$ , and some of the  $\beta$ -isomeride, m.p. 133.5—134°,  $[\alpha]_{\text{D}}^{20} + 15.0^\circ$ ,  $[\alpha]_{\text{D}}^{20} + 17.5^\circ$  (cf. loc. cit.). By similar methods (II) and  $\text{MgEtX}$  give the same two products (with slightly higher  $[\alpha]$ ), the relative amounts being inverted. These results show that a  $\beta$ -asymmetric C with respect to the CO causes the double linking of the CO to react partly unsymmetrically. H. G. M.

**Camphor series.** I. D. C. SEN (J. Indian Chem. Soc., 1935, 12, 647—652).—dl- or l-Camphor,  $\text{HCl}$ , and  $\text{H}_2\text{S}$  in dry  $\text{EtOH}$  at 0° give 50% of dl-thiocamphor (I), m.p. 145°, but d-camphor gives l-thiocamphor, m.p. 146°,  $[\alpha]_{\text{D}}^{20} - 12^\circ$  in  $\text{EtOH}$ ; (I) gives nearly quantitatively camphoroxime and the semicarbazone and phenylhydrazone, and with  $\text{Zn-HCl-EtOH}$  yields thioborneol, m.p. 120° (lit. 65°), converted by I into dibornyl disulphide, m.p. 198° (lit. 178°). R. S. C.

**6-Hydroxycamphor.** K. MIYAKE and M. WATANABE (Proc. Imp. Acad. Tokyo, 1935, 11, 322—323; cf. A., 1935, 754).—4-Carboxymethyl-2:3:3-trimethylcyclopentan-1-one at 280—300° affords 6-hydroxycamphor, m.p. 194—195° [dioxime, m.p. 241—242° (decomp.); disemicarbazone, m.p. 228°], which is hydrolysed to the original acid; its semicarbazone is reduced to camphane. J. L. D.

**Synthesis of "ketonopinone."** P. C. GUHA and K. GANAPATHI (Current Sci., 1935, 4, 312—313).—Me pinonate (cf. A., 1935, 975) with Na in PhMe or NaOMe in MeOH gives ketonopinone, m.p. 104° (Cu derivative, sinters 238°), which is (A), since with  $\text{Ba(OH)}_2$  it gives pinonic acid. F. R. G.

**Sulphur compounds of terpenes.** VI. Action of gold chloride on  $\text{C}_{10}\text{H}_{18}\text{S}$  ( $\geq \text{C-S-C} \leq$  type). VII. Action of gold chloride on  $\text{C}_{10}\text{H}_{18}\text{S}$  ( $\geq \text{C-S-C} \leq$  type) at higher temperature. VIII. Action of gold chloride on thioborneol and thiocamphor. IX. Action of gold chloride on various terpene sulphur compounds. A. NAKATSUCHI (J. Soc. Chem. Ind., Japan, 1935, 38, 511—512B, 512—513B, 617B, 617—618B).—VI.  $\text{C}_{10}\text{H}_{18}\text{S}$  (I) (cf. A., 1932,





1038) and  $\text{AuCl}_3\text{-H}_2\text{O}$  at  $30^\circ$  yield  $\text{C}_{10}\text{H}_{18}\text{S}\cdot\text{AuCl}_3$  (II), which on keeping with (I) and  $\text{H}_2\text{O}$  yields  $\text{C}_{10}\text{H}_{18}\text{S}\cdot\text{AuCl}$  (III),  $\text{C}_{10}\text{H}_{18}\text{SO}$ , and  $\text{HCl}$ . In the presence of excess of (I), the reaction between (I) and (II) is pseudo-unimol. (II) in  $\text{CHCl}_3$  at  $50^\circ$  is partly reduced to Au by limonene,  $\text{PhNO}_2$ , and amyl alcohol, but not by (I).

VII. (II) when heated at  $116\text{--}120^\circ$  (sealed vessel; 30 min.) is reduced to Au, but when (I) is present, the amount of Au formed is diminished. Similarly the amount of Au obtained when (III) is heated at  $120^\circ$  (sealed; 5 hr.) with  $\text{H}_2\text{O}$  is diminished by addition of (I), but is increased at  $109\text{--}111^\circ$  if colophony, ester gum, and ethylcellulose, but not organo-sulphur compounds, are also added. (III) with excess of (I) is stable at  $100^\circ$ , but at  $120^\circ$  decomposes rapidly giving Au and  $\text{Cl}_2$ . (I) and  $\text{AuCl}_3\text{-H}_2\text{O}$ , and (I) and (II) at  $110^\circ$  yield a compound, decomp.  $166^\circ$ , which contains 71.35% Au and 8.11% S.

VIII. A white Au compound,  $\text{C}_{10}\text{H}_{17}\text{SAu}$ , obtained from thioborneol, has m.p.  $194\text{--}195^\circ$ , decomp.  $206^\circ$ . Thiocamphor gives rise to a greenish-black amorphous compound, and a compound, m.p.  $179\text{--}180^\circ$  (decomp.).

IX. Similarly the S compound from  $\Delta^3$ -*p*-menthene (cf. A., 1933, 830) and  $\text{AuCl}_3\text{-H}_2\text{O}$  yield a Au compound,  $\text{C}_{10}\text{H}_{17}\text{SAu}$ , m.p.  $92^\circ$ , decomp.  $171^\circ$ , whilst the S compound from  $\Delta^{8(9)}$ -*p*-menthene and  $\text{AuCl}_3\text{-H}_2\text{O}$  yield a Au compound, decomp.  $169.5\text{--}171^\circ$ . The Au compounds obtained from the S compounds of  $\alpha$ -phellandrene, linaloolene, and linalyl acetate decompose at  $158\text{--}163^\circ$ ,  $161^\circ$ , and  $192\text{--}193^\circ$ , respectively. Most of the above Au compounds are sol. in certain org. solvents.

H. G. M.

Diterpene, "sciadopitene," from leaf- and wood-oil of *Sciadopitys verticillata*, S. and Z. I. Properties. K. NISHIDA and H. UOTA (J. Agric. Chem. Soc. Japan, 1935, 11, 489—494).—Fractional distillation/1—2 mm. affords approx. 5% of a diterpene, *sciadopitene*,  $\text{C}_{20}\text{H}_{32}$ , m.p.  $95\text{--}96^\circ$ ,  $[\alpha]_D^{25} + 11.06^\circ$  in  $\text{CHCl}_3$  [nitrosochloride, decomp.  $127\text{--}128^\circ$ ; nitrosate,  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{N}_2$ , decomp.  $126\text{--}127^\circ$ ; monohydrochloride, m.p.  $106^\circ$  (decomp.), which with  $\text{KOAc-EtOH}$  yields the isomeride, *isosciadopitene*, m.p.  $106\text{--}107^\circ$ , also prepared (m.p.  $108\text{--}109^\circ$ ) by isomerisation of the diterpene with  $\text{H}_2\text{SO}_4$ , but not  $\text{HCO}_2\text{H}$ ]. F. O. H.

Number of primary dicyclic terpene alcohols. R. BOUSSER (Bull. Soc. chim., 1935, [v], 2, 2187).—Myrtenol is not the first of these alcohols, as claimed by Dupont *et al.* (A., 1935, 624; cf. A., 1930, 1591; 1935, 219).

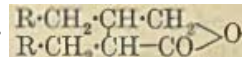
R. S. C.

Balata resin. I. Crystalline constituents of Surinam sheet balata resin. Y. TANAKA, T. KUWATA, and T. SUZUKI (J. Soc. Chem. Ind. Japan, 1935, 38, 504—505b).—The cryst. constituents of the resin are the acetates of three triterpene alcohols,  $\beta$ -amyrin (Bz derivative, m.p.  $229\text{--}230^\circ$ ), *isolupeol* (Bz derivative, m.p.  $269\text{--}270^\circ$ ), and *balatol* (Ac, m.p.  $100\text{--}101^\circ$ , and Bz derivative, m.p.  $121\text{--}121.5^\circ$ ).

H. G. M.

Constitution of matairesinol. L. H. BRIGGS, D. A. PEAK, and J. L. D. WOOLLOXALL (J. Proc. Roy. Soc. New South Wales, 1935, 69, 61—67).—Contrary to Easterfield (J.C.S., 1910, 97, 1028), matairesinol (I) [ $\text{B}_7$ -derivative, m.p.  $169\text{--}169.5^\circ$ ;  $\text{Ac}_2$  (lit.,  $\text{Ac}_1$ )

derivative, m.p.  $110^\circ$ ] is  $\text{C}_{20}\text{H}_{32}\text{O}_6$ , isomeric with pinoresinol (lit.,  $\text{C}_{19}\text{H}_{20}\text{O}_6$ ). With  $\text{Me}_2\text{SO}_4$  in  $\text{NaOH}$  it affords a  $\text{Me}_2$  derivative (II), m.p.  $126.5\text{--}127^\circ$ , hydrolysed ( $\text{NaOH}$ ) to *dimethylmatairesinolic acid*, m.p.  $80\text{--}84^\circ$ , which indicates the persistence of the lactone ring in the former derivative, and of two phenolic groups. (I) is not reduced by  $\text{Pd-H}_2$ , but with  $\text{KMnO}_4$  in  $\text{NaOH}$  at  $100^\circ$  affords veratric acid in  $> 50\%$  yield, which shows that two veratryl residues are present, and as no veratroylformic acid is obtained (cf. A., 1929, 1064), the aromatic nuclei must be linked through  $\text{-CH}_2\text{-}$ . The formula



[ $\text{R} = 4 : 3\text{-C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$ ] is proposed on chemical and phytochemical evidence.

J. L. D.

Pigment of ebony wood. E. WEDEKIND (Ber., 1935, 68, [B], 2363—2366).—West African ebony sawdust is freed from lignin by treatment with dioxan containing 3—5% of conc.  $\text{HCl}$  at  $100^\circ$  and the residue after being washed with dioxan and  $\text{COMe}_2$  is shaken with 72%  $\text{H}_2\text{SO}_4$  or treated with superconc.  $\text{HCl}$  at  $0^\circ$  to remove cellulose. The black, amorphous residue contains small amounts of adsorbed lignin, which are removed by  $\text{PhOH}$ . The composition of the black pigment (I), which is insol. in all org. and inorg. media, corresponds closely with the formula  $\text{C}_9\text{H}_6\text{O}_3$ . Alkali hydroxides partly dissolve (I) to colloidal solutions. Fusion with  $\text{KOH}$  does not lead to recognisable products. Powerful oxidising agents, particularly  $\text{NaOCl}$ , cause decomp., but no defined product could be isolated. The possible relationship of (I) to lignin  $\text{C}_9\text{H}_{12}\text{O}_3$  (Freudenberg's min. empirical formula) is examined by dehydrogenating the lignin extracted by dioxan from ebony wood with S at  $180\text{--}200^\circ$ , whereby  $\text{H}_2\text{S}$  is only very slowly evolved, giving a black, amorphous, completely insol., non-homogeneous product containing somewhat less C and somewhat more H than (I) and also 0.92% of S. A closely similar product is obtained from beechwood (dioxan) lignin. Dehydrogenation with Se is impossible, since the requisite high temp. induces decomp. of (I). Similar treatment of the wood of *Eucalyptus marginata* gives a red-brown pigment the H content of which is  $<$  that of lignin. H. W.

Hydrolysis of pine and beech wood. K. STORCH (Ber., 1935, 68, [B], 2367—2374).—Treatment of pine wood with 64%  $\text{H}_2\text{SO}_4$  at  $15\text{--}20^\circ$  during 3—48 hr. shows the presence of 28—30% of lignin; when hydrolysis of the cellulose has proceeded so far that the solution remains clear when diluted, it is immaterial whether or not the mixture is diluted with  $\text{H}_2\text{O}$  previous to filtration. Under similar conditions red beech wood appears to contain about 12% of lignin when the mixture is directly filtered and about 24% when it is diluted (and boiled) previously to filtration. After 16 hr. the lignin retains the fibrous structure of the wood; that from pine contains C 65.0, H 5.4, OMe 14.9%, whereas that from beech has C 63.0, H 5.6, and OMe 19.2%. Pine lignin retains 84% of the OMe in wood; the filtrate contains about 5% as  $\text{MeOH}$  and the remaining 11% is present in sol. org. compounds. In the beech residue (12% of wood) only 37% of the total OMe is retained. The matter pptd. by dilution contains 39% of the

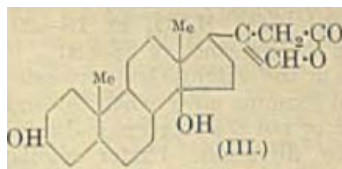
OMe whereas  $\approx 9\%$  is present as MeOH and the remaining 15% in OMe-compounds. Hilpert's view that beech lignin is a product of the action of conc. acid on the carbohydrates of wood is difficult to reconcile with the fibrous structure of insol. beech lignin. The beech lignin sol. in acid is sol. also in NaOH,  $C_5H_5N$ , and  $COMe_2 \cdot H_2O$  and retains this property after intense desiccation. Pine-wood ( $H_2SO_4$ ) lignin is not appreciably sol. in NaOH. Similar behaviour is shown by the woods. Beech wood is dissolved by 5% NaOH to the extent of 28% and 35% at room temp. and 100°, respectively, and the treatment does not cause enrichment of the residue in lignin. It is therefore probable that the sol. and insol. lignin components of beech are in some manner (possibly anatomically) separated from one another. The insol. component has the same composition when isolated after 16 or 48 hr. treatment; after complete hydrolysis, the sol. portion closely resembles it in elementary composition and OMe content. H. W.

**Sapinic acids from various species of pine and spruce.** T. HASSELSTROM and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2118—2121).—These are shown by hydrogenation and isomerisation to be a mixture of *l*- (I) and *d*-pimaric acid. Since (I) belongs to the abietic class, it is renamed *l*-sapietic acid.

R. S. C.

**An acid ester contained in the root of official valerian.** E. CIONGA (Compt. rend., 1935, 201, 1152—1154).—From industrial residues, an acid (I),  $C_{10}H_{18}O_4$ , b.p. 120—122°/0.6 mm.,  $[\alpha]_D^{20} +4.83^\circ$ , has been separated, yielding on hydrolysis  $Bu^sCO_2H$  and *d*- $\alpha$ -hydroxy- $\beta$ -methylbutyric acid, b.p. 124—125°/13 mm., m.p. 66.5—67.5°,  $[\alpha]_D^{24} -1.56^\circ$  in  $H_2O$ . (I) is therefore  $Bu^sCO_2O \cdot CHPr^s \cdot CO_2H$ . W. O. K.

**Vegetable heart poisons. VII. Constitution of uzarigenin.** R. TSCHESCHE and K. BOHLE [with, in part, P. T. P. SAH] (Ber., 1935, 68, [B], 2252—2256).—Fresh analyses of anhydrouzarigenin (I) [obtained by Windaus *et al.* (A., 1930, 1024) from *Gomphocarpus* root] and its derivatives ( $\alpha$ -benzoate, m.p. 261—262°) shows it to be a monoanhydro-compound,  $C_{23}H_{32}O_3$ . This view is in harmony with the observed absence of conjugation in the  $\alpha$ - or  $\beta$ -compound or in  $\alpha$ -anhydrouzarigenone, m.p. 255° [oxime, m.p. 283—285° (decomp.); semicarbazone, dc-comp. 266—268°], and with the catalytic



absorption of  $2H_2$ . Uzarin (II) is therefore  $C_{35}H_{54}O_{14} \cdot 2H_2O$ . (I) is pptd. by digitonin and hence contains OH attached to C-3. Since (II) is converted by the successive action of KOH-MeOH and AcOH into isouzarin,  $C_{35}H_{54}O_{14} \cdot 3H_2O$ , m.p. 240° (decomp.),  $[\alpha]_D^{21} -6.7^\circ$  in MeOH, the *tert*-OH is very probably united to C-14 and uzarigenin is (III). (I) is also obtained from uzaren, the second *Gomphocarpus* glucoside. H. W.

**Manchurian kaoliang (*Andropogon sorghum*, Brot.).**—See this vol., 124.

**Carotenoids of purple bacteria.**—See this vol., 259.

**New type of plant lipochrome.**—See this vol., 259.

**Carotenoids from the anthers of *Lilium tigrinum*: antheraxanthin.**—See this vol., 259.

**Antineuritic vitamin.**—See this vol., 253.

**Oxidation-reduction during dehydration of furyl alcohols.** R. PAUL (Bull. Soc. chim., 1935, [v], 2, 2220—2227).—Partly already reviewed (A., 1935, 867). 2- $\alpha$ -Hydroxypropylfuran at 400° gives 2- $\Delta^2$ -propenylfuran, b.p. 132—133°/756 mm., and 2-propionylfuran. 2- $\alpha$ -Hydroxy-*n*-butylfuran gives 2- $\Delta^2$ -*n*-butenyl-, b.p. 59—60°/24 mm., 2-*n*-butyl-, b.p. 48—49°/24 mm., and 2-*n*-butyryl-furan, b.p. 92—94°/18 mm. (semicarbazone, m.p. 182°). 2-Alkylene-furans are stable under  $N_2$  in presence of a trace of quinol. R. S. C.

**$\delta$ -Diketones and 1:4-pyrans.** A. P. DE CARVALHO (Ann. Chim., 1935, [xi], 4, 449—522).—PhCOMe with  $CO(p-C_6H_4Br)_2$  or  $COPH_2$  in  $Et_2O$  yields  $\alpha\epsilon$ -diphenyl- $\gamma\gamma$ -di-*p*-bromophenyl-, m.p. 195—196°, or  $\alpha\gamma\gamma\epsilon$ -tetraphenyl-penta- $\alpha\epsilon$ -dione (I), m.p. 182—183° ( $\beta\delta$ - $Br_2$ -derivative, m.p. 133—134°; dioxime, m.p. 191—192°; diphenylhydrazone, m.p. 184.5—185.5°).  $\alpha\alpha\epsilon\epsilon$ -Tetrachloro- $\alpha\gamma\gamma\epsilon$ -tetraphenylpentane has m.p. 159—160°. The dione with the appropriate Grignard reagent gives  $\alpha\alpha\gamma\gamma\epsilon\epsilon$ -hexaphenylpentane-(II), m.p. 193—194°,  $\alpha\gamma\gamma\epsilon$ -tetraphenyl- $\alpha\epsilon$ -diethylpentane-, m.p. 189—190° (alcoholate, m.p. 130°), and  $\alpha\gamma\gamma\epsilon$ -tetraphenyl- $\alpha\epsilon$ -dimethylpentane- $\alpha\epsilon$ -diol, m.p. 166—167°. When heated at 200° it gives  $\alpha$ -benzoyl- $\beta\beta$ -diphenylethylene; with  $CrO_3$  it gives BzOH and  $CHPh_2 \cdot CO_2H$ , with  $P_2O_5$  in boiling xylene gives 2:4:4:6-tetraphenyl-1:4-pyran, m.p. 157—158° (3:5- $Br_2$ -derivative, m.p. 215—216°), and with  $NH_4OAc$  in AcOH yields 2:4:4:6-tetraphenyl-1:4-dihydropyridine, m.p. 235—236°. With deficiency of the above Grignard reagent there are formed 2:4:4:6-tetraphenyl-2-ethylidihydropyran, m.p. 167—168° (5- $Br$ -derivative, m.p. 112—113°), and 2:2:4:4:6:6-hexaphenyltetrahydropyran (3:5- $Br_2$ -derivative, m.p. 177—178°), also obtained by dehydration of (II). Hydrogenation ( $PtO_2$ ) of (I) gives 2:4:4:6-tetraphenyltetrahydropyran (III), m.p. 145—146°. PhCHO and (I) give 3:5-dibenzoyl-2:4:4:6-tetraphenyltetrahydropyran (IV), m.p. 178—179°. The phototropy of (I), (III), and (IV) is discussed. F. R. G.

**Dibenzfuran. [Diphenylene oxide.] VII. Derivatives of tetrahydrodibenzfuran.** H. GILMAN, E. W. SMITH, and L. C. CHENEY (J. Amer. Chem. Soc., 1935, 57, 2095—2099; cf. A., 1935, 985).—With 1:2:3:4-tetrahydrodibenzfuran (I) the Friedel-Crafts reaction, sulphonation, and nitration involve the 7- and metalation the 8-position. (I) gives the 7- $NO_2$ -derivative (II), m.p. 124—125°, giving with Br 2-nitrodibenzfuran and on reduction 7-amino-1:2:3:4-tetrahydrodibenzfuran (III) (Ac derivative, m.p. 146°). (I) with  $Ac_2O-SnCl_4$  in  $C_6H_6$  gives the 7-Ac derivative (IV), m.p. 66—67°, b.p. 210°/15 mm. [and a little dibenzfuran (V)], oxidised by NaOI to 1:2:3:4-tetrahydrodibenzfuran-7-carboxylic acid, m.p. 247—248° (Me ester, m.p. 72.5—



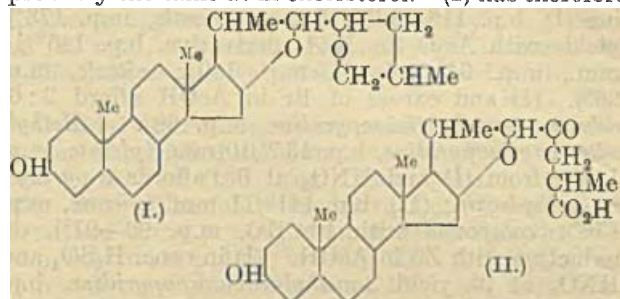
73.5°), giving dibenzfuran-2-carboxylic acid with Br. (I) and  $\text{ClSO}_3\text{H}$  in  $\text{CCl}_4$  at 10° yield the 7-sulphonic acid (Ba salt), the amide, m.p. 207.5—208.5°, of which with Br affords dibenzfuran-2-sulphonamide, m.p. 241—242°, which was synthesised (diazo-reaction;  $\text{Cu-SO}_2$ ) from 2-aminodibenzfuran by way of the sulphonyl chloride, m.p. 148.5°. (I) with  $\text{LiPh}$  or, less well,  $p\text{-C}_6\text{H}_4\text{MeLi}$  or  $\text{LiBu}^+$  gives a product which with  $\text{CO}_2$  affords 1:2:3:4-tetrahydrodibenzfuran-8-carboxylic acid, m.p. 197°, dehydrogenated by Br to dibenzfuran-1-carboxylic acid. The latter acid with  $\text{Na-EtOH}$  gives 1:2:3:4-tetrahydrodibenzfuran-1-carboxylic acid, m.p. 168°. The structure of 8-methoxy-1:2:3:4-tetrahydrodibenzfuran is confirmed by dehydrogenation by S at 275° to 1-methoxydibenzfuran. The "dihydrodibenzfuran" of Honigschmidt (A., 1901, i, 700) was impure (V). Hexahydrodibenzfuran (von Braun, A., 1923, i, 103) may exist, but the so-called  $\text{H}_6$ -derivatives are really (II), (III), and (IV), and it gives a picrate, m.p. 97°, whence (I) is formed by distillation in steam. Hydrogenation of (V) in presence of noble metals at moderate temp. and pressure gives only decahydrodibenzfuran, b.p. 258—259°/740 mm., 108—110°/7 mm. R. S. C.

**Amino-alcohols from dibenzfuran [diphenylene oxide].** E. MOSETTIG and R. A. ROBINSON (J. Amer. Chem. Soc., 1935, 57, 2186—2189).—2- $\beta$ -Amino- $\alpha$ -hydroxyethylidibenzfuran (I) and certain *N*-derivatives thereof have no morphine-like pharmacological action on the cat; they are more analgesic and toxic than similar phenanthrene derivatives. 2-Acetyldibenzfuran (II) and Br in dry  $\text{Et}_2\text{O}$  at 0° give 55% of 2- $\alpha$ -bromoacetyldibenzfuran, m.p. 105—106° [with  $\text{NaOCl}$  gives dibenzfuran-2-carboxylic acid (III)], which with the appropriate amine in  $\text{Et}_2\text{O}$  affords 2-dimethyl-, m.p. 82—83° (hydrochloride,  $+\text{H}_2\text{O}$ , m.p. 212—235°), -diethyl-, an oil (hydrochloride, m.p. 200—212°), -piperidino-, sinters at 97—98° (hydrochloride, m.p. 255—265°), ?-methyl- (IV) (hydrochloride, m.p. 225—250°), and -ethyl-aminoacetyldibenzfuran, unstable, m.p. 65—75° [hydrochloride, m.p. 254—256° (decomp.); 30% yield; some (III) also obtained]. (IV) (30% yield) is accompanied by some (III) and di(dibenzfuran-2-carbonylmethyl)methylamine (hydrochloride, m.p. 235—245°). Hydrogenation of 2-oximinoacetyldibenzfuran gives 64% of 2-aminoacetyldibenzfuran, decomp. from 171° [hydrochloride, m.p. 245—255° (decomp.)]. Hydrogenation of the keto-base or its hydrochloride affords - $\beta$ -dimethyl-, m.p. 88—89° (hydrochloride, m.p. 173—174°; O-benzoate, m.p. 99—100°), -diethyl-, m.p. 75—76° (hydrochloride, m.p. 157—159°), -piperidino-, m.p. 116.5—117.5° (hydrochloride, m.p. 250—251°; O-benzoate, m.p. 119°), and -ethyl-amino- $\alpha$ -hydroxyethylidibenzfuran, m.p. 99.5—101° (hydrochloride, m.p. 19—219.5°), and (I), m.p. 132° [hydrochloride, m.p. 261° (decomp.)]. (II) affords 2- $\alpha$ -hydroxyethylidibenzfuran, m.p. 63—64°. The Friedel-Crafts reaction in  $\text{PhNO}_2$  affords 2-propionylidibenzfuran, m.p. 101.5—102.5° (semicarbazone, m.p. 184—186°), oxidised to (II) by  $\text{NaOCl}$ . M.p. are corr. R. S. C.

**Constitution of calycopterin.** H. S. MAHAL and K. VENKATARAMAN (Current Sci., 1935, 4, 311—

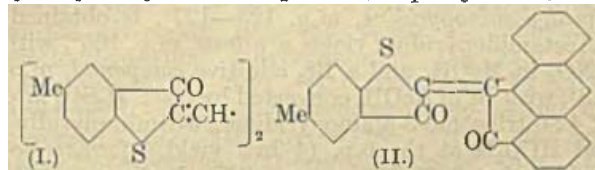
312).—Calycopterin (cf. Ratnagiriswaran, A., 1935, 246) is shown to be 6:4'-dihydroxy-3:5:7:8-tetramethoxyflavone, since with  $\text{AlCl}_3$  it yields either 5:6:4'-trihydroxy-3:7:8-trimethoxy- or 3:5:6:4'-tetrahydroxy-7:8-dimethoxy-flavone. F. R. G.

**Saponins of the cyclopentanohydrophenanthrene group. III. Constitution of *Digitalis* saponins.** R. TSCHESCHE and A. HAGEDORN (Ber., 1935, 68, [B], 2247—2252; cf. A., 1935, 1126).—Reduction of cholestan-4-one with Na and boiling  $\text{EtOH}$  affords cholestan-4-ol, m.p. 189°,  $[\alpha]_D^{25} +3.9^\circ$  in  $\text{CHCl}_3$ , whereas hydrogenation (Adams-Shriner) yields epicholestan-4-ol, m.p. 132°,  $[\alpha]_D^{25} +29.0^\circ$  in  $\text{CHCl}_3$ . Neither substance is pptd by digitonin. It is therefore established that OH in tigogenin (I) is attached to C-3 and that its steric position is probably the same as in cholesterol. (I) has therefore



the structure shown. The acid  $\text{C}_{27}\text{H}_{42}\text{O}_5$  obtained by drastic oxidation of tigogenin acetate (*loc. cit.*) gives an *Et* ester, m.p. 134°, which contains 1 active H (Zerevitinov), does not yield an oxime or semicarbazone, and is not hydrogenated catalytically. It is formulated as in (II). H. W.

**Indigoid dyes.** S. K. GUHA (J. Indian Chem. Soc., 1935, 12, 659—664).—2-Hydroxy-4-methylthionaphthen, the appropriate aldehyde, and  $\text{HCl}$  in hot  $\text{EtOH}$  give 1-*p*-, m.p. 264°, and -*m*-nitro-, m.p. 233°, -*p*-chloro-, m.p. 178°, -*p*-methoxy-, m.p. 157°, -*p*-, m.p. 252°, and -*m*-hydroxy-, m.p. 200°, -4'-hydroxy-methoxy-, m.p. 194°, and -3':4'-dihydroxy-benzylidene-, m.p. 248°, 1-*p*-tolylidene-, m.p.



159°, 1-piperonylidene-, m.p. 231°, 1-cinnamylidene-, m.p. 184°, and 1-benzylidene-2-keto-1:2-dihydrothionaphthen, m.p. 147°, and the compound (I), m.p. >300°. Aceanthracenequinone affords the compound (II), m.p. >310°. R. S. C.

**Chemical investigation of the liana "Efiri."** IV.—See this vol., 259.

**Syntheses of 1:2-dimethyl- and 2-methylpyrrolidine-5-carboxylic acid.** K. WINTERFELD and H. E. RONSBERG (Arch. Pharm., 1936, 274, 40—47).— $\delta$ -Hexolactone (prep. from  $\text{CH}_2\text{I-CH}_2\text{-CO}_2\text{H}$ ) and  $\text{HBr}$  at 100° give  $\delta$ -bromohexic acid, which leads, by way of the chloride, to *Et*  $\alpha$ -dibromohexoate, b.p. 136°/11 mm. With 25%  $\text{NH}_3\text{-MeOH}$  at 110—

120° this gives 2-methylpyrrolidine-5-carboxylamide, m.p. 193°, hydrolysed by conc. HCl at 100° to the corresponding acid, m.p. 207° (Cu salt, +2H<sub>2</sub>O, m.p. 228°; reineckate, decomp. 159°; Et ester platnichloride, m.p. 130°; with PhNCO gives the anhydride, m.p. 130°, of the 1-NPh-CO-derivative). NH<sub>2</sub>Me affords similarly 1:2-dimethylpyrrolidine-5-carboxylic acid, m.p. about 123—125° (Cu salt, +2H<sub>2</sub>O; reineckate, decomp. 156°). Neither acid is identical with the product from dehydrosparteine methoacetate.

**Alkali bromo-salts and bromo-pyridine derivatives of rhodium.**—See this vol., 175.

**3-Aminopyridine. II. Methyl derivatives, and acetamido- and formamido-pyridine.** E. PEŁAZEK, A. MARCINKÓW, and C. STAMMER (Rocz. Chem., 1935, 15, 365—377).—3-Methylaminopyridine (I), b.p. 118—120°/12 mm. (picrate, m.p. 178°), yields with Ac<sub>2</sub>O the N-Ac derivative, b.p. 145°/11 mm., m.p. 64° (picrate, m.p. 150°; nitrate, m.p. 96°). (I) and excess of Br in AcOH afford 2:6-dibromo-3-methylaminopyridine, m.p. 69°. 3-Methylnitrosoaminopyridine, b.p. 135°/10 mm. (picrate, m.p. 136°), from (I) and HNO<sub>2</sub> at 0°, affords 3-pyridyl-methylhydrazine (II), b.p. 141°/11 mm. (picrate, m.p. 176°; compound with PhCHO, m.p. 96—97°), on reduction with Zn in AcOH. (I) in conc. H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> at 0° yield 3-methylnitroaminopyridine, b.p. 124—125°/1.2 mm., m.p. 54—55° (picrate, m.p. 141°), reduced to (II) by Zn in AcOH, and converted by conc. H<sub>2</sub>SO<sub>4</sub> at 0—5° into 2-nitro-3-methylaminopyridine (III), m.p. 110°, together with 6-nitro-3-methylaminopyridine, m.p. 188°. 2-Amino-3-methylaminopyridine, m.p. 124° (picrate, m.p. 234°), is prepared by reduction of (III) with SnCl<sub>2</sub>, or from (I) and NaNH<sub>2</sub> in cymene (205—210°; 4—5 hr.), and 6-amino-3-methylaminopyridine, m.p. 70° (picrate, m.p. 228°), is obtained from 3-bromo-6-aminopyridine and NH<sub>2</sub>Me (110—115°; 20 hr.). Br and 3-dimethylaminopyridine in MeOH give a mixture of 2:6(?) dibromo-, b.p. 113—115°/0.5 mm., and (?) bromo-3-dimethylaminopyridine, m.p. 64—66° (picrate, m.p. 192—194°), whilst with HNO<sub>3</sub> in Ac<sub>2</sub>O trinitro-3-dimethylaminopyridine, m.p. 125—127°, is obtained. 3-Acetamidopyridine yields a nitrate, m.p. 165°, with HNO<sub>3</sub> in MeOH, and a Br<sub>2</sub> additive compound, m.p. 118°, with Br in AcOH, converted by conc. H<sub>2</sub>SO<sub>4</sub> into 2:4:6-tribromo-3-aminopyridine. 3-Aminopyridine and HCO<sub>2</sub>H at the b.p. (4 hr.) yield 3-formamido-pyridine, b.p. 200°/25 mm., m.p. 96° (nitrate, m.p. 158°; Br<sub>2</sub> additive compound, m.p. 92°). R. T.

**Pyridine series. II.** U. BASU and B. BANERJEE (J. Indian Chem. Soc., 1935, 12, 665—671).—The syntheses previously described (A., 1935, 1250) are generalised. NH<sub>2</sub>·CMe·CH·COMe with COPh·CH·CH·OH (I), p-C<sub>6</sub>H<sub>4</sub>·Me·CO·CH·CH·OH, or COEt·CMe·CH·OH in Et<sub>2</sub>O gives 3-acetyl-6-phenyl-, m.p. 90° (hydrochloride, m.p. 143—144°; picrate, m.p. 166°; semicarbazone, m.p. 212°; oxime, m.p. 106°), and p-tolyl-2-methylpyridine, m.p. 78° (hydrochloride, m.p. 150—151°; picrate, m.p. 163—164°; semicarbazone, m.p. 207°; oxime, m.p. 127°), and 3-acetyl-2:5-dimethyl-6-ethylpyridine, m.p. 60° (picrate, m.p. 118°; semicarbazone, m.p. 201°; oxime, m.p.

128°), respectively. NH<sub>2</sub>·CMe·CH·COPh affords similarly in EtOH or Et<sub>2</sub>O-EtOH 3-benzoyl-6-phenyl-, m.p. 77° (picrate, m.p. 196°; no semicarbazone), and p-tolyl-2-methylpyridine, m.p. 84°. NH<sub>2</sub>·CMe·CH·CO<sub>2</sub>Et with (I) in Et<sub>2</sub>O gives Et 2:5-dimethyl-6-ethylpyridine-3-carboxylate, b.p. 145°/10 mm. (picrate, m.p. 120°), hydrolysed by KOH to the corresponding acid, m.p. 193—194° (decomp.), which, when heated/vac. with soda-lime, affords 2:5-dimethyl-6-ethylpyridine, b.p. 181—182°/756 mm. (picrate, m.p. 127°). 6-Phenyl-, b.p. 285—287° (picrate, m.p. 180°), and 6-p-tolyl-2:5-dimethylpyridine, b.p. 291—292° (picrate, m.p. 146°), and 2:5:6-trimethylpyridine, b.p. 176—178°, are similarly obtained. R. S. C.

**Indole series. VI. Synthesis of [1:3-dimethylketo]tryptophan.** 3-Alkylation of oxindoles. P. L. JULIAN, J. PIKL, and F. E. WANTZ (J. Amer. Chem. Soc., 1935, 57, 2026—2029; cf. A., 1935, 765).—1:3-Dimethyloxindole, NaOEt, and CH<sub>2</sub>Br·CH(OEt)<sub>2</sub> in hot EtOH give a good yield of 1:3-dimethyl-3-β-dimethoxyethyloxindole, b.p. 182.5—183.5°/11 mm., hydrolysed by cold 5% HCl to 1:3-dimethyloxindolyl-3-acetaldehyde, b.p. 177—178°/12 mm., which by the Strecker synthesis affords the cyanohydrin, m.p. 142°, and β-1:3-dimethyloxindolyl-3-alanine (1:3-dimethylketotryptophan), m.p. 188° (decomp.), which above the m.p. in vac. loses CO<sub>2</sub> to give the base. Oxindole (2 active H) and 1-methyloxindole, however, with bromoacetals give only tars. CH<sub>2</sub>Cl·COCl and p-OEt·C<sub>6</sub>H<sub>4</sub>·NHMe yield 5-ethoxy-, m.p. 92°, and 1-hydroxy-5-methyl-oxindole. Oxindoles condense with esters in presence of NaOEt-EtOH. Thus are obtained 3-formyl-, -acetyl-, m.p. 109°, -carbethoxy-, m.p. 67°, and -dimethylaminoacetyl-1-methyloxindole, m.p. 219°, 3-acetyl-1:3-dimethyl- (I), m.p. 79°, and 3-dimethylaminoacetyl-5-ethoxy-1-methyl-oxindole, m.p. 196°, and 3-formyl-2-methoxy-1-methylindole; CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> gives also the bi-, m.p. 67°, and ter-mol., m.p. 225°, condensation products. Hydrogenation (PtO<sub>2</sub>; 1.5 atm.) of the acyl derivatives in EtOH at room temp. or, in some cases, AcOH at 50° gives the alkyl derivatives, viz.: 1:3-dimethyl-, 1-methyl-3-ethyl-, m.p. 169° (Br<sub>2</sub>-derivative), and 3-β-dimethylaminoethyloxindole, b.p. 185°/16 mm. (picrate, m.p. 168°), 5-ethoxy-1-methyl-3-β-dimethylaminoethyloxindole, b.p. 221°/17 mm. (picrate, m.p. 157°), β-1-methyloxindolyl-3-propionic acid, b.p. 160°/1 mm., and 2-methoxy-1-methylindolyl-3-carbinol, m.p. 62° (readily hydrolysed to 1-methyloxindolyl-3-carbinol). (I), which has no enolisable H, resists hydrogenation. R. S. C.

**Synthesis of derivatives of indole which contain sulphur.** H. WUYTS and (Mlle.) A. LACOURT (Bull. Soc. chim. Belg., 1935, 44, 587—592).—The S-Me derivative of β-phenylthioacet-α-phenyl-α-methylhydrazide (cf. A., 1933, 498) with warm MeOH-10% HCl (gas) gives 2-methylthiol-3-phenyl-N-methylindole, m.p. 96°, which loses 1 Me with HI at 120° and another at a high temp. The S-Me derivative of β-o-thiotolu-α-o-tolylhydrazine gives no indole because the hydrazine is substituted solely by aromatic groups. The S-Me derivative, m.p. 59°, of β-m-tolylthioacet-α-phenyl-α-methylhydrazide, m.p. 91°, with



MeOH-10% HCl affords 2-methylthiol-3-m-tolyl-N-methylindole, an oil (picrate, m.p. 84°), from which 2 Me are removed by energetic demethylation.  $\beta$ -Phenylthioacet- $\alpha$ -phenyl- $\alpha$ -methylhydrazide, m.p. 82°, affords 2-thion-3-phenyl-N-methyl-2:3-dihydroindole, m.p. 57° (picrate, m.p. 141°), insol. in alkali.  $\beta$ -Phenylthioacet- $\alpha$ -phenylhydrazide affords no indole, but is hydrolysed. J. L. D.

**Action of sodium methoxide on ethyl isatin-N-acetate.** N. I. PUTCHIN (J. Gen. Chem. Russ., 1935, 5, 1176—1184).—Et isatin-N-acetate and NaOMe in MeOH (75—80°; 2—3 hr.) give first the compound,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{ONa})(\text{OMe})_2$ , decomp. 230°, and then either (8 hr.; 75—80°) 3:4-diketol-1:2:3:4-tetrahydroquinoline-2-carboxylic acid (I) (Na, Ag<sub>1</sub>, and Ag<sub>2</sub> salts; Et<sub>2</sub> derivative, m.p. 119—120°) or (80—100°) o-glycinobenzoylformic acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . (I) is reduced (HI) to 1:2:3:4-tetrahydroquinoline-2-carboxylic acid. R. T.

**Reactions of mixed aromatic ketones with disubstituted thiocarbamides containing different aryl radicals.** K. DZIEWOŃSKI, L. GIZLER, and J. MOSZEW (Rocz. Chem., 1935, 15, 400—407).—Diarylthiocarbamides and substituted ketones yield quinoline derivatives when fused together; the reaction consists of three stages, viz., conversion of diarylthiocarbamide into amine and thiocarbimide, condensation of the former with the ketone to yield an anil, and condensation of the anil with the latter to yield a substituted quinoline. COPhMe (I) and *as*-phenyl-*p*-tolylthiocarbamide (5 hr. at 180—210°, then 30 min. at 270°), or acetophenone-*p*-tolil and PhNCS (2 hr. at 210—220°, then 30 min. at 270°) afford 4-anilino-2-phenyl-6-methylquinoline, m.p. 161° (hydrochloride, m.p. 171°; picrate, m.p. 210°; 4-N-NO-, m.p. 137—138°; 4-N-Ac-, m.p. 142°; 4-N-MeI-, m.p. 235°; 4-N-Me derivative, m.p. 167°), converted into 4-hydroxy-2-phenyl-6-methylquinoline by EtOH-KOH (200°; 4 hr.). *as*-Phenyl- $\beta$ -naphthylthiocarbamide (II) and (I) (4 hr. at 180°, then 30 min. at 280°) give 4- $\beta$ -naphthylamino-2-phenyl-5:6-benzoquinoline, m.p. 202—203° [hydrochloride, m.p. 286—287°; picrate, m.p. 260—261°; methiodide, m.p. 293—294°; 4-N-NO-, m.p. 250—251° (decomp.)]; 4-N-Ac derivative, m.p. 172—173°], yielding 4-hydroxy-2-phenyl-5:6-benzoquinoline with EtOH-KOH (200°; 4 hr.). (II) and *p*-tolyl Me ketone (5 hr. at 180—260°, then 30 min. at 290°) yield 4- $\beta$ -naphthylamino-2-*p*-tolyl-5:6-benzoquinoline, m.p. 226° [hydrochloride, m.p. 195°; picrate, m.p. 297° (decomp.)]; 4-N-NO-derivative, m.p. 195° (decomp.)], giving 4-hydroxy-2-*p*-tolyl-5:6-benzoquinoline, m.p. 314—315°, with EtOH-KOH (200°; 4 hr.). R. T.

**Fries-Rosenmund rearrangement of N-acetylcarbazole.** E. MEITZNER (J. Amer. Chem. Soc., 1935, 57, 2327—2328).—N-Acetylcarbazole with  $\text{AlCl}_3$  in  $\text{PhNO}_2$  gives 50—60% of 3- and some 1-acetylcarbazole, m.p. 136° (oxime, m.p. 179—180°; with molten KOH gives the 1-carboxylic acid), also obtained with tars from carbazole,  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$ .  $\text{AlCl}_3$  alone is unsatisfactory. R. S. C.

**Some amino-alcohol esters of acridine-5-carboxylic acid.** B. SAMDAHL and C. F. WEIDER

(Bull. Soc. chim., 1935, [v], 2, 2008—2016).—The following esters of acridine-5-carboxylic acid (I) were prepared by heating the hydrochloride, m.p. 215—216° (decomp.), of the acid chloride of (I) with the appropriate alcohol in  $\text{C}_6\text{H}_6$ . They are feebly anaesthetic, but not antiseptic.  $\beta$ -Aminoethyl, m.p. 238—240° (decomp.) [monohydrochloride, m.p. 238—240° (decomp.)];  $\beta$ -dimethylaminoethyl [mono-, m.p. 189—190° (decomp.), and di-hydrochloride, m.p. 172—173° (decomp.)];  $\beta$ -diethylaminoethyl [mono-, m.p. 179—180° (decomp.), and di-hydrochloride, m.p. 179—180° (decomp.)];  $\beta$ -dipropylaminoethyl [mono-, m.p. 177—178° (decomp.), and di-hydrochloride, m.p. 177—178° (decomp.)];  $\beta$ -diisobutylaminoethyl [mono-, m.p. 178—180° (decomp.), and di-hydrochloride, m.p. 168—169° (decomp.)];  $\beta$ -diisooamylaminoethyl [mono-, m.p. 130—146°, and di-hydrochloride, m.p. 167—168° (decomp.)]. The following appear to be new:  $\beta$ -dipropyl-, b.p. 90—92°/22 mm.,  $\beta$ -diisobutyl-, b.p. 96—98°/15 mm., and  $\beta$ -diisooamyl-aminoethyl alcohol, b.p. 126—128°/15 mm. H. G. M.

**Optical crystallographic study of some derivatives of barbital and luminal.** M. E. HULTQUIST and C. F. POE (Ind. Eng. Chem. [Anal.], 1935, 7, 398—399).—The following derivatives of veronal are described: o-, m.p. 140°, m-, m.p. 91°,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot$ , m.p. 146°, o-, m.p. 127°, m-, m.p. 102°,  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot$ , m.p. 142°,  $p\text{-C}_6\text{H}_4\text{I}\cdot\text{CH}_2\cdot$ , m.p. 122°, m-, m.p. 159°,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot$ , m.p. 192°,  $\text{PhCO}\cdot\text{CH}_2\cdot$ , m.p. 191°,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot$ , m.p. 191.5°. The following derivatives of 5-phenyl-5-ethylbarbituric acid are described: o-, m.p. 116°, m-, m.p. 130°,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot$ , m.p. 117°, m-, m.p. 111°,  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot$ , two forms, m.p. 111° and 113°,  $p\text{-C}_6\text{H}_4\text{I}\cdot\text{CH}_2\cdot$ , m.p. 127—128°, m-, m.p. 149.5°,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot$ , m.p. 182.5°,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot$ , m.p. 164°.  $n_D$ ,  $n_A$ ,  $n_F$ , crystallographic data, and block m.p. are recorded. F. R. G.

**4(5)-Amino-5(4)-methylglyoxaline.** R. WEIDENHAGEN and R. HERRMANN (Ber., 1935, 68, [B], 2205—2209).—Reduction of 4(5)-nitro-5(4)-methylglyoxaline by cold  $\text{SnCl}_2$  and conc. HCl and evaporation of the Sn-free solution in vac. causes little fission of the glyoxaline ring and yields 4(5)-amino-5(4)-methylglyoxaline dihydrochloride (I), m.p. 186° (decomp.), in 67% yield. (I) is transformed by NaOAc and PhCHO into 4(5)-benzylideneamino-5(4)-methylglyoxaline, m.p. 216°, by NaOAc, EtOH, and  $\text{Ac}_2\text{O}$  into 4(5)-acetamido-5(4)-methylglyoxaline, m.p. 216°, by  $\text{BzCl}$  (1 and 2 mols., respectively) in  $\text{C}_6\text{H}_5\text{N}$  into 4(5)-benzamido-, m.p. 262°, and 4(5)-benzamido-1-benzoyl-, m.p. 170°, -5(4)-methylglyoxaline, and by KOAc and PhNCO in  $\text{H}_2\text{O}$  into phenyl-5(4)-methylglyoxalinylicarbamide, m.p. 283°. H. W.

**Glyoxalinecarboxylic esters.** W. JOHN (Ber., 1935, 68, [B], 2283—2291).—Contrary to Oddo et al. (A., 1928, 1381) the product of the action of Mg glyoxalyl bromide (I) on  $\text{ClCO}_2\text{Et}$  is Et glyoxaline-1-carboxylate (II), b.p. 100°/16 mm. (picrate, m.p. 124°), the constitution of which follows from its ready conversion by dil. acid into glyoxaline. Similarly Mg 5-methylglyoxalyl bromide and  $\text{ClCO}_2\text{Et}$  afford Et 5-methylglyoxaline-1-carboxylate (III), b.p.

118—119°/21 mm. (*picrate*, m.p. 148—149°; *nitrate*, m.p. 116—117°), readily hydrolysed to 5-methylglyoxaline. The discrepancy in the m.p. of the *picrates* obtained by Oddo and the author respectively suggests the possibility of an isomerisation of (I) or (II) during the experiments. (I) appears unchanged when heated at 200° and yields the same product with  $\text{ClCO}_2\text{Et}$  as under normal conditions. (II) is very rapidly transformed at 250—260° into 1-ethylglyoxaline, b.p. 110°/16 mm. (*picrate*, m.p. 170°), identical with the product derived from glyoxaline and  $\text{EtBr}$ . Similarly, but less smoothly, (III) is converted into 5-methyl-1-ethylglyoxaline (*picrate*, m.p. 140°) mixed with 5-methylglyoxaline. Gradual addition of  $\text{NH}_3$  to  $\text{AcCHO}$  and  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  in  $\text{EtOH}$  leads to 2-styryl-5-methylglyoxaline (V), m.p. 235° [*nitrate*, m.p. 168° (decomp.); *picrate*, m.p. 248° (decomp.)], and small amounts of 2-phenyl-5-methylglyoxaline. Oxidation of (V) by  $\text{KMnO}_4$  in  $\text{COMe}_2$  affords 5-methylglyoxaline-2-carboxylic acid, m.p. 175° (decomp.) (*Et* ester and its *nitrate*, m.p. 124°), decarboxylated when heated above its m.p. to 5-methylglyoxaline (*picrate*, m.p. 159—160°). Oxidation of (V) with  $\text{CrO}_3$  gives  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ . H. W.

**Organic cupric tetrachlorides and tetrabromides.** J. AMIEL (Compt. rend., 1935, 201, 964—966; cf. A., 1935, 312).—The previous method was applied in preparing the compounds  $[\text{CuCl}_4](\text{NH}_3\text{Ph})_2$ ;  $[\text{CuCl}_4](\text{NH}_3\text{C}_6\text{H}_5)_2$ ;  $[\text{CuCl}_4](\text{C}_6\text{H}_5\text{NH})_2$ ;  $[\text{CuCl}_4](\text{NH}_2\text{C}_5\text{H}_9)_2$ ;  $[\text{CuCl}_4][(\text{NH}_2)_2\text{C}_4\text{H}_8]$ ;  $[\text{CuBr}_4](\text{C}_6\text{H}_7\text{NH})_2$ ;  $[\text{CuBr}_4](\text{C}_6\text{H}_5\text{NH})_2$ ;  $[\text{CuBr}_4](\text{NH}_2\text{C}_5\text{H}_9)_2$ ;  $[\text{CuBr}_4][(\text{NH}_2)_2\text{C}_4\text{H}_8]$ ;  $[\text{CuBr}_4](\text{C}_9\text{H}_7\text{NH})_2$ . The Cl and Br compounds were yellow and black, respectively. The piperazine (I) compounds formed dihydrates. With a large excess of halide of (I), or of Cu halide, respectively, the compounds  $\text{CuX}_2\cdot 2\text{X}\cdot[(\text{NH}_2)_2\text{C}_4\text{H}_8]\cdot 4\text{H}_2\text{O}$  and  $[\text{CuX}_3]_2[(\text{NH}_2)_2\text{C}_4\text{H}_8]$  were formed ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ). H. J. E.

**Organic sulphur compounds. III. Action of hydrogen cyanide, ammonia, and hydrogen sulphide on  $\alpha\beta$ -unsaturated ketones.** K. ABE (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 3, 17—27).—Treatment of mesityl oxide with  $\text{EtOH}\cdot\text{HCN}$  (from  $\text{KCN}$  and  $\text{AcOH}$ ) followed by  $\text{NH}_3$  and  $\text{H}_2\text{S}$  affords  $\alpha$ -amino- $\alpha$ -methylpyrrolerebic thionamide, m.p. 220°; similarly, benzylideneacetone (I) affords a mixture of  $\alpha$ -amino- $\beta$ -benzylidene- $\alpha$ -methylpropionic thionamide, m.p. 165—166°, and 2:5-dithioketo-3:6-distyryl-3:6-dimethylpiperazine, m.p. 172—173°. Under the same conditions furfurylideneacetone (II) gives  $\alpha$ -amino- $\beta$ -furfurylidene- $\alpha$ -methylpropionic thionamide, m.p. 190—191°. (I) with the same reagents but using  $\text{NaCN}+\text{NH}_4\text{Cl}$  as source of  $\text{HCN}$  affords duplo-benzylidenedithioacetaminine. Phenylacetonitrile was not obtained from (I) and  $\text{HCN}$ , and (II), under the same conditions, gave a substance, sinters at 210°, m.p. > 210°. P. G. C.

**Pyrimidines. CXLVIII. Action of chlorine on mercaptopyrimidines.** J. M. SPRAGUE and T. B. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 2252—2255).—Four known 4-chloro-2-ethylthiopyrimidines are prepared from the corresponding 4-CO-compounds by  $\text{POCl}_3$ . The 4-Cl-

compounds and  $\text{NaOEt}\cdot\text{EtOH}$  at room temp. give 2-ethylthiol-4-ethoxy-, b.p. 123—124°/11 mm., and 4-ethoxy-5-methyl-, b.p. 135—136°/12 mm., and 5-bromo-2-ethylthiol-4-ethoxy-pyrimidine, b.p. 140°/6 mm. 4-Chloro-2-ethylthiol-5-carbethoxypyrimidine is unstable to  $\text{NaOEt}$  in  $\text{EtOH}$ , but in hot  $\text{C}_6\text{H}_6$  gives the 4-OEt-compound (I), b.p. 175°/18 mm. 2:4-Diethylthiol- (II), b.p. 135—137°/6 mm., and 2:4-diethylthiol-5-methyl-pyrimidine (III), b.p. 158—161°/11 mm., are obtained from the 2:4- $\text{Cl}_2$ -compounds and  $\text{NaEtS}$  in  $\text{PhMe}$ . 2-Ethylthiopyrimidines with  $\text{Cl}_2$  in  $\text{H}_2\text{O}$  at < 20° give 2-EtSO<sub>2</sub>-derivatives. Thus are obtained (a) 2-ethylsulphonyl-4-ethoxy-, b.p. 183—185°/4 mm., and 4-ethoxy-5-methyl-, m.p. 67—68°, (b) 4-chloro-2-ethylsulphonyl-5-methyl-, m.p. 67·5—68°, and 5-carbethoxy- (IV), m.p. 72·5—73·5°, (c) 4-chloro-, m.p. 57—58°, and 4-chloro-5-bromo-2-ethylsulphonyl-, m.p. 81—82°, (d) 5-bromo-2-ethylsulphonyl-4-ethoxy-, m.p. 89·5—90·5°, 4-amino-2-ethylsulphonyl-5-carbethoxy- (prepared in  $\text{HCl}$  at 0°), m.p. 143·5—144·5°, and 2:4-diethylsulphonyl-pyrimidine, m.p. 87—88°. At < 5° (I) gives 60% of (IV) and 15—20% of 2:4-dichloro-5-carbethoxypyrimidine (V), m.p. 36—37°, but at 30—40° 7% of (IV), 69—75% of (V), and 47—75% of  $\text{EtSO}_2\text{Cl}$ ; (V) is probably formed by way of the 2-sulphoxide. (II) and (III) give amorphous products. The structure of the  $\text{EtSO}_2$ -compounds is proved by hydrolysis by 20%  $\text{HCl}$  to the diketopyrimidines,  $\text{SO}_2$ , and a little  $\text{EtSO}_3\text{H}$  (probably formed from  $\text{EtSO}_2\text{H}$  produced as a primary product of hydrolysis). R. S. C.

**Complex dipyridyl salts of nickel and copper.**—See this vol., 175.

**3:3'-Dipyridyl derivatives.** W. BRYDOWNA and W. WISZNIIEWSKI (Rocz. Chem., 1935, 15, 378—382).—The Ag salt of 3:3'-dipyridyl-2:2'-dicarboxylic acid (I) and  $\text{EtI}$  or  $\text{MeI}$  in  $\text{C}_6\text{H}_6$  (at the b.p.; 2·5 hr.) yield the *EtI*, m.p. 82—84°, and *MeI*, m.p. 153—153·5°, esters of (I), which with  $\text{EtOH}\cdot\text{NH}_3$  (8 hr.; 135—145°) afford the diamide, m.p. 268·5—270° (decomp.) of (I), converted by the Hofmann reaction into 2:2'-diamino-3:3'-dipyridyl, m.p. 181—182·5°, together with some 2-amino-3:3'-dipyridyl-2'-carboxylic acid lactam, m.p. 366—368° (decomp.). The chloride, m.p. 147—150°, of (I) is prepared from (I) and  $\text{SO}_2\text{Cl}_2$ . R. T.

**Reactions between indoles and Schiff's bases.** M. PASSERINI and F. ALBANI (Gazzetta, 1935, 65, 933—938).—The product from indole and  $\text{NPh}\cdot\text{CHPh}$  (A., 1933, 615) is converted by boiling 20%  $\text{HCl}$  into a substance (I),  $\text{C}_{30}\text{H}_{22}\text{N}_2$ , m.p. > 350°, regarded as  $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CHPh}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}\cdot\text{CHPh}\cdot\text{C}\cdot\text{NH}$ . Indole and  $\text{NPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$  yield anisylidi-indolylmethane, m.p. 180°, converted by boiling  $\text{HCl}$  into a substance,  $\text{C}_{32}\text{H}_{26}\text{O}_2\text{N}_2$ , m.p. > 350°, similar to (I). Phenylidi- $\alpha$ -methylindolylmethane is unchanged by  $\text{HCl}$ . E. W. W.

**Pyrrolidine derivatives. II. Ring enlargement from the indolizidine to the norlupinane series.** E. OCHIAI, K. TSUDA, and J. YOKOYAMA (Ber., 1935, 68, [B], 2291—2298; cf. A., 1934, 901).—Pyrrole is converted by the successive action of  $\text{K}$  and  $\text{Bu}^n\text{Br}$  in boiling  $\text{C}_6\text{H}_6$  into 1-n-butylpyrrole,

catalytically hydrogenated ( $\text{PtO}_2$  in  $\text{AcOH}$ ) to 1-n-butylpyrrolidine, b.p.  $88^\circ/63$  mm. (picrate, m.p.  $124.5^\circ$ ; methiodide, m.p.  $183^\circ$ ; platinichloride, m.p.  $122.5^\circ$ ). The corresponding bromocyanide, b.p.  $120^\circ/0.01$  mm., is converted by  $\text{KCN}$  in boiling  $\text{EtOH-H}_2\text{O}$  into  $\omega$ -cyanobutylbutylamine cyanide (I)  $\text{CN}[\text{CH}_2]_4\text{N}^+\text{Bu}^+\text{CN}$ , b.p.  $167^\circ/1$  mm., and  $\omega$ -butylamino-n-valeronitrile (II), b.p.  $125^\circ/9$  mm. (hydrochloride, m.p.  $211^\circ$ ). (I) or (II) with conc.  $\text{HCl}$  at  $150^\circ$  gives  $\omega$ -butylamino-n-valeric acid hydrochloride, m.p.  $124.5^\circ$ ; the corresponding acid, m.p.  $112.5^\circ$ , when heated at  $150^\circ$  gives 1-n-butylpiperid-2-one (III), b.p.  $120^\circ/5$  mm. (platinichloride, m.p.  $150-151^\circ$ ), also obtained by oxidising butylpyridinium bromide with  $\text{K}_3\text{Fe}(\text{CN})_6$  in alkaline solution and catalytic reduction ( $\text{PtO}_2$ ) of the pyridone.

2-Methylindolizidine bromocyanide (*loc. cit.*) is converted by  $\text{KCN}$  into 2- $\gamma$ -cyano- $\beta$ -methylpropylpiperidine cyanide, b.p.  $159^\circ/0.003$  mm., hydrolysed by conc.  $\text{HCl}$  to  $\gamma$ -2-piperidyl- $\beta$ -methylbutyric acid hydrochloride, m.p.  $145^\circ$ , converted by successive treatment with  $\text{Ag}_2\text{CO}_3$  and heating at  $150^\circ$  into 3-methyl- $\alpha$ -norlupinone (IV), b.p.  $107^\circ/2$  mm. (platinichloride, decomp.  $175^\circ$ ). Similarly, indolizidine is transformed successively into 2- $\gamma$ -cyanopropylpiperidine cyanide, b.p.  $175^\circ/0.12$  mm.,  $\gamma$ -2-piperidyl-butyric acid hydrochloride, m.p.  $188-189^\circ$ , and  $\alpha$ -norlupinone, b.p.  $105^\circ/3$  mm. (hydrochloride, m.p.  $146-147^\circ$ ). Reduction of (III) cannot be effected by  $\text{HCl}$  and  $\text{Zn-Hg}$ , electrolytically at a  $\text{Pb}$  cathode, or by  $\text{Na}$  and boiling  $\text{C}_5\text{H}_{11}\text{OH}$ ; with  $\text{MgMeI}$  it yields 1-n-butyl- $\alpha$ -pipecoline, b.p.  $85-90^\circ/11$  mm. (hydriodide, m.p.  $166.5^\circ$ ), hydrogenated ( $\text{PtO}_2$  in  $\text{AcOH}$ ) to 1-n-butyl- $\alpha$ -pipecoline, b.p.  $115-120^\circ/60$  mm. (hydrochloride, m.p.  $177.5^\circ$ ; picrate, m.p.  $116^\circ$ ; perchlorate, m.p.  $127.5^\circ$ ; aurichloride, m.p.  $114^\circ$ ; methiodide, m.p.  $224^\circ$ ; hydrobromide, m.p.  $203^\circ$ ; hydriodide, m.p.  $193^\circ$ ), also obtained from butylpecolinium bromide. Similar treatment of (IV) gives  $\Delta^1$ -1:3-dimethylnorlupinene, b.p.  $115^\circ/22$  mm. (hydriodide, decomp.  $237^\circ$ ), reduced ( $\text{PtO}_2$ ) to 1:3-dimethylnorlupinane, b.p.  $127^\circ/69$  mm., (hydrochloride, decomp.  $280^\circ$ ; perchlorate, decomp.  $228^\circ$ ; picrate, m.p.  $142.5^\circ$ ; methiodide, m.p.  $168^\circ$ ). H. W.

Reaction of  $\alpha\beta$ -diketonic acids with *o*-phenylenediamine. H. OHLE and W. GROSS (Ber., 1935, 68, [B], 2262-2269; cf. A., 1934, 634).— $\text{Et}_2$  mesoxalate (I) and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{EtOH}$  or  $\text{EtOH-H}_2\text{O}$  afford *Et* 2-hydroxyquinoxaline-3-carboxylate (II), m.p.  $175^\circ$ , hydrolysed to 2-hydroxyquinoxaline-3-carboxylic acid (III), m.p.  $265^\circ$  (decomp.). With a larger proportion of  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in boiling  $\text{AcOH-EtOH-H}_2\text{O}$  (I) gives 2-hydroxyquinoxaline-3-carboxy-2'-aminoanilide, m.p. about  $350^\circ$  after becoming yellow at  $250^\circ$  and subliming at about  $300^\circ$ , is obtained, which is not readily hydrolysed by boiling dil. acid or alkali, is not attacked by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at  $40^\circ$ , but is transformed by boiling  $\text{Ac}_2\text{O}$  into the  $\text{Ac}_2$  derivative, m.p.  $225^\circ$ , relatively readily hydrolysed to (III). Since it is indifferent towards  $\text{CH}_2\text{N}_2$ , it probably has a spiran structure at room temp., and the open form when heated. (II) reacts readily with  $\text{CH}_2\text{N}_2$  in  $\text{CHCl}_3$  giving *Et* 2-keto-1-methyl-1:2-dihydroquinoxaline-3-carboxylate, m.p.  $125-126^\circ$ , hydrolysed to the corre-

sponding acid, m.p.  $173^\circ$ , from which  $\text{Me}$  is not appreciably removed under the conditions of Zeisel's determination. Even with an excess of  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ,  $\alpha\beta$ -diketobutyric esters give 2-methylquinoxaline-3-carboxylic esters.  $\text{Me}_2$  dihydroxymaleate is transformed by the successive action of benzoquinone in boiling  $\text{MeOH}$  and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  into *Me*<sub>2</sub> quinoxaline-2:3-dicarboxylate, m.p.  $325^\circ$ . Hydroxytetronic acid acid when similarly treated yields the *o*-aminoanil of 2-hydroxy-1:2-dihydroquinoxaline 3-hydroxymethyl

ketone (IV),  $\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m.p.

$167.5-168.5^\circ$ , in which the presence of  $\text{NH}_2$  is established by the formation of a monohydrochloride, by diazotisation and coupling with  $\beta\text{-C}_{10}\text{H}_7\text{OH}$ , by condensation with  $\text{COMe}$ , to the compound,

$\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{COMe}_2$ , m.p.  $184.5-$

$186^\circ$ , and by the formation of a  $\text{Ac}_3$  derivative, m.p.  $182^\circ$  (with small amounts of a  $\text{Ac}_2$  compound, m.p.  $212-213^\circ$ ), converted by cautious hydrolysis into the  $\text{N-Ac}$  compound, m.p.  $233.5^\circ$ , and by  $\text{Ag}_2\text{O}$  and  $\text{MeI}$  into the substance

$\text{N}\cdot\text{C}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}\cdot\text{C}(\text{CH}_2\cdot\text{OMe})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , m.p.

$136.5-137.5^\circ$ . In contrast to the derivative  $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4$  from isoascorbic acid (*loc. cit.*), (IV) does not yield  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  when boiled with dil. acid, although extensive decomp. occurs. H. W.

Oxidation of uric acid.—See this vol., 233.

Reaction between aminoantipyrine and phenylhydrazine. M. PASSERINI and M. RINDI (Gazzetta, 1935, 65, 930-933; cf. A., 1935, 501).—Pyrimidone and  $\text{NHPh-NH}_2$  at  $180-190^\circ$  give 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone (I), with bis-(1-phenyl-3-methylpyrazol-5-on-4-yl), also obtained from (I) and  $\text{NHPh-NH}_2$ . Aminoantipyrine and *p*-tolylhydrazine yield 4-*p*-tolueneazo-1-*p*-tolyl-3-methyl-5-pyrazolone. E. W. W.

Occurrence of decomposition products of chlorophyll. III. Isolation of pyrroporphyrin from ox bile. P. ROTHMUND (J. Amer. Chem. Soc., 1935, 57, 2179-2180; cf. A., 1935, 110).—Fractional extraction of ox bile pigments from  $\text{Et}_2\text{O}$  by  $\text{HCl}$  gives a trace of coproporphyrin by 0.5%  $\text{HCl}$ , pyrroporphyrin by 3%  $\text{HCl}$ , phylloerythrin by 10%  $\text{HCl}$ , traces of other pigments by 15 and 20%  $\text{HCl}$ , but no phyllo- or rhodo-porphyrin. R. S. C.

Susceptibility of complex porphyrin-nickel salts. F. HAUROWITZ and W. KLEMM (Ber., 1935, 68, [B], 2312-2313).—Re-examination of the  $\text{Ni}$  salt of dimethylmesoporphyrin confirms its diamagnetic properties (Klemm, A., 1935, 1311), whereas the behaviour of  $\text{Ni}$ -tetramethylhaematoporphyrin ester (Haurowitz, A., 1935, 1384) varies, probably owing to non-uniformity. H. W.

Spectrophotometric studies. II—V.—See this vol., 221.

Alcoholic ammonia as a reagent in the nitrostilbene series. D. E. WORRALL (J. Amer. Chem. Soc., 1935, 57, 2299-2301).— $\alpha$ -Nitrostilbene (I) and  $\text{NH}_3\text{-EtOH}$  give  $\text{PhCHO}$ , much 3:4:5-triphenylisooxazoline oxide (II), and some dibenzoylphenyl-



methaneoxime ( $\alpha$ -oximino- $\gamma$ -keto- $\alpha\beta\gamma$ -triphenylpropane) (III), m.p. 152—153°; the same products are formed from (I) and  $\text{CH}_3\text{Ph}\cdot\text{NO}_2$  or from the latter and  $\text{PhCHO}$  with  $\text{NH}_3\text{-EtOH}$ . (III) gives (II) immediately with hot  $\text{HCl}$  or alkali and slowly above the m.p. The intermediate formation of some (III) in the prep. of (II) by more strongly alkaline reagents (cf. Heim, A., 1911, i, 717) is thus proved. In abs.  $\text{EtOH-NH}_3$  some  $\alpha$ -nitro- $\beta$ -benzylideneaminodibenzyl, m.p. 137—138°, is also formed. Similarly are obtained 3:5-diphenyl-4-p-bromophenyl-, m.p. 172—173°, 4-anisyl-, m.p. 145—146°, and 4-piperonyl-, m.p. 165—166°, 3:4-diphenyl-5-p-bromophenyl-, m.p. 213—215° (decomp.), 3-phenyl-4:5-di-p-bromophenyl-, m.p. 160—161°, and 5-p-bromophenyl-4-piperonyl-isooxazoline oxide, m.p. 192—193°; 3:5-diphenyl-4-p-bromophenyl-, m.p. 182—183°, 4-piperonyl-, m.p. 227—228°, 4-o-chlorophenyl-, m.p. 127—128°, 3-phenyl-4:5-di-p-bromophenyl-, m.p. 179—180°, 5-p-bromophenyl-4-anisyl-, m.p. 188—189°, and 5-p-bromophenyl-4-piperonyl-isooxazole, m.p. 204—205°;  $\alpha$ -nitro- $\beta$ -o-chlorobenzylideneamino- $\alpha$ -phenyl- $\beta$ -o-chlorophenylethane, m.p. 144—145°. R. S. C.

**Synthesis and pharmacological study of some derivatives of aminomethyl-dihydro-oxazine which exhibit an adrenaline-like action.** (MLLE.) G. BENOIT and D. BOVET (J. Pharm. Chim., 1935, [viii], 22, 544—548).— $o$ - $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  with  $\text{C}_3\text{H}_5\text{Br}$  in  $\text{COMe}_2$  containing  $\text{K}_2\text{CO}_3$  affords the  $O$ -allyl ether, the  $\text{Br}_2$ -derivative of which is hydrolysed ( $\text{HCl}$ ) to the  $\beta\gamma$ -dibromoallyl ether (hydrochloride, m.p. 171°) of  $o$ - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . The latter is cyclised with  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$  in  $\text{N}_2$  and then reacts with  $\text{NHEt}_2$  to give 3-diethylaminomethyl-2:3-dihydro-oxazine, m.p. 130° (dihydrochloride, m.p. 188°). 2-Diethylaminomethyl-, b.p. 195°/23 mm. (dihydrochloride, m.p. 190—192°), and 2-piperidinomethyl-2:3-dihydro-oxazine, b.p. 170—175°/1.5 mm., are prepared from  $o$ - $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  with diethyl- $\beta\gamma$ -dibromopropylamine, b.p. 105—110°/769 mm. [from  $\text{C}_3\text{H}_5\text{Br}$  and  $\text{NHEt}_2$ , followed by bromination] and 1- $\beta\gamma$ -dibromopropylpiperidine, b.p. 147—152°/753 mm. [from  $\text{C}_3\text{H}_5\text{Br}$  and piperidine, followed by bromination], respectively. The pharmacological effects are described. J. L. D.

**Synthesis of phenylated benzoxazoles and [their] derivatives.** V. J. MIKESKA and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2121—2124).—The prep. of  $o$ - and  $p$ - $\text{C}_6\text{H}_4\text{Ph}\cdot\text{OH}$  and  $\text{PhSO}_2$  from commercial  $\text{PhOH}$  residues is described. 3-Nitro-4-hydroxydiphenyl (I) ( $p$ -toluenesulphonate, m.p. 114.8°) with conc.  $\text{H}_2\text{SO}_4$  at 70° gives a sulphonic acid (Ba salt). 3-Amino-4-hydroxydiphenyl with  $\text{BzCl}$  gives 1:4-diphenyl-, m.p. 132.8°, and with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  at 210° 4-phenyl-1-p-nitrophenyl-benzoxazole (II), m.p. 288.8° (with a little 3-p-nitrobenzamido-4-hydroxydiphenyl, m.p. 249.3°). (II) or the  $p$ -nitrobenzoate, m.p. 169°, of (I) with  $\text{SnCl}_4\text{-HCl-AcOH}$  gives 4-phenyl-1-p-aminophenylbenzoxazole, m.p. 174.2°, which with 60% oleum gives (?) 6-sulpho-4-phenyl-1-4'-amino-(?) 3'-sulphophenylbenzoxazole and with  $\text{NaNO}_2$ , in conc.  $\text{HCl}$  4-phenyl-1-( $p$ -benzenediazonium chloride)benzoxazole, m.p. 270°. The Na salt of 3:5-dinitro-2-hydroxydiphenyl and  $\text{BzCl}$  in  $\text{COMe}_2$  gives the benzoate, m.p. 119.5°, reduced to

4-amino-2:6-diphenylbenzoxazole, m.p. 220.8° (sulphonic acid,  $+\text{H}_2\text{O}$ , decomp.  $>375^\circ$ ). M.p. are corr. R. S. C.

**Crystalline by-product, obtained in the large-scale extraction of theelin and theelol.** A. W. DOX, W. G. BYWATER, and F. H. TENDICK (J. Biol. Chem., 1935, 112, 425—430).—Human pregnancy urine contains a non-œstrogenic, acidic substance,  $\text{C}_{21}\text{H}_{23}\text{O}_3\text{N}_4$ , decomp. 360° [3 active H; *Et* ester or ether m.p. 277—278° (decomp. from 275°)], stable to 25%  $\text{KOH}$  and hot conc. acid, oxidised by  $\text{CrO}_3\text{-AcOH}$  to an acid,  $\text{C}_{18}\text{H}_{19}\text{O}_7\text{N}_2$ , decomp. 253—269°, and giving a pyrrole pine-splinter reaction and a red solution in conc.  $\text{H}_2\text{SO}_4$  (green fluorescence when heated), but no protein,  $\text{NH}_2$ -acid, or purine reactions. R. S. C.

**Unsaturation and tautomeric mobility of heterocyclic compounds. VI. Mobility of 5-substituted 1-hydroxybenzthiazoles, and the ultra-violet absorption of mobile and static derivatives of 1-hydroxybenzthiazole.** R. F. HUNTER and E. R. PARKEN. VII. Selenazole derivatives. C. HASAN and R. F. HUNTER (J.C.S., 1935, 1755—1761, 1762—1766).—VI. 1-Hydroxy-5-methylbenzthiazole (I), m.p. 168—169° (*Ac* derivative, m.p. 109°; *Ag* salt; *Na* salt, decomp. 260—261°), obtained by hydrolysis of the 1-*OEt*-compound, m.p. 35—36°, which is prepared from  $p$ -tolylthiourethane, is methylated ( $\text{Me}_2\text{SO}_4$ ) to 1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole, m.p. 76—77°, also obtained by heating the corresponding 1-nitrosoimino-compound, explodes 144° (from the methosulphate of 1-amino-5-methylbenzthiazole and  $\text{NaNO}_2$ ). 1-Methoxy-5-methylbenzthiazole, m.p. 32—33°, obtained from *Me p*-tolylthioncarbamate, m.p. 79—80°, is not present in the methylation product of (I). (I) is brominated to 4(or 6)-bromo-1-hydroxy-5-methylbenzthiazole, m.p. 239—240°, methylated to 4(or 6)-bromo-1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole (II), m.p. 145°. *o*-Bromo- $p$ -tolylthiourethane, m.p. 32—33°, gives 3-bromo-1-ethoxy-5-methylbenzthiazole, m.p. 36—37°, hydrolysed to the 1-*OH*-compound, m.p. 209°, which is methylated to 3-bromo-1-keto-2:5-dimethyl-1:2-dihydrobenzthiazole, m.p. 116°, not identical with (II). 2-Bromo- $p$ -tolylthiocarbimide, m.p. 44—45°, forms 2-bromo- $p$ -tolylthiourethane, m.p. 106°, which yields 4(or 6)-bromo-1-ethoxy-5-methylbenzthiazole, m.p. 50—51°, hydrolysed to the 1-*OH*-compound.

A similar series of reactions leads to the following:  $p$ -phenetylthiourethane, m.p. 93—94°; 1:5-diethoxy-, m.p. 54°, 1-hydroxy-5-ethoxy-, m.p. 147°, and 1-keto-5-ethoxy-2-methyl-1:2-dihydro-benzthiazole, m.p. 85°; *Me p*-phenetylthioncarbamate, m.p. 68—69°, 1-methoxy-5-ethoxybenzthiazole, m.p. 75—76°,  $p$ -iodophenylthiourethane, m.p. 106—107°, *o*-iodo-1-ethoxy-, m.p. 76—77°, and -hydroxy-benzthiazole, m.p. 225—226°, 5-iodo-1-keto-, m.p. 135°, and 5-iodo-1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole, explodes 160°; *Me p*-bromophenylthioncarbamate, m.p. 99—100°, 5-bromo-1-methoxybenzthiazole, m.p. 82—83°; *Me* phenylthioncarbamate, m.p. 93°, oxidised to 1-methoxybenzthiazole, m.p. 88—89°; 5-bromo-1-hydroxybenzthiazole is methylated to 5-bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole; 5-chloro-1-ethoxy-, m.p. 60—61°,





PLATZER (Ber., 1935, **68**, [B], 2221—2226).—Pyrrolidone and isatoic anhydride (I) at 120—180° afford  $\Delta^9$ -pegen-8-one, m.p. 110—111°, reduced at a Pb electrode to 1-o-aminobenzylpyrrolidine. Condensation of *o*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Cl with Me  $\delta$ -aminovalerate [obtained from piperidone (II)] yields 1-o-nitrobenzylpiperidone, m.p. 117°, reduced by Zn dust and 20% AcOH to 1-o-aminobenzylpiperidone, m.p. 92.5—93.5°, which is dehydrated by POCl<sub>3</sub> to the base (III), *o*-C<sub>6</sub>H<sub>4</sub> $\begin{matrix} \text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{N}=\text{C}\cdot\text{CH}_2\cdot\text{CH}_2 \end{matrix}$  m.p. 82—83° (corresponding H<sub>2</sub>-derivative, m.p. 71—72°). Alternatively (I) is condensed with (II) to piperidino-4-ketodihydroquinazoline, C<sub>6</sub>H<sub>4</sub> $\begin{matrix} \text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{N}=\text{C}\cdot\text{CH}_2\cdot\text{CH}_2 \end{matrix}$  m.p. 99—100°, reduced by Zn and acid to (III). H. W.

**Lupin alkaloids. VIII.** G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1935, 1743—1745).—*Et* pyridyl-2- $\beta$ -propionate, b.p. 95°/1 mm. (*picrolonate*, m.p. 141°, *picrate*, m.p. 84°), with CH<sub>2</sub>Br·CO<sub>2</sub>Et gives *Et* pyridinium-1-acetate-2- $\beta$ -propionate bromide, m.p. 159°, reduced to *Et* piperidyl-1-acetate-2- $\beta$ -propionate, b.p. 138—140°/1 mm. Ring-closure of this ester gives 3-keto-octahydropyridocoline, b.p. 74—76°/1 mm. (*picrate*, m.p. 185°), which with Zn-Hg-HCl yields octahydropyridocoline-A, identical with norlupinane, confirming the structure previously assigned. *Et* pyridyl-2-acetate, b.p. 134—135°/21 mm. (*picrate*, m.p. 136—137°), is reduced to the piperidyl ester, b.p. 105°/14 mm. (*picrate*, m.p. 125°), which with CHBrMe·CO<sub>2</sub>Et forms *Et* piperidyl-2-acetate-1- $\alpha$ -propionate, b.p. 135—140°/1 mm., cyclised to 3-keto-2-methyloctahydropyrrocoline, b.p. 67—69°/1 mm. (*picrate*, m.p. 162°). The ketone with Zn-Hg-HCl yields 3-hydroxy-2-methyloctahydropyrrocoline, b.p. 100—105°/16 mm. (*picrate*, m.p. 159°; *picrolonate*, m.p. 181°), and with N<sub>2</sub>H<sub>4</sub> followed by Na gives 2-methyloctahydropyrrocoline, b.p. 32—35°/1 mm. (*picrate*, m.p. 197°; *picrolonate*, m.p. 208°).

F. R. S.

**Lupin alkaloids. X.** Degradation of dehydrosparteine methoacetate by oxidation. K. WINTERFELD and H. E. RONSBERG (Arch. Pharm., 1935, **273**, 521—532).—The CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> oxidation product of dehydrosparteine methoacetate (A., 1930, 1300) yields the platinumchloride, m.p. 250°, of a substance which is not C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>, as thought by Winterfeld and Ipsen (*loc. cit.*), but the acid C<sub>15</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub> (I), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -38.2° in H<sub>2</sub>O (*aurichloride*, m.p. 205°). (I) is decarboxylated to a resinous substance; with CH<sub>2</sub>N<sub>2</sub>, (I) loses H<sub>2</sub>O and forms the Me ester, C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>, which with Pd-CaCO<sub>3</sub> absorbs 1 H<sub>2</sub>. A second CrO<sub>3</sub> oxidation product forms a Cu salt, and a reineckate, m.p. 186°; it is decarboxylated, and with MeOH-HCl yields two esters, b.p. 136°/15 mm. and 155—160°/1 mm., respectively. It consists of a mixture of the acid, C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>N<sub>2</sub>, with a similar substance. Methylpyrrolidinedicarboxylic acid is absent. E. W. W.

**Lupin alkaloids. XI.** Oxidative degradation of  $\alpha$ -didehydrosparteine. K. WINTERFELD and H. E. RONSBERG (Arch. Pharm., 1936, **274**, 48—60).— $\alpha$ -Didehydrosparteine (I) with CrO<sub>3</sub> gives only NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H and CO<sub>2</sub> (8 mols.), indicating that one ethylenic linking is in position 4 : 5. (I) gives an

unstable Bz derivative, indicating that the second ethylenic linking is  $\alpha\beta$  to the second N and attached to a *tert*.-C. (I) and KMnO<sub>4</sub> in dil. H<sub>2</sub>SO<sub>4</sub> give (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, which must have come from ring IV and thus favours the symmetrical formula for sparteine. R. S. C.

**Solanidine t. I.** H. DIETERLE and H. ROCHELMEYER (Arch. Pharm., 1935, **273**, 532—539).—Solanidine (I) is hydrogenated in AcOH to dihydrosolanidine, m.p. 219—220°. Action of MeI on (I) for 24 hr. at 125° yields not solanidine methiodide (II) (cf. Schaffnit, Diss., Frankfurt, 1932), but solanthrine, C<sub>27</sub>H<sub>41</sub>N, also obtained by heating (II) at 325°. Se at 320° converts (I) into phenanthrene, chrysene, and another hydrocarbon, with pyridine and other bases. E. W. W.

**Solanthrine. II.** H. DIETERLE and H. ROCHELMEYER (Arch. Pharm., 1935, **273**, 539—540).—Dihydrosolanthrine (I) (A., 1933, 171) is identical with solanidine (*ibid.*, 290), but not with dihydrosolanidine (II) (*ibid.*, 1061); both (I) and (II) are, however, hydrogenated to tetrahydrosolanthrine (*ibid.*, 729). Thus (I) and (II) are isomerides differing in the position of a double linking. E. W. W.

[Attempted synthesis of] ergot alkaloids. **Synthesis of 4-carbolinedicarboxylic acids.** W. A. JACOBS and L. C. CRAIG (Science, 1935, **82**, 421—422).—Condensation of tryptophan with CH<sub>3</sub>O, MeCHO, paralalol, and PhCHO gives 3 : 4 : 5 : 6-tetrahydro-4-carboline-5-carboxylic acid, the 3-Me, m.p. 295° (decomp.), 3- $\beta$ -hydroxypropyl-, m.p. 261°, and 3-Ph derivative, m.p. 223—226°, respectively. Crotonaldehyde gives an amorphous substance. Using *N*-methyltryptophan instead of tryptophan in the condensations, PhCHO gives 3-phenyl-4-methyltetrahydro-4-carboline-5-carboxylic acid, m.p. 199—201° (decomp.). These substances, however, and those obtained by direct methylation, do not give the colour reaction with *p*-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO characteristic of lysergic acid and its derivatives. L. S. T.

**Strychnine and brucine. XXXV.** Hofmann degradation of dihydrobrucine. O. ACHMатович, (Miss) P. LEWIS, and R. ROBINSON (J.C.S., 1935, 1685—1694).—N(b)-Methyl-dihydrobrucidinum carbonate and N(a)N(b)-dimethyl-dihydrobrucidinum dicarbonate (+16H<sub>2</sub>O), m.p. 190—192° (decomp.), undergo thermal decomp., the dicarbonate giving more satisfactory results; the products are N(b)-methyl-dihydrobrucidine-a (I) (methyl- $\psi$ -dihydrobrucidine, m.p. 221—222°) and -b (II), dihydrobrucidine, and hydroxymethyltetrahydrobrucidine (III), m.p. 169°. (I) and MeI at low temp. yield N(b)-methyl-dihydrobrucidine-a dimethiodide (+4H<sub>2</sub>O), m.p. 284—286° (decomp.) [dimethochloride (+3H<sub>2</sub>O), decomp. 296—298°], and at high temp. form allo-N(b)-methyl-dihydrobrucidine-a dimethiodide (+3H<sub>2</sub>O), m.p. 245—246° [dimethochloride (+4H<sub>2</sub>O, 3MeOH), m.p. 202—204° (decomp.)]. The *allo*-dimethochloride and NaOMe give dimethyldebrucidine, m.p. 155—156°. (I) absorbs 2 H (Pd-C) to give (NaI) N(b)-methyl-dihydrobrucidinum-d (+2H<sub>2</sub>O), m.p. 317—318° (decomp.) [chloride (+3H<sub>2</sub>O), m.p. 304—306° (decomp.)], and -c iodide (+2.5H<sub>2</sub>O), m.p. 304—306° (decomp.) [chloride (+3H<sub>2</sub>O), m.p. 233—235°]. (III) with



$\text{Ac}_2\text{O}-\text{NaOAc}$  gives *acetoxymethyltetrahydrobrucidine*, m.p. 258—260° (decomp.), is methylated ( $\text{Me}_2\text{SO}_4-\text{NaI}$ ) to methoxymethyltetrahydrobrucidine methiodide, and with hot aq.  $\text{H}_2\text{SO}_4$  leads to methylidihydrobrucidinum H sulphate. (II) is isolated as the *methiodide* (+ $\text{CHCl}_3$ ), decomp. 242—244° (+2MeOH), m.p. 80—82°, decomp. 242—244°, converted into the *methochloride*, m.p. 165—170°, solidifies 175—180°, decomp. 245—248°, from which the base is obtained. The constitution of the compounds is discussed.

F. R. S.

**Strychnos alkaloids. LXXXVIII.** Transformation of dihydrobrucine into three isomerides and preparation of *isodihydrostrychnine*. H. LEUCHS and A. DORNOW (Ber., 1935, 68, [B], 2234—2241).—Treatment of dihydrobrucine with  $\text{NaOMe}$  affords a mixture of *isodihydrobrucine* III, m.p. 235—245°,  $[\alpha]_D^{20} +28.8^\circ$  in abs. EtOH, which gives a very sparingly sol. *perchlorate*,  $[\alpha]_D^{20} +13^\circ$  in  $\text{H}_2\text{O}$ , a *methiodide*, decomp. 310° after darkening at 280°,  $[\alpha]_D^{20} +41.7^\circ$  in 90% AcOH, and an *acetate* (*perchlorate*, softens at 240°,  $[\alpha]_D^{20} -18^\circ$  in  $\text{H}_2\text{O}$ ), and *isodihydrobrucine* I (I),  $\text{C}_{23}\text{H}_{28}\text{O}_5\text{N}_2$ , m.p. 225—235°,  $[\alpha]_D^{20} -165^\circ$  in abs. EtOH,  $-195^\circ$  in  $\text{CHCl}_3$  [identical with the so-called dihydrobrucine hydrate of Wieland *et al.* (A., 1930, 1455)], which affords a *sulphate*, m.p. > 290°,  $[\alpha]_D^{20} -223^\circ$  in  $\text{H}_2\text{O}$ , a *perchlorate*,  $[\alpha]_D^{20} -231^\circ$  in  $\text{H}_2\text{O}$ , a *methiodide*, decomp. 310° after softening at 280—300° (vac.), and an *acetate* [*perchlorate*, m.p. 240—260° (decomp.),  $[\alpha]_D^{20} -133^\circ$  in  $\text{H}_2\text{O}$ ]. In addition, small amounts of *isodihydrobrucine* II, m.p. 215—216° (vac.),  $[\alpha]_D^{20} -10.2^\circ$  in  $\text{CHCl}_3$ ,  $+4.3^\circ$  in abs. EtOH, are occasionally produced; this becomes the main product when less drastic conditions of isomerisation are used. It gives a *perchlorate*, m.p. 215—230°,  $[\alpha]_D^{20} +24^\circ$  in  $\text{H}_2\text{O}$ , *methiodide*, m.p. 208—218° (sealed tube),  $[\alpha]_D^{20} +17.2^\circ$  in 90% AcOH, and *acetate*, m.p. 103—105° (*perchlorate*, m.p. 138—143°,  $[\alpha]_D^{20} +12^\circ$  in  $\text{H}_2\text{O}$ ). It is not hydrogenated in presence of  $\text{PtO}_2$  and AcOH and is isomerised to (I) by  $\text{NaOMe}$ . The presence of the *isostrychnine* type is established for all isomerides, and isomerism is caused by new, asymmetric C atoms. Treatment of dihydrostrychnine with  $\text{NaOMe}$  leads to *isodihydrostrychnine* (II), m.p. 249—250°,  $[\alpha]_D^{20} +6.5^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{20} +23^\circ$  in abs. EtOH, but other isomerides do not appear to be formed. (II) gives a *perchlorate*, m.p. 258—260° (decomp.),  $[\alpha]_D^{20} +37^\circ$  in  $\text{H}_2\text{O}$ , *methiodide*, m.p. about 318° (decomp.), and an *acetate*, m.p. 202° [*perchlorate*, m.p. 260° (decomp.),  $[\alpha]_D^{20} +25^\circ$  in  $\text{H}_2\text{O}$ ]. It is hydrogenated ( $\text{PtO}_2$ -dil. AcOH) to the base  $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$ , m.p. 228°,  $[\alpha]_D^{20} -4.02^\circ$  in  $\text{CHCl}_3$  [*perchlorate*, m.p. about 141° (decomp.),  $[\alpha]_D^{20} -14.3^\circ$  in  $\text{H}_2\text{O}$ ].

Dihydrobrucine methiodide separates from hot with 1 mol. of  $\text{H}_2\text{O}$  and has m.p. 245° or m.p. 255—258° (vac.). From MeOH it gives crystals  $+0.5\text{MeOH}$ , m.p. 290—295° (decomp.). The anhyd. salt has m.p. 290—295° (decomp.). H. W.

**Alkaloids of Papaver types. II. Alkaloids of . floribundum.** R. KONOVALOVA, S. YUNUSOV, and A. OREKHOV (Ber., 1935, 68, [B], 2277—2282; cf. this vol., 88).—The air-dried foliage of *P. floribundum* is moistened with 10%  $\text{NH}_3$  and percolated

with  $\text{C}_2\text{H}_4\text{Cl}_2$  and the mixture of alkaloids thus obtained (0.36% yield) is separated into phenolic (I) and non-phenolic (II) bases. Crystallisation of (I) from EtOH affords *floripavine* (III),  $\text{C}_{18}\text{H}_{21}\text{O}_4\text{N}$ , m.p. 200—201°,  $[\alpha]_D^{20} +90.5^\circ$  in  $\text{CHCl}_3$  (*hydrochloride*, m.p. 235—236°; *picrate*, m.p. 223—224°; *methiodide*, m.p. 220—221°), which contains 1 OH and 2 OMe. Treatment of the mother-liquors from (III) with  $\text{H}_2\text{C}_2\text{O}_4$  in EtOH gives *armepavine*. (II), when preserved, deposits crystals which are transformed into the corresponding hydrochlorides; these after repeated crystallisation from  $\text{H}_2\text{O}$  and subsequent treatment with  $\text{NH}_3$  yield *floripavidine* (IV),  $\text{C}_{21}\text{H}_{29}\text{O}_5\text{N}$ , m.p. 241—242°,  $[\alpha]_D^{20} -156.25^\circ$  in MeOH (*hydrochloride*, m.p. 209—210°; *hydriodide*; *methiodide*, m.p. 228—230°), which contains  $\text{CH}_2\text{O}_2$  but not  $\cdot\text{OH}$  (Zerevitinov). The mother-liquors from (IV) afford *floribundine* (V),  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$ , m.p. 193—195°,  $[\alpha]_D^{20} -204.28^\circ$  in  $\text{CHCl}_3$  (*tartrate*, m.p. 181—183°; *methiodide*, m.p. 178—180°), which contains  $\cdot\text{OH}$ ,  $\cdot\text{OMe}$ , and  $\cdot\text{NMe}$ . The mother-liquors from (V) give small amounts of "base V," m.p. 200—203°.

H. W.

**Deoxymorphine-C, deoxycodine-C, and their hydrogenated derivatives.**—See this vol., 107.

**Percaine.**—See this vol., 240.

**Alkaloids of Hanfangchi. II. Hanfangchin B.** C. F. HSU [with, in part, G. H. WANG and T. W. LU] (J. Chinese Chem. Soc., 1935, 3, 365—371; cf. A., 1935, 1257).—Hanfangchin B,  $\text{C}_{36}\text{H}_{40}\text{O}_6\text{N}_2$ , m.p. 241—242°,  $[\alpha]_D^{25} +272.4^\circ$  in  $\text{CHCl}_3$  (*COMe* compound, m.p. 134—136°; *picrate*, m.p. 186°; *aurichloride*, m.p. 172°; *methiodide*, m.p. 252°; *platinichloride*, m.p. 260°; *phosphate*, m.p. 215°; forms an Ac derivative with  $\text{Ac}_2\text{O}$  at 150—160°), was isolated by extracting the evaporated alcoholic mother-liquors from the prep. of hanfangchin A (*loc. cit.*) with  $\text{C}_6\text{H}_6$  and then crystallising from  $\text{COMe}_2$ . It contains 2 double linkings, 3 OMe, and 1 NMe, but no phenolic OH, N-NO, C=O,  $\text{O}_2\text{CH}_2$ , ester, or lactone groups. Intraperitoneal injection of the *hydrochloride* into the albino rat has no characteristic effect (minimal lethal dose, 250 mg. per kg. body-wt.). No alkaloids were found in Mofangchi or Kwangfangchi. H. G. M.

**Sulpharsphenamine. New method of preparation.** W. J. C. DYKE and H. KING (J.C.S., 1935, 1745—1747).— $\text{Na}_2$  3:3'-diamino-4:4'-dihydroxy-arsenobenzene-*NN'*-dimethylenesulphite, prepared from salvarsan and Na formaldehydebisulphite, with aq.  $\text{CH}_2\text{O}$  followed by  $\text{NaHSO}_3$  in  $\text{CO}_2$  gives sulpharsphenamine; it is not essential to isolate the  $\text{Na}_2$  salt. The mono-*N*-methylenesulphite of 4-nitro-2-aminophenol with  $\text{CH}_2\text{O}$  followed by  $\text{NaHSO}_3$  affords  $\text{Na}_2$  5-nitro-2-hydroxyanilino-*NN*-dimethylenesulphite.

F. R. S.

**Arsenicals containing the furan nucleus. II. Action of chlorine. Substituted furan arsenicals.** W. G. LOWE and C. S. HAMILTON (J. Amer. Chem. Soc., 1935, 57, 2314—2317; cf. A., 1935, 997).—Furyldichloroarsine, difurylchloroarsine (I), trifurylarsine, or 2-chlorofuran with  $\text{Cl}_2$  in  $\text{CHCl}_3$  give 2-chlorofuran tetrachloride, an oil, which loses HCl with  $\text{KOH}-\text{EtOH}$ , dil.  $\text{HNO}_3-\text{EtOH}$ , or  $\text{AgNO}_3-\text{HNO}_3-$

EtOH. Crude (I) and  $\text{Cl}_2\text{-CHCl}_3$  give also some *difurylarsinic acid*, m.p.  $138^\circ$ , and *trifurylarsine dichloride*, m.p.  $132^\circ$ . 5-Chloro-2-chloromercurifuran, m.p.  $181^\circ$ , and  $\text{AsCl}_3$  in  $\text{C}_6\text{H}_6$  give *tri-5-chlorofurylarsine*, m.p.  $63^\circ$ . *Tri-5-bromofurylarsine*, m.p.  $106^\circ$ , is similarly prepared. These compounds do not readily react with  $\text{HgCl}_2$ . R. S. C.

**Constitution of some additive compounds of tertiary phosphines.** W. C. DAVIES and (in part) W. P. WALTERS (J.C.S., 1935, 1786—1792).—The stability of  $\text{CS}_2$  compounds of phosphines is determined by measuring the total dissociation pressure of the compound; the stability of  $\text{PPhMe}_2\text{CS}_2$  is taken as 1 and that of any other compound obtained by comparing the temp. at which the dissociation pressure of the latter and of the standard become 50 mm. The m.p. of the additive compounds of  $\text{PRMe}_2$  and  $\text{PREt}_2$  run parallel, with one exception, to the stabilities in the two groups. The factors which affect stability are nuclear substituents in *p*- and *o*-positions and the change from aryl-dimethyl- to -diethyl-phosphine. The formulae of the compounds are discussed. The following have been prepared: *triethylphosphine-p-tolyl*, m.p.  $88\text{--}90^\circ$ , and *p-nitrophenyl-thiocarbimide*, m.p.  $97^\circ$ , *triethylphosphine-p-benzoquinone*, m.p. about  $180^\circ$ , *tri-n-butyl*, m.p.  $180\text{--}190^\circ$ , and *p-tolyl dimethyl-phosphine-p-benzoquinone*, m.p. above  $250^\circ$ . F. R. S.

**Derivatives of allyl ethers of phenols having mercury substituted in the nucleus.** A. N. NESMEJANOV and R. K. SCHATZKAJA (J. Gen. Chem. Russ., 1935, 5, 1268—1272).— $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$  in boiling  $\text{COMe}_2$  and  $\text{RBr}$  ( $\text{R}=\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot$ ) (7 hr.) yield the ether  $\text{o-OR}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$  (I), m.p.  $89^\circ$ , whilst when  $\text{RCl}$  is taken in place of  $\text{RBr}$  the product is  $(\text{o-OR}\cdot\text{C}_6\text{H}_4)_2\text{Hg}$ , m.p.  $59\cdot5\text{--}60\cdot5^\circ$ , into which (I) is converted by the action of  $\text{Na}_2\text{SnO}_2$ . With  $\text{C}_5\text{H}_5\text{N}$  in place of  $\text{COMe}_2$  in the above reaction (at  $-10^\circ$ ) the sole product is  $2\text{C}_5\text{H}_5\text{N}\cdot 2\text{RBr}\cdot\text{HgBr}_2$ , m.p.  $120\cdot5\text{--}121\cdot5^\circ$ .  $\text{PhOR}$  in aq.  $\text{AcOH}$ ,  $\text{HgO}$ , and  $\text{NaCl}$  (at the b.p.) yield the *p-isomeride* of (I), m.p.  $101\text{--}101\cdot5^\circ$ , converted by  $\text{Na}_2\text{SnO}_2$  into  $(\text{p-OR}\cdot\text{C}_6\text{H}_4)_2\text{Hg}$ , m.p.  $108\cdot5\text{--}110^\circ$ . The compound  $\text{OR}\cdot\text{C}_{10}\text{H}_6\cdot\text{HgCl}$ , m.p.  $161\text{--}162^\circ$ , is obtained from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  in  $\text{AcOH}$ ,  $\text{HgO}$ , and  $\text{NaCl}$ , as above. R. T.

**Arylation of mercuri-organic hydroxides by means of organic derivatives of tin, antimony, and boron.** R. C. FREIDLIN, A. A. KOTSCHESKOV, and A. N. NESMEJANOV (J. Gen. Chem. Russ., 1935, 5, 1171—1175).—The following compounds of the type  $\text{HgRR}'$  have been prepared by the general reaction  $\text{RHgX} + \text{R}'_m\text{MX}_n \rightarrow \text{HgRR}' + \text{R}'_m\text{MX}_{n+1}$  ( $\text{M}=\text{Sn}$ ,  $\text{Sb}$ , or  $\text{B}$ ;  $\text{X}=\text{halogen}$  or  $\text{OH}$ ):  $\text{R}=\text{Me}$ ,  $\text{R}'=\alpha\text{-C}_{10}\text{H}_7$ , m.p.  $80\text{--}82^\circ$ , from  $\text{RHgI}$  and  $\text{R}'_2\text{SnCl}_2$ , in  $\text{EtOH-NaOH}$  at the b.p.;  $\text{R}=\text{Ph}$ ,  $\text{R}'=\text{m-}$ , m.p.  $113\text{--}116^\circ$ , or  $\text{p-C}_6\text{H}_4\cdot\text{NO}_2$ , sintering at  $144\text{--}145^\circ$ , from *m-* or *p-R'HgCl* and  $\text{R}_2\text{SnCl}_2$ , as above;  $\text{R}=\text{p-C}_6\text{H}_4\text{Cl}$ ,  $\text{R}'=\text{CH}_2\text{Ph}$ , m.p.  $104\text{--}108^\circ$ , from  $\text{R'HgCl}$  and  $\text{RSbO}$ . R. T.

***o*- and *p*-Tolylstannic acids.** K. A. KOTSCHESKOV and M. M. NADJ (J. Gen. Chem. Russ., 1935, 5, 1158—1167).— $\text{R}_4\text{SnCl}_2$  (I) ( $\text{R}'=\text{o-}$ ,  $\text{R}=\text{p-C}_6\text{H}_4\text{Me}$ ) and  $\text{HgCl}_2$  in  $\text{EtOH}$  yield  $\text{RHgCl}$ , whilst in presence

of alkali the product is  $\text{HgR}_2$ .  $\text{RSnCl}_3$ , b.p.  $157^\circ/23\text{ mm.}$  (1 : 2 compound with  $\text{C}_6\text{H}_5\text{N}$ ), prepared from  $\text{SnCl}_4$  and  $\text{SnR}_4$ , or from (I) and  $\text{SnCl}_4$ , is converted into *p-tolylstannic acid*, decomp. at  $295^\circ$ , by aq.  $\text{KOH}$  at room temp.  $\text{R}'_2\text{SnCl}_2$ , m.p.  $49\text{--}50^\circ$ , obtained from  $\text{SnCl}_4$  and  $\text{SnR}'_4$ , yields  $\text{R}'\text{SnCl}_3$ , b.p.  $157\text{--}158^\circ/20\text{ mm.}$ , with  $\text{SnCl}_4$ , and is converted into  $(\text{R}'\text{SnS})_2\text{S}$  by  $\text{H}_2\text{S}$ , and into *o-tolylstannic acid* (II) by  $\text{KOH}$ . (II) is oxidised by  $\text{K}_3\text{Fe}(\text{CN})_6$  at room temp. to yield  $\text{PhMe}$ ,  $\text{R}'\text{CN}$ , and  $\text{H}_2\text{SnO}_3$ . R. T.

**Separation of diketopiperazines and amino-acids in protein hydrolysates by ionophoresis.** II. V. S. BALABUCHA-POPOVA, N. I. GAVRILOV, and A. M. RIKALEVA (Biochem. Z., 1935, 283, 62—70).—Mixtures of anhydrides and  $\text{NH}_2$ -acids are quantitatively separated by electrophoresis of the cathode fluid 3 or 4 times. In protein hydrolysates, the anhydride fraction can also be removed by electrophoresis, the cathodic fluid only retaining traces of anhydride.  $\text{Hg}$ ,  $\text{Ag}$ , or  $\text{Pb}$  but not  $\text{Ni}$  is usable as cathode; the c.d. at the cathode should be  $>10\text{--}13$  milliamp. per sq. cm. cathode surface and the liquid in cathode and anode chambers should be feebly acidified with  $0\cdot1\text{N-H}_2\text{SO}_4$  beforehand. With protracted electrophoresis, loss of N occurs. P. W. C.

**Derivatives of keratin.** D. R. GODDARD and L. MICHAELIS (J. Biol. Chem., 1935, 112, 361—371).—Keratin (I) (keratin reduced by  $\text{SNa}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ ) with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$ ,  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$ , and  $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{OH}$  gives *S-derivatives*, differing from (I) in solubility and isoelectric point, and digestible by pepsin or trypsin. The product from  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$  is fractionally pptd. by  $(\text{NH}_4)_2\text{SO}_4$ , indicating non-homogeneity of (I). The substance formed by re-oxidation of (I) is called metakeratin. *N-Derivatives* are not formed by the above procedure. R. S. C.

**Formation of thio-derivatives of proteins using carbon disulphide.** M. LOISELEUR (Compt. rend., 1935, 201, 966—968).— $\text{CS}_2$  and casein in  $0\cdot1\text{N-NaOH}$  at  $40\text{--}45^\circ$  give after pptn. by acid a red-orange product, which decomposes on drying and probably has  $\text{CS}_2\text{K}$  groups attached to protein- $\text{NH}_2$ . F. A. A.

**Acid autoclaving of blood-albumin.**—See this vol., 222.

**Direct simultaneous micro-determination of carbon, hydrogen, and oxygen.** II. Analysis of pure compounds containing carbon, hydrogen, oxygen, and sulphur. III. Analysis of pure compounds containing carbon, hydrogen, oxygen, and nitrogen. W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1935, 7, 363—365, 366—368; cf. A., 1934, 1239).—II.  $\text{Ph}_2\text{SO}_2$  and  $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Ph}$  analysed by the method previously described give vals. for S accurate to  $0\cdot4\pm0\cdot1\%$ .

III. The ratio of  $\text{NO}_2$  and  $\text{N}_2$  is determined in micro-combustions by the same method for various compounds containing N. F. R. G.

**[Determination of] chlorine in organic compounds.** I. Rapid lamp method. W. N. MALISOFF (Ind. Eng. Chem. [Anal.], 1935, 7, 428).—Cl can be determined accurately by the lamp method (cf. Kennedy, B., 1928, 559). F. R. G.



Action of perchloric acid on iodine and iodine derivatives.—See this vol., 177.

Semi-micro-Kjeldahl determination of nitro- and azo-nitrogen. R. A. HARTE (Ind. Eng. Chem. [Anal.], 1935, 7, 432—433).—A modification of the method of Elek *et al.* (A., 1926, 632). F. R. G.

Micro-determination of protein-nitrogen in the presence of ammonium salts. A. ROCHE and F. MARQUET (Bull. Soc. Chim. biol., 1935, 17, 1630—1632).—The protein is pptd. with tannin in aq. AcOH and N determined in the ppt. A. L.

Determination of protein-nitrogen. H. W. GERRITZ and J. L. ST. JOHN (Ind. Eng. Chem. [Anal.], 1935, 7, 380—383).—0.8 of the sulphates in the Kjeldahl-Gunning-Arnold method are replaced by phosphate, giving a reduction of digestion time to 10—25 min. F. R. G.

Determination of selenium in organic matter. K. T. WILLIAMS and H. W. LAKIN (Ind. Eng. Chem. [Anal.], 1935, 7, 409—410).—Modification of the method of Robinson *et al.* (B., 1934, 798) results in a saving of 4—6 hr. in the time of digestion. F. R. G.

Determination of the nitrogen of the nitro-groups of cyclotrimethylenetrinitroamine (T.). E. VERNAZZA (Chim. e l'Ind., 1935, 17, 685—687).—0.02—0.05 g. of the substance is treated with 10 c.c. of  $H_2SO_4$  and 0.3—0.4 g. of  $KMnO_4$  for 10 min. at room temp. and then at  $100^\circ$  until no more gas is evolved (about 20 min.). When cool, 1—3 drops of a saturated solution of I in  $H_2SO_4$ , followed by 0.1—0.2 c.c. of glacial  $HCO_2H$ , are added and the mixture is heated at  $100^\circ$  until colourless (1 min.). The excess of  $KMnO_4$  is thus reduced to  $Mn^{++}$  and the of the  $NO_2$  groups is converted quantitatively into  $NO_2 \cdot SO_3H$ , which is determined by adding an excess of standard  $KMnO_4$ , followed by an excess of standard  $FeSO_4$ , and titrating with  $KMnO_4$ . D. R. D.

"Glacial acetic acid" method of determination of amino- or other basic groups in amino-acids etc. L. J. HARRIS (Biochem. J., 1935, 29, 2820—2829).—The considerable "blank" correction in the aq. titration of basic groups in  $NH_2$ -acids, polypeptides, etc. is obviated by using glacial AcOH solvent,  $HClO_4$  in glacial AcOH as titrant, and brilliant-cresyl-blue as indicator. With 2 ml. of 0.1N solution (micro-method, 0.05 ml. of 0.025N) and in absence of  $H_2O$ , the error is  $< 2\%$ . Examples are given. F. O. H.

Colorations given by phenols with nitrous acid. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 97—1298).—PhOH, cresol, and thymol do not give any coloration with aq.  $HNO_2$ , pyrocatechol gives a brown coloration with  $< 0.002\%$   $HNO_2$ , resorcinol a grey ppt. with 1% and a yellow coloration with 0.005—0.1%  $HNO_2$ , quinol gives a yellow coloration 0.1%, pyrogallol with 0.001—1%, and phloroglucinol with 0.1—1%  $HNO_2$  (pink with 0.002—0.005%  $HNO_2$ ). R. T.

Volumetric extraction analysis. A. BOLLIGER (J. Proc. Austral. Chem. Inst., 1935, 2, 312—317).—o-polytropenols (I), e.g., picric or styphnic acid, are titrated with aq. methylene-blue hydrochloride

(II). The insol. salt formed is extracted with  $CHCl_3$ , and titration continued until (I) is completely removed from the  $H_2O$  layer. Cations forming insol. picrates or picrolonates may be so pptd., the ppt. being subsequently titrated as indicated. Other acids forming with (II) or other coloured bases salts insol. in  $H_2O$  but sol. in org. solvents may be titrated similarly. The method is suitable for about 1 mg. of material. J. S. A.

Determination of cholesterol. II. I. LIFSCHUTZ (Biochem. Z., 1935, 282, 441—443; cf. A., 1918, ii, 179; 1935, 1363).—Cholesterol is recovered quantitatively from its compound (I) with digitonin (II) by grinding (I) with NaOAc, boiling the mixture for 30 min. with 95% EtOH, and adding excess of  $Et_2O$ . (II) and NaOAc are pptd. W. McC.

Microchemical determination [detection] of cholesterol, carbamide, glycerol, etc., based on the formation of liquid crystals. P. GAUBERT (Compt. rend., 1935, 201, 1202—1204).—A very small quantity of cholesterol (I) may be detected by melting it on a heated microscope slide together with a fragment of  $CO(NH_2)_2$ , or other substance which when mixed with (I) forms liquid crystals (cf. A., 1913, i, 264); the latter show the presence of (I). Similarly urine, or glycerol in wine, may be detected by adding fragments of (I) to a drop evaporated on a slide, and heating; if necessary the liquid crystals are made visible by pressure on the cover-slip. Lemon juice is similarly detected; in this case the liquid crystals, due to citric acid, persist at room temp. E. W. W.

Application of "Original Hanau" artificial sunlight lamp in qualitative analysis. I. Photoanalysis in pyridine and indole series. H. FREYTAG (Z. anal. Chem., 1935, 103, 334—340).—A drop of solution containing  $C_5H_5N$ , applied to filter-paper impregnated with 0.2% alcoholic 1-phenyl-3-methylpyrazolone, gives on irradiation with ultraviolet light a blue spot, due to formation of a pyridine dye from the products of photochemical oxidation. 4-Methyl- but no other methylated pyridine similarly gives a violet colour. Limit,  $10^{-5}$  g. for each. Indole, and 2-, 5-, and 7-methylindole, irradiated as drops on filter-paper, give oxidation products possessing a strong yellow-green fluorescence. With skatole a sp. bluish fluorescence is obtained.  $2 \times 10^{-6}$  g. of indole may be detected by the formation of a pink colour on irradiation of a drop of liquid on filter-paper soaked in  $H_2SO_4$ . 2-, 5-, and 4-Methylindole (sp. blue colour) may be similarly detected. J. S. A.

Specific reaction for yohimbine. L. ROSSI, A. DEL BOCA, and R. LOBO (J. Pharm. Chim., 1935, [viii], 22, 566).—The authors claim priority (cf. Anal. Farm. Bioquim., 1932, 3, 51; A., 1935, 1260). J. L. D.

Aminometry of alkaloids. I. Aminometric determination in anhydrous chloroform solution. R. DIETZEL and W. PAUL (Arch. Pharm., 1935, 273, 507—515).—Alkaloids are determined by a modification of Vorlander's "aminometric" method (A., 1934, 198, 314). The amine groups are titrated in anhyd.  $CHCl_3$  with  $p-C_6H_4Me \cdot SO_3H$  in  $CHCl_3$  [standardised against  $N(CH_2Ph)_3$ ], using

$\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{Ph}$  in  $\text{CHCl}_3$  as indicator. Accurate results are obtained with brucine, strychnine, hyoscyamine, veratrine, atropine, papaverine, quinine, aconitine, cocaine, codeine, narcotine, and cinchonine. The method is applied to the determination of alkaloids in drugs and pharmaceutical preps. The drug is (if necessary) digested with aq.  $\text{HCl}$  or aq.  $\text{H}_2\text{SO}_4$  and extracted with  $\text{CHCl}_3$ . In general the alkaloid is then set free by  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{MgO}$ , or aq.  $\text{NH}_3$ , and extracted with  $\text{CHCl}_3$  (mixed, if necessary, with  $\text{Et}_2\text{O}$ ); the dried solution is then titrated as above. Details are given of the method as applied to cortex chinæ (and other quinine preps.), cortex granati, radix and tinctura ipecacuanhæ, extractum and tinctura strychni, extractum belladonnæ and hyoscyami, and secale cornutum (which requires special treatment). Application to semen strychni and to folia belladonnæ or hyoscyami is difficult. For semen and tinctura colchici, and for caffeine and theobromine, no suitable indicator is found. E. W. W.

**Extraction of lead by means of diphenylthiocarbazone.**—See this vol., 179.

**Glucoproteins. I. Determination of glucosamine.** R. BOYER and O. FÜRTH (Biochem. Z., 1935, 282, 242—256).—The colorimetric method of Elson and Morgan (A., 1934, 910) for determination of glucosamine (I) is adapted, with modifications, for use with the step photometer. Addition of carbohydrates or  $\text{NH}_2$ -acids to solutions of (I) causes errors; that of protein hydrolysates renders the method useless. Separation of (I) from the hydrolysates by pptn. by the  $\text{Cu-CaO}$  method is not possible, since considerable destruction of (I) occurs. For determinations of (I) in protein hydrolysates the more tedious method of Zuckerkandl *et al.* (A., 1931, 1081) must still be employed, since it is less sensitive to these errors. The structure of the pigment and its precursor is discussed. P. W. C.

**Determination of tryptophan in proteins by means of the Pulfrich photometer.** F. BÖHM and G. GRÜNER (Biochem. Z., 1935, 282, 230—234).—A method is described and tables summarise the tryptophan contents of caseinogen and serum when determined both by the colorimetric and photometric methods. P. W. C.

## Biochemistry.

**Carbonic acid and respiratory activity.** A. RISI (Z. Biol., 1935, 96, 615—633).—Inhalation of  $\text{CO}_2$ -rich (5—15%) air by cats and dogs markedly stimulates the respiration in both frequency and depth. The effect is increased by admixture with  $\text{O}_2$ , and occurs, although to some extent modified, after administration of certain alkaloids etc.

F. O. H.

**Equilibrium time of the gaseous nitrogen in the dog's body following changes of nitrogen tension in the lungs.** L. A. SHAW, A. R. BEHNKE, A. C. MESSER, R. M. THOMSON, and E. P. MOTLEY (Amer. J. Physiol., 1935, 112, 545—553).—The  $\text{N}_2$  content of the body  $\propto$  the partial pressure of  $\text{N}_2$  in the lungs under conditions of equilibrium at pressures up to 4 atm. The rates of  $\text{N}_2$  elimination from the completely and partly saturated body are equal, as are the saturation and desaturation times.  $\text{N}_2$  is held by the blood and tissue-fluids in a high state of supersaturation. R. N. C.

**Intravenous injection of oxygen with the animal under ordinary and increased atmospheric pressure.** I. SINGH (J. Physiol., 1935, 84, 315—322).—Cats absorb about 5 c.c. of  $\text{O}_2$  injected intravenously in 10 min. With animals of different species the vol. absorbed per kg.  $\propto$  the size of the animal. Increase of atm. pressure increases the amount of  $\text{O}_2$  that can be absorbed. R. N. C.

**Influence of hyperpnœa and of variations of oxygen and carbon dioxide tension in the inspired air on hearing, after images, and nystagmus.** E. GELLHORN and I. G. SPIESSMAN (Amer. J. Physiol., 1935, 112, 519—527, 620—626, 662—668).

R. N. C.

**Excitability of the respiratory centre in dependence on the thyroid and spleen.** J. FELDER

(Z. ges. exp. Med., 1934, 94, 384—388; Chem. Zentr., 1935, i, 2691). R. N. C.

**Dependence of the excitability of the respiratory centre on the thyroid.** R. SPIELMANN (Z. ges. exp. Med., 1934, 94, 378—383; Chem. Zentr., 1935, i, 2691).—The excitability of the respiratory centre of the rabbit is determined by measurement of the gross respiration in a special apparatus. Injection of thyroxine or thyrotropic hormone increases the excitability. Thyroid preps. can be evaluated biologically by the method. R. N. C.

**Effects of suppression of the mesotergal organ on the gaseous exchange of *Lepidoptera*.** A. RAFFY and G. GUIGNON (Compt. rend. Soc. Biol., 1935, 120, 765—766).—Gaseous exchange is depressed by destruction of the mesotergal organ, and the increases produced by nicotine are  $<$  normal. R. N. C.

**Neuro-central regulation of hæmatic nitrogen.** P. JEDŁOWSKI (Boll. Soc. ital. Biol. sperim., 1935, 10, 225—227).—Hæmatic N is increased by destruction of one or both of the hemispherical cortices in the rabbit, and to a small extent by lesions of different parts of the encephalic base. R. N. C.

**Evidence for a potassium shift from plasma to muscles in response to an increased carbon dioxide tension.** W. O. FENN and D. M. COBB (Amer. J. Physiol., 1935, 112, 41—55).—Experiments described indicate that increased  $\text{CO}_2$  tension tends to cause K shift from plasma to muscles, but the same increase would shift K from the muscle to Ringer's solution, because the muscle is intermediate between Ringer's solution and blood in its buffering capacity.

**Kinetics of the elimination of the dye water-blue from dog plasma after intravenous injection.** A. HEMINGWAY, F. H. SCOTT, and H. N. WRIGHT (Amer. J. Physiol., 1935, 112, 56—64).—The concn. of water-blue falls rapidly in the first 2 hr. after injection, following an exponential curve; it follows a slower exponential curve during the next 48—72 hr., and proceeds at an approx. const. rate during the last 7—8 days. The equation for time and concn. is given. R. N. C.

**Erythrocyte and hæmoglobin increase in human blood during and after exercise.** E. C. SCHNEIDER and C. B. CRAMPTON (Amer. J. Physiol., 1935, 112, 202—206). R. N. C.

**Adsorption of creatine and creatinine by erythrocytes.** K. KACL (Compt. rend. Soc. Biol., 1935, 120, 916—917).—Creatine is not adsorbed by erythrocytes of cattle, and only by those of adult horses. Creatinine (I) is adsorbed by the cells of both species to the extent of 10—50%. Equilibrium is established rapidly. The abs. quantity of (I) adsorbed increases, whilst the relative quantity decreases, with rise of concn.; the phenomenon is reversible. R. N. C.

**Effect of  $p_H$  on the adsorption of creatinine by erythrocytes.** K. KACL (Compt. rend. Soc. Biol., 1935, 120, 918—920).—The optimum  $p_H$  for the adsorption is 7.3. The amount of adsorption increases with rise of temp. In presence of acids or alkalis,  $p_H$  tends to revert to its natural val. during adsorption. R. N. C.

**Permeability of erythrocytes for malonamide.** F. SCHONHEYDER (Skand. Arch. Physiol., 1934, 71, 39—60; Chem. Zentr., 1935, i, 2837—2838).—The permeability in buffered NaCl solution is independent of the treatment of the blood, of the composition of the outer fluid [addition of  $\text{Na}_2\text{CO}_3$  or  $\text{Hg}(\text{CN})_2$ ], or the amount of swelling, but rises with decreasing  $p_H$ . J. S. A.

**Glutathione of the erythrocytes in hyper- and hypo-thyroidism.** A. R. BEAUX (Compt. rend. Soc. Biol., 1935, 120, 822—823).—Glutathione in red corpuscles of dogs is decreased by feeding with thyroid, and increased by thyroidectomy. R. N. C.

**Alleged effect of electrical stimulation on the metabolism of red cell suspensions.** E. PONDER and J. MACLEOD (J. Gen. Physiol., 1935, 19, 265—281).—Electrical stimuli applied to red cell suspensions lead to a permanent vol. decrease (0.1%) in the system, and not to an increase in  $\text{O}_2$  consumption (cf. von Hattingberg, A., 1934, 541). The effect, which may occur in absence of red cells, disappears when platinised Pt electrodes are substituted for bright Pt. Using serum, a vol. increase occurs with platinised, not with bright, Pt electrodes. F. A. A.

**Electrokinetic potential of thrombocytes.** H. D. REMIER (Biochem. Z., 1935, 281, 345—348).—The potential is 20—42 mv. The val. varies during the day, but no certain relationship between potential and time of day, absorption of food, amount of protein, serum-albumin-globulin ratio, or plasma viscosity was detectable. P. W. C.

**Optical activity of horse's globinhæmochromogen and of hæmoglobin dissolved in 0.25N-sodium hydroxide (globin+hæmatin), with special reference to the sulphur contents.** S. SIMONOVITS and G. BALASSA (Biochem. Z., 1935, 281, 333—338).—A 0.16% solution of horse-globinhæmochromogen in 0.25N-NaOH after keeping 24 hr. has  $[\alpha]_{D^{20}}^{20} -45.2^\circ$ ; globin+hæmatin under the same conditions has  $[\alpha]_{D^{20}}^{20} -45.7^\circ$ . The vals. are dependent on the S content of the prep., but are independent of the concn. (0.20—0.92%) and of the methods of crystallisation. It is suggested that in globinhæmochromogen the reduced prosthetic group is coupled not with the whole globin mol., but only with the N bases of globin which are split off by NaOH. P. W. C.

**Spectrophotometric studies. II. Preparations from washed blood cells; nitric oxide-hæmoglobin and sulphæmoglobin.** D. L. DRABKIN and J. H. AUSTIN. III. Methæmoglobin. J. H. AUSTIN and D. L. DRABKIN. IV. Hæmochromogens. V. Technique for analysis of undiluted blood and concentrated hæmoglobin solutions. D. L. DRABKIN and J. H. AUSTIN (J. Biol. Chem., 1935, 112, 51—65, 67—88, 89—104, 105—114; cf. A., 1933, 81).—II. Solutions prepared from washed erythrocytes are preferable to hæmolysed whole blood, and absorption spectra of oxyhæmoglobin (I), hæmoglobin (II), CO-(II), cyanomethæmoglobin (III) are presented. NO-hæmoglobin (IV) solutions are prepared from reduced (II) and NO in the absence of  $\text{O}_2$ , and are converted into methæmoglobin (V) by  $\text{K}_3\text{Fe}(\text{CN})_6$ , and further into (III) by KCN. (IV) appears to be analogous to (I), but is less readily converted into (II). (I) treated with  $\text{H}_2\text{S}$  gives mixtures of (II) and sulphæmoglobin (VI). A curve for pure (VI) is deduced; from this a quant. estimate of (VI) in the blood of a patient with clinical sulphæmoglobinæmia is obtained. (VI) is formed from (II) only in the presence of  $\text{O}_2$ . It is convertible into hæmochromogens, but not into (II) or (III). Sulph-methæmoglobin is produced when (V) or (III) is treated with  $\text{H}_2\text{S}$ .

III. Absorption data are given for (V) between  $p_H$  6.0 and 9.4. Between  $p_H$  7.0 and 9.2 the change is reversible; at about  $p_H$  9.4 a reaction apparently leading to hæmatin occurs. (I) is converted into (V) in 20 min. at  $p_H$  6.0 by an equiv. amount of  $\text{K}_3\text{Fe}(\text{CN})_6$  in air. At higher  $p_H$  excess of  $\text{K}_3\text{Fe}(\text{CN})_6$  is required to complete the reaction.  $\text{NaNO}_2$ , above a crit. amount, reacts with (I) giving (V). This reaction is faster at lower  $p_H$  vals. Benzoquinone reacts slowly with (I) giving (V), and (I) in very dil. solution is partly converted into (V) in 84 hr.

IV. Spectra are given of oxidised and reduced hæmins, and of various hæmochromogens. (II) reacts slowly with NaOH, giving one of these. Another is produced when  $\text{C}_5\text{H}_5\text{N}$  is added to reduced hæmins; the reaction is complete only when excess of  $\text{C}_5\text{H}_5\text{N}$  is used. (II) and  $\text{C}_5\text{H}_5\text{N}$  yields a hæmochromogen; the reduced form of this reacts reversibly with CO, the oxidised form with KCN.

V. A spectroscopic cell, 0.07 mm. in depth, allows direct measurements to be made on undiluted blood

and solutions of (II) up to 42.7 g. per 100 c.c. Beer's law holds, no significant change in the spectrum of (II) being observed down to  $10^{-4}$  of this concn.

F. A. A.

**Physiological degradation of blood-pigments.** III. Derivation of urinary pigments from hæmoglobin. R. NOTTHAAS (Klin. Woch., 1935, 12, 1438—1441; Chem. Zentr., 1935, i, 2837).—By oxidation of hæmoglobin with  $\text{H}_2\text{O}_2$ , a pigment identical in absorption spectrum, adsorptive properties, and solubility with urochrome B was obtained.

J. S. A.

**Acid autoclaving of blood-albumin at 220°.** V. S. SADIKOV and E. V. LINDQUIST-RISAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 271—272).—The ppt. (54 g.) obtained by acting on blood-albumin (6 kg.) with 4%  $\text{H}_2\text{SO}_4$  at 220° for 10 min. is purified by washing with  $\text{Et}_2\text{O}$  and 20 recrystallisations from hot  $\text{EtOH}$ ; the product (I) (3.4 g.) begins to sublime at 230° and to decompose at 250°; m.p. 275—276°, mol. wt. 209, 210. Analysis indicates the formula  $\text{C}_{11}\text{H}_{20}\text{O}_2\text{N}_2$ . The results of hydrolysis with 25%  $\text{HCl}$  suggest that (I) is a cyclic leucylisovaline,

P G C

**Genesis of the proteins of the blood-plasma.** I. Variations in albumin and globulin in course of plasmaphoresis. II. Restoration of the serum-proteins after repeated plasmaphoresis. III. Importance of the bone-marrow in the synthesis of serum-albumin. A. DALLA VOLTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 163—166, 167—171, 342—346).—I. Repeated plasmaphoresis at 3—5-day intervals in the dog causes an initial rise followed by a fall in total serum-proteins, serum-albumin, the albumin/globulin ratio, and the vol. of circulating plasma, immediately before withdrawal of the blood, whilst the serum-proteins fall steadily for 24 hr. after replacement of the withdrawn corpuscles. Serum-globulins remain unchanged.

II. Protein and plasma regeneration takes place rapidly after repeated plasmaphoresis; albumins and globulins increase independently of each other.

III. X-Irradiation of the bone-marrow of plasma-phorised dogs induces a rapid increase of serum-albumin, whilst globulins decrease. Destructive X-irradiation of the whole body induces small variations of total serum-proteins, with a slight increase during cachexia; globulins rise whilst albumins fall. The bone-marrow is hence a place of origin of serum-albumins.

R. N. C.

**Behaviour of serum-proteins under various metabolic conditions.** H. KEILHACK (Arch. exp. Path. Pharm., 1935, 180, 1—11).—Transfer of precipitin blood from rabbits to rabbits inhibits the pptn., due probably to the presence of a non-sp., heat-stable but  $\text{O}_2$ -sensitive factor. Transfer of hæmagglutinin blood to normal, fed animals results in the detection of serum-proteins (I) in the blood after 3—4 weeks. In starved, febrile, or growing animals (I) disappear more rapidly from the blood. The difference between normal and other animals indicates that (I) can be used in an emergency to replace N loss, or consumed directly.

J. N. A.

**Determination of the isoelectric point of blood-serum.** N. I. JOUKOVSKY and W. A. L. DEKKER (Compt. rend. Soc. Biol., 1935, 120, 805—808).—The isoelectric point of cattle serum is determined by measurement of the velocity of cataphoresis of colloidal particles in the serum. Colloidal Pt, Au,  $\text{Fe}_2\text{O}_3$ , Se, and  $\text{TiO}_2$  suspension all have the same velocity in serum, although their velocities in  $\text{H}_2\text{O}$  differ; specificity of adsorption does not interfere. The isoelectric point obtained is identical with that found by the turbidity method.

R. N. C.

**Lipins of human blood.** E. M. BOYD and J. H. TWEDDELL (Trans. Roy. Soc. Canada., 1935, [iii], 29, V, 113—121).—The free cholesterol and phospholipin of whole blood remain approx. const. during the 24 hr. Cholesteryl esters are max. at 4 a.m. and lowest in the early afternoon, whilst neutral fats are highest during the day and lowest about 4 a.m.

W. O. K.

**Relation between blood-lipin level and fat content of milk in cows.** P. SCHROORL (Landbouw. Tijdschr., 1935, 47, June).—The lipin content of the blood of calves 1 week to 14 months old is 0.63—0.85%. In two herds there seemed to be a correlation between the mean fat production of the cows and the lipin content of the blood of their calves.

NUTR. ABS. (m)

**Physico-chemical state of acetylcholine in the blood.** D. BROWN and H. SCHEINER (Compt. rend., 1935, 201, 1046—1048).—When acetylcholine is added to blood-serum, the greater part is destroyed by the choline-esterase, but a small portion is inactivated by forming a complex with the serum constituents, from which it may be liberated in an active form by the addition of alkali.

W. O. K.

**Reflex influence of the content of acetylcholine in the blood of the coronary veins.** O. KRAYER and E. B. VERNEY (Arch. exp. Path. Pharm., 1935, 180, 75—92).—Electrical stimulation of the carotid sinus increases the acetylcholine (I) content of the coronary venous blood (dog) when physostigmine is previously administered. Increase of blood pressure in the isolated sinus does not increase (I), an effect achieved by adrenaline (which is inactive unless producing an arterial pressor action) in heart-lung preps. with intact vagi.

J. N. A.

**Creatine compounds.** III. Phosphocreatine of the blood. I. CIACCIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 308—310).—Blood contains 0.40—0.80 mg.-% of phosphocreatine as determined by the method of Dulière; it occurs in the erythrocyte fraction.

R. N. C.

**Some recently-proposed methods for determination of glyoxaline derivatives in serum.** E. TRABUCCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 264—267).—A criticism of the method of Loeper *et al.* (cf. A., 1935, 422). The Pauly reaction in serum is considered to be due to histidine or ergothioneine, rather than to histamine, which is pptd. by phosphotungstic acid.

R. N. C.

**Alimentary post-hyperglycæmic hypoglycæmia in the normal dog.** R. SARIC, A. LACOSTE, and E. AUBERTIN (Compt. rend. Soc. Biol., 1935, 120, 1104—



1107).—The fall of blood-sugar (I) after alimentary hyperglycæmia is of regular occurrence. It may take place in one or two stages, and in some cases a second fall occurs after partial recovery; the type of curve varies with the animal. There is no correlation between the max. rises and falls of (I) or the two sections of the (I) curve. Initial hypoglycæmia never occurs before hyperglycæmia. R. N. C.

**Variations of the blood-sugar and the influence of adrenaline and insulin.** H. HOLMGREN (Acta med. Scand. Suppl., 1934, 59, 104—115).—The daily blood-sugar (I) picture of the rabbit shows regular fluctuations associated with the rhythmic changes of the liver function. Liver-glycogen (II) reaches its max. between the successive (I) max. The action of adrenaline at the (I) max. is < at the (I) min., but that of insulin is greater. The effects are associated with (II). R. N. C.

**Behaviour of blood-sugar in poisoning by potassium atractylate.** A. MARRAS (Boll. Soc. ital. Biol. sperim., 1935, 10, 355—357).—K atractylate increases blood-sugar in rabbits and pigeons when given in sublethal doses, and decreases it in lethal doses. The increase in rabbits is > in pigeons, and is reduced by atropine and ergotamine. R. N. C.

**Blood-alcohol curve after ingestion of malt beer and sugar solutions.** A. BICKEL (Arch. Verdauungskr., 1935, 57, 239—243).—After taking 400 ml. of malt beer by mouth, the blood-EtOH (Widmark's method) reached only 0.067—0.100 g. per litre. After sugar by mouth no EtOH appeared in the blood. NUTR. ABS. (m)

**General theory of the solubility of volatile acids in blood.** F. LUCE (Biochem. Z., 1935, 281, 383—394).—A theory of the solubility of foreign substances (particularly volatile acids) is developed from the physico-chemistry of hæmoglobin and from the acid-base equilibrium in blood. The difficulties due to inadequate knowledge of the influence of high concns. of protein and hæmoglobin on the individual activities of acid anions are discussed. P. W. C.

**Effect of pyruvic acid on blood-oxalic acid.** S. SUZUKI (Japan. J. Med. Sci., 1935, II, 3, 91—94).—Intravenous (but not oral) administration of  $\text{AcCO}_2\text{H}$  (< 0.05 g. per kg.) lowers the blood- $\text{H}_2\text{C}_2\text{O}_4$  in rabbits and men (cf. A., 1934, 1122). Lactic acid is ineffective. F. O. H.

**Determination of lactic acid in blood.** J. RNST and J. TRUKA (Magyar orvosi Arch., 1934, 35, 386—391; Chem. Zentr., 1935, i, 2417).—Blood is diluted with aq. NaCl and centrifuged. The plasma is pptd. successively with  $\text{Ca(OH)}_2$  and  $\text{ZnSO}_4$ , and lactic acid in the clear filtrate is determined colorimetrically with  $\text{FeCl}_3$ . J. S. A.

**Lactic acid content of the blood in pregnancy and in puerperium.** T. J. TRUKA (Magyar orvosi Arch., 1934, 35, 482—486; Chem. Zentr., 1935, i, 2400).—The normal lactic acid content of the blood varies with the season of the year. It is increased by 40—50% in the ninth month of pregnancy and returns to normal after several days of puerperium. R. N. C.

**Oxalic acid content of blood.** A. THOMSEN (Z. physiol. Chem., 1935, 237, 199—213).—The method of Merz *et al.* (A., 1931, 1440) for the determination of  $\text{H}_2\text{C}_2\text{O}_4$  in blood and serum involves a series of indifferent compounds, and the high vals. observed are due largely if not exclusively to these impurities. The content of ox serum, determined by the  $\text{Et}_2\text{O}$  extraction method, is > 0.001%. After administration of spinach to a rabbit, the max. content of  $\text{H}_2\text{C}_2\text{O}_4$  in the serum is 0.0011%. Small amounts of  $\text{H}_2\text{C}_2\text{O}_4$  are detected in the kidneys and liver. Izumi's method (A., 1934, 201) and Suzuki's modification thereof (*ibid.*, 1122) are untrustworthy. H. W.

**Acid-base balance of blood. IV. Characterisation and interpretation of displacement of the acid-base balance.** N. W. SMOCK and A. B. HASTINGS (J. Biol. Chem., 1935, 112, 239—262; cf. A., 1934, 542).—The results produced by varying the factors which control the acid-base balance in human blood indicate that individuals may be characterised in terms of the rate at which the balance is restored to normal after experimental displacement and that abnormal acid-base conditions may be characterised in terms of the physiological factors involved. W. McC.

**Blood of salmon during the spawning season.** H. OKAMURA (Japan. J. Med. Sci., 1935, II, 3, 85—89).—Analytical data are given. F. O. H.

**Changes in blood [produced] by experimental ammonia poisoning.** I. G. FAZEKAS (Arch. exp. Path. Pharm., 1935, 180, 93—104).—In rabbits there is marked hyperglycæmia, increase of serum-inorg. P, decrease of serum-Ca, pronounced acidosis, and lipæmia. J. N. A.

**Apparatus for the micro-determination of certain volatile substances. IV. Blood-ammonia, with observations on normal human blood.** E. J. CONWAY (Biochem. J., 1935, 29, 2755—2772).—Refinements in the method of determination of  $\text{NH}_3$  (A., 1933, 654) have been made. In venous blood, collected directly into the absorption vessel through a paraffined tube in an atm. of alveolar air or pure  $\text{CO}_2$ , there is practically no free  $\text{NH}_3$  for approx. 12 min.; after this time a slow rise occurs. In blood collected in an open vessel a rapid rise in  $\text{NH}_3$  content occurs, followed by a slower one; extrapolation of the curves corresponding with these rises to zero time gives in the first case a zero val. for blood- $\text{NH}_3$  and in the second 0.038 mg. of  $\text{NH}_3$ -N per 100 ml. It is concluded that there is no free  $\text{NH}_3$  in normal blood, and that that produced on shedding is due to the decomp. of a carbamino-compound. H. D.

**Blood-bromine. I. Determination. II. Control of the method and values for normal subjects.** R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1935, 10, 189—191, 191—192).—I. See A., 1935, 375.

II. The sensitivity of the method (*loc. cit.*) is double that of the gravimetric or Volhard's method. The time of heating required for the destruction of org. matter does not affect the result. Vals. found for

dibromothyroxine agree with the calc. val. Vals. are given for Br in ox blood and human blood.

R. N. C.

**Detection of lead in blood.** K. HOLL (Pharm. Ztg., 1935, 80, 1342—1343).—Various methods are discussed.

F. O. H.

**Diffusion of potassium from resting skeletal muscle following a reduction in the blood supply.** A. M. BAETJER (Amer. J. Physiol., 1935, 112, 139—146).—Blood-K in the femoral vein of the cat is not affected by reduction of the blood supply to the leg muscles to vals.  $\leq 80\%$  of the normal val., below which level it increases rapidly through loss of K from the muscles. Sympathetic stimulation increases venous plasma-K owing to reduction in the blood flow by vaso-constriction.

R. N. C.

**Inflammation and hydrogen-ion concentration of the blood.** F. LAMMERHIRT (Arch. exp. Path. Pharm., 1935, 180, 52—68).—Inflammation on the backs of rabbits, produced by mustard oil, is inhibited by intravenous injection of isotonic  $\text{Na}_2\text{CO}_3\text{--NaHCO}_3$  buffer. These solutions have no appreciable effect on  $[\text{H}^+]$  of the blood.  $\text{NH}_4\text{Cl}$  and Na atophan solutions both lower the  $p_{\text{H}}$ ; the latter, however, produces alkalosis within a few hr.

J. N. A.

**Action of zinc salts on blood.** G. PIOTROWSKI (Compt. rend. Soc. Biol., 1935, 120, 830—832).—Zn salts increase the time of coagulation of blood *in vitro* but not *in vivo*. Leucocytes and the polynuclear/lymphocyte ratio are temporarily increased.

**Chemical examination of moranylised or liquoidised blood.** R. NATTAN-LARRIER and P. TCHERNIAKOVSKY (Compt. rend. Soc. Biol., 1935, 120, 857—859).—Moranyl and liquoid used as anticoagulants do not affect the composition of blood except to raise the Na content.

R. N. C.

**Immunological specificity of the euglobulin and pseudoglobulin fractions of horse and human serum.** T. HARRIS and H. EAGLE (J. Gen. Physiol., 1935, 19, 383—396).—The sera of rabbits injected with either euglobulin or pseudoglobulin fractions from human and horse sera give ppts. with both, but two distinct antibodies are present. Neither fraction, as usually prepared, is free from the other. Lipins associated with the proteins do not determine the immunological specificity of the fractions.

F. A. A.

**Properties of the dried diphtheria toxin-aluminium hydroxide complex.** S. SCHMIDT (Compt. rend. Soc. Biol., 1935, 120, 1148—1150).—The complex loses its dissociability and its toxicity when dried.

R. N. C.

**Preparation of aluminium hydroxide for adsorption of toxins (anatoxins) and ultraviruses.** A. HANSEN and S. SCHMIDT (Compt. rend. Soc. Biol., 1935, 120, 1150—1152).— $\text{Al}(\text{OH})_3$  prepared by Willstatter's method does not lose its adsorbing power or gelatinous appearance if autoclaved immediately when prepared.

R. N. C.

**Adsorption of the antibodies from syphilitic and tuberculous sera.** G. D'ALESSANDRO and F. SOFIA (Boll. Soc. ital. Biol. sperim., 1935, 10,

193—195).—The antibodies are adsorbed by kaolin or animal C in presence of the corresponding antigens.

R. N. C.

**Nature of diphtheria toxin: pulverulent purified anatoxin.** S. HOSOYA, K. KAGABE, T. TANAKA, and A. MOMMA (Compt. rend. Soc. Biol., 1935, 120, 1030—1032).—The purified anatoxin does not produce flocculation with horse-serum as does the crude anatoxin, and is not an anaphylactic antigen. It does not reduce Fehling's solution except after hydrolysis with 5% HCl at 80°. An osazone, m.p. 189—191°, can be prepared from the hydrolysate after pptn. of proteins with Pb salts.

R. N. C.

**Aninsulin.** P. BARRAL (Compt. rend. Soc. Biol., 1935, 120, 993—995).—*Aninsulin*, prepared by heating insulin with  $\text{CH}_2\text{O}$ , does not produce hypoglycæmia, but is antigenic. These properties are unstable at most temp., the optimum temp. for storage being 60°.

R. N. C.

**Complement deviation reaction of aninsulin.** P. BARRAL (Compt. rend. Soc. Biol., 1935, 120, 995—998).

R. N. C.

**Nature of tubercle antibodies.** K. MEYER and A. PIC (Compt. rend. Soc. Biol., 1935, 120, 946—949).—Sera of animals prepared with tubercle bacilli contain antibodies to the proteins and fats of the bacilli, but no antibodies capable of reacting with both at once.

R. N. C.

**Precipitin titration of types I and II anti-pneumococcus sera.** L. K. VIKTOROV, L. A. GUINTZE-VERNER, and M. V. DEMIDOVA (Ann. Inst. Pasteur, 1936, 56, 52—67).—An *in-vitro* technique, using a precipitin titration with the sp. polysaccharide fraction prepared from cultures deproteinised by  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  and pptd. by 60% EtOH, is described.

F. O. H.

**Immunising power of certain soluble metallo-protein complexes, formed from anti-swine fever serum.** H. DIACONO (Compt. rend. Soc. Biol., 1935, 120, 699—701).—Cu and Hg complexes with the antiserum retain a considerable part of the immunising power.

R. N. C.

**Analysis of type I pneumococcus specific precipitate.** H. O. CALVERY (J. Biol. Chem., 1935, 112, 167—169).—Analytical data for the ppt. obtained from type I pneumococcus haptene and antisera are given. The cystine and tryptophan vals. are  $>$ , and the tyrosine val. is  $<$ , those for diphtheria toxin-antitoxin flocculates.

J. N. A.

**Nature of tuberculous antibodies.** K. MEYER and A. PIC (Compt. rend. Soc. Biol., 1935, 120, 772—774).—The antibodies of antiprotein and antilipin sera are fixed by their sp. antigens, and when liberated, remain sp.

R. N. C.

**Serological flocculation rate in the region of considerable antibody excess.** S. B. HOOKER and W. C. BOYD (J. Gen. Physiol., 1935, 19, 373—378).—Mainly theoretical. When antibody concn. is  $> 3$  times the equiv. amount, the velocity of flocculation approx.  $\propto$  antigen dilution.

F. A. A.

**Microscopy of powdered desiccated endocrine organs.** H. W. YOUNGKEN (Amer. J. Pharm., 1935,

107, 463—471).—Examination and identification of thyroid, adrenal, pituitary, ovary, and corpus luteum of cattle, sheep, and hogs are described. W. McC.

**Cerium in the organs and excreta.** C. PROVINCIALI (Arch. ital. Sci. farmacol., 1932, 1, 101—119).—Ce cannot be detected in the organs with  $\text{H}_2\text{O}_2$ - $\text{NH}_3$  owing to the interference of Fe. A solution of strychnine in  $\text{H}_2\text{SO}_4$  or of benzidine in AcOH is used under determined conditions. Ce injected intravenously remains in the blood stream for 8 hr., but later appears in most of the organs. In chronic Ce poisoning *per os*, Ce appears in the liver and kidneys, and also in the gall-bladder if administered as a double salt. It is excreted exclusively by the intestine. Resorption on oral administration is small. R. N. C.

**Distribution of chlorine in the tissues of the rabbit, after intravenous injection of sodium chloride.** F. SCICLOUNOFF and R. S. MACH (Compt. rend. Soc. Biol., 1935, 120, 941—942).—Max. increase of Cl in all organs appears rapidly after injection. The Cl is largely taken up by the organs that normally show high Cl contents. R. N. C.

**Occurrence of lead in the organs and bones of healthy domestic animals.** P. W. DANCKWORTT and K. HOLL (Deut. tierarztl. Woch., 1934, 42, 586—589).—Liver, spleen, kidneys, and brains, or mixed samples of these were analysed. The average Pb content of organs (200 g.) of cows and horses was 0.051 mg., and of pigs 0.33 mg. For the bones (200 g.) of cows the mean val. was 0.66 mg. and of pigs 1.15 mg. NUTR. ABS. (m)

**Silica in silicoderms.** E. KAHANE (Bull. Soc. Chim. biol., 1935, 17, 1554—1558).—Digestion by  $\text{HNO}_3$ - $\text{HClO}_4$  of silicoderms (*Oncidium*, *Paraperonia*, *Oncidiella*) yields cryst. residues containing 55—85% of  $\text{SiO}_2$ . A. L.

**Effects of magnesium deficiency on the teeth and their supporting structures in rats.** H. KLEIN, E. R. ORENT, and E. V. MCCOLLUM (Amer. J. Physiol., 1935, 112, 256—262). R. N. C.

**Chemical composition of teeth. II. Composition of human enamel and dentine.** J. H. BOWES and M. M. MURRAY (Biochem. J., 1935, 29, 2721—2727; cf. A., 1935, 234).—N, Ca, Mg, Na, K, P,  $\text{CO}_2$ , Cl, and F were determined in the enamel and dentine from sound teeth with only a slight degree of hypoplasia. It is concluded that the enamel consists chiefly of hydroxyapatite, and that dentine contains less apatite than enamel, but more  $\text{CO}_3$ ;  $\text{CaHPO}_4$  is probably also a constituent of dentine. Only small quantities of Si and F were found in teeth. H. D.

**Early stages in the formation of the enamel organ.** E. DELORENZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 279—280).—Glycogen is present in considerable quantities in early stages of formation of the organ in the guinea-pig, rabbit, and calf, but disappears with the metamorphosis into the stellate form of the cells of the central mass. R. N. C.

**Human epidermis. II. Isoelectric points of the stratum corneum, hair, and nails as determined by electrophoresis.** V. A. WILKERSON

(J. Biol. Chem., 1936, 112, 329—335; cf. A., 1934, 1381).— $p_{\text{H}}$ -electrophoretic mobility curves are plotted for the stratum corneum of human skin, hair, and nails, giving isoelectric points of  $p_{\text{H}}$  3.70, 3.67, and 3.78, respectively. H. D.

**Oxidation-reduction potential of the tissues of the ovary: effect of urine on this potential.** M. MAGARA (Compt. rend. Soc. Biol., 1935, 120, 1015—1018).—The initial  $E_h$  of the tissues of the rabbit ovary is approx. +0.3 mv., and falls in 2—3 hr. to a steady val. of +0.1 mv. In presence of urine it falls to -0.2 mv.; urine shows the same effect to a smaller degree on  $E_h$  of other tissues. R. N. C.

**Chemical composition of the muscle of marine animals. II. Nitrogenous extractives in muscle of *Mugil cephalus*.** A. CARTENI and A. MORELLI (Quad. Nutrizione, 1934—1935, 1, 433—449).—In the aq. extract of the muscle total extractive N constitutes 0.40% of the fresh tissue, the composition being:  $\text{NH}_3$ -N 4.30; purine-N 4.03; albumin-N 20.73; creatine- and creatinine-N 24.74; N of other bases 23.02;  $(\text{NH}_2)_1$ -acid-N 15.16; polypeptide-N 2.05; urea-N 2.55; undetermined N 3.43%. NUTR. ABS. (m)

**Glycogen content of tape worms (cestoids).** I. A. SMORODINCEV and K. V. BEBESHIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 413—414).—The glycogen content of *Taenia saginata* (60% of the dry solids) is 3—4 times that of *T. solium* or *Diphyllobotrium latum*. H. G. R.

**Growth and glycogen content of the foetal liver and placenta.** E. L. COREY (Amer. J. Physiol., 1935, 112, 263—267).—The foetal liver of the rat is progressively hydrated during the last third of the gestation period, placental  $\text{H}_2\text{O}$  remaining const. At foetal wt. of 0.3 g., foetal liver-glycogen (I) is > placental glycogen, which falls relatively steadily until birth, although maternal (I) varies widely, showing that the two are independent. R. N. C.

**Size, fat, and vitamin-A content of the liver of some cartilaginous fishes.** S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (Kong. Norske Vidensk. Selsk. Forhandl., 1934, 7, 47—50; Chem. Zentr., 1935, i, 2913; cf. B., 1934, 970).—The fat content of the liver is up to 80—90% and generally  $\propto$  liver-wt. Large variations in fat and vitamin-A (I) contents occur, even in the same species. Fat melted out from the liver is poorer in (I) than the extracted liver-oil. The total (I) content is  $\leq 14$  units, sometimes >5000; in *Galens vulgaris* and *Lamna cornubia* it is >10,000—40,000, i.e., as great as in halibut etc. The (I) content of rays is < that of sharks. H. N. R.

**Separation of physeteric acid from sardine and pilot-whale oils.**—See this vol., 189.

**Effect of sex on the lipins of some marine molluscs.** J. TIMON-DAVID and G. CERESOLA (Compt. rend., 1935, 201, 853—854).—The lipin contents of the female *Eledone moschata*, *Murex brandaris*, and *Mytilus galloprovincialis* are > those of the corresponding males. R. N. C.

**Separation of selacholeic acid from cod-liver, "sukesso-dara" liver, sei-whale, and pilot-**

**whale oils.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 684—687B).—Selacholeic ( $\Delta^8$ -tetracosic) acid has been isolated as a minor component of the fatty acids from the liver oils of cod and *Theragra chalcogramma*, and from sei- and pilot-whale oils; some impure *n*-tetracosic acid was also isolated from the whale oils. H. G. M.

**Unsaponifiable matter of sei-whale oil.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1935, 38, 687—690B).—The unsaponifiable matter contains oleyl and a little cetyl alcohol and cholesterol. Hexadecanol, octadecanol, and some highly unsaturated alcohols are possibly also present. H. G. M.

**Fatty oil of *Chanoschanos* (Forsk.)**. K. KAFUKU and C. HATA (J. Soc. Chem. Ind. Japan, 1935, 38, 650B).—Analytical data for the oils from the body, liver, and intestines of this tropical fish are recorded. Only the liver oil gives a strong colour reaction for vitamin-A. J. S. A.

**Visual purple system in marine fishes.** G. WALD (Nature, 1935, 136, 913).—The visual purple system in the eye tissues of *Prionotus carolinus*, *Centropomus striatus*, and *Stenotomus chrysops* is identical chemically with that in frogs (this vol., 96). L. S. T.

**Carotenoids and the visual cycle.** G. WALD (J. Gen. Physiol., 1935, 19, 351—371).—Fuller details of work already reported (A., 1934, 913; this vol., 96) are given. The xanthophyll content of the epithelium and choroid layer of frogs' eyes falls 10—20% during light-adaptation. Light-adapted retinas contain  $0.2\text{--}0.3 \times 10^{-6}$  g. of vitamin-A. F. A. A.

**Dissociation between intestinal and glandular permeability to carotenoids in the descendance of some crossings between different species of silkworm.** C. JUCCI (Boll. Soc. ital. Biol. sperim., 1935, 10, 218—219). R. N. C.

**New phosphorus fraction in blood and tissues.** T. KALAJA (Suomen Kem., 1935, 8, B, 41—42).—The filtrate obtained from the addition of blood (but not of serum) (man, cow, rabbit, rat) and liver and muscle (rabbit, rat) to  $\text{CCl}_3\text{CO}_2\text{H}$  gives a lower % of inorg. P by the Fiske-Subbarow method in the freshly prepared filtrate than after some hr. It is inferred that blood etc., but not serum, contains a thermo-labile compound which hydrolyses in acid or alkaline (but not neutral) protein-free filtrate. In the usual colorimetric method inorg. P must be determined immediately after filtering in the case of blood, whereas serum filtrates may be kept. The nature of the P compound is discussed. R. S. B.

**Dielectric properties and chemical constitution of phosphatides.** R. KUHN, I. HAUSSER, and W. BRYDOWNA (Ber., 1935, 68, [B], 2386—2388).—Sphingomyelin and lecithin (I) in EtOH have a dielectric const. > that of the solvent and therefore exist as zwitterions. In  $\text{C}_6\text{H}_6$  (I) and cephalin are dielectrically inactive. The inactivity of (I) is due to association. H. W.

**Lignoceryl sphingosin in ox lung.** C. TROPP (Z. physiol. Chem., 1935, 237, 178—180; cf. A., 1934, 97).

—Dried ox lung contains 0.06% of lignoceryl-sphingosin (I) together with a phosphatide of the sphingomyelin series. (I) probably exists preformed in the spleen, the content of which is not subject to seasonal variations. (I) does not occur in the heart, kidney, lymph glands, testes, or white and red bone marrow of the ox. W. McC.

**Determination of molecule size of nucleic acids and mononucleotides by the free diffusion method.** Size of the molecule of pancreatic pentosepolynucleotide and of cozymase. K. MYRBACK and E. JORPES (Z. physiol. Chem., 1935, 237, 159—164; cf. A., 1935, 232).—The diffusion of nucleic acids (I) [yeast-nucleic acid (II), pentosepolynucleotide (III)] is not affected by  $[\text{H}^+]$ , but is greatly affected by their electric charge and by presence of salts (e.g., NaCl) which restrict the diffusion to an extent  $\propto$  the mol. size of (I). In the determination of approx. mol. wt. of (I) by the free diffusion method, comparison must be made with known substances of similar structure and tendency to ionise. The method gives a mol. wt. of about 3000 for (III), and proves that it is not a mixture of (II) with guanylic acids. The mol. wt. of cozymase is approx. 500. W. McC.

**Isolation of cystine from wool hydrolysates.** G. TOENNIES and M. A. BENNETT (J. Biol. Chem., 1935, 112, 39—50).—Yields of *l*-cystine (I) up to 44% of theoretical calc. on total S are obtained by hydrolysis of wool with 50%  $\text{H}_2\text{SO}_4$ , addition of  $\text{Na}_2\text{SO}_4$  (to salt out humins), pptn. of (I) with  $\text{Cu}^{++}$ , and its conversion into hydrochloride. Negative biuret tests, or cyanide-nitroprusside tests corresponding with the total S content of the wool, do not prove complete hydrolysis. Max. yields of (I) are obtained at stages before complete hydrolysis, owing to loss of (I) by racemisation. F. A. A.

**Distribution of cystine and cysteine in the body.** K. INATOMI (Japan. J. Med. Sci., 1935, II, 3, 115—157).—Data for the cystine-cysteine (I) content of blood and other tissues (rabbit, dog, ox, man) are tabulated. The level increases in the blood during anæmia and in the spleen (but decreases in the liver) during hunger. Splenectomy produces first a fall, then a rise (to subnormal vals.), in the content of the corpuscles, a rise in that of liver and bone-marrow (a gradual decrease commences in the latter after 1 week), and a fall in that of kidney and muscle. The origin and storage of (I) are discussed. F. O. H.

**Acetylcholine equivalent of nervous tissues.** G. S. BARSOUM (J. Physiol., 1935, 84, 259—262).—The splanchnic and vagal nerve trunks in the dog show the highest acetylcholine (I) contents of all the tissues. EtOH extracts of tissues lose their (I) activity when kept at room temp.; the activity is largely restored by addition of  $\text{CCl}_3\text{CO}_2\text{H}$ . R. N. C.

**Carbon monoxide-ferroglutathione.**—See this vol., 194.

**Heparin.** F. LIPMANN and A. FISCHER (Z. physiol. Chem., 1935, 237, 273—274).—In agreement with Schmitz (A., 1935, 1394) highly purified hepa-



rin (I) is free from S. (I) prepared from ox lung by the method of Charles and Scott (A., 1933, 1317) gives a Ba salt which, after fractionation from neutral solution, contains Ba and org. S in the approx. ratio 2 : 3 in agreement with Jorpes' results (A., 1935, 1144), but % C and N are too high for a chondroitin-sulphuric acid. The preps. are about 30% more active than those of Jorpes. Under the action of 0.1N-HCl at 100° loss of physiological activity is much more rapid than elimination of H<sub>2</sub>SO<sub>4</sub>.

H. W.

**Potentiometric study of hepatoflavin.** F. J. STARE (J. Biol. Chem., 1935, 112, 223—229; cf. Stern, A., 1934, 846).—The redox potentials of hepatoflavin (from horse liver) at  $p_H$  0.32—13.38 have been determined by titration with reducing agents [Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>]. The titration curves branch in the more acid region. There are ionisation consts. at  $p_H$  about 6.8 (reduction) and 9.6 (oxidation). The normal potential is 0.188 volt.

W. McC.

**Dietary requirements for lactation. IV. Nature of factor-L.** W. NAKAHARA, F. INUKAI, and S. UGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 152—160).—Factor-L is pptd. from aq. EtOH extracts (previously treated with "acid earth"; A., 1934, 930) of liver by Ba(OH)<sub>2</sub>-MeOH. Dissolution of this ppt. by removal of Ba etc. and treatment with WO<sub>3</sub>.2H<sub>3</sub>PO<sub>4</sub> gives an active ppt. (0.176% of the liver used). The factor is not identical with glutamic acid.

F. O. H.

**Isolation of nicotinamide from heart muscle.** R. KUHN and H. VETTER (Ber., 1935, 68, [B], 2374—2375).—Protracted extraction with CHCl<sub>3</sub> of concentrates of a vitamin-B component (free from -B<sub>1</sub> and -B<sub>2</sub>) in feebly alkaline and neutral condition and heating of the residue at 150—160°/5 × 10<sup>-4</sup> mm. gives a waxy distillate from which nicotinamide is isolated.

H. W.

**Probable occurrence of tunicin in the dorsal sac of Sepia.** S. MÜLLER (Magyar chem. Foly., 1934, 40, 112—114; Chem. Zentr., 1935, i, 2551).—The product prepared by Ambronn from the dorsal sac of Sepia contains no tunicin, but a mixture of decomp. products of albumin, with a high N content.

R. N. C.

**Amide-nitrogen of ovalbumin.** A. SHORE, H. WILSON, and G. STUECK (J. Biol. Chem., 1936, 112, 407—413).—The NH<sub>3</sub> produced by the hydrolysis of ovalbumin (I) in 5, 1, and 0.2M-HCl is plotted against time and the probable amide content of (I) deduced by extrapolation to be 24 equivs. per mol.

H. D.

**Crystalline ovalbumin. II. Fractionation of peptic hydrolysis products.** H. O. CALVERY (J. Biol. Chem., 1935, 112, 171—174).—Pepsin hydrolysed one third of the peptide linkings of ovalbumin. Five distinct fractions were obtained, one of which contains free NH<sub>2</sub>-acids. Hydrolysis was also effected by erepsin, aminopolypeptidase, protaminase, and dipeptidase, the last yielding dipeptides.

J. N. A.

**Denaturation of ovalbumin by ultra-violet radiation.** J. H. CLARK (J. Gen. Physiol., 1935, 19, 199—210).—Three processes are involved, (a) a light-

denaturation, (b) a reaction between the product of (a) and H<sub>2</sub>O, (c) formation of a coagulum. (a) is unimol., independent of temp. and (largely) of  $p_H$ ; (b) has a temp. coeff. > 10, and occurs at lower temp. than does heat-denaturation.

F. A. A.

**Composition of the gelatinous mass from Rhizostoma Cuvieri.** R. ZEYNEK and A. DIMTER (Z. physiol. Chem., 1935, 237, 247—253).—The jelly is regarded as a gelatin-giving tissue differing from that of the higher animals in its ready decomp., low content of glycine (which is replaced by other NH<sub>2</sub>-acids), and high S content. It is undecided whether the L-aminobutyric acid present is to be regarded as a structural component.

H. W.

**Structure of silk fibroin.** H. MÜNCH (Angew. Chem., 1935, 48, 797—799).—A discussion of the effects of enzyme action.

E. S. H.

**Cryolysis and its relation to cell physiology.** F. F. NORD (Protoplasma, 1934, 21, 116—128).—Cryolysis of colloidal solutions followed by determination of physico-chemical vals. indicates that lyophilic colloids and their emulsions undergo irreversible changes consisting of aggregation or disaggregation according to their concns.

R. N. C.

**Physico-chemical researches on the proteins.**—See this vol., 158.

**Affinities between proteins and fatty acids, fats, and lipins.**—See this vol., 155.

**Colloid chemistry of edestin. II.**—See this vol., 158.

**Diphasic aspect of the curdling of milk by rennin.** A. G. SMITH and H. C. BRADLEY (Science, 1935, 82, 467).—A method for separating the enzymic and the aggregation phase is described. The former occupies < 60% of the time required for the appearance of the curd. Addition of CaCl<sub>2</sub> accelerates curdling by shortening the aggregation time; the enzymic activity of the rennin is unaffected. An increase in [H<sup>+</sup>] accelerates both phases.

L. S. T.

**Carotenoids of butter.** A. E. GILLAM and I. M. HEILBRON (Biochem. J., 1935, 29, 834—836).—The carotenes of various butters examined consisted of mixtures of  $\alpha$ - and  $\beta$ -forms. Lycopene and kryptoxanthin occurred in some highly coloured butters.

H. D.

**Adsorption of grass and butter carotenes on alumina.**—See this vol., 155.

**Carbon dioxide content and combining power and  $p_H$  of cervical lymph.** J. W. HEIM and O. C. LEIGH (Amer. J. Physiol., 1935, 112, 699—703).—The CO<sub>2</sub> dissociation curve of the cervical lymph of the dog is logarithmic. For a given CO<sub>2</sub> tension the combining power of the lymph is slightly > that of plasma. The average difference between the CO<sub>2</sub> contents of lymph saturated at 30 and 60 mm. of CO<sub>2</sub> tension is < the corresponding difference for separated plasma. The lymph contains about 58.8 vols. of CO<sub>2</sub> per 100 c.c. and its  $p_H$  is about 7.41 (plasma 7.34).

R.

**Substance in human seminal fluid affecting uterine muscle.** J. R. COCKRILL, E. G. MILLER, jun., and R. KURZROK (Amer. J. Physiol., 1935,

112, 579—580).—Human semen contains acetylcholine or some similar substance that in large amounts causes contraction, and is probably also responsible for the normal relaxation, of uterine muscle.

R. N. C.

**Identification of sperm in medico-legal investigations.** V. PRÉREZ (Crónica med. Valencia, 1934, 38, No. 810).—Solutions of  $\text{AuI}_3$  give characteristic crystals with dil. sperm.

CH. ABS. (e)

**Effect of intravenous injection of sucrose and glucose on the reducing power of cerebrospinal fluid, before and after hydrolysis.** M. I. GREGERSEN and L. WRIGHT (Amer. J. Physiol., 1935, 112, 97—108).—The average glucose (I) concn. of the spinal fluids of normal dogs is 77.5 mg. per 100 c.c. No hydrolysable reducing material is present; the apparent increase in reducing power on acid hydrolysis can be imitated in known (I) solutions by addition of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , or neutralised  $\text{HCl}$ . Injection of (I) causes an increase in cerebrospinal fluid-(I), but sucrose (II) does not increase hydrolysable reducing material, indicating that (I), but not (II), passes the blood-spinal fluid barrier. Spectrophotometric analysis is recommended in (I) determination by Folin's micro-method.

R. N. C.

**Use of hypertonic sucrose solutions intravenously to reduce cerebrospinal fluid pressure without a secondary rise.** L. T. BULLOCK, M. I. GREGERSEN, and R. KINNEY (Amer. J. Physiol., 1935, 112, 82—96).—Hypertonic glucose or  $\text{NaCl}$  solution reduces cerebrospinal fluid pressure in the dog, but the fall is followed by a secondary rise to vals. > the initial pressure. Sucrose causes the reduction without the secondary rise.

R. N. C.

**Calcium excretion by the pancreas.** G. ÅGREN (Biochem. Z., 1935, 281, 358—362).—The  $[\text{Ca}]$  in pancreatic juice is dependent on the rate of secretion and is always > that in blood. The serum- $\text{Ca}$  curves after injection of 5—10 mg. of  $\text{CaCl}_2$  per kg. body-wt. are very different for cats before and after injection of secretin. The difference may be utilised as a test for pancreatic function.

P. W. C.

**Excretion of uric acid and urea by the pancreas and the liver under the action of secretin.** G. ÅGREN (Biochem. Z., 1935, 281, 363—366).—The uric acid and residual N contents of pancreatic juice and of bile varied from the blood concn. down to 1/15 this amount. Intravenous injection of uric acid and urea, in amounts sufficient to increase the blood concn. considerably, led to a considerable increase also in the concns. of these substances in the pancreatic juice and in bile.

P. W. C.

**Stable histochemical reaction for detection of bilirubin.** J. STEIN (Compt. rend. Soc. Biol., 1935, 120, 1136—1138).—Bilirubin in fixed sections of tissue is coloured green by I, no other oxidiser showing this reaction except  $\text{FeCl}_3$ , with which it is very feeble.

R. N. C.

**Pyrroporphyrin from ox bile.**—See this vol., 213.

**Determination of the chloride index.** A. E. LEWIN and O. B. MAKAREVIĆ (Arch. Verdauungskr., 1935, 57, 263—268).—The chloride index of a gastric juice is defined as neutral  $\text{Cl} \times 100 / \text{total Cl}$ . Hist-

amine,  $\text{EtOH}$ , or any  $\text{Cl}'$ -free test meal may be used to promote the flow of juice. The  $\text{HCl}$  of the juice and the total  $\text{Cl}'$  are determined by titration with  $\text{NaOH}$  and  $\text{AgNO}_3$ , respectively, neutral  $\text{Cl}'$  being obtained by difference. Bile-stained juice must not be used. The index remained relatively const. in the same person, in spite of wide fluctuations in  $\text{HCl}$  and total  $\text{Cl}'$ .

NUTR. ABS. (m)

**Origin and significance of neutral chloride in the secretions of the stomach and duodenum.** C. M. WILHELMJ, L. C. HENRICH, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1935, 112, 15—20).—Neutral  $\text{Cl}'$  in the non-acid secretions of the stomach and the mixed duodenal secretions are approx. the same. When 0.1N- $\text{HCl}$  is added to the secretions, only about one third of the neutral  $\text{Cl}'$  represents neutralised  $\text{HCl}$ .

R. N. C.

**Action of gastric and duodenal juice and of bile on ascorbic acid.** A. CARTENI and A. MORELLI (Boll. Soc. ital. Biol. sperim., 1935, 10, 327—329).—Ascorbic acid is destroyed by gastric and duodenal juice and by bile, the % reduction generally  $\propto p_{\text{H}}$ .

R. N. C.

**Acidic components of wool grease.**—See B., 1936, 66.

**Formation of wax within the organism of bees.** G. BUCHNER (Fettchem. Umschau, 1935, 42, 208—209).—Shortly before the wax is discharged by the bees (i.e., during its formation) the temp. of the hive rises markedly, indicating an energetic oxidation due to the  $\text{O}_2$  derived from the conversion of sugar into wax. Possible reactions are discussed.

E. L.

**Urinary modifications in the dog and rabbit following vagotomy.** E. TRIA and A. NICOLAZZO (Boll. Soc. ital. Biol. sperim., 1935, 10, 329—331).—Vagotomy induces aciduria in the rabbit and alkaluria in the dog, irrespective of the normal effect of the diet on urinary  $p_{\text{H}}$ .

R. N. C.

**Physico-chemical characters of the urine of rats on a diet of fibrin and kept in glass cages.** F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 292—294).—The urine shows decreases in  $\eta$ ,  $\sigma$ , and f.p., and increases in  $\kappa$  and the f.p./ $\kappa$  ratio, which are > those obtained when the animals are kept in metal cages. The fluorescence spectrum and spectrophotometric curve are normal.

R. N. C.

**Elimination of organic acids in urine during childhood and relation of acids to basal metabolism in adults.** S. A. SIVÉ (Svenska Lak. sällsk. Hand., Stockholm, 1934, 60, 157).—Elimination of org. acids, both in the total amount and in the  $\text{Et}_2\text{O}$ -sol. fraction, often varies considerably from case to case and in the same person from day to day. In premature and weak infants, in rickets, and in nutritional disturbances the vals. are high. In diabetes establishment of the org. acids in the urine presents an improved method for determining acidosis. In children elimination of org. acids seems to diminish with age and daily variations become less. There is a relatively const. ratio of 3 : 2 between the org. acids eliminated during the day and during the night. In adults there is no relation between basal metabolism and org. acid elimination.

NUTR. ABS. (m)

**Excretion of oxalic acid by guinea-pigs.** S. BORGSTROM (Biochem. Z., 1935, 281, 377—382).— $\text{H}_2\text{C}_2\text{O}_4$  is excreted even when the diet is devoid of it.  $\text{H}_2\text{C}_2\text{O}_4$  given by mouth is to a large extent decomposed in the body, but injected subcutaneously is mainly excreted in the urine. P. W. C.

**Butyric acid content of normal urine.** L. KLINC (Bull. Soc. Chim. biol., 1935, 17, 1540—1545).—In normal urine 4—8 mg. of  $\text{Pr}^n\text{CO}_2\text{H}$  (determined by oxidation to  $\text{COMe}_2$  followed by iodometric titration) are excreted daily.  $\text{Pr}^n\text{CO}_2\text{H}$  is absent. A. L.

**Water and chloride excretion of decerebrate cats.** M. SUMWALT, W. H. ERB, and H. C. BAZETT (Amer. J. Physiol., 1935, 112, 386—396).

R. N. C.

**Bromine index of the urine as an indication of the normal physiological state.** N. BEZSSONOFF, A. VALLETTE, and R. SACREZ (Bull. Soc. Chim. biol., 1935, 17, 1573—1598).—The Br index of urine (mg. of Br taken up by 1 ml.) is not dependent on the concn. of mineral or org. substances, but on the presence of phenolic, indole, and glyoxaline derivatives, i.e. on the protein metabolism. The index increases with age, and reflects pathological conditions. Fever and rickets increases, and administration of vitamin-C decreases, the val. A. L.

**Renal excretion of urea.** R. DOMINGUEZ (Amer. J. Physiol., 1935, 112, 529—544).—Theoretical.

R. N. C.

**Application to urine of Tollens' naphthoresorcinol test for conjugated glycuronides.** H. B. SALT (Biochem. J., 1935, 29, 2705—2709).—An improved technique is described. It is sensitive to 0.5 mg. of glycuronic acid in 5 c.c. of urine. Interfering substances are first pptd. by  $\text{Pb}(\text{OAc})_2$ , and then the glycuronide by basic Pb acetate; the test is done on this ppt. Using aspirin as a glycurogenic drug, a method of testing the detoxicatory efficiency of the liver is described. J. N. A.

**Factors affecting appearance and duration of glycosuria.** C. S. ROBINSON, R. C. DERIVAUX, and B. HEWELL (Amer. J. Med. Sci., 1935, 189, 795—803).—In female patients without disturbance of carbohydrate metabolism and with normal fasting blood-sugar (I), after intravenous injection of 10 g. of glucose the peak (I) vals. were 0.131—0.304%. When urine excretion was small in vol., glycosuria persisted longer. The (I) level at which glycosuria ceased was usually < that at which it commenced.

NUTR. ABS. (m)

**Excretion of vitamin-C in human urine.** B. AHMAD (Biochem. J., 1936, 30, 11—15).—The reducing capacity of urine excreted under diets with (a) low vitamin-C (I), (b) low protein, (c) high protein, and (d) purine-free high protein contents has been determined. Meat diets favour excretion of (I), which possibly forms most of the reducing substance of urine. J. N. A.

**Detection of small quantities of gonadotropic hormone in the urine of normal subjects.** O. THOMSEN and K. PEDERSEN-BJERGAARD (Compt. rend. Soc. Biol., 1935, 120, 1143—1147).

R. N. C.

**Tungstic acid precipitation method for extraction of oestrogenic substance from urine.** S. C. FREED, I. A. MIRSKY, and S. SOSKIN (J. Biol. Chem., 1935, 112, 143—147).—Oestrogenic substances are extracted, without loss of activity, by treating urine with  $\text{Na}_2\text{WO}_4$ , acidifying with  $\text{H}_2\text{SO}_4$ , and extracting the ppt. with  $\text{EtOH-Et}_2\text{O}$ . J. N. A.

**Determination of urinary oestrin.** G. VAN S. SMITH and O. W. SMITH (Amer. J. Physiol., 1935, 112, 340—350).—Oestrin (I) cannot be recovered completely from untreated pregnancy urines by  $\text{CHCl}_3$ , olive oil,  $\text{EtOAc}$ , or  $\text{C}_6\text{H}_6$ ; the largest quantity is extracted by  $\text{C}_6\text{H}_6$ . In some cases  $\text{C}_6\text{H}_6$  extracts more (I) than can be demonstrated in the untreated urines. Pregnancy urines boiled with HCl increase in their (I) content. Total (I) after boiling with HCl can be extracted completely by  $\text{C}_6\text{H}_6$ ; none is destroyed by boiling with 15% HCl. Pure "theelin" is fixed in the alkaline solution in which it is supplied, and is less potent when first diluted than if kept for 10 days; acid treatment does not increase the potency further. The action of the HCl is therefore considered to be a liberation of "bound" (I). There is no apparent relation between the "free" (I) content of the urine and its  $p_H$ . The "free" (I) of the urine of a pregnant woman varies widely daily, but total (I) increases uniformly. The procedure adopted for the assay of (I) is outlined.

R. N. C.

**The Donaggio reaction. [Protective colloid in pathological urine.]** G. SOILLAZZO and V. CORTESE (Boll. Chim. farm., 1935, 74, 625—628, 631—634, 637).—The property of urine of febrile patients of inhibiting pptn. of a lake from thionine by  $(\text{NH}_4)_2\text{MoO}_4$  is due to a protective colloid, and can be imitated by gum arabic, and counteracted by addition of mannitol. The protective action is destroyed by pepsin or by dil.  $\text{AcOH}$ . Properties of the colloidal substance are discussed. E. W. W.

**Butyric acid content of faeces.** K. KLINC (Bull. Soc. Chim. biol., 1935, 17, 1546—1548).—The meconium does not contain  $\text{PrCO}_2\text{H}$ , which, however, is present in the faeces of suckling infants for a short time (until lactic acid fermentation predominates). In the adult, 40—130 mg. of  $\text{PrCO}_2\text{H}$  are present per 100 g. of faeces. A. L.

**Secreted nitrogen in the faeces and dietary protein utilisation.** W. HEUPKE and F. BELZ (Arch. Hyg. Bakteriol., 1935, 114, 56—62).—In man ingestion of various N-poor foodstuffs for 3—4-day periods indicated that faecal N (which was in all cases > the intake) tended to vary with the dry wt. of the faeces, suggesting that part of this N must be derived from intestinal secretion and that the utilisability of a foodstuff can be assessed only if the amount of the secreted N is known. About 1.5—2 g. of N are secreted per day for every 50 g. of dry wt. of faeces.

NUTR. ABS. (m)

**Variation in water content of the faecal material along the colon.** F. R. STEGGERDA (Amer. J. Physiol., 1935, 112, 559—564).

R. N. C.

**Disease of metabolism in sheep.** J. G. WRIGHT (Vet. Rec., 1935, 15, 1253—1255).

R. N. C.

**Uric acid excretion following administration of creatinine in man under normal and pathological conditions with special reference to renal insufficiency.** R. GARDSTAM (*Acta med. Scand.*, 1935, Suppl. 67, 296 pp.).—In toxic and orthostatic albuminuria and in the residual condition which follows acute nephritis, in essential hypertonia and gout, and to a certain extent in congestive cardiac conditions with albuminuria the ratios *concn. index of uric acid (I) : concn. index of creatinine (II)* and *(I) content of urine : concn. index of (II)* were within normal limits. Raised vals. were found in acute and chronic nephritis, pyelonephritis, and advancing arteriosclerosis of renal origin. NUTR. ABS. (m)

**Role of the pituitary in experimental chronic adrenal insufficiency.** A. GROLLMAN and W. M. FIROR (*Amer. J. Physiol.*, 1935, 112, 310—319).

R. N. C.

**Correlation between adrenals and thyroid.** I. ABELIN (*Z. ges. exp. Med.*, 1934, 94, 353—358; *Chem. Zentr.*, 1935, i, 2690).—Adrenalectomy and hyperfunction of the thyroid result in a similar series of effects. In both cases glycogen (I) falls in muscle and disappears from the liver, which undergoes fatty degeneration. A diet known to maintain liver-(I) in hyperthyroid rats has the same effect in adrenalectomised animals; di-iodotyrosine also maintains liver-(I). R. N. C.

**Gastric secretion in anaemia.** J. W. OGILVIE (*Arch. Dis. Childhood*, 1935, 10, 143—148).—A marked diminution in the secretion of free HCl and total acidity was found in 13 out of 34 anæmic children, but there was no significant variation in the other constituents of the juice. No type of anaemia showed any const. change in secretion of free acid. NUTR. ABS. (m)

**Effect of acute anoxaemia on hunger, digestive contractions, and the secretion of hydrochloric acid in man.** F. A. HELLEBRANDT, E. BROGDON, and S. L. HOOPES (*Amer. J. Physiol.*, 1935, 112, 451—460).—Acute anoxaemia of the pre-coma type has relatively little inhibitory effect on gastric motility or HCl secretion. R. N. C.

**Human anthrax in Barotseland treated with novarsenobenzene.** F. W. GILBERT (*Lancet*, 1935, 229, 1283—1285). L. S. T.

**Alimentary azotæmia in rats.** F. FUCHS (*Wien. klin. Woch.*, 1935, 48, 582—584).—In rats, a diet of green food with  $\text{NaHCO}_3$  in the drinking  $\text{H}_2\text{O}$  resulted in sickness and death in >14 days (high blood-N, very alkaline urine). NUTR. ABS. (m)

**Hyperglycæmia and glycosuria associated with disease of the biliary tract.** H. LANDE and H. POLLACK (*Arch. Int. Med.*, 1935, 56, 1097—1108).—A direct correlation was obtained between the disturbance of carbohydrate metabolism and the impairment of hepatic function. Disease of the gall bladder is accompanied by diabetes, which disappears on normal functioning of the liver and adequate biliary drainage. H. G. R.

**Cancer as a problem in metabolism.** H. H. BEARD (*Arch. Int. Med.*, 1935, 56, 1143—1170).—A review. H. G. R.

**Blood modifications in cancer.** J. LOISELEUR (*Compt. rend. Soc. Biol.*, 1935, 120, 1038—1042).—Blood- $\text{NH}_2$ -acids and -residual N in patients with cancerous lesions are increased, whilst urea falls. The corpuscle-/plasma-Cl ratio is lowered, and is inversely  $\propto$  total Cl. The alkaline reserve approaches the lower limit of its normal vals., whilst plasma- $\text{pH}$  approaches the upper limit. During radiological treatment residual N is increased, whilst urea, Cl, hydræmia, and alkalosis fall. R. N. C.

**Induction of cancer by cracked mineral oils.** C. C. TWORT and J. M. TWORT (*Lancet*, 1935, 229, 1226—1228).—Mice exposed to fumes from a mineral oil cracked on a heated plate showed no definite increase in the incidence of lung tumours, but the polynuclear count is increased. Heavier Diesel oils, but not light-grade oils, are carcinogenic for the skins of mice. Lubricating oils recovered from the sump of motor cars are more carcinogenic than the original oils. The carcinogenicity of crude shale oils decreases as the cracking temp. is lowered, but oil cracked at  $385^\circ$  is still carcinogenic. L. S. T.

**Growth-promoting and growth-inhibiting substances of normal organs.** J. MAISIN and Y. POURBAIX (*Amer. J. Cancer*, 1935, 24, 357—385).—Addition of liver, pancreas, and intestinal mucosa to the diet of tarred mice promoted growth of tar tumours. Brain, thymus, bone marrow, dried gastric mucosa, and lymph-tissue inhibited growth. The growth-promoting substances are mostly  $\text{H}_2\text{O}$ -sol. and relatively insol. in  $\text{Et}_2\text{O}$ , whilst the growth-inhibiting substances are sol. in  $\text{Et}_2\text{O}$  and relatively insol. in  $\text{COMe}_2$ . NUTR. ABS. (m)

**Anterior pituitary hormones and formation of experimental tar carcinoma.** J. ZELDENRUST (*Acta Brev. Neerl. Physiol.*, 1934, 4, 182—184).—Prolan stimulates growth of tumours produced in mice by tar, but the Evans alkaline pituitary extract prevents tumour formation. R. N. C.

**Phosphoric esters in normal and malignant tissues.** E. L. OUTHOUSE (*Trans. Roy. Soc. Canada*, 1935, [iii], 29, V, 77—84).—From lymphosarcoma was isolated  $\text{C}_6\text{H}_{13}\text{O}_8\text{NPBa}(\text{?})$ ,  $[\alpha]_{\text{D}}^{25} +2.86^\circ$ , probably the Ba salt of an aminohexahydric alcohol phosphoric acid (or possibly hexosaminephosphoric acid). From tumours other than lymphosarcomata, ethanolaminephosphoric acid has been isolated. Both these acids form insol. Pb salts. Phosphoric esters forming sol. Pb salts are present to the greatest extent in tumour tissue and least in skeletal muscle. Hexose phosphates are absent from the acid-sol. phosphates of tumour. W. O. K.

**Copper metabolism and experimental rat cancer.** S. SUMEGI (*Frankfurter Z. Path.*, 1935, 48, 35—42).—During implantation of Ehrlich-Putnoky rat cancer the Cu content of the tumour formed rises steeply until the 10th day and remains at the same level until death occurs. A disturbance of assimilation takes place in which the Cu content of



the liver rises from 34.2 to 40.8 mg. per 100 g., whilst that of the stomach falls from 38.9 to 23.2 mg. Withdrawal of Cu from normal function is advanced as a cause of cancer anæmia. When loss of Cu was compensated by injections of  $\text{CuSO}_4$  the Cu content of the stomach of tumour rats was raised to 59% > that of controls, and 11.3% < that of Cu-treated non-implanted rats. The treatment decreased the loss of red blood corpuscles and hæmoglobin and increased the no. of reticulocytes in tumour animals.

NUTR. ABS. (m)

**Determination of blood-oxalic acid in cancer.** E. AUJALEV, F. H. COLOMBIES, and A. MONTARIOL (Compt. rend. Soc. Biol., 1935, 120, 954—955).— $\text{H}_2\text{C}_2\text{O}_4$  is determined by the method of Maugeri. In cases of hyperoxalæmia, blood-sugar and cholesterol are generally increased, but not  $\propto \text{H}_2\text{C}_2\text{O}_4$ ; urea remains normal.

R. N. C.

**Intimate mechanism of diabetes from superabundance.** M. WIERZUCHOWSKI, Z. BORKOWSKI, and A. GOSTYNSKA (Compt. rend. Soc. Biol., 1935, 120, 1133—1135).—Absorption by the organs from the blood-stream of continuously-injected glucose in the dog increases with the rate of injection up to the extreme limit of tolerance.

R. N. C.

**Effect of total thyroidectomy on experimental diabetes insipidus in dogs.** W. MAHONEY and D. SHEEHAN (Amer. J. Physiol., 1935, 112, 250—255).

R. N. C.

**Calorigenic action of fat and carbohydrate in pancreatic diabetes.** G. C. RING (Amer. J. Physiol., 1935, 112, 124—129).

R. N. C.

**Effect of equivalent amounts of glucose and starch on glycæmia and glycosuria in diabetics.** M. WISHNOFSKY and A. P. KANE (Amer. J. Med. Sci., 1935, 189, 545—550).—No significant difference was observed.

NUTR. ABS. (m)

**Lipase content of the normal liver and the liver in fatty degeneration.** N. FIESSINGER and A. GAJDOS (Compt. rend. Soc. Biol., 1935, 120, 666—668).—The lipase content of the human liver decreases considerably in fatty degeneration.

R. N. C.

**Pathogenic mechanism of the green diarrhoea of pigeons in avitaminosis.** G. RENOSTO (Boll. Soc. ital. Biol. sperim., 1935, 10, 297—299).—The capacity of strains of *B. coli*, isolated from the intestines of pigeons in avitaminosis-B, to ferment carbohydrates, liberate  $\text{H}_2\text{S}$ , and cause hæmolysis is equal to that of strains from normal pigeons.

R. N. C.

**Structure of the striated muscular fibres in normal and pathological conditions. I. Lipidosis of the striated muscular fibres and localisation of the lipin material in some toxic actions.** A. BASILE (Boll. Soc. ital. Biol. sperim., 1935, 10, 302—304).—Intoxication of guinea-pigs by diphtheria toxin, *B. typhosus*, P, or As provokes a rise of lipins in the striated muscular fibres.

R. N. C.

**Influence of progressive toxæmic liver damage on the glucose tolerance curve.** S. SOSKIN and A. MIRSKY (Amer. J. Physiol., 1935, 112, 649—

656).—The curves obtained in dogs after administration of diphtheria toxin do not show the normal increase in tolerance. The cycle of events following the onset of toxæmia depends on the amount of sugar used; the curve becomes alternately normal and "diabetic" in type.

R. N. C.

**Infantile allergic eczema. II. Serum-lipins; saturation of the fatty acids.** H. K. FABER and D. B. ROBERTS (J. Paediat., 1935, 6, 490—493).—In eczema, serum-fatty acids tend to be less unsaturated than normally.

NUTR. ABS. (m)

**Hyperoxalæmia in acute eczema and dermatitis.** S. SUZUKI (Japan. J. Med. Sci., 1935, 11, 3, 95—97).—A slight hyperoxalæmia occurs.

F. O. H.

**Treatment of hæmorrhagic disorders with vitamin-C.** H. ENGELKES (Lancet, 1935, 229, 1285—1287).—Capillary hæmorrhages are successfully treated.

L. S. T.

**Pathological physiology of infarct. III. Ammonia and lactic acid during necrosis and autolysis.** G. BORGER, H. BAYERLE, T. MAYR, and E. PETERS (Z. physiol. Chem., 1935, 237, 113—120; cf. A., 1935, 1269).—The  $\text{NH}_3$  content of normal and infarct kidney remains fairly const. for 50 hr., whilst that of autolysing kidney steadily increases. The lactic acid levels vary, both that of autolysing and infarct kidney being > normal for the first 2 hr., after which (2—96 hr.) the infarct content alone decreases to normal levels.

F. O. H.

**Non-diabetic ketosis with acidosis.** D. C. DARROW and M. K. CARY (J. Paediat., 1935, 6, 676—694).

NUTR. ABS.

**Ketosis in cows.** G. F. BODDIE (Vet. Rec., 1935, 15, 1539—1546).—Blood-sugar in a normal cow is not increased after parturition; it falls in severe cases of post-parturient dyspepsia. Blood-ketones are slightly increased after parturition; in severe post-parturient dyspepsia there is a considerable increase due to formation of  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ , which is low in normal animals.

R. N. C.

**Flocculation of sera in distilled water and Henry reaction.** R. O. PRUDHOMME (Compt. rend. Soc. Biol., 1935, 120, 944—946).—Malaria sera contain a substance that is pptd. by  $\text{H}_2\text{O}$ ; it is present in normal serum in smaller quantities, demonstrable by melanin.

R. N. C.

**Pathology of infantile marasmus.** Z. VON GUTACSY (Arch. Kinderheilk., 1935, 105, 43—53).

NUTR. ABS.

**Blood- and cerebrospinal fluid-sugar. Permeability to sugar of the brain-membranes in meningitis.** A. V. TSHERKASSOV and E. E. JOLKVER (Rev. franc. Pediat., 1935, 11, 350—364).

NUTR. ABS.

**Renal elimination of vitamin-C in experimental nephritis.** F. PINOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 314—317).—Vitamin-C elimination by the kidneys is increased by intoxication with  $\text{UO}_2(\text{OAc})_2$  or  $\text{HgCl}_2$ , the increase from  $\text{HgCl}_2$  persisting longer.

N. C.

**Uric acid crystals in the blood plasma of a fowl suffering from pyo-nephrosis consequent**

on vitamin-A deficiency. G. SANKARAN (Current Sci., 1935, 4, 314).—A fowl fed during 12 weeks on a diet deficient in vitamin-A had 375 mg. of uric acid per 100 c.c. of plasma (control 8.34 mg.).

F. R. G.

Cerebrospinal fluid in periodic paralysis. G. GUILLAIN, L. ROQUES, and C. RIBADEAU-DUMAS (Compt. rend. Soc. Biol., 1935, 120, 841—842).—The cerebrospinal fluid shows hyperalbuminosis, a slightly positive Pandy reaction, and a broadening of the colloidal benzoin pptn. curve.

R. N. C.

Specific value of crude iron compounds in the treatment of "pine" in cattle and sheep. J. BROWN (Vet. Rec., 1935, 15, 1233—1234).

R. N. C.

Rheumatic disease (osteo-arthritis and allied conditions) in the horse. W. M. MITCHELL (Vet. Rec., 1935, 15, 1501—1507).—A lecture. Vitamin deficiency is the probable cause.

R. N. C.

Rickets due to strontium. (A) Nature of injury to calcifying mechanism. (B) Phosphatase activity and calcification. A. E. SOBEL, J. COHEN, and B. KRAMER (Biochem. J., 1935, 29, 2640—2645, 2646—2650).—(A) With Sr rickets in rats, a marked diminution occurs in *in-vitro* calcifying power of the bones, an injury removed both *in vivo* and *in vitro* by bathing the bone cells in Sr-free fluids. Sr<sup>++</sup> directly inhibits calcification, apparently combining with a factor involved in this process.

(b) No significant difference occurs in the phosphatase activities of bones from rats with Sr- or Ca-rickets, whilst Sr<sup>++</sup> (up to 0.08%) does not influence the hydrolysis by bone-phosphatase preps.; hence the loss of *in-vitro* calcifying power due to Sr<sup>++</sup> is not related to the phosphatase activity.

F. O. H.

Activity of *p*-aminophenylsulphonamide on experimental streptococcal infections in the mouse and rabbit. J. TREFOUEL, (MME.) J. TREFOUEL, F. NITTI, and D. BOVET (Compt. rend. Soc. Biol., 1935, 120, 756—758).—Resistance to hæmolytic streptococci is increased.

R. N. C.

Bordet-Wassermann reaction: inhibiting power of the fraction of the serum precipitated by hydrochloric acid. C. AUGUSTE (Compt. rend. Soc. Biol., 1935, 120, 885—886).—Complement-fixation by syphilitic sera is increased considerably by pptn. with HCl; it is reduced to normal by the return of the pptd. fraction.

R. N. C.

Relation of diet and serum-calcium to tetany in the parathyroidectomised rat. M. M. HOSKINS (Endocrinol., 1935, 19, 453—460).—Rats are protected from tetany by diets with high Ca/P ratios, which keep serum-Ca (I) high. In cases where (I) is low, tetany cannot be correlated closely with the blood-Ca level, and apparently depends on some endogenous factor.

R. N. C.

Thrombo-angiitis obliterans (Buerger) X. Reduction in blood volume following bilateral oophorectomy. M. FRIEDLANDER, N. LASKEY, and S. SILBERT (Endocrinol., 1935, 19, 461—465).—Cholesterol, fibrinogen, and  $\gamma$  are increased.

R. N. C.

Metabolism of tonic and non-tonic muscle. H. SCHONFELDER (Arch. exp. Path. Pharm., 1935,

180, 24—27).—Under anaerobic conditions the lactic acid (I) produced by finely minced muscle from newborn rabbits is increased by 28% by addition of glucose (II), but by only 5% by glycogen (III). With mature muscle, (II) increases (I) by only 7%, whilst (III) increases it by 116%; if the same muscles have been paralysed by section of the nerves 3—4 weeks before, the yield of (I) is increased by 30% by (II), and only by 1% by (III).

J. N. A.

Role of tissue metabolism in the radio-sensitivity of the thymus of the guinea-pig. M. CHEVRE-MONT (Arch. Biol., 1935, 46, 507—598).

Chemical mediation of sympathetic vasodilator nerve impulses. A. ROSENBLUETH and W. B. CANNON (Amer. J. Physiol., 1935, 112, 33—40).

R. N. C.

Water metabolism in normal and hypophysectomised frogs. M. E. JONES and F. R. STEGGERDA (Amer. J. Physiol., 1935, 112, 397—400).

R. N. C.

Colloid model for illustration of biological processes. I. Triple salt effect in the germination of crustacean eggs and with phosphatides. H. G. B. DE JONG, J. VAN DER MEER, and L. G. M. B. BECKING (Kolloid-Beih., 1935, 42, 384—407).—The concn. region of the system KCl-MgCl<sub>2</sub>-NaCl-H<sub>2</sub>O in which the germination of crustacean eggs is possible has been determined. Analogous regularities have been found in the behaviour of a desensitised, EtOH-insol. plant phosphatide as regards stability and reversal of change in these solutions. The biological significance of the results is discussed.

E. S. H.

Role of phosphatides in nutrition. A. K. PICKAT, O. J. KURTSINA, and N. S. ZENIN (Problems of Nutrition, Moscow, 1935, 4, No. 2, 30—37).—Small doses of lecithin (I) had no beneficial effect on the growth of rats receiving also all vitamins. (I) is probably not essential to the diet.

NUTR. ABS. (m)

Nutrient value of cow's milk and of modified milk for various mammals. R. JACQUOT and H. TRIMBACH (Bull. Soc. Sci. aliment., 1934, 22, 134—156; Chem. Zentr., 1935, i, 2553—2554).—Varying levels of utilisation of milk by animals receiving an all-milk diet are discussed. For smaller and more rapidly growing animals cow's milk is deficient in Ca, P, Fe, and lactalbumin (lysine). Lactose is relatively poorly utilised even by calves. Isoenergetic replacement of milk-fat by starch improves growth and increases N retention.

Digestibility of foodstuffs. H. STEUDEL (Z. ges. exp. Med., 1935, 95, 580—588; Chem. Zentr., 1935, i, 2553).—A discussion.

A. G. P.

Influence of rations low in minerals on the composition of the blood and milk of cows, and on the blood of their progeny. J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1935, 4, 93—165).—The only mineral element, a shortage of which in the ration was reflected in the composition of the blood of the heifers, was P, the blood-inorg. P decreasing from 7.2 to 3.4 mg. per 100 ml. The average composition of the blood-minerals of all the cows except those on low P intake was: Ca 8.4, P

Mg 2.7, K 58.7, Na 302, Cl 314 mg. per 100 ml. Slight depressions occurred in these levels during lactation. The variations in the composition of the rations had no effect on the mineral composition of the milk. In the calves, the blood-Ca was > that of the dam during the first month, and the inorg. P higher during the first 3 months. The K, which was very high in calf's blood at birth, declined rapidly and steadily, reaching the adult level at 10 weeks, whereas for Na the reverse was true.

NUTR. ABS. (m)

Effects of a diet poor in salts on the growth and composition of the incisors of the rat. M. F. CLARKE and A. H. SMITH (Amer. J. Physiol., 1935, 112, 286—293). R. N. C.

Relation between the motor and secretory functions of the human fasting stomach. F. A. HELLEBRANDT (Amer. J. Physiol., 1935, 112, 162—165). R. N. C.

Reserve store of hæmoglobin-producing substances in growing dogs as influenced by diet. F. S. ROBSCHT-ROBBINS and G. H. WHIPPLE (Amer. J. Physiol., 1935, 112, 27—32).—Growing dogs can store hæmoglobin-producing substances on a diet of liver or ox skeletal muscle. R. N. C.

Phytin in human nutrition. R. A. McCANCE and E. M. WIDDOWSON (Biochem. J., 1935, 29, 2694—2699).—Small amounts of phytin (I) can be determined by extraction with HCl, pptn. as the  $\text{Fe}^{\text{III}}$  salt, and determination of the P in the latter after  $\text{H}_2\text{SO}_4\text{-HClO}_4$  incineration. The (I) content of 64 foodstuffs has been determined, in many cases 40—50% of the total P being in the form of (I). Green leaf and stem vegetables and the pulp of fresh and dried fruits contain no (I). When (I) is ingested, 40—60% is excreted unchanged in the faeces. (I)-P constitutes < 5% of the total P of the average diet in this country. J. N. A.

Permeability of frog capillaries to protein. R. E. CONKLIN (Amer. J. Physiol., 1935, 112, 401—411).—The skin capillaries are highly permeable to protein, but normally do not admit protein mols. from the lymph spaces. R. N. C.

Deaminating and urea-forming power of the liver in normal pregnancy; intermediary metabolism. L. HEROLD (Arch. Gynakol., 1935, 159, 166—171).—Compared with normal women, normal pregnant women exhibit a delay in the decline of the free  $\text{NH}_2\text{-N}$  of the blood and a delayed rise in the bound  $\text{NH}_2\text{-N}$  following intravenous injection of 1 g. of glycine. NUTR. ABS. (m)

Effect of restricted diet on deamination in the organism. I. Effect of high-carbohydrate diet. AGNOLI and L. UNTERSTEINER (Arch. Sci. biol., 1934, 20, 474).—Deaminative power is reduced. NUTR. ABS. (m)

Nitrogen metabolism in protein starvation. OUBOT (Compt. rend., 1935, 201, 1044—1046).—In N<sup>o</sup> starvation the relative amount of the various actions excreted is a function of the total N excreted per kg. body-wt. per 24 hr. (i). Thus, as i increases, the proportion of urea also increases at

first rapidly, then more slowly, becoming const. at about 80% of the total N, when i is 400 mg. Conversely the amount of undetermined N falls with increasing i and becomes insignificant at the above val. of i. The nature of the N products excreted is thus determined primarily by the intensity of the oxidation process in the tissues. W. O. K.

Tyrosine metabolism of *Bombyx mori* (silkworm). J. HOLTZMANN (Biochem. J., 1936, 30, 28—30).—There is no need to assume synthesis of tyrosine (I) by the grubs, as the (I) intake in the ingested mulberry leaves exceeds the amount of (I) in the cocoon and contained grub. J. N. A.

Effect of an alkaline reaction and of the physico-chemical environment on the oxidation of uric acid. J. SULA (Compt. rend. Soc. Biol., 1935, 120, 911—915).—Uric acid (I) is oxidised by  $\text{O}_2$  in pure solutions at  $p_{\text{H}} > 7.6$ , the extent of oxidation increasing with  $p_{\text{H}}$ . Oxidation takes place in human serum at  $p_{\text{H}} > 7.6$  only if the (I) concn. is > 3 mg. per litre; otherwise it begins at  $p_{\text{H}}$  8.0. The inhibition is not due to the sp. proteins, since serum-globulins and -albumins and ovalbumin in pure solutions permit oxidation at  $p_{\text{H}}$  7.6. R. N. C.

Absorption of gluten peptone and of glutamic acid introduced into a Vella intestinal loop. G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 173—175).—The rate of absorption of gluten peptone in the dog is < that of Witte's peptone, but > that of glutamic acid. R. N. C.

Feeding experiments with mixtures of highly purified amino-acids. VII. Dual nature of the "unknown growth essential." M. WOMACK and W. C. ROSE. VIII. Isolation and identification of an essential amino-acid. R. H. MCCOY, C. E. MEYER, and W. C. ROSE (J. Biol. Chem., 1935, 112, 275—282, 283—302; cf. A., 1935, 113).—VII. The unknown substance essential for growth is a mixture of isoleucine (I) and a substance (II) less sol. in  $\text{Bu}^{\text{O}}\text{H}$  than is (I).

VIII. The isolation of pure (II) from blood-fibrin is described. (II) is  $\alpha$ -amino- $\beta$ -hydroxybutyric acid, m.p. 255—257° (decomp.) (N-benzoate, m.p. 151°, picrate m.p. 139.5—141°), which with red P and HI gives  $d$ - $\alpha$ -aminobutyric acid. An otherwise adequate diet must contain < 0.6% of (II) for max. growth. Bromination of methoxyethylmalonic acid (Palomaa *et al.*, A., 1931, 710) followed by heating at 150° gives  $\alpha$ -bromo- $\gamma$ -methoxybutyric acid, b.p. 145—148°/5 mm., which, with conc. aq.  $\text{NH}_3$  gives  $\alpha$ -amino- $\gamma$ -methoxybutyric acid (III), m.p. 224—225° (decomp.). (III) boiled for 3 hr. with 48% HBr gives  $\alpha$ -amino- $\gamma$ -hydroxybutyric acid, which has no growth-promoting effect. Hydroxyglutamic acid and citrulline are not essential constituents of food. W. McC.

Amino-acid metabolism. I. Fate of glycine,  $dl$ - and  $d$ -alanine in the normal animal. J. S. BUTTS, M. S. DUNN, and L. F. HALLMAN (J. Biol. Chem., 1935, 112, 263—274; cf. Wilson *et al.*, A., 1930, 367).—Those  $\text{NH}_2$ -acids, fed to male rats, favour the production of glycogen,  $d$ - being twice as effective as  $dl$ -alanine (I), which is much more effective than is glycine. The ketone-suppressing activities

of the acids are in the same order. Probably the *l*-component of (I) has no effect on glycogen production.

W. McC.

**Model experiment in respiration using croton oil in the presence and absence of carotenoids.** R. RETOVSKY (Bull. Soc. Chim. biol., 1935, 17, 1614—1628).—A study is made of the autoxidation of croton oil in the presence and absence of carotenoids (I). The length of the period of incubation  $\propto$  the intensity of the light, and is shorter in absence of (I). With daylight the course of the autoxidation in absence of (I) eventually follows that in presence of (I).

A. L.

**Behaviour in the body of peat extracts (humic substances) after oral or intravenous administration.** R. SCHMID (Biochem. Z., 1935, 281, 329—332).—Humic substances, orally administered to man, were absorbed to a small extent and led to an increase in the normal urinary excretion of humic substances. 1% aq. solutions injected intravenously into rabbits were lethal but smaller concns. were tolerated.

P. W. C.

**Action of choline and other substances in the prevention and cure of fatty livers.** C. H. BEST and H. J. CHANNON (Biochem. J., 1935, 29, 2651—2658).—The influence of dietary constituents (*e.g.*, protein) on the fat content of the liver and the correlation and significance of available data are discussed (cf. A., 1935, 244, 524, 890).

F. O. H.

**Influence of caseinogen content of diets on the nature of "cholesterol" fatty liver.** A. W. BEESTON, H. J. CHANNON, and H. WILKINSON (Biochem. J., 1935, 29, 2659—2667).—In rats fed on a diet containing 20% of fat, 2% of cholesterol, and only small amounts of choline (I), variations in the protein (II) content cause marked changes in the contents of the various lipins in the resulting fatty livers. Dosage with (I) (80 mg. per day per rat) largely prevents deposition of glycerides, but not that of cholesteryl esters. (II), but not (I), increases liver-phosphatides.

F. O. H.

**Metabolism of polycyclic compounds. I. Production of dihydroxydihydroanthracene from anthracene.** E. BOYLAND and A. A. LEVI (Biochem. J., 1935, 29, 2679—2683).—Rats fed on a diet containing anthracene excrete 1:1:2-dihydroxy-1:2-dihydroanthracene (I),  $C_{14}H_{12}O_2$ , m.p. 160—161°,  $[\alpha]_D^{20}$  —154° in  $COMe_2$ , —100° in dioxan (diacetate,  $C_{18}H_{16}O_4$ , m.p. 149°,  $[\alpha]_D^{20}$  —375.5° in  $C_6H_6$ , —362° in dioxan; dibenzoate,  $C_{28}H_{20}O_4$ , m.p. 138°,  $[\alpha]_D^{20}$  —452°), yielding  $\alpha$ -anthrol on boiling with dil. acid. Hydrogenation of (I) yielded dihydroxytetrahydroanthracene (II), m.p. 149°,  $[\alpha]_D^{20}$  +99° in dioxan (diacetate, m.p. 91°,  $[\alpha]_D^{20}$  —74° in dioxan). Oxidation of (II) gave 3- $\beta$ -carboxyethyl-2-naphthoic acid (III), m.p. 210° (decomp.). On boiling with dil. acid, (II) affords 2-ketotetrahydroanthracene. Rabbits fed on the same diet excreted a *d*-form of (I), m.p. 184°,  $[\alpha]_D^{20}$  +16° in dioxan (diacetate, m.p. 184°,  $[\alpha]_D^{20}$  +309° in dioxan). Hydrogenation yielded a dihydroxytetrahydroanthracene, m.p. 162°,  $[\alpha]_D^{20}$  —1° (diacetate, m.p. 84°,  $[\alpha]_D^{20}$  —3°), which on oxidation yielded (III). Rats probably excrete 1(or 2)-hydroxy-1:2-dihydroanthracene in addition to (I).

J. N. A.

**Comparison of the actions of certain dietary lipins in producing acetonaemia.** R. LECOQ and R. CAREL (Compt. rend., 1935, 201, 1154—1156).—Ingestion of castor oil in man, dog, rabbit, and rat is followed by a rise of the total ketones in the blood and especially of  $\beta$ -hydroxybutyric acid, similar to that following administration of butter-fat or olive oil.

W. O. K.

**Effect of ingested fat on the sterol metabolism of the white rat.** H. C. ECKSTEIN and C. R. TREADWELL (J. Biol. Chem., 1936, 112, 373—378).—Rats on diets supplemented with soya-bean or maize oils showed increased concns. of sterols in their livers which were not due to mobilisation from the tissues. The supplements appear to increase the difference between faecal and ingested sterols.

H. D.

**Fat metabolism in fishes. VIII. Changes in the fat of ripening salmon eggs.** J. A. LOVERN (Biochem. J., 1936, 30, 20—24).—At all stages of the ripening the degrees of unsaturation of the  $C_{20}$  and  $C_{22}$  acids are higher than in the depot fat, and two possible explanations are discussed. During ripening there is a marked rise in the amount of  $C_{18}$  acids together with a fall in the mean unsaturation of this group.

J. N. A.

**Dicarboxylic acids as intermediates in the biological degradation of normal saturated fatty acids and their derivatives.** P. E. VERKADE and J. VAN DER LEE (Rec. trav. chim., 1935, 54, 893—898).—Mainly a priority claim against Flaschen-träger *et al.* (A., 1935, 1151) and a recapitulation of the authors' views on biological oxidation of fatty acids (cf. A., 1933, 417; 1935, 1273, etc.).

J. W. B.

**Fat metabolism. VII.  $\beta$ -Oxidation of normal saturated dicarboxylic acids administered *per os*.** P. E. VERKADE, J. VAN DER LEE, and A. J. S. VAN ALPHEN (Z. physiol. Chem., 1935, 237, 186—190; cf. A., 1934, 1393).—Suberic and adipic acid were detected in the urine of a dog to which Na sebacate had been administered; similarly azelaic and pimelic acids were found after administration of Na undecanedicarboxylate. The incidence of  $\beta$ -oxidation is thus established.

H. W.

**Absorption in phloridzinised animals. I. Absorption of fats.** G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 197—198).—Fat excretion in the faeces of pigeons given high doses of phloridzin increases, but the % of fat absorbed is not displaced considerably.

R. N. C.

**Spontaneous ketonuria and ketonuria from administration of stearic acid in normal subjects and hepatic patients.** L. CANNAVÒ (Boll. Soc. ital. Biol. sperim., 1935, 10, 180—182).—Ketonuria is min. in normal subjects on a mixed diet, but is increased to non-pathological vals. by ingestion of Na stearate (I). It is increased in patients with hepatic parenchymatic trouble and after carbohydrate-rich food. (I) acts according to the type of hepatic lesion; ketonuria appears in local lesions where large parts of the parenchyma are functioning normally, and in more extensive lesions associated with cellular degeneration. The keto-acids are mostly eliminated as  $\beta$ -hydroxybutyric acid. (I) provokes in



most cases an increase in total org. acids in the urine, but there is no relation existing between ketonuria and aciduria.

R. N. C.

**Fat and calcium metabolism. III. Influence of butter and margarine on the faecal output of calcium in full-grown rats.** A. WESTERLUND (Lantbrukshögsk. Ann., 1935, 2, 51—70).—In rats on low or moderate Ca diets the faecal but not the urinary Ca excretion was much greater in those receiving margarine as sole source of fat than in those receiving butter.

NUTR. ABS. (m)

**Glycogen formation from lower fatty acids with an even number of carbon atoms. III. Fate of acetoacetic acid in the animal organism.** R. STÖHR (Z. physiol. Chem., 1935, 237, 165—170; cf. A., 1933, 1193; Snapper *et al.*, A., 1929, 94).—The respiration of surviving rat's liver and kidney is restricted and that of diaphragm is increased by addition of  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ . The glycogen content of the livers of fasting rats is not increased by feeding  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Na}$  and  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et} + \text{glucose}$ .

W. McC.

**Ketosis. VII. Quantitative studies on  $\beta$ -oxidation. Glycogen formation from various fatty acids.** H. J. DEVEL, jun., J. S. BUTTS, L. F. HALLMAN, and C. H. CUTLER (J. Biol. Chem., 1935, 112, 15—23).—Liver-glycogen (I) of fasting male rats rises approx. 100% following the ingestion of the Na salts of fatty acids with an odd no. of C. No such rise follows the ingestion of the Na salts of the even acids. Trivalerin causes an increase in (I) > that caused by tributyrin; Wesson oil causes no increase. Oleic acid does not cause an increased (I) formation, but nonoic acid does, indicating that fissure of the double linking is not a primary change in the metabolism of oleic acid.

F. A. A.

**Effect of administration of fat on blood-sugar.** H. SCHONFELD (Monatsschr. Kinderheilk., 1935, 61, 432—435).—Olive oil caused a fall in blood-sugar in fasted children and rabbits, but when fasted for 24—48 hr. after the administration, hyperglycaemia occurred.

NUTR. ABS. (m).

**Conversion of fat into sugar.** W. HAARMANN (Biochem. Z., 1935, 282, 406—418; cf. A., 1933, 1193). The production of lactic acid (I) by surviving organs (skeletal and heart muscle, liver, brain of rabbit, dog, pig) is increased (optimal with 0.005—0.01M solutions) by addition of  $\text{Pr}^n\text{CO}_2\text{Na}$  and a  $\beta$ -hydroxybutyrate (II), the increases being > equiv. to the corresponding decrease in the degradation of carbohydrate. When glucose is added this degradation is increased by addition of  $\text{Pr}^n\text{CO}_2\text{Na}$  and to a lesser extent by that of (II) but the production of (I) from carbohydrate is usually decreased.

W. McC.

**Fat metabolism. IV. Acetoacetic acid breakdown in the kidney.** J. H. QUASTEL and A. H. M. HEATLEY (Biochem. J., 1935, 29, 2773—2786).—The rate of  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$  (I) by the kidney cortex *in vitro* under the conditions previously described (1935, 1408) is investigated. The anaerobic breakdown of (I) is similar to the aerobic breakdown in the presence of  $\text{CN}^-$  or glucose, and is

accelerated by glutathione but not by ascorbic acid. The aerobic breakdown of (I) is inhibited by salts of  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{PrCO}_2\text{H}$ , and malonic acid (II). The inhibition by (II) may be neutralised by Na fumarate and lactate and by alanine. The aerobic inhibition by  $\text{BzOH}$  with guinea-pig kidney is much > that with rat kidney.  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  and  $\text{H}_3\text{AsO}_3$  inhibit strongly under aerobic conditions. Mincing the kidney decreases the breakdown of (I). Production of  $\beta$ -hydroxybutyric acid accounts chiefly for the anaerobic decomp. of (I) and for about 1/3 to 1/4 of the aerobic decomp.

H. D.

**Relation of the spleen to formation of glycogen in the liver; rate of absorption of glucose and lactic acid.** M. KERLY and C. REID (J. Physiol., 1935, 84, 302—314).—Glycogen (I) formation in the liver in normal or splenectomised cats under chloralose takes place with equal readiness when glucose (II) or lactic acid (III) is injected into a vein or absorbed from the intestine. Unanæsthetised normal and splenectomised rats form (I) in the liver after administration of (II) or (III) by stomach tube. Anæmia after splenectomy reduces (I) formation. (I) formation after feeding with (III) is < that after (II) and less regular. Acetylcholine and choline chloride do not increase (I) formation. Cats absorb 1.1N-(II) and -(III) from the intestine at the same mol. rate, but rats absorb 50—60% (II) from the stomach 6—7 times as fast as 10—17% (III); the rate of (III) absorption is not increased by the use of more conc. solutions, and the unabsorbed fraction is mostly found in the stomach, suggesting that control by this organ is responsible for the different rates of absorption in cats and rats.

R. N. C.

**Cyclic changes in liver-glycogen of rats after removal of the adrenals.** G. ÅGREN (Biochem. Z., 1935, 281, 367—369).—The periodic changes in the liver-glycogen level normally observed in rats are not obtained after adrenalectomy.

P. W. C.

**Functional and anatomical state of the endocrine pancreas, and its insulin content, in dogs subjected to prolonged fasting.** E. AUBERTIN, A. LACOSTE, R. SARIC, and E. CASTAGNOU (Compt. rend. Soc. Biol., 1935, 120, 1107—1110).—The alimentary blood-sugar curve in dogs subjected to prolonged fasting resembles that of diabetic dogs, but a subsequent hypoglycaemia is observed. The insulin (I) of the pancreas is > in normal animals.

R. N. C.

**Comparison of the influence of fasting on the tolerance to glucose and galactose.** E. M. MACKAY, H. C. BERGMAN, and R. H. BARNES (Amer. J. Physiol., 1935, 112, 591—594).—The blood-sugar curve in the rabbit following administration of galactose (I) is not influenced by fasting, whereas that after glucose (II) is lower. The alimentary hyperglycaemia produced by (I) is not affected by previous administration of (II), nor is the blood-sugar curve of a second dose of (I) essentially different from that of the first. The data support the theory that metabolism of (I) and (II) is fundamentally different.

**Rate of absorption of glucose from the intestinal tract of the rabbit.** E. M. MACKAY, H. C.

BERGMAN, and R. H. BARNES (Proc. Soc. Exp. Biol. Med., 1934, 32, 323—326).—The rate of absorption decreases with time after the glucose is administered, and is related to the amount of glucose available for absorption.  
R. N. C.

Origin of the specific dynamic action of intravenous fructose at the three levels of assimilation in a normal dog. M. WIERZUCHOWSKI (Compt. rend. Soc. Biol., 1935, 120, 1127—1130).—Fructose (I) assimilation, fructolysis, and fat formation are dependent on the levels of assimilation, whilst the sp. dynamic action and oxidation quotient of (I) are independent of these and hardly variable. The sp. dynamic action hence originates from none of the above factors.  
R. N. C.

Utilisation of carbohydrate during aerobic activity in isolated frogs' muscle. C. L. GEMMILL (Amer. J. Physiol., 1935, 112, 294—300).—The average utilisation of carbohydrate by muscles stimulated at regular short intervals for long periods in oxygenated Ringer's solution accounts for only 42% of the total energy exchange as calc. from the  $O_2$  consumption, so that other material besides carbohydrate is oxidised to supply the energy for aerobic contraction of muscle.  
R. N. C.

Carbohydrate changes following recovery from muscular contraction. J. SACKS and W. C. SACKS (Amer. J. Physiol., 1935, 112, 565—572).—The lactic acid (I) formed during anaerobic activity in the muscle diffuses into the blood during recovery, no glycogen (II) being formed. The "Meyerhof cycle" is of no significance in recovering mammalian muscle. Hexose phosphate formed during contraction is resynthesised directly to (II) during recovery, at a practically const. rate. Further evidence is shown that the sole function of phosphocreatine hydrolysis is the maintenance of const.  $p_H$  in the fibre. The data confirm the theory that the energy of muscular activity is derived primarily from oxidative reactions.  
R. N. C.

Hypothalamic nuclei in the regulation of chloride and sugar metabolism. F. H. LEWY and F. K. GASSMAN (Amer. J. Physiol., 1935, 112, 504—510).  
R. N. C.

Hexose monophosphate changes in muscle in relation to rate of stimulation and work performed. R. E. FISHER and G. T. CORI (Amer. J. Physiol., 1935, 112, 5—14).—The work output and lactic acid (I) formation by rapidly-stimulated, isolated frogs' gastrocnemii are the same as by slowly-stimulated muscle, but hexose monophosphate (II) formation is increased, indicating an increased breakdown of glycogen (III); a short tetanus causes an even greater increase. (I) and (II) formation in unloaded muscle is < in muscles attached to a tension spring. (II) formation is not directly related to the work performed. The increase per mg. of (I) formed is greatest in contractions without load, and decreases as the work output increases; it is concluded that a muscle exhibits max. working efficiency with reference to (III) expenditure if it is producing max. tension at a slow rate of stimulation. Short tetani against a spring permitting considerable con-

traction do not produce delayed (I) or (II) formation, but after-formation of (I) is observed.  
R. N. C.

Aerobic and anaerobic production of lactic acid and degradation of carbohydrate in tissues. W. HAARMANN and H. BRINK (Biochem. Z., 1935, 282, 419—433).—Production of lactic acid (I) and degradation of carbohydrate in organs (heart and skeletal muscle, brain of ox, dog, rabbit) are differently affected by  $O_2$ , being restricted in some cases and unaffected or increased in others. In some case the production of (I) after addition of glucose (II) and glycogen (III) is decreased in presence of  $O_2$ . Usually the degradation of carbohydrate in absence of  $O_2$  is more than equiv. to the amount of (I) produced. Oxidation of (II) and (III) in some organs is decreased by  $O_2$ , but is unaffected in others. Production by the organs of (I) from  $AcCO_2H$  and  $AcCHO$  is not prevented by  $O_2$  and that from fumaric and succinic acid (IV) is increased by  $O_2$  [no (I) is produced anaerobically from (IV)].  
W. McC.

Aerobic and anaerobic disappearance of lactic acid in tissues. W. HAARMANN and H. BRINK (Biochem. Z., 1935, 282, 434—440).—The amount of added lactate which disappears from pulped tissues in 3 hr. is the same whether or not  $O_2$  is present.  
W. McC.

Vascular balance of lactic acid in the organs of the dog, after saturation of the organism with glucose. M. WIERZUCHOWSKI and T. CHMIELEWSKI (Compt. rend. Soc. Biol., 1935, 120, 1131—1133).—Lactic acid is discharged into the blood-stream from the motor apparatus, head organs, and portal vein system, and is absorbed in small quantities by the liver.  
R. N. C.

Resynthesis of phosphocreatine after muscular contraction. J. SACKS and W. C. SACKS (Amer. J. Physiol., 1935, 112, 116—123).—Removal of lactic acid (I) and resynthesis of phosphocreatine (II) proceed *pari passu* in the early stages of recovery of the muscle of the cat and the rabbit after contraction. The amounts of (I) removed and (II) synthesised in a given time are equiv. (II) resynthesis from its hydrolysis products after contraction takes place at a rate much < that required by Lundsgaard's hypothesis. Reconversion of hexose phosphate-P into (II)-P is slow in the early stages of recovery.  
R. N. C.

Liver-ketogenesis and its auto-regulation. S. LEITES and A. I. ODINOV (Biochem. Z., 1935, 282, 345—361).—In rabbit's liver pulp kept at 37—38° for 24 hr. autoxidation produces  $CH_3Ac\cdot CO\cdot H$  (I) and  $\beta$ -hydroxybutyric acid (II). Ketogenesis is more pronounced in the liver pulp of fasting than in that of non-fasting rabbits. With non-fasting rabbits production of (I) is optimal at  $p_H$  5.6 and of (II) at 7.0, whilst with fasting rabbits the val. for (I) and (II) is 5.6. When the amount of preformed ketone in the pulp is low, ketogenesis is > when it is high.  $Pr^oCO_2H$  added to the pulp produces (II) if ketogenesis was previously slight. Addition of  $NaOAc$  and  $AcCO_2Na$  has no effect on ketogenesis. These results indicate that the intermediate products of fat metabolism directly control ketogenesis in the liver to an extent dependent on that of previous

ketogenesis. The auto-regulation also depends on the glycogen content.

W. McC.

**$\alpha$ -Glycerophosphoric acid and brain metabolism.** R. E. JOHNSON (Biochem. J., 1936, 30, 33—42).—In the presence of  $\text{Na}_4\text{P}_2\text{O}_7$  (I) the extra  $\text{O}_2$  uptake by pigeon's brain tissue *in vitro* due to the addition of  $\alpha$ -glycerophosphate (II) is additive to that due to lactate (III). (I) increases the rate of disappearance of (II); (III) has little effect. There is no interaction between  $\text{AcCO}_2\text{H}$  and (II) with or without added (I), so it is concluded that the Embden-Meyerhof scheme does not apply to pigeon's brain tissue. The 2:4-dinitrophenylhydrazones of  $\text{AcCHO}$  and of a compound containing probably 6 C were isolated from the reaction products of brain with (II).

H. D.

**Role of glutathione in anaerobic tissue glycolysis.** A. GEIGER (Biochem. J., 1935, 29, 811—823).—Aq. KCl extracts and suspensions of muscle, brain, liver, and heart of rats, dialysed free from glutathione (I), produced no lactic acid (II) from glucose (III) or  $\text{AcCHO}$ , but did so if glycogen (IV) was the substrate. Addition of reduced (I) caused (II) formation from (III) and  $\text{AcCHO}$ , but slightly inhibited that from (IV). Oxidised (I) inhibited (II) formation from (III),  $\text{AcCHO}$ , and (IV). Inhibition of glycolysis by oxidising agents is probably due to the formation of oxidised (I). Borate inhibits glycolysis by brain, the effect being counteracted by  $\text{CaCl}_2$ . Probably inorg. P is not essential for glycolysis.

H. D.

**Intermediate metabolism of internal secretory glands. IV. Proteolysis and ammonia formation.** S. EPSTEIN and E. MIMA (Biochem. Z., 1935, 281, 339—344).—The proteolytic activity and  $\text{NH}_3$  formation in the thyroid, thymus, adrenal, and pancreatic glands were investigated. Proteolysis was very feeble (except with the pancreas), but was more marked at acid reactions.

P. W. C.

**Nitrogen metabolism of pre-school children.** L. C. KUNG and W. Y. FANG (Chinese J. Physiol., 1935, 9, 375—381).—In children on a controlled diet supplemented with soya-bean milk or cow's milk, the N intake and retention were 0.47—0.53 and 0.046—0.140 g. per kg., respectively; with a freely chosen diet the vals. were 0.39—0.56 and 0.030—0.064.

H. G. R.

**Chemical changes in metabolism in severe malnutrition in infants. V. Nitrogen metabolism.** L. GAROT, R. VIVARIO, and (Mlle.) COMHAIRE (Rev. franç. Pédiat., 1935, 11, 1—36).—Absorption of protein in malnutrition is little altered, the recovery of N from the faeces being < 20% of the intake. N retention is often increased in spite of stationary body-wt. Excretion in the early stages is normal, but in more severe cases the partition of urinary N is altered. Urea-N falls below 60% of the total,  $\text{NH}_3$ -N is almost absent, and  $\text{NH}_2$ -acid and residual N are greatly increased. Possibly intermediary metabolism is deranged.

NUTR. ABS. (m)

**Phosphorus metabolism of invertebrate nerve.** G. L. ENGEL and R. W. GERARD (J. Biol. Chem., 1936, 112, 379—392).—The P of the nerves of

*Homarus americanus* was determined as inorg., arginine (I), adenylypyrophosphate (II), and stable (resistant to 7 min. acid hydrolysis) fractions. The changes in these fractions during recovery in  $\text{O}_2$  after dissection are interpreted as being due to the reaction:  $(\text{II}) + 2 (\text{I}) \rightarrow 2 (\text{I}) \text{ phosphate} + \text{adenylic acid}$ . If the time of dissection was long the synthesis of (I) phosphate was > the apparent breakdown of (II), due probably to the re-synthesis of (II) at a later stage. During anoxia extensive hydrolysis of (II) and (I) phosphate occurs; on aerobic recovery from anoxia all the (I) phosphate is re-formed in 5 hr. and 2/3 of the (II) in 1 hr.

H. D.

**Minimum endogenous sulphur metabolism: magnitude, origin, character.** R. RAZAFIMAHERY (Ann. Physiol. Physicochim. biol., 1935, 11, 261—300).—Administration to pigs, rats, rabbits, and dogs of a carbohydrate diet sufficient for energy requirements but deficient in N and S led to a continual loss of N and S from the body. The N:S ratio of the negative balance was always different from that found in the tissues, being higher in the dog and rabbit and lower in the rat and pig. When the total energy expenditure was lowered the loss of both N and S per unit of body-wt. was also lowered. The partition of S between faeces and urine differed from that of N, the gut excreting a higher proportion of S than N. In the dog the faecal S was 66% of the total output, in the rat 50, in the rabbit 33, and in the pig 20%. 30—50% of urinary S was neutral S. In all species observed about 15% of the total acid S consisted of conjugated S; it persisted in the urine even with a protein-free diet.

NUTR. ABS. (m)

**Sulphur metabolism. I. Absorption and excretion of flowers of sulphur.** J. H. KELLER-MANN (Onderstepoort J. Vet. Sci., 1935, 4, 199—228).—The rates of absorption and excretion of S flowers, when fed to rats or sheep, were relatively low. When the S was removed from the ration there was a very marked lag before the urinary inorg.  $\text{SO}_4$  returned to its normal level, and also a long retention of S in the digestive tract. When the basal ration was relatively high in easily available S the absorption of the S flowers was low and vice versa, and thus the level of the food-S may control the toxic level of S flowers when added to the ration.

NUTR. ABS. (m)

**Continuous nitrogen and mineral balances during pregnancy, puerperium, and lactation.** H. A. HUNSCHER, F. COPE, H. R. STERNBERGER, B. N. ERICKSON, and I. G. MACY (Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl., 13—14).—During the latter half of pregnancy in a healthy woman the mean daily intakes were: Ca 3.1, Mg 0.6, Na 5.0, K 6.6, N 19.0, P 2.7, Cl 7.7, S 1.5 g., and the corresponding daily retentions: 0.37, 0.11, 0.56, 1.40, 3.06, 0.26, 0.60, and 0.34 g. During the first 53 days of lactation the daily balances were often negative; the averages were: Ca -0.48, Mg -0.03, Na +0.47, K +0.87, N -0.56, P -0.37, Cl +0.30, S -0.22 g.

NUTR. ABS. (m)

**Calcium, phosphorus, and nitrogen retention of rats on soya bean-egg powder and whole milk powder diets.** E. REID (Chinese J. Physiol., 1935,

9, 307—313).—Soya bean-egg powder promotes Ca and P retention equal to, and N retention and digestibility >, that of whole milk powder. H. G. R.

**Composition and action on calcium metabolism of Ah-Chiao (donkey-skin) glue and commercial gelatin.** T. G. NI (Chinese J. Physiol., 1935, 9, 329—338).—Donkey-skin glue contains N 16.49, ash 0.92, Ca 0.099, lysine 6.2—7.0, arginine 7, lysine 0.41—2.19, and cystine 0.15%. Donkey-skin glue, pure gelatin, and glycine all increase the absorption and retention of Ca. H. G. R.

**Serum-calcium response to ingested calcium.** S. FREEMAN, E. R. KANT, and A. C. IVY (J. Biol. Chem., 1935, 112, 1—7).—The serum-Ca of fasting adults is raised 5—6% 2 hr. after ingestion of 2.3 g. of  $\text{CaCl}_2$  or 10 g. of Ca gluconate (I). Daily ingestion of  $\text{CaCl}_2$  for one month before the experiment does not affect this response. In dogs the serum-Ca response increases with Ca dosage, and  $\text{CaCl}_2$  produces a greater max. response than (I), but the increase produced by (I) persists longer. F. A. A.

**Magnesium deficiency in animals. VII. Effects of magnesium deprivation, with a superimposed calcium deficiency, on the animal body, as revealed by symptomatology and blood changes.** H. G. DAY, H. D. KRUSE, and E. V. MCCOLLUM (J. Biol. Chem., 1936, 112, 337—359; cf. A., 1934, 1253).—Dogs on a diet deficient in Mg and Ca show decreases in serum-Ca, -Mg, -alkali reserve, - $p_{\text{H}}$ , and -inorg. P, and erythrocyte vol. and increases in blood-Cl, -fibrinogen, and -non-protein-N, and no changes in serum-Na, -K, -lipins, -bile pigments, -albumin, and -globulin. H. D.

**Metabolism of inorganic substances in the liver of calves during foetal development. I. Iron, phosphorus, and calcium.** Z. GRUZEWSKA and M. G. ROUSSEL (Ann. Physiol. Physicochim. biol., 1935, 11, 176—198).—There appears to be a local reserve of Fe in the foetal liver; the content is at a min. at 6—7 months, rising suddenly at 8½—9 months. The P content (chiefly org.) at about the 4th month is approx. 0.9%; it then decreases throughout gestation, at first rapidly, then more slowly. The Ca content showed only small variations throughout development. NUTR. ABS. (m)

**Disappearance of digestive inhibition with the repetition of exercise.** F. A. HELLEBRANDT, E. BROGDON, and S. L. HOOPES (Amer. J. Physiol., 1935, 112, 442—450).—The inhibition of HCl secretion disappears with the repetition of all but extreme grades of work. It disappears also in extremely severe work when the response has been conditioned. R. N. C.

**Some immediate physiological effects of reduced cooling powers on human subjects.** D. H. K. LEE and A. G. MULDER (J. Physiol., 1935, 84, 279—295).—Exposure in the post-absorptive state to high temp. in dry or humid atm. causes similar responses. Respiratory changes become marked after 3 hr. Alveolar  $\text{CO}_2$  tension falls only after the respiratory vol. has increased. Urinary acid excretion is lowered from the 3rd to the 6th hr.  $\text{CO}_2$  in cutaneous venous blood from the forearm

falls before alveolar  $\text{CO}_2$  tension, probably due to increased  $\text{CO}_2$  excretion through the skin; the fall may be increased when the tension falls. The evidence for a true arterial alkalemia is not conclusive. Blood-lactate is not increased. After ingestion of food the response in dry atm. is > that in humid atm. R. N. C.

**Nervous system and remote action of ultra-violet rays.** G. VIALE and E. RONCALLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 311—314).—Irradiation of the normal rabbit's foot depresses blood-sugar, but scarcely affects it in the denervated foot. R. N. C.

**Diuresis associated with direct stimulation of the pituitary.** W. R. INGRAM and R. W. BARRIS (Endocrinol., 1935, 19, 432—440). R. N. C.

**Comparative study of sodium chloride and blood pressure changes induced by adrenal insufficiency, trauma, and intraperitoneal administration of glucose.** W. M. PARKINS, A. R. TAYLOR, and W. W. SWINGLE (Amer. J. Physiol., 1935, 112, 581—590; cf. A., 1935, 1422). R. N. C.

**Comparative values of butter and margarine in medical nutrition.** S. BADILKES, E. EINHORN, V. KUDASCHEVITSCH, and V. SIKOV (Arch. Verdauungskrankh., 1934, 56, 293—306; Chem. Zentr., 1935, i, 2694). R. N. C.

**Physiological action of silage on the digestive process of farm animals.** A. KRATINOV (Probl. Tierzucht, 1933, 5, 18—25; Bied. Zentr., 1935, A, 5, 615).—Silage stimulates the gastric and salivary glands of cows, sheep, and pigs and induces changes in the composition of digestive juices, whereby digestion is improved. A. G. P.

**Influence of ingestion of raw pancreas on the blood-lipins of completely depancreatized dogs maintained with insulin.** I. L. CHAIKOFF and A. KAPLAN (J. Biol. Chem., 1935, 112, 155—165).—The blood-lipin level is lowered soon after pancreatectomy, but addition of raw pancreas to the diet increases it to a val. > the normal, which is maintained as long as the tissue is supplied. Ingestion of raw pancreas after a low lipin level has been established causes a rapid and pronounced rise in all lipin constituents and fatty acids, particularly the cholesteryl esters. J. N. A.

**State of bismuth in body-fluids and tissues.** P. J. HANZLIK and A. P. RICHARDSON (J. Pharm. Exp. Ther., 1935, 55, 447—463).—Electromigration experiments show that the Bi of  $\text{NaBiO}_3$ ,  $\text{Na}_2\text{BiI}_5$ , and Na Bi tartrate and thioglycollate (I) exists in the electronegative state in aq., glycol, or sucrose solutions, in the presence of salt and of acidity or alkalinity according to the Bi compound, in urine, blood, and liver-tissue *in vitro*, and in the urine, plasma, and liver of rabbits after intramuscular injection of toxic and fatal doses. The  $\text{BiI}_5$  ion exists as such in both solutions and body-fluids. Bi of  $\text{BiOCl}$  and Bi hydroxysalicylate in aq. suspension migrates electropositively in traces only, but in the presence of salt and the above body-fluids and tissues *in vitro*, and after intramuscular injection, the Bi is strongly electronegative. Bi always exists in the



electronegative state in the body, the originally electro-positive ions being transformed slowly into electro-negative complexes by the action of salts. Blood-Bi is mostly in plasma solution, only traces occurring in the corpuscles; the highest concn. of plasma-Bi is obtained after administration of (I). R. N. C.

**Incidents and toxic accidents of calcium intravenotherapy.** L. TOCCO (Boll. Soc. ital. Biol. sperim., 1935, 10, 348—350).—The disturbances produced during Ca therapy, or immediately after, are the result of rapid reaction or saturation of the blood with Ca, and have no connexion with the toxic effects sometimes encountered, which are probably due to micro-crystals present in the Ca solution, or produced by contact with the blood. R. N. C.

**Effect of potassium and calcium on the contractions of mammalian skeletal muscle.** A. M. BAETJER (Amer. J. Physiol., 1935, 112, 147—151). R. N. C.

**Effect of potassium and calcium ions on the blood-sugar.** K. KIYOHARA, M. MORITA, and S. MUTA (Compt. rend. Soc. Biol., 1935, 120, 1011—1014).—Perfusion of the isolated pancreas of the dog with blood containing KCl or CaCl<sub>2</sub> does not affect blood-sugar (I). Both increase (I) in rabbits when injected intravenously; the increase is not affected by atropine, and is not reduced after double adrenalectomy. R. N. C.

**Biochemistry of copper. XI. Pigmentation of skin and hair.** U. SARATA. XII. Beneficial effect on blood-transfusion. M. ITIZYO (Japan. J. Med. Sci., 1935, II, 3, 79—84, 99—113).—XI. The Cu content of non-pigmented skin of cats and dogs (approx. 0.0004% of the dry wt.) is < that of pigmented skin. This fact, together with the increase in oxidation of *l*-3:4-dihydroxyphenylalanine by skin extracts due to certain concns. of Cu (A., 1931, 1186), indicate that Cu is concerned with melanin formation. XII. Blood-regeneration due to blood-transfusion in hæmorrhagic rabbits is accelerated by addition of Cu (0.6—2.0 mg. per kg. body-wt.), but not of Mn, Fe, Co, or Ni, to the transfused blood. F. O. H.

**Effect of fluorine on the phosphatase content of plasma, bones, and teeth of albino rats.** M. C. and E. M. LANTZ (J. Biol. Chem., 1935, 112, —311; cf. Phillips, A., 1932, 1278).—Feeding of harmful doses of NaF and injection of doses sufficient to cause acute poisoning have no significant effect on the phosphatase content of their plasma, bones, and teeth. W. McC.

**Effect of ammonia on acid-base equilibrium.** VENULET, F. GOEBEL, and R. TISLOWITZ (Compt. rend. Soc. Biol., 1935, 120, 1139—1142).—NH<sub>3</sub> added to milk or distilled or tap-H<sub>2</sub>O ingested by dogs abolishes alkalosis and displaces the acid-base equilibrium of the blood towards the acid side. The alkalosis produced by ingestion of NaHCO<sub>3</sub> or alkaline salt mixture is also decreased by addition of NH<sub>3</sub>, and intravenous injection of NH<sub>3</sub> decreases the alkaline reserve. R. N. C.

**Apparent intoxication in poultry, due to nitrogenous bases.** S. F. COOK and K. G. SCOTT (Science, 1935, 82, 465—467).—Intoxication induced

by N bases apparently occurred in poultry fed on a special diet which included functionally low-S fish-meal. Replacement of the latter by meat scrap, casein, skim-milk, or high-S fish-meal relieved the hæmorrhagic symptoms. Addition of NMe<sub>3</sub>, NHMe<sub>2</sub>, NH<sub>2</sub>Me, NHEt<sub>2</sub>, etc., ergot, and nicotine to a non-hæmorrhagic diet produced symptoms similar to those resulting from the special diet. Methylamines were present in the low-S fish-meal in amounts sufficient to produce the intoxication. The S compounds in the high-S fish-meal were sufficient to detoxicate the methylamines. Addition of dried blood, S, cystine, or cysteine to hæmorrhagic diets alleviated the symptoms. L. S. T.

**Effect of intravenous injections of amino-acids on the motility of the stomach in normal and fasting dogs.** H. BOWMAN, J. F. REGAN, and E. U. STILL (Amer. J. Physiol., 1935, 112, 438—441). R. N. C.

**Sensitivity to acetylcholine and velocity of hydrolysis by blood of acetylcholine in man.** G. INGVARSSON (Biochem. Z., 1935, 281, 370—376).—No difference could be detected in the rate of hydrolysis of acetylcholine (I) by bloods of sensitive and resistant individuals or in blood taken before and after injection of (I). Such differences in sensitivity arise in the nervous system rather than in any varying degree of inactivation of (I) by blood. P. W. C.

**Pharmacological properties of the acetylene linking.**—See this vol., 188.

**Action of acetylcholine on gaseous metabolism.** C. ZUMMO, D. ELIA, and A. PAGANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 195—197).—Acetylcholine (I) does not affect gaseous metabolism in rats or pigeons; hence the increase caused by pilocarpine is not due to liberation of (I). R. N. C.

**Co-operative action of sympathetic nerve impulses, adrenaline, and sympathin on the nictitating membrane of the cat.** A. C. LIU (Amer. J. Physiol., 1935, 112, 690—694). R. N. C.

**Tyramine. II. Moderating effect on human basal metabolism: therapeutic assays in hyperthyroidism.** III. Effects on the different systems of the human organism. P. JACCHIA and F. CAPOCASALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 201—204, 205—208).—II. Tyramine (I) depresses basal metabolism in hyperthyroid patients when given orally or intramuscularly; metabolism remains low when (I) is administered over long periods.

III. (I) given as above reduces gastric acidity, and in some cases increases blood-sugar. R. N. C.

**Derivatives of aminomethyldihydro-oxazine which exhibit adrenaline-like action.**—See this vol., 214.

**2:4-Dinitrophenol and respiration of tissues *in vitro*.** G. DOMINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 362—364).—Sections of surviving liver and spleen show no change in their metabolism *in vitro* if taken from animals treated with fatal doses of 2:4-dinitrophenol (I). Metabolism is unaffected by addition of small quantities of (I) to the respiratory medium, but is depressed by higher concns. If the (I)

is added to the medium during the development of the manometric registration, small quantities are still ineffective, moderate quantities cause a rise of metabolism followed by a fall, whilst large quantities inhibit it, and  $O_2$  consumption falls. R. N. C.

**Influence of sodium taurocholate, hepatic bile, and gall-bladder bile on the absorption of oleic acid from the small intestine.** C. RIEGEL, K. O. ELSOM, and I. S. RAVDIN (Amer. J. Physiol., 1935, 112, 669—672).—Oleic acid introduced alone into an intestinal loop in the dog is practically unabsorbed, but the absorption is increased by the presence in the loop of Na taurocholate, and to a small degree by hepatic or gall-bladder bile. R. N. C.

**Therapy of poisoning by the active principle (potassium atractylate) of *Carlina gummifera*.** A. MARRAS (Boll. Soc. ital. Biol. sperim., 1935, 10, 357—359).—Correction by glucose or adrenaline of the hypoglycaemia induced in rabbits poisoned by K atractylate prevents or delays death, which is, however, due to other causes besides hypoglycaemia. R. N. C.

**Variations of the absorption spectrum of the blood of leucæmic fowls after intravenous injection of a lecithin-hydrogen peroxide complex.** J. MAGAT, D. ABRAGAM, and M. MAGAT (Compt. rend. Soc. Biol., 1935, 120, 1091—1093).—The absorption curve of the leucæmic fowl after injection of lecithin- $H_2O_2$  complex lies above that of the normal fowl between 450 and 600  $m\mu$ , with a feeble max. at 510  $m\mu$ , whilst the band at 600—640  $m\mu$  is less intense. The leucæmic blood probably contains a principle that inhibits the formation of peroxyhaemoglobin. R. N. C.

**Toxic action of pyrethrins on marine animals.** M. O. GAUDIN (Compt. rend. Acad. Agric. France, 1935, 21, 277—281).—Effects of administration of pyrethrins by injection or through respiratory organs are examined. A. G. P.

**Action of tetralin, 5-tetralol, and 5-tetralone on body temperature and metabolism.** H. R. KANITZ, A. LOHMEYER, and J. SCHOLZ (Arch. Hyg., 1935, 113, 234—244; Chem. Zentr., 1935, i, 2841).—Administration of tetralin caused a moderate fall in body temp., followed by a more permanent rise;  $O_2$  consumption was not changed, while the urinary quotient was increased. H. N. R.

**Action of chlorophyll on the mobilising effects of adrenaline with respect to sugar.** K. E. LARSSON (Compt. rend. Soc. Biol., 1935, 120, 1124—1126).—Injection of large doses of chlorophyll in rabbits suppresses to some extent the hyperglycæmic action of adrenaline. R. N. C.

**Hæmatopoietic action of Ah-Chiao (donkey-skin glue).** T. G. NI (Chinese J. Physiol., 1935, 9, 383—393).—The hæmatopoietic action was of a similar order to that of gelatin and was independent of Fe and Cu. H. G. R.

**Solvents of the active principles of chamæpitium.** A. BORSANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 240—242).— $COMe$ ,  $EtOH$ ,  $Et_2O$ , and  $CHCl_3$  extracts of *Ajuga chamæpitys* show a transitory

pressor effect, whilst the corresponding residues show a depressor effect without an initial rise, indicating the presence of two active principles. The depressor principle is sol. in  $H_2O$  and is pptd. by  $EtOH$ . R. N. C.

**Synergism of narcotic poisons.** R. J. LESZCZYŃSKI (Poznań. Towarz. Przyj. Nauk. Prace Kom. Lek., 1934, 4, 1—16; Chem. Zentr., 1935, i, 2559).—Morphine, scopolamine, and the *Cannabis indica* alkaloids act synergistically with one another in the production of narcosis in dogs. R. N. C.

**Theories of narcosis.** (A) K. H. MEYER and H. HEMMI. (B) I. TRAUBE. (C) K. H. MEYER (Biochem. Z., 1935, 282, 444, 445—446, 447).—Polemical. W. McC.

**Absorption of bilirubin, rose Bengal, and tetrabromophenolsulphonephthalein by the liver.** M. ROYER (Compt. rend. Soc. Biol., 1935, 120, 809—812).—Absorption of bilirubin by the liver of the normal dog is > that of rose Bengal or tetrabromophenolsulphonephthalein; all three diminution coeffs. are < that of urobilin, and are reduced by intoxication with  $CHCl_3$ . R. N. C.

**Toxic action of local anæsthetics on the amphibian heart.** L. DONATELLI (Arch. Farm. sperim., 1935, 60, 482—496).—Comparative data are given for the lethal and toxic action of novocaine, stovaine, cocaine, pantocaine, and percaine on the heart of frogs and toads. F. O. H.

**Influence of diuretics on the chlorine of rat organs.** K. A. WINTER (Med. Klinik, 1934, 30, 1727—1728; Chem. Zentr., 1935, i, 2842—2843).—Salyrgan causes no diminution in tissue-Cl, but kidney-Cl falls by 75%. Euphyllin causes a considerable general fall in Cl. H. N. R.

**Action of curare and atropine on the secretions of the pancreas.** R. GAYET and M. GUILLAUME (Ann. Physiol. Physicochim. biol., 1934, 10, 532—533; Chem. Zentr., 1935, i, 2841).—The action of the two drugs is similar. H. N. R.

**Percaine.** F. FALCO (Rev. Fac. Quím. Ind. Agric., 1934, 3, 185—191).—Percaine (I) is extracted from viscera with  $EtOH$ . Photomicrographs are reproduced of the compounds of (I) with picric acid, Mayer's reagent,  $K_2Cr_2O_7$ ,  $HgCl_2$ ,  $AuCl_3$ , and  $K_4Fe(CN)_6$ . F. R. G.

**Fate of procaine in the dog.** J. G. DUNLOP (J. Pharm. Exp. Ther., 1935, 55, 464—481).—Procaine (I) in the normal dog disappears rapidly from the circulation, and is excreted slowly in the urine as non-toxic end-products; in the absence of the kidneys these are found in the blood during survival. Blood alone does not affect (I). The liver is not essential for detoxication of (I), but its action is more rapid and efficient than that of other tissues. R. N. C.

**Phenanthrene derivatives.** VI. Amino-alcohols of the ethanalamine and propanolamine type. N. B. EDDY (J. Pharm. Exp. Ther., 1935, 55, 419—429).—The pharmacological properties of 3- $\beta$ -diethylamino- $\alpha$ -hydroxyethylphenanthrene are described. Similar derivatives with the  $NH_2$  unsubstituted, or with the  $NEt_2$  attached to an Ac or a

hydroxy-*n*-propyl side-chain are less effective analgesics, and less like morphine in other respects. Phenanthrene and  $\text{NEt}_2 \cdot [\text{CH}_2]_6 \cdot \text{OH}$  are not analgesic. R. N. C.

**Removal of cardiac glucosides from the frog's ventricle.** G. KINGISEPP (*J. Pharm. Exp. Ther.*, 1935, **55**, 377—389).—Washing-out of cardiac glucosides from the heart produces recovery; the combination between the drugs and heart muscle resembles an absorption, but hysteresis must be assumed to occur. R. N. C.

**Mechanism of the action of fish serum on warm-blooded animals.** A. VON BEZNAK and L. VON TÓTH (*Arch. exp. Path. Pharm.*, 1935, **180**, 69—74).—Intravenous or subcutaneous injection of shad serum causes death, the min. lethal dose for rabbits being  $1.2 \pm 0.2$  c.c. per kg. There is a decrease in respiration, temp., and blood pressure. The lytic and lethal factors are retained by an ultrafilter. The toxic action is reduced by atophan. J. N. A.

**Effect of poisons of different pharmacological types on the chromatic function of frog's skin.** R. J. LESZCZYŃSKI (*Poznań. Powarz. Przyj. Prace Kom. Lek.*, 1934, **4**, 17—44; *Chem. Zentr.*, 1935, **i**, 2559).—Adrenaline lightens, and pituitrin (I) darkens, the colour of the skin by peripheral action. Ergotamine lightens the colour by sympathetic action; (I) abolishes, but does not invert, this action. Pilocarpine, eserine, acetylcholine,  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{BaCl}_2$ , strophanthin, papaverine, Ca, K, and conc. NaCl solution produce a temporary lightening followed by darkening;  $\text{NaNO}_2$  lightens, and  $\text{C}_5\text{H}_{11}\text{NO}_2$  darkens, the colour, whilst atropine is without effect. The characteristic action is shown only by poisons that affect the sympathetic system. R. N. C.

**Detoxification of strychnine by sodium pentobarbital.** E. E. SWANSON (*J. Amer. Pharm. Assoc.*, 1935, **24**, 959—961).—Na pentobarbital is an antidote for strychnine poisoning in rabbits; the effect is < that of Na amytal. F. O. H.

**Potassium polythionates as antidotes for hydrocyanic acid poisoning.** A. CHISTONI and B. FORESTI (*Arch. int. Pharm. Ther.*, 1935, **49**, 439—444; *Chem. Zentr.*, 1935, **i**, 2843).— $\text{K}_2\text{S}_4\text{O}_6$  and  $\text{K}_2\text{S}_5\text{O}_6$  are not suitable antidotes for HCN poisoning, since the  $\text{K}^+$  assists the paralytic action of the poison on the nerve centres. H. N. R.

**Enzyme chemistry.** R. WILLSTATTER (*Scientia*, 1935, **57**, 210—220; *Chem. Zentr.*, 1935, **i**, 2548).—The nature, constitution, and specificity of enzymes are discussed. A. G. P.

**Progress in enzyme chemistry.** ANON. (*Nature*, 1936, **137**, 53—55).—An expansion of the paper read by E. Waldschmidt-Leitz before the British Association. L. S. T.

**Enzyme activity and anion effects.** W. KOPACZEWSKI (*Bull. Sci. Pharm.*, 1934, **41**, 391—402; *Chem. Zentr.*, 1935, **i**, 2383).—Activity is influenced by  $[\text{H}^+]$  and by the associated ions, but much more by the age of the prep., the concn. and physical condition of the substrate, and the purity of the enzyme. A. G. P.

**Thermodynamics of enzymic equilibria. Aspartase system.** K. P. JACOBSON and J. TAPADINHAS (*Biochem. Z.*, 1935, **282**, 374—382; cf. A., 1935, 121, 1530; Quastel *et al.*, A., 1926, 868).—The position of equilibrium attained in the aspartase (I) system is dependent on temp. and since the heat of amination (calc. from the temp. coeff. of *K*) accords with the val. for the difference in the heats of formation of the components of the system, it follows that (I) is a true catalyst. W. McC.

**High-pressure ultrafiltration with Cellophane as a means of enzyme purification and determination of particle size.** G. GORBACH and K. NITSCHKE (*Biochem. Z.*, 1935, **281**, 306—309).—The prep. of the membrane and its application to the concn. of invertase in yeast autolysates are described. P. W. C.

**Stereochemical specificity and equilibrium in the fumarase system.** Biochemical production of *d*-malic acid. K. P. JACOBSON and M. SOARES (*Biochem. Z.*, 1935, **282**, 383—386).—In solutions containing aspartase and relatively high  $[\text{NH}_4\text{Cl}]$ , fumarase produces *d*-malic acid in 100% yield from *dl*-malic acid and hence exhibits abs. configurative specificity. W. McC.

**Uricase and its action. VIII. Extraction and precipitation of ox-kidney uricase.** R. TRUSZKOWSKI and S. GUBERMANOWNA (*Biochem. J.*, 1935, **29**, 2787—2797; cf. A., 1934, 451).—Uricase (I) powder is prepared by thorough washing of minced kidney with  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{Et}_2\text{O}$  and drying at  $30^\circ$ . The apparent activity of the preps. depends on the availability of  $\text{O}_2$ . Active solutions are obtained by extracting the powder with aq.  $\text{Na}_2\text{CO}_3$  at  $p_{\text{H}} > 9.8$  for 48 hr. at room temp.  $\text{AcOH}$  and  $(\text{NH}_4)_2\text{SO}_4$  ppt. (I) from the extracts. (I) has an optimum  $p_{\text{H}}$  of 8.8 and is completely inactivated at  $p_{\text{H}} < 5.8$  or by tryptic digestion. The quantity of P removable by 2% aq. NaOH in the powder approx.  $\propto$  the activity.

**Uricase, amino-acid oxidase, and xanthine oxidase.** D. KEILIN and E. F. HARTREE (*Proc. Roy. Soc.*, 1935, **B**, **119**, 114—140).—Uricase (I) and  $\text{NH}_2$ -acid oxidase (II), like xanthine oxidase (III), function as true dehydrogenases. (I) is prepared by drying minced pig's liver with  $\text{COMe}_2$ . This prep. shows optimum activity at  $p_{\text{H}}$  9.25. Its inhibition by  $\text{CN}^-$  is reversible.  $\text{CO}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaF}$ , and urethane have very small or no inhibitory effects.  $\text{P}_2\text{O}_7^{4-}$  has a slight activating effect. Small amounts of Cu and Fe inhibit (I), but this inhibition is abolished when the metals are added in phosphate buffer containing  $\text{P}_2\text{O}_7^{4-}$ . (I) is sp. for uric acid (IV); alkyl derivatives of (IV) are not oxidised, although they may act as competitive inhibitors.  $\text{H}_2\text{O}_2$  is formed when  $\text{O}_2$  is the H acceptor for the oxidation. On the addition of *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  (V) and peroxidase (VI) a coupled oxidation of (V) by  $\text{H}_2\text{O}_2$  occurs, doubling the  $\text{O}_2$  uptake due to the oxidation of (IV) alone. (V) alone increases the  $\text{O}_2$  uptake owing to the (VI) activity of haematin compounds in (I) preps. It is suggested that the primary stage of the reaction is the oxidation of (IV) to uric acid 4:5-glycol; this then rearranges to form hydroxyacetylenediureinecarboxylic acid,

which gives allantoin on decarboxylation. The Michaelis const. for (II) with *dl*-alanine as substrate is about  $5 \times 10^{-3} M$ . (II) is irreversibly inhibited by  $H_2S$  in the presence of  $O_2$ . An inhibition by ethylurethane may be only a salt effect as other narcotics have no effect. (II) is inhibited by various tissue extracts such as liver-(I) and heart-muscle oxidase. Incubation with (III) almost completely inhibits (II), but this effect is considerably reduced if (III) is first boiled. Destruction of (III) by incubation with  $CN'$  does not affect this inhibition. A similar inhibition is shown by charcoal. The rate of oxidation of *l*-alanine by (II) is unaffected by the addition of *d*-alanine. The formation of  $H_2O_2$  on aerobic dehydrogenation is best shown by the coupled oxidation of EtOH (cf. following abstracts). (II) oxidises *N*-monomethyl- but not *N*-dimethyl- or  $\alpha$ -methyl-alanine. In addition to oxidative deamination, kidney slices promote the oxidation of *d*- and *l*-dihydroxyphenylalanine due to their polyphenol-oxidase content.

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dehydrase system, dehydrogenation is accompanied by dismutation. H. W.

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**Nature and specificity of Ricinus lipase.** H. E. LONGENECKER and D. E. HALEY (J. Amer. Chem. Soc., 1935, 57, 2019—2021).—Dry *Ricinus* lipase loses only a portion of its activity in many years. The activity is favoured by factors favouring the stability of  $H_2O$ -in-oil emulsions. For 14 oils examined there was no specificity when the no. of mols. hydrolysed is considered. R. S. C.

**Voltinism of the silkworm (*Bombyx mori*, L.).**  
**I. Activity of the lipase in relation to voltinism.** H. SATO and I. CHINO (Bull. Sericult. Japan, 1935, 8, 403).—The lipase of eggs incubated at 15° has an activity > that of eggs incubated at 25°. This and similar phenomena are due to instability of the voltinism determiner. P. G. M.

**Influence of oral administration and injection of various nutrients on enzyme actions of body-fluid of the silkworm.** S. MATSUMURA and T. OKA (Bull. Sericult. Japan, 1935, 8, 403—404).—Enzyme activity is increased by feeding or injection of the appropriate substrate only. P. G. M.

**Activation of enzymes. III. Role of metal ions in activation of arginase. Hydrolysis of arginine induced by certain metal ions with urease.** L. HELLERMAN and M. E. PERKINS (J. Biol. Chem., 1935, 112, 175—194).—A method for obtaining an arginase (I) prep. of high activity is described. So obtained it is neither activated nor, after treatment with oxidising agents, reactivated by cysteine; but it is activated by Ni<sup>++</sup>, Mn<sup>++</sup>, Fe<sup>++</sup>, and especially by Co<sup>++</sup>, and Co<sup>++</sup> effects complete reactivation after H<sub>2</sub>S inactivation. Arginine, without (I), best in presence of urease and any of the above ions, is hydrolysed. The effect is diminished by CN<sup>-</sup>, which, however, does not prevent hydrolysis of any urea in the mixture. The mol. of (I) probably contains a metallic component which can be separated by oxidising or other agents. The pronounced effect of Co<sup>++</sup> may be due to its ability to form complex mols. J. N. A.

**Quantitative measurement of tyrosinase.** M. GRAUBARD and J. M. NELSON (J. Biol. Chem., 1935, 112, 135—141).—A method for determining the activity of tyrosinase (I) is described. A unit is the amount of (I) which under specified conditions will bring about an uptake of 10 cu. mm. of O<sub>2</sub> per min. (I) appears to consist of one enzyme, the oxidation of *p*-cresol and dehydrogenation of pyrocatechol being both effected by active O<sub>2</sub>. J. N. A.

**Peptidase system of *Aspergillus parasiticus*.** M. J. JOHNSON and W. H. PETERSON (J. Biol. Chem., 1935, 112, 25—34).—The aminopolypeptidase (I) is preferentially pptd. from mixtures with dipeptidase by addition of 1.5—2.5 vols. of 95% EtOH. The (I) of *A. parasiticus* attacks peptide linkings adjacent to free NH<sub>2</sub>. Dipeptides are not attacked unless decarboxylated, and peptides composed entirely of glycine are not attacked. The crude enzyme from the mould also contains three distinct peptidases, capable of hydrolysing peptides in which Cl or Me is substituted in the NH<sub>2</sub>. The apparent basic dissociation consts.  $\times 10^{12}$  of leucyldiglycine, leucylglycine, triglycine, and diglycine are 19.0, 16.0, 19.0, and 14.0, respectively. F. A. A.

***a*- and *b*-Thymonucleic acid and the enzyme transforming the *a*- into the *b*-form (nucleogelase).** R. FEULGEN (Z. physiol. Chem., 1935, 237, 261—267).—Na *a*-thymonucleate (I) is transformed into the *b*-salt (II) by nucleogelase (pancreatic prep.) at *p*<sub>H</sub> 6.8—6.9. The tetranucleotide structure of the product follows, since (*a*) elimination of H<sub>2</sub>PO<sub>4</sub> or

purines does not occur, (*b*) protracted exposure of (II) to the action of the enzyme does not diminish the amount pptd. by mineral acid or increase the solubility in acid, (*c*) the at. ratio P:Na = 4:4 in both (I) and (II), (*d*) [ $\alpha$ ] of (II) resembles that of (I) in its unusual dependence on temp., and in its disappearance after addition of NaOH and return after neutralisation, (*e*) complete hydrolysis of (I) or (II) yields identical products in identical amounts, and (*f*) the analytical data for (II) are those required for a tetranucleotide based on the presence of deoxyribose as carbohydrate. H. W.

**Enzymic histochemistry. II. Micro-method for determination of tryptic activity.** L. WEIL (Biochem. J., 1936, 30, 5—10).—The CO<sub>2</sub>H groups liberated by the action of trypsin on tissue sections are determined by titration with 0.05*N*-NMe<sub>4</sub>-OH, the NH<sub>2</sub> having been blocked by CH<sub>2</sub>O. The reproducibility of the method is  $\pm 0.00007$  mg. of NH<sub>2</sub>-N. The tryptic activity in tumour tissue is independent of the thickness of the slice and time of extraction. J. N. A.

**Platinum potential corresponding to the inactivation of the proteolytic power of papain by oxidisers.** P. REISS (Compt. rend. Soc. Biol., 1935, 120, 908—910).—The proteolytic action of papain is arrested by oxidisers above a definite *E*<sub>h</sub>, which increases with fall of *p*<sub>H</sub>. R. N. C.

**Isolation and properties of pepsin and trypsin.** J. H. NORTHROP (Current Sci., 1935, 4, 370—376).—A summary.

**Acetylation of tyrosine in pepsin.** R. M. HERRIOTT (J. Gen. Physiol., 1935, 19, 283—299; cf. A., 1934, 1239).—“Cryst. 60% active acetylpepsin” contains 7 Ac per mol.; 3 of these may be removed by hydrolysis at *p*<sub>H</sub> 0.0 or 10. The phenolic OH of glycyltyrosine is acetylated by keten under the conditions used for pepsin, and it is probable that the 3 labile Ac, responsible for the decrease in activity, are attached to tyrosine phenolic groups in the pepsin mol. F. A. A.

**Enzymic histochemistry. XVI. Digestion of keratin by the larva of the moth *Tineola biselictella*.** Humm. K. LINDERSTRÖM-LANG and F. DUSPIVA (Z. physiol. Chem., 1935, 237, 131—158; cf. A., 1935, 784).—The intestinal cells and juice (*p*<sub>H</sub> 9.6—10.2) of the larvæ contain a proteinase (I) which degrades caseinogen (optimum *p*<sub>H</sub> 9.3) but does not attack wool (at *p*<sub>H</sub> 9.2 or 9.6—10.2). Juice from larvæ which have eaten wool, but not that from fasting larvæ and larvæ on diets poor in S (cotton wool, caseinogen), contains a -SH compound (or compounds) which rapidly oxidises in air. At *p*<sub>H</sub> 10, in presence of reducing agents (LiSH, SH·CH<sub>2</sub>·CO<sub>2</sub>H), (I) attacks wool liberating equiv. amounts of NH<sub>2</sub> and CO<sub>2</sub>H. When trypsin-kinase replaces (I) the wool remains unaffected. The mid-gut cavity contains a reducing agent the presence of which is independent of that of -SH compounds. The action of (I) is not inhibited by low concns. (0.01*N*) of -SH compound. W. McC.

**Changes of wheat proteins under the action of flour and yeast enzymes.** A. V. BLAGOVESHCHENSKI and M. P. YURGENSON (Biochem. J., 1935, 29, 805—



810).—Variations on treatment with flour enzyme (A., 1933, 1331) in the leucosine- and non-protein-N, gliadin, globulin, and glutenin fractions of flour and baking mixtures (obtained by extracting with  $H_2O$ , 72% EtOH, 10% NaCl, and 2% NaOH, respectively) indicate that the solvent effect of the enzyme is one of disaggregation as opposed to the proteolytic action of yeast enzymes. H. D.

**Does protease secretion occur in bacteria?** W. MOYCHO (Compt. rend., 1935, 201, 859—860).—Cultures of *B. prodigiosum* in peptone media develop to a greater extent if shaken, and the appearance of the red colour of prodigiosin is delayed. The secretion of proteases (I) does not occur until after the death of the cell. (I) are not liberated if the bacteria are killed by PhMe,  $CHCl_3$ , or  $Et_2O$ . R. N. C.

**Action of proteases on the protein of ungerminated cereals and on amylolytic activity** T. CHRZĄSZCZ and J. JANICKI (Biochem. Z., 1935, 281, 408—419).—The action of trypsin, papain, pepsin, and rennin on the protein and active amylase (I) content of ungerminated cereals was investigated. (I) is present in cereals, and the activity is increased by the action of proteases to an extent varying with different proteases and cereals. No abs. relationship exists between the increase of active (I) and the extent of protein degradation. The increase depends not exclusively on these factors, but also on the formation of substances having elutrient and kinase activity. Rennin, since it degrades oat- and buckwheat-protein (unattacked by pepsin), must contain protease. P. W. C.

**Phosphatases of the brain.** K. V. GIRI and N. C. DATTA (Current Sci., 1935, 4, 324).—In brain (of sheep) both "acid" (I) and "alkaline" phosphatase (optimum  $pH$  5.0 and 9.6, respectively) are present. (I) is not activated by  $Mg^{++}$ , and is therefore not identical with erythrocyte phosphatase (cf. Waldschmidt-Leitz, A., 1935, 534). F. R. G.

**Variations of serum-phosphatase after ingestion of chloroform.** H. METZGER, P. BARTHELME, and M. URBAN (Compt. rend. Soc. Biol., 1935, 120, 896—897).— $CHCl_3$  ingested by dogs daily for long periods causes an increase of serum-phosphatase, which disappears with cessation of administration. Bile secretion is not affected. R. N. C.

**Serum-phosphatase during gestation.** J. CAYLA and F. FABRE (Compt. rend. Soc. Biol., 1935, 120, 748—750).—Phosphatase increases by about 136% in pregnancy, and does not depend on the age of the mother.  $CaO$  fixation by the foetus is increased 7-fold during the last 2 months. R. N. C.

**Action of some chemical compounds on vegetable phosphatases.** J. COURTOIS (Compt. rend., 1935, 201, 855—856).—The affinity of any phosphatase for glycerophosphate depends on its origin; emulsin (I) and white mustard phosphatase react differently from takadiastase (II). NaF accelerates hydrolysis by the grain enzymes, and restrains that by (II); EtOH exhibits an inverse activity to NaF, whilst glycerol restrains (II) without affecting (I).  $AsO_4^{+++}$  and  $PO_4^{+++}$  inhibit all three to equal degrees. All these agents influence the affinity of each enzyme

for both glycerophosphates to the same degree.  $Mg^{++}$  does not accelerate any of the three, nor does 8-hydroxyquinoline (cf. A., 1935, 122). R. N. C.

**Phosphatase activity of tissues and plasma in tumours of bone.** C. C. FRANSEEN and R. McLEAN (Amer. J. Cancer, 1935, 24, 299—317).—The phosphatase activity of the blood-plasma is raised significantly in the osteoblastic type of osteogenic sarcoma, and on removal of the tumour mass the plasma-phosphatase val. falls to normal, rising again with recurrence of the tumour. The tumour tissue is also higher in phosphatase than are all other types of tumour tissue examined. The results support the theory of the synthesis of phosphatase by the osteoblasts. NUTR. ABS. (m)

**Micro-determination of phosphatase in serum.** E. MÜLLER (Z. physiol. Chem., 1935, 237, 35—39).—Amidol or metol is suitable as reducing agent in the colorimetric  $[(NH_4)_2MoO_4-sulphite]$  determination of  $PO_4^{+++}$  by the step-photometer. With Na  $\beta$ -glycerophosphate as substrate, the application of the method to phosphatase activity in serum (0.5 c.c.) is described. F. O. H.

**Energy relationships in the enzymic formation of lactic acid and synthesis of phosphagen.** O. MEYERHOF and W. SCHULZ (Biochem. Z., 1935, 281, 292—305).—The reaction phosphopyruvic acid (I) + creatine  $\rightarrow$  creatinephosphoric acid +  $AcCO_2H$  is associated with a negative heat val. of  $-3000$  g.-cal., whereas the analogous reaction (I) + arginine  $\rightarrow$  argininephosphoric acid +  $AcCO_2H$  is almost thermoneutral. P. W. C.

**Enzymic synthesis of creatinephosphoric acid by phosphate transfer from phosphopyruvic acid.** H. LEHMANN (Biochem. Z., 1935, 281, 271—291).—The synthesis of creatinephosphoric acid (I) in muscle poisoned with  $CH_2I \cdot CO_2H$  on addition of phosphoglyceric acid (II) and phosphopyruvic acid (III) is investigated using dialysed muscle extracts. The synthesis, which takes place only in presence of adenylic acid (IV) or adenylyl pyrophosphate (V), occurs particularly in old extracts dialysed for a long time in which spontaneous dephosphorylation no longer occurs.  $PO_4^{+++}$  transfer occurs in two stages: (IV) + (III)  $\rightarrow$  (V) +  $AcCO_2H$ ; (V) + creatine  $\rightarrow$  (I) + (IV). A small amount of (IV) may thus generate 100 times its amount of (I).  $Mg$  is necessary for both reactions. (III) permits a quicker and more complete transfer of  $PO_4$  than does (II). The reaction may be used for the prep. of (I) and also for the synthesis of argininephosphoric acid in crab's muscle extract. P. W. C.

**Dephosphorylation of starch by phosphatase.** H. PRINGSHEIM and F. LOEW (Bull. Soc. Chim. biol., 1935, 17, 1607—1613).—Complete dephosphorylation of amylopectin without maltose formation is not effected by several phosphatase preps. The dephosphorylation becomes proportionately easier, however, as diastatic action proceeds. A. L.

**Cozymase.** H. VON EULER, H. ALBERS, and F. SCHLENK (Z. physiol. Chem., 1935, 237, I—II; cf. A., 1935, 1024; Warburg *et al.*, *ibid.*, 400).—Improved methods of purification enable cozymase

(I) to be obtained almost pure and not as a mixture of isomerides. On acid hydrolysis (I) yields adenine (19.5%), nicotinamide, and  $\text{NH}_3$  (but no  $\text{CO}_2$ ). (I), which is probably a dinucleotide,  $\text{C}_{24}\text{H}_{35}\text{O}_{18}\text{N}_8\text{P}_2$ , is a monobasic acid. W. McC.

**Stability of the heat-stable glycolysis activator in cozymase, and of Warburg's co-enzyme.** H. VON EULER and G. GÜNTHER (Svensk Kem. Tidskr., 1935, 47, 285—290).—The glycolysis-activating power of cozymase is slightly enhanced when its oxidation-reduction activation is destroyed by heat. A study of lactic acid production indicates that the mechanism of glycolysis activation is the same for both "active" and "inactive" cozymase. The glycolysis activation is only slowly inactivated by 0.1N-NaOH at 100°, 0.5N-NaOH, or 0.5N-HCl. The relative activities at  $p_{\text{H}}$  5 (from fermentation measurements) after 1 hr. at 85° are approx.: cozymase 85%, Warburg's co-enzyme 30%. M. H. M. A.

**Cozymase as a hydrogen carrier.** H. VON EULER, E. ADLER, and H. HELLSTRÖM (Svensk Kem. Tidskr., 1935, 47, 290—293).—Substrate-dehydrogenase-cozymase systems give a reduced cozymase stable to atm.  $\text{O}_2$ , and reoxidised by flavin-enzyme. Cozymase is thus identified with the co-enzyme in the system substrate-dehydrogenase-co-enzyme-flavin-enzyme-acceptor. M. H. M. A.

**Action of cozymase.** H. VON EULER and R. VESTIN (Z. physiol. Chem., 1935, 237, 1—7).—Cozymase (I) [both highly purified ( $A_{C_0}=4 \times 10^5$ ) and relatively crude preps.] rendered fermentation-inactive by heat (A., 1935, 782, 1162, 1165, 1278) and normal (I) promote phosphorylation and formation of lactic acid by rat muscle in presence of hexose diphosphate (II) to approx. the same extent. Adenosine triphosphate can replace (I)+(II) in muscle glycolysis but not in yeast fermentation (cf. A., 1932, 778). Direct phosphorylation of  $\text{AcCO}_2\text{H}$  by yeast enzyme system (apozymase) in presence of (I) does not occur. Phosphorylation in muscle extract-glycogen-(I) preps. with (II) equals that with  $\text{AcCO}_2\text{H}$ . The nature of the various active centres of (I) (which are differentiated by reagents, e.g.,  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ , as well as by heat) is discussed. F. Ö. H.

**Oxidative inactivation of cozymase with Schar-dinger enzyme preparations.** F. LIPMANN (Nature, 1935, 136, 913—914).—An inhibition of fermentation occurs when yeast macerate is mixed with a milk prep. containing xanthine oxidase in presence of  $\text{O}_2$ . Fermentation recommences on addition of boiled yeast macerate or purified cozymase. L. S. T.

**Activators of glycolysis. II.** H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1935, 237, 221—226; cf. A., 1035, 1162).—Repetition of previous work with a much purer cozymase prep. shows that the ability to accelerate glycolysis is increased by heating the material at 100°. H. W.

**Fermentative enzymes. IV. Specificity of yeast-phosphatase.** E. BAUER, A. SCHAFFNER, and F. KRUMEY (Z. physiol. Chem., 1935, 237, 191—198; cf. A., 1935, 661).—Repetition of previous work following criticisms of Schuchardt (*ibid.*, 1026) and

Collatz (*ibid.*, 1026) shows that dried yeast of various origins yields phosphatase preps. identical within the limits of experimental error with those described previously with respect to sp. action on  $\alpha$ -glycerophosphate.  $\beta$ -Glycerophosphate is relatively slowly attacked. H. W.

**Phosphate transference by means of phosphopyruvic acid in alcoholic fermentation of sugar.** O. MEYERHOF and W. KIESSLING (Biochem. Z., 1935, 281, 249—270).—The velocity of degradation of phosphopyruvic acid (I) by yeast is increased by addition of sugar to an extent dependent on the fermentation velocity of the latter, to which  $\text{PO}_4'''$  of (I) is transferred. In presence of NaF, 2 mols. of (I), 2 mols. of hexose, and 2 mols. of  $\text{PO}_4'''$  are used and 2 mols. of  $\text{CO}_2$ , 2 mols. of EtOH, 1 mol. of hexose diphosphate (II), and 2 mols. of phosphoglyceric acid (III) are formed. The velocity is similarly increased in presence of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  and (II) is again formed. The MeCHO arising remains, however, as such, the conversion into (III)+EtOH not taking place. By using different sugars as  $\text{PO}_4'''$  acceptors in systems containing NaF or  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ , the velocity of degradation of (I) is shown to correspond with the fermentation velocities of the various sugars. The latter velocity must therefore be determined by the ability and readiness of the sugar to act as  $\text{PO}_4'''$  acceptor. Including this new reaction in the general mechanism of alcoholic fermentation, a scheme is obtained which accounts both for the fermentation velocity of the sugars and for the requirements of the Harden-Young equation. P. W. C.

**Theory of mitogenetic radiation. V. Yeast as detector for mitogenetic rays.** M. MOISSEJEVA (Biochem. Z., 1935, 281, 349—357).—Using liquid yeast cultures as detector in a chamber with quartz base or wall and using blood which had been dried on filter-paper and immersed in  $\text{H}_2\text{O}$  as inductor, the detector and inductor being hermetically separated, a positive induction effect (max. 50%, average 21%) on the multiplication of the yeast occurs. P. W. C.

**Preparation and determination of trehalose in yeast.** A. STEINER and C. F. CORI (Science, 1935, 82, 422—423).—Treatment of yeast with  $\text{N}\cdot\text{H}_2\text{SO}_4$  followed by pptn. with  $\text{HgSO}_4+\text{Fe}_2(\text{SO}_4)_3$  in 7.5%  $\text{H}_2\text{SO}_4$  completely extracts the trehalose (I), and only traces of polysaccharide which are pptd. on neutralisation with  $\text{BaCO}_3$ . After removal of the added metals, concn. in vac., and addition of EtOH, cryst. (I) is obtained in 0.3—0.7% yield. A method for the determination of (I) in yeast is outlined. L. S. T.

**Relation of oxygen tension and temperature to the time of reduction of cytochrome.** T. J. B. STIER (J. Gen. Physiol., 1935, 19, 339—350).—The time for the appearance of the cytochrome absorption band in yeast suspensions at various temp. is linearly related to the  $\text{O}_2$  tension. Crit. tensions, increasing with rise of temp., are found below which the cytochrome band appears. The  $\text{O}_2$  tension within the suspension is lowered by respiration by the cells; the rate of lowering can be calc. from the data and agrees approx. with direct measurements. F. A. A.

**Constitution of cytochrome c.** J. ROCHE and M. T. BÉNEVENT (Bull. Soc. Chim. biol., 1935, 17, 1473—1493).—Hæmatin, prepared from pig's blood, successively oxidised and reduced with  $K_3Fe(CN)_6$  and  $Na_2S_2O_4$  gives a hæmochromogen with  $C_5H_5N$  which has an absorption spectrum almost identical with that of the corresponding hæmochromogen of cytochrome c from yeast. A. L.

**Fixation and exchange of cations in living organisms.** General character of the laws of base exchange. J. LAVOLLAY (Compt. rend., 1935, 201, 1150—1152).—If  $x$  is the concn. of a cation in a medium and  $Y$  the concn. in the organisms cultivated thereon, then the equation  $Y = Kx^{1/p}$  (where  $K$  and  $p$  are consts. and  $1/p < 1$ ) holds within certain limits of concn. for K in *Penicillium glaucum*, Mg in *Aspergillus niger*, and for Ca and Pb in brewer's yeast. If  $C_1$  and  $C_2$  represent the concns. of two cations, then in certain cases  $[C_1/C_2]_{fixed} = [C_1/C_2]_{medium}^a$ . The formal similarity of these laws to those controlling base exchange in zeolites and in soil indicates a close relationship to these phenomena. W. O. K.

**Yield of citric acid from sugar as a basis for estimating the schemes of its formation from the latter.** V. S. BUTKEVITSCH and M. S. GAJEVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 405—408).—Yield tests show that, with *A. niger*, the whole of the sugar is converted into citric acid, according to the scheme of either Raistrick or Virtanen.

H. G. R.

**Diffusible nature of the inhibitory agent produced by fungi.** J. C. CARTER (Phytopath., 1935, 25, 1031—1034).—Agar media staled by growth of *Helminthosporium sativum* and a bacterium inhibit the further growth of *H. sativum*. The inhibitory agent is diffusible and thermostable, and retains its activity after sterilisation. A. G. P.

**Biochemistry of micro-organisms. XLVII. Production of polysaccharides by *Penicillium luteum*.** Zukal. C. G. ANDERSON and H. RAISTRICK (Biochem. J., 1936, 30, 16—19).—When *P. luteum*, Zukal, is grown on a Czapek–Dox medium with glucose as sole source of C, the principal metabolic product is luteic acid, a malonylpolyglucose. In the early stages of growth a polymannose is present which tends to be replaced by a polygalactose with increasing age of the culture. No pentose is produced. J. N. A.

**Vitamin-A activity of the stem of a *Mucor*.** W. H. SCHOPFER and A. JUNG (Compt. rend. Soc. Biol., 1935, 120, 1093—1095).—The stem of *Phycomyces oakesleeanus* when completely developed contains carotene and exhibits considerable vitamin-A activity. R. N. C.

**Slime-mould pigment as indicator of acidity.** W. SEIFRIZ and M. ZETZMANN (Protoplasma, 1935, 23, 175—179).—The yellow pigment,  $C_{13}H_{13}O_2N_4$ , of *Physarum polycephalum* changes from greenish-yellow at  $p_H$  8 to orange-red at  $p_H$  1. Within the mould the pigment shows changes in the plasmodium from  $p_H$  8 when fruiting to  $p_H$  1.6 when a sclerotium is formed. The pigment is probably a flavin. A. G. P.

**Nature of inhibition between certain fungi parasitic on citrus.** J. G. ARRILLAGA (Phytopath., 1935, 25, 763—775).—Inhibitory action of *Diaporthe citri* towards *Phytophthora parasitica* or *P. citrophthora* results from the action of metabolic products of *D. citri*. The inhibitory agent is not an enzyme, is diffusible, filterable, and relatively thermostable, and is constantly produced in various substrates whether *Phytophthora* is present or not. A. G. P.

**Influence of *Phytomonas tumefaciens* and *P. rhizogenes* on the actual acidity of certain liquid and agar substrates.** A. R. WILSON (Phytopath., 1935, 25, 854—863).—Differences in the rate and direction of  $p_H$  changes effected by these organisms in a no. of media are determined. On carrot infusion free  $NH_3$  is produced. A. G. P.

**Relation between sulphur in various forms and rate of growth of the colourless flagellate *Chilomonas paramecium*.** S. O. MAST and D. M. PACE (Protoplasma, 1935, 23, 297—325).—*Chilomonas* synthesises starch (I), fat, protein, and protoplasm from inorg. compounds, without intervention of light. Energy is probably derived from oxidation of  $NH_3$ . With all S compounds examined the rate of fission increases to a max. and subsequently declines as the S source is progressively increased. The optimum concn. of S varies with the source. Growth, fission, and synthesis of (I) and fat continue in the absence of S. With insufficient S fat accumulates (defective oxidation) and death ultimately occurs. Insufficient C causes death through (I)-starvation. Excessive S or C causes the formation of substances inhibiting cell division. Neither S nor C is necessary for fission. A. G. P.

**Role of bacteria, particularly anaerobes, in the corrosion of steel.** R. VEILLON (Compt. rend. Soc. Biol., 1935, 120, 1045—1047). R. N. C.

**Action of microbes on fats.** L. M. HOROVITZ-VLASOVA and M. J. LIVSCHITZ (Zentr. Bakt. Par., 1935, II, 92, 424—435).—Lipolysis by a no. of bacteria and fungi is indicated principally by the increased acid val. of the fatty phase. Glycerol is not detectable in cultures. The Nile-blue and "potash" tests are suitable for detecting lipolysis. Oxidation of fats by the organisms yields peroxides, OH-acids, and aldehydes and is indicated by the presence of labile O compounds (pyrogallol test), increased acidity in the aq. phase, lowered I val., and increased  $n$ . Neither the lipase nor the oxidative enzyme of moulds appears in the substrate. Bacterial lipase is thermostable. A. G. P.

**Phytochemical reduction of lactaldehyde.**—See this vol., 191.

**Optical properties of fermentation lactic acids. I. Bacteria producing inactive lactic acid.** H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 997—1007).—Yeast mashies for sake manufacture contain both *d* and *l*-lactic acid formers; the resultant lactic acid from the sake produced is optically inactive. P. G. M.

**Formation of succinic acid by *B. coli*. Production of succinic acid in relationship to synthesis of proteins.** M. MICHAELIS (Z. physiol. Chem., 1935,

237, 181—185).—Determination of lactic and succinic acid (I). EtOH, AcOH, and  $\text{HCO}_2\text{H}$  formed by the growth of *B. coli* in sucrose solutions in presence of increasing amounts of  $\text{NH}_3$  shows that only in the case of (I) does a relationship between yield and  $[\text{NH}_3]$  exist; with increasing  $[\text{NH}_3]$  the yield of (I) declines. No relationship exists between the yields of (I) and AcOH. Apparently (I) is a product of the fission of the sugar, and in presence of sufficient  $\text{NH}_3$  is transformed by aspartase through fumaric acid into aspartic acid and thence into proteins. H. W.

Nature of the "sporogenes vitamin," an essential growth factor for *Cl. sporogenes* and related organisms. A. M. PAPPENHEIMER, jun. (Biochem. J., 1935, 29, 2057—2063; cf. Fildes *et al.*, this vol., 113).—The isolation of a highly conc. prep. of the sporogenes growth factor (I) from a conc. HCl extract of the  $\text{C}_5\text{H}_5\text{N}$ -Et<sub>2</sub>O solution of the saponifiable and unsaponifiable material of mare's urine is described. (I) is probably an unsaturated OH-acid of mol. wt. 200, and is purified by distillation of its Me ester, which is inactive.  $0.04 \times 10^{-6}$  g. of (I) per ml. added to an  $\text{NH}_2$ -acid medium promoted visible growth of *sporogenes*. (I) is distinct from other growth factors previously described. A. L.

*Leptothrix echinata*, a new iron bacterium, precipitating principally manganese. H. BEGER (Zentr. Bakt. Par., 1935, II, 92, 400—406).—The Mn-accumulating properties of the organism are described. A. G. P.

Carotenoids of purple bacteria. I. P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1935, 18, 1306—1315).—The isolation (by extraction with various solvents and chromato-absorption) of the following cryst. carotenoids from purple bacteria (called strain Z, as yet unidentified) is described: *rhodoviolascin*, m.p. 218° (max. at 573.5, 534, 496  $\text{m}\mu$ ;  $\text{SbCl}_3$  compound, max. at 642  $\text{m}\mu$ ) (C 84.15, H 10.23%), *rhodopin*, m.p. 159—160° (547, 508, 478  $\text{m}\mu$ ) (C 82.83, H 10.58%), both of which contain 2 O, which is not OH, and *rhodopurpurin*, m.p. 161—162°,  $\text{C}_{40}\text{H}_{50}\text{O}_5$  (550, 511, 479  $\text{m}\mu$ ). An amorphous pigment *flavorhodin* (502, 472  $\text{m}\mu$ ) was also isolated. All absorption max. are in  $\text{CS}_2$ . J. W. B.

Action of some sulphur compounds on fermentation of glucose by propionic bacteria (*Propionibacterium* II). P. CHAIX (Compt. rend., 1935, 201, 857—858).—*Propionibacterium* II does not affect glucose in absence of S derivatives, but ferments it in presence of cystine, cysteine, or glutathione (I). Max. action occurs with a (I) concn. of 1 : 25,000. R. N. C.

Photochemical reactions of SH-compounds in solution.—See this vol., 171.

Utilisation of  $\text{CO}_2$  in the dissimilation of glycerol by propionic acid bacteria. H. G. WOOD and C. H. WERKMAN (Biochem. J., 1936, 30, 48—53).—The mechanism of formation of the products of fermentation of glycerol (I) is investigated. Yeast is incubated anaerobically with (I) and  $\text{CaCO}_3$  and the volatile and non-volatile acids formed, and the  $\text{CO}_2$  and (I) utilisation, are determined. AcOH, EtCO<sub>2</sub>H, PrCO<sub>2</sub>H, succinic and sometimes lactic acid were

isolated;  $\text{CO}_2$  obtained from  $\text{CaCO}_3$  is utilised by propionic bacteria in the fermentation of (I). H. D.

Sulphur bacteria in the "pink" waters of the Surakhani oil fields.—See this vol., 48.

New autotrophic and thermophilic sulphur-bacteria association. V. CZURDA (Zentr. Bakt. Par., 1935, II, 92, 407—414).—In sulphated hot springs (Pystian) organisms utilising S as an energy source included two variants of *Thiobacterium* and a new *Thiospirillum* (*T. pistiense*). A. G. P.

Specific polysaccharide from the bacillus Calmette-Guerin (BCG). E. CHARGAFF and W. SCHAEFER (J. Biol. Chem., 1936, 112, 393—405).—Sp. polysaccharides were obtained from BCG by the Heidelberger-Menzel method and separated into H<sub>2</sub>O-sol. and -insol. fractions which on purification gave polysaccharide A,  $[\alpha]_D + 77.4^\circ$ , containing mannose, arabinose, and small quantities of inositol, and polysaccharide S, sol. in acids, and containing  $\text{Ca}_3(\text{PO}_4)_2$ . A protein,  $[\alpha]_D^{25} - 50^\circ$ , is also prepared with weak tuberculin activity. The A and S fractions are haptens without antigenic activity. H. D.

Refractometric study of diphtheria toxin. C. SIEBENMANN (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 41—43).—Under const. conditions, the quantity of toxin produced by cultures of *B. diphtheriae*  $\propto$  the amount of bacterial growth, which in turn is correlated with the fall in  $n$  of the medium. In general, high toxin production is associated with low vals. of  $n$ . W. O. K.

Variations of  $p_H$  in culture media designed for the production of staphylococcal toxin. J. SCHWARTZ (Compt. rend. Soc. Biol., 1935, 120, 1085—1086). R. N. C.

Relation of growth to toxin production of the Dochez N.Y. 5 strain of hæmolytic streptococcus. H. C. PLUMMER (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 45—52).—With various carbohydrate-free media, the quantity of toxin formed is related to the extent of growth. In presence of glucose or maltose, growth, but not necessarily the quantity of toxin produced, is increased; at neutral reactions both growth and toxin are regularly increased. W. O. K.

Neutralising action of two streptococcal antisera. F. H. FRASER and H. C. PLUMMER (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 63—68).—Of the toxins produced by 174 strains of hæmolytic streptococci, 157 were neutralised by N.Y. 5 antitoxin, 15 of the remainder by Smith antitoxin, whilst 2 strains were neutralised only by a mixture of the two antitoxins. One toxin was neutralised by each of the two antitoxins separately. W. O. K.

Action of quinoline derivatives on pneumococci and streptococci *in vitro*. I. BÜHRMANN (Z. Immunität., 1935, 84, 300—307; Chem. Zentr., 1935, i, 2833—2834).—18 quinoline derivatives [mostly 6-hydroxyquinoline-4-carboxylic acid (I) and 4-amino-2-phenylquinoline (II) derivatives] were examined in 0.01% solution. The growth of pneumococci was inhibited by the hydrochlorides of (I) Pr<sup>a</sup> ester, 4-amino-6-hydroxyquinoline (III), (II), 4-amino-2-*p*-tolylquinoline (IV), Bu<sup>s</sup> 3-2-phenyl-4-



quinolylaminoacetate, and 3:4-dihydro-1:2-naphth-acridineamine (V). Growth of streptococci was inhibited by (II), (III), (IV), and (V). J. S. A.

**Lipins of tubercle bacilli. XL. Presence of sterols.** R. J. ANDERSON, R. SCHOENHEIMER, J. A. CROWDER, and F. H. STODOLA (*Z. physiol. Chem.*, 1935, 237, 40—45).—Only traces of sterol-like substances were found in the  $\text{COMe}_2$ -sol. fat and crude  $\text{CHCl}_3$ -sol. waxes. They probably arise from extraneous sources (cf. A., 1935, 407, 663).

F. O. H.

**Active immunisation in poliomyelitis.** S. FLEXNER (*Science*, 1935, 82, 420—421). L. S. T.

**Nature of filterable viruses.** R. G. GREEN (*Science*, 1935, 82, 443—445). L. S. T.

**Titration of the *L* and *S* antigens of vaccinia virus in extracts of the vaccinated skin of the rabbit, calf, and guinea-pig.** J. CRAIGIE and F. O. WISHART (*Trans. Roy. Soc. Canada*, 1935, [iii], 29, V, 57—62).—Extracts of infected skin contain both the *L* (heat-labile) and *S* (heat-stable) antigens as demonstrated by reaction with pure anti-*L*- and anti-*S*-serum. The presence of the same *L* and *S* antigens in the infected skin of three different species suggests that the antigens of vaccinia are sp. products of the virus analogous to bacterial antigens. W. O. K.

**Purification of bacteriophage by electrophoresis and its therapeutic use.** L. MARMIER and V. GRYZEZ (*Ann. Inst. Pasteur*, 1935, 55, 641—653).—Details are given for obtaining bacteriophage preps. free from protein material, which on intravenous injection do not produce anaphylactic shock. The bacteriophage loses but little of its activity in purification. P. G. M.

**Action of medicinal substances on the cell.** G. ROSKIN (*Z. Immunität.*, 1935, 84, 251—267; *Chem. Zentr.*, 1935, i, 2697).—The action of medicinal substances on trypanosomes can be detected by failure to form the blue dye from Rongalit-white, and by the shifting of the isoelectric point of the cells (indicator, methylene-blue). The sensitivity of *Paramecia* to quinine (I) fluctuates periodically; saccharated  $\text{Fe}_2\text{O}_3$  renders them more sensitive to (I) in acid than in alkaline solution. The sensitivity of *Paramecia* to ultra-violet light is increased in presence of dil. (I) solutions. R. N. C.

**[Trypanocidal action of] antimony compounds.** F. G. CAWSTON (*Vet. Rec.*, 1935, 15, 1280).—Stibilase and trystibine are more effective than tartar-emetic against trypanosomes and schistosomes. R. N. C.

**Synthesis of chemotherapeutic compounds.**

**Synthetic "Naganin" in the U.S.S.R.** I. L. KRITSHEVSKI and I. S. MEERSON. II. Quinoline derivatives [for use] against malaria. I. L. KRITSHEVSKI and E. J. STERNBERG (*Z. Immunität.*, 1935, 79, 180—186, 438—459; *Chem. Zentr.*, 1935, i, 2843).—I. The synthesis of a compound as active against trypanosomes as "Fournau 309" is claimed.

II. A no. of 8-substituted aminoquinolines have been studied with regard to their action against d-malaria. 8- $\gamma$ -Diethylaminopropylamino-6-methoxyquinoline ("Plasmizide") has a therapeutic

index of 26.6; the corresponding OH-compound is also active. Lengthening of the C-chain in position 8 and the introduction of branched chains lower the val. of the product. H. N. R.

**Germicidal efficiency of chloramine-T and calcium hypochlorite.**—See B., 1936, 46.

**Integration of the endocrine system.** (Sir) W. LANGDON-BROWN (*Lancet*, 1935, 229, 1155—1161).—A lecture. L. S. T.

**Endocrine organs of the blue whale.** A. P. JACOBSEN (*Nature*, 1935, 136, 1029).—The presence of various hormones in the pituitary, thyroid, pancreas, ovary, and corpus luteum graviditatis is described. L. S. T.

**Reversion of the action of adrenaline and other active substances.** V. SUSANNA (*Arch. Int. Pharm. Ther.*, 1935, 49, 460—469; *Chem. Zentr.*, 1935, i, 2836).—Ergotamine reverses the pressor action of adrenaline, pituitrin, eserine, ephedrine, racetrine, strychnine,  $\text{NMe}_3$ , and  $\text{NH}_2\text{Bu}$ . Ethylurethane and chloral are without influence. A. G. P.

**Comparative study of sympathin and adrenaline.** W. B. CANNON and A. ROSENBLUETH (*Amer. J. Physiol.*, 1935, 112, 268—276).—The effects of sympathin from different sources in the cat are compared with those of adrenaline (I) on physiological indicators. It is concluded that there are two sympathins, one excitatory and the other inhibitory; the latter differs from acetylcholine, and both differ from (I). R. N. C.

**Response of the hyperthyroid heart to adrenaline.** C. H. McDONALD, W. L. SHEPARD, M. F. GREEN, and A. F. DE GROAT (*Amer. J. Physiol.*, 1935, 112, 227—230).—Prolonged thyroid feeding to terrapins increases the rate of  $\text{O}_2$  consumption in the isolated heart and the response of the rate of  $\text{O}_2$  consumption to adrenaline. R. N. C.

**Action of the hormone of adrenal cortex on the glycogen content of the liver.** H. A. HOCHFELD (*Biochem. Z.*, 1935, 282, 392—398).—In rats the glycogen content of the liver, after a 24-hr. fast, is progressively increased by administration of fat, of the hormone, and of fat + hormone. Possibly the hormone stimulates conversion of fat into carbohydrate. W. McC.

**Adrenaline and sugar content of foetal blood.** O. MACCHIARULO (*Arch. Gynakol.*, 1935, 159, 349—354).—Variable amounts of adrenaline (I) were detected in the blood and urine of infants following birth; comparable amounts were present 8 days later. There was no relationship between the sugar and (I) of the blood. (I) was present in the maternal blood several days before delivery and increased during labour. NUTR. ABS. (m)

**Tono-glycaemic index of adrenaline.** B. ENOCKSSON and A. GIERTZ (*Acta med. Scand.*, 1934, 59, Suppl., 116—126).—There is a relation ("tono-glycaemic index") in normal men between the hyperglycaemic and pressor actions of adrenaline, injected subcutaneously. This is about 3 in normal men and about 7 in normal women. Its variability depends chiefly on that of the pressor effect. The

hyperglycæmic and pressor effects in women are respectively  $>$  and  $<$  those in men. The dissociation of the two effects becomes manifest in certain diseases; the index rises in hypertonia and asthma, and falls in jaundice. R. N. C.

**Adrenaline in the venom of *Bufo arenarum*.** V. DEULOFEU (Z. physiol. Chem., 1935, 237, 171—172).—0.18 mg. of adrenaline was isolated from 45 g. of the dried venom. W. McC.

**Effect of continuous injection of adrenaline on the ketone content of the urine.** A. BAUDOUIN, H. BENARD, J. LEWIN, and J. SALLET (Compt. rend. Soc. Biol., 1935, 120, 860—862).—Urinary ketones in the dog are increased slightly by chloralose anaesthesia, and very considerably by continuous injection of adrenaline. The acidosis produced is  $<$  in diabetics. R. N. C.

**Inactivation of histamine in perfused organs.** F. R. STEGGERDA, H. E. ESSEX, and F. C. MANN (Amer. J. Physiol., 1935, 112, 70—73).—The kidneys and (less) the liver are most effective in inactivating histamine. R. N. C.

**Effect of dietary lipæmias on the insulin and adrenaline blood-sugar curves.** H. J. HAMBURGER (Klin. Woch., 1935, 14, 96—97).—The insulin blood-sugar curve in children fed with albumin paste containing cholesterol and pig's bile shows a fall  $>$  normal; the rise produced by adrenaline is weakened. R. N. C.

**Hypoglycæmic action of insulin in dogs with the pancreatic duct ligatured, and with or without secondary fatty degeneration of the liver.** E. AUBERTIN and E. CASTAGNOU (Compt. rend. Soc. Biol., 1935, 120, 1101—1104).—Ligature of the pancreatic ducts does not diminish the response to insulin in an otherwise healthy animal. Fatty degeneration of the liver causes a broadening of the blood-sugar curve, recovery being much slower. R. N. C.

**Hypoglycæmic action of insulin phosphotungstate and phosphotungstic acid administered by mouth.** H. N. MUKHERJEE (J. Physiol., 1935, 84, 362—366).—Insulin phosphotungstate suspension in phosphotungstic acid (I) solutions, or (I) alone, produces hypoglycæmia when administered to rabbits by mouth; the effect is apparently due to both constituents. R. N. C.

**Augmentation of the physiological response to insulin.** L. C. MAXWELL and F. BISCHOFF (Amer. J. Physiol., 1935, 112, 172—175).—The response to insulin in rats and rabbits is augmented by addition of basic  $\text{Fe}^{III}$  chloride to the insulin. R. N. C.

**Continuous injection of insulin in the dog: threshold dose by the intra-arterial and the mesenteric-intravenous routes.** A. BAUDOUIN, J. LEWIN, and E. AZERAD (Compt. rend. Soc. Biol., 1935, 120, 865—866).—The threshold dose by either route is approx. 0.01 unit per kg. per hr. R. N. C.

**Effect of hypophysectomy and cerebral manipulation in the dog on the response of the blood-sugar and -inorganic phosphorus to insulin.** I. L. CHAIKOFF, F. L. REICHERT, P. S. LARSON, and M. E. MATHES (Amer. J. Physiol., 1935, 112, 493—

503).—The response of blood-sugar and -inorg. P to insulin is augmented to successively increasing extents by craniotomy, radial incision of the dura, retraction of the right temporal lobe, and complete hypophysectomy. R. N. C.

**Continuous injection of insulin in the dog. Threshold dose by the peripheral intravenous route.** A. BAUDOUIN, E. AZERAD, and J. LEWIN (Compt. rend. Soc. Biol., 1935, 120, 769—771).—The threshold dose is about 0.05 unit per kg. per hr. R. N. C.

**Excretion of insulin by the dog.** J. A. SHANNON (Amer. J. Physiol., 1935, 112, 405—413).—The rate of insulin (I) excretion  $\propto$  plasma concn. of (I) between 0.013 and 0.565%. Intravenous injection of (I) does not affect the urea, xylose (II), or creatinine (III) excretion. The simultaneous excretion ratio of (III) and (I) is about 0.994. (II) excretion with moderate to high urine vols. is  $<$  the simultaneous (I) excretion (mean ratio 0.734). Phloridzin raises the glucose excretion to the level of that of (III) or (I), the excretion of (II) increasing to  $>90\%$  of that of (I). R. N. C.

**Reactions of ammonolysed parathyroid hormone.** R. G. ROBERTS, W. R. TWEEDY, and G. H. SMULLEN (J. Biol. Chem., 1935, 112, 209—214).—Parathyroid hormone (I) reacts as a typical protein with Na in liquid  $\text{NH}_3$ . The activity of (I) varies inversely with the liberation of the acidic  $\text{H}_2$ , and is diminished by the action of  $\text{NH}_3$  alone; it is not dependent on  $\text{S}\cdot\text{S}\cdot$  or any linkings readily reduced by  $\text{Na}\cdot\text{NH}_3$ . (I) has no prosthetic group (either with or without Fe) which catalyses the action of Na on  $\text{NH}_3$ . J. N. A.

**Action of small doses of parathyroid hormone on the magnesium of the organism.** M. COPPO and M. PISA (Z. ges. exp. Med., 1935, 95, 675—678; Chem. Zentr., 1935, i, 2390).—Total Mg and ash in the body of the rat are reduced by administration of 1 unit of parathormone (I) a day. The action of (I) on mineral metabolism probably results from its effect on Mg. R. N. C.

**Relation of contracture and tetany to experimentally-produced calcium deficiency in cats, with and without lesions of the cortical motor areas.** H. C. COOMBS, F. H. PIKE, and D. S. SEARLE (Endocrinol., 1935, 19, 421—431). R. N. C.

**Idiopathic hypoparathyroidism and tetany in the fowl.** F. B. HUTT and W. L. BOYD (Endocrinol., 1935, 19, 398—402).—A case is reported of a pullet with tetany and low blood-Ca, due to temporary idiopathic hypoparathyroidism. Parathormone, but not Ca gluconate, showed a curative effect. R. N. C.

**Depressor hormone as the origin of protein shock.** G. DE NITO (Deut. med. Woch., 1935, 61, 339—341).—Lymphoganglin (I), formed in the lymph glands, is considered to be the most important depressor factor of the animal organism. Injection produces effects characteristic of protein shock. Protein shock is probably due to (I) being discharged by the lymph glands on stimulation of the lymphatic

system by the foreign protein. A (I)-like substance can be extracted from plants. R. N. C.

**Existence of prosecretin.** V. B. SCOTT and E. U. STILL (Amer. J. Physiol., 1935, 112, 511—517).—Of the secretin (I) present in untreated duodenal mucosa one fraction is extracted by neutral 0.9% NaCl, and the other completely by acids, and partly by weak bases and aq. EtOH. (I) is present in the mucosa if digestive acids have been excluded. The prosecretin (II) theory of Bayliss and Starling is not considered to be entirely tenable; the acid-sol. (I) is probably held by adsorption on the protein mols., and, if (II) exists, by combination. R. N. C.

**Role of duodenal hormones (secretin) in carbohydrate metabolism.** J. LA BARRE (Bull. roy. Acad. Med. Belg., 1934, 14, 469—486).—A lecture. R. N. C.

**Effect of lactogenic hormone preparations on the blood-sugar level of rabbits and monkeys.** W. O. NELSON, C. W. TURNER, and M. D. OVERHOLSER (Amer. J. Physiol., 1935, 112, 714—717).—Lactogenic hormone preps., believed to be relatively free from other pituitary hormones, do not affect blood-sugar in either species. R. N. C.

**Action of pituitrin on venous blood pressure.** V. I. VON GONCZY and J. KISS (Z. ges. exp. Med., 1934, 94, 400—404; Chem. Zentr., 1935, i, 2835).—In most cases the pressure is increased by injection of pituitrin. Negative results sometimes obtained are associated with a predominance of histamine-like substance in the pituitrin prep. A. G. P.

**Acetonuria after administration of the (pituitary) fat-metabolism hormone.** K. J. ANSELMINO and F. HOFFMANN (Z. ges. exp. Med., 1934, 94, 305—308; Chem. Zentr., 1935, i, 2835; cf. A., 1935, 411).—Administration of the hormone increased the COME<sub>2</sub>, AcOH, and  $\beta$ -hydroxybutyric acid contents of blood and urine. A. G. P.

**Erythrophore and melanophore hormone.** A. JORES and G. WILL (Z. ges. exp. Med., 1934, 94, 389—393; Chem. Zentr., 1935, i, 2690).—The melanophore hormone (I) is not identical with Zondek's erythrophore hormone (II). (I) is > (II) in the basophile section of the pre-pituitary, whilst in the anterior lobe the (I)/(II) ratio is inverted. H<sub>2</sub>O extracts only a small quantity of (I) from pituitary powder, but the activity of the extract is increased considerably by treatment with alkali or contact with food, suggesting that the extract contains an inactive precursor of (I). The (II) potency of the extract is weakened by this treatment. (II) is extracted completely, but (I) only partly, from the powder by repeated treatment with 0.6% NaCl. (II) is readily sol. EtOH, but (I) only with difficulty. R. N. C.

**Melanophore hormone and adrenals.** A. JORES and H. BECK (Z. ges. exp. Med., 1934, 94, 295—299; Chem. Zentr., 1935, i, 2690).—The adrenal cortex is increased in size in rabbits or rats by injection of melanophore hormone (I). The adrenaline content is also increased. (I) may be identical with the corticotropic hormone. R. N. C.

**Influence of various hormones on spread of melanophores caused by posterior pituitary lobe extract.** H. MATSUDA (Folia Pharmacol. Japon., 1935, 19, 377—393). CH. ABS. (*p*)

**Effect of the thyrotropic hormone of the pituitary on blood-function.** S. THADDEA and A. WALY (Z. ges. exp. Med., 1934, 94, 359—369; Chem. Zentr., 1935, i, 2690). R. N. C.

**Comparison of the actions of the corticotropic hormone of the anterior pituitary in different species of animals.** K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Z. ges. exp. Med., 1934, 94, 323; Chem. Zentr., 1935, i, 2690).—The hormone acts similarly on the adrenals in rats, guinea-pigs, rabbits, and mice. The growing male mouse is best suited for assay. R. N. C.

**Action of alkaline anterior pituitary extract on the mineral substances of the plasma.** R. GERSONMAN and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 817—820).—In normal and thyroidectomised dogs the extract evokes an increase of total plasma-CO<sub>2</sub>, sugar, Ca, Mg, and inorg. P, and a fall of Cl and Na. The Ca increase appears in hypophysectomised, but not thyro-parathyroidectomised, dogs. R. N. C.

**Cows' milk as a possible excretory source of the anterior pituitary-like hormone.** A. I. WEISMAN, I. S. KLEINER, and E. ALLEN (Endocrinol., 1935, 19, 395—397).—The hormone is absent from pregnancy milk. R. N. C.

**Influence of pituitary growth-hormone on the phosphatase activity of bone and kidney.** W. E. WILKINS, J. A. CALHOUN, C. PILCHER, and E. M. REGEN (Amer. J. Physiol., 1935, 112, 477—480).—The phosphatase activity of the bones and kidney of the adult rat is slightly reduced. R. N. C.

**Growth-promoting hormone and tumour growth.** P. ENGEL (Z. Krebsforsch., 1935, 41, 488—496; Chem. Zentr., 1935, i, 2835).—The tumour-stimulating action of the pituitary growth-hormone is lowered by simultaneous injection of "preptan," but not by that of gonadotropic hormone. The direct inhibitory action of the latter on tumour growth is due to its influence on metabolic changes. A. G. P.

**Action of posterior pituitary hormone on the blood-sugar of the rabbit.** H. C. ELLSWORTH (J. Pharm. Exp. Ther., 1935, 55, 435—438).—Pitressin increases blood-sugar in very high doses only; pitocin is without effect. R. N. C.

**Posterior pituitary and carbohydrate metabolism.** F. HOGLER and F. ZELL (Wien. Arch. inn. Med., 1935, 27, 141—158).—In rabbits the posterior pituitary hormone affects carbohydrate metabolism. Tonephin acts on the liver cell, mobilising glycogen and raising blood-sugar. Hence injuries to the posterior pituitary may cause disturbances of carbohydrate metabolism. NUTR. ABS. (*m*)

**Chemistry of the pituitary gonadotropic hormone.** L. C. MAXWELL and F. BISCHOFF (J. Biol. Chem., 1935, 112, 215—221; cf. Wallen-Lawrence, A., 1934, 1039).—Partial or complete inactivation

of pituitary powder results from treatment with powerful oxidising agents and substances which react with  $\text{NH}_3$ ,  $\text{NH}_4$ , and  $\text{OH}$ , but mild oxidising and reducing agents have no effect. In 3 hr. at  $37^\circ$  0.1N-NaOH produces complete, whilst 0.033N-NaOH and 0.1N-HCl produce partial, inactivation. There is no evidence that the preps. contain two hormones, and  $\text{CH}_2\text{O}$ , although it produces inactivation, does not exert a selective destructive action.

W. McC.

**Prolan excretion in senility.** H. SAETHRE (Acta med. Scand., 1934, 59, Suppl., 440—442).—Prolan excretion is high in old women, but absent in girls of 13—15 years. Healthy men excrete about 5 mouse units per litre of urine, but elderly men almost as much as elderly women.

R. N. C.

**Effect of adrenals and pituitary on regulation of blood-pressure and inversion of the sex characters in man.** J. BAUER (Acta brev. Neerl. Physiol., 1934, 4, 157—161).—Theoretical.

R. N. C.

**Oxytocic properties of blood extracts and their physiological significance.** G. H. BELL and J. M. ROBSON (J. Physiol., 1935, 84, 351—361).—Oxytocic activity has been found in a no. of extracts from the blood of pregnant cows, women in labour, and rabbits before and after injection of posterior pituitary extract. The extracts also contain a factor inhibiting the reaction of the uterus to oxytocin *in vitro*; this activity increases on keeping.

R. N. C.

**Chemistry of oestrogenic substances.** J. W. COOK, E. C. DODDS, and F. L. WARREN (Nature, 1935, 136, 912—913).—Previous work is confirmed (cf. A., 1935, 1033, 1173).

L. S. T.

**Pineal gland and gonadotropic hormone.** P. ENGEL (Z. ges. exp. Med., 1934, 94, 333—345; Chem. Zentr., 1935, i, 2692).—The extract from  $\text{CO}_2$ -dried pineal powder with 0.5% alkali acts antagonistically to the gonadotropic hormone (pre-pitan).

R. N. C.

**Rate of disappearance and fate of mare's gonadotropic hormone following intravenous injection.** H. R. CATCHPOLE, H. H. COLE, and P. B. PEARSON (Amer. J. Physiol., 1935, 112, 21—26).—The hormone (I) after injection in large quantities in the rabbit and gelding disappears from the blood without being excreted or stored. The rate of disappearance in the gelding is  $>$  in the pregnant mare. Castration of the rabbit does not affect the rate of disappearance of (I). Thus (I) is not prolan, which is excreted in the urine.

R. N. C.

**Influencing of the time of coagulation of blood by the sex hormone and its variation in hormonal hermaphroditism and experimental sex changes.** E. LUNDBERG (Acta med. Scand., 1934, 59, Suppl., 432—438).—Injection of folliculin in growing female rabbits shortens the time of coagulation of the blood by approx. 50%; the effects appear 1—2 hr. after injection, and persist for  $>$  24 hr. In man the time is shortened by approx. 20%. There is little reaction in young female animals, and none in infants.

R. N. C.

**Hormones of the corpus luteum.** E. JARLOV (Acta. med. Scand., 1934, 59, Suppl., 438—440).—Corner's corpus luteum extract is adsorbed on excess of kieselguhr and the powder exhaustively extracted with  $\text{H}_2\text{O}$ . The extract, which should contain only folliculin (I), exhibits an action ("pre-pregnancy reaction") on the rabbit's uterus. Pure (I) preps. give the reaction only at certain places in the uterus.

R. N. C.

**Crystalline by-product obtained in large-scale extraction of theelin and theelol.**—See this vol., 214.

**Presence, in the urines of certain women, of a substance antagonistic to the oestrous hormones.** A. DURUPT, J. LAGARDE, and P. BREGOU (Compt. rend. Soc. Biol., 1935, 120, 852—853).—The antagonistic substance appears in the urine of dysmenorrhœics.

R. N. C.

**Standardisation of sex-stimulating substances: therapeutic efficiency.** E. LAQUEUR (Klin. Woch., 1935, 14, 339—341).—The min. dose of ketohydroxy-oestrin (I) necessary to produce "heat" in the castrated rat is 10—16 times that necessary for mice, whilst the rat unit of oestradiol monobenzoate (II) is 4 times the mouse unit. Hence the rat is 4—5 times as sensitive to (II) as to (I); in mice the two substances are equally potent.

R. N. C.

**Effects of the oestrogenic and the galactopoietic hormones on the mammary gland of the rabbit.** W. U. GARDNER, E. T. GOMEZ, and C. W. TURNER (Amer. J. Physiol., 1935, 112, 673—683).

R. N. C.

**Effect of injection of residual ovarian extracts.** H. W. MARLOW and F. GROETSEMA (Endocrinol., 1935, 19, 415—420).

R. N. C.

**Inhibition of thyroid activity by the follicular hormone (menformone).** J. G. HEYL, S. E. DE JONGH, and R. KOOR (Acta brev. Neerl. Physiol., 1934, 4, 126—127).

R. N. C.

**Inhibition of the oestrogenic effect of follicular hormone by progestin.** P. DE FREMERY, S. KOBER, and M. TAUSK (Acta brev. Neerl. Physiol., 1934, 4, 119—121).—The effect of the min. oral dose of oestrin in spayed mice is inhibited by 3 rabbit units of progestin injected simultaneously.

† C

**Isolation of folliculin and equilenin by chromatographic adsorption.** R. DUSCHINSKY and E. LEDEBER (Bull. Soc. Chim. biol., 1935, 17, 1534—1539).— $\alpha$ -Folliculin (I) is readily isolated from the  $\text{C}_6\text{H}_6$  extract of pregnant mares' urine after adsorption on  $\text{CaCO}_3$ ; with  $\text{Al}_2\text{O}_3$ , (I) and equilenin (II) are adsorbed, (II) being isolated as picrate.

A. L.

**Equilin prepared from pregnant mare urine.** G. F. CARTLAND and R. K. MEYER (J. Biol. Chem., 1935, 112, 9—14).—Equilin (I) prepared by Girard's method and further recrystallisation from EtOH has m.p. 238—240°,  $[\alpha]_D^{25} +331^\circ$  in EtOH. Assayed biologically in 10% aq. EtOH + 0.5%  $\text{Na}_2\text{CO}_3$ , the product has approx. 75% of the activity of standard theelin (II); assayed without the addition of  $\text{Na}_2\text{CO}_3$  its biological activity is only 30% that of (II). Colorimetrically (cf. A., 1935, 791) (I) has approx. 11% o



the val. of (II); this val. is not altered during the final recrystallisations. F. A. A.

**Difference between "male hormone" extracts from urine and from testicles in hypophysectomised rats.** J. FREUD (Acta brev. Neerl. Physiol., 1934, 4, 145—147).—The response of the seminal vesicles, ventral prostate, and periurethral tissue in hypophysectomised rats to testicle extracts is considerably > to male urine extracts. The "male hormone" of the testicle extracts is considered therefore to be different from that of the urine, or to be associated with some "co-substance" which acts synergistically. R. N. C.

**Use of gonadotropic hormones in the treatment of imperfectly-migrated testes.** A. W. SPENCE and E. F. SCOWEN (Lancet, 1935, 229, 1335—1338). L. S. T.

**Enzymic determination of vitamins.** F. PIRONE (Annali Chim. Appl., 1935, 25, 292—309).—The action of solutions of vitamin-A, -B, -C, and -D, of known biological activity, on the alcoholic fermentation of sucrose is studied by means of the CO<sub>2</sub> evolved. Acceleration of the fermentation (X)  $\propto$  concn. of the vitamin. The vitamin units are given by the following expressions: for -A and -D,  $11.36 \times (X-100)+23$ ; for -B,  $0.0823(X-100)+2.34$ ; for -C,  $0.0625(X-100)+0.19$ . T. H. P.

**Absorption of carotene and vitamin-A.** J. C. DRUMMOND, M. E. BELL, and E. T. PALMER (Brit. Med. J., 1935, ii, 1208—1210).—The carotene (I) and vitamin-A (II) content of the chylous fluid of a patient suffering from an effusion of chyle into the thoracic cavity were studied before and after oral administration, on separate occasions, of (II) (0.125 mg. in 9 days) and (I) (100 mg. in 7 days). A rise of the level of both followed the administration, but, relative to the amount ingested, was much more marked in the case of (II). Little (I) and (II) could be extracted directly from the fluid with Et<sub>2</sub>O, but treatment with EtOH rendered (I) easily extractable. (II) was present as ester. NUTR. ABS. (m)

**Do the ascorbic acid contents of the organs of the rat vary according to the presence or absence of vitamin-A in the diet?** L. RANDOIN, A. GROUD, and C. P. LEBLOND (Compt. rend. Soc. Biol., 1935, 120, 1082—1085).—Ascorbic acid is high in the organs of the rat, the presence or absence of vitamin-A causing no important variations. R. N. C.

**Determination of vitamin-A in body-fluids.** ROSENTHAL (Klin. Woch., 1935, 14, 307; Chem. centr., 1935, i, 2554).—Wendt's method gives uncertain results. The author's colour test (A., 1934, 149, 1413) is suitable for sera and other body-fluids. A. G. P.

**Determination of vitamin-A by means of its influence on the vaginal contents of the rat.** K. H. COWARD, M. R. CAMDEN, and E. M. LEE (Biochem. J., 1935, 29, 2736—2741).—The disappearance of keratinised cells from the vaginal smears of rats deficient in vitamin-A on feeding -A is used as a basis for the assay of -A. Results are rather less accurate than by the growth response method. H. D.

**Antineuritic vitamin. IV.** A. WINDAUS, R. TSCHESCHE, and R. GREWE (Z. physiol. Chem., 1935, 237, 98—104; cf. A., 1934, 1415).—Oxidation with BaMn<sub>2</sub>O<sub>8</sub> of the sulphate of the vitamin, removal of Ba, SO<sub>4</sub>, and Mn oxides from the solution, concn. in a vac., and treatment with picronic acid yields the picrolonate (I) of a base (II), C<sub>6</sub>H<sub>10</sub>N<sub>4</sub> (probably 5:6-diamino-2:4-dimethylpyrimidine) [hydrochloride (III), m.p. 265° (decomp.); picrate, m.p. 224.5° (decomp.)]. The liquors from (III) yield a second base, subliming at 110—120°/13 mm. (hydrochloride, m.p. 224°), probably the Ac derivative of (II). The liquors from (I) yield two cryst. fractions, m.p. 180° and 225°, of acidic character, containing N but free from S and Cl. The structure of vitamin-B<sub>1</sub> is discussed. F. O. H.

**Consumption of the antineuritic factor in the oryzanin feeding of different birds.** G. MARTINO (Boll. Soc. ital. Biol. sperim., 1935, 10, 300—302; cf. A., 1934, 460, 706). R. N. C.

**Is lactic impregnation of the tissues the true cause of avian polyneuritis?** R. LECOQ (Compt. rend. Soc. Biol., 1935, 120, 958—961).—Addition of lactic acid to the diet increases the vitamin-B requirements of the pigeon, and the normal protective doses of yeast for polyneuritis are no longer effective. R. N. C.

**Isolation of pyruvic acid from the blood of vitamin-B<sub>1</sub>-deficient pigeons.** R. E. JOHNSON (Biochem. J., 1936, 30, 31—32).—AcCO<sub>2</sub>H has been isolated as the 2:4-dinitrophenylhydrazone from the blood of vitamin-B<sub>1</sub>-deficient pigeons. AcCHO is not present. J. N. A.

**Content of vitamin- in (A) germinating wheat, (B) Italian wheats.** V. FAMIANI (Atti R. Accad. Lincei, 1935, [vi], 22, 84—85, 86—88).—(A) The vitamin-B<sub>1</sub> content of wheat tends to increase during germination.

(B) Data for 8 varieties are given. F. O. H.

**Gastro-intestinal symptoms of vitamin-(B) deficiency.** E. SCHTODT (Acta med. Scand., 1935, 84, 456—495). R. N. C.

**Extraction and stabilities of vitamin-B<sub>1</sub> and of lactoflavin.** B. BISBEY and H. C. SHERMAN (J. Biol. Chem., 1936, 112, 415—420).—Vitamin-B<sub>1</sub> is almost completely extracted from dried milk by 80% EtOH but scarcely at all by abs. EtOH; about half of the lactoflavin is extracted by 80% EtOH, the remainder being found active in the residue. H. D.

**Lactoflavin (vitamin-B<sub>2</sub>).** R. KUHN (Angew. Chem., 1936, 49, 6—10).—A lecture.

**Growth-promoting activity of l- and d-araboflavin [6:7-dimethyl-9-l-(or d-)-1'-arabityliso-alloxazine].** H. VON EULER, P. KARRER, and M. MALMBERG (Helv. Chim. Acta, 1935, 18, 1336—1338; cf. A., 1935, 1286).—Growth in rats given 10—40  $\times 10^{-6}$  g. daily doses of l-araboflavin (*ibid.*, 1134) ceases after 30—40 days, and even with the latter dose no const. growth-promoting activity is observed. Doses of 10  $\times 10^{-6}$  g. of d-araboflavin produce a const. wt. increase of 0.8 g. per day over the period of observation (50 days). Doses of 10  $\times 10^{-6}$  g. of l-riboflavin

and  $3 \times 10^{-6}$  g. of the *d*-form produce wt. increases of 1.3 g. and 0.9 g. per day, respectively. The synthetic stereoisomeride thus exhibits higher growth-promoting activity than does natural lactoflavin, although it differs only in the stereoisomerism of one OH in the sugar residue.

J. W. B.

**Vitamin- $B_2$  complex.** Differentiation of anti-blacktongue and "P.-P." factors from lactoflavin and vitamin- $B_6$  ("rat pellagra" factor). I—VI. T. W. BIRCH, P. GYORGY, and L. J. HARRIS (Biochem. J., 1935, 29, 2830—2850).—Data for the distribution of human pellagra-preventing ("P.-P.") factor (I), vitamin- $B_6$  ("rat pellagra" factor) (II), and lactoflavin (III) in various foodstuffs are tabulated. Rats fed on (I)-producing diets (A., 1929, 476) remain free from skin lesions; such diets cure (II)-deficiency disease. Hence rat pellagra is not analogous to human pellagra, rats having no need of, or being able to synthesise, (I). With maize diets (*ibid.*) containing (II), dogs develop "blacktongue," a condition rapidly cured by administration of autoclaved yeast, fresh fish, or anti-anæmia prep., but not of (III). The anti-blacktongue factor is therefore distinct from (II) and (III), but may be identical with (I). The "chicken pellagra" of Elvehjem and Koehn (A., 1935, 669) appears to be distinct from (II)-deficiency; its relation to human pellagra and blacktongue is not clear. The term "rat acrodynia factor" is proposed for (II). The extrinsic factor for pernicious anæmia (A., 1932, 1156) appears to be different from (II) or (III). Factors in the vitamin- $B_2$  complex are discussed.

F. O. H.

**Maintenance nutrition in the pigeon.** Influence of dietary protein and vitamin- $B_3$ . C. W. CARTER and J. R. O'BRIEN (Biochem. J., 1935, 29, 2746—2754).—For the normal growth of pigeons a diet of polished rice plus vitamin- $B_1$  must be supplemented with protein and - $B_3$  (liver concentrates).

H. D.

**Maintenance nutrition in the pigeon.** Vitamin- $B_3$  concentrates. C. W. CARTER and J. R. O'BRIEN (Biochem. J., 1936, 30, 43—47).—A prep. containing vitamin- $B_3$  activity is obtained by extraction of liver with 97% EtOH, concn. and addition of Et<sub>2</sub>O, extraction with H<sub>2</sub>O, and addition of COMe<sub>3</sub>.

H. D.

**"Enteral" vitamin- $I-B_7$ .** Behaviour of the vitamin towards primary alcohols. E. CENTANNI (Biochim. Terap. sper., 1935, 22, 137, 153).—The extract obtained from rice polishings with 95—100% EtOH, administered to pigeons on a diet of polished rice, did not protect from progressive emaciation ending fatally, but prevented digestive disturbances. The same extract, administered orally or intravenously, stimulated appetite markedly. The existence of an "enteral" vitamin (*I-B*.) regulating the digestive functions is therefore affirmed. MeOH (most effective), Pr<sup>o</sup>OH, Bu<sup>o</sup>OH, and C<sub>5</sub>H<sub>11</sub>·OH extracted the vitamin from rice polishings, in varying degree. The vitamin probably consists of several factors.

NUTR. ABS. (m)

**Behaviour of the enteral vitamin towards solvents.** E. MONTEVECHI (Biochim. Terap. sper., 1935, 22, 143).—The vitamin is insol. in fat solvents,

but sol. in 95% EtOH, which does not extract the antineuritic and growth-promoting vitamins. With 70% EtOH, the last two are completely, the first partly, extracted from rice polishings.

NUTR. ABS. (m)

**Synthesis of ascorbic acid in the tissues *in vitro*.** M. LAPORTA and E. RINALDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 319—322).—Minced animal tissues in Ringer-Locke solution at *p*<sub>H</sub> 7.38 in presence of sugars, or their H<sub>2</sub>O or glycerol extracts, show no definite increase in their ascorbic acid content; the results of Guha and Ghosh (cf. A., 1935, 416) are not confirmed.

R. N. C.

**Cellular fixation and non-fixation of ascorbic acid in dystrophies from avitaminosis-C.** G. MOURIQUAND and A. COEUR (Compt. rend. Soc. Biol., 1935, 120, 1007—1009).—The Giroud-Leblond reaction after administration of ascorbic acid in avitaminosis-C is negative in certain cases.

R. N. C.

**Effect of thyroxine on vitamin-C metabolism.** J. MOSONYI (Z. physiol. Chem., 1935, 237, 173—177; cf. Demole *et al.*, A., 1935, 1423).—In guinea-pigs (but not in rats) administration of thyroxine or extract of thyroid gland markedly decreases the ascorbic acid (I) content of the adrenals and slightly decreases that of the liver. Simultaneous administration of vitamin-A counteracts the effect. In rats extirpation of the thyroid gland increases the (I) content of the adrenals (but not that of the liver), apparently due to increased synthesis in the adrenals.

W. McC.

**Seasonal variation in vitamin-C content of the organism.** F. IPPEN (Schweiz. med. Woch., 1935, 66, 431—432).—In healthy people receiving 200 ml. of orange juice by mouth or 0.1 g. of ascorbic acid orally or intravenously the urinary excretion of vitamin-C (I) showed a max. in all cases after 1 hr. Low curves are held to indicate a (I) deficit in the organism.

NUTR. ABS. (m)

**Polyploidy and vitamin-C.** F. W. SANSOME and S. S. ZILVA (Biochem. J., 1936, 30, 54—56; cf. A., 1934, 227).—There is no evidence that the ascorbic acid content of tomatoes is conditioned by their size (McHenry, A., 1935, 1287).

H. D.

**Effect of incomplete diets on concentration of ascorbic acid in the rat's organs.** Identity of ascorbic acid and the reducing agent of rat's gut. F. G. HOPKINS [with B. R. SLATER and G. A. MILLIKAN] (Biochem. J., 1935, 29, 2803—2819).—With rats on a normal mixed diet, the concn. of ascorbic acid (I) in liver and gut is 0.26 mg. per g. After a 48-hr. fast, the level in the gut rises to 0.40 mg., whilst that in the liver is unaffected. With diets of carbohydrate (II) alone, the concn. of (I) in the liver rises to 0.33 mg., whilst that in the gut remains normal; with protein+fat or fat alone, the liver and gut vals. are 0.19 and 0.37 mg., respectively. Diets of protein+(II) or of fat+(II) produce no significant effect. Determination of the velocity of reduction of 2:6-dichlorophenol-indophenol indicates the identity of the reducing agent in CCl<sub>3</sub>·CO<sub>2</sub>H extracts of rat's gut with (I). The bimol. coeff. of reduction

is unaffected over a considerable range of concn. of (I) and dye (cf. A., 1934, 1145). F. O. H.

**Reversible oxidation of vitamin-C in biological media.** N. BEZSSONOFF and M. WOLOSZYŃ (Compt. rend. Soc. Biol., 1935, 120, 893—895).—Vitamin-C (I) forms a reversible oxidation-reduction system with its oxidation product, which contains no dienolic group and is probably dehydroascorbic acid (II).  $E_h \propto$  the (I) concn., the variation being due to considerable ionisation differences between (I) and (II). The characteristic reducing agents of biological media increase the stability of the system and modify the properties of (I) from those observed in pure solution. R. N. C.

**Oxidation-reduction processes in experimental deficiency.** I. Alteration of capacity of tissues to reduce 2:6-dichlorophenol-indophenol in avian heriberi. M. MITOLO (Arch. Fisiol., 1934, 34, 102).—The capacity of tissues to reduce the indophenol is diminished in all organs, and particularly in the lungs and intestine. NUTR. ABS. (m)

**Variations of the power of vitamin-C in biological media to decolorise dichlorophenol-indophenol.** N. BEZSSONOFF and M. WOLOSZYŃ (Compt. rend. Soc. Biol., 1935, 120, 890—892).—The results obtained by dichlorophenol-indophenol titration of urine, milk, and cerebrospinal fluid to which known quantities of ascorbic acid have been added are untrustworthy. R. N. C.

**Reeds as a source of vitamin-C.** S. BALACHOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 3, 270).—Leaves of the common reed (*Phragmites communis*) contain up to 0.2% of ascorbic acid. Anaerobic treatment of an aq. extract with lactic bacilli resulted in an increased reducing power. P. G. C.

**Vitamin-C (ascorbic acid) content of [East] Indian fruits.** J. P. SPRUYT and W. F. DONATH (Geneesk. Tijds. Nederl.-Indie, 1935, 75, 1944—1950).—The ascorbic acid content of various fruits was determined by the 2:6-dichlorophenol-indophenol titration method, both before and after treatment with  $H_2S$ . Addition of  $Hg(OAc)_2$  has no effect on the result. *Capsicum annum* (0.07—0.25%) and the banana (0.04—0.15%) have the highest vitamin-C contents. S. C.

**Origin of the vitamin-C in the organs of rats fed on vitamin-C-free diets.** H. VON EULER, C. GARTZ, and M. MALMBERG (Biochem. Z., 1935, 282, 399—405; cf. Guha *et al.*, A., 1935, 131).—*In vitro* rats liver and brain do not convert mannose (I) into ascorbic acid. Brain- and liver-hexosedehydrase, after addition of cozymase (II), dehydrogenate (I) and glucose. The (II) of the liver undergoes rapid spontaneous destruction. W. McC.

**Vitamin-C in invertebrates.** A. GIROUD and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1935, 120, 763—765).—Vitamin-C (I) is high in the hepatopancreas and sex glands of invertebrates, low in the muscles, and scarcely detectable in the intestine and gills. The ovaries of *Pecten maximus*, which contain a carotenoid, contain more (I) than the carotenoid-free testicles. R. N. C.

**Ascorbic acid content of certain organs of chicks raised on vitamin-C-deficient ration.** H. C. HOV (Science, 1935, 82, 423).—Chicks fed on such a diet, with or without ultra-violet irradiation, showed a high ascorbic acid (I) content in the adrenals, intestine, and intestinal mucosa; pancreas and kidney had approx. one third of the content of the liver or intestine, whilst muscle contained none. Part of (I) appeared to be excreted through the intestinal wall to the lumen. L. S. T.

**Examination of the cerebrospinal fluid for the detection of hypovitaminosis-C.** F. PLAUT and M. BULOW (Klin. Woch., 1935, 14, 276—277).—Young patients on a vitamin-C-deficient diet exhibit a low -C content of the cerebrospinal fluid. -C falls in old age. R. N. C.

**Reduction of 1-phospho-18-tungstic acid by ascorbic acid.** M. LAPORTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 318—319).—Ascorbic acid and reductone are the only substances that reduce 1-phospho-18-tungstic acid (I) in the cold to any considerable extent; in neutral or alkaline solution it is reduced by many other substances. With org. liquids containing vitamin-C the intensity of the blue colour  $\propto$  -C content. The reduction is quantitatively reversible, and (I) can be determined by titration of the reduced (I) with 2:6-dichlorophenol-indophenol or I. R. N. C.

**Reactions of vitamin-C.** E. PITTARELLI and M. PITTARELLI (Biochem. Terap. sper., 1935, 22, 100).—Three reactions are described for the identification of ascorbic acid, based on the reduction of  $Fe(CNS)_3$ ,  $Cu(CNS)_2$ , and  $HgCl_2$ . The first and last might be used quantitatively. NUTR. ABS. (m)

**Determination of ascorbic acid.** M. VAN EEKELLEN and A. EMMERIE (Biochem. J., 1936, 30, 25—27).—In determining the ascorbic acid content of various substances and fluids by the  $Hg(OAc)_2$  method the extract must be made with  $CCl_3 \cdot CO_2H$  and the  $Hg(OAc)_2$  added at  $p_H$  5, an excess being avoided. The time between the pptn. and passage of  $H_2S$  must be  $> 5$ —10 min. Other methods are criticised. J. N. A.

**Conditions for the silver nitrate reaction as a test for ascorbic acid.** A. GIROUD, C. P. LEBLOND, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1935, 120, 967—968). R. N. C.

**Provitamin-D from plant and animal sources.** R. M. BETHKE, P. R. RECORD, and O. H. M. WILDER (J. Biol. Chem., 1935, 112, 231—238; cf. Waddell, A., 1934, 1043).—In chicks, irradiated cholesterol (I) is more efficacious in preventing rickets than is irradiated ergosterol (II) and calciferol (III), irradiated (II) and (III) being equally efficacious. Irradiated (I) is as potent as is cod-liver oil. Since equiv. rat units of vitamin-D (IV) from irradiated animal products (hog-brains, butter, lard) are more efficacious than (IV) from irradiated plant products (cottonseed oil, wheat middlings, lucerne leaf meal, yeast, fungus mycelium), it follows that the pro-(IV) of animal is not identical with that of plant products. The (IV) efficiencies of irradiated products from higher and lower plants are equal. W. McC.

**Vitamin-D content of egg yolk. II. Influence of various sources of vitamin-D on the antirachitic value. III. Antirachitic value of market eggs.** H. D. BRANION, T. G. H. DRAKE, and F. F. TISDALL (U.S. Egg and Poultry Mag., 1934, 40, No. 8, 22, 23, 58; No. 9, 22, 23, 52, 54).—Egg yolks are a good source of the antirachitic vitamin. Addition of 1% of cod-liver oil to the ration of hens increased the antirachitic potency of yolks 6–8 times. Large quantities of irradiated ergosterol (I) are transferred to the yolk with relative inefficiency. Small doses of (I) are transferred to the yolk as efficiently as is cod-liver oil. Ultra-violet irradiation of the birds, or exposure to sunshine during summer, causes only slight increase in the antirachitic val. of the eggs. Cold-storage for 8–11 months has little or no effect on the vitamin-D content of the eggs. NUTR. ABS. (m)

**Effect of vitamin-D on the calcium content of dentine.** E. W. FISH (J. Physiol., 1935, 84, 272–278).—Max. doses of vitamin-D administered with  $\text{CaCO}_3$  to dogs over long periods do not affect the Ca content of the dentine. Blood-Ca and the opacity of the bones to X-rays are increased, and new deposits of highly-calcified bone matrix are produced. R. N. C.

**Comparative antirachitic efficiency of irradiated milk, yeast milk, and cod-liver oil.** R. M. BETHKE, W. E. KRAUSS, P. R. RECORD, and O. H. M. WILDER (Proc. Amer. Inst. Nutrition, J. Nutrition, 1935, 9, No. 6, Suppl., 7).—Irradiated milk and cod-liver oil, fed to chicks, showed the same antirachitic potency, but the milk from cows fed on irradiated yeast had only about 10% of this val. When fed to rachitic infants, the two milks were equally efficient. NUTR. ABS. (m)

**Vitamin-D activity of cacao shell. I. Effect of fermenting and drying of cacao on the vitamin-D potency of cacao shell. II. Origin of vitamin-D in cacao shell.** A. W. KNAPP and K. H. COWARD (Biochem. J., 1935, 29, 2728–2735).—Vitamin-D is absent from the shell of the cacao bean dried in the dark, whether previously allowed to ferment or not; 21 I.U. per g. were found in that which had fermented and dried in the sun for 22 days. It is concluded that the occurrence of -D in the cacao bean is associated with the growth of ergosterol-producing yeast on it during fermentation. H. D.

**Use of purpurin as an indicator of the action of vitamin-D.** L. BUTTURINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 215–217).—Purpurin colours the bone sections of rachitic rats whether or not vitamin-D is administered. R. N. C.

**Physiological system of products eliminated by plants.** A. FREY-WYSSLING (Protoplasma, 1935, 23, 393–409).—Secretions, excretions, and resorbed materials which are not subsequently assimilated ("recretions") are differentiated and their nature is discussed. A. G. P.

**Osmotic ratios of some Bengalese plants.** J. SEN-GUPTA (Ber. deut. Bot. Ges., 1935, 53, 783–795).—Cryoscopic determinations of the osmotic

pressure of saps of a no. of species from various localities and at different periods are recorded.

A. G. P.

**Mechanism of salt absorption by plant cells.** (A) W. J. V. OSTERHOUT. (B) F. C. STEWARD (Nature, 1935, 136, 1034–1035, 1035).—Discussions.

L. S. T.

**Intake of caesium by potato plants.** K. HELLER, K. PEH, and J. PINDUR (Z. Pflanz. Düng., 1935, 41, A, 36–37).—Addition of Cs salts to nutrient media for potatoes had no appreciable effect on the % of dry matter or of K, but increased the % of Cs in the plants. In higher proportions Cs tended to lower the total wt. of the plants. A. G. P.

**Incorporation of deuterium into growing organisms. II.** O. REITZ and K. F. BONHOEFFER (Z. physikal. Chem., 1935, 174, 424–434).—The experiments with green algæ (A., 1935, 661) have been continued, using water of higher D content. It has been possible to replace > half the H in the dry substance of the organisms with D without the algæ being killed. As the D content of the culture solution increases, the rate of growth of the algæ falls, and at a D content of 85–90% growth of *Scenedesmus acutus* ceases. After many days in culture solutions made with practically pure  $\text{D}_2\text{O}$ , however, a considerable proportion of the organisms start to grow again if placed in water of lower D content. Under conditions where any growth by chlorophyll assimilation occurs the assimilation of D is only half as rapid as that of H. R. C.

**Isotope exchange in soya beans.** K. OKABE and T. TITANI (Bull. Chem. Soc. Japan, 1935, 10, 552–554).—The exchange of H in soya beans by D has been observed by leaving the beans in contact with dil.  $\text{D}_2\text{O}$ . The exchange corresponds with a  $\text{H}_2\text{O}$  content of 25%, whereas analysis gives 10%, probably because of the replacement in the beans of H other than those of  $\text{H}_2\text{O}$  by D. R. S. B.

**Chlorophyll deficiencies in rice.** K. RAMIAH and S. RAMANUJUM (Proc. Indian Acad. Sci., 1935, 11, B, 343–368).—Genetic factors are examined. A. G. P.

**Action of electromagnetic short waves on the development of the plant embryo.** A. HERZUM (Magyar Orvosi Arch., 1934, 35, 392–395; Chem. Zentr., 1935, i, 2387–2388).—Exposure to short waves (12 m.) retards the growth of embryos of *Lupinus albus*. The action is sp. and increases with the period of exposure. The direct thermal effect is secondary. Brief exposure has a stimulative action.

**Hydrocyanic acid and nitrates in the germination of sorghum.** C. HAMANT (Compt. rend., 1935, 201, 1503–1505).—The total N in the grains, which contain an emulsin-like enzyme, is about 0.535%, of which about 0.046% is  $\text{NO}_3\text{-N}$ .  $\text{NO}_3\text{-N}$  of the germinating plant first increases and then decreases, the loss being found as HCN in a glucoside, formed exclusively in the plant, which also contains fructose and a hydroxybenzaldehyde as components.

**Occurrence of methoxyl, ethoxyl, and methylenedioxy-groups in substances of vegetable**



origin; mechanism of their formation by the plant. C. A. BROWNE and M. PHILLIPS (J. Washington Acad. Sci., 1935, 25, 517—524).—A theoretical discussion. Pictet's conception of the formation of OMe and CH<sub>2</sub>O<sub>2</sub> from CH<sub>2</sub>O in plants is inapplicable to *Penicillium*. The groups may be derived from hexoses by changes involving, in turn, hydrolysis, oxidation, reduction, and dehydration. Lignin, derived from carbohydrates, may be the precursor of many OMe-containing constituents of plants. A. G. P.

**Relationship between vitamin-A and plastids.** P. J. LAVERGNE (Compt. rend., 1935, 201, 1042—1044).—The plastids of the cells of *Elodea canadensis* and other plants give locally the SbCl<sub>3</sub> reaction for vitamin-A. W. O. K.

**Physiology of delayed germination in *Avena fatua*.** L. P. V. JOHNSON (Canad. J. Res., 1935, 13, C, 283—300).—Delayed germination is associated with a condition of the seed-coat tissues (brought about by post-fertilisation agencies) which restricts access of O<sub>2</sub> to the embryo. Normal germination may be restored by breaking the seed coat over the embryo or by soaking in 1—2% aq. KNO<sub>3</sub>. Exposure to artificially increased [O<sub>2</sub>] under germinating conditions had a stimulative effect. Treatment with pure O<sub>2</sub>, Et<sub>2</sub>O, or NaCNS produced irregular results. CH<sub>2</sub>Cl·CH<sub>2</sub>·OH and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> were injurious. After-ripening probably induces changes in the seed coat which increase its permeability to O<sub>2</sub>. A. G. P.

**Chemical studies on methods of mulberry culture for young silkworms.** C. NAKASONE (Bull. Sericult. Japan, 1935, 8, 398). P. G. M.

**Concentration of cell sap of mulberry leaves.** Y. IMAMURA, K. KOIKE, and M. FURUYA (Bull. Sericult. Japan, 1935, 8, 396—397).—An investigation of cell sap concn. in different varieties by a method of plasmolysis. The concn. is lower in spring than in autumn. P. G. M.

**Atomic dynamics of plant growth.** G. HEVESY, K. LINDERSTRÖM-LANG, and C. OLSEN (Nature, 1936, 137, 66—67; cf. A., 1935, 1531).—Using radioactive P as indicator, it is found that the P atoms of maize leaves are present in a mobile state, and that during growth a continuous interchange of P occurs between different leaves. L. S. T.

**Action of follicular hormone on the growth of culture plants.** K. SCHARRER and W. SCHROPP (Biochem. Z., 1935, 281, 314—328).—The effects of increasing amounts (500—1000 mouse units) of cryst. preps. [both phenolic and the Na salt (I)], free from auxin but not completely free from equilin and hippulin, were investigated. With wheat, increased yields of grain and straw resulted, the effect being greater with (I). With rye and barley, the increases were within the limits of error except with 1000 units. Positive results were not obtained with oats.

With horse beans, 500 units led to an increase of 24% and 1000 units of 39% in the fruit, but the yield of straw was decreased. No significant effects were obtained with rape-seed or soya bean, but with sugar beet the yield was increased by 14%. This increase, however, affected only the dry substance wt., no increase in sugar or leaf being obtained. P. W. C.

**Developmental growth and the amino-acids.** I. *l*-Histidine. F. S. HAMMETT (Protoplasma, 1935, 23, 326—336).—*l*-Histidine (I) has no direct action on developmental growth, anabolism, or catabolism in *Obelia geniculata*. In concns. of *M*/31,000—21,000 (I) sustains the metabolic activity of maintenance. It is toxic in concns. > *M*/16,000. A. G. P.

**Influence of season on photosynthesis in the tropics.** B. N. SINGH and K. KUMAR (Proc. Indian Acad. Sci., 1935, 11, B, 437—456; cf. A., 1935, 794).—Seasonal variations are recorded in the intensity of assimilation of CO<sub>2</sub> by radish leaves of different ages under controlled conditions. Artificially increased illumination accelerates photosynthesis more effectively in winter than in summer. Summer rates of assimilation are increased by rise of temp. in the range 29—37°, but are not greatly affected by increases of [CO<sub>2</sub>]. The temp. coeff. of assimilation (21—31°) does not vary much from season to season, but at higher temp. ranges vals. are high in summer and low in winter. The chlorophyll content of leaves reaches max. during rains, is smaller, although still high, in winter, and is least in summer. The dry matter content and total leaf area in winter are > in summer. A. G. P.

**Role of potassium in the production of plant substance.** K. MAIWALD and A. FRANK (Z. Pflanz. Düng., 1935, 41, A, 8—28).—A discussion. A. G. P.

**Growth substance and cell division.** L. JOST (Ber. deut. Bot. Ges., 1935, 53, 733—750).—The response (elongation or division) of plant cells to growth substance (I) from various sources (bean sap, extracts of *Boletus edulis*) and of yeast preps. varies with the nature, position, age, and physiological condition of the cell, and with the concn. of (I) applied to it. Cell division may be induced by indolylacetic acid, and also by many unrelated substances, e.g., citric acid, NaCl, fructose. The possibility of the necessary presence of co-substances for the activity of (I) is discussed. The concn. of (I) necessary to cause cell division is approx. 1 in 10<sup>3</sup>—10<sup>4</sup>, whereas cell elongation is stimulated by 1 in 10<sup>7</sup>. A. G. P.

**Ascorbic acid (vitamin-C) and phytochemicals.** L. HAVAS (Nature, 1935, 136, 989; cf. A., 1935, 1431, 1548).—Injection of ascorbic acid into tomato plants increased the size of the tumours produced in them by *B. tumefaciens*. No marked change in *p<sub>H</sub>* of the sap of treated plants occurred. L. S. T.

**Pathological histology and phytochemistry of Psyllid yellows.** J. R. EYER (Phytopath., 1935, 25, 895).—Tissue surrounding feeding stylets of the potato psyllid nymph is examined. Sheath materials are of animal origin and contain chitosan and mucin. Surrounding tissue contains plant degradation products, arginine, tryptophan, and tyrosine. Diseased leaves and stems have abnormally high starch contents. The relationship between hexoses and starch in healthy plants is disturbed by the disease. Sucrose, the principal sugar of translocation, is absent or its formation is inhibited in diseased plants. A. G. P.

**Biochemical modifications in phytopathology. Disequilibrium of organic and mineral composition in parasite infections.** R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 780—782).—Fats, insol. carbohydrates (I), and ash in *Medicago lupulina*, L., are reduced during infection by *Septoria medicaginis*, Rob. and Desm., whilst proteins and sol. (I) are increased. Ca falls and P and K rise in the ash. The increase in sol. (I) is due to one of reducing sugars, whilst the fall in insol. (I) is due to disappearance of amyloids and hemicelluloses. R. N. C.

**Low-temperature masking of tobacco mosaic symptoms.** J. GRAINGER (Nature, 1936, 137, 31—32).—These symptoms are masked when the host plant is grown at a temp.  $< 11^{\circ}$  approx. L. S. T.

**Effect of tannic acid on infectivity of tobacco-mosaic virus.** H. H. THORNBERRY (Phytopath., 1935, 25, 931—937).—Inhibition of the virus by tannic acid (I) depends on the concn. of acid applied and the period of action. Removal of (I) by pptn. with gelatin or by ultrafiltration restores virus activity. Treatment of plants with (I) prior to inoculation inhibits infection to extents  $\propto$  the concn. of (I) used. When applied after inoculation, (I) in concns. of 0.01—10% has little effect on infection. A. G. P.

**Virus of tobacco mosaic. IV. Effects of different chemical agents on infectivity. V. Optimum hydrogen-ion concentration for purification by precipitation with lead acetate.** W. M. STANLEY (Phytopath., 1935, 25, 899—921, 922—930).—IV. Substances directly inactivating the virus are usually oxidising agents, protein precipitants, or agents inducing a change in  $[H^+]$  known to inactivate the virus. Prolonged action of  $HgCl_2$  in germicidal concns. did not affect the virus. In higher concns.  $HgCl_2$  affected purified virus preps. more markedly at  $p_H$  6—8 than at  $p_H$  3—5. The infectivity of the virus on *Phaseolus vulgaris* was increased by  $PO_4^{3-}$  buffers at  $p_H$  7.0, but on *Nicotiana* was unaffected or somewhat decreased. Charcoal completely adsorbed the virus from solutions, notably at  $p_H$  3—5.

V. The optimum  $p_H$  for pptn. by basic Pb acetate was 9.0, and for  $Pb(OAc)_2$ , 5.5. For elution from  $Pb(OAc)_2$  ppts. the optimum  $p_H$  was 7.0. A. G. P.

**Inhibiting influence of a virus on one of its mutants.** H. H. McKINNEY (Science, 1935, 82, 463—464).—Tobacco plants inoculated with virus mixtures in which the extract of yellow mosaic is much  $>$  that of the common mosaic develop at first symptoms of the former, but ultimately show those of the latter. With plants having yellow mosaic reinoculation with the common mosaic eventually suppresses symptoms of the former. L. S. T.

**Toxicity of ethyl alcohol towards dried and germinating seeds.** S. LALLEMAND and S. LALLEMAND (Bull. Soc. Chim. biol., 1935, 17, 1509—1521).—The toxicity of EtOH towards germinating seeds of *Lens esculenta* is  $<$  that towards the dry seeds, although in the former case the EtOH concn. is greater. A. L.

**Biological distribution of metals.** H. RAMAGE (Nature, 1936, 137, 67).—Spectroscopic determin-

ations of various metals in apple seeds, india-rubber tree seeds, Brazil nuts, etc. are recorded and discussed. L. S. T.

**Influence of soil sand on the determination of radium in plants.** K. G. KUNASCHEVA and B. K. BRUNOVSKI (Trav. Lab. biogeochem. Acad. Sci. U.R.S.S., 1935, 3, 45—48).—The anomalously high Ra content of *Struthiopteris germanica* does not depend on the presence of a large amount of sand, which has no influence on the Ra content of plants. CH. ABS. (e)

**Iodine contents of Chinese marine algæ.** P. S. TANG and C. S. CHANG (Chinese J. Physiol., 1935, 9, 369—374).—The I content of 12 further species (cf. A., 1935, 1436) is determined. H. G. R.

**Mode of combination of acetic acid in ginkgo wood (*Ginkgo biloba*).** K. KURSCHNER (Cellulosechem., 1935, 16, 107).—Polemical against Tang *et al.* (this vol., 123). R. S. C.

**Fructose anhydride from the leaves of the barley plant.** H. K. ARCHBOLD and A. M. BARTER (Biochem. J., 1935, 29, 2689—2693).—An aq. extract of barley leaves yielded a fructose anhydride (or a mixture of anhydrides) which on hydrolysis yielded reducing sugar equiv. to 105% of the wt. of anhydride taken, of which 94% was fructose. The more sol. fractions had  $[\alpha]_D^{25} -27^{\circ}$  and were more readily attacked by invertase than the less sol., which had  $[\alpha]_D^{25} -37^{\circ}$ . J. N. A.

**Pectin of ramie bast.** F. EHRLICH and R. HAENSEL (Cellulosechem., 1935, 16, 97—107, 109—114).—This pectin is much "altered." It contains much cyclic tetragalacturonic (pectolic) acid as  $H_2O$ -insol. Ca salt and only small amounts of  $\alpha$ -D-galacturonic acid, whilst most of the  $H_2O$ -sol. portion is a non-cyclic digalacturonic acid bound to carbohydrates, which include a disaccharide, large amounts of D-galactose, and some L-arabinose and methylpentose (? D-fucose). R. S. C.

**Properties of kelp colloids.** G. B. RICE and B. DUNSFORD (Proc. 5th Pacific Sci. Congr., 1934, 3, 2115—2121).—Colloidal preps. from *Nereocystis* were dialysed in collodion sacs. The solid matter in the initial and dialysed preps. averaged 0.079 and 2.4%, respectively. The respective  $p_H$  were 5.58 and 6.43. The dialysed preps. gave a flaky ppt. with electrolytes, but no ppt. on boiling. CH. ABS. (e)

**Unsaponifiable matter of algæ fats. I. Sterol.** K. SHIRAHAMA (J. Agric. Chem. Soc. Japan, 1935, 11, 980—984).—A sterol, "pervesterol," was isolated from various algæ and named. The consts. given agree with those reported by Heilbron *et al.* for fucosterol (A., 1934, 1347). The sterol from *Chishima nori* could not be purified. P. G. M.

**Chemical investigation of the seeds of *Allanblackia klainei*, Pierre.** L. ADRIAENS (Mat. grasses, 1933, 25, 9961—9962; Chem. Zentr., 1935, i, 2911—2912).—The acids from the seed-fat are 62.0% saturated (mainly stearic acid) and 37.5% unsaturated

(almost wholly oleic acid). Fractional crystallisation of the fat from COMe<sub>2</sub> affords an *oleodistearin*, m.p. 43.9—44.5°, I val. 27.8. H. N. R.

**African oil seeds.**—See B., 1936, 66.

**Wheat-germ oil.**—See B., 1936, 67.

**Essential oil from the rhizomes of *Cyperus rotundus*, Linn.**—See B., 1936, 44.

**Crystalline substance from the essential oil of *Lachnophyllum gossypinum*, Bge.** V. V. VILJAMS, V. S. SMIRNOV, and V. P. GOLMOV (J. Gen. Chem. Russ., 1935, 5, 1195—1204).—The oil contains β-pinene, camphene, and about 30% of a cryst. ester (I), CPr<sup>a</sup>:C:C:C:CH:CH:CO<sub>2</sub>Me, m.p. 32.6—32.8°, which when hydrolysed with aq. NaOH yields a mixture of products, of which COMeBu<sup>a</sup>, *n*-valeric and maleic acids were identified. When heated at 100° with 50% HNO<sub>3</sub> (I) yields Pr<sup>a</sup>CO<sub>2</sub>H and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Catalytic hydrogenation (Pd-C) of (I) affords CH<sub>2</sub>Me[CH<sub>2</sub>]<sub>7</sub>CO<sub>2</sub>Me. R. T.

**Diterpene, from leaf- and wood-oil of *Sciadopitys verticillata*, S. and Z.**—See this vol., 207.

**Carotenoids from the anthers of *Lilium tigrinum*: antheraxanthin.** P. KARRER and A. OSWALD (Helv. Chim. Acta, 1935, 18, 1303—1305).—Hydrolysis (NaOEt-EtOH) of the ligroin extract of the anthers affords a mixture of pigments separated by chromato-absorption from EtOH solution by Ca(OH)<sub>2</sub> into capsanthin, and *antheraxanthin*, C<sub>20</sub>H<sub>58</sub>(56)O<sub>3</sub>, m.p. 211° (corr.), which has absorption max. at 490.5, 460.5, and 428 mμ in CHCl<sub>3</sub>, and gives a blue colour (max. 587 mμ) with SbCl<sub>3</sub>. J. W. B.

**New type of plant lipochrome.** I. M. HEILBRON, B. LYTTHGÖE, and R. F. PHIPERS (Nature, 1935, 136, 989).—A pigment, *myoxanthin*, m.p. 117—118° (uncorr.), has been isolated from the unsaponifiable fraction of *Rivularia nitida*. Unlike other phyto-carotenoids, it exhibits only one absorption band (max. 488—490 mμ) in CS<sub>2</sub>, resembling astacene in this respect, but differing from it in other respects. No hypophasic xanthophylls were detected in *R. nitida*. L. S. T.

**Plastid pigments of marsh dodder.** G. MACKENNEY (J. Biol. Chem., 1936, 112, 421—424).—2—3 mg. of rubixanthin, 4—6 mg. of lycopene, and 20—25 mg. of γ-carotene per kg. of fresh wt. were isolated from *Cuscuta subinclusa* and *salina*; traces of chlorophyll were detected. H. D.

**Hanfangchin B.**—See this vol., 217.

**Alkaloids obtained from jaborandi leaves.**

**Synthesis of pilocarpidine.**—See this vol., 215.

**Chemical investigation of the liana "Efiri."** IV. E. CASTAGNE (Congo, 1935, I, 32—37; Chem. Zentr., 1935, i, 2828; cf. this vol., 133).—From the EtOH extract of the stem of *Trichlistia gillettii* are isolated two alkaloids, *trichlisine*, C<sub>16</sub>H<sub>31</sub>O<sub>10</sub>N, m.p. about 255—260° (decomp.), [α]<sub>D</sub><sup>20</sup> +116.66° in 0.5N-HCl, and *trichliseine*, C<sub>23</sub>H<sub>40</sub>O<sub>7</sub>N, m.p. 135°, [α]<sub>D</sub><sup>20</sup> +68.49° in 0.5N-HCl. H. N. R.

**"Sotetsu" (*Cycas revoluta*, Thunb.). IV. Sotetsu-emulsin.** K. NISHIDA (Bull. Chem. Soc. Japan, 1935, 10, 524—530).—Sotetsu seed contains

a glucoside of CH<sub>2</sub>O, which splits off CH<sub>2</sub>O under the influence of an emulsin (I) which is also present. The isolation of (I) is described. (I) effects complete hydrolysis of salicin, the optimum conditions being *p*<sub>H</sub> 5.1 and 55—60°; the unimol. coeff. for the reaction increases with time and the velocity α the amount of (I) used (cf. following abstract). J. W. B.

**"Sotetsu" (*Cycas revoluta*, Thunb.). V. Sotetsu pollen.** I. K. NISHIDA (J. Agric. Chem. Soc. Japan, 1935, 11, 143—148).—The pollen does not contain starch, protamine, or spermine. Free adenine and choline are present, 2.24 g. of the latter (as aurichloride) being obtained from 1 kg. of pollen. P. G. M.

**Proteins of the cowpea (*Vigna sinensis*).** W. H. ADOLPH and H. C. CHIANG (Chinese J. Physiol., 1935, 9, 347—353).—The protein has been fractionated into vigin (globulin A) 45, glutelin 25, albumin 15, globulin B 10, and globulin C 5%, and the distribution of N determined in each fraction by the Van Slyke method. H. G. R.

**Artificial medium for epithelial cells and fibroblasts.** L. E. BAKER (Compt. rend. Soc. Biol., 1935, 120, 932—934). R. N. C.

**Air analysis apparatus.** T. C. SHEN (Chinese J. Physiol., 1935, 9, 363—368). H. G. R.

**Manometric device for gas analysis.** B. N. SINGH and P. B. MATHUR (Current Sci., 1935, 4, 313—314).—A simplified apparatus alternative to that of Haldane for measuring the respiratory gaseous exchange in plants is briefly described. N. M. B.

**Technique of toxicology.** R. FABRE (Chem. Weekblad, 1935, 32, 691—697).—Various techniques used in the isolation of foreign substances from tissues (destruction of org. matter, electrodialysis, extraction with solvents, etc.) are discussed. F. O. H.

**Determination of protein-nitrogen.**—See this vol., 219.

**Determination of salicylates in body-fluids.** L. E. ONTANEDA and A. V. J. FERLONI (Compt. rend. Soc. Biol., 1935, 120, 820—822).—Salicylates are determined as phenol in blood by Marenzi's modification of the method of Theiss and Benedict, and in urine by the method of Marenzi. R. N. C.

**Determination of phenols in blood and urine.** R. F. BANFI and A. D. MARENZI (Compt. rend. Soc. Biol., 1935, 120, 812—814).—More exact details are given for some of the steps in Marenzi's modification of the method of Theiss and Benedict. R. N. C.

**Modification of Young's method for the determination of inositol in animal tissues.** R. A. GREGORY (Biochem. J., 1935, 29, 2798—2802).—The method (A., 1934, 1246) is modified by replacing the COMe<sub>2</sub> extraction by dissolution of the tissue in 10% KOH followed by pptn. of impurities by ZnCl<sub>2</sub>. H. D.

**Modification of the copper-lime technique for the separation and recovery of carbohydrates from biological fluids.** R. M. ARCHIBALD (Trans. Roy. Soc. Canada, 1935, [iii], 29, V, 97—103).—A modification of the Van Slyke's CuSO<sub>4</sub>-Ca(OH)<sub>2</sub>

method for removing carbohydrates from solution is described which allows small quantities to be separated from urine and recovered in good yield. At most only a small fraction of the fermentable sugar originally present is converted into non-fermentable reducing material. W. O. K.

**So-called normal alcohol of the body.** R. N. HARGER and A. L. GOSS (*Amer. J. Physiol.*, 1935, **112**, 374—381).—Steam-distillates of fresh urine, blood, or minced tissues contain reducing substances. Any EtOH added to the fluid distils over in the first fraction of distillate, so that the reducing material of the second fraction cannot be EtOH. The difference between the reducing powers of the first and second fractions represents the normal EtOH of the tissue or fluid used, and is never  $> 0.3$  mg.-%; vals. are given for blood, urine, and certain tissues. The reducing substances of the first fraction of distillate are increased by storing the tissues in the refrigerator before distillation. R. N. C.

**Determination of thiocyanates in biological fluids by double distillation.** P. R. ORELLA (*Anal. Farm. Bioquim.*, 1935, **6**, No. 2, 41—51).—In this rapid modification of Chelle's method, the sample is distilled with 0.1N- $\text{H}_2\text{PO}_4$  or  $\text{H}_2\text{SO}_4$  to separate  $\text{CN}'$ , and then aq.  $\text{K}_2\text{CrO}_4$  and dil.  $\text{H}_2\text{SO}_4$  are added to decompose  $\text{CNS}'$ , liberating HCN, which is distilled separately. The HCN is collected in each case in NaOH and determined colorimetrically as Prussian-blue.  $\text{CNS}'$  was detected in human and horse's saliva and cow's milk, but not in human urine or human milk. No cyanides were found in any of these fluids. E. L.

**Rapid titrimetric determination of arsenic in biological material.** R. ALLCROFT and H. M. GREEN (*Biochem. J.*, 1935, **29**, 824—833).—Org. matter is destroyed with  $\text{HClO}_4$  and  $\text{HNO}_3$ , and As is distilled into aq.  $\text{AgNO}_3$  as  $\text{AsH}_3$  by addition of  $\text{SnCl}_2$ ,  $\text{H}_2\text{SO}_4$ , and Zn. 88% of As added to various org. materials in concns. of 1.3 p.p.m. was recovered. H. D.

**Application of the nitro-sulpho-perchloric acid method in the destruction of organic matter for the toxicological determination of arsenic.** E. KAHANE and M. POURTOY (*J. Pharm. Chim.*, 1936, [viii], **23**, 5—22).—Loss of As by entrainment during distillation is more liable with  $\text{As}^{\text{III}}$  than with  $\text{As}^{\text{V}}$  and during wet destruction of org. matter the tendency for the formation of  $\text{As}^{\text{III}}$  should be prevented by using excess of oxidising agent. In the  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$ - $\text{HClO}_4$  method (B., 1934, 380) this is attained by continuous addition of  $\text{HNO}_3$  or  $\text{HNO}_3$ - $\text{HClO}_4$ . Redistillation of the distillate is then unnecessary except as a precaution. E. H. S.

**Determination of chlorides in biological fluids by the use of adsorption indicators.** Use of dichlorofluorescein for the volumetric micro-determination of chlorides in cerebrospinal fluids and blood-serum. A. SAIFFER and M. KORNBLUM (*J. Biol. Chem.*, 1935, **112**, 117—122).—The liquid is treated with EtOH-Et<sub>2</sub>O, an EtOH solution of dichlorofluorescein is added, and then

titrated with standard  $\text{AgNO}_3$ . 1 mg. of NaCl can be rapidly determined with an error  $> 2\%$ .

J. N. A.

**Micro-methods for the determination of magnesium.** B. BASSANI and V. ZAMBOTTI (*Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 261—263).—The presence of Zn in plasma and tissues introduces an error that may reach 2.5% in determinations of Mg by pptn. as  $\text{MgNH}_4\text{PO}_4$  (I) after ashing.  $\text{ZnNH}_4\text{PO}_4$  is pptd. at a lower  $p_{\text{H}}$  than (I), and either fails to redissolve on addition of excess  $\text{NH}_3$ , or more probably is carried down or adsorbed by the pptd. (I), since there is no definite ratio between the total and pptd. Zn, and the amount of Zn pptd. increases with the Mg/Zn ratio.

R. N. C.

**Extraction of lead by means of diphenylthiocarbazone.**—See this vol., 179.

**Determination of potassium in organs and parts of organs.** H. WILLSTAEDT (*Acta med. Scand.*, 1934, **84**, 104—107; *Chem. Zentr.*, 1935, i, 2860).—The sample is dried at  $110^\circ$  and ashed in presence of  $\text{H}_2\text{SO}_4$ . The ash is extracted with little  $\text{H}_2\text{O}$ , and K determined by the method of Jendrassik and Szél. J. S. A.

**Determination of small quantities of zinc.**—See this vol., 178.

**Spectrophotometric micro-determination of zinc in organic material.** J. DABROWSKI and L. MARCHLEWSKI (*Biochem. Z.*, 1935, **282**, 387—391).—After destruction of org. matter (cf. Ridge *et al.*, B., 1933, 858) the part of the ash sol. in HCl is freed from Cu by treatment with  $\text{H}_2\text{S}$ , and the Zn, after pptn. as  $\text{ZnS}$  and dissolution in HCl, is repptd. with 8-hydroxyquinoline (I). The amount of (I) (and hence the Zn content) in the ppt. is determined spectrophotometrically after separating the components by dissolving in HCl. W. McC.

**Determination of copper in organs.** Z. GRUZEWSKA and G. ROUSSEL (*Compt. rend. Soc. Biol.*, 1935, **120**, 934—936).—Cu is determined in organs after incineration by extraction of the ash with  $\text{H}_2\text{O}$ , oxidation of Fe with  $\text{HNO}_3$  and pptn. with excess of  $\text{NH}_3$ , and pptn. of Cu with 1-nitroso- $\beta$ -naphthol in AcOH. The ppt. is ignited in presence of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and Cu weighed as  $\text{CuO}$ . The Cu of rabbit liver remains in the insol. ash, Fe passing into the sol. fraction. R. N. C.

**Determination of total phosphorus in organs and organic liquids.** I. Technique. S. FIANDACA. II. Technical observations and physiological values. S. FIANDACA and I. CAPIZZI (*Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 183—185, 185—186).—I. The sample is incinerated with  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , and Ca removed from the neutral solution with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . P is pptd. as  $\text{MgNH}_4\text{PO}_4$ , which is washed with  $\text{H}_2\text{O}$ , dissolved in 20%  $\text{H}_2\text{SO}_4$ , and N determined by the micro-Kjeldahl method.

II. Vals. obtained with solutions of  $\text{Na}_2\text{HPO}_4$  and  $\text{Na}_2\text{HPO}_4 + \text{Na}$  glycerophosphate oscillate between limits on either side of the calc. val. Vals. are given for the P of the blood and organs of the rabbit.

R. N. C.



# BRITISH CHEMICAL ABSTRACTS

## A—PURE CHEMISTRY

MARCH, 1936.

### General, Physical, and Inorganic Chemistry.

Absorption spectrum of hydrogen. II. The  $D$  state in the term scheme of hydrogen from photographs of  $H_\alpha$  and  $D_\alpha$ . H. BEUTLER, A. DEUBNER, and H. O. JÜNGER (Z. Physik, 1935, 98, 181—197; cf. A., 1935, 1291). A. B. D. C.

Ground state of  $(H_2)$ , the molecular ion  $(H_2^+)$ , and wave mechanics. O. W. RICHARDSON (Proc. Roy. Soc., 1935, A, 152, 503—514).—The agreement between the vals. of the fundamental consts. of the ground state of the  $H_2$  mol. (i) as determined by experiment, and (ii) as calc. by wave mechanics, is discussed. The properties of the mol. ion  $(H_2^+)$  as predicted by wave mechanics are compared with those predicted empirically from a study of various excited states of  $(H_2)$ . L. L. B.

Fine structure of  $D_\alpha$  with increased resolution. R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1936, [ii], 49, 40; cf. this vol., 127).—A correction. N. M. B.

Energy states of doubly excited helium. T. Y. WU (Physical Rev., 1934, [ii], 46, 239). L. S. T.

Doubly-excited states in helium. F. G. FENDER and J. P. VINTI (Physical Rev., 1934, [ii], 46, 77—78). L. S. T.

Absorption of fluorspar [transmitted] ultra-violet light by carbon black, gold, and rhombic sulphur. G. RATHENAU (Physica, 1936, 3, 42—60). Carbon black has an absorption max. at approx. 2500 Å., and a min. at approx. 1700 Å.; Au has an absorption max. at about the latter  $\lambda$ . S layers, transparent to ultra-violet light, were made by vaporisation in vac. on to a  $CaF_2$  plate at  $-80^\circ$ . S absorbs at about 2000 Å., and there is another band at 1800 Å. The results are discussed in relation to the at. and mol. spectra. A. J. M.

Light yield in the nitrogen spectrum excited by electron collision. O. HERRMANN (Ann. Physik, 1936, [v], 25, 166—184).—The excitation function, negative bands of the N spectrum and the abs. yield for 3 negative and 5 of the second positive group of  $N_2^+$  and  $N_2$  band spectra have been determined. A. J. M.

Dependence of intensities of rotation lines of band on the conditions of excitation. O. HERRMANN (Physikal. Z., 1936, 37, 100—103).—The lines in the  $R$  branch of the an. of the negative N<sub>2</sub> group at 3914 Å. have been determined for excitation with electrons of various velocities. A. J. M.

Excitation of the auroral green line by metastable nitrogen molecules. J. KAPLAN (Physical Rev., 1936, [ii], 49, 67—69; cf. A., 1934, 827).—The excitation in tubes which show the two new afterglow spectra of  $N_2$  is described. The conditions of excitation are compared with those in the night-sky and in the aurora borealis, in which cases, it is suggested, the  $^1S_0$  state of O which is responsible for the green line is produced by collisions of O atoms and metastable  $N_2$  mols. in the  $A^3\Sigma$  state. N. M. B.

Hopfield's Rydberg series and the ionisation potential and heat of dissociation of nitrogen. R. S. MULLIKEN (Physical Rev., 1934, [ii], 46, 144—146; cf. A., 1931, 1343). L. S. T.

Predissociation of the oxygen molecule. P. J. FLORY (J. Chem. Physics, 1936, 4, 23—27).—Optical data for  $O_2$  are interpreted as indicating that the initial process in the photochemical reactions of  $O_2$  due to light in the region of Schumann–Runge band absorption is the formation of normal  $^3P$  atoms by predissociation rather than the reaction of an optically excited mol. with a normal mol., as hitherto supposed. M. S. B.

Arc spectra of fluorine and potassium. B. EDLÉN (Z. Physik, 1936, 98, 445—460).—85 F I lines between 6000 and 9500 Å. are tabulated. A. B. D. C.

Intensity measurements in the spectra of neon and argon excited by electron collision. O. HERRMANN (Ann. Physik, 1936, [v], 25, 143—165).—Efficiency determinations for the excitation of the Ne and Ar spectra by electron collision have been made by an abs. method. The scattering of electrons and their angular distribution are taken into account. The abs. yield and excitation probabilities for 54 Ar lines, and the excitation functions for 52 Å and 16 Ne lines are recorded. Comparison of the abs. yields of 7 Ne and 7 Ar lines belonging to the same term shows no simple connexion between the two gases. A. J. M.

Intensity distribution of neon lines. E. LAU (Physikal. Z., 1936, 37, 110).—Polemical against Schütz *et al.* (A., 1935, 907). A. J. M.

[Intensity distribution of neon lines.] W. SCHÜTZ (Physikal. Z., 1936, 37, 110—111).—A reply to the above. A. J. M.

Absolute transition probability of potassium. E. F. M. VAN DER HELD and J. H. HEIERMAN (Physica, 1936, 3, 31—41).—The abs. intensity of light emitted

by K atoms in a  $C_2H_2$ -air flame, the flame temp., and the no. of emitting particles have been determined, and the abs. transition probabilities of the resonance lines of K calc. The abs. transition probabilities were also obtained for the sharp and diffuse series by photographic comparison with the resonance lines, using light of known colour temp. A. J. M.

**Arc spectrum of rubidium.** K. W. MEISSNER (Z. Physik, 1935, 98, 353—354). A. B. D. C.

**Fine structure in the ( $^2D$ ) series limit terms of the  $I^+$  spectrum.** S. TOLANSKY (Proc. Physical Soc., 1936, 48, 49—56; cf. A., 1935, 137).—Classifications and fine-structure data are tabulated for  $I^+$ , and fine structure analyses of 14 lines of the  $-D$  system and interval factors for 12 terms are given. Large interval factors associated with the  $5d$  electron terms of the  $^4S$  and  $^2D$  systems are correlated with observations for Sn II, and are due to perturbation by terms with large fine structure. Two types of perturbation in the fine structures are observed.

N. M. B.

**Nuclear spin of iodine. II. Fine structure in the arc spectrum and a fine structure perturbation effect.** S. TOLANSKY (Proc. Roy. Soc., 1935, A, 152, 663—672; cf. A., 1935, 137).—The fine structures of 13 of the classified lines of the I arc spectrum (6300—4760 Å.) have been measured. The nuclear spin is confirmed as  $5/2$ . The  $6s^4P_{5/2}$  is perturbed.

L. L. B.

**Absorption spectra of cerium, neodymium, and samarium.** F. W. PAUL (Physical Rev., 1936, [ii], 49, 156—162; cf. King, this vol., 2).—Data for  $\lambda$  and intensities of 600 Ce, 450 Nd, and 1500 Sm lines are tabulated in the region 12,000—2500 Å.

N. M. B.

**Absolute intensities in the spectrum of a low-pressure quartz mercury-vapour discharge burner.** A. J. MADDOCK (Proc. Physical Soc., 1936, 48, 57—62).—Abs. intensities of the main  $\lambda\lambda$  in the range 6000—2400 Å. are tabulated and discussed theoretically in relation to results for high-pressure arcs (cf. A., 1935, 800). Therapeutic effects are examined.

N. M.

**Collision-induced emission.** W. M. PRESTON (Physical Rev., 1936, [ii], 49, 140—144).—A new continuous spectrum associated with the weak forbidden Hg 2269-80 Å. line has been found in a low-pressure Hg discharge with a few cm. pressure of A or He added. It is attributed to radiation from excited Hg atoms in the  $^3P_2$  metastable state perturbed by the close approach of rare gas atoms. N. M. B.

**Thallium II spectrum.** C. B. ELLIS and R. A. SAWYER (Physical Rev., 1936, [ii], 49, 145—150). The Tl spectrum from the hollow-cathode discharge in He has been photographed in the range 9250—600 Å. Full data, classifications, and assignments for 115 previously known lines and 160 new lines which locate 35 new levels are tabulated. N. M. B.

**Hyperfine structure and the depolarisation of resonance radiation by a magnetic field.** A. ELLETT (Proc. Iowa Acad. Sci., 1934, 41, 251).

CH. ABS. (e)

**New "bright" method for investigation of the Stark effect with a homogeneous field.** W. STEUBING and J. A. SCHAEFER (Ann. Physik, 1936, [v], 25, 97—123).—The method enables very bright spectra to be produced in a measurable homogeneous electric field, and makes it possible to examine the Stark effect of some atoms and mols. which are difficult to excite by other methods. A. J. M.

**Analysis and interpretation of the nebular spectrum of Nova Herculis.** M. BLOCH and J. DUFAY (Compt. rend., 1935, 201, 1463—1465).—Lines are due to H I, He I, He II, O II, N II, C II, O III, N III, and probably C III. T. G. P.

**Absorption of monochromatic X-ray beams, of wave-length in the region 50—20 X units, in lead, tin, copper, and iron.** J. READ (Proc. Roy. Soc., 1935, A, 152, 402—417; cf. A., 1934, 577).—A curve relating the absorption coeff. of Pb and the  $\lambda$  has been obtained. The photo-electric absorption coeffs. calc. from this are 7—20% > corresponding vals. obtained from Gray's empirical law (A., 1931, 281).

L. L. B.

**Fluorescence X-ray yields from K shells of atoms.** R. J. STEPHENSON (Physical Rev., 1934, [ii], 46, 73—74).—A criticism and a revision of vals. (cf. A., 1934, 577).

L. S. T.

**Dose measurement of very soft X-rays.** E. WILHELMY (Physikal. Z., 1936, 37, 103—107).—The method employs an ionisation chamber of sufficient length to absorb the rays almost completely.

A. J. M.

**Effects of chemical binding on the X-ray  $K\alpha_{1,2}$  doublet lines of sulphur studied with a two-crystal spectrometer.** L. G. PARRATT (Physical Rev., 1936, [ii], 49, 14—16).—Using FeS,  $Cu_2S$ ,  $MgSO_4$ ,  $BaSO_4$ , and PbS targets, ionisation curves were recorded, and effects of binding on  $\lambda$ , on the  $\alpha_1$ ,  $\alpha_2$  separation, and on the doublet contour were measured. The  $\lambda$  shift of the  $SK\alpha_{1,2}$  lines from sulphates to sulphides was observed in the process of shifting.

N. M. B.

**Excitation potential of  $K\alpha_{3,4}$  satellite lines.** L. G. PARRATT (Physical Rev., 1936, [ii], 49, 132—139).—The  $K\alpha$  satellite lines intensity-X-ray tube voltage curve has been determined for the Ti  $K\alpha_{3,4}$  lines. For voltages > 11 kv. the ratio satellite intensity/Ti  $K\alpha_1$  line intensity is 2.21%; the ratio of peak intensities  $\alpha_4/\alpha_1$  is 0.69%. The Ti  $K\alpha_{3,4}$  excitation potential is  $5450 \pm 100$  volts, in good agreement with the calc. voltage, 5455, required to produce a state of  $KL_{III}$  ionisation in the Ti atom, and supporting the Wentzel-Dryvesteyn theory of satellite line origins.

N. M. B.

**Absorption ratio within the L-shell.** H. SCHWARZ (Ann. Physik, 1935, [v], 23, 571—588).—Measurements of the fluorescence radiation of Sn excited by the  $K\alpha$  lines of Cr (2.285 Å.), Cu (1.54 Å.), and Mo (0.71 Å.) lead to intensity ratios for the three lines, which correspond with the three L-levels.

A. J. M.

**Asymmetry of the electric charge distribution in the  $^{201}_{80}Hg$  nucleus.** H. SCHULER and T. SCHMIDT (Z. Physik, 1935, 98, 239—251).

A. B. D. C.

**Emission constants of single- and poly-crystalline materials.** A. RÖCKNAGEL (Z. Physik, 1935, 98, 355—362).—Theoretical. Richardson's emission const.  $A$  for a single crystal can be double that for polycryst. samples of the same material. A. B. D. C.

**Thermionic emission from tungsten and thoriated tungsten filaments.** W. B. NOTTINGHAM (Physical Rev., 1936, [ii], 49, 78—97).—Electron emission has been investigated as a function of applied potential from a few volts retarding to 1400 volts accelerating. The electron energy distribution was deficient in slow electrons. The negative temp. coeff. of the work function for pure W is  $4.3 \times 10^{-5}$  volt per degree. Electron emission data in accelerating fields show large deviations from the Schottky mirror image theory. N. M. B.

**Photo-electric effect for the L-shell.** H. HALL and W. RARITA (Physical Rev., 1934, [ii], 46, 143) L. S. T.

**Spark potential for electrolytic valve action.** W. BÄR (Z. Physik, 1935, 98, 267—279). A. B. D. C.

**Shot effect of secondary emission.** I. M. ZIEGLER (Physica, 1936, 3, 1—11).—A method of measuring fluctuations in the current in a vac. tube by comparing them with the definite fluctuations brought about in another tube by the pure shot effect is described. A. J. M.

**Electron-microscopic investigations of electron emission from cold metals.** A. WEHNELT and W. SCHILLING (Z. Physik, 1935, 98, 286—287).—A cold Mo cathode emits electrons from independent points; these centres last for several min. and then suddenly cease to emit, whilst new centres appear. A. B. D. C.

**Electron-optical structural image and emission from barium-nickel cathodes.** E. BRÜCHE (Z. Physik, 1935, 98, 77—107).—Changes in heated cathodes during electron emission have been followed by the electron microscope. A. B. D. C.

**Electron-optical images of emitting wires.** H. MAHL (Z. Physik, 1935, 98, 321—323).—Images of W and Mo wires are reproduced. A. B. D. C.

**Pressure of a degenerate electron gas and related problems.** (Sir) A. EDDINGTON (Proc. Roy. Soc., 1935, A, 152, 253—272).—A straightforward deduction of the formula  $P = K\sigma^{5/3}$  ( $P$  = min. electron pressure corresponding with an electron density  $\sigma$ ) from relativistic principles is given. The pressure is found directly, and not by way of the amutonian. The usual (Dirac) theory of at. phenomena follows from the present basis. The results are applied to a determination of the val. of the cosmical const. The existence of a vast no. of occupied negative energy levels is one of the essential consequences of the analysis. L. L. B.

**Reflexion coefficient of electrons.** M. J. COPLEY and F. E. PHIPPS (Physical Rev., 1934, [ii], 46, 144). L. S. T.

**Scattering of slow electrons by diatomic molecules.** J. B. FISK (Physical Rev., 1936, [ii], 3).—Mathematical. The Ramsauer effect is treated by a method analogous to that used for

atoms. Total cross-sections for elastic scattering are calc. in terms of three parameters related with band spectroscopy. Results for incident electron velocities 0—40 volts for  $N_2$ ,  $O_2$ , and  $H_2$  are in good agreement with experiment. N. M. B.

**Electron attachment and ion formation in gases.** W. ROGOWSKI (Z. Physik, 1935, 98, 399—414). The mass action law is applied with success to formation of ions in gases. A. B. D. C.

**Energy losses by positive ions to probes in the plasma of gas discharges.** W. MOLTAN (Z. Physik, 1935, 98, 227—238).—Probe heating  $\propto$  probe potential to 200 volts, indicating that the accommodation coeff. for the ions is much  $< 1$ , and that there is a negligible electron emission from the probe. A. B. D. C.

**Retardation of hydrogen positive rays by metals.** H. BÄTZNER (Ann. Physik, 1936, [v], 25, 233—262).—The velocity decrease of  $H^+$  particles with 4—60 e.k.v. in passing through films of Al, Cu, Ag, Sn, and Au has been measured. The relative at. retarding powers for this energy region depend on the at. vol. rather than on the at. no., in contrast to the relation for high energy. Vals. for the range of the particles in Al are calc. L. J. J.

**Negative atomic hydrogen ions.** W. H. BENNETT and P. F. DARBY (Physical Rev., 1936, [ii], 49, 97—99). Negative at. H ions have been directly observed at the heads of striations in discharges in  $H_2O$  vapour; they form readily in these regions of high density of slow electrons, but are easily lost by collision. N. M. B.

**Determination of the conditions for inelastic collision with the aid of slow  $K^+$  ions.** O. SCHMIDT (Z. Elektrochem., 1935, 42, 8—21).—Theoretical. The significance of experimental results (A., 1934, 863, 937) is discussed. E. S. H.

**Collision of  $K^+$  ions with inorganic and organic gases. III. Effective cross-section [of particles] and area of mass-spectrographic distribution curves.** O. SCHMIDT (Ann. Physik, 1936, [v], 25, 92—96; cf. A., 1935, 5).—For const. max. intensity, the area  $F$  of the curve of scattering  $\propto$  pressure of the gas and is related to the effective cross-section  $Q$ . For pure scattering in similar gases  $F/Q = a = \text{const.}$  (Xe, Kr, Ar, and  $CO_2$ ,  $N_2$ ,  $MeCl$ ). For other gases, the val. of  $a$  and the loss of energy on impact either increase (inert gases) or decrease (paraffins and olefines and He) with decreasing mass. L. J. J.

**Relative at. wt. of oxygen in water and in air.** M. DOLB (J. Amer. Chem. Soc., 1935, 57, 2731).—The at. wt. of O in air is 16.00008 if that of O in Lake Michigan  $H_2O$  is 16.00000. E. S. H.

**At. wt. of gallium.** G. E. F. LUNDELL and J. I. HOFFMANN (J. Res. Nat. Bur. Stand., 1935, 15, 409—420).—Conversion of pure Ga into  $Ga_2O_3$  through  $Ga_2(SO_4)_3$ ,  $Ga(OH)_3$ , or  $Ga(NO_3)_3$  and ignition at 1200—1300° gave at. wt. of Ga 69.74.  $Ga_2O_3$  has  $d$  5.95. A. R. P.

**At. wt. of rubidium.** E. H. ARCHIBALD, J. G. HOOLEY, and N. W. F. PHILLIPS (Trans. Roy. Soc.

Canada, 1935, [iii], 29, III, 155—162, and J. Amer. Chem. Soc., 1936, 58, 70—72).—The at. wt., determined from the Ag : RbCl ratio, and using Johnson's method of determining the nephelometric end-point, was 85.48 (cf. A., 1931, 584). H. J. E.

**Mass ratio of hydrogen and deuterium from band spectra.** W. W. WATSON (Physical Rev., 1936, [ii], 49, 70—72).—Corrections of  $B_e$  rotational const. for uncoupling terms and interactions between nuclear and electronic motions for some diat. hydride and deuteride mols. are calc. If  $H-1.0081$ , D must be  $>$  the generally accepted val. 2.01423, and is approx. 2.0148 (cf. Aston, A., 1935, 677). N. M. B.

**Mass ratio of the lithium isotopes from the spectrum of  $Li_2$ .** G. M. ALMY and G. R. IRWIN (Physical Rev., 1936, [ii], 49, 72—77; cf. *ibid.*, 1935, [ii], 48, 104).—Rotational and vibrational analyses of the  $\rightarrow Li_2$  band system are tabulated. The mass ratio  $Li^7/Li^6$  calc. from the observed isotope effect is  $1.16640 \pm 0.00016$ , and the mass coeff.  $1.04077 \pm 0.00004$ . A small electronic isotope shift,  $-0.064 \pm 0.010$  cm.<sup>-1</sup>, has been found. N. M. B.

**Alpha-particle yield from lithium under proton bombardment.** N. P. HEYDENBURG, C. T. ZAHN, and L. D. P. KING (Physical Rev., 1936, [ii], 49, 100—101).—Observed thick film yields for the proton energy range 40—225 kv. are in good agreement with those of Herb (cf. A., 1935, 1186) at higher voltages. N. M. B.

**Measurement of  $\beta$ -radiation from radium in  $r$ -units.** H. SMEREKER and K. JURIS (Strahlenther., 1935, 52, 327—337; Chem. Zentr., 1935, i, 3249).—Measurement by the method described shows the unfiltered  $\beta$ -radiation to be 200 times as strong as the  $\gamma$ -radiation. J. S. A.

**Quantum energy of some nuclear  $\gamma$ -rays.** R. FLEISCHMANN (Naturwiss., 1936, 24, 77—78).—The quantum energy of  $\gamma$ -rays emitted by neutron bombardment was determined by the coincidence method of Bothe *et al.* (A., 1929, 116), to avoid scattering effects. The absorption of secondary electrons emitted by the action of the  $\gamma$ -rays on Al was determined. The quantum energies are  $>$  those obtained by the direct absorption method (this vol., 6). Quantum energy shows dependence on at. no. similar to the packing fraction. A. J. M.

**Emission of  $\gamma$ -quanta on disintegration of lithium by fast protons.** K. ALEXOPOULOS (Z. Physik, 1935, 98, 336—341).— $\gamma$ -Quanta are emitted on bombardment with protons of 450 e.kv. A. B. D. C.

**Rayleigh scattering of hard radiation by heavy atoms.** W. FRANZ (Z. Physik, 1935, 98, 314—320).—Theoretical. Rayleigh scattering of 4.7 X  $\gamma$ -radiation by Pb should amount to 1% of the Klein-Nishina scattering. A. B. D. C.

**Scattering of the Th-C''  $\gamma$  rays.** C. C. LAURITSEN and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 46, 81). L. S. T.

**Production of electron-pairs by  $\gamma$ -rays in krypton.** M. N. S. IMMELMAN (Naturwiss., 1936, 24, 61—62).—The probability of production of an

electron-pair in Kr by  $\gamma$ -rays from Th-C'' ( $h\nu=2.6 \times 10^6$  ev.) is about  $\frac{1}{6}$  of the probability of production of Compton electrons with energy  $> 1.25 \times 10^6$  ev. Examination of 300 Wilson photographs gave 51 Compton electrons of the above energy, and 4 electron-pairs. A. J. M.

**Determination of neutron intensities by means of Fermi electrons from rhodium.** R. DOPEL (Physikal. Z., 1936, 37, 96—100).—The Fermi effect with Rh has been investigated with a view to its use for determining the intensity of a weak beam of neutrons mixed with strong  $\gamma$ -rays. There are two emissions of electrons, half-life 35 sec. and 3.8 m. The initial intensity ratio of the short- to the long-lived is 6.7, and half-val. thickness of Al for absorption of the electrons is 0.45 mm. for both emissions. The optimum conditions for the determination of neutron intensities are examined, and the prep. of neutron standards for comparative work is described. A. J. M.

**Neutrons from the disintegration of deuterium by deuterons.** T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1936, [ii], 49, 19—21; cf. this vol., 6; Crane, A., 1934, 714; McMillan, A., 1935, 559).—The excitation functions for the emission of neutrons from D and Be by  $D_2$  were investigated in the energy range 0.5—0.9 m.e.v. The yield of neutrons from a  $D_3PO_4$  target varied nearly linearly, and from a Be target nearly exponentially, with the bombarding energy. The no. of neutrons from Be increases from 1 to 3 times as many as from  $D_3PO_4$  in the range. The neutrons from D are nearly homogeneous, with 2.55 m.e.v. max. energy. The energy of the disintegration is  $3.21 \pm 0.13$  m.e.v. N. M. B.

**Absorption of residual neutrons.** J. TUTIN (Nature, 1936, 137, 34).—Neutrons may be captured in energy levels outside the nucleus. L. S. T.

**Absorption law for slow neutrons.** F. RASETH, E. SEGRE, G. FINK, J. R. DUNNING, and G. B. PEGRAM (Physical Rev., 1936, [ii], 49, 104).—The validity of the Fermi-Bethe absorption law was tested by measuring the absorption of neutrons by a thin film of Cd and of Ag on the edge of a disc rotating at high velocity with and against, respectively, the neutron beam. For Ag the law is obeyed, but for Cd a change of 6.3% in the absorption coeff. indicates that the capture cross-section varies with the velocity less rapidly than  $1/v$ , where  $v$  is the neutron velocity (cf. following abstract). N. M. B.

**Velocities of slow neutrons.** G. A. FINK, J. R. DUNNING, G. B. PEGRAM, and D. P. MITCHELL (Physical Rev., 1936, [ii], 49, 103; cf. A., 1935, 1441).—Velocity distribution curves for slow neutrons from sources at room temp. and liquid air temp. are given and discussed. N. M. B.

**Slowing down of neutrons.** G. C. WICK (Physical Rev., 1936, [ii], 49, 192—193).—Fermi's statement, that an impact of a neutron with a proton reduces, on an average, the neutron energy by  $1/e$ , is explained (cf. A., 1935, 910). N. M. B.

**Influence of the velocity of slow neutrons on their capture by certain nuclei.** P. PREISWERTK and H. VON HALBAN, jun. (Nature, 1935, 136, 1027).



The radioactivation of Ag by neutrons from a Be+Rn source at different temp. after traversing paraffin wax with a Cd shield interposed at various distances indicates that the cross-section for neutron capture varies inversely as the velocity of the neutrons relative to the Ag atoms. Contrary to Moon and Tillman (A., 1936, 802), cooling the paraffin wax to 90° abs. increases the radioactivity induced in I by 10%.

L. S. T.

**Energy of disintegration of radio-phosphorus [ $P^{30}$ ].** C. D. ELLIS and W. J. HENDERSON (Proc. Roy. Soc., 1935, A, 152, 714—723).—The energy of the upper limit of the positrons from [ $P^{30}$ ] is found to be  $2.9 \pm 0.1 \times 10^6$  volts, corresponding with the formation of the product nucleus  $Si^{30}$  in its ground state. Assuming that this energy determines the difference of internal energy of  $Si^{30}$  and  $P^{30}$ , it is found, on the basis of existing data, that the difference in mass of  $Al^{27}$  and  $Si^{30}$  is the same whether calc. from  $_{13}Al^{27} + _2He^4 \rightarrow _{14}Si^{30} + _1H^1$ , or from the two stages  $_{13}Al^{27} + _2He^4 \rightarrow _{15}P^{30} + _0n^1$  and  $_{15}P^{30} \rightarrow _{14}Si^{30} + e^+$ .

L. L. B.

**New artificial radioactive elements. II.** O. D'AGOSTINO (Gazzetta, 1935, 65, 1071—1087; cf. A., 1935, 276).—The identification of 17 active elements obtained by neutron bombardment of Li, B, Na, Al, P, Cl, K, Mn, Cu, Zn, Ga, As, Se, Ag, Cd, In, Sb, I, Ba, W, and Re and some experiments on the separation of radioactive isotopes are described.

O. J. W.

**Radioactivity produced in thorium and in uranium by means of neutron bombardment.** O. D'AGOSTINO and E. SEGRE (Gazzetta, 1935, 65, 1088—1098; cf. A., 1934, 826).—In the Th activity produced by neutron bombardment two periods have been established, viz., 1 min. and 24 min. The latter is due to a new isotope of Th. The 13 and 100 min. activities of U are not due to any element of at. no. 80—92, but to an element 93 or 94 and at. wt. 239.

O. J. W.

**Angular distribution of the products of artificial nuclear disintegration.** J. GIARRATANA and C. G. BRENNECKE (Physical Rev., 1936, [ii], 49, 35—40). Using special technique, measurements, accurate to  $\pm 8\%$ , of the angular distribution of  $\alpha$ -particles from the disintegration of Li by fast protons showed that the emission is random in direction.

N. M. B.

**Capacity of the elements for disintegration. Results of old and new methods.** G. STETTER (Physikal. Z., 1936, 37, 88—95).—A critique of the scintillation method of investigating at. disintegration, and discussion of results obtained by more modern methods.

A. J. M.

**Production of cosmic-ray showers at a considerable depth below ground-level.** D. H. LITTLE and J. D. CRAWSHAW (Nature, 1935, 136, 1026).—Much of the radiation which penetrates must consist of positive or negative electron

L. S. T.

**Secondary effect of cosmic rays.** A. SCHWEG (Physik, 1935, 98, 288; cf. A., 1935, 1297).

A. B. D. C.

**Fluctuations in cosmic-ray ionisation as given by several recording meters at the same station.** R. L. DOAN (Physical Rev., 1936, [ii], 49, 107—122).—Intensity variations over 10 weeks are recorded and analysed. Statistical agreement is found. The barometer effect is 1—2% per cm. Hg. Marked ionisation increase during rainfall is probably due to  $\gamma$ -radiation from active deposits brought down from the upper atm. Time distribution of ionisation bursts is purely random, with no evidence of barometer effect on burst frequency.

N. M. B.

**Super-Novae and cosmic rays.** W. BAADE and F. ZWICKY (Physical Rev., 1934, [ii], 46, 76—77).

L. S. T.

**Penetrating power of asymmetric component of cosmic radiation.** S. A. KORFF (Physical Rev., 1934, [ii], 46, 74—75).

L. S. T.

**Analysis of ultra-radiation.** B. GROSS (Physikal. Z., 1936, 37, 12—18).—Theoretical. The energy of a primary ray is calc. as a function of depth and range.

A. J. M.

**Excitation function of lithium under proton bombardment.** M. OSTROFSKY, G. BREIT, and D. P. JOHNSON (Physical Rev., 1936, [ii], 49, 22—34).—The yield of  $\alpha$ -particles in the bombardment of Li with protons for different depths and widths of the "potential well," and the asymptotic form of the dependence of the collision cross-section on velocity at low velocities, are calc. Estimates of the theoretical variation of the yield with velocity are made for  $Li^7 + H^2$ . The "well" for the quant. representation of the  $\alpha$ -particle reaction is compared with the mass of  $Be^8$ , and both can be fitted by attributing the formation of  $Be^8$  from  $Li^7$  to the addition of a proton into a  $p$  level.

N. M. B.

**Radiative collision between fast charged particles.** C. MÖLLER (Proc. Roy. Soc., 1935, A, 152, 481—496).—Mathematical. A correspondence method, which is relativistically invariant and forms an immediate generalisation of the method previously used in the treatment of the non-radiative collision of fast particles, is developed for the treatment of the radiative collision between two particles. (Cf. A., 1931, 1109.)

L. L. B.

**Apparent failure of the photon theory of scattering.** R. S. SHANKLAND (Physical Rev., 1936, [ii], 49, 8—13).—Using Ra-C  $\gamma$ -radiation and air, Al, Be, filter-paper, and paraffin scatterers, coincident discharges were recorded in special Geiger-Müller electron and photon counters at various angles. There were fewer coincidences in the correct positions than expected, and those observed could be accounted for as chance coincidences due to the finite resolving time of the apparatus. Results do not agree with the photon theory of scattering.

N. M. B.

**Exchange forces and the structure of the nucleus.** J. H. BARTLETT, jun. (Physical Rev., 1936, [ii], 49, 102; cf. Feenberg, this vol., 134).—The possibility of a Heisenberg exchange followed by a Majorana exchange, i.e., an interchange of spin co-ordinates and not of space co-ordinates, is examined.

N. M. B.

**Interaction of light nuclei. II. Binding energies of the nuclei and  $\text{He}_2^3$ .** H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1935, A, 152, 693—705).—The validity of the variation method as applied to  $\text{H}_1^2$  is examined by comparing results obtained by its use with exact solutions. The method must be used with caution in determining binding energies due to short-range interactions. The binding energies of  $\text{H}_1^3$  and  $\text{He}_2^3$  can be explained by introducing attractive forces between the neutrons on the one hand and the protons on the other. The attraction between two neutrons must be much  $<$  that between a neutron and a proton, so the existence of a stable  $n_0^2$  nucleus is precluded. The anomalous attraction between two protons at small distances must also be much  $<$  that between a neutron and a proton, and cannot be sufficient to produce a stable nucleus  $\text{He}_2^3$ . (Cf. A., 1935, 274.) L. L. B.

**Energies of nuclear reactions.** H. A. WILSON (Proc. Roy. Soc., 1935, A, 152, 497—502).—The energies of 17 nuclear reactions are discussed, and in order to make the reaction equations consistent, the vals. of some of the energies are revised. The at. wts. of the 13 light elements involved are calc. from the reaction energies, and vals. obtained in good agreement with those of Bethe (Physical Rev., 1935, [ii], 47, 634) and of Oliphant *et al.* (A., 1935, 803).

L. L. B.

**Recombination of neutron with proton.** S. KIKUCHI, K. HUSIMI, and H. AOKI (Nature, 1936, 137, 30—31).—From the relative intensities of the  $\gamma$ -rays emitted under neutron bombardment by  $\text{H}_2\text{O}$  and aq.  $\text{H}_3\text{BO}_3$  and an aq. solution of a Cd salt, the mean cross-section found for the recombination of neutron with proton lies between  $8.3 \times 10^{-28}$  and  $3.0 \times 10^{-28}$  cm.<sup>2</sup>

L. S. T.

**Spontaneous disintegration of proton or neutron according to the Fermi theory.** H. C. WOLFE and G. E. UHLENBECK (Physical Rev., 1934, [ii], 46, 237).

L. S. T.

**Neutron collisions and the  $\beta$ -ray theory of Fermi.** A. NORDSIECK (Physical Rev., 1934, [ii], 46, 234—235).

L. S. T.

**Energy of removal of neutrons and  $\alpha$ -particles from nuclei and  $\alpha$ -instability below the radio-elements.** E. D. EASTMAN (Physical Rev., 1934, [ii], 46, 238—239).—A discussion emphasising the  $\alpha$ -instability of elements of relatively low at. no. (cf. A., 1934, 939).

L. S. T.

**Hydrogen atom.** V. FOCK (Z. Physik, 1935, 98, 145—154).—Group theory describes very simply many of the phenomena associated with the H atom, including the Compton effect for bound electrons.

A. B. D. C.

**Singular magnetic poles.** B. O. GRONBLOM (Z. Physik, 1935, 98, 283—285).—Theoretical.

A. B. D. C.

**Creation of electron pairs by fast charged particles.** H. J. BHABHA (Proc. Roy. Soc., 1935, A, 152, 559—586).—Mathematical. The creation of electron pairs by the collision of fast charged particles is calc., taking into account the effect of screening. The probability of the creation of a pair

as a function of impact parameter is investigated, and various cases are treated which have not been considered before. Most of the formulæ can be derived by a method similar to that given by Weizsäcker (A., 1934, 712).

L. L. B.

**Light aberration and the Doppler effect.** K. PAPELLO (Z. Physik, 1936, 98, 490—495).—Aberration of light from stars depends on the distance of the star from the earth, and the relative or abs. velocity of the observer, indicating that the velocity of light is a function of time.

A. B. D. C.

**Orbits of electrons in magnetrons with space charge.** H. AWENDER, A. THOMA, and D. M. TOMBS (Z. Physik, 1936, 98, 534—535).—A correction (cf. this vol., 4).

A. B. D. C.

**Probability of radiative processes for very high energies.** L. W. NORDHEIM (Physical Rev., 1936, [ii], 49, 189—191).—Mathematical. The present theory (cf. Bethe, A., 1934, 1150) is modified for high energies and cosmic-ray phenomena.

N. M. B.

**Temperature dependence of free electron susceptibility.** E. C. STONER (Proc. Roy. Soc., 1936, A, 152, 672—692).—Mathematical. Various formulæ required in the application of the Fermi-Dirac statistics to the calculation of magnetisation are given in a convenient form, and calculations are made of the magnetisation as a function of  $H$  and  $T$  for the spin and diamagnetic effects considered separately or together, at both low and high temp. Under certain conditions the formulæ derived will hold approx. for electrons in metals.

L. L. B.

**Magnetic moment of the neutron.** A. LANDÉ and D. R. INGLIS (Physical Rev., 1934, [ii], 46, 76).—Disagreement with Schuler's val. of  $-1.65$  magnetons (A., 1934, 580) is expressed.

L. S. T.

**Interpretation of present values of nuclear moments.** G. BREIT and I. I. RABI (Physical Rev., 1934, [ii], 46, 230—231).—A discussion of recent speculations on the magnetic moment and nature of the neutron and proton.

L. S. T.

**Progression of nuclear resonance levels with atomic number.** H. MARGENAU and E. POLLARD (Physical Rev., 1934, [ii], 46, 228; cf. A., 1935, 804).

L. S. T.

**Disintegration of  $\text{H}^2$  and the stellar abundance of  $\text{H}^2$  and  $\text{H}^3$ .** H. H. GOLDSMITH (Physical Rev., 1934, [ii], 46, 78—79).

L. S. T.

**Electric quadrupole moments of some atoms and the magnetic moment of the proton.** H. SCHÜLER and T. SCHMIDT (Z. Physik, 1936, 98, 430—436).—Lack of symmetry shown by Cu, As, Eu, Lu, Hg, and Bi nuclei indicates rod- and plate-like electric charge distribution, and gives a magnetic moment of  $1.5$  for the proton in these nuclei.

A. B. D. C.

**Relativistic self-consistent field.** (Miss) B. SWIRLES (Proc. Roy. Soc., 1935, A, 152, 625—649).—Mathematical. A relativistic treatment of a many-electron atom on the lines of the self-consistent field method with "exchange" is developed. Tables are given from which the expression for the

total energy of an atom containing  $s$ ,  $p$ ,  $d$  electrons may be constructed.

L. L. B.

**Band spectrum of  $\text{OH}^+$ .** F. W. LOOMS and W. H. BRANDT (Physical Rev., 1936, [ii], 49, 55—67).—Full data are given for two bands at 3332 and 3565 Å. in the electrodeless discharge in pure  $\text{H}_2\text{O}$  vapour (cf. Rodebush, A., 1934, 39) and for new bands at 3695 and 3893 Å., which are, respectively, the (1,0), (0,0), (1,1), and (0,1) bands of  $\text{OH}^+$ . Rotational analysis shows that they correspond with a  $^3\Pi \rightarrow ^3\Sigma^-$  transition in which the  $^3\Pi$  state is inverted. Multiplet intervals in both states are determined from the 9 strong branches and the satellite branches.  $\Delta$ -type doubling and perturbations are examined. The  $^3\Sigma^-$  state concerned in the transition and the perturbing state are mol. levels which dissociate into the ground states of O and  $\text{H}^+$  and  $\text{O}^+$  and H, respectively.

N. M. B.

**Rotation constants  $B$ ,  $D$ , and  $\gamma$  for the  $^3\Pi$  terms of  $\text{TiO}$ ,  $\text{C}_2$ ,  $\text{CO}$ ,  $\text{PH}$ ,  $\text{AlH}$ , and  $\text{NH}$ .** A. BUDÓ (Z. Physik, 1936, 98, 437—444).

A. B. D. C.

**Absorption spectrum of copper hydride.** B. GRUNDSTROM (Z. Physik, 1935, 98, 128—132).

A. B. D. C.

**Strontium deuteride and hydride spectra.** W. W. WATSON, W. R. FREDRICKSON, and M. E. HOGAN, jun. (Physical Rev., 1936, [ii], 49, 150—155; cf. A., 1932, 439; 1935, 1443).—Analyses of the  $B$  and  $C$  band systems of  $\text{SrD}$  and of part of the  $D$  system of  $\text{SrH}$  are reported.

N. M. B.

**Isotope effect for gold hydride ( $\text{AuH}/\text{AuD}$ ).** T. HEIMER (Naturwiss., 1936, 24, 78).—The arc emission band spectrum of  $\text{AuD}$  has been examined, and compared with results for  $\text{AuH}$ .

A. J. M.

**Anomalous rotation of  $\text{HgH}$  molecules.** F. F. RIEKE (Physical Rev., 1934, [ii], 46, 236—237).

L. S. T.

**Absorption bands of gaseous  $\text{HI}$ .** D. E. KIRKPATRICK (Physical Rev., 1936, [ii], 49, 104).—Measurements of the centres of the 1  $\leftarrow$  0 and 2  $\leftarrow$  0 absorption bands gave the vals.  $2260 \pm 30$  and  $4416 \pm 75 \text{ cm}^{-1}$ , in agreement with Salant (cf. A., 1931, 545) and Nielsen (cf. A., 1935, 806).

N. M. B.

**Band spectra of  $\text{BiBr}$ ,  $\text{BiCl}$ ,  $\text{BiF}$ , and  $\text{BiI}$  in absorption.** F. MORGAN (Physical Rev., 1936, [ii], 49, 41—46).—Data and vibrational analyses are reported.  $\text{BiBr}$  has two systems for each of the isotopes  $\text{Br}^{79}$  and  $\text{Br}^{81}$  with origins at 4045.7 and 4869.1 Å., the latter system degrading to the red.  $\text{BiCl}$  has a system in the range 3600—4000 Å. for both  $\text{Cl}$  and  $\text{Cl}^{37}$ , in addition to a system at 4300—5500 Å. (cf. Saper, A., 1933, 207). Vibrational analyses are confirmed by the respective isotope shifts. A system 4150—4900 for  $\text{BiF}$ , and a system 4150—4300 Å. for  $\text{BiI}$  have been observed and analysed.

N. M. B.

**Absorption spectra of  $\text{PbF}$ ,  $\text{PbCl}$ , and  $\text{PbBr}$ .** MORGAN (Physical Rev., 1936, [ii], 49, 47—50).—Data and vibrational analyses are given.  $\text{PbF}$  has a single system of double-headed bands in the 4100—5300 Å.  $\text{PbCl}$  has a system with origin for each the isotopes  $\text{Cl}^{35}$  and  $\text{Cl}^{37}$ .  $\text{PbBr}$  has a system in the range 4400—5400 Å. for

both  $\text{Br}^{79}$  and  $\text{Br}^{81}$ . Analyses are confirmed by the respective isotope shifts; all the bands degrade to the red.

N. M. B.

**End-isotope effect for triatomic molecules.** M. WEHRLI (Naturwiss., 1936, 24, 14—15).—The end-isotope effect has been investigated for  $\text{TeCl}_2$ , the relative abundance of the mols. being  $\text{TeCl}_2^{35} : \text{TeCl}_2^{35}\text{Cl}^{37} : \text{TeCl}_2^{37} = 1 : 0.32 : 0.10$ . In contrast to diat. mols. there is no simple connexion between the isotopic splitting,  $\Delta\nu$ , and the frequency, except in two special band series, one due to excitation of symmetrical vibrations only, and the other to excitation of the antisymmetrical and deformation vibrations. The isotopic factor,  $f_1$ , is 0.0131 (theory for linear mol. 0.0139).

A. J. M.

**Absorption spectra of the chlorides and oxychlorides of sulphur.** R. K. ASUNDI and R. SAMUEL (Proc. Physical Soc., 1936, 48, 28—34; cf. A., 1935, 680).—Absorption curves, in the visible and ultra-violet, are given for the vapours of  $\text{SCl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SOCl}_2$ , and  $\text{SO}_2\text{Cl}_2$ . Heats of formation and linking energies are derived, and results are correlated with photodissociation processes.

N. M. B.

**Spectrophotometric studies. II—V.**—See this vol., 221.

**Extinction of mesomorphic liquids in a magnetic field.** Y. BJORNSTAHL (Z. physikal. Chem., 1935, 175, 17—37).—Melts of  $p$ -azoxyanisole,  $p$ -azoxyphenetole, and  $p$ -azoxyanisolephenetole have been examined. The extinction coeff.,  $\epsilon$ , is unaffected by a transverse field, and there is no dichroism in the field. The depolarisation of linearly polarised light by the liquid is changed in the field. In a longitudinal field  $\epsilon$  decreases with increasing field strength,  $F$ , ultimately approaching a limit. If  $\epsilon$  is measured with rising and falling  $F$ , hysteresis may appear. For moderate  $F$   $\epsilon$  decreases in jumps with rising  $F$ . In a given longitudinal field  $\epsilon$  is independent of the temp. It is difficult to account for these observations on the swarm theory of mesomorphic liquids. Ornstein's theory (A., 1935, 20) is criticised.

R. C.

**Absorption spectra of tautomeric selenazoles.** R. F. HUNTER (Nature, 1935, 136, 1030).—The ultra-violet absorption curve of 1-hydroxylbenzelenazole (I) in  $\text{MeOH}$  is practically identical with that of 1-keto-2-methyl-1 : 2-dihydrobenzelenazole and distinct from that of the  $O$ -Me ether. In aq.  $\text{NaOH}$  the curve of (I) is moved to the left (deformation) and there is a decrease in the max. due to the production of the ion  $\text{C}_6\text{H}_4\text{<N>CO}$  on which tautomeric change depends. 1-Thiolbenzelenazole shows marked similarity to thiazole analogues in the ultra-violet region; the curve for  $\text{MeOH}$  solution is similar to that of 1-thio-2-methyl-1 : 2-dihydrobenzelenazole.

L. S. T.

**Ultra-violet absorption spectra of some complex aromatic hydrocarbons.** I. W. V. MAYNEORD and E. M. F. ROE (Proc. Roy. Soc., 1935, A, 152, 298—324).—An investigation has been made of the ultra-violet absorption spectra of  $\text{EtOH}$  solutions of  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ , anthracene, 1 : 2-benzanthracene, 1 : 2 : 5 : 6-dibenzanthracene, phenanthrene, and their

derivatives, and of chrysene, picene, pyrene and its derivatives. The spectra of chemically related compounds are compared, and the effects of the addition of various groups are noted. Changes have been observed in the absorption spectra on cooling the solutions to  $-183^{\circ}$ .  
L. L. B.

**Ionic dispersion in the extreme infra-red.** C. H. CARTWRIGHT (Physical Rev., 1936, [ii], 49, 101—102).—A study of the absorption coeff. and reflecting power curves of  $\text{H}_2\text{O}$  and of KI and KCl solutions indicates that the dispersion of electrolytes in the extreme infra-red can be pictured classically, according to Maxwell's equations, by considering the ions to follow in translation the alternations of electromagnetic waves. The motion of the ions decreases in amplitude, because of inertia and friction, with increasing frequency of radiation. In electrolytes of KCl and KI the ions seem to move with respect to the  $\text{H}_2\text{O}$  mols. except for friction. N. M. B.

**Choice of spectral reference rays in the study of every infra-red region (photographic infra-red), especially for the determination of fluorescence spectra.** C. DHÉRE and O. BIERMACHER (Compt. rend. Soc. Biol., 1935, 120, 1162—1166).—Standard reference lines for the infra-red are A 912.4 and 1064  $\text{m}\mu$ , Hg 1014 and the combined He, Cu, and Ag spectra for 500—850  $\text{m}\mu$ . Acid porphyrin solutions show fluorescence bands between 667.8 and 728.2  $\text{m}\mu$ , coincident with the two Cu lines.  
R. N. C.

**Infra-red absorption spectrum of water and alcohols in non-polar solvents.** E. L. KINSEY and J. W. ELLIS (Physical Rev., 1936, [ii], 49, 105).—Absorption curves in the range 1.0—2.5  $\mu$  for  $\text{H}_2\text{O}$  dissolved in  $\text{CS}_2$  and for  $\text{MeOH}$  in  $\text{CCl}_4$ , compared with those for liquid and vapour  $\text{H}_2\text{O}$  and  $\text{MeOH}$ , show vapour-like characteristics and strong OH bands, indicating that the interaction between mols. in the liquid is weakened or destroyed in solution, and that the interaction affects, relatively, only the polar part of the mol.  
N. M. B.

**Rotation-vibration spectrum of acetylene in the photographic infra-red.** G. W. FUNKE and G. HERZBERG (Physical Rev., 1936, [ii], 49, 100).—Data and interpretations of 3 new  $\perp$  and 6 new  $\parallel$  bands are reported and discussed.  
N. M. B.

**Quantitative absorption measurements of the CH overtones for simple hydrocarbons. I. Halogen derivatives of methane, ethane, and ethylene.** B. TIMM and R. MECKE (Z. Physik, 1935, 98, 363—381).—Photometer measurements are given for the third CH overtone in spectra of  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{MeCl}$ ,  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{MeBr}$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ ,  $\text{C}_2\text{H}_3\text{Cl}_3$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $\text{EtCl}$ ,  $\text{Pr}^n\text{Cl}$ ,  $\text{C}_2\text{H}_2\text{Br}_4$ ,  $\text{C}_2\text{H}_3\text{Br}_3$ ,  $\text{EtBr}$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_2$ , and  $\text{C}_2\text{H}_3\text{Cl}$ . Absorption intensity  $\propto$  to the no. of CH groups, the halide atom having little influence on the electrical properties of an aliphatic CH linking. Transition moments are calc. and used to determine variation of dipole moment with nuclear separation in a homopolar linking.  
A. B. D. C.

**Rotation-vibration spectra of methyl halides in the photographic infra-red to 1.11  $\mu$ .** H.

VERLEGER (Z. Physik, 1935, 98, 342—352).—Resolved vibration bands are given for  $\text{MeCl}$ ,  $\text{MeBr}$ , and  $\text{MeI}$ , and give moments of inertia for the axis normal to the symmetry axis of 60, 80, and  $90 \times 10^{-40}$  g.-cm.<sup>2</sup>; that about the symmetry axis is  $4.1 \times 10^{-40}$  for all three.  
A. B. D. C.

**Infra-red evidence for the existence of an isomeric form of HCN.** D. WILLIAMS (J. Chem. Physics, 1936, 4, 84).—The infra-red spectrum of a saturated solution of HCN has a strong band at 4.76  $\mu$  and a much fainter band at 4.95  $\mu$ . Since a shift of approx. 0.2  $\mu$  represents the difference between the band for org. cyanides and their isomeric forms at 4.5  $\mu$  the absorption at 4.95  $\mu$  is attributed to a small quantity (about 2%) of the isomeride HNC.

M. S. B.  
**Relations between electrochemical constants, infra-red spectrum, and reaction properties.** F. VLES (Compt. rend., 1935, 201, 1475—1477).—The  $\lambda\lambda$  of the bands calc. from the previous relationship (A., 1935, 444) for  $\text{BzOH}$ ,  $\text{NH}_2\text{Ph}$ , anthranilic acid, and methylene-blue, and for the decomp. of  $\text{CO}(\text{NH}_2)_2$  by urease, are ascribed to sp. groups of atoms.  
T. G. P.

**Infra-red spectra of amino-acids and polypeptides.** E. HEINTZ (Compt. rend., 1935, 201, 1478—1480; cf. A., 1935, 1053).—Data are recorded for glycine, *dl*-alanine, *l*-cystine, cysteine, *l*-leucine, *d*-glutamic acid, *d*-arginine, *dl*-proline, tyrosine, *l*-histidine, phenylalanine, three peptones, and an albuminose of casein. The vals. confirm the previous relationship (A., 1935, 444).  
T. G. P.

**Raman spectrum of deuterium. II. Intensity and polarisation characters.** S. BHAGAVANTAM (Proc. Indian Acad. Sci., 1935, 2, A, 477—482; cf. A., 1935, 1445).—Data are recorded and classified. Vibration lines are polarised; rotation lines are nearly completely depolarised.  
H. J. E.

**Raman spectra of carbon and silicon tetrachlorides.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1935, 2, A, 452—458).—Two new lines of low intensity were found for  $\text{CCl}_4$  (434, 145  $\text{cm}^{-1}$ ). A new line at 440.5  $\text{cm}^{-1}$  was found for  $\text{SiCl}_4$ . The origin of these lines is discussed.  
H. J. E.

**Raman spectrum and fundamental vibration frequencies of silane ( $\text{SiH}_4$ ).** F. B. STITT and D. M. YOST (J. Chem. Physics, 1936, 4, 82).—Two Raman lines have been found for  $\text{SiH}_4$  and, combined with the infra-red data of Steward and Nielsen (A., 1935, 914), have led to the following arrangements of fundamentals:  $\nu_1$  2187,  $\nu_2$  978,  $\nu_3$  2183, and  $\nu_4$  910  $\text{cm}^{-1}$ .  
M. S. B.

**Raman spectra of some formates and the constitution of formic acid.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 615—620).—The Raman spectra of  $\text{HCO}_2\text{Na}$ ,  $(\text{HCO}_2)_2\text{Ca}$ ,  $(\text{HCO}_2)_2\text{Cd}$ , and  $(\text{HCO}_2)_2\text{Pb}$  have been measured for the solids and their aq. solutions; average frequencies for the  $\text{HCO}_2$  ion are 2834, 2732, 1717, 1534, 1347, and 857  $\text{cm}^{-1}$ . These frequencies are compared with those of  $\text{HCO}_2\text{H}$ ,  $\text{HCO}_2\text{Me}$ ,  $\text{AcOH}$ , and  $\text{NaOAc}$ . The existence of the lines 2834 and 2732  $\text{cm}^{-1}$  proves the presence of the



CH group. The 1534  $\text{cm}^{-1}$  line, of doubtful origin, is characteristic of formates. J. W. S.

**Raman spectrum of oxalic acid.** W. R. ANGUS and A. H. LECKIE (J. Chem. Physics, 1936, 4, 83—84).—Contrary to Hibben's conclusion (this vol., 9), the frequencies 1661 and 1759 are present in the spectrum of solid  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and are as strong as the corresponding frequencies in aq. solution. This agrees with Rao's data (A., 1935, 807) on the assumption that the latter were obtained from the  $2\text{H}_2\text{O}$  crystals. M. S. B.

**Raman spectrum of dioxan.** A. SIMON and F. FEHER (Ber., 1936, 59, [B], 214—217).—Repeated freezing and melting of dioxan causes a gradual lowering of the m.p., apparently due to the formation of a polymeric form. Evidence of isomerisation to acetaldehyde ethylene diacetal is not obtained. The Raman spectrum of dioxan gives results correcting and expanding those of Villars (A., 1931, 145). H. W.

**Raman effect of acetylenes. II. Di-iodoacetylene, liquid acetylene, and deuteroacetylenes.** G. GLOCKLER and C. E. MORRELL (J. Chem. Physics, 1936, 4, 15—22; cf. A., 1935, 146).—A new type of apparatus is described. Data are recorded for  $\text{C}_2\text{I}_2$ , liquid  $\text{C}_2\text{H}_2$ , and gaseous  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{HD}$ , and  $\text{C}_2\text{D}_2$ . Marked differences between the spectra of liquid and gaseous  $\text{C}_2\text{H}_2$  indicate mol. distortion in the liquid state, so that the mol. is no longer linear. Free energies have been calc. and the equilibrium const. for  $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2 \rightleftharpoons 2\text{C}_2\text{HD}$  has been determined at temp. 273—700° abs. M. S. B.

**Fundamental frequencies of acetylene.** G. GLOCKLER and C. MORRELL (Physical Rev., 1934, [ii], 46, 233).—The frequencies 382 (5), 618 (2), 631 (5), 1762 (1), 1959 (10), 3338 (5)  $\text{cm}^{-1}$  have been found by Raman scattering in liquid  $\text{C}_2\text{H}_2$ . L. S. T.

**Spectrum and force constants of the ethylene molecule.** L. G. BONNER (J. Amer. Chem. Soc., 1936, 57, 34—39).—The Raman and infra-red absorption spectra in the photographic region have been reinvestigated. Three new Raman lines and 1 new infra-red absorption bands have been found. frequency vals. have been assigned to all the 12 fundamental vibration modes of the  $\text{C}_2\text{H}_4$  mol., on the basis of the new data, and 8 of the force consts. of the mol. have been obtained. E. S. H.

**Constitution of the  $\alpha\beta$ -dihalogen derivatives of ethane.** H. C. CHENG (J. Chim. phys., 1935, 32, 724).—Cabannes and Rousset's apparatus (A., 1933, 446) has been used for measuring depolarisation. Raman lines of  $(\text{CH}_2\text{Cl})_2$ ,  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Br}$ , and  $(\text{CH}_2\text{Br})_2$ . It is concluded that the *cis*- and *trans*-forms of these compounds should coexist in the liquid state, and an attempt is made to classify the fundamental frequencies due to each form. J. W. S.

**Raman spectrum of deuterobenzene.** R. C. ORD, jun. (J. Chem. Physics, 1936, 4, 82—83).—The Raman spectrum given by Wood (A., 1935, 1189) for  $\text{C}_6\text{D}_6$  requires force consts. much > usually attributed to benzene linkings. It is suggested that some of the lines are attributable to  $\text{C}_6\text{D}_5\text{H}$ . M. S. B.

**Raman spectra of benzene and its derivatives.** K. W. F. KOHLRAUSCH (Physikal. Z., 1936, 37, 58—79).—A review. A. J. M.

**Partial interpretation of the Raman and infra-red spectra of benzene.** E. B. WILSON, jun. (Physical Rev., 1934, [ii], 46, 146—147).—Raman-active and infra-red-active fundamentals of  $\text{C}_6\text{H}_6$  have been assigned to definite modes of vibration of the regular plane hexagon model. The doublet at 1600  $\text{cm}^{-1}$  in the Raman spectrum is explained on the basis of quantum-mechanical resonance between  $\nu_8$  and  $\nu_1 + \nu_6$ . The suggestion that the spectra of  $\text{C}_6\text{H}_6$  are incompatible with hexagonal symmetry is not justified. L. S. T.

**Molecular scattering of light: Cabannes-Daure effect, critical opalescence of binary mixtures.** A. ROUSSET (Ann. Physique, 1936, [xi], 5, 5—135; cf. A., 1934, 473, 830, 1302).—The continuous spectrum surrounding the exciting line in the scattering of light by liquids (Cabannes-Daure effect) is attributed to part of the anisotropic scattering due to variations of mol. orientations. The arrangement of cybotactic groups limiting the relative orientations of the axes of the mols. changes the statistical wt. of the rotational levels so that the intensity max. of the *P* and *R* branches are approx. identical with that of the fundamental line. In presence of strong permanent moments the anisotropic scattering of a vibrating mol. is wholly in the *Q* branch, explaining the weak intensity of the Cabannes-Daure effect in strongly polar mols. Measurements of the depolarisation factors  $\rho$  for  $\text{H}_2\text{O}-\text{Pr}^n\text{CO}_2\text{H}$ ,  $\text{C}_6\text{H}_{14}-\text{PhNO}_2$ ,  $\text{NH}_2\text{Ph}-\text{cyclohexane}$ , and  $\text{H}_2\text{O}-\text{NEt}_3$  show that on approaching the crit. temp. of complete miscibility  $\rho$  reaches a min. and increases rapidly near the crit. point, indicating that the scattering due to variations of the mol. field increases more slowly than the opalescence near the crit. point. The sharp rise of  $\rho$  is attributed to a partly depolarised secondary scattering increasing more rapidly in intensity than in the case of the primary scattering. The law of variation of opalescence with  $\lambda$  is deduced, intensity of scattering in two directions relative to the incident beam and variations of  $\lambda\lambda$  are examined, and results are discussed in relation to available theory. N. M. B.

**Raman spectra of amino-acids and related compounds. I. Ionisation of the carboxyl group.** J. T. EDSALL (J. Chem. Physics, 1936, 4, 1—8).—Raman spectra have been determined for four  $\text{NH}_2$ -acids, their hydrochlorides and Et esters of two,  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{CH}_2\text{Cl}-\text{CO}_2\text{H}$ , and their Na salts,  $\text{NH}_3\text{MeCl}$ ,  $\text{NH}_3\text{EtCl}$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{MeOAc}$ , and  $\text{COMe}_2$ . For aliphatic acids there is a shift of the C:O frequency from 1670 to 1720 on dissolution in  $\text{H}_2\text{O}$ , but no similar shift for  $\text{MeOAc}$  and  $\text{COMe}_2$ . The presence of  $\text{NH}_3^+$  attached to the  $\alpha$ -C increases the same frequency by approx. 20. On ionisation of  $\text{CO}_2\text{H}$  the C:O frequency vanishes, lines of the region 1200—1420 undergo characteristic changes, and, in general, the frequency of a powerful line in the region 750—930 is increased by 20—40, whilst each additional Me group on the  $\alpha$ -C decreases it by approx. 50, and, finally, the C-H frequency in  $\text{HCO}_2\text{H}$  is

decreased. Certain strong frequencies in  $\text{NH}_3\text{Me}$  and  $\text{NH}_3\text{Et}$  are decreased by ionisation. M. S. B.

**Dust effects.** L. ŠPLAIT (Z. Physik, 1935, 98, 396—398).—Polemical, against Mitra (A., 1935, 1301). A. B. D. C.

**Collision broadening of Rayleigh lines in compressed gases.** E. KAPPLER (Ann. Physik, 1936, [v], 25, 272—278).—Theoretical. The undisplaced component is not broadened by collisions, provided that the incident frequency is far removed from any characteristic frequency of the mol. The intensity distribution observed by Weiler (A., 1935, 1190) is not the effect of collisions on the rotational wings of the Rayleigh line. L. J. J.

**Collision broadening of the undisplaced component of radiation scattered by carbon dioxide at high pressures.** E. KAPPLER and J. WEILER (Ann. Physik, 1936, [v], 25, 279—280).—Up to 59 atm. pressure, radiation scattered through  $90^\circ$  shows no broadening either in the  $Q$  branch or in the polarised Tyndall scattering (cf. preceding abstract). L. J. J.

**Resonance fluorescence of benzene.** II. G. R. CUTHBERTSON and G. B. KISTIAKOWSKY (J. Chem. Physics, 1936, 4, 9—15).—Previous work (A., 1932, 1189) has been amplified and corr. On absorption of the Hg line 2536 Å. the changes of the quantum no. of one vibration only ( $990\text{ cm}^{-1}$ ) of the non-excited  $\text{C}_6\text{H}_6$  mol. are unrestricted in fluorescence. The changes for other vibrations are  $>1$  (or 2 if required by selection rules). Five frequencies other than the above have been identified: 432, 791, 1542, 2557, and  $3174\text{ cm}^{-1}$ . For  $\text{C}_6\text{D}_6$  the frequencies 944 ( $\Delta\nu$  unrestricted) and 2460 have been observed. The quenching of the resonance fluorescence of  $\text{C}_6\text{H}_6$  in  $\text{He}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and cyclohexane consists in a change to high-pressure fluorescence, and some new high-pressure fluorescence bands have been observed. The resonance spectra of PhF and PhMe are nearly continuous even at 0.01 mm. pressure. The fluorescence of PhEt and PhCl is too faint to be examined. M. S. B.

**Fluorescence of ruby, sapphire, and emerald.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1935, 2, A, 459—465).—New bands in the fluorescence spectrum of ruby have been measured. That of sapphire is very similar. Emerald gave two sharp lines at  $\lambda\lambda$  6806, 6835 Å., together with diffuse bands. H. J. E.

**Fluorescence of some pure substances.** E. CANALS, P. PEYROT, and R. NOËL (Compt. rend., 1935, 201, 1488—1489; cf. A., 1935, 1058).—Vals. for the depolarisation factors ( $\rho$ ) and the relative intensities of fluorescence for eight alcohols are recorded. The spectra lie between 4400 and 4900 Å. T. G. P.

**Extinction of fluorescence of methylene-blue by ferrous iron.** H. HELLSTRÖM (Naturwiss., 1935, 24, 76—77; cf. A., 1935, 1087).—The relative intensity of fluorescence of methylene-blue (I) at various  $[\text{Fe}^{2+}]$  and  $p_{\text{H}}$  3 (citrate buffer), and at various  $p_{\text{H}}$  and const.  $[\text{Fe}^{2+}]$  has been determined. The intensity of fluorescence rapidly diminishes on adding  $\text{Fe}^{2+}$ , the extinction velocity being dependent on  $p_{\text{H}}$ . There

may be an unstable compound of (I) and  $\text{Fe}^{2+}$  which readily dissociates. A. J. M.

**Fluorescence of porphyrins.** I. A. STERN and H. MOLVIG (Z. physikal. Chem., 1935, 175, 38—62; cf. A., 1926, 885; A., 1935, 808, 1444).—Fluorescence spectra in dioxan have been determined. Porphyrins which in the positions 1—8 of porphin have substituted Me, Et, and various Me ester groups have five fluorescence bands in the visible. As with the absorption spectra, the position of the max. varies little with the nature of the substituents. The positions of the max. of the principal bands are near those of the red bands in the absorption spectra. Porphyrins with vinyl groups have four fluorescence bands in the visible, the max. of which are shifted towards the red compared with those of porphyrins without unsaturated groups. Porphyrins containing both unsaturated and CO groups and  $\gamma$ -substituted porphyrins may have fluorescence spectra different from the above. The effect of varying substitutions in dihydroporphin on the fluorescence spectrum is much greater and more complicated than with porphin, but certain regularities, observable in absorption spectra, emerge, and may assist in the determination of constitution. The fluorescence spectra of two solid porphyrins and an Al salt have been determined. Solid pyromethenes have one fluorescence band in the visible, usually between 590 and 640  $\mu$ . R. C.

**Porphyrin-gelatin phosphorescence.**—See this vol., 346.

**Quantum theory of the phosphorescence of crystal phosphors.** T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, 28, 171—206).—Mathematical. J. W. S.

**Optimum " concentration of active foreign substances in crystal phosphors.** G. SCHUMANN (Z. Physik, 1935, 98, 252—261).—This optimum concn. is not uniquely defined, factors such as prep. of the crystal and conditions of observation having been overlooked. A. B. D. C.

**Optical and electrical properties of didymium glass.** K. PROSAD, D. K. BHATTACHARYA, and L. M. CHATTERJEE (Z. Physik, 1935, 98, 324—335). Fluorescence bands of Dy glass are identical with the Raman spectrum obtained from incident  $\lambda\lambda$  equal to those of absorption bands. Photo-conductivity has been determined using sunlight and that transmitted by yellow and blue filters. A. B. D. C.

**Luminescence of solid solutions of rhoduline.** S. I. GOLUB (Physikal. Z. Sovietunion, 1935, 7, 49—57).—The spectra of the fluorescence and phosphorescence of solid solutions of rhoduline in sugar are identical. CH. ABS.

**Study of thermoluminescence in some crystals.** T. MUTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 207—220).—Thermoluminescence is studied in terms of the excitation of an electron of an impurity atom, usually a rare-earth metal, by a heat quantum, followed by photo-emission. Variation of bands with temp., disappearance of

time, and the effect of heating the crystal and then treating with X-rays are interpreted theoretically.

R. S. B.

**Mitogenetic radiation.** J. B. BATEMAN (Biol. Rev. Camb. Phil. Soc., 1935, 10, 42—71; Chem. Zentr., 1935, i, 3294).—A crit. review. The existence of mitogenetic radiation is unproven, and its allocation to the ultra-violet region is improbable.

J. S. A.

**Relation between the photo-potential and the chemical properties of photo-sensitive organic substances.** H. T. NGA (J. Chim. phys., 1935, 32, 725—740).—As with inorg. electrodes, the photo-electric potential of org. substances appears only in presence of  $H_2O$ . The effect appears instantaneously only with mols. containing atoms of variable valency, the  $NH_2$ -group being the most active. All compounds containing this group are not photo-sensitive, nor are their leuco-derivatives, but a mixture shows the effect, as does a dye to which is added the leuco-base of a less readily reducible dye. It is concluded that in these compounds the effect is due to displacement of the oxidation-reduction equilibria, produced by the primary photolysis of  $H_2O$ .

J. W. S.

**Flow method applied to space charge and ionic processes in oil.** K. CHRIST (Z. Physik, 1935, 98, 23—65).—The method of a fluid flowing at right angles to an electric field has been applied to dielectric liquids; it shows the transference of a positive charge from metal to oil, and the presence of space charge when an electric current passes through the oil. It can be used to measure ionic mobilities.

A. B. D. C.

**Superposition of field distribution and conductivity.** W. O. SCHUMANN (Z. Physik, 1935, 98, 44—74).—Theoretical discussion of inhomogeneous dielectrics.

A. B. D. C.

**Determination of dielectric constants of organic liquids at radio-frequencies. I. Carbon tetrachloride and chloroform.** R. M. DAVIES (1936, [vii], 21, 1—41).—The resonant circuit method was used to obtain the dielectric constants of  $CCl_4$  and  $CHCl_3$ ,  $C_6H_6$  being employed as standard. Vals. obtained at  $20^\circ$  and  $25^\circ$ , respectively, :  $CCl_4$  2.236<sub>0</sub>, 2.226<sub>7</sub>;  $CHCl_3$  4.796<sub>4</sub>, 4.708<sub>6</sub>.

A. J. M.

**Density and molecular polarisation of menthol and borneol.** H. HARMS (Z. physikal. Chem., 1935, 135, 440—442).—The dipole moments of *l*-menthol are  $(1.62 \pm 0.03) \times 10^{-18}$  and  $(1.65 \pm 0.03)$  e.s.u., respectively. The association in  $C_6H_6$  solutions has been examined.

R. C.

**Molecular volume of alkanes.**—See this vol., 309.

**Dispersion of air, krypton, and xenon in the ultra-violet.** W. KRONJÄGER (Z. Physik, 1935, 98, 22).—Dispersion is given down to  $\lambda = 2000$  Å.

A. B. D. C.

**Refractive indices and dispersions of volatile compounds of fluorine and boron.** Carbon tetrafluoride, nitrogen trifluoride, fluoroform, carbon tetrachloride, nitrogen compound of fluorine  $(CF_3N)_2$ , boron trifluoride, nitrogenous boron hydride,  $N_3H_6$ . K. L. RAMASWAMY (Proc. Indian

Acad. Sci., 1935, 2, A, 630—636).—Measurements have been made with a Rayleigh type interferometer at room temp. and for  $\lambda$  4359—6440 Å. Combining with dielectric const. data (this vol., 139) the vals. of the electronic and at. polarisation are deduced.  $(CF_3N)_2$  and  $B_3N_3H_6$  have appreciable vals. of at. polarisation. From the variations of  $n$  with pressure the compressibilities of the gases have been deduced.

J. W. S.

**Refractometric investigations in the series of saturated normal nitriles.** B. DARAGAN (Bull. Soc. chim. Belg., 1935, 44, 597—624).— $d_4^{20}$  vals. for various temp., and  $n_D^{20}$ ,  $n_D^{54.4}$ ,  $n_D^{74}$ , and  $n_D^{95}$  for the  $He_{red}$ ,  $He_{yellow}$ ,  $He_{green}$ ,  $Hc_{violet}$ ,  $H_a$ ,  $D$ ,  $H_s$ , and  $H_v$  lines are recorded for the series MeCN to  $C_{13}H_{27}CN$ . The mol. refractions are calc. and the increments for each  $CH_2$  deduced. The results are in accord with data for paraffins (A., 1934, 132), but diverge from those for glycols.

J. W. S.

**Rotatory dispersion of aliphatic aldehydes.** P. A. LEVENE and A. ROTHEN (J. Chem. Physics, 1936, 4, 48—52; cf. A., 1934, 12, 1293).—Rotatory dispersion curves of aldehydes of the type  $CHMeEt[CH_2]_nCHO$  have been determined in the visible and ultra-violet regions. The  $\cdot CHO$  band at  $\lambda$  2950 is active and the sign of its contribution changes as  $n$  changes from 0 to 1 and higher members. The magnitude of the contribution varies periodically with the no. of C between the  $\cdot CHO$  and the asymmetric C.

M. S. B.

**Photographic measurement of the magnetic rotatory dispersion of water.** I. T. PIERCE and R. W. ROBERTS (Phil. Mag., 1936, [vii], 21, 164—176).—The magnetic rotation of  $H_2O$  for 11 lines of the Hg spectrum from 5780 to 2483 Å. has been determined, and a formula has been derived for the dispersion of the Verdet const.

A. J. M.

**Magnetic birefringence in solutions of organic substances.** I. S. W. CHINCHALKAR (Proc. Indian Acad. Sci., 1935, 2, A, 525—531).—Data are recorded for several aromatic hydrocarbons with two or more  $C_6$  rings in the mol., dissolved in  $CCl_4$ , EtOH,  $Et_2O$ , or EtOAc. For  $Ph_2$  and most of its simple derivatives the mol. magnetic birefringence is approx. 4 times, for  $m-C_6H_4Ph_2$  approx. 9 times, and for  $C_6H_5Ph_3$  approx. 16 times that of  $C_6H_6$ , indicating that the  $C_6$  rings in these mols. are either coplanar or parallel. When the  $C_6$  rings are condensed, the magnetic and optical anisotropies are  $>$  when they are separate.

H. J. E.

**Thiele's theory of partial valency in terms of electrons.** F. E. RAY (Proc. Iowa Acad. Sci., 1934, 41, 157—160).—A discussion.

CH. ABS. (e)

**Theory of liquids.** V. T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 466—476; cf. A., 1935, 1198).—The application of the theory in the calculation of surface tension, internal pressure, cohesion, mol. vibration, internal latent heats, and compressibilities is reviewed.

H. J. E.

**Parachors and chemical constitution. VI. Quadrivalent tellurium compounds.** B. SINGH and R. KRISHNAN (J. Indian Chem. Soc., 1935, 12, 711—714; cf. A., 1928, 355).—The parachors of

$\alpha$ -dimethyltelluri-dichloride, -dibromide, and -dinitrate have been determined and are in good agreement with vals. calc. on the basis of a shell of 10 Te valency electrons. R. S.

**Parachor and molecular refraction of hydrazine and [its] aliphatic derivatives.** L. D. BARRICK, G. W. DRAKE, and H. L. LOCHE (J. Amer. Chem. Soc., 1936, 58, 160—162).—Vals. for parachors (figures given after compound) agree with those calc. from Sugden's consts. (A., 1924, ii, 662), but differ considerably from those calc. from the consts. of Mumford and Phillips (A., 1929, 1219):  $N_2H_4$ , 90.7,  $(CMe_2 \cdot N)_2$ , 302.2,  $(CMeEt \cdot N)_2$ , 379.8,  $(\cdot NHPr^B)$ , 327.1,  $(\cdot NH \cdot CHMeEt)$ , 400.8,  $(\cdot NPr^B)$ , 318.4,  $(\cdot N \cdot CHMeEt)$ , 395.5,  $CMe_2 \cdot N \cdot NHPr^B$ , 313.7,  $CMeEt \cdot N \cdot NH \cdot CHMeEt$ , 387.6, 3 : 5 : 5-trimethylpyrazoline 288.4. The mol. refractions of these compounds agree with the calc. vals. provided (i) each N in the N-N and N-N linkings is given the primary amine val. and (ii) the C-N linking is given the val. of C-C and the N that of a sec.-amine. H. B.

**Predissociation limit of CO at 11.6 volts.** R. SCHMID (Physikal. Z., 1936, 37, 55—56).—New spectral evidence is given for the existence of a predissociation limit for CO at 11.6 volts (cf. A., 1935, 1299). A. J. M.

**Highly dilute flames of K-I<sub>2</sub>.** E. E. ROTH (Magyar chem. Fol., 1934, 40, 65—81; Chem. Zentr., 1935, i, 2311).—The heat of the secondary gas reaction is sufficient to excite only the red, but not the violet, K doublet. The heat of dissociation of K<sub>2</sub> is calc. as 187 kg.-cal. from the diminution in light intensity on superheating the reaction zone. J. S. A.

**Plano-radiate compounds.** H. J. BACKER (Chem. Weekblad, 1936, 33, 67—71).—A survey of published data indicates that, whilst in compounds of the type CX<sub>4</sub> the X are distributed symmetrically in space, in compounds of the type C<sub>6</sub>X<sub>6</sub> (C<sub>6</sub>=benzene ring) they take up a symmetrical radial arrangement in the plane of the C<sub>6</sub> ring. The resultant compounds are characterised by high m.p., readiness to crystallise, chemical stability, and volatility. D. R. D.

**Exchange of energy between diatomic gas molecules and a solid surface.** J. M. JACKSON and A. HOWARTH (Proc. Roy. Soc., 1935, A, 152, 515—529).—The theory of the accommodation coeff. developed by Jackson and Mott for monat. gases (A., 1932, 1074) has been extended for diat. mols. The gas mol. is treated (a) as an oscillator, when the exchange of energy between the rotations of the gas mol. and the vibrations of the solid is negligible, and (b) as a plane rotator, when the effect of the rotations is small for H<sub>2</sub> and larger for O<sub>2</sub>. L. L. B.

**Distance between molecules and the determination of the volume they occupy in the liquid state (by density).** A. E. MAKOVETZKI (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 83—102).—Expressions are derived for calculating intermol. distances in liquids, the results differing from those derived from van der Waals' equation. CH. ABS. (e)

**Dependence of interatomic distance on single linking-double linking resonance.** L. PAULING, L. O. BROCKWAY, and J. Y. BEACH (J. Amer. Chem. Soc., 1935, 57, 2705—2709).—Using experimental vals. for C-C linkings, a function showing the dependence of interat. distance on linking character for single-double linking resonance is plotted. The electronic structure of mols. containing double or triple linkings or aromatic nuclei and of mols. containing C-Cl linkings adjacent to double linkings, and the dependence of linking angles on single-double linking resonance are discussed. E. S. H.

**Radial distribution method of interpretation of electron diffraction photographs of gas molecules.** L. PAULING and L. O. BROCKWAY (J. Amer. Chem. Soc., 1935, 57, 2684—2692).—Tests on CCl<sub>4</sub> and other tetrahalides, Br, Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, CS<sub>2</sub>, and COS show that the radial distribution function given by a sum of Fourier terms corresponding with the rings of an electron diffraction photograph of gas mols. provides vals. of the important interat. distances accurate to 1 or 2%. Revised vals. of interat. distances and linking angles for several substances are given. E. S. H.

**Effect of electric and magnetic fields on the properties of gases.** A. A. ZAITZEV (Uspek. Fiz. Nauk. U.S.S.R., 1934, 14, 1009—1019).—A discussion. CH. ABS. (e)

**Dissociation of some molecules with free valencies.** H. LESSHEIM and R. SAMUEL (Phil. Mag., 1936, [vii], 21, 41—64; cf. A., 1935, 1057).—In the case of the mols. BeF, MgF, CaF, SrF, BeO, MgO, CdF, BeCl, MgCl, and CaCl, there is good agreement between the energy of excitation of the products of dissociation and the terms of the metal atom if the ground level of the mol. is correlated to the  $sp^3P$  term of the metal. Correlation of the ground level to the repulsive term  $s^2 \ ^1S$  is also possible in some of these mols. A. J. M.

**Statistical perturbation theory. II. Perturbation calculations with exchange for the Thomas-Fermi theory.** P. GOMBAS (Z. Physik, 1936, 93, 417—429; cf. this vol., 134). A. B. D. C.

**Polymerisation and condensation.** E. K. RIDEAL (Trans. Faraday Soc., 1936, 32, 3—10).—A general review of the present state of knowledge regarding types of linking, mechanical properties, swelling and dispersion, and mol. wt. of highly polymerised substances, and the kinetics of their production. F. L. U.

**Influence of van der Waals forces and primary linkings on binding energy, strength, and orientation, with special reference to artificial resins.** J. H. DE BOER (Trans. Faraday Soc., 1936, 32, 10—37; cf. A., 1934, 727).—The mutual orientation of C<sub>6</sub>H<sub>6</sub> rings parallel to their planes is discussed with reference to the van der Waals and repulsive forces. In calculating the tensile strength of either NaCl or synthetic resins of the PhOH- or *m*-cresol-CH<sub>2</sub>O type, the inclusion of van der Waals forces still further increases the discrepancy between theory and observation, which is attributed to weakness due respectively to defects in the lattice and to the



smallness of the no. of C-C linkings actually formed compared with the no. possible. In the case of well-oriented cellulose derivatives the calc. vals. agree with experiment. Calculation of the relative positions of  $C_6H_6$  rings in polystyrene indicates that they will tend to lie perpendicular to the direction of the aliphatic C chains, a conclusion in agreement with the observed strongly negative fluxional birefringence.

F. L. U.

Absolute measurement of efficiency of X-ray fluorescent screen. O. GAERTNER (Z. tech. Phys., 1935, 16, 9—12; Chem. Zentr., 1935, i, 3100; cf. A., 1935, 273).—A Cd tungstate screen absorbed 50% of the incident X-radiation, and emitted 0.54% as visible light.

J. S. A.

Intensity of interference lines in Debye X-ray diagrams. N. SELJAKOV, A. STEFANOVSKI, and J. HURGIN (Z. Physik, 1935, 98, 66—71).—Variation of the lattice area covered by the incident beam when its angle is varied accounts for anomalous intensities of different orders of reflexion from chemical catalytic lattices; these anomalies measure the extent of defects in the lattice.

A. B. D. C.

Precision measurements with the Debye-Scherrer method. II. M. STRAUMANIS and A. IRVING (Z. Physik, 1936, 98, 461—475; cf. this vol., 181).—The film is extended to give interference rings around the incident and exit portions of the primary beam; this allows measurement of the film to be made independently of camera and film curvature dimensions. Accurate lattice consts. are tabulated for Al,  $As_2O_3$ , Au, Fe,  $Fe_2O_3$ , MgO, NaCl, Pb,  $Pb(NO_3)_2$ , Si,  $TiCl_3$ , W, and  $WO_3$ .

A. B. D. C.

Relation between mechanical strain and intensity of X-rays reflected by a quartz plate. III. E. FUKUSHIMA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1—14; cf. this vol., 15).—The increase in intensity of the interior reflexion of X-rays transmitted through a quartz plate under the influence of heterogeneous strain has been studied theoretically.

R. S. B.

Effect of temperature on the reflexion of X-rays by crystals. I. Isotropic crystals. C. ZENER and G. E. M. JAUNCEY. II. Anisotropic crystals. C. ZENER (Physical Rev., 1936, [ii], 49, 17—18, 122—127).—I. A short derivation of the Debye-Waller temp. factor in the reflexion of X-rays from isotropic crystals is given.

II. Mathematical. The temp. factor  $e^{-M}$  is a function of reflexion plane orientation. The case of metals with hexagonal symmetry is treated. The ratio of the const.  $M$  for reflexion  $\perp$  to and  $\parallel$  to the principal axis is 1.80 and 1.73 for Zn and Cd, respectively.

N. M. B.

X-Ray studies of crystals vibrating piezoelectrically. C. V. BERTSCH (Physical Rev., 1936, [ii], 49, 128—132; cf. Colby, A., 1934, 1296).—Intensity investigations for quartz and Na K tartrate, using the patterns and regular reflexion from the crystal surfaces, are reported.

N. M. B.

Systematic packing of spheres, with particular relation to porosity and permeability. L. C.

GRATON and H. J. FRASER (J. Geol., 1935, 43, 785—909).—The geometry of close-packing is discussed.

L. S. T.

Orientation of molecules of liquids from the X-ray scattering pattern. A. PETERLIN (Physikal. Z., 1936, 37, 43—52).—The theoretical scattering curve for  $CCl_4$  is calc., and agrees well with the experimental curve of Pierce (A., 1932, 12).

A. J. M.

Schiller structure. R. T. COLONY (Amer. Min., 1935, 20, 828—837).—A discussion.

L. S. T.

Tabulation of crystal forms and discussion of form-names. A. F. ROGERS (Amer. Min., 1935, 20, 838—851).

L. S. T.

Metallic surfaces and thin films with particular reference to aluminium. BRITISH ALUMINIUM Co. (Intelligence Memo., 49 pp.).—An exhaustive review.

Disperse structures. I. Systematics. V. S. VESELOVSKI. II. X-Ray investigation of the disperse structures of graphitic substances. V. S. VESELOVSKI and K. V. VASILIEV (J. Phys. Chem. U.S.S.R., 1934, 5, 977—981, 982—995).—I. A review of crystal structure and classification.

II. X-Ray data for graphitic substances are discussed.

CH. ABS. (e)

Crystalline boron. S. VON NARAY-SZABÓ (Naturwiss., 1936, 24, 77).—Cryst. B (Morck) consists chiefly of the adamantine form, together with irregular hexagonal leaflets of the graphitic form. X-Ray investigation gave for the adamantine form (tetragonal),  $a$  12.55,  $c$  10.18, identity period along [110], 17.61 Å., and for the graphitic form (rhombohedral),  $a$  17.64,  $b$  25.0,  $c$  10.26 Å.

A. J. M.

Crystal structure of solid oxygen. L. VEGARD (Z. Physik, 1935, 98, 1—16).— $\gamma$ - $O_2$  has a cubic structure, space-group  $T_h^h$ , the unit cell containing 8 rotating mols. ordered in pairs; the pair centres form a face-centred cubic structure of closest spherical packing for the pairs.  $\beta$ - $O_2$  has a rhombohedral cell of 6 mols.

A. B. D. C.

Crystalline properties and magnetic anisotropy of distilled bismuth. A. GOETZ, O. STIERSTADT, and A. B. FOCKE (Z. Physik, 1935, 98, 118—127).—High-vac. distillation of Bi produces a microcryst. layer 0.5—0.1 mm. thick carrying a macrocryst. conglomerate of similarly oriented crystals.

A. B. D. C.

Isomorphism of  $Mg_3Al_2$  and  $\alpha$ -manganese. F. LAYES, K. LOHBERG, and P. RAHLFS (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 67—71; Chem. Zentr., 1935, i, 3103).—Complete analysis of the crystal structure of " $Mg_3Al_2$ " shows the space-group to be  $T_h^h$ ,  $a$  10.54 Å., with 58 atoms per unit cell, giving a true formula  $Mg_{17}Al_{12}$ .

J. S. A.

Structure of aluminium carbonitride,  $Al_5C_3N$ . M. VON STACKELBERG and K. F. SPIESS (Z. physikal. Chem., 1935, 175, 140—153).— $Al_5C_3N$  has a hexagonal structure;  $a$  3.280,  $c$  21.55 Å.,  $Z=2$ , space-group  $C_{6h}^{2h}$ . The lattice consists of hexagonal planes, 5 Al planes interleaved with 3 C planes and 1 N plane forming a layer, which consists of two parts similar in structure to  $Al_4C_3$  and AlN, respect-

ively. The lattice of AlN has  $a$  3.104,  $c$  4.965 Å. 2.15 Å. is deduced by Zachariasen's method as the mean "univalent radius" of the N<sup>III</sup> ion. Apparently AlN is able to hold some Al<sub>4</sub>C<sub>3</sub> in solid solution.

R. C.

**Crystal structure and colloid-chemical properties of vanadium pentoxide.** J. A. A. KETELAAR (Chem. Weekblad, 1936, 33, 51-57). V<sub>2</sub>O<sub>5</sub> forms hemimorphic rhombic crystals of space-group  $C_{2v}^2$ , with 2 mols. in the unit cell;  $a$  11.48,  $b$  4.360,  $c$  3.555 Å., and  $d_{\text{calc}}$  3.37. The structure is built up of chains of O tetrahedra linked by shared corners, accounting for formation of elongated micelles in colloidal solution.

D. R. D.

**Structure of thin films of metallic oxides and hydrates.** N. SMITH (J. Amer. Chem. Soc., 1935, 58, 173-179).—Electron diffraction indicates that oxide films removed from heated metals are polycryst., showing no evidence of preferred orientation or pseudomorphism. The film on Ni is NiO, Cu<sub>2</sub>O on Cu, and Fe<sub>3</sub>O<sub>4</sub> mainly on Fe. Hydroxide pptts. from salt solutions are cryst., but show evidence of distortion.

E. S. H.

**Complex nitrites of iron, cobalt, nickel, and copper: structure and magnetic susceptibility.** L. CAMBI and A. FERRARI (Gazzetta, 1935, 65, 1162-1190).—The prep. of 15 compounds  $M^I[M^II(Fe(NO_2)_6)]$  is described ( $M^I=K, NH_4, Tl$ ;  $M^II=Ba, Sr, Ca, Pb, Hg, Cd$ ). Vals. of lattice consts. and  $d_{\text{calc.}}$ , obtained from X-ray measurements, are given. Comparison with previous data shows that the mol. vols. of the complex ions  $[Fe(NO_2)_6]^{IV}$ ,  $[Co(NO_2)_6]^{IV}$ , and  $[Ni(NO_2)_6]^{IV}$  are 120.3, 123.5, and 128.9, respectively. Magnetic susceptibility measurements show that  $[Fe^{II}(NO_2)_6]^{IV}$  is predominantly diamagnetic like  $[Co^{III}(NO_2)_6]^{IV}$ , whereas  $[Co^{II}(NO_2)_6]^{IV}$  is paramagnetic (1 Bohr magneton) like  $[Cu^{II}(NO_2)_6]^{IV}$ .

O. J. W.

**Crystallography of hexa- $\omega$ -bromomethylbenzene.** J. BEINTEMA, P. TERPSTRA, and W. J. VAN WEERDEN (Rec. trav. chim., 1935, 54, 962-969).—The hexagonal unit cell of  $C_6(CH_2Br)_6$  contains 3 mols. and has  $a$  11.373,  $c$  5.377 Å., but the crystal has a rhombohedral lattice with  $a$  9.621 and  $\alpha$  116° 36'. It is concluded that the atoms of each mol. are coplanar, and that each Br lies on a circle of radius 3.75 Å.

J. W. S.

**X-Ray study of symmetrical trinitrotoluene and cyclotrimethylenenitroamine.** R. HULTGREN (J. Chem. Physics, 1936, 4, 84).— $C_6H_2Me(NO_2)_3$  is orthorhombic with  $a$  14.85,  $b$  39.5,  $c$  5.96 Å. For 16 mols. per unit cell  $d_{\text{calc.}}$  is 1.710 (lit. 1.654). The crystals of cyclotrimethylenenitroamine are also orthorhombic. X-Ray analysis gives  $a$  11.5,  $b$  13.2,  $c$  10.6 Å. For 8 mols. per unit cell  $d_{\text{calc.}}$  is 1.82.

M. S. B.

**Alkaline-earth cacodylates. II.** R. TROLLAIS (Bull. Soc. chim., 1936, [v], 3, 87-95).—Cacodylates of Ca, Sr, and Ba belong to the monoclinic system, with  $a:b:c=3.363:1.2414, 1.813:1.2335, 1.5737:1.13332$ , respectively. Forms found present are Ca:  $ph_1m$  and  $pa_1h_1m$ , Sr:  $pmb_{1/3}b_1h_{1/2}$  and  $pme_1b_{1/3}b_1h_{1/2}$ , Ba:  $pa_1h_1m$ ,  $pa_1e_1h_1m$ ,  $pa_1m$ , and

$pa_1h_1mb_{1/2}$ . The Sr salt shows twinning (cf. *ibid.*, 70).

E. E. A.

**Fine structure of plant chitin.** G. VAN ITERSOM, jun., K. H. MEYER, and W. LOTMAR (Rec. trav. chim., 1936, 55, 61-63).—X-Ray examination of plant chitin from *Phycomyces* is described and the results are compared with those previously recorded for animal chitin (cf. A., 1935, 753). An arrangement of the acetylglucosamine residues in the elementary cell of plant chitin fibres is suggested.

E. E. A.

**X-Ray spectrography of polymerides, particularly those having rubber-like extensibility.** J. R. KATZ (Trans. Faraday Soc., 1936, 32, 77-94).—A general discussion of the interpretation of X-ray spectrograms of cryst. and amorphous polymerides. Synthetic rubbers should be made under control by X-ray analysis. No polymeride of isoprene has yet been found to have the X-ray characteristics of natural rubber. Spectrographic data indicate that the extensible units in rubber and in polymerides with similar properties are single mols.

F. L. U.

**Dependence of cybotactic groups on specific volume.** R. D. SPANGLER (Proc. Iowa Acad. Sci., 1934, 41, 253-254; cf. A., 1935, 1297).—X-Ray diffraction data are recorded for Et<sub>2</sub>O near its crit. point. The cybotactic groupings depend more on sp. vol. than on temp. The indications of groups disappear at about the crit. sp. vol.

CH. ABS. (c)

**Effect of crystal size on lattice dimensions.** G. I. FINCH and S. FORDHAM (Proc. Physical Soc., 1936, 48, 85-94).—Lattice consts. of the Li, Na, and K halides are determined by the electron-diffraction method. Slight divergences from results by X-ray diffraction indicate that crystal size appreciably influences lattice dimensions.

N. M. B.

**Electron-diffraction investigation of carbonyl chloride, the six chloroethylenes, thiocarbonyl chloride,  $\alpha$ -methylhydroxylamine, and nitromethane.** L. O. BROCKWAY, J. Y. BEACH, and L. PAULING (J. Amer. Chem. Soc., 1935, 57, 2693-2704).—The C-Cl distances determined vary between 1.67 and 1.73 Å., which is 5-20% < the normal single linking val. The decrease is due to the partial double linking character caused by resonance resulting from the conjugation of an unshared pair of electrons on the Cl atom with the adjacent double linking. The vals. for the angle Cl-Cl-X are smaller than the tetrahedral val. for the angle between a single and a double linking for the same reason. The vals. for other interat. distances are in good agreement with the accepted covalent radii.

E. S. H.

**Diffuse rings produced by electron scattering.** L. H. GERMER (Physical Rev., 1936, [ii], 49, 163-166; cf. A., 1933, 657).—Two diffuse diffraction rings have been obtained by electrons scattered from vaporized ZnS, and from unpolished surfaces of  $Cu_2O$ , contrary to the view that such rings from polished metal surfaces are evidence that surfaces are amorphous. The possibility of an amorphous layer on polished metals is not excluded.

**Structure of ice II.** R. L. McFARLAN (J. Chem. Physics, 1936, 4, 60—64).—X-Ray analysis of ice II indicates a side-centred orthorhombic cell,  $a$  7.30,  $b$  4.50,  $c$  5.56 Å. The cell contains 8 mols., has the symmetry of space-group  $V^5-C222_1$ , and gives  $d$  1.21. The transition from ice I to II breaks up the  $H_2O$  mol. and gives an ionic crystal for II.

M. S. B.

**Structure of ice.** W. H. BARNES (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 53—60).—A crit. discussion of the structure proposed by Bernal and Fowler (A., 1933, 1106).

H. J. E.

**Structure and entropy of ice and of other crystals with some randomness of atomic arrangement.** L. PAULING (J. Amer. Chem. Soc., 1935, 57, 2680—2684).—The  $H_2O$  mols. in ice are so arranged that each is surrounded by 4 others, each mol. being oriented so as to direct its 2 H towards two of the four neighbours, forming H linkings. Only one H lies near each 0-0 axis. There are  $(3/2)^N$  such configurations for  $N$  mols., giving a residual entropy of  $R \log_e 3/2 = 0.805$  e.u., in good agreement with the experimental val.

E. S. H.

**Crystal structure from data on magnetic susceptibilities.** O. M. JORDAHL (Physical Rev., 1934, [ii], 46, 79).—Experimental results on the crystal structure of  $CuSO_4 \cdot 5H_2O$  (A., 1934, 243) agree with the conclusions of the author (*ibid.*, 241) deduced from an analysis of the magnetic data.

L. S. T.

**X-Ray investigation of the solid solution nature of nitrate-contaminated barium sulphate precipitates.** G. H. WALDEN, jun., and M. U. COHEN (J. Amer. Chem. Soc., 1935, 57, 2591—2593). Apparatus and technique for determining the lattice parameters of powdered crystals with a precision of 0.01% are described. A study of the lattice parameters of  $BaSO_4$  ppts., containing  $NO_3^-$  in absence of all foreign cations other than  $H^+$ , shows that the contaminant enters the  $BaSO_4$  lattice with formation of a solid solution. The general problem of ppt. contamination is discussed in the light of the results.

E. S. H.

**Crystal structure and constitution of  $BF_3 \cdot 2H_2O$ .** J. KLINKENBERG and J. A. A. KETELAAR (Rec. trav. chim., 1935, 54, 959—961).— $BF_3 \cdot 2H_2O$  is isomorphous with  $NH_4ClO_4$ , its orthorhombic unit containing 4 mols. and having  $a$  8.74±0.06,  $b$  4.7±0.03,  $c$  7.30±0.10 Å. These cell dimensions are almost identical with those of  $NH_4BF_4$ , viz.,  $a$  8.7±0.05,  $b$  4.68±0.05, and  $c$  7.21±0.03 Å., respectively. This is interpreted as indicating that the formula should be written  $(OH_3)(BF_3OH)$ .

J. W. S.

**Physical investigations on alkali halide crystals.** R. HILSCH (Angew. Chem., 1936, 49, 69—73).—Reference to published work concerning optical properties and electrical conductivity, especially of crystals containing excess of alkali or halide ions.

E. S. H.

**Effect of thermal and mechanical tempering on electromotive force and current-voltage curves of rock-salt crystals.** A. VENDERVINSCH and R. DRISINA (Z. Physik, 1935, 98, 108—117). The effects of tempering NaCl crystals

on deviations from Ohm's law show that these deviations are due to the presence of a high-voltage polarisation.

A. B. D. C.

**Variation of alternating-current resistance of nickel in longitudinal magnetic fields.** M. M. SEN GUPTA, H. B. MOHANTY, and S. SHARAN (Z. Physik, 1935, 98, 262—266).—A.-c. measurements are free from many irregularities found with d.c. Hysteresis is less for a.c. (cf. A., 1935, 267).

A. B. D. C.

**Phenomenon in transformations [in metals and alloys] extending over a temperature range.** A. SCHULZE (Z. Metallk., 1935, 27, 251—255).—Magnetic transformations and the change from regular to random orientation of the atoms in the lattice are preceded by inflexions in the curves of electrical resistance, temp. coeff. of resistance, and thermal expansion. This anomaly is shown by Fe, Ni, and Ni-Fe alloys (magnetic transformations) and by Au-Cu and  $\beta$ -Zn-Cu alloys (lattice reorientation).

A. R. P.

**Magnetic behaviour of nickel wire under high torsion.** R. GANS (Ann. Physik, 1936, [v], 25, 77—91).—Theoretical.

L. L. J.

**Processes of technical magnetisation. I. Weiss' theory of the technical magnetisation curve.** K. H. R. WEBER (Z. Physik, 1935, 98, 155—180).

A. B. D. C.

**Relation of spontaneous and true magnetisation to [optical] emissivity.** W. GERLACH (Ann. Physik, 1936, [v], 25, 209—212).—The anomalous resistance-temp. curve of Ni in the neighbourhood of the Curie point is associated with a similar anomaly in the emissivity-temp. curve for long  $\lambda$ , in accordance with the Hagen-Rubens relation. Both effects are quantitatively related to the spontaneous magnetisation; data for  $\lambda$  24  $\mu$  and 8.7  $\mu$  are recorded from 100° to 310°. True magnetisation depresses the emissivity, in further agreement with theory.

L. J. J.

**[Optical] emissivity of nickel.** E. LOWE (Ann. Physik, 1936, [v], 25, 213—222; cf. preceding abstract).—Measurements of total radiation and radiation at a series of  $\lambda$  from < 4.5 to 24  $\mu$  for polished Ni between 100° and 450° are recorded. Magnetisation has no effect on the total emission, but for  $\lambda > 8$ —10  $\mu$  the emission at the Curie point is depressed 0.6% in a field of 4000 gauss.

L. J. J.

**Effect of tension on magnetisation [of nickel] above the Curie point.** G. SCHARFF (Ann. Physik, 1936, [v], 25, 223—232).—The Curie temp. is independent of tension. Ferromagnetic and true magnetisation can be distinguished by the effect of tension, since the former is depressed, the latter unaffected. Ferromagnetisation can be detected up to 12° above the Curie point.

L. J. J.

**Transverse magnetic effect.** J. E. VERSCHAFFELT (Wis. nat. Tijds., 1934, 7, 53—66; Chem. Zentr., 1935, i, 3638).—Theoretical.

J. S. A.

**Surface magnetisation in ferromagnetic crystals.** L. W. MCKEEHAN and W. C. ELMORE (Physical Rev., 1934, [ii], 46, 226—228; cf. this vol., 145).

L. S. T.

**Variation of volume magnetostriction and Weiss' factor with temperature and lattice constant.** M. KORNETZKI (*Z. Physik*, 1935, 98, 289—313).—Ferromagnetic substances showing vol. magnetostriction should have Curie points that vary with vol. Measurements on Fe, Fe-Ni, and Ni-Cu alloys between 20° and 90° confirm this. A. B. D. C.

**Behaviour of single crystals of aluminium of different degrees of purity prepared from the molten metal and by recrystallisation.** F. GISEN (*Z. Metallk.*, 1935, 27, 256—261).—Single crystals of 99.5—99.998% Al can be prepared (i) by maintaining the metal at 800—820° until all nuclei disappear, then cooling very slowly without disturbance to < the m.p., or (ii) by drawing rod to 40—45% reduction, annealing at 250° for 15 hr. to obtain a fine-grained structure, stretching 0.5—1%, and slowly heating from 430° to 480° during 45 hr. The crit. shear strength of crystals prepared by method (ii) decreases almost linearly with decreasing purity from about 300 g. per sq. mm. for the 99.998% metal to 70 g. per sq. mm. for the 99.5% metal, whereas that of crystals prepared by method (i) is < 20 g. per sq. mm. irrespective of the purity. This difference is ascribed to the more pronounced mosaic structure of crystals prepared by method (ii); X-ray examination confirms this theory. A. R. P.

**Strength and modulus of elasticity of amorphous materials, related to their internal structure.** R. HOUWINK (*Trans. Faraday Soc.*, 1936, 32, 122—131).—The internal structure of asphalts, resins, and glass is discussed, and their tensile strengths and vals. of Young's modulus are compared. Smekal's theory of "Lockerstellen" is adopted to account for the discrepancy between calc. and observed strengths, weaknesses in macromols. of an insol. PhOH-CH<sub>2</sub>O resin being due to non-reaction between such reactive groups as happen to be out of alignment. F. L. U.

**High elasticity of three-dimensionally polymerised amorphous materials in relation to their internal structure.** R. HOUWINK (*Trans. Faraday Soc.*, 1936, 32, 131—143; cf. preceding abstract).—"High elasticity," i.e., elastic deformation which > 1%, is observed in asphalts and glass, in which it may reach 20% and is connected with a viscosity range of 10<sup>11</sup>—10<sup>13</sup> poises. In hardening resins at about 120° it reaches 240%. A relation between the conditions for high elasticity and the formation of insol. elastic three-dimensional networks is shown, and calculations are given to explain changes of Young's modulus, yield val., and strain at the yield val. when such structures are formed. F. L. U.

**Inorganic substances with rubber-like properties.** K. H. MEYER (*Trans. Faraday Soc.*, 1936, 32, 148—152; cf. A., 1935, 1450).—The elastic behaviour and X-ray patterns of elastic S and of polyphosphonitrilic chloride are described. They present many analogies with org. polymerides, and their extensibility is attributed to long flexible chains of mols. which become straight when stretched, and undergo flexion by Brownian movement when ten-

sion is relaxed, with consequent shortening of the specimen. F. L. U.

**Constitution of the crystallised part of cellulose. IV. Elasticity of cellulose.** K. H. MEYER and W. LOTMAR (*Helv. Chim. Acta*, 1936, 19, 68—86).—The influence of moisture, temp., orientation, and tension on the modulus of elasticity *E* of several natural cellulose (I) fibres and some derivatives of (I) has been determined using Polanyi's dynamometer and also an acoustic method of measurement. The temp. coeffs. of the tension are zero or negative except for (I) acetate, which gives a positive val. like rubber, because of its amorphous structure. In the other fibres, with a cryst. network, the attractive forces between the atoms, or the deformation of the valency angles, are responsible for the elasticity. *E* for natural fibres of high orientation, such as ramie, hemp, and linen, approaches a val. of approx. 11,000 kg. per sq. mm.  $\pm 10\%$ , which is close to the val. calc. for the (I) model if the angular forces are 20% of the principal valency force. Artificial (I) fibres or (I) derivatives have vals. of *E* between 100 and 5000 kg. per sq. mm. M. S. B.

**Crystal plasticity. V. Completion of the rate of slip formula.** E. OROWAN (*Z. Physik*, 1935, 98, 382—387; cf. A., 1934, 949).—A term is added to the earlier rate of slip formula to take account of forces arising in the crystal opposed to the applied force: these are likely to be significant for org. crystals. A. B. D. C.

**Variation of the adiabatic elastic moduli of rock-salt between 80° and 270° abs.** F. C. ROSE (*Physical Rev.*, 1936, [ii], 49, 50—54).—Balamuth's method for measuring Young's modulus of a cubic crystal (cf. A., 1935, 154) is extended to the measurement of all the elastic moduli of any solid crystal below 0°. Data for the variation with temp. of the adiabatic and isothermal elastic moduli and elastic consts. of rock-salt in the range 80—270° abs. are given. N. M. B.

**Relation between heat of transition and transition point of enantiotropic modifications.** J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1935, 54, 934—936).—An equation is derived connecting heat of transmission with the temp., and the at. frequencies and densities of the modifications at the transition temp. Direct confirmation is lacking owing to absence of data, but by substituting the ratio of the at. frequencies by the ratio of the abs. temp. at which the forms have equal sp. heats, the calc. transition temp. for Sn and S are of the same order as the experimental vals. J. W. S.

**Rates of vaporisation of metals in a gaseous atmosphere.** J. A. M. VAN LIEMPT (*Rec. trav. chim.*, 1936, 55, 1—6).—A formula is derived which is in agreement with experimental data and with Weber's formula. The deviations which are observed at high pressures are explained. E. E. A.

**Mol. wt. of polystyrenes and shape of the molecules in solutions.** R. SIGNER (*Trans. Faraday Soc.*, 1936, 32, 296—307).—Experiments on mol. wts. of polystyrenes as determined by u r centrifuging and on their fluxional birefringence a.



to the conclusion that in certain solvents the mols. are linear, straight for the fractions of lower, and curved for those of higher, mol. wt. (cf. A. 1933 '93, 902; 1935, 162, 700). F. L. U.

Rendering visible standing ultrasonic waves in transparent solid substances. III. Optical strain analysis of elastic vibrations. E. HIEDEMANN and K. H. HOESCH (Z. Physik, 1935, 98, 141—144; cf. A., 1935, 1312).—Longitudinal and transverse waves give different patterns. A. B. D. C.

Determination of ultrasonic velocity in 52 organic liquids. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1935, 2, A, 497—511).—Data for 52 liquids (hydrocarbons, alcohols, ketones, halogen derivatives, etc.) at 23—24.5° are given. Aromatic compounds in general gave higher velocities than did aliphatic compounds. Mols. with electric moment, or long mols., also gave high velocities. Adiabatic compressibility data are tabulated. H. J. E.

Longitudinal thermoelectric effect. VI. Mercury. J. L. CH'EN and W. BAND (Proc. Physical Soc., 1936, 48, 164—167; cf. A., 1935, 1312).—The Benedicks e.m.f. in Hg in an unconstricted glass tube undergoes a reversible decrease with rising temp. It is suggested that there is an anisotropic quasi-cryst. arrangement of the surface mols. depending on temp. N. M. B.

Thermomagnetic properties of nickel. II. W. BAND and Y. K. HSU (Proc. Physical Soc., 1936, 48, 168—177; cf. *ibid.*, 1935, 47, 910).—Curves are given for the homogeneous thermoelectric e.m.f. in pure Ni wire 1 mm. diameter for tensions  $\geq$  8 kg. Benedicks coeffs. are found as functions of magnetic field and tension. An antisymmetric part of the e.m.f. with respect to the magnetisation has been discovered. Evidence suggests that the homogeneous effect is controlled by the regularity of the micro-crystals in the wire. N. M. B.

Ionic complexes of polymeric compounds. v. WALTER (Trans. Faraday Soc., 1936, 32, 396—397).—Determination of the electrical conductivity of mono- and poly-meric methylenecarbamides in  $\text{HCO}_2\text{H}$  in conjunction with that of the mol. wt. in the same solvent and of the  $\text{NH}_2$  end-groups reveals the presence of ionic complexes. The role of the latter in the formation of resins from  $\text{CO}(\text{NH}_2)_2$  and  $\text{CH}_2\text{O}$  is discussed. F. L. U.

Electrical conductivity of alkali metal flames. KISSELMANN and A. BECKER (Ann. Physik, 1936, [1], 25, 49—73).—The conductivity of Li, Na, K, Rb, and Cs chloride vapours in the Meker burner flame at 1250—1950° abs. has been investigated. The metal-free flame the conductivity-temp. relation corresponds with electron emission by a component of ionisation potential 2.50 volts. For the metal vapour, the conductivity  $\propto$  the square of the total metal concn.; the conductivity-temp. relation is independent of the concn., and corresponds approx. with electron emission by free metal ions formed by chemical dissociation. L. J. J.

Phase-equilibrium of superconductors in a magnetic field. H. LONDON (Proc. Roy. Soc., 1935, A, 150, 650—663).—Mathematical. The disturbance

of superconductivity by a magnetic field is treated thermodynamically (A., 1935, 689). A threshold val. of the c.d. and not of the magnetic field is the decisive quantity. L. L. B.

Superconductivity of thin metallic films. A. D. MISENER and J. O. WILHELM (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 5—11).—The transition temp. for Pb films falls rapidly as the film thickness is decreased below  $9 \times 10^{-5}$  cm. The films were deposited electrolytically on constantan wire cores. H. J. E.

Effect of magnetic fields on the superconductivity of thin films of tin. A. D. MISENER, H. G. SMITH, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 13—21).—The critical magnetic field necessary to interrupt the superconducting state of Sn is greater for thin films than for massive Sn. Hysteresis effects occurred in thin films. H. J. E.

Magnetic anisotropy of naturally occurring substances. I. Mother of pearl. P. NILAKANTAN (Proc. Indian Acad. Sci., 1935, 2, A, 621—629).—From measurements of the abs. susceptibility and magnetic anisotropy of the nautilus *Turbo, Haliotis, M. margaritifera, Mytilus viridis*, and *Nautilus pompilius* it is concluded that the *c* axes are in each case normal to the elementary lamina. The *a* and *b* axes are probably in some cases distributed at random and in others the *a* axis is approx. along the line of growth. J. W. S.

Magnetism and polymerisation. J. FARQUHARSON (Trans. Faraday Soc., 1936, 32, 219—226).—Polymerisation is accompanied by a change in diamagnetic susceptibility, measurement of which can be used to find the mol. wt. of the product with an accuracy which decreases with increase in the degree of polymerisation. Results of experiments with  $(\text{CH}_2\text{CMe})_2$ , cyclopentadiene,  $\text{CNCl}_3$ , and  $\text{PhNO}$  are given. F. L. U.

Electrical resistance and magnetic susceptibility of sugar carbon submitted to various thermal treatments. P. CORRIEZ (Compt. rend., 1935, 201, 1486—1488; cf. this vol., 143).—Vals. are recorded for specimens heated from 1000° to 2000°. T. G. P.

Character of linking in the carbon monoxide molecule. R. I. JANUS and J. S. SCHUR (Physikal. Z. Sovietunion, 1935, 7, 19—25).—A simple method of measuring the magnetic susceptibility of gases is described. The val. for CO is  $-118 \pm 6 \times 10^{-7}$ . CO contains a triple linking. CH. ABS. (e)

Diamagnetism and change of state. P. S. VARADACHARI (J. Annamalai Univ., 1935, 5, 18—26).—Evidence is given that the decreased magnetic susceptibility of many aromatic compounds on solidification is due to the decomp. on fusion of polymerides present in the solid state. The sharp lines in solid  $\text{C}_6\text{H}_6$  and  $\text{Ph}_2\text{O}$  (cf. Gross, A., 1935, 564) may be due to such polymerides.  $\text{H}_2\text{O}$  is considered in the light of Raman data. Differences between the susceptibilities of the liquid and vapour states of org. compounds are eliminated if the v.d. is taken into account in calculating mol. susceptibility. N. M. B.

**Magnetochemistry of rhenium : metallic rhenium and septavalent rhenium.** N. PERRAKIS and L. KAPATOS (*Praktika*, 1934, 9, 121—125; *Chem. Zentr.* 1935, i, 3110).—Measurement of the magnetic susceptibility of  $\text{Re}_2\text{O}_7$  gives for  $\text{Re}^{\text{VII}}$  the same val. as found by Albrecht and Wedekind for metallic Re. For Re prepared by reduction of  $\text{NH}_4\text{ReO}_4$ , the author's previous val. was confirmed.  $\chi$  for  $\text{KReO}_4$  and  $\text{NH}_4\text{ReO}_4$  are recorded. J. S. A.

**Diamagnetic susceptibilities of salts forming ions with inert gas configurations. II. Alkaline halides.** G. W. BRINDLEY and F. E. HOARE (*Proc. Roy. Soc.*, 1935, A, 152, 342—353).—The method previously described (A., 1935, 149) has been used to determine the diamagnetic susceptibilities of the halides of Li, Rb, and Cs. The results indicate that the susceptibilities are additive within the limits of experimental error except for  $\text{LiCl}$ ,  $\text{LiBr}$ , and  $\text{LiI}$ , and  $\text{CsCl}$ ,  $\text{CsBr}$ , and  $\text{CsI}$ . It is suggested that the low vals. in the latter cases are due to deformation of the ions produced by (a) the close approach of the negative ions in the Li salts, and (b) the change of crystal structure in the Cs salts. A series of ionic susceptibilities for ions in crystals of the rock-salt type is derived. L. L. B.

**Temperature coefficient of susceptibility of tetrahydronaphthalene.** B. N. RAO (*Current Sci.*, 1935, 4, 404—405).—The susceptibility, studied in the range 23—70°, showed no temp. effect. The abs. val. was  $-0.688 \times 10^{-6}$ , showing no variation with field strength. N.

**Temperature of the Langmuir hydrogen flame.** H. VON WARTENBERG and H. J. REUSCH (*Nachr. Ges. Wiss. Göttingen*, 1934, [ii], 1, 141—145; *Chem. Zentr.*, 1935, i, 2654).—The temp. of an at. H flame was determined by the reversal of lines of the Li flame, using the solar image as comparison. Near the electrode 4600—4800° was recorded. J. S. A.

**Temperature rise in a material of which the thermal properties vary with temperature.** J. H. AWBERRY (*Proc. Physical Soc.*, 1936, 48, 118—124).—Mathematical. N. M. B.

**Polymorphism.** H. E. PHIPPS and J. H. REEDY (*J. Physical Chem.*, 1936, 40, 89—100).—An accurate method for determining the transition temp. of sol. substances by means of a dipping refractometer is described. Examination of  $\text{NH}_4\text{NO}_3$  III petrographically indicates that it is orthorhombic. Redetermination of the transition point of  $\text{CCl}_4$  by heating and cooling curves gives  $-47.66 \pm 0.2^\circ$ . The effect of impurities on this is much > on the m.p. M. S. B.

**Temperature dependence of free electron specific heat.** E. C. STONER (*Phil. Mag.*, 1936, [vii], 21, 145—160).—Mathematical. The Fermi-Dirac statistics are applied to obtain the variation of energy and sp. heat over the whole temp. range, the range of validity of the formulæ being specially considered. A. J. M.

**Equation for approximating heat capacities of gases calculated from spectral data.** I. N. GODNEV (*J. Amer. Chem. Soc.*, 1936, 58, 180—181). The proposed equation has been applied satisfactorily

to data for  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{S}$  in the range 100—5000° abs.

**Rotation and entropy of hydrogen sulphide.** K. CLUSIUS and A. FRANK (*Naturwiss.*, 1936, 24, 62).—There is no difference between the entropy of  $\text{H}_2\text{S}$  calc. thermodynamically and statistically, in contrast with  $\text{H}_2\text{O}$ . There is therefore no zero-point rotation of its *o*-modification. This difference between  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  is connected with the existence of a no. of solid phases of  $\text{H}_2\text{S}$  under ordinary pressures, whereas only one stable form of  $\text{H}_2\text{O}$  exists. A. J. M.

**Thermal data on organic compounds. XV. Heat capacity, entropy, and free energy data for the isomeric butenes.** S. S. TODD and G. S. PARKS (*J. Amer. Chem. Soc.*, 1936, 58, 134—137; cf. A., 1935, 825).—The heat capacities of the four isomeric butenes have been determined between liquid-air temp. and their respective b.p. The mol. entropies and free energies of formation have been calc. The thermodynamic stability varies considerably with the configuration of the mol. E. S. H.

**Glass. XII. New heat capacity data for organic glasses. Entropy and free energy of *dl*-lactic acid.** G. S. PARKS, S. B. THOMAS, and D. W. LIGHT. **XIII. Glass formation by a hydrocarbon polymeride.** J. D. FERRY and G. S. PARKS (*J. Chem. Physics*, 1936, 4, 64—69, 70—75).—XII. Sp. heat measurements have been made on  $\text{Bu}^n\text{OH}$ , *dl*-lactic acid (I), and  $\gamma$ -methylhexane in glassy, liquid, or incompletely cryst. states by Nernst's method. As with other glass-forming substances (cf. A., 1930, 1359), there is a transition region over a temp. interval of 8—20°, depending on the nature of the glass and its thermal history. Through this temp. interval the material passes from a hard glass to a more or less viscous liquid, whilst the sp. heat rises rapidly. The sp. heat of cryst. (I) has also been determined at different temp. The heat of fusion of the crystals at 289.9° abs. is 30.1 g.-cal. per g. The entropy and free energy of formation of (I) have been calc.

**XIII. Polyisobutene**, average mol. wt. 4000, forms a glass of nature similar to those of low mol. wt. The transition region, through which the sp. heat increases by 32%, is 192—202° abs. The expansion coeff. has been measured at 160—300° abs. and increases by 200% between 185° and 205° abs. In agreement with the behaviour of other glass-forming substances,  $\eta$ , at the mean transition temp., is approx.  $10^{13}$  poises. The influence of mol. structure on glass formation is discussed. M. S.

**Purification and physical properties of organic compounds. XII. Lower aliphatic bromides.** E. L. SKAU and R. McCULLOCH (*J. Amer. Chem. Soc.*, 1935, 57, 2439—2440; cf. this vol., 290).—Revis data for the b.p., f.p., and *d* of  $\text{Et}$ ,  $\text{Pr}^n$ ,  $\text{Pr}^i$ ,  $\text{Bu}^n$ ,  $\text{Bu}^i$ , and *n*-amyl bromides are recorded. E. S. H.

**Regularities in the m.p. of polyenes.** R. and C. GRUNDMANN (*Ber.*, 1936, 69, [B], 224). The same regularities are observed in the absorption and fluorescence spectra of the purely aliphatic polyenes and of the  $\omega\omega'$ -diphenylpolyenes. In ex

ation of further physical regularities it is found that the m.p. of polyenes are to a first approximation a linear function of the no. of conjugated double linkings. The inclination of the graphs is nearly identical for aldehydes, carboxylic acids, and their Me esters, but is steeper for the alcohols. Among *cis-trans*-isomerides the *cis*-forms ( $H_2C_2O_4$ , maleic, *cis-cis*-muconic acid) show a different sequence of m.p., and the 2-furylidene-polyene-aldehydes and -carboxylic acids do not conform to the scheme. The following new or amended m.p. are recorded: sorbaldehyde, m.p. sorbate, m.p. 15°; decatetraenoic acid, m.p. 226.5°.

H. W.

Time of melting of thin fuses. II. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Z. Physik 1935 13—40; cf. A., 1935, 289).—Currents, *I*, up to 20 times the limiting current require a time *t*, for fusion, where  $I^2t = \text{const.}$

A. B. D. C.

Thermochemical properties of nitrous oxide. SUTTON, H. R. AMBLER and G. W. WILLIAMS, (Proc. Physical Soc., 1936, 48, 189—202).—The conditions of initiation and of pressure under which direct decomp. will propagate progressively and explosively through  $N_2O$  are examined. The heat of formation, determined by explosive thermal decomp. at 42 atm., is  $-19.52 \pm 0.1$  g.-cal. per mol. at const. pressure. A simple method for comparing *p* for two gases is applied to  $N_2O$  and  $CO_2$  over 10—45 atm.

N. M. B.

Continuation of vapour-pressure curve above critical. F. KRUGER (Physikal. Z., 1936, 37, 100).—Theoretical. The methods of Eucken (A., 1934, 1062) and of Trautz and Ader (*ibid.*, 1923) gave identical results in the neighbourhood of the crit. point.

A. J. M.

Vapour pressure of glycols. O. J. SCHIERHOLTZ (J. Amer. Chem. Soc., 1935, 57, 2709—2711).—V.p. (10—760 mm.), and *d* are recorded for ethylene,  $\alpha\beta$ - and  $\alpha\gamma$ -propylene,  $\gamma$  and  $\beta\gamma$ -butylene glycols.

E. S. H.

Isopiestic method of determining the vapour pressures of salt solutions. A. JANIS (Proc. Roy. Soc. [iii], 29, III, 87—89).—A modification of Smclair's method for use with larger samples is described (cf. A., 1933, 587).

H. J. E.

of expansion of silver iodide and of thallium. G. JONES and F. C. JONES (J. Amer. Chem. Soc., 1935, 57, 2532—2536).—A differential dilatometer, which acts simultaneously as a thermo-regulator, is described. The following mean cubical coeffs. of expansion have been determined: pyrex glass  $9.85 \times 10^{-6}$ , PhMe  $1.111 \times 10^{-3}$ , AgI  $1.1 \times 10^{-4}$ , TiCl  $1.59 \times 10^{-4}$ , TiBr  $1.53 \times 10^{-4}$ , TH  $1.35 \times 10^{-4}$ .

elastic curves and compressibilities of nitrogen and argon. P. W. BRIDGMAN (Proc. Amer. Acad. Sci., 1935, 70, 1—32; cf. A., 1935, 156).—*p* and *v* changes on melting were determined at pressures up to 6000 atm. The heats of fusion were calculated. *P-V-T* data are given.

CH. ABS. (e)

Viscosity of uranium oxide and its mixtures with water at 25°. G. JONES and B. J. FERNWALT

(J. Chem. Physics, 1936, 4, 30—33).— $\eta$  is nearly a linear function of *d*. An expression relating fluidity to the increase in *d* over that of ordinary H<sub>2</sub>O is shown to be valid to 0.006% over the whole concn. range whilst Bingham's equation is valid to 0.01%.

M. S. B.

Absolute measurement of the viscosity of liquid tin. A. J. LEWIS (Proc. Physical Soc., 1936 48, 102—110; cf. Stott, A., 1933, 895).—Using the capillary flow method,  $\eta$ , with independent correction was measured for the temp. range 235—330°. The temp. variation of  $\eta$  and the val. at the f.p. agree with Andrade's theory (cf. A. 1934 356).

N. M. B.

Association of substances which are solid at ordinary temperatures [determined] by the fluidity method. E. C. BINGHAM and J. E. HATFIELD (Physics, 1935, 6, 64—68).—The fluidities of  $BzOH$ ,  $C_{10}H_8$ ,  $CH_3Ph \cdot OBz$ ,  $Me_2C_2O_4$ ,  $Et_2C_2O_4$ ,  $Pr_2C_2O_4$ , and succinic, glutaric, and adipic acids and of mixtures of  $BzOH$  and  $C_{10}H_8$  with  $CH_3Ph \cdot OBz$  were measured. A viscosimeter bath suitable for use up to 230° is described.

CH. ABS. (e)

Molecular dimensions from viscosity studies. R. M. THEIS and H. B. BULL (J. Physical Chem., 1936, 40, 125—131).—The viscosity of stearic acid and lecithin in  $CCl_4$  has been determined and a linear relation observed between  $c\eta_0/(\eta - \eta_0)$  and *c*, where  $\eta_0$  and  $\eta$  are the viscosities of the solvent and solution, respectively. The possibility of applying Eisen-schitz' equation (A., 1932, 121) to determine the ratio of the length of the solute mols. to their diameter is discussed.

M. S. P.

Partial molal volumes of ammonia and hydrogen in liquid ammonia-hydrogen mixtures under pressure at 100°. R. WIEBE and T. H. TREMEARNE (J. Amer. Chem. Soc., 1935, 57, 2601—2603).—Data are recorded and their thermodynamic significance is discussed.

E. S. H.

Density of solutions of alkali metal halides in liquid ammonia. W. C. JOHNSON and R. I. MARTENS (J. Amer. Chem. Soc., 1936, 58, 15—18).—Data are recorded for solutions of the chlorides, bromides, and iodides of Li, Na, and K in liquid  $NH_3$ , between  $-32^\circ$  and  $-60^\circ$  over as wide a concn. range as solubility permits.

E. S. H.

[Refractive index of] mixtures of piperine and iodides. S. GRUM-GRSHIMAILO (Trans. Inst. Econ. Min. U.S.S.R., 1934, No. 61, 21—23, 27—28).—The vals. of *n* recorded for piperine,  $SbI_3$ , and  $AsI_3$  differ from those given by Larsen (U.S. Geol. Surv. Bull. 679, 1921).

CH. ABS. (e)

Raman effect in mixtures of oleum and nitric acid. J. CHÉDIN (Compt. rend., 1936, 202, 220—222; cf. A., 1935, 807).—The mixtures afford evidence of association between  $N_2O_5$  and  $SO_3$ ; the characteristic spectral effects are very different from those accompanying the association of  $SO_3$  and  $H_2SO_4$  in  $H_2S_2O_7$ .

T. G. P.

Magnetic susceptibilities of nitric acid solutions. S. P. RANGANADHAN and M. QURESHI (Current Sci., 1935, 4, 404).—The susceptibility-concn.

curve over the range 4–65%  $\text{HNO}_3$  shows marked departure from linearity. The  $g$ -ionic susceptibility of the  $\text{NO}_2$  ion is  $-20.83 \times 10^{-6}$ . Min. in the curve correspond with  $\text{HNO}_3 + 50\text{H}_2\text{O}$ ,  $+6\text{H}_2\text{O}$ ,  $+4\text{H}_2\text{O}$ , and  $2\text{HNO}_3 + 5\text{H}_2\text{O}$ . N. M. B.

**Constitution of liquid zinc amalgams.** H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1935, 57, 2657–2662).—Analysis of published e.m.f. data shows that the deviations can be explained on a polymerisation hypothesis which assumes the existence of  $\text{Zn}_2$  and  $\text{Zn}_3$  in equilibrium with monat. Zn. E. S. H.

**Binary mixtures.** IV. L. PIATTI (Angew. Chem., 1936, 49, 77–78; cf. A., 1934, 1301).—The b.p. of binary mixtures (0–100%) of *o*-, *m*-, and *p*-cresol with  $\text{COMe}_2$  and  $\text{C}_6\text{H}_6$ , respectively, have been determined. The vals. are < those calc. from the mixture rule. E. S. H.

**Azeotropic and constant evaporating mixtures.** S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 203–213; cf. this vol., 281).—It is deduced that  $v_1/v_2 = (p_1/p_2)\sqrt{(D_1/D_2)}$ , where  $v_1$  and  $v_2$  are the rates of evaporation of the components of a binary liquid mixture having the diffusion coeffs.  $D_1$  and  $D_2$  and partial v.p.  $p_1$  and  $p_2$ . A mixture in which  $x_1$  and  $x_2$  are the mol. fractions of the components will evaporate without change in composition if  $x_1/x_2 = (p_1/p_2)\sqrt{(D_1/D_2)}$ , an equation which has been confirmed by experiment. Mixtures for which the vapour given off at a particular temp. has the same composition as the liquid do not, in general, evaporate without change of composition at that temp. R. C.

**Orthobaric azeotropes. Esters-hydrocarbons.** M. LECAT (Ann. Soc. Sci. Bruxelles, 1935, 55, B, 253–265; cf. A., 1930, 680).—315 binary systems involving 44 hydrocarbons and 72 esters have been studied. The b.p., composition, and heats of formation of the azeotropes are given. R. S.

**B.p. and composition of the vapour phase of the ternary system ethyl acetate-ethyl alcohol-water.** V. A. KIREEV, I. J. KLINOV, and A. N. GRIGOROVITSCH (J. Chem. Ind. Russ., 1935, 12, 936–940).—B.p. data and the composition of the vapour phases are recorded. R. T.

**Viscosity measurements of the ternary system diopside-albite-anorthite at high temperatures.** S. KÔZU and K. KANI (Proc. Imp. Acad. Tokyo, 1935, 11, 383–385).—Data are recorded for the temp. range 1150–1575°. In a homogeneous melt,  $\eta$  varies linearly with the temp. but the slope increases suddenly when the primary phase begins to crystallise. E. S. H.

**X-Ray and electrical investigation of the copper-gold system.** C. H. JOHANSSON and J. O. LINDE (Ann. Physik, 1936, [v], 25, 1–48; cf. A., 1926, 112; 1927, 400).—A new regular structure ( $\text{CuAu II}$ ) in the region 50 at.-% has been identified, and its lattice dimensions are measured.  $\text{CuAu II}$  has rhombic symmetry, and is a modification of the tetragonal form ( $\text{CuAu I}$ ). The unit cell is the 4-atom face-centred cell repeated 10 or 11 times.  $\text{CuAu II}$  is stable at low temp. for the regions 36–47 and 53–

65 at.-% Au; for 47–53% it can be obtained only by quenching from 420°. The relations between the lattice structures, and the influence of heat-treatment, are discussed. In the region 65–80 at.-% Au a cubic structure is found. The sp. resistance for the entire range has been measured. L. J. J.

**Ferromagnetic increment of resistance of copper-nickel alloys.** B. SVENSSON (Ann. Physik, 1936, [v], 25, 263–271).—Data are recorded for the sp. electrical resistance of nine Cu-Ni alloys with 11–90 at.-% Ni between 0° and 500°. The ferromagnetic component of the resistance has a max. val. at approx. 80 at.-% Ni. L. J. J.

**Solid solubility of magnesium in aluminium.** S. KISHINO (J. Chem. Soc. Japan, 1935, 56, 322–324).—The determination of the solubility of Mg in Al by microscopic examination, or by electrical resistance measurements, is difficult for < 5% of Mg. CH. ABS. (e)

**M.p. of eutectics.** Lipowitz alloy and Wood's metal. S. J. FRENCH (Ind. Eng. Chem., 1936, 28, 111–113).—The cooling and melting curves of the Lipowitz alloy (Bi 50, Pb 27, Sn 13, Cd 10%) and Wood's metal (Bi 50, Pb 25, Sn 12.5, Cd 12.5%) coincide approx. over the greater part of the const.-temp. region, giving the same m.p. and f.p., viz., 71.7° and 69.7°. The former approaches the quaternary eutectic more closely than does Wood's metal. Discrepancies in published vals. may be due to undercooling or to Hg as an impurity. It is suggested that names for the alloys should be discarded, and that composition and m.p.—f.p. range should be substituted. R. S. B.

**Ternary diagram of aluminium-copper-silicon system.** K. MATSUYAMA (Kinz.-no-Kenk., 1934, 11, 461–490).—The Al-Cu, Cu-Si, and Al-Si diagrams have been reinvestigated. In the system Al-Cu-Si there are 18 monovariant curves and 8 nonvariant points. The  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  solid solutions of the systems Cu-Al and Cu-Si are contiguous. In the solid state there are 9 monovariant curves and 2 nonvariant points. CH. ABS. (e)

**System iron-cementite-manganese carbide-manganese.** R. VOGEL and W. DÖRING (Arch. Eisenhüttenw., 1935–1936, 9, 247–252).—Contrary to previous statements, Mn and  $\text{Mn}_3\text{C}$  do not form a continuous series of solid solutions, but a complicated series of reactions occurs during cooling. The liquidus curve passes through a min. at 3.5% C, 1160°, and  $\text{Mn}_3\text{C}$  undergoes a transformation at 1050°, the temp. of which is gradually decreased by addition of Mn to 920° at 3.5% C (eutectoidal point). At 740° in alloys with > 1.2% C the  $\gamma$ -Mn solid solution undergoes a eutectoidal transformation into  $\alpha$ -Mn +  $\alpha$ - $\text{Mn}_3\text{C}$ . The  $\gamma$ - $\beta$ -transformation point of Mn is lowered by addition of C from 1140° to 840°, whereas the  $\beta$ - $\alpha$  point is raised from 740° to 840° (0.9% C). The complete diagram and micrographs showing characteristic structures of alloys within the various fields are included. In the ternary system Fe-Mn-C the equilibria resemble those in the Fe-C system up to 60% Mn; in alloys with a higher Mn content complicated reactions occur due to the allotropic changes



in Mn and  $\text{Mn}_3\text{C}$ ; thus the section through 70% Mn contains 17 phase fields. In the Mn corner of the ternary diagram there are 4 planes of four-phase equilibrium, one of which corresponds with a ternary eutectoidal change:  $\gamma\text{-Mn} = \alpha\text{-Mn} + \gamma\text{-Fe} + \alpha\text{-Mn}_3\text{C}$ ; the eutectoid contains Fe 25, Mn 77.95, C 2.05% (640°).  
A. R. P.

Properties of the oxides of nitrogen. II. Binary system  $\text{N}_2\text{O}_3\text{-H}_2\text{O}$ . III. Pseudo-binary system  $\text{N}_2\text{O}_4\text{-H}_2\text{O}$ . T. M. LOWRY and J. T. LEMON. IV. Formation of two liquid layers in mixtures of nitrogen peroxide and water. T. M. LOWRY, E. LLOYD, and W. V. LLOYD (J.C.S., 1936, 1—6, 6—10, 10—17).—II. Two liquid phases are formed over a wide range of mixtures. The limiting mixtures correspond with 42—97 wt.-%  $\text{N}_2\text{O}_3$  at 0° and 48—95% at 20°. A max. temp. of separation was observed at 55° and 65%  $\text{N}_2\text{O}_3$ . Escape of NO into the gaseous phase lowers all the temp. and the crit. solution temp. is possibly 20° > that recorded. A quaternary point, at which the gaseous and two liquid phases are in equilibrium with ice, occurs at -33.3° and 36%  $\text{N}_2\text{O}_3$ , and another, with  $\text{N}_2\text{O}_3$  as the solid phase, may occur below -103° at > 98%  $\text{N}_2\text{O}_3$ .

III. Two liquid phases are formed over a wide range. A max. temp. of separation was observed at 67° and 89%  $\text{N}_2\text{O}_4$ . Escape of NO into the gaseous phase probably lowers the temp. Homogeneous aq. solutions deposit ice down to -50° and up to 33%  $\text{N}_2\text{O}_4$  and a compound of unknown composition over a narrow range down to -56° and up to 44%  $\text{N}_2\text{O}_4$ . Non-homogeneous mixtures containing > 44%  $\text{N}_2\text{O}_4$  deposit  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  from the upper aq.-acid layer, at temp. up to a max. of -22.5°. The lower layer of liquefied gas deposits  $\text{N}_2\text{O}_4$ , either in the ordinary stable form or in a metastable form which melts 11° lower.

IV. The composition of the two liquid layers has been determined by analysis. The limits within which two liquid layers are formed in the system  $\text{H}_2\text{O-N}_2\text{O}_3\text{-N}_2\text{O}_5$  at 0° and 20° are shown on triangular diagrams.  
E. E. A.

Solubility of gas mixtures in liquids under pressure. I. Solubility in water of carbon dioxide from admixture with hydrogen at 20° and 30° and under total pressures up to 30 kg. per sq. cm. I. R. KRITSCHESKI, N. M. SHAVORON, and V. A. AEPPELBAUM (Z. physikal. Chem., 1935, 175, 232—238).—A thermodynamic method is described for calculating the solubility of components gas mixtures in liquids in the case where the thermodynamic potential of the dissolved gas is not affected by the presence of other dissolved gases. The experimental results show that if the pressure is not so high the solubility of  $\text{CO}_2$  in  $\text{H}_2\text{O}$  at a given fugacity is the same whether the gas is pure or mixed.  
R. C.

Ratio of rates of evaporation of different gases in moving air. S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 195—202).—It is deduced theoretically and confirmed experimentally that for two liquids of v.p.  $p_1$  and  $p_2$  evaporating under the same conditions in a current

of air  $v_1/v_2 = (p_1/p_2) \sqrt{[D_1/(B - \frac{1}{2}p_1)]/[D_2(B - \frac{1}{2}p_2)]}$ , where  $v_1$  and  $v_2$  are the rates of evaporation, and  $D_1$  and  $D_2$  the diffusion coeffs. of the vapours, and  $B$  is the barometric pressure.  
R. C.

Dependence of rate of evaporation on nature of gas flowing over the surface of the evaporating liquid. S. I. SKLJARENKO and M. K. BARANAJEV (Z. physikal. Chem., 1935, 175, 214—218; cf. preceding abstract and this vol., 280).—If the vapour of the liquid is heavier than the gas passing over the surface,  $v_1/v_0 = \sqrt{(D_1/D_2)}$ , where  $v_1$  and  $v_0$  are the rates of evaporation into, and  $D_1$  and  $D_0$  the diffusion coeffs. of the vapour into, the gas and air, respectively. If the vapour is the lighter, as in the evaporation of  $\text{H}_2\text{O}$  into air, allowance must be made for convection currents.  
R. C.

Principles of gas exsorption. III. A. GUYER, B. TOBLER, and H. FARMER (Chem. Fabr., 1936, 9, 5—7; cf. A., 1934, 592, 1065).—The apparent "evaporation coeff." and rate of loss of gas from falling drops of  $\text{H}_2\text{O}$  is independent of the height of fall, and therefore of the velocity of fall. The relative loss of gas increases with increasing height of fall. The relative loss of gas from a  $\text{H}_2\text{O}$  stream falling against an air resistance increases with the height of fall and with decreasing cross-section of the stream. Reduced pressure has only a slight influence on the loss of gas. This is related to the degree of disturbance of the  $\text{H}_2\text{O}$ , which is a function of the air pressure.  
J. W. S.

Diffusion of gases through metals. II. Diffusion of hydrogen through aluminium. C. J. SMITHELLS and C. E. RANSLEY (Proc. Roy. Soc., 1935, A, 152, 706—713; cf. A., 1935, 692).—The rate of diffusion of  $\text{H}_2$  through Al above 400° depends on the state of the surface. The highest rate is given with a surface freshly scraped in  $\text{H}_2$ , but it rapidly falls, and after several hr. reaches a steady val. which is only 0.1 of the initial rate. This low rate is obtained with an anodically oxidised surface. The effects of temp. and pressure are represented by Richardson's equation.  
L. L. B.

Diffusion of water vapour through copper. J. H. DE BOER and J. D. FAST (Rec. trav. chim., 1935, 54, 970—974).—At about 800°  $\text{H}_2\text{O}$  vapour diffuses at the rate of about  $1.9 \times 10^{-12}$  g.-mol. per sq. cm. per sec. through Cu 1 cm. thick, when the pressure difference is 1 atm. The rate of diffusion of  $\text{H}_2$  under similar conditions is  $230 \times 10^{-12}$  g.-mol. per sq. cm. per sec. The diffusion of  $\text{N}_2$  through Cu, if existent, is very slow.  $\text{H}_2\text{O}$  vapour does not diffuse through chrome-Fe, whilst at 900° the rate of diffusion of  $\text{N}_2$  is  $> 6.9 \times 10^{-12}$  g.-mol. per sq. cm. per sec.  
J. W. S.

Diffusion of helium through fused silica. E. O. BRAATEN and G. F. CLARK (J. Amer. Chem. Soc., 1935, 57, 2714—2717).—Measurements at -78° to 562° show that the rate of diffusion  $\propto$  pressure and inversely  $\propto$  the thickness of  $\text{SiO}_2$ . Two vals. for the activation energy have been obtained, depending on the temp. region.  
E. S. H.

Diffusion of silver in glass. O. KUBASCHESKI (Z. Elektrochem., 1936, 42, 5—7).—The rate of diffusion and variation with temp. have been

determined. The amount of Ag taken up depends primarily on the availability of  $O_2$ , showing that it is not a case of simple diffusion of  $Ag^+$ . E. S. H.

**Equilibrium between strontium sulphate and water at various temperatures.** G. GALLO (Annali Chim. Appl., 1935, 25, 628—631).—The solubility of  $SrSO_4$  in  $H_2O$  increases from 0.0121 (g. per 100 c.c. of solution) at  $5^\circ$  to 0.0141 at  $40^\circ$ , then decreases to 0.0113 at  $95^\circ$ ; both pptd.  $SrSO_4$  and calcined celestine give similar vals. The influence of  $NH_4Cl$ ,  $NH_4NO_3$ , and  $(NH_4)_2SO_4$  on the solubility is studied. E. W. W.

**Re-determination of the solubility of chloropentammine cobaltic chloride.** F. J. GARRICK (Nature, 1935, 136, 1027—1028).—The compound purified by an improved method (A., 1935, 1335) gave 0.00925 and 0.0211 g.-mol. per litre at  $0.20^\circ$  and  $25.00^\circ$ , respectively. L. S. T.

**Solubilities and free energies of some metallic sulphides.** S. E. RAVITZ (J. Physical Chem., 1936, 40, 61—70).—The solubility data for the sulphides of Zn, Pb, Cu, Tl, Ag, and Cd have been examined and the solubilities recalcd. with the help of recent activity data. Free energies of formation have also been calc. M. S. B.

**Solubility of oxalic acid and oxalates of the alkaline earths in mineral acids.** I. H. TRAPP (J. pr. Chem., 1936, [ii], 144, 193—210).—The solubility of  $H_2C_2O_4$  in 0—16.46%  $HCl$ , 0—46.96%  $H_2SO_4$ , and 0—29.35%  $H_3PO_4$  at  $20+2^\circ$  is recorded. With  $K_2SO_4$  and  $CaSO_4$  it forms  $KHC_2O_4 \cdot H_2C_2O_4$  and  $CaC_2O_4 \cdot 2H_2O$ , respectively, until the concn. of  $H_2SO_4$  is 12 and 13%, respectively, at  $20+2^\circ$ . Lower concns. of  $H_2SO_4$  suffice to dissolve the salts at higher temp.  $NaCl$  and  $MgSO_4$  form  $Na_2C_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$  and  $MgC_2O_4 \cdot 2H_2O$ , respectively.  $BaCl_2$  gives  $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$  until the concn. of  $HCl$  is 4.5% and above this concn.  $BaC_2O_4 \cdot H_2C_2O_4 \cdot 3H_2O$ . R. S. C.

**Equilibrium in the system lithium phthalate-phthalic acid-water.** S. B. SMITH, W. A. STURM, and E. C. ELY (J. Amer. Chem. Soc., 1935, 57, 2406—2408).—Solubility data at  $0^\circ$ ,  $25^\circ$ , and  $50^\circ$  have been obtained. The compound  $LiHC_8H_4O_4 \cdot 2H_2O$  is formed at these temp. and can be crystallised at temp.  $< 60^\circ$ . E. S. H.

**Solubility of metals in crystals of halides.** G. TAMMANN (Z. anorg. Chem., 1935, 226, 92—96).—Solutions of metals in their solid halides (e.g., Na in  $NaCl$ , Ca in  $CaF_2$ ) are discussed from the point of view of their similarity to solutions of one metal in crystals of another. F. L. U.

**Precipitation processes. I. Connexion between ratio of concentrations of reactants and precipitation of silver thiocyanate and cyanide.** B. TEZAK (Z. physikal. Chem., 1935, 175, 219—231; cf. A., 1934, 593).—The pptn. curve (graph of turbidity 4 min. after mixing the reacting solutions against reactant concn.) exhibits two max. if the stabilising effects of the two reacting ions are large but approx. equal. The max. at the lower concn. is due to the isoelectric point, and the other to the reduction in solubility and stability and to the rapid formation

of pptn. centres. If the stabilising effect of the ion of variable concn. is very great, or there is considerable tendency to complex formation, the first max. only is observed, whilst if both ions have but a slight stabilising effect the second max. only is present. R. C.

**Distribution of thorium-C'' in thallium salt solutions.** J. ZIRKLER (Z. Physik, 1935, 98, 75—76).—The separation of the Tl isotope  $Th-C''$  from a solution containing  $Tl'$  and  $Tl$  does not depend on the total mass of the ions present, but on the amounts of  $Tl^{205}$  and  $Tl^{203}$ . A. B. D. C.

**Adsorption of hydrogen and deuterium on copper at low pressures.** R. A. BEEBE, G. R. LOW jun., E. L. WILDNER, and S. GOLDWASSER (J. Amer. Chem. Soc., 1935, 57, 2527—2532).—At  $-78^\circ$  and 0—2 mm. the rate of adsorption is less for  $D_2$  than for  $H_2$ , but equal amounts are adsorbed at equilibrium. At  $0^\circ$   $H_2$  is more strongly adsorbed, but at  $125^\circ$  it is adsorbed  $< D_2$ . The differential heats of adsorption are identical for  $H_2$  and  $D_2$ . E. S. H.

**Adsorption of hydrogen on tungsten.** J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 445—463).—The method used depends on the fact that the accommodation coeff. of Ne is different for a bare surface and for a surface with an adsorbed film on it. Saturation occurs at a partial pressure of  $H_2$  of the order of  $< 10^{-1}$  mm. and the process is one of chemisorption, which takes place rapidly at these low pressures at  $79^\circ$  abs. The heat of adsorption and amount of gas adsorbed have been measured on a single fine wire. The film is stable at negligibly low pressures at room temp. There is strong evidence for the view that the  $H_2$  is adsorbed as atoms, with one atom for each W atom in the surface. The binding is of the same type as that of  $O_2$  on W. The bearing of the data on the general problem of  $H_2$  adsorption and on that of activated adsorption is considered. L. L. B.

**Composite films of oxygen and hydrogen on tungsten.** J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 477—480).—When an  $O_2$  mol. is adsorbed on a W surface already covered with  $H_2$ , a mol. of  $H_2$  is ejected into the gas phase. The behaviour of  $H_2$  in the presence of a surface partly covered with  $O_2$  is also considered. The data support the theory that activated adsorption of  $H_2$  is connected with the interaction between  $H_2$  and surface  $O_2$ , either adsorbed or forming an integral part of the solid lattice. L. B.

**Adsorbed films of oxygen on tungsten.** J. K. ROBERTS (Proc. Roy. Soc., 1935, A, 152, 464—477; cf. preceding abstract).—Experiments show that a second mol. film of  $O_2$ , which is quite stable at room temp., is formed on top of the well-known stable film (A., 1931, 782). The heats of adsorption and no. of mols. adsorbed in each film have been measured. Consideration of the process of building up an immobile film by the adsorption of the two atoms of diat. mol. on neighbouring solid atoms shows that such a film necessarily has gaps in it. The no. of these gaps has been measured, and the amount of  $O_2$  in the second film found to correspond with adsorption on the gaps in the first. The possible

role of these gaps in the diffusion of  $O_2$  into W is discussed. The accommodation coeffs. for Ne striking the at. and the mol. film are deduced.

L. L. B.

**Sorption of ammonia and other gases by arsenic trisulphide.** N. MORITA (J. Chem. Soc. Japan, 1935, 56, 325—332).—The sorption velocity of  $NH_3$  by  $As_2S_3$  varies with the mode of prep. of the  $As_2S_3$ . The product at room temp. corresponds with  $As_2S_3 \cdot NH_3$ . The behaviour of  $NH_3$  is similar.

CH. ABS. (c)

**Adsorption of gases by virgin salt surfaces.** F. DURAU and A. HORN (Z. Physik, 1935, 98, 198—226).—Observations have been made with NaCl,  $CdCl_2$ , and  $NaNO_3$  which were melted, freed from impurities, and powdered in high vac. A. B. D. C.

**Adsorption on chromite catalysts.** J. C. W. FRAZER and C. G. ALBERT (J. Physical Chem., 1936, 40, 101—112).—The "activated adsorption" of  $O_2$  and CO on Cu chromite (I) at 100—200°, as distinct from the van der Waals adsorption, has been determined in order to see what relation it bears to the catalytic activity of (I) in the oxidation of CO. Activation energies of the adsorption have been calc. The activated adsorption of  $O_2$  increases with rise of temp., but that of CO attains a max. and then falls. This behaviour may be due to entirely separate processes taking place at the surface of (I). The results suggest that it is the activated adsorption of  $O_2$  which determines the catalytic activity of the surface. Possible mechanisms are discussed. M. S. B.

**Adsorption at crystal-solution interfaces.** VIII. Influence of dyes and other organic compounds on the crystal habits of barium and lead nitrates. (Miss) P. P. DAVIS and W. G. FRANCE (J. Physical Chem., 1936, 40, 81—87).—The habit assumed by crystals of  $Pb(NO_3)_2$  and  $Ba(NO_3)_2$ , separating from pure solutions and solutions containing dyes or other org. substances, indicates that they approximate most closely to the distorted  $CaF_2$  structure. The results are in general agreement with the theory previously put forward to account for the adsorption and habit modification (cf. A., 1933, 20). The effect of a mixture of two dyes is approximate. M. S. B.

**Adsorption of dyes on previously ignited gels.** SPILCHAL (Coll. Czech. Chem. Comm., 1935, 7, 536).—Basic dyes, e.g., methylene-blue, Me-are not adsorbed from aq. solution by ignited alumina gel (I). The adsorption of acid dyes, e.g., Congo-red (II), eosin, and Bordeaux-red, is high, but decreases to very low vals. as the drying temp. of (I) is raised to 1200°. Ignited  $Fe(OH)_3$  gels behave similarly. An unstable space lattice of the  $\gamma-Al_2O_3$  is indicated. The adsorption on bauxites (III), which have a smaller internal surface than (I), and of (II) on (I), decreases as the grain size increases. The adsorptive power of (III), heated at 1000°, increases towards basic dyes, probably owing to an increase of the internal surface of the grains.

J. G. A. G.

**aximal adsorption.** I. Maximal adsorption of sparingly soluble acids and bases by

different active charcoals. H. BRINTZINGER, A. SCHALL, and H. G. BEIER (Kolloid-Z., 1936, 74, 29—32).—Max. adsorption is defined as the amount of substance adsorbed at a given temp. by 1 g. of the adsorbent from a saturated solution. Determinations with salicylic acid and quinine are reported.

E. S. H.

**Adsorption of lead nitrate by metastannic acid.** A. G. BOSIN and M. M. SHILKINA (J. Appl. Chem. Russ., 1935, 8, 1287—1290).—When Sn—Pb alloys are dissolved in  $HNO_3$  part of the  $Pb(NO_3)_2$  formed is adsorbed on the  $SnO_2$ ; the amount ( $C_2$ ) of Pb adsorbed by a const. amount of  $SnO_2$  is given by  $C_2 = 4\sqrt{C_1}$ , where  $C_1$  is the amount of Pb found in the solution.

R. T.

**Adsorption at the interface between two fluids.**

I. Adsorption of methylene-blue, methyl-orange, Congo-red, and orange II at benzene-water and chlorobenzene-water interfaces. C. W. GIBBY and C. C. ADDISON (J.C.S., 1936, 119—127).—The adsorption, at various concns. in  $H_2O$ , at  $H_2O$ — $C_6H_6$  and  $H_2O$ —PhCl interfaces and the interfacial tensions have been measured. The results show marked quant. deviations from the predictions of Gibbs' equation in all cases, although this equation gives vals. of approx. the right order and in closer agreement with the observed results than with Lewis' data. Two types of concn.—adsorption curve are found. The type differs according to the adsorbate, but is independent of whether the interface is  $H_2O$ — $C_6H_6$  or  $H_2O$ —PhCl. Curves for Congo-red and Me-orange have the qual. features of a Gibbs curve; those for methylene-blue and orange II have not. The area of the interface occupied by the adsorbed mol., reckoned as monomeric, in the region of max. adsorption is calc. For methylene-blue and orange II, the adsorbed layer, on either interface, is unimol., but for the other two dyes, the surface concn. on  $C_6H_6$  is <, and on PhCl about twice as great as, that which is represented by a unimol. layer. E. E. A.

**Kinetics of adsorption of vapours by highly active adsorbents.** M. V. POLJAKOV, I. E. NEIMARK, and I. M. MALKIN (J. Phys. Chem. U.S.S.R., 1934, 5, 1079—1081).—Data for the adsorption of  $C_6H_6$  and PhMe by a mixture of C and  $SiO_2$  gel at 0—36° are recorded. The change in the character of the isotherm with fall in temp. is attributed to the onset of capillary condensation. CH. ABS. (c)

**Application of Polanyi's potential theory to the van der Waals adsorption of gases on iron synthetic ammonia catalysts.** P. H. EMMETT and S. BRUNAUER (J. Amer. Chem. Soc., 1935, 57, 2732—2733).—Isotherms for the adsorption of A and  $N_2$  by  $Fe_2O_3$ — $Al_2O_3$  catalysts are in accordance with the theory. E. S. H.

**Specific heat and binding conditions of adsorbed argon on charcoal.** H. M. CASSELL (J. Amer. Chem. Soc., 1935, 57, 2724).—Published sp. heat evidence suggests that the adsorbed atoms are capable of one-dimensional vibration only.

E. S. H.

**Temperature dependence of the surface tension of solutions.** R. V. MERTZLIN and N. A.

TRIFONOV (J. Phys. Chem. U.S.S.R., 1934, 5, 1146—1163; cf. A., 1935, 928).—Data are recorded for the systems  $\text{PhMe-Pr}^n\text{CO}_2\text{H}$  (12—100°),  $\text{C}_5\text{H}_5\text{N-NPhEt}_2$  (18—100°), allylthiocarbimide-NPhEt<sub>2</sub> (16—130°), quinoline-Bu<sup>o</sup>OH (0—140°), thymol-EtOAc (15—70°)

CH. ABS. (e)

Effect of light on surface tension of soap solutions. II. L. D. MAHAJAN (Z. Physik, 1935, 98, 388—395; cf. A., 1931, 1228).—Max. lowering by irradiation is observed with  $6.25 \times 10^{-4}$  g. of Na oleate per c.c., and with ultra-violet light.

A. B. D. C.

Electrokinetics. XVI. Streaming potentials in small capillaries. H. B. BULL and L. S. MOYER (J. Physical Chem., 1936, 40, 9—20).—A mathematical treatment is given for the streaming potential in capillaries < those to which Smoluchowski's theory in its simple form applies. The change in the viscosity of H<sub>2</sub>O with capillary size is discussed and an equation is derived to show the relationship between the back pressure produced by electro-osmotic effects and the mechanical pressure. A method for determining the average pore radius is described. For quartz and glass diaphragms, the theoretical crit. pore radius is not the same as that found experimentally. The potential-concn. and flow-concn. curves are anomalous for quartz and glass diaphragms with pores < the crit. size, but normal for cellulose.

M. S. B.

Wetting and spreading properties of aqueous solutions. Oleic acid-sodium carbonate mixtures. H. L. CUPPLES (Ind. Eng. Chem., 1936, 28, 60—62; cf. B., 1935, 1129).—The surface tensions and interfacial tensions against mineral oil have been determined for oleic acid-aq. Na<sub>2</sub>CO<sub>3</sub> mixtures containing approx. 0.1—1% of oleic acid, and approx. 1—4 mols. of Na<sub>2</sub>CO<sub>3</sub> per mol. of oleic acid. The spreading coeff.  $s = \sigma_{\text{oil}} - \sigma_{\text{soap solution}} - \sigma_{\text{interface}}$  varies much less with the ratio of alkali to acid than with oleic acid-NaOH mixtures, especially at high concn. of acid. Unlike the NaOH mixtures, the Na<sub>2</sub>CO<sub>3</sub> mixtures at high acid concn. have excellent wetting properties over the whole range of mol. ratios, and a high val. of  $s$  is easy to maintain.

R. S. B.

Wetting hysteresis caused by dispersity. I. R. KLJATSKO (Kolloid-Z., 1936, 74, 90—97).—Wetting isotherms for several minerals have been determined and the importance of the adsorption of surface-active substances is confirmed. The relation to flotation is discussed.

E. S. H.

Spreading of ovalbumin. (Miss) M. G. TER HORST (Rec. trav. chim., 1936, 55, 33—42).—The area of spreading increases with rise of temp., but the velocity of spreading shows an optimum at 25°. The area of the coherent film is little influenced by temp., but that of the compressed film rapidly increases with rise in temp. until at 50° both films probably become identical and the p.d. between the two films vanishes.

E. E. A.

Ageing of surface of solutions. K. S. G. DOSS (Current Sci., 1935, 4, 405).—A freshly formed surface of 0.002M solution of benzopurpurin, investigated by the surface-pressure method, showed a regular fall of surface tension with time, accompanied by the

formation of a surface film. If overcrowding of the surface mols. is produced by shifting the barrier, the surface tension increases with time. The observed rate of accumulation of solute mols. is far < the calc. collision frequency and is > doubled for 20° temp. rise, in agreement with the view that the adsorption is of the activated type.

N. M. B.

Collapse of unimolecular films of palmitic acid on acid solutions. R. J. MYERS (J. Amer. Chem. Soc., 1935, 57, 2734—2735).—The curve obtained when the collapse pressure vals. are plotted against  $p_H$  is S-shaped. The mid-point of the curve differs from that of the neutralisation curves for fatty acids. This appears to indicate increased activity of palmitic acid when oriented at a H<sub>2</sub>O surface.

E. S. H.

Periodic phenomena in diffusion and adsorption. I. Use of membranes. H. WAELSCH, S. KITTEL, and A. BUSZTIN (Kolloid-Z., 1936, 74, 22—29).—Periodic variations in concn. have been observed in the diffusion of salts in blood corpuscles and plasma. Similar periodicity has been obtained in a colloid model by allowing KCl to diffuse from aq. solution into a gelatin sol, from which it is separated by a membrane.

E. S. H.

Effects of some factors on rhythmic crystallisation. M. J. MACMASTERS, J. E. ABBOTT, and C. A. PETERS (J. Amer. Chem. Soc., 1935, 57, 2504—2508).—The periodic crystallisation of aq. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> has been investigated. Differences in temp. and concn. have little effect, but the phenomenon may be inhibited by foreign anions, the effect increasing in the order  $\text{Cl}^- < \text{SO}_4^{2-} < \text{NO}_3^-$ . The spacing of the periods agrees with that observed in the Liesegang phenomenon and in the crystallisation of periodic structures from melts.

E. S. H.

Structural changes taking place on ageing of freshly-prepared crystalline precipitates. V. Thermal ageing of freshly-prepared lead sulphate. VI. Perfection and ageing of lead sulphate precipitated under various conditions. VII. Kinetics of the distribution of thorium-B through fresh lead sulphate. VIII. Influence of agitation on the ageing and speed of distribution of thorium-B. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1935, 57, 2573—2577, 2577—2579; 1936, 58, 116—120, 121—122; cf. A., 1935, 715).—V. Sintering of the particles occurs markedly at 400° and very slowly at 300°. At lower temp. internal thermal ageing occurs, due to the high speed of evaporation of lattice ions on the active surface. At still lower temp. thermal ageing is promoted by adsorbed and occluded H<sub>2</sub>O.

VI. The effects of concn. of Pb(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>SO<sub>4</sub> and of temp. on the nature of PbSO<sub>4</sub> ppts. and their rate of ageing have been studied.

VII. During the initial stages of the ageing of fresh PbSO<sub>4</sub> the recrystallisation is mainly unidirectional and an enrichment of Th-B in the recryst. sulphate occurs; with prolonged shaking, successive recrystallisations occur, ultimately leading to homogeneous distribution.

VIII. The speed of distribution of Th-B when



shaken with freshly-pptd.  $\text{PbSO}_4$  is independent of the speed of agitation so long as the ppt. is prevented from settling. The speed of ageing of  $\text{PbSO}_4$  in aq.  $\text{Pb}(\text{NO}_3)_2$  is independent of the amount of ppt. and the speed of agitation. The recrystallisation is not an Ostwald-ripening process. E. S. H.

**Influence of nature of the membrane and temperature on the osmotic system of water and oxalic acid.** F. A. H. SCHREINEMAKERS, (Miss) J. C. LANZING, and C. L. DE VRIES (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1067—1074; cf. A., 1931, 1007; 1932, 334, 691).—The system  $\text{H}_2\text{O}$ -membrane-aq.  $\text{H}_2\text{C}_2\text{O}_4$  has been investigated when one of the liquids is maintained invariant. With Cellophane at  $20^\circ$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4$  diffuse in opposite directions, with pig's bladder both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4$  diffuse to the left at  $0^\circ$ , but at  $20^\circ$  with invariant aq.  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4$  diffuse to the left until the  $\text{H}_2\text{O}$  contains approx. 5% of  $\text{H}_2\text{C}_2\text{O}_4$  and then  $\text{H}_2\text{O}$  diffuses to the right. The relations at  $0^\circ$  and  $20^\circ$  are discussed. J. G. A. G.

**Osmotic complex with two stationary liquids.** F. A. H. SCHREINEMAKERS and J. P. WERRE (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 982—988).—Changes in composition with time have been investigated for the system  $A|B|C|D$ , where  $A$  is  $\text{H}_2\text{O}$ ,  $D$  is a  $\text{NaCl}$  solution of definite concn., and  $B$  and  $C$  represent solutions of  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$ . The concn. of  $\text{NaCl}$  in  $B$  passes through a min. J. W. S.

**Osmotic complexes in which one or more liquids proceed along a closed curve during osmosis.** I. F. A. H. SCHREINEMAKERS and C. L. DE VRIES (Rec. trav. chim., 1935, 54, 945—955).—The changes of composition with time in systems consisting of solutions in series contact through semipermeable membranes are discussed, with special reference to aq.  $\text{NaCl}+\text{Na}_2\text{CO}_3$  solutions,  $\text{H}_2\text{O}$  forming one invariant phase. J. W. S.

**Electrodialysis.** G. S. VOZDVISHENSKI (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 99—111).—If the  $\text{H}_2\text{O}$  in the electrode spaces in electrodialysis is left unchanged, the c.d. and rate of dialysis increase, even if the voltage is kept const. Gluten containing  $\text{NaCl}$  (ash content 1.70%) was electrolysed by this method, using a parchment membrane. It took 5 hr. at 30 volts, or 1 hr. at 100 volts, to obtain a product with 0.14% of ash. CH. ABS. (e)

**Simple lyotropic effects (viscosity).** E. M. DRUINS (Rec. trav. chim., 1936, 55, 13—16).—Different lyotropic formulæ are discussed and the idea of crit. ions is explained. The viscosities of 0.25*N* solutions of electrolytes containing (1, 1)-, (1, 2)-, (2, 1)-, and (2, 2)-valent salts can be calc. from a single formula. E. E. A.

**Optical behaviour of dissolved ions and its significance for the structure of solutions of electrolytes.** I. Influence of temperature and effect of salts on optical absorption of 2:4-dinitrophenoxide ion. G. KORTÜM (Z. physikal. Chem., 1936, B. 30, 317—355).—The extinction coeff,  $\epsilon$ , of the 2:4-dinitrophenoxide ion (I) at 436

$m\mu$  in aq. solution at  $20^\circ$  and  $25^\circ$  remains const., in presence of foreign salts independent of the salt concn.,  $c$ , up to concns. beyond those at which the ionic properties influenced by electrostatic interactions, e.g., conductivity, vary appreciably with  $c$ . At higher salt concns. ( $c > 0.01$ ) the absorption bands of (I) shift, but the magnitude and direction of the shift are an individual property of the foreign salt present. At these concns. there is no parallelism between the change of  $\epsilon$  with  $c$  and the change of the activity coeff. of (I) with  $c$ . The effects cannot be explained by deformation by the cations accumulating in the ionic atmosphere or by ionic association. In general, the salt anion has a sp. effect on  $\epsilon$  commensurate with that of the cation. The effects of salts on the optical properties of an ion seem to depend on the interaction between the ion and the solvent, rather than on direct deformation in the Coulomb field of force of the added ions. Calculation shows that small changes in the field of force due to ion-dipole interaction will have optical effects as large as deformation in the Coulomb field of the ions. The optical effects of non-electrolytes on (I) are similar to those of electrolytes. The effect of temp. on the long-wave absorption band of (I) suggests an electron affinity spectrum. A review of the entire optical data for aq. solutions of electrolytes indicates that at small and moderate concns. the solute is present as isolated solvated ions, the mutual deformation of which is largely negligible compared with their interaction with the  $\text{H}_2\text{O}$  mols. R. C.

**Optical rotation and circular dichroism, and absorption and refraction in solutions.** W. KUHN (Z. physikal. Chem., 1935, B, 30, 356—378).—The non-sp. part of the effect of the solvent results in the circular dichroism,  $D$ , and the optical rotation,  $\alpha$ , each being multiplied by the factor  $(n^2+2)/3$  on passage from the gaseous to the dissolved state, whilst the contribution of an absorption band to the normal absorption and sp. refractive power,  $r_L$ , is multiplied by the factor  $K=[(n^2+2)/3]^2/n$ . Consequently, relations between  $D$  and  $\alpha$  and between  $r_L$  and absorption are not changed by going over from the gaseous to the dissolved state, provided that the magnitudes for the appropriate state are consistently used. This is confirmed by existing experimental data. The anisotropy-activity factor observed with a solution must be multiplied by  $(n^2+2)/3n$  to reduce it to the gaseous state. In calculating  $f$  vals. from the intensity of absorption bands in solutions, allowance must be made for the factor  $K$ . R. C.

**Dielectric constants of strong electrolytes and the Debye-Falkenhagen theory.** M. JEZEWSKI (Physikal. Z., 1936, 37, 52—55).—New measurements of the dielectric consts. of strong electrolytes by a resonance method show that the Debye-Falkenhagen theory is in agreement with experiment for dil. solutions. At higher concns. and higher temp. the change of dielectric const. is  $<$  that given by the theory. A. J. M.

**Form and dielectric behaviour of thread-like molecules in solutions.** W. KUHN (Z. physikal. Chem., 1935, 175, 1—16).—The dipole moment of a zwitterion  $\propto \sqrt{Z}$ , where  $Z$  is the chain length, and

$r^2 \propto Z$ , where  $r^2$  is the mean square distance between the positive and negative charges on the ion.  $r^2$ , the mean square of the distance between the ends of the mol. taking account of the attraction between the two charges, increases slightly more rapidly than  $\propto Z$ , which agrees with the observation that  $dD/dc \propto Z$  ( $D$ —dielectric const.,  $c$ —concn.). Only when  $Z > 25$  does the difference between  $r^2$  and  $r^2$  fall below about 40%. The calc. orientation polarisation on applying a field to a solution containing zwitterions is the same whether the zwitterions are supposed to behave as rigid dipoles capable of rotating, but not of changing in length in the field, or whether the variation in the distance between the charges with the field strength is taken into account. The internal field in aq. solutions of  $\text{NH}_2$ -acids is much weaker than  $(4/3)P$  (cf. A., 1934, 959, 1291). R. C.

**Diffusion of compounds of high mol. wt. IV. Rod-like molecules.** M. TANIGUCHI and I. SAKURADA (J. Soc. Chem. Ind. Japan, 1935, 38, 728—730B; cf. A., 1935, 1072).—The diffusion consts. ( $D$ ) of squalene and fractions crystallised from solid paraffin have been determined in  $\text{C}_6\text{H}_{14}$  and  $\text{Et}_2\text{O}$ .  $D = \eta kT (\log l/d + 0.69)/2\pi l$ , where  $l$  and  $d$  are the mol. length and thickness,  $\eta$ —viscosity of the medium, and  $k$ —gas const. For squalene  $l=31.2$ ,  $d=5.3$  Å., and for the paraffin fractions  $l=29.2$ —39.7,  $d=4.0$  Å. These vals. are in good agreement with those deduced from X-ray measurements.

R. S. B.

**Spierer lens and colloidal structure.** W. SEIFRIZ (Ind. Eng. Chem., 1936, 28, 136—140).—A reply to criticism of the use of the lens (A., 1926, 931) in the study of colloidal structure. R. S. B.

**Preparation of colloid solutions by the silent electric discharge. IV.** S. MIYAMOTO (Kolloid-Z., 1936, 74, 32—35; cf. A., 1935, 932).—The prep. of hydrosols and alcossols of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{S}$ , and also of hydrosols of Hg and  $\text{HgS}$  from corresponding salt solutions is described. The relative stability of the sols is indicated. E. S. H.

**Water-soluble colloidal lead.** A. F. GERASIMOV and B. M. KOZUIREV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 119—125; cf. A., 1930, 1114).—The prep. of a substance containing 16.5% of Pb is described. The properties of a 1% colloidal Pb solution after dialysis are described.

CH. ABS. (e)

**Emulsification of mercury.** L. J. KREMNEV (J. Phys. Chem. U.S.S.R., 1934, 5, 1051—1061; cf. A., 1934, 729).—Suspensions of oxides and certain slightly sol. salts stabilise the Hg globules by forming protecting layers. Results obtained with oxides or hydroxides of Ca, Mg, Ba, Zn, Hg, Pb, Cu, Fe, and Si, and  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgI}_2$ ,  $\text{HgBr}_2$ ,  $\text{ZnCO}_3$ ,  $\text{PbSO}_4$ ,  $\text{BiONO}_3$ , and  $\text{HgS}$  in association with various electrolytes are described. Stabilisation is also produced by Prussian-blue, Congo-red, night-blue, benzopurpurin-4B, benzopurpurin-10B, and chrysophenin. In presence of oxidising or chlorinating agents,  $\text{HgO}$  or  $\text{Hg}_2\text{Cl}_2$  can act as an emulsifier for Hg.

CH. ABS. (e)

**Application of a simple air-driven spinning-top centrifuge to colloid-chemical problems.**

J. W. MCBAIN and R. F. STUEWER (Kolloid-Z., 1936, 74, 10—16).—Apparatus, technique, and applications are described, with some preliminary results on the sedimentation velocity of agar sols and swelling pressure of the gels. E. S. H.

**Effect of heat-treatment on hydrous chromic oxide sols.** G. H. AYRES (J. Amer. Chem. Soc., 1936, 58, 18—22).—The effect of heating the sols at temp. up to  $260^\circ$  is to decrease  $\eta$  in the lower temp. ranges, but to increase  $\eta$  at the higher temp. At  $250$ — $260^\circ$  conc. sols set to rigid gels and dil. sols are finally pptd. Heat-treatment reduces the stability of the sols towards flocculation by  $\text{K}_2\text{SO}_4$ . E. S. H.

**Electrolytic double layer.** E. J. W. VERWEY (Wis. nat. Tijds., 1934, 7, 89—100; Chem. Zentr., 1935, i, 3640).—The formation of a double layer with AgI sols is discussed. H. J. E.

**Viscosity relationships in emulsions containing milk fat.** A. LEVITON and A. LEIGHTON (J. Physical Chem., 1936, 40, 71—80).—The viscosity  $\eta$  of emulsions containing milk fat does not vary, within the limits of experimental error, with variations in the degree of dispersion of the fat phase, provided that fat clusters enclosing a portion of the continuous medium are not formed. Such formation causes a rise in  $\eta$ . An empirical expression for the relation between  $\eta$  and the fat content of these emulsions has been found. For low concns. of fat it reduces to Taylor's equation (A., 1932, 1195). The apparent vol. of the continuous medium associated with the fat clusters per unit vol. of dispersed fat represents the clumping index of cream and ice-cream mixes. It is determined from  $\eta$  vals. of the mix and the continuous medium. M. S. B.

**Relation between absorption and scattering of light in white sols.** B. TEZAK (Kolloid-Z., 1936, 74, 16—22).—Determinations of absorption and scattering of light in different spectral regions by sols of colophony and cellulose acetate of different concn. are in accordance with the Lambert-Beer law. The influence of  $\lambda$ , particle radius, and polydispersity is discussed. E. S. H.

**Dispersion of the Kerr effect of certain colloidal solutions.** Time of relaxation of the electrokinetic potential. J. ERRERA, J. T. G. OVERBEEK, and H. SACK (J. Chim. phys., 1935, 32, 681—704; cf. A., 1929, 135).—The electrical birefringence of colloidal solutions of  $\text{V}_2\text{O}_5$ , benzopurpurin (I), polystyrene (II), and  $p$ -azoxyanisole (III) has been measured at frequencies  $10^3$ — $6 \times 10^7$  cycles per sec. The birefringence of  $\text{V}_2\text{O}_5$  sols increases with increasing field towards a saturation val., and it also increases with increasing concn. and age. The dispersion suggests that there are two components, one positive and decreasing rapidly at frequencies  $>10^6$  and the other negative and decreasing at frequencies  $>10^7$ . The dispersion of the dielectric const. ( $\epsilon$ ) of these sols is confirmed and the negative part of the birefringence is attributed to high vals. of  $\epsilon$ . The birefringence of (I) is negative and diminishes rapidly at frequencies  $>10^6$ , whilst that of (III) is positive and accompanied by marked dichroism. No bire-

fringence could be detected with (II). The dispersions at  $>10^6$  cycles per sec. can be explained in terms of the time of relaxation of the electro-kinetic potential.

J W S.

**Maxwell effect in colloids.** A. M. TAYLOR (Trans. Faraday Soc., 1936, 32, 307—310).—Methods are suggested for discriminating between theories of streaming double refraction which assume on the one hand optical anisotropy of the particles and on the other hand the production of elastic strain in particles normally isotropic.

F L U

**Constitution of hydrous oxide sols from X-ray diffraction studies.** H. B. WEISER and W. G. MILLIGAN (J. Physical Chem., 1936, 40, 1—7).—X-Ray diffraction photographs of moist  $\text{Al}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$  gels prepared from the hydrous  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  give the patterns for  $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $\text{SnO}_2$ , and  $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , respectively. In sols containing chloride this is not present as basic salt, but is adsorbed.

M S B

**Constitution of hydrous oxide gels and sols.** H. WEISER and W. O. MILLIGAN (Trans. Faraday Soc., 1936, 32, 358—374).—A review of evidence leads to the conclusion that gelatinous ppts. of oxides consist of agglomerates of minute crystals of oxide or hydroxide which hold large amounts of  $\text{H}_2\text{O}$  by adsorption and capillary forces. In hydrous oxide sols containing chloride the latter is adsorbed, not bound in the form of basic salts or Werner complexes.

**Colloid-chemical processes at high temperatures.** S. I. DJATSCHKOVSKI (Kolloid-Z., 1936, 74, 51—57).—The effect of heating several hydrosols at high temp. in an autoclave has been investigated. Typical hydrophobic sols undergo coagulation; hydrophilic sols undergo complex changes, involving loss of electrolyte and desolvation.  $\text{Fe}(\text{OH})_3$  is resolvated at the highest temp. used.  $\text{V}_2\text{O}_5$  passes into a mol. form, leading to crystallisation of  $\text{HVO}_3$ .

E. S. H.

**Acclimatisation phenomenon in colloid-chemical processes.** V. N. KRESTINSKAJA (Kolloid-Z., 1936, 74, 45—51).—Published work is discussed.

E. S. H.

**Reaction of organic anions with basic thorium chloride hydrosols. Reversal of charge with salts of the hydroxy-acids and with nitric acid.** A. W. THOMAS and C. B. KREMER (J. Amer. Chem. Soc., 1935, 57, 2538—2541).—Hydroxy-org. anions reverse the charge of the sol, producing anionothorate micelles. Negative sols are also produced by peptising  $\text{ThO}_2 \cdot x\text{H}_2\text{O}$  with K salts of the above anions. Conc.  $\text{HNO}_3$  also reverses the charge of the positive sols. The order of deolation of basic  $\text{TiCl}_4$  sols and subsequent formation of crystalloid solutions with conc. inorg. acids is  $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$ .

E. S. H.

**Ageing and reactivation *in vitro*.** I. Ageing of gum arabic. D. KOTSOVSKY (Kolloid-Z., 1936, 74, 88—90).—Gum arabic sols age at a rate which is inversely  $\propto$  to the vol. of solution. The surface tension-time curves show irregular, periodic variations, the amplitude of which is greater in dil. than in conc.

solutions. The shape of the curve, but not the general rate, is influenced by addition of electrolytes.

E S H

**Heat of imbibition of cellulose in water and in certain technical organic solvents at 25°.** K. P. MISCHTSCHENKO and M. Z. PRONINA (J. Appl. Chem. Russ., 1935, 8, 1164—1169).—The heat of imbibition of cellulose has been measured in an ice calorimeter on  $\text{H}_2\text{O}$ ,  $\text{HCO}_2\text{H}$ ,  $\text{MeOH}$ , and triacetin. Vaseline oil gives no heat effect, whilst the rate of evolution of heat in  $(\text{CH}_2\text{OH})_2$  and glycerol is too slow to permit measurement.

R T

**Interaction of cellulose esters with solvents.** A. I. OKATOV and Z. I. EMMANUILOVA (J. Appl. Chem. Russ., 1935, 8, 1248—1264).—When  $\text{SiO}$  gel is immersed in  $\text{H}_2\text{O}$  or  $\text{C}_6\text{H}_6$ , heat is evolved in two stages which correspond with wetting of the surfaces and with swelling of the gel. When cellulose nitrate is placed in  $\text{EtOH-Et}_2\text{O}$ , the greatest heat effect is obtained for equimol. mixtures, which have also the greatest negative heat of mixing; the evolution of heat in this case involves a third factor, viz. disruption of aggregates to yield sols. Imbibition proceeds most rapidly at low temp. and high pressures, whence it follows that the most homogeneous films would be obtained by cold-pressing the partly solvated product.

P

**Dependence of the swelling power of potato starch in warm water on the kind and amount of cations contained therein.** E. WIEGEL (Kolloid-Z., 1936, 74, 58—66).—The effect of acid treatment on the viscosity ( $\eta$ ) of starch sols has been investigated. After neutralisation with alkalis the sol has relatively greater initial  $\eta$  and a lower end  $\eta$ . Alkaline-earth cations cause a relatively lower initial  $\eta$ , but scarcely change the end val.; the sols are more turbid and less sensitive to electrolytes than those containing alkali ions. The practical significance of the results is discussed.

E. S. H.

**Relation between the chemical and colloidal structure of proteins.** A. FODOR and S. KUK (Kolloid-Z., 1936, 74, 66—87).—Results obtained by non-hydrolytic degradation of gelatin and casein by glycerol at 930—150° are further discussed (cf. A. 1933, 730).

E. S. H.

**Laws of motion of thixotropic plastic liquids.** M. BUNIN (J. Phys. Chem. U.S.S.R., 1934, 5, 996—1003).—A discussion.

CH. ABS. (e)

**Lyophilic colloids. XXVI. Coacervation. III. Complex coacervation of the system gum arabic-gelatin.** II. H. G. B. DE JONG (Kolloid-Beih., 1936, 43, 213—271; cf. A., 1935, 821).—The composition of the two layers formed by mixing aq. gum arabic and gelatin sols has been investigated. Under optimal conditions of coacervation the coacervate contains the components in the same ratio as in the whole system for a series of isohydric mixtures. The  $\text{H}_2\text{O}$  content of such a coacervate is at a min. between  $p_H$  3.3 and 3.5. Addition of a desolvating non-electrolyte (e.g.,  $\text{EtOH}$ ) increases the colloid content of the coacervate, but addition of neutral salts decreases it. The coacervate can take up excess of one of the components. The aq. layer also con-



tains gum arabic and gelatin; the conditions determining the amount of these components are discussed.

E. S. H.

**Silicic acid gels. VI. Influence of temperature and acid on the time of set.** C. B. HURD (J. Physical Chem., 1936, 40, 21—26).—The times of set of silicic acid gels made by mixing aq. Na silicate with aq. AcOH, tartaric, citric, or succinic acids of varying concn. have been determined at 25.1°, 38.4°, and 53.0°. The relation between log (time of set) and  $1/T^\circ$  abs. is shown to be linear and heats of activation have been deduced. The average vals. for the four acids are 17,140, 17,530, 16,940, and 17,190 g.-cal., respectively (cf. A., 1932, 1202).

M. S. B.

**Diffusion coefficient and apparent radius of the cupric ion in silica gels.** W. G. EVERSOLE and E. W. DOUGHTY (J. Physical Chem., 1936, 40, 55—60; cf. A., 1935, 702).—The rate of diffusion of  $\text{CuCl}_2$  into  $\text{SiO}_2$  gels has been determined by a photometric method. The most probable val. of the diffusion coeff. of  $\text{Cu}^{++}$  in  $\text{H}_2\text{O}$  is  $4.6 \times 10^{-6}$  sq. cm. per sec. The effective radius of hydrated  $\text{Cu}^{++}$  appears to be approx.  $5.2 \times 10^{-8}$  cm.

M. S. B.

**Influence of neutral salts on the optical rotation of gelatin. III. Effect of the halides of lithium, sodium, rubidium, and caesium. IV. Rotatory dispersion of gelatin in sodium iodide solutions.** D. C. CARPENTER and F. E. LOVELACE (J. Amer. Chem. Soc., 1935, 57, 2337—2342, 2342—2346).—III. The  $[\alpha]_D$  at 0.5° and 40° of a 0.7% solution of gelatin (calfskin) (I) at  $p_H$  6—7 is lowered (more marked at 0.5°) by the halides in the order  $\text{I} > \text{Br} > \text{Cl}$ ; when the concn. of added salt is fairly high the cation exerts a minor lowering effect, viz.,  $\text{Li} > \text{Cs} > \text{Rb} > \text{Na}$ . For the alkali gelatinates in absence of added salt the magnitude of  $[\alpha]_D$  is in the order  $\text{K} > \text{Rb} > \text{Cs} > \text{Na} > \text{Li}$ .

IV. The  $[\alpha]_D$  of solutions of (I) (0.7704 g. per 100 solution) containing NaI have been measured at 0.5° and 40° for 5 wave-lengths. The rotatory dispersion, which obeys a single-term Drude equation, is governed by an absorption band at 2200 Å., in which region (I) has a high absorption. The "gel"  $\rightarrow$  "sol" transformation is considered to be a process of dissociation or association of the mol. of (I). Application of Lucas' method (A., 1930, 1095) of analysis to the data shows that only two optically active species exist in solutions or gels of (I).

H. B.

**Myoglobin. I. Solubility in ammonium sulphate solutions.**—See this vol., 359.

**Colloid chemistry of edestin. III. Capillary-electric effects produced during the peptisation of edestin by solutions of electrolytes.** K. HOLWERDA (Biochem. Z., 1936, 283, 253—262; cf. this vol., 158).—The shifting of the zone of peptisation towards higher salt concns. on the acid side of the isoelectric point is a consequence of the auto-complex capacity of edestin (I), but diminution or removal of this does not suffice to cause peptisation and the solubility of (I) in neutral salt solutions does not depend on this capacity alone.

W. McC.

**Salting-out and peptisation of edestin by mixtures of two salt solutions.** K. HOLWERDA (Bio-

chem. Z., 1936, 283, 280—291; cf. Büchner *et al.*, A., 1931, 1125).—The effects of small amounts of NaCl, NaI, and NaCNS on the salting-out of edestin by  $\text{Na}_2\text{SO}_4$  are similar to those produced in the case of gelatin, there being no antagonistic effects, but KF has an antagonistic effect on peptisation by NaCl, adsorption of F' being then negative. The antagonism observed between NaCl and multivalent cations probably has another cause (effect of oppositely charged centres, auto-complex action).

W. McC.

**Plant colloids. XLII. Influence of crystalloids on the state of amyloses, with special reference to thread-forming power.** M. SAMEC [with P. BENKOVIČ] (Kolloid-Beih., 1936, 43, 272—286; cf. A., 1935, 165).—The viscosity of dil. amylose solutions is lowered by small amounts of electrolytes, but raised by larger amounts; the spontaneous coagulation by ageing is retarded by electrolytes or org. crystalloids. Conc. amylose solutions (6%) increase in consistency as the concn. of the added crystalloid is increased; at a certain stage the mixtures have good thread-forming properties.

E. S. H.

**Phase rule in colloid chemistry.** W. D. BANCROFT (J. Physical Chem., 1936, 40, 43—45). Theoretical.

M. S. B.

**Exchange reactions with deuterium. I. Deuterium and hydrogen chloride.** P. C. CROSS and P. R. LEIGHTON (J. Chem. Physics, 1936, 4, 28—30).—An apparatus for measuring exchange equilibria and rates of exchange between  $\text{D}_2$  and H-containing compounds is described. Data for the equilibria  $\text{H}_2 + 2\text{DCl} \rightleftharpoons \text{D}_2 + 2\text{HCl}$  and  $\text{H}_2 + \text{DCl} \rightleftharpoons \text{HD} + \text{HCl}$  have been obtained and are in satisfactory agreement with theoretical vals.

M. S. B.

**Thermal equilibrium of the cis-trans-isomerides of dichloroethylene at high temperatures.** W. MARONEY (J. Amer. Chem. Soc., 1935, 57, 239, 2398).—The investigations previously reported (A., 1934, 831) have been extended to 975°.

E. S. H.

**Present state of the problem of electrolytic solutions.** C. A. KRAUS (J. Chem. Educ., 1936, 12, 567—573).—At lower concns. the properties of electrolytes in solvents are satisfactorily accounted for by interaction between ions in accord with the Coulomb law of force. In solvents of high  $\epsilon$ , electrolytes are completely dissociated into ions and only long-range interactions need be considered, but when  $\epsilon$  is low, short-range interactions must be taken into account. As  $\epsilon$  falls, these interactions become of increasing importance and the formation of triple ions as well as ion pairs must be considered. In solvents of very small  $\epsilon$  more complex interactions, which occur at higher concns., lead to the formation of complex neutral, and probably charged aggregates. The present theory adequately accounts for the properties of electrolytic solutions at higher concns. Conductance data for various electrolytes in aq.  $\text{NH}_3$ , and  $\text{C}_2\text{H}_4\text{Cl}_2$ , the f.p. and the  $\epsilon$  of solutions of  $\text{C}_2\text{H}_6$ , are recorded and discussed.

**Statistical treatment of strong electrolytes.** S. LEVINE (Proc. Roy. Soc., 1935, A, 152, 559).—It is shown that Kramer's theory of s



electrolytes (A., 1927, 626) is valid if the ordinary Coulomb forces between the ions are assumed. The deviations from the inverse square law, due to saturation and hydration effects on the  $H_2O$  dipoles, and to the polarisation, van der Waals, and exchange forces between two typical ions are accounted for by means of a correction term in the expression for the energy of interaction. L. L. B.

**Transition cases in the distribution of ions.** R. M. FUOSS (J. Amer. Chem. Soc., 1935, 57, 2604—2607).—A crit. concn. exists, above which free and pair-associated ions become indistinguishable (cf. A., 1935, 488). At higher concns. the simple laws of dil. electrolyte solutions are no longer obeyed

E. S. H.

**Hydration of ions.** O. SCHMITZ-DUMONT (Z. anorg. Chem., 1935, 226, 33—45).—Theoretical. Brntzinger's method (A., 1935, 579, 582, 824) based on the coeff. of dialysis does not enable electrostatically bound  $H_2O$  to be distinguished from that present as an aquo-complex.

F. L. U.

**Sourness of acids.** R. M. BEATTY and L. H. CRAGG (J. Amer. Chem. Soc., 1935, 57, 2347—2351).—Sourness is defined in terms of the normality of aq. HCl of equal sourness. The sourness of unbuffered solutions of some org. acids is given by  $x/K$ , where  $x$  is the vol. of a  $PO_4^{'''}$  buffer required to bring a unit vol. of the acid to  $p_H$  4.4, and  $K$  is a const. characteristic of the buffer used.

E. S. H.

**Monoalkyl phosphites and their hydrolysis.**—See this vol., 312.

**Effect of temperature on the ionisation constants of some dibasic acids.** I. JONES and F. G. COOPER (J.C.S., 1936, 133—137).—When the distance ( $r$ ) between the ionising centres is  $> 4.0$  Å., corrections for anisotropy and compressibility may be ignored without appreciable error, and it has been possible to determine  $r$  for many symmetrical dibasic acids at various temp. The  $p_H$  changes during the neutralisation of *cis*-caronic acid (I) show no marked displacement with temp. change, and with phenolphthalein, contrary to the observation of Baeyer, there is no indication of monobasicity at room temp., although temp. markedly affects the inflexion point at the second neutralisation. The second ionisation const. of (I) is  $0.49 \times 10^{-8}$ , and the disappearance of the ion at higher temp. is attributed to increased hydrolysis of the salt. To obtain a sharp end-point in the titration of such weak acids, titrations should be made at low temp. For a const. val. of  $r$ , the  $K_1/K_2$  ratio or the first and second ionisation consts.  $K_1/K_2$  increases with temp. for all acids studied, except those having *cis*-structures, and possible causes of this are discussed. Values of  $K_1 \times 10^5$  for (I) and *trans*-caronic acid are 459 and 15.2 respect. Caronic acid is compared with other dicarboxylic acids.

E. S. H.

**Effect of certain sugar alcohols and their anhydrides on the dissociation of boric acid.** J. C. KRANTZ, jun., (Miss) M. OAKLEY, and C. J. CARR (J. Physical Chem., 1936, 40, 151—154).—The two polyhydric alcohols, mannitol and dulcitol, have an effect on the titration curve of  $H_3BO_3$  much  $>$  that

of the anhydrides mannitan, mannide, and dulcitan. *iso*Mannide has no effect.

M. S. B.

**Hydrogen-ion dissociation curve of the crystalline albumin of the hen's egg.**—See this vol., 360.

**Physico-chemical properties of mercurous perchlorate solutions.** E. NEWBURY (Electrochem. Soc. Preprint, 1936, 69, 57—73).—The prep. and purification of  $Hg_2(ClO_4)_2$  is described. The existence of the tetrahydrate is confirmed and this is shown to be stable below  $36^\circ$ . From  $36^\circ$  to  $>100^\circ$  the stable hydrate is  $2H_2O$ . The transition point is lowered in strongly acid solution. Hydrolysis occurs in three stages the products being  $Hg_2O, Hg_2(ClO_4)_2$  (I),  $Hg_2(OH) \cdot ClO_4$  (II), and  $HgO$ , respectively. The degree of hydrolysis is 2.5% in 0.1M solution. In more conc. solution the hydrolysis is  $>$  anticipated because (I) is a weaker base than (II). The degree of ionisation ( $\alpha$ ) of the salt appears to increase with the concn. Conductivity data suggest that  $\alpha=128\%$  in the saturated solution (3.93M) at  $25^\circ$ . The view is expressed that in dil. solution the basic salt formed by hydrolysis is non-ionised and that, in very conc. solutions,  $Hg_2^{++}$  is dissociated into  $2Hg^+$  by the action of the negatively charged ions present in large concn.  $Hg^+$  perchlorate may be used for a Hg coulometer, for sp. gr. determinations in mineralogy, for cleaning Hg, for the prep. of pure  $Hg_2Cl_2$  or  $Hg_2SO_4$ , and as a reagent for halogens,  $SO_4^{--}$ ,  $PO_4^{--}$ ,  $AsO_4^{--}$ , and  $CrO_4^{--}$ .

M. S. B.

**Equilibria in solutions of tri-ionic electrolytes.** K. JABECZYNSKI and R. LEGAT (Rocz. Chem., 1935, 15, 351—359).—Cryoscopic and conductivity data are applied in the estimation of the equilibria const. for the ionisation of Ba, Sr, Ca, and Mg chlorides in accordance with the general formula  $MCl_3 \rightleftharpoons M^{++} + 2Cl^-$ .

R. T.

**Carbamate equilibrium.** I. Equilibrium of amino-acids, carbon dioxide, and carbamates in aqueous solution; with a note on the Ferguson-Roughton carbamate method. W. C. STADIE and H. O'BRIEN (J. Biol. Chem., 1936, 112, 723—758).—It is the amphiprotic  $COO^- \cdot R \cdot NH_2$  and not the zwitterion  $COO^- \cdot R \cdot NH_3^+$  of  $NH_2$ -acids which forms carbamates with  $CO_2$ . The ionisation of these, which behave as dibasic salts at  $p_H > 7$ , is discussed. Mass-action equations for the carbamate equilibrium of  $NH_2$ -acids and  $CO_2$  in aq. solution are given, together with const. calc. under various conditions. By the use of carbonic anhydrase, the Ferguson-Roughton carbamate method can be used when much free  $CO_2$  is present.

J. N. A.

**Activity coefficient of ions.** (Mlle.) M. QUINTIN (Compt. rend., 1936, 202, 123—125; cf. A., 1935, 826).—The e.m.f. of the cells Cd (amalgam, two phases) |  $CdCl_2(m)$  | KCl sat. |  $KCl 0.1N$  |  $Hg_2Cl_2$  | Hg and  $Ag | AgCl | CdCl_2(m) | KCl sat. | KCl 0.1N$  |  $Hg_2Cl_2$  | Hg have been measured at  $25^\circ$  for  $m=0.001-0.1$ . From the data the calc. radii (Debye  $a$ ) of  $Cd^{++}$  and  $Cl^-$  are 5.4 and 2 Å., respectively. The former val. agrees with the  $6 \pm 1$  Å. calc. from data using  $CdSO_4$  (A. 1927, 729).

T. G. P.

**Activity coefficients of lead chloride in aqueous solutions of barium nitrate.** H. D. CROCKFORD

and H. O. FARIL, jun. (J. Amer. Chem. Soc., 1936, 58, 87-89).—Activity coeffs. and the  $a$  parameter have been calc. from e.m.f. determinations of the cell  $\text{Pb Hg (2-phase)} | \text{PbCl}_2 (m_1) | \text{Ba(NO}_3)_2 (m_2) | \text{AgCl-Ag}$ .  
E. S. H.

Activity coefficients of sulphuric acid in anhydrous ethyl alcohol from electromotive force data. A. W. SCHOLL, A. W. HUTCHISON, and G. C. CHANDLER (J. Amer. Chem. Soc., 1935, 57, 2542-2544).—The data have been obtained from e.m.f. measurements of the cell  $\text{H}_2 | \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4(s) | \text{Hg}$ .  
E. S. H.

Fundamentals of chemical thermodynamics. P. VAN RYSELBERGHE (Chem. Rev., 1935, 16, 37-51).—A review.  
CH. ABS. (e)

Exact significance of the thermodynamic quantities  $\Delta F$  and  $\Delta F'$ . P. VAN RYSELBERGHE (Chem. Rev., 1935, 16, 29-35).—Theoretical.  
CH. ABS. (e)

Independent components in the phase rule. A. P. GERASIMOV (Trans. Butlerov Inst. Chem. Tech. Kuzan, 1934, No. 1, 114-119).—A discussion.  
CH. ABS. (e)

Integrated form of the equation for calculating change of equilibrium with temperature. J. B. AUSTIN (J. Amer. Chem. Soc., 1935, 57, 2428-2434). The equations relating change of solubility with temp. are converted into a more convenient form. Experimental vals. fall on a straight line when plotted against temp., or the reduced temp., on double logarithmic co-ordinates. The approx. equation for v.p. leads directly to the rules of Ramsay and Young and of Dühring.  
E.

System stannic chloride-hydrogen chloride. A. CURÉTHEN and G. VARGA (Compt. rend., 1935, 201, 1491-1493).—Thermal data show the formation of  $\text{SnCl}_4 \cdot 5\text{HCl}$ , m.p.  $-94.7^\circ$ , and  $\text{SnCl}_4 \cdot 2\text{HCl}$ , m.p.  $85^\circ$ , and three eutectic points.  
T. G. P.

System antimony iodide sodium iodide-water. F. FRANÇOIS (Compt. rend., 1935, 201, 1489-1491).—Isotherms at 15, 35°, and 60 indicate the formation of  $\text{SbI}_3 \cdot 2\text{NaI} \cdot 8\text{H}_2\text{O}$  and  $\text{SbI}_3 \cdot \text{NaI} \cdot 6\text{H}_2\text{O}$ .  
T. G. P.

Thermal analysis of the systems iodine LiI, KI, RbI, or TlI. J. A. FIALKOV and G. A. KUZMENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 127-139).—Polyiodides are not formed when the iodides are fused with I, indicating that the presence of a solvent is essential for their formation.  
R. T.

Purification and physical properties of organic compounds. X. F.p. diagram for the system acetanilide propionanilide. E. L. SKAT and L. F. ROWE (J. Amer. Chem. Soc., 1935, 57, 2437-2438; cf. A., 1935, 1077).—The Beckmann method is unsatisfactory. A static method shows that the system forms a compound with incongruent m.p.  
E. S. H.

Binary systems of *p*-dichlorobenzene with diphenyl, naphthalene, and triphenylmethane. R. E. MORRIS and W. A. COOK (J. Amer. Chem. Soc., 1935, 57, 2403-2406).—A simple eutectic is shown

in each system. Solubilities, eutectic temp., and compositions are approx. those calc. for ideal solutions.  
E. S. H.

Physical-chemical properties of the chlorohydrin and of the dichloride of  $\Delta^2$ -butene. I. N. BUSCHMAKIN, M. M. GOLIDMAN, and K. I. KUBTSHINSKAJA (Sintet. Kautschuk, 1935, 4, No. 1, 33-35).—Equilibrium data are recorded for the binary and ternary systems formed with  $\text{H}_2\text{O}$ .  
CH. ABS. (e)

Solid-liquid equilibria in ternary systems in which incongruently melting compounds are formed. III. K. HRYNAKOWSKI and M. SZMYT (Z. physikal. Chem., 1935, 175, 83-98).—The systems salicylic acid- $\text{CO}(\text{NH}_2)_2$ -urethane and  $\text{PhOH-CO}(\text{NH}_2)_2$ -urethane each exhibit one eutectic point and two peritectic points.  
R. C.

(A) Lower transition point of the mutual system  $\text{Na}_2\text{SO}_4\text{-NH}_4\text{HCO}_3\text{-H}_2\text{O}$ . (B) Mutual aqueous system  $\text{Na}_2\text{SO}_4\text{-NH}_4\text{HCO}_3\text{-H}_2\text{O}$  at  $-17^\circ$ . A. P. BELOPOLSKI and S. J. SCHUPIT (J. Appl. Chem. Russ., 1935, 8, 1126-1135, 1136-1142).—(A) The transition point, corresponding with the equilibrium  $2\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + 2\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O} + 2\text{NaHCO}_3 + 16\text{H}_2\text{O}$ , is shown by solubility measurements to be at  $-17^\circ$ .  
(B) Equilibrium relations have been determined at  $-17^\circ$ . (I), which is unstable at  $< -16^\circ$ , can exist at lower temp. in presence of  $\text{NH}_4\text{HCO}_3$ .  
R. T.

Equilibria in the systems (A)  $\text{MgCO}_3\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ , (B)  $\text{Na}_3\text{PO}_4\text{-NaCl-H}_2\text{O}$ . A. P. OBUCHOV (J. Appl. Chem. Russ., 1935, 8, 1143-1148, 1149-1151).—(A) [with E. I. GORDON]. The double salt  $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$  crystallises from an aq. solution of  $\text{Na}_2\text{CO}_3$  which has been saturated with  $\text{MgCO}_3$  at  $35^\circ$ .  
(B) [with M. N. MICHAILOVA]. Equilibrium data are recorded for the systems at 25 and  $105^\circ$ . The solubility of  $\text{Na}_3\text{PO}_4$  falls rapidly with increasing  $\text{NaCl}$ .  
R. T.

System cobalt chloride, ammonium chloride, ammonia, water. M. CHATELET (Compt. rend., 1936, 202, 216-217).—The formation of the ions  $[\text{CoNH}_3]$  and  $[\text{Co}(\text{NH}_3)_3]$  is said to have been detected by calorimetric measurements.  
T. G. P.

Determination of change of free energy in reactions of type  $A(s) + B(s) = AB(s)$  and application to dolomite problem. F. HALLA [with F. RITTER] (Z. physikal. Chem., 1935, 175, 63-81). A method for determining the change in free energy,  $\Delta F$ , in the formation of double compounds by solubility measurements is described. Application the formation of dolomite (I) from its solid components shows that under 1 atm. this occurs spontaneous above  $-34^\circ$  and  $\Delta F^\circ$  is  $590 \pm 50$  g.-cal. at 25 and  $740 - 30$  g.-cal. at  $38.8^\circ$ , and that  $\Delta H$  is  $-2840 \pm 300$  g.-cal. at  $25-32^\circ$ . For dolomitisation,  $2\text{CaCO}_3 + \Delta F = -190 \pm 50 + 1430 \log \frac{[\text{Ca}^+]}{[\text{Mg}^{++}]}$  g.-cal. at  $25^\circ$  and  $120 \pm 30 - 1365 \log \frac{[\text{Ca}^+]}{[\text{Mg}^{++}]}$  g.-cal. at  $38.8^\circ$ . The direction of this process is therefore determined almost entirely the ratio  $[\text{Ca}^+] : [\text{Mg}^{++}]$  in the solution, and under the conditions of temp. and concn. prevailing in t dolomitisation should occur spontaneously.



following solubility products have been obtained:  $\text{MgCO}_3$ ,  $1.8 \times 10^{-8}$  at  $25^\circ$ ,  $1.6 \times 10^{-8}$  at  $38.8^\circ$ ;  $\text{CaCO}_3$ ,  $3.83 \times 10^{-9}$  at  $38.8^\circ$ ; (I),  $3 \times 10^{-17}$  at  $25^\circ$ ,  $1.8 \times 10^{-17}$  at  $38.8^\circ$ . Lewis and Randall's sp. ionic activity coeffs. have been successfully used to calculate solubility product from a single solubility. The variation in solubility of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  with temp is given by  $m = 0.4344 - 0.0111t + 0.004953t^2$ . Heats of dissolution in  $2N\text{-HCl}$  have been measured.

R. C.

Heats of dissolution of ferric chloride in water and in aqueous hydrochloric acid. W. KANGRO and R. FLÜGGE (Z. physikal. Chem., 1935, 175, 187—194).—Differential and integral heats of dissolution and dilution at  $20^\circ$  have been determined. The heat of dissolution in aq.  $\text{HCl}$  falls rapidly with increasing  $[\text{HCl}]$ . When  $[\text{HCl}]$  is  $\approx 10\%$  the decrease is quantitatively accounted for by fall in the activity of the  $\text{H}_2\text{O}$ , but at higher concns. there are discrepancies, which are probably connected with association. Sp. heats of aq.  $\text{FeCl}_3$  solutions have been determined at  $20^\circ$ .

R. C.

Hydrazine. Heats of dissolution of hydrazonium salts at  $25^\circ$ . II. E. C. GILBERT and V. C. BUSHNELL (J. Amer. Chem. Soc., 1935, 57, 2611—2612, cf. A., 1935, 303).—Data for hydrazonium dibromide (anhyd. and hydrated) and sulphate are recorded. Partial mol. heats of dissolution of solute and solvent ( $\text{H}_2\text{O}$ ) have been calc. for the bromide. The heat capacity of aq. hydrazonium sulphate at  $25^\circ$  has been determined.

E. S. H.

Thermochemistry of azoimide. P. GÜNTHER, R. MEYER, and F. MÜLLER-SKJOLD (Z. physikal. Chem., 1935, 175, 154—169).— $\text{HN}_3$  is conveniently prepared by heating  $\text{NaN}_3$  with stearic acid in vac. and condensing at not below  $-75^\circ$ . When the gas explodes under reduced pressure very little  $\text{NH}_3$  is formed. The heat of formation of the gas at const. is  $-70.9 \pm 0.5$  kg.-cal. per mol. The v.p. of the liquid has been determined from near the triple point to near the b.p. ( $35.7^\circ$ ). At  $12.4^\circ$  the mol. heat of evaporation is  $-7.3 \pm 0.1$  kg.-cal. The total heat of dissolution of the gas to give a  $0.16N$  solution is  $3.1 \pm 0.1$  kg.-cal. per mol. These data confirm the recorded heat of formation (Roth and Müller, A., 1929, 133). For the liquid at  $0-21^\circ$   $d = 1.126/(1 + 0.0013t)$ .

R. C.

Heat of combustion of isobutane. F. D. ROSSINI (J. Res. Nat. Bur. Stand., 1935, 15, 357—361).—The heat of combustion of  $\text{iso-C}_4\text{H}_{10}$  in  $\text{O}_2$  to form  $\text{CO}_2$  (gas) and  $\text{H}_2\text{O}$  (liquid) at  $25^\circ/1$  atm. is  $686.31 \pm 0.13$  kg.-cal. per mol., hence the heat of formation of  $\text{iso-C}_4\text{H}_{10}$  at  $25^\circ$  is  $32.2 \pm 0.43$  and the heat of conversion of the  $n$ - into the  $\text{iso}$ -form is  $1.63 \pm 0.15$  kg.-cal. per mol.

A. R. P.

Direct carboxylation of carbon compounds. III. Free energy of benzoic acid at  $522^\circ$  abs. W. D. BONNER and C. R. KINNEY (J. Amer. Chem. Soc., 1935, 57, 2402—2403; cf. A., 1933, 1159).—Calculation from published data gives  $\Delta F_{522}^\circ = -36.491$  g.-cal.

E. S. H.

Heats of organic reactions. III. Hydrogenation of some higher olefines. IV. Hydrogen-

ation of dienes and of benzene. G. B. KISTIAKOWSKY, J. R. RUHOFF, H. A. SMITH, and W. E. VAUGHAN (J. Amer. Chem. Soc., 1936, 58, 137—145, 146—153; cf. A., 1935, 825).—III. Heats of hydrogenation (in g.-cal. per mol.) are recorded for  $\Delta^2$ -heptene ( $-30,137 \pm 37$ ), *as*-methylethylethylene ( $-28,491 \pm 36$ ),  $\Delta^2$ -pentenes (*cis* and *trans*) ( $-27,954 \pm 28$ ),  $\text{CMePr}^2\text{CH}_2$  ( $-27,997 \pm 24$ ), cyclohexene ( $-28,592 \pm 10$ ),  $\text{CMe}_2\text{CHMe}$  ( $-26,920 \pm 10$ ), and  $\text{CMe}_2\text{CMe}_2$  ( $-26,633 \pm 19$ ). With increasing no. of substituent alkyl groups the heat of hydrogenation is progressively lowered, and the differential effect decreases with increasing no. of substituents. This effect is independent of the chain length of substituent *n*-alkyls, but branched groups have a greater influence.

IV. Heats of hydrogenation are given for allene +  $2\text{H}_2$  ( $-71,280 \pm 103$ ), *zy*-butadiene +  $2\text{H}_2$  ( $-57,067 \pm 28$ ),  $\alpha\delta$ -pentadiene +  $2\text{H}_2$  ( $-60,790 \pm 64$ ),  $\alpha\epsilon$ -hexadiene +  $2\text{H}_2$  ( $-60,525 \pm 43$ ),  $\Delta^{1,3}$ -cyclohexadiene +  $2\text{H}_2$  ( $-55,367 \pm 56$ ),  $\text{C}_6\text{H}_6 + 3\text{H}_2$  ( $-49,802 \pm 44$ ), cyclopentadiene +  $2\text{H}_2$  ( $-50,865 \pm 47$  g.-cal. per mol.). The data are discussed.

E. S. H.

Single linking energies. I. C-C linking in hexaphenylethane. H. E. BENT, G. R. CUTHBERTSON, M. DORFMAN, and R. E. LEARY. II. C-C linking in hexaphenylethane. H. E. BENT and G. R. CUTHBERTSON (J. Amer. Chem. Soc., 1936, 58, 170, 170 1/3).—I. Apparatus and technique for determining heats of reaction, especially for easily oxidised substances, are described. The v.p. of  $\Delta^2$ -heptene (I) has been determined from  $0^\circ$  to  $90^\circ$  and the heat of vaporisation calc. The heat of hydrogenation of (I), the heat of oxidation of  $(\text{CPh}_3)_2$ , and the heats of dissolution of the compounds involved in these reactions have been determined. The dissociation of  $(\text{CPh}_3)_2$  is due to weakening of the C-C linking and the stabilising effect of the resonance energy of  $\text{CPh}_3$ .

II. The heat of hydrogenation of  $(\text{CPh}_3)_2$  to form  $\text{CPh}_2$  is  $-40.5$  kg.-cal. for solids and  $-34.8$  kg.-cal. in  $\text{EtOAc}$  solution. The C-C linking is weaker than a normal linking by about 30 kg.-cal.

E. S. H.

Electrical conductivity of potassium chloride in certain mixed solvents. R. N. AGARWALA and D. C. MANDERVILLE (J. Indian Chem. Soc., 1935, 12, 699—705).—Viscosities and sp. conductivities of  $\text{H}_2\text{O}$ - $\text{MeOH}$ ,  $\text{H}_2\text{O}$ - $\text{EtOH}$ , and  $\text{H}_2\text{O}$ - $\text{COMe}_2$  mixtures have been determined together with equiv. conductivities  $\Lambda$  of the corresponding  $\text{HCl}$  solutions. The plot of  $\Lambda$  against  $[\text{KCl}]^{1/2}$  is linear for  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ - $\text{EtOH}$ , but regularly spaced max. and min. appear in the case of  $\text{H}_2\text{O}$ - $\text{MeOH}$  and  $\text{H}_2\text{O}$ - $\text{COMe}_2$  which bear no relation to the viscosity. An explanation involving "dipole association" chains of hydrated  $\text{COMe}_2$  etc. between the ions has been advanced.

R. S.

Electrical conductivity of solutions of electrolytes in methyl alcohol and acetone at high temperatures. P. C. BLOKKER (Rec. trav. chim., 1935, 54, 975—987).—The conductivities and sp. vols. of solutions of  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ,  $\text{NaI}$ ,  $\text{KI}$ ,  $\text{CaI}_2$ , and  $(\text{Pr}^n[\text{CH}_2]_2)_4\text{NI}$  in  $\text{MeOH}$  and  $\text{COMe}_2$  have been measured at temp. up to  $218^\circ$  in special soft steel

bombs lined with Pt. The equiv. conductivities of these solutions show max. at temp. which are the lower the higher is the salt concn. It is shown that the max. are caused by decrease in the dielectric const. J. W. S.

Conductivity of calcium, strontium, and barium chlorides in anhydrous glycerol. J. SZFER and Z. GAJEWSKI (J. Chim. phys., 1935, 32, 705—714).—For 1—1/16 molar solutions and at 25—200°, the mol. conductivities of  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$  in anhyd. glycerol follow the Kohlrausch law  $-\Lambda_\infty = k'\sqrt{c}$ . The limiting mol. conductivity is  $3.67 \times 10^{-4}$  at 25° and 35° for all three salts. The mobilities of the cations increase with the mol. wt. The mol. conductivity increases exponentially with temp. at low temp., but above 130° increases linearly. J. W. S.

Electrochemical investigation of the ternary system  $\text{AlBr}_3$ - $\text{AsBr}_3$ -benzene. V. A. PLOTNIKOV and S. I. JAKUBSON (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 99—109).—Thermal analysis does not suggest compound formation, but freshly prepared solutions of the salts in  $\text{C}_6\text{H}_6$  conduct electricity, the conductivity falls rapidly to a const. val. after 23 days. The unstable compound  $\text{AlBr}_3\cdot\text{AsBr}_3$  is postulated. R. T.

Determination of transference numbers in dilute solutions from limiting ionic conductances. B. B. OWEN (J. Amer. Chem. Soc., 1935, 57, 2441).—Theoretical. E. S. H.

Ionic mobility. J. J. HERMANS (Z. Physik, 1935, 97, 681—689).—An equation is obtained for the effect of solvent dipoles on ionic mobility, and is solved for infinite dilution. Extension to finite dilution shows that the mobility  $\propto (\text{concn.})^{1/2}$ . A. B. D. C.

Electrical transport of an active deposit of radium in some organic liquids. Z. KLEMENSIEWICZ and K. PROJEKT (Acta Phys. Polon., 1933, 2, 409—415).—Solutions in  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ ,  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ , and  $\text{EtOH}$  have been examined in an electric field. The amount of Ra deposited on the electrodes decreases with rise in the dielectric const. and the viscosity of the liquid. CH. ABS. (e)

Absolute single potential of [calomel] electrode. K. HIROTA and T. MURATA (Bull. Chem. Soc. Japan, 1935, 10, 594—596).—The variation of p.d. with interfacial tension ( $\sigma$ ) of Hg has been studied by forcing the Hg upwards through a fine orifice immersed in  $\text{KNO}_3$ . The height of the jet varies approx. parabolically with the p.d. between jet and the N-calomel electrode, the min. corresponding with the position of max.  $\sigma$ . The mean val. for the N-calomel electrode is  $0.563 \pm 0.004$  volt at 20.6°, in agreement with vals. determined by the dropping Hg electrode. R. S. B.

Unknown property of the calomel half-cell and the determination of bromide-chloride mixtures. F. L. HAHN (J. Amer. Chem. Soc., 1935, 57, 2537).—The potential is strongly influenced by even very small amounts of  $\text{Br}^-$  in the KCl. The effect may be adapted to the determination of  $\text{Br}^-$ . E. S. H.

Mercury-mercuric oxide-saturated barium hydroxide and calcium hydroxide electrodes. G. J. SAMUELSON and D. J. BROWN (J. Amer. Chem. Soc., 1935, 57, 2711—2714).—The potential  $\text{Hg}|\text{HgO}(\text{s}), \text{Ba}(\text{OH})_2(\text{s})$  with reference to the  $\text{N-H}_2$  electrode is  $+0.1462 - 0.00060(t-25) \pm 0.0002$  volt; that of  $\text{Hg}|\text{HgO}(\text{s}), \text{Ca}(\text{OH})_2(\text{s})$  is  $+0.1923 + 0.00010 \times (t-25) \pm 0.0010$  volt. The ease of prep., constancy, reproducibility, and temp. coeff. of the electrodes have been studied. E. S. H.

Potential of the  $\text{Ag}(\text{s})|\text{Ag}_2\text{CrO}_4(\text{s})|\text{CrO}_4^{2-}$  electrode. J. Y. CANN and G. B. MUELLER (J. Amer. Chem. Soc., 1935, 57, 2525—2527).—E.m.f. measurements of the cell  $\text{Ag}(\text{s})|\text{Ag}_2\text{CrO}_4(\text{s})|\text{K}_2\text{CrO}_4(\text{aq.})|\text{KCl}(\text{aq.})|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$  at 25° give  $-0.4463$  volt for the normal electrode potential of  $\text{Ag}(\text{s}), \text{Ag}_2\text{CrO}_4(\text{s}), \text{CrO}_4^{2-}$ ;  $\Delta F^\circ = 20,596$  g.-cal. E. S. H.

Volta effect of electrolytic solutions against water, and characteristics of acidity and basicity. (MILLER) S. VEIL (Compt. rend., 1936, 202, 121—123).—The electrometric potentials of the system  $\text{Pt-H}_2\text{O}$  (gelatin)-salt solution-Pt have been measured (A., 1935, 822). They depend on the concn. and nature of the salt, and are positive at  $p_{\text{H}} < 7$ . T. G. P.

Anomalous redox potentials of thiol-disulphide systems. J. W. H. LUGG (J. Indian Chem. Soc., 1935, 12, 706—711).—A theory involving the formation of an ionisable compound between RS and the electrode surface is suggested. R. S.

Oxidation-reduction potential of reductone. R. WURMSER and N. MAYER (Compt. rend., 1935, 201, 1366—1368; cf. A., 1934, 1072).—The oxidation-reduction potential of the system  $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CHO} \rightleftharpoons \text{CO}(\text{CHO})_2$  at 38° has been studied between  $p_{\text{H}}$  2 and 9.  $E_0$  at  $p_{\text{H}}$  0 is  $+0.28$  volt. T. G. P.

Oxidation-reduction potentials. II. Investigation of a coupled oxidation-reduction equilibrium by photo-electric measurement of light extinction. G. HOLST (Z. physikal. Chem., 1935, 175, 99—126; cf. A., 1934, 968).—The mol. extinction coeff.,  $\alpha$ , of methylene-blue (I) at 20° in 0.01N-HCl for  $\lambda = 546$  m $\mu$  increases with the dye concn.  $\text{PhN}\cdot\text{N}\cdot\text{SO}_3\text{K}$  (II), as a result of chemical interaction, depresses  $\alpha$ , whilst  $\text{NHPh}\cdot\text{NH}\cdot\text{SO}_3\text{K}$  (III) does not affect  $\alpha$ . The equilibrium  $(\text{I}) + (\text{III}) \rightleftharpoons \text{leucomethylene-blue (IV)} + (\text{II})$  is reversibly displaced by light. In 0.01N-HCl at 20° the equilibrium const. of the dark reaction is 8.2. Irradiation with blue light shifts the equilibrium towards larger concns. of (I), yellow light has the reverse effect. The  $\alpha$  of the mixture equilibrated in the dark increases during irradiation when the (I) concn. is small and falls when it is large, in either case it attains a limiting val. as irradiation continues. The p.d.,  $\Delta E$ , between the two reaction-reduction-oxidation systems at 20—40° is const. at 0.027 volt, corresponding with an equilibrium const. of 8.5 at 20°. This val. of  $\Delta E$  is  $\ll$  that recorded by Clark *et al.* (U.S. Hyg. Lab. Bull., 19, No. 151), a discrepancy which may be connected with the variation of potential with dye concn. The heat changes for  $(\text{II}) - \text{H}_2 \rightleftharpoons (\text{III})$  and  $(\text{I}) +$



$H_2 \rightleftharpoons$  (IV) (at  $p_H$  2.0) are 30.3 and 31.5 kg.-cal., respectively. R. C.

**Decomposition potential of solutions of bromides of metals in fused cadmium bromide.** V. A. IZBEKOV and G. J. ZACHARTSCHENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 121—126).—The decomp. potentials of a no. of bromides in fused  $CdBr_2$  fall in the order  $Zn < Cd < Pb < Cu < Ag < Sn < Co < Ni < Bi$ ; the same order holds in fused  $AlBr_3$  or  $ZnBr_2$ . Any member of the above series is displaceable from  $CdBr_2$  solution by any of the preceding metals. R. T.

**Nature of the residual current [observed with the moving cathode].** I. ZLOTOWSKI (J. Chim. phys., 1935, 32, 750—753).—Polemical against Thon (A., 1935, 705). J. W. S.

**Nature of the residual current [observed with the moving cathode].** N. THON (J. Chim. phys., 1935, 32, 754).—Polemical against Zlotowski (cf. preceding abstract). J. W. S.

**Simultaneous cathodic and anodic direct-current polarisation of electrodes. II. Anodes of platinum, palladium, and gold.** P. S. TUTUNDZIC (Z. Elektrochem., 1936, 42, 21—27; cf. A., 1935, 1205).—The influence of superimposed d.c. of varying direction, p.d., and c.d. on the potential and decomp. potential of Pt, Pd, and Au anodes in  $2N-H_2SO_4$  at room temp. has been investigated. E. S. H.

**Oxide film on passive iron.** W. D. BANCROFT and J. D. PORTER (J. Physical Chem., 1936, 40, 3, 42).—The data of earlier investigators suggest that the oxide film on passive Fe (I) is  $FeO_3$ . This is confirmed by e.m.f. measurements in  $HNO_3$  ( $d$  1.20) on Fe made passive by adsorption from aq. K ferrate, by anodic polarisation in KOH, and by treatment with  $H_2O_2$ ,  $CrO_3$ , acid  $KMnO_4$ , or  $HNO_3$  ( $d$  1.35—1.47). The activation of (I) by conc.  $H_2O_2$  is due to decomp. of  $FeO_3$  by the heat evolved when the  $H_2O_2$  is catalytically decomposed at the surface of (I) and not by a reducing action of the  $H_2O_2$ . M. S. B.

**Electrometric studies of the precipitation of hydroxides. XIII. Reactions between silver nitrate and methylamine, mono-, di-, and triethylamine, ethylenediamine, aniline, and pyridine in solution.** H. T. S. BRITTON and W. G. WILLIAMS (J.C.S., 1936, 96—100; cf. A., 1935, 936).—The formation of complex Ag cations when various org. bases are added to  $AgNO_3$  has been studied. The extent to which bases ppt.  $Ag_2O$  and the amounts required for redissolution depend on the instability const. of the complex cation, the solubility product of the  $Ag_2O$ , and the dissociation const. of the base. Glass electrode titration curves at 18° of  $AgNO_3$  with solutions of the bases and electro-titration curves are given.  $(CH_3NH_2)_2$  forms the ion  $Ag[(CH_3NH_2)_2]^+$ . The modes of pptn. of  $Ag_2O$  by the org. bases and by  $NH_3$  are compared. Unlike  $NH_3$ , none of the bases causes the  $Ag_2O$  to redissolve when 2 mols. per mol. of  $AgNO_3$  have been added. From  $p_H$  vals. and e.m.f. data, the instability consts.  $K_1$  of  $Ag(NH_2Me)_2^+$  and  $Ag(NH_2Et)_2^+$  have been calc. The relatively large vals. of  $K_1$  for complex cations

from  $NH_2Ph$  and  $C_5H_5N$  show that these are relatively much less stable. E. E. A.

**Energy levels in electrochemistry** W. D. BANCROFT and J. E. MAGOFFIN (J. Amer. Chem. Soc., 1935, 57, 2561—2565).—The oxidation of dil. aq.  $H_2SO_3$  or  $Na_2SO_3$  is irreversible because, for reduction to occur, the system must pass through an energy level which is  $>$  the energy level for nascent H as obtained by electrolysis. The energy level decreases with decreasing concn., rising temp., and activating adsorption. The stabilities of  $NaClO_3$  and  $NaClO_4$  relatively to  $NaOCl$  are related to the intermediate energy levels which must be surmounted for reduction to occur. An irreversible reaction may give a definite c.m.f. E. S. H.

**Homogeneous unimolecular decomposition reactions of gases.** F. PATAT (Z. Elektrochem., 1936, 42, 85—98).—A review.

**Thermal interaction of deuterium and ammonia.** A. FARKAS (J.C.S., 1936, 26—35).—The kinetics of the homogeneous exchange reaction between  $NH_3$  and  $D_2$  have been investigated at 680—790 and at 25—400 mm. total pressure. The apparent energy of activation is 62 kg.-cal. and the reaction mechanism (i)  $D_2 \rightarrow 2D$ , (ii)  $NH_3 + D \rightarrow NH_2D + H$ , and (iii)  $H + D_2 \rightarrow HD + D$  accords with the data assuming that the rate-determining step (ii) is 30—40-fold slower than reaction (iii). The atoms responsible for the exchange reaction are produced by the thermal process (i), the dissociation  $NH_3 \rightarrow NH_2 + H$  being negligible. The lower speed of (ii) is due to the higher activation energy,  $11 \pm 1$  kg.-cal., required, and may be partly due to a lower steric factor. This result is in agreement with preliminary experiments on the Hg-sensitised photochemical exchange reaction between D and  $NH_3$ . J. G. A. G.

**Occurrence of radicals in the thermal decomposition of molecules and the reaction  $Me + H_2$ .** F. PATAT (Naturwiss., 1936, 24, 62—63).—The radical chain theory of Rice and Herzfeld (A., 1934, 369) can be tested by the  $p-H_2$  method of Geib and Harteck (A., 1931, 1252). In the case of the reactions (i)  $Me + H_2 \rightarrow CH_4 + H$  and (ii)  $H + \text{org. substance} \rightarrow H_2 + \text{org. radical}$ ,  $[H]/[Me] = k_1[H_2]/k_2[\text{org. substance}]$ , where  $k_1$  and  $k_2$  are the velocity coeffs. of (i) and (ii), respectively.  $[Me]$  can be determined from  $[H]$  if  $k_1/k_2$  is known. In the photochemical decomp. of  $MeCHO$  and azomethane in  $p-H_2$ , the difference in energy of activation for reactions (i) and (ii) is negligible. The similar reactions involved in the thermal decomp. of  $Me_2O$  etc. give the same result, showing that the radical concn. is  $< 1/1000$  of that expected if the decomp. followed the chain mechanism of Rice and Herzfeld. A. J. M.

**Rate of combination of bromine atoms.** K. HILFERDING and W. STEINER (Z. physikal. Chem., 1935, B, 30, 399—439).—The rate of homogeneous formation of  $HBr$  in light, all wall effects being absent, has been measured, and simultaneously the abs. amount of energy absorbed. For a total pressure of 258—1308 mm. the relation between velocity,  $v$ , and total pressure agrees with Herzfeld's reaction scheme (A., 1919, ii, 503), so that over this pressure

range  $[\text{Br}]$ , which is measured by  $v$ , is determined solely by the rate of energy absorption and the rate of recombination of Br atoms. From the reaction have therefore been deduced the rate of recombination of Br atoms in triple collision with various foreign mols. at  $490^\circ$  abs. A "yield factor,"  $f$ , can be separated from the velocity coeffs. of these reactions, which has the dimension time and measures the sp. energy transfer. From the vals. of  $f$  it appears that the no. of effective triple collisions is practically equal to the total no. of triple collisions calc. by the gas-kinetic theory. For the val. of  $f$  it is immaterial whether the mol. takes up energy solely as translational energy or also as rotational and vibrational energy. The variations in effectiveness between different mol. species are due to perturbation of the potential curve of the pair of atoms by the mol. At pressures  $< 258$  mm. the wall exerts an effect. For the transport to the wall of Br atoms formed by the radiation, convection rather than diffusion is responsible, except in a thin film immediately on the wall. R. C.

Zero-point energy of an activated complex and the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ . O. K. RICE (J. Chem. Physics, 1936, 4, 53—59).—Theoretical. A reaction of which the rate is determined by a transitory activated complex in the formation of which classical degrees of freedom must be frozen out into vibrations must have, at all temp., a positive activation energy increasing with rise of temp. A negative activation energy means the formation of a more or less stable mol. complex. The theory has been applied to the oxidation of NO to  $\text{NO}_2$ . M. S. B.

Mechanism of reactions of nitric oxide with oxygen, chlorine, and bromine. I. M. BODENSTEIN. II. Rate of formation and equilibrium of nitrosyl bromide. W. KRAUSS (Z. physikal. Chem., 1936, 175, 294, 295—303).—I. Introductory.

II. At  $264$ — $290^\circ$  abs.  $K$  ( $p$  in atm.) for  $2\text{NO} + \text{Br}_2$  is given by  $\log K = -13,100/4.571T' + 8.025$ . The formation of  $\text{NOBr}$  at all temp. and concns. is a termol. reaction with temp. coeff.  $1.10$ ; reported deviations from the termol. law (A., 1918, ii, 162) disappear if the reverse reaction is allowed for.

Kinetics of the oxidation of gaseous hydrocarbons. III. Oxidation of acetylene. E. W. R. STEACIE and R. D. McDONALD (J. Chem. Physics, 1936, 4, 75—81).—Measurements have been made by a static method in an apparatus previously employed (A., 1935, 172). The rate of reaction is variable and depends on the condition of the surface of the reaction vessel. It is approx. expressed by  $-(d/dt)[\text{C}_2\text{H}_2] = k[\text{C}_2\text{H}_2]^{3/2}/[\text{O}_2]^{0.1}$  if  $\text{O}_2$  is in excess. The order diminishes with increase of surface and may fall to  $1.4$  in a packed vessel. In an empty vessel the ratio  $\text{CO}/\text{CO}_2$  is independent of pressure, but it falls in a packed bulb and still further decreases with diminishing pressure. The apparent heat of activation is approx.  $35,000$  g.-cal. Addition of glyoxal causes no change in velocity, but  $\text{CH}_2\text{O}$  decreases it. The oxidation is apparently a chain reaction, the chains being initiated at the walls but not appreciably destroyed there. It is possible that the chain carrier is some

product that precedes glyoxal in the oxidation process. A reaction scheme is suggested. M. S. B.

Explosion waves and shock waves. III. Initiation of detonation in mixtures of ethylene and oxygen and of carbon monoxide and oxygen. W. PAYMAN and H. TITMAN (Proc. Roy. Soc., 1935, A, 152, 418—445; cf. A., 1928, 1099).—The inflammation of mixtures of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$ , which detonate with ease, and of  $\text{CO}$  and  $\text{O}_2$ , which detonate with comparative difficulty, has been studied with a wave-speed camera. The speed of the flame in a tube before shock waves of appreciable intensity are produced depends on the fundamental speed of propagation of flame by the transfer of heat, and on the motion of the gas in which the flame is moving. Detonation may be set up ahead of or within the flame front, due to waves travelling in front of or from behind the flame, to the collision or overtaking of wave and flame or wave and wave, or to the collision of a wave with an obstruction or the closed end of the tube. L. L. B.

Combustion of hydrocarbons. I. Influence of molecular structure on hydrocarbon combustion. II. Absorption spectra and chemical properties of intermediates. A. R. UBBELOHDE (Proc. Roy. Soc., 1935, A, 152, 354—378, 378—402).—I. Theoretical. A review is made of methods which have been adopted to investigate the combustion of hydrocarbons. The chemical identification of intermediates of oxidation, reaction kinetics, chemiluminescence and emission spectra, the induction period and wall effects, the action of positive and negative catalysts, and the behaviour of isomerides and of substituted hydrocarbons are discussed. The probable importance of vibrational energy, particularly at low temp., is verified, using simple mol. models, and a mechanism for the combustion of the longer-chain hydrocarbons is suggested. This involves a mechanism of chain-branching which accounts for special phenomena observed in the low-temp. region of combustion. Evidence in support of this is obtained from the oxidation of hydrocarbon mols. sufficiently long to permit ring-closure.

II. A study has been made of all the compounds with characteristic absorption spectra which might arise in slow combustion, and of the influence of certain catalysts, such as  $\text{NO}_2$ , on the slow combustion of hydrocarbons. The absorption spectra and slow combustion of ring compounds including one O atom have been investigated in an attempt to discover the origin of the band X arising in the slow combustion of the higher hydrocarbons. Since this first appears for  $\text{C}_4\text{H}_{10}$ , it would seem to depend on ring formation of some kind. The conclusion is reached that the formation of O ring compounds is of importance in elucidating the oxidation mechanism of the higher paraffins at low temp. It is suggested that the formation of saturated O rings, such as methyltetrahydrofuran, corresponds with an internal oxidation by the energy-rich peroxide,  $\text{Me}[\text{CH}_2]_4\text{OOH} \rightarrow \text{CHMe} < + \text{H}_2\text{O}$ , and that the formation of unsaturated O rings occurs when a similar process



takes place with an energy-rich peroxide radical,  $\text{Me}[\text{CH}_2]_4\text{O}_2 \rightarrow \text{OH} \cdot \text{CH} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CH} \end{array} \right\rangle \text{CH}_2 + \text{H} \cdot$ . These two compounds are the only ones the presence of which has been definitely indicated, but other modes of ring-closure are not excluded. The formation of peroxides which combine the properties of an olefine and an alkoxy-peroxide is probably due to the peroxidation of unsaturated O ring compounds, since the vinyl ether peroxides which would be formed have the required behaviour. The formation of a substance X with intense absorption band is probably due to the decomp. of a peroxide first formed. Its structure may resemble that of ascorbic acid. L. L. B.

**Thermal decomposition of silane.** T. R. HOGNESS, T. L. WILSON, and W. C. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 108—112).—Determinations at 380—490° over a considerable pressure range show the reaction to be of the first order. The  $\text{H}_2$  produced inhibits the decomp.; this does not appear to be due to adsorption of  $\text{H}_2$  by Si, and there is no evidence of reaction between Si and  $\text{H}_2$  to form  $\text{SiH}_4$ . The mechanism of decomp. is discussed. E. S. H.

**Thermal decomposition of *tert.*-butyl and *tert.*-amyl chlorides, gaseous homogeneous unimolecular reactions.** D. BREARLEY, G. B. KISTIAKOWSKY, and C. H. STAUFFER (J. Amer. Chem. Soc., 1936, 58, 43—47).—The reactions have been investigated at 543—645° abs. The activation energies are 45,000±1900 and 46,200±700 g.-cal., respectively; the rate expressions are  $k=1.9 \times 10^{14} e^{-46,000/RT}$  sec.<sup>-1</sup> and  $k=4.5 \times 10^{14} e^{-46,000/RT}$  sec.<sup>-1</sup> if the activation energies are regarded as identical. The data are compared with those for the corresponding alcohols. E. S. H.

**Thermal decomposition of silver oxalate.** J. Y. MACDONALD (Nature, 1936, 137, 152—153).—The rate at which  $\text{Ag}_2\text{C}_2\text{O}_4$  decomposes with a rise in temp.  $\propto$  the concn. of the original solutions and the relative amounts of the reacting substances,  $\text{Ag}_2\text{O}_3$  and  $\text{Na}_2\text{C}_2\text{O}_4$ . A complex mechanism, which disagrees with the conclusions of Benton *et al.* (this vol., 37), is discussed. L. S. T.

**Relative rates of ozonisation of unsaturated compounds.**—See this vol., 313.

**Carbon dioxide cleavage from dibromomalonic acid. II.** (Miss) J. MUUS (J. Physical Chem., 1936, 43, 121—124).—The rate at which  $\text{CBr}_2(\text{CO}_2\text{H})_2$  gives up  $\text{CO}_2$  at 25° (A., 1935, 709) is also the approx. rate at which it can simultaneously take up Br. A fraction only of the acid reacts with Br and this fraction is independent of [Br] within a large range. It is suggested that an intermediate unsaturated compound is formed on  $\text{CO}_2$  cleavage (cf. Pedersen, A., 1934, 737). This may either lead directly to  $\text{CHBr}_2 \cdot \text{CO}_2\text{H}$  or form a compound reacting with Br to give  $\text{CBr}_3 \cdot \text{CO}_2\text{H}$ . M. S. B.

**Highly polymerised compounds. CXXII. Relation between reaction velocity and composition of product of reaction in macropolymerisation processes.** G. V. SCHULZ (Z. physikal. Chem., 1935, B, 30, 379—398).—The distribution of mol. wts. in a mixture of polymeride-homologues

has been calc. statistically, assuming that the homologues are built up by chain reactions. The no. of mols. of the degree of polymerisation  $P \propto \alpha^P$ , where  $\alpha=1-k$  ( $k$ —ratio of the velocity of the chain-breaking reaction to that of the polymerisation reaction) and is  $< 1$ , but the proportion of such mols. by wt.  $\propto P\alpha^P$  and thus passes through a max., the val. of  $P$  at which is equal to the mean degree of polymerisation,  $P$  (1 base-mol. of the mixture contains  $1/P$  g.-mols.). For an unfractionated polymerisate the val. of  $P$  determined from the viscosity by Staudinger's law is twice the true val. The above deductions have been confirmed by fractionation of a mixture of polymerised isobutylenes. R. C.

**Polymerides and polyfunctionality.** W. H. CAROTHERS (Trans. Faraday Soc., 1936, 32, 39—49).—Polymerisations do not conform to a single reaction type (e.g., opening of double linkings), but are to be regarded as intermol. combinations functionally capable of indefinite continuation in one or more dimensions. If  $f$ —no. of reactive functions per monomeric mol., then if  $f=2$ , only linear polymerides can be formed, whereas for any higher val. of  $f$  growth may be in two or three dimensions. In general, the extent of reaction (*i.e.*, fraction of original reactive functions lost)  $= 2/f - 2/xf$ , where  $x$ —average degree of polymerisation. Attention is directed to the importance of the distribution of mol. wt., and not merely its average val., in determining the properties of a polymerisation product. F. L. U.

**Mechanism of polymerisation.** H. DOSTAL and H. MARK (Trans. Faraday Soc., 1936, 32, 54—69).—Polymerisation of unsaturated compounds, not involving condensation, proceeds in two stages, of which the first is the formation of "nuclei," e.g., by collision of two monomeric mols., requires an activation, and may be unimol. or bimol. The second stage, rapid compared with the first, is the growth of chains which may occur and be modified in a variety of ways. Formulæ consistent with the mechanism suggested are derived for the reaction velocity. Quant. agreement with experiment is obtained in the case of  $\text{CHPh} \cdot \text{CH}_2$ . F. L. U.

**Kinetics of long-chain disintegration applied to cellulose and starch.** K. FREUDENBERG (Trans. Faraday Soc., 1936, 32, 74—75).—Velocity coeffs. ( $K$ ) of hydrolysis of cello-biose (I), -triose (II), -tetraose (III), and cellulose (IV), and of maltose and starch are given. The vals. of  $K$  for (II) and (III) lie between those for (I) and (IV), indicating a continuous sequence from biose to polysaccharide. Heats of activation and steric factors are calc. F. L. U.

**Highly polymerised compounds. CXX. Formation of high polymerides of unsaturated substances.** H. STAUDINGER (Trans. Faraday Soc., 1936, 32, 97—115; cf. A., 1935, 1319).—A general review of the conditions of formation and the properties of synthetic polymerides is given. In polymerisations not involving condensation a chain mechanism originating in an activated monomeric mol. is best in accord with experimental observations. The physical and colloidal properties of homopolar

polymerides are determined by chain length and are independent of chemical composition. Measurement of the sp. viscosity of dil. solutions of polymerides as a method of determining chain length is valid even for the most highly polymerised substances, but as a measure of mol. wt. only when the chains are unbranched and cross-linkings are absent.

F. L. U.

**Kinetics of ring formation and polymerisation in solution.** G. SALOMON (Trans. Faraday Soc., 1936, 32, 153—175).—In condensation of substances of the type of  $\text{Br}[\text{CH}_2]_x\text{NH}_2$  intramol. ring-closure is greatly influenced by the chain length but is nearly independent of the concn., whereas intermol. polymerisation, largely independent of chain length, is affected by the solvent which is a sp. factor in the reaction velocity. A theory of ring-closure by the interaction of terminal groups is advanced, and supported by analysis of kinetic measurements in different solvents, for  $x=3-17$ .

F. L. U.

**Kinetics of polymerisation reactions.** C. E. H. BAWN (Trans. Faraday Soc., 1936, 32, 178—183; cf. preceding abstract).—The transition state method, applied to the calculation of reaction velocities, leads to a simple interpretation of the steric factor of bimol. association reactions in terms of the probability of the transition state. Assuming a chain mechanism, the degree of polymerisation is shown to be determined by the magnitude of the steric factor, which is calc. for some simple reactions.

F. L. U.

**Kinetics of polymerisation of  $\Delta^2$ -butadiene in presence of metallic sodium.** A. ABKIN and S. MEDVEDEV (Trans. Faraday Soc., 1936, 32, 286—295).—Polymerisation of  $(\text{CH}_2\cdot\text{CH})_2$  in presence of Na takes place in both the gaseous and the liquid phase. The reaction is heterogeneous and its rate, at a given pressure, is the same in both phases. An initial period of acceleration is followed by reaction at a const. rate, the former being connected with the formation of primary compounds with Na. Polymerisation proceeds by the successive addition of monomeric mols. to the Na compounds. The inhibiting effect of  $\text{O}_2$  has been studied. Experiments were done at  $30-35^\circ$ .

F. L. U.

**Kinetic consequences of complex formation in solution.** E. A. MOELWYN-HUGHES and A. SHERMAN (J.C.S., 1936, 101—110).—Theoretical. The solvent is responsible for differences between kinetics of reaction in the gas phase and in solution, and the effect is, in general, electrostatic in origin. For convenience, reactions in solution involving other than the rupture or formation of homopolar linkings in non-ionised mols. are divided into the following types: (i) ion-ion, (ii) dipole-dipole, (iii) dipole-induced dipole, (iv) ion-induced dipole, and (v) ion-permanent dipole. The Debye-Huckel expression refers only to interionic attractions, whereas the so-called ionic reactions, in the kinetic study of which the expression has been extensively applied, usually involve interaction between an ion and a dipole as well. Interaction between two mols. with permanent dipoles probably accounts for the existence of several intermol. complexes, and the low velocity of certain

bimol. reactions is attributed to interaction of either dipolar reactant with the solvent. Certain catalytic effects, e.g.,  $\text{AlCl}_3$  in the Friedel-Crafts reaction, and the existence of hydrates of  $\text{CH}_4$  and the rare gases are traced to the interaction of a permanent dipole with an induced dipole. The solvation of ions and the formation of cryst. hydrates imply an ion-permanent dipole interaction, the relation of which to the co-ordinate linking is discussed.

J. G. A. G.

**Hydrolysis of aryl sulphuric acids.** I. G. N. BURKHARDT, W. G. K. FORD, and E. SINGLETON. II. **Kinetic considerations.** G. N. BURKHARDT, A. G. EVANS, and E. WARHURST (J.C.S., 1936, 17—25, 25—26).—I. The hydrolysis by aq.  $\text{HCl}$  of  $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_3\text{K}$ , where  $\text{X}=\text{o-}, \text{m-}, \text{p-NO}_2, \text{-Cl}, \text{-Br}, \text{-Me}, \text{and } \text{-OMe}$ , at  $48.6^\circ$  and  $78.7^\circ$  is of first order with respect to aryl sulphate and partly autocatalytic owing to the increase of  $[\text{H}^+]$  due to partial dissociation of  $\text{HSO}_4^+$  formed in the hydrolysis. The  $\text{SO}_4$  group is most readily hydrolysed when attached to a position of low electron availability. The logarithms of the velocity coeff. for the *m*- and *p*-compounds give a straight-line relation of the type previously described (A., 1935, 1465). Existing data show that the linear relationship is of wide application in the case of *m*- and *p*-substituted compounds and is valid for some series of *o*-derivatives. In terms of the transition-state conception, the influence of substituents on the free-energy changes associated with the equilibria between the initial and transition states, in the reactions considered in respect of velocity,  $\propto$  their influence on the free-energy changes between the initial and final states in corresponding dissociations.

II. The acid hydrolysis of  $\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{SO}_3\text{K}$  is not catalysed by  $\text{HSO}_4^+$ .

J. G. A. G.

**Elimination of chlorine in the hydrolysis of aqueous solutions of chloroacetic acid and chloroacetates.** H. M. DAWSON and E. R. PYCOCK (J.C.S., 1936, 153—158; cf. A., 1933, 1125; 1934, 848).—Measurements at  $25^\circ$  and  $45^\circ$  of the initial velocity of hydrolysis of the  $\text{CH}_2\text{Cl}\cdot\text{CO}_2$  group, *A*, in solutions containing (i) undissociated mols. only, (ii) ions only, and (iii) mols. and ions, show that the reaction is, in general, the sum of four independent processes represented by  $v=k_1[\text{A}^+]+k_2[\text{A}']^2+k_3[\text{HA}]+k_4[\text{HA}][\text{A}']$ . Collisions involving  $\text{H}^+$  and those between *HA* mols. are not measurably effective. At high  $[\text{HA}]$ , and in presence of much  $\text{HNO}_3$  and  $\text{HClO}_4$ , *v* falls below the calc. val. probably owing to a decrease in  $k_3$ .  $k_1$  and  $k_3$  probably relate to bimol. processes involving the  $\text{H}_2\text{O}$  mol., and the relative bimol. velocity coeffs. of the processes at  $45^\circ$  are: mol- $\text{H}_2\text{O}$  1, ion- $\text{H}_2\text{O}$  1.22, ion-ion 228, mol.-ion 880.

J. G. A. G.

**Kinetics of the reaction between  $\alpha$ -bromopropionate and silver ions.** A. N. KAPPANNA (Proc. Indian Acad. Sci., 1935, 2, A, 512—524).—The hydrolysis of aq.  $\text{C}_2\text{H}_4\text{Br}\cdot\text{CO}_2\text{Na}$  is a very slow reaction. The reaction with aq.  $\text{AgNO}_3$  at  $27^\circ$  occurs at the surface of  $\text{AgBr}$  particles. The rate in dil. solution  $\propto$  the concn. of each of the reactants, showing the latter to be weakly adsorbed on the catalyst surface. In dil. solutions the rate  $\propto$  the amount of suspended  $\text{AgBr}$ .

H. J. E.



**Kinetics of the synthesis of ketones by Friedel and Crafts' method.** S. C. J. OLIVIER (Rec. trav. chim., 1935, **54**, 943—944).—The conclusions of Ulich and Heyne (A., 1935, 1207) were anticipated by the author (A., 1918, i, 228), but no irregularities in the reaction const. were observed. J. W. S.

**Kinetics of gaseous Diels-Alder reactions.** G. B. KISTIAKOWSKY and J. R. LACHER (J. Amer. Chem. Soc., 1936, **58**, 123—133).—Rate coeffs. have been determined as follows: acraldehyde and cyclopentadiene,  $k=1.50 \times 10^9 e^{-15,200/RT}$ ; acraldehyde and isoprene,  $k=1.02 \times 10^9 e^{-18,700/RT}$ ; acraldehyde and butadiene,  $k=1.46 \times 10^9 e^{-19,700/RT}$ ; crotonaldehyde and butadiene,  $k=0.90 \times 10^9 e^{-22,000/RT}$ . The reactions are of the second order, homogeneous, and only slightly complicated by side reactions. The product of the first of the above reactions, endomethylenetetrahydrobenzaldehyde (A., 1928, 1019), is unstable at elevated temp.: the rate of decomp. is given by  $k=2.2 \times 10^{12} e^{-33,600/RT}$ . E. S. H.

**Constitution and reactivity. XV. Kinetics of the nitration of aromatic compounds in sulphuric acid.** K. LAUER and R. ODA (J. pr. Chem., 1936, [ii], 144, 176—192; cf. A., 1935, 1465).—The rate of nitration of anthraquinone (I) by  $\text{HNO}_3$  or  $\text{KNO}_3$ , measured in 87—100%  $\text{H}_2\text{SO}_4$  at 15°, 20°, and 25°, is a max. in 89%  $\text{H}_2\text{SO}_4$ .  $Q$  is about 21,750 g.-cal. for  $\text{HNO}_3$  and 5 nitrates in 87—95.6%  $\text{H}_2\text{SO}_4$ , but only 13,300 for  $\text{KNO}_3$  in 100%  $\text{H}_2\text{SO}_4$ . The "action const." varies with the concn. of the acid, being a min. for 87% acid, and is thus responsible for the variation in  $k$ . The rate of nitration is affected by the nature of the cation in the order,  $\text{H} < \text{NH}_4 < \text{K} < \text{Na} < \text{Ag} < \text{Li}$ , which is also the order of relative ease of formation of pyrosulphates. Cations thus act by removal of free  $\text{SO}_3$  to form pyrosulphate with consequent diminution in  $[\text{H}_2\text{SO}_4]$ . Martensen's data for  $\text{PhNO}_2$  (A., 1905, ii, 149) lead to similar results. Nitration in aq.  $\text{H}_2\text{SO}_4$  is considered to be due to  $\text{OH}\cdot\text{NO}_2$ , but in 100%  $\text{H}_2\text{SO}_4$  mainly to  $[\text{N}(\text{OH})_3]^+$ .  $\text{H}_2\text{SO}_4$  containing 3—5% of  $\text{SO}_3$  causes sulphonation of (I) in presence, but not in absence, of  $\text{KNO}_3$ ; reaction is due to addition of  $[\text{N}(\text{OH})_3]^+$  to the  $\alpha$ -C and of  $[\text{HSO}_4]^-$  to the  $\beta$ -C, with subsequent elimination of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ .  $m$ -Nitration of  $\text{PhNO}_2$  is due to  $\text{OH}\cdot\text{NO}_2$ , and  $o$ - $p$ -nitration to  $[\text{N}(\text{OH})_3]^+$ , as is shown by increase in the latter from 11.7% in 90%  $\text{H}_2\text{SO}_4$  to 13.8% in 100%  $\text{H}_2\text{SO}_4$ . R. S. C.

**Benzoin reaction. IV. Kinetics of the benzoin reaction in presence of organic solvents.** REGE and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, **2**, A, 483—489; cf. A., 1935, 938, 1084, 1200).— $\text{C}_6\text{H}_6$ ,  $\text{C}_5\text{H}_{12}$ ,  $\text{CCl}_4$  are added to a mixture of solid KCN and  $\text{PhCHO}$  cause pptn. of part of the dissolved KCN, and so retard the homogeneous autocatalytic reaction. They do not affect the heterogeneous reaction. OH-compounds [e.g.,  $\text{MeOH}$ ,  $(\text{CH}_2\cdot\text{OH})_2$ ] accelerate the reaction, the effect increasing with the no. of OH groups in the mol. H. J. E.

**Determination of linear crystallisation velocity.** T. FORSTER (Z. physikal. Chem., 1935, **175**,

177—186).—In the usual method of determining the crystallisation velocity,  $v$ , of a non-metallic substance in a tube the temp. of the solid-liquid interface rises with the distance from the wall. This is responsible for the presence on the graph of  $v$  against amount of supercooling of a portion of const.  $v$ , followed by an abrupt fall, whilst the true curve must exhibit a sharp max. A method of determining the true form of the curve is described. R. C.

**Atmospheric corrosion of metals.** Iron. I, II.—See B., 1936, 150.

**Kinetics of reactions in heterogeneous systems. I. Reaction between carbon disulphide and alkali. II. Reaction between benzoyl chloride and water.** D. KARVE and K. K. DOLE (J. Indian Chem. Soc., 1935, **12**, 719—732, 733—739).—I. The influence of speed of shaking, temp., amount and concn. of alkali solution, and amount and concn. of  $\text{CS}_2$  alone and in petroleum, light petroleum,  $\text{PhMe}$ , xylene,  $\text{PhCl}$ , and  $\text{PhBr}$  has been studied. Reaction occurs chiefly in the homogeneous aq. phase and to a smaller extent heterogeneously. The rate is increased by addition of  $\text{H}_2\text{O}_2$ , but decreases with additions of  $\text{NaCl}$ , and does not follow a simple kinetic law.

II. The reaction is purely heterogeneous and the velocity is increased by shaking. Solutions of  $\text{BzCl}$  in  $\text{CCl}_4$ , xylene,  $\text{CS}_2$ ,  $\text{PhCl}$ ,  $\text{PhBr}$ , and  $\text{CHCl}_3$  react according to a unimol. law and with velocities which decrease in the order named. R. S.

**Hydrolysis rates of some monoacid triglycerides under the influence of pancreas extract. I. Influence of the fineness of division of the triglyceride on the hydrolysis rate.** K. HOLWERDA, P. E. VERKADE, and A. H. A. DE WILLIGEN (Rec. trav. chim., 1936, **55**, 43—57).—Detailed examination of the heterogeneous system triglyceride-pancreas extract has yielded reaction rates which are greatly influenced by the fineness of division of the triglyceride and the relative amounts of the phases. A method for obtaining uniform results has been worked out. E. E. A.

**Theory of proton transfer.** J. HORIUTI and M. POLANYI (Acta Physicochim. U.R.S.S., 1935, **2**, 505—532).—The authors' theory of ionogenic reactions (cf. A., 1934, 1185) is extended to reactions involving proton transfer, viz., electrolytic dissociation of acids (proton donors), prototropy, spontaneous ionisation and separation of H at electrodes, and H-ion catalysis. The order of magnitude of the activation energy of the first three processes, the relation between electrolytic dissociation const. of acids and bases and their catalytic activity, and the Tafel relationship for H overvoltage, are all derived from the theory. The order of magnitude of the catalytic activity of H ions is explained. O. J. W.

**Factors governing the formation of nitric acid in the course of combustion of organic substances under a high pressure of oxygen.** L. KEFFLER (J. Chim. phys., 1935, **32**, 741—749).—The quantity of  $\text{HNO}_3$  produced during org. combustions in the bomb calorimeter  $\propto$  the rise in temp. in the bomb and the pressure. It increases with

increasing  $[N_2] : [O_2]$  ratio in the bomb, but there is evidence that the  $HNO_3$  first formed tends to oppose the further oxidation of  $N_2$ . The results also indicate that there is a negative catalyst for the reaction present in cylinder  $O_2$ , and that its concn. increases as the pressure in the cylinder decreases.

J. W. S.

**Polymerisation of gaseous formaldehyde and acetaldehyde.** J. E. CARRUTHERS and R. G. W. NORRISH (Trans. Faraday Soc., 1936, 32, 195—208).—Polymerisation of gaseous  $CH_2O$  is promoted by  $HCO_2H$  vapour. The reaction occurs only on the walls of the vessel, and is complete at  $18^\circ$ . At higher temp. depolymerisation takes place simultaneously and leads to an equilibrium, whilst if the whole vessel is at  $100^\circ$  only the monomeric form can be detected. Polymerisation is bimol. with reference to the  $CH_2O$ ; that of  $MeCHO$  vapour is also promoted by  $HCO_2H$  but not by  $AcOH$ , and that of  $CH_3O$  is promoted by  $AcOH$ . With  $(-CHO)_2$  and  $HCO_2H$  reaction does not go beyond the formation of an additive compound. The results are explained by a branching chain mechanism in which the  $HCO_2H$  is responsible for both initiation and branching. The ease with which depolymerisation occurs indicates that the simple mols. are linked through O. The results support Staudinger's theory of the catalysis.

F. L. U.

**Acid-catalysed enolisation of sec.-butyl ketones.**—See this vol., 317.

**Kinetics of Friedel-Crafts reaction and activity of mixed catalysts.**—See this vol., 322.

**Enzymic hydrolysis of glucosides in heavy water.**—See this vol., 377.

**Adsorption and heterogeneous catalysis.** E. C. C. BALY (J.S.C.I., 1936, 55, 9—12r).—The equations already developed (A., 1935, 1084) are extended to cases involving supported catalysts. On certain assumptions, the reaction velocity is a function of one half of the total energy of activation of the reaction. A supported catalyst has a max. efficiency when of a sp. composition, e.g., a unimol. layer of  $Al(OH)_3$  on kieselguhr (I), or a termol. layer of  $NiO$  or  $CoO$  on (I) (cf. A., 1935, 1070). The structure of these surfaces is discussed.

J. G. A. G.

**Polymerisation in monolayers.** G. GEE (Trans. Faraday Soc., 1936, 32, 187—195).—Changes occurring during the "drying" of the compound of  $\beta$ -claeostearin with maleic anhydride have been followed by measuring the surface pressures at different areas per mol. of a unimol. film on  $0.01N$ - $H_2SO_4$ . The initial reaction gives rise to an unstable peroxide which may polymerise either directly or after transformation into a more stable form, according to the experimental conditions. The velocity curves indicate that polymerisation proceeds by a chain mechanism in which the chains are terminated by a steric factor. Addition of inert substances like  $Me-[CH_2]_{13}-CO_2Et$  to the film inhibits polymerisation by breaking the chains, but does not affect the oxidation. The polymerisation stage is also accelerated by  $CoSO_4$ , and retarded by quinel. Activation energies are calc.

F. L. U.

**Polymerisation of phosphorus.** H. W. MELVILLE and S. C. GRAY (Trans. Faraday Soc., 1936, 32, 271—285).— $P_4$  mols. dissociate to  $P_2$  when passed through a  $SiO_2$ -glass jet at  $500$ — $800^\circ$ , or by contact with a hot W filament. If  $P_2$  thus formed is condensed under such conditions that it cannot combine to  $P_4$ , the product is red P. The kinetics of dissociation on hot W have been studied in detail. It is shown that only  $P_2$  mols. are in equilibrium with red P, and that discrepancies in the thermal data regarding the interconversion of red and white P are removed by taking into account the thermal change accompanying the dissociation  $P_4 \rightleftharpoons 2P_2$ .

F. L. U.

**Change of magnetic and catalytic properties during the transformation of a mixture of calcium oxide and ferric oxide into calcium ferrite.** G. F. HUTTIG, J. FUNKE, and H. KITTEL (J. Amer. Chem. Soc., 1935, 57, 2470—2477).—Products obtained by heating  $CaO + Fe_2O_3$  and  $CaCO_3 + Fe_2O_3$  in mol. ratio at different high temp. under varying conditions have been investigated with regard to catalytic activity in the decomp. of  $N_2O$ , magnetic susceptibility, powder  $d$ , colour, and  $CO_2$  content. The heat of activation and no. of active centres are given for each product. An "active intermediate," which no longer possesses the properties of the original mixture nor those of the cryst.  $CaFe_2O_4$ , is formed. The most active samples contain up to 60% of the intermediate, which has a magnetic susceptibility of  $51.5 \times 10^{-6}$  and heat of activation (for decomp. of  $N_2O$ ) of 20,000—25,000 g.-cal. The intermediate is formed as a film at the surface of the particles.

E. S. H.

**Platinum catalysts on metallic carriers.**—See B., 1936, 101.

**System vanadic acid-cupric oxide-silicic acid as catalyst in the formation of sulphuric acid.**—See B., 1936, 144.

**Is sintering the cause of inactivation of barium-vanadium catalysts?**—See B., 1936, 101.

**Catalytic air-oxidation of petroleum in the vapour phase.**—See B., 1936, 83.

**Catalytic hydrogenation of phenolic oil in low-temperature tar.** II.—See B., 1936, 132.

**Condensation of benzyl chloride and benzene.**—See B., 1936, 138.

**Ternary catalyst  $Cu-ZnO-Cr_2O_3$  as a hydrogenation catalyst.** S. S. BALIASNI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 175—182).—Reduction of  $COPhMe$  to  $PhEt$  is catalysed more efficiently by Ni than by  $91.8 : 6.5 : 1.7$   $Cu-Zn-Cr_2O_3$  at  $250^\circ$ , whilst at  $284$ — $289^\circ$  the latter catalyst has no hydrogenating activity.

R. T.

**Decompositions of esters and acids by anhydrous zinc chloride.**—See this vol., 313.

**Electrolytic preparation of deuterium and the separation coefficient  $\alpha$ .** M. P. APPLEBEY and G. OGDEN (J.C.S., 1936, 163—168).—The large discrepancy between the observed and the theoretical vals. of  $\alpha$  ( $= [D_2]$  in gas/ $[D_2]$  in liquid phase) is discussed, and the following principles are adopted in the design

of cells for producing  $D_2O$ : (a) the electrode metal must be a poor catalyst for the exchange reactions, (b) the  $H_2$  evolved must be removed rapidly from the electrode surface, and (c) local concn. of  $D_2O$  at the electrode must be avoided. With very low  $[D_2O]$ , vals. of  $\alpha$  the calc. vals. (0.05—0.10) were obtained, but this is not necessarily a proof that quantum-mechanical leakage is an important factor in the difference of reactivity of H and D atoms, since the observed val. of  $\alpha$  is controlled by the uncertain val. of  $[D]$  in standard  $H_2O$ . J. G. A. G.

**Direct introduction of deuterium into benzene by high-frequency current.** J. HORIUTI and T. KOYANO (Bull. Chem. Soc. Japan, 1935, 10, 601).—Pure  $C_6H_6$  in presence of 8%  $D_2O$  and Pt-black after standing on a pole of a Tesla coil for 10 hr. at room temp. acquired a D content of 0.69%; no change in temp. occurred. In a second experiment the pure  $C_6H_6$  was kept between the poles of a high-frequency oscillator of  $\lambda$  4 m., and was cooled, the % of D rising from 0 to 0.41.  $C_6H_6$  similarly treated with ordinary  $H_2O$  gave no change in  $d$  and f.p. No exchange occurred at room temp., even with an oscillator, unless a catalyst was present. R. S. B.

**Preparation of oxygen by electrolysis of baryta.** E. M. STODDART (Proc. Roy. Soc., 1935, A, 152, 273—277).—Electrolysis of  $Ba(OH)_2$ , using Ni electrodes, does not always give pure  $O_2$  at the anode. After some time  $H_2$  is liberated as well, probably owing to the reaction  $OH + OH = H_2 + O_2$ . This can be prevented by coating the anode with a layer of  $Ni(OH)_2$ . L. L. B.

**Influence of small amounts of agar-agar and gelatin on the  $KG_1$  of the anode deposit of silver peroxide.** A. GLAZUNOV and K. VALEČKA (Chem. Listy, 1935, 29, 359—361).—The velocity of crystallisation of  $Ag_2O_2$  at the anode in electrolysis of  $AgNO_3$  falls with increasing concn. of agar-agar or gelatin from 0 to 0.15%. R. T.

**Spectroscopic studies of luminescence at cathode during electrolysis.** I. UHARA (Bull. Chem. Soc. Japan, 1935, 10, 559—563).—The spectrum of the luminescence at a Pt wire cathode on electrolysis of 1—3*N*-salt or -acid solutions shows lines identical with those of the arc, and in some cases the spark spectra of the metals forming cations. The lines of H and  $H_2$  are observed, but anions have no influence on spectra. It is suggested that no luminescence occurs until the c.d. is sufficient to form a film of H on the cathode. The metals which give insol. hydroxide and consequent disappearance of the luminescence with d.c. give prolonged luminescence with 100 volts a.c. R. S. B.

**Electrolytic manufacture of aluminium-magnesium alloys.**—See B., 1936, 151.

**Electrodeposition of bronze.**—See B., 1936, 151.

**Electrodeposition of zinc and cadmium on aluminium and aluminium alloys.**—See B., 1936,

**Electrodeposition of cadmium.**—See B., 1936, 152.

**Hardness of electrolytic chromium.** II.—See B., 1936, 152.

**Effect of imprisonment of resonance radiation in the decomposition of ammonia and of deuterio-ammonia.** H. W. MELVILLE (Proc. Roy. Soc., 1935, A, 152, 325—341; cf. A., 1934, 1078, 1183).—Velocity coeffs. in Hg-photosensitised reactions are usually determined by comparison with the mean life of the Hg atom, which is assumed to be const. At high Hg-vapour pressures, however, at which experiments are usually made, there is appreciable imprisonment of resonance radiation with the result that the effective mean life is much > its actual val. of  $10^{-7}$  sec. A re-examination of the Hg-photosensitised decomp. of  $NH_3$ ,  $ND_3$ ,  $PH_3$ , and  $PD_3$ , under conditions where reabsorption is negligible, leads to lower velocity coeffs., in agreement with expectation. It is suggested that the decomp. of  $NH_3$  and  $ND_3$  are brought about in collisions between  $NH_3$  ( $ND_3$ ) and metastable atoms, derived from quenching collisions between  $3P_1$  atoms and  $NH_3$  ( $ND_3$ ). The former collisions are equally efficient for  $NH_3$  and  $ND_3$ . To account for the greater reactivity of  $NH_3$ , secondary reactions, unconnected with Hg atom processes, are assumed to occur. The suggested mechanism is supported by the fact that in the direct photo-decomp.  $NH_3$  also reacts more quickly, and that the decomp. of  $ND_3$  is more susceptible to inhibition by D than is that of  $NH_3$  by H. L. L. B.

**Mathematical representation of photographic blackening curves deduced from the coagulation theory of latent images and using the fundamental hypothesis of Bose-Einstein statistics.** G. UNGAR (Z. Physik, 1936, 98, 517—533).—The equation deduced permits closer correlation of blackening with properties of the emulsion. A. B. D. C.

**Mercury-photosensitised polymerisation of acetylene.** H. W. MELVILLE (Trans. Faraday Soc., 1936, 32, 258—271).—Kinetic analysis of results obtained in polymerising  $C_2H_2$  by light from a quartz-Hg lamp in presence of Hg vapour (pressure  $\approx 0.0003$  mm.) indicates that excited Hg atoms form with a  $C_2H_2$  mol. a complex which then adds on more  $C_2H_2$  mols. by a chain mechanism. The chain length is independent of the  $C_2H_2$  pressure, of surface, and of the rate at which chains are started, and exhibits a max. (100) at  $250^\circ$ . Cessation of growth is due to collision between a  $C_2H_2$  mol. and the growing polymeride, but of a different kind from that causing propagation. The pressure and temp. ranges were 0.05—10 mm. and  $20$ — $500^\circ$ . Polymerisation of  $C_2H_4$  also occurs under the same conditions, but is preceded by formation of  $C_2H_2$  and  $H_2$ , the final product being partly hydrogenated. F. L. U.

**Explanation of the course of photolysis of fructose in quartz light using long-wave ultra-violet light.** R. CANTENI (Helv. Chim. Acta, 1936, 19, 86—93).—In long-wave ultra-violet light (glass-filtered quartz light) fructose with the ketone structure decomposes with the evolution of CO, whilst, simultaneously, the ring structure in equilibrium gives  $CO_2$ . In long- and short-wave ultra-violet

light (unfiltered quartz light)  $H_2$  is obtained in addition, but polarimetric measurements also indicate that some of the fructose undergoes change without any evolution of gas. M. S. B.

**Connexion between decomposition velocity and concentration of fructose in long-wave ultra-violet light.** It. CANTINI (Helv. Chim. Acta, 1936, 19, 94—96; cf. preceding abstract).—The rate of decomp. of fructose by long-wave ultra-violet light, as measured by gas evolution, reaches a max. for a fructose concn. of 150 g. per 100 c.c. of  $H_2O$ . Above this concn. the rate of decomp. remains const., at least up to 200 g. per 100 c.c. of  $H_2O$ . The gas evolution from such a solution is approx. half that from an equal vol. of solution of concn. 1 : 10 irradiated by unfiltered quartz light.

M. S. B.

**Acidity and yellow coloration of fructose at higher temperatures in quartz light.** R. CANTINI (Helv. Chim. Acta, 1936, 19, 96—98).—The acid formation which takes place in fructose solution under the influence of ultra-violet light, and more rapidly at shorter  $\lambda$ , is probably due to  $HCO_2H$  formed by the oxidation of the  $CH_2O$  proved to be produced by ultra-violet light. The yellow coloration is due to a dark reaction accelerated by the presence of acid and requiring the addition of heat, either directly or by the transformation of light energy into heat.

M. S. B.

**Influence of solvent on the course of chemical reactions.** I. Absorption spectrum of anthracene in various solvents. K. LAUER and M. HORIO. II. Photochemical reaction, anthracene dianthracene, in various solvents. III. Kinetics of bromination of anthracene in various solvents. IV. Changes in energy of activation and action constants in substitution reactions of organic compounds as effect of solvent. K. LAUER and R. ODA (Ber., 1936, 69, [B], 130—137, 137—140, 141—145, 146—148).—I. Examination of the absorption spectrum of anthracene in hexane (I), cyclohexane (II), cyclohexene (III),  $C_6H_6$ , EtOH, and AcOH shows that solvents containing double linkings cause displacement of the absorption max. of dissolved aromatic compounds without dipole character or polar groups towards the region of longer  $\lambda$ . Dipolar solvents have so little effect on these solutes that the displacements are within the limits of experimental error. Solvents with double linkings but without dipole act on polar mols. in such a manner that the spectrum proper to the polar group and that due to the aromatic portion of the solute is displaced towards the longer  $\lambda$ . Dipolar solvents have a greater influence than dipole-free solvents on that part of the spectrum due to the dipole of the solute and a less, though distinct, influence on the aromatic portion of the spectrum. The displacements are always in the same sense as those caused by the linear anellation of  $C_6H_6$  nuclei to  $C_{10}H_8$ .

II. The rate of the photochemical reaction, anthracene dianthracene, has been determined in (I), (II), (III),  $C_6H_6$ , EtOH, and AcOH. Within the limits of experimental error it has the same val. in (I), (II), (III), and EtOH, but is considerably

higher in AcOH and particularly in  $C_6H_6$ . The photo-reaction is parallel to the displacement of the absorption spectra, and double linkings in the solvent have a distinct, accelerating action on the change.

III. Bromination of anthracene in (I) or (II) takes place relatively slowly and at about the same rate in each solvent. In  $C_6H_6$  and EtOH it is equally rapid at  $10^\circ$ , but about twice as fast in EtOH as in  $C_6H_6$  at  $15^\circ$ . In (I), (II), and  $C_6H_6$  (dipole-free solvents) the change occurs with a uniform energy of activation (about 6800 g.-cal.) and the greater rate in  $C_6H_6$  is due to the higher action const. In EtOH and AcOH the energies of activation are 18,600 g.-cal. and 10,850 g.-cal., respectively, and the action consts. are considerably higher, hence the greater rate of change.

IV. The heat of dissolution of Br in (I), AcOH, and EtOH, respectively, is determined at dilutions and temp. similar to those used in the bromination of anthracene. These vals. subtracted from the heats of activation gave a very nearly const. val. which is regarded as the energy val. of the action, anthracene-Br, in the absence of solvent. It is considered that the solvent without dipole exerts an "impact action" which affects the no. of successful collisions of the reacting mols.; whether this is a numerical or spatial action remains undecided. Dipolar solvents, in addition to this action, cause also a change in the heat of activation of the subsequent reaction due to alteration in the energy conditions on dissolution of the reaction partner ("energy action"). H. W.

**Photochemical stability of crotonaldehyde.** F. E. BLACET and J. G. ROOF (J. Amer. Chem. Soc., 1936, 58, 73—75).—Although ultra-violet light is absorbed by the vapour phase, no decomp. or appreciable polymerisation was observed. The concept of a predominating reverse reaction is put forward as an explanation.

E. S. H.

**Photochemical decomposition of nitrated phenols.** J. MOLNAR (Compt. rend., 1935, 201, 1482—1484).—At  $p_H > 13.0$  picric acid is decomposed in ultra-violet light to give picramic and isopurpuric acids,  $HNO_2$ ,  $NH_3$ , and HCN, whilst the usual yellow form existing at  $p_H < 13.0$  is unaffected. An analogous reaction occurs with 2 : 5-OH- $C_6H_3(NO_2)_2$ , *o*- and *p*- $NO_2$ - $C_6H_4$ -OH, 2 : 4- and 2 : 6-OH- $C_6H_3(NO_2)_2$ , and 2 : 4-dinitro-*o*-cresol decompose at  $p_H$  where the red forms exist, the rate of decomp. increasing with  $p_H$ .

T. G. P.

**Catalysed photo-reduction of vat dyes.** K. WEBER (Naturwiss., 1935, 23, 849—850).—If 0.001% aq. solution of thionine (Lauth's violet) (I) containing a small amount of  $FeSO_4$  and  $H_2SO_4$  is cooled to  $10^\circ$  and exposed to the light of a powerful arc lamp, the dye is rapidly bleached. The process is reversible. The bleaching takes the longer the higher is the temp. and the weaker the light. Methylene-blue (II), Nile-blue, phenosafranin, and neutral-red, all of which have negative normal reduction potentials, do not behave similarly. (I) has a positive reduction potential. In the case of (II) photo-reduction takes place if the  $FeSO_4$  is replaced by  $K_4Fe(CN)_6$ , which has a more negative reduction potential. The phenomenon can be explained by



supposing that the photo-excited dye mol.  $F^*$  has a more positive reduction potential than the unexcited mol.  $F$ . The systems  $F$ -leuco-base, and  $F^*$ -leuco-base are both present. In the dark,  $Fe^{++}$  does not react, but in the light the potential of  $F^*$  becomes more positive than that of the  $Fe^{+++}$ - $Fe^{++}$  system, and equilibrium is reached by the formation of leuco-base and  $Fe^{+++}$ . The max. of the absorption band of (I) is at 600  $m\mu$ , corresponding with an absorption of energy  $>$  sufficient for the above change. (II) has a more negative reduction potential than (I) and its absorption max. is at higher  $\lambda$ ; consequently the energy absorbed is in this case insufficient for the reaction to occur. The fact that the photo-reduction does not occur in alkaline solution is explained on similar grounds. A. J. M.

**Radiochemical decomposition of deutero-ammonia.** J. C. JUNGERS (J. Physical Chem., 1936, 40, 155—158).—The rate of decomp. of  $ND_3$  by  $\alpha$ -radiation is  $<$  that of  $NH_3$  and also increases more slowly, relatively, with rise of temp. M. S. B.

**Action of radioactive substances on proteins.** J. LOISELEUR (Compt. rend., 1935, 201, 1511—1513).—Proteins are first hydrolysed; and flocculation follows in the presence of electrolytes. T. G. P.

**Heavy hydrogen and heavy water.** H. MARK and M. WALD (Protoplasma, 1935, 23, 109—127).—A review.

**Production and identification of helium of mass three.** W. BLEAKNEY, G. P. HARNWELL, W. W. LOZIER, P. T. SMITH, and H. D. SMYTH (Physical Rev., 1934, [ii], 46, 81—82; cf. this vol., 130).—Evidence for the production of  $He^3$  from  $D_2$  in a mass spectrograph is advanced. The life of the  $H^3$  and  $He^3$  produced is at least  $10^8$  years. No evidence of the production of  $He^4$  was obtained. Attempts to find  $He^3$  and  $He^5$  in ordinary He were unsuccessful. L. S. T.

**Purification and spectroscopic evidence for  $He^3$ .** G. P. HARNWELL, H. D. SMYTH, and W. D. URRY (Physical Rev., 1934, [ii], 46, 437).—The purification and isolation of small amounts of  $He^3$  from circulating in a canal-ray discharge tube are described (cf. preceding abstract). L. S. T.

**Preparation of calcium chromate in the wet way.** J. MILBAUER and J. DOSKAR (Shorn. Masaryk. Akad. Prace, 1934, 8, 42—59; Chem. Zentr., 1935, i, 3259; cf. B., 1933, 963).—Full details are given. J. S. A.

**Common occurrence of trimercury group ( $HgX_2.Hg_2$ ) in complex compounds of mercury (family of turpeths).** G. DENIGES (Bull. Trav. Soc. Pharm. Bordeaux, 1933, 71, 97—109; Chem. Zentr., 1935, i, 3260).—Basic Hg compounds with 3 atoms of Hg per mol. are referred to a common structural unit  $Hg\langle\begin{smallmatrix} X.Hg \\ X.Hg \end{smallmatrix}\rangle A$ , where  $X=O, S, Se, NH, NR$  or  $NH_2OH, N_2H_4$ , and  $CO(NH_2)_2$  residues;  $A=Cl_2, Br_2$ , or a dibasic acid. The compounds are termed "turpeths" (turpeth mineral,  $A=O, X=SO_3$ ), and the compounds with  $X=O, A=(NO_3)_2, SeO_4, TeO_4, (BrO_3)_2, (IO_3)_2, Cl_2$ , and  $Br_2$ ;  $X=S, A=SO_4, Cl_2$ ,

$Br_2, F_2, (NO_3)_2, (OAc)_2, (O-COEt)_2, (O-COPr)_2$  are described. J. S. A.

**Aluminium carbide,  $Al_4C_3$ , and aluminium carbonitride,  $Al_5C_3N$ .** M. VON STACKELBERG, E. SCHNORRENBERG, R. PAULUS, and K. F. SPIESS (Z. physikal. Chem., 1935, 175, 127—139).—The compound  $Al_4C_3N$ , almost indistinguishable in appearance and properties from  $Al_4C_3$ , is formed by regulated admission of  $N_2$  to a mixture of Al and C at  $1800^\circ$ , being an intermediate product in the nitridation of carbide to nitride,  $5Al_4C_3 \cdot 10N_2 = 4Al_5C_3N + 3C + 8N_2 = 20AlN + 15C$ .  $Al_4C_3$  takes up at high temp. excess of Al, which separates again on cooling, and the supposed carbides  $Al_9C_3$  and  $Al_3C_2$  (A., 1934, 600) are merely finely disperse mixtures of  $Al_4C_3$  and Al, whilst  $Al_8C_9$  is a mixture of Al and  $Al_2C_3$ . "Amorphous"  $Al_4C_3$  (A., 1933, 917) is identical with the cryst. variety. R. C.

**Carbonyl chloride.** A. PERRET and R. PERROT (Bull. Soc. d'Encour., 1935, 134, 552—560).—The reactions of  $COCl_2$  are summarised and its action on the blood is discussed, especially with reference to the analogy between the effects of  $COCl_2$  and of CO. J. W. S.

**Colour reaction between nitroprusside and sulphite (Bodeker's reaction).** G. SCAGLIARINI (Atti R. Accad. Lincei, 1935, [vi], 22, 155—159).—Treatment of equimol. aq. mixtures of Na nitroprusside and  $Na_2SO_3$  with conc. aq. Zn, Cd, or Ni acetate and  $(CH_2)_6N_4$  affords the compounds (Zn or Cd) $_2[Fe^{++}(CN)_5(NO \cdot SO_3)] \cdot 2C_6H_{12}N_4 \cdot 12H_2O$  and  $Ni_2[Fe^{++}(CN)_5(NO \cdot SO_3)] \cdot 2C_6H_{12}N_4 \cdot 8H_2O$  (see A., 1896, i, 197). F. O. H.

**Germanium chlorofluorides.** H. S. BOOTH and W. C. MORRIS (J. Amer. Chem. Soc., 1936, 58, 90—93).—By reaction of  $GeCl_4$  with  $SbCl_3$  in presence of  $SbCl_5$ , there are formed  $GeCl_3F$ , b.p.  $37.5^\circ$ , m.p.  $-49.8^\circ$ ,  $GeCl_2F_2$ , b.p.  $-2.8^\circ$ , m.p.  $-51.8^\circ$ ,  $GeClF_3$ , b.p.  $-20.3^\circ$ , m.p.  $-66.2^\circ$ , and  $GeF_4$ . The chlorofluorides hydrolyse in moist air more readily than does  $GeCl_4$ ; they are unstable, tending to rearrange to  $GeCl_4$  and  $GeF_4$  even at  $-78^\circ$ . Under certain conditions they are reduced explosively by Cu to  $Ge^{II}$  salts. E. S. H.

**Lead ferrites.** L. I. PARAMONOV (Tsvet. Metal., 1934, No. 3, 79—88).—Formation of  $PbO.Fe_2O_3$  (I) by heating PbO with  $Fe_2O_3$  begins at  $665^\circ$ , and is a max. at  $725^\circ$ . Addition of  $SiO_2$  favours the decomp. of (I).  $CaO$  decomposes (I) at  $600$ — $800^\circ$  and combines partly with the PbO. CO begins to reduce PbO from (I) at  $400^\circ$ . The reduction is complete at  $550^\circ$ . CH. ABS. (e)

**Ammonium salts of arsenic, phosphoric, and antimonie acids, and direct determination of heats of oxidation of arsenic.** A. DE PASSILLE (Ann. Chim., 1936, [xi], 5, 83—146).—Full details of the author's prep. of pure As (cf. A., 1934, 742) and work on  $NH_4$  phosphates and arsenates (cf. *ibid.*, 377, 966; 1935, 344, 936) are given. The prep. of  $NH_4SbO_3 \cdot 3H_2O$  (I) is described. (I) readily loses  $H_2O$  and  $NH_3$ , affording probably  $HSbO_3 \cdot 0.5NH_3$  at  $110^\circ$ , and  $Sb_2O_5$  at  $270^\circ$ . When As is burned in  $O_2$  at  $15$ — $40$  atm., the ratio  $As_2O_5 : As_2O_3$  increases with  $[O_2]$ . The heats

of formation from As metal are :  $\text{As}_2\text{O}_3$  (cubic) 154.7 and  $\text{As}_2\text{O}_5$  (cubic) 218.3 kg.-cal. J. G. A. G.

**Dehydrogenating action of sulphur monoxide.** B. S. RAO and M. R. A. RAO (Current Sci., 1935, 4, 406).—On absorption in paraffin or decalin at low temp. SO yielded  $\text{H}_2\text{S}$ .  $\text{C}_2\text{Cl}_4$  gave no result, the SO being comparatively stable in solution, but yielding  $\text{H}_2\text{S}$  on adding paraffin or decalin. SO gave  $\text{H}_2\text{S}$  readily on treatment with MeOH, and more slowly with EtOH. Micro-analysis confirmed the reaction  $2\text{SO} + \text{MeOH} = \text{H}_2\text{S} + \text{CH}_3\text{O} + \text{SO}_2$ . The general dehydrogenation is  $\text{RH}_2 + 2\text{SO} = \text{R} + \text{H}_2\text{S} + \text{SO}_2$ , or possibly in some cases  $\text{RH}_2 + \text{SO} = \text{RO} + \text{H}_2\text{S}$ .

N. M. B.

**Fluorination of sulphuryl chloride : sulphuryl chlorofluoride.** H. S. BOOTH and C. V. HERRMANN (J. Amer. Chem. Soc., 1936, 58, 63—66).— $\text{SO}_2\text{ClF}$ , b.p.  $7.1 \pm 0.1^\circ$ , m.p.  $-124.7 \pm 0.1^\circ$ , has been prepared by the action of  $\text{SbF}_3$  on  $\text{SO}_2\text{Cl}_2$  in presence of  $\text{SbCl}_5$  under pressure. The latent heat of vaporisation at the b.p. is 6338 g.-cal. At  $0^\circ$  the liquid has  $d$  1.623 and surface tension 17.2 dynes per cm. The gas is hydrolysed by  $\text{H}_2\text{O}$  and readily absorbed by aq. NaOH.

E. S. H.

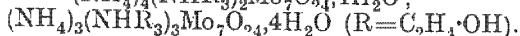
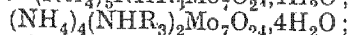
**Preparation of selenic acid.** L. I. GILBERTSON and G. B. KING (J. Amer. Chem. Soc., 1936, 58, 180).— $\text{SeO}_2$  is oxidised by refluxing with aq.  $\text{H}_2\text{O}_2$ .

E. S. H.

**Molybdenum-blue.** F. HEIN, I. BURAWOY, and H. SCHWEDLER (Kolloid-Z., 1936, 75, 35—45).—The reduction of heteromolybdic acids by  $\text{SnCl}_2$  has been studied colorimetrically. This reaction and titration of the Mo-blue with  $\text{KMnO}_4$  indicate that the product is  $\text{Mo}_4\text{O}_{11}$ .

E. S. H.

**Mixed molybdates.** F. GARELLI and A. TETTMANZI (Gazzetta, 1935, 65, 1009—1015; cf. A., 1934, 1208).—The prep. of the following compounds is described :  $(\text{NH}_4)_5\text{NHR}_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ;



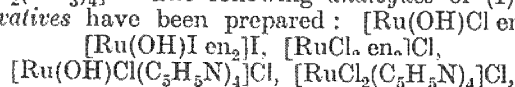
O. J. W.

**Action of chlorine and bromine on chlorites.** G. R. LEVI and M. TABET (Gazzetta, 1935, 65, 1138—1144).—The action of  $\text{Cl}_2$  on aq. solutions of  $\text{Ca}(\text{ClO}_2)_2$  is quant :  $2\text{ClO}_2' + \text{Cl}_2 = 2\text{Cl}' + 2\text{ClO}_2$ . With Br a similar reaction takes place in the initial stages, but is followed by an oxidation-reduction process :  $3\text{ClO}_2' = 2\text{ClO}_3' + \text{Cl}'$ , nearly all the Br remaining in the free state.

O. J. W.

**Residual affinity and co-ordination. XXXVI. Constitution of "ruthenium-red."** G. T. MORGAN and F. H. BURSTALL (J.C.S., 1936, 41—45).—Ru-red (I) is best prepared by treating  $\text{RuCl}_3$  with conc. aq.  $\text{NH}_3$ . The constitution of (I),  $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$ , is supported by the prep. therefrom of the following compounds :

$[\text{RuCl}_2(\text{NH}_3)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ,  $[\text{RuCl}(\text{NO}_3)(\text{NH}_3)_4]\text{NO}_3 \cdot 4\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{OH})\text{Br}(\text{NH}_3)_4]\text{Br} \cdot \text{H}_2\text{O}$ ,  $[\text{RuBr}_2(\text{NH}_3)_4]\text{Br} \cdot \text{H}_2\text{O}$ ,  $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_3)_4]\text{I}$ ,  $[\text{Ru}(\text{OH})\text{I}(\text{NH}_3)_4]\text{I}$ , and  $[\text{RuI}_2(\text{NH}_3)_4]\text{I}$ . The following analogues of (I) and derivatives have been prepared :



$[\text{RuCl}_2(\text{NH}_2\text{Et})_4]\text{Cl}$ , and  $[\text{Ru}(\text{OH})\text{Cl}(\text{NH}_2\text{Et})_4]\text{Cl}$ . The analogues of (I) are less strongly coloured than (I).

J. G. A. G.

**Detection and separation of sparingly soluble compounds by concentrated hydriodic acid.** E. R. CALEY and M. G. BURFORD (Ind. Eng. Chem. [Anal.], 1936, 58, 63—67).—Examples of the use of conc. HI in the detection and separation of compounds that are insol. in HCl,  $\text{HNO}_3$ , or aqua regia are given.

E. S. H.

**Calculating the blank [in volumetric determinations].** B. PARK (Ind. Eng. Chem. [Anal.], 1936, 8, 32).—Arithmetical procedure is described.

E. S. H.

**Theory of titration in stages of mixtures of acids and bases.** S. KILPI (Z. physikal. Chem., 1935, 175, 239—254; cf. A., 1935, 1214).—The conditions for the titratability of such mixtures and of ampholytes have been derived.

R. C.

**Colorimetric chemical analyses by means of photo-electric cells.** F. CARRANZA (Bol. Soc. Quím. Peru, 1935, 1, No. 5, 7—27).—The % of the incident light transmitted by the unknown solution is determined by means of a photo-electric cell and the concn. deduced by comparison with solutions of known concn. The sensitivity may be increased or decreased by the use of filters of complementary or similar colour, respectively, to the solution. Examples are given of the determination of  $\text{KMnO}_4$  in aq. solution, of  $\text{NH}_2$ -acids (glycine) by means of the ninhydrin reaction, and of vitamin-A in cod-liver oil.

D. R. D.

**Volumetric determination of water in liquids and solids.**—See B., 1936, 127.

**Argentometric titration of halide, thiocyanate, selenocyanate, and cyanate with adsorption indicators.** R. RIPAN-TILICI (Z. anal. Chem., 1936, 104, 16—22).— $\text{CN}'$  is titrated with  $\text{AgNO}_3$  by Liebig's method, and the titration of  $\text{Cl}'$ ,  $\text{SCN}'$ ,  $\text{SeCN}'$ ,  $\text{CNO}'$ , etc. continued using fluorescein as indicator.

J. S. A.

**Determination of sulphuric acid in solutions containing aluminium, chromium, and ferric sulphate. III.** S. A. TOLKATSHEV and J. G. TIROVA (J. Appl. Chem. Russ., 1935, 8, 1271—1283).—25 ml. of aq.  $\text{Al}_2(\text{SO}_4)_3$  are titrated with 0.5N-NaOH, an excess of 12 ml. of which is then added; the solution is diluted to 100 ml., and saturated with  $\text{CO}_2$  at the b.p., cooled, and diluted to 250 ml., filtered, and excess of alkali in an aliquot part of the filtrate is titrated with 0.5N- $\text{H}_2\text{SO}_4$  (Me-orange).  $\text{Cr}_2(\text{SO}_4)_3$  is determined analogously, an excess of 10 ml. of 0.5N-NaOH being added per 0.1 g. of  $\text{Cr}_2\text{O}_3$  in the solution. In the case of  $\text{Fe}_2(\text{SO}_4)_3$  treatment with  $\text{CO}_2$  is not necessary; the excess of alkali should be 8 ml. per 0.1 g. of  $\text{Fe}_2\text{O}_3$ . The mean error is  $\pm 0.2$ — $0.3\%$ .

R. T.

**Stabilisation of 0.1N-sodium thiosulphate solution.**—See B., 1936, 144.

**Determination of selenium in sulphur.**—See B., 1936, 101.

**Source of loss of ammonia in Kjeldahl distillations.** Method of eliminating this loss. H. S.

MILLER (Ind. Eng. Chem. [Anal.], 1936, 8, 50—51).—Dilution of  $\text{NH}_3$  with air in the initial stages causes low absorption, giving an average loss of 1.26% N. By using a modified delivery tube, provided with holes which cause the air bubbles to be broken up, this loss can be reduced to 0.06% N. E. S. H.

**Titrimetric determination of phosphoric acid in perchloric acid solution as bismuth phosphate.** J. HARMS and G. JANDER (Angew. Chem., 1936, 49, 106—109).—The conductometric titration of  $\text{H}_3\text{PO}_4$  in  $\text{HClO}_4$  solution with aq.  $\text{BiOClO}_4$  has been investigated in presence of Mg, Ca, Cu, Zn, Ni,  $\text{Fe}^{II}$ , Mn, Al, small amounts of  $\text{Fe}^{III}$ ,  $\text{NO}_3$ , Cl,  $\text{H}_2\text{SiO}_3$ , and in artificial fertilisers. With suitable precautions, the method is rapid (10—15 min.) and satisfactory.

T. G. P.

**Influence of fluorine on precipitation of phosphoric acid with molybdic acid.** H. T. BUCHERER and F. W. MEIER (Z. anal. Chem., 1936, 104, 23—28).—Quant. results for  $\text{P}_2\text{O}_5$  by the molybdate method of Lorenz, or in presence of 8-hydroxyquinoline, cannot be obtained in presence of F, which must first be removed. J. S. A.

**Micro-determination of arsenic in must and wine.**—See B., 1936, 119.

**Determination of silicon in aluminium alloys.**—See B., 1936, 151.

**Determination of free carbonic acid in waters containing humus.** Y. KAUKO (Ann. Acad. Sci. Fenn., 1934, 39, A, No. 2; Chem. Zentr., 1935, i, 3177).—The method previously described (A., 1935, 34; this vol., 159) is applied to soft surface waters. Decomposition of dissolved H carbonates introduces an error if applied to hard waters. J. S. A.

**System of qualitative analysis for the [commoner] anions.** J. T. DOBBINS and H. A. LJUNG (J. Chem. Educ., 1935, 12, 586—588).—The anions are separated into six groups, the detailed analysis of which is described. Group I, containing  $\text{CO}_3^{''}$ ,  $\text{F}'$ ,  $\text{C}_2\text{O}_4^{''}$ ,  $\text{SO}_3^{''}$ ,  $\text{AsO}_3^{'''}$ ,  $\text{AsO}_4^{'''}$ ,  $\text{PO}_4^{'''}$ , and tartrate, is pptd. as the Ca salts in alkaline solution; II,  $\text{SO}_4^{''}$  and  $\text{CrO}_4^{''}$ , as the Ba salts from alkaline solution; III,  $\text{CN}'$ ,  $\text{BO}_3^{'''}$ ,  $\text{Fe}(\text{CN})_6^{'''}$ ,  $\text{S}''$ , and  $\text{Fe}(\text{CN})_6^{''''}$ , as the Zn salts in alkaline solution; IV,  $\text{S}_2\text{O}_3^{''}$ ,  $\text{CNS}'$ ,  $\text{Br}'$ , and  $\text{I}'$ , as the Ag salts from slightly acid ( $\text{HNO}_3$ ) solution; V,  $\text{ClO}_3'$ ,  $\text{NO}_2'$ ,  $\text{OAc}'$  and VI,  $\text{NO}_3'$  are identified without pptn. Sensitivities are recorded. L. S. T.

**Use of formaldehyde for the elimination of ammonia and of ammonium salts in qualitative and quantitative analysis.** II. Application to detection of metals of the sixth group. A. HEMMELER (Annali Chim. Appl., 1935, 25, 610—617).— $\text{NH}_4$  salts, and their disturbing effect on group VI analysis, may readily be removed by adding  $\text{CH}_2\text{O}$ , thus converting them into  $(\text{CH}_2)_6\text{N}_4$  (cf. A., 1934, 1189). The group V filtrate so treated is divided into portions A and B. To A, conc. aq. or solid  $\text{NaOH}$  is added and  $\text{Mg}(\text{OH})_2$  completely pptd.; in half the filtrate  $\text{Li}'$  is detected in the usual way. In the remainder,  $\text{K}'$  is detected by adding  $\text{AcOH}$  to neutralise (phenolphthalein) followed by freshly prepared  $\text{Na}_2\text{Co}(\text{NO})_6$ ; if there is no ppt., or one of  $(\text{CH}_2)_6\text{N}_4$

*cobaltinitrite* which dissolves completely when treated with conc.  $\text{NaOH}$  followed by  $\text{AcOH}$ ,  $\text{K}'$  is absent, whilst if a yellow ppt. remains,  $\text{K}'$  is present. In portion B,  $\text{Na}'$  is detected as  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ .  $(\text{CH}_2)_6\text{N}_4$  interferes with other qual. tests for  $\text{K}'$ .

E. W. W.

**Methyl-red as an adsorption indicator.** D. M. MUKHERJEE (J. Indian Chem. Soc., 1935, 12, 748—749).—The  $p_H$  and the sp. conductivity of the solution have been determined after pptn. of  $\text{AgCl}$  in presence and in absence of Me-red. R. S.

**Determination of the radium content of rocks.** W. D. URRY (J. Chem. Physics, 1936, 4, 40—48).—The differential method for determining Ra has been applied to rock analysis. The apparatus has an observational limit of  $5.5 \times 10^{-14} \times n^{-0.5}$  g. Ra for  $n$  hourly readings. He, Ra, U, and Th, and age data are given for Keweenaw trap rocks from different levels, and also data for a geological time scale.

M. S. B.

**Detection of cadmium.** F. I. TRISCHIN (J. Appl. Chem. Russ., 1935, 8, 1269—1270).—Ag, Pb, Hg, Bi, Fe, Al, Cr, Mn, and Sn are pptd. by adding dil. aq. KI, conc. aq.  $\text{NH}_3$ , and 5—6 drops of  $\text{H}_2\text{O}_2$  to 1 c.c. of solution, the solution is filtered, and excess of KCN and a few drops of aq.  $\text{Na}_2\text{S}$  are added to the filtrate (containing Zn, Co, Ni, Cu, and Cd), when a yellow ppt. is obtained in presence of  $< 0.00056$  mg. of Cd. R. T.

**Salts of thiolbenzthiazole.**—See this vol., 215.

**Direct detection of lead with diphenylthiocarbazone.** M. KASAHARA and T. KASAHARA (Klin. Woch., 1934, 13, 1857—1858; Chem. Zentr., 1935, i, 3320).—A colorimetric variation of the method of Bohnenkamp and Linneweh (A., 1934, 1030) is described. H. N. R.

**Use of the iodine monochloride end-point in volumetric analysis.** III. Titration of thallos salts with permanganate, iodate, and ceric sulphate. E. H. SWIFT and C. S. GARNER (J. Amer. Chem. Soc., 1936, 58, 113—115; cf. A., 1930, 561).— $\text{KMnO}_4$  and  $\text{Ce}(\text{SO}_4)_2$  are unsatisfactory. The use of  $\text{KIO}_3$  is recommended. E. S. H.

**Iodometric determination of copper.** Adjustment of hydrogen-ion concentration. W. R. CROWELL, T. E. HILLIS, S. C. RITTENBERG, and R. F. EVENSON (Ind. Eng. Chem. [Anal.], 1936, 8, 9—11).—Park's procedure (A., 1931, 454) is modified. K H phthalate has no material effect on  $p_H$  of the solution and may be omitted. E. S. H.

**Spectrophotometric determination of copper in ores and mattes.**—See B., 1936, 105.

**Separation of precipitated mercuric sulphide and sulphur in the gravimetric determination of mercury.** E. R. CALEY and M. G. BURFORD (Ind. Eng. Chem. [Anal.], 1936, 8, 43).—The  $\text{HgS-S}$  mixed ppt. is dried and weighed;  $\text{HgS}$  is dissolved by treatment with cold, conc.  $\text{HI}$ , and the residual S weighed.

**Gravimetric determination of cerous salts.** P. SPACU (Z. anal. Chem., 1936, 104, 28—30).  $\text{Ce}^{III}$  salts give with  $\text{K}_4\text{Fe}(\text{CN})_6$  at room temp. a

ppt. of  $\text{CeK}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$  which may be weighed as such or dried to the trihydrate at  $100^\circ$ . J. S. A.

**Volumetric determination of indium.** H. B. HOPE, M. ROSS, and J. F. SKELLY (Ind. Eng. Chem. [Anal.], 1936, 8, 51—52).—In acetate is titrated with  $\text{K}_4\text{Fe}(\text{CN})_6$ , using diphenylbenzidine as internal indicator.  $\text{Cl}^-$  must be absent. E. S. H.

**Determination of rhenium. I. Qualitative.** L. C. HURD (Ind. Eng. Chem. [Anal.], 1936, 8, 11—15).—In the Prescott and Johnson system of analysis Re concentrates with As. Confirmatory tests for Re are described. E. S. H.

**Standardisation of permanganate solutions with sodium oxalate.** R. M. FOWLER and H. A. BRIGHT (J. Res. Nat. Bur. Stand., 1935, 15, 493—501).—Titration of  $\text{Na}_2\text{C}_2\text{O}_4$  with  $\text{KMnO}_4$  at  $60-90^\circ$  gives vals. for the normality of the latter which may be 0.4% high. 90—95% of the  $\text{KMnO}_4$  solution should be added to the aq.  $\text{Na}_2\text{C}_2\text{O}_4$  (+5% of  $\text{H}_2\text{SO}_4$ ) at  $25-30^\circ$ , the solution warmed to  $55-60^\circ$ , and the titration completed as usual. H. J. E.

**Colorimetric determination of manganese [in soils] in presence of titanium.**—See B., 1936, 114.

**Determination of manganese and magnesium in soils and silicate rocks.**—See B., 1936, 114.

**Use of potassium stannochloride dihydrate  $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  in determination of iron.** E. VOYATZAKIS (Praktika, 1934, 9, 108—111; Chem. Zentr., 1935, i, 3317).—To the strongly acid ( $\text{HCl}$ )  $\text{Fe}^{+++}$  solution,  $\text{NaHCO}_3$  is added, and then an excess of  $\text{K}_2\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  (I) (prep. described). The excess of (I) is titrated back with 0.01N-I. J. S. A.

**Determination of iron in phosphorites and apatites.**—See B., 1936, 144.

**Oxidimetric determination of molybdenum. I. Vanadate method.** R. LANG and S. GOTTLIER (Z. anal. Chem., 1936, 104, 1—16).—A neutral  $\text{MoO}_4^{--}$  solution is acidified with 15—20 vol.-% of conc.  $\text{HCl}$ , and 0.2N- $\text{SnCl}_2$  is added until no further brown coloration occurs on each addition, reducing  $\text{Mo}^{\text{VI}}$  to  $\text{Mo}^{\text{V}}$ . The excess of  $\text{SnCl}_2$ , but not  $\text{Mo}^{\text{V}}$ , is oxidised by adding aq.  $\text{Br} + \text{KBr}$ ,  $\text{Br}$  being removed by an equal vol. of 0.3N- $\text{As}_2\text{O}_3$ .  $\text{NaF}$  is added, and then  $\text{NHPh}_2$  in  $\text{H}_3\text{PO}_4$  as indicator.  $\text{Mo}^{\text{V}}$  is oxidised by addition of 0.1N- $\text{NH}_4\text{VO}_3$  (I), the excess of which is titrated back with  $\text{FeSO}_4$ . Alternatively, after addition of  $\text{As}_2\text{O}_3$ , the  $\text{Mo}^{\text{V}}$  may be titrated directly with (I), previously oxidised diphenylamine-sulphonic acid being added as indicator shortly before the end-point. The acidity during reduction must be as stated to avoid reduction to  $\text{Mo}^{\text{III}}$  or  $\text{Mo}^{\text{IV}}$ , which oxidises directly to  $\text{Mo}^{\text{VI}}$  with  $\text{Br}$ . Neutral salts or non-reducible metals do not interfere. In presence of  $\text{Fe}$  and  $\text{V}$  the method is impracticable, due to oxidation of  $\text{Mo}^{\text{V}}$  by  $\text{Fe}^{\text{III}}$  and  $\text{V}^{\text{IV}}$ . Large amounts of  $\text{Cu}$  interfere similarly.  $\text{Mo}$  may be determined in presence of  $\text{W}$  by adding  $\text{NaF}$  before reduction to keep  $\text{WO}_3$  in solution; a trace of  $\text{Cu}$  is added to catalyse the reoxidation of  $\text{W}$  compounds by  $\text{Br}$ . J. S. A.

**Reduction of uranyl ion in the uranyl oxalate actinometer.** E. C. PITZER, N. E. GORDON, and

D. A. WILSON (J. Amer. Chem. Soc., 1936, 58, 67—70).—A method for determining  $\text{U}^{\text{IV}}$  in presence of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{UO}_2^{++}$  is described. In the photolysis of actinometer solutions the complex undergoing unimol. decomp. is  $\text{UO}_2(\text{C}_2\text{O}_4)_2^{--}$ , and the source of  $\text{U}^{\text{IV}}$  is  $\text{UO}_2\text{C}_2\text{O}_4$ . The ionisation of the complex is discussed. E. S. H.

**Oxidation of stannous chloride by permanganate.** V. V. ZACHAROV and N. V. ZACHAROVA (J. Appl. Chem. Russ., 1935, 8, 1284—1286).— $\text{SnCl}_2$  may be titrated with  $\text{KMnO}_4$  in presence of  $\text{FeSO}_4$  and  $\text{H}_3\text{PO}_4$ . R. T.

**Determination of the thorium content of rocks.** W. D. URRY (J. Chem. Physics, 1936, 4, 34—40).—A method of measuring  $\text{Th}$  in quantities of the order of  $10^{-5}$ — $10^{-6}$  g. by determining the  $\alpha$ -particle activity of thoron ( $\text{Tn}$ ) in a streaming gas by a counter is described. It is possible to make a simultaneous determination of the  $\text{Pa/Ra}$  ratio in common rocks. M. S. B.

**Organic compounds as analytical reagents. II. Cinchonine iodide as reagent for determination of bismuth.** J. B. FICKLEN, I. L. NEWELL, and N. R. PIKE (Z. anal. Chem., 1936, 104, 30—34).—Cinchonine iodide is not strictly sp. for  $\text{Bi}$ . Data are given as to the interfering effect of other cations. J. S. A.

**Stable standardised gold solution.** W. C. WILLIAMS (J. Lab. Clin. Med., 1935, 80, 545—549).—Patterson's method (A., 1932, 225) is modified by use of 0.02N-KOH, the acid  $\text{Au}$  salt, and a solution of edestin for standardisation. CH. ABS. (p)

**Calorimetric apparatus.** W. A. ROTH (Chem. Fabr., 1936, 9, 10—12).—A summary of recent developments in calorimetry. J. W. S.

**Maquenne block.** R. P. JACQUEMAIN (Bull. Soc. chim., 1936, [v], 3, 142—143).—The disadvantages of the usual Maquenne block are reviewed. A Cr block is recommended. E. E. A.

**Combined hydrogen and helium liquefier.** B. V. ROLLIN (Proc. Physical Soc., 1936, 48, 18—27).—An apparatus needing only liquid air for the initial cooling, and designed for low-temp. laboratory experiments, is described. N. M. B.

**Semi-micro-Cottrell b.-p. apparatus.** M. L. WILLARD and D. E. CRABTREE (Ind. Eng. Chem. [Anal.], 1936, 8, 79—80).—The apparatus can be used with 5 c.c. of liquid and gives results accurate to  $0.1^\circ$ . E. S. H.

**Electrically-heated m.-p. apparatus.** E. DOWZARD and M. J. RUSSO (Ind. Eng. Chem. [Anal.], 1936, 8, 74—75).—The apparatus avoids the use of heating liquids and is suitable for substances with m.p.  $> 310^\circ$ , with a reproducibility of  $0.5^\circ$ . E. S. H.

**Stem correction for mercury thermometers.** M. EDENHOLM and G. OLSSON (IVA, 1935, 5—10; Chem. Zentr., 1935, i, 3692).—The formula  $\Delta t = n_1(t_a - t_c)/(k - n_1 + t_c)$ , where  $t_c$  = temp. of exposed stem, observed temp.,  $n_1$  = length of exposed stem in degrees, and  $1/k$  = apparent coeff. of cubical expansion, is proposed. H. N. R.



**General source of radiation for the visible and infra-red spectrum.** A. H. PFUND (Science, 1935, 82, 597—598). L. S. T.

**Curved quartz crystal X-ray spectrograph.** J. W. M. DuMOND and B. B. WATSON (Physical Rev., 1934, [ii], 46, 316—317). L. S. T.

**Large-aperture spectrograph suitable for the ultra-violet.** A. ARNULF and B. LYOT (Compt. rend., 1935, 201, 1480—1482).—A quartz spectrograph, aperture  $f/1$ , has been constructed using a spherical Al mirror in place of the usual objective.

T. G. P.

**Self-rectifying gas X-ray tube.** R. W. G. WYCKOFF and J. B. LAGSDIN (Rev. Sci. Instr., 1936, [ii], 7, 35—37).—An instrument previously described (Radiology, 1930, 15, 42) is improved. C. W. G.

**Simplified apparatus for fluorescence analysis.** A. KARSTEN (Zement, 1935, 24, 158—159; Chem. Zentr., 1935, i, 3315).—An apparatus, using activated metal electrodes, is described. H. N. R.

**Application of photo-electric methods to the Duboscq colorimeter.** G. BERNHEIM and G. REVILLON (Ann. Falsif., 1936, 29, 5—10).—The photo-electric cell described has a range of sensitiveness similar to that of the human eye, and consists of a small Fe plate supporting semi-conductors which are covered (by cathodic treatment) with a thin layer of an alloy of a precious metal. One of these is inserted under each of the eyepiece prisms of the Duboscq colorimeter, the two being connected through a milliammeter in opposition. Solutions tested and the corresponding max. relative matching errors are 0.6% 1.2, 0.05%  $\text{KMnO}_4$  10, 2%  $\text{CuSO}_4$  (in aq.  $\text{NH}_3$ ) 6, and 10 mg. per litre of methylene-blue 2.2%. J. G.

**Determinations with registering spherical cadmium cells.** M. BENDER (Physikal. Z., 1936, 37, 107—110).—Cd photo-cells can be used for determining the ultra-violet in sunlight. A. J. M.

**Differential refractometer.** D. RAU and W. E. ROSEVEARE (Ind. Eng. Chem. [Anal.], 1936, 8, 72—73).—The apparatus uses white light and has a sensitivity of  $5 \times 10^{-7}$ . It has been used to determine the concn. of aq. solutions with  $n=0.0004-0.002 > n$  for  $\text{H}_2\text{O}$ . The scale readings are nearly a linear function of the difference in  $n$ . E. S. H.

**Visual conductometry.** L. WOLF (Chem. Fabr., 1936, 9, 46—49).—Two galvanometer-Se-rectifier instruments are used, one in series with the titration cell and the other in parallel. The current in the main circuit is kept const. and the deflexion of the second galvanometer is observed after each addition of alkali. The accuracy can be increased by taking readings with different currents in the main circuit.

R. S.

**Directionally selective ion counter.** L. M. LANGER and R. T. COX (Rev. Sci. Instr., 1936, [ii], 7, 31—33).—A particle passing between a pair of parallel wire electrodes in a direction parallel to them produces a greater total discharge than one passing in another direction. C. W. G.

**Universal camera for electron diffraction at 10 100 kv.** H. J. YEARIAN and J. D. HOWE

(Rev. Sci. Instr., 1936, [ii], 7, 26—30).—Reflected or transmitted electron beams from a hot-filament cathode or from a discharge tube can be used. A wide range of temp. and exposures is available.

C. W. G.

**Ion sources for mass spectroscopy.** A. J. DEMPSTER (Rev. Sci. Instr., 1936, [ii], 7, 46—49; cf. A., 1935, 677).—A high-frequency alternating spark coupled inductively to a primary oscillating spark circuit is a more convenient source than a vac. vibrator or a large condenser discharge. C. W. G.

**Measurement of the breakdown and current-voltage characteristics of liquid dielectrics with direct potentials.** E. B. BAKER and H. A. BOLTZ (Rev. Sci. Instr., 1936, [ii], 7, 50—58).—Currents from  $10^{-16}$  to  $10^{-3}$  amp. can be measured. C. W. G.

**High-speed, high-sensitivity photo-electric potentiometer.** R. W. GILBERT (Rev. Sci. Instr., 1936, [ii], 7, 41—46).—The response to changes of input is instantaneous. C. W. G.

**Electro-ultra-filtration apparatus.** E. J. CZARNETZKY (Science, 1935, 82, 625—626).—An apparatus for the prep. of solutions of protein-Hg compounds is described. L. S. T.

**Mounting cell for the bulb type of glass electrode.** J. H. HIGHBERGER (J. Amer. Leather Chem. Assoc., 1936, 31, 32—34).—The apparatus described previously (A., 1935, 1097) is modified to permit the flushing of the saturated aq. KCl and the electrode chamber. D. W.

**Modified Gouy's balance for the accurate and quick measurement of diamagnetic susceptibilities.** M. B. NEVGI (Current Sci., 1935, 4, 403).—The modified instrument consists of two tubes, one of which is sealed and contains the paramagnetic substance and acts as a stopper to the other tube containing the diamagnetic specimen. An equation is deduced, and calc. results for nine org. substances are in good agreement with available data.

N. M. B.

**Utility of broken automatic pipettes.** B. N. SINGH and P. B. MATHUR (Science, 1935, 82, 626).

L. S. T.

**Apparatus for sugar and other titrations.** E. S. WEST (Ind. Eng. Chem. [Anal.], 1936, 8, 62).

E. S. H.

**Precision pycnometer for liquids.** S. T. YUSTER and L. H. REYERSON (Ind. Eng. Chem. [Anal.], 1936, 8, 61—62).—A modified apparatus is described.

E. S. H.

**Method of obtaining perfectly polished metallic surfaces.** P. JACQUET (Compt. rend., 1935, 201, 1473—1475; cf. B., 1935, 730).—The Cu specimen, polished in the ordinary way on fine emery, is made the anode in the electrolysis, at a suitable c.d., of aq.  $\text{H}_3\text{PO}_4$  or  $\text{H}_4\text{P}_2\text{O}_7$  containing at least 400 g. per litre, and maintained between  $15^\circ$  and  $25^\circ$ . T. G. P.

**Quick method of depositing polonium on silver.** M. D. WHITAKER, W. BJORKSTED, and A. C. G. MITCHELL (Physical Rev., 1934, [ii], 46, 629—630). L. S. T.

**Safety device for use with gas-heated Soxhlet.** J. C. MACRAE (Chem. and Ind., 1936, 53).—The device cuts off the gas supply if the  $H_2O$  supply to the condenser or bath begins to fail. E. S. H.

**Efficient fume hood [for laboratories].** G. W. MUHLEMAN (J. Chem. Educ., 1935, 12, 591).

L. S. T.

**Apparatus for producing vapours of constant concentration by evaporation of mixtures of liquids of different b.p.** E. V. ALEXEEVSKI and G. M. CHRAMOV (J. Appl. Chem. Russ., 1935, 8, 1319—1320).

R. T.

**Stirring apparatus for small amounts of liquid.** K. PACKENDORFF (J. pr. Chem., 1936, [ii], 144, 211—213).—An electrically operated plunger-stirrer, suitable for mixing small amounts of liquid in a gas-tight or evacuated tube, is described.

R. S. C.

**Low-pressure measurements.** W. GAEDE (Z. tech. Physik, 1934, 15, 664—668; Chem. Zentr., 1935, i, 3164).—A piece of Al foil is suspended by a quartz fibre in a glass vessel, the pressure and mol. wt. of the gas in the apparatus being deduced from observations of the vibration and damping of the Al. The range of operation is  $10$ — $10^{-7}$  mm. Hg. H. J. E.

**Laboratory hints.** A. VOSMAER (Chem. Weekblad, 1936, 33, 61—62).—The best methods for cutting different kinds of glass tubing and for cutting and boring glass plate are described.

D. R. D.

**Laboratory hints.** W. VAN TONGEREN (Chem. Weekblad, 1936, 33, 62).—A hole bored in the rubber ejector bulb of a wash-bottle is closed during use by means of a finger.

D. R. D.

**Ultramicrometer.** C. L. UTTERBACK and H. WIRTH (Physical Rev., 1934, [ii], 46, 323).—Changes in pressure of the order  $10^{-3}$  dyne per sq. cm. can be measured by the arrangement described. L. S. T.

**Organic liquids suitable for cloud expansion work.** D. D. LOUGHRIDGE and H. C. TRUEBLOOD (Physical Rev., 1934, [ii], 46, 323).—28 liquids have been studied with reference to their min. expansion ratio for condensation on  $\alpha$ -particle tracks.

L. S. T.

**Amplifier and recording apparatus for  $\alpha$ -particles, high-speed protons and neutrons.** M. C. HENDERSON (Physical Rev., 1934, [ii], 46, 324).

L. S. T.

**Measurement of very low relative humidities.** A. SIMONS (Proc. Physical Soc., 1936, 48, 135—144).—An apparatus for measuring dew points down to  $-40^\circ$ , corresponding with 0.5—10% R.H., and a hygrometer using wet and dry thermocouples are described. Calibration curves for the hygrometer for 0.5—10% R.H. and  $10$ — $90^\circ$  air temp. are given.

N. M. B.

**Automatic recording balance.** D. S. BINNINGTON and W. F. GEDDES (Ind. Eng. Chem. [Anal.], 1936, 8, 76—79).—The balance is electrically operated, fitted with oil damping, and counterbalanced for an initial load of 100 g. Wt. losses up to 17 g., with an accuracy of 0.01 g., are recorded without manual attention by an automatic device which places wts. on the pan. A continuous record is obtained on a paper chart by the use of a timed spark.

E. S. H.

**Micro-Dumas generation of carbon dioxide.** W. S. IDE (Ind. Eng. Chem. [Anal.], 1936, 8, 56).— $MgCO_3$  is introduced into the closed end of the micro-combustion tube. Before combustion, air is removed from the tube by heating the  $MgCO_3$ .

E. S. H.

**Check valve.** E. L. GREEN (Ind. Eng. Chem. [Anal.], 1936, 8, 40).—The device is designed to prevent the sucking back of liquids when passing a gas through them.

E. S. H.

**Ball mill.** L. L. QUILL (Ind. Eng. Chem. [Anal.], 1936, 8, 27).

E. S. H.

**Determination of the wall correction for the falling-sphere viscosimeter.** E. I. FULMER and J. C. WILLIAMS (J. Physical Chem., 1936, 40, 143—149).—Viscosity data have been obtained in the falling-sphere viscosimeter for castor oil, glycerol, solutions of colophony in turpentine, and two samples of honey. An equation has been derived giving the wall correction for vals. of  $r/R$  up to approx. 0.500.  $r$  and  $R$  are the radii of the sphere and the inside of the cylinder, respectively.

M. S. B.

**Surface tension by the ring method. Applicability of the Du Nouy apparatus.** R. MACY (J. Chem. Educ., 1935, 12, 573—576).—Methods by which data obtained by this method can be brought into line with those given in the International Critical Tables are described.

L. S. T.

**Practical application of lifting plate method to determination of surface tension.** W. DE KEYSER (Wis. nat. Tijds., 1934, 7, 107—118; Chem. Zentr., 1935, i, 3640—3641).—An expression is developed for the accurate determination of surface tension from the force required to lift a disc from the surface of a liquid.

J. S. A.

**Determination of surface tension of saturated aqueous solutions.** F. DE BLOCK (Wis. nat. Tijds., 1934, 7, 80—88; Chem. Zentr., 1935, i, 3641).—A lifting-disc method is applied to the determination of the surface tension of saturated solutions, and its dependence on temp.

J. S. A.

**Further applications of chemistry to archaeology.** W. FOSTER (J. Chem. Educ., 1935, 12, 577—579).—Ancient mortars and cements (Mayan), beeswax, and Pb are described.

L. S. T.

## Geochemistry.

**Temperature of atmospheric ozone.** J. DEVAUX (Compt. rend., 1935, 201, 1500—1501; cf. A., 1932, 108).—Infra-red spectra indicate a temp.  $< 0^\circ$ , which does not suffer appreciable diurnal or seasonal variation.

T. G. P.

**Penetration of solar and cosmic rays into fresh-water lakes.** G. A. LINHART (J. Physical Chem., 1936, 40, 113—119).—An equation previously deduced (Amer. Math. Month., 1935, 42, 224) is applied.

M. S. B.

**Origin of bore-hole water.** N. V. TAGEEVA (Nefit. Choz., 1934, 26, No. 7, 63—65).—Analyses are given. The  $H_2O$  originated from the ocean, and was later changed by contact with minerals.

CH. ABS. (e)

**Radium minerals.** V. CHARRIN (Rev. ind., 1935, 65, 19—20; Chem. Zentr., 1935, i, 3701).—A review of the occurrence and extraction of Ra. J. S. A.

**Occurrence of minerals in Hungary.** R. REICHERT (Foldtani Kozlony., 1934, 64, 348—356; Chem. Zentr., 1935, i, 3651).—Microscopic, chemical, and crystallographic data are given concerning Hungarian occurrences of marcasite, quartz in pyroxene andesite, hornblende and biotite, and phillipsite. J. S. A.

**Crystallographic data for Hungarian copper pyrites.** SZÁVA-KOVÁTS and K. RESCH (Foldtani Kozlony, 1934, 64, 334—341; Chem. Zentr., 1935, i, 3651).—Measurements on Cu pyrites from four sources are given. J. S. A.

**Granodiorite deposit of Štěnovic (near Pilsen) and its relation to neighbouring massifs.** A. ORLOV (Věst. stát. Geol. Ust. Česk. Repub., 1934, 10, 97—103; Chem. Zentr., 1935, i, 3651).—The oligoclase granodiorite of Štěnovic contains plagioclase (of oligoclase type, with zoned structure) 50%, quartz 20%, and orthoclase 10%, with amphibole and biotite. J. S. A.

**Chemical-mineralogical investigation of eruptive rocks of the central Sahara and the Sudan.** M. E. DENAEYER (Bull. Soc. franç. Min., 1934, 57, 284—337; Chem. Zentr., 1935, i, 3651).—A comprehensive résumé of chemical and mineralogical data. J. S. A.

**Bohmite and bayerite.** H. LEHL (J. Physical Chem., 1936, 40, 47—54).—Four definite crystalline forms of Al hydroxide are known. Diaspore gives  $\alpha$ -corundum on removal of  $H_2O$ . The other three forms, on losing  $H_2O$ , give cubic  $\gamma$ - $Al_2O_3$ . They are, in order of increasing stability, bohmite,  $Al_2O_3 \cdot H_2O$ , bayerite,  $Al_2O_3 \cdot 1.5H_2O$ , and gibbsite,  $Al_2O_3 \cdot 3H_2O$ . M. S. B.

**Helium content of minerals not emitting  $\alpha$ -rays and its explanation.** H. J. BORN (Naturwiss., 1936, 24, 73—76).—The origin of He in beryl and in alkali halides, particularly sylvine, is discussed. The He content of beryl is probably due to the action of  $\gamma$ -rays on  ${}^4Be^9$  giving  ${}^4Be^8$  and  ${}_0^1n$ , the  ${}^4Be^8$  breaking down to  ${}^2He^4$ . Sylvine and rock-salt often contain Pb, and the difference in He content of these minerals may depend on the concn. of U, Ra, and Ra-D in the  $H_2O$  from which they were originally deposited. Primary rock-salts contain only minute amounts of He. Those containing greater amounts have all been in contact with  $H_2O$  at some later period, and the high He content is connected with the high [Ra] in deep waters. A. J. M.

**Thermal decomposition of talc.** R. H. EWELL, E. N. BUNTING, and R. F. GELLER (J. Res. Nat. Bur. Stand., 1935, 15, 551—556).—Wt. losses and X-ray data are given. No change in crystal structure occurs up to 800°. At 800—840°, enstatite (I), amorphous

$SiO_2$ , and  $H_2O$  are formed. (I) forms clinoenstatite at 1200°, and amorphous  $SiO_2$  forms cristobalite at 1300°. H. J. E.

**Ejected blocks of the Laacher See district.** G. KALB (Tsch. Min. Petr. Mitt., 1936, 47, 185—210).—The sanidinites derived from crystalline schists are of two types: aegirine-augite-sanidinite (fenite) formed by pneumatolytic injection metamorphism with a phonolitic magma; and biotite-sanidinite formed by pneumatolytic contact metamorphism with an alkali-trachyte magma. L. J. S.

**Aphrosiderite from the granite of the Tatra Mts.** B. MAURITZ (Mat. Term. Ért., 1935, 53, 238—247, and Tsch. Min. Petr. Mitt., 1936, 47, 262—269).—Analysis of a chloritic mineral coating a block of granite identifies it with aphrosiderite. L. J. S.

**Yellow rock-salt from Hall in Tirol.** K. PRZIBRAM (Nature, 1936, 137, 107—108).—The discovery by Schaubberger of light-sensitive yellow rock-salt from this locality supplies the link, hitherto missing, in the formation of natural blue rock-salt. The absorption spectrum is the same as for rock-salt coloured artificially by Ra rays. The salt shows thermoluminescence, and on exposure to Ra rays it colours quickly; the artificial colour is likewise sensitive to light. L. S. T.

**Petrology of common volcanic rocks of Japan.** S. TSUBOI (Proc. V Pacific Sci. Congr., 1934, 3, 2271—2273).—The alkali-lime index for the Japanese volcanic rock series is 65.5. The compositions of pyroxenes are plotted. CH. ABS. (e)

**Chemical composition of the Deccan trap flows of Linga, Chhindwara District, Central Provinces.** L. L. FERMOR (Rec. Geol. Surv. India, 1934, 68, 344—360).—The minerals are described. Analyses are given. CH. ABS. (e)

**Occurrence of sphalerite at Ellsworth, Ohio.** G. U. GREENE (Amer. Min., 1935, 20, 882—883).—Sphalerite associated with barite or calcite is described. L. S. T.

**Morphology of phenacite from two new occurrences [at Klein-Spitzkopje, South West Africa, and the Morefield mine, Winterham, Amelia Co., Virginia].** F. H. POUGH (Amer. Min., 1935, 20, 863—874). L. S. T.

**Vectorial chemical alteration of crystals.** C. FRONDEL (Amer. Min., 1935, 20, 852—862).—Vectorial chemical alteration of crystals occurring in nature is described for pyrite (to hematite), enargite, stibnite (probably to wurtzite), and tourmaline. With barite and celestite, a partial overgrowth of a white opaque substance of later generation may simulate a vectorial alteration. Chemical changes in crystals may be affected by twinning, zoning in composition, and the physical nature of the bounding surface. Nucleation on crystal edges or surface imperfections is described for the topochemical alteration of azurite to malachite. L. S. T.

**Monticellite from San Bernardino County, California, and the monticellite series.** W. T. SCHALLER (Amer. Min., 1935, 20, 815—827).—Small

grains of monticellite (I) disseminated throughout a dolomite from the Dewey mine are the purest samples of (I) so far described. The FeO and MnO replacing MgO is < 1.50%.  $\alpha$  1.641,  $\beta$  1.649, and  $\gamma$  1.655 are < any other recorded vals. The components of the series  $\text{MgO}, \text{CaO}, \text{SiO}_2$  (I)— $\text{FeO}, \text{CaO}, \text{SiO}_2$ — $\text{MnO}, \text{CaO}, \text{SiO}_2$  (glaucochroite) are discussed and their refractive indices given. L. S. T.

**Experimental study of the porosity and permeability of clastic sediments.** H. J. FRASER (J. Geol., 1935, 43, 910—1010). L. S. T.

**Biotite system.** A. N. WINCHELL (Amer. Min., 1935, 20, 773—779).—A revision of data and diagrams (cf. A., 1925, ii, 592; 1926, 494). L. S. T.

**Occurrence and origin of celestite and fluorite at Clay Centre, Ohio.** R. B. MORRISON (Amer. Min., 1935, 20, 780—790).—Descriptive. L. S. T.

**Enargite and plumbojarosite at Picher, Oklahoma.** A. L. RANSOME (Amer. Min., 1935, 20, 799—805).—Crystals of enargite and plumbojarosite in a specimen from the Barr mine are described. L. S. T.

**Thulite in New Mexico.** S. A. NORTHPROP (Amer. Min., 1935, 20, 805—807).—Thulite,  $d$  3.15, occurs in quartz, associated with some actinolite, at Pilar Post Office, Taos Co., New Mexico. An analysis is given. L. S. T.

**Quartz paramorphs after tridymite and cristobalite.** R. S. MOEHLMAN (Amer. Min., 1935, 20, 808—810).—Abnormal forms of quartz, probably the result of inversion from tridymite and cristobalite, have been observed in Miocene volcanic rocks southwest of Ouray, Colorado. L. S. T.

**Composition of asbestos and other fibres of Thetford district, Quebec.** H. C. COOKE (Trans. Roy. Soc. Canada, 1935, [iii], 29, IV, 7—19).—Several analyses are given of carefully selected chrysotile of different degrees of softness and harshness, and these are interpreted as mixtures of serpentine ( $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ ), chlorite, talc, brucite, periclase, etc. Harshness seems to be connected with excess of  $\text{SiO}_2$  and the presence of more talc and periclase and less  $\text{H}_2\text{O}$ . Analyses of fibrous materials occurring on slickensided surfaces and in faults show that these may range from serpentine to brucite. L. J. S.

**Manganese concretions in Nova Scotia lakes.** E. M. KINDLE (Trans. Roy. Soc. Canada, 1935, [iii], 29, IV, 163—180).—The nodular or more often disc- or saucer-shaped concretions (3—6 in. across) are formed around pebbles on the bottom of the lakes, and contain  $\text{MnO}_2$  35.29,  $\text{Fe}_2\text{O}_3$  16.56%. They have probably been formed by the action of algae extracting Mn and Fe from the lake water. L. J. S.

**Role of manganese in minerals.** H. OTTO (Tsch. Min. Petr. Mitt., 1935, 47, 89—140).—Several new chemical analyses together with optical data are given of various manganese-bearing minerals (phosphates and silicates), and the results are plotted, together with data from the lit., showing a decrease in  $n$  with isomorphous replacement of  $\text{Fe}^{II}$  by  $\text{Mn}^{II}$  and an increase with replacement of Zn, Mg, Li,

Ca by  $\text{Mn}^{II}$  and of Al by  $\text{Mn}^{III}$ . The varied coloration of Mn minerals and the occurrence of Mn in different kinds of rocks are discussed. L. J. S.

**Pyrometasomatic vein deposits at Tepezala, Aguascalientes, Mexico.** A. WANDKE and T. G. MOORE (Econ. Geol., 1935, 30, 765—782).—The rock types and ore deposits are described. CaO-silicate minerals occur both as products of wall rock alteration and as gangue minerals in the veins proper. The sulphide ore, chiefly chalcopyrite with minor amounts of pyrite, sphalerite, and galena, is associated with abundant diopside (I), hedenbergite (II), garnet, epidote (III), fluorite, quartz (IV), etc. as vein gangue minerals. The marginal alteration associated with the veins consists of an intergrowth of (I), (II), (III), and (IV). This alteration affects both intruded and intrusive rock and is probably the first work of the solutions as they rose in the fractures. The sequence of mineral deposition is discussed, and a comparison with other pyrometasomatic districts is made. The deposits are considered to be of Tertiary age. L. S. T.

**Iron ore deposits of the Ilmpeia River, Eastern Siberia.** V. SOBOLEV (Econ. Geol., 1935, 30, 783—791).—The geology and petrology of the district are briefly discussed. The Fe ore deposits, which present a new instance of a special type of magnetite deposits, are described and analyses are given. Their origin also is discussed. L. S. T.

**Kaldurga conglomerates and the iron ore series of the Bababudans, Kadur district, Mysore.** (A) M. B. R. RAO. (B) C. S. PICHAMUTHU (Current Sci., 1935, 4, 415—417, 417—418).—(A) A criticism of Pichamuthu (cf. A., 1935, 1479). (B) A reply. N. M. B.

**Some deposits of lead ores in the state of Minas Geraes.** B. A. WENDEBORN (Bol. Min. Agric. [Brazil], 1935, 24, 35—77).—The geology of the region studied (a zone of 1100 km. from Sete Lagoas through Pirapora to Montes Claros, and about 10—20 km. wide) is described with especial reference to, and analyses of, the Pb ores found. E. L.

**Lead-bismuth ores in Bleka, Svartdal, Norway.** C. BUGGE (Econ. Geol., 1935, 30, 792—799).—The ore (analyses given) occurring at Bleka in quartz (I) veins in a gabbro dyke is mainly galenobismutite with small amounts of bismutite ( $\text{Bi}_2\text{S}_3$ ) and traces of galena. Emplectite has also been found. Au-bearing veins also occur and the gangue consists of dominant (I), barite, brown spar, tourmaline, and traces of fluor spar. Chalcopyrite is also important. L. S. T.

**Spectrographic evidence on origin of ores of Mississippi Valley type.** L. C. GRATON and G. A. HARCOURT (Econ. Geol., 1935, 30, 800—824).—Spectrographic examination shows that sphalerites from many deposits of the so-called Mississippi Valley type appear to contain amounts of Fe, Cu, and Pb, and of the less common elements, especially Cd, Ga, Ge, and In, commensurate with those found in deposits formed by solutions of magmatic origin. The geochemistry of the latter group of elements



in this connexion is discussed. A definite and systematic serial relationship between these sphalerites and those of hydrothermal sphalerites of a magmatic group is indicated. L. S. T.

**Steigerite, a new vanadium mineral.** E. P. HENDERSON (Amer. Min., 1935, 20, 769—772).—Steigerite (I),  $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 6.5\text{H}_2\text{O}$ , similar to fervanite (II), has been found in the U-V deposits of the Gypsum Valley, San Miguel Co., Colorado. (I),  $n$  1.71  $\pm$  0.005, has  $\text{V}_2\text{O}_5$  44.44,  $\text{Al}_2\text{O}_3$  25.14,  $\text{Fe}_2\text{O}_3$  1.50,  $\text{H}_2\text{O}$ —8.08,  $\text{H}_2\text{O} +$  21.04, total 100.20%. It is bright canary-yellow in colour, insol. in  $\text{H}_2\text{O}$ , and is easily decomposed by mineral acids. X-Ray examination shows that (I) is cryst. giving a pattern different from that of (II). L. S. T.

**Pegmatite minerals from near Amelia, Virginia.** J. J. GLASS (Amer. Min., 1935, 20, 741—768).—31 mineral species have been identified from the pegmatites of Amelia and eight of these, viz., bertrandite, biotite, chalcopyrite, phenacite, pyro-lusite, topaz, triplite, and zinnwaldite, are described in detail for the first time. The physical and optical properties of the two varieties of microlite which occur are compared, and several varieties of sericite (with analyses) are described. The zinnwaldite has  $\text{SiO}_2$  43.70,  $\text{Al}_2\text{O}_3$  22.96,  $\text{Fe}_2\text{O}_3$  0.59,  $\text{FeO}$  11.67,  $\text{TiO}_2$  0.32,  $\text{MgO}$  0.03,  $\text{CaO}$  0.02,  $\text{Na}_2\text{O}$  0.74,  $\text{K}_2\text{O}$  9.58,  $\text{H}_2\text{O}$ —0.08,  $\text{H}_2\text{O} +$  1.35,  $\text{MnO}$  1.95,  $\text{F}$  5.52,  $\text{Li}_2\text{O}$  1.92,  $\text{Rb}_2\text{O}$  1.04,  $\text{Cs}_2\text{O}$  0.10, total 101.58, (less O 2.32) 99.26%. New optical determinations and other properties of nearly all the minerals which occur at Amelia are tabulated. The less common elements, identified by spectrographic analyses in many of these minerals, are recorded. L. S. T.

**Lithology of the precipitation of "domanic" shales from the upper Devonian of the western**

**slope of the Ural mountains.** A. A. VAROV (Nef't Choz., 1934, 26, No. 7, 32—37).—The shales contain  $\text{TiO}_2$  0.2–0.3,  $\text{Mn} > 2.23$ ,  $\text{Fe}_2\text{O}_3 > 2$ , total S 2—3,  $\text{SO}_4^{2-}$  0.2—0.3%. The  $\text{P}_2\text{O}_5$  (0.1—0.5%) is higher in the carbonate shales than in the siliceous shales. CH. ABS. (e)

**Lithology of the clay facies of the carboniferous in the Samara U-bend of the Volga river.** L. A. GULJAEVA (Nef't. Choz., 1934, 26, No. 7, 26—31).—The clay from various depths ( $> 1000$  m) contained alkalis 6—10,  $\text{CO}_2 < 6$ ,  $\text{Mg}$  1—3%. It was low in Mn, Cl, and  $\text{H}_2\text{SO}_4$ . CH. ABS. (e)

**Enrichment of titania in clays.** A. SALMINEN (Suomen Kem., 1936, 9, A, 1—4).—The average  $\text{TiO}_2$  content of 27 Finnish clays was 0.68%; that of 12 sands was 0.40%. S. M. N.

**Geological aspects of recent research on coal.**—See B., 1936, 82.

**Geology and presence of petroleum in northern Ferghana.** G. I. SCHATOV (Nef't. Choz., 1934, 26, No. 10, 21—22). CH. ABS. (e)

**Geological characterisation of the Tschikischlyar oil-bearing district in Turkmenia.** A. I. KOSUIGN (Nef't. Choz., 1934, 26, No. 7, 49—55).—Analytical data are given for various volcanic, and other, gas and oil producers, on the east shore of the Caspian Sea. CH. ABS. (e)

**Athabasca oil sands: apparent example of local origin of oil.** M. W. BALL (Bull. Amer. Assoc. Pet. Geol., 1935, 19, 153—171).—The oil occurs as a film around each grain of sand. It is of asphaltic base, very heavy, high in S, and is readily cracked at  $<$  the normal temp., yielding 20—35% of gasoline. It is probably a young oil, which has not been geologically cracked. CH. ABS. (e)

## Organic Chemistry

**Comparison and critical analysis of physical properties of homologues and isomerides. Molecular volume of alkanes.** G. CALINGAERT and J. H. HLADKY (J. Amer. Chem. Soc., 1936, 58, 153—161).—A series of parallel curves is obtained by plotting  $\log V$  against no. of C atoms in the longest chain;  $n$  on a rare scale is used. Certain irregularities and the need of new data are discussed. H. B.

**Combustion of hydrocarbons I, II.**—See this vol., 294.

**Occurrence of radicals in the thermal decomposition of molecules and the reaction  $\text{CH}_3 + \text{H}_2$ .**—See this vol., 293.

**Formation of condensation products from simple hydrocarbons.** M. W. TRAVERS (Trans. Faraday Soc., 1936, 32, 236—246).—Work previously (A., 1935, 40) on the pyrolysis of  $\text{C}_2\text{H}_6$  and condensation of  $\text{C}_2\text{H}_4$  is reviewed. In presence of  $\text{H}_2$  at  $50^\circ$   $\text{CHMe} \cdot \text{CH}_2$  yields  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$ , whilst at the same time condensation proceeds from initial reactions  $2\text{C}_3\text{H}_6 = (\text{C}_3\text{H}_6)_2$  and  $\text{C}_3\text{H}_6 + \text{C}_2\text{H}_4 = \text{C}_5\text{H}_{10}$ . Preliminary experiments with  $\text{C}_2\text{H}_2$  indicate

that the state of the  $\text{SiO}_2$ -glass surface influences the nature of the reaction. F. L. U.

**Development of the intermolecular and intramolecular chains in oxidation of  $n$ -hexane.** W. M. ZAIKOVSKY (Physical Rev., 1934, [ii], 46, 329). Analytical data of the oxidised air- $n$ -hexane mixture are discussed. L. S. T.

**Isomerisation of  $n$ -heptane.** G. CALINGAERT and H. A. BEATTY (J. Amer. Chem. Soc., 1936, 58, 51—54; cf. A., 1935, 843).— $n\text{-C}_7\text{H}_{16}$  heated with  $\text{AlCl}_3$  gives pentanes (+lower hydrocarbons) 64.6% (of  $\text{C}_7\text{H}_{16}$  reacting),  $\beta$ - and  $\gamma$ -methylpentane 3.4 and 2%, respectively,  $n\text{-C}_6\text{H}_{14}$  0.4%,  $\beta\delta$ -dimethylpentane 1.5%,  $\beta\gamma$ -trimethylbutane 0.5%,  $\gamma\gamma$ -dimethylpentane 0.4%,  $\beta$ - and  $\gamma$ -methylhexane 1.2 and 1.6%, respectively, and polymerisation products 24.4%. The above % are deduced from vals. of  $n$ , b.p., and crit. solution temp. in  $\text{NH}_2\text{Ph}$ . H. B.

**Highly polymerised compounds. [Viscosity of solutions of aliphatic hydrocarbons.]** H. STAUDINGER (Ber., 1936, 69, [B], 203—208).—A reply to Meyer *et al.* (A., 1935, 1318). H. W.

**Paraffin hydrocarbon from urine of pregnancy.**—See this vol., 362.

**Mechanism of addition of halogens to ethylenic linkings.** R. A. Ogg, jun. (J. Amer. Chem. Soc., 1935, 57, 2727—2728).—The following mechanism, which applies to reactions in solution and in the dark, is suggested:  $\text{CHR}:\text{CHR} + \text{Br}^- \rightarrow \text{CHRBr}:\text{CHR}^-$   $\xrightarrow{\text{Br-Br}}$   $\text{CHRBr}:\text{CHRBr} + \text{Br}^-$ . Addition is thus catalysed by  $\text{Br}^-$ ; evidence (lit.) supporting this view is given. Since the intermediate carbanion has a stable configuration, stereoisomerides should be formed from *cis*- and *trans*-isomerides; the theories of Carothers (A., 1924, ii, 814) and Ingold (Chem. Reviews, 1934, 15, 225) lead to identical additive products. The above theory also explains the generally observed *trans* addition of Hal. H. B.

**Mechanism of polymerisation.**—See this vol., 295.

**Polymerides and polyfunctionality.**—See this vol., 295.

**Formation of high polymerides of unsaturated substances.**—See this vol., 295.

**Polymerisation of unsaturated hydrocarbons.** H. I. WATERMAN and J. J. LEENDERTSE (Trans. Faraday Soc., 1936, 32, 251—257; cf. A., 1935, 480).—A review of work previously published.

F. L. U.

**Peroxide effect in addition of reagents to unsaturated compounds. XI. Solvent effect in addition of hydrogen bromide to isobutene.** M. S. KHARASCH and W. M. POTTS (J. Amer. Chem. Soc., 1936, 58, 57—59; cf. A., 1934, 792).—Addition of HBr to isobutene in a vac. in presence of antioxidants and solvents (pentane,  $\text{CS}_2$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{EtBr}$ ,  $\text{PhCN}$ ,  $\text{PhNO}_2$ ,  $\text{H}_2\text{O}$ ) gives 80—92% yields of  $\text{Bu}^\gamma\text{Br}$ . In presence of ascaridole (0.03—0.04 mol.) and the same solvents a mixture of  $\text{Bu}^\beta\text{Br}$  (75—87% except in  $\text{CS}_2$  when 100%) and  $\text{Bu}^\gamma\text{Br}$  (13—25%) results. The data now obtained confirm the conclusion (*loc. cit.*) that solvents affect the velocity, but not the direction, of addition. H. B.

**Photoiodination of ethylenic linking at low temperatures.** G. S. FORBES and A. F. NELSON (J. Amer. Chem. Soc., 1936, 58, 182—183).—Illumination (through 10 cm.  $\text{H}_2\text{O}$ ) of an equimol. mixture of  $\Delta^a$ -butene (0.01M in  $\text{CHCl}_3$ ) and I at  $-70^\circ$  to  $-60^\circ$  with light from incandescence lamps causes 98% disappearance of I after 3 hr. (90% in  $\text{CH}_2\text{Cl}_2$  at  $90^\circ$  to  $-60^\circ$ ); I does not react with the solvent. Subsequent exposure of the solution in quartz to light from a W-steel spark causes quant. elimination of the I within 1 hr.; when the solution is kept at  $20^\circ/100$  hr., 84% elimination of I occurs. H. B.

**Dibromide method of determination of butene mixtures.** W. G. YOUNG and S. WINSTEIN (J. Amer. Chem. Soc., 1936, 58, 102—104).—Contrary to Pines (A., 1933, 1138) and Komarewsky *et al.* (A., 1935, 192), the reaction rate-dibromide method (A. 1930, 888) is trustworthy. Conversion of mixtures into dibromides (composition not altered by distillation at atm. pressure) does not cause an appreciable change in composition. Differences in composition

of the  $\text{C}_4\text{H}_8$  prepared by catalytic decomp. of  $\text{Bu}^\alpha\text{OH}$  are ascribed to the effects of catalyst and temp. rather than to analytical procedure. H. B.

**Application of the structure theory of reactions to Lebedev's synthesis of butadiene from alcohol and to Rice's theory of pyrolysis.**—See this vol., 167.

**Polymerisation of  $\Delta^a$ -butadiene in presence of metallic sodium.**—See this vol., 296.

**Induced substitution of pentene by chlorine.** T. D. STEWART and B. WEIDENBAUM (J. Amer. Chem. Soc., 1936, 58, 98—100).—The following reactions occur between  $\Delta^a$ -pentene and  $\text{Cl}_2$  in  $\text{CCl}_4$  at  $-10$  or  $25.1^\circ$ :  $\text{CH}(\text{Et}):\text{CHMe} + \text{Cl}_2 \rightarrow \text{CH}(\text{Et})\text{Cl}:\text{CHMeCl}$ ;  $\text{CH}(\text{Et}):\text{CHMe} + \text{Cl}_2 \rightarrow \text{CH}(\text{Et})\text{CH}:\text{CH}_2\text{Cl}$  (I) + HCl. Substitution is favoured by decreasing the  $[\text{Cl}_2]$ ; addition of  $\text{H}_2\text{O}$ , HCl, or powdered glass has no effect. Substitution also occurs, but to a smaller extent, with  $\text{CH}_2:\text{CH}:\text{CH}_2\text{Ph}$  but not with  $\text{CH}_2:\text{CMeCl}$  (II). A reaction mechanism is discussed. The pseudo-unimol. velocity coeffs. (mols. per litre at  $25^\circ$ ) of quaternary salt formation between  $\text{NMe}_3$  (ten-fold excess) and (I),  $\text{CH}_2:\text{CH}:\text{CH}_2\text{Cl}$  (II), and  $\text{CCl}_4$  are 0.109, 0.045, 0, and 0, respectively. H. B.

**Dicrotyl [ $\Delta^a$ -octadiene].** R. LESPIEAU and P. HEITZMANN (Bull. Soc. chim., 1936, [v], 3, 273—277).— $\text{CHMe}:\text{CH}:\text{CH}_2\text{MgBr}$  and  $\text{H}_2\text{O}$  give a mixture of dicrotyls [ $\Delta^a$ -octadienes], b.p.  $122$ — $125^\circ$  [does not add I; hydrogenated to  $n\text{-C}_8\text{H}_{18}$ ; oxidised to  $\text{AcOH}$  and  $(-\text{CH}_2\text{CO}_2\text{H})_2$ ], *trans-trans-dicrotyl*, b.p.  $124^\circ/747$  mm., m.p. about  $-76^\circ$  (*tetra-bromide*, m.p.  $84$ — $84.5^\circ$ , and *-iodide*, decomp. about  $100^\circ$ ), and *trans- $\gamma$ -methyl- $\Delta^a$ -heptadiene*, b.p.  $115^\circ$ , m.p. about  $-57^\circ$  (*di-iodide*, m.p.  $155$ — $156^\circ$ ; oxidised to  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{CO}_2\text{H}:\text{CH}_2:\text{CHMe}:\text{CO}_2\text{H}$ ; hydrogenated to  $\gamma$ -methylheptane, b.p.  $118.5^\circ$ ). R. S. C.

**Mercury-photosensitised polymerisation of acetylene.**—See this vol., 299.

**Peroxide effect in addition of reagents to unsaturated compounds. X. Addition of hydrogen bromide to methylacetylene (allylene).** M. S. KHARASCH, J. G. McNAB, and M. C. McNAB (J. Amer. Chem. Soc., 1935, 57, 2463—2465).—“Normal addition (in a vac. in absence or presence of antioxidant) of HBr to  $\text{CH}_3\text{CMe}$  (I) gives  $\text{CMe}_2\text{Br}_2$ . In presence of ascaridole (II),  $\text{CHMeBr}:\text{CH}_2\text{Br}$  is formed; the HBr must be passed into the (I)+(II) at  $-40^\circ$  to  $-33^\circ$ . (I) is not very sensitive to  $\text{O}_2$ . H. B.

**Divinylacetylene and its derivatives.** P. V. SHAVERONKOV, A. P. ALECHINA, and R. S. SCHTER (Sintet. Kautschuk, 1934, No. 2, 12—14; cf. A., 1933, 694).—Divinylacetylene (I), b.p.  $46$ — $47^\circ/200$  mm., obtained as a by-product in the prep. of chloroprene from  $\text{C}_2\text{H}_2$ , polymerises in 7—8 days in air to a gel which explodes on drying and cannot be used in the production of protective films. Antioxidants retard the formation of explosive films, whilst chlorination gives “safety” films. (I) yields *vinyl allyl ketone*, b.p.  $85$ — $86^\circ/20$  mm., by the addition of  $\text{H}_2\text{O}$ .

CH. ABS. (r)

**Reaction of butylacetylene with oxygen.** C. . . YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 55—56; cf. A., 1935, 325).—



CH<sub>3</sub>CBu, freed from olefine by regeneration from CBr<sub>4</sub>:C<sub>6</sub>H<sub>5</sub>AgNO<sub>3</sub> with aq. NaCN, forms a peroxide (attempted isolation by distillation caused decomp.); when kept in O<sub>2</sub> at 35–45°/3 months, valeric acid (8 g. from 123 g.) and polymeric material are produced.

H. B.

**Catalytic dechlorination of tetrachloroethane.** I. Decomposition by active carbon. II. Order of the decomposition reaction of tetrachloroethane. S. YAMAGUCHI (J. Chem. Soc. Japan, 1934, 55, 1227–1231, 1232–1235).—I. The effect of temp. and of various added materials is described.

II. The reaction  $2C_2H_2Cl_4 \xrightarrow{C} 2C_2H_2Cl_2 + HCl$  is of the second order in the presence of active C.

CH. ABS. (r)

**Constitution of the  $\alpha\beta$ -halogen derivatives of ethane.**—See this vol., 269.

**Allylic rearrangements.** I. Crotyl and methylvinylcarbinyl bromides. S. WINSTEIN and W. G. YOUNG (J. Amer. Chem. Soc., 1936, 58, 104–107).—Largely a more detailed account of work previously reviewed (A., 1935, 1480). Mixtures of CHMe:CH:CH<sub>2</sub>Br, b.p. 2°/5 mm., and CH<sub>3</sub>:CH:CHMeBr (I), b.p. –2°/14 mm., 31°/93 mm., are separated by fractional distillation at low temp. in a vac.; higher temp. cause rearrangement. Slow distillation/atm. pressure of a mixture [13% (I)] gives a product containing 87.5% of (I) (cf. loc. cit.).

H. B.

**Mechanism of the catalytic conversion of alcohols into diethylene hydrocarbons.** S. V. LEBEDEV, J. A. GORIN, and S. N. CHUTORETZKAJA (Sintet. Kautschuk, 1935, 4, No. 1, 8–27).—Catalytic decomp. of a mixture of EtOH and MeCHO affords butadiene (I). The influence of varying conditions on the yield of (I) is described. Catalytic decomp. of a mixture of EtOH and Et<sub>2</sub>O yields (I), together with C<sub>2</sub>H<sub>4</sub> and (CHMe)<sub>2</sub>, the proportions depending on the conditions. Mixtures of EtOH with H<sub>2</sub>O, H<sub>2</sub>, and BuOH behave similarly; the influence of varying conditions on the yield of (I) is described.

CH. ABS. (r)

containing  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butene (about 70%)  $\gamma\gamma$ -dimethyl- $\Delta^{\alpha}$ -butene (about 3%), and  $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -butene (about 27%). The formation of a radical and its immediate isomerisation,  $CH_3\cdot C^*\cdot CMe_2 \rightarrow CH_2\cdot CMe_2\cdot C^*\cdot Me$ ,  $C^*\cdot H_2\cdot CMe_2\cdot CMe_2$ , is assumed, hydrogenation at the expense of Bu<sup>2</sup> occurring at C\* atoms. The dehydration of methyltert.-butylcarbinol is explained similarly.

H. W.

**Fission and isomerisation of olefines which contain a tertiary radical.** I. N. NASAROV (Ber. 1936, 69, [B], 21–24).—Methylisopropyltert.-butylcarbinol (I) is transformed by distillation with a trace of I into  $\gamma$ -methylene- $\beta\beta\delta$ -trimethylpentane smoothly transformed by 1:4-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H into  $\beta$ -methyl- $\Delta^{\alpha}$ -propene and  $\beta$ -methyl- $\Delta^{\beta}$ -butene, also obtained directly from (I). Ethylisopropyltert.-butylcarbinol, b.p. 188–191°, is dehydrated by I to  $\delta\delta$ -dimethyl- $\gamma$ -isopropyl- $\Delta^{\beta}$ -butene, b.p. 153–158°, which is transformed by 1:4-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H into  $\beta$ -methyl- $\Delta$ -propene and, apparently,  $\beta$ -methyl- $\Delta^{\beta}$ -pentene and  $\beta$ -methyl- $\Delta^{\alpha}$ -pentene.

H. W.

**Pyrolysis of geraniol and citral.** J. DÈUVRE and R. DESMULE (Bull. Soc. chim., 1936, [v], 3, 196–206).—In presence of Pt or glass wool at 505–510° geraniol (p-xenylurethane, m.p. 69°) gives much isoprene and CMe<sub>2</sub>:CH:CHO [semicarbazone, m.p. 240° (block)]; p-nitro-, m.p. 161°, and 2:4-dinitro-phenylhydrazones, m.p. 187–188°, with CH<sub>3</sub>O, MeCHO. CHMe:CH:CO<sub>2</sub>H, (?) CMe<sub>2</sub>:CH:CH<sub>2</sub>:OH, and a mixture of (? $\beta\eta$ - and  $\beta\zeta$ -)dimethyl- $\Delta^{\beta\delta}$ -octadienes, b.p. 67–68°/20 mm., all of which arise by fission of the  $\delta\epsilon$ -linking or formation and fission of an internal  $\gamma$ -oxide. Citral gives much CH<sub>3</sub>:CHMe and other gases with a complex mixture containing  $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -nonadiene, b.p. 141–143° (corr.)/750 mm., a hydrocarbon, C<sub>10</sub>H<sub>18</sub>, b.p. 66°/19 mm., a little isoprene, and a trace of CMe<sub>2</sub>:CH:CHO.

R. S. C.

(A) Hexadecenol and tetradecenol in sperm head oil. Y. TOYAMA and T. TSUCHIYA. (B) Hexadecenol in sperm blubber oil. Y. TOYAMA and G. AKIYAMA (Bull. Chem. Soc. Japan, 1935, 10, 572–579, 579–584).—(A) Fractionation of the Ac derivatives of the unsaponifiable matter, b.p. < 180°/15 mm., of sperm head oil, conversion of the unsaturated acetates into their bromides, debromination, and refractionation of the unsaturated acetates affords the Ac derivative, b.p. 195–198°/15 mm. (oxidised by KMnO<sub>4</sub>-AcOH to *n*-C<sub>6</sub>H<sub>13</sub>·CO<sub>2</sub>H and OAc[CH<sub>2</sub>]<sub>8</sub>·CO<sub>2</sub>H), of  $\Delta^1$ -hexadecen- $\alpha$ -ol (I) (zoomaryl alcohol), I val. 98.6, and the Ac derivative, b.p. 165–170°/15 mm. (oxidised to *n*-C<sub>8</sub>H<sub>17</sub>·CO<sub>2</sub>H and  $\gamma$ -hydroxyvaleric acid), of  $\Delta^1$ -tetradecen- $\alpha$ -ol (physeteryl alcohol), I val. 111.2.

(B) The isolation (by similar methods) of (I) (16 g.) from the unsaponifiable portion (10 kg.; 36.1% of the oil) of sperm blubber oil, is described. J. W. B.

**Lipins of tubercle bacilli.** XLI. 1. Composition of timothy bacillus wax. 2. Isolation of  $\alpha$ -eicosan- $\beta$ -ol and  $\alpha$ -octadecan- $\beta$ -ol from the unsaponifiable matter of timothy bacillus wax. M. C. PANGBORN and R. J. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 10–14).—The wax (A., 1931, 526), purified by repeated pptn. from Et<sub>2</sub>O with

**Action of sulphuric acid on sec.-butyl alcohol.** N. L. DRAKE and F. P. VEITCH, jun. (J. Amer. Chem. Soc., 1935, 57, 2623–2625).—sec.-BuOH and 75% H<sub>2</sub>SO<sub>4</sub> at 80°/48 hr. under pressure give a mixture of (sec.-Bu)<sub>2</sub>O and  $\gamma\delta$ -dimethyl- $\Delta^{\beta}$ -hexene (I) [ozonolysis products, MeCHO, AcOH, and Me sec.-Bu ketone (II) (2:4-dinitrophenylhydrazones, m.p. 71.2°)]. Distillation of (I) with a trace of acid gives substances of higher mol. wt. (II) is oxidised (NaOBr) to  $\alpha$ -methylbutyric acid (p-phenylphenacyl ester, m.p. 70.6°). Whitmore's mechanism of polymerisation by acids explains the production of (I) better than that of Kline and Drake (A., 1935, 192).

H. B.

**Dehydration of methyltert.-butylcarbinol.** Fission and isomerisation of ditert.-butylethylene. I. N. NASAROV (Ber., 1936, 69, [B], 18–21; cf. Whitmore et al., A., 1933, 1140).—Distillation of methyltert.-butylcarbinol with I affords essentially  $\gamma$ -methylene- $\beta\beta\delta$ -tetramethylpentane, which readily suffers fission when heated with 1:4-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H into  $\beta$ -methyl- $\Delta^{\alpha}$ -propene and a liquid mixture

COMe., has m.p. 45°, I val. 20.5, sap. val. 66.9,  $[\alpha]_D +10.1^\circ$  in  $\text{CHCl}_3$ . Hydrolysis (5% EtOH-KOH in  $\text{N}_2$ ) gives glycerol, trehalose, optically active higher fatty acids, and a dibasic OH-acid,  $\text{C}_{70}\text{H}_{138}\text{O}_6$ , m.p. 56–57°,  $[\alpha]_D +6.1^\circ$  in  $\text{CHCl}_3$  [Ac derivative, m.p. 40–41°; Me ester, m.p. 49° (Ac derivative, m.p. 41°)]. The unsaponifiable matter consists almost entirely of higher alcohols since treatment with  $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  gives nearly quant. conversion into H phthalates. Fractional crystallisation of the alcohols (from MeOH) and their phenylcarbamates affords d-eicosan- $\beta$ -ol (I), m.p. 62.5–63°,  $[\alpha]_D +4.2$  in  $\text{CHCl}_3$  (acetate, m.p. 35–37°; benzoate, m.p. 39–40°; m.p. 78–78.5°, solidifies at 76° and remelts at 81°;  $\bar{H}$  m.p. 60–61), and d-octadecan- $\beta$ -ol (II), m.p. 56°,  $[\alpha]_D +5.7$  in  $\text{CHCl}_3$  (phenylcarbamate, m.p. 72–73°, solidifies at 66° and remelts at 76–77°). (I) is oxidised ( $\text{CrO}_3\text{-AcOH}$ , 30–40°) to eicosan- $\beta$ -one, m.p. 58–59° (oxime, m.p. 73–74°; semicarbazone, m.p. 128°), which is also prepared by alkaline hydrolysis of the product from n-heptadecyl bromide and  $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ . (II) is similarly oxidised to octadecan- $\beta$ -one, m.p. 52° (semicarbazone, m.p. 127.5°), also synthesised from n-heptadecoyl chloride and  $\text{ZnMeI}$ . H. B.

**Stability of pinacolates in liquid ammonia solution.** C. B. WOOSTER and D. S. LATHAM (J. Amer. Chem. Soc., 1936, 58, 76–78).— $(\text{CMe}_2\cdot\text{OH})_2$  (I) and  $(\text{CPhMe}\cdot\text{OH})_2$  (II) with  $\text{NaNH}_2$  (or  $\text{CNaPh}_2$ ) in liquid  $\text{NH}_3$  give the colourless  $(\text{CRMe}\cdot\text{ONa})_2$ , which are hydrolysed ( $\text{NH}_4\text{Cl}$ ) to the pinacols but no  $\text{CORMe}$ ; ketyl formation [as with  $(\text{CPh}_2\cdot\text{OH})_2$  (cf. Kraus and Bien, A., 1933, 1120)] does not occur. (I) and (II) can be titrated with  $\text{NaNH}_2$  using  $\text{CHPh}_3$  as indicator. (I) and Na in liquid  $\text{NH}_3$  give  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{ONa}$ ; (II) undergoes fission to  $\text{CHPhMe}\cdot\text{ONa}$ . Hydrobenzoin is too insol. in liquid  $\text{NH}_3$  to react with  $\text{NaNH}_2$ . H. B.

**Compounds of bivalent carbon.** XIV. Bromodimethoxymethane (formyl bromide dimethyl acetal) and its reaction with sodium triphenylmethyl. H. SCHEIBLER and H. J. SCHMIDT (Ber., 1936, 69, [B], 12–15; cf. this vol., 66).— $(\text{OMe})_2\text{CH}\cdot\text{CO}_2\text{H}$  is readily converted by Br in warm  $\text{CHCl}_3$  in direct sunlight into bromodimethoxymethane (I) b.p. 55°/12 mm., and Me H oxalate, b.p. 75°/12 mm. (K salt). (I) and  $\text{CNaPh}_3$  in  $\text{Et}_2\text{O}$  under  $\text{N}_2$  yield the unstable triphenylacetaldehyde Me., acetal, which immediately decomposes into  $\text{CHPh}_3$  and (not-isolated) dimethoxymethylene ( $\text{CO Me}_2$  acetal). H. W.

**Small-scale experiments on the autoxidation of ether.** A. RIECHE and R. MEISTER (Angew. Chem., 1936, 49, 101–103).— $\text{PhCHO}$  treated with  $\text{H}_2\text{O}_2$ , followed by  $\text{CH}_2\text{Ph}\cdot\text{OH}$  and  $\text{P}_2\text{O}_5$ , yields dibenzyl ether peroxide,  $(\text{CH}_2\text{Ph}\cdot\text{O})_2$ , m.p. 11°.  $\text{OH}\cdot\text{CHMe}\cdot\text{O}\cdot\text{H}$  (I) dehydrated with  $\text{P}_2\text{O}_5$  in  $\text{Me}_2\text{O}$  at low temp. yields the compound  $(\text{CHMe}\cdot\text{O}\cdot\text{H})_2\text{O}$ . (I) treated with  $\text{MeCHO}$  and  $\text{H}_2\text{O}_2$  in  $\text{Et}_2\text{O}$  at 20°, the mixture cooled in  $\text{Et}_2\text{O}$ -solid  $\text{CO}_2$ , and MeCl added followed by  $\text{P}_2\text{O}_5$  yields  $\alpha$ -ethoxyethyl H peroxide, which under appropriate conditions of decomp. gives EtOH, MeCHO, AcOH,  $\text{H}_2\text{O}_2$ , and polymerised

ethylidene peroxide. A complete mechanism for the autoxidation of  $\text{Et}_2\text{O}$  is suggested. T. G. P.

**Preparation of ketals of alkylacetylenes with higher alcohols.** D. B. KILLIAN, G. F. HENNING, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 80–81; cf. A., 1934, 867).—Addition of  $\text{CH}_2\text{CBu}$  to ROH ( $\text{R}=\text{Et}$ -hexyl) containing small amounts of  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  and a catalyst (prepared from red HgO and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  in MeOH) at  $\geq 70^\circ$  gives  $\text{CMeBu}(\text{OR})_2$ , which are hydrolysed (dil.  $\text{H}_2\text{SO}_4$ ) to  $\text{COMeBu}$ .  $\beta\beta$ -Diethoxy-, b.p. 68–69°/18 mm.,  $\beta\beta$ -dipropoxy-, b.p. 95–97°/18 mm.,  $\beta\beta$ -dibutoxy-, b.p. 115–117°/18 mm.,  $\beta\beta$ -diamyloxy-, b.p. 141–143°/18 mm., and  $\beta\beta$ -dihexyloxy-, b.p. 143–144°/8 mm., -hexanes are described.  $\beta\beta$ -Diethoxy-, b.p. 81–83°/18 mm.,  $\beta\beta$ -dipropoxy-, b.p. 107–109°/18 mm.,  $\beta\beta$ -dibutoxy-, b.p. 134–136°/18 mm., and  $\beta\beta$ -diamyloxy-, b.p. 148–150°/17 mm., -heptanes are similarly prepared from  $\Delta^2$ -heptinene. Ketals could not be prepared from branched-chain AlkOH. H. B.

**Thermal decomposition of methyl hydrogen peroxide.**—See this vol., 164.

**Monoalkyl phosphites and their hydrolysis.** P. NYLÉN (Svensk Kem. Tidskr. 1936, 48, 2–22). The following monoalkyl phosphites, prepared by the action of NaOH on the appropriate dialkyl phosphite, are isolated as their Na salts: Me, m.p. 125 (decomp.); Et, m.p. 183–185°;  $\text{Pr}^\alpha$ , m.p. 195–196°;  $\text{Pr}^\beta$ , m.p. 132–133°; Bu $^\alpha$ , m.p. 177.5–178.5°. K for these H esters is determined in 3.98M-NaCl at 25°. Only the undissociated H ester is oxidised by acid 1; the anion is stable towards I. A method for following the hydrolysis of the esters by acids and alkalis is described, and the equilibrium of the system  $\text{H}_3\text{PO}_4\text{-EtOH-EtH}_2\text{PO}_3\text{-Et}_2\text{HPO}_3\text{-H}_2\text{O}$  is determined. The structure of the mono- and di-alkyl phosphites is discussed. J. N. A.

**Hydrolysis of the phosphoric ester of starch and glycogen.**—See this vol., 243.

**Formation of high polymerides by condensation between metal polysulphides and dihalogenated hydrocarbons and ethers.** J. C. PATRICK (Trans. Faraday Soc., 1936, 32, 347–357). Aliphatic hydrocarbons and ethers having a halogen on each of the terminal C condense with metal polysulphides, e.g.,  $\text{Na}_2\text{S}_4$ , to form linear polymerides of high mol. wt. with the respective empirical formulae  $\text{C}_2\text{H}_4\text{S}_4$  and  $\text{C}_4\text{H}_8\text{OS}_4$ . Both types frequently exhibit rubber-like properties. By treatment with NaOH half the S is removed, the residual substance losing its rubbery nature if formed from a hydrocarbon, but retaining it if formed from an ether. S can be re-introduced, and (in the former case) rubbery properties restored, by a process analogous to the vulcanisation of rubber. Theories of chemical structure and of the mechanism of the heat-vulcanisation are advanced. F. L. U.

**Preparation of lower alkanesulphonic acids.** D. L. VIVIAN and E. E. REID (J. Amer. Chem. Soc., 1935, 57, 2559–2560).—Anhyd. Alk $\cdot\text{SO}_3\text{H}$  are obtained from conc. aq. solutions after 4–5 distillation at 1 mm.; the pure acids soon darken even in a vac. The following are described: n-propane,



b.p. 136°/1 mm., m.p. 7.5°, *n*-butane-, b.p. 147°/0.5 mm., -15.2°, *n*-pentane-, b.p. 163°/1 mm., m.p. 15.9, and *n*-hexane, b.p. 174°/1 mm., m.p. 16.1°, -sulphonic acids. The alternation in m.p. resembles that for  $\text{Alk}\cdot\text{CO}_2\text{H}$ . H. B.

**Interaction of diazonium salts and acetone-sulphonic acid.** G. D. PARKES and S. J. M. FISHER (J.C.S., 1936, 83—85).—Diazotised  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$  and Na acetonesulphonate give Na methylglyoxal-*p*-bromophenylhydrazone- $\omega$ -sulphonate, m.p. 224° (decomp.). The following are similarly obtained: Na methylglyoxal-phenyl-, m.p. 195° (decomp.), -*p*-chlorophenyl-, m.p. 228° (decomp.), -2:4-dichlorophenyl-, m.p. 210° (decomp.), -2:4-dibromophenyl-, m.p. (decomp.), -*o*-nitrophenyl-, m.p. 256° (decomp.), -*m*-nitrophenyl-, m.p. 251° (decomp.), and -*p*-nitrophenylhydrazone- $\omega$ -sulphonate, m.p. 265° (decomp.). Na methylglyoxalphenylhydrazone- $\omega$ -sulphonate with 1 or 2 mols. yields  $\alpha$ -bromomethylglyoxal-*n*-bromophenylhydrazone, with 3 mols. of Br gives  $\beta\omega$ -dibromo- $\alpha$ -ketopropaldehyde-*p*-bromophenylhydrazone, and with excess of Br forms  $\beta\beta\omega$ -tribromo- $\alpha$ -ketopropaldehyde-2:4-dibromophenylhydrazone.

**Esterification as a gas reaction.**—See this vol.,

**Hydrolysis rates of some monoacid triglycerides under the influence of pancreas extract.** I.—See this vol., 297.

**Catalytic hydrogenation of acid chlorides in the vapour phase at atmospheric pressure.** N. and C. G. DANOV (J. pr. Chem., 1936, 217—224).—Hydrogenation (Pd-asbestos) of the appropriate acid chloride at the b.p. gives some  $\text{CHPr}\cdot\text{CHEt}\cdot\text{CHO}$ , isovaleryl-butyrolactone (54%), from succinyl chloride,  $\text{PhCHO}$  (89%),  $\text{CH}_2\text{Ph}\cdot\text{OH} + \text{PhEt}$ , and  $n\text{-C}_6\text{H}_{13}\text{COCl}$ . S and P compounds must be entirely absent. Raney Ni cannot be used. R. S. C.

**Catalysis in organic chemistry. V. Decompositions of esters and acids by anhydrous zinc chloride.** H. W. UNDERWOOD, jun., and O. L. BARN (J. Amer. Chem. Soc., 1935, 57, 2729—2730).— $\text{Alk}\cdot\text{CO}_2\text{H}$  (I) and their Me, Et, Pr, and Bu esters are unaffected by anhyd.  $\text{ZnCl}_2$  (II) (cf. A., 1930, 321; 1931, 1034); the amyl esters undergo slow decomposition (I) and unsaturated hydrocarbon (III). The rate of decomp. of  $\text{Alk}\cdot\text{CO}_2\text{Alk}'$  increases with the no. of C atoms in  $\text{Alk}'$ . The esters of aliphatic dibasic acids (IV) give the Zn salt of (IV) and HCl [which reacts with (III) to form  $\text{AlkCl}$ ].  $\text{ArCO}_2\text{R}$  decompose to (III) and  $\text{ArCO}_2\text{H}$  (which then gives  $\text{CO}_2$  and  $\text{ArH}$ ). All the (III) produced undergo polymerisation; the amount increases with the no. of C atoms. When (II) is insol. in the hot acid or ester no decomp. occurs. Numerous examples are given.  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  gives  $\text{CO}$ ,  $\text{CH}_2\text{O}$ , and HCl;  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  affords  $\text{CO}$ ,  $\text{COCl}_2$ , and HCl. H. B.

**Preparation of acetylenecarboxylic acids with sodamide. Synthesis of ethylpropionic acid.** A. E. FAVORSKI and V. O. MOCHNATSK (Bull. Far. Eastern Branch Acad. Sci. U.S.S.R., 1934, No. 9,

3 6; cf. A., 1888, 1168).—Treatment of  $\alpha\beta\text{-C}_4\text{H}_8\text{Br}_2$  with  $\text{NaNH}_2$  in kerosene, followed by passage of  $\text{CO}_2$ , gives a 46% yield of  $\Delta^2$ -pentenoic acid, b.p. 81—m.p. 50–6°. The prep. from  $\text{COMeEt}$  and  $\text{PCl}_5$ , followed by  $\text{NaNH}_2$  and  $\text{CO}_2$ , gave only poor yields. CH. ABS. (r)

**Tetradecenoic and dodecenoic acids in sperm oil.** I. Tetradecenoic and dodecenoic acids in sperm blubber oil. II. Dodecenoic acid in head oil. Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1935, 10, 563—569; 570—573).—I. After fractionation of their Me esters and hydrolysis, the fatty acids (2.4%) of sperm blubber oil (from *Physeter macrocephalus*, L.) are separated into fractions (i) b.p. 172—177°/15 mm., and (ii) b.p. 192 197°/15 mm. By the Pb-soap method (i) affords  $\Delta^8$ -dodecenoic acid (I), termed *denticetic acid*, converted into a Me dihydroxylaurate which gives  $n\text{-C}_6\text{H}_{13}\cdot\text{CO}_2\text{H}$  and glutaric acid (II) when oxidised with  $\text{KMnO}_4$  in  $\text{COMe}_2$ . Similarly (ii) gives  $\Delta^8$ -tetradecenoic acid (identical with physeric acid from sperm head oil), converted into a Me dihydroxy-myristate, oxidised ( $\text{KMnO}_4$ ) to  $n\text{-C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$  and (II). Neither  $\Delta^8$ -tetradecenoic nor  $\Delta^8$ -dodecenoic acid (Hilditch *et al.*, B., 1928, 307) could be detected.

II. (I) is isolated from the unsaturated fatty acids, b.p. 172 177°/15 mm., obtained by usual methods from sperm head oil, and its structure is established as above. J W

**Drying of oils and related unsaturated compounds.** R. S. MORRELL and W. R. DAVIS (Trans. Faraday Soc., 1936, 32, 209—215; cf. this vol., 298).—Of the possible combinations between maleic anhydride and  $\alpha$ - and  $\beta$ -elaeostearic acids, only one is formed with each, viz., at the pair of conjugated double linkings remote from the  $\text{CO}_2\text{H}$  in the  $\alpha$ - and nearer the  $\text{CO}_2\text{H}$  in the  $\beta$ -acid. The former (I) does not, and the latter (II) does, exhibit "drying" properties at room temp. Changes occurring in both compounds have been studied by measurements of the  $\text{O}_2$  absorbed, peroxide val., I val., and viscosity, and by examination of the chemical structure of the products. In (I) only the ethenoid linking in the aliphatic chain is oxidised, yielding a product with  $\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot$ , which undergoes no further change. In (II) a similar oxidation occurs at the ring ethenoid linking, whilst the remote aliphatic linking gives rise to a peroxide which is solely responsible for the ensuing polymerisation. Polymerisation in this, and in similar materials such as tung oil, is shown by a steady increase of viscosity which is accompanied by a concomitant disappearance of the peroxide radical. A chemical interpretation, supported by structural evidence, is put forward. The influence of polar and non-polar solvents is discussed.

F. L. U.

**Polymerisation in monolayers.**—See this vol., 298.

**Relative rates of ozonisation of unsaturated compounds.** C. R. NOLLER, J. F. CARSON, H. MARTIN, and K. S. HAWKINS (J. Amer. Chem. Soc., 1936, 58, 24—27).—The  $\text{O}_3$ -absorption curves (cf. Brus and Peyresblanques, A., 1930, 449, 588) for

oleic and elaidic acids, Me oleate, 1-phenyl- $\Delta^1$ -cyclohexene, and stilbene show that rapid addition of 1 mol. to the C:C occurs. The rate of addition decreases considerably with CHPh.CPh<sub>2</sub> and compounds containing  $\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot$  (e.g., vinylacetic, crotonic, cinnamic, and itaconic acids; CHMe:CH $\cdot$ CHO); a further decrease is observed with CPh<sub>2</sub>.CPh<sub>2</sub> and CHCl:CHCl. With compounds containing 2 or 3 double linkings (e.g., diphenylbutadiene; sorbic and elaeostearic acids), rapid addition of 1 mol. occurs; the rate then decreases. With geometrical isomerides which undergo relatively slow addition (e.g., Me fumarate and maleate; mesaconic and citraconic acids), the *trans*-form reacts more rapidly. H. B.

**Lipins of tubercle bacilli. XLII. Phthioic acid.** M. A. SPIELMAN and R. J. ANDERSON (J. Biol. Chem., 1936, **112**, 759—767; cf. this vol., 24).—Phthioic acid, C<sub>26</sub>H<sub>52</sub>O<sub>2</sub>, m.p. 20—21° (best purified by way of the Me ester, b.p. 158°/0.003 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.2° in Et<sub>2</sub>O, and characterised as *amide*, m.p. 45°), with CrO<sub>3</sub>-AcOH gives only a branched-chain acid, C<sub>11</sub>H<sub>20</sub>O<sub>2</sub> (p-C<sub>4</sub>H<sub>9</sub>CO $\cdot$ CH<sub>2</sub> ester, m.p. 49—50°; tribromoanilide, m.p. 111°). The *methylamide*, m.p. 27°, with PCl<sub>5</sub>-C<sub>6</sub>H<sub>6</sub> gives indefinite Cl nos. of no constitutive val. Grignard-CrO<sub>3</sub> degradation of the ester gives a mixture (impure *semicarbazone*, m.p. 55—65°). The acid is a polymethylated long-chain acid and probably has at least one Me close to the CO<sub>2</sub>H since [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.56° in Et<sub>2</sub>O, is high. The very pure acid retains the physiological properties previously reported. R. S. C.

**$\epsilon$ -Hexolactone.** F. J. VAN NATTA, J. W. HILL, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1936, **58**, 183).—Partly a reply to Stoll and Rouvé (A., 1935, 1351). Further details (cf. A., 1934, 392) for the prep. of  $\epsilon$ -hexolactone are given. H. B.

**Highly polymerised compounds. CXXXIII. Viscosity of solutions of glycol esters and dicarboxylic esters.** H. STAUDINGER and H. MOSER (Ber., 1936, **69**, [B], 208—213).—The observed sp. viscosities of C<sub>6</sub>H<sub>6</sub> and CHCl<sub>3</sub> solutions of esters of higher fatty acids and decane- $\alpha\kappa$ -diol and of esters of sebacic and thapsiaic acid agree with those calc. from the formula  $\eta_{sp.}/c = 1.4\%$  and the temp. coeff. is the same as that observed with other aliphatic compounds of similar structure, thus showing that  $\eta_{sp.}$  of a solution depends essentially on the length of the mol. and is independent of its special structure. With derivatives of propane- $\alpha\gamma$ -diol the observed  $\eta_{sp.}$  is lower than the calc. but the temp. effect is normal. A shortening of the chain due to inter-attraction of the O atoms appears to be indicated. The following are incidentally described: *dilaurate*, m.p. 47—48°, *dimyristate*, m.p. 56—57°, and *dipalmitate*, m.p. 62—63°, of decane- $\alpha\kappa$ -diol; *dicetyl sebacate*, m.p. 53.5—54.5°; *dicetyl*, m.p. 62.5—63°, and *dioleyl*, m.p. 35—35.5°, *thapsiate*; *dilaurate*, m.p. 38—39°; *dimyristate*, m.p. 49.0—49.5° and *dipalmitate*, m.p. 54.5—55.5°, of propane- $\alpha\gamma$ -diol. H. W.

**Influence of heat and of the presence of various cations on oxalic acid solutions.** A. M. VASILIEV and N. I. PANOVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 79—82).—H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is volatile

from conc. aq. solution on boiling. Most salts are stable but Mn causes loss of acid even in dil. solution.

CH. ABS. (7)

**Oxidation of ethyl hydrogen methylmalonate and of ethyl hydrogen succinate with potassium persulphate.** F. FICHTER and J. HEER (Helv. Chim. Acta, 1936, **19**, 149—154).—CO<sub>2</sub>K $\cdot$ CHMe $\cdot$ CO<sub>2</sub>Et and CO<sub>2</sub>K $\cdot$ CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et behave when oxidised with KSO<sub>4</sub> in the same manner as when electrolysed according to Crum Brown and Walker, EtCO<sub>2</sub>Et and CH<sub>2</sub>:CH $\cdot$ CO<sub>2</sub>Et being obtained in addition to ( $\cdot$ CHMe $\cdot$ CO<sub>2</sub>Et)<sub>2</sub> from the former and Et<sub>2</sub> adipate from the latter. Electrosynthesis is therefore an oxidation in the sense 2CO<sub>2</sub>H $\cdot$ CHMe $\cdot$ CO<sub>2</sub>Et + O = 2CO<sub>2</sub> + H<sub>2</sub>O + ( $\cdot$ CHMe $\cdot$ CO<sub>2</sub>Et)<sub>2</sub> and 2CO<sub>2</sub>H $\cdot$ CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et + O = ( $\cdot$ CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et)<sub>2</sub> + 2CO<sub>2</sub> + H<sub>2</sub>O. The yields of Et<sub>2</sub> esters are less by the oxidative than by the electrolytic method and decrease with increasing mol. wt. of the initial material. Et H methylmalonate has b.p. 111°/1 mm. H. W.

**Carbon dioxide cleavage from dibromomalonic acid. II.**—See this vol., 295.

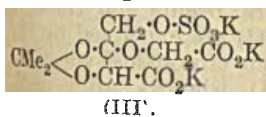
**Formation of succinic acid by *B. coli*.**—See this vol., 247.

**Lichen substances. LXII. Components of *Cetraria islandica*, Ach.** Y. ASAHINA and M. YANAGITA (Ber., 1936, **69**, [B], 120—125).—*C. islandica*, Ach., from Hokkaido contains about 4% of a mixture of fatty acids which affords *d-protolichesteric acid* (I), m.p. 106°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.07 in CHCl<sub>3</sub> when crystallised from AcOH, and *l-allo-protolichesteric acid* (II), m.p. 88°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -56.34° in EtOH, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -49.53° in CHCl<sub>3</sub>. Since (II) is transformed by warm Ac<sub>2</sub>O into *l*-lichesteric acid and converted by CH<sub>3</sub>N<sub>3</sub> into a *pyrazoline* derivative. C<sub>22</sub>H<sub>36</sub>O<sub>4</sub>N<sub>2</sub>, m.p. 68—69°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -73.69° in CHCl<sub>3</sub>, it is structurally identical with *protolichesteric acid*. It is oxidised by alkaline KMnO<sub>4</sub> to myristic acid. Treatment of the mixture of fatty acids with Ac<sub>2</sub>O at 100° gives *dl-lichesteric acid*, m.p. 115°, also obtained from its components. Catalytic hydrogenation (Pd in AcOH) of (II) affords *dihydro-l-allo-protolichesteric acid*, m.p. 92—93°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -7.41 in CHCl<sub>3</sub>. Similarly, (I) gives *dihydro-d-protolichesteric acid*, m.p. 106°, [ $\alpha$ ]<sub>D</sub><sup>15</sup> +34.60° in CHCl<sub>3</sub>, transformed by CH<sub>3</sub>N<sub>3</sub> into a *pyrazoline* derivative, m.p. 54—55°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> +190.60° in CHCl<sub>3</sub>. Extraction of the thall of Japanese *C. tenuifolia*, Retz, with H<sub>2</sub>O yields *d-protolichesteric acid*, m.p. 106°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -12.12° in CHCl<sub>3</sub>, hydrogenated to *dihydro-l-protolichesteric acid*, m.p. 106°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -30.96°, whence the *pyrazoline* derivative, m.p. 54—55°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -183.1° in CHCl<sub>3</sub>. H. W.

**Action of periodic acid on tartaric acid.** P. FLEURY and (MLLE.) G. BON-BERNATETS (J. Chim., 1936, [viii], 23, 85—99; cf. A., 1933, 591, Malaprade, A., 1934, 1090).—In the first stage of the reaction, which is complete in 5—10 min., H<sub>2</sub>O<sub>2</sub> gives up O, 2CHO $\cdot$ CO<sub>2</sub>H (I) being produced; in the second, which is complete in 36—48 hr. at room temp. (2 hr. at 37°), (I) is oxidised to HCO<sub>2</sub>H and CO<sub>2</sub>, taking O from HIO<sub>4</sub>. Hence each mol. of tartaric acid requires 3HIO<sub>4</sub> for completion of the reaction.



**Constitution of isopropylidenefurtondicarboxylic acids.** H. OHLE and N. SENGEL (Ber., 1936, 69, [B], 160—170; cf. A., 1929, 913; 1931, 72; 1932, 144, 148).—Oxidation of  $\beta$ -diisopropylidene-fructose (I) with  $\text{KMnO}_4$  ( $\equiv 4\text{O}$ ) gives  $K_2$   $\beta$ -isopropylidene-*l*-furtondicarboxylic acid, ( $+\text{H}_2\text{O}$ ) (II),  $[\alpha]_D^{25} +53.2^\circ$  in  $\text{H}_2\text{O}$  [corresponding  $\text{Ag}_2$  ( $+\text{H}_2\text{O}$ ),  $\text{Ba}$  ( $+\text{H}_2\text{O}$ ), and  $\text{Ca}$  ( $+\text{H}_2\text{O}$ ) salts]. (II) is transformed by pyridine-*l*-sulphonic acid in  $\text{C}_5\text{H}_5\text{N}$  into  $K_2$   $\beta$ -isopropylidene-*l*-furtondicarboxylate *l*-sulphate (III) (*loc. cit.*), so that (II) is the parent of (III). Methylation of the  $\text{Ag}$  salt of (II) affords  $\alpha$ -isopropylidenedioxy- $\beta$ -carbomethoxymethoxy- $\gamma$ -butyrolactone (IV) m.p.  $89.5^\circ$ ,  $[\alpha]_D^{25} +56.6^\circ$  in  $\text{MeOH}$ ,  $+64.2^\circ$  in  $\text{C}_6\text{H}_6$ , which regenerates (II) when hydrolysed by alkali, and *Me*  $\gamma$ -methoxy- $\alpha$ -isopropylidenedioxy- $\gamma$ -carbomethoxymethoxy-*n*-butyrate, b.p.  $140^\circ$  (bath)/0.05 mm.,  $[\alpha]_D^{25} +33.8^\circ$  in  $\text{MeOH}$ , hydrolysed by  $\text{KOH-MeOH}$  to  $K_2$   $\gamma$ -methoxy- $\alpha$ -isopropylidenedioxy- $\gamma$ -carbomethoxy-*n*-butyrate (V),  $[\alpha]_D^{25} +45.85^\circ$  in  $\text{H}_2\text{O}$  (corresponding  $\text{Ag}_2$  contains an active  $\text{H}$  of unknown location. When hydrolysed by acid it evolves  $\text{CO}_2$  with much greater difficulty than does (II). When treated with boiling  $\text{HCl-MeOH}$  it gives (in about 90% yield) hydroxyketonic acid, identified by dehydrogenation with  $p\text{-O:C}_6\text{H}_4\text{:O}$  and coupling with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  to the quinoxaline derivative,  $\text{C}_{16}\text{H}_9\text{O}_4\text{N}_2$ . Analogously (IV), (V) decomposes into  $\text{COMe}_2$ ,  $\text{CO}_2$ , and  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , but the expected dihydroxymethylacetone could not be detected with certainty. (III) therefore the structure shown and the analogy between fermentative and



Oxidative fission is purely formal. Examination of the graphs of the oxidation of (III) by  $\text{KMnO}_4$  in alkaline and neutral solution together with previous observations (*loc. cit.*) show that oxidation of (I) proceeds in two fundamentally different manners determined by  $[\text{H}^+]$  and  $[\text{OH}^-]$ , respectively. In alkaline solution the oxidant at first attacks almost exclusively the  $\text{OH}$  of  $\text{CH}_2\cdot\text{OH}$ . In neutral solution oxidation takes place preferentially at the  $\text{CH}$  linkings of the etherified  $\text{OH}$  groups.

H. W.

**Synthesis of vitamin-C from starch.** P. P. T. SAH (Ber., 1936, 69, [B], 158—159).—The synthesis of *l*-ascorbic acid (I) through the following steps is announced; the details will follow.  $\text{Starch} \rightarrow d\text{-saccharic acid} \rightarrow l\text{-gulonic acid} \rightarrow l\text{-gulonolactone} \rightarrow l\text{-glucose} \rightarrow l\text{-gulosazone} \rightarrow l\text{-gulosone} \rightarrow \alpha\text{-keto-}l\text{-gulonic acid} \rightarrow \text{Me } \alpha\text{-keto-}l\text{-gulonate} \rightarrow \text{(I)}$ .

H. W.

**Starch as a starting material for the synthesis of vitamin-C.** P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, C, 3, 265—277).—A detailed account of the work already reviewed (cf. preceding abstract). The possible, similar use of lactose is suggested.

H. W.

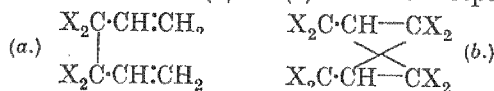
**Reactions of vitamin-C.**—See this vol., 255.

**Constitution of glauconic acids.** IV. H. SUTTER, F. ROTTMAYR, and H. PORSCH (Annalen, 1936, 521, 180—197; cf. A., 1935, 1224).—Proof that the thermal decomp. product of glauconic acid (A., 1933, 1143) is  $\text{CH}_2\text{Et}\cdot\text{CET}\cdot\text{CHO}$  is obtained by its oxidation with  $\text{Ag}_2\text{O}$  to the acid, b.p.  $116^\circ/13$  mm. (chloride,

b.p.  $62^\circ/13$  mm.; *amide*, m.p.  $117^\circ$ ), identical with a specimen synthesised by condensation of  $\text{CH}_2\text{EtBr}\cdot\text{CO}_2\text{Et}\cdot\text{Zn}\cdot\text{EtCHO}$  to give the *OH*-ester b.p.  $107\text{—}122^\circ/18$  mm., converted by  $\text{PCl}_5$  and subsequent hydrolysis with  $\text{KOH-EtOH}$  into  $\text{CH}_2\text{Et}\cdot\text{CET}\cdot\text{CO}_2\text{H}$ . The *amides* of tiglic, m.p.  $77^\circ$ , and of  $\beta\beta$ -dimethylacrylic acid, m.p.  $108^\circ$ , were prepared for comparison. Glauconic acid (I) m.p.  $188^\circ$ ,  $[\alpha]_D^{25} +189.6^\circ$  in  $\text{CHCl}_3$ , has equiv. 83, and gives a  $\text{Ag}_4$  salt which, with  $\text{MeI-MeOH}$  affords only a *Me*<sub>2</sub> ester, m.p.  $145^\circ$ . (I) gives a compound,  $\text{C}_{18}\text{H}_{21}\text{O}_6\text{N}$ , m.p.  $207\text{—}208^\circ$ , with  $\text{NH}_2\text{OH}$ , and a compound,  $\text{C}_{20}\text{H}_{22}\text{O}_4\text{H}_4$ , m.p.  $122^\circ$ , with  $\text{NHPh}\cdot\text{NH}_2$ . Reduction of (I) with  $\text{Zn-AcOH}$  affords (mainly) a dicarboxylic acid,  $\text{C}_{18}\text{H}_{27}\text{O}_7$ , m.p.  $209^\circ$  (*Me*<sub>2</sub> ester, m.p.  $161^\circ$ ), and traces of an acid,  $\text{C}_{20}\text{H}_{24(26)}\text{O}_7$ , m.p.  $201^\circ$  (*Me* ester, m.p.  $193\text{—}194^\circ$ ), and a neutral substance,  $\text{C}_{18}\text{H}_{22}\text{O}_6$ , m.p.  $192^\circ$ . (I) is stable to most oxidising agents, but with  $\text{NaOCl-NaOH}$  it gives a substance,  $\text{C}_{16}\text{H}_{20(22)}\text{O}_4\text{Cl}_2$ , m.p.  $200^\circ$ . The structure of (I), which probably contains the system  $\text{OH}\cdot\text{C}\cdot\text{C}\leq\text{C}\cdot\text{CO}\cdot\text{O}$  reduced to  $>\text{C}\cdot\text{C}\leq\text{C}\cdot\text{CO}$ , is briefly discussed.

J. W. B.

**Possibility of ring-chain mesomerism.** II. **Properties of  $\Delta^{\alpha\alpha}$ -hexadiene- $\alpha\gamma\gamma\delta\zeta\zeta$ -octacarboxylic esters.** C. K. INGOLD, M. M. PAREKH, and C. W. SHOPPEE (J.C.S., 1936, 142—153).—The work of Guthzeit and Hartmann (A., 1910, i, 386) on the ester obtained from Et sodiodicarboxyglutaconate and I has been repeated, without complete confirmation. The *Me* series has also been prepared and the constitution of the compounds is discussed. The observations do not support the *dicyclobutane* formula for the ester nor a structure with fused *cyclobutane* rings, but are in favour of (a) or (b). The corresponding



*Me* compounds are given in brackets. Oxidation of Et  $\Delta^{\alpha\alpha}$ -hexadiene- $\alpha\gamma\gamma\delta\zeta\zeta$ -octacarboxylate (I) [*Me*<sub>8</sub> ester (II), m.p.  $139^\circ$ ] with  $\text{KMnO}_4$  gives Et<sub>6</sub> H<sub>2</sub>  $\Delta^{\alpha\alpha}$ -hexadiene- $\alpha\gamma\gamma\delta\zeta\zeta$ -octacarboxylate [*Me*<sub>6</sub> ester m.p.  $218^\circ$  (decomp.)], which with  $\text{SOCl}_2$  yields the Et<sub>6</sub> ester dichloride,  $\text{C}_6\text{H}_2(\text{CO}_2\text{Et})_6(\text{COCl})_2$ , m.p.  $65\text{—}66^\circ$ . (I) and  $\text{HCl}$  afford Et<sub>4</sub> H<sub>2</sub> 3-hydroxy-2:4:4:5:5-pentacarboxycyclopentane-1-acetate, m.p.  $152^\circ$ , and its *anilide*, m.p.  $152^\circ$  [*Me* ester, m.p.  $245^\circ$  (decomp.)], converted into the neutral Et<sub>6</sub> ester, m.p.  $71^\circ$  [*Me*<sub>6</sub> ester, m.p.  $168^\circ$ ]. 3-Hydroxy-2:4:5-tricarboxycyclopentane-1-acetate, prepared by hydrolysis of the foregoing esters, has m.p.  $193^\circ$ , is stable to  $\text{KMnO}_4$ , and gives *Me* and *Et* esters; the constitution of this substance was given incorrectly by previous authors. Ozonolysis of (I) and (II) gives Et and *Me* ethane-tetracarboxylate, respectively. (II) and  $\text{NaOMe}$  afford *Me* 3-methoxy-2:2:4:4:5:5-hexacarboxycyclopentane-1-malonate, m.p.  $193^\circ$ , whilst thermal decomp. of (II) leads to *Me* 6-methoxy- $\alpha$ -pyrone-3:5-dicarboxylate. Electrolysis of (II) in  $\text{H}_2\text{SO}_4$  gives *Me*<sub>8</sub> dihydro-2:2:4:4:5:5-hexacarboxycyclopentane-1-malonate, m.p.  $149^\circ$ , which with  $\text{HCl}$  forms the *Me*<sub>6</sub> H<sub>2</sub> ester, m.p.  $252^\circ$  (decomp.), hydrolysed to 2:4:5-tricarboxycyclopentane-1-acetic acid, m.p.  $225^\circ$  [*Ag*



salt; *amide*, m.p. 280° (decomp.). The red  $\text{Na}_4$  salt of Guthzeit does not exist. *Me* 3-hydroxy-2:4:5-tricarboxycyclopentane-1-acetate is dehydrated ( $\text{KHSO}_4$ ) to a mixture of isomeric -pentene-1-acetates, reduced to a mixture of acids. F. R. S.

**Photochemical reactions of SH-compounds in solution.**—See this vol., 171.

**Derivatives of  $\beta$ -sulphopropionic acid.** L. A. BIGELOW, H. W. SIGMON, and D. H. WILCOX, jun. (J. Amer. Chem. Soc., 1935, 57, 2521—2524).—*Me*<sub>2</sub>, b.p. 132—133° (slight decomp.)/1 mm., m.p. 17°, *Et*<sub>2</sub>, m.p. 4°, *Pr*<sup>a</sup><sub>2</sub>, m.p. -7°, *Bu*<sup>a</sup><sub>2</sub>, m.p. -25°, and *di*-(phenylethyl), m.p. 59°,  $\beta$ -sulphopropionates are prepared from the anhyd.  $\text{Ag}_2$  salt (cf. Rosenthal, A., 1886, 866) and  $\text{RI}$ . The dry  $\text{K}_2$  salt and  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  afford the unstable acid chloride ( $\text{I}$ ),  $\text{COCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Cl}$ , m.p.  $-9\pm 1^\circ$  (cf. *loc. cit.*); the normal *dianilide*, m.p. 161°, is prepared. ( $\text{I}$ ) and dry  $\text{NH}_3$  in  $\text{C}_6\text{H}_6$  give (probably)  $\text{NH}_4$   $\beta$ -sulphopropionimide,  $\begin{matrix} \text{CH}_2\cdot\text{SO}_2 \\ \text{CH}_2\cdot\text{CO} \end{matrix} \text{N}\cdot\text{NH}_4$ , m.p. 164—168° (decomp.); the corresponding *Ba* salt and  $\text{H}_2\text{SO}_4$  (1 equiv.) do not give the imide, but afford some ( $\text{NH}_4$ )<sub>2</sub>  $\beta$ -sulphopropionate, m.p. 175—176° (shrinks at 170°), which passes at 111°/3—4 mm. into the  $\text{NH}_4$  *H* salt. H. B.

**Kinetics of reaction between peracetic acid and aldehydes.**—See this vol., 165.

**Reduction of aldehydes with aluminium isopropoxide.** W. G. YOUNG, W. H. HARTUNG, and F. S. CROSSLEY (J. Amer. Chem. Soc., 1936, 58, 100—102).— $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$  is best prepared (58—60% yield) by reduction of  $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$  with  $\text{Al}(\text{OPr}^i)_3$  ( $\text{I}$ ) (from  $\text{Al}$  and  $\text{HgCl}_2$  in  $\text{Pr}^i\text{OH}$ ) in  $\text{Pr}^i\text{OH}$  at 110° (bath);  $\text{COMe}_2$  is removed continuously. Citronellal and  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  similarly give citronellol (32%) and  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$  (68%), respectively.  $\text{PrCHO}$  in  $\text{EtOH}$  at 25° or  $\text{C}_6\text{H}_6$  (b.p.) with ( $\text{I}$ ) gives 30 or 28%, respectively, of  $\text{Bu}^a\text{OH}$ ;  $\text{Al}(\text{OEt})_3$  and  $\text{OEt}\cdot\text{MgCl}$  (Meerwein and Schmidt, A., 1925, i, 1239) are much less efficient. The reaction mechanism is considered not to be a simple adaptation of the Cannizzaro reaction (cf. *loc. cit.*). H. B.

**Constitution of bisulphite additive compounds of aldehydes and ketones.** W. M. LAUER and C. M. LANGKANIMERER (J. Amer. Chem. Soc., 1935, 57, 2360—2362).— $\text{CH}_2\text{I}\cdot\text{SO}_3\text{K}$  ( $\text{I}$ ) (from  $\text{CHI}_3$  and aq.  $\text{K}_2\text{SO}_3$ ) and  $\text{KOAc}$  at 200—205° give *K* acetoxymethanesulphonate ( $\text{II}$ ) (crystallographic data given), also formed by acetylation ( $\text{Ac}_2\text{O}\cdot\text{AcOH}$ ) of the  $\text{KHSO}_3$  additive compound ( $\text{III}$ ) of  $\text{CH}_2\text{O}$ . ( $\text{III}$ ) is, therefore, *K* hydroxymethanesulphonate. ( $\text{I}$ ) is reduced ( $\text{Zn}$  dust,  $\text{EtOH}\cdot\text{AcOH}$ ) to  $\text{MeSO}_3\text{K}$  and with aq.  $\text{K}_2\text{SO}_3$  gives  $\text{CH}_2(\text{SO}_3\text{K})_2$ . ( $\text{II}$ ) and  $\text{NH}_2\text{Ph}$  afford *K* anilino-methanesulphonate ( $+\text{H}_2\text{O}$ ), converted by aq.  $\text{KCN}$  into  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CN}$  (hydrolysed to  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ). ( $\text{II}$ ) and aq.  $\text{KCN}$  give  $\text{OAc}\cdot\text{CH}_2\cdot\text{CN}$ . Hydrolysis (dil.  $\text{H}_2\text{SO}_4$ ) of ( $\text{II}$ ) affords  $\text{CH}_2\text{O}$ .  $\text{CH}_2\text{I}\cdot\text{SO}_3\text{Na}$  ( $+\text{H}_2\text{O}$ ) is prepared as ( $\text{I}$ ). H. B.

**[Asymmetric] catalysis with organic fibres.**—See this vol., 170.

**Polymerisation of gaseous formaldehyde and acetaldehyde.**—See this vol., 298.

**Polymerides of acetaldehyde.** M. W. TRAVERS [in part with R. G. SOLLERS] (Trans. Faraday Soc., 1936, 32, 246—249).—By distilling dry air-free  $\text{MeCHO}$  into a bulb cooled in liquid air, a viscous or gelatinous product is obtained, the v.p. of which is, however, not measurably < that of the ordinary mobile liquid. On exposure to a vac., the product froths and ultimately becomes glassy. It slowly regenerates  $\text{MeCHO}$  in a sealed tube at 100°. Treatment of  $\text{MeCHO}$  with  $\text{H}_2\text{SO}_4\cdot\text{EtOH}$  at temp. not below -105° produces rapid polymerisation, a liquid compound, b.p. 73—75°, being formed. Its mol. wt., determined cryoscopically, corresponds with  $(\text{MeCHO})_n$ . It dissociates rapidly at 100°. F. L. U.

**Synthesis of deuteroacetaldehyde.** J. E. ZANNETTI and D. V. SICKMAN (J. Amer. Chem. Soc., 1935, 57, 2735).—Deuteroacetaldehyde (v.p. 327 mm. at 0°), prepared from  $\text{C}_2\text{D}_2$  and  $\text{D}_2\text{O}$ -acid-Hg salt, shows the usual aldehyde reactions. H. B.

**Decomposition of acraldehyde catalysed by iodine.**—See this vol., 167.

**Aldehyde condensations with secondary amines (Knoevenagel reaction).** R. KUHN, W. BADSTURNER, and C. GRUNDMANN (Ber., 1936, 69, [B], 98—107; cf. A., 1931, 1273).—The apparent discrepancy between the authors' results and those of Bernhauer *et al.* (A., 1932, 834) are explained by the observations that homogeneous crotonaldehyde ( $\text{I}$ ) is unchanged by piperidine ( $\text{II}$ ), whereas, after insolation, discoloration and separation of  $\text{H}_2\text{O}$  occur readily. The change is due to crotonic acid ( $\text{III}$ ) formed by autoxidation of ( $\text{I}$ ).  $\text{AcOH}$ ,  $\text{BzOH}$ , citric or cholic acid can replace ( $\text{III}$ ), but phenols are less efficient. It is therefore probable that the Knoevenagel reaction is generally catalysed by salts of *sec.* bases rather than by the bases themselves and an equimol. mixture of ( $\text{II}$ ) and glacial  $\text{AcOH}$  diluted with a little abs.  $\text{EtOH}$  is found very serviceable. Decatetraenal,  $\text{Me}\cdot[\text{CH}\cdot\text{CH}]_4\cdot\text{CHO}$ , m.p. 107—107.5° (hydrazone, complete decomp. 280° after softening and darkening at 190°), is thus derived from ( $\text{I}$ ) and sorbaldehyde or from  $\text{MeCHO}$  and octatrienal. It condenses with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  to decatetraenalmalonic acid, which gradually decomposes when heated and is decarboxylated, best by boiling  $\text{AcOH}\cdot\text{Ac}_2\text{O}$ , to dodecapentaenoic acid, m.p. 247° (decomp.); the *Me* ester, m.p. 190.5°, becomes polymerised and autoxidised when exposed to air. Citrylideneacetaldehyde,  $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ , b.p. 93—94/0.02 mm., obtained from citral and excess of  $\text{MeCHO}$  in presence of ( $\text{I}$ )- $\text{AcOH}$  but not of ( $\text{I}$ ), can be preserved unchanged in vac. in the dark, but rapidly resinifies when exposed to air; it has a strong odour of over-ripe pears, and differs in this respect and in its physical consts. from the product of von Braun *et al.* (A., 1934, 1335). The possibility of *cis-trans*-isomerism is not supported by attempted isomerisation by irradiation,  $\text{I}$ , etc. It gives a semicarbazone, m.p. 166—167°, and a 2:4-dinitrophenylhydrazone, m.p. 132—133°. It is transformed by boiling 10%  $\text{K}_2\text{CO}_3$  into  $\text{MeCHO}$  and methylheptenone. When



heated with  $\text{Ag}_2\text{O}$  it is oxidised (with partial hydrolysis) to *citrylideneacetic acid*, b.p. 115—120°/0.002 mm., hydrogenated ( $\text{PtO}_2$ ) to *dl-80-dimethyldecoic acid*, b.p. 160—162°/12 mm. (*p*-bromophenacyl ester, m.p. 56°). Treatment of it with  $\text{Al}(\text{OPr}^i)_3$  affords *citrylidene-ethyl alcohol* ( $\epsilon\epsilon$ -dimethyl- $\Delta^{8,10}$ -decatrienyl alcohol), b.p. 102—105°/0.03 mm. H. W.

**Detection of methylglyoxal and fission of caoutchouc by ozone.** R. PUMMERER, G. MATTHÄUS, and W. SOCIAS-VINALS [with, in part, F. BRAUN] (Ber., 1936, 69, [B], 170—183).—The possibility of recognising  $\text{AcCHO}$  in presence of laevulaldehyde (I),  $\text{MeCHO}$ , and  $\text{CH}_2\text{O}$  (as products of ozonisation of caoutchouc) is impeded by the impossibility of separating (I) and  $\text{AcCHO}$  by means of  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ . The pptn. of Ni methylglyoxime is not sufficiently complete in dil. solution. The most suitable reagent is  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , which in very dil. solution gives 91% yields of methylglyoxaldisemicarbazone (II) without co-pptn. of laevulaldehydesemicarbazone. (II) is subsequently transformed by 17%  $\text{H}_2\text{SO}_4$  into methylglyoxal-2 : 4-dinitrophenylosazone (yield 95%). A more complex separation of  $\text{AcCHO}$  and (I) is effected by *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ . Comparative experiments with  $\text{O}_3$  and mesityl oxide in  $\text{CCl}_4$  and  $\text{H}_2\text{O}$  give only 7.4% and 18% yields of  $\text{AcCHO}$ , which are increased to 29% in  $\text{CHCl}_3$  at 0° followed by very cautious fission of the ozonide by  $\text{SO}_2$ . The mean yield of  $\text{MeCHO}$  from caoutchouc is 1%, but this is observed only after over-ozonisation. If the action of  $\text{O}_3$  is interrupted as soon as the  $\text{CHCl}_3$  solution has become stable to Br, the production of  $\text{AcCHO}$  is  $\approx 0.1\%$  in any case. The view that  $\text{AcCHO}$  is a secondary product is discounted by the observation that, after a certain period, further over-ozonisation does not affect the yield of  $\text{AcCHO}$ . If aq.  $\text{SO}_2$  is used for fission of the ozonide,  $\text{AcCHO}$  is not detected even after prolonged ozonisation. A terminal isoprene group with a conjugated system is therefore not present in 1000 isopentene groups of caoutchouc. *Uttapercha* behaves similarly, giving no  $\text{AcCHO}$  without over-ozonisation if  $\text{SO}_2$  is used for fission of the ozonide and about 1% of  $\text{AcCHO}$  if  $\text{H}_2\text{O}$  at 0° is employed. The occurrence of  $\text{MeCHO}$  among the products of ozonisation is unexplained. Methylglyoxaldehyde when ozonised or over-ozonised and then treated with  $\text{SO}_2$  does not give  $\text{AcCHO}$ . Over-ozonisation and subsequent treatment with  $\text{H}_2\text{O}$  at 0° gives 0.6—0.8% of the C skeleton as  $\text{AcCHO}$  and an almost equiv. amount of  $\text{H}_5\text{C}_2\text{O}_4$ . H. W.

**Enolisation as directed by acid and basic catalysts. III. Acid-catalysed enolisation of sec.-butyl ketones.** P. D. BARTLETT and C. H. STAUFFER (J. Amer. Chem. Soc., 1935, 57, 2580—2583).—The rates of racemisation ( $k_R$ ) and iodination ( $k_I$ ) of *d*-COPh-CHMeEt in AcOH containing  $\text{HNO}_3$  (1.19N) (catalyst) at 36.75° are identical. Similarly,  $k_R$  and  $k_I$  are determined for *d*-COR-CHMeEt ( $\text{R} = \text{Me, Et, CH}_2\text{Ph, and cyclohexyl}$ ) at 25° (and other temp.); the competitive rates of the enolisations involving the H of CHMeEt and R are calc. The mechanism previously advanced (A., 1934, 607) does not permit an explanation of the relationship

between enolisation and alkyl substitution. The vals. of  $k_R$  and  $k_I$  for menthone (*ibid.*, 153) are revised.

H. B.

**Reactions of tagetone. I.** T. G. H. JONES (Proc. Roy. Soc. Queensland, 1934, 45, 45—49; cf. A., 1926, 72).—Tagetone (I) is represented as a tautomeric mixture:  $\text{COBu}^s\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ ,  $\text{OH}\cdot\text{CBu}^s\cdot\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CH}_2$ ,  $\text{COBu}^s\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHMe}$ ,  $\text{CH}\cdot\text{CH}_2$ . Reduction of (I) with Na-EtOH yields *dihydrotagetol*,  $\text{C}_{10}\text{H}_{20}\text{O}$ , b.p. 197°/760 mm., which is not  $\gamma$ -0-dimethyl- $\Delta^8$ -octen- $\epsilon$ -ol. Reduction of (I) with Zn dust and EtOH- $\text{NH}_4\text{Cl}$  yields a non-homogeneous *dihydrotagetone* (II),  $\text{C}_{10}\text{H}_{18}\text{O}$ , b.p. 186—190°, with two dimeric products,  $\text{C}_{20}\text{H}_{36}\text{O}$ , b.p. 115—120°/4 mm., and  $\text{C}_{20}\text{H}_{34}\text{O}_2$ , b.p. 140—150°/4 mm. (II) on oxidation yields  $\text{Bu}^s\text{CO}_2\text{H}$  and a *CO-acid*,  $\text{C}_9\text{H}_{16}\text{O}_3$ ; it is, therefore,  $\text{COBu}^s\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}$  containing a little  $\text{COBu}^s\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2$ . Reduction of (I) with Zn and EtOH-NaOH yields a *monoketone*,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , b.p. 140—150°/4 mm. (*monoxime*), and an isomeric *diketone*, b.p. 160—170°/4 mm. (*dioxime*), together with a little low-boiling liquid (*semicarbazone*, m.p. 92.5°). Reduction of (I) with Na-Hg and EtOH or with Al-Hg and EtOH affords intractable mixtures of pinacols. Treatment of (I) with  $\text{H}_2\text{S}$  in  $\text{NH}_3$ -EtOH yields a S-containing substance b.p. 90°/4 mm. With  $\text{Ba}(\text{OH})_2$  in MeOH (I) affords a *CO-alcohol*,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , b.p. 75—80°/4 mm., with  $\text{COMeBu}^s$ . (I) with  $\text{MgMeI}$  yields a substance, b.p. 66°/3 mm., and two *polymerides*,  $\text{C}_{10}\text{H}_{32}\text{O}_2$ , b.p. 130—140°/4 mm., and 150—160°/4 mm. With  $\text{NH}_2\text{OH}$  in alkaline solution an oxime is formed, whilst in dil.  $\text{H}_2\text{SO}_4$  an *oximinoketone*, b.p. 100—102°/4 mm., is produced.

CH. ABS. (r)

**Steric transformation of sugars.** F. JUST (Z. Spiritusind., 1936, 59, 25, 33—34).—A review of the methods used in effecting steric transformation of sugars leads to the conclusion that Walden inversion during fission of the O bridge in anhydro-sugars is more promising preparatively than treatment of the sugars with alkali or  $\text{C}_2\text{H}_5\text{N}$  or of unsaturated sugar derivatives with  $\text{BzO}_2\text{H}$ .

H. W.

**Structure of *d*-xylomethylose.** P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1936, 112, 775—783).—*iso*Propylidene-*d*-xylomethylose and  $\text{MeI}-\text{Ag}_2\text{O}$  at 50° give the 3-*Me ether*, b.p. 58—60°/0.3 mm.,  $[\alpha]_D^{25} -49.4^\circ$ , hydrolysed by hot 1%  $\text{H}_2\text{SO}_4$  to 3-methyl-*d*-xylomethylose, b.p. 101—102°/0.8 mm.,  $[\alpha]_D^{25} +8.1^\circ$  (*phenylosazone*, m.p. 128—130°), which with  $\text{HCl}-\text{MeOH}$  affords  $\alpha$ -, b.p. 58—62°/0.3 mm.,  $[\alpha]_D^{25} +124.5^\circ$ , and  $\beta$ -methyl-3-methyl-*d*-xylomethyloside, b.p. 72—75°/0.3 mm., m.p. 48—50°,  $[\alpha]_D^{25} -127.9^\circ$ . These with  $\text{MeI}-\text{Ag}_2\text{O}$  at 50° yield  $\alpha$ -, m.p. 34—35°, b.p. 39—41°/0.5 mm.,  $[\alpha]_D^{25} +154^\circ$ , and  $\beta$ -methyl-2 : 3-dimethyl-*d*-xylomethyloside, b.p. 38—40°/0.5 mm.,  $[\alpha]_D^{25} -102.4^\circ$ , respectively, both oxidised by conc.  $\text{HNO}_3$  to *d*-[CH(OMe) $\cdot\text{CO}_2\text{H}$ ] $_2$ . *d*-Xylomethylose (I) and  $\text{Ag}_2\text{O}-\text{H}_2\text{O}$  at 80° give only  $\text{AgOAc}$ . The rate of lactonisation of *d*-gulomethylonic acid indicates formation of  $\gamma$ - and  $\delta$ -lactones. The structure of (I) is thus confirmed.  $[\alpha]$  are in  $\text{H}_2\text{O}$ . R. S. C.

**Ring closure in sugar benzoates.** M. L. WOLFROM and C. C. CHRISTMAN (J. Amer. Chem. Soc.,

1936, 58, 39—43).—Successive treatment of *l*-arabinose  $\text{Et}_2$  mercaptal with  $\text{CPh}_3\text{Cl}$  and  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  at room temp. gives 5-triphenylmethyl-*l*-arabinose  $\text{Et}_2$  mercaptal tribenzoate, m.p. 111—112°,  $[\alpha]_D^{25} -25^\circ$  in  $\text{CHCl}_3$ , converted by  $\text{AcOH-HBr}$  followed by  $\text{CdCO}_3 + \text{HgCl}_2$  in aq.  $\text{COMe}_2$  into *l*-arabinose 2:3:4-tribenzoate (I), m.p. 162—163°,  $[\alpha]_D^{25}$  (in  $\text{C}_5\text{H}_5\text{N}$ )  $+143^\circ \rightarrow +196^\circ$ . Equilibration of *l*-arabinose in  $\text{C}_5\text{H}_5\text{N}$  and subsequent treatment with  $\text{BzCl}$  affords  $\alpha$ -*l*-arabinose tetrabenzoate (II), m.p. 160—161°,  $[\alpha]_D^{25} +112.5^\circ$  in  $\text{CHCl}_3$  [also prepared by benzylation of (I)], converted by cold  $\text{AcOH-HBr}$  into benzobromo-*l*-arabinose, m.p. 144—145°,  $[\alpha]_D +203^\circ$  in  $\text{CHCl}_3$ , which is hydrolysed (method: Fischer and Noth, A., 1918, i, 225) to (I).  $\beta$ -*l*-Arabinose tetrabenzoate has m.p. 173—174°,  $[\alpha]_D +325^\circ$  in  $\text{CHCl}_3$  (cf. Gehrke and Aichner, A., 1927, 544). The above reactions are considered to support the pyranose structure of (II). *d*-Galactose  $\text{Et}_2$  mercaptal tetrabenzoate, m.p. 127—128°,  $[\alpha]_D^{25} -16.5^\circ$  in  $\text{CHCl}_3$  [from the 6-CPh<sub>3</sub> ether (III) (A., 1935, 734) and  $\text{AcOH-HBr}$ ], with  $\text{CdCO}_3 + \text{HgCl}_2$  in aq.  $\text{COMe}_2$ , gives *d*-galactose tetrabenzoate (+MeOH), m.p. 112—113°,  $[\alpha]_D^{25}$  (in  $\text{CHCl}_3$ )  $-10^\circ \rightarrow +6.5^\circ$ .  $\text{HBr}$  converts (III) (in  $\text{CHCl}_3$ ) into 6-bromo-*d*-galactose  $\text{Et}_2$  mercaptal tetrabenzoate, m.p. 103—104°,  $[\alpha]_D^{25} -1.4^\circ$  in  $\text{CHCl}_3$ ,  $\alpha$ -*d*-Galactose pentabenzoate, m.p. 128—129°,  $[\alpha]_D +187^\circ$  in  $\text{CHCl}_3$ , is prepared by Levene and Meyer's method (A., 1928, 398). Triphenylmethyl-*d*-mannose  $\text{Et}_2$  mercaptal tetrabenzoate, m.p. 105—106°,  $[\alpha]_D^{25} 0^\circ$ ,  $[\alpha]_D^{50} -10.5^\circ$  in  $\text{CHCl}_3$  (corresponding tetraacetate, m.p. 133.5—134.5°,  $[\alpha]_D^{25} +36^\circ$  in  $\text{CHCl}_3$ ), is converted [as for (III)] into *d*-mannose  $\text{Et}_2$  mercaptal tetrabenzoate, m.p. 116—117°,  $[\alpha]_D^{25} -5^\circ$  in  $\text{CHCl}_3$ , and thence into *d*-mannose tetrabenzoate,  $[\alpha]_D^{25} -115^\circ$  in  $\text{CHCl}_3$ . Glucose  $\text{Et}_2$  mercaptal pentabenzoate (Brigl and Muchschlegel, A., 1930, 1022) with  $\text{CdCO}_3 + \text{HgCl}_2$  in aq.  $\text{COMe}_2$  gives aldehydoglucose pentabenzoate, m.p. 81—82°,  $[\alpha]_D^{25} +40^\circ$  in  $\text{EtOH}$  (cf. *loc. cit.*). Kunz and Hudson's method of hydrolysis (A., 1926, 941) is applicable to sugar benzoates provided they are appreciably sol. in  $\text{H}_2\text{O}$ . H. B.

**Esters of aldehydol form of sugars.** M. L. WOLFROM (J. Amer. Chem. Soc., 1935, 57, 2498—2500).—aldehydoGalactose penta-acetate  $\text{Et}$  hemiacetal (A., 1930, 1023) with  $\text{AcHal}$  gives aldehydo-1-chloro-, m.p. 174—175°,  $[\alpha]_D^{25} -44^\circ$  in  $\text{CHCl}_3$ , -1-bromo-, m.p. 179—181°,  $[\alpha]_D^{25} -79^\circ$  in  $\text{CHCl}_3$ , and -1-iodo-, m.p. 152—153°,  $[\alpha]_D^{25} -111^\circ$  in  $\text{CHCl}_3$ , -*d*-galactose hexa-acetates; these compounds are the open chain analogues of the cyclic halogenosugar acetates. Acetylation ( $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  or  $\text{ZnCl}_2$  at room temp.) of aldehydo-*d*-glucose penta-acetate affords the hepta-acetate, m.p. 118.5—119.5°,  $[\alpha]_D^{25} +8^\circ$  in  $\text{CHCl}_3$ ; aldehydo-*l*-arabinose tetra-acetate gives the hexa-acetate, m.p. 89.5°,  $[\alpha]_D^{25} -27^\circ$  in  $\text{CHCl}_3$ . These  $\text{C}_5\text{H}(\text{OAc})_2$  derivatives are much more stable than the aldehydo-forms. H. B.

**Action of hot alkali solutions on carbohydrates.** R. S. HILPERT and A. WOLTER (Angew. Chem., 1936, 49, 54—55).—Carbohydrates are heated with aq.  $\text{Na}_2\text{CO}_3$ , and the amount of acid produced is determined from the  $\text{CO}_2$  evolved. This varies from zero for gum arabic to 0.18 g. of  $\text{CO}_2$  per g. of mono-

saccharide at 100°. The amount increases rapidly with rise of temp. up to 0.3 at 170°. Sucrose is stable up to 130°.  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  was not found in the liquors. S. M. N.

**Constitution of osazones.** L. L. ENGEL (J. Amer. Chem. Soc., 1935, 57, 2419—2423).—The absorption spectra of the osazones (I) of various sugars (e.g., glycerose, glucose, lactose, 3:4:6-trimethyl-, tetra-acetyl- and -benzoyl-glucose) are all markedly similar; the group responsible for the sp. absorption is considered to be

$\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{OR}$  ( $\text{R}=\text{H}$ , alkyl, or acyl). The difference between the curves for (I) and the osazones of  $\text{AcCHO}$  and  $\text{Ac}_2$  (both of which are almost identical) is ascribed to the  $\text{C}_3\cdot\text{O}$  in (I). The mutarotation of (I) may be due to the establishment of an equilibrium between (I) and their hydrolysis products. A related equilibrium appears to be established between 3:4:6-trimethylglucosephenylosazone,  $[\alpha] -48.8^\circ \rightarrow +61.5^\circ$  (after 188 hr.) (in  $\text{EtOH-C}_5\text{H}_5\text{N}$ ), and  $\text{NHPh}\cdot\text{NH}_2$  (16.3 mols.); the change  $[\alpha] -50.6^\circ \rightarrow +30^\circ$  (after 155 hr.) being observed.

Acetylation ( $\text{Ac}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$ ) of glucosephenylosazone (II) and fructosephenylmethylosazone (III) gives the  $\text{Ac}_4$  derivatives, m.p. 102—104° (corr.),  $[\alpha]_D^{25} -58.5^\circ$  in 95%  $\text{EtOH}$ , and m.p. 126—127° (corr.),  $[\alpha]_D^{27} -184.8^\circ$  in 95%  $\text{EtOH}$ . (III) and  $\text{NHPh}\cdot\text{NH}_2$  in  $\text{MeOH}$  at room temp. afford glucosephenylphenylmethylosazone; the *p*-nitrophenylphenylmethylosazone, m.p. 223.5—224.5° (corr.), is similarly prepared using *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ . isoPropylidene-galactosephenylosazone, m.p. 183.5—184.5° (corr.), is formed from the galactosazone,  $\text{COMe}_2$ , and  $\text{P}_2\text{O}_5$  at 0°. Acetylglucose-2:4-dinitrophenylosazone, m.p. 196—197° (corr.), is obtained from  $\text{CO}(\text{CH}_2\cdot\text{OAc})_2$  [prep. by oxidation ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{AcOH-H}_2\text{SO}_4$ ) of diacetin described]. Methylation (various conditions) of (II) gives non-homogeneous products. Votoček and Valentin's results (A., 1931, 1274) on the mutarotation of (III) could not be confirmed. H. B.

**Photolysis of fructose in ultra-violet light.**—See this vol., 299, 300.

**Hydrolysis of glucosides and of certain organic compounds by ultra-violet rays.**—See this vol., 171.

**Synthesis and properties of  $\beta$ -alkylglucosides.** S. VEIBEL and F. ERIKSEN (Bull. Soc. chim., 1936, [v], 3, 277—283).— $\beta$ -Methyl-, -ethyl-, m.p. 81—83°,  $[\alpha]_D^{20} -38.6^\circ$  in  $\text{H}_2\text{O}$  (tetra-acetate, m.p. 105—106°,  $[\alpha]_D^{20} -29^\circ$  in  $\text{C}_5\text{H}_5$  or  $\text{EtOH}$ ), -propyl-, forms, m.p. 77—78° (I) and 102—103° (II), respectively,  $[\alpha]_D^{20} -39.3^\circ$  in  $\text{H}_2\text{O}$  [(I)  $\rightarrow$  (II) at 90—95°; (II)  $\rightarrow$  (I) in  $\text{PhMe}$  slowly at 30° and rapidly if boiled and then cooled to 70°; tetra-acetate, m.p. 102—103°,  $[\alpha]_D^{25} -27^\circ$  in  $\text{EtOH}$ ], and -isopropyl-glucoside, m.p. 128—129°,  $[\alpha]_D^{20} -40.9^\circ$  in  $\text{H}_2\text{O}$  (tetra-acetate, m.p. 136—137°,  $[\alpha]_D^{25} -30.6^\circ$  in  $\text{EtOH}$ ), are prepared (a) from penta-acetylglucosidyl bromide and subsequent hydrolysis by a trace of  $\text{NaOMe}$  and (b) by emulsin from glucose with removal of the excess of glucose  $\gamma$  yeast. M.p. are corr. R.



**Synthesis of 1-*d*-glucosidocytosine.** G. E. HILBERT and E. F. JANSEN (J. Amer. Chem. Soc., 1936, 58, 60—62).—2:4-Diethoxypyrimidine and acetobromoglucose at 65° give 2-*keto*-4-ethoxy-1-tetra-acetyl-*d*-glucosido-1:2-dihydropyrimidine, m.p. 206° (corr.),  $[\alpha]_D^{25} + 36.1^\circ$  in CHCl<sub>3</sub>, converted by EtOH-HCl into 1-*d*-glucosidouracil (I) (A., 1931, 100) and by EtOH-NH<sub>3</sub> at 80°/96 hr. in sealed tube into 1-*d*-glucosidocytosine (II) (+ $\frac{1}{3}$ EtOH), m.p. 197—199° (sinters at 192°) [picrate, m.p. 216—218° (decomp.); nitrate (+H<sub>2</sub>O), m.p. 143° (decomp.)], which when kept in a moist atm. passes into a hydrate, m.p. about 128° (decomp.). Crystallisation from 90—95% EtOH gives a hydrate-alcoholate, m.p. 194—195° (decomp.). Anhyd. (II) is hygroscopic and has  $[\alpha]_D^{25} + 25.6^\circ$  in H<sub>2</sub>O. (II) with 25% H<sub>2</sub>SO<sub>4</sub> at 150° gives (probably) a mixture of (I) and (II). 7-Acetyl-1-tetra-acetylglucosidocytosine has m.p. 225°,  $[\alpha]_D^{25} + 38.1^\circ$  in CHCl<sub>3</sub>. H. B.

**Influence of crystalloids on the state of amyloses.**—See this vol., 288.

**Plant colloids. XLIII. Influence of chlorine dioxide on the chemical reactions of potato- and wheat-starch.** M. SAMEC [with F. ULM] (Kolloid-Beih., 1936, 43, 287—294).—When treated with ClO<sub>2</sub> solutions, starch loses P and N. A considerable amount of P in potato- (but not wheat-) starch resists this action. The treatment also renders the starch more sol., and in some cases causes feeble oxidation. E. S. H.

**Kinetics of long chain disintegration applied to cellulose and starch.**—See this vol., 295.

**Origin of nitrous oxide and hydrogen cyanide formed by certain methods of decomposition of cellulose nitrate.** H. MURAUOR (Bull. Soc. chim., 1936, [v], 3, 265—267).—Decomp. of cellulose nitrate leads to HNO, which at low temp. gives N<sub>2</sub>O and at high temp. reacts with CH<sub>4</sub> to produce HCN. R. S. C.

**Highly polymerised compounds. CXXIII. Measurements of the viscosity of aliphatic amines with long chains.** H. STAUDINGER and K. RÖSSLER (Ber., 1936, 69, [B], 49—60).—Determinations of the viscosity of long-chained aliphatic nitriles and primary and *sec.*-amines show the compounds to be unimol. in C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub>, since the observed  $\eta_{sp}$ . (1.4%) vals. agree with those calc. from the expression  $\eta_{sp}$ . (1.4%) =  $\eta\eta$ . The temp. coeff. is the same as that of hydrocarbons. With short-chain compounds the observed vals. are < the calc., since the abs. viscosity of the dissolved substance is not sufficiently high in comparison with that of the solvent. The amine mol. has therefore the form R-NH-R, not NHR<sub>2</sub>. *tert.*-Amines with three long chains have the mol. structure  $\begin{matrix} R & R & R \\ & \diagdown & / \\ R-N & -N- & N-R \\ & / & \diagdown \\ R & R & R \end{matrix}$ , not  $\begin{matrix} R & R \\ & \diagdown & / \\ R-N & -N- & N \\ & / & \diagdown \\ R & R \end{matrix}$ , and are thus comparable with the glyceryl esters. The viscosity of long-chained amines in heteropolar solvents is quite irregular and is little affected by the addition of electrolytes. Since micelle formation is not involved, an adequate explanation of the high sp. viscosity in AcOH is not forthcoming. Amines

and nitriles, like hydrocarbons and esters, exist in solution as thread mols. with the most extended form; from these the crystals are formed and m.p. and solubility of the solids depend greatly on the length of the chains. Nitriles have a somewhat higher m.p. (about 9°) than hydrocarbons with the same no. of chain links. Primary amines and primary alcohols have the same m.p. (20—30° > that of the corresponding hydrocarbons); their mols. are therefore coordinatively united but so weakly that the union is broken in solution. The very low m.p. of *tert.*-amines is explained by their branched structure. *sec.*-Amines with two long chains have m.p. slightly < the corresponding hydrocarbons due to the slightly less regular structure, whilst Me-substituted *tert.*-amines have m.p. similar to that of hydrocarbons containing Et attached to the central C. The following compounds are incidentally described: *dimyristylamine*, m.p. 56—58.5°; *dicetylamine*, m.p. 65—66°; *dimethylmyristylamine*, liquid at 0°; *dimethylcetylamine*, m.p. about 12°; *dimethylstearylamine*, m.p. about 25°; *methylmyristylamine*, m.p. 24—25°; *methylcetylamine*, m.p. 34—35°; *methylstearylamine*, m.p. 40°; *trimyristylamine*, m.p. 33—34°; *tricyetylamine*, m.p. 42—43.5°; *tristearylamine*, m.p. 54—55°. H. W.

**Possible rearrangement reactions of monochloroamine and Grignard reagents.** G. H. COLEMAN and R. A. FORRESTER (J. Amer. Chem. Soc., 1936, 58, 27—28).—CH<sub>2</sub>Ph·MgCl and NH<sub>2</sub>Cl give 92% of CH<sub>2</sub>Ph·NH<sub>2</sub>;  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·MgCl affords 47% of  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>·NH<sub>2</sub>; CHPh·CH·CH<sub>2</sub>·MgCl (at -20°) yields 14% of CHPh·CH·CH<sub>2</sub>·NH<sub>2</sub>. No indication of the formation of rearrangement products (viz., *o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>, 1:2-C<sub>10</sub>H<sub>6</sub>Me·NH<sub>2</sub>, and NH<sub>2</sub>·CHPh·CH·CH<sub>2</sub>, respectively) was obtained. H. B.

**Kinetics of ring formation and polymerisation in solution.**—See this vol., 296.

**Reduction of organic compounds by ethanolamines.** M. MELTSNER, C. WOHLBERG, and M. J. KLEINER (J. Amer. Chem. Soc., 1935, 57, 2554).—Reduction of anthraquinone, (NPh)<sub>2</sub>, and COMe<sub>2</sub> occurs when these are heated with N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>3</sub> (I); anthranol, NH<sub>2</sub>Ph, and Pr<sup>2</sup>OH, respectively, are formed. Mixtures of the azo-, azoxy- (II), and NH<sub>2</sub>-derivatives are similarly produced from PhNO<sub>2</sub> and *o*-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub> with (I), NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH, or, preferably, NH(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>2</sub> in presence of aq. NaOH; (II) is not formed in absence of NaOH. Chrysoidine is reduced [? by (I)] to 1:2:4-C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>3</sub>. Aq. solutions of Ag, Pb, Hg, and other metal salts are also reduced. H. B.

**Mixed molybdates.**—See this vol., 302.

**[Derivatives of] ruthenium-red.**—See this vol., 302.

**Preparation and properties of  $\beta$ -*n*-alkylcholine chlorides and their acetyl esters.** R. T. MAJOR and H. T. BONNETT (J. Amer. Chem. Soc., 1936, 58, 22—24).—OH·CHR·CH<sub>2</sub>·NMe<sub>2</sub> (from OH·CHR·CH<sub>2</sub>Cl and NHMe<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> at 115—120°) are converted (MeI followed by AgCl) into OH·CHR·CH<sub>2</sub>·NMe<sub>2</sub>Cl (R=Et—*n*-C<sub>7</sub>H<sub>15</sub>), which are acetylated (method:

A., 1932, 257) to  $\text{OAc}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$ . The following are described:  $\alpha$ -chlorononan- $\beta$ -ol, b.p. 114.5—116.5°/13 mm. (prep.: Levene and Haller, A., 1928, 737);  $\alpha$ -dimethylamino- $\beta$ -hydroxybutane, b.p. 142—144°/760 mm., -hexane, b.p. 89—90°/25 mm., -octane, b.p. 99—101°/10 mm., and -nonane, b.p. 104—106°/5 mm.;  $\beta$ -ethylcholine chloride, m.p. 174—176° (acetate, m.p. 144—146°), and iodide, m.p. 162—163°;  $\beta$ -n-propylcholine chloride, m.p. 115—117° (acetate, m.p. 168—169°), and iodide, m.p. 198—200°;  $\beta$ -n-butylcholine chloride, m.p. 100.5—102° (acetate, m.p. 186—187°), and iodide, m.p. 90—92°;  $\beta$ -n-amylcholine chloride, m.p. 72—74° (acetate, m.p. 182—184°), and iodide, m.p. 98—100° (lit. 106—108°);  $\beta$ -n-hexylcholine chloride, m.p. 69—71° (acetate, m.p. 169—171°), and iodide, m.p. 109—110°;  $\beta$ -n-heptylcholine chloride, m.p. 97—99° (acetate, m.p. 176—177°), and iodide, m.p. 122.5—123.5°. Pharmacological data are given; none of the acetates is as active as  $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$  (cf. Simonart, A., 1932, 1284).

H. B.

**Equilibrium of amino-acids, carbon dioxide, and carbamates in aqueous solution.**—See this vol., 289.

**Feeding experiments with purified amino-acids.** VIII.—See this vol., 233.

**Synthesis of  $\alpha$ -amino- $\beta$ -hydroxy- $n$ -butyric acids.** H. E. CARTER (J. Biol. Chem., 1936, 112, 769—773).—The mixture of isomerides,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$  (I), of Abderhalden *et al.* (A., 1934, 638) has no physiological activity. Formylation gives  $\alpha$ -formamido- $\beta$ -methoxy- $n$ -butyric acid, m.p. 173—174°, which after epimerisation by hot  $\text{Ac}_2\text{O}$ -NaOH and hydrolysis with HBr yields a mixture of stereoisomerides of (I), which has about 25% of the activity of the natural acid.

R. S. C.

**Canavanine.** VI. M. KITAGAWA and A. TAKANI (J. Agric. Chem. Soc. Japan, 1935, 11, 1077—1082).—The similarity in properties of  $\text{ONH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and canaline confirms the structure of  $\text{ONH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ . Guanidation of  $\alpha$ -benzoylcanaline with methylisocarbamide followed by hydrolysis yields (as flavianate) canavanine, which therefore is  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{N}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$  (cf. A., 1934, 993).

F. O. H.

**Specific rotation of *l*-cystine in relation to degree of neutralisation and  $p_H$ .** G. TOENNIES, T. F. LAVINE, and (MISS) M. A. BENNETT (J. Biol. Chem., 1936, 112, 493—496).— $[\alpha]_{25}^{25}$  at  $p_H$  0—10.6 are recorded for 0.005*M*-*l*-cystine, prepared from 98—99% pure Li cystinate by adding varying amounts of LiOH and/or HCl.  $[\alpha]_{H_2O}$  is  $-225^\circ$  at  $p_H$  about 0.1,  $-97^\circ$  at  $p_H$  11.6, and  $-325^\circ$  at  $p_H$  3—7 (the isoelectric range).  $d[\alpha]/dt$  is  $+1.5^\circ$  between 19.3° and 32.05°.

R. S. C.

**New synthesis of methionine and a scheme relating certain  $\alpha$ -amino-acids.** E. M. HILL and W. ROBSON (Biochem. J., 1936, 30, 248—251).—*Et*  $\gamma$ -chloro- $\alpha$ -benzamidobutyrate, m.p. 45°, prepared by treatment of  $\alpha$ -benzamido- $\gamma$ -butyrolactone with HCl in EtOH, gave benzoylmethionine on treatment with NaSMe and subsequent alkaline hydrolysis.

Acid hydrolysis gave methionine (carbamide, m.p. 171—172°; hydantoin, m.p. 117—118°). H. D.

**Determination of the stereochemical purity of *l*-cysteine.** G. TOENNIES and (MISS) M. A. BENNETT (J. Biol. Chem., 1936, 112, 497—502).—*l*-Cysteine (modified prep.),  $[\alpha]_{D}^{20} + 9.68 \pm 0.05^\circ$ ,  $[\alpha]_{D}^{15} + 7.6 \pm 0.1^\circ$  (*M* solution in *N*-HCl;  $d\alpha/dt = -1\%$  between 23° and 33°), is determined within  $\pm 0.25\%$  by oxidation with  $\text{H}_2\text{O}_2$  (2% excess) in *N*-HCl in presence of 0.003*M*- $\text{CuSO}_4$  and determination of the max.  $[\alpha]$  (due to cystine) during 1 hr.

R. S. C.

**Detection of cysteine in presence of cystine.** C. B. DI CAPUA (Boll. Soc. ital. Biol. speriment., 1935, 10, 428—429).—Grothe's reagent can be used for detection of cysteine, but the supposed blue cystine (I) coloration appears in acid solution without (I) and is probably due to formation of Prussian-blue.

R. N. C.

**Highly polymerised compounds. CXXIV.** Measurements of the viscosity of amides and anilides of fatty acids. H. STAUDINGER and K. ROSSLER (Ber., 1936, 69, [B], 61—73).—The m.p. of the normal fatty amides is considerably  $>$  that of the corresponding acids; the lower m.p. of *sec.*- and *tert.*-amides may be caused by the presence of branched chains. Correspondingly the methylamides and more particularly the dimethylamides are more freely sol. in  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , or  $\text{CHCl}_3$  than the simple amides. The relatively high m.p. of primary amides depends on peculiarities of structure as well as on the formation of co-ordinative mols. Measurements of  $\eta_{sp}$ , dimethylamides in  $\text{C}_6\text{H}_6$  gives vals.  $>$  expected, which do not depend on concn. Since the temp. effect is normal the  $\text{CO}\cdot\text{NH}_2$  group causes exaltation; this view is confirmed by the behaviour of the piperidides. Similarly,  $\eta_{sp}$  of amides and methylamides in  $\text{CHCl}_3$  is  $>$  expected. Methylanilides in  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , or  $\text{CHCl}_3$  behave similarly to the dimethylamides. On the hypothesis that mols. in solution assume the longest possible form, the normal mols. of anilides have

the structure  $\text{Me}\cdot[\text{CH}_2]_n\cdot\overset{\text{O}}{\text{C}}\cdot\text{NHPh}$ . Co-ordinative mols. can have the structure  $\text{Me}\cdot[\text{CH}_2]_n\cdot\text{C}(\text{O})\cdot\text{NH}\cdot\text{Ph}\cdot\text{HN}(\text{O})\text{C}(\text{O})\cdot[\text{CH}_2]_n\cdot\text{Me}$  or

$\text{PhNH}\cdot\text{COR}\cdot\text{HN}\cdot\text{Ph}\cdot\text{COR}$  dependent on whether or not

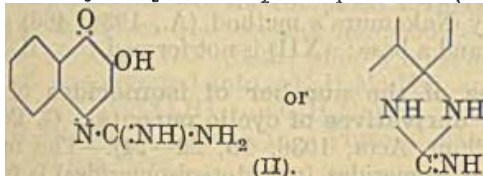
$\text{Me}\cdot[\text{CH}_2]_n\cdot\text{CO}$  is longer than Ph. Support for this view is found in the observation that the m.p. of fatty acid anilides passes through a min. at octoanilide.  $\eta_{sp}$  of anilides in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , or  $\text{C}_5\text{H}_5\text{N}$  shows progression similar to that of the m.p. In AcOH the viscosity of anilides appears to depend on the ionogenic groups rather than on the chain length. The following compounds are incidentally described. *methylamides* of undecenoic, myristic (I), and palmitic (II) acid, m.p. 48—49°, 78—79°, and 86°, respectively; *dimethylamides* of lauric (III), (I), (II), and stearic acid (IV), b.p. 180°/15 mm., m.p. 18—20°, b.p. 210—213°/15 mm., m.p. 31—32°, m.p. 41° and m.p. 50—51.5°, respectively; *stearyl* piperidide, m.p. 37—38°; *methylanilides* of (III), (I), (II), and (IV), b.p. 1°/0.2 mm., m.p. 15°, b.p. 204.5—206°/0.5 mm., m.p.



29–30°, b.p. 202–203°/0.01 mm., m.p. 40–45° and m.p. 48.5–49.5°, respectively. H. W.

**Condensation of carbamide and formaldehyde.** G. WALTER (Trans. Faraday Soc., 1936, 32, 377–395).—A summary of work previously published (cf. B., 1931, 357; A., 1932, 150). F. L. U.

**Coloured compound formed in Sullivan reaction for guanidine.** M. X. SULLIVAN and W. C. HESS (J. Amer. Chem. Soc., 1936, 58, 47–48; cf. this vol., 195).—The compound, decomp. about 250°, formed from guanidine (I) and Na 1:2-naphthaquinone-4-sulphonate in aq. NaOH at 90°, followed by acidification (conc. HCl+conc. HNO<sub>3</sub>), is considered to be (II) since it is hydrolysed (conc. H<sub>2</sub>SO<sub>4</sub>, 95% EtOH) to 2-hydroxy-1:4-naphthaquinone. (II) is



rose-coloured in acid, purple in alkali, and forms NH<sub>4</sub>, m.p. 285–288°, and Na, m.p. 297–300°, salts. 1:2-Naphthaquinone, (I), and a little HNO<sub>3</sub> in aq. EtOH give the compound, 1:2-O:C<sub>10</sub>H<sub>6</sub>:N·C(NH)·NH<sub>2</sub>, m.p. 265–267° (decomp.), hydrolysed (20% HCl) to α-C<sub>10</sub>H<sub>7</sub>·OH. H. B.

**Reduction of nitroguanidine. II. Preparation and properties of nitrosoguanidine.** V. J. SABETTA, D. HIMMELFARB, and G. B. L. SMITH. III. **Synthesis of aminoguanidine.** G. B. L. SMITH and E. ANZELMI. IV. **Preparation of nitrosoguanidine by catalytic hydrogenation** [of nitroguanidine]. E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1935, 57, 2478–2479, 2730, 2739–2480).—II. Slightly impure nitrosoguanidine (I), detonates at 161°, is obtained in 40–60% yield by reduction (Zn dust and aq. NH<sub>4</sub>Cl at < 50°) of nitroguanidine (II). Methods for the determination of (I) are given.

Methylisothiocarbamidesulphate and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O give MeSH and the sulphate (yield 90%) of aminoguanidine (*K<sub>b</sub>* 1.1 × 10<sup>-3</sup>), the H carbonate of which is CH<sub>6</sub>N<sub>4</sub>·H<sub>2</sub>CO<sub>3</sub>.

1. Reduction [H<sub>2</sub> (slightly > 1 mol.), PtO<sub>2</sub> or Raney Ni, H<sub>2</sub>O] of (II) affords 36–62% of (I).

**Vinyldiazomethane.** C. D. HURD and S. C. LUI (J. Amer. Chem. Soc., 1935, 57, 2656–2657).—Vinyldiazomethane (I), obtained from nitrosoallylurethane (m.p. 110°, prep.) by Nirdlinger and Acree's method (A., 1910, i, 341), with BzOH gives allyl benzoate. Appreciable isomerisation of (I) to pyrazole (cf. Adamson and Turner, A., 1935, 479) occurs during its distillation. H. B.

**Parachor and molecular refraction of hydrazine and its aliphatic derivatives.**—See this vol., 279.

**Dibutylphosphorous acid chloride and preparation of butylpyrophosphorous acid from it.** BUSOV and V. S. ABRAMOV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 28–33).—

BuO·PCl<sub>2</sub> is converted by NaOBu into (BuO)<sub>2</sub>PCl<sub>2</sub>; this, with (BuO)<sub>2</sub>P·ONa, affords *butylpyrophosphorous acid*, b.p. 175–176°, which, with H<sub>2</sub>O, yields (BuO)<sub>2</sub>P·OH, and, with Br, a Br<sub>4</sub>-compound.

CH. ABS. (r)

**Acetoacetic acid O-phosphoric ester.** P. KARRER and H. BENDAS (Helv. Chim. Acta, 1936, 19, 98–99).—Cautious treatment of ONa·CHMe·CH·CO<sub>2</sub>Et with POCl<sub>3</sub> give *Et<sub>3</sub> acetoacetate O-phosphate*, isolated as the salt PO<sub>3</sub>Ba·O·CMe·CH·CO<sub>2</sub>Et. The corresponding Na<sub>2</sub> salt is hydrolysed to the compound (I), PO<sub>3</sub>Na<sub>2</sub>·O·CMe·CH·CO<sub>2</sub>Na. Hot, dil. acids convert (I) into CH<sub>2</sub>Ac·CO<sub>2</sub>H or COMe<sub>2</sub>; kidney phosphatase readily removes ·OPO<sub>3</sub>Na<sub>2</sub> from (I) at *p<sub>H</sub>* 9. H. W.

**Phosphate transferences by means of phosphopyruvic acid in alcoholic fermentation of sugar.**—See this vol., 246.

**Preparation of boron alkoxy-halides and their reaction with metals.** C. R. KINNEY, H. T. THOMPSON, and L. C. CHENEY (J. Amer. Chem. Soc., 1935, 57, 2396–2397).—A mixture of triisomyl borate (I) (2 mols.) and BCl<sub>3</sub> (1 mol.) is kept for 24 hr. and then fractionated; *B diisomylloxy-chloride* (II), b.p. 110–115°/14 mm., is obtained in 45% yield. (II) and Na in C<sub>6</sub>H<sub>6</sub> at 70° give HCl, isopentene, H<sub>2</sub>, (I), and B<sub>2</sub>O<sub>3</sub>. BCl(OEt)<sub>2</sub> warmed with Na or Zn dust similarly affords B(OEt)<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>. H. B.

**Colour reaction for detection of cyclopentadiene.** B. N. AFANASIEV (Ind. Eng. Chem. [Anal.], 1936, 8, 15).—A violet colour is produced when one drop of cyclopentadiene dissolved in CHCl<sub>3</sub> (1 c.c.) and AcOH (1 c.c.) is treated with conc. H<sub>2</sub>SO<sub>4</sub>. A similar coloration is obtained with higher terpenes but only when Ac<sub>2</sub>O is used. S. C.

**Ozonisation of hydrogenated diphenyls.** C. R. NOLLER and G. K. KANEKO (J. Amer. Chem. Soc., 1935, 57, 2442–2443).—1-Phenyl-Δ<sup>1:1</sup>-cyclohexene (I) and di-Δ<sup>1:1</sup>-cyclohexenyl add 1 and 2 mols., respectively, of O<sub>3</sub>, indicating that steric hindrance in the 1 and 1' positions is not the factor involved in the failure of Ph<sub>2</sub> to give a hexaozonide (cf. Harries and Weiss, A., 1906, i, 228). Decomp. of the ozonides affords δ-benzoylvaleric and adipic acid, respectively. The tetrahydrodiphenyl obtained (cf. Bamberger and Lodter, A., 1888, 292) by reduction (Na, amyl alcohol) of Ph<sub>2</sub> is mainly (I). H. B.

**Dehydration of benzylcyclohexanols.** J. W. COOK and C. L. HEWETT (J.C.S., 1936, 62–71).—2-Methylcyclohexanone and CH<sub>2</sub>Ph·MgCl (I) give impure 1-benzyl-2-methylcyclohexanol, b.p. 115°/0.8 mm., dehydrated (KHSO<sub>4</sub> at 160–175°) to 1-benzyl-2-methyl-Δ<sup>1</sup>-cyclohexene, b.p. 158–160°/19 mm., converted by AlCl<sub>3</sub> in CS<sub>2</sub> at 0° into a saturated hydrocarbon, C<sub>14</sub>H<sub>18</sub>, b.p. 141°/18 mm., which could not be dehydrogenated (Se at 300–320°; Pd-C at 300°) and is oxidised (dil. HNO<sub>3</sub> at 180–185°) to α-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>. Tetrahydrocarvone and (I) afford 1-benzyl-2-methyl-5-isopropylcyclohexanol, b.p. 140–142°/0.6 mm., dehydrated (ZnCl<sub>2</sub> at 160°) to 1-benzyl-2-methyl-5-isopropyl-Δ<sup>1</sup>-cyclohexene, b.p. 159°/12 mm., similarly converted into a saturated hydrocarbon, C<sub>17</sub>H<sub>24</sub>, b.p. 160–161°/13 mm., which could

not be dehydrogenated. Phenylcyclohexylcarbinol (II) and 1- (III) and 2-benzylcyclohexanol, b.p. 154°/11 mm., m.p. 75.5—76° (prepared by reduction of the hexanone with Na and H<sub>2</sub>O in Et<sub>2</sub>O), are all converted by P<sub>2</sub>O<sub>5</sub> at 150° into 30—70% of 2:3-benz-1:3:3-dicyclo-Δ<sup>2</sup>-nonene (IV), b.p. 85°/0.3 mm., 123°/15 mm., and not (XII) (below) (see A., 1933, 1042); (IV) is oxidised (dil. HNO<sub>3</sub> at 180°) to *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, thus showing that cyclisation involves the attachment of the alicyclic part of the mol. at C2 of the C<sub>6</sub>H<sub>6</sub> ring.

(IV) could not be dehydrogenated (Pt-black or -asbestos); it is oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH) to 2:3-benz-1:3:3-dicyclo-Δ<sup>2</sup>-nonen-4-one (V), b.p. 108—110°/0.2 mm. (oxime, m.p. 123—124°; semicarbazone, m.p. 222—224°), which is reduced (Clemmensen) to pure (IV). The complete absence of strain in (IV) is probably the determining factor in its formation. (V) and HNO<sub>3</sub> (*d* 1.5) give the 3'-NO<sub>2</sub>-derivative, m.p. 118.5—119.5°, reduced (SnCl<sub>2</sub>, conc. HCl, EtOH) to the 3'-NH<sub>2</sub>-derivative, m.p. 122.5—123.5°, which is oxidised (CrO<sub>3</sub>, AcOH) to *cis*-hexahydrosophthalic acid (VI) and converted (through the diazonium sulphate) into 3'-hydroxy-2:3-benz-1:3:3-dicyclo-Δ<sup>2</sup>-nonen-4-one, m.p. 160.5—161.5° [oxidised (KMnO<sub>4</sub>, aq. KOH) to (VI)]. (V) could not be methylated (MeI, NaNH<sub>2</sub>). No reaction occurs between (V) and Br in CS<sub>2</sub>, indicating the absence of enol.

1-Benzyl-Δ<sup>1</sup>-cyclohexene (VII), obtained (cf. von Auwers and Treppmann, A., 1915, i, 789; Prévost *et al.*, A., 1934, 649) by dehydration (KHSO<sub>4</sub>) of (III), is converted into the nitrosochloride, m.p. 116—117° (lit. 110°), and thence by boiling C<sub>5</sub>H<sub>5</sub>N into 2-benzyl-Δ<sup>2</sup>-cyclohexenoneoxime, m.p. 138.5—139.5° (lit. 136—138°), which when hydrolysed (6*N*-H<sub>2</sub>SO<sub>4</sub>) and then reduced (H<sub>2</sub>, Pd-black, Et<sub>2</sub>O) gives 2-benzylcyclohexanone (VIII). Dehydration (ZnCl<sub>2</sub> at 170—180°) of (II) affords a mixture of (IV) [proved by oxidation to (V)] and unsaturated material, which is not (VII) (cf. von Auwers, this vol., 195) but may be benzylidenecyclohexane. Contrary to von Auwers and Treppmann (*loc. cit.*), there is no evidence of the change CHPh:C< CH<sub>2</sub>Ph:C<. *Et*-2-benzylcyclohexanone-2-carboxylate, b.p. 144—145°/0.4 mm., m.p. 34.5—35° (semicarbazone, m.p. 182—183°), prepared from *Et* sodiocyclohexanone-2-carboxylate and CH<sub>2</sub>PhCl in C<sub>6</sub>H<sub>6</sub>, is hydrolysed (EtOH-KOH) to *α*-benzylpimelic acid, m.p. 81—82°, which when distilled (from bath at 360—380°) gives (VIII). *trans*-2-Ketodecahydronaphthalene and (I) give β-decahydronaphthylbenzylcarbinol, b.p. 171°/6 mm. (3:5-dinitrobenzoate, m.p. 162.5—164°), dehydrated (KHSO<sub>4</sub> at 160—170°) to 2-benzyldecahydronaphthalene, b.p. 151°/6 mm., which is reduced (H<sub>2</sub>, Pd-black, AcOH) to 2-benzyldecahydronaphthalene (IX), b.p. 173—175°/10 mm., and dehydrogenated (Se at 310—320°) to 2-benzyldecahydronaphthalene [also formed from (IX) and Pt-black at 300—305° but not with Se at 320—330°]. Successive oxidation (CrO<sub>3</sub>, cold AcOH) and reduction (H<sub>2</sub>, Pd-black, AcOH) of 2-phenyl-Δ<sup>3</sup>-tetrahydrobenzaldehyde (Lehmann and Paasche, A., 1935, 978) gives 2-phenylhexahydro-

benzoic acid (X), m.p. 105—107°, better prepared by reduction (Na, amyl alcohol) of *o*-C<sub>6</sub>H<sub>4</sub>Ph-CO<sub>2</sub>H [the acid obtained by catalytic reduction (Raneco and León, A., 1925, i, 665) is not a stereoisomeride of (X) but is *o*-cyclohexylbenzoic acid, m.p. 104°, oxidised (alkaline KMnO<sub>4</sub>) to *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>]. The chloride of (X) with AlCl<sub>3</sub> in CS<sub>2</sub> at 0° affords 1:2:3:4:10:11-hexahydrofluorenone (XI), m.p. 41.5—42° (oxime, m.p. 183—185°; semicarbazone, m.p. 212—213°), reduced (Clemmensen) to 1:2:3:4:10:11-hexahydrofluorene (XII), b.p. 127°/15 mm., which is readily dehydrogenated (Se at 300—320°; Pt at 250—260°) to fluorene. Oxidation (CrO<sub>3</sub>, AcOH) of (XII) gives resinous products but no (XI). The hexahydrofluorenone of Vocke (A., 1934, 189) is probably (XI). Reduction of fluorenone-oxime by Nakamura's method (A., 1930, 466) gives fluorene and a base; (XII) is not formed. H. B.

Tables of the number of isomerides of the simpler derivatives of cyclic parents. G. PÓLYA (Helv. Chim. Acta, 1936, 19, 22—24).—The no. of structural isomerides (not stereoisomerides) is tabulated which can be derived by replacement of H of C<sub>6</sub>H<sub>6</sub>, C<sub>10</sub>H<sub>8</sub> (anthraquinone), anthracene (pyrene), phenanthrene or thiophen (furan) by the univalent radicals X, Y, and Z provided that the introduction of X<sub>a</sub>, Y<sub>b</sub>, and Z<sub>c</sub> into the parent does not lead to the same mol. formula as the introduction of X<sub>b</sub>, Y<sub>k</sub>, and Z<sub>l</sub>. The case of alkyl derivatives receives extended treatment. H. W.

#### Kinetics of nitration of aromatic compounds.

—See this vol., 297.

#### Direct introduction of deuterium into benzene.

—See this vol., 299.

Reaction of paraffins with aromatic hydrocarbons (destructive alkylation). A. V. GROSSE and V. N. IPATIEV (J. Amer. Chem. Soc., 1935, 57, 2415—2419; cf. A., 1935, 1348).—In presence of suitable catalysts paraffins and aromatic hydrocarbons react thus: C<sub>(m+n)</sub>H<sub>2(m+n)+2</sub> + ArH > C<sub>n</sub>H<sub>2n+2</sub>. Ar·C<sub>m</sub>H<sub>2m+1</sub>. Dry HCl is passed through ββ-trimethylpentane (I), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> at 25—50° (or ZrCl<sub>4</sub> at 50—75°); isobutane, PhBu<sup>+</sup>, and C<sub>6</sub>H<sub>4</sub>Bu<sup>+</sup> (only the *p*-compound is isolated pure) [formed by further reaction of PhBu<sup>+</sup> with (I)] are produced. (I) and C<sub>6</sub>H<sub>6</sub> do not react in presence of MgCl<sub>2</sub>-HCl at 200°/20 atm. or BF<sub>3</sub> (promoted by Ni and H<sub>2</sub>O) at 55°. H. B.

Kinetics of Friedel-Crafts reaction and activity of mixed catalysts in the reaction of benzoyl chloride with toluene. L. F. MARTIN, P. PIZZOLATO, and L. S. McWATERS (J. Amer. Chem. Soc., 1935, 57, 2584—2589).—The reaction between Phale and BzCl in presence of AlCl<sub>3</sub>, FeCl<sub>3</sub>, and mixtures (I) of AlCl<sub>3</sub> and FeCl<sub>3</sub> is investigated using Steele's method (J.C.S., 1903, 83, 1470). All the (I) are more active than either of the components; the velocity coeff. increases with rise in the % of FeCl<sub>3</sub> and is max. with > 50 mols.-% in (I). For each mol. of total metal chlorides used, < 1 mol. of C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>· is produced; evidence showing that this is due to the removal of the catalyst as the complex,



COPh·C<sub>6</sub>H<sub>4</sub>Me, AlCl<sub>3</sub>, FeCl<sub>3</sub>, is given. The variation of the velocity coeff. with concn. is of the same order as that found by Olivier (A., 1918, i, 228) for the reaction between C<sub>6</sub>H<sub>6</sub> and BzCl. The velocity coeff. for the reaction between PhMe and CH<sub>2</sub>PhCl is greatly increased by a small % of FeCl<sub>3</sub>; a subsequent decrease occurs when substantial amounts are present. The results support the reaction mechanism proposed by Steele (*loc. cit.*). H. B.

**Decomposition of di-*o*-tolylidonium iodide.** H. J. LUCAS, E. R. KENNEDY, and C. A. WILMOT (J. Amer. Chem. Soc., 1936, 58, 157—160).—*o*-C<sub>6</sub>H<sub>4</sub>Me·IO, *o*-C<sub>6</sub>H<sub>4</sub>Me·IO<sub>2</sub>, and Ag<sub>2</sub>O [which catalyses the reaction C<sub>7</sub>H<sub>7</sub>IO + C<sub>7</sub>H<sub>7</sub>IO<sub>2</sub> → (C<sub>7</sub>H<sub>7</sub>)<sub>2</sub>I<sup>+</sup> + IO<sub>3</sub><sup>-</sup>] are triturated in CHCl<sub>3</sub> + successive small amounts of H<sub>2</sub>O; treatment of the combined aq. extracts with SO<sub>2</sub> or KI gives di-*o*-tolylidonium iodide (I). Decomp. of (I) at 155° (bath) affords only *o*-C<sub>6</sub>H<sub>4</sub>MeI (which is converted into *o*-C<sub>6</sub>H<sub>4</sub>Me·MgI and thence into *o*-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>H) : (*o*-C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>I·I → *o*-C<sub>6</sub>H<sub>4</sub>MeI + *o*-C<sub>6</sub>H<sub>4</sub>Me<sup>+</sup> + I<sup>-</sup>. Physical data for the C<sub>6</sub>H<sub>4</sub>MeI are given. H. B.

**Chloro-derivatives of xylene.** H. WAHL (Ann Chim., 1936, [xi], 5, 5—82).—Partly a detailed account of work already reported (A., 1933, 815; 1934, 177, 181, 772, 878; 1935, 739). The following is new. Chloro-*p*-xylene (I) and H<sub>2</sub>SO<sub>4</sub> give 2-chloro-*p*-xylene-5-sulphonic acid, +2H<sub>2</sub>O, m.p. about 100° (a, +H<sub>2</sub>O, and Ca salts, +3H<sub>2</sub>O; chloride, m.p. 50; amide, m.p. 185°; anilide, m.p. 155°), obtained (diazo-reaction) also from *p*-xylylene-5-sulphonic acid and converted by HNO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub> at 50—60° into a mixture of 65—70% of 2-chloro-3-nitro-*p*-xylene-5-sulphonic acid (K, Ca, +4H<sub>2</sub>O, and Na, +2H<sub>2</sub>O, m.p. 101°) and 20% of 2-chloro-3:5-dinitro-*p*-xylene (II), m.p. 95° [also obtained from 2-chloro-3- and -5-nitro-*p*-xylene and HNO<sub>3</sub> at about 10° and (diazo-reaction) from 3:5-dinitro-*p*-xylylene]. Reduction (Fe—HCl) affords 3-chloro-*p*-xylylene-6-sulphonic acid, +H<sub>2</sub>O. The prep. of the 3-NO<sub>2</sub>, m.p. 36° (Ac derivative, m.p. 190°), and 5-NO<sub>2</sub>-derivatives of acet-*p*-xylylene is described. The third aldehyde (phenylhydrazone, m.p. 145°), obtained by nitration of (I), has m.p. 101°. 2-Chloro-6-nitro-*p*-xylene and HNO<sub>3</sub> at about 10° give 2-chloro-5:6-dinitro-*p*-xylene, m.p. 101°, reduced by Zn and AcOH—EtOH to the (NH<sub>2</sub>)<sub>2</sub>-compound, m.p. 50°, which affords a phenanthrazine, m.p. 235°. 5-Chloroacet-*p*-xylylene (III) and HNO<sub>3</sub> give 5-chloro-3-nitroacet-*p*-xylylene, m.p. 200—200·5°, hydrolysed (H<sub>2</sub>SO<sub>4</sub>) to 5-chloro-3-nitro-*p*-xylylene, m.p. 100—101° (Bz derivative, m.p. 160°), the structure of which is proved by conversion into 2-chloro-6-nitro-*p*-xylene. The Cl of the chloronitro-*p*-xylenes is unreactive owing to steric hindrance. The K salts, +H<sub>2</sub>O, of 2:3- and 2:6-dichloro-*p*-xylenesulphonic acids are described. 2:5-Dichloro-*p*-xylene and HNO<sub>3</sub> give the 6-NO<sub>2</sub>-derivative, m.p. 95°, b.p. 155—160°/15 mm., reduced (Fe) to the 6-NH<sub>2</sub>-derivative, m.p. 81°, b.p. 155—160°/15 mm. (Ac, m.p. 198°, and Bz derivative, m.p. 205°). (III) and Cl<sub>2</sub> in AcOH give 3:5-dichloroacet-*p*-xylylene, m.p. 172°, hydrolysed to the base, m.p. 48°, b.p. 160—162°/15 mm. (Bz derivative, m.p. 179—180°), which (diazo-reaction) yields 2:6-dichloro-*p*-xylene. *p*-Xylylene with Cl<sub>2</sub> in conc.

H<sub>2</sub>SO<sub>4</sub> at about 40° affords the 5:6-Cl<sub>2</sub>-derivative, m.p. 78—80°, b.p. 165—170°/15 mm. [Ac, m.p. 165° (corr.), and Bz derivative, m.p. 173° (corr.)], converted (diazo-reaction) into 2:3-dichloro-*p*-xylene. Hot chlorination of (III) affords 3:5:6-trichloroacet-*p*-xylylene, m.p. 220°, and thence the base, m.p. 206°. Dyes obtained by coupling each of 10 diazotised xylylenes with 9 2-hydroxy-1-naphthxylylenes and 9 naphthols are described. The fastness of these dyes to light, Cl<sub>2</sub>, and washing is good. The following are prepared: 2-hydroxy-1-naphth-xylylene, m.p. 200°, -3-, m.p. 230°, -5'-, m.p. 258°, and -6'-chloro-, m.p. 180°, -3'-, m.p. 150° (decomp.), -5'-, m.p. 255° (decomp.), and -6'-nitro-, m.p. 145°, and -3':5'-, m.p. 223°, -3':6'-, m.p. 250°, and -5':6'-dichloro-*p*-xylylene, m.p. 233°. R. S. C.

**Jacobsen reaction.** IV. L. I. SMITH and C. L. MOYLE (J. Amer. Chem. Soc., 1936, 58, 1—10).—The Jacobsen rearrangement is not a general reaction; it is limited (with few exceptions) to C<sub>6</sub>H<sub>5</sub>Me<sub>3</sub>, C<sub>6</sub>HMe<sub>5</sub>, C<sub>6</sub>HMe<sub>4</sub>Et, and halogeno-derivatives of C<sub>6</sub>H<sub>5</sub> and methylbenzenes. Labile groups are Cl, Br, I, Me, Et, and SO<sub>3</sub>H; no rearrangement occurs when NO<sub>2</sub>, Ac, OMe, or CO<sub>2</sub>H is present. In general, except when Hal is present, < 4 substituents must be in the C<sub>6</sub>H<sub>5</sub> nucleus to obtain rearrangement; the course (and ease) of the reaction is determined by the substituents. Results now and previously obtained (A., 1933, 600) show that for all the C<sub>6</sub>HMe<sub>4</sub>Cl and C<sub>6</sub>HMe<sub>4</sub>Br, the ease of migration is Br > Me > Cl, whilst for C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>Cl and C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>Br the order is Br > Cl > Me (when rearrangement occurs). There appears to be some correlation between the ease of hydrolysis of ArSO<sub>3</sub>H and its ability to undergo rearrangement. Whenever rearrangement occurs, side reactions leading to amorphous solids or tars and SO<sub>2</sub> also occur. Attempts to rearrange C<sub>6</sub>Me<sub>5</sub>·SO<sub>3</sub>H, using conditions designed to avoid such reactions, failed; rearrangement could not be effected with reagents [e.g., PhSO<sub>3</sub>H, H<sub>3</sub>PO<sub>4</sub>, CaCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub>] other than H<sub>2</sub>SO<sub>4</sub>. The constitutions of the compounds described below are established by conversion into known or proved derivatives.

Chlorodurene (from durene and Cl<sub>2</sub> in CHCl<sub>3</sub> at 0° and conc. H<sub>2</sub>SO<sub>4</sub> at 65° give 99% of chloropentamethylbenzene (I), m.p. 154·5—155° [reduced (red P, 45% HI, 220°) to C<sub>6</sub>HMe<sub>5</sub>], and 81% of 3-chloro-*ψ*-cumene-5-sulphonic acid (II) [also prepared by short treatment of 3-chloro-*ψ*-cumene (III) with oleum]. Chlorosodurene, b.p. 139°/41 mm., m.p. -1° to 1° (obtained with a little of the Cl<sub>2</sub>-derivative, m.p. 188°, from isodurene and Cl<sub>2</sub> in CHCl<sub>3</sub>), similarly affords (I) (96·4%), (II) (70%), and a little of a compound, C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>, m.p. 209·5°, whilst chloroprehnitenene, b.p. 131—132°/24 mm., m.p. 24°, and approx. 14% oleum at 25—30° yield (I) (98%) and (II) [or, by hydrolysis, (III)]. At least two rearrangements are considered to occur with the above C<sub>6</sub>HMe<sub>4</sub>Cl. 5-Chloro-*ψ*-cumene, m.p. 70·5—71° [formed with (III) from *ψ*-cumene and Cl<sub>2</sub> in CHCl<sub>3</sub> at 0°, and 20% oleum at 65—70° give (II) (71%) and tar. (II) (44%) and a small amount of an unidentified product, m.p. 148—153°, are formed from 6-chloro-*ψ*-cumene (IV), b.p. 127—128°/20 mm. [3:5-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p.

162° (lit. 162° and 169—170°), and approx. 15% oleum at 25—30°. Intramol. migration of Cl thus occurs in both cases. (IV) is prepared by deamination of 6-chloro-5- $\psi$ -cumidine [from  $\psi$ -cumidine (V) (in EtOH-I) and  $\text{Cl}_2$  (in  $\text{CHCl}_3$ )]. Chloromesitylene [ $\text{SO}_3\text{H}$  derivative ( $\text{Na}$  salt +  $0.5\text{H}_2\text{O}$ ; *amide*, m.p. 165.5—166°)] and 4-chlorohemimellitene, b.p. 86—87°/16 mm. [5:6- $\text{Br}_2$ -derivative, m.p. 229—230°], prepared from hemimellitene and  $\text{Cl}_2$  in  $\text{CHCl}_3$ -I at 0°, do not rearrange; sulphonation occurs with 20% oleum at 70—75°. Bromomesitylene [ $\text{SO}_3\text{H}$  derivative ( $\text{Na}$  salt +  $0.5\text{H}_2\text{O}$ ; *amide*, m.p. 160—160.5°)] and 20% oleum at 25—30° give *dibromomesitylene*, m.p. 65.5°, and 2:4:6- $\text{C}_6\text{H}_3\text{Me}_3\text{SO}_3\text{H}$  (not isolated; hydrolysed to  $s\text{-C}_6\text{H}_3\text{Me}_3$ ); at 70°, *tribromomesitylene*, m.p. 223.5—224°, is formed in 68.5% yield. 5-Bromo- $\psi$ -cumene [from  $\psi$ -cumene-5-sulphonic acid (VI) and Br in aq. EtOH] and 20% oleum at 25—30°/6 weeks afford a little *tribromo- $\psi$ -cumene*, m.p. 232°, and 90% of 3-bromo- $\psi$ -cumene-5-sulphonic acid [ $\text{Na}$  salt, also prepared from the  $\text{Na}$  salt of (VI) in EtOH with Br in  $\text{CHCl}_3$ ], hydrolysed (dil.  $\text{H}_2\text{SO}_4$  at 145°) to 3-bromo- $\psi$ -cumene. The following compounds did not undergo any rearrangement when treated with conc.  $\text{H}_2\text{SO}_4$  or oleum: (V), hemimellitene, 5-nitro- $\psi$ -cumene, 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$ ,  $p\text{-C}_6\text{H}_4\text{PhBr}$ , pentamethylcyclohexane, b.p. 98—98.5°/38 mm., 188°/730 mm. [prepared by reduction ( $\text{H}_2$ , Ni-kieselguhr, 225°) of  $\text{C}_6\text{HMe}_5$ ], and *Me pentamethylbenzenesulphonate*, m.p. 91—91.5° (from  $\text{C}_6\text{Me}_5\text{SO}_2\text{Cl}$  and  $\text{MeOH-NaOMe}$ ).

Reduction (Zn, dil. HCl) of 3-chloro- $\psi$ -cumene-5-sulphonamide, m.p. 182°, affords  $\psi$ -cumene-5-sulphonamide, m.p. 180°.  $\text{Na}$  3-chloro- $\psi$ -cumene-5-sulphonate (VII) is reduced ( $\text{Na-Hg}$ ,  $\text{H}_2\text{O}$ ) to  $\text{Na}$   $\psi$ -cumene-5-sulphonate (nitrated to trinitro- $\psi$ -cumene, m.p. 183.5°), is converted by red P and 45% HI into  $\psi$ -cumene, and is hydrolysed (dil.  $\text{H}_2\text{SO}_4$  at 135—155°) to 3-chloro- $\psi$ -cumene, b.p. 127°/61 mm. [5:6-( $\text{NO}_2$ )<sub>2</sub>-derivative (VIII), m.p. 173.5—174°, also formed by nitration of (VII)]. 3-Chloro-5:6-diamino- $\psi$ -cumene, m.p. 136.5° [from (VIII),  $\text{SnCl}_2$ , and EtOH-conc. HCl], and phenanthraquinone (IX) in EtOH-AcOH afford 12-chloro-10:11:13-trimethylphenanthrophenazine, m.p. 330.5—331°, whilst reduction ( $\text{SnCl}_2$ , HCl) of (VIII) in AcOH gives 6-chloro-2:4:5:7-tetramethylbenziminazole, m.p. 250—251°. 3-Chloro-5:6-dibromo- $\psi$ -cumene, m.p. 224°, is obtained from (VII) and Br in AcOH at 70°. 2-Chloro-4:6-diaminomesitylene, m.p. 137—138°, is prepared by reduction ( $\text{SnCl}_2$ ) of the ( $\text{NO}_2$ )<sub>2</sub>-derivative. 3-Bromo-5:6-dinitro- $\psi$ -cumene is reduced ( $\text{SnCl}_2$ , EtOH-HCl) to 5:6-diamino- $\psi$ -cumene, which with (IX) yields 10:11:13-trimethylphenanthrophenazine, m.p. 253°; reduction in AcOH affords 2:4:5:7-tetramethylbenziminazole, m.p. 233°. 6-Bromo- $\psi$ -cumene, b.p. 117°/17 mm., 233° (corr.)/724 mm., is obtained by deamination of 6-bromo-5- $\psi$ -cumidine, m.p. 69° [from (V) (in dil. HCl) and Br in AcOH]. 4-Chloro-5:6-dinitrohemimellitene, m.p. 183°, is similarly reduced to the ( $\text{NH}_2$ )<sub>2</sub>-derivative, m.p. 137—137.5°, which with Ac. and (IX) gives 8-chloro-2:3:5:6:7-pentamethylquinoxaline, m.p. 160.5°, and 13-chloro-10:11:12-trimethylphenanthrophenazine, m.p. 346.5—347°; reduction in AcOH yields 7-chloro-2:4:5:6-tetramethylbenziminazole, m.p. 288.5°. The ( $\text{NO}_2$ )<sub>2</sub>-

derivative, m.p. 196.5°, of 4-bromohemimellitene, b.p. 103—103.5°/12 mm., 229.5°/750 mm., m.p. 1°, on reduction ( $\text{SnCl}_2$ , HCl) and treatment with (IX) gives 10:11:12-trimethylphenanthrophenazine, m.p. 311°. H. B.

**Oxidation in benzene series by gaseous oxygen. V. Oxidation of tertiary hydrocarbons.** H. N. STEPHENS and F. L. RODUTA (J. Amer. Chem. Soc., 1935, 57, 2380—2381).—Slow oxidation ( $\text{O}_2$ ) of  $\text{CHPhMeR}$  ( $\text{R}=\text{Et}$ ,  $\text{Pr}^n$ ,  $\text{Bu}^n$ ) at 119° (bath) gives  $\text{COPhMe}$  but no  $\text{COPhR}$ ;  $\text{CHPh}_2\text{Me}$  and  $\text{CHPh}_3$  similarly afford  $\text{COPh}_2$ . These reactions, unlike that with  $\text{CH}_2\text{Ph}_2$  ( $\rightarrow \text{COPh}_2$ ) (cf. A., 1928, 1233), are not inhibited by  $\text{H}_2\text{O}$ . H. B.

**Reactions between organomercury compounds and nitrosyl compounds.** L. I. SMITH and F. L. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 2460—2463).—Acetoxymercuridurene (I) (in  $\text{CHCl}_3$ ) and  $\text{NOCl}$  (from EtO-NO and AcOH-conc. HCl) give *nitroso-durene* (II), m.p. 160° (decomp.) (rapid heating). *Nitroso-isodurene* (III), m.p. 134°, *pentamethylbenzene*, m.p. 160° (decomp.) (rapid heating), *prehnitene*, m.p. 72°, *mesitylene*, and  $\psi$ -cumene are similarly prepared:  $\text{ArHgX} + \text{NOCl} \rightarrow \text{ArNO} + \text{HgXCl}$ . (I) and (II) are both converted by  $\text{HNO}_3$  (d 1.26) at 70° into *nitrodurene*, m.p. 112—113°; (III) and acetoxymercuridurene (IV) similarly afford *nitroisodurene*, m.p. 38—39°, also prepared from (III) and  $\text{NO}_2$  in  $\text{CHCl}_3$ .  $\text{N}_2\text{O}_3$  distilled into (IV) (in  $\text{CHCl}_3$ ) gives a colourless ppt. of (probably) *nitritomercuroisodurene* contaminated with  $\text{Hg}(\text{NO}_2)_2$ , which subsequently redissolves; a brown ppt. is then formed and the  $\text{CHCl}_3$  contains (III) [similarly obtained from (IV) and  $\text{NO}_2$ ]. The reaction between  $\text{HgPh}_2$  and  $\text{N}_2\text{O}_3$  (Bamberger, A., 1897, i, 288; 1900, i, 145) is considered to give  $\text{PhNO}$  as the primary product;  $\text{PhN}\cdot\text{NO}_3$  is then formed from  $\text{PhNO}$  and  $\text{NO}$ . Diazonium nitrates are formed only when  $\text{N}_2\text{O}_3 + \text{NO}$  (excess) act on Hg compounds. H. B.

**Reaction between chlorodiphenylmethane and ethyl alcohol.** F. G. KNY-JONES and A. M. WARD (J. Amer. Chem. Soc., 1935, 57, 2394—2396). Re-examination of the method previously used (A., 1927, 1061) in greater detail again shows that the reaction,  $\text{CHPh}_2\text{Cl} + \text{EtOH} \rightarrow \text{CHPh}\cdot\text{OEt} + \text{HCl}$ , is irreversible (cf. Norris and Morton, A., 1928, 1000). H. B.

**Polystyrene and the mechanism of polymerisation.** G. S. WHITBY (Trans. Faraday Soc., 1936, 32, 315—323).—Evidence is presented for the view that polymerisation of unsaturated compounds is due to successive additions to the double linking present in the monomeric or the preceding polymeric stage, a H atom going to one side of the double linking and the rest of the addendum to the other. F. L. U.

**Highly polymerised compounds. CXXI. Insoluble polystyrene.** H. STAUDINGER [with HEUER and E. HUSEMANN] (Trans. Faraday Soc., 1936, 32, 323—332).—When styrene (I) is polymerised in presence of *p*-divinylbenzene (II) as product, although highly turgescible, is insol. in the usual solvents. The proportion of (II) needed to render the resulting polystyrene (III) insol. decreases as the chain-length of (III) increases, being, e.g. (11)



(I)=1/50,000 for a highly polymerised product. The insol. product is thus chemically indistinguishable from sol. (III), and the striking difference in physical properties is due to the relatively small no. of "bridges" effected by (II) between the long chains of (III), converting a linear into a three-dimensional polymeride. The results are discussed with reference to sol. and insol. caoutchouc, and to highly polymerised biological materials.

F L U

**Synthesis of diacetylene derivatives.** J. S. SALKIND and F. B. FUNDYLER (Ber., 1936, 69, [B], 128—130).—CPh:CH is converted by heating with a feebly acidified solution of  $\text{NH}_4\text{Cl}$  and excess of  $\text{CuCl}$  into the compound,  $\text{C}_{16}\text{H}_{10}\text{CuCl}$ , immediately decomposed by  $\text{Et}_2\text{O}$  into  $\alpha\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -butindine (I), m.p. 86—87°. The change appears to be balanced. (I) is hydrogenated (Pt-sponge) to  $\alpha\delta$ -diphenylbutane. The liberated H is involved in the formation of resinous material (?  $\text{C}_{16}\text{H}_{14}$ ). Analogous reactions are given by  $\gamma$ -hydroxy- $\gamma$ -methyl- $\Delta^{\alpha}$ -butinene and hydroxycyclohexylacetylene.

H. W.

**Rearrangements of polyinenes. VII. Formation of allenenes.** J. H. FORD, C. D. THOMPSON, and C. S. MARVEL (J. Amer. Chem. Soc., 1935, 57, 2619—2623).—COPhBu $\gamma$  (I) (2 : 4-dinitrophenylhydrazine, m.p. 194—195°), prepared in 67% yield from  $\text{MgPhBr}$  and  $\text{Bu}^{\gamma}\text{COCl}$  in  $\text{Et}_2\text{O}$  and  $\text{N}_2$ , with  $\text{CBu}^{\gamma}\text{C}^{\gamma}\text{MgBr}$  gives phenyltert.-butyltert.-butylethynylcarbinol (II), b.p. 125—128°/4 mm., converted by  $\text{PBr}_3$  in light petroleum into the carbinyl bromide (III), b.p. 115—117°/1 mm., and by  $\text{AcOH}$ -conc.  $\text{H}_2\text{SO}_4$  into  $\gamma$ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- $\Delta^{\gamma}$ -hepten- $\epsilon$ -one, b.p. 96—97°/1 mm., m.p. 30.5° (2 : 4-dinitrophenylhydrazine, m.p. 150—151°). A hydrocarbon could not be prepared from (II) and  $\text{TiCl}_3$  or from (III) and  $\text{Ag}$  or  $\text{Cu}$ . (III) and moist  $\text{Ag}_2\text{O}$  in  $\text{COMe}_2$  give (II). Decomp. of the Grignard reagent (A) from (III) with  $\text{H}_2\text{O}$  affords the allenic hydrocarbon  $\gamma$ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- $\Delta^{\gamma\epsilon}$ -heptadiene (IV), b.p. 78—80°/1 mm. [ozonolysis products,  $\text{Bu}^{\gamma}\text{CO}_2\text{H}$  and (I)].  $\text{ClCO}_2\text{Me}$  and (A) similarly give Me  $\gamma$ -phenyl- $\beta\beta\zeta\zeta$ -tetramethyl- $\Delta^{\gamma\epsilon}$ -heptadiene- $\epsilon$ -carboxylate, b.p. 116—120°/2 mm. [free acid, m.p. 160—161°, also formed from (A) and  $\text{CO}_2$ ], which is oxidised ( $\text{O}_3$ ) to the Me ester (2 : 4-dinitrophenylhydrazine, m.p. 205—206°) of trimethylpyruvic acid [2 : 4-dinitrophenylhydrazine, m.p. 169—171° (decomp.)]. (III) does not give a stable Na alkyl when treated with 40% Na-Hg in  $\text{Et}_2\text{O}$  and  $\text{N}_2$ ; decomp. of the product with  $\text{H}_2\text{O}$  affords (IV) and two isomeric hydrocarbons,  $\text{C}_{34}\text{H}_{46}$ , m.p. 148—149° and 115—125°. The same mixture is obtained by reduction (Zn dust,  $\text{EtOH}$ ) of (III) or treatment with Li.  $\alpha$ -Phenyl- $\beta\beta$ -dimethylbutyric acid, m.p. 105°, is prepared from  $\text{CO}_2$  and  $\text{CHPhBu}^{\gamma}\text{MgBr}$ . The acids and esters formed from metallic derivatives of the type  $\text{CR}:\text{C}:\text{CR}'_2\text{M}$  may all be  $\text{CO}_2\text{R}''\text{CR}:\text{C}:\text{CR}'_2$ . H. B.

**Rearrangements of polyinenes. VIII. Formation of diallenes.** E. D. FARLEY and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 29—34).—The hydrocarbon obtained (A., 1932, 505) from diphenyltert.-butylethynylcarbinyl bromide and  $\text{Ag}$  or  $\text{Cu}$ -bronze is now considered to be  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\gamma\delta$ -ditert.-butyl- $\Delta^{\alpha\beta\gamma\delta}$ -hexatetraene (I),  $(\text{CPh}_2\text{C}^{\gamma}\text{CBu}^{\gamma})_2$ , since oxidation

(dry  $\text{O}_2$  in  $\text{C}_6\text{H}_4\text{Me}_2$  at 140°) gives 52% of  $\text{COPh}_2$ , (apart from products derived from the  $\text{C}_6\text{H}_4\text{Me}_2$ ). (I) could not be oxidised by  $\text{PbO}_2$ ; with  $\text{O}_3$  the products previously reported (*loc. cit.*) and  $\text{BzOH}$  are obtained. The hydrocarbon  $\text{C}_{12}\text{H}_{16}$  [obtained (*ibid.*, 496) from  $\text{CMeEt}_2\text{C}^{\gamma}:\text{C}^{\gamma}:\text{CPh}_2\text{Br}$ ] is also oxidised ( $\text{O}_2$ ) to  $\text{COPh}_2$  (38%); definite products could not be isolated from the hydrocarbon prepared by Moureu *et al.* (A., 1927 355) from  $(\text{CPh}:\text{C}^{\gamma}\text{CPh}_2)_2$ . Reduction of diphenyltert.-butylethynylcarbinol with  $\text{TiCl}_3$  gives (I) and a compound,  $\text{C}_{38}\text{H}_{39}\text{Cl}$ , m.p. 201°. Reduction (Na, amyl alcohol) of (I) affords hydrocarbons,  $\text{C}_{38}\text{H}_{38}$ , m.p. 132 (II), and  $\text{C}_{38}\text{H}_{44}$  [described previously (A., 1932, 505) as  $\text{C}_{19}\text{H}_{22}$ ], m.p. 182°; with red P and 47% HI in  $\text{AcOH}$ , a hydrocarbon,  $\text{C}_{30}\text{H}_{42}$  (III), m.p. 210—211° [which may be the dimeride of 3-phenylindene (Blum-Bergmann, A., 1931, 208)], results. The hydrocarbon,  $\text{C}_{38}\text{H}_{38}$ , m.p. 176°, obtained (*cf. loc. cit.*) from (I) and  $\text{AcOH-HCl}$ , is not oxidised by  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{AcOH}$ , does not give a Na alkyl with 40% Na-Hg, but is reduced (P, HI,  $\text{AcOH}$ ) to (III). (I) and 40% Na-Hg in  $\text{Et}_2\text{O}$  and  $\text{N}_2$  afford a product (A) containing  $\text{CNaPh}_2\text{C}^{\gamma}:\text{C}^{\gamma}\text{CBu}^{\gamma}$  [since treatment with  $\text{CO}_2$  gives a little  $\text{CBu}^{\gamma}:\text{C}^{\gamma}\text{CPh}_2\text{CO}_2\text{H}$  (A., 1932, 50)] and an additive compound  $\text{C}_{38}\text{H}_{38}\text{Na}_2$  [since the action of  $\text{H}_2\text{O}$  affords a hydrocarbon,  $\text{C}_{38}\text{H}_{40}$  (IV), m.p. 163° (*loc. cit.*), whilst  $\text{ClCO}_2\text{Me}$  gives an ester,  $\text{C}_{38}\text{H}_{38}(\text{CO}_2\text{Me})_2$ , m.p. 173°, which when (partly) hydrolysed ( $\text{MeOH-KOH}$ ) and then heated passes into an ester,  $\text{C}_{38}\text{H}_{39}\text{CO}_2\text{Me}$ , m.p. 162°]. Oxidation of (IV) with  $\text{KMnO}_4$  in  $\text{COMe}$  gives a neutral compound,  $\text{C}_{38}\text{H}_{39}\text{O}_2$ , m.p. 217—218°; with  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{AcOH}$ , a neutral compound,  $\text{C}_{38}\text{H}_{28}\text{O}_3$  (V), m.p. 169°, results. Reduction (Na, amyl alcohol) of (IV) affords a hydrocarbon,  $\text{C}_{38}\text{H}_{42}$  (VI), m.p. 197°, and a mixture (B) of (VI) and a more fusible isomeride; the hydrocarbon,  $\text{C}_{38}\text{H}_{42}$ , m.p. 181—182°, previously described (A., 1932, 505), is identical with (B). (VI) is also obtained by successive treatment of (IV) with 40% Na-Hg and  $\text{H}_2\text{O}$ . The hydrocarbon,  $\text{C}_{38}\text{H}_{38}$ , m.p. 179—180° (*loc. cit.*), prepared from (A) and  $\text{C}_2\text{Me}_4\text{Br}_2$ , is oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{AcOH}$ ) to (V), is reduced (Na, amyl alcohol) to (VI) and an isomeride, m.p. 155—156°, and is converted by successive treatment with 40% Na-Hg and  $\text{H}_2\text{O}$  into (IV).

The Na alkyl from  $\alpha\alpha$ -diphenyl- $\delta\delta$ -dimethyl- $\Delta^{\alpha\beta}$ -pentadiene (A., 1932, 50) and 40% Na-Hg with  $\text{C}_2\text{Me}_4\text{Br}_2$  gives a hydrocarbon,  $\text{C}_{38}\text{H}_{40}$ , m.p. 143—144°; the dimeride (VII) (*loc. cit.*) similarly regenerates (VII), but decomp. with  $\text{H}_2\text{O}$  affords a hydrocarbon,  $\text{C}_{38}\text{H}_{44}$ , m.p. 133° [probably formed also by reduction (Na, amyl alcohol) of (VII)], which differs from (II). Reduction (red P, 47% HI,  $\text{AcOH}$ ) of (VII) affords a hydrocarbon,  $\text{C}_{38}\text{H}_{42}$ , m.p. 134—135°, whilst oxidation ( $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{AcOH}$ ) gives a little of a neutral compound,  $\text{C}_{26}\text{H}_{26}\text{O}_2$ , m.p. 227°, but no  $\text{COPh}_2$ . H. B.

**Mol. compounds of polycyclic hydrocarbons and their quinones with polynitro-compounds and with metallic salts.** K. BRASS and K. FANTA (Ber., 1936, 69, [B], 1—11).—Examination of many compounds fails to confirm Bruni's view (A., 1906, i, 491) that the power of adding  $\text{NO}_2$ -compounds depends essentially on the  $\text{C}_6\text{H}_6$  nucleus and that the no. of added mols. is in the limit equal to the no. of independent  $\text{C}_6\text{H}_6$  nuclei present in the hydrocarbon



and that polynuclear condensed mols. add only 1 mol. of  $\text{NO}_2$ -compounds. Perylene does not add dipicric acid (I), but with styphnic acid (II) gives a compound (1:1), m.p.  $211^\circ$ . 2:3:10:11-Dibenzperylene affords the compounds,  $\text{C}_{28}\text{H}_{16}$ ,  $2\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ , m.p.  $240^\circ$  (decomp.),  $\text{C}_{28}\text{H}_{16}$ ,  $2\text{C}_6\text{H}_5\text{O}_8\text{N}_3$ , decomp.  $236^\circ$ ,  $\text{C}_{28}\text{H}_{16}$ ,  $\text{SbCl}_5$ , and  $\text{C}_{28}\text{H}_{16}$ ,  $\text{SnCl}_4$ . 1:12-Benzperylene does not add (I), but affords the substances,  $\text{C}_{22}\text{H}_{12}$ ,  $\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ , m.p.  $267^\circ$ ,  $\text{C}_{22}\text{H}_{12}$ ,  $\text{C}_6\text{H}_5\text{O}_8\text{N}_3$ , m.p.  $234^\circ$ ,  $2\text{C}_{22}\text{H}_{12}$ ,  $\text{SbCl}_5$ , and  $\text{C}_{22}\text{H}_{12}$ ,  $2\text{SnCl}_4$ . 2:3-Benzanthracene does not unite with picric acid (III), dibromopicric acid (IV), (I), or (II), but gives the substances,  $2\text{C}_{18}\text{H}_{12}$ ,  $\text{SbCl}_5$  and  $\text{C}_{18}\text{H}_{12}$ ,  $2\text{SnCl}_4$ . Addition of (I), (II), (III), or (IV) to 2:3-benzanthraquinone is not observed, but the compounds,  $\text{C}_{18}\text{H}_{10}\text{O}_2$ ,  $2\text{SbCl}_5$  and  $\text{C}_{18}\text{H}_{10}\text{O}_2$ ,  $2\text{SnCl}_4$ , have been isolated. 1:2-Benzanthracene gives the compounds,  $\text{C}_{18}\text{H}_{12}$ ,  $\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ , m.p.  $141.5\text{--}142.5^\circ$ ,  $\text{C}_{18}\text{H}_{12}$ ,  $\text{C}_6\text{H}_5\text{O}_8\text{N}_3$ , m.p.  $153^\circ$ , and  $2\text{C}_{18}\text{H}_{12}$ ,  $\text{SbCl}_5$ . 1:2-Benzanthraquinone does not add (I), (II), (III), or (IV), but affords the substances,  $\text{C}_{18}\text{H}_{10}\text{O}_2$ ,  $\text{SbCl}_5$  and  $2\text{C}_{18}\text{H}_{10}\text{O}_2$ ,  $\text{SnCl}_4$ ,  $\text{CHCl}_3$ . (III) is not added by 3-isopropyl-, m.p.  $154\text{--}155^\circ$ , 7-isopropyl-, m.p.  $114^\circ$ , 4-methyl-, m.p.  $168\text{--}169^\circ$ , 5-methyl-, m.p.  $173.5\text{--}174.5^\circ$ , or 6-methyl-, m.p.  $174^\circ$ , 1:2-benzanthraquinone. Additive compounds of 9:9'-dianthryl with (II), (III), or (IV) could not be isolated;  $\text{SnCl}_4$  causes halochromism, whilst  $\text{SbCl}_5$  affords the substance,  $\text{C}_{28}\text{H}_{18}$ ,  $\text{SbCl}_5$ . 9:9'-Dianthranthylquinone does not add (I), (II), (III), or (IV), but gives the compounds,  $\text{C}_{28}\text{H}_{16}\text{O}_2$ ,  $2\text{SbCl}_5$  and  $\text{C}_{28}\text{H}_{16}\text{O}_2$ ,  $2\text{SnCl}_4$ . H. W.

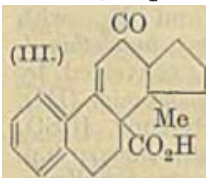
**Action of oleum on decahydronaphthalene.** E. I. PROKOPETZ (J. Appl. Chem. Russ., 1935, 8, 1214—1215).—When *cis-trans*-decahydronaphthalene is shaken with 20% oleum, only the *cis*-isomeride is oxidised, leaving the pure *trans*-isomeride. R. T.

**Rubrene problem.** A. SCHONBERG (J. Amer. Chem. Soc., 1936, 58, 182; cf. A., 1934, 643).—A question of priority (cf. Eck and Marvel, A., 1935, 1492). H. B.

**Attempts to obtain rubenes soluble in water. Hexabromotetraphenylrubene; its transformation into rubenepolycarboxylic acids.** C. DUFRAISSE and L. VELLUZ (Bull. Soc. chim., 1936, [v], 3, 254—265).— $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{C}\cdot\text{MgBr}$  and  $\text{CO}(\text{C}_6\text{H}_4\text{Br}\cdot p)_2$  give  $\alpha\gamma\gamma$ -tri-*p*-bromophenylpropinen- $\gamma$ -ol, m.p.  $141\text{--}142^\circ$  (*Me* ether, m.p.  $101\text{--}102^\circ$ ); this with  $\text{H}_2\text{SO}_4\text{--Bu}_2\text{O}$  gives *p*- $\text{C}_6\text{H}_4\text{Br}$  *pp'*-dibromohydrindenylmethyl ketone, m.p. ( $+ \text{C}_6\text{H}_6$ )  $114\text{--}115^\circ$  and (anhyd.)  $135\text{--}136^\circ$ , which with  $\text{PCl}_3$  in ligroin affords the chloride, m.p.  $130\text{--}131^\circ$  (dimeride, m.p.  $273\text{--}275^\circ$ ), converted in quinoline at  $100^\circ/15\text{--}16$  mm. into 5:5'- (or 5:6'-)dibromo-1:3:1':3'-tetra-*p*-bromophenylrubene (bisindenyl formulation), m.p.  $401\text{--}402^\circ$  (cryst. peroxide loses 75% of its O at  $150\text{--}200^\circ$ ). Four Br readily and the last two very slowly react with Mg;  $\text{CO}_2$  then leads to an amorphous acid ( $\text{H}_2\text{O}$ -sol. Na salt), which forms a dissociable peroxide. M.p. are taken on a block. R. S. C.

**Chemical interrelationships in the cholane group.** H. JENSEN (J. Chem. Educ., 1935, 12, 559—564).—A review. L. S. T.

**Synthesis of compounds related to sterols, bile acids, and oestrus-producing hormones.** VIII. C. L. HEWETT. IX. A. COHEN, J. W. COOK, and C. L. HEWETT. X. Ruzicka's hydrocarbon " $\text{C}_{21}\text{H}_{36}$ " from cholic acid. W. E. BACHMANN, J. W. COOK, C. L. HEWETT, and J. IBALL (J.C.S., 1936, 50—52, 52—53, 54—61).—VIII. Dihydroresorcinol (I) (1 mol.) and  $\text{CH}_2\text{PhCl}$  (1 mol.) in  $\text{EtOH-NaOEt}$  (1 mol.) give some benzylcyclohexane-2:6-dione, m.p.  $184\text{--}185^\circ$ , converted by conc.  $\text{H}_2\text{SO}_4$  at  $-15^\circ$  into a  $\text{SO}_3\text{H}$  derivative ( $+ \text{H}_2\text{O}$ ), m.p.  $193\text{--}194^\circ$ .  $\beta$ -*m*-Methoxyphenylethyl bromide (II), b.p.  $138^\circ/12$  mm., and (I) similarly afford (mainly) the  $\beta$ -*m*-methoxyphenylethyl ether, b.p.  $205\text{--}207^\circ/0.5$  mm., of (I) and a little  $\beta$ -*m*-methoxyphenylethylcyclohexane-2:6-dione, m.p.  $149\text{--}150^\circ$  (cf. Robinson and Schittler, A., 1935, 1498), which is best converted into 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (*loc. cit.*) by 80%  $\text{H}_2\text{SO}_4$  at  $100^\circ$  (bath).  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  and (I) give 3-keto- $\Delta^1$ -cyclohexenyl  $\beta$ -1-naphthylethyl ether, m.p.  $138\text{--}139^\circ$ , hydrolysed (aq.  $\text{EtOH-KOH}$  or  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in  $\text{C}_5\text{H}_5\text{N}$  at  $100^\circ$ ) to  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ . Hydrolysis (dil.  $\text{HCl}$ ) of the product from *m*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$  and  $(\text{CH}_2)_2\text{O}$  at  $100^\circ$  ( $\text{Et}_2\text{O}$  removed first) gives  $\beta$ -*m*-methoxyphenylethyl alcohol, b.p.  $150\text{--}155^\circ/18$  mm. (3:5-dinitrobenzoate, m.p.  $106.5\text{--}107.5^\circ$ ), converted by  $\text{PBr}_3$  in  $\text{CCl}_4$  into (II). Modified preps. of *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OH}$  (from *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$  and *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{OMe}$  are given. 2-Acetyl-1-methyl- $\Delta^1$ -cyclopentene (from 1-methyl- $\Delta^1$ -cyclopentene and  $\text{AcCl}$  in  $\text{CS}_2\text{--SnCl}_4$ ) and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$  in  $\text{EtOH-NaOEt}$  afford a little of (probably) the acid (III), m.p.  $242^\circ$ .

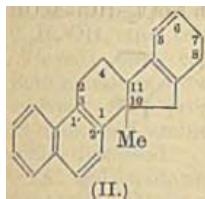


IX.  $\beta$ -6-Methoxy-1-naphthylethyl bromide and  $\text{CHK}(\text{CO}_2\text{Et})_2$  in  $\text{PhMe}$  at  $120\text{--}130^\circ$  give the *Et* ester, b.p.  $200\text{--}205^\circ/0.3$  mm., of  $\beta$ -6-methoxy-1-naphthylethylmalonic acid, m.p.  $160^\circ$  (decomp.), decarboxylated at  $190^\circ$  to  $\gamma$ -6-methoxy-1-naphthylbutyric acid, m.p.  $150\text{--}151^\circ$  [*Et* ester (I), b.p.  $169^\circ/0.2$  mm.]. 1-Keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene (Butenandt and Schramm, this vol., 76) and a little of the 7-OH-ketone are formed from (I) and 80%  $\text{H}_2\text{SO}_4$  at  $100^\circ$ . The product from (I) and  $\text{Et}_2\text{C}_2\text{O}_4$  in  $\text{Et}_2\text{O}+\text{KOEt}$  is converted by warm 80%  $\text{H}_2\text{SO}_4$  into 7-methoxy-3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p.  $217.5\text{--}218.5^\circ$ , which is demethylated [ $\text{HBr}$  (d 1.48) in  $\text{AcOH}$ ] to 7-hydroxy-3:4-dihydrophenanthrene-1:2-dicarboxylic anhydride, m.p.  $275\text{--}278^\circ$  (previous sintering), and dehydrogenated ( $\text{Pt-black}$  at  $300^\circ$ ) to 7-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p.  $260\text{--}261^\circ$  (corr.) (cf. this vol., 71).

X (cf. A., 1935, 1359). The carbinol from 2-methylhydrindone and  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr}$  (I) is dehydrated ( $\text{KHSO}_4$  at  $160^\circ$ ) (general procedure) to 3- $\beta$ -1'-naphthylethyl-2-methylindene, m.p.  $99\text{--}99.5^\circ$  (dipicrate, m.p.  $161\text{--}161.5^\circ$ ), which is cyclised by  $\text{AlCl}_3$  in  $\text{CS}_2$  at  $0^\circ$  (general method) to 10-methyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene (II), m.p.  $111\text{--}112^\circ$ , dehydrogenated (Se at  $310^\circ$ ; general method) to 2':1'-naphtha-1:2-fluorene, m.p.  $328^\circ$  (*ibid.*, 74). *p*-Methylbenzylmethylmalonic acid, m.p.  $178\text{--}180^\circ$



(decomp.) [the *Et* ester, b.p. 203—210°/26 mm., is prepared from  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$  and  $\text{CNaMe}(\text{CO}_2\text{Et})_2$  in  $\text{EtOH}$ ], is decarboxylated at 180° to  $\beta\text{-}p\text{-tolyl-}\alpha\text{-methylpropionic acid}$ , b.p. 181—182°/23 mm., m.p. 30—31·5°, the chloride, b.p. 139—141°/21 mm., of which with  $\text{AlCl}_3$  in ligroin gives 2:6-dimethylhydrindone, b.p. 145—



148°/21 mm. [*phenylhydrazone*, m.p. 173—175° (decomp.)]. This and (I) lead to  $\beta\text{-}1'\text{-naphthylethyl-2:5-dimethylindene}$ , m.p. 81—81·5° (*dipicrate*, m.p. 144—144·5°), converted into 6:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 106·5—107° (*semipicrate*, m.p. 133·5—134°), and thence into 6-methyl-2':1'-naphtha-1:2-fluorene, m.p. 330° (varies with rate of heating), which is oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{AcOH}$ ) to the -1:2-fluorenone, m.p. 225—226°. *m*-Methylbenzylmethylmalonic acid, m.p. 152—153° (decomp.), is similarly converted through  $\beta\text{-}m\text{-tolyl-}\alpha\text{-methylpropionic acid}$ , b.p. 178—179°/20 mm. (chloride, b.p. 137—138°/21 mm.), into 2:5-dimethylhydrindone, b.p. 142—144°/21 mm. [2:4-dinitrophenylhydrazone, m.p. 225—226° (decomp.)], which with (I) gives  $\beta\text{-}3\text{-}1'\text{-naphthylethyl-2:6-dimethylindene}$ , b.p. 184—186°/0·05 mm., cyclised to 7:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 134·5—135° [accompanied by some  $\alpha\delta\text{-di-1-naphthylbutane}$ , m.p. 101° (*dipicrate*, m.p. 174—175°), which is undoubtedly present as an impurity in the indene; it is now prepared from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  and  $\text{Mg}$ ]. 7-Methyl-2':1'-naphtha-1:2-fluorene, m.p. 334—336°, is oxidised to the -1:2-fluorenone, m.p. 175—176·5°. *o*-Methylbenzylmethylmalonic acid, m.p. 125—123°, similarly yields  $\beta\text{-o-tolyl-}\alpha\text{-methylpropionic acid}$ , b.p. 179—180°/20 mm. (chloride, b.p. 137—138°/21 mm.), and thence 2:4-dimethylhydrindone, b.p. 147—149°/20 mm. [*semicarbazone*, m.p. 224—225° (decomp.)]. This and (I) lead to  $\beta\text{-}3\text{-}1'\text{-naphthylethyl-2:7-dimethylindene}$ , m.p. 96°, resolidifying with m.p. 113·5—114°, cyclised to 8:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 121—122° (*semipicrate*, m.p. 130·5—131·5°), dehydrogenated to 8-methyl-2':1'-naphtha-1:2-fluorene (III), m.p. 281—281·5° (corr.) (fluorenone, m.p. 237—238°). Hydrolysis (aq.  $\text{MeOH-KOH}$ ) of the product from  $\text{CNaMe}(\text{CO}_2\text{Et})_2$  and 4-bromo-3-bromomethyltoluene, b.p. 148—152° (from  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$ ,  $\text{Br}$ , and  $\text{Fe}$  powder at 0°), or a mixture of 4-bromo-2- and -3-chloromethyltoluenes (Fieser and Seligman, A., 1935, 853), gives 2-bromo-5-methylbenzylmethylmalonic acid, m.p. 179—180° (decomp.), converted through  $\alpha\text{-2-bromo-5-methylbenzylpropionic acid}$ , m.p. 84—85° (chloride, b.p. 173—174°/20 mm.), into 4-bromo-2:7-dimethylhydrindone, b.p. 115—117°/0·15 mm. This and (I) lead to 7-bromo-3- $\beta\text{-}1'\text{-naphthylethyl-2:4-dimethylindene}$ , m.p. 84—85° (*dipicrate*, m.p. 142·5—143·5°), which is cyclised to 8-bromo-5:10-dimethyl-3:4:10:11-tetrahydro-2':1'-naphtha-1:2-fluorene, m.p. 137·5—138·5°, dehydrogenated to 5-methyl-2':1'-naphtha-1:2-fluorene (IV), m.p. 275—276° (corr.) (fluorenone (V), m.p. 209—210°). Hydrolysis (aq.  $\text{NH}_4\text{Cl}$ ) of the product obtained from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  and propylene oxide at 100° ( $\text{Et}_2\text{O}$  first removed)

gives  $\alpha\text{-1-naphthylisopropyl alcohol}$ , b.p. 148—155°/25 mm. [3:5-dinitrobenzoate, m.p. 171—172°; chloride (VI), b.p. 131°/6 mm.]. Cyclisation of a fraction, b.p. 195—215°/0·8 mm., obtained from 2-methylhydrindone, the Grignard reagent from (VI), and  $\text{MgEtBr}$  (1 mol.) gives  $\alpha\delta\text{-di-1-naphthyl-}\beta\text{-}\gamma\text{-dimethylbutane}$ , m.p. 131—132° (removed as picrate), and resinous material, dehydrogenated with  $\text{Se}$  to a little 4-methyl-2':1'-naphtha-1:2-fluorene, m.p. 202—203° (corresponding fluorenone, m.p. 214—215°). All the methylnaphthafluorenones give intense purple colours, gradually changing to magenta, with conc.  $\text{H}_2\text{SO}_4$ .

Comparison (m.p.; colour with  $\text{H}_2\text{SO}_4$ ) of (V) and the ketone obtained by oxidation of the hydrocarbon,  $\text{C}_{21}\text{H}_{16}$  (VII), of Ruzicka *et al.* (A., 1933, 278; 1934, 398) shows their identity. Powder photographs of (IV) and (VII), which are first fused under identical conditions, are very similar; the slight difference is ascribed to impurity in (VII). Crystallographic data for (III) and (IV) are given. The production of (VII) [*i.e.*, (IV)] from cholic acid is due to simple cyclisation of the side-chain during dehydrogenation. H. B.

**Alkali fusion. I. Fusion of potassium sulphanilate with alkali.** N. N. VOROSCHCOV and M. M. SCHEMJAKIN (Ber., 1936, 69, [B], 148—152).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$  when heated with a large excess of  $\text{KOH}$  at 350—355° in  $\text{N}_2$  gives  $\text{NH}_3$  (76·7%); the normal exchange of  $\cdot\text{SO}_3\text{K}$  for  $\cdot\text{OK}$  occurs to only a slight extent since only 1·5% of  $\text{SO}_3$  is observed. At higher temp. (> 400°) the yield of  $\text{SO}_3$  increases but the product becomes carbonised. Although  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$  enters almost quantitatively into reaction the product does not contain  $\text{NH}_2\text{Ph}$ ,  $\text{PhOH}$ , or  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  is formed in 77·53% yield. H. W.

**Action of sodium on aromatic nitro- and nitroso-compounds.** V. O. LUKASHEVITSCH (Annalen, 1936, 521, 198—214).—The Na compounds of aryl  $\text{NO}_2$ - and  $\text{NO}$ -derivatives (Schmidt, A., 1900, i, 20) are best prepared by the action of 0·5% Na-Hg on the  $\text{NO}_2$ - or  $\text{NO}$ -compound in dry  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , or  $\text{PhMe}$  ( $\text{N}_2$  atm.). The structures  $\text{R}\cdot\text{N}(\text{ONa})_2$  (I), and  $\text{R}\cdot\text{NNa}\cdot\text{ONa}$  (II), respectively, are suggested. The reactions (I) +  $\text{R}'\text{NO}_2 \rightleftharpoons \text{R}'\text{N}(\text{ONa})_2 + \text{RNO}_2$  (A), and (II) +  $\text{R}'\text{NO} \rightleftharpoons \text{R}'\text{NONa}_2 + \text{RNO}$  (B), are reversible, but the reaction (I) +  $\text{R}'\text{NO} \rightarrow \text{R}'\text{NONa}_2 + \text{RNO}_2$  (C) proceeds only from left to right. These relationships are established by investigation of the products of interaction of (I) or (II) (or mixtures in accordance with equations A, B, or C) with  $\text{BzCl}$ , dil.  $\text{H}_2\text{SO}_4$ , or  $\text{H}_2\text{O}$ , numerous examples being given. Thus with  $\text{BzCl}$  (I) reacts: (I) +  $2\text{BzCl} \rightarrow \text{RN}(\text{OBz})_2 \rightarrow \text{Bz}_2\text{O} + \text{RNO}$ , which then reacts as C to give (II), which with  $\text{BzCl}$  affords  $\text{RNBz}\cdot\text{OBz}$  (III). The isolation of  $\text{Bz}_2\text{O}$  and various dibenzoylarylhydroxylamines in yields closely corresponding with these equations is described. With  $\text{H}_2\text{O}$  or dil.  $\text{H}_2\text{SO}_4$  (I) gives the corresponding  $\text{NHR}\cdot\text{OH}$  (isolated cryst., and determined in the mother-liquor by reduction of 2—3%  $\text{AgNO}_3$ ), and with  $\text{PhNO}_2$ , *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeNO}_2$  the yields of  $\text{NHR}\cdot\text{OH}$  are, respectively, 79·1, 90·9, 85·3, and 83·3%. By the action of  $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$  on the appropriate  $\text{NHR}\cdot\text{OH}$  in dry  $\text{Et}_2\text{O}$  ( $\text{N}_2$ ) are obtained  $\text{NO}$ -



*dibenzoyl-phenyl*-, m.p. 118—118.8°, -o-, m.p. 137—138°, -m-, m.p. 114.5—115.5°, and -*p*-tolyl-, m.p. 127—127.8°, and -*p*-chlorophenyl-, m.p. 86—87°, -*hydroxylamine* [all identical with the derivatives (III)], from which, by hydrolysis with cold NaOH-MeOH, are obtained *N*-benzoyl-phenyl-, m.p. 121—122°, -*p*-tolyl-, m.p. 109—110°, and -o- (? -*p*-)chlorophenyl-, m.p. 157° (decomp.), -*hydroxylamine*. J. W. B.

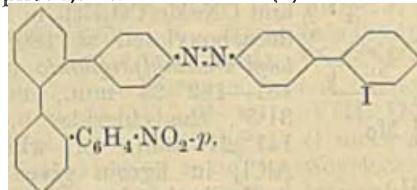
**Manufacture of derivatives of *N*-butylaniline.**—See B., 1936, 91.

**Synthesis of aromatic nitro-compounds with the azide group in the side-chain.** J. JUSCHT-SCHENKO (Mem. Inst. Ukrain. Acad. Sci., 1935, 2, 195—205).—o-, b.p. 121—122°/2 mm., and *p*-Nitrobenzyl azide, b.p. 144—148°/2 mm., and 2 : 4-dinitrobenzyl azide, m.p. 46—47°, have been prepared from NaN<sub>3</sub> or AgN<sub>3</sub> and the appropriate chlorides or iodides in EtOH or Et<sub>2</sub>O (8—10 hr. at the b.p.). The azides yield the corresponding aldehydes, NH<sub>3</sub>, and N<sub>2</sub> when treated with hot dil. H<sub>2</sub>SO<sub>4</sub>. R. T.

**Interaction of amines and ammonia with di(diphenylene)ethylene.** L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1935, 57, 2398—2402).—Di(diphenylene)ethylene (I) and NH<sub>2</sub>Et at 65° for 2 days give 9-ethylamino-9 : 9'-difluorenyl (II), m.p. 165° [hydrochloride, m.p. 210—215° (decomp.)]; picrate, m.p. 228° (decomp.); NO-derivative, m.p. 217°, and small amounts of fluorene (III) and 9 : 9'-difluorenyl (IV). (II) heated with EtOH for 10 days affords (III), 9-ethyliminofluorene (V) [picrate, m.p. 206° (decomp.)], and fluorenone (VI) [formed by hydrolysis of (V)]; in NH<sub>2</sub>Et at 85° (sealed tube), (III) and (IV) are produced. (I) and NH<sub>2</sub>Me at room temp. similarly afford 9-methylamino-9 : 9'-difluorenyl, m.p. 151° (Ac, m.p. 232°, and NO-, m.p. 203°, derivatives). 9-Dimethylamino-9 : 9'-difluorenyl has m.p. 215° (decomp.). (I) and CH<sub>3</sub>Ph·NH<sub>2</sub> at 100°/6 days give 9-benzylamino-9 : 9'-difluorenyl (VII), m.p. 168° (hydrochloride, m.p. 215—218°; NO-derivative, m.p. 217—218°), (III), (IV), a base, C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>, m.p. 90° (dihydrochloride, m.p. 212°), and a hydrocarbon, m.p. 318°; at room temp./6 months, (VII) appears to be the sole product. (VII) heated in EtOH at 100° (sealed tube) gives (III), (VI), PhCHO, and a little of an unidentified product, m.p. 202°. (I) and liquid NH<sub>3</sub> at 65° for 3 weeks afford (III), 9-iminofluorene, m.p. 123° [hydrochloride, m.p. 303° (decomp.)] [which with NH<sub>2</sub>Et at 55° gives (V)], and a compound, m.p. 300°. The rate of addition of amines to (I) is NH<sub>2</sub>Me > NH<sub>2</sub>Et > NHMe<sub>2</sub> > CH<sub>3</sub>Ph·NH<sub>2</sub> > NH<sub>3</sub> > NHEt<sub>2</sub>, NH<sub>2</sub>Ph. All m.p. are corr. H. B.

**Attempted formation of rings attached to the *p*-positions of the phenyl groups in 2 : 2'-diphenyldiphenyl.** S. SAKO (Bull. Chem. Soc. Japan, 1935, 10, 585—592).—4'-Nitro-2-aminodiphenyl hydrochloride (improved prep.) is converted by diazotisation-KI into 2-iodo-4'-nitro-, m.p. 100—101.5°, reduced (SnCl<sub>2</sub>-HCl-EtOH) to 2-iodo-4'-amino-diphenyl (hydrochloride; Ac derivative, m.p. 162—163°), converted by Cu powder (1.4 times the theoretical quantity gives highest yield of 53%) at 220—225° into 2 : 2'-bis-(*p*-nitrophenyl)diphenyl (I), m.p. 290°, and (?) 4-o-iodophenyl-4'-(2''''-*p*-nitrophenyl-2''-di-

phenyl)azobenzene (annexed), m.p. 312—313° (dimorphous). Reduction of (I) with SnCl<sub>2</sub>-HCl-AcOH



at 60—70°, or with Na<sub>2</sub>S-EtOH, affords 2 : 2'-bis-*p*-aminophenyl- (II), b.p. 290°/5 mm., m.p. 163—164°, converted (Sandmeyer) into 2 : 2'-bis-*p*-iodo- (III), m.p. 205—206°, and 2 : 2'-bis-*p*-bromophenyl- (IV), m.p. 170—171°, -diphenyl. With Na in boiling Et<sub>2</sub>O (III) and (IV) give only 2 : 2'-diphenyldiphenyl, and various other attempts to prepare large rings from (I) and (II) by ring-closure between the substituent groups were unsuccessful. J. W. B.

**Synthesis of 2 : 2'-diphenylbenzidine.** S. SAKO (Bull. Chem. Soc. Japan, 1935, 10, 593—594).—Diazotised 5-nitro-2-aminodiphenyl with KI affords 2-iodo-*o*-nitrodiphenyl, b.p. 191—192°/4 mm., m.p. 114°, converted by heating with Cu powder at 215—225° into 4 : 4'-dinitro-2 : 2'-diphenyldiphenyl, b.p. 290°/4 mm., m.p. 218—219°, reduced (SnCl<sub>2</sub>-HCl-AcOH) to 2 : 2'-diphenylbenzidine, m.p. 151—152°. J. W. B.

***o*-Quinonephenylhydrazones.** A. BURAWOY (Annalen, 1936, 521, 298—302).—A criticism of the views of Kuhn *et al.* (A., 1935, 613). The author's earlier views regarding the *o*-quinonephenylhydrazone structure of *o*-hydroxyazobenzenes (A., 1934, 401 and references there cited) are maintained. J. W. B.

**Diazo-compounds. VII. Diazo-resins. VIII. Coupling and oxidising power of normal diazotates during their decomposition. IX. Reversion of isodiazotates into normal diazotates; its application in dyeing and in negative diazo-type [printing]. X. Rapid preparation of solutions of alkali diazotates from diazonium salts. XI. Constitution of diazonium salts and of alkali diazotates.** G. ODDO and R. INDOVINA (Gazzetta, 1935, 65, 1037—1054, 1054—1067, 1099—1104, 1104—1105, 1105—1127; cf. this vol., 199).—VII. The yield of the resins from 32 diazotised amines decomposing in presence of 0.4, 0.8, and 1.6% NaOH (cf. A., 1899, i, 543) varies with the nature of the amine (least from *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>; most from halogenated amines, and anisidine), and irregularly with the alkalinity. The resins contain N in varying amount and may be separated into fractions richer and poorer in N by pptn. by light petroleum from C<sub>6</sub>H<sub>6</sub> solution. *o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> yields indazole and its *o*-tolueneazo-derivative; *p*-xylylene gives 6-methylindazole and its *p*-xylyleneazo-derivative; *ψ*-cumidine, dimethylindazole and its *ψ*-cumeneazo-derivative; mesidine forms similar products. The resins all contain hydroxyazo- or bisazo-compounds, and are sulphated by oleum. Some contain diazoamino-compounds. The results are tabulated and discussed; formation of resins is considered due essentially to coupling of diazo-compounds with decomp. products, e.g. phenols, amines, or indazole; autoxidation plays an insignificant part.



VIII. As diazotised amines decompose in presence of NaOH they lose their power to couple with  $\beta$ - $C_{10}H_7OH$ , and take progressively longer to give a (delayed) blue coloration with starch-KI paper. Both reactions are negative when  $N_2$  has ceased to be evolved; their progressive decrease with decomp. of 32 diazotised amines is tabulated, and the oxidising action discussed.

IX. *iso*Diazotates (I) are reconverted into normal diazotates (II) by the action of heat or light (sun, ultra-violet, or electric). Azo-pigments are formed when (I) are mixed with 1%  $\beta$ - $C_{10}H_7OH$  in 1% NaOH and exposed to light. The reaction is given by (I) from  $NH_2Ph$ , *o*-4-xylydine, and *o*-, *m*-, and *p*- $C_6H_4XNH_2$  ( $X=Cl, Br, \text{ or } I$ ), but not by those from *o*- $C_6H_4MeNH_2$ , *m*-4-xylydine,  $\psi$ -cumidine, or mesidine. The interconversion is represented:  $NR:N\cdot ONa$  (II)  $\rightleftharpoons$   $NR:N\cdot ONa$  (I). Application of (I) to dyeing, and to "diazotype" photographic printing, is discussed; good prints have been obtained using (I) from *p*- $C_6H_4BrNH_2$  or from *p*- $C_6H_4INH_2$ .

X. (I) may be rapidly prepared by adding solutions of diazonium salts to 1-6% NaOH heated to 100°, and keeping at 100° until (after a few min.) coupling power is completely lost ( $\beta$ - $C_{10}H_7OH$  paper). Yields are: from  $NH_2Ph$ , 29%; from its *m*- and *p*-Me, *p*-Br-, *p*-I-, and *m*- $NO_2$ -derivatives, 31, 8, 39, 52, and 61%; when 0.4 or 0.8% NaOH is used, yields are smaller.

XI. A historical review, summed up in favour of the structures:  $NR:NCl \rightarrow NR:N\cdot OH \rightarrow NR:N\cdot OK \rightleftharpoons NR:N\cdot OH$  (see Part IX). On this view, "(I)" ("antidiazotates" of Hantzsch) should be renamed "diazotates," and "(II)" ("syndiazotates" of Hantzsch) be renamed "diazoniates." The very small depressions of f.p. of aq. NaOH caused by diazonium salts (A., 1895, i, 661) support the view that slightly hydrolysed diazotates are formed, and are in contrast to the great depressions now observed with methylpyridinium and *o*-tolyltrimethylammonium iodides. An aq. solution of benzenediazoxycarbonamide (III) (A., 1922, i, 1071) [but not anhyd. (III)] reacts with Br to form a substance, m.p. 102–103°, decomposed by boiling  $H_2O$ . (III) heated in  $H_2O$  with Br, and treated with  $SO_2$ , yields an insol. substance, m.p. 222°, and an acid, m.p. 142° (decomp. to a substance, m.p. 136°), which couples with  $\beta$ - $C_{10}H_7OH$  and is regarded as benzenediazoxycarboxylic acid,  $Ph\cdot N_2O\cdot CO_2H$ , together with a substance, m.p. 75°. The action of NaOH on (I) is formulated:  $NPh\cdot N(O)\cdot CO\cdot NH_2 \rightarrow NPh\cdot N\cdot NH\cdot O \rightarrow NPh\cdot N\cdot OH \rightarrow NPh\cdot N\cdot ONa$ . (I) treated with aq. or conc.  $H_2SO_4$ , or with  $PCl_5$ , does not give  $PhNO_2$  [which would be expected if (I) were  $NPh(O)\cdot N\cdot CO\cdot NH_2$  as suggested by Angeli (A., 1917, i, 418)], but only, after prolonged action,  $PhOH$ .

E. W. W.

Identification of phenols with 1-chloro-2:4-dinitrobenzene. R. W. BOST and F. NICHOLSON (J. Amer. Chem. Soc., 1935, 57, 2368–2369).—Aryl 2:4-dinitrophenyl ethers are prepared by heating  $NaOAr$  (0.01 mol. in 5 c.c. of  $H_2O$ ) with 1:2:4- $C_6H_3Cl(NO_2)_2$  (0.01 mol. in 30 c.c. of 95% EtOH). The following are described: *Ph*, m.p. 69°; *o*-, m.p. 90°, and *m*-, m.p. 74°, -tolyl; *p*-tolyl, m.p. 33.5°; *thymyl*, m.p. 67°; *o*-anisyl, m.p. 97°;  $\alpha$ - $C_{10}H_7$ , m.p. 128°;  $\beta$ - $C_{10}H_7$ , m.p. 95°; *p*-diphenyllyl,

m.p. 118°; *m*-OH- $C_6H_4$ , m.p. 194° (lit. 184°); *eu*-genyl; *isoeugenyl*, m.p. 130°; 2:4-(OMe)(CHO) $C_6H_3$ ; *o*-, m.p. 142° (lit. 119°), *m*-, m.p. 138°, and m.p. 120° (lit. 114°),  $NO_2\cdot C_6H_4$ ; 6-chloro-*m*-tolyl, m.p. 112°; *o*- $C_6H_4I$ , m.p. 95°; *p*- $C_6H_4I$ ; *o*-, m.p. 99°, *m*-, m.p. 75°, and *p*-, m.p. 126°, *C.H.Cl*; 2:4- $C_6H_3Cl_2$ , m.p. 119°; 2:4:6- $C_6H_2Cl_3$ , m.p. 136°; *o*-, m.p. 89°, and *p*-, m.p. 141°,  $C_6H.Br$ ; 2:4- $C_6H_3Br_2$ , m.p. 135°; 2:4:6- $C_6H_2Br_3$ , m.p. 135°.

H. B.

*m*-2-Xylyl  $\alpha$ -naphthylcarbamate. C. D. HURD and M. A. POLLACK (J. Amer. Chem. Soc., 1936, 58, 181).—The xylenol obtained (A., 1932, 857) by pyrolysis of furfuraldehyde is 2:6- $C_6H_3Me_2OH$  ( $\alpha$ -naphthylcarbamate, m.p. 176.5°).

H. B.

Synthesis of alkyl- and aryl-cryptophenols. M. E. MCGREAL and J. B. NIEDERL (J. Amer. Chem. Soc., 1935, 57, 2625–2627).— $CMe_2Pr^{\beta}OH$  (1 mol.),  $PhOH$  (1 mol.), and  $ZnCl_2$  (1.5 mols.) at 180° give  $\beta$ -*p*-hydroxyphenyl- $\beta$ - $\gamma$ -dimethylbutane, m.p. 105° (45);  $CMe_2Bu^{\alpha}OH$  similarly affords  $\beta$ -*p*-hydroxyphenyl- $\beta$ -methylhexane, b.p. 280°/760 mm., but  $\beta\delta\delta$ -trimethylpentan- $\beta$ -ol yields *p*- $C_6H_4Bu^{\alpha}OH$  (I); the methylcyclohexanols give *p*-2-, m.p. 107° (50), -3-, m.p. 101° (105), and -4-, m.p. 108° (70), -methylcyclohexylphenols, but 4-*tert*.-octylcyclohexanol affords (I);  $CH_2PhOH$  yields *p*-benzylphenol;  $CH_2Ph\cdot CH_2OH$  or  $CHPhMeOH$  gives  $\alpha$ -phenyl- $\alpha$ -*p*-hydroxyphenylethane, m.p. 64° (40) (dehydration of the former presumably preceding addition of the  $PhOH$ );  $CPhMeEtOH$  affords  $\beta$ -phenyl- $\beta$ -*p*-hydroxyphenylbutane, b.p. 145–148°/2.5 mm., also prepared (method: A., 1935, 79) from  $PhOH$  and  $\beta$ -phenyl- $\Delta^{\beta}$ -butene;  $CPhMePr^{\beta}OH$  yields  $\beta$ -phenyl- $\beta$ -*p*-hydroxyphenyl- $\gamma$ -methylbutane, b.p. 157–160°/3 mm., also prepared from the appropriate phenylpentene. The nos. quoted in parentheses are the  $PhOH$ -coeffs. (using *Staph. aureus*).

H. B.

Reduction of isosafrole with sodium and ethyl alcohol. K. ONO and M. IMOTO (J. Chem. Soc. Japan, 1934, 55, 991–1001).—A mixture of *m*- and *p*- $C_6H_4PrOH$  is produced. Addition of active C increases the yield.

CH. ABS. (r)

Phenols of anthracene oil. O. KRUBER (Ber., 1936, 69, [B], 107–114).—The liquid products obtained by centrifuging a crude phenanthrene fraction, b.p. 320–340°, after extraction with NaOH and distillation of the extracted matter in vac., yielded *p*-hydroxydiphenyl, m.p. 163°. Similar treatment of crude  $C_{10}H_8$  press-cake yielded  $\beta$ - $C_{10}H_7OH$  and a diphenol,  $C_{16}H_{18}O_2$ , m.p. 135°, b.p. 341°/755 mm. [*Me\_2 ether*, b.p. 200–201°/15 mm., m.p. 85°; *diphenylurethane*, m.p. 199–200°; compound,  $C_{42}H_{36}O_4N_2$ , m.p. 192–193°, with  $CO(NHPh)_2$ ]. Separation of the phenols of the anthracene oil fraction, b.p. 340–370°, is rendered difficult by the presence of complex, non-phenolic substances with feebly acidic properties; it is best effected by repeated alternate extraction with NaOH and distillation of the extracted matter, whereby the complex materials are extensively decomposed. Distillation of the phenolic fraction over Zn dust or a Mo contact affords diphenylene oxide and fluorene. Further fraction-

ation and prolonged keeping of the individual fractions in PhMe at 0° causes the separation of a solid material which cannot be separated into its components by crystallisation. When treated with NaOH and Me<sub>2</sub>SO<sub>4</sub> it yields a mixture of ethers, non-separable by crystallisation, from which 2-methoxydiphenylene oxide (I), m.p. 98°, is isolated after partial oxidation with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in AcOH at 70°. Treatment of (I) with NH<sub>2</sub>Ph.HCl at 250° affords 2-hydroxydiphenylene oxide, b.p. 348°/758 mm., m.p. 142—143° (phenylurethane, m.p. 173°). The synthesis of (I) from 2-aminodiphenylene oxide is recorded. Treatment of the mother-liquors from (I) with NH<sub>2</sub>OH.HCl and BaCO<sub>3</sub> leads to the isolation of 2-methoxyfluorenoneoxime, m.p. 174° after softening, whence 2-methoxyfluorenone, m.p. 78°. Separation of the crude methylated product into its components can also be effected by Na at 180—200° but is complicated by many by-reactions. H. W.

**Phenylether series. IV. 4:4'-Dithioldiphenyl ether and related compounds.** C. M. SUTER and P. H. SCRUTCHFIELD (J. Amer. Chem. Soc., 1936, 58, 54—55).—Reduction (SnCl<sub>2</sub>, AcOH-HCl) of (p-SO<sub>2</sub>Cl-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>O (A., 1931, 616) gives 4:4'-dithioldiphenyl ether, m.p. 103—104° (Me<sub>2</sub> ether, m.p. 81—81.5°), converted by CH<sub>2</sub>Cl.CO<sub>2</sub>K into the 4:4'-dithioglycollic acid, m.p. 165—166° (chloride, converted by AlCl<sub>3</sub> into a red tar), which could not be cyclised by oleum or ClSO<sub>3</sub>H to a thionaphthen derivative.

(+)- and (-)-γ-Phenyl-α-methylallyl alcohols. J. KENYON, S. M. PARTRIDGE, and H. PHILLIPS (J.C.S., 1936, 85—88).—CHPh.CH<sub>2</sub>CHO and MgMeBr give dl-γ-phenyl-α-methylallyl alcohol (I), b.p. 129—131°/11 mm., m.p. 33° [p-nitrobenzoate, m.p. 58—59°; H phthalate (II), m.p. 92—93.5°, prepared by the action of o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O on (I) (in C<sub>5</sub>H<sub>5</sub>N) or the Grignard complex], which could not be separated (distillation; partial fusion; crystallisation) into *cis*- and *trans*-forms. Recrystallisation (from EtOAc) of the cinchonidine salt of (II) affords the cinchonidine salt, m.p. 179° (decomp.), of (+)-γ-phenyl-α-methylallyl H phthalate (III), m.p. 68.5°, [α]<sub>5461</sub> +44.71° in CS<sub>2</sub>, -15.4° in EtOH (vals. for many solvents and different λ given). Hydrolysis of (III) with aq. Na<sub>2</sub>CO<sub>3</sub> gives (I); 5*N*-NaOH and subsequent crystallisation from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum lead to the (+)-alcohol (IV), m.p. 61°, [α]<sub>5461</sub> +28.3° in CS<sub>2</sub> (p-xenylcarbamate, m.p. 179—180°; p-nitrobenzoate, m.p. 41°; acetate, b.p. 132—133°/9 mm.), reduced (Adams) to (-)-CH<sub>2</sub>Ph.CH<sub>2</sub>CHMe.OH (V) (phenylcarbamate, m.p. 47—48°) (J.C.S., 1914, 105, 1124). The recovered H phthalate [from (III)] gives the brucine salt, decomp. about 110°, of (-)-γ-phenyl-α-methylallyl H phthalate, m.p. 68.5°, [α]<sub>5461</sub> -44.53° in CS<sub>2</sub>, and thence (as above) the (-)-alcohol, m.p. 61°, [α]<sub>5461</sub> -28° in CS<sub>2</sub>. Comparison of the rotatory powers of (IV), (V), (-)-CHMeEt.OH, and (+)-CH<sub>2</sub>:CH:CHMe.OH shows that introduction of Ph [as in (IV) and (V)] causes [M] to be approx. doubled; the introduction of the Δ<sup>2</sup>-double linking doubles [M] and reverses the sign. H. B.

**Resolution of phenyl-*n*-propylcarbinol.** J. KENYON and S. M. PARTRIDGE (J.C.S., 1936, 128—

129).—CHPhPr.OH (H phthalate, m.p. 90—91°) is resolved through the quinidine salt, m.p. 168—169°, of the *d*-H phthalate, m.p. 53—54°, [α]<sub>5461</sub> -11.5° in Et<sub>2</sub>O, into the *d*-form, b.p. 115°/14 mm., m.p. 49°, [α]<sub>5461</sub> +52.2° in C<sub>6</sub>H<sub>6</sub>, and afterwards through the strychnine salt, m.p. 184—185° (decomp.), of the *l*-H phthalate, m.p. 52—53°, [α]<sub>5461</sub> -11° in Et<sub>2</sub>O, into the *l*-form, m.p. 48—49°, [α]<sub>5461</sub> -53.5°, [α]<sub>5893</sub> -45.9° in C<sub>6</sub>H<sub>6</sub> (cf. Levene and Marker, A., 1932, 1027). Vals. for other solvents and λ are given.

H. B.

**epialloCholesterol, a new isomeride of cholesterol.** E. A. EVANS, jun., and R. SCHOENHEIMER (J. Amer. Chem. Soc., 1936, 58, 182).—Reduction of cholestenone with Al(OPr<sup>i</sup>)<sub>3</sub> gives epiallocholesterol (I), m.p. 84°, [α]<sub>D</sub><sup>25</sup> +120.8° in C<sub>6</sub>H<sub>6</sub> (acetate, m.p. 82.5°), and an isomeride [pptd. by digitonin whereas (I) is not]. (I) is reduced (catalytically) to a mixture of epidihydrocholesterol and epicoprosterol, indicating that (I) contains C<sup>3</sup>-OH *trans* to C<sup>10</sup>-Me; an intense Rosenheim reaction also indicates that the double linking is between C<sup>4</sup> and C<sup>5</sup>. (I) is dehydrated by dil. HCl in 95% EtOH to a hydrocarbon, C<sub>27</sub>H<sub>44</sub>, m.p. 79°, [α]<sub>D</sub><sup>25</sup> -118.2° in C<sub>6</sub>H<sub>6</sub>, the absorption max. (244, 235, and 229 mμ) of which differ from those of cholesterolene (Heilbron *et al.*, A., 1928, 219). H. B.

**Androsterone and related sterols.** R. E. MARKER, F. C. WHITMORE, and O. KAMM (J. Amer. Chem. Soc., 1935, 57, 2358—2360).—α-Cholestyl chloride (I), m.p. 112°, is prepared (a) by reduction (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) of cholesteryl chloride, (b) from epicholesterol (II) and PCl<sub>5</sub>, and (c) from β-cholestanol (III) and SOCl<sub>2</sub>; Walden inversion occurs in (a) and (c). (I) is hydrolysed (KOAc in valeric acid followed by EtOH-KOH) to (II). β-Cholestyl chloride, m.p. 102—103°, obtained from (II) and SOCl<sub>2</sub> or (III) and PCl<sub>5</sub>, is similarly hydrolysed to (III). Oxidation (CrO<sub>3</sub>, AcOH) of (I) gives α-chlorocholelanic acid, m.p. 174—175°, and α-chloroandrosterone, m.p. 170—171° (Butenandt and Dannenbaum, A., 1935, 413; cf. Ruzicka *et al.*, *ibid.*, 1125). H. B.

**Alkaline halogenation. Bromination of sodium benzoate.** P. L. HARRIS and J. C. SMITH (J.C.S., 1936, 168; cf. A., 1934, 405).—BzOH (61 g.) in aq. NaOBr [2 litres from NaOH (40 g.) and Br (80 g.)] at 35°/7 days gives approx. 5 g. each of *o*-, *m*-, (I), and *p*-C<sub>6</sub>H<sub>4</sub>Br.CO<sub>2</sub>H; the results vary owing to rapid decomp. of NaOBr. Use of 2 equivs. of NaOH (*i.e.*, NaOBz:NaOBr=1) almost inhibits bromination. In agreement with Stark (A., 1910, i, 234), (I) is the main product from BzOH and HOBr in H<sub>2</sub>O. H. B.

**Syntheses in the anæsthetic group. I.** G. SANNA (Annali Chim. Appl., 1935, 25, 638—643).—*Et p-chloroacetamidobenzoate*, m.p. 115°, is prepared by treating anæsthesine (I) in C<sub>6</sub>H<sub>6</sub> with CH<sub>2</sub>Cl.COCl, and is converted (NHMe<sub>2</sub>) into *Et p-dimethylglycylamidobenzoate* (II), m.p. 95° (hydrochloride, m.p. 193°) and (NH<sub>4</sub>Et<sub>2</sub>) into the corresponding Et<sub>2</sub> compound (III), m.p. 115° (hydrochloride, m.p. 211°). (II) and (III) are more sol. than (I) in H<sub>2</sub>O, and have anæsthetic properties, which are being examined. E. W.

**Preparation of α-naphthoic acid.** D. J. and F. C. WHITMORE (J. Amer. Chem. Soc., 1935, 57,



2727).— $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>Et, obtained in 70% yield from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·MgBr and Et<sub>2</sub>CO<sub>3</sub>, is hydrolysed to the acid (yield > 90%). H. B.

**Synthesis of alkeines derived from O-phenyl-lactic and -mandelic acid.** E. PLÁZEK, Z. RODEWALD, and D. KRZYŻANIAK (Rocz. Chem., 1935, 15, 360—364).—O-Phenylmandetyl chloride, b.p. 135°/0.6 mm., yields the *tropyl* ester, b.p. 208°/1 mm. (*picrate*, m.p. 171°; *picrolonate*, m.p. 187°), with tropine, and  $\beta$ -dimethylaminoethyl O-phenylmandelate, b.p. 148—150°/0.2 mm. (*picrolonate*, m.p. 141—142°), with NEt<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH. KOPh and CHMeBr·CO<sub>2</sub>Me (2 hr.; 100°), followed by hydrolysis of the product with EtOH-KOH, yield O-phenyl-lactic acid (I), m.p. 114°, the *chloride*, b.p. 115°/20 mm., of which affords the *tropyl*, b.p. 140—150°/0.6 mm. (*picrate*, m.p. 175°; *picrolonate*, m.p. 200—202°), and  $\beta$ -dimethylaminoethyl esters of (I), m.p. 75° (*picrate*, m.p. 113°; *picrolonate*, m.p. 148°). R. T.

**Dehalogenation of  $\beta$ -bromo-acids.** IV.  $\beta$ -Bromophenylpyruvic acid. B. SOBIN and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2458—2460).— $\beta$ -Bromophenylpyruvic acid (I), m.p. 103—104° (from CH<sub>2</sub>Ph·CO·CO<sub>2</sub>H and Br in CCl<sub>4</sub>), is converted by boiling with H<sub>2</sub>O or shaking with Ag<sub>2</sub>O in H<sub>2</sub>O into CH<sub>2</sub>Ph·CO<sub>2</sub>H (II) (yield 77 and 94%, respectively); the following reactions are considered to occur: CHBrPh·CO·CO<sub>2</sub>H  $\rightarrow$  CO<sub>2</sub> + HBr + CHPh·C'O; CHPh·C'O + H<sub>2</sub>O  $\rightarrow$  CH<sub>2</sub>Ph·CO<sub>2</sub>H. CH<sub>2</sub>Ph·CO<sub>2</sub>Et is similarly obtained in 36% yield from (I) and Ag<sub>2</sub>O in EtOH. (I) and aq. Na<sub>2</sub>CO<sub>3</sub> give benzoyl-carbinol (III) (by rearrangement of the intermediate OH·CHPh·CHO); with aq. NaHCO<sub>3</sub>, a mixture of (II) and (III) and a little of an acid, C<sub>23</sub>H<sub>15</sub>O<sub>5</sub>, m.p. 218—219° (Ac derivative, m.p. 162—163°), result. Tars (free from CHPh·C'O) are produced from (I) and C<sub>2</sub>H<sub>5</sub>N or NPhMe<sub>2</sub>. H. B.

**General reaction for the preparation of keto-acids, unsaturated acids, and disubstituted lactones.** II. G. KOMPPA and W. ROHRMANN (Annalen, 1936, 521, 227—242).—*apo*Camphoric anhydride (I) (1 mol.) and MgMeI (1 mol.) at -15° (cf. A., 1934, 650) give, after esterification, *Et cis-3-acetyl-2-dimethylcyclopentane-1-carboxylate*, b.p. 122—123°/11 mm., isolated as its *semicarbazone*, m.p. 142—142.5°, not identical with the *trans-ester* [*semicarbazone*, m.p. 196—200° (decomp.); *semicarbazone* of the free acid, m.p. 191° (decomp.)] obtained by Winzer's method (A., 1890, 1152) by the action of LiNa(CO<sub>2</sub>Et)<sub>2</sub> on (I) in C<sub>6</sub>H<sub>6</sub> to give *malonylapo-camphoric anhydride*, m.p. 63.5—64°, b.p. 216°/12 mm., and subsequent hydrolysis with NaOEt-EtOH. With 2 mols. of MgMeI (I) affords *dimethylapo-campholide* (45% yield), m.p. 102—103°, and *3-isopropylidene-2:2-dimethylcyclopentane-1-carboxylic acid*, (35% yield), m.p. 103—104° (gives 2:2-dimethylcyclopentanone-3-carboxylic acid on ozonolysis). Similarly *d*-camphoric anhydride (II) with MgMeI (1 mol.) gives *Et cis-3-acetyl-2:2:3-trimethylcyclopentane-1-carboxylate*, b.p. 133—135°/8 mm. (*semicarbazone* m.p. 177°, hydrolysed to the acid, +H<sub>2</sub>O, 76—78° (*semicarbazone*, m.p. 223—224°), probably identical with the acid, m.p. 73°, obtained

by Quadrat-i-Khuda (A., 1930, 471), but different from Winzer's acid (*loc. cit.*), which is *cis-3-acetyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (IV) (*semicarbazone*, m.p. 218°, indefinite). With 2 mols. of MgMeI (II) gives *dimethylcampholide* and *3-isopropenyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (V), the m.p., 68.5—70.5°, of which (Komppa. A., 1908, i, 353) is raised to 87—88° by repeated crystallisation, probably by conversion into the *3-isopropylidene acid* (VI); ozonolysis of (V) gives a *3-acetyl-1:2:2-trimethylcyclopentane-1-carboxylic acid* (*semicarbazone*, m.p. 220—221°) not identical with either (III) or (IV), whereas (VI) gives an indefinite oil with O<sub>3</sub>. The results of Houben *et al.* (A., 1908, 539) on the interaction of CH<sub>2</sub>Ph·MgCl on (II) are confirmed and, in addition, are isolated an *Et phenyl-acetyltrimethylcyclopentanecarboxylate*, b.p. 217—218° [converted into the bicyclic compound (VII) by hydrolysis], and an *Et  $\beta$ -phenyl- $\alpha$ -benzylethylidenetrimethylcyclopentanecarboxylate*, b.p. 230—234°/9 mm. (*acid*, m.p. 166—167°). *Santenic anhydride* (VIII) with MgMeI gives *cis-3-acetyl-2:3-dimethylcyclopentane-1-carboxylic acid*, m.p. 63—65° (*semicarbazone*, m.p. 218°), not identical with *cis-3-acetyl-1:2-dimethylcyclopentane-1-carboxylic acid*, m.p. 95—96° (*semicarbazone*, m.p. 219°), obtained by Winzer's method. With 2 mols. of MgMeI (VIII) affords *dimethylsantolide*, b.p. 136—138°/15 mm., and a trace of an unsaturated acid.

J. W. B.

**Preparation of tetrachlorophthalic acid.** J. S. SALKIND and M. BELIKOVA (J. Appl. Chem. Russ., 1935, 8, 1210—1213).—*o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O at 240—250° and Cl<sub>2</sub> (in presence of 3% of Fe) yield tetrachlorophthalic acid in 90—95% yield. The product loses H<sub>2</sub>O of crystallisation (1.5 mols.) at 100°, and is converted into the anhydride at 110°. R. T.

**Lithium phthalate.**—See this vol., 282.

**Synthesis of hydrogenated phenanthrenes.**

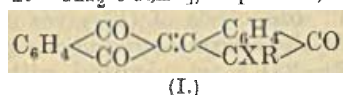
E. E. GRUBER and R. ADAMS (J. Amer. Chem. Soc., 1935, 57, 2555—2556; cf. Barnett and Lawrence, A., 1935, 1243).—1:1'-Dihydroxy-1:1'-dicyclohexyl (from cyclohexanone, Mg, and HgCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>) is dehydrated (10% H<sub>2</sub>SO<sub>4</sub>) to di- $\Delta^{1,1'}$ -cyclohexene, b.p. 101—102°/5.5 mm., which with maleic anhydride in C<sub>6</sub>H<sub>6</sub> gives the anhydride, m.p. 122.5—123.5°, of *dodecahydrophenanthrene-9:10-dicarboxylic acid*, m.p. 242° (Maquenne block) (*imide*, m.p. 182—183°), and with CH<sub>2</sub>CH·CHO in C<sub>6</sub>H<sub>6</sub> at 50—60° affords *dodecahydrophenanthrene-9-aldehyde*, b.p. 136—137°/4 mm. (*semicarbazone*, m.p. 179—180°). H. B.

**Synthesis of 1-methylcyclopentane-1:3-dicarboxylic acid (1-methylnorcamphoric acid).** N. J. TOIVONEN, A. JOHN, E. SAINIO, and T. KUUSINEN (Suomen Kem., 1935, 8, B, 46—47).—Et<sub>3</sub> 2-methylcyclopentanone-2:4:5-tricarboxylate with glycerol-H<sub>2</sub>O at 170—200° affords Et<sub>2</sub> 2-methylcyclopentanone-2:4-dicarboxylate, b.p. 153—156°/11 mm., which with K-Hg in EtOH-dil. H<sub>2</sub>SO<sub>4</sub> gives Et<sub>2</sub> 2-methylcyclopentan-1-ol-2:4-dicarboxylate, b.p. 126—128°/0.5 mm. [*acid*, m.p. 172—174°, converted by HBr followed by Zn in AcOH-HCl into *cis*- (cf. this vol., 339) and *trans*-1-methylcyclopentane-1:3-dicarboxylic acid, m.p.

114—115°, the former of which with  $\text{PCl}_5$  and excess of Br gives the 3-Br-derivative, m.p. 136—138°].

J. L. D.

**Condensation of bindone with  $\alpha$ -halogeno-carboxylic esters.** G. WANAG (Ber., 1936, 69, [B], 189—194; cf. A., 1935, 623).—Bindone [(I)  $\text{X}=\text{R}=\text{H}$ ] condenses with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  in boiling EtOH containing  $\text{K}_2\text{CO}_3$  to *Et bindonylacetate* [(I)  $\text{X}=\text{H}$ ;  $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$ ], m.p. 109°, converted by Br in boiling



$\text{CHCl}_3$  into *Et bromobindonylacetate* [(II) (I)  $\text{X}=\text{Br}$ ;  $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$ ], m.p.

153°, by fuming  $\text{HNO}_3$  in boiling AcOH into *Et nitrobindonylacetate* [(I)  $\text{X}=\text{NO}_2$ ;  $\text{R}=\text{CH}_2\cdot\text{CO}_2\text{Et}$ ], m.p. 154—155°, and hydrolysed by acid or alkali to *bindonylactic acid*, m.p. 242—244°. Treatment of (II) with conc. HCl in AcOH affords (?) *indandionylene- $\alpha$ -naphthaquinone* [(I) with  $\text{CH}:\text{CH}$  for CXR], m.p. 310—312°. Analogously, (I) and  $\text{CHBrMe}\cdot\text{CO}_2\text{Et}$  yield *Et  $\alpha$ -bindonylpropionate* [(I)  $\text{X}=\text{H}$ ;  $\text{R}=\text{CHMe}\cdot\text{CO}_2\text{Et}$ ], m.p. 126—127°, whence *Et  $\alpha$ -nitrobindonylpropionate*, m.p. 154—155°, and  *$\alpha$ -bindonylpropionic acid*, m.p. 230°. *Et bindonylphenylacetate* [(I)  $\text{X}=\text{H}$ ;  $\text{R}=\text{CHPh}\cdot\text{CO}_2\text{Et}$ ], m.p. 153°, *Et nitrobindonylphenylacetate*, m.p. 158—159°, and *bindonylphenylacetic acid*, m.p. 234°, are obtained with  $\text{CHBrPh}\cdot\text{CO}_2\text{Et}$ . Treatment of (I) with  $\text{CHCl}(\text{CO}_2\text{Et})_2$  leads to *trans-dibindonylene*, production of which does not appear to be due to simple dehydrogenation, since it is also formed when  $\text{Pr}^{\beta}\text{I}$  or  $\text{C}_2\text{H}_4\text{Br}_2$  is used and (in small amount) when  $\text{MeI}$  is employed; it is suggested that these substances accelerate autoxidation.

H. W.

#### Mechanism of the Perkin-Oglialoro synthesis.

(SIGNA.) M. BAKUNIN and D. PECCERILLO (Gazzetta, 1935, 65, 1145—1161).—The yield of *o*-nitrocinamic acid (I) from the reaction (at 90°) between *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (II) and various metallic salts of  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  (III), in presence of  $\text{Ac}_2\text{O}$ , increases in the order  $\text{Ba} < \text{Li} < \text{Na} < \text{K} < \text{Rb}$ .  $\text{NH}_4$  and  $\text{NH}_3\text{Ph}$  salts do not give (I). With (II) and the anhydride of (III), the catalytic action of bases etc. is in the order  $\text{NHET}_2 < \text{C}_5\text{H}_{11}\text{N} < \text{NaOAc} < \text{NMe}_3 < \text{NEt}_3$ . From (II) and (III) in absence of  $\text{Ac}_2\text{O}$ , or of catalyst, no (I) is formed; the effects of various bases in presence of  $\text{Ac}_2\text{O}$ , and of various anhydrides in presence of  $\text{NEt}_3$ , are tabulated. (II) and (III) react in presence of  $\text{NaOBz}$ .  $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  does not react with (II). *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OAc})_2$  with  $\text{CH}_2(\text{CO}_2\text{H})_2$  yields *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})_2$ , but does not react appreciably with (III). The reaction  $\text{Ac}_2\text{O} + 2\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{M} \rightarrow (\text{CH}_2\text{Ph}\cdot\text{CO}_2)_2\text{O} + 2\text{MOAc}$  has been shown to take place, and to depend on the nature of M (Na, Li, Ba), and on temp. The effect of inorg. salts as catalysts is ascribed to formation of  $\text{MOAc}$ ; KI, which does not yield  $\text{KOAc}$ , is not a catalyst. Mol. compounds are formed between anhydrides or acids, and salts of the same (or perhaps even of a different) acids, e.g., the compound  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$  (IV), m.p. 95° (stable in org. solvents). (IV) reacts with (II) in the presence, but not in the absence, of  $\text{Ac}_2\text{O}$  or  $\text{Bz}_2\text{O}$ .  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$  and  $\text{Ac}_2\text{O}$  react to form a mol. com-

pound, m.p. 60°, together with (IV);  $\text{AcCl}$  reacts similarly, as do other substances. It is concluded that the Perkin synthesis depends on the intermediate formation of acid-salt or anhydride-salt compounds (which are decomposed by  $\text{H}_2\text{O}$ ), on their stability at the temp. of reaction, and their solubility in the medium, and on the homogeneous presence in the formation of substances capable of absorbing  $\text{H}_2\text{O}$ . The formation of Ac and imide derivatives of aldehydes impedes the reaction.

E. W. W.

**Removal of hydrogen and acid radicals from organic compounds by bases. II. Removal of acetic acid from acetylaldoximes by alkalis.** C. R. HAUSER and E. JORDAN (J. Amer. Chem. Soc., 1935, 57, 2450—2456; cf. A., 1934, 73).—Acetyl- $\alpha$ - and - $\beta$ -araldoximes undergo the same types of reaction with alkalis; the oxime is formed by hydrolysis and the ArCN by elimination (which occurs more readily with the  $\beta$ -derivatives) of AcOH. The yields of products depend on the relative rates of the two (competing) reactions. Acetyl- $\beta$ -*p*-methoxy-, -3:4-methylenedioxy- (I), and -*p*-nitro-benzaldoximes with 2*N*-NaOH give mixtures of ArCN (predominates at 30°) and the  $\alpha$ -oxime (II) (predominates at 0°); the first two with aq. 10%  $\text{Na}_2\text{CO}_3$  at 0° or 30° give ArCN and a little (II) (cf. loc. cit.). Hydrolysis (2*N*-NaOH) of acetyl- $\alpha$ - (III), -*m*-, and -*p*-nitro-, -*p*-methoxy-, and -3:4-methylenedioxy- (IV) -benzaldoximes, prepared by a modification of Brady and Dunn's method (J.C.S., 1, 13, 103, 1619), at 30° and 97—100° gives (usually) the  $\alpha$ -oxime (V) and a little  $\text{ArCO}_2\text{H}$  at 61—64° (III) affords an appreciable amount *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ . (IV) and acetyl- $\alpha$ -chloro-, -*p*-methoxy-, and -*m*-nitro-benzaldoximes with  $\text{KNH}_2$  in liquid  $\text{NH}_3$  give ArCN (major product) and (V) the first three with boiling 2*N*-EtOH-NaOEt afford mainly (I) (as Na salts). (I) is hydrolysed more readily than (IV) by an excess of  $\text{Na}_2\text{CO}_3$  in aq. COM.e<sub>2</sub>.

#### Reactions of aldoxime derivatives with bases.

**II. Reactions of carbethoxy- $\alpha$ -benzaldoximes with sodium hydroxide.** C. R. HAUSER, E. JORDAN, and R. O'CONNOR (J. Amer. Chem. Soc., 1935, 57, 2456—2458).—Carbethoxy- $\alpha$ -benzaldoxime and its *o*- (I), *m*- (II), and *p*-nitro-, *o*- and *p*-chloro-, *o*- and *p*-methoxy- (III), and 3:4-methylenedioxy derivatives with 2*N*-NaOH give mixtures of the corresponding  $\alpha$ -oxime (IV) [predominates at 30°; except for (I) and ArCN (or  $\text{ArCO}_2\text{H}$ ) [the yield at 97—100° is > at 30° and often exceeds that of (IV)]] and ArCN (or  $\text{ArCO}_2\text{H}$ ) [the yield at 97—100° is > at 30° and often exceeds that of (IV)]. The yields of ArCN are generally > those from the acetyl- $\alpha$ -araldoximes (preceding abstract). (II) and (III) with  $\text{KNH}_2$  in liquid  $\text{NH}_3$  give ArCN and a little (IV). Some of the above  $\text{CO}_2\text{Et}$  derivatives are wrongly described as  $\beta$ -isomerides by Brady and McHugh (J.C.S., 1923, 123, 1190).

**Derivatives of dihydrovanillin. Catalytic hydrogenation of nitrostyrenes.** (A) O. S. CHALES. (B) K. MAURER (J. pr. Chem., 1936, [ii], 144, 214—215, 216).—Concerning priority (A., 1935, 1232, 1497).

**Iodine substitution products of vanillin and their derivatives.** L. C. RAIFORD and E. H. WELLS



(J. Amer. Chem. Soc., 1935, 57, 2500—2503).—2-Aminovanillin is converted (Sandmeyer) into 2-iodovanillin (I), m.p. 155—156° [Ac derivative, m.p. 70—72°; oxime (+0.5H<sub>2</sub>O), softens ca. 122°, m.p. (anhyd.) 142.5—143.5°; semicarbazone, m.p. 199—200°; p-nitrophenylhydrazone, m.p. 211—212°; benzidine condensation product, decomp. ca. 232—233°], methylated (Me<sub>2</sub>SO<sub>4</sub>, aq. KOH) to 2-iodo-3:4-dimethoxybenzaldehyde, m.p. 82°. 5-Aminovanillin (hydrochloride; stannichloride; ON-Ac, m.p. 174—176°, and ON-Bz, m.p. 161—162°, derivatives), prepared by reduction (SnCl<sub>2</sub>, conc. HCl, EtOH) of the NO<sub>2</sub>-compound, similarly gives 5-iodovanillin, m.p. 179—180° [Ac (II), m.p. 105—106°, and Bz, m.p. 135.5—136.5°, derivatives; oxime, m.p. 178—179°; semicarbazone, m.p. 205—205.5°; p-nitrophenylhydrazone, m.p. 242—243° (decomp.); benzidine condensation product, m.p. 232° (decomp.); Me ether, m.p. 69—70°], which is identical with the iodovanillin of Carles (A., 1872, 708). (II) or 5-iodo-4-acetoxy-3-methoxybenzylidene diacetate, m.p. 132—133°, with fuming HNO<sub>3</sub> at < gives derivative, m.p. 124—125°, of 5-iodo-2-nitrovanillin, m.p. 146—147° [oxime, m.p. 128—129°; semicarbazone, m.p. 187—188° (decomp.); p-nitrophenylhydrazone, (+0.5EtOH), m.p. 228—230° (decomp.); benzidine condensation product], reduced [Fe(OH)<sub>2</sub>, aq. NH<sub>3</sub>] to 5-iodo-2-aminovanillin (III), m.p. 155°. (I) and I in AcOH-NaOAc give 2:5-di-iodovanillin, m.p. 200° [Ac derivative, m.p. 127—128°; oxime, m.p. 174.5—175.5°; semicarbazone, m.p. 235° (decomp.); p-nitrophenylhydrazone, m.p. 252—253° (decomp.); benzidine condensation product; Me ether, m.p. 94°], also prepared (Sandmeyer) from (III). H. B.

**Synthesis of dicyclo-[1:2:3]-octanone and dicyclo-[1:2:3]-octane.** G. KOMPPA, T. HIRN, W. ROHRMANN, and S. BECKMANN (Annalen, 1936, 521, 242—261).—The following methods of prep. of hexahydrohomoisophthalic acid (I) (A., 1904, i, 60) have been investigated. (a) Homoisophthalic acid (II), m.p. 185° [diamide, m.p. 228°; Et, b.p. 175°/12 mm., and Me, b.p. 152—153°/10 mm., esters; Ba (+2H<sub>2</sub>O), Ag, Cd (+2H<sub>2</sub>O), and Zn (+0.66H<sub>2</sub>O) salts], is reduced by Na-Hg-NaOH to its H<sub>2</sub>-derivative (III) (Br<sub>2</sub>-derivative, m.p. 193—194°), which with HBr-AcOH at 100° gives the bromohexahydro-acid, m.p. 283° (decomp.) (and a substance, m.p. 157—158°), converted by Ag<sub>2</sub>O in EtOH into an unsaturated acid, C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>, m.p. 141—143°, and reduced (Na-Hg) to (?) trans-hexahydrohomoisophthalic acid (IV), m.p. 156—158° [diamide, m.p. 277—278° (decomp.); Ag and Ba salts]. (b) Direct reduction of (III) with H<sub>2</sub>-Pd, or, better, direct catalytic reduction (Skita) of (II) (85% yield) is the best method of prep. (c) Reduction of (II) with Na-C<sub>5</sub>H<sub>11</sub>·OH gives a mixture, m.p. 120—127°, of stereoisomerides of (I). (d) cycloHexanone-3-carboxylic acid, obtained from m-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (Einhorn et al., A., 1896, i, 530), with CH<sub>2</sub>Br·CO<sub>2</sub>Et-Zn and dehydration of the OH-ester with NaHSO<sub>4</sub> at 120—140°, gives the Et<sub>2</sub> ester, b.p. 151—156°/16 mm., of (III), reduced (Skita) to the Et ester, b.p. 138—144°/8 mm., of (I). (e) (IV) is obtained by condensation of Et 3-bromocyclohexane-1-carboxylate

with either CHNa(CO<sub>2</sub>Et)<sub>2</sub> or CN·CHNa·CO<sub>2</sub>Et and complete hydrolysis of the products. Reduction of hexahydroisophthalic anhydride with H<sub>2</sub>-Ni at 280—290° affords the lactone, b.p. 111—113°/8 mm f p -5° to -10°, of 3-hydroxymethylcyclohexane-1-carboxylic acid, also obtained by the action of I at 150° on the Ag salt of (IV). dicyclo-[1:2:3]-Octanone (V) (loc. cit.) [oxime, m.p. 66—67°; semicarbazone, m.p. 183—183.5° (corr.), and not 189—190° as previously recorded] is best obtained by distillation of the Ca salt of (IV). Oxidation of (V) with HNO<sub>3</sub> at 50° gives cis-hexahydroisophthalic acid, and reduction (Na-EtOH) affords dicyclo-[1:2:3]-octanol, b.p. 200—205°, m.p. 170° (corr.) [phenylurethane, m.p. 133° (corr.)], the chloride, b.p. 73—75°/14 mm., m.p. 43—45°, of which is reduced (Na-EtOH) to dicyclo-[1:2:3]-octane, m.p. 133—134°.

J. W. B.

**Preparation of m-nitroacetophenone.** V. G. MORGAN and H. B. WATSON (J.S.C.I., 1936, 55, 29—30T).—A method of nitration, using HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>, is described, differing in some details from the procedure given in "Organic Syntheses," 1930, 10, 74, and leading to a better yield of a very pure product. The m.p. of m-nitroacetophenone is 79.5° (corr.).

**Synthesis of mixed acetones by means of ethyl malonate.** A. GIACALONE [in part with F. Russo] (Gazzetta, 1935, 65, 1127—1138).—Acyl chlorides react with CHNa(CO<sub>2</sub>Et)<sub>2</sub> (I) to form acyl compounds of type R·CO·CH(CO<sub>2</sub>Et)<sub>2</sub> (II), and acyl derivatives of the enolic form of these, viz., R·CO<sub>2</sub>·CR'C(CO<sub>2</sub>Et)<sub>2</sub> (II). (II) and (III) with NH<sub>2</sub>Ph, NHPh·NH<sub>2</sub>, or NH<sub>2</sub>OH yield CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> and R·CO·NHR'. BzCl and (I) give Et<sub>2</sub> benzoylmalonate, b.p. 198°/8 mm., and dibenzoylmalonate, m.p. 45°, b.p. 249°/6 mm. With NHPh·NH<sub>2</sub> these yield NHPh·NHBz, new m.p. 170—171°; both are hydrolysed to CPhMe. 6-Amino-3-methylacetophenone (IV), m.p. 50—51°, is prepared [with a view of synthesising 2-(4'-amino-m-tolyl)-4:6-dimethylquinoline (cf. A., 1935, 758)] as follows. 4-Nitro-m-toluic acid (V) (this vol., 69) is converted into the chloride, m.p. 45—46°, and this combined with (I) to form Et<sub>2</sub> 4-nitro-m-toluoyle- (VI), sol. in aq. NaOH, and di-(4-nitro-m-toluoyle)-malonate (VII), m.p. 106—107°, insol. in aq. NaOH. (V) is hydrolysed (80% H<sub>2</sub>SO<sub>4</sub>) to 6-nitro-3-methylacetophenone (VIII), and (VI) to (V) and (VIII). (VIII) is then reduced (Sn-HCl) to the stannichloride, (C<sub>9</sub>H<sub>4</sub>ON<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>SnCl<sub>6</sub>, m.p. 187° (decomp.), of (I), with the stannichloride, m.p. 215° (decomp.), of 4-amino-m-tolylmethylcarbinol, m.p. 35°. 2-Nitro-m-toluic acid (IX) similarly yields, through its chloride, m.p. 82—83°, Et<sub>2</sub> 2-nitro-m-toluoyle- (X), m.p. 73°, and di-(2-nitro-m-toluoyle)-malonate (XI), m.p. 134—135°. (X) is hydrolysed to 2-nitro-3-methylacetophenone (XII), m.p. 85°, and (XI) to (IX) and (XII). (XII) is reduced to the stannichloride, m.p. 208°, of 2-amino-3-methylacetophenone.

E. W. W.

**Autoxidation of ketones.** S. S. JENKINS (J. Amer. Chem. Soc., 1935, 57, 2733).—o-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H and PhCHO are formed when o-C<sub>6</sub>H<sub>4</sub>Cl·CO·CH<sub>2</sub>Ph is kept. Similar autoxidation occurs with several ketones of the type COR·CH<sub>2</sub>Ph. H. B.

**Reaction between (A) phenyl  $\alpha\beta$ -dibromo- $\beta$ -phenylethyl ketone and azides, (B) phenyl  $\alpha\beta$ -dibromo- $\beta$ -*m*-nitrophenylethyl ketone and sodium azide.** V. A. KUZMIN and N. I. ZEMLIANSKI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 183—190, 191—194).—(A)  $\text{NaN}_3$  and  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COPh}$  in aq.  $\text{COMe}_2$  (12 hr. at 60—65°) yield a Br-containing oil, and a monoazide of Ph styryl ketone, m.p. 64—65°, both decomposed by  $\text{H}_2\text{SO}_4$  with evolution of  $\text{N}_2$ .

(B)  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$  and  $\text{NaN}_3$  in aq. EtOH or  $\text{COMe}_2$  (12—14 hr. at 65—70°) afford a monoazide, m.p. 76—77° (decomp.) of Ph 3-nitro-styryl ketone. R. T.

**New route to hydroaromatic ketones related to anthracene and phenanthrene.** J. W. COOK, C. L. HEWETT, and C. A. LAWRENCE (J.C.S., 1936, 71—80).—2-Chlorocyclohexanol and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  (I) lead (by ring-contraction) to cyclopentylcarbinol, b.p. 120° (bath)/0.1 mm., m.p. 30° (3:5-dinitrobenzoate, m.p. 100.5—101.5°), oxidised ( $\text{CrO}_3$ , AcOH) to phenylacetylcyclopentane (semicarbazone, m.p. 117—118°). cycloHexene oxide (II) and (I) give 2-benzylcyclohexanol (III), m.p. 76.5—77.5° (3:5-dinitrobenzoate, m.p. 133—135°) (oxidised to 2-benzylcyclohexanone), and a mixture (A) of *cis*- and *trans*-2-chlorocyclohexanols. The  $\text{Mg}(\text{CH}_2\text{Ph})_2$  present in the Grignard reagent thus appears to be more reactive than the  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  [responsible for the production of (A)] towards (II). 2-Phenylcyclohexanol (IV), b.p. 153—154°/16 mm., m.p. 56—57° (lit. 54—55°) (3:5-dinitrobenzoate, m.p. 121—121.5°), prepared from (II) and LiPh in  $\text{Et}_2\text{O}$  and  $\text{N}_2$ , is oxidised ( $\text{CrO}_3$ , AcOH) to  $\delta$ -benzoylvaleric acid and 2-phenylcyclohexanone (V). The poor yield of (IV) from (II) and  $\text{MgPhBr}$  (Bedos, A., 1926, 508) is due to cyclopentylcarbinol formation.  $\alpha\text{-C}_{10}\text{H}_7\text{Li}$  and (II) afford 2-1'-naphthylcyclohexanol, b.p. 183°/1 mm., m.p. 129—130° (3:5-dinitrobenzoate, m.p. 162—163°; phenylcarbamate, m.p. 134—135°), dehydrated ( $\text{ZnCl}_2$  at 160—170°) to 1-naphthyl- $\Delta^1$ -cyclohexene, m.p. 46° (lit. 36°), also prepared by Weiss and Woidich's method (A., 1926, 509), and from the alcohol and  $\text{PBr}_3$  in cold  $\text{CCl}_4$ .  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ , (V), and Zn in  $\text{C}_6\text{H}_6$  give *Et* 1-hydroxy-2-phenylcyclohexylacetate, b.p. 146—154°/0.8 mm. (free acid, m.p. 128—129°), dehydrated ( $\text{SOCl}_2$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{N}$  at 0°) to the *Et* ester, b.p. 123—125°/0.8 mm., of 2-phenyl- $\Delta^1$ -cyclohexenylacetic acid (VI), b.p. 150—155°/0.4 mm., m.p. 92.5—93.5°. Reduction ( $\text{H}_2$ , Pd-black, AcOH) of (VI) affords 2-phenylcyclohexylacetic acid (VII), m.p. 168—170°, and an impure isomeride (?) (cf. below) [converted by conc.  $\text{H}_2\text{SO}_4$  at 100° into a ketone,  $\text{C}_{14}\text{H}_{16}\text{O}$ , m.p. 95—96° (oxime, m.p. 175—177°), which is probably stereoisomeric with (VIII) (below)]. The bromide from (IV) and  $\text{PBr}_3$  in  $\text{CCl}_4$  with  $\text{CHK}(\text{CO}_2\text{Et})_2$  in  $\text{C}_6\text{H}_6$  gives (after hydrolysis and decarboxylation) a stereoisomeric (?) 2-phenylcyclohexylacetic acid, m.p. 84—85° (cf. Ghose, A., 1935, 1495). The chloride of (VII) with  $\text{AlCl}_3$  in  $\text{CS}_2$  at 0° gives 9-keto-1:2:3:4:9:10:11:12-octahydrophenanthrene (hexahydrophenanthrene) (VIII), b.p. 137—138°/0.5 mm. (oxime, m.p. 123.5—124.5°; semicarbazone, m.p. 195—196°), also formed from (VII) and conc.  $\text{H}_2\text{SO}_4$  at 100°. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) of (VIII) affords the 9-hydroxyoctahydrophen-

anthrene, m.p. 114—115°, dehydrogenated (Pt-black at 310—320°) to 9-phenanthrol and dehydrated ( $\text{ZnCl}_2$  at 180°) to hexahydrophenanthrene, b.p. 125—126°/2.5 mm., which is similarly dehydrogenated to phenanthrene. *as*-Octahydrophenanthrene (A., 1933, 1042) is oxidised ( $\text{CrO}_3$ , AcOH) to a mixture of (VIII) and an isomeride (?) (oxime, m.p. 186.5—187.5°). The Grignard reagent from impure 1-chloro-2-benzylcyclohexane, b.p. 85—100°/0.2 mm. [from (III) and  $\text{SOCl}_2$  in  $\text{NPhMe}_3$ ], and  $\text{CO}_2$  give *cis*- (IX), m.p. 86—88°, and *trans*- (X), m.p. 133—134°, -2-benzylhexahydrobenzoic acids. The Grignard reagent from 1-bromo-2-benzylcyclohexane, b.p. 120°/0.4 mm. [from (III) and  $\text{PBr}_3$  in cold  $\text{CCl}_4$ ], with  $\text{ClCO}_2\text{Et}$  affords (after hydrolysis with aq. EtOH-KOH) (X), probably 4-benzylhexahydrobenzoic acid, m.p. 140—141° (the formation of which involves a migration), and 2:2'-dibenzyl-dicyclohexyl, m.p. 180—181° (cloudy; clear at 191°).  $o\text{-CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  is reduced by Na and amyl alcohol to (X) and by  $\text{H}_2$  and  $\text{PtO}_2$  in AcOH to *o*-hexahydrobenzylbenzoic acid, m.p. 95.5—96.5° [oxidised (alkaline  $\text{KMnO}_4$ ) to  $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ]. (X) with cold conc.  $\text{H}_2\text{SO}_4$ , or its chloride with  $\text{AlCl}_3$  in cold  $\text{CS}_2$ , leads to *trans*-hexahydroanthrone (XI), m.p. 109—109.5° (oxime, m.p. 174.5—175.5°); (IX) similarly gives *cis*-hexahydroanthrone (XII), m.p. 79—80° (cloudy; clear at 85°) (oxime, m.p. 150—151°), and some (XI). Dehydrogenation (Pt-black at 300°) of (XI) and (XII) affords anthracene. A mixture of (XI) and (XII) is formed from either (IX) or (X) and conc.  $\text{H}_2\text{SO}_4$  at 100°; interconversion of the ketones probably occurs through an intermediate enolic form.

[By R. ROBINSON.] Contrary to the previous statement (A., 1934, 75), cyclohexene oxide and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$  (XIII) give cyclopentyl- $\beta$ -phenylethylcarbinol (XIV), also prepared from (XIII) and cyclopentylformaldehyde. The following corrections should be made in the abstract: the chloride and *p*-nitrobenzoate of 2- $\beta$ -phenylethylcyclohexanol are those of (XIV); the 2- $\beta$ -phenylethylcyclohexanone is cyclopentyl  $\beta$ -phenylethyl ketone; 2- $\beta$ -phenylethyl-1-ethylcyclohexanol is cyclopentyl- $\beta$ -phenylethylethylcarbinol; 1:2:3:4:9:10:11:12-octahydrophenanthrene is 1-cyclopentylhydrindene; 2- $\beta$ -phenylethyl-1-ethyl- $\Delta^1$ -cyclohexene and ethyloctahydrophenanthrene are best described as hydrocarbons, both  $\text{C}_{16}\text{H}_{22}$ . The apparent difference between the previous results and those of Bardhan and Sen-Gupta (A., 1932, 1241) no longer exists. H. B.

**Preparation of 9:10-dihydrophenanthrene and its derivatives.** A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1935, 57, 2731—2732).—Reduction of phenanthrene with  $\text{H}_2$  at 2000—4000 lb. per sq. in. at 220° in presence of a Cu—Cr—BaO catalyst (Connor *et al.*, A., 1932, 477) gives 60—80% of the 9:10- $\text{H}_2$ -derivative, m.p. 31—32°, which with AcCl in  $\text{CS}_2$  or  $\text{PhNO}_2$  affords 2-acetyl-9:10-dihydrophenanthrene (I), m.p. 51—52° (oxime, m.p. 146—147.5°; semicarbazone, m.p. 236—237°). (I) is oxidised by  $\text{CrO}_3$  to 2-acetyl-9:10-phenanthraquinone, m.p. 223—224°, and by NaOCl to 9:10-dihydrophenanthrene-2-carboxylic acid, m.p. 211.5—212.5° [*Me* ester, an oil, dehydrogenated (Se at 300°) to phenanthrene-2-carboxylic acid].

2-Bromoacetyl-9:10-dihydrophenanthrene has m.p. 93.5—95°. 9:10-Dihydroanthracene is obtained in nearly quant. yield by reduction ( $H_2$ ; Cu chromite; 160°) of anthracene. H. B.

Higher benzenoid hydrocarbons. II. Isomeric bromofluorenones. III. Isomeric bromo-9-fluorenols and bromofluorenes. H. F. MILLER and G. B. BACHMAN (J. Amer. Chem. Soc., 1935, 57, 2443—2446, 2447—2450).—II. The chloride, m.p. 162—163°, of 4-bromobenzophenone-2'-carboxylic acid (I) is converted by liquid  $NH_3$  into the amide, m.p. 184.5—185°, and thence by alkaline NaOBr into 4-bromo-2'-aminobenzophenone (II), m.p. 108°, also prepared by hydrolysis (90%  $H_2SO_4$ , AcOH) of the reaction product from 2-*p*-toluenesulphonamidobenzoyl chloride, PhBr, and  $AlCl_3$ , and from (I) and  $N_3H$  (method: Oesterlin, A., 1932, 1030). When the diazo-solution from (II) is warmed, 3-bromofluorenene, m.p. 162°, is obtained. The chloride, m.p. 119—120°, of 3-bromobenzophenone-2-carboxylic acid with  $NH_4HCO_3$  affords the amide, m.p. 135—140°, converted (NaOBr) into 3-bromo-2-aminobenzophenone, m.p. 128—130°, and thence (as above) into 4-bromofluorenene, m.p. 190—191°, which is also prepared from 2-bromodiphenyl-2'-carboxylic acid, m.p. 186—187° (from  $o$ - $C_6H_4$ - $CO_2Me$ ,  $o$ - $C_6H_4Br$ , and Cu at 260—290°), and conc.  $H_2SO_4$  at 100° (bath).

III. Bromofluorenones (A) are reduced (Zn dust, conc. aq.  $NH_3$ , EtOH) to bromofluorenols (B), which are reduced further to bromofluorenes [also prepared by Clemmensen reduction of (A)] by red P and I in AcOH. (B) with HBr and HCl in EtOH give the dihalogenofluorenes. The following are new: 3-, m.p. 142—145°, and 4-, m.p. 149—150°, -bromo-9-fluorenols; 3- (III), m.p. 90—91°, and 4- (IV), m.p. 165°, -bromofluorenes; 2:9-, m.p. 107.5—108.5°, 3:9-, m.p. 124—125°, and 4:9-, m.p. 194—195°, -dibromofluorenes; 9-chloro-3-, m.p. 116—117°, and 4-, m.p. 141—142°, -bromofluorenes. Fluorene and  $Hg(OAc)_2$  give (mainly) the 4-OAc-Hg-derivative [converted by successive treatment with  $CaCl_2$  and Br into (IV)]; in the absence of solvent some of the 3-derivative [converted into (III)] is also formed. In the latter case, the intermediate mixture of  $CHg$ -derivatives differs considerably from the product obtained by Goswami and Das-Gupta (A., 1931, 1435).

$\omega$ -Benzyl derivatives of acetophenone and their reduction products. G. A. HILL and A. J. COFRANCESCO (J. Amer. Chem. Soc., 1935, 57, 2426—2428).—In  $\alpha$ -diphenylisopropyl ketone (I) (oxime, m.p. 157°), formed together with  $COPh \cdot CH_2 \cdot CH_2Ph$  (II) from  $COPhMe$ ,  $CH_2PhCl$ , and  $NaNH_2$  in xylene, is reduced (Na, EtOH) to  $\alpha$ -diphenyl- $\beta$ -benzylpropyl alcohol (phenylcarbamate, m.p. 185°). (II) is benzylated (above method) to Ph  $\beta$ -phenyl- $\alpha$ -dibenzylethyl ketone (tribenzylacetophenone) (III), m.p. 111—128°, which is reduced by Na and EtOH to  $\alpha$ -diphenyl- $\beta$ -dibenzylpropyl alcohol, decomp. when heated at low pressure, and by red P and 47% HI to  $C(CH_2Ph)_4$  (yield 13%). (I)—(III) could not be reduced by Clemmensen's method. H. B.

Structure of metallic derivatives formed by adding Grignard reagents to unsaturated ket-

ones. E. P. KOHLER, M. TISHLER, and H. POTTER (J. Amer. Chem. Soc., 1935, 57, 2517—2521).—The compound,  $[CHPh_2 \cdot CH \cdot CO \cdot C_6H_2Me_3]MgBr$  (A), obtained from mesityl styryl ketone (I) and  $MgPhBr$ , with  $BzCl$  gives  $\approx 96\%$  of  $\gamma$ -diphenyl- $\alpha$ -mesityl- $\Delta^a$ -propenyl benzoate (II), m.p. 162°. Mesityl  $\beta$ -diphenylethyl (III) or  $\alpha$ -bromo- $\beta$ -diphenylethyl ketones and  $MgEtBr$  afford an isomeride (B) of (A); a geometrical isomeride (IV), m.p. 148°, of (II) is obtained from (B) and  $BzCl$ . (II) and (IV) are both hydrolysed (EtOH-NaOH) to (III). Ability to combine with  $RCHO$  is no indication of the structure of such Mg derivatives. Thus, (B) and  $PhCHO$  afford  $\beta$ -trimethylbenzoyl- $\alpha$ - $\gamma$ -triphenylpropyl alcohol, m.p. 132°, oxidised ( $CrO_3$ , AcOH) to  $\alpha$ -benzoyl- $\alpha$ -trimethylbenzoyl- $\beta$ -diphenylethane (V), m.p. 107°, and polymeric material. Acidification of a solution of (V) in  $MeOH$ -NaOH gives an enol, m.p. 137°, which reverts to (V) in presence of org. bases; the relative stability of the enol is due to the  $C_6H_2Me_3$  group since the enol of  $CHBz_2 \cdot CHPh$ , is mobile. The Mg derivative from  $CHPh_2 \cdot CH_2 \cdot COPh + MgEtBr$  with  $C_6H_2Me_3 \cdot COCl$  affords (V) and  $\alpha$ - $\gamma$ -triphenyl- $\Delta^a$ -propenyl trimethylbenzoate, m.p. 93°. The product from (I) +  $MgMeI$  treated with  $BzCl$  gives (after removal of ester with cold  $MeOH$ -NaOH) a little of the enol, m.p. 128°, of  $\alpha$ -benzoyl- $\alpha$ -trimethylbenzoyl- $\beta$ -phenylpropane, m.p. 130°; this enol has the same stability as that of (V). Reduction (Adams) of (I) affords mesityl  $\beta$ -phenylethyl ketone, b.p. 191—192°/about 5 mm.; successive treatment of this with  $MgEtBr$ ,  $BzCl$ , and  $MeOH$ -NaOH gives 12% of  $\alpha$ -benzoyl- $\alpha$ -trimethylbenzoyl- $\beta$ -phenylethane (VI), m.p. 118°, fresh solutions ( $MeOH$ ) of which contain 4% of enol (equilibration with piperidine gives approx. equal amounts of keto- and enol forms). (VI) is also prepared from  $CH_2PhCl$  and the Na derivative of  $CH_2Bz \cdot CO \cdot C_6H_2Me_3$  (VII), and by catalytic reduction of  $\alpha$ -benzoyl- $\alpha$ -trimethylbenzoyl- $\beta$ -phenylethylene, obtained in poor yield (method: Knoevenagel and Erler, A., 1903, i, 636) from (VII) and  $PhCHO$ .  $\alpha$ -Diphenyl- $\gamma$ -mesityl- $\Delta^a$ -propenyl benzoate (?), m.p. 110°, is formed from Ph trimethylstyryl ketone +  $MgPhBr$  and  $BzCl$ . Decomp. of (A) with cold dil. HCl and treatment of the product (in moist light petroleum) with  $O_2$  gives the peroxide, m.p. 116—117° (decomp.), of  $\gamma$ -diphenyl- $\alpha$ -mesityl- $\Delta^a$ -propen- $\alpha$ -ol [*i.e.*, the enolic form of (III), stabilised by the  $C_6H_2Me_3$  group]. H. B.

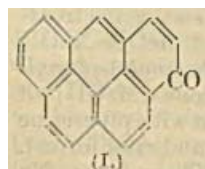
Preparation of benzanthrone compounds and benzanthronecarboxylic acids.—See B., 1936, 92.

Additions to conjugated systems in anthracene series. III. Factors influencing mode and extent of reaction of Grignard reagent with ketones. P. L. JULIAN, W. COLE, and T. F. WOOD (J. Amer. Chem. Soc., 1935, 57, 2508—2513).—10-Benzylideneanthrone and  $MgMeI$  give (by 1:2-addition) 10-benzylidene-9-methyl-9:10-dihydroanthranol, m.p. 148°, converted by Br in  $CHCl_3$  into 10- $\alpha$ -bromobenzyl-9-bromomethylanthracene (I), m.p. 168 (decomp.), which with  $NaOAc$ -AcOH affords 10- $\alpha$ -acetoxybenzyl-9-acetoxymethylanthracene, m.p. 188; treatment of the initial reaction product (in solution) with  $O_2$  gives a small amount of a peroxide, decomp. 74° [to anthraquinone (II)]. (I) and Br in  $CHCl_3$



afford  $\text{CH}_2\text{PhBr}$  and 10-bromo-9-bromomethylanthracene. The formation of (II) and  $\text{MeCHO}$  from 10-hydroxy-10-ethylanthrone (III), m.p.  $107^\circ$  [from (II) and  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$ ], and  $\text{AcOH-conc. H}_2\text{SO}_4$  in  $\text{O}_2$  supports the view that 10-ethylideneanthrone (IV), b.p.  $245-247^\circ/20$  mm. [obtained when (III) is distilled at atm. pressure in  $\text{N}_2$ ], reacts as 9-hydroxy-10-vinylanthracene. The ready oxidation ( $\text{O}_2$ ) of (IV) to (II) and vinyl alcohol through the peroxide, and the oxidative decomp. of (IV) to (II) and  $\text{C}_2\text{H}_2$  during attempted distillation at atm. pressure, are thus satisfactorily explained. Anthraphenone, which resembles an  $\alpha\beta$ -unsaturated ketone, is reduced by  $\text{MgPhBr}$  to 10 : 10'-dibenzoyl-9 : 10 : 9' : 10'-tetrahydro-9 : 9'-dianthryl; no reaction occurs with  $\text{MgMeI}$ . 9 : 10-Dihydroanthraphenone similarly affords 9- $\alpha$ -hydroxybenzhydryl-9 : 10-dihydroanthracene, m.p.  $173^\circ$ , dehydrated ( $\text{AcOH-conc. H}_2\text{SO}_4$ ) to 9-benzhydrylidene-9 : 10-dihydroanthracene, m.p.  $258^\circ$ , which is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to  $\text{COPh}_2$  and (II). Pure products could not be isolated from 9-benzoyl-10-phenylanthracene (V); the 9 : 10- $\text{H}_2$ -derivative of (V) similarly gives (V), presumably owing to oxidation of the intermediate  $\text{Mg}$  compound. H. B.

**Action of glycerol and sulphuric acid on pyrene: history of benzanthrone.** R. SCHOLL and H. K. MEYER (Ber., 1936, 69, [B], 152-158).—Pyrene is converted by  $\text{H}_2\text{SO}_4$  and glycerol at  $100-110^\circ$  into 1 : 9 : 8-diperinaphth-2 : 9-anthra-2-one (I), m.p.  $243^\circ$  after darkening, which is not further affected by the reactants at  $140^\circ$  and is not transformed into pyranthrone-like substances by  $\text{NaCl-AlCl}_3$  and  $\text{BzCl}$ . (I) readily gives a



(?)  $\text{-Br}_2$ -derivative and is converted by boiling  $\text{HNO}_3$  ( $d$  1.42) into a ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $>330^\circ$ , whence the ( $\text{NH}_2$ )<sub>2</sub>- and ( $\text{NHAc}$ )<sub>2</sub>-compounds. When treated with red P and boiling HI ( $d$  1.7), (I) is transformed into 1 : 9 : 8-diperinaphth-2 : 3 : 4 : 9-tetrahydroanthracene, m.p.  $107-108^\circ$  (picrate), re-oxidised to (I) by  $\text{H}_2\text{SO}_4$  and glycerol and converted by passage over heated Cu into 1 : 9 : 8-diperinaphth-2 : 9-dihydroanthracene. (I) is oxidised by  $\text{CrO}_3$  in boiling  $\text{AcOH}$  to the quinone,  $\text{C}_{19}\text{H}_8\text{O}_2$ , m.p.  $>330^\circ$  after darkening at  $300^\circ$ . The history of the discovery of benzanthrone is given (cf. A., 1929, 1305). H. W.

**cis- and trans-1 : 3-Diketodecahydronaphthalene.** C. K. CHUANG and Y. L. TIEN (Ber., 1936, 69, [B], 31).—Condensation of cyclohexenyl Me ketone with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  by a slight modification of the method of Kon *et al.* (A., 1927, 150) affords Et 1 : 3-diketodecahydronaphthalene-4-carboxylate (I), m.p.  $114^\circ$  (semicarbazone, m.p.  $229^\circ$ ), in 87% yield. It is hydrolysed by boiling 20%  $\text{KOH-EtOH}$  to trans-1 : 3-diketodecahydronaphthalene (II), m.p.  $152-153^\circ$  (lit. m.p.  $142^\circ$ ) [dioxime, m.p.  $207^\circ$  (decomp.); disemicarbazone, m.p.  $241^\circ$  (decomp.); trans-1 : 3-diketo-2-benzylidenedecahydronaphthalene, m.p.  $229^\circ$ ; methylenedi-trans-1 : 3-diketodecahydronaphthalene, m.p.  $172-173^\circ$ ]. The configuration of (II) follows from its oxidation by  $\text{NaOBr}$  to trans-o-carboxycyclohexaneacetic acid and by  $\text{KMnO}_4$  to trans-cyclohexane-

1 : 2-dicarboxylic acid. Treatment of (I) with dil.  $\text{KOH-EtOH}$  at  $15-20^\circ$  gives the corresponding acid, which passes with loss of  $\text{CO}_2$  into cis-1 : 3-diketodecahydronaphthalene (III), m.p.  $124-125^\circ$  (dioxime, m.p.  $152-153^\circ$ ; methylenedi-cis-1 : 3-diketodecahydronaphthalene, m.p.  $147-148^\circ$ ). Oxidation of (III) with  $\text{NaOBr}$  leads to cis-o-carboxycyclohexaneacetic acid, m.p.  $146^\circ$ . (III) is isomerised to (II) by treatment with boiling 20%  $\text{KOH-EtOH}$ . Hydrolysis of (I) with boiling 15%  $\text{HCl}$  (cf. Ruzicka *et al.*, A., 1931, 1302) followed by distillation of the product in vac. gives an acid,  $\text{o-C}_6\text{H}_{10}\text{Ac}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  or  $\text{o-CH}_2\text{Ac}\cdot\text{C}_6\text{H}_{10}\cdot\text{CO}_2\text{H}$ , m.p.  $52-53^\circ$  (Ag salt; semicarbazone, m.p.  $158-160^\circ$ ); the corresponding crude Et ester is converted by  $\text{NaOEt}$  in  $\text{Et}_2\text{O}$  into (II). H. W.

**Preparation of diaryl  $\alpha$ -diketones.** H. H. HATT, A. PILGRIM, and W. J. HURRAN (J.C.S., 1936, 93-96).— $\text{COAr}\cdot\text{CH}_2\text{Ph}$  (1 mol.) are oxidised by  $\text{SeO}_2$  (1.5 mols.) in  $\text{Ac}_2\text{O}$  at  $140-150^\circ$  to  $\text{COAr}\cdot\text{COPh}$  (I) in almost quant. yields; the following are prepared: benzil; 4-phenyl-, m.p.  $104-105^\circ$ ; 4-chloro-, m.p.  $73^\circ$ , 4-bromo-, m.p.  $86.5^\circ$ , and 4-methyl- (II), m.p.  $31^\circ$ , -benzils; 2 : 4-, b.p.  $228^\circ/16$  mm., 2 : 5-, m.p.  $41^\circ$ , and 3 : 4-, m.p.  $63.5^\circ$ , -dimethylbenzils, oxidised ( $\text{H}_2\text{O}_2$ ,  $\text{N-NaOH}$ ,  $\text{C}_6\text{H}_5\text{N}$ ) to  $\text{BzOH}$  and 2 : 4-, 2 : 5-, and 3 : 4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$ , respectively; 2 : 4 : 6-trimethylbenzil, m.p.  $136-137^\circ$ . (I) and  $\text{CO}(\text{NH}_2)_2$  in  $\text{EtOH-KOH}$  give 5-phenyl-5-arylhydantoin and varying amounts of phenylarylacetylenediureide,

$\text{CO} < \begin{array}{c} \text{NH}\cdot\text{CPh}\cdot\text{NH} \\ \text{NH}\cdot\text{CAr}\cdot\text{NH} \end{array} > \text{CO}$ . The following are described: 5-phenyl-5-p-diphenyl-, m.p.  $242-242.5^\circ$ , -5-p-chlorophenyl-, m.p.  $243^\circ$ , -5-p-bromophenyl-, m.p.  $239^\circ$ , -5-o-4'-xylyl-, m.p.  $225^\circ$ , -5-m-4'-xylyl-, m.p.  $269^\circ$ , -5-p-xylyl-, m.p.  $226^\circ$ , and -5-p-tolyl-hydantoin; phenyl-p-diphenyl-, m.p.  $316-318^\circ$ , -p-chlorophenyl-, m.p.  $339^\circ$ , -o-4'-xylyl-, m.p.  $333^\circ$ , and d-p-tolyl-, m.p.  $335^\circ$ , -acetylenediureides. The compound (m.p.  $99-101^\circ$ ) described as (II) by Weiss (A., 1920, i, 555) is impure p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , m.p.  $110-111^\circ$ , now shown to be formed [together with (II)] by hydrolysis ( $\text{EtOH}$ ) of p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CPhBr}_2$  (*loc. cit.*). (II) undergoes the benzilic acid change (cf. *loc. cit.*) yielding phenyl-p-tolylglycolic acid, m.p.  $132^\circ$ . Hydrolysis ( $\text{MeOH-NaOMe}$ ) of p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CHPhBr}$ , m.p.  $87.5-88^\circ$  (from p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$  and Br in boiling  $\text{CHCl}_3$ ), gives r-p-toluoylphenylcarbinol, m.p.  $110-111^\circ$ ; this prep. is more convenient than those of McKenzie *et al.* (J.C.S., 1914, 105, 1583) and Weissberger *et al.* (A., 1930, 475). H. B.

**Constitution of campnospermonol.** T. G. H. JONES (Proc. Roy. Soc. Queensland, 1934, 45, 38-40).—Campnospermonol (I) is  $\text{C}_{25}\text{H}_{40}\text{O}_2$  and not  $\text{C}_2\text{H}_{42}\text{O}_2$  or  $\text{C}_{28}\text{H}_{44}\text{O}_2$  (Jones and Smith, A., 1928, 291); the structure  $\text{m-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{Me}$  is assigned to (I). Decomp. of oximinohydrocampnospermonyl Me ether (II) with  $\text{PCl}_5$  yields m- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$  (III) and stearic acid; similarly oximinocampnospermonyl Me ether (IV) yields (III) and oleic acid. Oxidation of (IV) yields suberic, azelaic, nonoic, and m-methoxybenzoic acids. The fatty acid previously isolated by oxidation of (II) is



shown to be a mixture of margaric and stearic acids.

CH. ABS. (r)

**Hydroxypolyketones. II. Dibenzoylcarbinol.** A. H. BLATT and W. L. HAWKINS (J. Amer. Chem. Soc., 1936, 58, 81—84).—Dibenzoylcarbinyl acetate (I), solutions of which in 95% EtOH at room temp. contain 5.1% enol (indirect Br titration), is hydrolysed (a) by aq.  $\text{Na}_2\text{CO}_3$  to AcOH, BzOH, and  $\text{CH}_2\text{Bz}\cdot\text{OH}$ , (b) by aq. 5% NaOH to AcOH and BzOH, (c) by aq.  $\text{NaHCO}_3$  in MeOH (EtOH) to AcOH,  $\text{CH}_2\text{Bz}\cdot\text{OH}$ , and MeOBz (EtOBz), (d) by short treatment with cold  $\text{H}_2\text{SO}_4$  to dibenzoylcarbinol (II), m.p. 111—112° (yield 25%) (Bigelow *et al.*, A., 1935, 346). Alkalis and (II) give the same products as (I). (II) is acetylated to (I), is oxidised [ $\text{Cu}(\text{OAc})_2$  in 60% AcOH] to benzil, and when distilled at 4 mm. rearranges to  $\text{CH}_2\text{Bz}\cdot\text{OBz}$ . (II) is not oxidised by I in neutral or acid solution, indicating the non-formation of  $\text{OH}\cdot\text{CPh}\cdot\text{CBz}\cdot\text{OH}$  under these conditions. (II) does not give colours with  $\text{NH}_2$ -acids.

H. B.

**Chalkones and chalkone oxides. I. Phenyl 3:4-methylenedioxy-styryl ketone.** R. P. DODWADMATH and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 438—451).—A comparative study of the reactivities of Ph 3:4-methylenedioxy-styryl ketone (I) and of Ph 6-nitro-3:4-methylenedioxy-styryl ketone (II). With Br (1 mol.) (I) yields Ph  $\alpha\beta$ -dibromo- $\beta$ -3:4-methylenedioxyphenylethyl ketone (A., 1922, i, 1035), which with EtOH and MeOH gives respectively Ph  $\alpha$ -bromo- $\beta$ -ethoxy-, m.p. 143—144°, and  $\beta$ -methoxy-, m.p. 115—116°,  $\beta$ -3:4-methylenedioxyphenylethyl ketone. With Br (2 mols.) (I) gives Ph  $\alpha\beta$ -dibromo- $\beta$ -6-bromo-3:4-methylenedioxyphenylethyl ketone, m.p. 174—175°, which yields  $\alpha$ -bromo- $\beta$ -ethoxy-, m.p. 126—127°, and  $\alpha$ -bromo- $\beta$ -methoxy-, m.p. 131—132°, compounds as above, and which with KI in  $\text{COMe}_2$  forms Ph 6-bromo-3:4-methylenedioxy-styryl ketone, m.p. 146—147°, which is synthesised from 6-bromopiperonal and COPhMe. Treatment of (I) in AcOH with  $\text{Cl}_2$  gives first a product converted by recrystallisation from EtOH into Ph  $\alpha$ -chloro- $\beta$ -ethoxy- $\beta$ -3:4-methylenedioxyphenylethyl ketone, m.p. 118—119°; on longer treatment, Ph  $\alpha\beta$ -dichloro- $\beta$ -6-chloro-3:4-methylenedioxyphenylethyl ketone, m.p. 127—128°, is formed. With KCN-EtOH, (III) forms  $\beta$ -benzoyl- $\alpha$ -3:4-methylenedioxyphenylpropionitrile, m.p. 132—133°, hydrolysed to the acid, m.p. 143—144°. The structure of (III) and of these derivatives is confirmed by the similar formation of  $\beta$ -benzoyl- $\alpha$ -phenylpropionitrile from Ph  $\alpha\beta$ -dibromo- $\beta$ -phenylethyl ketone. With Br (1 mol.), (II) yields Ph  $\alpha\beta$ -dibromo- $\beta$ -6-nitro-3:4-methylenedioxyphenylethyl ketone, m.p. 174—175°; this does not react with EtOH or further with Br; with KI it regenerates (II). With  $\text{Cl}_2$ , (II) gives the corresponding  $\alpha\beta$ -dichloro-compound, m.p. 151—152°. (I) with NaOEt and  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  in EtOH yields Et 4-phenyl-2-(3':4'-methylenedioxyphenyl)- $\Delta^6$ -cyclohexen-6-one-1-carboxylate, m.p. 151—152°; (II) does not react. (I) is catalytically reduced (Pd) to  $\alpha$ -phenyl- $\gamma$ -3:4-methylenedioxyphenylpropyl alcohol, m.p. 95—96°, without formation of the saturated ketone; (II) is not reduced. With  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , (I) forms 3-phenyl-5-(3':4'-methylenedioxyphenyl)pyrazoline (?), decomp. on drying

(hydrochloride, m.p. 197—198°; picrate, m.p. 185—186°; Ac derivative, m.p. 153—154°); this substance does not give Knorr's pyrazoline reaction, but its formation of a hydrochloride, and failure to give  $\text{NH}_3$  when reduced by Na-Hg, are against its being a hydrazone. With  $\text{NHPh}\cdot\text{NH}_2$ , (I) forms 1:3-diphenyl-5-(3':4'-methylenedioxyphenyl)pyrazoline, m.p. 129—130° (pyrazoline reaction; NO-derivative).

Action of  $\text{H}_2\text{O}_2$  (6%) on (I) in MeOH and  $\text{COMe}_2$  yields Ph 3:4-methylenedioxyphenylstyryl ketone oxide (IV), m.p. 99—100°; with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  this forms a hydrazone, m.p. 173—174° (regarded as such and not as a pyrazoline, since it does not form a NO-derivative), which with NaOEt or  $\text{Ac}_2\text{O}$  condenses to 3-phenyl-5-(3':4'-methylenedioxyphenyl)pyrazole, m.p. 194—195°. With MeOH or EtOH and  $\text{H}_2\text{SO}_4$ , the O-ring opens, and Ph  $\alpha$ -hydroxy- $\beta$ -methoxy- (V), m.p. 117—118°, and Ph  $\alpha$ -hydroxy- $\beta$ -ethoxy- $\beta$ -3:4-methylenedioxyphenylethyl ketone, m.p. 93—94°, respectively, are obtained. When (V) is heated with NaOAc-AcOH or with aq. NaOH, or (IV) boiled (30 sec.) with aq. NaOH-EtOH, Ph 3:4-methylenedioxybenzyl diketone, m.p. 114—115°, is formed, which with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  yields 2-phenyl-3-(3':4'-methylenedioxybenzyl)quinoxaline, m.p. 137—138°. If (IV) is boiled with aq. NaOH-EtOH for 4 hr.,  $\alpha$ -phenyl- $\beta$ -3:4-methylenedioxyphenyl- $\alpha$ -lactic acid, m.p. 149—150°, is produced, oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ ) to Ph 3:4-methylenedioxybenzyl ketone (A., 1930, 1041). (II) is oxidised by  $\text{H}_2\text{O}_2$  (6%) in  $\text{COMe}_2$  to Ph 6-nitro-3:4-methylenedioxy-styryl ketone oxide (VI), m.p. 159—160°, but this is not readily isolated, and is better prepared by adding NaOEt to  $\text{CH}_2\text{Br}\cdot\text{COPh}$  and 6-nitropiperonal in EtOH at 0°. (VI) does not react with EtOH or MeOH, or with NaOH, but with HCl in AcOH gives Ph  $\beta$ -chloro- $\alpha$ -hydroxy- $\beta$ -6-nitro-3:4-methylenedioxyphenylethyl ketone, m.p. 183—184°. Action of  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  on (II) in AcOH gives Ph 6-nitro-3:4-methylenedioxy-styryl ketone-N-acetylhydrazone, m.p. 244—245°; with  $\text{NHPh}\cdot\text{NH}_2$ , the  $\beta$ -phenylhydrazone, m.p. 159—160°, is formed, which is condensed (AcOH) to 1:3-diphenyl-5-(6'-nitro-3'-4'-methylenedioxyphenyl)pyrazoline, m.p. 203—204°, from which  $\text{AgNO}_3$  forms the corresponding  $\beta$ -pyrazole, m.p. 163—164°, also obtained from (VI) and  $\text{NHPh}\cdot\text{NH}_2$ . Results show that the 6- $\text{NO}_2$  removes the enhanced reactivity which  $\text{CH}_2\text{O}_2$  confers on one of the Br of the chalkone dibromide, and reduces the reactivity of the oxide towards EtOH or MeOH, but not towards HCl.

E. W. W.

**Synthesis of 2:6-dihydroxy-4-methoxyphenyl  $\beta$ -phenylethyl ketone** obtained from the oil of *Ponulus balsamifera*, L. A. GORIS and H. CANAL (Compt. rend., 1935, 201, 1520—1521).—2:4:6-Trihydroxyphenyl  $\beta$ -phenylethyl ketone (cf. A., 1926, 1135) with  $\text{Me}_2\text{SO}_4$  affords 2:6-dihydroxy-4-methoxyphenyl  $\beta$ -phenylethyl ketone, m.p. 168°, identical with the natural product.

J. L. D.

**Organic salts of a diaminobenzoquinonedisulphonic acid.** (MILLE.) Y. GARREAU (Compt. rend., 1935, 201, 1515—1517; cf. A., 1935, 338).—Diaminobenzoquinonedisulphonates of the following bases are prepared from the  $\text{NH}_4$  salt and the base

in dil. HCl: glycine (+2H<sub>2</sub>O, decomp. about 240°), creatine [+2H<sub>2</sub>O, 245—248° (decomp.)], adenine (+4H<sub>2</sub>O, which at 105—110° is converted into +1H<sub>2</sub>O), aliphatic NH<sub>2</sub>-acids, uric acid and guanidine bases, and many alkaloids. J. L. D.

**Anthragallol esters.** M. TANAKA (J. Chem. Soc. Japan, 1935, 55, 196—197).—The methylation of anthragallol with Me<sub>2</sub>SO<sub>4</sub>-NaOH, and the 1:2:3-Me<sub>3</sub>, m.p. 173°; 2:3-Me<sub>2</sub>, m.p. 166°, and 3-Me, m.p. 143°, ethers, are described. CH. ABS. (r)

**Mechanism of the conversion of 2-aminoanthraquinone into indanthrone.** M. TANAKA (J. Chem. Soc. Japan, 1935, 56, 192—195).—Fusion of NH<sub>2</sub>Ph with alkali, in the presence of an oxidising agent or PhNO<sub>2</sub>, does not give phenazine or the *N*-oxide. Under similar conditions, 2-aminoanthraquinone (I) gives 2-amino-1-hydroxyanthraquinone (II) and dihydro-2'-amino-1:3'-dianthraquinonylamme (III). Alkali fusion of (II) gives, not indanthrone (IV), but a dihydrophenazinecarboxylic acid; (III), treated similarly, affords (IV). A mechanism is advanced for the formation of (IV) from (I), by way of (III). CH. ABS. (r)

**Manufacture of derivatives of chrysenequinones.**—See B., 1936, 139.

**Vat dyes of the benzanthrone series.** XV. **Synthesis of 5-methoxybenzanthrone and 5:5'-dimethoxyviolanthrone.** T. MAKI. XVI. **Constitution of dichlorinated violanthrone and preparation of some new Bz-3:3'-violanthrone derivatives.** T. MAKI and T. AOYAMA (J. Soc. Chem. Ind. Japan, 1935, 38, 630—636B, 636—642B; cf. this vol., 206).—XV. 1-Chloro-9-anthrone, m.p. 114° (corr.) (cf. B., 1923, 1216A) (obtained from 1-chloroanthraquinone and H<sub>2</sub>SO<sub>4</sub>-Al), when heated at 120° during 6 hr. with H<sub>2</sub>SO<sub>4</sub> and glycerol and the product boiled with 1% NaOH solution yields *o*-chlorobenzanthrone (I), m.p. 181.5°, and a compound, m.p. 121°, probably 4-chlorobenzanthrone. (I) is probably identical with  $\alpha$ -chlorobenzanthrone (B.P. 278.496; B., 1928, 9), and is oxidised by CrO<sub>3</sub>-H<sub>2</sub>O-AcOH to 5-chloroanthraquinone-1-carboxylic acid. (I) with KOH-MeOH at 150° for 7 hr. affords 5-methoxybenzanthrone (II), m.p. 191° (corr.). The OMe is very resistant to HI. (II) when heated at 210° with KOH-PhOH affords mainly 5:5'-dimethoxyviolanthrone (III), sol. in NaOH-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-EtOH-H<sub>2</sub>O, and about 35% of a compound (IV), sol. with difficulty in alcoholic alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and considered to be similar to the *B* dyes described previously (cf. B., 1934, 752). (III) dyes cotton blue, fast to acids and alkalis. (IV) dyes cotton grey-blue. (I) when heated at 220° with KOH, or, better, KOH-PhOH, affords 5:5'-dihydroxyviolanthrone, almost insol. in the ordinary org. solvents and in alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>; addition of H<sub>2</sub>O to its solution in H<sub>2</sub>SO<sub>4</sub> gives a greenish-black ppt.

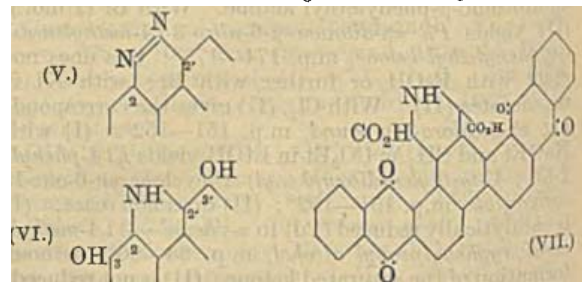
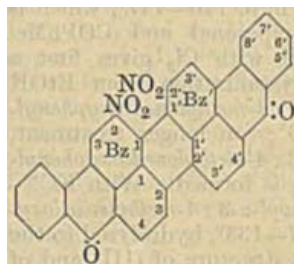
XVI. Careful chlorination of violanthrone in AcOH affords Bz-3:3'-dichloroviolanthrone (V) (cf. A., 1934, 754) and a little of a dark green vat dye, separated by means of PhNO<sub>2</sub>. (V) at 150° with KOH-MeOH affords Bz-3:3'-dimethoxyviolanthrone (cf. Jap. P. 109,582), which fairly readily forms a blue hyposulphite vat and dyes cotton fast indigo-blue.

The OMe groups are very resistant to HI. (V) when treated with H<sub>2</sub>SO<sub>4</sub>-MnO<sub>2</sub>-H<sub>3</sub>BO<sub>3</sub> at 60° during 1 hr. affords Bz-3:3'-dichloro-Bz-2:2'-dihydroxyviolanthrone, a violet-black cryst. powder, which dyes cotton from a blue Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> vat a dull green, similar to that obtained with Bz-2:2'-dihydroxyviolanthrone. (V) with NH<sub>3</sub>, H<sub>2</sub>O, and Cu at 200° for 7 hr. yields Bz-3:3'-diaminoviolanthrone, which dyes cotton from a blue Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> vat a dark violet-blue, almost unaffected by NaOCl. Similarly (V) when refluxed during 9 hr. with *p*-toluidine, anhyd. NaOAc, and Cu affords Bz-3:3'-di-*p*-toluidinoviolanthrone, a violet-black cryst. powder, which dyes cotton dark violet-blue from a blue vat. Reasons are given for the constitution assigned to (V).

H. G. M.

**Vat dyes of the benzanthrone series.** XVII. **Preparation and purification of dinitroviolanthrone.** XVIII. **Constitution of dinitroviolanthrone.** T. MAKI, Y. NAGAI, and Y. HAYASHI (J. Soc. Chem. Ind. Japan, 1935, 38, 710—715B, 715—720B).—XVII. The % of N in the product when violanthrone (I) is nitrated with HNO<sub>3</sub> (*d* 1.48)-AcOH increases with increase in the proportion of HNO<sub>3</sub>. Optimum conditions for the formation of the almost pure (NO<sub>2</sub>)<sub>2</sub>-derivative (II) are the nitration of 3 parts of (I) in 50 parts of AcOH with 30 parts of HNO<sub>3</sub> in 30 parts of AcOH at 60° for 12 hr. The small amount of by-product formed is removed either by crystallisation of (II) from C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, or by extraction with 80% H<sub>2</sub>SO<sub>4</sub> in which it is sol. When only 10 parts of HNO<sub>3</sub> at room temp. are used, a mixture of NO<sub>2</sub>- and (NO<sub>2</sub>)<sub>2</sub>-derivatives is formed. Nitration of (I) with HNO<sub>3</sub> (*d* 1.48)-H<sub>2</sub>SO<sub>4</sub> at 0—5° does not give (II), but a substance (III), probably a dinitrodihydroxyviolanthrone. The tinctorial properties of these derivatives are described.

XVIII. The following reactions prove that (II) is Bz-2-Bz-2'-dinitroviolanthrone (annexed formula). Reduction with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-NaOH affords the (NH<sub>2</sub>)<sub>2</sub>-derivative (IV), the green colour of which, on wool, is oxidised by 0.5% NaOCl to a black (V), which is reconverted into (IV) by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>-NaOH. Oxidation of (IV) with CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> affords first a substance, probably (VI), insol. NH<sub>3</sub>, and finally a substance,



NH<sub>3</sub>-sol., to which the structure (VII) is assigned. Oxidation of (II) with MnO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> gives



its Bz-3-Bz-3'-(OH)<sub>2</sub>-derivative, which is not identical with the Bz-3-Bz-3'-dinitro-Bz-2-Bz-2'-dihydroxy-derivative obtained by nitration of the Bz-2-Bz-2'-(OH)<sub>2</sub>-compound (preceding abstract) with HNO<sub>3</sub> (d 1.48)-AcOH at 60°, but appears to be identical with (III). J. W. B.

**Carbamide derivatives in terpene series.** R. L. BATEMAN and A. R. DAY (J. Amer. Chem. Soc., 1935, 57, 2496—2498).—*l*-Menthylcarbamide, m.p. 140.2—140.6° (lit. 134—136°) [Ac, m.p. 118—119°, CH<sub>2</sub>Br·CO·, m.p. 111.8—112.3°, cinnamoyl, m.p. 144.3—145.1°, *p*-nitro-, m.p. 158.7—159.2°, and *p*-amino-benzoyl, m.p. 208—210° (decomp.), derivatives; additive compound, C<sub>10</sub>H<sub>19</sub>·NH·CO·NH·CH(OH)·CCl<sub>3</sub>, m.p. 146.2—147.2°, with chloral], *d*-bornylcarbamide, m.p. 165.7—166.3° [Ac, m.p. 129—129.5°, CH<sub>2</sub>Br·CO·, m.p. 136.1—136.5°, cinnamoyl, m.p. 220.2—220.8°, *p*-nitrobenzoyl, m.p. 230° (decomp.), and *p*-amino-benzoyl, m.p. 233° (decomp.), derivatives; additive compound, m.p. 180° (decomp.), with chloral], and 3-carbamido-2-ketocamphane (+0.5H<sub>2</sub>O), m.p. 177.8—178.4° (lit. 169°) (*p*-nitrobenzoyl derivative), are prepared from the appropriate RNH<sub>2</sub>·HCl and NO<sub>2</sub>·NH·CO·NH<sub>2</sub> in aq. NaHCO<sub>3</sub>. All m.p. are corr. Some of the above compounds possess narcotic activity. H. B.

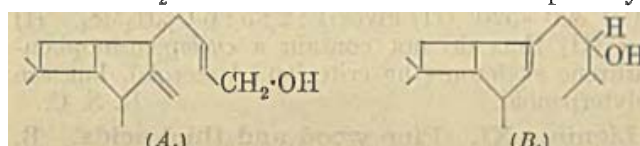
**Anomalous mutarotation of salts of Reychler's acid.** IV. Comparison of 2-anilo-*d*-camphane-10-sulphonic acid with *d*-camphor-10-sulphonanilide. H. SUTHERLAND and R. L. SHRINER (J. Amer. Chem. Soc., 1936, 58, 62—63; cf. A., 1935, 1503).—The differences in properties of *d*-camphor-10-sulphonanilide, m.p. 120.5—121°, [α]<sub>D</sub><sup>25</sup> +76° in CHCl<sub>3</sub> (no mutarotation in 95% EtOH) [hydrolysed (25% HCl) with difficulty], and the dehydration product (I), [α]<sub>D</sub><sup>25</sup> −170.5° in CHCl<sub>3</sub>, of NH<sub>2</sub>Ph *d*-camphor-10-sulphonate support the view (A., 1935, 1118) that (I) is 2-anilo-*d*-camphane-10-sulphonic acid. H. B.

**Structure of methylsantene obtained by the catalytic dehydration of fenchyl alcohol by weak acids.** N. J. TOIVONEN, T. VEIJOLA, and S. FRIBERG (Suomen Kem., 1935, 8, B, 44—46).—Mild dehydration of fenchyl alcohol (cf. A., 1930, 348) gives, by intramolecular change, 1-methylsantene (A., 1935, 865), which with O<sub>3</sub> gives 1:3-diaceto-1-methylcyclopentane, b.p. 0.6/109°/6 mm. [semicarbazone, m.p. 230—232° (decomp.)]; this with NaOBr, followed by Zn-AcOH, gives 1-methylcyclopentane-1:3-dicarboxylic acid, m.p. 97° (anhydride, m.p. 81°). J. L. D.

**Determination of the constitution of sesquiterpenes by powerful oxidative degradation.**

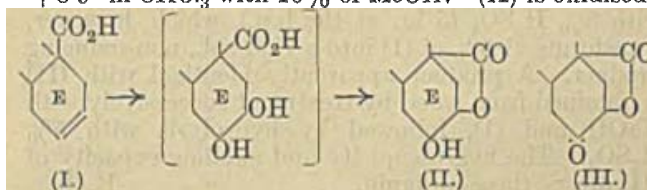
**Betulol.** W. TREIBS (Ber., 1936, 69, [B], 1—46).—The unesterified betulol of birch-bud oil (isolated through the non-cryst. H phthalate) has in agreement with Soden *et al.* (A., 1905, i, 174), whereas that obtained by hydrolysis of the betulyl acetate has α<sub>D</sub> −19.5°. Betulol (I) is therefore a mixture of at least two bicyclic, closely related alcohols. The alcoholic group is not exclusively primary, since the oxidation product of tetrahydro-*β*-betulol (Semmler *et al.*, A., 1918, i, 301) is only partly aldehydic. Since both components of the oil behave qualitatively, the following work was per-

formed with the mixture. Treatment of the latter with powdered KMnO<sub>4</sub> in COMe<sub>2</sub> affords small amounts of neutral products, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.5 mol.), a little AcOH, and an acid mixture (II) oxidised by hot dil. HNO<sub>3</sub> to *betulolic acid* (III) [Me<sub>2</sub> ester, (IV), b.p. 132—136°/18 mm., [α]<sub>D</sub> +48°]. The physical properties of (IV) indicate the presence of a 4-C ring, which is confirmed by the stability of (III) towards oxidants. Protracted action of boiling dil. HNO<sub>3</sub> partly converts (III) into H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and CO<sub>2</sub>H·CH<sub>2</sub>·CMe<sub>2</sub>·CO<sub>2</sub>H without affecting the properties of the unattacked acid, so that (III) is probably a homocaryophyllenic acid belonging to the *trans*-series, since it is not dehydrated by Ac<sub>2</sub>O or AcCl. Since (II) is transformed by MeOH-H<sub>2</sub>SO<sub>4</sub> and subsequent vac. distillation into the Me<sub>2</sub> ester, b.p. 200—202°/20 mm., α<sub>D</sub> +32°, of a saturated OH-dicarboxylic acid, C<sub>13</sub>H<sub>20</sub>O<sub>5</sub> (V), and by protracted esterification into the ester of unsaturated acids, and since (V) is oxidised by hot dil. HNO<sub>3</sub> to (III), it follows that the side-chain must have the termination ·CH:CH·CH<sub>2</sub>·OH. The structures *A* and *B* for primary



and *sec.* (I) are most probable. The portion of the oil which does not react with *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O yields *betulene*, C<sub>15</sub>H<sub>22</sub>, b.p. 130—132°/20 mm., α<sub>D</sub> −78°, a bicyclic sesquiterpene with three double linkings. Treatment of a similar portion with H<sub>3</sub>BO<sub>3</sub> yields the unstable, strongly unsaturated compound, C<sub>15</sub>H<sub>22</sub>O, b.p. 140°/20 mm., α<sub>D</sub> −9.2°. The paraffin of the oil is C<sub>20</sub>H<sub>42</sub>, m.p. 49°. H. W.

**Polyterpenes and polyterpenoids. XCIX.** Primary products of the oxidation at the double linking of sumaresinolic acid and oleanolic acid. L. RUZICKA, H. HOSLI, and K. HOFMANN (Helv. Chim. Acta, 1936, 19, 109—114).—Treatment of sumaresinolic acid (I) with O<sub>3</sub> in 80% AcOH at 80° or with H<sub>2</sub>O<sub>2</sub> in AcOH at room temp. affords the corresponding OH-lactone (II), m.p. 322—324° (decomp.), [α]<sub>D</sub> +8.9° in CHCl<sub>3</sub> with 10% of MeOH. (II) is oxidised



by CrO<sub>3</sub> in AcOH at 50° to *sumaresinonoketolactone* (III), m.p. 311—312°, [α]<sub>D</sub> −24.2° in CHCl<sub>3</sub>, also obtained from (I) and CrO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>-AcOH. Acetyl-oleanolic acid is oxidised by H<sub>2</sub>O<sub>2</sub> in AcOH at 80° to the corresponding OH-lactone (IV), m.p. 292—294°, further transformed into the ketolactone (V), m.p. 279—280° (oxime, m.p. 220—221°) (Kitasato, A., 1932, 1035). (IV) differs from the corresponding compound of Aumüller *et al.* (A., 1935, 865) only in the steric configuration of the OH group, since each yields (V) when oxidised. Hydrolysis of (V) with KOH-MeOH affords *hydroxyketodihydro-oleanolic acid*, m.p. 306—307°. H. W.

**Differentiation of sterols from other polyterpene alcohols. Structure of lanosterol and onocerol.** H. SCHULZE (Z. physiol. Chem., 1936, 238, 35—53).—"isoCholesterol" (I) (modified prep.), m.p. 136—137°,  $[\alpha]_D^{25} + 61.9^\circ$  in  $\text{CHCl}_3$ , or its acetate with Se at 320—335° gives 1:2:8-trimethylphenanthrene, a hydrocarbon, m.p. 212—213°, and an alkali-sol. substance, (?) a hydroxytrimethylphenanthrene (Me ether, m.p. 179—180°, b.p. 215—230°/14 mm.), but (I) is largely unchanged by Pt at 300°. Onocerol (II) (modified prep.),  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , dimorphic, m.p. 232° and 202°,  $[\alpha]_D^{25} + 5.04^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  [diacetate (III), m.p. 224°,  $[\alpha]_D^{25} + 28.3^\circ$ ; dibenzoate, m.p. 237—238°,  $[\alpha]_D^{25} + 21.5^\circ$ ; dichloroacetate, m.p. 238—244°,  $[\alpha]_D^{25} + 11.4^\circ$ ; di-3:5-dinitrobenzoate, m.p. 291° (decomp.),  $[\alpha]_D^{25} + 19.3^\circ$ ; dianisate, m.p. 232—234°,  $[\alpha]_D^{25} + 9^\circ$ ; all  $[\alpha]$  are in  $\text{CHCl}_3$ ], gives no  $\text{PhCHO}$  on ozonisation (cf. lit.) and does not resemble  $\text{CH}_2\text{:CHPh}$  or neoergosterol in absorption spectrum, reacts with 2 mols. of  $\text{BzO}_2\text{H}$ , and is difficultly reducible. (III), however, readily absorbs 2H (PtO<sub>2</sub> in AcOH). With Se at 300—320° (II) gives 1:2:5:6- $\text{C}_{10}\text{H}_4\text{Me}_4$ . (I) and (II) thus do not contain a cyclopentanophenanthrene skeleton (the criterion of sterols), but are polyterpenoid. R. S. C.

**Lignin. XI. Pine wood and thiol acids.** B. HOLMBERG (Ber., 1936, 69, [B], 115—119; cf. A., 1935, 1502).—The treatment of pine wood with thiolacetic,  $\alpha$ -thiolpropionic,  $\alpha$ -thiolisobutyric, thiolsuccinic, and  $\alpha$ -thiol- $\alpha$ -methylsuccinic acid is described, but it is difficult to find a theoretical basis for the interpretation of the results. The change appears to proceed in two stages, during the first of which the lignin reacts with the SH-acid giving acids containing S which in the subsequent stage become sol. in  $\text{H}_2\text{O}$  or alkali. H. W.

**Action of ethylene oxide on wood and lignin.** II. N. I. NIKITIN and T. I. RUDNEVA (J. Appl. Chem. Russ., 1935, 8, 1176—1183).—Willstätter lignin treated with 18% NaOH and  $(\text{CH}_2)_2\text{O}$  (I) (2 hr. at 70°, or 2 days at room temp.) yields amorphous hydroxyethyl-lignin (II), containing 38.76% of  $\text{OEt} + \text{OMe}$ , and 5.18% of acetylable OH. (I) is eliminated from (II) by HI at 135—140°, but not by hydrolysis with 5%  $\text{H}_2\text{SO}_4$  (5 hr. at the b.p.), which, however, transforms 21.6% of (I) into a  $\text{H}_2\text{O}$ -sol., non-reducing product. A product apparently identical with (II) is obtained from wood by treatment successively with NaOH and (I), followed by hydrolysis with 5%  $\text{H}_2\text{SO}_4$ . The hygroscopicity and swelling capacity of (II) are > those of lignin. R. T.

**Elemic acid from elemi resin. VIII.  $\beta$ -Elemionic acid.** M. M. MLADENOVIC and I. BERKEŠ (Monatsh., 1935, 67, 36—41; cf. A., 1935, 495).— $\beta$ -Elemionic acid (I), m.p. 220.5° [modified prep. from  $\alpha$ -elemionic acid (II); oxime, m.p. 218°, hydrolysed to (I) by  $\text{HNO}_2$ ], gives (Pd-C in AcOH) a  $\text{H}_4$ -acid (III), m.p. 244° [oxime, m.p. 245°, hydrolysed to (III); also obtained by hydrogenation of crude (II)], and is identical with  $\delta$ -elemic acid (A., 1932, 749). R. S. C.

**Toad poisons. VIII. Dehydrogenation of cinobufagin.** H. JENSEN (J. Amer. Chem. Soc., 1935, 57, 2733—2734).—Dehydrogenation (Se at

310—340°) of cinobufagin (I),  $\text{C}_{25}\text{H}_{26}\text{H}_{32}\text{O}_6$  (cf. A., 1934, 412), gives a little of (probably) methylcyclopentenophenanthrene. (I) and (probably) other bufagins appear to contain the same ring system as the sterols and cardiac aglucones. H. B.

**Carotenoids of purple bacteria. II. Rhodoviolascene.** P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 3—5; cf. this vol., 248).—Rhodoviolascene is  $\text{C}_{42}\text{H}_{60}\text{O}_2$ . It contains 2 OMe and absorbs 26 H when catalytically hydrogenated. It affords  $\text{COME}_2$  when treated with  $\text{O}_3$ , and hence is probably a  $(\text{OMe})_2$ -derivative of lycopene (I) or similar hydrocarbon. It appears to be optically inactive in  $\text{C}_6\text{H}_6$ . It does not react with  $\text{NH}_2\text{OH}$  or give a  $\text{H}_2$ -derivative by short treatment with  $\text{Zn-AcOH-C}_5\text{H}_5\text{N}$ . The bacteria contain also rhodovibrene, but rhodopurpurin is possibly identical with (I). H. W.

**Preparation and reactions of tertiary tetrahydrofurylcarbinols.** A. L. DOUNCE, R. H. WARDLOW, and R. CONNOR (J. Amer. Chem. Soc., 1935, 57, 2556—2559).—Reduction ( $\text{H}_2$  at 100—130 atm., Raney Ni, 150°) of Et furoate (I) gives 93.3% of Et tetrahydrofuroate (II), b.p. 188—190°/740 mm., which with  $\text{MgPhBr}$  affords diphenyl-2-tetrahydrofurylcarbinol (III), m.p. 79—80°, dehydrated (anhvd.  $\text{MgSO}_4$ ) to 2-benzhydrylidene tetrahydrofuran (IV), b.p. 195°/10 mm., m.p. 107.5—108.5° [ozonolysis products,  $\text{COPh}_2$  and  $\gamma$ -butyrolactone (V)]. Prolonged treatment of (III) with  $\text{MgPhBr}$  (3 equivs.) in xylene does not cause ring fission; hydrolysis and removal of the xylene gives (IV). 2-Tetrahydrofuryl-diethyl-, b.p. 200—203°/740 mm., and -di-n-butyl- (VI), b.p. 151—152°/24 mm., 251—252°/740 mm., -carbinols, best prepared from (II) and  $\text{MgRBr}$ , are also obtained by reduction of 2-furyl-diethyl-, b.p. 92—95°/14 mm., and -di-n-butyl-, b.p. 128—131°/14 mm., -carbinol, respectively [from (I) and  $\text{MgRBr}$ ]. Dehydration ( $\text{MgSO}_4$ -KOH) of (VI) gives an inseparable mixture. (V) is obtained in 10% yield by reduction ( $\text{H}_2$  at 90—130 atm., Cu-Cr-BaO catalyst, 250°) of Et succinate. (V) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  give a little succinhydrazide and (mainly)  $\gamma$ -hydroxybutyrylhydrazide, m.p. 89—90°. H. B.

**Dicarboxylic acid esters of tetrahydrofurfuryl alcohol.** J. N. BORGLIN (Ind. Eng. Chem., 1936, 28, 35—36).—Tetrahydrofurfuryl alcohol reacts (48 hr.; 170—190°) with the calc. amount of terpinene, maleic, maleic, or phthalic anhydride to form the corresponding acid ester or di-ester. F. N. W.

**Production of furfuraldehyde from xylose solutions by means of hydrochloric acid-sodium chloride systems.** E. I. FULMER, L. M. CHRISTENSEN, R. M. HIXON, and R. L. FOSTER (J. Physical Chem., 1936, 40, 133—141).—Xylose-HCl-NaCl mixtures were refluxed with  $\text{PhMe}$  and the furfuraldehyde (I) yields determined from the  $d$  of the resulting (I)- $\text{PhMe}$  solutions. The yield of (I) diminishes as the concn. of xylose increases, being twice as great for 4% as for 60% xylose. It increases with increasing concn. of NaCl, i.e., it is a linear function of the  $p_{\text{H}}$  or of the activity coeff. of the acid. M. S. B.



**Terpene furoates.** J. N. BORGLIN (Ind. Eng. Chem., 1936, 28, 31—32).—Borneol and fenchyl alcohol heated (40 hr.; 160°) with furoic acid give, respectively, *bornyl*, b.p. 275°/760 mm., and *fenchyl furoate*, b.p. 275°/760 mm., hydrogenated (PtO<sub>2</sub>) to fenchyl tetrahydrofuroate. F. N. W.

**Orientation in the dibenzfuran series.** W. G. BYWATER, E. W. SMITH, G. E. BROWN, and H. GILMAN (Proc. Iowa Acad. Sci., 1934, 41, 166).—Sulphonation and chlorination take place at position 2, nitration at position 3, whilst metals attack in position 4. Rules governing the position of entry of a second substituent are given. Sulphonation of *dibenzfuran-2-sulphonic acid* yields the *-2:8-disulphonic acid*; nitration of 2-bromo- and bromination of 3-nitro-dibenzfuran give the same *7-bromo-3-nitro-dibenzfuran*. Bromination of *3-acetamidodibenzfuran* yields *2-bromo-3-aminodibenzfuran*. CH. ABS. (r)

**Constituents of *Matteucia orientalis*.** II. Constitution of *demethoxymatteucinol*. S. FUJISE and T. NISHI (J. Chem. Soc. Japan, 1934, 55, 1020—1023, 1024—1027; cf. A., 1935, 91).—II. Condensation of dimethylphloroglucinol with cinnamoyl chloride affords *5:7-dihydroxy-6:8-dimethylflavanone*, m.p. 202.7—203°; although the m.p. is lowered about 1° on admixture with *demethoxymatteucinol*, the identity of all other properties leads to the conclusion that they are identical. CH. ABS. (r)

**General method for synthesis of flavonol derivatives.** T. OYAMADA (J. Chem. Soc. Japan, 1934, 55, 1256—1261).—Flavonols are formed when *o*-hydroxychalcones are treated with H<sub>2</sub>O, in the presence of dil. alkali. Several examples are given. *Methoxyflavone* has m.p. 114°. CH. ABS. (r)

**Preparation of homogeneous anthocyanins by chromatographic analysis.** P. KARRER and F. M. STRONG (Helv. Chim. Acta, 1936, 19, 25—28).—Al<sub>2</sub>O<sub>3</sub>, activated by cautious treatment with tap-H<sub>2</sub>O, is a suitable adsorbent for anthocyanins. Since the slightly basic material partly converts the oxonium salt into colour base, carbinol base, and phenolbetaine, a given pigment does not necessarily produce a homogeneous zone. *Paonin*, obtained according to Willstätter *et al.* (A., 1915, i, 288), is found to contain cyanin; the colour of a solution of the pure material and FeCl<sub>3</sub> in EtOH is unchanged by addition of H<sub>2</sub>O. H. W.

**Pigments of cotton flowers.** II.—See this vol., 395.

**Bark of *Terminalia arjuna*.** I. *Arjunin*.—See this vol., 395.

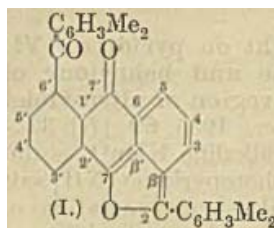
**Catalytic chlorination of dioxan.** J. J. KUCERA and D. C. CARPENTER (J. Amer. Chem. Soc., 1935, 57, 2346—2347).—Dioxan and Cl<sub>2</sub> in presence of a little SnCl<sub>4</sub> or I at 90° give 96.6% of the 2:3-Cl<sub>2</sub>-derivative, chlorinated further (in absence or presence of catalyst) at 145° to 83—85% of a mixture of *s*-(32%) and *as*-Cl<sub>2</sub>-derivatives. H. B.

**Dioxan series.** II. Aryl-substituted dioxans. **Synthesis of *p*-dioxen.** R. K. SUMMERBELL and L. N. BAUER (J. Amer. Chem. Soc., 1935, 57, 2364—2368; cf. A., 1934, 80).—2:3-Diphenyl-, m.p.

49—50°, 2:3-di-*o*-, m.p. 105.7—106.2° (corr.), -*m*-, m.p. 84.2° (corr.), and -*p*-, m.p. 56—57.2° (corr.), -*tolyl*-, 2:3-di-*p*-chlorophenyl-, m.p. 152—153° (corr.), 2:3-di-*p*-anisyl-, m.p. 79—80.2° (corr.), 2:3-di-*α*-naphthyl-, b.p. 255—258°/3—4 mm., 2:3-di-*xylenyl*-, m.p. 144.5—146° (corr.), and 2:3-di-*benzyl*-, m.p. 62.2° (corr.), -*dioxans* are prepared from 2:3-dichlorodioxan (I) and MgRX. The main product from (I) and MgMcBr, MgEtBr, or MgBuBr is *p*-*dioxen* (II),  $\text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} = \text{CH} \end{array} \text{O}$ , b.p. 94.2°/749.9 mm. [ozonolysis products, HCO<sub>2</sub>H and C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>]; small amounts of the 2:3-dialkyldioxans (Et<sub>2</sub>, b.p. 164—175°/747.9 mm.; Bu<sub>2</sub>, b.p. 120—122°/16—17 mm.; not characterized) are also produced. (II) and Hal in CCl<sub>4</sub> at 0° give (I) and 2:3-di-*bromodioxan*, m.p. 69—70° (softens at 64°). (I) and HCl at 0° afford *chlorodioxan* (III), b.p. 62—63°/14 mm., which is unstable even at room temp.; in presence of a little BiCl<sub>3</sub>, a polymeride of (II) results. (III) and MgPhBr give *phenyldioxan*, m.p. 45—46°. Chlorination of dioxan (IV) to (I) is considered to occur thus: (IV) → (III) → (II) → (I). H. B.

**Dimorphism of rotenone.** E. L. GOODEN and C. M. SMITH (J. Amer. Chem. Soc., 1935, 57, 2616—2618).—Rotenone exists in two enantiotropic forms, m.p. 163° (stable) and approx. 180° (unstable); optical data are given. H. B.

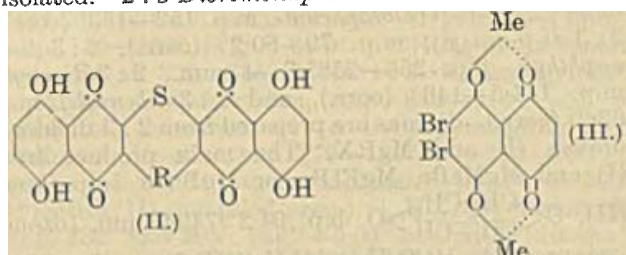
**6:7-Benzoylene-ββ'-benzofurans from 1:5-di-aryolanthraquinones.** R. SCHOLL and S. HASS (Ber., 1936, 69, [B], 194—197).—1:5-Di-*m*-xyloylantraquinone is transformed by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in boiling 80—85% EtOH in absence of air into *9-hydroxy-1:5-di-m-xyloylanthr-10-one*, m.p. 230° in a preheated bath (pyridinium salt; *p*-bromobenzoate, m.p. 288°), which in indifferent media or when subjected to



pressure passes into an equilibrium mixture with 1:5-di-*m*-xyloylanthraquinol. It is converted by boiling AcOH or conc. H<sub>2</sub>SO<sub>4</sub> at 15—20° into 2-*m*-xylyl-6:7-6'-*m*-xyloxybenzoylene-ββ'-benzofuran (I), m.p. 193°, which is not reduced by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and NaOH and suffers fission of the furan ring with hot C<sub>5</sub>H<sub>5</sub>N-NaOH. H. W.

**Tetrahydroxydibenzothianthrenediquinone; chemistry of naphthazarin.** K. BRASS, R. PFLUGER, and K. HONSBURG (Ber., 1936, 69, [B], 80—87).—The interaction of Na<sub>2</sub>S (1.5 mols.) with dibromonaphthazarin (I) does not proceed as smoothly as with 2:3-dichloro-*α*-naphthaquinone, but gives Na<sub>1</sub>, Na<sub>3</sub>, and Na<sub>5</sub> derivatives converted by dil. acid into *tetrahydroxydibenzothianthrenediquinone* (II; R=S), m.p. > 300°, best obtained from (I) and Na<sub>2</sub>S (1 mol.) at 200°. (II) cannot be acetylated, but is reduced and then benzoylated to *octabenzoyldibenzothianthren*, m.p. 283°. It is not attacked by cold conc. or fuming HNO<sub>3</sub> and is completely oxidised by the hot reactants. The complex course of the prep. is shown by the occasional formation of the compound (II; R=S-S). *Dibromonaphthazarin Me<sub>2</sub> ether* (III), m.p. 179—180°, and Na<sub>2</sub>S give products containing

Br from which a homogeneous material could not be isolated. 2:3-Dibromonaphthazarin is best obtained



by the action of a slight excess of Br on naphthazarin in AcOH; it does not react with  $\text{CH}_3\text{N}_2$  or  $\text{Me}_2\text{SO}_4$ , but is transformed by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$  and anhyd.  $\text{Na}_2\text{CO}_3$  in  $o\text{-C}_6\text{H}_4\text{Cl}_2$  at  $170^\circ$  into (III). Under similar conditions naphthazarin affords the  $\text{Me}_2$  ether, m.p.  $160^\circ$ . Reasons are advanced for assigning the above constitution to (III) and for considering its reduction product to be 2:3-dibromo-1,4-dihydroxy-5:8-dimethoxynaphthalene. H. W.

**Syntheses by means of magnesylpyrroles.**  
**Series II. XXI.** B. ODDO and G. ACUTO (Gazzetta, 1935, 65, 1029—1036).—Mg 2:5-dimethylpyrrol bromide in  $\text{Et}_2\text{O}$  with  $\text{AcCl}$  yields 3-acetyl-2:5-dimethylpyrrole, m.p.  $89^\circ$  [semicarbazone, m.p.  $234^\circ$  (decomp.)]. The 3-propionyl, m.p.  $102.5^\circ$  [semicarbazone, m.p.  $197^\circ$  (decomp.)], 3-butyryl, m.p.  $60^\circ$ , and 3-benzoyl, m.p.  $132^\circ$ , compounds are similarly prepared. With  $\text{CO}_2\text{Et}\cdot\text{COCl}$ , Et 2:5-dimethylpyrrol-3-glyoxylate, m.p.  $83.5^\circ$ , is obtained, hydrolysed to the acid, m.p.  $196\text{--}197^\circ$  (decomp.) ( $\text{NH}_4$ ,  $\text{Pb}$ , and other salts); this gives, when heated, an aldehyde, and, with  $\text{EtOH}\cdot\text{NH}_3$  at  $120^\circ$ , 2:5-dimethylpyrrol-3-glyoxamide, m.p.  $225^\circ$  (decomp.). E. W. W.

**Occurrence of piperidine in black pepper.**—See this vol., 395.

**Action of ultra-violet light on pyridine. VI.**  
**Reactions of photopyridine and behaviour of pyridine derivatives in the region of ultra-violet radiations.** H. FREYTAG (Ber., 1935, 69, [B], 32—40; cf. A., 1934, 303).—Dil. alkaline  $\text{KMnO}_4$  is unsuitable for the detection of photopyridine [ $\text{NH}_4$  salt of enolglutacondialdehyde (I)], since irradiation of  $\text{H}_2\text{O}$  causes formation of  $\text{H}_2\text{O}_2$ . The applicability of dimedon (I), 1-phenyl-3-methylpyrazol-5-one (II), and indole (III) has therefore been tested with the Na salt of (I); coloured derivatives are obtained which could not be completely purified. Anaesthesin (IV), however, yields glutacondianæstheside, m.p. about  $154\text{--}155^\circ$ . The effect of irradiation of  $\text{C}_5\text{H}_5\text{N}$ , 2-, 3-, and 4-methyl-, 2:4- and 2:6-dimethyl-, 2:4:6-trimethyl-, and 2-benzyl-pyridine in presence of (I), (II), (III), and (IV), respectively, is tabulated, whereby it appears that Me in position 3 hinders the photo-reaction. Several  $\text{C}_5\text{H}_5\text{N}$  derivatives become coloured yellow to yellowish-brown in  $\text{H}_2\text{O}$  or  $\text{EtOH}$ , but do not give an aldehydic reaction. Substances with halogen and carbalkoxy-groups become hydrolysed and give halogen ions. 5-Bromo-3-aminopyridine becomes very rapidly discoloured with elimination of Br; since discoloration commences at the boundary of solution and air a photo-oxidative attack on the  $\text{NH}_2$  appears to occur. This applies also to 5-amino-

2-methylpyridine, whereas 5-aminopyridine-3-carboxylic acid is unaffected. 4-Chloropicolinic acid and 4-chloro-2-aminopyridine are resistant to irradiation, whilst pyridine-2:3-dicarboxylic acid and -3-carboxydiethylamide are completely unchanged. The behaviour of  $\cdot\text{CHO}$  in 5:6-dichloropyridine-3- and 4:6-dichloropyridine-2-aldehyde is uncertain. 4-Iodopyridine-2-carboxylic acid yields I formed by photo-oxidation of primarily-formed HI.  $\text{Et}_2$  2:6-dimethylpyridine-3:5-dicarboxylate is rapidly hydrolysed. H. W.

**Alkylated benzeneazoaminopyridines.**—See B., 1936, 124.

**Aldehydes of the indole series.**—See B., 1936, 140.

**Condensation of indolealdehydes with hippuric acid.** E. RESTELLI (Anal. Assoc. Quim. Argentina, 1935, 23, 58—62).—Indole-3-aldehyde and hippuric acid, when heated with  $\text{NaOAc}$  in addition to  $\text{Ac}_2\text{O}$ , give 2-phenyl-4-(1'-acetylindolylidene)oxazolone, m.p.  $205^\circ$  (2'-Me derivative, m.p.  $185^\circ$ ). F. R. G.

**Catalytic decomposition of ethyl propyl ketone phenylhydrazone.** A. E. ARBUSOV and I. A. ZAITZEV (Trans. Butlerov Inst. Chem. Tech. Kazan, 1934, No. 1, 33—38; cf. A., 1932, 1236).—A substance,  $\text{C}_{12}\text{H}_{15}\text{N}$ , b.p.  $167/15$  mm. (picrate, m.p.  $144^\circ$ ), is obtained, which may be either 2:3-diethyl- or 2-methyl-3-propyl-indole. CH. ABS. (r)

**Quinolone-acids from oxindole derivatives.**  
 E. ZRIKE and H. G. LINDWALL (J. Amer. Chem. Soc., 1936, 58, 49—50).—Isatin (I) and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$  in  $\text{EtOH}\cdot\text{NH}_4\text{Et}$  at room temp. for 5 days give 3-hydroxy-3- $\alpha$ -carbethoxybenzylloxindole, m.p.  $154\text{--}156^\circ$ , converted by warm 1%  $\text{NaOH}$  into (I) and by conc.  $\text{HCl}$  in  $\text{EtOH}$  into 2-keto-3-phenyl-1:2-dihydroquinoline-4-carboxylic acid. 3-(Dicyanomethylene)oxindole (II) (Walter, A., 1902, i, 373) is reduced (aq.  $\text{Na}_2\text{S}_2\text{O}_4$ ) to 3-(dicyanomethyl)oxindole, m.p.  $183\text{--}185^\circ$  (darkens about  $160^\circ$ ), which is unstable in hot solvents and is converted by 10%  $\text{NaOH}$  (or acid) into 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (III).  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  and (I) in  $\text{EtOH}$ -piperidine afford 3-(cyanoformamidomethylene)oxindole, m.p.  $248\text{--}250^\circ$ ; this and (II) are hydrolysed (conc.  $\text{HCl}$ ) to a dibasic acid,  $\text{C}_{11}\text{H}_7\text{O}_5\text{N}$ , m.p.  $>340^\circ$  ( $\text{Ag}_2$  salt; ester, m.p.  $150\text{--}151^\circ$ ), also formed from  $\text{Et}_3\text{O}$  oxindole-3:3-dimalonate (A., 1935, 758) and 10%  $\text{NaOH}$ , which is reduced ( $\text{Zn}$ ,  $\text{AcOH}$  or  $\text{Na}\text{--Hg}$ ,  $\text{H}_2\text{O}$ ) to (II). H. B.

**Amino-compounds of the quinoline series.**—See B., 1936, 92.

**Preparation of 4-alkyl- and 4-aryl-quinolines.**  
 J. KENNER and F. S. STATHAM (Ber., 1936, 69, [B], 16—18).—The following % yields of 4-arylquinoline are obtained from the requisite arylamine and  $\alpha$ -ketone (cf. Blaise *et al.*, A., 1907, i, 241) without and with  $\text{PhNO}_2$  (1 mol.),  $\text{As}_2\text{O}_5$  (0.5 mol.),  $\text{SnCl}_4\cdot 8\text{H}_2\text{O}$  (1 mol.), and  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (2 mols.) as oxidising agent: 4-phenyl (10, —, —, 52.6, —);  $p$ -tolyl (7, 9, 14, 36.6, 44.6); 2-methoxy-5-methylphenyl (5, —, —, 1.5, —), and  $\beta$ -naphthyl (—, —, —, 41, —) quinoline. The respective % yields of 4-alkylquinolines with  $\text{PhNO}_2$  (1 mol.),  $\text{SnCl}_4$  (1 mol.),  $\text{SnCl}_4\cdot 8\text{H}_2\text{O}$  (1 mol.),



and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2 mols.) as oxidants are as follows: Me- (28, 21, 40, 35—40); Et- (20, —, 40, —); Pr<sup>n</sup>- (25, —, 40, —); Bu<sup>n</sup>- (28, —, 40, —).

$\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  afford  $\beta$ -chloroethyl 2-naphthyl ketone, m.p.  $83^\circ$ , converted by KOH at  $280^\circ$  into  $2\text{-C}_{10}\text{H}_7\text{-CO}_2\text{H}$  and by  $\text{NHPH-NH}_2$  in warm EtOH into 1-phenyl-3- $\beta$ -naphthylpyrazoline, m.p.  $181\text{--}182^\circ$ . The picrates, m.p.  $200^\circ$  (decomp.),  $205^\circ$  (decomp.), and  $185\text{--}189^\circ$  (decomp.), of 4-ethyl-, 4-n-propyl-, and 4-n-butyl-quinoline, respectively, are described.

H W

**Tetrahydrocarbazoles with substituents in the 7-position.** S. G. P. PLANT and (Miss) K. M. ROGERS (J.C.S., 1936, 40—41).—9-Acetyltetrahydrocarbazole (I),  $\text{AcBr}$ , and  $\text{AlCl}_3$  give 7:9-diacetyltetrahydrocarbazole (II), m.p.  $110^\circ$ , hydrolysed to 7-acetyltetrahydrocarbazole (S) to 2-acetylcarbazole and reduced ( $\text{Zn-Hg}$ ) to 7-ethylhexahydrocarbazole, m.p.  $44\text{--}46^\circ$ . (I) and  $\text{BzCl}$  afford 7-benzoyl-9-acetyl-, m.p.  $126^\circ$ , hydrolysed to 7-benzoyl-, m.p.  $165^\circ$ , which is also obtained from 1,3-dibenzoyl-tetrahydrocarbazole, m.p.  $121^\circ$ . 9-Benzoyl-7-acetyltetrahydrocarbazole, m.p.  $149^\circ$ , hydrolysed to (II), is similarly obtained.

F. R. S.

**Chemotherapeutic studies in the acridine series.** I. 2:6- and 2:8-Diaminoacridines. A. ALBERT and W. H. LINNELL (J.C.S., 1936, 88—93).—Na 2-chloro-4-nitrobenzoate,  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$ , and Cu yield 5:5'-dinitrodiphenylamine-2-carboxylic acid (I), m.p.  $263^\circ$  (Ag salt), reduced ( $\text{SnCl}_2\text{-HCl}$ ) to 3:3'-diaminodiphenylamine, m.p.  $94\text{--}95^\circ$  ( $\text{Ac}_2$  derivative), also obtained by reduction of 3:3'-dinitrodiphenylamine, m.p.  $186\text{--}5^\circ$ . Ring-closure of (I) yields a mixture of 5-chloro-2:6- (II), m.p.  $200\text{--}203^\circ$  (principally), and 2:8-dinitroacridine (III), with 2:8-dinitroacridone. (II) is hydrolysed ( $\text{HCl}$ ) to 2:6-dinitroacridone, reduced to the 2:6- $(\text{NH}_2)_2$ -compound ( $+0\text{.5H}_2\text{O}$ ), m.p.  $306^\circ$ , which with  $\text{H}_2$  gives 2:6-diaminoacridine, m.p.  $213\text{--}216^\circ$  (p.). 2:8-Diaminoacridine, obtained from (III), forms dibenzylidene, m.p. approx.  $370^\circ$  (decomp.), above  $350^\circ$ , and  $\text{Bz}_2$  derivatives, m.p. above  $350^\circ$ .

F. R. S.

**10-Hydroxyacridone and "acridol."** II. A. KIEGL and A. BRÖSAMLE (Ber., 1936, 69, [B], 197—202; cf. A., 1914, i, 867).—Oxidation of acridine (I) in  $\text{C}_6\text{H}_6$  with  $\text{BzO}_2\text{H}$  affords acridine 10-oxide, identical with "acridol" (loc. cit.; cf. Tanasescu et al., A., 1934, 1010; Lehmnstedt, A., 1935, 1251). Similar treatment of 5-methoxyacridine gives 5-methoxyacridine 10-oxide (II), m.p. about  $158^\circ$  (also  $+1\text{H}_2\text{O}$ ), which is not identical with the Me ether obtained by methylation of 10-hydroxyacridone (III) (Kiegl, loc. cit.). Both ethers give 10-hydroxyacridone when treated with  $\text{HCl}$  and decompose at about the same temp. into  $\text{CH}_2\text{O}$  and (I), but (II) is pronouncedly basic and dissolves readily in  $2\text{N-HCl}$  at  $15\text{--}20^\circ$ . (III) is tautomeric, the free compound passing under the influence of alkali into 5-hydroxyacridine 10-oxide.

H. W.

**2:8-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups on the 5-carbon atom.** V. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium hydroxides. VI.

**Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium iodides.** VII. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium oxalates. VIII. Synthesis of 5-amino-2:8-dialkoxy-10-alkylacridinium derivatives and 5-(2':8'-dialkoxy-N'-alkylacridonamino)-2:8-dialkoxy-10-alkylacridinium derivatives. IX. Synthesis of (2':8'-dialkoxy-10'-alkyl-10'-substituted-acridine)-5:5'-ethylenediamino-2:8-dialkoxy-10-alkylacridinium derivatives. K. ISHIIHARA (J. Chem. Soc. Japan, 1934, 55, 945—958, 1028—1039, 1040—1050, 1185—1206, 1277—1294; cf. A., 1935, 1132).—V. The following 5-anilino-, 5-o-, -m-, and -p-toluidino-, and 5-p-phenetidin-derivatives of substituted-acridinium hydroxides have been prepared by hydrolysis of the chlorides: 2:8-dimethoxy-10-methyl-, m.p.  $148\text{--}149^\circ$ ,  $133\text{--}134^\circ$ ,  $137\text{--}138^\circ$ ,  $133\text{--}134^\circ$ ,  $180^\circ$ ; 2:8-dimethoxy-10-ethyl-, m.p.  $145\text{--}146^\circ$ ,  $157\text{--}158^\circ$ ,  $165\text{--}166^\circ$ ,  $167\text{--}168^\circ$ ,  $154\text{--}155^\circ$ ; 2:8-diethoxy-10-methyl-, m.p.  $164\text{--}165^\circ$ ,  $131\text{--}132^\circ$ ,  $172\text{--}173^\circ$ ,  $158\text{--}159^\circ$ ,  $167\text{--}168^\circ$ ; 2:8-diethoxy-10-ethyl-, m.p.  $156^\circ$ ,  $138\text{--}139^\circ$ ,  $176^\circ$ ,  $174\text{--}175^\circ$ ,  $171^\circ$ .

VI. The -acridinium iodide derivatives (as above) are obtained from the hydroxides and  $\text{AcOH-KI}$ : 2:8-dimethoxy-10-methyl-, m.p.  $237\text{--}238^\circ$ ,  $236\text{--}237^\circ$ ,  $243\text{--}244^\circ$ ,  $253\text{--}254^\circ$ ,  $238^\circ$ ; 2:8-dimethoxy-10-ethyl-, m.p.  $249^\circ$ ,  $224\text{--}225^\circ$ ,  $243\text{--}245^\circ$ ,  $230\text{--}231^\circ$ ,  $227\text{--}228^\circ$ ; 2:8-diethoxy-10-methyl-, m.p.  $252\text{--}253^\circ$ ,  $248^\circ$ ,  $263^\circ$ ,  $257^\circ$ ,  $251^\circ$ ; 2:8-diethoxy-10-ethyl-, m.p.  $255^\circ$ ,  $248^\circ$ ,  $262^\circ$ ,  $274^\circ$ ,  $234\text{--}235^\circ$ .

VII. Similarly the corresponding 20 oxalates are prepared from the hydroxides and  $\text{H}_2\text{C}_2\text{O}_4$  in  $\text{AcOH}$ ; respective m.p., in the order given above, are  $232^\circ$ ,  $214\text{--}215^\circ$ ,  $220\text{--}221^\circ$ ,  $214\text{--}215^\circ$ ,  $180^\circ$ ;  $206\text{--}207^\circ$ ,  $200\text{--}201^\circ$ ,  $204\text{--}205^\circ$ ,  $184\text{--}185^\circ$ ,  $209^\circ$ ;  $231\text{--}232^\circ$ ,  $210\text{--}211^\circ$ ,  $212\text{--}213^\circ$ ,  $224\text{--}226^\circ$ ,  $202\text{--}203^\circ$ ,  $212^\circ$ ,  $234\text{--}235^\circ$ ,  $212\text{--}214^\circ$ ,  $212^\circ$ ,  $218\text{--}219^\circ$ .

VIII. 5-Amino-2:8-dimethoxy-10-methylacridinium chloride (I), m.p.  $324\text{--}325^\circ$ , is prepared from the 5-Cl-compound with aq.  $\text{NH}_3$ . The corresponding hydroxide, m.p.  $74\text{--}78^\circ$ , iodide, m.p.  $339\text{--}340^\circ$  and oxalate, m.p.  $252\text{--}253^\circ$ , are described. (I), with  $\text{AcOH}$ , yields 2:8-dimethoxy-5-(2':8'-dimethoxy-N'-methylacridonamino)-10-methylacridinium chloride, m.p.  $269\text{--}270^\circ$ . The following are prepared similarly: 5-amino-2:8-dimethoxy-10-ethylacridinium chloride, m.p.  $282\text{--}283^\circ$  (hydroxide, m.p.  $140\text{--}142^\circ$ ; iodide, m.p.  $294^\circ$ , oxalate, m.p.  $190^\circ$ ); 2:8-dimethoxy-5-(2':8'-dimethoxy-N'-ethylacridonamino)-10-ethylacridinium iodide, m.p.  $295^\circ$ ; 5-amino-2:8-diethoxy-10-methylacridinium chloride, m.p.  $311\text{--}312^\circ$  (hydroxide, m.p.  $153\text{--}154^\circ$ ; iodide, m.p.  $312^\circ$ ; oxalate, m.p.  $228^\circ$ ); 2:8-diethoxy-5-(2':8'-diethoxy-N'-methylacridonamino)-10-methylacridinium chloride, m.p.  $287\text{--}288^\circ$  (iodide, m.p.  $288\text{--}290^\circ$ ); 5-amino-2:8-diethoxy-10-ethylacridinium chloride, m.p.  $294\text{--}295^\circ$  (hydroxide, m.p.  $149\text{--}150^\circ$ ; iodide, m.p.  $303^\circ$ ; oxalate, m.p.  $237\text{--}238^\circ$ ); 2:8-diethoxy-5-(2':8'-diethoxy-N'-ethylacridonamino)-10-ethylacridinium chloride, m.p.  $218^\circ$  (iodide, m.p.  $269^\circ$ ).

IX. 5-Chloro-2:8-dimethoxy-10-methylacridinium chloride with  $(\text{CH}_2\text{NH}_2)_2$  yields (10'-hydroxy-2':8'-dimethoxy-10'-methylacridino)-5:5'-ethylenediamino-2:8-dimethoxy-10-methylacridinium hydroxide, m.p.  $230^\circ$  (tetrapicrate, m.p.  $231\text{--}232^\circ$ ); this with  $\text{AcOH}$

affords (10'-chloro-2': 8'-dimethoxy-10'-methylacridino)-5 : 5'-ethylenediacetamido-2 : 8-dimethoxy-10-methylacridinium chloride, m.p. 250°. The 10'-chloro-chloride, m.p. 231—232°, 10'-iodo-iodide, m.p. 282—283°, and 10'-oxalato-oxalate, m.p. 233—234°, are obtained similarly. The following are described: (10'-hydroxy-2': 8'-dimethoxy-10'-ethylacridino)-5 : 5'-ethylenediamino-2 : 8-dimethoxy-10-ethylacridinium hydroxide, m.p. 218—220°, and the derived 10'-chloro-chloride, m.p. 253°, 10'-iodo-iodide, m.p. 271—272°, and 10'-oxalato-oxalate, m.p. 235°; (10'-hydroxy-2': 8'-diethoxy-10'-methylacridino)-5 : 5'-ethylenediamino-2 : 8-diethoxy-10-methylacridinium hydroxide, m.p. 236—238°, and the derived 10'-chloro-chloride, m.p. 267—268°, 10'-iodo-iodide, m.p. 290°, and 10'-oxalato-oxalate, m.p. 253°; (10'-hydroxy-2': 8'-diethoxy-10'-ethylacridino)-5 : 5'-ethylenediamino-2 : 8-diethoxy-10-ethylacridinium hydroxide, m.p. 204—206°, and the derived 10'-chloro-chloride m.p. 241—242°, and 10'-oxalato-oxalate, m.p. 249—250°. CH. ABS. (r)

**Action of alkalis and alkali salts on antipyrine.** L. E. HARRIS and E. D. TEBOW (J. Amer. Pharm. Assoc., 1935, 24, 1069—1070).—The immiscible liquid obtained on the addition of antipyrine to conc. solutions of alkalis or alkali salts is apparently an isomeride. E. H. S.

**Derivatives of 1 : 3-diaryl-5-pyrazolones and of 1 : 1'-diaryl-3 : 3'-arylene-5 : 5'-bispyrazolones.**—See B., 1936, 92.

**Alkylglyoxalidines.** H. C. CHITWOOD and E. E. REID (J. Amer. Chem. Soc., 1935, 57, 2424—2426).—2-Methylglyoxalidine (I), m.p. 105° (205°), obtained in 68% yield when  $(\text{CH}_2\text{NHAc})_2$  is heated with Mg powder at 270°, is hydrolysed (aq. alkali) to  $(\text{CH}_2\text{NH}_2)_2$ . 2-Ethyl-, m.p. 38.1° (137.1°), 2-propyl-, m.p. 35.3° (129°), 2-butyl-, m.p. 41° (125.8°), 2-amyl-, m.p. 33.8° (128.4°), 2-hexyl-, m.p. 46.2°, 2-heptyl-, m.p. 60° (104.8°), 2-octyl-, m.p. 52.1°, 2-nonyl-, m.p. 71.4° (122°), 2-decyl-, m.p. 79.5° (82°), and 2-undecyl-, m.p. 79.8° (61.5°), glyoxalidines are similarly obtained (in some cases Mg is replaced by Na) in 5.6—49% yield from the appropriate  $(\text{CH}_2\text{NH}\cdot\text{COR})_2$ . The temp. given in parentheses are m.p. of the picrates; the aurichlorides are analysed. The toxicity (towards *Lupinus albus* and animals) of the first 5 compounds decreases with increase in size of the alkyl group. (I) and Br in  $\text{CHCl}_3$  give (probably) the N-Br-derivative hydrobromide, hydrolysed ( $\text{H}_2\text{O}$ ) to (I). H. B.

**Preparations of methyl  $\beta$ -( $\zeta$ -methyl- $\Delta^7$ -heptenyl)amine.**—See B., 1936, 124.

**Piperazine.** VIII. Condensation with aldehydes. W. T. FORSEE, jun., and C. B. POLLARD (J. Amer. Chem. Soc., 1935, 57, 2363—2364).—Piperazine (I) and RCHO in presence or absence of solvent give insol. products of the type  $(\text{N} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_5 \end{smallmatrix} > \text{N}\cdot\text{CHR})_n$ ; those where R=H, m.p. > 300° [also formed from (I) and  $\text{CH}_3\text{I}$ , Ph, m.p. 270° (decomp.)] [also formed from (I) and  $\text{CHPhCl}_2$ ], *o*-OH- $\text{C}_6\text{H}_4$ , m.p. 210° (decomp.), *p*- $\text{C}_6\text{H}_4\text{Me}$ , m.p. 275° (decomp.), *o*- $\text{C}_6\text{H}_4\text{Cl}$ , m.p. 240° (decomp.), and *p*-OMe- $\text{C}_6\text{H}_4$ , m.p. 290° (decomp.), are described. N-Phenylpiperazine with

$\text{CH}_3\text{O}$ , MeCHO, PhCHO, *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$ , and *o*-OMe- $\text{C}_6\text{H}_4\cdot\text{CHO}$  gives di-(N-phenyl-N'-piperazyl)-methane, m.p. 123—124° (also formed using  $\text{CH}_3\text{I}_2$ ), -ethane, m.p. 121—123°, -phenylmethane, m.p. 125—126°, -*o*-tolylmethane, m.p. 144—144.5°, and -*o*-anisylmethane, m.p. 135—136°, respectively. H. B.

**Synthesis of 6-amino-4-ethylpyrimidine.** W. T. CALDWELL and W. M. ZIEGLER (J. Amer. Chem. Soc., 1936, 58, 78—79).—6-Hydroxy-2-ethylthiol-4-ethylpyrimidine [best prepared from  $\text{EtCO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $\text{SEt}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ , HBr in MeOH-KOH at 0°] is hydrolysed to 4-ethyluracil, m.p. 204—205°, converted by POCl<sub>3</sub> into 2 : 6-dichloro-4-ethylpyrimidine, b.p. 90—95°/4 mm., 103—107°/7 mm., which with red P and HI (b.p. 127°) gives 6-hydroxy-4-ethylpyrimidine hydriodide, m.p. 170.5—171.5° (sinters at 160°). This with POCl<sub>3</sub> affords 6-chloro-4-ethylpyrimidine, b.p. 193°, which with EtOH-NH<sub>3</sub> at 150° gives 6-amino-4-ethylpyrimidine (+3H<sub>2</sub>O), m.p. 47.5—48°, m.p. (anhyd.) 87.5—88° (picrate, m.p. 204—205°; hydrochloride, m.p. 198—199°; aurichloride, m.p. 150—151°). H. B.

**Reaction products of aromatic amidines with diketones, dialdehydes, and their monoximes.** J. B. EKELEY and J. L. ELLIOTT (J. Amer. Chem. Soc., 1936, 58, 163—164).—The following 5-hydroxy-2-phenyl-4-arylpyrimidines are prepared (cf. A., 1936, 1133) from  $\text{NH}_2\cdot\text{CPh}\cdot\text{NH}$  (I),  $(\text{CHO})_2$ , and the appropriate ArCHO in aq. EtOH-KOH at room temp.: 4-*o*-carboxyphenyl, m.p. 259—260°; 4-*o*-, m.p. 260°, and -*p*-, m.p. 305—306°, -chlorophenyl; 4-2' : 4', m.p. 248—249°, -2' : 5', m.p. 268—269°, and -3' : 4', m.p. 259—260°, -dimethoxyphenyl; 4-*p*-dimethylamino-phenyl, m.p. 277—278°, 4-*p*-phenetyl, m.p. 292—293°; 4-*m*-hydroxyphenyl, m.p. 265—265.5°; 4-dibromo-*o*-hydroxyphenyl, m.p. 311°; 4-*o*-hydroxybenzyl, m.p. 287—288°; 4-5'-nitro-2'-hydroxyphenyl, m.p. > 300°; 4-*p*-cumyl, m.p. 246—247°; 4-6'-methoxy-*m*-tolyl, m.p. 253—254°; 4-3' : 4'-methylenedioxyphenyl, m.p. 283—287°; 4-*m*-tolyl, m.p. 237—238°. The following 5-hydroxy-2-*m*-tolyl-4-arylpyrimidines are similarly prepared from  $(\text{CHO})_2$ , *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  (II) and ArCHO : 4-2' : 4', m.p. 250—251°, -2' : 5', m.p. 229—230°, and -3' : 4', m.p. 238—239°, -dimethoxyphenyl; 4-*p*-phenetyl, m.p. 237—238°; 4-*p*-cumyl, m.p. 263—264°; 4-*o*-, m.p. 272—273°, and -*p*-, m.p. 229°, -anisyl; 4-3' : 4'-methylenedioxyphenyl, m.p. 4-6'-methoxy-*m*-tolyl, m.p. 237—239°. Phenanthraquinone with (I), (II), and *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  (hydrochlorides) in 50% alkali gives compounds:  $\text{C}_{21}\text{H}_{14}\text{ON}_2$ , m.p. 277—278°,  $\text{C}_{22}\text{H}_{16}\text{ON}_2$ , m.p. 269—270°, and  $\text{C}_{22}\text{H}_{16}\text{ON}_2$ , m.p. 287.5—288°, respectively. (I) and (II) with  $\text{CAcMe}\cdot\text{N}\cdot\text{OH}$  similarly afford compounds,  $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_4$ , m.p. 105—107°,  $\text{C}_{16}\text{H}_{24}\text{O}_4\text{N}_4$ , m.p. 94—96°, respectively. Phenanthraquinoneoxime (in amyl alcohol) with (I), (II), *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$  (in  $\text{CHCl}_3$ +KOH) gives compounds,  $\text{C}_{21}\text{H}_{17}\text{O}_2\text{N}_3$ , m.p. 186°,  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_3$ , m.p. 165—166°, and  $\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_3$ , m.p. 182—183°, respectively. A compound,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_3$ , m.p. 182—183°, is described. U. B.

**Synthesis of nitrated 2 : 3-dihydropyrimidinazole.** O. BREMER (Annalen, 1936, 521, 286—287).—With  $\text{SOCl}_2$ , 3-nitro-4- $\beta$ -hydroxyethylaminopyrimidine gives the 4- $\beta$ -chloroethylamino-compound, m.p.



reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to 3-amino-4- $\beta$ -chloroethylamino-pyridine, m.p. 85–80°. 3-Nitro-4- $\beta$ -hydroxyethoxy-pyridine, m.p. 112–113° [from 4-chloro-3-nitropyridine, Na and  $(\text{CH}_2\cdot\text{OH})_2$ ], similarly affords the 4- $\beta$ -chloroethoxy-compound, m.p. 70–71°, sinters 44°. 4-Chloro-3-nitropyridine, m.p. 74–75° (lit. m.p. 45°), is reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to the 3- $\text{NH}_2$ -compound, m.p. 82°. 2-Chloro-5-nitropyridine (I) and its 3-Br-derivative with  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  in EtOH at 100° give, respectively, o-nitro-2- $\beta$ -hydroxyethylaminopyridine (II), m.p. 131–132° (hydrochloride, m.p. 182°), and its 3-Br-derivative (III), m.p. 136°; 2-chloropyridine gives 2- $\beta$ -hydroxyethylamino-, m.p. 65° (hydrochloride, m.p. 158.5°), converted by  $\text{SOCl}_2$  into 2- $\beta$ -chloroethylamino-pyridine (IV) (hydrochloride, m.p. 146°). (I) and  $(\text{CH}_2\cdot\text{OH})_2\text{-Na}$  give 5-nitro-2- $\beta$ -hydroxyethoxy-, m.p. 113–114°, converted ( $\text{SOCl}_2$ ) into 2- $\beta$ -chloroethoxy-pyridine, m.p. 131–132°, converted by  $\text{NH}_4\text{Et}$  into 5-nitro-2- $\beta$ -diethylaminoethoxy-pyridine, b.p. 170°/3 mm. [reduced by  $\text{SnCl}_4$  and condensed with  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  to give the 5- $p$ -dimethylaminobenzylideneamino-derivative, m.p. 163–164 (picrate, m.p. 131°)], also obtained from (I) and  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{ONa}$  in  $\text{Et}_2\text{O}$ . Similarly (I) and the appropriate base afford o-nitro-2- $\beta$ -amino-enylamino-, m.p. 123°, 2- $\beta$ -(diethylamino)ethylamino-, 2- $\beta$ -hydroxydiethylamino- (V), m.p. 59–60°, and 2-allylamino-, m.p. 97° [converted by  $\text{HBr}$  to 2- $\beta$ -bromopropylamino- (VI)], pyridine. (VI) is converted by warming in  $\text{H}_2\text{O}$  into 5-nitro-3-methyl-2:3-dihydropyriminazole, m.p. 185°. Gentle heat converts (IV) into dihydropyriminazolium chloride, converted by  $\text{KOH}$  into 2:3-dihydropyriminazole, m.p. 64–65° (picrate, m.p. 213°), also obtained by the action of  $\text{SOCl}_2$  and alkali on 1- $\beta$ -hydroxyethylpyridoneimine (Kunjanaz, A., 1935, 627).  $\text{SOCl}_2$  converts (II), (III), and (V) into, respectively, 5-nitro- (VII), m.p. 258° (decomp.) (chloride, not melting at 280°), 7-bromo-5-nitro-, m.p. 222° (decomp.) [also from (VII) and  $\text{Br}\cdot\text{AcOH}$  at 100°], and 5-nitro-8-hydroxy-1-ethyl-2:3-dihydropyriminazole. J. W. B.

$\alpha\beta$ -Naphthoquinoxaline-2:3-dicarboxylic acid. G. B. CRIPA and G. PERRONCITO (Annali Chim. Appl., 1935, 25, 618–620).—1-Benzeneazo- $\beta$ -naphthylamine condenses with  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  at 190° to form *Et*,  $\alpha\beta$ -naphthoquinoxaline-2:3-dicarboxylate (I), m.p. 119°, and a substance, m.p. 205–210°. (I) is hydrolysed to the dicarboxylic acid, m.p. 195° (decomp.) (anhydride, m.p. 235°). E. W. W.

**Pyrrole-blues. III.** P. PRATESI and A. ZANETTA (Atti R. Accad. Lincei, 1935, [vi], 22, 159–165).—Isatin (1 mol.) in AcOH with 2:3:4-trimethylpyrrole (1 mol.) yields 3-(3':4':5'-trimethyl-2'-pyrrolyl)oxindole. Oxidation of opsopyrrole-blue (A., 1935, 1134) with  $\text{H}_2\text{O}_2$  or  $\text{CrO}_3$  affords isatin and methyllethylmaleinimide; that of pyrrole-blue B (I) (A., 1905, i, 841; 1907, i, 657) gives maleinimide and isatin. Dry distillation of (I) in a vac. affords oxindole. The production of isatin-5-sulphonic acid indicates that the sulphonic acid of (I) (*ibid.*) is 3-(2'-pyrrolyl)oxindole-5-sulphonic acid. The constitution of the pyrrole-blues is discussed. F. O. H.

**Indoles and isatogens. XXI.** Condensation of the three phthalaldehydes with nitrated tolu-

enes and preparation of di-isatogens. P. RUGGLI and E. WOLFF (Helv. Chim. Acta, 1936, 19, 5–15).— $p\text{-C}_6\text{H}_4(\text{CHO})_2$  and 2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  in presence of piperidine at 160° give 2:4:2':4'-tetranitro-*p*-distyrylbenzene, m.p. 294°, transformed by  $\text{Cl}_2$  in AcOH at 110° into the corresponding tetrachloride, m.p. (indef.) 92–99°, which passes in boiling  $\text{C}_5\text{H}_5\text{N}$  into 2:4:2':4'-tetranitro-*p*-dichlorostyrylbenzene (I), m.p. 248°. Protracted insolation of (I) suspended in  $\text{C}_5\text{H}_5\text{N}$  yields 6:6'-dinitro-2:2'-*p*-phenylenedi-isatogen,  $p\text{-C}_6\text{H}_4(\text{C} \begin{smallmatrix} \text{CO} \\ \text{NO} \end{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NO}_2)_2$ , m.p. 294°, reduced by  $\text{NHPh}\cdot\text{NH}_2$  in EtOH at 100° to dinitro-*p*-phenylenedi-indoxyl, isolated as the *Ac*, derivative, gradual decomp. > 280°. Similarly,  $m\text{-C}_6\text{H}_4(\text{CHO})_2$  gives 2:4:2':4'-tetranitro-*m*-distyrylbenzene, m.p. 243°, the tetrachloride, m.p. (indef.) 90–108°, of which gives 2:4:2':4'-tetranitro-*m*-dichlorostyrylbenzene, m.p. 215°, whence 6:6'-dinitro-2:2'-*m*-phenylenedi-isatogen, m.p. 289° (decomp.), reduced to dinitro-*m*-phenylenedi-indoxyl (*Ac*, derivative, m.p. 304°). Under like conditions *o*- $\text{C}_6\text{H}_4(\text{CHO})_2$  undergoes one-sided condensation giving *o*-2':4'-dinitrostyrylbenzaldehyde, m.p. 186° (phenylhydrazone, m.p. 193°).  $p\text{-C}_6\text{H}_4(\text{CHO})_2$  and *o*-nitro-*p*-toluonitrile give 2:2'-dinitro-4:4'-dicyano-*p*-distyrylbenzene, m.p. 350° (decomp.), whence the corresponding tetrachloride, m.p. 218°, 2:2'-dinitro-4:4'-dicyano-*p*-dichlorostyrylbenzene, m.p. 296°, and (?) 6:6'-dicyano-2:2'-*p*-phenylenedi-isatogen, blackens > 300°. 2:2'-Dinitro-4:4'-dicyano-*m*-distyrylbenzene, m.p. 298°, gives a tetrachloride, m.p. (indef.) 80–100°, or cryst. m.p., 248°, and thence 2:2'-dinitro-4:4'-dicyano-*m*-dichlorostyrylbenzene, m.p. 268°, and 6:6'-dicyano-2:2'-*m*-phenylenedi-isatogen, decomp. about 300° after darkening at 270°. *o*-2'-Nitro-4'-cyanostyrylbenzaldehyde, m.p. 210°, and its phenylhydrazone, m.p. 182°, are described. H. W.

**Quaternary ammonium compounds of derivatives of the anthracene series** [mainly pyrimidines].—See B., 1936, 140.

**Absorption spectra of 1:2:3-benzotriazoles.** A. K. MACBETH and J. R. PRICE (J.C.S., 1936, 111–119).—1:2:3-Benzotriazole and its derivatives absorb in two main regions, the shorter-wave region being attributed to an electron in the C:C system of the  $\text{C}_6\text{H}_6$  nucleus, and the other being assigned to the N:N of the triazole ring. Introduction of alkyl substituents into the nucleus results in improved separation of the two regions. No absorption characteristic of  $\text{NO}_2$  is observed unless an aq. solvent is used or OMe or OH is present in the triazole ring. 1-Hydroxy-1:2:3-benzotriazole and its 6-Me derivative exist in EtOH as equilibrium mixtures of two tautomeric forms, whilst  $\text{NO}_2\cdot\text{OH}$ -compounds exist as the stable OH-form in EtOH and aq. solution. Displacements of the max. are found, on change of solvent from EtOH to  $\text{H}_2\text{O}$ , in the  $\text{NO}_2\cdot\text{OH}$ -compound. 3-Nitro-4-chlorotoluene with  $\text{N}_2\text{H}_4$  gives 1-hydroxy-6-methyl-1:2:3-benzotriazole, m.p. 178–179°.

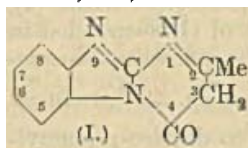
F. R. S.

**New soluble derivative of caffeine.** G. BARGIONI (Boll. Chim. farm., 1935, 74, 869–871).—Bromocaffeine and  $\text{CHNa}(\text{CO}_2\text{Et})_2$  give *Et*, caffeine-



malonate, converted into the acid, and into *caffeine-acetic acid*, of which the very sol. *Na* salt has the pharmacological character of caffeine, without toxicity. E. W. W.

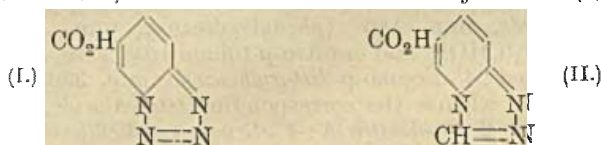
**A new heterocyclic grouping: benzopyrimidazole.** C. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 1067—1070).—2-Aminobenziminazole and



$\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  give 2-methyl-3:4-dihydrobenzopyrimidazol-4-one (I), m.p.  $280^\circ$ , converted by boiling 25%  $\text{NaOH}$  into  $\beta$ -2-benziminazolyl-iminobutyric or -aminocrotonic acid, m.p.  $> 300^\circ$ . With

$\text{Br}$  in  $\text{AcOH}$  (I) forms a 3:3- $\text{Br}_2$ -derivative, m.p.  $> 300^\circ$ . E. W. W.

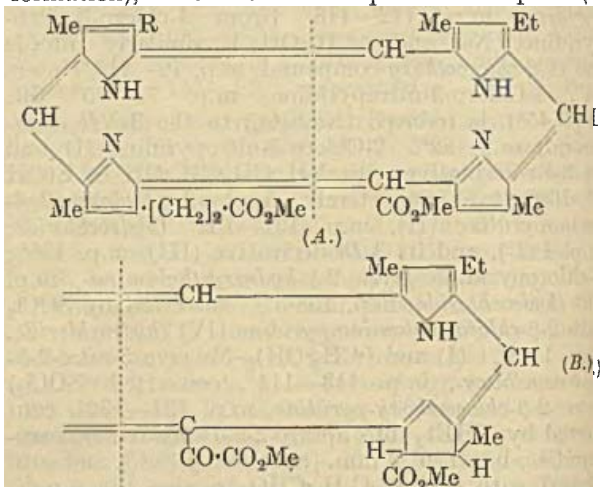
**Stereochemistry of tervalent nitrogen.** J. KENNER and F. S. STATHAM (Ber., 1936, 69, [B], 187—188).—The *brucine*, m.p.  $240\text{--}244^\circ$ ,  $[\alpha]_D^{18} +1.113^\circ$  in  $\text{CHCl}_3$ , *quinine*, m.p.  $205\text{--}210^\circ$ ,  $[\alpha]_D^{17} -145.2^\circ$  in  $\text{AcOH}$ , *strychnine*, m.p.  $220\text{--}224^\circ$ ,  $[\alpha]_D^{17} -1.559^\circ$  in  $\text{CHCl}_3$  and *cinchonine*, m.p.  $220^\circ$ ,  $[\alpha]_D^{15} +144.0^\circ$  in  $10N\text{-AcOH}$ , salts of benzotetrazolecarboxylic acid (I)



and the *brucine*, m.p.  $218^\circ$ ,  $[\alpha]_D^{20} -18.71^\circ$  in  $10N\text{-AcOH}$ , and *quinine*, m.p.  $135\text{--}145^\circ$ ,  $[\alpha]_D^{17.5} -161.6^\circ$  in  $\text{AcOH}$ , salts of benzotriazolecarboxylic acid (II) give no indication (I) of the possible resolution of (I) and (II) into optical antipodes; a plane configuration of this type of compound of  $\text{N}^{III}$  is therefore regarded as established experimentally. H. W.

**Chlorophyll. LXV. Synthesis of oxorhodophorphyrin, its conversion into 1:3:5:8-tetramethyl-4-ethyl-2-hydroxyethylporphin-6-carboxylic acid-7-propionic acid; pseudoverdoporphyrin.** H. FISCHER and G. KRAUSS (Annalen, 1936, 521, 261—285).—Oxorhodophorphyrin  $\text{Me}_2$  ester (I) ( $A$ ,  $R=\text{Ac}$ ) (A, 1934, 420; improved prep.) (semicarbazone, decomp.  $270^\circ$ ; *hæmin*, decomp.  $287^\circ$ ) with cold  $\text{Br}\cdot\text{HCO}_2\text{H}$  affords (by replacement of 2-Ac by  $\text{Br}$ ) the 2-*Br*-derivative (II), m.p.  $300^\circ$  ( $\text{Cu}$  complex salt, m.p.  $268^\circ$ , decomp.  $278^\circ$ ), of 2-*de*-ethyl-rhodophorphyrin (III), m.p.  $230\text{--}232^\circ$ , which is obtained either by the resorcinol fusion of the *hæmin* of (II) (together with 2-*de*-ethylpyrroporphyrin) or, better, by  $\text{KOH}\cdot\text{MeOH}$  hydrolysis of (II) and reduction with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot\text{Pd}\cdot\text{CaCO}_3$ . Reacetylation of the *hæmin* ester of (III) with  $\text{Ac}_2\text{O}\cdot\text{SnCl}_4$  and re-esterification of the product with  $\text{CH}_3\text{N}_2$  gives [2-*de*-ethyl-2-acetyl-rhodophorphyrin  $\text{Me}_2$  ester identical with (I), and reduced by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\cdot 3\%$   $\text{NaOMe}$  to rhodophorphyrin (IV). In agreement with the structure assigned oxidation of (I) with  $\text{PbO}_2\cdot\text{H}_2\text{SO}_4$  at  $0^\circ$  gives methylethylmaleimide. 2-Hydroxyethylrhodophorphyrin (V), m.p.  $255^\circ$  (*loc. cit.*; by  $\text{MeOH}\cdot\text{KOH}$  reduction of the 2-Ac compound) ( $\text{Cu}$  complex salt, m.p.  $222^\circ$ ), is reduced by  $\text{AcOH}\cdot\text{HI}$  (*d* 1.96) to (IV), and is reoxidised by cold 20% oleum-S to the 2-Ac derivative. With  $\text{HBr}\cdot\text{AcOH}$  at  $45^\circ$  and treatment of the product with  $\text{KOH}\cdot\text{MeOH}$ ,  $\text{AcOH}$ , and  $\text{CH}_2\text{N}_2$

(V) gives a porphyrin with 3-OMe (partial ether formation), which does not depress the m.p. of (V),



and could not be converted into the 2-vinyl derivative by heating with  $\text{Cu}$  powder in quinoline. The *hæmin* ester of (III) with  $\text{CHCl}_3\cdot\text{OEt}\cdot\text{POCl}_3\cdot\text{SnCl}_4$  (cf. A., 1934, 1234) and subsequent re-esterification gives [2-*de*-ethyl-2-formylrhodophorphyrin ester, m.p.  $283^\circ$  (VI) (*oxime*, m.p.  $262^\circ$ ), converted by  $\text{MgMeI}$  in  $\text{C}_6\text{H}_5\text{N}\cdot\text{Et}_2\text{O}$  into [2-*de*-vinyl-2-hydroxyethylpseudoverdoporphyrin (VII), m.p.  $250^\circ$ . Treatment of the  $\text{HBr}\cdot\text{AcOH}$  rearrangement product of pseudoverdoporphyrin  $\text{Me}_2$  ester with  $\text{KOME}\cdot\text{MeOH}$  gives [2-*de*-vinyl-2-methoxyethylpseudoverdoporphyrin ester, m.p.  $196^\circ$ , not identical with (VII), but with 20% aq.  $\text{KOH}$  the  $\text{Me}_2$  ester, m.p.  $252^\circ$ , of (VII) is obtained. Pseudoverdoporphyrin (VIII) ( $A$ ;  $R=\text{CH}\cdot\text{CH}_2$ ) therefore contains a vinyl group and its  $\text{Me}_2$  ester with  $\text{Br}\cdot\text{HCO}_2\text{H}$  followed by  $\text{MeOH}\cdot\text{KOH}$  gives a *Br*-derivative,  $\text{C}_{37}\text{H}_{46}\text{O}_6\text{N}_4\text{Br}$ , m.p.  $190^\circ$  [side-chain  $\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OMe}$  or  $\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\text{Br}$ ].  $\text{CHN}_2\cdot\text{CO}_2\text{Me}$  the  $\text{Me}_2$  ester of (VIII) gives the compound  $\text{C}_{37}\text{H}_{46}\text{O}_6\text{N}_4$  (IX), m.p.  $247^\circ$ , and with  $\text{PhN}_3$  it is converted into (VI). Phætopurpurin 7 (X) must also contain a  $\cdot\text{CH}\cdot\text{CH}_2$  group and its  $\text{Me}_2$  ester reacts with  $\text{CHN}_2\cdot\text{CO}_2\text{Me}$  to give a liquid product, converted by  $\text{C}_6\text{H}_5\text{N}\cdot\text{MeOH}$  into (IX). (X) has, therefore, structure B ( $R=\text{CH}\cdot\text{CH}_2$ ). With  $\text{AcOH}\cdot\text{HI}$  (XI) and purpurin 18 give a mixture of (IV) and its  $\gamma$ -carboxylic acid, and chlorin  $p_6$  gives only the latter product. J. W. B.

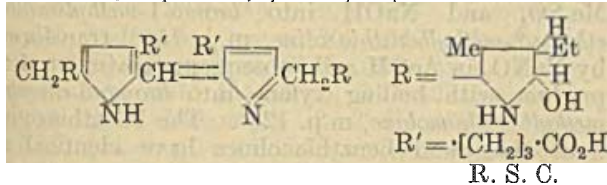
**Optical activity of horse's globin-hæmochromogen and of hæmoglobin.**—See this vol., 221.

**Porphyrin-gelatin phosphorescence.** F. DOW and E. J. KLAUS (Z. physiol. Chem., 1936, 238, 1—13).—The absorption and fluorescence spectra of porphyrins in gelatin films closely resemble the absorption spectra of solutions. The fluorescence spectra are less intense and the max. are shifted slightly towards the red.  $p_H$  has great influence, and is changed by buffering or by variation of the solvent used for the porphyrin. No chemical or physical change occurs during prep. of the films. R. S. A.

**Constitution of stercobilin.** H. FISCHER and H. HALBACH (Z. physiol. Chem., 1936, 238, 59—Stereobilin (I) (modified prep.),  $\text{C}_{33}\text{H}_{46}\text{O}_6\text{N}_4$ , m.p. -



readily absorbs 2H in AcOH (Pd-black), but 4H in 0.05*N*-NaOH; it cannot be converted into or obtained from mesobilirubinogen (II). (II) with O<sub>2</sub> in HCl gives mesobiliviolin and a little urobilin [reduced to (II) by Na-Hg]. (I) and HNO<sub>3</sub> give (·CH<sub>2</sub>-CO<sub>2</sub>H)<sub>2</sub>, but no methylethylmaleinimide which is readily so obtained from mesobilirubin (III) or glaucobilin (IV). (I) and HI-AcOH at 100° give pyrrole bases but no bilirubinic acid. With HBr-AcOH at 180° (I) gives an unidentified porphyrin. With PhN<sub>3</sub>Cl (II) and (III) give the ester *hydrochloride*, m.p. 193°, of a dye, *stercobilinogen* gives an uncrystallisable dye, but (I) does not react; (I) also does not react with PhCHO. With conc. H<sub>2</sub>SO<sub>4</sub> at 100° (I), (II), and (III) give (IV). (I) is strongly levorotatory (hydrochloride, [ $\alpha$ ]<sub>D<sup>20</sup></sub><sup>0.550</sup> -1733°, [ $\alpha$ ]<sub>D<sup>20</sup></sub><sup>0.550</sup> -1007° in AcOH), but is readily racemised by various reagents. (I) is probably as shown. Opsopyrrole and *p*-C<sub>6</sub>H<sub>4</sub>Me-N<sub>2</sub>Cl give a monazo-dye, m.p. 238° (*hydrochloride*, m.p. 208°; *hydrobromide*, m.p. 185°; *picrate*, m.p. 182°).



R. S. C.

Preparation and tinctorial properties of benzoxazole dyes. V. J. MIKESKA and M. T. BOGERT (J. Amer. Chem. Soc., 1935, 57, 2513—2517).—A series of substantive cotton dyes are prepared from diazotised 4-phenyl-1-*p*-aminophenylbenzoxazole (I) [and its  $\text{SO}_3\text{H}$  derivative (II)] and 4-amino-1 : 6-diphenylbenzoxazole (III) (and its  $\text{SO}_3\text{H}$  derivative) by coupling with  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ ,  $\text{PhOH}$ ,  $m\text{-C}_6\text{H}_4(\text{OH})_2$ , and  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ ; those prepared from (I) are more substantive than those from (III). The dyes resemble, but give lighter shades than, the corresponding derivatives from dehydrothio-*p*-toluidine (1.) (A., 1927, 679). Absorption curves for "ingrain red" [from (IV) and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ ] and "oxazole red" [from (II) and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ ] are given; the former shows wider absorption. Oxidation (aq.  $\text{EtOH-NaOCl}$  at  $0-10^\circ$ ) of (I) gives  $\text{pp}'$ -di-(4-phenyl-1-benzoxazolyl)azobenzene, decomp.  $>300^\circ$  [ $(\text{SO}_3\text{Na})_2$  derivative (V);  $(\text{SO}_3\text{Na})_4$  derivative, prepared by similar oxidation of 4-phenyl-1-*p*-aminophenylbenzoxazolesulphonic acid]. Similar "chloramine yellow" dyes are prepared from 1-*p*-aminophenyl-4-methylbenzoxazole [resembles (V)] and (III) [inferior to (V)]. Fabrics dyed directly retain (after 5 years) a better colour than those dyed by the "ingrain" process.

Н. 1

Pyridine and quinoline derivatives of dibenzfuran and their physiological properties. W. H. KIRKPATRICK and H. GILMAN (Proc. Iowa Acad. Sci., 1934, 41, 172).—The physiological properties of a no. of amino- and substituted amino-dibenzfurans and their amino reduction products have been studied. In many cases the  $\text{NH}_2$ -compounds undergo cyclisation, yielding pyridinodibenzfurans. CH. ABS. (r)

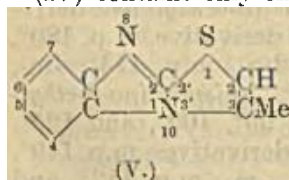
Alkyl derivatives of aryl-substituted thiazolones. J. A. DAVIS and F. B. DAINS (J. Amer.

Chem. Soc. 1935, 57, 2627—2630; cf. A., 1933, 1174).—Alkylation (alkyl halide on Na salt in EtOH) of 2-arylamino-4-thiazolidones [prepared (a) from  $\text{NHAr}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  and KCNS in EtOH, or (b) from  $\text{NHAr}\cdot\text{CS}\cdot\text{NH}_2$  and equimol. amounts of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  and  $\text{C}_5\text{H}_5\text{N}$  in EtOH] gives generally a mixture of a little 2-arylimino-3-alkyl-4-thiazolidone (I) [the 5-benzylidene derivatives of which are hydrolysed (EtOH—conc. HCl) to  $\text{NH}_2\text{Ar}$  and 2:4-diketo-5-benzylidene-3-alkyltetrahydrothiazoles] and much 2-N-alkylarylamino-4-thiazolidone (II) (the 5-benzylidene derivatives are hydrolysed to  $\text{NHArAlk}$  and 2:4-diketo-5-benzylidenetetrahydrothiazoles). Certain exceptions are noted. (I) are also synthesised from  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  and  $\text{NHAr}\cdot\text{CS}\cdot\text{NHalk}$ . The 3-aryl-2-ethylimino-4-thiazolidones of Beckurts and Frerich (A., 1916, i, 744) are (II). The following are described: (a) substituted thiocarbamides: *p*-cymyl-, m.p. 152°; *N*-o-, m.p. 88°, and -*p*-, m.p. 112°, -ethoxyphenyl-, *N*-*ψ*-cumyl-, m.p. 138°; *N*-o-, m.p. 77°, -*m*-, m.p. 112°, and -*p*-, m.p. 147°, -anisyl-, *N*-*p*-cymyl-, m.p. 126°, *N*-*p*-iodophenyl-, m.p. 147·5°, and *N*-2:4-di-iodophenyl-, m.p. 164°, -*N'*-ethyl-, *N*-*ψ*-cumyl-, m.p. 179°, and *N*-*p*-iodophenyl-, m.p. 171°, -*N'*-methyl-, *N*-*p*-iodophenyl-*N'*-amyl-, m.p. 130°, and -*N'*-benzyl-, m.p. 149°; (b) substituted 4-thiazolidones: 2-*p*-ethoxyanilo-3-ethyl-, m.p. 93° (5-benzylidene derivative, m.p. 135°); 2-*o*-ethoxyanilino-, m.p. 172°; 5-benzylidene derivative, m.p. 210°, of 2-*N*-ethyl-*p*-ethoxyanilino-; 2-*N*-ethyl-*o*-ethoxyanilino-, m.p. 99° (5-benzylidene derivative, m.p. 164°); 2-*o*-ethoxyanilo-3-ethyl-, m.p. 79° (5-benzylidene derivative, m.p. 113°); 2-*ψ*-cumylimino-3-methyl-, m.p. 91° (5-benzylidene derivative, m.p. 136°), and -3-ethyl-, m.p. 77° (5-benzylidene derivative, m.p. 141°); 5-benzylidene derivative, m.p. 180°, of 2-*N*-ethyl-*ψ*-cumylamino-; 2-*o*-, m.p. 114°, -*m*-, m.p. 65—66°, and -*p*-, m.p. 83°, -anisylimino-3-ethyl- (5-benzylidene derivatives, m.p. 99°, 109°, and 125°, respectively); the 5-benzylidene derivatives, m.p. 149°, 135°, and 198°, of 2-*N*-ethyl-*o*-, -*m*-, m.p. 112°, and -*p*-anisidino-, respectively; 2-*m*-anisidino-, m.p. 165°; 2-*p*-cymylamino-, m.p. 174°; 2-*N*-ethyl-*p*-cymylamino-, m.p. 85° (5-benzylidene derivative, m.p. 169°); 2-*p*-cymylimino-3-ethyl-, m.p. 64° (5-benzylidene derivative, m.p. 73°); 2-2':4'-di-iodoanilino-, m.p. 233°; 2-2':4'-di-iodoanilo-3-ethyl-, m.p. 173° (5-benzylidene derivative, m.p. 210—211°); 2-*p*-iodoanilino-, m.p. 226°; 2-*N*-methyl-, m.p. 207°, -ethyl-, m.p. 116°, -amyl-, m.p. 116°, and -benzyl-, m.p. 176°, -*p*-iodoanilino- (5-benzylidene derivatives, m.p. 246°, 231°, 202°, and 221°, respectively); 2-*p*-iodoanilo-3-methyl-, m.p. 152°, -ethyl-, m.p. 103°, -amyl-, m.p. 57°, and -benzyl-, m.p. 137° (5-benzylidene derivatives, m.p. 167°, 172°, 105°, and 162°, respectively); 2-anilino-3-amyl-, an oil (5-benzylidene derivative, m.p. 78°); 2-benzylimino-3-benzyl-, m.p. 74° (5-benzylidene derivative, m.p. 109°); (c) miscellaneous: chloroacet-2-*p*-cymidide, m.p. 85°, and -2:4-di-iodoanilide, m.p. 153°; *p*-nitrobenz-*o*-phenetidide, m.p. 155°; benzenesulphon-*N*-ethyl-*o*-phenetidide, m.p. 61°, -*N*-ethyl-*o*-anisidide, m.p. 90°, and -*N*-methyl-*p*-iodoanilide, m.p. 78°; *N'*-phenyl-*N*-*p*-ethoxyphenyl-*N*-ethyl-, m.p. 93°, and *N*-*p*-tolyl-*N'*-*o*-ethoxyphenyl-, m.p. 172°, -carbamides; 2:4-diketo-5-benzylidene-3-amyl-, m.p. 74°, and -3-benzyl-, m.p. 134°, -tetrahydrothiazoles.

H. B.

H. B.

**Aneurine. II. Synthesis of N-arylthiazolium salts; details in the constitution of aneurine and thiochrome.** A. R. TODD, F. BERGEL, and KARIMULLAH (Ber., 1936, 69, [B], 217—223).— $\text{CH}_2\text{PhBr}$  and 2:4-dimethylthiazole at  $100^\circ$  give 3-benzyl-2:4-dimethylthiazolium bromide, m.p.  $173^\circ$ . Addition of thioacetmethylamide to  $\text{CH}_2\text{Cl}\cdot\text{COMe}$  at  $80^\circ$  yields 2:3:4-trimethylthiazolium chloride, m.p.  $235^\circ$  (decomp.). Similarly thioacetanilide and  $\text{CH}_2\text{Cl}\cdot\text{COMe}$  at  $100^\circ$  afford 3-phenyl-2:4-dimethylthiazolium chloride (I), m.p.  $184^\circ$  (decomp. in sealed capillary; corresponding picrate, m.p.  $115^\circ$ ). If reaction is effected at  $15\text{--}20^\circ$ , S-acetylthioacetanilide hydrochloride (II), m.p.  $112^\circ$  [corresponding perchlorate, m.p.  $130^\circ$ , unstable free base and its semicarbazone, m.p.  $230^\circ$  (decomp.)], is formed. It passes at  $100^\circ$  into (I) and is hydrolysed by boiling  $\text{H}_2\text{O}$  or dil. acid to  $\text{NH}_3\text{Ph}$ ,  $\text{NHAcPh}$ , and a substance (III), (?)  $\text{SH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{COMe}$  [semicarbazone,  $\text{C}_7\text{H}_{13}\text{ON}_3\text{S}_2$ , m.p.  $213^\circ$  (decomp.)]. 3-o-Tolyl-2:4-dimethylthiazolium chloride, perchlorate, m.p.  $172^\circ$ , picrate, m.p.  $150^\circ$ , and iodide, m.p.  $217\text{--}218^\circ$  (decomp.), are obtained analogously. S-Acetylthioacet-o-toluidide hydrochloride, m.p.  $125^\circ$ , is more stable than (II); its hydrolysis leads to  $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ ,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ , and (III).  $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  is converted by cautious treatment with  $\text{P}_2\text{S}_5$  into o-nitrothioacetanilide, m.p.  $114^\circ$ , whence 3-o-nitrophenyl-2:4-dimethylthiazolium perchlorate, m.p.  $205^\circ$ . Determination of C-alkyl by oxidation with  $\text{CrO}_3$  of thiazolium, pyrimidine, and allied compounds shows that Williams' pyrimidine compound from aneurine (IV) contains only one alkyl; (IV) and thiochrome



each contains two alkyls, the higher val. indicated (Kuhn) for (IV) being observed with other compounds which lose CMe quantitatively.  $\text{o-C}_6\text{H}_3(\text{NH}_2)_2$  and  $\text{CS}(\text{NH}_2)_2$  yield thiobenziminazoline, m.p.  $295\text{--}300^\circ$ , converted by  $\text{CH}_2\text{Cl}\cdot\text{COMe}$  into 3-methylthiazolo-2':3':2:1-glyoxaline (V), m.p.  $164\text{--}165^\circ$ .

H. W.

**1-Amino-5-ethoxy-2-methylbenzthiazolium hydroxide and its derivatives.** O. BEHAGHEL and E. SCHNEIDER (Ber., 1936, 69, [B], 88—98).—Repetition of the work of Hunter *et al.* (A., 1930, 1452) shows that *p*-ethoxyphenylthiocarbamide is transformed by an excess of Br in  $\text{CHCl}_3$  into bromo-1-amino-5-ethoxybenzthiazole (I), m.p.  $196^\circ$ , and by the calc. quantity into 1-amino-5-ethoxybenzthiazole, m.p.  $162^\circ$ . Treatment of (I) with  $\text{Me}_2\text{SO}_4$  yields the corresponding methosulphate, converted by NaOH into bromo-1-imino-5-ethoxy-2-methylbenzthiazoline, m.p.  $144^\circ$ , also derived from *as-p*-ethoxyphenylmethylthiocarbamide, m.p.  $139^\circ$  (prepared from *N*-methyl-*p*-phenetidine hydrochloride and  $\text{NH}_4\text{CNS}$ ), and Br in  $\text{CHCl}_3$ . *N*-Methyl-*p*-phenetidine and KCNS in 95% AcOH are transformed by Br in warm AcOH into 1-amino-5-ethoxy-2-methylbenzthiazolium bromide, decomp.  $295^\circ$ , whereas in MeOAc the corresponding thiocyanate, m.p.  $187^\circ$ , is produced. Treatment of the salts with cold  $\text{Na}_2\text{CO}_3$  affords 1-amino-5-ethoxy-2-methylbenzthiazolium hydroxide (II), m.p. about  $64^\circ$ , which readily loses  $\text{H}_2\text{O}$  when kept over  $\text{H}_2\text{SO}_4$

giving 1-imino-5-ethoxy-2-methylbenzthiazoline (III), m.p.  $98^\circ$ . 1-Amino-5-ethoxybenzthiazole (III) is transformed by  $\text{Me}_2\text{SO}_4$  at  $100^\circ$  into 1-amino-5-ethoxy-2-methylbenzthiazolium methosulphate, m.p.  $187\text{--}189^\circ$ , converted by NaOH into 1-methylimino-5-ethoxy-2-methylbenzthiazoline, m.p.  $86^\circ$ . 1-Amino-5-ethoxy-2-methylbenzthiazolium iodide, m.p.  $245^\circ$ , results from (II) and HI or from (IV) and MeI in MeOH at  $100^\circ$ , whilst the corresponding chloride, m.p.  $308^\circ$  (decomp.), is obtained from (II) and boiling HCl. The presence of NH in (III) is established by the isolation of 1-nitrosoimino-5-ethoxy-2-methylbenzthiazoline, which evolves  $\text{N}_2$  quantitatively when boiled with xylene and gives 5-ethoxy-2-methylbenzthiazolone, m.p.  $87^\circ$ . (III) is converted by boiling  $\text{Ac}_2\text{O}$ , BzCl, or valeric anhydride, respectively, into 1-acetimido-, m.p.  $172^\circ$ , 1-benzimido-, m.p.  $191^\circ$ , and 1-valerimido-, m.p.  $119^\circ$ , -5-ethoxy-2-methylbenzthiazoline, which essentially yield salts with mineral acids. Bromo-1-amino-5-ethoxy-2-methylbenzthiazolium methosulphate is transformed by  $\text{Me}_2\text{SO}_4$  and NaOH into bromo-1-methylimino-5-ethoxy-2-methylbenzthiazoline, m.p.  $158^\circ$ , transformed by  $\text{NaNO}_2$  in AcOH and subsequent treatment of the product with boiling xylene into bromo-5-ethoxy-2-methylbenzthiazolone, m.p.  $126^\circ$ . The benzthiazolium hydroxides and benzthiazolines have identical absorption spectra in MeOH possibly owing to conversion of the former into the latter. The absorption spectra of 2-methylated benzthiazole, benzoxazole, benz-selenazole, and benziminazole are compared. *p*-Chlorophenyl-thiolacetic and -selenolacetic acid have closely similar absorption spectra which differ considerably from that of *p*-chlorophenoxyacetic acid.

H. W.

**Compounds for treatment of textiles [benzthiazoles].**—See B., 1936, 92.

**Cyanine dye series. II. Carbocyanines with substituents in the three-carbon chain.** L. G. S. BROOKER and F. L. WHITE (J. Amer. Chem. Soc., 1935, 57, 2480—2488).—Substituted thiocarbocyanine iodides,  $\text{C}_6\text{H}_4\text{--}\langle\text{S--NR}\rangle\text{--C}\cdot\text{CH}\cdot\text{CR}'\cdot\text{CH}\cdot\text{C}\langle\text{S--NRI}\rangle\text{--C}_6\text{H}_4$ ,

are prepared from various ortho-esters (I), *e.g.*,  $\text{CR}'(\text{OMe})_3$  ( $\text{R}'=\text{H}$ , Me, Et, Pr, Bu, amyl,  $\text{CH}_2\text{Ph}$ ,  $\text{OPh}\cdot\text{CH}_2$ , Ph) and 1-methylbenzthiazole alkiodides or alk-*p*-toluenesulphonates (followed by aq. KI) in boiling  $\text{C}_5\text{H}_5\text{N}$ . The following are described: 2:2'-diallyl-, m.p.  $264\text{--}266^\circ$  (decomp.); 2:2'-di-*n*-propyl-, m.p.  $296\text{--}297^\circ$  (decomp.); 2:2'-di-*n*-butyl-, m.p.  $275\text{--}277^\circ$  (decomp.); 8-methyl-2:2'-diallyl-, m.p.  $267\text{--}268^\circ$  (decomp.), -2:2'-di-*n*-propyl-, m.p.  $295\text{--}296^\circ$  (decomp.), and -2:2'-di-*n*-butyl-, m.p.  $236\text{--}237^\circ$  (decomp.); 2:2'-dimethyl-8-ethyl-, m.p.  $286\text{--}287^\circ$  (decomp.); 2:8:2'-triethyl-, m.p.  $236\text{--}237^\circ$  (decomp.); 8-ethyl-2:2'-diallyl-, m.p.  $214\text{--}216^\circ$  (decomp.), -2:2'-di-*n*-propyl-, m.p.  $248\text{--}250^\circ$  (decomp.), and -2:2'-di-*n*-butyl-, m.p.  $241\text{--}243^\circ$  (decomp.); 2:2'-dimethyl-8-*n*-propyl-, m.p.  $268\text{--}269^\circ$  (decomp.), -8-*n*-butyl-, m.p.  $168\text{--}169^\circ$  (decomp.), -8-*n*-amyl-, m.p.  $217\text{--}219^\circ$  (decomp.), -8-isoamyl-, m.p.  $241\text{--}242^\circ$  (decomp.), -8-benzyl-, m.p.  $288\text{--}289^\circ$  (decomp.), -8-phenoxyethyl- (bromide), m.p.  $255\text{--}257^\circ$  (decomp.), and -8-phenyl-, m.p.  $275\text{--}277^\circ$  (decomp.); 2:2'-diethyl-8-*n*-propyl-, m.p.  $246\text{--}$

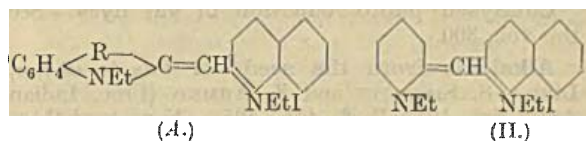


248° (decomp.), -8-*n*-butyl-, m.p. 233—234° (decomp.), -8-*n*-amyl-, m.p. 237—238° (decomp.), -8-isoamyl-, m.p. 219—220° (decomp.), -8-benzyl-, m.p. 242—243° (decomp.), -8-phenoxymethyl-, m.p. 202—204° (decomp.), and -8-phenyl-, m.p. 300—301° (decomp.); 8-benzyl-, m.p. 225—227° (decomp.), and 8-phenoxymethyl-, m.p. 211—213° (decomp.), -2:2'-diallyl-. In the above series introduction of 8-Me (for H) causes a shift in the absorption max. (in MeOH) of about 150 Å. towards the blue; replacement of 8-Me by Et (or higher alkyl) causes a shift of about 50 Å. back towards the red. The following substituted 5:6:5':6'-dibenzthiacarbocyanine bromides are similarly prepared from (I) and 1-methyl- $\alpha$ -naphthothiazole meth-*p*-toluenesulphonate, m.p. 232—233°, or etho-*p*-toluenesulphonate followed by aq. KBr: 2:2'-dimethyl-, m.p. 285° (decomp.); 2:2'-diethyl-, m.p. 280° (lit. 274°) (decomp.); 2:8:2'-trimethyl-, m.p. 278—281° (decomp.); 8-methyl-2:2'-diethyl-, m.p. 261° (decomp.); 2:2'-dimethyl-8-ethyl-, m.p. 299° (decomp.); 2:8:2'-triethyl-, m.p. 296° (decomp.); 8-phenyl-2:2'-dimethyl-, m.p. 308—310° (decomp.), and -2:2'-diethyl-, m.p. 296° (decomp.). 2:2'-Dimethyl-, m.p. 237° (decomp.), 2:8:2'-trimethyl-, m.p. 240—241° (decomp.), 2:2'-dimethyl-8-ethyl-, m.p. 230° (decomp.), 2:8:2'-triethyl-, m.p. 247° (decomp.), and 8-phenyl-2:2'-dimethyl-, m.p. 242—244° (decomp.), and -2:2'-diethyl-, m.p. 252° (decomp.), -3:4:3':4'-dibenzthiacarbocyanine bromides are similarly obtained from 2-methyl- $\beta$ -naphthothiazole meth-*p*-toluenesulphonate, m.p. 189—190°, or the etho-*p*-toluenesulphonate. 1-Methylbenzelenazole meth- and etho-*p*-toluenesulphonates lead to 2:8:2'-trimethylselenacarbocyanine bromide, m.p. 290—291° (decomp.), and 2:2'-dimethyl-8-ethyl-, m.p. 271—272° (decomp.), 2:8:2'-triethyl-, m.p. 146—148°, and 8-phenyl-2:2'-dimethyl-, m.p. 271—272° (decomp.), and -2:2'-diethyl-, m.p. 280—281° (decomp.), -selenacarbocyanine iodides. 2:8:2'-Trimethyl-, m.p. 290—292° (decomp.), 2:2'-dimethyl-8-ethyl-, m.p. 280—282° (decomp.), and 2:8:2'-triethyl-, m.p. 269—270° (decomp.), -oxacarbocyanine iodides, prepared from the appropriate benzoxazole salts and (I) in  $C_5H_5N$ -NEt<sub>3</sub>, are sensitizers for the green and blue-green. Absorption curves for many of the dyes are given. The following are new: *Me* ortho-propionate, b.p. 126—128°, -*n*-butyrate, b.p. 145—147°, -*n*-valerate, b.p. 167—170°, -*n*-hexoate, b.p. 187—190°, and -isohexanoate, b.p. 178—181°; *Et* ortho-phenoxyacetate, b.p. 99—100°/1.5 mm., and -benzoate, b.p. 239.5—240.5°; 1-methylbenzthiazole *n*-propyl iodide, m.p. 173—175°, -*n*-butyl iodide, m.p. 186—187°, allyl iodide, m.p. 192—193°, and meth-*p*-toluenesulphonate, m.p. 183.5—184.5°.

H. B.

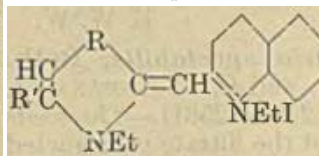
**Cyanine dye series. III. Improvements in the 2'-cyanine condensation.** L. G. S. BROOKER and G. H. KEYES. IV. [Thiazolo-2'-cyanines and related compounds.] L. G. S. BROOKER, G. H. KEYES, and F. L. WHITE (J. Amer. Chem. Soc., 1935, 57, 2488—2492, 2492—2496).—III. 2:1'-Diethyl-oxa-2'-cyanine iodide (A, R=O), m.p. 290—292° (decomp.), obtained in 43—56% yield from 2-iodoquinoline ethiodide (I) and 1-methylbenzoxazole ethiodide in EtOH-NEt<sub>3</sub>, is best prepared using NPhEt<sub>2</sub> (at 100°)

as the condensing agent; EtOH-KOH (cf. Hamer, A., 1928, 307) leads to a 3% yield. The following are prepared in yields of 10—87% usually in Pr<sup>4</sup>OH-NEt<sub>3</sub>: 2:1'-diethylseleno-2'-cyanine iodide (A, R=Se), m.p. 280—282° (decomp.), from (I) and 1-methylbenzelenazole ethiodide; 1:1'-diethyl-2-pyridyl-2'-cyanine iodide (II), m.p. 237—239° (decomp.), from (I) and 2-methylpyridine ethiodide (III) or from 2-iodopyridine ethiodide (IV) and 2-methylquinoline ethiodide (thus affording further evidence of the virtual tautomerism of the cyanine dyes); 1:1'-diethyl-2-pyridyl-4'-cyanine iodide, m.p. 194—196° (decomp.), from (IV) and 4-methylquinoline ethiodide;



1:1'-diethyl-4-pyridyl-2'-cyanine perchlorate, m.p. 211—214° (decomp.), from (I) and 4-methylpyridine etho-*p*-toluenesulphonate (V) followed by aq. KClO<sub>4</sub>; 1:1'-dimethyl-2:2'-pyridocyanine iodide, m.p. 315—317° (decomp.), from 2-iodopyridine methiodide (VI) and 2-methylpyridine methiodide; 1:1'-diethyl-2:2'-pyridocyanine iodide (VII), m.p. 237—239° (decomp.), from (III) and (IV); 1:1'-dimethyl-2:4'-pyridocyanine iodide, m.p. 214—217° (decomp.), from (VI) and 4-methylpyridine meth-*p*-toluenesulphonate; 1:1'-diethyl-2:4'-pyridocyanine iodide, m.p. 163—166° (decomp.), from (IV) and (V). Absorption curves for the above dyes are given. All the compounds containing the  $C_5H_5N$  ring show sensitising action.

IV. 2-Methylthiazole ethiodide, m.p. 195—197°, and 2-iodoquinoline ethiodide (I) in EtOH-NEt<sub>3</sub> give 3:1'-diethylthiazolo-2'-cyanine iodide (B, R=S; R'=H), m.p. 267—269° (decomp.); the 4-Me, m.p. 255—257° (decomp.), and 4-Ph, m.p. 256—258° (decomp.),



derivatives of this are similarly formed from (I) and 2:4-dimethylthiazole ethiodide and 4-phenyl-2-methylthiazole ethiodide, m.p. 175.5—176.5°, respectively.

Similarly, (I) with 2:4-dimethyl- (II) and 4-phenyl-2-methyl-oxazole etho-*p*-toluenesulphonates affords 4-methyl- (B, R=O; R'=Me), m.p. 255—258° (decomp.), and 4-phenyl-, m.p. 262—264° (decomp.), -3:1'-diethyloxazolo-2'-cyanine iodide, respectively, whilst (I) and the ethiodide, m.p. 157—158°, of 2:4-dimethylselenazole, b.p. 54—55°/12 mm. [from selenoacetamide (modified prep.) and COMe·CH<sub>2</sub>Cl], give 4-methyl-3:1'-diethylselenazolo-2'-cyanine iodide (B, R=Se; R'=Me), m.p. 259—260° (decomp.). 2-Iodo- $\beta$ -naphthquinoline ethiodide and the above S, O, and Se salts [except (II)] afford 3:1'-diethyl-, m.p. 268—270° (decomp.), 4-methyl-3:1'-diethyl-, m.p. 278—280° (decomp.), and 4-phenyl-3:1'-diethyl-, m.p. 274—276° (decomp.), -5':6'-benzthiazolo-, 4-phenyl-3:1'-diethyl-5':6'-benzoxazolo-, m.p. 279—282° (decomp.), and 4-methyl-3:1'-diethyl-5':6'-benzelenazolo-, m.p. 275—277° (decomp.), -2'-cyanine iodides, respectively. 3:1'-Diethyl-, m.p. 260—262°

(decomp.), 4-methyl-3:1'-diethyl-, m.p. 255—257° (decomp.), and 4-phenyl-3:1'-diethyl-, m.p. 247—249° (decomp.), -thiazolo-, and 4-methyl-3:1'-diethylselenazolo-, m.p. 232—233° (decomp.), -2'-pyridocyanine iodides are prepared from 2-iodopyridine ethiodide and the above S and Se salts. All the above dyes are sensitizers; absorption spectra are given.

H. B.

**Sensitisation of photographic emulsions.**—See B., 1936, 125.

**Manufacture of unsymmetrical heptacarbo-cyanine and hexamethine dyes.**—See B., 1936, 93.

**Catalysed photo-reduction of vat dyes.**—See this vol., 300.

**Alkaloids from the seeds of *Cassia absus*, Linn.** S. SIDDIQUI and Z. AHMED (Proc. Indian Acad. Sci., 1935, 2, A, 421—425).—Kernels of these seeds extracted with MeOH-HCl give a product from which the quaternary alkaloids *chaksine* (I) and *iso-chaksine* (II) are separated through their iodides. *Chaksine iodide* (III), m.p. 168° (decomp.), is converted into the (impure) base,  $[\alpha]_D^{25} + 32^\circ$  in EtOH, which absorbs CO<sub>2</sub> from the air to give *chaksine H carbonate*, C<sub>12</sub>H<sub>20</sub>ON<sub>3</sub>·HCO<sub>3</sub>·0.5H<sub>2</sub>O, m.p. 167—169° (decomp.). *Chaksine sulphate* (IV), m.p. 316° (decomp.), and *picrate*, m.p. 239—240° (decomp.), are prepared; the *platinichloride*, (C<sub>12</sub>H<sub>20</sub>ON<sub>3</sub>·HCl)<sub>2</sub>PtCl<sub>6</sub>, m.p. 232° (decomp.), loses HCl at 120°. *isoChaksine iodide* gives (II); this is also obtained by treating (IV) with Ba(OH)<sub>2</sub>, and its *carbonate*, (C<sub>12</sub>H<sub>20</sub>ON<sub>3</sub>)<sub>2</sub>CO<sub>3</sub>, m.p. 128° (decomp.), by heating *chaksine H carbonate* in EtOH. *isoChaksine chloride* loses H<sub>2</sub>O at 90° to form a *product*, m.p. 250—252°; the *picrate* has m.p. 184°; the *platinichloride*, (C<sub>12</sub>H<sub>20</sub>ON<sub>3</sub>·HCl)<sub>2</sub>PtCl<sub>6</sub>, m.p. 172° (decomp.), is stable at 120°. (III) gives no evidence of containing OMe or N-Me; (I) and (II) appear to be quaternary bases, with a second N feebly basic. (IV) is a general depressant (heart, respiration, nerves); lethal dose for frogs, 0.1 g. per kg.

E. W. W.

**Alkaloid from *Crotalaria spectabilis*, Roth.** W. M. NEAL, L. L. RUSOFF, and C. F. AHMANN (J. Amer. Chem. Soc., 1935, 57, 2560—2561).—The seeds are soaked in 5% aq. NH<sub>3</sub> and the filtrate is extracted with CHCl<sub>3</sub>; *monocrotaline* (I), probably C<sub>16</sub>H<sub>26</sub>O<sub>6</sub>N, m.p. 196—197°, is thus obtained. (I) is the toxic principle of *C. spectabilis*; pharmacological data are given.

H. B.

**Alkaloid of *Stemona sessilifolia*.** H. SCHILD (Ber., 1936, 69, [B], 74—80).—The isolation from *S. sessilifolia* is described of an alkaloid (I), m.p. 86—87°, b.p. about 220°/0.0006 mm.,  $[\alpha]_D^{20} - 47.1^\circ$  in CHCl<sub>3</sub>, analyses of which together with those of its *perchlorate*, m.p. 243°, and *methiodide monohydrate* (II), decomp. 230—233°, agree most closely with the formula C<sub>22</sub>H<sub>33</sub>O<sub>2</sub>N. (II) is transformed by AgCl into the *methochloride dihydrate*, m.p. 169°, and by Ag<sub>2</sub>O into the *betaine*, C<sub>23</sub>H<sub>37</sub>O<sub>3</sub>N·H<sub>2</sub>O, decomp. 227—229°, which re-forms (II) when heated with HI. (I) is a *tert.* base which does not evolve CH<sub>4</sub> with MgMeI. 2 O are present in a lactone group, since it dissolves in 1 mol. of hot KOH. Further groups sensitive to alkali are not present. Catalytic hydrogenation of

(I) in neutral solution yields the *substance*, m.p. 118—120°,  $[\alpha]_D^{20} - 10.8^\circ$  in CHCl<sub>3</sub>, whereas in acid solution a *compound*, C<sub>22</sub>H<sub>35</sub>O<sub>4</sub>N, m.p. 134,  $[\alpha]_D^{20} - 13.2^\circ$  in CHCl<sub>3</sub> (*hydrochloride*), is produced. Since (I) does not give an ultra-violet absorption spectrum above 234—313 mμ the presence in it of an aromatic ring is excluded. The presence of a pyrrolidine ring is possible since in conjunction with I, MeI, or EtI it is oxidised by air to a neutral *substance*, C<sub>22</sub>H<sub>29</sub>O<sub>4</sub>N, m.p. 186°, which retains the lactone ring, readily gives the Ehrlich pyrrole reaction, and has a characteristic ultra-violet absorption spectrum. Electrolytic reduction of (I) yields the di-deoxo-base, C<sub>22</sub>H<sub>37</sub>O<sub>2</sub>N (*perchlorate*, m.p. 244—245°; *methiodide*, m.p. 261—262°), which does not contain a lactone group; the second replaced O is attributed to the presence of non-reactive CO. (I) is very stable towards HNO<sub>3</sub> and CrO<sub>3</sub> but is oxidised by KMnO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> to *l*-methylsuccinic acid, m.p. 108—109°,  $[\alpha]_D^{20} - 9.3^\circ$  in CHCl<sub>3</sub>, and by alkaline KMnO<sub>4</sub> to a *substance*, C<sub>17</sub>H<sub>25</sub>O<sub>3</sub>N, m.p. 134—135° after softening at 130°.

H. W.

**Conessine series. I. Isomerisation of conessine and its nor-bases.** S. SIDDIQUI (Proc. Indian Acad. Sci., 1935, 2, A, 426—437; cf. A., 1934, 787).—Conessine dissolved in cold conc. H<sub>2</sub>SO<sub>4</sub>, poured on to ice, and treated with NaOH, AcOH, and KI, gives, with oxidation products, the *hydriodide*, m.p. 325—326° (decomp.), of *isoconessine* (I), C<sub>24</sub>H<sub>40</sub>N<sub>2</sub>, b.p. 239—241°/3 mm.,  $[\alpha]_D^{25} + 97^\circ$  in EtOH [*hydrochloride* (+2H<sub>2</sub>O), m.p. 318° (decomp.),  $[\alpha]_D^{25} + 72^\circ$ ; *platinichloride*, m.p. 271—273°; *aurichloride*, m.p. 293—295° (decomp.); *picrate*, m.p. 240—242° (decomp.); *hydrobromide* (II), m.p. 318—322° (decomp.); *dimethiodide*, m.p. 316—318° (decomp.)]. (I) with Br in CHCl<sub>3</sub> or AcOH yields (II) and an oily *product*. With H<sub>2</sub>SO<sub>4</sub>, *isoconessimine* similarly isomerises, to *isonorisconessimine* (III), C<sub>23</sub>H<sub>38</sub>N<sub>2</sub>,  $[\alpha]_D^{25} + 101^\circ$  in EtOH [*hydriodide*, m.p. 289° (decomp.); *hydrochloride*, m.p. 335° (decomp.),  $[\alpha]_D^{25} + 72.80^\circ$  in H<sub>2</sub>O; *picrate*, m.p. 166°; *platinichloride*, m.p. 290—292° (decomp.)]. (III) with MeI gives an ill-defined *product*, m.p. 280—300°; with CH<sub>2</sub>O-HCO<sub>2</sub>H followed by KI it furnishes the *hydriodide* of (I). (III) in HCl with NaNO<sub>2</sub> forms a *NO*-derivative (*hydrochloride*, m.p. 282—284°). *Conimine* in H<sub>2</sub>SO<sub>4</sub> gives rise to *isoconimine* (IV), C<sub>22</sub>H<sub>36</sub>N<sub>2</sub>,  $[\alpha]_D^{25} + 89^\circ$  in EtOH [*hydriodide*, m.p. 332° (decomp.); *carbonate*; *hydrochloride*, m.p. 335—336° (decomp.); *picrate*, m.p. 135°; *platinichloride*, m.p. 285—288° (decomp.); (*NO*)<sub>2</sub>, m.p. 123—125°, and *Ac*, m.p. 139—140° [*bromination product*, m.p. 185—186° (decomp.)], derivatives. The Me<sub>2</sub> derivative of (I) (CH<sub>2</sub>O-HCO<sub>2</sub>H) is identical with (I). *isoConessine* is about three times as active (respiration of frogs) as conessine.

E. W. W.

**Alkaloids of *Erythrophloeum guineense*.** G. DALMA (Annali Chim. Appl., 1935, 25, 569—571). From the bark of the West African red-water tree were isolated *cassaine*, C<sub>24</sub>H<sub>36</sub>O<sub>4</sub>N, m.p. 141,  $[\alpha]_D^{20} - 103^\circ$  in EtOH, *cassaidine*, C<sub>24</sub>H<sub>43</sub>O<sub>5</sub>N, m.p. 131°, *norcassaidine*, C<sub>23</sub>H<sub>41</sub>O<sub>5</sub>N, m.p. 131°, and *omofteit*, C<sub>56</sub>H<sub>90</sub>O<sub>9</sub>N<sub>2</sub>. Colour reactions are given.

O H

**Reduction in morphine series. VII. *ψ*-Codemone.** R. E. LUTZ and L. SMALL (J. Amer. Chem.



Soc., 1935, 57, 2651—2656).—The alicyclic double linking in  $\psi$ -codeinone (I) [*hydrochloride* (+H<sub>2</sub>O) (II), m.p. 201—203° (decomp.)] is considered to be between C6 and C7 [as suggested by Gulland and Robinson (A., 1926, 83)] since treatment with an excess of semicarbazide gives (as with  $\alpha\beta$ -unsaturated ketones) *semicarbazinodihydro- $\psi$ -codeinonesemicarbazone* (+H<sub>2</sub>O), m.p. 225—227° (uncorr.; decomp.). Condensation of (I), which is prepared by oxidation (method: Knorr and Horlein, A., 1907, i, 547) of  $\psi$ -codeine or *allo- $\psi$ -codeine*, with PhCHO does not indicate the  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  group since codeine undergoes the same reaction. Reduction (H<sub>2</sub>, PtO<sub>2</sub>, AcOH) of (II) affords the non-phenolic *dihydro- $\psi$ -codeinone* (III), m.p. 113°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +37° in EtOH [*hydrochloride* (+H<sub>2</sub>O), m.p. 172—173°; *hydriodide*, m.p. 250—255° (decomp.); *H tartrate* (?), m.p. 199—200° (uncorr.); *oxime*, m.p. 244—245°], reduced (Na, EtOH) to *dihydro- $\psi$ -codeine-A* (A., 1933, 170) and converted by Ac<sub>2</sub>O-NaOAc into *de-N-acetyldihydro- $\psi$ -codeinone enol acetate*, m.p. 191.5—192°. Reduction (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) of (I) gives the phenolic *tetrahydro- $\psi$ -codeinone* (+0.5H<sub>2</sub>O) (IV), m.p. 137—138.5°, m.p. (anhyd.) 170—171°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +8° in EtOH [*hydrochloride* (+2H<sub>2</sub>O), m.p. 165—166° (decomp.); *hydriodide* (+H<sub>2</sub>O), m.p. 154—155°; *Ac derivative*; *oxime*, m.p. 218—219° (lit. 137°)], which differs considerably from Hill's description (Diss., Frankfurt, 1925). (IV) does not react with CH<sub>2</sub>N<sub>2</sub>; it is reduced, as is (I), by Na and EtOH in N<sub>2</sub> to *tetrahydro- $\psi$ -codeine*. Demethylation (48% HBr) of (III) gives *dihydroisomorphinone* (V), m.p. 198°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +46° in EtOH. (I) and MgMeI afford the phenolic *methylidihydro- $\psi$ -codeinone* (VI), m.p. 213.5—214.5°, which could not be reduced (various methods); no oxime or semicarbazone could be prepared. (VI) may be formed by 1:2- or 1:4-addition involving fission of the  $\cdot\text{O}\cdot$  ring. All m.p. are corr. unless stated otherwise. Pharmacological data for (III) and (V) are given. H. B.

**Strychnos alkaloids. LXXXIX. Behaviour of strychninonic acid towards barium peroxide.** H. LEUCHS and W. DIELS (Ber., 1936, 69, [B], 47—48).—Treatment of strychninonic acid with Ba(OH)<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> at 85—90° gives the *NH<sub>2</sub>-acid* (I), C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub>, m.p. 248—255°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -18.8° in H<sub>2</sub>O [*monoperchlorate*, m.p. 240—243° (decomp.) after softening at 230°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -17.4° ( $\pm$ 8°); *semiperchlorate* (I) with NaOH-MeOH-MeI gives the *product*, C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> (*perchlorate*, decomp. 262°), and a mixture of neutral products. H. W.

**Sinomenine. XLIII.** K. GOTO and H. SHISHIDO Bull. Chem. Soc. Japan, 1935, 10, 597—600).—*Bromodemethoxydihydrosinomenine methiodide* (A., 1931, 1171) with hot 2% NaOH affords *1-bromode-N-methyl-demethoxydihydrosinomenine* (A; R' = Br), m.p. 130°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +7.00° in MeOH (*methiodide*, m.p. 278—279°), which gives a *racemate*, m.p. 148°, with *1-bromode-N-methylidihydro-codeinone*, m.p. 132°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -8.00° in MeOH. Similarly *de-N-methyl-demethoxydihydrosinomenine* (I) (A; R' = H), m.p. 120°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +4.00° in MeOH, gives a

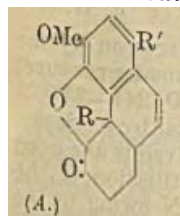
*racemate*, m.p. 114—116°, with *de-N-methyldihydro-codeinone* (II), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -4.00° in MeOH (Freund *et al.*, A., 1921, i, 125). Reduction (H<sub>2</sub>-Pd-BaSO<sub>4</sub> in 0.3% HCl) of (I) gives its *H<sub>2</sub>-derivative*, m.p. 93—97°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +50.00° in EtOH, which gives a *racemate*, m.p. 113—116°, with the *H<sub>2</sub>-derivative*, m.p. 95—98°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -50.5° in EtOH, of (II). Catalytic reduction of thebaine in < N-HCl affords *dihydrothebaine* (III) and a little *dihydrothebainone* (IV); in 2.5N-HCl (IV), *dihydrocodeinone* (V), and *metathebainone* (VI), are obtained, whereas in 5N-HCl a 75% yield of (VI) is obtained (Cahn, A., 1933, 1061). (III) is hydrolysed by cold 2N-HCl to (V). The mixture (A., 1930, 1600) of *demethoxydihydrosinomenine* [(+)-*dihydrothebainone*] [*hydrobromide*, m.p. 291° (decomp.); *hydrochloride*, m.p. 293° (decomp.)] and *demethoxydihydrosinomeninol* [(+)-*dihydrothebainol*] is separated by dissolution in HBr or HCl, salts of the former crystallising. 1-Bromodemethoxydihydrosinomenine (*oxime*, m.p. 177—178°: the m.p. 263° given in A., 1930, 795, is that of the oxime hydrochloride) has been obtained in a form, m.p. 167°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +78.67° in CHCl<sub>3</sub>, which gives a *racemate*, m.p. 190—193°, with 1-bromodihydrothebainone. J. W. B.

**New alkaloid of ergot.** S. SMITH and G. M. TIMMIS (Nature, 1936, 137, 111).—Ergot contains an *alkaloid*, probably C<sub>30</sub>H<sub>35</sub>O<sub>5</sub>N<sub>5</sub>, decomp. approx. 228°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +522° in CHCl<sub>3</sub>. L. S. T.

**Dimorphism of ergometrine.** R. L. GRANT and S. SMITH (Nature, 1936, 137, 154).—A second *modification*, m.p. 212° (decomp.), of ergometrine, m.p. 162—163° (decomp.), has been cryst. in long needles from COMe<sub>2</sub>. The form of low m.p. tends to pass into the less fusible on keeping, and is the more sol. Both forms have [ $\alpha$ ]<sub>D</sub><sup>20</sup> +62.6°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +42.2° in EtOH. L. S. T.

**Aconitine. I. Oxonitin and the oxidation of aconitine with nitric acid and chromic acid.** A. LAWSON (J.C.S., 1936, 80—83).—Oxonitin is oxidised (HNO<sub>3</sub>) with loss of OMe to an *acidic compound*, C<sub>31</sub>H<sub>35</sub>O<sub>14</sub>N<sub>3</sub>, m.p. 263° (decomp.). Aconitine (I) is oxidised (CrO<sub>3</sub>) to *aconitoline*, C<sub>30</sub>H<sub>37</sub>O<sub>9</sub>N, m.p. 220°, hydrolysed (NaOEt) with loss of BzOH to a base, C<sub>30</sub>H<sub>33</sub>O<sub>8</sub>N [*hydrochloride* (+3H<sub>2</sub>O), m.p. 222°; *Ac derivative*, m.p. 239°]. (I) with HNO<sub>3</sub> gives an *acid*, C<sub>30</sub>H<sub>35</sub>O<sub>13</sub>N<sub>2</sub>, m.p. 268° (decomp.), containing NO, hydrolysed with loss of BzOH and AcOH to a *substance*, C<sub>22</sub>H<sub>29</sub>O<sub>11</sub>N<sub>3</sub>, m.p. 201°, and with HCl converted into an *amino-acid*, C<sub>31</sub>H<sub>36</sub>O<sub>12</sub>N<sub>2</sub>·HCl·2H<sub>2</sub>O, m.p. 218° (decomp.). Aconitoline with HNO<sub>3</sub> yields a *nitroso-acid*, C<sub>29</sub>H<sub>33</sub>O<sub>13</sub>N<sub>3</sub>, m.p. 186° (decomp.), which with HCl forms an *NH<sub>2</sub>-acid*, C<sub>29</sub>H<sub>31</sub>O<sub>12</sub>N<sub>2</sub>, m.p. 250° (decomp.), hydrolysed (NaOEt) to an *acid*, C<sub>22</sub>H<sub>30</sub>O<sub>11</sub>N<sub>2</sub>·HCl·H<sub>2</sub>O, m.p. 218° (decomp.). Oxidation of (I) with HNO<sub>2</sub> gives a *substance*, C<sub>31</sub>H<sub>40</sub>O<sub>12</sub>N<sub>2</sub>, m.p. 276° (decomp.). These results are in agreement with the formula for (I) of Spath and Galinovsky (A., 1931, 1313). F. R. S.

**Arsenical derivatives of thymol.** V. BELLAVITA and M. BATTISTELLI (Annali Chim. Appl., 1935, 25, 631—634).—2-Aminothymol is diazotised and converted by As<sub>2</sub>O<sub>3</sub> in NaOH (Cu) into 2-hydroxy-6-methyl-3-propylphenylarsinic acid (I), m.p. 189—190° (decomp.). (I) is resistant to reduction by H<sub>3</sub>PO<sub>2</sub>; with



(A.)

R =  $\cdot[\text{CH}_2]_2\cdot\text{NH}_2$

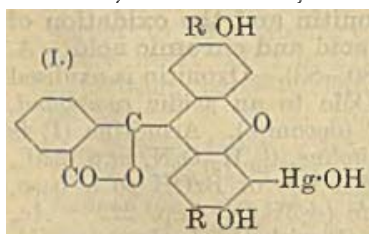
R' = H, m.p. 120°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +4.00° in MeOH, gives a

$\text{Na}_2\text{CO}_3$ -KI- $\text{SO}_2$  it gives after 10 days 2-hydroxy-6-methyl-3-propylphenylarsinoxide, unaltered at  $320^\circ$ . In EtOH with HCl (or HBr) and  $\text{SO}_2$ , (I) yields respectively 2-hydroxy-6-methyl-3-propylphenyldichloro-, m.p.  $60-62^\circ$ , and dibromo-arsine, b.p.  $140^\circ/12$  mm. With Br in AcOH, (I) forms 5-bromo-2-hydroxy-6-methyl-3-propylphenylarsinic acid, m.p.  $204-205^\circ$ ; the corresponding 5-I-compound, m.p.  $195^\circ$ , is obtained in alkaline solution using 0.1N-I. (I) gives no colour with  $\text{FeCl}_3$ . E. W. W.

**Polymethylbenzenes. XIII. Mercuration.** L. I. SMITH and F. L. TAYLOR (J. Amer. Chem. Soc., 1935, 57, 2370-2372).—The hydrocarbons are heated with  $\text{Hg}(\text{OAc})_2$  in MeOH-AcOH; the resulting  $\text{OAc}\cdot\text{Hg}\cdot$  derivatives (in  $\text{CHCl}_3$ , EtOH, or EtOH- $\text{CHCl}_3$ ) with aq. EtOH-HCl, -NaBr, and -NaI (<1 equiv.) give the  $\text{HalHg}$ -compounds. The following are described: pentamethylbenzene ( $\text{OAc}\cdot\text{Hg}\cdot$ , m.p.  $180^\circ$ ,  $\text{ClHg}\cdot$ , m.p.  $205^\circ$ , and  $\text{BrHg}\cdot$ , m.p.  $195-196^\circ$ , derivatives); durenene ( $\text{OAc}\cdot\text{Hg}\cdot$ , m.p.  $158-159^\circ$ ,  $\text{ClHg}\cdot$ , m.p.  $188-189^\circ$ ,  $\text{BrHg}\cdot$ , m.p.  $174^\circ$ , and  $\text{IHg}\cdot$ , m.p.  $161-162^\circ$ , derivatives); isodurenene ( $\text{OAc}\cdot\text{Hg}\cdot$ , m.p.  $108^\circ$ ,  $\text{ClHg}\cdot$ , m.p.  $174^\circ$ ,  $\text{BrHg}\cdot$ , m.p.  $160^\circ$ , and  $\text{IHg}\cdot$ , m.p.  $163-164^\circ$ , derivatives); prehnitene ( $\text{OAc}\cdot\text{Hg}\cdot$ , m.p.  $147^\circ$ ,  $\text{ClHg}\cdot$ , m.p.  $216-217^\circ$ ,  $\text{BrHg}\cdot$ , m.p.  $213-214^\circ$ , and  $\text{IHg}\cdot$ , m.p.  $200^\circ$ , derivatives); mesitylene ( $\text{OAc}\cdot\text{Hg}\cdot$  derivative, m.p.  $102-103^\circ$ );  $\psi$ -cumene (5- $\text{OAc}\cdot\text{Hg}\cdot$  derivative, m.p.  $145-147^\circ$ );  $\text{Hg}(\text{C}_6\text{Me}_5)_2$ , m.p.  $278^\circ$  (lit.  $266^\circ$ ), and  $\text{Hg}$  diduryl, m.p.  $242-243^\circ$ , diisoduryl, m.p.  $217-218^\circ$ , and diprehnityl, m.p.  $200^\circ$ , are prepared from the appropriate  $\text{IHg}\cdot$  derivative and NaI (4 mols.) in EtOH.

H. B.

**Antiseptics. Mercury salts of alkylfluoresceins.** A. NOVELLI (An. Farm. Biochim., 1933, 4, 29-35; Chem. Zentr., 1935, i, 3691).—Mercuration of diacetyl-, dipropionyl-, diethyl-, dipropyl-, dibutyl-, and dihexyl-fluoresceins leads to  $\text{Hg}$  compounds



(I). The antiseptic activity increases with increasing length of the side-chain, R.

Presence of  $\text{CO}$  in R diminishes antiseptic power.

H. N. R.

**Action of radioactive substances on proteins.**—See this vol., 301.

**Multivalent amino-acids and peptides. VI.**—See this vol., 379.

**Influence of neutral salts on the optical rotation of gelatin. III, IV.**—See this vol., 288.

**Colloid chemistry of edestin. III.**—See this vol., 288.

**Salting-out and peptisation of edestin by mixtures of two salt solutions.**—See this vol., 288.

**Reducing groups of proteins.** A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1936, 19, 451-459).—Proteins contain, besides SH groups, others which will react with  $\text{K}_3\text{Fe}(\text{CN})_6$ , and are probably in the tyrosine and tryptophan units. Their activity is enhanced by denaturation and by increase of  $p_{\text{H}}$  and

temp., but they differ from SH groups in that their activity depends on the concn. and time of exposure to  $\text{K}_3\text{Fe}(\text{CN})_6$ . F. A. A.

**Thiol and disulphide groups of proteins. II. Relation between number of SH and S-S groups and quantity of insoluble protein in denaturation and in reversal of denaturation. III. Thiol groups of native proteins: haemoglobin and the proteins of the crystalline lens.** A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1936, 19, 427-438, 439-450).—II. No SH groups are detectable (see A., 1935, 506) in native ovalbumin, but on heat-coagulation as many are found as in the fully hydrolysed protein. The same no. of them appears when ovalbumin is denatured by ultra-violet radiation, or at surfaces. The sol. fraction of partly heat-coagulated ovalbumin shows no SH. When serum-albumin is denatured, S-S groups appear, but disappear when denaturation is reversed.

III. Native haemoglobin and the proteins of the cryst. lens contain SH groups, the no. increasing with rise of  $p_{\text{H}}$  from 6.8 to 9.5. On denaturation, more SH groups appear; these latter are active at  $p_{\text{H}}$  vals. so low that those in the native proteins are barely detectable, and thus may be differentiated from them. At  $p_{\text{H}}$  6.8,  $\text{K}_3\text{Fe}(\text{CN})_6$  oxidises the Fe-porphyrin of haemoglobin without affecting the SH groups; at 9.6, the SH groups may be oxidised, by cystine, without affecting the Fe-porphyrin. F. A. A.

**Characterisation and determination of the hydrolysis products of elastin. Isolation of the monoamino-acids by a new technique.** R. ENGELAND (Bull. Soc. Chim. biol., 1935, 17, 1790-1804).— $\text{NH}_2$ -acids are separated by fractional pptn. of the hydrochlorides from MeOH solution. From elastin two  $\text{NH}_2$ -acids,  $\text{C}_{11}\text{H}_{22}\text{O}_4\text{N}_2$  and  $\text{C}_{17}\text{H}_{38}\text{O}_4\text{N}_2$ , are isolated as the Cu salt,  $\text{C}_{11}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu}$ , and the aurichloride,  $\text{C}_{17}\text{H}_{36}\text{O}_4\text{N}_2\cdot 2\text{AuCl}_4$ , respectively. A. L.

**Determination of the m.p. of organic substances.** F. FRANCIS and F. J. E. COLLINS (J.C.S., 1936, 137-142).—A description of apparatus for setting point and m.p. determination. Setting point gives more accurate experimental vals. for transition temp. from solid to liquid. With the apparatus described, existence of metastable forms fusing within  $1^\circ$  of each other can be detected, transition temp. recorded, and a judgment reached on the purity of the specimen. F. R. S.

**Organic micro-analytical practice.** C. WEYGAND and H. HENNIG (Chem. Fabr., 1936, 9, 8-10).—The technique of methods of C, H, N, halogen, S, and OMe-determination, as applied to samples of 0.001-0.01 g., is detailed. J. W. S.

**Determination of carbon and nitrogen by the action of chromic acid under reduced pressure.** C. N. ACHARYA (Biochem. J., 1936, 30, 241-247).—C and N are determined in org. material by oxidation with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$  and the  $\text{CO}_2$  evolved is absorbed and weighed. Subsequent direct distillation of the digest with alkali gives low vals. for N owing to the formation of  $\text{NO}_3^-$  so that a preliminary reduction is necessary. The disturbing influence of Cl is avoided by addition of  $\text{HgO}$ . H. D.



**Analysis of organic compounds containing H and D.** H. ERLÉNMEYER and H. GARTNER (Helv. Chim. Acta, 1936, 19, 129—144).—The customary determination of H in org. compounds which contain H and D gives accurate results only when the content of H is very high. In the general case a differentiation between a H- and D-compound cannot thus be effected or only very inexactly. Generally, the differences in the % of C allow an approx. differentiation between H- and D-compounds but for accurate results a high % of C and H is necessary. Suitable relationships exist in hydrocarbons particularly in those of the paraffin series. A method is described in which the substance (0.05 to 0.15 g.) is burnt with CuO and the water is collected in a tube cooled in solid  $\text{CO}_2\text{-CCl}_4\text{-CHCl}_3$ . It is mixed with 10 c.c. of standard  $\text{H}_2\text{O}$ ; the mixture is distilled and its  $d$  is determined. The sensitiveness is such that in a mixture of isotopic benzenes, approx. PhD, it is just possible to discriminate between  $\text{C}_6\text{H}_{4.995}\text{D}_{1.005}$  and  $\text{C}_6\text{H}_{5.005}\text{D}_{0.995}$ . H. W.

**Determination of organic sulphur by the liquid ammonia-sodium method.** F. J. SOWA, V. G. ARCADE, and J. A. NIEUWLAND (Ind. Eng. Chem. [Anal.], 1936, 8, 49—50).—0.1 g. of substance is dissolved in 175 c.c. of liquid  $\text{NH}_3$  with the help if necessary of an inert solvent and Na is added until the blue colour is permanent. The solution is evaporated (20 c.c.), 3—5 g. of  $\text{NH}_4\text{Cl}$  are added, and the mixture is evaporated to dryness. The residue is taken up in  $\text{H}_2\text{O}$ , oxidised with 2 g. of  $\text{Na}_2\text{O}_2$ , and the S pptd. as  $\text{BaSO}_4$ . The method is accurate and of general applicability. S. C.

***p*-Bromobenzhydrazide as a reagent for the identification of aldehydes and ketones.** S. M. WANG, CHENG-HENG KAO, CHUNG-HSI KAO, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1935, A, 3, 279—284).—*p*-Bromobenzhydrazide, m.p.  $164^\circ$  (prep. from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  described), condenses with aldehydes and ketones in boiling 95% EtOH containing a few drops of glacial AcOH yielding *p*-bromobenzoylhydrazones of the following substances: MeCHO, m.p.  $192\text{--}193^\circ$ ; EtCHO, m.p.  $172\text{--}173^\circ$ ;  $\text{Pr}^\text{t}$ CHO, m.p.  $157\text{--}158^\circ$ , Bu $^\text{t}$ CHO, m.p.  $153\text{--}154^\circ$ ; hexaldehyde, m.p.  $144\text{--}145^\circ$ ; *n*-heptaldehyde, m.p.  $124\text{--}125^\circ$ ; PhCHO, m.p.  $242\text{--}243^\circ$ ; *p*-, m.p.  $250\text{--}251^\circ$ , and *m*-, m.p.  $217\text{--}218^\circ$ ;  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ ; furfuraldehyde, m.p.  $218\text{--}219^\circ$ ;  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ , m.p.  $235\text{--}236^\circ$ ; COMe., m.p.  $198\text{--}199^\circ$ ; Me hexyl ketone, m.p.  $131\text{--}132^\circ$ ; CPhMe, m.p.  $192\text{--}193^\circ$ ; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ , m.p.  $212\text{--}213^\circ$ ; benzylideneacetophenone, m.p.  $219\text{--}220^\circ$ ; *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , m.p.  $219\text{--}220^\circ$ ; CPh., m.p.  $160\text{--}161^\circ$ ; lævulic acid, m.p.  $158\text{--}159^\circ$ ; Et, m.p.  $128\text{--}129^\circ$ , and  $\text{C}_6\text{H}_5\text{Ph}$ , m.p.  $123\text{--}124^\circ$ , lævulate;  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ , m.p.  $74\text{--}75^\circ$ . Primary and sec. alcohols are oxidised and then identified by this method. H. W.

**Determination of thiol and disulphide compounds, with special reference to cysteine and cystine.** IV. Accurate determination of thiol compounds. Standardisation of cysteine hydrochloride. V. Cystine determination by sulphite and phospho-18-tungstic acid reagent. K. SHINO-

HARA. VI. Reaction of ascorbic acid and glutathione with phospho-18-tungstic acid reagent. VII. Modified phospho-18-tungstic acid method of determining cysteine, cystine, and ascorbic acid in urine. K. SHINOHARA and K. E. PADIS (J. Biol. Chem., 1936, 112, 671—682, 683—696, 697—708, 709—721; cf. this vol., 60).—IV. Cysteine (I) and  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  are allowed to react with a deficiency of  $\text{HgCl}_2$  and the excess is determined colorimetrically by phospho-18-tungstic acid (II).  $\text{H}_2\text{O}$  and a little cystine (III) are the chief impurities in commercial (I). (III) does not interfere with the determination of (I) by this method.

V. (III) is reduced by  $\text{NaHSO}_3$  and then determined colorimetrically by (II).  $\text{NaHSO}_3$  alone develops little colour;  $\text{HgCl}_2$  inhibits formation of colour by (III). Various reducing agents, but not (I), interfere.

VI. Ascorbic acid (IV) is determined colorimetrically by (II), the colour being twice as intense as that due to equimolar amounts of (I). The colour is not affected under specified conditions by  $\text{HgCl}_2$ , or small amounts of  $\text{CH}_2\text{O}$ . (I), (III), and (IV) are thus determined in the same solution by use of  $\text{CH}_2\text{O}$ ,  $\text{HgCl}_2$ , and (II). Oxidised (IV) gives no colour. Glutathione gives irregular results, probably due to hydrolysis, and interferes with the methods.

VII. Modifications are necessary for determinations in urine. Fresh normal urine contains 0—0.9 mg. of (I), 1.1—4.8 mg. of (III), and 3.2—26.8 mg. of (IV) per 100 c.c. R. S. C.

**Determination of cystine by Sullivan's method:** supposed cleavage of cystine from casein by dilute alkali. H. J. LEE (Austral. J. Exp. Biol., 1936, 13, 229—237).—Various factors may interfere with the determination of cystine (I) by Sullivan's method. The conclusion of Jones and Gersdorff (A., 1934, 313) that treatment of casein by dil. alkali destroys some of the (I) is vitiated by their failure to make allowance for the interfering effect of the casein hydrolysate on the determination of (I).

W. O. K.

**Titration of amino-acids in glacial acetic acid solution.** G. F. NADEAU and L. E. BRANCHEN (J. Amer. Chem. Soc., 1935, 57, 1363—1365).— $\text{NH}_2$ -acids (I) (in glacial AcOH) are determined by titration with 0.1*N*- $\text{HClO}_4$  using crystal-violet,  $\alpha$ -naphtholbenzein, or benzoylauramine as indicator; picric acid does not interfere. (I) insol. in AcOH are determined by dissolution in an excess of 0.1*N*- $\text{HClO}_4$  and back-titration with guanidine acetate. The results agree with potentiometric titration (in AcOH using chloranil electrode). H. B.

**Colorimetric determination of allantoin.** G. MOURROT (Bull. Soc. Chim. biol., 1935, 17, 1845—1850).—The method is a modification of that of Fosse (A., 1931, 976). The allantoinic acid is hydrolysed to glyoxylic acid, which is determined colorimetrically using  $\text{NHPh}\cdot\text{NH}_2$ . A. L.

**Weydel reaction for xanthines.** G. DENIGÈS (Bull. Trav. Soc. Pharm. Bordeaux, 1934, 72, 345—355; Chem. Zentr., 1935, i, 3162).—Colour reactions for caffeine, theobromine, theophylline, xanthine, and

guanine are described; the underlying mechanism and the influence of constitution are discussed.

H. N. R.

**Spectrophotometric determination of chlorophyll *a* and *b*, carotene, and xanthophyll.**—See this vol., 396.

## Biochemistry.

**Effect of respiration of pure oxygen on metabolism.** P. BIELCHOWSKY and S. THADDEA (Z. klin. Med., 120, 330—340; Chem. Zentr., 1934, ii, 3399).—Blood-ketones in man, if high, are diminished, and  $p_H$  is shifted towards the alkaline side as the result of decreased alveolar  $CO_2$  tension. The lactic acid curves obtained by injections of Na lactate and adrenaline in man or the dog lie considerably lower in  $O_2$  respiration.

R. N. C.

**Respiration of carbon dioxide in narcosis and in paralysis of the respiratory centre.** H. FRANKEN (Schmerz, Narkose, Anästhesie, 1934, 7, 26—36; Chem. Zentr., 1934, ii, 3646).

R. N. C.

**Simple valveless apparatus for determination of gaseous metabolism in man.** F. FOLDES (Biochem. Z., 1935, 282, 303—307).—The apparatus (cf. the similar apparatus for dogs, A., 1935, 238) is described. The error of duplicate experiments is  $\pm 3\%$ .

P. W. C.

**Respiratory characteristics of the blood of the seal.** L. IRVING, O. M. SOLANDT, D. Y. SOLANDT, and K. C. FISHER (J. Cell. Comp. Physiol., 1935, 6, 393—403).—The capacity of the blood for  $CO_2$  and its buffering power are  $<$  those of human blood.  $O_2$  capacity vals. and dissociation curves are given.

R. N. C.

**Vapour pressure of the blood of arthropods from swift and still waters.** H. M. FOX and E. J. BALDES (J. Exp. Biol., 1935, 12, 174—178).—No correlation was apparent between the v.p. of blood and the  $O_2$  consumption.

CH. ABS. (p)

**Effect of oxygenation of the external medium on the composition of blood in *Scyllium canicula*.** E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 194—196).—Total osmotic pressure, Na, Ca, proteins, org. substances, and the alkaline reserve are increased, whilst plasma-Cl falls; corpuscular Cl is unaffected. Mineral salts in serum and muscle increase simultaneously, and  $H_2O$  passes from the blood to the muscles.

R. N. C.

**Variation of blood- $p_H$  and blood-gas after injection of sodium silicate.** K. DAIKOKU (Trans. Soc. Path. Japon., 1934, 24, 72—76).—Continuous injection caused a decrease in blood- $p_H$  and -gas.

CH. ABS. (p)

**Regeneration of blood in fish following bleeding.** L. BAUDIN (Compt. rend. Soc. Biol., 1936, 121, 330—332).

R. N. C.

**Effects of extracts of pituitary gland on sedimentation of red blood corpuscles of normal and hypophysectomised dogs.** T. ICHIJO (Sei-i Kwai Med. J., 1934, 53, No. 6, 123—132).—Data obtained by Kowarski's apparatus are given.

CH. ABS. (p)

**Determination of rate of sedimentation of blood corpuscles. Effect of globulin solutions**

**on the rate *in vitro*.** I. BINET and I. KRASZNAI (Biochem. Z., 1936, 283, 190—198).—Westergreen's method gives trustworthy results only if const. temp. and  $p_H$  are maintained in the tubes. *In vitro* the rate of sedimentation of washed red blood corpuscles and to a smaller extent that of blood is diminished by addition of globulin.

W. McC.

**"Urea surcharge" (Delaunay) of the erythrocytes of *Sipunculus*: distribution of urea between erythrocytes and plasma in the coelomic liquids charged with erythrocytes.** M. FLORKIN (Compt. rend. Soc. Biol., 1936, 121, 158—160).—The erythrocytes of the coelomic liquid of *Sipunculus* are surcharged with urea, but not those of *Echiurus*, *Glycera*, or *Capitella*.

R. N. C.

**Effect of heparin on the permeability of the erythrocytes to adrenaline.** M. KUCZAROW (Klin. Woch., 1934, 13, 734—735; Chem. Zentr., 1934, ii, 3780—3781).

R. N. C.

**Characteristics of the stability of corpuscular glucose subjected to washing with physiological solution.** G. PATRASSI and U. TEODORI (Boll. Soc. ital. Biol. sperim., 1935, 10, 525—526).—Repeated washing of erythrocytes with 0.9% NaCl reduces their glucose to a steady min., which in erythrocytes from diabetics is slightly  $>$  from normal subjects.

R. N. C.

**Corpuscle resistance and bilirubinæmia in young mammals with trychophytia after slow dosage with thallium acetate.** I. GATTO and G. MELODIA (Pediatria, 40, 230—235; Chem. Zentr., 1934, ii, 3397).—Corpuscle resistance is increased and bilirubinæmia diminished or abolished.

R. N. C.

**Diurnal variations in concentration of red blood cells and hæmoglobin.** J. J. SHORT (J. Lab. Clin. Med., 1935, 20, 708—713).

CH. ABS. (p)

**Percentage of hæmoglobin compared with the volume of erythrocytes. Importance of this relation in correcting the Van Allen determination of the volume of platelets.** K. K. NYGAARD and D. L. DUXBURY (J. Lab. Clin. Med., 1935, 20, 767—772).—The hæmoglobin content expressed as g. per 100 c.c. is closely related to the vol. of erythrocytes expressed as vol.-% of the sample. Tables for intercalculation are given.

CH. ABS. (p)

**0.1N-Hydrochloric acid as diluent for combined leucocyte and hæmoglobin determinations.** C. A. PONS and W. P. BELK (J. Lab. Clin. Med., 1935, 20, 766—767).—Blood diluted with 0.1N-HCl is suitable for white cell counts and for examination in the Huden-Hausser hæmoglobinometer.

CH. ABS. (p)

**Birth pains and the blood of the new-born.** Z. HORVATH and C. HOLLÓSI (Amer. J. Dis. Children, 1935, 49, 689—694).

CH. ABS. (p)

**Determination of hæmoglobin in experimental anæmia in rabbits.** R. DAMADE, L. SERVANTIE, and J. FERVILLE (Compt. rend. Soc. Biol., 1936, 121, 229—232).—The methods of Sahli and Autenrieth and of Wong are recommended. R. N. C.

**Solutions of hæmoglobin stabilised with time.** I, II. W. DUCE (Boll. Soc. ital. Biol. sperim., 1935, 10, 376—379, 379—382).—I. Solutions of hæmoglobin (I) after prolonged dialysis are coagulated by boiling, and by 2*N*-NaCl, or EtOH, are coloured red by slight acidification or alkalis, and pptd. by HNO<sub>3</sub>, AcOH, Hg(NO<sub>3</sub>)<sub>2</sub>-HNO<sub>3</sub>, and K<sub>4</sub>Fe(CN)<sub>6</sub> (II), but not by CuSO<sub>4</sub>, NiSO<sub>4</sub>, AgNO<sub>3</sub>, basic Pb acetate, or HgCl<sub>2</sub>. After prolonged storage at room temp. dialysed (I) is coagulated only by 2*N*-NaCl, is coloured brown by acids and alkalis, and pptd. by all the above reagents except (II).

II. The absorption bands of (I) in the red are displaced towards the red end by prolonged dialysis and storage. The absorption quotient falls.

R. N. C.

**Sulphur content of hæmoglobin with special reference to blood-groups.** G. BALASSA (Biochem. Z., 1936, 283, 222—228).—In man the hæmoglobin (I) of the blood of some individuals contains 0.611% of S whilst that of others contains 0.662%, the corresponding Fe:S ratios and min. mol. wts. being, respectively, 4:13, 4:14, and 68,000, 34,000. The blood of individuals belonging to blood-groups A and B contains the second, that of the blood of individuals belonging to blood-group O the first, kind of (I).

W. McC.

**Optical properties of acidified solutions of -<sub>2</sub> and CO-hæmoglobin in blood.** G. BARKAN (Z., 1936, 283, 241—252; cf. A., 1930, 107).—Spectrophotometric examination indicates that the darker colour of the solutions containing CO is due to a difference in the degree of dispersion.

W. McC.

**Analysis of the spectra of hæmoglobin derivatives.** D. L. DRABKIN (Amer. J. Med. Sci., 1935, 189, 154).—Absorption curves are represented as ions a no. individual bands. Oxy- (I), ca h (II), cyano-, and two forms of met-hæmo- n e certain bands in common. Their position is discussed. The α-bands of (I) and (II) do not belong to this series and probably represent the union of hæmoglobin with a gas.

CH. ABS. (p)

**Aliphatic amino-content of the oxyhæmoglobins of animals.** K. GERGELY (Biochem. Z., 1936, 283, 263—272; cf. A., 1933, 107).—The average NH<sub>2</sub>-N contents of h dog-, and ox-oxyhæmoglobin are, respectively, 1.96—12.48, 13.14, and 13.28%. The vals. are not altered by repeated recrystallisation.

W. McC.

**Differentiation of the pigments of human serum.** R. SULLMANN, E. SZECSENYI-NAGY, and F. VARRÓ (Biochem. Z., 1936, 283, 263—272; cf. A., 1933, 107).—The pigments may be determined by advantage of their differing solubilities in ac. F<sub>3</sub> and light petroleum and may be separated by autographic adsorption on Al<sub>2</sub>O<sub>3</sub>. With the exception of very small amounts of non-diazotisable bilirubin-like pigments the only pigments in normal

human serum are bilirubin (I), carotene, and xanthophyll. (I) in aq. EtOH is determined after treatment with SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl. The pigments produced by ultra-violet irradiation of (I) are insol. in light petroleum and cannot be diazotised. W. McC.

**New crystalline derivative of blood-pigments.** M. WAGENAAR (Z. anal. Chem., 1935, 103, 417—418).—The object to be tested for blood is moistened on a microscope slide with COMe<sub>2</sub>, and a drop of dil. mineral acid is added. Characteristic crystals of acetone-hæmin are produced with the dried residue from 0.05 mg. of blood.

J. S. A.

**Spectrophotometric investigation of cyano-compounds of blood-pigments.** S. SCHONBERGER and P. BALINT (Biochem. Z., 1936, 283, 210—221; cf. A., 1935, 999).—In the visible part of the spectrum the absorption curves of cyanomethæmoglobin (I), cyano-NH<sub>2</sub>-parahæmatin, cyano-C<sub>5</sub>H<sub>5</sub>N-parahæmatin, and cyanohæmatin are identical and exhibit a max. at 541 mμ. In the ultra-violet (I) and cyanoparahæmatin (but not cyanohæmatin) exhibit an intense well-defined band at 424 mμ. The sp. extinctions in the visible are decreased 15% by increasing the alkalinity. The results throw light on the constitution of blood-pigments.

W. McC.

**Variations of osmotic pressure and of the size of hæmocyanin molecules during a long fast (in summer or hibernating) of varieties of *Helix*.** A. ROCHE and J. ROCHE (Compt. rend., 1935, 201, 1522—1524; cf. A., 1934, 673).—The mol. size of hæmocyanin in *H. pisana* and *H. pomatia* is about halved by fasting. This may be the mechanism for H<sub>2</sub>O retention within the animal.

J. L. D.

**Reticulo-endothelial origin of fibrinogen: comparative study of the fibrinogenetic action of some carioclasts.** P. CAMPELLONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 497—499).

R. N. C.

**Micro-Kjeldahl technique for determining fibrinogen.** H. R. GARBUTT and R. S. HUBBARD (J. Lab. Clin. Med., 1935, 20, 758—761).—Plasma (0.5 c.c.) is mixed with 24 c.c. of 0.85% NaCl and 0.5 c.c. of 2.5% CaCl<sub>2</sub> solution. The clot is removed centrifugally, washed with 0.05% CaCl<sub>2</sub> solution, digested with the Folin-Wu mixture, and diluted to 10 c.c. N is determined by nesslerisation.

CH. ABS. (p)

**Protein and electrolyte contents of the plasma and transudates (serous effusions and subcutaneous fluid).** L. ANTOGNETTI (Pathologica, 1935, 27, 182—189).—A progressive and parallel decrease occurs in the [H<sup>+</sup>] and protein concn. in the order erythrocytes, plasma, serous effusions, subcutaneous transudates. Variations in [HCO<sub>3</sub><sup>-</sup>] are in the reverse order. The Donnan membrane equilibrium explains the facts.

CH. ABS. (p)

**Protein equilibrium of blood-serum in anaphylactic states.** AUBRY, THIODET, and RIBERE (Compt. rend. Soc. Biol., 1935, 120, 1257—1259).—Protein equilibrium is disturbed in anaphylactic states, particularly urticaria, albumins remaining steady whilst globulins fall considerably.

R. N. C.

**Protein, lipin, and total cholesterol content of the serum of the normal cat.** L. BLANCHARD (Bull. Soc. Chim. biol., 1935, 17, 1677—1692).—The vals. for the serum-protein, -serine, -globulin, total serum-lipins, and cholesterol of the normal cat are  $73.44 \pm 8.64$ ,  $38.35 \pm 6.97$ ,  $34.78 \pm 8.72$ ,  $8.63 \pm 1.92$ , and  $1.03 \pm 0.20$  g. per 1000 g., respectively. These vals. are of the same order as those for the dog and for man. A. L.

**Influence of ingestion of colostrum on proteins of the blood sera.** I. P. EARLE (J. Agric. Res., 1935, 51, 479—490).—Sera of new-born foals, kids, pigs, and lambs are deficient in euglobulin (I) and low in pseudoglobulin I (II). On ingestion of colostrum (I) and (II) increase rapidly. With foals the amounts of (I) and (II) absorbed are related to the quantity of colostrum ingested. E. P.

**Determination of the tyrosine index of serum polypeptides.** R. LEFAUX (Bull. Soc. Chim. biol., 1935, 17, 1822—1827).—The difference in colour intensity between the  $\text{CCl}_3\text{-CO}_2\text{H}$  and phosphotungstic acid filtrates of the material after treatment with conc.  $\text{HNO}_3$  and aq.  $\text{NaOH}$  is measured. A. L.

**Polypeptidaemia in anaphylactic shock.** M. POLONOVSKI, C. GERNEZ, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 121, 37—38).—Blood-polypeptides show no significant modification either in anaphylactic shock or during sensitisation. R. N. C.

**Polypeptidaemia during anaphylactic shock.** F. MAIGNON (Compt. rend. Soc. Biol., 1936, 121, 225—226).—A reply to Polonovski, Gernez, and Driessens (see above). R. N. C.

**Hyperazotæmia of neuro-central origin.** P. JEDŁOWSKI (Boll. Soc. Ital. Biol. sperim., 1935, 10, 615—618). R. N. C.

**Variation of residual nitrogen in blood after injection of sodium silicate solution.** H. AKABANE (Trans. Soc. Path. Japon., 1934, 24, 76—81).—Residual N increased after injection. CH. ABS. (p)

**Influence of protein feeding on the nitrogenous blood constituents in the dog.** L. SAS (Biochem. Z., 1935, 282, 308—316).—The blood-residual-N is greatly increased by protein feeding, due in the initial stages to increase in blood-urea. The polypeptide-N shows no characteristic changes. In animals receiving a N-free diet, blood-urea decreases, but residual N remains unchanged. P. W. C.

**Blood- and urinary nitrogen of a lamelli-branch mollusc (*Anodonta cygnea*).** M. FLORKIN and G. BOSSON (Compt. rend. Soc. Biol., 1935, 120, 1368—1369).—Total, protein-, and non-protein-N vals. for blood and urine at different seasons are given. R. N. C.

**Non-protein-nitrogen content of blood of healthy Korean adults.** H. S. LEE (J. Chosen Med. Assoc., 1934, 24, 1541—1548).—In most cases, vals. varied from 29 to 43 mg. per 100 c.c. of blood (mean for 79 cases  $36.11 \pm 0.83$ ). CH. ABS. (p)

**Adenine nucleotide content of human blood.** II. Correlation with hæmoglobin. M. V. BUELL (J. Biol. Chem., 1936, 112, 523—530; cf. A., 1935,

373).—There is a statistically significant correlation between the adenine nucleotide and hæmoglobin contents of the erythrocytes. J. N. A.

**Oxidised/reduced glutathione ratio in acute oxidosis.** W. LIBBRECHT and A. MASSART (Compt. rend. Soc. Biol., 1935, 120, 1330).—The oxidised/reduced glutathione (I) ratio of rabbits' blood is increased by prolonged exposure to air or  $\text{O}_2$  *in vitro*, but is reduced by exposure to pure  $\text{O}_2$  at high pressures *in vivo*; the state of (I) depends therefore on oxidation in the tissues. R. N. C.

**Liver and glutathione.** L. BINET and G. WELLER (Compt. rend., 1935, 201, 992—993).—In fasting dogs, total glutathione (I) (oxidised+reduced) in the blood from the portal vein is 9%, and in the suprahepatic vein 44%, > in blood from the femoral artery. During digestion, the figures are 51% and 27%, respectively, indicating that during fasting the blood absorbs (I) from the liver, and deposits (I) during digestion. F. A. A.

**Determination of glyoxalines in serum.** A. SCHWARTZ and A. RIEGERT (Compt. rend. Soc. Biol., 1935, 120, 1309—1312).—The method of Loeper *et al.* is unsatisfactory. R. N. C.

**Does the blood contain acetylcholine?** R. AMMON (Klin. Woch., 1935, 14, 453—456).—Acetylcholine cannot be detected chemically or biologically in the blood. R. N. C.

**Arginine as the cause of the non-specificity of analytical methods for blood-guanidine.** M. ZAPPACOSTA (Diagnostica tec. lab. [Napoli], 1934, 5, 919—927).—Reagents for colorimetric tests give the same colour intensity with guanidine (I) as with equimol. quantities of arginine (II). (II), like (I), is adsorbed by C and 70% of it may be eluted with 0.02N-HCl in EtOH. CH. ABS. (p)

**Indole. II. Effect of indole on blood-sugar, urea-nitrogen, and blood-amino-acids.** III. Indolæmia provoked by ligaturing the hepatic peduncle: indican-indole index. E. MACCHIA (Boll. Soc. Ital. Biol. sperim., 1934, 9, 1314—1315, 1935, 10, 528—530).—II. Indole (I) temporarily increases blood-sugar in dogs, but scarcely affects non-protein-N and  $\text{NH}_2$ -acids.

III. Ligature of the hepatic peduncle in the dog after injection of (I) increases blood-(I) and reduces blood-indican. The liver is hence concerned in (4) metabolism. The indican-(I) index is defined. R. N. C.

**Blood-lipins, -calcium, and -potassium during experimental excitation of the hypothalamus, in dogs.** A. VAN BOGAERT and L. VAN MEEL (Compt. rend. Soc. Biol., 1936, 121, 199—201).—Blood-lipins are temporarily depressed, the fall being almost exclusively due to decrease of fatty acids. Cholesterol and unsaponifiable material are scarcely affected.  $\text{Ca}$  sometimes shows a slight temporary rise, and  $\text{K}$  slight fall. R. N.

**Serum-lipins by a micro-gravimetric technique.** W. R. WILSON and A. E. HANSEN (J. Biol. Chem., 1936, 112, 457—468).—The inorg. P and the wt., total acidity, and I val. of the fatty acids or saponifiable fraction and the I val. of the unsaponi-



able fraction of the serum-lipins were determined in 2.5–5 c.c. of serum. The mean total, unsaponifiable, and saponifiable lipins were 0.657, 0.260, and 0.362%, respectively. 81% of the lipin-P is found in the saponifiable fraction. H. D.

**Carotenæmia.** E. BOUNIN and M. LÉVINSON (Z. Vitaminforsch., 1935, 5, 12–21).—Carotenæmia is associated with tuberculosis, diabetes, typhus, malaria, metabolic disturbances, spleen and liver diseases, and in normal persons with a carotene-rich diet. The subnormal oxidation of carotenoids is related to the concomitant hypocholesterolaemia. F. O. H.

**Blood-cholesterol in the carotid artery, venæ cavæ, and portal vein.** F. H. SHILLITO, E. H. BIDWELL, and K. B. TURNER (J. Biol. Chem., 1936, 112, 551–556).—The level of the blood-cholesterol (I) in these vessels was the same for a given animal, whether the whole blood or serum was used, and whether or not cholesterol was administered previously. Passage through the lungs had no effect on (I). Large doses of KI given for 2–14 days produced no variation in the distribution of (I).

J. N. A.  
**Variations in blood-cholesterol in man and in animals.** L. I. PUTSCHINSKI and T. T. GLUHENKI (Bull. Soc. Chim. biol., 1935, 17, 1836–1844).—The cholesterol (I) content of (fasting) human blood over a 24-hr. period varies between 50 and 130 mg. per 100 g. (I) of rabbit and dog blood varies likewise. A. L.

**Influence of a hyperthermal sulphuretted radioactive environment on some constituents of the blood.** A. KRIJANOVSKY (Compt. rend. Soc. Biol. 1935, 120, 1236–1238).—Blood-sugar, -N, -cholesterol, and plasma-Cl are depressed, whilst corpuscular Cl rises, in man in the Luchon radio-vaporarium. R. N. C.

**Blood-sugar of *Cancer pagurus*: nature of reducing substances and factors of variation of blood-sugar.** J. ROCHE and C. DUMAZERT (Compt. rend. Soc. Biol., 1935, 120, 1225–1227).—The hæmolymp contains glucose (I) and non-fermentable reducing substances pptd. by Cd(OH)<sub>2</sub>. The average content is 0.21 g. per 1000; it is temporarily increased by removal from the aquarium, is unaltered by insulin, adrenaline, or muscular work. R. N. C.

**Hypoglycæmia by conditioned reflex.** C. C. HON and A. RUDEANU (Compt. rend. Soc. Biol., 1935, 121, 185–186).—Rabbits injected with 0.9% daily injections of insulin exhibit a fall of blood-sugar. R. N. C.

**Hourly constancy of phenolæmia in man in normal and pathological states.** R. BANFI, E. L. M., D. MARENZI (Compt. rend. Soc. Biol., 1935, 121, 359).—Free phenols (I) in nephrotoxic blood are > in normal blood, whilst conjugated phenols (II) are more variable. The constancy in normal blood is > that of (II) over a period of 28 hr. P. C.

**Rate of alcohol in the blood in putrefaction in vitro.** NICLOUX (Compt. rend. Soc. Biol., 1935, 120, 1304–1306).—The rate of disappearance

of EtOH from putrefying blood increases with rise of temp. R. N. C.

**Organic phosphorus of the blood studied by the method of prolonged spontaneous hydrolysis, in man and in some domestic animals.** G. DE TONI (Arch. Ist. Biochim. Ital., 1935, 7, 303–340).—The autolysis curves at 37° of org. P in infantile and adult human and animal blood are described. The curves are essentially the same in lactating animals of all species. Autolysis is rapid during the first 24 hr., but slackens very considerably afterwards. In the adult animals inorg. P is always < in the corresponding lactating animals, and the autolysis curves show wide variations from each other. Autolysis is most extensive in rabbit blood, moderate in human and horse blood, whilst sheep's and cows' bloods contain little or no org. P. R. N. C.

**Influence of pituitary body and preparations of other endocrine organs on inorganic salts of the blood.** S. NISHIDA (Sei-i-Kwai Med. J., 1934, 53, No. 6, 133–175).—Hypophysectomy causes a decrease in blood-Cl, -Na, -K, and -Mg and an increase in -Ca. Pituitrin, antuitrin, and pituglandol produce a reciprocal effect in normal dogs and restoration to normal levels in hypophysectomised animals. Oophormin, thyroxine, and adrenaline cause a decrease in Mg and K and an increase in Ca. Insulin produces no change in Mg in normal, but a decrease in that of hypophysectomised, dogs. CH. ABS. (p)

**Blood, bile, and liver of animals with permanent biliary fistulas.** F. CAVAZZA (Pathologica, 1935, 27, 241–250).—In dogs blood-Ca and alkaline reserve are lowered and blood-K increases. No marked changes occur in Ca content of bile and hepatic tissues. CH. ABS. (p)

**Effect of changes in the concentration of plasma-electrolytes on the concentration of electrolytes in the red blood cells of dogs, monkeys, and rabbits.** H. YANNET, D. C. DARROW, M. K. CARY (J. Biol. Chem., 1936, 112, 477–488).—In monkeys and rabbits changes in the plasma-Na, produced by intraperitoneal injection of aq. glucose or NaCl, caused changes in erythrocyte-Na and -K due to shift of H<sub>2</sub>O alone. In the dog a certain migration of cations occurred. H. D.

**Bromine in blood and spinal fluid; its relation to blood-iodine.** U. C. BONORINO, M. SCHTEINGART, and R. FERRAMOLA (Prensa med. Argentina, 1934, Mar. 7).—Blood-Br varied from 0.6 to 3.6 mg. per 100 c.c. Br and I vary in a parallel manner, I:Br ranging between 70 and 170. Spinal fluid contains 0.2 mg. of Br per 100 c.c. CH. ABS. (p)

**Blood-chloride in healthy Koreans.** M. S. KIM (J. Chosen Med. Assoc., 1934, 24, 1537–1540).—Vals. for Koreans who eat excessive amounts of salt fall within normal variations found in occidentals. CH. ABS. (p)

**Effects of hydrochloric acid and sodium hydrogen carbonate administrations on distribution of blood-chlorine.** N. MATSUOKA and K. DAITA (Trans. Soc. Path. Japon., 1934, 24, 82–91).—

$\text{NaHCO}_3$  increases blood-Cl and decreases plasma-Cl. Both vals. increase after administration of HCl.

CH. ABS. (p)

Metabolism of iodine. I. Blood-iodine. II. Influence of ascorbic acid on blood-iodine. H. LOHR (Arch. exp. Path. Pharm., 1936, 180, 332—343, 344—353).—I. Improvements in methods for the micro-determination of I are described. The blood-I (I) of healthy men and women is  $20\text{--}30 \times 10^{-6}\%$  and is not influenced by sex or season; it is greatly increased by exercise (rowing) for 1 hr., returning to normal after 1 hr. rest, but increasing again after 24 hr.

II. Ascorbic acid lowers the (I) of normal and thyroidectomised dogs and antagonises the (I)-increasing action of thyroxine. F. O. H.

Diffusible calcium in the serum of laying and non-laying hens. M. W. TAYLOR and W. C. RUSSELL (J. Agric. Res., 1935, 51, 663—667).—No difference in the level of diffusible Ca was apparent. Non-diffusible Ca was much higher in the laying condition. A. G. P.

Variability of non-haemoglobin iron. T. G. KLUMPP (J. Clin. Invest., 1935, 14, 351—355).—Non-haemoglobin Fe varies widely and is a significant fraction of the total Fe. CH. ABS. (p)

Chemical and physico-chemical sexual differences in the blood of selachians. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 105—107).—Corpuscular vol. and Cl, and  $\kappa$  in the blood of males are  $>$  in females, whilst the alkaline reserve is less. The osmotic pressure and inorg. salts in the male are  $>$  in the female in *Scyllium canicula*, but less in *Raia undulata*, whilst with blood-proteins and org. substances of the serum the reverse is the case. R. N. C.

Chemical and physico-chemical sexual differences of the blood of *Labrus bergylla*. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 102—105).—The osmotic pressure,  $\kappa$ , blood-, serum-, and corpuscular Cl, serum-Na, and total inorg. substances in the blood of the male are  $>$  in the female, whilst K, Ca, proteins, the alkaline reserve, corpuscular vol., and org. substances are less. The fraction of the osmotic pressure due to NaCl in the male is  $>$  in the female. R. N. C.

Action of indole on hydræmia, chloræmia, and glycaemia. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 441—443).—Injection of indole in guinea-pigs increases  $\text{H}_2\text{O}$  and depresses Cl in the blood; blood-sugar behaves variably. R. N. C.

Blood-modifications from administration of indole. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 439—441). R. N. C.

Composition of the blood of some marine invertebrates and vertebrates. E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 291—293).—From the analytical data given, the osmotic pressure of poikilosmotic marine animals is slightly  $>$  that of the external medium, whilst that of homeosmotic animals is less.  $\kappa$  of the serum of poikilosmotic animals differs from that of the external medium. The % of the osmotic pressure due to NaCl in selachians is

$<$  in teleosts. Blood-Cl in cephalopods is approx. equiv. to Cl in the sea; in selachians it is half, and in teleosts a quarter, of the cephalopod val. Proteins are high in cephalopods. R. N. C.

New antagonistic property of normal sera: the cercaricidal action. J. T. CULBERTSON and S. B. TALBOT (Science, 1935, 82, 525—526).—Sera of many animals have a definite cercaricidal action. L. S. T.

Investigations [on sera] in the ultra-violet. W. GRAUBNER (Z. ges. exp. Med., 81, 1—5; Chem. Zentr., 1934, ii, 3397).—The absorption spectra of different human sera vary considerably, but no significant deviation appears in any single serum. Pptn. with EtOH or dialysis shifts the spectrum about  $10 \text{ m}\mu$  towards the visible, but deproteinisation with  $\text{Fe}(\text{OH})_3$  or large  $p_{\text{H}}$  changes with  $\text{H}_2\text{SO}_4$  or NaOH are ineffective. The substance responsible for the spectrum is not one of the known serum constituents, and probably contains a CO or a  $\text{C}_6\text{H}_6$  ring. Urine always shows a band between 260 and  $280 \text{ m}\mu$ ; the max. is indefinite. The spectra of both sera and urine are probably due to the same substance, which is also present in cerebrospinal and pathological fluids. R. N. C.

Behaviour of calcium in the electrodialysis of blood-serum and its dialysate. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1333—1336).—Ca transport is anodic with small currents and cathodic with large currents in both serum and its dialysate; this confirms the existence in serum of diffusible non-ionisable Ca complexes. R. N. C.

Calcium metabolism in the first phase of blood clotting. III. Mechanism of thrombin formation. H. SCHEURING (Biochem. Z., 1935, 283, 1—11).—The mechanism of the earlier described (A., 1935, 1263) shift of Ca from the ionised to the negative Ca complex condition during thrombin formation is further investigated. The governing reaction results from the affinity of  $\text{Ca}^{++}$  for prothrombogen (I), the reaction conforming to the mass law and the complex formed being identical with thrombogen (II). The union of thrombokinase (III) with (II) also conforms to the mass law. Normal dog serum contains  $\text{Ca}^{++}$  corresponding with the (II) content, whilst (I) is present in about twice the amount required by the (III) content. P. W. C.

Action *in vitro* of iron-vitamin-C complexes with different bases on the coagulation of blood. F. ARLOING, A. MOREL, and A. JOSSERAND (Compt. rend. Soc. Biol., 1936, 121, 39—41).—Na ascorbate restrains slightly the coagulation of blood *in vitro*. Ferriscorbone complexes with inorg. and org. base exhibit greater restraining action, Ca ferriscorbone being the least anticoagulant. With ferrosorbone the time of coagulation is always  $> 1 \text{ hr.}$  R. N. C.

Influence of splenic fractions on blood coagulation. I. Effect of splenectomy, spleen diet, and spleen extract. S. BOKU, I. HIRAI, and K. GON (J. Chosen Med. Assoc., 1935, 25, 48—50).—Splenectomy accelerates coagulation for 2 days and subsequently delays it. Administration of spleen material restores normal conditions. CH. ABS. (p)

**Mechanism of the action of anticoagulant substances.** H. GOLDIE (Compt. rend. Soc. Biol., 1935, 120, 1181—1185).—The anticoagulant power of compounds of the moranyl group corresponds exactly with, or is slightly  $>$ , the alexin-destroying power; these compounds therefore affect a coagulant agent, probably prothrombin, the structure of which resembles that of alexin (I). Naphthalenesulphonates with high anticoagulant power exert only a feeble effect on (I). The incoagulable plasma exhibits variable characteristics as regards pptn. by acids, and contains "protective colloids." R. N. C.

**Toxicity of ricin and body temperature.** H. MORIYAMA (Japan. J. Exp. Med., 1934, 12, 591—600). CH. ABS. (p)

**Ricin. II.** H. MORIYAMA (Japan J. Exp. Med., 1934, 12, 437—453).—Effects of various substances on the hæmagglutinating power of ricin are recorded. The lyophilic character of the protein is associated with the presence of a double linking, the loss of which causes changes in colloidal state, toxicity, and agglutinating power. CH. ABS. (p)

**Distribution of isoagglutinins in blood-serum fractionated by electrophoresis.** A. GRONWALL (Biochem. Z., 1935, 282, 257—262).—Human serum of individuals of blood group O is fractionated by electrophoresis and the agglutinin titre, protein-N, and precipitability with  $(\text{NH}_4)_2\text{SO}_4$  are determined. Isoagglutinin is distributed uniformly through the fractions pptd. by 30% saturation with  $(\text{NH}_4)_2\text{SO}_4$ . P. W. C.

**Antigenic properties of detoxicated Indian and African venoms: cross-reaction exerted by the respective antivenins.** E. GRASSET and A. ZOUTENDYK (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 391—398; cf. A., 1934, 1022).—Venoms were rendered atoxic by 1%  $\text{CH}_2\text{O}$ . The potency of these preps. is compared with that of African viperine and colubrine venoms. Multivalent antivenins of colubrine venoms may be produced either by unmodified venoms by anavenoms. CH. ABS. (p)

**Toxic and antigenic properties of S. African venoms with special reference to multivalency of S. African antivenin.** E. GRASSET, A. ZOUTENDYK, and A. SCHAAFSMA (Trans. Roy. Soc. Med., 1935, 28, 601—612).—The potency of horse antivenin can be titrated with venoms of the puff adder and Cape cobra. A special evaluation is shown with these venoms and the antivenin. CH. ABS. (p)

**Precipitin reaction to phosphatides of tubercle bacilli.** G. R. DUNCAN, C. C. VAN WAGENINGEN, E. S. MARIETTE, and E. P. K. FENGER (Amer. J. Tuberc., 1935, 31, 307—322).—Human tubercle bacillus (Anderson S-1) does not act as an antigen for precipitation of antibodies in rabbits. S-2 is a very poor and bovine, avian, and lepra phosphatides are good antigens. No type specificity among these phosphatides was apparent. CH. ABS. (p)

**Relation between type-specific carbohydrates of human cord and blood group-specific substances.** F. WITEBSKY, E. NETER, and H. SOBOTKA (J. Exp. Med., 1935, 61, 703—715).—Hæmolysis of

sheep cells is inhibited by human group-sp. A-antiserum. Differences between the acetylated and deacetylated polysaccharides of *Pneumococcus* type I are demonstrated by inhibition of hæmolysis, by complement fixation, and by inhibition of group-sp. isoagglutination tests. Destruction of potency of acetylated polysaccharides by faeces filtrates is not due to fission of Ac. CH. ABS. (p)

**Effect of various enzymes on toxin and anatoxin.** Y. ANAZAWA (Sei-i-Kwai Med. J., 1934, 53, No. 10, 1—62).—Trypsin detoxicates diphtheric and tetanic toxins and destroys their antigenic property. Anatoxins prepared by heating these toxins with  $\text{CH}_2\text{O}$  are not destroyed by trypsin. Neither diastase nor lipase destroys the toxins or anatoxins. CH. ABS. (p)

**Antibody production through the cutaneous route.** Y. HIROSE (Sei-i-Kwai Med. J., 1934, 53, No. 6, 1—73).—The antibody for cholesterol was produced in rabbits by smearing cholesterol or dehydrated lanoline over the skin. CH. ABS. (p)

**Antibody-forming accelerator in spleen. IV. Influence of spleen diet on hæmolysin and agglutinin formation.** S. BOKU, I. HIRAI, and K. GON (J. Chosen Med. Assoc., 1934, 24, 1508—1518).—Splenectiony delays hæmolysin and agglutinin formation. Oral administration of spleen counteracts this effect. CH. ABS. (p)

**Chemical composition of pig's stomach.**—See B., 1936, 168.

**Structure of protoplasm.** W. SEIFRIZ (Bot. Rev., 1935, 1, 18—36). CH. ABS. (p)

**Isoelectric point of mucoproteins.** A. ROCHE (Compt. rend. Soc. Biol., 1935, 120, 1229—1231).—The isoelectric point of the mucoprotein of the submaxillary of the ox is  $p_H$  2.70. R. N. C.

**Isoelectric point of mucoproteins.** A. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 71—73).—The isoelectric points of a no. of mucoproteins from invertebrate tissues are given. That of the vitreous humour is about  $p_H$  3.0, whilst those of the skin are generally higher. R. N. C.

**The myogen volume in relation to the volume of the muscle fibre.** W. HAUMANN and H. H. WEBER (Biochem. Z., 1935, 283, 146—152).—The myogen solution of mammalian muscle occupies 35% of the vol. of the minced muscle and may amount to  $< 20\%$  of the vol. of the intact muscle fibre. Close agreement was obtained by different methods in the determinations of the non-solvent space for myogen. P. W. C.

**Myoglobin. I. Solubility in concentrated ammonium sulphate solutions.** V. E. MORGAN (J. Biol. Chem., 1936, 112, 557—563).—The solubility of carboxymyoglobin (I) in conc. solutions of  $(\text{NH}_4)_2\text{SO}_4$  at  $p_H$  6.6 and  $25^\circ$  is expressed by  $\log S = 8.00 - 0.94(\Gamma/2)$ , where  $S$  is the solubility in g. and  $\Gamma/2$  is the ionic strength per litre. (I) is quite sol. in buffer solutions at  $p_H$  6.6 up to a  $[\text{PO}_4^{''}]$  of  $\approx 3M$ . J. N. A.

**Decomposition of tuberculo-protein, starch, and gelatin by dry grinding.** C. H. BOISSEvain

(Amer. Rev. Tuberc., 1935, 31, 542—546).—Prolonged grinding of starch causes its transformation into erythro-dextrin, and then into achroo-dextrin. Similarly, gelatin is changed to a  $H_2O$ -sol. peptone-like compound incapable of forming a gel even at  $0^\circ$ . Tuberculo-protein (I) is decomposed by grinding into  $H_2O$ -sol. protein, peptone, and polysaccharide. Boiling with dil. acid or treatment with 4% aq. NaOH produces the same change in (I). CH. ABS. (p)

**Factors affecting the affinity of the pulmonary proteins and their degradation products for the lung.** P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 459—461).—The proteins of the portion of the lung juice expelled by 400 atm. pressure are able to fix Co and convey it to the lungs, the effect being unaffected by tryptic digestion. The effect is not shared by aq. lung extracts or the proteins of the juice expelled by 200 atm. pressure. R. N. C.

**Relation of protein coagulation to oxidation-reduction potential.** Y. NAKAMURA (J. Agric. Chem. Soc. Japan, 1935, 11, 1101—1104).—Treatment of ov- and serum-albumin by heat or ultra-violet irradiation and of milk by enzyme action lowers the potential, indicating a relation between coagulation and hydrolysis. F. O. H.

**Hydrogen-ion dissociation curve of the crystalline albumin of the hen's egg.** R. A. KEKWRICK and R. K. CANNAN (Biochem. J., 1936, 30, 227—234).—The  $H^+$  dissociation curve of ovalbumin has been constructed. The  $H^+$ -combining capacity reaches a max. of 30—32 eqvs. per mol. just below  $p_H$  2. Evidence of a max. dissociating capacity was observed at  $p_H$  8—9 (corresponding with a dissociation of 11 eqvs. of  $H^+$  per mol.), but not at  $p_H$  11.5—12.0. H. G. R.

**Effect of formaldehyde on the hydrogen-ion dissociation curve of ovalbumin.** R. A. KEKWRICK and R. K. CANNAN (Biochem. J., 1936, 30, 235—240).— $H^+$  dissociation curves of ovalbumin (I) in presence of  $CH_2O$  indicate the presence of 16—18  $NH_2$  groups, other than  $\alpha-NH_2$ , which are identified with the  $\epsilon-NH_2$  of lysine. The action of  $HNO_3$  on (I) indicates the presence of 19—20  $NH_2$  groups per mol. and the lysine-N of the phosphotungstate ppt., 17—18 mols. of lysine per mol. H. G. R.

**Relations between some alkaloids and protein substances.** P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 464—467).—Brucine (I) and strychnine in ovalbumin solutions form non-dialysable complexes with the protein. They also form complexes with serum-proteins, the quantity of alkaloid fixed by ox-serum being > by sheep serum. A method of determining (I) is described. R. N. C.

**Electric cataphoresis of brucine and strychnine in solutions of ovalbumin or in blood-serum from different animals.** P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1935, 10, 461—464).—Brucine and strychnine in the free state in solutions of ovalbumin or animal sera travel to the cathode, but when bound to the protein they travel to the anode. R. N. C.

**Bioluminescence. II. Partial purification of Cypridina luciferin.** R. S. ANDERSON (J. Gen. Physiol., 1935, 19, 301—305).—The powdered organ-

ism is extracted with MeOH under  $H_2$ , Bu<sup>o</sup>OH is added, the MeOH removed, and the BuOH solution treated with BzCl. Bz or Ac derivatives of luciferin (I) are more stable to  $O_2$  than is (I) itself. Preps. of (I) 2000 times as active as the starting material are obtained, in yields up to 65%, by two benzoylations followed by hydrolysis with  $N-HCl$ . F. A. A.

**Organic bases, especially spermine, in the muscle of higher animals.** K. YOSHIMURA, Y. HIWATASHI, and T. SAKAMOTO (J. Chem. Soc. Japan, 1935, 56, 280—288).—Vals. for creatine, hypoxanthine, carnosine, creatinine, methylguanidine, carnitine, and spermine are given for muscles of cattle, horse, pig, and hen. CH. ABS. (p)

**Antianæmic principle of liver.** H. B. SREERANGACHAR and M. SREENIVASAYA (Current Sci., 1936, 4, 468—472).—A review.

**Hæmatin pigments of Actinia (actiniohæmatin) and cytochrome-b.** J. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 69—71).—The muscle of *Actinia* is rich in cytochrome-b (I), but contains little or no cytochrome-c (II).  $C_5H_5N$  extracts of (II)-free muscles contain protohæmatin and the hæmatin of (II), with traces of that of cytochrome-a. Hence (I) and (II) of *Actinia* contain the same prosthetic group. R. N. C.

**Hæmatin of cytochrome-c and nature of the combination of hæmatins with globins.** J. ROCHE and M. T. BENEVENT (Compt. rend. Soc. Biol., 1935, 120, 1227—1229).—Hæmatin-c (I), the prosthetic group of cytochrome-c (II), shows absorption bands at 614, 568, 535, 498, and 395  $m\mu$ .  $C_5H_5N$  transforms it into a parahæmatin (bands at 578 and 538  $m\mu$ ), which is reduced to a hæmochromogen (bands at 550, 521, and 410  $m\mu$ ) identical with that formed from (II) by  $C_5H_5N$ . (I) and (II) are reduced to the same porphyrin. (I) and natural globin in neutral or slightly alkaline solution form another parahæmatin (bands at 505 and 538  $m\mu$ ), whereas other hæmatins form methæmoglobins. The results suggest that hæmoglobins and hæmochromogens are not formed by the action of the same group in the hæmatin mol. R. N. C.

**Contents of glutathione and vitamin-C in anti-anæmic liver preparations.** F. G. KOSER (Arch. exp. Path. Pharm., 1936, 180, 183—188).—Glutathione does not occur in several (commercial) liver preps., whilst the vitamin-C content varies considerably. F. O. H.

**Glycogen in the central nervous system of human embryos.** O. FUSEJIMA (Sei-i-Kwai Med. J., 1934, 53, No. 9, 80—93).—A histological study. CH. ABS. (p)

**Laracein from the scale of the insect Cero-plastes rubens, Maskell.** R. KOYAMA (J. Chem. Soc. Japan, 1935, 56, 365—372).—The wax from insects grown on tea and on citrus trees had  $n_D^{20}$  0.69694, 0.99208, m.p. 54—56°, 55—57°, sap. val. 152.8, 126.0, acid val. 22.9, 46.6, I val. 76.3, 130.2, respectively. From the wax were obtained, melissic, ceromelissic,  $C_{33}H_{66}O_2$ , m.p. 94°, ceroplastic,  $C_{33}H_{70}O_2$ , m.p. 96—98°, and a resin acid,  $C_{22}H_{34}O_2$ . The unsaponifiable fraction contained ceromelissyl, cero-



plasyll, and melissyll alcohols, all of which are primary. The wax does not contain ceryl or ibotaceryl alcohols or the corresponding acids. CH. ABS. (p)

**Lipin composition and physiological activity in the ovaries of pregnant guinea-pigs.** E. M. BOYD (J. Biol. Chem., 1936, **112**, 591—595).—Ovaries from guinea-pigs at various stages of gestation showed the same average phospholipin content of about 1.25% as those from non-pregnant controls at the pre-ovulatory stage. Similarly there was no significant variation from the mean (0.30%) for the free cholesterol. There is no increase in physiological activity in the ovaries of gravid guinea-pigs. J. N. A.

**Liver-fat and blood determinations after adrenalectomy.** J. F. B. BARRETT and A. T. WILSON (J. Physiol., 1934, **81**, 43—45p).—In doubly adrenalectomised cats increased blood viscosity causes an increase in residual blood in the liver and a consequent fall in the % of total solids. No correlation is apparent between adrenalectomy and the amount and nature of liver-fat. CH. ABS. (p)

**Jaboty fat. Composition of mink fat. New alcohols and hydrocarbons in sperm oil.**—See B., 1936, 158.

**Hexadecenol and tetradecenol in sperm head oil. Hexadecenol in sperm blubber oil.**—See this vol., 311.

**Tetradecenoic and dodecenoic acids in sperm oil.** I, II.—See this vol., 313.

**Change in the solubility of calcium compounds during the autolysis of muscle tissue.** I. A. SMORODINCEV and J. N. LASKOVSKAJA (Bull. Soc. Chim. biol., 1935, **17**, 1814—1821).—The  $H_2O$ -sol. Ca of autolysing beef increases with time in parallel with the lactic acid, but not the  $PO_4^{'''}$  content of the extract. A. L.

**Analysis of otoliths and endolymphatic sac deposits in *Amblystoma tigrinum*.** A. B. HASTINGS (J. Comp. Neurol., 1935, **61**, 295—296).—Saccus deposits and otoliths contained 26.7 and 15.9% of  $Ca_3(PO_4)_2$  as dahlite and 64.5 and 83.2% of  $CaCO_3$  as aragonite, respectively. CH. ABS. (p)

**Role of iron and silica in the structure of the radular teeth of certain marine molluscs.** E. I. JONES R. A. McCANCE, and L. R. B. SHACKLETON (J. Exp. Biol., 1935, **12**, 59—64).—In the *Patellidae* radular teeth consist largely of Si and Fe, the former comprising the skeleton of the teeth. Fe is present as oxide, carbonate, or org. compound. In *Chitonidae* occurs without Si and in *Deutalium* Si, but not Fe, is present. CH. ABS. (p)

**Modifications in the quantity of some phosphorus compounds in the muscle of the pigeon deprived of its cerebellum.** M. F. DE MIRA and DA CRUZ (Compt. rend. Soc. Biol., 1936, **121**, 261).—Extirpation of the cerebellum diminishes inorg. P,  $P_2O_7^{'''}$ , and (particularly) phosphagen. R. N. C.

**Detection of heavy metals in the retina.** E. BARONI (Monatsh., 1935, **67**, 129—130).—Traces of Cu have been found in fresh retina and choroid. Zn is absent. F. L. U.

**Action of lipins on lacteal secretion and the chemical composition of milk. I. Action of lecithin and cholesterol introduced by the parenteral route in the goat. II. Action of the total lipins of egg-yolk introduced by the parenteral route in the goat.** D. TORRISI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 443—445, 445—447).—I. Lecithin (I) in small quantities increases, and in larger quantities reduces, body-wt. and lacteal secretion; small quantities increase total milk-lipins (II) and cholesterol (III). Cholesteryl oleate (IV) increases body-wt., (II), and (III) without affecting secretion. Mixtures of (I) and (IV) in small quantities increase body-wt., lacteal secretion, total, inorg., and casein-P, (II), and (III), without affecting acid-sol. and lecithin-P. Larger quantities reduce body-wt. slightly without affecting lacteal secretion or the composition of the milk.

II. Injection of egg-yolk lipins in well-fed animals increases body-wt., lacteal secretion, total, inorg., and casein-P of the milk, (II), and (III); org. acid-sol. P and kephalin-P are unaffected. In sparingly-fed animals body-wt. and lacteal secretion are diminished, whilst small quantities also diminish (II) and kephalin. A succession of small daily doses influences favourably body-wt., lacteal secretion, (II), and the various P fractions in the milk. R. N. C.

**Monohydroxypalmitic acid in butter fat.** A. W. BOSWORTH and G. E. HELZ (J. Biol. Chem., 1936, **112**, 489—492).—A *monohydroxypalmitic acid*, m.p. 16.5—17.5°,  $[\alpha]_D^{20} +2.40^\circ$  to  $+2.47^\circ$  in  $CHCl_3$ , was separated from butter fat. H. D.

**Biological effects of feeding with the milk of cows in oestrus.** F. USUELLI (Boll. Soc. Eustachiana, 1934, **32**, 57—64; Chem. Zentr., 1934, ii, 3783). R. N. C.

**Detection of oxytocic, pressor, and diuresis-inhibitory components of posterior pituitary secretion in cerebrospinal fluid.** S. DELEONARDI (Arch. exp. Path. Pharm., 1936, **180**, 135—141).—All three components (oxytocic in amount corresponding with approx.  $0.4 \times 10^{-6}$  g. of fresh pituitary prep. per c.c.) were detected in cerebrospinal fluid (rabbit, dog) and in fluid from the second and third ventricles (man). F. O. H.

**Colour reaction of cerebrospinal fluid in cerebrospinal meningitis.** R. REITLER (Trans. Roy. Soc. Trop. Med. Hyg., 1935, **28**, 405—406).—The centrifuged fluid (1 c.c.) is poured over a layer (1 c.c.) of  $H_2SO_4$ . In pathological, but not in normal, fluids a violet ring is produced in 24 hr. CH. ABS. (p)

**Stability of sugar in cerebrospinal fluid.** P. G. SCHUBE (J. Lab. Clin. Med., 1935, **20**, 752—753).—The sugar content of the fluid stored under sterile conditions at  $10^\circ$  remains unchanged for  $\leq 21$  days. CH. ABS. (p)

**Inorganic phosphorus and sugar of cerebrospinal fluid.** P. UJSACHY (Orvosi Hetilap, 1935, **79**, 381—382).—Some proportionality between the two vals. was observed, but no regularities were apparent. The occurrence of high or normal P contents was no indication of the presence or absence of meningitis. CH. ABS. (p)

**Modifications of the thiocyanate concentration of the nasal mucus and other secretions, in relation to stimulation of the trigeminum and the olfactorium.** P. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 431—432).—Stimulation of the olfactorium with eucalyptus oil increases CNS' in the nasal and lachrymal secretions and the urine, but not in the saliva. R. N. C.

**Saliva.** A. CASTELLANI, M. DOUGLAS, P. REDAELLI, and G. AMALFITANO (J. Trop. Med. Hyg., 1935, 38, 81—87).—A review. CH. ABS. (p)

**Presence of lactic acid in the saliva.** R. VLADESCO (Compt. rend. Soc. Biol., 1936, 121, 275—276).—Lactic acid is always present. R. N. C.

**Hæmolytic actions and surface tension of human and animal biles and cholates.** S. TSUJI (Japan. Z. Mikrobiol. Path., 1934, 28, 1534—1552).—Among various biles examined those of carp and toads had the greatest hæmolytic action and that of chicken the highest surface tension. CH. ABS. (p)

**Action of post-pituitary extracts on gastric secretion.** L. LANGERON, M. PAGET, and A. DANES (Compt. rend. Soc. Biol., 1936, 121, 33—35). R. N. C.

**Gastric acidity and its significance.** F. L. APPERLY (Lancet, 1936, 230, 5—9). L. S. T.

**Urine of the normal cat.** L. BLANCHARD (Bull. Soc. Chim. biol., 1935, 17, 1693—1706).—The vol., acidity, and urea,  $\text{NH}_3$ , and Cl' content of the urine of the cat are 37 c.c. per kg. wt. per day, 0.060 g. of H, 84.10—89.85, 1.88—2.69, and 3.05—4.67 g. per 1000 g., respectively. The normal urine contains albumin (0.5 g. per 1000 g.), and under certain conditions of feeding small amounts of lipins and cholesterol. A. L.

**Modifications of the urinary reaction following renal denervation.** E. TRIA and B. CAPALDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 502—504).—Renal denervation induces a fall of the actual and potential acidity of the urine, a slight rise in  $\text{NH}_3$ , and a considerable rise of combined  $\text{CO}_2$ , free  $\text{CO}_2$  being scarcely affected. Conditions tend to return to normal after 10—15 days. R. N. C.

**Partition of nitrogenous constituents of urine and its physiological significance. VII. Evolution of specific endogenous nitrogen metabolism during protein inanition.** G. MOUROT (Bull. Soc. Chim. biol., 1935, 17, 1741—1789).—In the urine of rats undergoing protein starvation, the total N, after remaining nearly const. for some time, increases before death. Whilst urinary creatinine, uric acid, and purine bases do not, the urea-,  $\text{NH}_3$ -, and  $\text{NH}_2\text{-N}$ , allantoin, and creatine losses do, follow the same course as that of the total N. A. L.

**Detection of leucine and tyrosine [in urine].** FISCHER and H. STRALLER (Pharm. Ztg., 1936, 81, 38—39).—A method is given for detecting 0.01% of leucine (I) and tyrosine (II) in urine. In fresh urine containing sediment, (I) and (II) are in the sediment and not in solution. Control tests are advisable when the microscopic test is used. (I) and (II) occur very rarely in urine. P. G. C.

**Micro-determination of trimethylamine in the urine.** G. MONASTERIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 385—386).—The urine is distilled with alkaline  $\text{NaOCl}$ , which decomposes all but the *tert.* bases.  $\text{NMe}_3$  is collected in 0.02N- $\text{H}_2\text{SO}_4$  and excess of  $\text{H}_2\text{SO}_4$  determined with I. R. N. C.

**Histidine in human urine.** F. FOLDES (Biochem. Z., 1936, 283, 199—209).—The frequency of the occurrence of histidine (I) in human urine increases as its *d* increases. (I) is detected more frequently in the urine of pregnant women than in that of non-pregnant, but a test for pregnancy cannot be based on this difference. No (I) could be detected in the urine of non-pregnant animals (dog, horse, cow, elephant, giraffe, tiger, antelope). A method described is more sensitive for the detection of (I) than is that of Kapeller-Adler (A., 1934, 1050). W. McC.

**Renal innervation and reducing substances in the urine.** E. MARTINI, A. BONSIGNORE, and F. PINOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 474—477).—The oxidised/reduced ascorbic acid ratio in the urine of the dog is increased by congelation of the vagi, renal denervation, or injection of atropine. It is reduced by excitation of the congealed vagi or injection of eserine. R. N. C.

**Determination of ascorbic acid in urine by titration.** H. VON EULER and D. BURSTROM (Biochem. Z., 1935, 283, 153—157).—The ascorbic acid contents of the same samples of urine as determined by the Bezssonoff method (using molybdophosphotungstic acid) are always very much > results on the same urines by the Tillmans method. P. W. C.

**Use of Mayer's reagent for detection of quinine in alkaline urine.** J. W. FIELD and M. KANDIAH (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 385—390).—Addition of  $\text{AcOH}$  to the reagent ensures pptn. of albumin (I), and of quinine (II) in clinically significant amounts. If (I) is present, urine and reagent are boiled and filtered while hot. On cooling (II) is pptd. CH. ABS. (p)

**Detection of acridine derivatives in urine.** G. FERRARI (Diagnostica tec. lab. [Napoli], 1934, 5, 928—932).—The sample (5 c.c.) is treated with 1—2 drops of 20% aq. Na caffeine benzoate. An intense green fluorescence or the enhanced intensity of an existing fluorescence indicates the presence of acridine derivatives. CH. ABS. (p)

**Determination of urinary ketones for clinical use.** E. MACCHIA (Diagnostica tec. lab. [Napoli], 1934, 5, 908—918).—An application of the nitroprusside reaction is described. CH. ABS. (p)

**Paraffin hydrocarbon from urine of pregnancy.** W. F. HART and M. A. NORTHUP (J. Amer. Chem. Soc., 1935, 57, 2726—2727).—The material extracted by light petroleum from the adsorbate (fuller's earth) from the acidified, aged urine is separated by warm MeOH into insol. *heptacosane*, m.p. 58—59°, and (probably) sol. *pentacosane*, m.p. 52—54°. H. B.

**Urinolysis in fat metabolism.** F. J. JIRKA and C. S. SCUDERI (J. Lab. Clin. Med., 1935, 20, 631—633).—Intracystic fat occurs exclusively in the last

few drops of urine excreted. It may be determined directly by centrifuging in a Babcock bottle.

CH. ABS. (p)

**Determination of glucose and chlorides in urines containing sodium formaldehydesulphoxylate.** E. HUG and R. H. DE MEIO (Compt. rend. Soc. Biol., 1936, 121, 370—372).—Na formaldehydesulphoxylate reduces  $\text{AgNO}_3$  and alkaline Cu solutions, and must be oxidised with  $\text{HNO}_3$  and  $\text{KMnO}_4$  before Cl<sup>-</sup> can be determined. Glucose can be determined polarimetrically, or by Cu after preliminary deproteinisation with  $\text{HgSO}_4$ — $\text{H}_2\text{SO}_4$  and  $\text{BaCO}_3$ , and removal of Hg with  $\text{H}_2\text{S}$ .

R. N. C.

**Enteric coatings. II. Excretion studies with sodium salicylate tablets.** M. WRUBLE (J. Amer. Pharm. Assoc., 1935, 24, 1074—1077).—The amounts of salicylate recovered from the urine by a modified Thoburn-Hanzlik method were approx. the same whether coated or uncoated tablets of Na salicylate were administered.

E. H. S.

**Approximate rapid determination of the barbital content of urine and drugs.** H. OETTEL (Arch. Pharm., 1936, 274, 1—10).—The barbital content of urine is determined within a few mg. by acidifying 10 c.c. with a few drops of 0.1N-HCl, extracting with 20 c.c. of  $\text{CHCl}_3$ , and adding small amounts of 0.2%  $\text{MeOH-Co(OAc)}_2$  and 0.2%  $\text{MeOH-LiOH}$  to the extract. Barbitals are detected in urine immediately and several days after administration.

R. S. C.

**"Donaggio phenomenon" in the urine of children affected with muscular dystrophy both at rest and after fatigue.** E. BOZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 586—587).

R. N. C.

**"Donaggio phenomenon" in the urine of horses in febrile conditions.** P. RUCCI BITTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 561—563).

R. N. C.

**"Donaggio reaction" in the urine of fatigued individuals.** A. TORBOLI (Boll. Soc. ital. Biol. sperim., 1935, 10, 548—550).

R. N. C.

**"Inhibition phenomena" of Donaggio.** T. ITALI (Diagnostica tec. lab. [Napoli], 1935, 6, 9—20).

CH. ABS. (p)

**Microdetermination of the  $p_H$  of fluid in renal glomeruli and tubules.** H. MONTGOMERY and A. PIERCE (Amer. J. Med. Sci., 1934, 187, 735).—A colorimetric method for 0.2-c.c. samples and a quinhydrone electrode for 0.02 c.c. are described. Vals. for glomerular, proximal, and intermediate tubular fluids in *Necturus* are the same as that for plasma. The  $p_H$  decrease occurs in the distal tubule, in which vals. are always < that of glomerular fluid and > that of the corresponding urine.

CH. ABS. (p)

**Determination of total lipins and lipin partition in faeces.** H. C. TYDWEIL and L. E. HOLT, jun. (Biol. Chem., 1936, 112, 605—613).—A method for determining the partition of lipins, unsaponifiable matter, neutral fat, fatty acid, and soap in a single sample is described.

J. N. A.

**Calcium precipitation in the pancreas.** M. EPER, A. LESURE, E. BIOY, and P. PERREAU

(Compt. rend. Soc. Biol., 1936, 121, 22—24).—Pancreatic Ca is 2—5 times as great as hepatic Ca in pathological states, which is probably the cause of its rapid petrification.

R. N. C.

**Blood and urinary phosphorus in various diseases.** T. IMIO (J. Chosen Med. Assoc., 1935, 25, 26—40).—Data are recorded.

CH. ABS. (p)

**Carbon disulphide and adrenals (Addison's disease).** L. DEVOTO (Arch. Gewerbepath. Gewerbehyg., 1934, 5, 429—432).—A case is reported of Addison's disease following prolonged work with  $\text{CS}_2$ .

R. N. C.

**Prophylaxis of simple anaemia in infancy with iron and copper. Effect on haemoglobin, weight, and resistance to infection.** S. J. USHER, P. N. MACDERMOT, and E. LOZINSKI (Amer. J. Dis. Children, 1935, 49, 642—657).—Daily administration of  $\text{Fe}^{III}$  glycerophosphate to infants increased the average haemoglobin concn. at 1 year by 15%. Simultaneous administration of  $\text{CuSO}_4$  enhanced the effect, and increased gains in wt. and resistance to infection.

CH. ABS. (p)

**Glutathione and anaemia.** G. C. DOGLIOTTI and T. CASTELLANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 521—523).—Total glutathione (I) in the blood is normal or slightly reduced in post-haemorrhagic or acute infectious anaemia, whilst corpuscular (I) is normal or slightly raised. In other anaemias total (I) is generally normal, whilst corpuscular (I) is raised; in polycythemia corpuscular (I) is reduced.

R. N. C.

**Further evidence for the presence of a toxic factor in pernicious anaemia.** G. E. WAKERLIN and H. D. BRUNER (Science, 1935, 82, 494—495).—The urine contains a thermolabile, comparatively toxic, reticulocyte-decreasing factor and a partly thermostable, relatively non-toxic, reticulocyte-stimulating principle for the pigeon. Normal human urine contains the latter, but not the former.

L. S. T.

**Non-identity of lactoflavin and the "extrinsic factor" in pernicious anaemia.** C. A. ASHFORD, L. KLEIN, and J. F. WILKINSON (Biochem. J., 1936, 30, 218—223).—Lactoflavin is not identical with either the liver anti-pernicious anaemia principle or the "extrinsic factor."

H. G. R.

**Effect of transfusion of heterogeneous formalised blood in experimental acetylphenylhydrazine anaemia in the rabbit.** O. MALAGUZZI-VALERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 453—455).

R. N. C.

**Effect of heterogeneous formalised transfusion in experimental anaemia from bleeding in the rabbit.** O. MALAGUZZI-VALERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 546—548).

R. N. C.

**Cholesterol content of plasma in arthritis.** E. F. HARTUNG and M. BRUGER (J. Lab. Clin. Med., 1935, 20, 675—681).—Plasma-cholesterol (I) decreased in rheumatoid and increased in osteo-arthritis. The ratio of free (I) : (I) esters is normal. Total (I) of the blood and sedimentation rate are not related.

CH. ABS. (p)

**Cholesterol-induced atherosclerosis: prevention in rabbits by feeding an organic iodine compound.** I. H. PAGE and W. G. BERNHARD (Arch. Path., 1935, 19, 530—536).—Administration of org. I compounds prevents atherosclerosis following feeding of cholesterol (I) in olive oil. Persistent lipæmia also occurring under these conditions is more marked when I compounds are given. The lipæmia differs from that occurring in nephrosis, in that total, free, and ester-(I) are increased relatively  $>$  are lipin-N,  $\text{-NH}_2\text{-N}$ , or  $\text{-P}$ . CH. ABS. (p)

**Separation of liver substances which are reticulocytogenic in the guinea-pig and therapeutically active in experimental canine black tongue.** Y. SUBARROW, B. M. JACOBSON, and C. H. FISKE (New England J. Med., 1935, 212, 663—664).—Approx. 50% of the activity of crude liver extract was due to *l*-tyrosine. A second active substance can be adsorbed on charcoal and eluted by EtOH. CH. ABS. (p)

**Serum-proteins in cancer.** W. KOPACZEWSKI (Compt. rend., 1935, 201, 1229—1231).—In cancer serum-globulin and -albumin are  $<$  and myxoproteins  $>$  normal. The hydrophobic colloid content, and the physical condition of the colloid, are concerned in the acceleration of lactogelatinisation of cancerous sera. A. G. P.

**Schubert-Dannmeyer test for cancer.** E. R. HOLIDAY and F. C. SMITH (Amer. J. Cancer, 1935, 23, 339—342).—The method, based on changes in serum-lipin in cancer, is not sufficiently trustworthy for clinical use. CH. ABS. (p)

**Early diagnosis of carcinoma by exact chemical measurement.** R. LINKS (Z. Krebsforsch., 1934, 41, 166—206; Chem. Zentr., 1934, ii, 3787—3788).—A formula is given for the diagnosis of carcinoma from serum-K and -Mg determinations. R. N. C.

**Inhibiting the development of tar-carcinoma in mice.** J. R. DAVIDSON (Canad. Med. Assoc. J., 1935, 33, 364—366).—A diet rich in vitamin-E and incidentally in  $\text{-B}_1$  and  $\text{-B}_6$  increased the resistance of mice to carcinogenic factors in tar. CH. ABS. (p)

**Carcinogenic action of 1:2-benzpyrene.** C. SANNIE, C. OBERLING, M. GUERIN, and P. GUERIN (Compt. rend. Soc. Biol., 1935, 120, 1196—1198). R. N. C.

**Physiological validity of enzyme [amylase] determinations in tumour tissue.** F. H. SCHARLES, P. ROBB, and W. T. SALTER (Amer. J. Cancer, 1935, 23, 322—327).—The method previously described (A., 1934, 1023) determines only the enzymic activity, and not the effect of accelerators or inhibitors. CH. ABS. (p)

**Plasma and erythrocyte glutathione in human cancer.** J. W. SCHOONOVER (Amer. J. Cancer, 1935, 23, 315—321).—In cancer the ratio of oxidised glutathione (I) to reduced (I) is increased in plasma and lowered in erythrocytes. The quotient of the ratio in plasma  $\div$  the ratio in erythrocytes is  $>$  normal. CH. ABS. (p)

**Blood-glutathione in human cancer.** J. W. SCHOONOVER (Amer. J. Cancer, 1935, 23, 311—314).—

The average concns. of oxidised and of reduced glutathione (I) remain normal in cancer, but vals. for reduced (I) in erythrocytes were slightly  $>$  normal. CH. ABS. (p)

**Aminoethyl phosphate from tumours.** E. L. outhouse (Biochem. J., 1936, 30, 197—201).—Bovine malignant tumours contain aminoethyl phosphate (I) [*Ba* salt; *brucine* salt (one equiv. of brucine); *flavianate*, m.p. 223°] identical with synthetic (I) from aminoethanol (II) phosphate and  $\text{POCl}_3$ . Hydrolysis of (I) with phosphatase gives (II) (flavianate, m.p. 198° and 212°). Probably the formula of (I) is  $\text{CH}_2\text{<NH}_3\text{O>PO-OH}$ , at least at  $p_H$  5—9. W. McC.

**Biodynamics of the pseudo-proteins. Chemotherapy of carcinoma by redox substances from osteocolla.** O. HUPPERT (Wien. med. Woch., 1934, 84, 624—628; Chem. Zentr., 1934, ii, 3788).—A thiogelatin, an org. Fe-heavy-metal complex with a synthetically-introduced thiazole-glyoxaline group of the character of glutathione, prepared from osteocolla, has an inhibitory effect on growth of *B. coli*, and is thus a possible therapeutic agent for cancer. R. N. C.

**Effect of bromohexic acid on rat sarcoma 39.** W. A. SELLE and M. BODANSKY (Amer. J. Cancer, 1935, 23, 289—296).—No sp. inhibition of growth was observed. CH. ABS. (p)

**Enzymes in rabbit sarcoma.** K. MIYAMA (Sei-Kwai Med. J., 1934, 53, No. 6, 105—123).—Necrotic and non-necrotic areas in rabbit sarcoma contain amylase and lipase, the latter being greater in necrotic sections. The lipase is resistant to atoxyl and quinine. Small amounts of trypsin and a pepsin-like enzyme occur in both areas. CH. ABS. (p)

**Dental caries. III. Rickets in relation to caries in deciduous and in permanent teeth.** A. F. HESS, H. ABRAMSON and J. M. LEWIS (Amer. J. Dis. Children, 1934, 47, 477—487). CH. ABS. (p)

**Mottled enamel in Texas.** H. T. DEAN, R. M. DIXON, and C. COHEN (U.S. Publ. Health Repts., 1935, 50, 424—442).—A review. CH. ABS. (p)

**Calcium and phosphorus metabolism of children with mottled enamel.** E. M. LANTZ, M. C. SMITH, and R. M. LEVERTON (J. Home Econ., 1935, 27, 236—239).—The Ca and P metabolism is not affected by feeding F. F probably causes mottled enamel by a sp. effect on the enamel-forming organ. CH. ABS. (p)

**Changes in teeth and bone in chronic fluoride poisoning.** C. J. SUTRO (Arch. Path., 1935, 19, 159—173).—Changes in the enamel and bone matrix caused by feeding NaF are due to chemical disturbances unrelated to the parathyroid glands. CH. ABS. (p)

**Glutathione and diabetes.** G. C. DOGLIOTTI and O. MELONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 523—525).—Total glutathione (I) in the blood of diabetics is normal whether or not insulin (II) has been administered. Corpuscular (I) is slightly  $>$  normal in moderate diabetes, and slightly  $<$  normal after (II); it is also  $<$  normal in severe cases. R. N. C.



**Diabetes mellitus, its differentiation into insulin-sensitive and insulin-insensitive types.** H. P. HIMSWORTH (Lancet, 1936, 230, 127—130).—One type appears to be caused by a deficiency of insulin (I), and the other to lack of an unknown factor which sensitises the body to (I). L. S. T.

**Effect of protein on carbohydrate tolerance of two patients having combined diabetes mellitus and pernicious anaemia.** N. JOLIFFE, H. BRANDALEONE, and H. MOST (J. Clin. Invest., 1935, 14, 357—365).—High-protein (II) diets reduced carbohydrate (I) tolerance. Use of high-(I) diets counteracted the immediate effects of (II), but loss in tolerance was permanent and not affected by insulin. CH. ABS. (p)

**Absorption curve of glucose by the red corpuscles of normal and diabetic subjects *in vitro*.** G. PATRASSI and U. TEODORI (Boll. Soc. ital. Biol. sperim., 1935, 10, 527—528).—The absorption curves of the corpuscles are very similar in the two cases, both rising to a steady max., the increases of the glucose contents being equal. R. N. C.

**Relations between bilirubinaemia and carbohydrate metabolism. I. Bilirubinaemia in fasting and glucose-fed diabetics.** E. SLAVICH (Boll. Soc. ital. Biol. sperim., 1935, 10, 531—532).—Bilirubinaemia in diabetics is considerably > normal. It is not affected by ingestion of glucose. R. N. C.

**Effect of thyroidectomy in poisoning by diphtheria toxin.** P. LOCATELLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1317—1318). R. N. C.

**Influence of acute infection and artificial fever on plasma-lipins.** A. V. STOEßER and I. McQUARRIE (Amer. J. Dis. Children, 1935, 49, 658—671).—Plasma-lipins decrease in acute febrile, but not in afebrile, disorders or induced fevers. Fever, in itself, does not cause lipin changes. CH. ABS. (p)

**Experimental goitre: functional, chemical, histological studies.** C. A. HELLWIG (Arch. Path., 1935, 19, 364—371).—A Ca-rich diet induces goitres in rats. The I content of goitres is related to that of the diet. Colloid (I-rich) goitres have a higher thyroid function than do parenchymatous, colloid-rich goitres. The latter induce the higher blood-Ca vals. CH. ABS. (p)

**Etiology of enzootic bovine haematuria. I.** A. DATTA (Indian J. Vet. Sci., 1934, 4, 341—344).—Oral administration of Ca lactate or intramuscular injection of  $\text{CaCl}_2$  caused no appreciable difference in coagulability of blood in affected cases. Serum-Ca was not affected, but serum- $\text{PO}_4^{'''}$  increased. CH. ABS. (p)

**Index and jaundice of the newborn.** H. HOLLÓSI and Z. HORVÁTH (Amer. J. Dis. Child., 1935, 49, 638—641).—The haemoglobin index is > 100% in normal and < 100% in jaundiced newborn. CH. ABS. (p)

**Ureum-phosphatase in toxic and haemolytic jaundice.** A. R. ARMSTRONG and E. J. KING (Canad. J. Biochem. Physiol., 1935, 32, 379—383; cf. A., 1935, 403).—The phosphatase increased markedly in toxic, but not in haemolytic, jaundice. CH. ABS. (p)

**Significance of thiocyanate in hepatic coma.** H. INOUE (J. Chosen Med. Assoc., 1934, 24, 1355—1365).—The  $\text{SCN}^-$  in blood and urine is lowered in hepatic coma. Vals. were also low in rabbits with total biliary obstruction and in dogs with Eck fistula. CH. ABS. (p)

**Pathological physiology of the liver. III. Impaired function in relation to nitrogen-containing substances.** I. MATSUO and K. INOUE (Acta Schol. Med. Kioto, 1935, 17, 417—432).—A review. CH. ABS. (p)

**Role of fats and cholesterol in the Henry reaction.** V. CHORINE (Compt. rend. Soc. Biol., 1936, 121, 297—300).—The intensity of the Henry reaction is reduced by washing the serum with  $\text{Et}_2\text{O}$ , which reduces surface tension and removes fats and cholesterol. The reaction is associated with protein modifications in the serum, the role of fats and cholesterol being secondary. R. N. C.

**Lipins and melano-flocculation (Henry reaction).** F. TRENSZ (Compt. rend. Soc. Biol., 1935, 120, 1268—1270).—The euglobulins of paludic sera that have been freed from fat by pptn. with  $\text{COMe}$ , no longer give positive melano-flocculation reactions. The isolated globulins also lose their melano-flocculability when treated with  $\text{COMe}_2$ ; the reaction is therefore dependent not on the protein part of the globulin mol., but on associated lipins or other  $\text{COMe}_2$ -influenced substances. R. N. C.

**Chemical factors of malaria-flocculation (Henry reaction) in anophelian paludism.** E. BENHAMOU and R. GILLE (Compt. rend. Soc. Biol., 1935, 120, 1259—1261).—The three factors controlling malaria-flocculation are euglobulin, serin, and cholesterol; the Henry reaction depends on their ratio (the index of flocculability), but not on any of them separately. R. N. C.

**Melano-precipitation serological reaction in malaria.** E. D. W. GRIEG, C. O. VAN ROOYEN, and E. B. HENDRY (Trans. Roy. Soc. Trop. Med. Hyg., 1934, 28, 175—191).—The substitution of a colloidal melanin (I) solution (prep. described) for the ox-choroid antigen (Henry) is suggested. In the course of a benign tertian infection the blood-phospholipin inversely  $\propto$  the reacting titre with (I). CH. ABS. (p)

**Malaria and blackwater fever. I. Malaria. II. Blackwater fever. Haemoglobinæmia. III. New blood pigment in blackwater fever and other biochemical observations.** N. H. FAIRLEY and R. J. BROMFIELD (Trans. Roy. Soc. Trop. Med. Hyg., 1933—1934, 27, 289—314).—I. Blood destruction in malaria is associated with hyperbilirubinaemia, urea increase, decrease in blood-cholesterol, and normal alkali reserve. Haemoglobinæmia does not occur. Sp. treatment (quinine etc.) decreases plasma-bilirubin and -urea and increases blood-cholesterol.

II. In blackwater fever blood is brownish-red and contains methaemoglobin (I). Washed red cells do not contain (I). Variations in (I) and oxyhaemoglobin (II) are recorded. (I) arises from (II) which has been liberated from corpuscles after lysis. Drug-methaemoglobinæmia is intracorpuseular in origin and does not

involve presence of (I) in plasma or excretion in urine.

III. The pigment resembles but is not identical with (I). The hæmolytic agent in blackwater fever arises from metabolic breakdown in chronic subtertian malarial infection, is pptd. by quinine, lysing the corpuscle and converting the liberated (II) into (I), or the new pigment. CH. Abs. (p)

**Function of the liver in malaria. Overloading with galactose and combined overloading with insulin-glucose-water.** K. TSCHELOV and I. MLADENOV (Arch. Schiffs- u. Tropen-Hyg., 1934, 38, 282—287; Chem. Zentr., 1934, ii, 3405).—Galactosuria following overloading with galactose does not indicate liver injury. In some patients blood-sugar (I) is increased without sugar excretion. Combined administration of glucose and  $H_2O$  after insulin produces a disturbance of the liver function, with hypoglycæmia and an abnormal difference between (I) in the unaffected and hypoglycæmic states. (I) is frequently delayed in reaching its max. R. N. C.

**Experimental chemotherapy in malaria.** W. KIKUTH (Deut. med. Woch., 1935, 61, 573—577). R. N. C.

**Chlorine metabolism in meningitis.** A. PRUNELL (Prensa med. Argentina, 1935, No. 2).—Bacillary meningitis is usually followed by decreased  $Cl'$  in spinal fluid; glucose content is lowered and fibrin is present. Blood- $NaCl$  is correspondingly decreased. CH. Abs. (p)

**Diagnostic and prognostic significance of the creatine-creatinine metabolism in various myopathies before and after amino-acid therapy.** H. H. BEARD, C. J. TRIPOLI, and J. E. ANDES (Amer. J. Med. Sci., 1934, 188, 706—712).—Clinical improvement is associated with increased creatine excretion (50—200% > that of control period) provided this increased creatinuria soon disappears or returns to the control level. Creatinuria probably has an exogenous origin from the  $NH_2$ -acids of the diet. CH. Abs. (p)

**Thiocyanate ions in blood and urine of nephritic cases.** H. INOUE and M. YAMASHITA (J. Chosen Med. Assoc., 1935, 25, 1—13).—Blood- $SCN'$  increases and urinary  $SCN'$  decreases in nephritis. A similar retention of  $SCN'$  occurs in experimental nephritis produced in rabbits by cantharidin, U, and  $HgCl_2$ . CH. Abs. (p)

**Phenol contents of blood of nephritic and hepatic patients.** D. YANAGIHARI (J. Chosen Med. Assoc., 1934, 24, 1562—1570).—Vals. for free, combined, and total  $PhOH$  in nephritic patients were <, and in hepatic patients >, normal. The free  $PhOH$  in blood increases with the gravity of the disease. No relationship was apparent between blood pressure and blood- $PhOH$ . CH. Abs. (p)

**An optimal diet in promoting nitrogen gain in nephrosis** S. H. LIU and H. I. CHU (J. Clin. Invest., 1935, 14, 293—303).—In Bright's disease of the nephrotic type, N retention was favoured by increasing the carbohydrate, fat, and N in the diet. Optimum

vals. are given. Changes in serum-protein level took place slowly even during N retention.

CH. Abs. (p)  
**Indican test on blood and urine in renal insufficiency.** S. H. POLAYES and E. A. ECKERT (J. Lab. Clin. Med., 1935, 20, 681—688).—High blood-indican (I) is always accompanied by high total non-protein-N (II). In some cases of severe renal disease normal (I) occurs with high (II). A persistent increase in (I), concomitant with a decrease in urinary indican, indicates a fatal prognosis. CH. Abs. (p)

**Influence of glycine on creatinuria in peripheral neuritis.** M. J. C. ALLISON, H. H. HENSTELL, and H. E. HIMWICH (Amer. J. Med. Sci., 1934, 188, 560—564).—Ingestion of glycine markedly increased creatinuria. Edetan and glutamic acid had no action. CH. Abs. (p)

**Nutritional oedema in the dog. II. Hypoalbuminaemia and the augmentation of tissue fluid.** A. A. WEECH, E. GOETTSCHE, and E. B. REEVES (J. Exp. Med., 1935, 61, 717—734).—Data relating to N metabolism and wt. changes indicate increasing retention of fluid during the pre-oedema stage. A positive correlation between the duration of oedema and the protein content of the oedema fluid is not demonstrable. CH. Abs. (p)

**Polypeptidæmia in pellagra.** P. TOMESCO, N. G. IONESCO, and P. CONSTANTINESCO (Compt. rend. Soc. Biol., 1936, 121, 190—192).—Polypeptidæmia is increased in pellagra, particularly in the more pronounced visceral forms. R. N. C.

**Behaviour of hepatic lipins in experimental rabies.** R. MACCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 580—583).—Hepatic lipins are > normal in the rabbit. R. N. C.

**Action of the lung on polypeptides: application to the study of scalds.** L. BINET and M. BURNSTEIN (Compt. rend. Soc. Biol., 1936, 121, 287—289).—Perfusion of blood through an isolated scalded lung causes an increase in the polypeptide content of the blood, which is reduced by subsequent perfusion through a normal lung. R. N. C.

**Chemotherapy of schistosomiasis.** M. KHALIL (J. Egypt Med. Assoc., 1935, 18, 284—295). CH. Abs. (p)

**Experimental scurvy. XX. Leucocytes in blood of guinea-pigs on a vitamin-C-free diet. XXII. Amounts of reducing substance and hydrolysed sugar in urine of guinea-pigs on a vitamin-C-free diet.** J. SHIMADA. XXIV. Gas metabolism. Y. SONEDA and Y. KATO (Sei-i-Kwai Med. J., 1934, 53, No. 6, 105—123, No. 10, 159—171, 172—186).—XXII. Scurvy does not affect the reducing substances in urine. Partial inanition causes a decrease in the amount and % of these substances.

XXIV Diets free from vitamin-C cause an initial decline (2 days), a return to normal (3 days), and from the tenth scorbutic day till death a steady decline in gaseous metabolism. The  $O_2$  intake of semi-starved guinea-pigs is reduced in abs. val., but practically unchanged if calc. on a body-wt. basis. CH. Abs. (p)

Complement fixation as related to resistance and allergy in experimental tuberculosis. A. B. BAKER (Amer. Rev. Tuberc., 1935, 31, 54—61).  
CH. ABS. (p)

Gastric acidity in pulmonary tuberculosis. I. GRAY and J. MELNICK (Amer. Rev. Tuberc., 1935, 31, 460—465).  
CH. ABS. (p)

Vitamin therapy in intestinal tuberculosis. M. M. STEINBACH and M. B. ROSENBLAT (Amer. Rev. Tuberc., 1935, 31, 35—43).—High-vitamin diets neither cured nor prevented intestinal tuberculosis.  
CH. ABS. (p)

Effect of applications of irradiated cholesterolised lanoline on the blood-cholesterol in pulmonary tuberculosis. A. DUFOUR and P. LAROUX (Compt. rend. Soc. Biol., 1936, 121, 43—45).  
R. N. C.

Standardised tuberculin (purified protein derivative) for uniformity in diagnosis and epidemiology. E. R. LONG, F. B. SEIBERT, and J. D. ARONSEN (Tubercle, 1935, 16, 304—322).  
CH. ABS. (p)

Old tuberculin, human tubercle bacillus protein, and trichloroacetic acid precipitate. C. A. STEWART (Amer. J. Dis. Children, 1935, 49, 625—628).—Simultaneous sensitivity to tuberculo-protein (by  $\text{CO}_2\text{H}$  pptn.) differs with age.  
CH. ABS. (p)

Effect of reduced glutathione on the curative action of neosalvarsan in the nagana-infected mouse. C. MONCORPS and R. M. BOHNSTEDT (Arch. Dermatologie, 1934, 170, 26—32; Chem. Zentr., 1934, ii, 3983).—Glutathione (I) increases the virulence of trypanosomes, and detoxifies neosalvarsan. In mice infected with *T. nagana* the action of (I) is weakened by small quantities of (I) (subcutaneous) but strengthened by large quantities (intravenous).  
N

Study of gastric acid secretion by fractional analyses in cases of gastric and duodenal ulcers. DELFINO (Pathologica, 1935, 27, 261—268).—representing changes of titratable acidity with time of extraction of the gastric secretion are parabolic in normal cases but not in cases of ulceration.  
CH. ABS. (p)

regulation of basal metabolism. L. AN (Orvosi Hetilap, 1935, 79, 311—314).—Basal metabolism is not influenced by agents affecting cerebral centres. Narcotics cause a change of 10%.  
CH. ABS. (p)

B in children of normal and a intelligence. Blood-cholesterol and creatinine values. B. ROTHBART (Amer. J. Dis. Children, 1935, 672—688).—No correlation was apparent between metabolic rates and intelligence quotients.  
CH. ABS. (p)

S action of amino-acids. I. E. effect of glucose on the specific-dynamic action of glycine. II. Effect of configuration on specific-dynamic action. III. Dependence of specific-dynamic action on amino-group content. Y. MASAI, T. UCHI, and T. FUKIWAKE (Biochem. Z., 1936, 283, 159—168, 169—173, 174—179).—I.

In fasting rabbits, distilled  $\text{H}_2\text{O}$ , orally administered, has no sp.-dynamic action and during the fast that of glucose (I) is very weak. The sp.-dynamic action of glycine (II) gradually decreases and finally disappears as fasting continues. The action of (II) is weakened and curtailed by administration of phloridzin. In both cases previous administration of (I) increases the action of (II). Hence the presence of (I) is essential for the development of the sp.-dynamic action of (II).

II. The sp.-dynamic action of *l*-alanine, *l*-glutamic acid, and *l*-aspartic acid is respectively > that of the corresponding *d*- and *dl*-acids, the action of *dl*-aspartic acid being very weak.

III. For each  $\text{NH}_2$ -acid there is an optimal amount which has the most powerful sp.-dynamic action, this being less powerful with larger or smaller amounts. There is no relation between the amount of  $\text{NH}_2$ -acid given or its  $\text{NH}_2$  content and the magnitude of the action. The action of urea is strong, but weaker than that of (II) and alanine.  
W. McC.

Diffusion of nitrogenous compounds from frog muscles in Ringer's solution. W. O. FENN (J. Cell. Comp. Physiol., 1935, 6, 469—485).—Frog muscles in Ringer's solution at 22° lose about  $52 \pm 6$  mg. of N per 100 g. of muscle in 5 hr., half the N lost being protein, and the remainder urea, creatine, and  $\text{NH}_2$ -acids. In solutions of varying  $[\text{K}^+]$  the loss in protein  $\propto$  the gain in  $\text{Cl}^-$ , with a min. at about 50 mg. of K per 100 g. Protein loss is increased by rise of temp., asphyxia, and frequent renewal of the solution; non-protein-N loss is increased by stimulation and asphyxia. Both N losses are reduced by previous perfusion of the muscle with Ringer's solution. During immersion in Ringer's solution  $p_{\text{H}}$  falls in the muscles and rises in the solution, owing to loss of  $\text{K}^+$  and gain of  $\text{Cl}^-$  by the muscle. Ringer's solution as a medium for muscle is abnormal.  
R. N. C.

Water balance of a marine mammal, the seal. L. IRVING, K. C. FISHER, and F. C. McINTOSH (J. Cell. Comp. Physiol., 1935, 6, 387—391).  
R. N. C.

Mechanism by which the acidity of an acid meal is reduced in the stomach. F. C. HILL, L. C. HENRICH, and C. M. WILHELMJ (Surg. Gynecol. Obstet., 1935, 60, 966—968).—The mechanism includes neutralisation and the regurgitation of duodenal fluids. The two factors may be determined by use of phenolphthalein. In dogs vals. were 35 and 65%, respectively.  
CH. ABS. (p)

Metabolism of injured tissue. (A) W. FLEISCHMANN. (B) H. DRUCKREY (Naturwiss., 1936, 24, 15; cf. this vol., 102).—The results of Druckrey are in harmony with previous work, e.g., that by Fleischmann on the metabolism of leucocytes.  
W. O. K.

Metabolism of injured tissue. H. DRUCKREY (Arch. exp. Path. Pharm., 1936, 180, 231—250; cf. this vol., 102).  
F. O. H.

Tissue metabolism. VIII. Effect of fumarate and succinate on tumour respiration. E. BOYLAND and M. E. BOYLAND (Biochem. J., 1936, 30, 224—226).—Respiration of tumour tissue, like

that of muscle, kidney, and liver, is increased by succinate or fumarate and decreased by malonate.

H. G. R.

**Exhaustion of the respiratory capacity *in vitro* of some tissues.** G. DOMINI and P. PERUZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 493—496).

R. N. C.

**Respiration *in vitro* of some tissues in relation to the growth-curve of the organism.** P. PERUZZI (Boll. Soc. ital. Biol. sperim., 1935, 10, 489—493).—O<sub>2</sub> consumption by surviving muscle, spleen, and liver sections of the albino rat rises to a max. during the period when body-wt. has reached 40—60 g., and then falls to a steady val.

R. N. C.

**Utilisation of oxygen by *Mya arenaria*.** L. VAN DAM (J. Exp. Biol., 1935, 12, 86—94).—The O<sub>2</sub> utilisation coeff. is normally 3—10%, but increases temporarily to 25% after a period of anaerobiosis.

CH. ABS. (p)

**Anoxybiosis of the embryo of *Rana fusca* in different stages of development.** I. LATINIR-VETULANI (Bull. Acad. Polonaise, 1935, B, 273—278).—The effect of anaerobic conditions on CO<sub>2</sub> production by the embryo varies with the stage of development. The mechanism of these effects is examined.

A. G. P.

**Respiratory quotients during embryonic development (Orthoptera).** E. J. BOELL (J. Cell. Comp. Physiol., 1935, 6, 369—385).—Bound CO<sub>2</sub> in eggs of *Melanoplus differentialis* increases during development. The O<sub>2</sub> consumption curve reaches a max. in 20 days at 25°. In diapause, respiration is maintained at a min. level, but afterwards it increases steadily. The R.Q. shows that fat is the chief metabolite oxidised during development; it decreases slowly in later stages and is probably converted into chitin.

R. N. C.

**Photodynamically-induced oxygen consumption in muscle and nerve.** A. J. KOSMAN and R. S. LILLIE (J. Cell. Comp. Physiol., 1935, 6, 505—515).—Exposure of eosin-stained muscle and nerve to visible light increases O<sub>2</sub> consumption by 135—183% and 133—144%, respectively. The increase is unaffected by Ca<sup>++</sup>, Na salt solutions, CN<sup>-</sup>, or boiling. Ovalbumin stained with eosin consumes O<sub>2</sub> in presence of light; glucose-eosin solutions, either alone or in presence of adsorbents, do not. Irradiated fat-free muscle extracts but not protein-free extracts consume O<sub>2</sub>. The photodynamic effect in skeletal muscle is possibly associated with the membrane proteins.

R. N. C.

**Energy sources in ontogenesis. VIII. Respiratory quotient of developing gastropod eggs.** E. BALDWIN (J. Exp. Biol., 1935, 12, 27—35).—Throughout development the R.Q. was 1.05. Fat synthesis is indicated. The increase in CO<sub>2</sub> content of the eggs coincides with the formation of true shell. Synthetic fat is probably not derived from protein. Uric acid is synthesised by the embryo during the later period of development.

CH. ABS. (p)

**Nutrition and national health.** (Sir) R. McCARRISON (Roy. Soc. Arts., 1936, 56 pp.).—Cantor Lectures.

**Nutritive value of canavanine.** M. KITAGAWA and M. WADA (J. Agric. Chem. Soc. Japan, 1935, 11, 1083—1088).—Dietary experiments on rats failed to elucidate the growth-promoting action of canavanine (cf. Ogawa, A., 1934, 1391).

F. O. H.

**Nutritive value of mustard oil.** B. B. BRAHMACHARI (Indian Med. Gaz., 1934, 62, 327—329).—The oil contains no vitamin-A and tends to inactivate -A in other foods. It has a nutritive val. similar to that of other fats provided the -A supply is adequate.

CH. ABS. (p)

**Comparison between the nutritive value of some legumes and some cereals.** V. ZAGAMI and V. FAMIANI (Arch. ital. Biol., 88, 119—127; Chem. Zentr., 1935, i, 3301).

G. H. F.

**Nutritive value of alcohol-extracted animal tissues, and supplements required for growth and lactation.** W. H. SEEGER and H. A. MATTIL (Proc. Iowa Acad. Sci., 1934, 41, 173—174).—Extracted tissues (beef heart, kidney, round, and liver) produced inferior growth in rats to that obtained with whole tissues. The deficiency was supplied by the EtOH-extract of liver.

CH. ABS. (p)

**Determination of digestibility coefficients. I. Method and computation for directly obtaining coefficients of individual nutrients in a mixed ration.** M. CARBERY, I. CHATTERJEE, and M. A. HYE (Indian J. Vet. Sci., 1934, 4, 295—340).—Methods utilising graphical and multiple regression equations are described.

CH. ABS. (p)

**Nutritional investigation of the porgy. IV. Fractionation of porgy meat.** Y. HATAKOSHI (J. Chem. Soc. Japan, 1935, 56, 221—229).—Max. dissolution of protein from ground meat was obtained with 0.1N-NaCl or 0.02N-NaOH.

CH. ABS. (p)

**"Disequilibrating" effect of fructose.** R. LECOQ (Compt. rend. Soc. Biol., 1936, 121, 226—228).—Fructose (I) causes disequilibrium when present in the diet to 80—84% of the total carbohydrates. The disequilibrium is not so accentuated as with galactose or lactose. Equilibrium is established with 35% of (I), and with 66% if yeast is added to the diet.

R. N. C.

**Metabolism of the lung-fish. II. Effect of feeding meat on metabolic rate.** H. W. SMITH (J. Cell. Comp. Physiol., 1935, 6, 335—349).—Lung-fish fed with meat exhibit a rise of O<sub>2</sub> consumption, and fasting causes a logarithmic decrease.

N C

**Organic matter in dissolved and colloidal form as food for *Daphnia magna*.** S. S. GELLIS and G. L. CLARKE (Physiol. Zool., 1935, 8, 127—137).—The animals require colloidal nutrients.

CH. ABS. (p)

**Nutrition: vegetable proteins.** L. B. MENDEL and H. B. VICKERY (Carnegie Inst. Wash. Yearbook, 1934, 33, 289—295).—In synthetic rations for rats in P-metabolism trials casein may be replaced lactalbumin or, less satisfactorily, partly purified ovalbumin. Highly purified vitamin-B<sub>2</sub> preps. are obtained from liver, protein-free milk, or yeast extraction with 5% HCl, adsorption on activated fuller's earth, and elution with NH<sub>3</sub> or C<sub>5</sub>H<sub>5</sub>.



Yellow solutions showing green fluorescence (especially in ultra-violet light) are produced. A yeast constituent other than  $-B_1$  or  $-B_2$  is required for satisfactory growth of rats. The cystine content of haemoglobin (Cu<sup>1</sup> mercaptide method) is: horse 0.41, sheep 0.61, dog 1.16%. Histidine was completely pptd. from protein hydrolysates by  $HgCl_2$ . In addition to nicotine, green tobacco leaves contain *N*-methylpyrrolidine and nornicotine, but no sol. quaternary bases other than volatile alkaloids.

CH. ABS. (p)

**Influence of protein on longevity.** C. Y. CHEN (Nat. Peiping Univ. Coll. Agric. Nutrition Bull., 1935, B, 2, 12—21).—On a 9% protein level the life span of rats was shortest on a beef diet and the longest on a mixed cereal diet containing maize protein 2, casein or soya-bean protein 1.

CH. ABS. (p)

**Protein metabolism and oxidation processes in experimental scurvy. III. Urea and creatinine excretions in experimental scurvy and the effect of iron.** L. D. KASHEVNIK and I. B. FRIDLAND (Biochem. Z., 1935, 282, 265—268).—The urinary creatinine in guinea-pigs increases during the development of scurvy and also by addition of Fe to the diets. Addition of Fe, however, does not affect urea excretion.

P. W. C.

**Histochemical studies of the development of fish. I. Vitellogenesis in the gudgeon (*Gobio fluviatilis*) and the carp (*Cyprinus carpio*).** B. KOSOPACKA (Bull. Acad. Polonaise, 1935, B, 163—). Appropriate histological technique is described and the stages of formation of vitellin during the growth of the oocyte are examined.

A. G. P.

**Synthesis of creatinephosphoric acid in organ extracts and in living spermatozoa.** I. TORRES (Z., 1935, 283, 128—133).—The transfer of  $PO_4^{'''}$  from phosphopyruvic acid (I) to creatine occurs in many organ extracts, most rapidly in muscle and next in extract of testicles, the activity in the latter case being related to the sperm content. In living sperms on addition of (I) and creatine show a considerable synthesis of creatinephosphoric acid.

P. W. C.

**Utilisation of tryptophan administered subcutaneously.** V. DU VIGNEAUD, R. R. SEALOCK, VAN ETTEN (J. Biol. Chem., 1936, 112, 451—).—view Alcock's contention (A., 1934, 1392) that tryptophan (I) produces no growth response in (I)-deficient animals, earlier work indicating the contrary (1933, 89) was repeated and confirmed. The discrepancies remained when Alcock's technique was used exactly.

H. D.

**Availability of tryptophan derivatives for supplementing diets deficient in tryptophan.** C. P. BLERG and H. E. HANSON (Proc. Iowa Acad. Sci., 1934, 31, 102—).—cf. A., 1935, 1405).—Utilisation of tryptophan by rats is prevented by benzoylation but not by acetylation or esterification (EtOH). The *p*-propyl and phenylpropionyl derivatives of (I) as well as *p*-Ph and  $CH_2Ph$  ester hydrochlorides (but not the phenylacetate) were utilisable.

CH. ABS. (p)

**Production of a deficiency involving cystine and homocysteine by the administration of cholic**

acid. A. WHITE (J. Biol. Chem., 1936, 112, 503—509).—Rats fed on a diet low in cystine (I) and containing cholic acid (II) lost wt., but addition of either *L*-(I) or *DL*-methionine (III) caused resumption of growth. Taurine and  $Na_2SO_4$  were ineffective. The deficiency in (I) and (III) produced by (II) may be due to the demand for taurine for the synthesis of taurocholic acid, or to a direct detoxication of (II) by (I) and (III).

J. N. A.

**Influence of feeding amino-acids and other compounds on the excretion of creatine and creatinine.** M. BODANSKY (J. Biol. Chem., 1936, 112, 615—624).—Comparatively large doses of arginine, aspartic acid, glutamic acid, cystine, histidine, tyrosine, choline, betaine, sarcosine, and salts of guanidine had no effect on the excretion of creatine (I) and creatinine in rats. Glycine, guanidinoacetic acid, and to a smaller extent, alanine increased the output of (I). 30—80% of (I) given in doses of 35—120 mg. was recovered in the urine within 48 hr.

J. N. A.

**Resorption of bile acids in the small intestine.** E. FROLICHER (Biochem. Z., 1936, 283, 273—279).—In the small intestine of rats taurocholic acid is more readily absorbed than are cholic and glycocholic acid. The absorption of the acids is more rapid in the lower than in the upper part of the intestine. The differences are not due to variations in  $p_H$  (5.9, 7.8) or to excretion of bile acids by the upper part of the intestinal mucous membrane.

W. McC.

**Indican. IV. Absorption of indoles and indican synthesis in the body. V. Excretion of indican by bile.** H. INOUE (J. Chosen Med. Assoc., 1934, 24, 1519—1536; 25, 121—135).—IV. In rabbits and dogs absorption of indoles can be greater in the small than in the large intestine. Some absorbed indole passes into blood by the lymphatics. Synthesis of indican (I) occurs in liver and lungs but not in kidneys or intestines. Emulsions from liver and lungs synthesise (I) *in vitro* (optimum  $p_H$  6.8—9.0).

V. Normal bile contains 0.06—0.12 mg. of (I) per 100 c.c., vals. being close to those in blood at the time of excretion.

CH. ABS. (p)

**Formation of xanthurenic acid: experiments on man.** F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 578—580).—Administration of kynurenine (I) to a healthy man produces the diazo-reaction in the urine, but none of the other reactions of xanthurenic acid. (I) is present in the urine, and is probably responsible for the diazo-reaction.

R. N. C.

**Phosphatide metabolism and the influence of thyroïdin.** L. PASTERNAK and I. H. PAGE (Biochem. Z., 1935, 282, 282—292).—Phosphatide (I) injected intraperitoneally into white mice is not stored, but is completely utilised. The muscle-(I) in rats after treatment with thyroïdin (II) increases by 96%. This increase is not due to any injury of the (I)-degrading power nor to any infiltration of (I) from other tissues. It is not a relative, but an abs. increase due probably to a synthesis of (I) under the action of (II), possibly as intermediate products in the degradation of fat.

P. W. C.

**Choline and dietary production of fatty livers.** C. H. BEST, H. J. CHANNON, and J. H. RIDOUT (J. Physiol., 1934, 81, 409—421).—Fatty liver caused by high-fat diet is due to an increase in the neutral fat fraction. That caused by cholesterol is due to excessive amounts of cholesteryl esters with an increase in neutral fat. The phosphatide (I) content of both types of fatty liver is inversely  $\propto$  the total lipin content. Choline prevents the occurrence of both types of fatty liver, and increases the % of (I) in the livers without disproportionate increases in lecithin and sphingomyelin. CH. ABS. (p)

**Physiology of lipins and sterols under complete and protein inanition.** S. VALLA (Bull. Soc. Chim. biol., 1935, 17, 1715—1740).—A comparison is made of the lipin and sterol content of normal mice and animals undergoing complete and protein starvation. Although the length of life under protein starvation is  $>$  that under complete starvation, the continuous carbohydrate intake in the first case does not prevent the complete utilisation of the fatty reserves. Fasting increases both cholesterol and total N of the animals. A. L.

**Fat metabolism. I. Effect of ingestion of olive oil on lipin contents of rabbit tissues. II. Effect on lipin contents of splenectomised rabbit tissues. III. Effect on sulphur distribution in rabbit tissues.** Y. SONEDA (Sci-i-Kwai Med. J., 1934, 53, No. 8, 49—65, 66—87, 88—91).—I. Daily administration of 10 c.c. of olive oil increased the fat acid (I) and lecithin (II) contents of spleen and adrenals, and the cholesterol (III) in spleen and (slightly) in kidneys. Other organs were unaffected.

II. Splenectomy lowered the (I), (II), and (III) in all organs. Administration of olive oil markedly increased the (I) of the lungs, decreased the (III) : (I) and (III) : (II) ratios of the kidneys, and increased the (II) : (I) ratio in the heart.

III. Feeding of olive oil caused a considerable increase in liver-S, and a slight increase in S of all other organs except lungs (decrease) and kidneys (no change). CH. ABS. (p)

**Combustion of odd-numbered fatty acids in the animal organism.** S. SKRAUP and E. STRIECK (Verh. Ges. Verdauungs- u. Stoffwechselkrankh., 1934, 132—136; Chem. Zentr., 1934, ii, 3784).—Saturated  $C_{11}$  and  $C_{13}$  fatty acids are not oxidised in the body of the dog when administered alone, but the oxidation is catalysed by small quantities of unsaturated fats which are not themselves oxidised. R. N. C.

**Central regulation of fat metabolism in the epidermis.** A. PERUTZ, B. LUSTIG, and A. E. KLEIN (Arch. Dermatol. Syphilis, 1934, 170, 511—520; Chem. Zentr., 1934, ii, 3784).—Destruction of the mid-brain followed by prolonged feeding with fatty substances in rabbits increases hair-fat and blood- $\beta$ -hydroxybutyric acid, blood-ketones being unaffected. Fat excretion by the skin is therefore probably regulated by a central mechanism. R. N. C.

**Fat metabolism in the course of gestation of *Trygon violacea*.** G. STOLFI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1315—1316).—The I vals. of the

fats of the uterine liquid and embryonal tissues are  $<$  that of the maternal liver, which hence must undergo a saturation process in order to be utilised by the foetus. R. N. C.

**Nutritive effect of plant gums on formation of fat and glycogen.** H. IWATA (Bul. Sci. Fak. Terkult. Kjusu, 1933, 5, 352—366).—Feeding gum arabic or starch to rabbits did not increase glycogen formation. Blood-protein-N and haemoglobin were unchanged but -total sugar increased somewhat. CH. ABS. (p)

**Influence of acid-base equilibrium on the glycogen content of the liver.** S. KUMAMURA (Trans. Soc. Path. Japan, 1934, 24, 2—5).—Acidosis decreases, and alkalosis increases, liver-glycogen. CH. ABS. (p)

**Glycogenic function of the liver in the chicken embryo.** A. GUELIN-SCHERINA (Compt. rend. Soc. Biol., 1936, 121, 144—146).—Insulin does not cause the premature appearance of liver-glycogen (I) in the developing chick embryo; (I) appears at a later stage than the pancreas. R. N. C.

**Glycogen metabolism of the organiser in amphibian gastrula.** C. P. RAVEN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1107—1109).—When pieces of ectoderm were inserted in the dorsal lips of the blastospore of the embryo, there was a definite decrease of glycogen (I) in those cells which had involuted. This loss of (I) is closely connected with the involution. J. N. A.

**Initial transformations of glycogenolysis: function of hexose monophosphoric ester.** P. OSTERN and J. A. GUTHKE (Compt. rend. Soc. Biol., 1936, 121, 232—235).—Glycogen is first broken down to hexose monophosphate, which then reacts with adenosinetriphosphoric acid to form hexose diphosphate. R. N. C.

**Utilisation of *d*-mannoheptulose (*d*-manno-ketoheptose) by adult rabbits.** J. H. ROE and C. S. HUDSON (J. Biol. Chem., 1936, 112, 443—449).—Rabbits fed with *d*-mannoketoheptose (I) showed an increased blood-sugar which was not accounted for by the blood-(I); (I) is converted into a reducing substance fermentable by yeast. The conversion does not occur in the liver, but during the process of intestinal absorption. Insulin accelerates the oxidation of the reducing substance formed from (I). H. D.

**Hydrolysis, oxidation, and energy changes in dogs. IV. Absorption of fructose by the organs of dogs *in vivo*.** M. WIERZUCHOWSKI and H. FISZEL (Biochem. Z., 1935, 283, 30—44).—Further work on the utilisation of fructose (I) is described (cf. A., 1935, 1017, 1542). The absorption velocities of (I) by the organs of the dog are, in mg. per g. per hr., for liver 21, organs of the portal system 3.5, motor system 0.4, muscle only 0.8, organs of the head 0.39, other organs 2.0. Simultaneously glucose is being formed by the liver and is being absorbed by the organs of the head with a velocity of 1.3, of the portal system 1.0, motor system 0.02, other organs 0.32. One fifth of the (I) absorbed is returned by the liver to the blood as lactic acid. The organs of

the head and portal system do not appear to give lactic acid in this way. The glucose-forming power of the liver is unchanged during the introduction of inositol, Na lactate, and MeCHO. P. W. C.

#### Chief method of lactic acid formation in muscle.

O. MEYERHOF and W. KRIESSLING (Biochem. 1935, 283, 83—113).—Lactic acid (I) arises in muscle chiefly by the oxidation of 1 mol. of triosephosphoric acid to phosphoglyceric acid with simultaneous reduction of 1 mol. of  $\text{AcCO}_2\text{H}$  to (I). This reaction proceeds much more rapidly than does the earlier described reaction in which  $\alpha$ -glycerophosphoric acid +  $\text{AcCO}_2\text{H}$  gave 2 mols. of (I). The stages of the new reaction can be separated using NaF and  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  in the same way as with alcoholic fermentation. A complete scheme of the intermediate reactions in muscle is given, and it is seen that in muscle  $\text{AcCO}_2\text{H}$  is the biological equiv. of MeCHO and (I) of EtOH of alcoholic fermentation.  $\text{PO}_4^{4-}$  changes involve the muscle-adenylic acid system. The scheme is in close agreement with the requirements of the Harden-Young equation. P. W. C.

Effect of hydrazine on the production of ketonic substances in the phloridzin-intoxicated animal. M. M. GREENBERG (J. Biol. Chem., 1936, 112, 431—436).—Phloridzinised rats, treated with  $\text{N}_2\text{H}_4$ , showed a decreased excretion of ketones which was not due to kidney retention, decreased deamination of  $\text{NH}_2$ -acids, or increased glucose or protein metabolism. H. D.

Comparison of the tendencies of different animal species to ketonuria and ammoniuria. E. F. TERROINE and H. TRIMBACH (Arch. int. Physiol., 1934, 39, 377—416; Chem. Zentr., 1934, ii, 3980).—Ketonuria in milk-fed animals is higher in those of smaller body-wt., but is independent of the amount of food ingested per kg. The ratio  $(\text{COMe}_2 + \text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H})/\beta$ -hydroxybutyric acid in the excreta is generally 30 : 70, but is less for the cat and hedgehog.  $\text{NH}_3$  excretion differs greatly with the species, and is independent of the type or quantity of the food. R. N. C.

Acetaldehyde in muscular work and avitaminosis-B. H. HANDOVSKY (Compt. rend. Soc. Biol., 1935, 120, 1357—1358).—Blood-MeCHO is not modified in the dog by muscular work. Injection of MeCHO in vitamin-B-deficient pigeons delays death. R. N. C.

Fate of alcohol in the corpse of an alcoholised mammal : formation of alcohol in non-alcoholised control animals. M. NICLOUX (Compt. rend. Biol., 1935, 120, 1306—1309).—The rate of disappearance of EtOH from the corpse of an alcoholised mouse increases with temp. Formation of EtOH occurs in non-alcoholised control animals; the rate of formation increases with temp., but it always rises to a max. and then falls. The highest max. occurs at 15—18°. R. N. C.

Mineral metabolism of pullets. II. R. H. SIMON (J. Agric. Sci., 1936, 26, 85—100; cf. A., 1933, 1326).—Heavy P excretion during egg laying increased excretion of  $\text{NH}_3\text{-N}$ . Probably the excess of P is eliminated as  $\text{NH}_4$

phosphate in the urine. Excreted P is not unduly high if the intake of  $\text{CaCO}_3$  is adequate. Pullets receiving 5% of  $\text{CaCO}_3$  in the ration produced eggs with a higher P content than when the  $\text{CaCO}_3$  was omitted. A. G. P.

Renal threshold of potassium. H. GRIFFON (Compt. rend. Soc. Biol., 1936, 121, 47—49).—Theoretical. R. N. C.

Aluminium in nutrition. H. H. KEIL and V. E. NELSON (Proc. Iowa Acad. Sci., 1934, 41, 161—164).—Of the salts examined the order of toxicity was  $\text{Al}(\text{OH})(\text{OAc})_2 < \text{K alum}$  and  $\text{Al}(\text{NO}_3)_3 < \text{AlCl}_3$ . CH. ABS. (p)

Influence of lungs on salt metabolism. S. RYU (J. Chosen Med. Assoc., 1934, 24, 1404—1410).—Blood-Cl in the right heart of the rabbit is  $>$ , and the plasma-Cl  $<$ , the corresponding amounts in the left. Passage of  $\text{CO}_2$  into arterial blood increases plasma-Cl and decreases corpuscular Cl. Reverse effects occur in venous blood. Lungs not only remove Cl from blood but regulate Cl distribution by the gaseous exchange. CH. ABS. (p)

Probable nervous mechanism of the increase of the reducing power of the aqueous humour under the action of light. A. BONSIGNORE (Boll. Soc. ital. Biol. sperim., 1935, 10, 505—509).—The increased ascorbic acid content is probably due to parasympathetic action. R. N. C.

Insolation and acidosis. G. DI MACCO (Boll. Soc. Ital. Biol. sperim., 1935, 10, 437—438).—Administration of HCl to rabbits delays death from insolation. R. N. C.

Increase of cell permeability by mitogenetic irradiation. (Chemical detection of the mitogenetic effect.) I. R. BACHROMEJEV (Biochem. Z., 1935, 282, 297—302).—The small amounts of inorg. P, phosphatide, phosphatase, sugar, and catalase separated from surviving mouse liver into Ringer's solution are very largely increased when the liver is previously subjected to mitogenetic irradiation for  $\frac{1}{2}$  hr. P. W. C.

Role of the reticulo-endothelial system in the fixation of radiothorium. K. SCHACHOWITZ, D. K. JOWANOWITSCH, and M. WISCHNITSCHewa (Glas Srpske kraljevske Akad., 1933, 78, 65—73; Chem. Zentr., 1934, ii, 3401). R. N. C.

Radioactive effect of potassium on the vegetative nervous system. O. MERCK (Strahlenther., 1934, 50, 471—475; Chem. Zentr., 1934, ii, 3786). R. C. N.

Influence of changes in the medium on the development of eggs of *Bothriocephalus scorpii* (Müller 1776). S. MARKOWSKI (Bull. Acad. Polonaise, 1935, B, 49—58).—Eggs are not susceptible to any but extreme changes in salt concn. in the medium. Light intensity is a more important factor. A. G. P.

Behaviour of the water-flea, *Daphnia pulex*, de Geer, in media of different hydrogen-ion concentrations. K. PASSOWICZ (Bull. Acad. Polonaise, 1935, B, 59—86).—Optimum development occurs at  $p_H$  7.3. With  $p_H$  5.7 and 6.0 the population

of *D. pulex* in a culture is restricted but the parthenogenetic increase of the survivors is not affected.

A. G. P.

**Embryonic and larval development in *Saccolina (Rhizocephala)* in media of changed osmotic condition.** M. RAMULT (Bull. Acad. Polonaise, 1935, B, 87—109).—Effects of hypo- and hypertonic solutions on the various stages of development are examined.

A. G. P.

**Water exchange and fatigue: effect of ingestion of water on tachycardia and hyperpnoea from work.** G. DI MACCO (Boll. Soc. ital. Biol. sperim., 1935, 10, 436—437).

R. N. C.

**Electromotive force in biological systems.**

IV. **Effect of carbon monoxide on the electromotive force of frog skin.** A. B. TAYLOR and E. J. BOELL (Proc. Iowa Acad. Sci., 1934, 41, 316—317; cf. A., 1934, 327).—The e.m.f. of frog skin is depressed by CO in CO-O<sub>2</sub> mixtures. The effect is not due to decreased [O<sub>2</sub>]. No additional change occurs in darkness. Aeration causes a return to normal (and sometimes > normal) vals.

CH. ABS. (p)

**Sensitisation of animals with simple chemical compounds.** K. LANDSTEINER and J. JACOBS (Proc. Soc. Exp. Biol. Med., 1934, 31, 790, 1079).—Positive effects on guinea-pigs are obtained with a no. of substances. The mechanism of the action is discussed.

CH. ABS. (p)

**Harmful effect of certain chemicals on the uterus of the rat.** F. E. D'AMOUR and N. KIVEN (Amer. J. Obstet. Gynecol., 1935, 29, 503—509).

CH. ABS. (p)

**Toxic action of heavy metal salts on the three-spined stickleback (*Gasterosteus aculeatus*).** J. R. E. JONES (J. Exp. Biol., 1935, 12, 165—173).—Toxic effects of the salts are largely due to the cations, although anions have some influence, e.g., SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>. Difference in toxicity is closely related to difference in electrical conductivity.

CH. ABS. (p)

**Mammalian organism and action of metallic salts.** L. E. WALBUM (Z. Immunitats., 1934, 82, 399—419).

R. N. C.

**Influence of neutral salts on the photodynamic stimulation of muscle.** R. S. LITTLE, M. A. HINRICHS, and A. J. KOSMAN (J. Cell. Comp. Physiol., 1935, 6, 487—501).—Pure Na salts in solution sensitise eosin-stained muscles to stimulation by light, the efficiencies of the anions being Cl<sup>-</sup> < Br<sup>-</sup> < NO<sub>3</sub><sup>-</sup> < I<sup>-</sup>. Stained muscles irradiated in Ringer's solution are sensitised to subsequent stimulation by Na salts: staining alone has a depressant action. Ca<sup>2+</sup> inhibits the photodynamic response, which is more sensitive to Ca<sup>2+</sup> than to Na<sup>+</sup>. O<sub>2</sub> is essential to photodynamic response.

R. N. C.

**Effect of iodine on the sexual organs and growth in the rat.** A. LIPSCHUTZ and E. MORALES (Compt. rend. Soc. Biol., 1936, 121, 337—340).

R. N. C.

**Iodine compounds and fertilisation. IX. Fertilisation in the starfish, *Asterias rubens*.** L. G. S. CARTER (J. Exp. Biol., 1935, 12, 108—118; cf. A., 1932, 1285).—Immature starfish sperm is activated and the fertilisability of unripe eggs is

improved by treatment with thyroxine (I). Ripe sperm and eggs are unaffected. (I) causes a temporary rise in the O<sub>2</sub> consumption of unripe eggs.

CH. ABS. (p)

**Interpretation of the [physiological] action of some preparations of bromine.** I. SIMON (Boll. Soc. ital. Biol. sperim., 1935, 10, 382—383).—Injection of dibromocholesterol in olive oil in rabbits causes a deposition of Br in the blood, liver, kidney, and adipose tissue, but not in the brain.

R. N. C.

**Effect of cupric, manganous, and ferric chlorides on cardiac explants in tissue culture.** D. C. HETHERINGTON and M. E. SHIPP (Biol. Bull., 1935, 68, 215—230).—Low concns. of the salts produced stimulatory and higher concns. toxic effects. A combination of the three chlorides was very toxic.

CH. ABS. (p)

**The combination of iron and copper and their relation to blood-formation and to general metabolism, and the connexion between their effects and the crystalline state of the metals.** S. ODA (Z. ges. exp. Med., 1932, 84, 719—727; Chem. Zentr., 1935, i, 3154).—Active Fe<sub>2</sub>O<sub>3</sub> (Siderac) (I) causes no polycythæmia in normal animals, but produces changes in the urinary C/N ratio. Cu-albumin compounds or Cu glycerophosphate cause polycythæmia, are efficacious in experimental anæmia, and affect the urinary ratio. Mixtures of (I) and Cu compounds have the greatest effect on blood and C/N ratio, but cryst. combinations of Cu and (I) have no effect on blood formation.

G. H. F.

**Therapeutic action of iron.** L. J. WITTS (Lancet, 1936, 230, 1—5).—Factors affecting the requirement, absorption, and utilisation of Fe are discussed. Absorption of Fe from food or drugs ∝ the ease with which Fe<sup>2+</sup> ions are liberated. Fe is a nutrient and not a stimulant for blood-forming organs.

L. S. T.

**Mercurial (novurit) suppository as a diuretic for cardiac oedema.** J. PARKINSON and W. A. R. THOMSON (Lancet, 1936, 230, 16—19).

L. S. T.

**Action of potassium on formation of lactic acid and breakdown of phosphagen in the isolated muscle of the frog.** D. NACHMANSOHN, J. WAJZER, and A. MARNAY (Compt. rend. Soc. Biol., 1936, 121, 141—142).—Excess of K<sup>+</sup> accelerates lactic acid formation and phosphagen breakdown in the isolated muscle in anaerobiosis.

R. N. C.

**Physiological and pharmacological action of sulphur.** F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1933, 8, 1511—1513).—S injected subcutaneously in dogs in aq. EtOH-glycerol solution increases the resistance of the erythrocytes, and also augments the alkaline reserve of the plasma, thus favouring the O<sub>2</sub>-fixing power of hæmoglobin and increasing the buffering power of the blood. The intracellular oxidation-reduction processes are maintained and accelerated.

R. N. C.

**Action of Viterbo sulphurous water on germination and on the activity of the epithelium of frog's oesophagus.** A. ROSSINI (Annali Chim. Appl., 1935, 25, 541—557).—The SO<sub>2</sub>-containing H<sub>2</sub>O (ana-



lyses given), after a brief initial retardation, accelerates the germination and growth of wheat and lentil when compared with controls in normal  $H_2O$  or Knop's solution. The movements of ciliated epithelial cells are depressed and finally (1—2 hr.) arrested. F. O. H.

Action of some natural mineral waters on the isolated heart. G. GUIDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 432—434). R. N. C.

Action of hydrocyanic acid on carbon dioxide assimilation and respiration of *Stichiococcus bacillaris*. F. VAN DER PAAUW (Planta, 1934, 24, 353—360).—Small amounts of HCN accelerate assimilation and respiration under conditions of high or low light intensity. The inhibitory effect of larger dosages of HCN is more marked in high light intensity. A. G. P.

Fixation of propyl bromide in the blood and brain of the guinea-pig, after preliminary administration of different poisons of the central nervous system. M. TIFFENEAU and D. BROWN (Compt. rend. Soc. Biol., 1935, 120, 1169—1170).—The  $Pr^{Br}$ -fixing capacity of the brain is reduced by hypnotics (chloralose, soneryl, urethane), but increased by stimulants such as caffeine. R. N. C.

Pharmacology of bromoacetic acid. H. FREUND (Arch. exp. Path. Pharm., 1936, 180, 199—208).—The mechanism of the sp. actions of  $CH_2BrCO_2H$  on carbohydrate metabolism of animals and bacteria and of the toxic action on ascarides (the muscular contraction of which is compared with that due to santonin) is discussed. F. O. H.

Elimination of sodium formaldehydesulphoxylate by the kidneys. E. HUG (Compt. rend. Soc. Biol., 1936, 121, 365—367).—The kidneys of the dog have a concentrating capacity of 2—2.5% for the compound. The greater part is excreted in 2—3 hr. after injection. R. N. C.

Pharmacology of tetraethylammonium phosphate. I. SIMON (Arch. int. Pharmacodyn. Thé., 1934, 47, 75—95; Chem. Zentr., 1934, ii, 3981). R. N. C.

$\beta$ -n-Alkylcholine chlorides and their acetyl esters.—See this vol., 319.

Influence of the water vapour content of an odorous gas on the olfactory sense. H. WOERDEMAN (Arch. Neerland. Physiol., 1935, 20, 591—595).—Intensity of the odour of isoamyl acetate when mixed with damp air is > when mixed with dry air. J. N. A.

Relations between simple odorous and odorous irritant stimuli and thiocyanate concentration in the nasal mucus. P. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 429—431).—The [CNS] of the mucus is increased by non-irritant and decreased by irritant odours. R. N. C.

Organic effects of hydrazine derivatives. W. C. HUEPER (J. Ind. Hyg., 1936, 18, 17—36).—The four derivatives examined produced lesions of the same type and in the same site, differing only in degree.  $\alpha$ -Ethyl- $\beta$ -propylacetaldehydehydrazone was the most toxic. Destruction of erythrocytes and leucocytes occurred in all cases. P. G. M.

Relation between the chemical constitution and pharmacological action of phenylhydrazine derivatives. W. F. VON OETTINGEN and W. DEICHMANN-GRUEBLER (J. Ind. Hyg., 1936, 18, 1—16).—Attempts to preserve the antipyretic action of  $NHPh \cdot NH_2$  while decreasing its toxicity have been unsuccessful. Substitution of one or more H by alkyl, aryl, alkoxy, or acyl decreases toxicity, which depends largely on the solubility in  $H_2O$  and the ease of hydrolysis. Introduction of  $Bu$ ,  $CH_2Ph$ , or  $CHO$  yields compounds which have no effect on blood pressure, respiration, etc. because of their stability at high temp. P. G. M.

Action of indole on the dehydrogenating power of tissues. G. F. DE GAETANI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1291—1294).—The dehydrogenating processes are generally diminished; blood-sugar is raised. R. N. C.

Action of diketopiperazines on fibroblasts cultivated *in vitro*. R. TRUHAUT and D. ODIETTE (Compt. rend. Soc. Biol., 1935, 120, 1198—1201).—Growth is stimulated by 2:5-diketopiperazine, and to a smaller extent by glycine. R. N. C.

Alkylglyoxalidines.—See this vol., 344.

Mercury salts of alkylfluoresceins.—See this vol., 352.

Action of  $\beta$ -dinitrophenol (1:2:6) on respiratory exchange and temperature of homeothermic animals. G. SARZANA and D. ELIA (Boll. Soc. ital. Biol. sperim., 1935, 10, 545—546).—2:6-Dinitrophenol increases  $O_2$  consumption in pigeons and rats by about 100%. R. N. C.

Pharmacology of the vegetative nervous system. IV. Point of attack of 2:4-dinitrophenol. B. DE BIASIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 383—385). R. N. C.

Action of phenylglyoxal on the vasomotor innervation of the kidney. E. MARTINI and G. FRANCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 473—474). R. N. C.

Vagal central action of phenylglyoxal. E. MARTINI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1709—1710).— $BzCHO$  acts similarly to  $AcCHO$ , but is effective in smaller concns. R. N. C.

Urinary sulphate determinations as a measure of benzene exposure. W. P. YANT, H. H. SCHRENK, R. R. SAYERS, A. A. HORVATH, and W. H. REINHART (J. Ind. Hyg., 1936, 18, 69—88).—A marked decrease in the % of inorg.  $SO_4^{--}$  in the urine occurs many weeks before symptoms of anaemia etc. P. G. M.

Proliferation-stimulating action of 1:2:5:6-dibenzanthracene on *Obelia geniculata*. S. P. REIMANN and F. S. HAMMETT (Amer. J. Cancer, 1935, 20, 343—349).—Hydranth development was stimulated in sea- $H_2O$  cultures containing this compound. CH. ABS. (p)

Hypoglycaemic action of methylene-blue. G. PIOTROWSKI (Compt. rend. Soc. Biol., 1935, 120, 1215—1216).—Methylene-blue does not reduce normal blood-sugar in rabbits, but apparently reduces hyperglycaemia caused by adrenaline or glucose. R. N. C.

**Secretion in tissue cultures. I. Inhibition of phenol-red accumulation in the chick kidney.** R. CHAMBERS, L. V. BECK, and M. BELKIN. **II. Effect of sodium iodoacetate on the chick kidney.** L. V. BECK and R. CHAMBERS (*J. Cell. Comp. Physiol.*, 1935, **6**, 425—439, 441—455). R. N. C.

**Influence of pyocyanine on respiration of sea-urchin's eggs.** J. RUNNSTROM (*Biol. Bull.*, 1935, **68**, 327—334).—Pyocyanine (I) increases the respiration of the eggs, the effect being further increased by HCN in unfertilised, but decreased in fertilised, eggs. The block in division of the egg caused by HCN is not removed by (I). The rate of respiration in presence of (I) is  $>$  that in the presence of methylene-blue. Neither the Fe-containing enzyme nor the dehydrase-substrate system acts as a limiting factor for the oxidation rate in the unfertilised or newly fertilised egg. CH. ABS. (p)

**Action of acetylcholine on energy exchange.** V. BASUNTI (*Minerva med.*, 1935, **i**, 486—489).—Subcutaneous injection of acetylcholine (0.2 c.c.) during fasting produces a slight but inconst. increase in respiratory exchange and a definite const. increase in the sp. dynamic effect of foods. CH. ABS. (p)

**Acetyl- $\beta$ -methylcholine (mecholine). Action on blood pressure, skin temperature, and the heart as exhibited by electrocardiograms of hypertensive patients.** I. H. PAGE (*Amer. J. Med. Sci.*, 1935, **189**, 55—64). CH. ABS. (p)

**Developmental growth and the amino-acids. II. *l*-Tryptophan.** F. S. HAMMETT and M. L. ELLIOTT. **III. *d*-Arginine.** F. S. HAMMETT and N. CHATALBASH (*Protoplasma*, 1935, **23**, 457—465, 492—502).—II. Effects of various concns. of *l*-tryptophan (I) on the development of *Obelia* are recorded. The chief function of (I) is that of retarding catabolic activity, hence its indispensability for wt. maintenance. In developmental growth (I) is a sp. determining participant in processes concerned in differentiation or organisation and in the prep. of the tissue reaction basis for new growth initiation.

**III. The function of arginine (II) in growth** is not the regulation of any particular metabolic activity, but participation in preparatory processes essential for organisation of the tissue reaction basis for new growth initiation. The possible significance of (II) in malignancy is discussed. A. G. P.

**Highly active pressor substance from cerebral ventricular fluid of human beings.** I. H. PAGE (*Science*, 1935, **82**, 550).—Intravenous injection into cats of extract of human cerebral ventricular fluid from malignant hypertension cases produces a sharp rise in arterial pressure. Similar extracts prepared from plasma produce a slower but more prolonged rise. L. S. T.

**Vasoconstrictive substance in blood.** M. ENOMOTO (*J. Chosen Med. Assoc.*, 1935, **25**, 14—25).—The amount of vasoconstrictive substances is increased in pulmonary tuberculosis, typhoid, nephritic and hepatic cases. The substance is not destroyed by  $O_2$ ,  $H_2$ , or  $CO_2$ , nor by heating at  $60^\circ$  for 30 min. It is destroyed at  $100^\circ$ . CH. ABS. (p)

**Effect of specific substances of the body on blood pressure in man. III. Action of lacarnol, myoston, padutin, "fourth substance" (Lange), and eutonone on intravenous application.** H. J. WOLF and H. A. HEINSEN (*Z. klin. Med.*, 1934, **127**, 1—14; *Chem. Zentr.*, 1934, **ii**, 3787). R. N. C.

(A) Antagonistic action of lipins to the toxic action of bile salt. (B) Effect of thyroid gland preparation on formation of gastric ulcer by bile salts, and antagonistic action of cholesteryl oleate. (C) Relationship between toxicity of bile salts and their antagonist. K. ISHII (*Sei-i-Kwai Med. J.*, 1934, **53**, No. 9, 94—191, 192—198, 199—211).—(A) Susceptibility to bile salt (I) toxicity in the male is  $>$  in the female starfish. The effect is antagonised by cholesteryl oleate (II) or phospholipin, but not by free cholesterol, oleic acid, castor or olive oil, glucose, Na K tartrate, Na citrate or lactate.

(B) Hyperthyroidic guinea-pigs are more susceptible to gastric ulcer formation by (I). (II) antagonises the thyroid effect.

(C) When (I) and diphtheria toxin are simultaneously injected into guinea-pigs the antagonistic ratio of (II) : (I) is 1 : 0.8. CH. ABS. (p)

**Influence of cell constituents of the pancreas on the external secretion of the pancreas. I. Influence of parenteral introduction of pancreas cell constituents into dogs with complete pancreatic fistulas. II. Influence of cell constituents of other organs. III. Influence of purified extracts of pancreas and other organs. IV. Mechanism of hypersecretion and nature of the exciting agent.** K. TABUCHI (*Japan. J. Exp. Med.*, 1934, **12**, 411—418, 419—421, 423—425, 427—435).—Pancreatic cell constituents and their purified extracts stimulate strongly the external secretion of the pancreas, independently of simultaneous secretion of gastric juice and bile. Secretion is not inhibited by atropine. The mechanism of stimulation differs from that of insulin and histamine and is effected by a hormone acting by way of the blood stream on the acinar cells. CH. ABS. (p)

**Action of some amines related to adrenaline: methoxyphenylmethoxyethylamines.** G. K. ELPHICK and J. A. GUNN (*J. Physiol.*, 1934, **81**, 422—433).—The physiological effects of *p*-methoxy-3 : 4-dimethoxy-, and 3 : 4 : 5-trimethoxy-phenyl- $\beta$ -methoxyethylamines are compared with corresponding compounds lacking OMe. Addition of OMe to the side-chain diminishes the activity. CH. ABS. (p)

**Importance of cholesterol in the action of calcium on heart muscle.** S. MENTL, J. KARASEK, and V. KRUTA (*Arch. int. Physiol.*, 1934, **40**, 158—172; *Chem. Zentr.*, 1935, **i**, 3158).—The heart of cholesterol-treated frogs reacts normally to Ca and adrenaline, although the isolated heart is abnormally sensitive in presence of cholesterol. The right auricle of cholesterol-fed guinea-pigs is more sensitive and contains more cholesterol than normal. G. H. F.

**Action of creatine on the double electric curve of fatigue in man.** G. BORGATTI (*Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 609—611). R. N. C.

**Variations of the dehydroascorbic/ascorbic acid ratio in the liver and adrenals after administration of parasympatheticotropic substances.** F. COPELLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 509—515).—The ratio is decreased by parasympathetic excitants, and increased by paralyzers, in the liver, but is not affected by either in the adrenals.

R. N. C.

**Theory of narcosis.** N. V. LAZAREV (Biochem. Z., 1935, 283, 158).—Claim of priority in respect of the work of Meyer and Hemmi (A., 1935, 893).

P. W. C.

**Effects of chloral hydrate on maternal and fetal organisms.** R. E. CAMPBELL (Amer. J. Obstet. Gynecol., 1934, 28, 83—88).—Chloral hydrate depresses respiration and urinary output.

CH. ABS. (p)

**Carbohydrate metabolism under barbiturate narcosis.** M. G. MULINOS (Arch. int. Pharmacodyn. Ther., 1934, 47, 111—112; Chem. Zentr., 1934, ii, 3403).—Blood-sugar (I) in rabbits and dogs is raised by amylal, pernocton (II), nembutal (III), and dial. (II) anaesthesia does not affect the action of subcutaneously-injected glucose, adrenaline, or insulin on (I). Oral administration of glucose to anaesthetised rabbits raises (I) to only 60% of the val. reached in unanaesthetised animals. The urine of (III)-anaesthetised cats contains a reducing substance that is not glucose.

R. N. C.

**Constitution and hypnotic action: bromoethyl- and diethyl-barbituric acid.** L. DONATELLI (Arch. Farm. sperim., 1935, 40, 497—516).—The Na salt of 5-bromo-5-ethyl- (I) has a stronger hypnotic action than that of 5:5-diethyl-barbituric acid (II), and is very toxic. In restricting the respiration, and is very toxic. In restricting the respiration, and diminishing the amplitude and the frequency of the cardiac function, and in vasodilatory action the effect of (I) is much > that of (II).

E. P.

**Effect of oxygen in the prevention of liver necrosis produced by volatile antiseptics.** S. GOLDSCHMIDT, I. S. RAVDIN, and B. LUCKÉ (Amer. J. Med. Sci., 1935, 189, 155—156).—In  $\text{CHCl}_3$  or ivinyl ether anaesthesia,  $\text{O}_2$  decreases subsequent necrosis.

CH. ABS. (p)

**Local anaesthetics with vasopressor action. Esters of aryethanolamines.** G. A. ALLES and R. K. KNOEFEL (Arch. int. Pharmacodyn., 1934, 47, 96—110; Chem. Zentr., 1934, ii, 3404).

R. N. C.

**Effects of drugs on the autonomic nervous and on protein metabolism in normal and hypophysectomised dogs.** Y. TAKIZAKI (Sci. Med. J., 1934, 53, No. 11, 98—117).—In action eserine increased protein and intermediate metabolism. The effect was reversed by administration of nicotine or atropine.

CH. ABS. (p)

**Action of decamethylenediguanidine bitartrate on blood-sugar.** B. L. MONIAS (Illinois Med. J., 1934, 66, 105—107).—Dosages of 12 mg. administered by stomach tube caused a temporary increase of blood-sugar. Larger amounts (24 mg.) caused convulsions and death even when glucose (I) was given after

convulsions started. Simultaneous injection with (I) was non-toxic.

CH. ABS. (p)

**Cardiazol as a reviver in animal experiments.** M. H. FISCHER and H. LOWENBACH (Klin. Woch., 1934, 13, 1401; Chem. Zentr., 1934, ii, 3983).

R. N. C.

**Carioclastic crisis in the reticulo-endothelial system and endogenous uric acid exchange.** G. DOMINI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1297—1300).—Carioclastic substances do not affect blood- or urinary uric acid in the dog, but allantoin excretion is increased.

R. N. C.

**Comparison of the effect of guanidine, synthalin, and "anticoman" on the muscle of cold-blooded animals.** R. RITTMANN and J. MAGERL (Arch. Verdauungskr., 1935, 57, 9—14; Chem. Zentr., 1935, i, 3158).—The fatigue induced in frog sartorius muscle, indicated by the acceleration in rate of production of lactic acid, gives the order: synthalin > guanidine > "anticoman" > "anticoman" + pancreatic enzyme prep. > "anticoman" tablets.

G. H. F.

**Action of ricin on the isolated heart of the rabbit.** R. ATTIMONELLI (Boll. Soc. ital. Biol. sperim., 1933, 8, 1524—1528).

R. N. C.

**Action of thevetin, a cardiac glucoside, and its clinical application.** H. L. ARNOLD, W. S. MIDDLETON, and K. K. CHEN (Amer. J. Med. Sci., 1935, 189, 193—206).—Thevetin from "be-still" nuts (*Thevetia neriifolia*) has a digitalis-like action with potency and toxicity approx. 1/7 of that of ouabain.

CH. ABS. (p)

**Mechanism and course of chemotherapeutic action.** F. AXMACHER (Arch. exp. Path. Pharm., 1936, 180, 142—166).—The action of various chemotherapeutic substances is ascribed to purely physical processes, e.g., changes in permeability and surface action, resulting in exclusion of nutritive substances from the cell and in inhibition of cell-enzymes. The action of germanin (I) on the fermentation of cell macerates does not depend on adsorption-inactivation of zymase, but is possibly related to the presence of  $\text{SO}_3\text{H}$  in (I); that of Sb preps. is due to inhibition or destruction of carboxylase. The mechanism of curative processes is discussed.

F. O. H.

**Mode of action of chemotherapeutics in spirochaete and protozoan infections.** E. SINGER (Med. Klinik, 1935, 31, 380—389).

R. N. C.

**New antipyretic: isopropylantipyrene.** G. ORESTANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 470—473).

R. N. C.

**Pharmacology of chenopodium oil. II.** M. AIAZZI-MANCINI and L. DOVATELLI (Boll. Soc. ital. Biol. sperim., 1934, 9, 1306—1307).

R. N. C.

**Theosan and its combinations.** F. ECKHARDT (Wien. med. Woch., 1934, 84, 1059; Chem. Zentr., 1934, ii, 3787).

R. N. C.

**Mechanism of the action of ephedrine on gaseous exchange.** G. ORESTANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 467—469).—The action of ephedrine on gaseous metabolism is similar to that of

adrenaline, and is effective in the same species, the effect persisting longer. R. N. C.

**Octaverine, a new spasmolytic.** P. ELLINGER, W. KOSCHARA, and H. SEEGER (Arch. int. Pharmacodyn. Thé., 1934, 48, 50—62; Chem. Zentr., 1934, ii, 3402).—Octaverine, a derivative of phenylisoquinoline, is less toxic and is less rapidly absorbed and detoxicated than papaverine. R. N. C.

**Action of bulbocapnine on the frog's heart.** F. M. CHIANCONE and U. POPPI (Boll. Soc. ital. Biol. sperim., 1935, 10, 573—575). R. N. C.

**Action of bulbocapnine on isolated frog muscle.** U. POPPI and F. M. CHIANCONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 570—573). R. N. C.

**Action of cocaine on fish.** R. DE MARCO (Boll. Soc. ital. Biol. sperim., 1933, 8, 1488—1490). R. N. C.

**Pharmacology of physostigmine.** C. R. LINEGAR, J. M. DILLE, and T. KOPPANYI (Science, 1935, 82, 497). L. S. T.

**New active principle in ergot: effects on uterine mobility.** M. E. DAVIS, F. L. ADAIR, G. ROGERS, M. S. KHARASCH, and R. R. LEGAULT (Amer. J. Obstet. Gynecol., 1935, 29, 155—167).—A yellow, stable, non-alkaloidal fraction is isolated. It provokes the characteristic uterine response. CH. ABS. (p)

**Physiological action of ergometrine and of ergometrine.** R. HAMET (Compt. rend. Soc. Biol., 1935, 120, 1208—1212).—The activity of ergometrine in the dog is the smaller. R. N. C.

**Effect of morphine and of heroin on blood-sugar and respiration in rabbits.** H. GYOKU (J. Chosen Med. Assoc., 1935, 25, 222—226).—Blood-sugar is increased by injection of morphine hydrochloride (0.05 g. per kg.), reaching a max. in 2—3 hr., and regaining normal in 6—7 hr. Heroin hydrochloride produces similar but smaller changes. CH. ABS. (p)

**Antagonism between nicotine and some quaternary hexamethylenetetramine iodides. Curare poisons.** J. GAUTRELET and N. HALPERN (Arch. int. Pharmacodyn. Thé., 1934, 47, 4—44; Chem. Zentr., 1934, ii, 3402). R. N. C.

**Effect of nicotine on sex and sexual hormone.** Y. C. LEE (Trans. Soc. Path. Japon, 1934, 24, 446—449).—Luteo-hormone had a marked antidotic action to nicotine. CH. ABS. (p)

**Action of pilocarpine and acetylcholine, introduced into a Vella loop, on enteric secretion.** G. SARZANA (Boll. Soc. ital. Biol. sperim., 1935, 10, 542—544). R. N. C.

**Action of pilocarpine on formation of lactic acid and breakdown of phosphagen in the isolated frog's muscle at rest.** D. NACHMANSOHN, J. WAJZER, and R. LIPPMANN (Compt. rend. Soc. Biol., 1936, 121, 139—141).—Pilocarpine accelerates both lactic acid formation and phosphagen breakdown in the isolated muscle in anaërobiosis. R. N. C.

**Tolerance of cells cultivated *in vitro* to the action of quinine dichloride.** L. PILATI (Boll. Soc. ital. Biol. sperim., 1935, 10, 414—416). R. N. C.

**Influence of quinine derivatives on the iodine contents of endocrine organs.** II. A. OHTA (Sei-i-Kwai Med. J., 1934, 53, No. 11, 78—97).—Quinine hydrochloride (10 c.c. of 10% solution per kg.) increased the I content of thyroid, adrenals, liver, ovaries, and testicles, and lowered that of blood, thymus, spleen, pituitary, and pancreas. Both cinchonine hydrochloride and 2-hydroquinine produced smaller increases in I in thyroid, adrenals, and testicle; the former lowered that of spleen, and the latter that of spleen and liver. Optoquin caused no changes (cf. A., 1935, 1396). CH. ABS. (p)

**Action of quinic and phenylcinchoninic acids on metabolism.** E. BECCARI (Boll. Soc. ital. Biol. sperim., 1935, 10, 402—405).—Injection of quinic (I) and phenylcinchoninic acids (II) in healthy human subjects increases uric acid excretion. (I) produces a negative and (II) a positive balance of N and P. The urinary urea-/total N ratio is reduced by (I) through an increase of non-urea-N excretion, whilst the variations produced by (II) are due to variations of urea. The azoturic coeff. is reduced by both acids. R. N. C.

**Alkaloids from the seeds of *Cassia absus*, Linn.**—See this vol., 350.

**Isomerisation of conessine and its nor-bases.**—See this vol., 350.

**Variable action of cobra venoms standardised for therapeutic use.** P. SEMOMIN and J. BRION (Compt. rend. Soc. Biol., 1935, 120, 1253—1255). R. N. C.

**Ultra-violet absorption spectra of snake venoms.** H. F. HOLDEN and C. G. SETTER (Austral. J. Exp. Biol., 1936, 13, 223—228).—The venoms of many snakes exhibit an ultra-violet absorption band at about 280 m $\mu$ , but no correlation exists between the toxicity of the venom and the position or intensity of the band. W. O. K.

**Carbon tetrachloride intoxication.** A. NASSAN and M. SALAH (J. Egypt. Med. Assoc., 1935, 18, 207—214).—Poisoning by CCl<sub>4</sub> used as an anthelmintic is not related to the amount used or to Ca deficiency, but is due to constitutional intolerance. CH. ABS. (p)

**Arrow poisons.** C. G. SANTESSON (Skand. Arch. Physiol., 1934, 70, 102—125; Chem. Zentr., 1935, i, 3310).—An arrow poison of central African pigmies is of the digitalis-strophanthus type. Investigation of two Celebes arrow poisons points to their glucosidic nature, one of them possibly being derived from *Antiaris toxicaria*, Lesch. H. N. R.

**Physiology of the treatment of barbiturate poisoning.** R. MASSIERE and G. BEAUMONT (Presse Méd., 1935, 43, 4—7; Chem. Zentr., 1935, i, 3310).—The efficacy of strychnine as an antidote for barbiturate poisoning is not due to antagonism, but is an adsorption effect analogous to the toxin-antitoxin reaction. H. N. R.

**Toxicity of methyl alcohol.** S. KAJIZUKA (J. Soc. Chem. Ind. Japan, 1935, 38, 746—747B).—MeOH stimulates the mucous membranes locally, but is not highly toxic. On a diet containing 10% MeOH,



rats show a turbidity of the urine and an increased excretion of  $\text{HCO}_2\text{H}$ . H. G. R.

**Cause of the toxicity of methyl alcohol.** I. SIMON (Boll. Soc. ital. Biol. sperim., 1935, 8, 1376—1379).—The toxic effect of  $\text{MeOH}$  is considered to be due to  $\text{MeOH}$  itself, no oxidation to  $\text{CH}_2\text{O}$  or  $\text{HCO}_2\text{H}$  occurring in the body. R. N. C.

**Distribution of arsenic a few hours after ingestion of small amounts.** G. VITTE (Bull. Trav. Soc. Pharm. Bordeaux, 1934, 72, 357—358; Chem. Zentr., 1935, i, 3159).—The distribution of As in the viscera with and without simultaneous dosing with  $\text{Na}_2\text{SO}_4$  has been investigated. J. S. A.

**Effect of Fowler's solution on animals.** E. ROBERTS and W. M. DAWSON (Illinois Agric. Exp. Sta. Bull., 1935, No. 413, 187—202).—The practice of feeding Fowler's solution to animals for show purposes diminishes respiratory activity and reproductive functions. In treated animals As may be detected in the urine, faeces, and hair. A. G. P.

**Increase in toxicity for mice of solutions of neoarsphenamine on exposure to air.** R. WIEN (Quart. J. Pharm., 1935, 8, 631—641).—The toxicity to rats of a solution of neoarsphenamine increased by 17.5 and 23% after exposure to air for 15 and 25 min., respectively, but this increase was prevented if the solution was protected by a layer of liquid paraffin. W. O. K.

**Toxicity of sodium cyanide and the efficiency of the nitrite-thiosulphate combination as a remedy for poisoned animals.** A. B. CLAWSON, v. F. COUCH, and H. BUNYEA (J. Washington Acad. Sci., 1935, 25, 357—361).— $\text{NaCN}$  is less toxic than  $\text{KCN}$  or  $\text{HCN}$ , whilst the two latter are similar. The ratio min. toxic/min. lethal doses is 1 : 2 for  $\text{KCN}$  and  $\text{HCN}$ , and 1 : 1.25 for  $\text{NaCN}$ . Intraperitoneal injection of 1 g. of  $\text{NaNO}_2$  and 2 g. of  $\text{Na}_2\text{S}_2\text{O}_3$  in  $\text{H}_2\text{O}$  1.5—4 min. after the  $\text{NaCN}$  effected recovery in 4 out of 7 cases. P. G. M.

**Use of sodium tetrathionate in cyanide poisoning.** E. MENEGETTI (Boll. Soc. ital. Biol. sperim., 35, 10, 386—391).—A criticism of the method of Aunsiechio and de Nito (cf. A., 1935, 1276). R. N. C.

**Treatment of cyanide poisoning of sheep and cattle.** H. BUNYEA (J. Amer. Vet. Med. Assoc., 656—661).—Injections of methylene-blue,  $\text{NaNO}_2$ , and  $\text{Na}_2\text{S}_2\text{O}_3$  had some val. 10 c.c. of  $\text{NaNO}_2$  followed immediately by 20 c.c. of 10%  $\text{Na}_2\text{S}_2\text{O}_3$  was preferable to either alone. CH. ABS. (p)

**acid and soaps are not antidotes for cyanide poisoning.** BELLECCI (Arch. Farm. sperim., 1935, 40, 517—533).—If intravenous injection of the min. lethal dose  $\text{HgCl}_2$  is followed by injection of tannic acid or Na oleate (II) death is not prevented; is retarded by small, accelerated by large, doses of (I) or (II). If  $\text{HgCl}_2$  is given *per os*, (I) or (II) (*per ven* in large excess retards but does not prevent death. E. P.

**Diagnosis of lead poisoning in children.** M. (Klin. Woch., 1934, 13, 1646—1647; Zentr., 1935, i, 3320).—X-Ray examination,

supplemented by the skin reaction with  $\text{Na}_2\text{S}$ , is best. H. N. R.

**Action of electromagnetic waves on enzyme systems.** A. DE P. FORJAZ (Biochem. Z., 1935, 283, 53—58).—Electromagnetic waves have no effect on the activity of fumarase, but increase the activity of the phosphatase of takadiastase by 20%. P. W. C.

**So-called "blood-group enzyme" content of saliva.** O. SIEVERS (Klin. Woch., 1934, 13, 1640—1641; Chem. Zentr., 1935, i, 3148).—The power of saliva to destroy blood-group characteristics is greatest when collected during starvation. G. H. F.

**Enzymic reactions in heavy water.** D. L. FOX (J. Cell. Comp. Physiol., 1935, 6, 405—424).—Catalase, amylase, and emulsin show no loss of activity in  $\text{D}_2\text{O}$  at the same temp. and  $p_{\text{H}}$  as controls in  $\text{H}_2\text{O}$ . The activity of amylase appears to be increased in conc.  $\text{D}_2\text{O}$ . R. N. C.

**Enzymic hydrolysis of glucosides in heavy water.** K. F. BONHOEFFER and F. SALZER (Naturwiss., 1935, 23, 867).—Glucosides with high affinities for emulsin (*e.g.*, salicin) are hydrolysed more slowly in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$ , whilst for those with low affinities (*e.g.*, methylglucoside) the reverse is the case.  $\text{D}_2\text{O}$  retards the hydrolysis of the enzyme-substrate complex, but may also increase the affinity of the enzyme for its substrate, in which case the higher concn. of the enzyme-substrate complex may compensate for the retardation of the hydrolysis, leading to an increase in the rate of reaction. E. A. H. R.

**Hydrogen-transporting co-enzyme, its composition and mode of action.** O. WARBURG, W. CHRISTIAN, and A. GRIESE (Biochem. Z., 1935, 282, 157—205).—The co-enzyme (I) from red blood cells, which is designated the H-transporting enzyme, was purified until its catalytic activity could not be further increased. The purest prep. (12.9% N, 12.3% P) was readily sol. in  $\text{H}_2\text{O}$ , did not crystallise, and on hydrolysis yielded 1 mol. each of adenine and nicotinamide together with 3 mols. of  $\text{H}_3\text{PO}_4$  and 2 mols. of pentose. Assuming that these are united with the loss of  $6\text{H}_2\text{O}$ , (I) is  $\text{C}_{21}\text{H}_{28}\text{O}_{17}\text{N}_3\text{P}_3$ . The  $\text{H}_2$  transportase of heart-muscle is probably, and that of yeast is certainly, identical with (I). (I) cannot replace cozymase (II) in yeast fermentation nor can (II) replace (I) in oxidation experiments. (I) is however, probably closely related to (II). (I) is active only in association with certain proteins, which are called intermediate enzymes (III). Hexosephosphoric acid (IV) in presence of traces of (I) + (III) + Warburg's yellow enzyme (V) is oxidised to hexosephosphonic acid (VI), (V) being reduced and, in presence of atm.  $\text{O}_2$ , reoxidised. (IV) is also oxidised by an equiv. amount of (I) in presence of (III), giving (VI) + (I)- $\text{H}_2$ , the latter then being able to react with (V) to give free (I) + (V)- $\text{H}_2$ . This then reacts with atm.  $\text{O}_2$  giving  $\text{H}_2\text{O}_2$  + (V). (I) can be hydrogenated reversibly by  $\text{Na}_2\text{S}_2\text{O}_4$  and irreversibly by  $\text{Pt} + 3\text{H}_2$ . In the latter reaction the  $\text{C}_5\text{H}_5\text{N}$  is converted into a piperidine ring and (I) loses its activity. The reversible hydrogenation of (I) is a partial hydrogenation of the  $\text{C}_5\text{H}_5\text{N}$  ring. P. W. C.

**Destruction of hydrogen transporting co-enzyme by ultra-violet light.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1935, 282, 221—223).—When 0.001 mg. of co-enzyme (I) in 1 c.c. of  $H_2O$  is irradiated in a quartz vessel at a distance of 30 cm., the activity of (I) is lost in 15 min. Irradiation in a glass vessel or of more conc. solutions (1 mg. per c.c.) in quartz vessels does not result in detectable loss in 15 min. Using dil. solutions, the time for half-destruction of (I) increases rapidly with the  $\lambda$ , being 520 times as great at 283  $m\mu$  as at 186  $m\mu$ .

P. W. C.

**Constitution of the prosthetic group of catalase.** K. G. STERN (J. Biol. Chem., 1936, 112, 661—669; cf. A., 1935, 1278).—Catalase (I) solutions from horse liver after an  $Al_2O_3$  gel adsorption were further conc. by  $COMe_2$ - $CO_2$  treatment. The (I) solution is then sufficiently conc. to allow the cleavage of (I) by the acid- $COMe_2$  treatment used for respiratory haem pigments, which ppts. the protein. On removal of the  $COMe_2$  the prosthetic group of (I) is pptd. The identity of this prosthetic group with the protohaematin of haemoglobin is established by the prep. from it of a mesoporphyrin  $Me_2$  ester and by its conversion into the haemoglobin of the same species by the substitution of native globin for the enzyme-protein.

E. A. H. R.

**Nutritive value of pentosans. V. Digestion by intestinal enzymes.** H. IWATA (J. Agric. Chem. Soc. Japan, 1935, 11, 1024—1027).—Xylanase occurs in rabbit's and pig's intestine to an extent < that of co-existing amylase. Optimum temp. and  $p_H$  are 38° and 6, respectively.

F. O. H.

**Action of lithium, sodium, and potassium bromides and iodides on the activity of the amylase of the fowl's crop. VII, VIII.** A. BERNARDI and M. A. SCHWARZ (Giorn. Biol. Appl. Ind. Chim., 1932, 2, 41—52; Chem. Zentr., 1935, i, 3679).— $LiBr > KBr > NaBr$  stimulates the amylase activity; otherwise they behave similarly to the chlorides.  $LiI < KI < NaI$  inhibits the activity.

R. N. C.

**Technique of diastase determination in blood according to Ottenstein.** J. BRINCK (Klin. Woch., 1934, 13, 1686—1688).—The technique is described and possible sources of error are discussed.

R. N. C.

**Relation of glycolysis to proteolysis in tissues.** V. M. RUBEL (Biochem. Z., 1936, 283, 180—189).—In healthy and diseased (tumour) tissue, glycolysis, increased by addition of glucose,  $AcCO_2H$  (I), and  $MeCHO$  or decreased by addition of  $NaF$  is accompanied, respectively, by increased or decreased proteolysis. Lactic acid (II) increases proteolysis and is probably the link which connects the two processes. When production of (II) is restricted by  $NaF$  the extent of proteolysis is restored to normal by addition of (I) and (II).

W. McC.

**Conversion of *p*-tolylglyoxal into *l*-*p*-methyl-mandelic acid by the enzyme of fresh cells.** S. FUJISE and M. IWAKIRI (Biochem. Z., 1936, 283, 298—300).—Fresh carp-muscle extract converts *p*-tolylglyoxal almost quantitatively into *l*-*p*-methyl-mandelic acid. The conversion of  $BzCHO$  into *l*-

mandelic acid by the extract is more rapid, but not so complete.

W. McC.

**Complete enzymic hydrolysis of chondroitin- and mucoitin-sulphuric acid.** C. NEUBERG and W. CAHILL (Atti R. Accad. Lincei, 1935, [vi], 22, 149—155).—Enzyme preps. from *B. fluorescens* hydrolyse chondroitinsulphuric acid to glucuronic acid (I), chondrosamine,  $AcOH$ , and  $H_2SO_4$  and mucoitinsulphuric acid to (I), glucosamine,  $AcOH$ , and  $H_2SO_4$ .

F. O. H.

**Glucosulphatase. XII. Purification of the enzyme and the effects of phosphate, sulphate, and fluoride on the enzyme action.** T. SODA and F. EGAMI (J. Chem. Soc. Japan, 1934, 55, 1164—1168).—Activity of the enzyme is inhibited by  $PO_4'''$  and  $F'$  in concns.  $> 0.0005M$  (cf. A., 1935, 659).

CH. ABS. (p)

**Pancreatic lipase. I. II. Influence of various compounds on the hydrolytic activity.** S. S. WEINSTEIN and A. M. WYNNE (J. Biol. Chem., 1936, 112, 641—648, 649—660).—I. The rate of hydrolysis of glycerides and alkyl esters of fatty acids by pancreatic lipase (I) is investigated. The initial rate of hydrolysis of triglycerides decreases in the order tripalmitin (II), tributyrin, trihexoin, triacetin, trivalerin. The initial rates of acid formation from mono-,  $\alpha\gamma$ -di-, and tri-acetin are in the ratio 1 : 2 : 2.66, indicating that the ester linking on the  $\beta$ -C is more slowly hydrolysed than the two end linkings. The rate of hydrolysis of the alkyl esters of the fatty acids increases with the length of the C chain of the acid radical, but decreases with its length in the alkyl. With phosphate buffers the initial rate of hydrolysis of (II) and of  $PrCO_2Me$  is greatest at  $p_H$  7.2, but in glycine buffers the optimum  $p_H$  is 9.3. The initial velocity of hydrolysis  $\propto$  (I) concn. and (II) concn. (in the range 0.016—0.16*M*). The vals. did not accord with the Michaelis equation.

II. Ketones and aldehydes markedly inhibit (I). The degree of inhibition depends on the time of preliminary incubation of (I) with the inhibitor, the mol. vol., the no. of CO groups present, and the presence or absence of the  $C_6H_5$  ring. Heavy metals are inhibitory.  $CN'$  and  $SH$  compounds activate (I). Phenols and cresols are inert, but a  $NO_2$ -group increases the toxicity. Di- but not tri-hydric phenols are inhibitory; the inhibitory action of the former increases with increased separation of the OH groups. Monohalogen derivatives of  $AcOH$  inhibit in the order  $I > Br > Cl$ , and halides in the order  $F > I > Br > Cl$ . Bile salts in neutral solution are without effect. Possible mechanisms of some of the inhibitions and activations are discussed, and it is suggested that  $NH_2$  may be an essential constituent of (I).

E. A. H. R.

**Castor bean lipase. VII. Relation between activity of highly active *Ricinus* lipase and some oxidising and reducing substances.** E. TAKAMURA (J. Agric. Chem. Soc. Japan, 1935, 11, 156; cf. A., 1935, 1416).—Exposure to air or  $H_2O_2$  retarded the activity of the lipase. Glutathione (I) accelerated activity to extents  $\propto p_H$ . Larger proportions of (I) or adjustment of  $p_H$  to 6.0 had a

retarding action. Cysteine (II),  $\text{CH}_2\text{O}$ , glucose, fructose, and  $\text{NaHSO}_3$  produced similar effects, but cystine had no action. Lipase, inactivated by oxidation, was not regenerated by addition of (I) and (II). CH. ABS. (p)

**Inhibitory action of formaldehyde on the activity of blood choline-esterase.** E. CORTEGGIANI, J. GAUTRELET, N. HALPERN, and A. SERFATY (Compt. rend. Soc. Biol., 1936, 121, 316—318).— $\text{CH}_2\text{O}$  inhibits the action of choline-esterase after a latent period which  $\propto$  the dilution of the  $\text{CH}_2\text{O}$ . The inhibition is probably the result of alterations of  $p_H$ . R. N. C.

**Formation of acetylcholine in the body, and an investigation of the choline-esterase. I—III.** F. H. SHAW (Austral. J. Exp. Biol., 1935, 13, 251—260).—Stimulation of the lingual nerve of the dog does not alter the choline content of the tongue. Two esterases exist in serum, of which only one is inhibited by eserine. In presence of pig's serum, acetylcholine (I) is synthesised from choline and  $\text{NaOAc}$ . Neither this action nor the enzymic synthesis of tributyrin is inhibited by eserine. The synthesis of (I) in the body is probably effected through the synthetic action of tissue-esterase. W. O. K.

**Enzymic histochemistry. I. Distribution of arginase activity in rabbit kidney.** L. WEIL and J. O. ELY (J. Biol. Chem., 1936, 112, 565—577).—The micro-method of Linderström-Lang *et al.* (A., 1935, 1163) for determining arginase (I) activity is suitable for histo-enzymic studies if the solution is buffered at  $p_H$  9.5. A micro-(I) unit is defined. (I) activity is present in the cortex only of rabbit kidney, and runs parallel with the no. of proximal convoluted tubular cells. The medulla shows no (I) activity, and as addition of inactive medullary tissue to cortical tissue causes no inhibition of (I) activity in the latter, it is concluded that the inactivity of the medulla is not due to inhibitors. E. A. H. R.

**Assay of aspartase.** K. P. JACOBSON and M. C. RES (Compt. rend. Soc. Biol., 1936, 121, 251—255).—Experiments described do not establish the presence of aspartase in the vegetable tissues examined, nor the amination of fumaric acid as a regular metabolic reaction in plants. R. N. C.

**Effect of various salts on the aspartase system.** F. B. PEREIRA and M. SOARES (Compt. rend. Soc. Biol., 1936, 121, 255—258).—Synthesis of acid by aspartase is accelerated by  $\text{SO}_4^{2-}$  and retarded by  $\text{Cl}^-$  relative to  $\text{Cl}^-$ . Atoxyl does not affect the action in presence of  $\text{PO}_4^{3-}$  buffer, but morphine slows it.  $\text{PO}_4^{3-}$  buffer alone exerts a restraining action, as does  $\text{Na}^+$  in presence of  $\text{Cl}^-$ . R. N. C.

**Peptic hydrolysis of caseinogen.** L. UTKIN (Biochem. Z., 1936, 283, 233—240).—In the early hydrolysis the liberation, at  $p_H$  4.6, of organic P compounds occurs in two (possibly more) defined phases. The P:N ratio of the compounds produced in the first phase differs from that of those produced in the second, the difference being due to differences in the composition of the

compounds, and not merely to differences in the amounts. W. McC.

**Physiology of digestion of plankton Crustaceæ. I. Digestive enzymes of *Daphnia*.** A. D. HASLER (Biol. Bull., 1935, 68, 207—214).—The  $p_H$  of the intestine of *D. magna* varied from 6.8 at the anterior to 7.2 at the posterior end. Tryptic digestion of casein is indicated. Glycerol extracts of the intestine digested gelatin. Hog-pancreas extract gave a similar hydrolysis curve. Extracts of defatted *D. pulex* contained amylase and lipase. CH. ABS. (p)

**Multivalent amino-acids and peptides. VI. Action of proteolytic enzymes on synthetic substrates.** J. P. GREENSTEIN (J. Biol. Chem., 1936, 111, 517—522; cf. this vol., 194).—Anhydro-*l*-lysyl-*l*-glutamamide,  $[\alpha]_D^{25} - 27.7^\circ$ , is unaffected by pepsin, trypsin, or papain-HCN (also without action on anhydro-*dl*-aminotricarballylic tetra-amide), which is inconclusive evidence against the existence of diketopiperazine rings in proteins. *l*-Lysyl-*l*-glutamamide and *l*-histidine are hydrolysed by yeast peptidase, the former more slowly. Glycyl-*dl*-aminotricarballylic acid is slowly split by yeast autolysate and intestinal erepsin, but not by carboxypeptidase. R. S. C.

**Inhibition of enzymic proteolysis by oxidising agents. Nature of the action of potassium bromate and analogous substances as improvers of wheat flour. II.** H. JØRGENSEN (Biochem. Z., 1935, 283, 134—145).—The inhibition of proteinases (I) in flour- $\text{H}_2\text{O}$  suspensions by  $\text{KBrO}_3$  and the consequent decrease of solubility of flour-N are greatly emphasised on adding yeast, due to the activation of (I) by the glutathione of the yeast (cf. B., 1935, 1115). P. W. C.

**Action of enzyme extracts on soluble keratin.** P. G. CASTELLINO (Arch. Ist. Biochim. Ital., 1935, 7, 417—424).—Extract of rabbit's skin is free from enzymes hydrolysing sol. keratin [prepared by the action of Na thioglycollate (A., 1934, 1238)] at  $p_H$  1.5, 3, or 8, but contains a tryptic enzyme hydrolysing caseinogen. F. O. H.

**Enzymic synthesis from thyroid di-iodotyrosine peptone of an artificial protein which relieves myxœdema.** W. T. SALTER and O. H. PEARSON (J. Biol. Chem., 1936, 112, 579—589).—A solution of di-iodotyrosine peptone (I) was prepared by peptic digestion of thyroglobulin (II) of human origin, followed by removal of thyroxine (III). (I) was conc. and then subjected to a peptic synthesis, with the formation of an artificial protein containing I, analogous in its properties to a true protein. Clinically, in equiv. I dosage, it relieves myxœdema as effectively as (II). The view is held that di-iodotyrosine is the precursor of (III) and that a naturally occurring protease in the thyroid cells is possibly responsible for the synthesis. E. A. H. R.

**Phosphatase content of blood-serum and tissues in the rat following administration of vitamin-D and -A.** P. D. CRIMM and J. W. STRAYER (J. Biol. Chem., 1936, 112, 511—515).—The mean phosphatase (I) content of rat serum is about 20 times that of human serum. Toxic doses of viosterol (II) lead to a marked decrease of (I) activity in blood

and kidney, and a considerable increase in the small intestine. The effect of (II) on the high (I) content of bones is variable. Liver and spleen contain small amounts of (I) both before and after administration of (II). The decrease in serum-(I) with rats deficient in vitamin-A (III) or with hypervitaminosis-A is attributed to impaired nutrition rather to the presence or absence of (III). E. A. H. R.

**Plasma-phosphatase in normal and rachitic children.** O. ANDERSEN (Jahrb. Kinderheilk., 1935, 144, 206—221; Chem. Zentr., 1935, i, 3148).—Antirachitic treatment of rachitic children (technique of Kay) produces a diminution of plasma-phosphatase. G. H. F.

**Intestinal phosphatase.** H. G. K. WESTENBRINK (Arch. Neerland. Physiol., 1935, 20, 566—590).—The activity of a solution of intestinal phosphatase (I) is not  $\propto$  its concn., and the rate of hydrolysis of Na glycerophosphate continually decreases with time of reaction. This is not due to inhibition by  $H_3PO_4$  or glycerol, or to decreasing substrate concn. or to inactivation by the buffer of  $p_H$  8.8. The activity of (I)  $\propto$  concn. if it is previously kept in contact with the buffer for some hr. at  $25^\circ$ . In determining (I) by the hydrolysis of  $H_3PO_4$  from a suitable substrate, it is best to work in a medium containing Ca. J. N. A.

**Determination of the phosphatase activity of whole blood, plasma, and serum.** J. CAYLA (Bull. Soc. Chim. biol., 1935, 17, 1707—1714).—A modification of the Mo colorimetric method for the determination of phosphatase (I) is described. In the normal adult the (I) content is 15 units per litre of serum, 1 unit of (I) liberating 1 mg. of  $H_3PO_4$  from 10% aq. Na  $\beta$ -glycerophosphate at  $p_H$  7.6. A. L.

**Specific pyrophosphatase.** E. BAUER (Naturwiss., 1935, 23, 866—867).—Glycerol extracts of yeast retain their ability to act on pyrophosphate after the  $\alpha$ -glycerophosphatase activity has largely been destroyed by heat, indicating the separate existence of a sp. pyrophosphatase. E. A. H. R.

**Glycerophosphatase of the brain.** F. CEDRANGOLO (Boll. Soc. ital. Biol. sperim., 1935, 10, 374—376).—Brain-glycerophosphatase shows optimum activity at  $p_H$  5.32 and 9.16, with a max. in 0.0016M-glycerophosphate. Prolonged electrodialysis abolishes the enzyme activity, which is restored by  $MgCl_2$ . Activity is inhibited by NaF,  $CH_2I-CO_2H$ ,  $As_2O_3$ , and phloridzin. The enzyme shows a preference for  $\alpha$ -glycerophosphate. R. N. C.

**Mode of action of intermediate enzymes.** E. NEGELEIN and E. HAAS (Biochem. Z., 1935, 282, 206—220).—In the reaction, co-enzyme (I) + hexosediphosphoric acid = (I)· $H_2$  + phosphohexonic acid, which occurs in presence of intermediate enzyme (II), the velocity of hydrogenation can be determined in terms of the rate of the resulting increase of absorption in the ultra-violet at 345 m $\mu$ . A study of the hydrogenation velocities with varying amounts of (I) and (II) shows that (II) functions not as a catalyst, but as the colloidal carrier of (I). (I) and (II) by a reversible reaction are converted into the H-transporting enzyme (III). At a concn. of (I)

of  $10^{-5}$  mol. per litre, half of the (III) is dissociated into (I) + (II). As a result of such dissociation, a small amount of (II) can effect hydrogenation of large amounts of (I). (II) therefore differs from the carrier of the yellow enzyme (IV), since it is combined with (IV), and the oxidational reaction requires therefore a stoicheiometric amount of pigment.

P. W. C.

**Oxidation, phosphorylation, and fermentation by apozymase in presence of reversible oxidation-reduction systems.** A. LENNERSTRAND and J. RUNNSTROM (Biochem. Z., 1935, 283, 12—29).—Oxidation and phosphorylation are studied in a system containing apozymase, cozymase, hexose diphosphate, glucose, and either methylene-blue (I) or pyocyanin (II), fermentation being inhibited by NaF. The system absorbs  $O_2$ , but forms practically no  $CO_2$ . Although (I) and (II) belong to the same potential range, the  $O_2$  absorption with (II) is three times that with (I) and moreover using  $\alpha$ -naphthol-2-sulphonate-indophenol, which has a much higher potential, the  $O_2$  absorption is  $<$  with (II). There is a definite connexion between oxidation and phosphorylation, 1 mol. of glucose being esterified with  $PO_4$  for each mol. of phosphoglyceric acid produced by oxidation from triose phosphate. P. W. C.

**Formation of flavin enzyme systems in germinating seeds.** H. VON EULER and O. DAHL (Biochem. Z., 1935, 282, 235—241).—The total flavin (I) content of barley in the first 5 days of germination is 3—7 times that of oats. The (I) synthesis is completed in barley by the 2nd day, but continues longer in oats. In extracts of germinated seeds, the ratio of non-dialysable to total (I) is 2 : 3, and is maintained fairly const. during germination. In peas (ungerminated) which contain considerable amounts of (I), almost all the (I) is in the non-dialysable form. Tables summarise the accompanying increases in respiration during germination. P. W. C.

**Nicotinamide and lumino-flavin.** O. WARBURG and W. CHRISTIAN (Ber., 1936, 69, [B], 228; cf. Kuhn *et al.*, this vol., 227).—Nicotinamide has been obtained previously from co-enzyme (I) and lumino-flavin by irradiation of an alkaline flavin solution obtained from milk. Since the yellow enzyme and (I) are universal components of cells, Kuhn's discoveries are not fundamentally new. H. W.

**Fermentation velocity of hexosediphosphoric acid and phosphate transfer to adenylic acid.** P. OHLMEYER (Biochem. Z., 1935, 283, 114—127).—Although muscle-adenylic acid (I) is not identical with and cannot replace cozymase in all its reactions, yet (I) has an activating role in some fermentation reactions. Thus hexose diphosphate in yeast maceration juice with added (I) is partly fermented and partly converted into hexose monophosphate (II), whilst (I) is converted into adenylyl pyrophosphate (III), which is identical with muscle-(III). The higher is the concn. of (I) in this reaction, the greater is the max. velocity. The fermentation velocity of (II) is also increased, but to a smaller extent by addition of (I), and (III) is again formed. Addition of (III) has no effect on the velocity of fermentation of the diphosphate. P. W. C.



**Action of extracts of liver and other organs on fermentation by yeast.** J. DADLEZ and W. KOSKOWSKI (Biochem. Z., 1936, 283, 292—297; cf. Zipf *et al.*, 1935, 253).—The stimulating effect on fermentation by yeast of liver extract is > that of extract of other organs (spleen, stomach, lung, heart, muscle, kidney, brain, testes, uterus, mammary gland, bone-marrow, pituitary, thymus, adrenals). With liver and spleen extracts the action does not always run parallel with the anti-anæmic effect. W. McC.

**Mechanism of oxidation processes.** XLIII. **Arrest of the respiration and fermentation processes of yeast.** H. WIELAND, K. RAUCH, and A. F. THOMPSON (Annalen, 1936, 521, 214—226).—The inhibiting action of various poisons on the fermentative action (glucose) of "impoverished" yeast is generally smaller than that on the aerobic dehydrogenation of EtOH at 30° and  $p_H$  6.8. 0.0002*M*-KCN reduces the  $O_2$  consumption to 56%, but 30 times this concentration is necessary to effect an equal retardation of the fermentation process.  $Na_2S$  is similar, but  $NaCNO$ , which is more potent than KCN, inhibits both processes to approx. the same extent;  $NaN_3$ , which inhibits the dehydrogenation as effectively as does KCN, has actually a small accelerating influence on the fermentation, and is equally effective under  $O_2$  as under  $N_2$ . The catalase activity is inhibited by  $NaCNO > NaN_3 > KCN$ . The inhibiting action of these poisons is largely removed by centrifuging the yeast with  $H_2O$ . The  $O_2$  consumption in the aerobic dehydrogenation of EtOH is greatly reduced if the  $[O_2]$  is only 2—5% (cf., A., 1932, 303). J. W. B.

**Effect of selenium on cellular metabolism.** **Rate of oxygen uptake by living yeast in presence of sodium selenite.** V. R. POTTER and C. A. ELVEHJEM (Biochem. J., 1936, 30, 189—196).—The uptake in presence of glucose, fructose, and mannose is diminished by 80% when  $Na_2SeO_3$  (min. effective concn. 0.0033*M*) is added. With lactate and pyruvate as substrates, the diminution is < 10%. The oxidation by yeast of EtOH, AcOH, and possibly succinic acid also appears to be diminished by  $Na_2SeO_3$ . The action is in all cases most marked in the acid zone and decreases rapidly at  $p_H$  7.0—7.5. Se appears to act primarily as inhibitor of glycolysis.  $a_3AsO_3$  (min. effective concn. 0.001*M*) is more toxic to oxidative systems than is  $Na_2SeO_3$ . W. McC.

**Effect of *m*-dinitrobenzene and its reduction derivatives on the metabolism of Fleischmann's yeast.** REAC'H (Compt. rend. Soc. Biol., 1936, 121, 248).—Respiration of liquid-cultured yeast is increased considerably by  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-NO}$  (I) and by  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  (II), whilst that of yeast is increased considerably by both possibly through the reduction of (II) to (I) by the organism.  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-OH}$  does not affect respiration. R. N. C.

**Action of dinitrothiophen on the metabolism of Fleischmann's yeast.** P. CREAC'H (Compt. Rend. Soc. Biol., 1936, 121, 248—250).—Dinitrothiophen is irreversibly after a period of latency  $\propto$  the concn. Respiration of the yeast

risers temporarily when reduction begins, afterwards falling rapidly to < the initial val. R. N. C.

**Catalytic fermentation of some fructoholosides.** R. GUILLEMET (Compt. rend., 1935, 201, 1517—1519).—Raffinose, gentianose, stachyose, and levosin are fermented by yeast juice to the extent of 100, 66, 50, and 30%, but in the absence of von Euler's Z factor fermentation is much reduced and levosin is not fermented. J. L. D.

**Action of methyl and ethyl alcohol on enzymes.** I. **Action on beer yeast and on the cytoplasm of castor seeds.** N. T. DELEANO and D. MEZINCESCO (Bull. Soc. Chim. biol., 1935, 17, 1805—1813).—Small quantities of MeOH and EtOH increase slightly the rate of carbohydrate fermentation by yeast, but larger amounts inhibit the reaction, MeOH being less toxic. The inhibition of lipase action by MeOH and EtOH is almost the same, but is more marked with olive oil than with castor oil as substrate. A. L.

**Yeast lipins.** III. **Lecithin and kephalin.** L. F. SALISBURY and R. J. ANDERSON (J. Biol. Chem., 1936, 112, 541—550).—The mixed phospholipins of yeast have been separated into lecithin (I) and kephalin (II). (I) was obtained free from  $NH_4-N$  and all the N of (II) was in the  $NH_2$ -form. On hydrolysis (I) gave a mixture of fatty acids, 86% of which were liquid, optically active glycerophosphoric acid (III), and choline, whilst (II) gave a similar mixture of acids, 84% of which were liquid, optically inactive (III), and  $NH_2\text{-CH}_2\text{-CH}_2\text{-OH}$ . The liquid component acids of both (I) and (II) gave a mixture of palmitic (IV) and stearic (V) acids on catalytic reduction. The solid acids consisted only of (IV) and (V). Methods of prep. of hydrolecithin and hydrokephalin are given. E. A. H. R.

**Biological value of two *Torula* from the cheese factory.** G. GUITTONNEAU and H. SIMONNET (Compt. rend. Soc. Biol., 1935, 120, 1166—1168).—The antineuritic vals. of both *Torula* are < that of brewer's yeast; the *Torula* with lactose-fermenting power is the more active of the two. R. N. C.

**Yeast growth-promoting substances.** N. NIELSEN (Compt. rend. Trav. Lab. Carlsberg, 1935, 21, No. 7, 151—183).—The effect of growth-promoting substances (I) (bios) on yeast can be shown by the increase in dry wt. of cultures. The heavier is the inoculation the less is the relative increase in growth. (I) can be quantitatively extracted from yeast with boiling  $H_2O$ . The (I) content of yeast cultures is determined by the (I) content of the culture medium. Yeast must contain more than a certain min. amount of (I) to grow on a (I)-free culture medium. Most of the utilised (I) undergoes no great chemical change, as it can be extracted again, but a certain proportion is so transformed that it cannot be extracted. A. H. R.

**Buffered and low oxygen content physiological salt solutions.** M. RANDALL and T. C. DOODY (Biol. Bull., 1935, 68, 258—262).— $Mn(OH)_2$  effectively removes  $O_2$  and buffers solutions from  $p_H$  7.0 to 9.0. Its use is convenient in the culture of protozoa.

CH. ABS. (p)

**Nature of crystals found in amoeba.** R. H. LUCE and A. W. POHL (Science, 1935, 82, 595—596).—The most prominent cryst. inclusions have  $n$  1.668, m.p. approx. 290°; they probably consist of Ca chlorophosphate. L. S. T.

**Ultra-violet irradiated amoebæ.** W. A. BLACK (Science, 1935, 82, 495—497).—*A. proteus* is negatively phototropic towards ultra-violet light. Irradiation appears to stop the digestion of food. L. S. T.

**Infection with *Trypanosoma equiperdum*.** D. PERLA (Arch. Path., 1935, 19, 505—523).—Infected but surviving rats acquired a secondary hæmolytic anæmia, and showed increased [Fe], without change in [Cu], in livers. [Fe] and [Cu] in the spleen declined. CH. ABS. (p)

**Action of certain derivatives of copper on *Treponema cuniculi* and *Trypanosoma brucei*.** R. SAZERAC and N. LARTHE (Compt. rend. Soc. Biol., 1935, 120, 1179—1181).—*T. cuniculi* lesions in the rabbit are cured by injections of  $\text{Na}_2\text{Cu}(\text{S}_2\text{O}_4)_2$ , but in the case of CuO they recur. *T. brucei* infection in the rat is reduced temporarily by  $\text{Cu}_2\text{O}$ , electrocuprol, or 1%  $\text{CuSO}_4$ . R. N. C.

**Changes in the nucleus of *Euglena gracilis*, Ehrbg., in chronic arsenical poisoning.** S. B. RYBINSKY and L. M. ZRYKINA (Arch. Protistenk., 1935, 85, 334—340).—Chronic  $\text{As}_2\text{O}_3$  poisoning results in an increase in the thymonucleic acid of the nucleus and changes in morphological characteristics. A. G. P.

**Relation of hydrogen-ion concentration to growth of *Chilomonas* and *Chlorogonium*.** J. B. LOEFFER (Arch. Protistenk., 1935, 85, 209—223).—Total growth ranges of  $p_{\text{H}}$  and optimum zones are determined for *Chilomonas paramecium*, *Chlorogonium euchlorum*, and *C. elongatum*. NaOAc prevents growth of *Chlorogonium* below  $p_{\text{H}}$  5.4 and of *Chilomonas* below 8.5. A. G. P.

**Influence of heat and storage on electrophoretic migration velocities of various micro-organisms.** K. P. DOZOIS and F. HATCHEL (J. Bact., 1935, 30, 473—477).—Migration velocities increased with rising temp. > 60°. A. G. P.

**Precision photometer for study of bacteria and other micro-organisms.** H. MESTRE (J. Bact., 1935, 30, 335—358).—A "densitometer" used in conjunction with a photo-electric cell is described. A. G. P.

**Growth and survival of micro-organisms at sub-freezing temperatures.** H. F. SMART (Science, 1935, 82, 525).—Many species of bacteria, yeasts, and moulds are able to survive in frozen fruit kept at  $-9.4^\circ$  for 3 years; some of these showed slow growth at  $-8.9^\circ$  in fresh cultures. L. S. T.

**Carbohydrate metabolism of *Aspergillus niger* is a function of the nitrogen source of the nutrient medium.** R. BONNET and J. JACQUOT (Compt. rend., 1935, 201, 1213—1215; cf. A., 1935, 1027).—*A. niger* produces citric (I) and oxalic acid (II) when N is supplied as peptone or  $\text{NH}_2$ -acids. The wt. of mycelium and its (I) content remained practically const. during 4—20 days, but accumulation of (II)

increased progressively. In  $\text{NO}_3'$  media (I) and (II) are produced from all sugars examined, except lactose. In no case was (II) formed in  $\text{NH}_4$  media.

A. G. P.

**Assimilation of oxalic acid by *Aspergillus niger*.** D. BACH and J. FOURNIER (Compt. rend., 1935, 201, 982—984).—5-day-old cultures of this organism consume  $\text{H}_2\text{C}_2\text{O}_4$ ; the amount diminishes with increasing  $p_{\text{H}}$ , and is practically zero at  $p_{\text{H}} > 5.8$ . The acid ion as well as the neutral mol. appears to be utilised. F. A. A.

**Proteolytic enzymes of *Aspergillus niger*.** H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 317—322).—Aq. or glycerol extracts of *A. niger* exhibit digestive properties typical of pepsin, trypsin, and erepsin. Optimum digestion of fibrin occurs at  $p_{\text{H}}$  7.1 or 2.0. CH. ABS. (p)

**Mould enzymes splitting nucleic acid.** H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 323—329).—Glycerol extracts of a no. of species of moulds hydrolysed nucleic acid. Optimum  $p_{\text{H}}$  vals. were between 4.2 and 6.2. CH. ABS. (p)

**Action of mould enzymes on benzene derivatives of amino-acids and dipeptides.** H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 330—333).—Mould enzymes readily decomposed benzoyl-*dl*-leucylglycine. In general hippuric acid was more strongly attacked than benzoyldiglycine. Benzoyl- and benzylglycyl-*dl*-phenylalanine are not attacked. CH. ABS. (p)

**Nutrient solution purification for removal of heavy metals in deficiency investigations with *Aspergillus niger*.** R. A. STEINBERG (J. Agric. Res., 1935, 51, 413—424).—The solution is treated with  $\text{CaCO}_3$  and filtered while hot. Supplementary use of C is unnecessary and lowers experimental precision. Extraction of spores of *A. niger* with aq.  $\text{KHCO}_3$  partly removes Fe, Cu, and Mn. Subsequent growth of treated spores leads to accentuated deficiency effects in respect of these metals.

**Pharmacodynamic action of zinc in general metabolism.** O. KAUFFMAN-COSLA and R. BRULL (Bull. Soc. Chim. biol., 1935, 17, 1828—1835).—The absence of Zn from cultures of *Aspergillus niger* leads to a decrease in the synthesis of carbohydrates, lipins, and protein. A. L.

**Mould tissue. X. Phospholipins of *Aspergillus sydowi*.** D. W. WOOLLEY, F. M. STRONG, W. H. PETERSON, and E. A. PRILL (J. Amer. Chem. Soc., 1935, 57, 2589—2591; cf. A., 1934, 697).—The phospholipins (0.4—0.7% of mycelium), purified by repeated pptn. from  $\text{Et}_2\text{O}$ -solution with COMe., consist of a mixture of lecithin and kephalin. Hydrolysis (5%  $\text{H}_2\text{SO}_4$ ) gives glycerophosphoric acid, choline, cholamine [*picrolonate*, m.p. 222—226° (decomp.)], oleic acid, and (probably) traces of palmitic, stearic, and a more unsaturated acid. H. B.

**Dissimilation of glucose by heterofermentative lactic acid bacteria.** M. E. NELSON and C. H. WERKMAN (J. Bact., 1935, 30, 547—557).—The end-products of fermentation of glucose by three heterofermentative species were lactic acid,  $\text{AcOH}$ ,  $\text{CO}_2$ ,

EtOH, and glycerol. The amount of  $\text{CO}_2$  produced was equiv. to the EtOH+AcOH (mols.), and that of glycerol to twice the AcOH (mols.). A tentative scheme representing these changes is presented.

A. G. P.

**Utilisation of amino-acids as common sources of carbon and nitrogen by soil bacteria: organisms decomposing betaine and valine.** H. HEIGENER (Zentr. Bakt. Par., 1935, II, 93, 81—113).—As simultaneous sources of N and C, valine (I), betaine (II), and glycine were but poorly utilised by soil bacteria; leucine, phenylalanine, alanine, and asparagine were rather more effective. Glutamic and aspartic acid were very generally utilised. Organisms decomp. (I) and (II) were isolated and described and their significance in humus formation is discussed.

A. G. P.

**Relation of oxidation-reduction potential to growth of an aerobic micro-organism.** W. B. WOOD, jun., M. L. WOOD, and I. L. BALDWIN (J. Bact., 1935, 30, 593—602).—Reversible oxidation-reduction indicators positive to, and including, methylene-blue when in oxidised forms inhibit the growth of *B. megatherium*. Indicators negative to this do not inhibit. Substances which are inhibitory in the oxidised form are not bacteriostatic when reduced. Bacteriostatic compounds affect growth only in the lag phase. Addition of inorg. reducing agents to broth renders it more favourable to the growth of the organism.

A. G. P.

**Effect of some alkaloids on soil micro-organisms: nitrogen fixers. I. Effect on *B. radicola*.** G. MEZZADROLI and L. SGARZI (Giorn. Biol. Appl. Ind. Chim., 1934, 4, 162—174; Chem. Zentr., 1935, i, 3679).—Development is stimulated by caffeine, quinine, and strychnine, the effect in nutrient solution being > that in soil mixture. Glucose can serve as a source of carbohydrate.

R. N. C.

(A) Action of radiation in the extreme ultra-violet on *Bacillus subtilis* spores. (B) Inhibition of growth of *B. subtilis* by ultra-violet-irradiated carbohydrates. I. H. BLANK and W. ARNOLD (J. Biol. Chem., 1935, 110, 503—506, 507—511).—(A) Radiation region —140 m $\mu$  has a marked germicidal action.

(B) Radiations of 235.7 m $\mu$  modify agar in a manner which prevents the growth on it of *B. subtilis*. A non-thermostable inhibitory agent, diffusible through agar, is formed. A similar inhibition is observed by irradiation of carbohydrate solutions used in the prep. of media.

A. G. P.

**decomposition of chitin.** H. BUCHE (Zentr. Bakt. Par., 1935, II, 93, 12—24).—Organisms decomp. chitin are isolated from soil and other sources.

A. G. P.

**Urea-decomposing microflora of soils. I.** See B., 1936, 114.

**Mannitol-forming bacteria isolated from potatoes (*Ipomoea edulis*, Makino), and Diospyros kaki.** Y. IWASAKI (Bull. Japan. Soc. Japan, 1935, 11, 159—164, 164). Both strains produce mannitol from

fructose, but not from glucose, mannose, or galactose. Morphological characteristics are given. F. O. H.

**Anaerobic bacteria capable of fermenting waste sulphite liquor.** A. M. PARTANSKY and B. S. HENRY (J. Bact., 1935, 30, 559—571).—Five new species of *Clostridium* are described, and their biochemical activities are recorded.

A. G. P.

**Production of *d*-lactic acid and of butyric acid.**—See B., 1936, 167.

**Amylase of *Clostridium acetobutylicum*.** W. W. JOHNSTON and A. M. WYNNE (J. Bact., 1935, 30, 491—501).—The amylase shows optimum activity at  $p_{\text{H}}$  4.8—5.05. NaOAc retards its action *in vitro*, but when added to the culture media increases the amount of amylase present in the nutrient at the end of the fermentation.  $\text{PO}_4'''$  and  $\text{Cl}'$  also retard starch hydrolysis at  $p_{\text{H}}$  4.95. Temp. effects are examined.

A. G. P.

**Effect of synthetic surface-active materials on bacterial growth. I. Effect of sodium di-sec-butyl-naphthalenesulphonate on growth of *Mycobacterium smegmatis*.** J. KATZ and A. LIPSITZ (J. Bact., 1935, 30, 419—422).—In concns. of 1:10,000 the salt inhibits growth. In small proportions (to 1:50,000) involution forms occur frequently. No synergistic action was apparent between the salt and neutral acriflavine.

A. G. P.

**Existence in *B. tumefaciens* of an endotoxin capable of causing the formation of tumours in plants.** A. BOIVIN, M. MARBE, I. MESROBEANU, and P. JUSTER (Compt. rend., 1935, 201, 984—986).— $\text{CCl}_3\cdot\text{CO}_2\text{H}$  extracts a "complete" antigen (I) from *B. tumefaciens* (II), corresponding with 3% of the dry wt. of the bacteria. (I) is a solid, aq. solutions of which are not dialysable. In dil. AcOH at 100° it yields fatty acids and a slowly dialysable polysaccharide (III) ("residual antigen"). Both (I) and (III) are pptd. specifically by serum from rabbits injected with (II). (I) is toxic to mice, whilst (II) is non-toxic. (I) produces tumours in *Helianthus annuus* stems similar to those produced by living (II).

F. A. A.

**Bactericidal action of organic acids towards Bang's bacillus.** E. ZIMMERMAN (Zentr. Bakt. Par., 1935, I, 215—221).—Lactic, tartaric, citric, and (especially) formic acid have marked toxic action on the bacillus. Lethal dosages are determined. Possible chemotherapeutic uses of org. acids are discussed.

A. G. P.

**Presence of hæmolysins in young cultures of cholera vibrios.** W. DOORENBOS (Compt. rend. Soc. Biol., 1936, 121, 128—129).

R. N. C.

**Cultural requirements of bacteria. VI. Diphtheria bacillus.** J. H. MUELLER. VII. Amino-acid requirements for the Park-Williams No. 8 strain of diphtheria. J. H. MUELLER and I. KAPNICK (J. Bact., 1935, 30, 513—524, 525—534). VI. Animal tissue extracts contain substances essential to the growth of the organism. Considerable amounts of the active substance occur in the 95% EtOH filtrate of aq. liver extract (beef), and may be adsorbed on C and eluted with acidified EtOH. The

filtrate from such C adsorptions also contains growth-stimulating materials, including K and Mg.

VII. This strain grows freely on media containing only *l*-cystine, *d*-glutamic acid, *dl*-valine, *dl*-leucine, *dl*-methionine, glycerol, inorg. salts, and liver "elute." The prep. of the latter is described. A. G. P.

Electrophoretic phenomena of bacteria. II. Electrophoretic velocities of virulent and non-virulent *C. diphtheriae*. III. Electrophoretic velocity in relation to growth, senescence, and death. C. W. BUGGS and R. G. GREEN (J. Bact., 1935, 30, 447—451, 453—463).—II. Although no strict line of demarcation was apparent, the average velocity of all non-toxicogenic strains is 18.8% > that of all toxicogenic strains.

III. The velocity of cultures was approx. const. from 6 hr. to 10 days, and showed variable changes after killing by heat, but not after treatment with  $\text{PhOH}$ ,  $\text{CH}_2\text{O}$ , or  $\text{HgCl}_2$ . Extraction of cultures with hot 70% EtOH lowered the velocities approx. to those of cells killed in  $\text{PO}_4^{'''}$  buffer solution.

A. G. P.

Metabolic activity of various colon group organisms at different phases of the culture cycle. G. MOONEY and C. E. A. WINSLOW (J. Bact., 1935, 30, 427—440).—The presence of a fermentable sugar (glucose) stimulates multiplication of *E. coli* and *Salmonella gallinarum* in aerated media, but tends to inhibit that of *S. pullorum*. Production of  $\text{CO}_2$  per cell per hr. by organisms in the same period of culture cycle is independent of species and culture medium. Metabolic rates vary considerably with the phase of the cycle. The period of physiological youth in cultures is characterised by relatively larger cells and by greater metabolic activity per unit of living matter concerned.

A. G. P.

*Escherichia coli* and three of its rough variants. E. H. RENNEBAUM (J. Bact., 1935, 30, 625—638).—As energy sources AcOH, lactic, and malic acids are more readily utilised by the parent cell, whilst tartaric, citric, and salicylic acids are preferentially utilised by one or more of the variants. A typical rough variant has less vigorous enzymes than the parent, in respect of glucose decomp. Injection of the normal strain into the ear vein of rabbits causes a sudden increase in blood-sugar and death in a few hr. Variants have no appreciable action. The fatal action of the normal form is probably due to a sol. exo-toxin which increases the permeability of lung capillaries.

A. G. P.

"Complete" somatic antigen contained in some *B. coli*. A. BOIVIN, L. MESROBEANU, G. MAGHERU, and A. MAGHERU (Compt. rend. Soc. Biol., 1935, 120, 1276—1279).—Eight strains of *B. coli* examined fall into six serological types. The "complete" antigens contain 38—48.4% of sugar and 9.9—20.7% of fatty acid (liberated by acid hydrolysis); the chemical composition is not const. for strains of the same type.

R. N. C.

"Residual" antigen of *B. coli*. G. MAGHERU, A. MAGHERU, A. BOIVIN, and L. MESROBEANU (Compt. rend. Soc. Biol., 1935, 120, 1279—1282). R. N. C.

Importance of the electric charge in certain aspects of immunity. H. C. BROWN and J. C. BROOM (Trans. Roy. Soc. Trop. Med. Hyg., 1935, 28, 357—376).—*Leptospira* are killed by colloidal Cu when suspended in immune but not when in normal serum. Victoria-blue is toxic in both sera. If the charge on red cells is diminished, a hæmolytic serum becomes inactive. CH. ABS. (p)

Violet agar reaction as a differential characteristic of the *Micrococcus catarrhalis* group. G. H. CHAPMAN (Stain Tech., 1936, 11, 25—26).—The crystal-violet-agar reaction is useful in the study of different strains of this group. P. G. M.

Cultural characteristics of *Pasteurella tularensis*. C. M. DOWNS and G. C. BOND (J. Bact., 1935, 30, 485—490). A. G. P.

Effects of quinine derivatives in experimental *Pneumococcus* studies. W. W. G. MACLACHLAN, H. H. PERMAR, J. M. JOHNSTON, and J. R. KENNEY (Amer. J. Med. Sci., 1934, 188, 699—705).—Toxicity of ethylapoquinine varies considerably, but decreased toxicity does not diminish its protective power. Hydroxyethylapoquinine is less toxic but has greater antipneumococcal power. Hydroxyethylhydrocyprene is the least toxic, and its protective action is < that of other derivatives. CH. ABS. (p)

Anaerobic surface cultures. II. Gaseous products of metabolism of organisms (yeast, *Staphylococcus aureus*, *B. coli*, *B. prodigiosum*): aldehyde content and bactericidal action at a distance. W. BACHMANN and OGAIT (Zentr. Bakt. Par., 1935, I, 134, 281—288).—The inhibitory action (at a distance) of certain yeasts etc. on aerobic and anaerobic bacteria depends on the production of appreciable amounts of MeCHO. A. G. P.

Denaturation of staphylococcal proteins. A. P. KRUEGER and V. C. NICHOLS (J. Bact., 1935, 30, 401—409).—Antigens separated by ultrafiltration contain < 10% of the total bacterial protein in the denatured form. On heating, the native proteins are denatured, become insol. at the isoelectric point, and show a considerable decrease in -SH. The denaturation process obeys the law of mass action. The facts are considered in relation to the prep. of vaccines and the preservation of active antigens.

A. G. P.

Organism of European foul-brood of bees. H. L. A. TARR (Nature, 1936, 137, 151—152).—Photomicrographs of two kinds of *Streptococcus apis*, which differ only in that one rapidly liquefies gelatin and coagulates and peptonises the casein of milk, are reproduced. L. S. T.

Donators and acceptors of hydrogen for *Streptococcus haemolyticus*. D. BACH (Compt. rend. Soc. Biol., 1936, 121, 215—217).—Fructose, glucose, mannose, xylose, galactose, lactose, sucrose, maltose, arabinose, glycerol,  $\text{CH}_3\text{CH}_2\text{OH}$ , EtOH, MeOH, Bu'OH, lactate, cysteine, fumarate, and pyruvate are active H donators; NaBrO<sub>3</sub> and NaIO<sub>3</sub> are the only active H acceptors. R. N. C.

Lipins of tubercle bacilli. XLI, XLII.—See this vol., 311, 314.



Comparison of antigenic properties of defatted tubercle bacilli and their derived proteins. C. H. BOISSEVAIN (Amer. Rev. Tuberc., 1935, 31, 547—552).—The  $H_2O$ -sol. proteins from ground or hydrolysed bacilli or from filtered culture media all have the same tuberculin activity. Guinea-pigs cannot be rendered hypersensitive to 1% tuberculoprotein by injection of 10—100 mg. of any  $H_2O$ -sol. protein or peptone derived from the bacillus. CH. ABS. (p)

Preparation of purified tuberculin. A. BOQUET and G. SANDOR (Compt. rend. Soc. Biol., 1936, 121, 99—100).—Tubercle bacilli filtrate is pptd. with phosphotungstic acid and  $H_2SO_4$ . The ppt. is collected by centrifuge, washed with 0.2N- $H_2SO_4$ , and eluted with  $Ba(OH)_2$  solution; the residue is washed twice with  $H_2O$  and the eluate and washings are combined and filtered. The stable filtrate contains tuberculin. R. N. C.

Cultural characters of *Trichomonas (Trichomonastix) colubrorum*. R. CAILLEAU (Compt. rend. Soc. Biol., 1936, 121, 108—110).—*T. colubrorum* ferments glucose, galactose, fructose, maltose, sucrose, raffinose, and lactose with production of acid. Horse serum, but not rabbit serum, can replace whole blood or organs as nutrient. R. N. C.

Nitrogen distribution in the protein of mouse typhoid bacillus. H. OTANI (Acta Schol. Med. Kioto, 1935, 17, 334—337).—Data are given for the dry defatted bacilli and for the fraction pptd. from a conc.  $H_2SO_4$  extract on dilution to 5%. CH. ABS. (p)

Variation of the hæmolytic power of the El Tor vibrio. W. DOORENBOS (Compt. rend. Soc. Biol., 1936, 121, 130—132). R. N. C.

Microbiological basis of chemotherapeutic action. III. Fixation of therapeutically administered gold compounds by various recurrent spirochætes. N. VON JANCsó and E. NOVAK (Zentr. Bakt. Par., 1935, I, 134, 159—169).—Fixation of Au by *Sp. obermeiri* is reversible. Washing with serum removes the Au. *Sp. usbekistanica* does not absorb Au to any appreciable extent. A unimol. surface fixation by this organism is postulated. A. G. P.

Bacteriostatic and bactericidal studies of dyes and allied compounds. S. A. PETROFF and W. S. GUMP (J. Lab. Clin. Med., 1935, 20, 689—698).—zine, oxazine, thiazine, and basic CHPh<sub>3</sub> dyes (I), anti-quinoline derivatives (II), and some alkaloids have bactericidal and bacteriostatic effects on Gram-positive organisms. The order of activity for Gram-negative organisms was (II) > (I) > acridine dyes. CH. ABS. (p)

Study of the relations between bacteria, ultra-ruses, bacteriophages, toxins, and enzymes, by means of the action of gonacrine. C. LEVADITI, ER, and G. HORNUS (Bull. Acad. med., 1934, 112, 573—586).—Gonacrine rapidly suppresses the virulence, and sp. activity of bacteria, bacteriophages, and ultraviruses (except that of poliomyelitis), but does not affect toxins or enzymes. R. N. C.

Production of a neurotropic strain of Rift Valley fever virus. R. D. MACKENZIE and G. M. FINDLAY (Lancet, 1936, 230, 140—141). L. S. T.

Action of sodium ricinoleate on rabies virus. H. VIOLLE and J. LIVON (Compt. rend. Soc. Biol., 1936, 121, 100—102).—Na ricinoleate injected with rabies virus in rabbits prevents the onset of rabies. R. N. C.

Cultivation of the virus of St. Louis encephalitis. J. T. SYVERTON and G. P. BERRY (Science, 1935, 82, 597). L. S. T.

Apparatus for determining the fermentative properties of aerobic and anaerobic micro-organisms. A. P. STRUYK (Chem. Weekblad, 1936, 33, 44—45). S. C.

Hormonal equilibrium and hormonal derangement in the interferometric picture of the serum. A. SCHITTENHELM, F. CHROMETZKA, and W. SPIEKER (Z. ges. exp. Med., 1935, 95, 149—167; Chem. Zentr., 1935, i, 3431). R. N. C.

Gaseous exchange after injection of adrenaline in cocks and owls. A. PAGANO (Boll. Soc. ital. Biol. sperim., 1935, 10, 540—542).—Gaseous exchange, as in pigeons, is scarcely affected. R. N. C.

Adrenal cortex and carbohydrate metabolism. S. THADDEA (Z. ges. exp. Med., 1935, 95, 600—626; Chem. Zentr., 1935, i, 3299).—Adrenal cortex hormone injected into guinea-pigs causes increase of blood-sugar and of liver- and muscle-glycogen; it counteracts the action of insulin. G. H. F.

Modifications of the hypertensive action of adrenaline by certain colloidal products. D. BROWN and A. BEAUNE (Compt. rend. Soc. Biol., 1935, 120, 1202—1204).—The action of adrenaline in the dog is reduced by colloidal lipins, and by certain colloidal metals and proteins. R. N. C.

Physiology of the autonomous nervous system. VI. Action of adrenaline on the blood-calcium of the dog with parathyroid insufficiency. F. MATHIEU and Z. M. BACQ. VII. Phosphagen in the muscle of the sympathectomised cat. W. L. DULIERE, Z. M. BACQ, and L. BROUHA (Arch. int. Physiol., 1934, 38, 160—163, 164—171; Chem. Zentr., 1934, ii, 3401).—VI. Serum-Ca falls 10—15 min. after intravenous injection of adrenaline, which therefore has only a secondary rôle in Ca regulation.

VII. P in the muscles affected is increased some time after sympathectomy, owing to the slackening of the process of resynthesis. After 3—5 months P metabolism in the resting state is scarcely affected, whilst in the muscle a compensating or adapting process has taken place. R. N. C.

Action of adrenaline and potassium on the phosphagen of muscle poisoned with iodoacetic acid. J. WAJZER, R. LIPPMANN, and A. MARNAY (Compt. rend. Soc. Biol., 1936, 121, 142—144).—Adrenaline scarcely affects phosphagen (I) in the isolated  $CH_2I-CO_2H$ -poisoned frog's muscle in anaerobiosis, no resynthesis occurring even when (I) is almost absent from the muscle. Excess of K<sup>+</sup> causes a breakdown of (I). R. N. C.

**Influence of rapidity of intravenous injection of adrenaline on hyperglycæmic action.** Y. SUGANUMA (*Folia Pharmacol. Japon.*, 1935, 19, 412—416).—The longer was the time of injection the stronger was the hyperglycæmic response (max. at 10—30 min.). CH. ABS. (p)

**Decomposition of adrenaline in tissues.** H. BLASCHKO and H. SCHLOSSMANN (*Nature*, 1936, 137, 110).—Rat-liver tissue accelerates the loss of adrenaline (I) activity in presence of O<sub>2</sub>. The O<sub>2</sub> uptake of liver tissue is not markedly influenced by (I), but that of liver extracts is increased when (I) is added. In presence of tissue extracts activity is approx. halved after the uptake of one O and practically abolished after that of 2 O per mol. of (I). L. S. T.

**Significance of the vegetative nervous system on the regulation of blood-sugar.** E. FYLLA (*Minerva med.*, 1935, I, 489—494).—Insulin (I) injection with adrenaline is less effective in producing hypoglycæmia than is (I) alone. Simultaneous injection of atropine and ginerin followed by (I) has a greater effect than (I) alone. CH. ABS. (p)

**Action on local glycæmia, *in vivo*, of insulin injected intravenously.** D. OLMER, J. OLMER, J. PAILLAS, and J. VAGUE (*Compt. rend. Soc. Biol.*, 1936, 121, 76—78).—Injection of insulin in a section of a limb that has been ligatured off from the circulation causes a local fall of blood-sugar that varies with the subject. The hypoglycæmic action of insulin probably depends on direct glycæmic and muscular glycolysis, but the hepatic factor is excluded. R. N. C.

**State of functional reactivity of the endocrine pancreatic tissue in normal dogs subjected to prolonged biquotidian injection of insulin.** E. AUBERTIN, A. LACOSTE, and R. SARIC (*Compt. rend. Soc. Biol.*, 1936, 121, 241—244).—The blood-sugar curve after glucose does not exhibit an abnormal rise in animals subjected to prolonged insulin treatment, but the post-hyperglycæmic fall is increased. R. N. C.

**Influence of insulin on the liver-glycogen level of frogs.** E. GEIGER [with H. HALMOS] (*Arch. exp. Path. Pharm.*, 1936, 180, 251—257).—Continuous electrical stimulation of the muscles in summer and spring (but not winter) frogs diminishes the liver-glycogen (I). Prior administration of insulin (II) inhibits this change. Administration of glucose causes production of (I) in all seasons, but the increase in (I) of summer frogs disappears after a few days unless (II) is injected. Hence the seasonal variation in (I) is due to deprivation of (II), which inhibits glycogenolysis but does not influence (I) formation. F. O. H.

**Direct action of glucose on secretion of insulin by the pancreas.** V. G. FOGLIA and R. FERNANDEZ (*Compt. rend. Soc. Biol.*, 1936, 121, 355—358).—Injection of glucose in a dog with a pancreatic graft on the neck causes an increase of insulin secretion in the graft, independent of extrinsic innervation. R. N. C.

**Effect of repeated injections of insulin on the histological state of the endocrine pancreatic tissue and its insulin content in the normal dog.**

A. LACOSTE, E. AUBERTIN, and R. SARIC (*Compt. rend. Soc. Biol.*, 1936, 121, 239—241).—The no. of islets of Langerhans and the insulin content are increased. R. N. C.

**Modifications of the cardiovascular action of acetylcholine by insulin.** D. BROWN and A. BEAUNE (*Compt. rend. Soc. Biol.*, 1935, 120, 1205—1208).—The action is reinforced by insulin. R. N. C.

**Effect on local glycæmia, *in vivo*, of parathyroid hormone injected intravenously.** J. OLMER, J. PAILLAS, and B. SICNAST (*Compt. rend. Soc. Biol.*, 1936, 121, 78—80).—Intravenous injection of parathormone (I) in a section of a limb that has been ligatured off from the circulation does not affect local blood-sugar; the action of (I) is therefore not due to direct glycolytic influence exercised by muscle or blood. R. N. C.

**Effect of parathyroid extract on blood coagulation.** R. BONNYNS (*Arch. Int. Physiol.*, 1934, 40, 189—208).—Parathyroid extract (I) does not affect coagulation of re-calcified oxalated blood *in vitro*. The time of coagulation of such blood of rabbits is reduced by intravenous injection of (I), reaching its min. 45 min. after injection, and returning to normal in 3 hr. The action takes place principally in the second phase of (I) action. Plasma-scrozyme is increased, and also, very slightly, the fibrinogen and platelet contents of the blood, the  $p_H$  and alkaline reserve being unaffected. R. N. C.

**Action of hormones on the secretion of digestive enzymes. Effect of (I) thyroid, (II) parathyroidectomy, (III) insulin, on the composition of gastric juice.** R. FERRARI (*Boll. Soc. ital. Biol. sperim.*, 1934, 9, 1320—1322, 1323—1325, 1325—1328).—I. Thyroid preps. fed to dogs increase the enzyme content of the gastric juice; thyroidectomy reduces it, whilst subsequent administration of thyroid preps. restores it to the normal val. Total acidity and free HCl are unaffected.

II. Parathyroidectomy increases the enzyme content and free HCl, but does not affect total acidity.

III. Insulin increases the enzyme content, total acidity, and free HCl as the blood-sugar falls, and vice versa; the rate of secretion is also increased. Glucose increases enzyme content and free HCl slightly, but does not affect total acidity. R. N. C.

**Rôle of cholesterol in thyroid-ovarian antagonism: ovarian and adrenal cholesterol in thyroidectomised and thyroxine-treated animals.** C. I. PARHON, C. PARHON-STEFANESCU, and I. ORNSTEIN (*Compt. rend. Soc. Biol.*, 1936, 121, 187—189).—Thyroidectomy in rabbits and guinea-pigs causes an increase in ovarian cholesterol (I), which is slightly further increased in rabbits and decreased in guinea-pigs by administration of excess of thyroxine (II). Adrenal (I) is decreased in guinea-pigs and increased in rabbits by both thyroidectomy and excess of (II). (I) is apparently concerned in thyroid-ovarian antagonism. R. N. C.

**Influence of thyroxine on the oxygen consumption of surviving tissue.** W. HAARMANN (*Arch. exp. Path. Pharm.*, 1936, 180, 167—182).—

The  $O_2$  consumption of surviving muscle or liver tissue is increased by addition of  $10^{-17}$ – $10^{-9}\%$  (max.  $10^{-12}$ – $10^{-14}\%$ ) of thyroxine: higher concns. have an inhibitory action. F. O. H.

**Influence of thyroxine on tissue respiration.** A. REUTER (Z. ges. exp. Med., 1935, 95, 214–216; Chem. Zentr., 1935, i, 3300).—Thyroxine caused a rise in  $O_2$  consumption of isolated organs of rat and cat (Warburg's method) of 20–35%; the effect vanished after 1–2 hr. Results on isolated organs may not be comparable with those on living organisms. G. H. F.

**Pathogenesis of the histological alterations of the myocardium with excessive administration of synthetic thyroxine.** C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 597–600). R. N. C.

**Mode of toxic action of excessive administration of thyroxine on the liver.** C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 594–597). R. N. C.

**Histological lesions of the liver with excessive administration of thyroxine.** C. MANZINI and E. COSTANTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 591–594). R. N. C.

**Influencing of the thyroxine-catechin balance of different types of blood by a growth-promoting principle.** H. EUFINGER and J. B. GOTTLIEB (Klin. Woch., 1934, 13, 1204–1205; Chem. Zentr., 1934, ii, 3396).—The effect of thyroxine (I) on *Rana temporaria* when added to the aquarium- $H_2O$  is restricted by addition of umbilical, retroplacental, or pubertal blood, which contain an inhibitory and growth-promoting substance. Lactic and uric acids increase the effect of (I), probably through shifting of  $pH$ . R. N. C.

**Occurrence of thyrotropic hormone in the central nervous system and cerebrospinal fluid.** A. SCHITTENHELM and B. EISLER (Z. ges. exp. Med., 1935, 95, 121–123; Chem. Zentr., 1935, i, 3434).—Thyrotropic hormone occurs in the mid-brain and cerebrospinal fluid of the cat. The mid-brain contains  
o 1/3 of the pituitary content. R. N. C.

**Transmission of thyrotropic hormone through the placenta and milk.** A. SCHITTENHELM and EISLER (Z. ges. exp. Med., 1935, 95, 124–125; Chem. Zentr., 1935, i, 3298).—Thyrotropic hormone administered to guinea-pigs, when pregnant or when nursing young, produced no change in the thyroids of the young. G. H. F.

**Anti-thyrotropic substance in blood and carbohydrate metabolism of the liver.** A. LOESER (Z. ges. exp. Med., 1936, 180, 325–331).—The principle (I) antagonistic to the anterior pituitary thyrotropic hormone (A., 1935, 1543) inhibits the characteristic symptoms of hyperthyroidism. The hepatic carbohydrate metabolism indicates that changes (e.g., glycogenolysis) due to thyroxine are independent of the thyroid gland are not influenced. The relation of (I) to thyroid activity is dis

**Effect of pituitary on protein metabolism. I. Pituitary preparations. II. Thyroid preparations. III. Pancreatic preparations. IV. Adrenal preparation. V. Ovarian preparations.** Y. TOKIZAKI (Sei-i-Kwai Med. J., 1934, 53, No. 9, 212–242, No. 10, 105–117, 118–129, 130–139, 140–148).—I. Hypophysectomy decreases protein (I) metabolism and only the anterior pituitary prep. can accelerate it.

II. Injection of thyroxine accelerates (I) metabolism in normal and hypophysectomised dogs, the action being less in the latter.

III. Injection of insulin into normal animals increases all N fractions in urine, and the total, non-protein-,  $NH_3$ -, and creatinine-N in blood. Blood-urea, -uric acid, -creatine, and  $-NH_2$ -acid decline. With hypophysectomised dogs all urinary N fractions increase, blood-uric acid increases, and all other N fractions together with  $HIO_3$  decrease.

IV. Adrenaline increases (I) metabolism in normal and hypophysectomised animals.

V. Ovarian prep. (oophormin) increases (I) metabolism in normal > in hypophysectomised dogs.

CH. ABS. (p)

**Influence of pituitary preparations on non-protein-nitrogen and urea in blood, and iodic acid in serum, of normal and hypophysectomised dogs.** Y. TOKIZAKI (Sei-i-Kwai Med. J., 1934, 53, No. 10, 149–158).—Pituitrin and pituglandol increased, but hypophorin decreased, the non-protein-N and urea in blood of normal and hypophysectomised dogs.  $HIO_3$  in serum increased in all cases.

CH. ABS. (p)

**Difference of response of the pituitary glands of male and female albino rats treated with the growth hormone.** H. S. RUBINSTEIN (Anat. Rec., 1934, 61, 131–140). R. N. C.

**Significance of the pituitary in kidney disease.** H. MARX (Klin. Woch., 1935, 14, 367–372; Chem. Zentr., 1935, i, 3153). G. H. F.

**Stability of anterior pituitary extract in aqueous solution.** I. W. ROWLANDS (Quart. J. Pharm., 1935, 8, 642–645).—Aq. extracts of anterior pituitary preps. lost about 50% of their gonadotropic activity in 9 days at room temp. and in about 1 year at 0–2°. W. O. K.

**Migraine as a pituitary disease and its treatment with ovarian preparations.** I. MUELLER (Med. Klinik, 1935, 31, 448–450).—The anterior pituitary hormone content of the urine of women suffering from migraine is frequently > normal. Progynon exerts a curative effect. R. N. C.

**Adrenaltropic action of the anterior pituitary.** K. J. ANSELMINO, L. HEROLD, and F. HOFFMANN (Klin. Woch., 1934, 13, 1724).—The chrome-pigmentability of the adrenal medulla is almost abolished and vacuole formation increased by injection of anterior pituitary extract in rats or mice. The active principle is sensitive to acids and alkali, but comparatively thermostable; it can be separated from the corticotropic hormone by ultrafiltration through collodion, which retains it. R. N. C.

Influence of hormones of the anterior and posterior lobes of the pituitary, the thyroid, and the adrenals on the spontaneous creatinuria of endocrine disturbances. A. SCHITTENHELM and F. BUHLER (Z. ges. exp. Med., 1935, 95, 206—213; Chem. Zentr., 1935, i, 3435).—Spontaneous creatinuria in males with gonadal insufficiency is abolished by prolant and orasthin, but not by prahormone. Thyrotropic hormone and thyroxine induce creatinuria in myxœdema. Spontaneous creatinuria in Addison's disease is abolished by small doses of cortical preps.; its appearance is due to increased breakdown of phosphagen in the muscles. R. N. C.

Glyco-chloro-proteinæmic curve in normal and diabetic individuals after injection of posterior pituitary extract. G. DELL'ACQUA (Boll. Soc. ital. Biol. sperim., 1935, 10, 423—447).—Injection of the extract in normal subjects induces a short rise of blood-sugar (I) followed by a prolonged fall and recovery to normal. Proteins (II) show a fall followed by a recovery to almost normal; NaCl falls without recovering. In diabetics (I) shows a marked rise followed by a fall without recovery. (II) rise rapidly at first, fall to vals. < normal, and then rise slowly to > the first max. NaCl rises irregularly. R. N. C.

Determination of the excretion of prolant by mature and by aged men. H. SAETHRE (Klin. Woch., 1935, 14, 376—378; Chem. Zentr., 1935, i, 3153).—The urinary prolant excretion of healthy men is 25—30 mouse units per litre. In old age there may be some increase. G. H. F.

Prepubertal reversal of the sex difference in the gonadotropic hormone content of the pituitary gland of the rat. H. M. CLARK (Anat. Rec., 1934, 61, 175—192).—The prolant content of the pituitary in the immature female rat is > that in the male; at puberty the male gland is more potent. From 4 to 6 months the sex difference is negligible, whilst at 7 months it is reversed. In the female the content rises sharply at 13—20 days, whilst in the male it increases gradually to a const. level at puberty. R. N. C.

Sex difference in the change of potency of the anterior pituitary following bilateral castration in newborn rats. H. M. CLARK (Anat. Rec., 1934, 61, 193—202).—Prolant in the male pituitary increases on castration; it fluctuates in females. R. N. C.

Is there an antagonism of sex hormones? O. O. FELLNER (Z. ges. exp. Med., 1935, 95, 373—377; Chem. Zentr., 1935, i, 3431—3432).—Hormones are extracted from urine by boiling with CaO and pptn. with  $\text{Na}_2\text{C}_2\text{O}_4$ , the hormones remaining in the filtrate. The masculin (I) content of pregnancy urine is > that of male urine, (I) probably originating from the placenta. The sex hormone antagonism hypothesis is discarded in favour of one of synergism between the hormones and gonads. R. N. C.

Physiology of  $\Delta^5$ -androstenediol. A. BUTENANDT (Naturwiss., 1936, 24, 16).— $\Delta^5$ -Androstenediol in pure condition displays the activities of both testicular and follicular hormones. W. O. K.

Action of the male hormone (androsterone) injected into the chicken embryo: experimental production of intersexuals. E. WOLFF (Compt. rend. Soc. Biol., 1935, 120, 1312—1314).

R. N. C.

Interpretation of the results obtained by injection of synthetic androsterone in the chicken embryo. E. WOLFF (Compt. rend. Soc. Biol., 1935, 120, 1314—1316).

R. N. C.

Influence of sex hormone on the spontaneous creatinuria of endocrine disturbances. A. SCHITTENHELM and F. BUHLER (Z. ges. exp. Med., 1935, 95, 197—205; Chem. Zentr., 1935, i, 3433).—Spontaneous creatinuria in males with gonadal insufficiency is abolished by "proviron," but not if muscle metabolism has been disturbed by degenerative muscle changes. Similar creatinuria in women at the climacteric is abolished by "progynon," but not so uniformly. In certain cases creatinuria is abolished also by the heterosexual hormone.

R. N. C.

Response of immature rats to various gonadotropic substances. R. DEANESLY (Quart. J. Pharm., 1935, 8, 651—668).—Various gonadotropic preps. were administered to male and female immature rats and their resulting actions observed. A method of assay which employs 10 rats with an error of  $\pm 10\%$  is described. W. O. K.

Relative activity of different gonadotropic preparations on œstrous rabbits, pregnant rabbits, and immature rats. I. W. ROWLANDS (Quart. J. Pharm., 1935, 8, 646—650).—Extracts of pituitary gland (cow, horse) and urine of pregnancy have been assayed on œstrous, 15 days- and 25 days-pregnant rabbits, and on immature rats. For ovulation, pregnant rabbits require more of all extracts tested than do œstrous rabbits. Horse pituitary and urine of pregnancy extracts are relatively equally potent when tested on rabbits and rats, but ox pituitary is less potent in rats. W. O. K.

Physiology of the corpus luteum. IX. Inhibition of œstrin by progestin-containing extracts of the corpus luteum. W. M. ALLEN and R. K. MEYER (Anat. Rec., 1935, 61, 427—439).—Progestin inhibits cornification by œstrin and the œstrous smear. R. N. C.

Structure of œstrin in alkaline solution. K. P. BJERGAARD and S. A. SCHOU (Quart. J. Pharm., 1935, 8, 669—673).—In neutral or acid EtOH solution, the max. ultra-violet absorption of œstrin occurs at 282 m $\mu$ , whilst in alkaline solution it is at 295 m $\mu$ . The shift is probably associated with enolisation of the keto-group. W. O. K.

Biological activity of theelol. R. K. MEYER, L. C. MILLER, and G. F. CARTLAND (J. Biol. Chem., 1936, 112, 597—604).—Theelol (I) has little biological activity compared with international standard theelin (II) when determined by the vaginal smear method, but it is 4 times as active when determined by the opening of the vagina of the immature rat. (II) is approx. 90 times as active as (I) when administered in oil and 250 times when injected in aq. 10% EtOH containing 0.5%  $\text{Na}_2\text{CO}_3$ . J. N. A.



**Follicular hormone content of eclamptic blood.** W. BICKENBACH and H. FROMME (Klin. Woch., 1935, 14, 496—497).—The follicular hormone content of the blood of eclamptic women is  $\times$  that of the blood of pregnancy. R. N. C.

**Sexual hormones in domestic animals.** KÜST (Klin. Woch., 1934, 13, 1782—1784).—Pregnancy is diagnosed in mares by the Aschheim-Zondek serum reaction from the sixth week to the fifth month, and later by increased follicular hormone (I) excretion in the urine. (I) excretion is increased in the 23rd week in cows, and after 3½ months in goats; in the sow it reaches max. in the fourth week and at the end of pregnancy. (I) is present in the urine of mature boars. R. N. C.

**Sexual hormones in domestic animals.** S. KOBER (Klin. Woch., 1935, 14, 381).—Excretion of follicular hormone in the urine of the pregnant mare appears before the 110th day, rises to a max. between the 6th and 8th months, and then falls to a trace at the conclusion of pregnancy (cf. preceding abstract). R. N. C.

**Artificial (hormonal) growth of the oviduct in female carp.** K. EHRLHARDT and K. KÜHN (Endokrinol., 1934, 15, 1—14; Chem. Zentr., 1935, i, 3433; cf. A., 1935, 413).—The oestrus hormone (I) is apparently not identical with the oviduct hormone (II); crude (I) affects the oviduct more strongly than the cryst. product, whilst (II), although resembling (I) in solubility, thermostability, and adsorbability on C, is difficult to elute from the adsorbate, and is destroyed by 15% NaOH or by AcOH. R. N. C.

**Embryological interpretation of changes induced by oestrogens in the male reproductive tract.** S. ZUCKERMAN (Lancet, 1936, 230, 135—136). L. S. T.

**Follicular and luteal hormones and their reaction on the anterior lobe of the pituitary.** CLAUERG and W. BREIPOHL (Klin. Woch., 1935, 14, 119—121; Chem. Zentr., 1935, i, 3298). G. H. F.

**Inhibitory effect of follicular hormone on the anterior lobe of the pituitary gland.** B. ZONDEK (Lancet, 1936, 230, 10—12). L. S. T.

**Biological determination of corpus luteum acts.** R. COURRIER (Compt. rend. Soc. Biol., 1935, 120, 1263—1266). R. N. C.

**Antigonadotropic hormone in the pineal gland, and organs.** P. ENGEL (Z. ges. exp. Med., 1935, 95, 441—457; Chem. Zentr., 1935, i, 3300).—Antigonadotropic hormone (I) of pineal gland is standardised by injecting into immature female rats simultaneously with standardised gonadotropic hormone anterior pituitary (II). The amount of (I) required to neutralise the effect of a rat unit of (II) is measured. (I) is found in small amounts in blood, kidney, and spleen. G. H. F.

**Effects of the melanophore hormone and prolantin pigmentation and growth of tadpoles.** M. AGLIALORO and U. CIULLA (Boll. Soc. ital. Biol. D D

sperim., 1935, 10, 538—540).—The melanophore hormone inhibits, whilst prolantin stimulates, these. R. N. C.

**Standardisation of the melanophore hormone.** M. AGLIALORO and U. CIULLA (Boll. Soc. ital. Biol. sperim., 1935, 10, 537—538). R. N. C.

**Villikin in the human intestine.** G. VON LUDANY (Klin. Woch., 1935, 14, 123—124; Chem. Zentr., 1935, i, 3301; cf. A., 1934, 331).—Human intestinal mucous membrane when extracted with HCl, neutralised, and the extract injected intravenously into fasting dogs caused great acceleration of the rate of contraction of villi. G. H. F.

**Colour reactions of vitamin-A, -D, and -E, and of some sterols.** S. UENO, Y. OTA, and Z. UEDA (J. Soc. Chem. Ind. Japan, 1935, 38, 742—744B).—The colour reactions of these vitamins and of cholesterol, ergosterol, and sitosterol, with fourteen new reagents (mainly PhOH + a second substance) are tabulated and briefly discussed. J. W. B.

**Vitamin-A storage of *Macrurus rupestris*.** S. SCHMIDT-NIELSEN, A. FLOOD, J. STENE, and N. A. SØRENSEN (Kong. Norske Vid. Selsk. Forhandl., 1935, 7, 174—177; Chem. Zentr., 1935, i, 3302).—Data for liver-fat and tintometer no. are given and correlated. H. J. E.

**Vitamin-A content of the liver and its variations.** A. CHEVALLIER and Y. CHORON (Compt. rend. Soc. Biol., 1935, 120, 1223—1225).—Vitamin-A (I) is decreased in the liver and increased in the blood of the rabbit by anaesthesia. In the guinea-pig, liver-(I) shows marked variations with the animal, whilst blood-(I) is practically const. R. N. C.

**Metabolism of rat liver in avitaminosis-A.** O. ROSENTHAL (Arch. Neerland. Physiol., 1935, 20, 539—551).—In about 2/3 of the avitaminotic rats examined, the energy of metabolism decreased considerably, and there was a slight decrease in respiration. These effects appeared as often in fatty as in de-fatted livers. Fatty degeneration, probably as a result of the respiration disorder, is assumed. Changes in metabolism and fatty degeneration of the liver are secondary effects of the vitamin-A deficiency. J. N. A.

**Effect of standard diet on liver metabolism in experimental avitaminosis-A in rats.** O. ROSENTHAL (Arch. Neerland. Physiol., 1935, 20, 552—558).—The changes in metabolism and the histological fatty degeneration of the liver are due to an unsp. diet deficiency. The importance of this in the problem of experimental avitaminosis-A is discussed. J. N. A.

**Size and vitamin content of liver of various animals.** S. SCHMIDT-NIELSEN, A. FLOOD, and J. STENE (Kong. Norske Vid. Selsk. Forhandl., 1934, 3, 81—84; Chem. Zentr., 1935, i, 2620).—Vitamin-A contents of livers of warm-blooded animals are < those of many fish. J. S. A.

**Effect of vitamin-A on fat and lipin metabolism.** P. E. SMOLA and T. KALAJA (Suomen Kem., 1935, 8, B, 43—44).—Rats and guinea-pigs fed a vitamin-A (I)-free diet show large decreases in the I val. and neutral fat content of the skin, whereas the cholesterol

content is increased, especially in rats. In rats fed on (I)-rich diets, the free cholesterol of the skin and the cholesteryl esters (II) of the liver and kidneys are increased. In guinea-pigs, the changes are indefinite, although the (II) content, the I val., and the neutral fats of the liver are increased.

J. L. D.

**Fate of carotene injected into the circulation of the rat.** J. C. DRUMMOND and R. J. MACWALTER (*J. Physiol.*, 1934, **83**, 236—242).—Vitamin-A and fat distribution is fairly uniform in the three main lobes of the liver. Carotene injected into the portal circulation is taken up uniformly by the lobes, and tends to disappear after a few days, -A not increasing simultaneously, but in some cases falling. Removal of one lobe may cause a fall in the -A of the other lobes.

R. N. C.

**Vitamin-A in the red corpuscles of the blood of vertebrates.** A. MAGNAN and H. GIRERD (*Compt. rend.*, 1935, **201**, 1219—1221).—Vitamin-A occurs in certain of the red corpuscles of the blood of the ray and is localised on the chondriome.

A. G. P.

**Determination of vitamin-A.** A. L. BACHARACH, J. C. DRUMMOND, and R. A. MORTON (*Nature*, 1936, **137**, 148—149).—A crit. discussion of the three approved methods of standardisation which may give three different results.

L. S. T.

**Effects of vitamin-B on female genital organs of white rats.** J. UENO (*Japan. J. Obstet. Gynecol.*, 1934, **17**, 388—411).

CH. ABS. (p)

**Deficiency of vitamin-B and endocrine glands of female white rats.** J. UENO (*Japan. J. Obstet. Gynecol.*, 1934, **17**, 267—278)

CH. ABS. (p)

**Effect of arginine and of liver and stomach extracts on vitamin-B deficiency in pigeons.** A. VON JENEY (*Klin. Woch.*, 1935, **14**, 379—380; *Chem. Zentr.*, 1935, i, 3155).—The length of life of pigeons on a vitamin-B-free diet was increased by administration of extracts from yeast, liver, or pig's stomach, or of arginine. The -B complex appears to contain an antianæmic factor resembling arginine.

G. H. F.

**Assay of vitamin-B<sub>1</sub> by the "beri-beri" quotient ( $Q_b$ ).** G. AMANTEA (*Atti R. Accad. Lincei*, 1935, [vi], **22**, 173—176).—Further details of the technique are given (cf. A., 1934, 460, 706).

F. O. H.

**Vitamin-B<sub>1</sub> and -B<sub>2</sub>.** J. F. FEASTER and V. E. NELSON (*Proc. Iowa Acad. Sci.*, 1934, **41**, 149—152).—Autoclaved yeast supplies a factor, probably vitamin-B<sub>2</sub>, enhancing lactation in rats.

CH. ABS. (p)

**Interrelationship of vitamins.** C. A. ELVEHJEM and A. ARNOLD (*Nature*, 1936, **137**, 109—110).—The cure of certain symptoms in experimental animals even with cryst. preps. of vitamin does not necessarily mean that the deficiency is due to a lack of the factor fed. Rats showing -B<sub>4</sub>-deficiency may be relieved by administration of -B<sub>1</sub>. The latter appears to relieve accompanying anorexia, and food consumption increases to a level which supplies adequate -B<sub>4</sub>. Synthetic diets used for -B<sub>1</sub> studies must be

amply supplied with -B<sub>4</sub>, especially when growth is used as a criterion of potency. The improved growth often obtained by adding large amounts of -B<sub>1</sub> to rats on a low -B<sub>1</sub> diet may be due to the additional effect of traces of -B<sub>4</sub> present as an impurity.

L. S. T.

**Objective method for fluorescence determination, with special application to the determination of vitamin-B<sub>2</sub>.** F. H. COHEN (*Acta Brev. neerl. Physiol.*, 1935, **5**, 18—19; *Chem. Zentr.*, 1935, i, 3306).—The apparatus previously described (A., 1935, 466) is applied to the determination of vitamin-B<sub>2</sub>.

H. N. R.

**Effect of adenine fed to rats on a diet deficient in vitamin-B<sub>4</sub>.** T. Y. LO (*Nat. Peiping Univ. Coll. Agric. Nutrition Bull.*, 1934, **B**, 1, 40—46).—Pure adenine from yeast does not serve as a source of vitamin-B<sub>4</sub> for rats.

CH. ABS. (p)

**Influence of some food factors on pellagra-like symptoms in rats.** F. J. GORTER (*Z. Vitaminforsch.*, 1936, **5**, 1—11).—The incidence and type of pellagra-like disease in rats depend on the composition of the basal diet. There exists an anti-pellagic growth-promoting factor other than flavin and perhaps identical with vitamin-B<sub>6</sub>. This factor is separated from caseinogen by hydrolysis. Factors causing dermatitis in rats are discussed.

F. O. H.

**Antiscorbutic activity of dehydroascorbic acid: its storage and that of ascorbic acid by the guinea-pig at different levels of intake.** F. W. FOX and L. F. LEVY (*Biochem. J.*, 1936, **30**, 211—217).—The antiscorbutic val. of dehydroascorbic acid has been confirmed (Hirst *et al.*, A., 1933, 1091). After reduction to ascorbic acid (I) it is stored in small amounts in the liver. Storage of (I) in the liver is dependent on the level of intake, being small at the min. protective dose and reaching an upper limit at higher levels.

H. G. R.

**Does vitamin-C affect the occurrence of normal pigmentation?** F. TENCHIO (*Klin. Woch.*, 1934, **13**, 1511—1512; *Chem. Zentr.*, 1934, ii, 3644—3645).

R. N. C.

**Reversibility of oxidation of ascorbic acid.** R. WURMSER and N. MAYER (*Compt. rend. Soc. Biol.*, 1936, **121**, 3—5).—Oxidation of ascorbic acid by 2 : 6-dichlorophenol-indophenol is as reversible as oxidation by I.

R. N. C.

**Reversible oxidation of ascorbic acid by norite charcoal.** F. W. FOX and L. F. LEVY (*Biochem. J.*, 1936, **30**, 208—210).—The C (and to a smaller extent other kinds) rapidly (10—15 min.) converts ascorbic acid almost quantitatively into dehydroascorbic acid. With small amounts of C, the effect  $\propto$  the amount of C. Probably the oxidation results from direct transfer of O<sub>2</sub> from the C surface.

W. McC.

**Biological oxidations.** V. Copper and hæmochromogens as catalysts for the oxidation of ascorbic acid. Mechanism of the oxidation. E. S. G. BARRON, R. H. DEMEIO, and F. KLEMPERER (*J. Biol. Chem.*, 1936, **112**, 625—640).—Ascorbic acid (I) is not autoxidisable in solutions free from Cu when the  $p_H$  is < 7.6. Above  $p_H$  7.6 the rate of

autoxidation increases rapidly with the  $p_H$ . KCN slightly accelerates the rate of  $O_2$  consumption. In neutral and acid solution  $Cu^{++}$  (alone of metallic ions) catalyses the oxidation of (I) in concns. as low as 0.046 mg. of Cu per litre. The  $O_2$  uptake is 1 O per mol. of substrate. The optimum  $p_H$  of the Cu-catalysed oxidation is 6.95. The haemochromogens of nicotine,  $C_5H_5N$ , and pilocarpine can also act as catalysts. 0.001M-KCN completely inhibits the catalytic effect of Cu, and CO, by combining with  $Cu_2Cl_2$  and thus inhibiting its reoxidation to  $CuCl_2$ , also considerably retards the reaction. The low val. of 1.65 for the temp. coeff. suggests that the reoxidation of  $Cu_2Cl_2$  is the reaction governing the rate of oxidation of (I). The oxidation product can be completely reduced by  $H_2S$  up to  $p_H$  5.0, but above this the amount of (I) recovered gradually decreases until at  $p_H$  7.6 the oxidation is mainly irreversible. E. A. H. R.

**Diagnosis of vitamin-C subnutrition by urine analysis.** M. A. ABBASY, L. J. HARRIS, S. N. RAY, and J. R. MARRACK (Lancet, 1935, 229, 1399—1405).—Data obtained by the method previously described (A., 1935, 417), together with its specificity, are discussed. The urinary excretion of vitamin-C by adults receiving graded doses of -C over long periods reaches levels  $\propto$  the intake. Little variation occurs between individual subjects; the same daily dose of -C soon produces an almost identical rate of excretion. During fever, output falls, and an additional dose is needed to restore the original level. A diet appears to be unduly low in -C whenever the daily excretion is  $<$  a titration val. of 10—15 mg. per day per 10 stone body-wt., or when the standard dose of 700 mg. produces no response on the second day. In England, the average daily excretion of normal adults receiving small allowances of fruit or other source of -C is approx. 20 mg. per day. L. S. T.

**Effect of vitamin-C on the growth of plants.** S. VON HAUSEN (Suomen Kem., 1935, 8, B, 50; cf. A., 1935, 1036).—Removal of the cotyledons of young pea seedlings reduces their ascorbic acid (I) content to a low val. and growth is almost completely retarded. Addition of (I) causes increased (approx. normal) growth; the (I) content of the treated plants is much  $>$  that of the untreated. J. L. D.

**Antiscorbutic value of dandelion.** I. S. KLEINER TAUBER (Science, 1935, 82, 552).—The ascorbic acid (I) content varies between 0.08 and 0.10 mg. per g. of fresh greens. Compared with the greens of other vegetables it is not a good source of (I).

L. S. T.

**Ascorbic acid content of plant tissue.** L. ANDOIN, A. GIROUD, and C. P. LEBLOND (Bull. Soc. Chim. biol., 1935, 17, 1649—1676).—Equal quantities of tissue containing chlorophyll and that containing no chlorophyll of the carrot, turnip, cress-grass, endive, lettuce, leek, and beetroot are administered to guinea-pigs in addition to a diet containing no vitamin-C. The chlorophyll tissue has much higher antiscorbutic val., as is shown by the survival curves and the ascorbic acid content of the renal glands, the kidney, liver, and testicles.

A. L.

**Sources of vitamin[-C]. XI—XVI.**—See B, 1936, 121.

**Vitamin-D requirements in relation to the calcium and phosphorus content of the diet.** A. QUERIDO (Arch. Neerland. Physiol., 1935, 20, 487—538; cf. A., 1935, 1431).—The daily requirement for rats varies between 0 and  $1 \times 10^{-6}$  g. of calciferol. It is influenced by the salt level of the ration, and diminishes with increase of the abs. concn. of P. Influence of vitamin-D on the ash content of bone is seen only with diets having a Ca : P ratio of 4. Unpreventable rickets produced by some diets can be changed into a preventable form by preliminary feeding with a diet rich in minerals. Rickets produced by a diet containing 0.2% of P and Ca : P = 1 resembles the human form  $>$  that produced with a Ca : P ratio of 4. J. N. A.

**Evaluation of the relative toxic effects of large doses of calciferol and the crystalline antirachitic preparation substance L.** J. VAN NIEKERK (Arch. Neerland. Physiol., 1935, 20, 559—561).—The ratio of toxic to antirachitic activity of the substance L of Reerink and van Wijk is identical with that of calciferol. J. N. A.

**Anti-infective power of vitamin-D.** G. SPAGNOL (Rev. sudamer. endocrinol., 1935, 18, 163—166).—Irradiated ergosterol prevented infection of rats with *Salmonella typhimurium*. CH. ABS. (p)

**Changes in composition of blood in rabbits by irradiated food.** A. FALASCHINI (Boll. Soc. Eustach., 1934, 32, 1—15; Chem. Zentr., 1934, ii, 3782—3783). R. N. C.

**Irradiation and growth.** F. ROGOZINSKI and Z. GLOWCZYNSKI (Bull. Acad. Polonaise, 1935, B, 123—136).—Ultra-violet irradiation had no apparent influence on the growth, food utilisation, or bone composition of rats receiving a complete diet, but afforded marked protection when a rachitogenic diet was used. A. G. P.

**Cereals and rickets. VI. Comparative rickets-producing properties of different cereals.** B. H. THOMAS and H. STEENBOCK (Biochem. J., 1936, 30, 177—188; cf. Green *et al.*, A., 1928, 333).—Rolled oats, patent flour, whole wheat, polished rice, and yellow maize fed to rats as 75% of a low-Ca diet do not differ as regards the severity of the rickets produced. W. McC.

**Hypervitaminosis-D.** L. THATCHER (Lancet, 1936, 230, 20—22).—Young infants may have idiosyncrasy to the vitamin-D (I) in cod-liver oil as well as to artificially-prepared calciferol. The current tendency to increase the (I) potency of cod-liver oil is deprecated. L. S. T.

**Vitamin-D content of calf, beef, lamb, and hog livers.** G. M. DEVANEY and H. E. MUNSELL (J. Home Econ., 1935, 27, 240—241).—Ox and hog livers have 0.5—0.4, lamb 0.2, and calf liver  $<$  0.1 international units per g. CH. ABS. (p)

**Vitamin-D content of New Zealand fish oils : prophylactic method of biological assay.** M. M. CUNNINGHAM (New Zealand J. Sci. Tech., 1935, 17, 563—567).—Vals. for a no. of oils are recorded.

That for proper-liver oil was exceptionally high. The trustworthiness of the prophylactic method of assay is confirmed. A. G. P.

**Vitamin-E. IV. Influence on fertility and condition of the young.** L. SCHIOPPA (Z. Vitaminforsch., 1936, 5, 22—26).—Administration of large doses of wheat-germ oil to doe rabbits increases their fertility and body-wt. F. O. H.

**Chemical properties of vitamin-E.** H. S. OLCOTT (Proc. Iowa Acad. Sci., 1934, 41, 173; cf. A., 1935, 1431).—The inactive product obtained by bromination of vitamin-E concentrates is reactivated by boiling with Zn and HCl in MeOH. Catalytic hydrogenation at 200°/200 atm. does not destroy -E.

CH. ABS. (p)

**Newly-discovered nutritional factor in milk.** G. VON WENDT (Z. Volksernahr., 1935, 10, 116—118; Chem. Zentr., 1935, i, 3686).—The milk of cows fed with green food contains a nutritional factor that stimulated growth and lacteal secretion in rats and in a nursing woman. It is not stored in the organism, nor bound to the milk fat. It is stable to drying of the milk, but not to drying for hay of the grass fed to the cows. R. N. C.

**Relationships between the chemistry of chlorophyll and its function in photosynthesis.** A. STOLL (Naturwiss., 1936, 24, 53—59).—A lecture.

**Photosynthesis in *Grimmia montana*.** E. MCKAY (Plant Physiol., 1935, 10, 803—809).—Photosynthesis begins within 10—20 min. of moistening the dry moss, and reaches equilibrium with respired CO<sub>2</sub> in 30 min. The reducing sugar contents of the plant increase from the beginning of photosynthesis and reach a steady level after 30 min.

A. G. P.

**Photochemical responses of wheat plant to spectral regions.** E. J. LEASE and W. E. TOTTINGHAM (J. Amer. Chem. Soc., 1935, 57, 2613—2616).—Elimination of  $\lambda < 390$  or 520 m $\mu$  from artificial sunlight decreases the assimilation of NO<sub>3</sub>' (I) and conserves carbohydrates in young wheat plants. The chlorophyll and SH-compounds in the tissue also decrease; these appear to influence the reducing power of the press sap. Increased assimilation of (I) is accompanied by a reduction in the pentosans. Most of the compositional effects in the tissue are associated with variations in the proportion of blue-violet light. Reduction of (I) to NO<sub>2</sub>' is, however, associated with long ultra-violet radiation. H. B.

**Histological variations in *Cosmos* in relation to photoperiodism.** O. BIDDULPH (Bot. Gaz., 1935, 97, 139—155).—Short-day treatment of *C. sulphureus* causes rapid initiation of flower primordia (7 days). Transition of foliar to flower primordia is accompanied by marked accumulation of carbohydrates and protein in the growing tip, and by hydrolysis of these at the base of the stem. The glutathione content of the tip shows diurnal variations during the short-day treatment, but remains permanently high from the time of the actual anatomical change from vegetative to flower primordia. Flower-bud formation is associated with somewhat higher asparagine and lower NH<sub>4</sub>' contents in the stem tip. A. G. P.

**Modification of [plant] leaf structure by X-rays.** Y. NOGUCHI (Plant Physiol., 1935, 10, 753—762).—Localised modifications of cellular structure and of the distribution of chloroplasts follow exposure to X-rays.

A. G. P.

**Theory of assimilation.** H. GAFFRON and K. WOHL (Naturwiss., 1936, 24, 81—90, 103—107).—A discussion.

**Metabolism of certain *Chlorella* and allied forms.** T. D. BECKWITH (Publ. Univ. Calif. Biol. Sci., 1933, 1, No. 1, 1—34).—Three among 8 examined species of unicellular algae produced NO<sub>2</sub>' from NO<sub>3</sub>'. None effected the reverse change, although several species grew well on NO<sub>2</sub>' media. As source of N urea was generally unsuitable, asparagine had a depressive action, peptone was favourable to some species, and in one case (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> was satisfactorily utilised. The end-products of N metabolism were bases. Neither indole nor tryptophan was formed. Complete protein was not essential to these organisms. In diffuse light only maltose and glucose favoured proliferation. The end-products of carbohydrate metabolism were alkaline whether grown in darkness or in light. The antigenic protein structure of *Chlorella* varies with the species.

A. G. P.

**Phosphorus metabolism in leaves of persistent-foilage plants, during yellowing.** E. MICHEL-DURAND (Compt. rend., 1935, 201, 1215—1217; cf. A., 1935, 265).—Fractionation of the P compounds of end-of-season green leaves and of yellowed leaves is recorded. Small amounts of phytin-P occurred in all green leaves. On yellowing this migrated completely in Algerian ivy and *Aucuba* (but not in cherry-laurel) before actual leaf-fall. Other forms of P declined in varying proportions at this stage.

A. G. P.

**Lipin metabolism in germinating mung bean.** H. C. KAO (Biochem. J., 1936, 30, 202—207).—During germination the N and ash contents of the whole bean (*Phaseolus aureus*) remain const., the amounts of Et<sub>2</sub>O and EtOH extracts increase, the chief constituents of the cotyledon are gradually transferred to the germinating portion, the sterols increase, and the phosphatides decrease. The total fatty acids first decrease and then increase. In the cotyledon the amount of fatty acids remains const., but the amount in the growing portion increases. The degree of saturation of the fatty acids in the sprouting portion increases.

W. McC.

**Effect of an atmosphere enriched in oxygen on development of plants.** M. MOLLARD (Compt. rend., 1935, 201, 1160—1162).—Dry matter production by radish plants decreased with rising [O<sub>2</sub>] (20—80% of the atm., probably as a result of chlorophyll injury. *A. niger* was similarly affected, but to a relatively smaller extent. In a current of O<sub>2</sub>, conidia produced after exhaustion of sugar in the medium were coloured brick-red.

A. G. P.

**Structure of the walls of higher plants.** D. B. ANDERSON (Bot. Rev., 1935, 1, 52—76).—A review.

CH. ABS. (p)

**Physiological characteristics of frost-resistant winter grains.** M. T. TIMOFEEV (Bull. Appl.



U.S.S.R., 1934, Ser. A, No. 9, 17—24).—The significance of the proteins, the  $p_H$  of the sap, and other physicochemical properties, in addition to the sugar and  $H_2O$  contents, is emphasised. CH. ABS. (p)

**Distribution of plant constituents in capillary form. II. Fluorescence of chlorophyll.** A. KUHN and G. SCHAFER (Pharm. Zentr., 1936, 77, 33—35).—With capillary formation, the green zone of chlorophyll (e.g., from tinctures) as viewed by daylight becomes black or red by filtered ultra-violet light. This is due to presence of essential or fatty oils. F. O. H.

**Cause of cold-resistance in plants.** W. KESSLER (Planta, 1935, 24, 312—352).—No causal relationship exists between cold-resistance and the osmotic pressure or  $[H^+]$  of the cell sap. The winter resting period of the plant is associated with changes in the condition of the plasma resulting in increased viscosity and hydration of the colloids and probably with greater  $d$  of the plasma. A. G. P.

**Course of stone cell formation in pear fruits.** W. W. SMITH (Plant Physiol., 1935, 10, 587—611).—Changes in the lignin, cellulose, reducing substances, and  $H_2O$ -, alkali-, and EtOH-extractives during the development of the fruit are recorded. The decrease in the % of lignocellulose (I) during growth of certain varieties of apple and pear is due not to a decline in abs. amounts present, but to a relatively rapid increase in EtOH-extractives. There is no evidence of a breakdown of (I) to simpler substances. Sugars are probably elaborated to form lignified tissue. Hemicellulose disappears during storage of fruit and probably serves as a source of respirable matter. A. G. P.

**Osmotic pressure and water content of prairie s.** L. A. STODDART (Plant Physiol., 1935, 10, 680).—The osmotic pressure of plant saps is characteristic of environment, i.e., the resultant of soil forces which supply  $H_2O$  and transpiration effects. A close inverse relationship is established between the osmotic pressure and  $H_2O$  contents of indi plants. The osmotic pressure in new was > that in old tissue. A. G. P.

**Comparison of the plasmolytic and cryoscopic methods for determining osmotic values in plants.** BUHMANN (Protoplasma, 1935, 23, 579).—Appropriate technique is described. The two methods yield comparable results. Extensive experimental data are recorded and discussed.

**Freezable and freezable water equilibrium in plant tissues as influenced by sub-zero temperatures.** A. GREATHOUSE (Plant Physiol., 1935, 10, 781—8).—The conception that normally "unfreezable"  $H_2O$  in plant tissues does actually freeze at low temp. ( $-18^\circ$  to  $-20^\circ$ ) applies to hardened but not to unhardened clover-root tissue or to potato tubers. A. G. P.

**Streamline flow and the movement of solutes in the transpiration stream.** R. C. McLEAN and I. R. CHINGS (Plant Physiol., 1935, 10, 773—780).—The diffusion of solutes in plants may be explained by consideration of the radical velocity

gradient due to streamline flow in tubes. Movement of solutes in the  $H_2O$  stream of the xylem may be considerably more rapid than that indicated by transpiration data. A. G. P.

**Temperature regulation of the dry matter production in marine algae as a plasmatic adjustment.** H. LAMPE (Protoplasma, 1935, 23, 534—578).—Respiration rates and the assimilation/respiration quotient of several species of marine algae are examined in relation to temp. and seasonal changes and to the distribution of species. A. G. P.

**Influence of the carbohydrate-nitrogen relation on nodule production by red clover.** C. E. GEORGI (J. Agric. Res., 1935, 51, 597—612).—The inhibitory action on nodulation of combined-N feeding of clover plants is partly counteracted by increasing carbohydrate synthesis, e.g., by  $CO_2$ -enrichment. The inhibitory influence is associated with increased concn. of sol. carbohydrates, and decreased % of N and concn. of inorg. N in the sap. A. G. P.

**Possible structure of chlorophyll granules in the plastid.** J. G. WAKKIE (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1082—1086).—Additional support is given for the granular model of the plastid. Anisotropic colloidal chlorophyll (I) models were made, which fluoresced in a hydrophilic environment by association with a "carrier-mol." Owing to the low concn. of (I) the models did not possess the required band spectrum. The results are in agreement with data for the diffusion of (I) in paraffin and MeOH. J. N. A.

**Formation of cell-wall substance [in plants].** A. KIESEL and R. JATZINA (Planta, 1935, 24, 308—311).—Both  $H_2O$ - and EtOH-sol. galacturonic acids occur on the cell wall. The EtOH-sol. form is probably stored within the cell. A transition into EtOH-insol. and probably into  $H_2O$ -insol. forms in the cell wall is indicated. A. G. P.

**Slime flux [of trees].** E. F. GUBA (10th Nat. Shade Tree Conf. Proc. Ann. Meet., 1934, 56—60).—Exudates from heartwood of shade trees become gritty through deposition of  $CaCO_3$  dissolved from cell walls. Exudates are alkaline and favour growth of numerous organisms. Exudates from wounds in inner bark or sapwood are usually acid and rich in sugars, proteins, and starch: many contain  $BzOH$ ,  $H_2C_2O_4$ , cinnamic acid, and traces of  $MeCHO$  and  $PhCHO$ . CH. ABS. (p)

***Digitalis lanata* and *D. purpurea*: comparative biological investigation.** E. BERTONASCO (Giorn. Farm. Chim. Sci. aff., 1934, 83, 421—424; Chem. Zentr., 1935, i, 3690). R. N. C.

**Plant pigments and reproduction.** R. H. ROBERTS and N. LIVINGSTON (Science, 1935, 82, 596).—With apple leaves, no correlation between fruitfulness and the carotenoid pigments could be detected (cf. A., 1934, 1045). L. S. I.

**Assimilation and respiration of Mediterranean macchia plants in rainy and dry seasons.** H. VON GUTTENBERG and H. BUHR (Planta, 1935, 24, 163—265).—Daily and seasonal changes in assimilation

ation and respiration rates and in the starch and sugar contents of leaves are recorded. The influence of temp., light conditions, and  $H_2O$  supply is examined.

A. G. P.

**Gaseous exchange in aquatic plants during photosynthesis.** F. GÓRSKI (Bull. Acad. Polonaise, 1935, B, 177—198).—Factors affecting the results of the "bubble" method are examined. Most of the  $O_2$  produced (70%) diffuses in the  $H_2O$ , the balance escaping in bubbles. Relatively less N passes from the  $H_2O$  into the intercellular spaces at higher rates of assimilation, since the rate of diffusion is slow. The size of the plant has little influence on the relative amounts of gases evolved.

A. G. P.

**Kinetics of an intracellular system for respiration and bioelectric potential at fluxequilibrium.** G. MARSH (Plant Physiol., 1935, 10, 681—697).—Mathematical.

A. G. P.

**Absorption and accumulation of potassium bromide by *Elodea* as related to respiration.** R. S. ROSENFELS (Protoplasma, 1935, 23, 503—519).—In *Elodea* tissue immersed in aq. KBr, artificially induced changes in respiration rate were paralleled by similar changes in  $Br^-$  absorption. The mechanism of these effects is discussed.

A. G. P.

**Hormones in relation to root formation on stem cuttings.** W. C. COOPER (Plant Physiol., 1935, 10, 789—794).—Application of  $\beta$ -indolylacetic acid to leafy or leafless cuttings of lemon and other species stimulates root formation. The hormone is translocated in the phloem.

A. G. P.

**Chemical nature of some growth hormones as determined by the diffusion method.** A. N. J. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1074—1081).—The growth hormone from root tips of *Vicia faba* is identical with auxin, and the latter is probably present in the regenerated tip of the coleoptile of *Avena*. The hormone obtained from the sporangiophore of *Phycomyces nitens* is probably  $\beta$ -indolylacetic acid.

J. N. A.

**Follicular and other hormones and plant growth.** M. A. H. TINCKER and S. E. JACOBS (Ann. Appl. Biol., 1935, 22, 619—629).—Administration of ketohydroxyœstrin and theelol to plants, by the roots, by injection, or by application to cut surfaces failed to produce any growth response or acceleration of flowering. Auxin stimulated the growth of *Bacterium auxinophilum* (nov. sp.) isolated from gelatin cultures of greenhouse cuttings.

A. G. P.

**Influence of ovarian hormone on plant development.** G. TEODORO and R. ZAMPETTI (Arch. Ist. Biochim. Ital., 1935, 7, 425—440).—The cryst. hormone tends to inhibit germination of some plants, but stimulates the subsequent growth especially of the roots (e.g., with *Lens esculenta*). Variations occur with different plants and also with different culture media.

F. O. H.

**Effect of artificial wind on growth and transpiration in *Helianthus annuus*.** E. V. MARTIN and F. E. CLEMENTS (Plant Physiol., 1935, 10, 613—636).

A. G. P.

**Action of sulphurous mineral waters on germination and plant development.** P. TESTONI (Annali Chim. Appl., 1935, 25, 558—563).—Mineral  $H_2O$  (analyses given) of Tivoli and Telese produces more rapid germination and growth of wheat and lentil than does normal  $H_2O$ .

F. O. H.

**Growth and seasonal changes in composition of oak leaves.** A. W. SAMPSON and R. SAMSON (Plant Physiol., 1935, 10, 739—751).—Protein (I) and fibre accumulate in the leaves at an early stage of growth. Assimilation of N ceases for a considerable period during active leaf expansion. Fibre production proceeds, only very slowly. Resorption of (I) of older leaves occurs in the late growth stage. The  $Et_2O$ -extractives increase steadily throughout growth. Accumulation of N-free extractives varies with the location. Rates of intake of Ca, Si, K, and P varied individually with advancing growth.

A. G. P.

**Formation of ethylene by plant tissues and its significance in the ripening of fruit.** R. GANE (J. Pomology, 1935, 13, 351—358).—Ripe apples generate gaseous products which produce epinastic effects on petioles and leaves of plants and abnormal growth of seedlings similar to those produced by  $C_2H_4$ . Esters evolved by ripe apples do not affect seedlings.  $C_2H_4$  is isolated from the "active substance" of apples (cf. A., 1935, 265).

A. G. P.

**Effects of ethylene on plant-growth hormone.** H. D. MICHENER (Science, 1935, 82, 551—552).—Experiments in which  $C_2H_4$  acts on plant growth in a manner different from heteroauxin are described. Action of  $C_2H_4$  on growth may be explained, not as direct effects of  $C_2H_4$  alone, but as effects of  $C_2H_4$  on a growth hormone.

L. S. I.

**Germination experiments with peas in heavy water.** J. BRUN and L. TRONSTAD (Kongl. Norske Vid. Selsk. Forh., 1935, 7, 171—173; Chem. Zentr., 1935, i, 3242).—Germination occurred in  $H_2O$  containing  $> 40\%$   $D_2O$ , but was inhibited at higher concns. Algal growth occurred up to  $94\%$   $D_2O$ .

J. S. A.

**Effect of the pyrrole nucleus on the formation of chlorophyll.** G. POLACCI, B. ODDO, and M. GALLOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 565—567).—Growth of algæ and formation of chlorophyll are not opposed by Mg pyrrole-2-carboxylate.

**Influence of sulphur deficiency on the metabolism of soya bean.** S. V. EATON (Bot. Gaz., 1935, 97, 68—100).—External symptoms of S deficiency resemble those of N, P, or K deficiency in many respects, and are probably the immediate effect of inferior assimilation of  $NO_3^-$  within the plant. Stem elongation is only slightly reduced by S deficiency, largely because of the ability of the soya bean to break down and re-utilise protein. Plants lacking S produce harder stems. Cell-wall thickness is more closely related to the accumulation of starch and hemicellulose (I) than to that of total carbohydrates. (I) probably acts as a reserve material. S-deficient plants contain much sol. org. N, but have a low sugar content. Proteolysis is active but resynthesis is incomplete through inadequacy of the S supply.

A. G. P.

**Biochemical modifications in phytopathology :** carbohydrate substances of the leaf of *Ampelopsis vitifolia*, Hort. R. SALGUES (Compt. rend. Soc. Biol., 1935, 120, 1212—1214).—Sol. polysaccharides in the healthy leaf increase during the late summer and fall in autumn, whilst insol. polysaccharides fall rapidly in summer and more slowly in autumn. In the leaf affected with *Phyllosticta altescheri*, Syd., the changes are similar but retarded. R. N. C.

**Effect of titanous chloride on the formation of chlorophyll in *Zea mays*.** O. L. INMAN, G. BARCLAY, and M. HUBBARD (Plant Physiol., 1935, 10, 821—822).—In chlorophyll formation Ti cannot replace Fe. Addition of Fe to nutrient media increases root formation. A. G. P.

**Calcium deficiency effects on *Pisum sativum*.** D. DAY (Plant Physiol., 1935, 10, 811—816).—Insufficient supplies of Ca are associated with shorter and less succulent growth, high % of dry matter in the tops and low % in the roots, and low Ca content in the whole plant. A. G. P.

**Serological studies of plant viruses.** J. M. BIRKELAND (Ann. Appl. Biol., 1935, 22, 719—727).—Precipitin reactions with plant viruses cultivated in serologically unrelated hosts show that the virus is, in itself, antigenic. Viruses of cucumber mosaic, tobacco ring-spot, and tobacco mosaic are serologically distinct, whereas tobacco mosaic, aucuba mosaic, and probably tomato streak virus are indistinguishable. A. G. P.

**Properties of virus causing degeneration diseases of beet.** G. VERPLANCKE (Succerie belge, 1935, 54, 118—127, 142—151, 162—168; Chem. Zentr., 1935, i, 3210).—The properties of the virus causing yellowing and mosaic diseases of beet leaves, and its resistance towards temp. and chemical agents, are reviewed. The virus in purified solutions is more sensitive than that in the juice. J. S. A.

**Chlorosis of hortensia (*Hydrangea hortensis*) in relation to iron.**—See B., 1936, 165.

**Effects of fuel oil on plants.** G. D. FULLER and DRETTNER (Plant Physiol., 1935, 10, 817—820).—Fuel oil injures plants when brought into contact with them, the effect becoming fatal when the quantity reaches a level critical for each species. Penetration of oil may not occur, but if it enters the root it acts principally in the primary xylem. A. G. P.

**Chemical composition of grasses in pure culture at different stages of growth.**—See B., 1936, 169.

**Content of plants and water.** B. K. SKI and K. G. KUNASCHIEVA (Trav. lab. Acad. Sci. U.S.S.R., 1935, 3, 31—41).—The content of plants varied from 0.89 to 20.5% on contained 10 times as much  $\text{H}_2\text{O}$  as the sea  $\text{H}_2\text{O}$  from which they were obtained. Yeast contained amounts of the same order. CH. ABS. (p)

**Comparative sulphur and phosphorus content of plants grown in the same soil.** G. BERTRAND and I. SILBERTEIN (Compt. rend., 1935, 201, 1449—1453).—The S/P ratio in the foliage of many plants grown under the same conditions varies from 0.377

to 4.021, which indicates that the S or P content depends on the physiological requirements of the plant. The capacity to "fix" S, probably present in org. combination, is more variable than for P.

J. L. D.

**Constituents of *Orthosiphon stamineus*, Benth.** R. DIETZEL and E. SCHMIDT (Arch. Pharm., 1936, 274, 10—16).—Cold and hot aq. extracts of *O. stamineus* are treated with urease at  $pH$  7.2 and the  $\text{CO}_2$  (modified Barcroft method) and  $\text{NH}_3$  liberated determined. 100 g. of air-dried drug contain 14 mg. of free and a further 26 mg. of combined urea.

R. S. C.

**Occurrence of piperidine in black pepper.** E. SPATH and G. ENGLAENDER (Ber., 1935, 68, [B], 2218—2221).—Distillation of a mixture of finely divided black pepper and  $\text{MgO}$  with steam in vac. at  $35^\circ$  affords an alkaline distillate which after neutralisation with  $\text{HCl}$  gives a mixture of  $\text{NH}_4\text{Cl}$  and piperidine hydrochloride separable by  $\text{CHCl}_3$ . Under these conditions piperine is not hydrolysed. Since similar results are obtained with an aq. extract of pepper free from piperine the presence of piperidine (0.0086%) as such or as a simple salt is established. The presence of 3-methylpyrrolidine could not be confirmed.

H. W.

**Odoriferous constituent of *Periploca graca*, L.** T. SOLACOLU, A. MAYRODIN, and G. HERRMANN (J. Pharm. Chim., 1935, [viii], 22, 548—556).—The bark contains 2-hydroxy-4-methoxybenzaldehyde, which is distributed fairly widely in the *Asclepiadaceae*.

J. L. D.

**Acids contained in the wood of *Libocedrus formosana*, Florin.** VII. N. ICHIKAWA (J. Chem. Soc. Japan, 1934, 55, 1124—1133).—Oxidation experiments with dihydroshonan acid indicate the presence of the 3-carboxy-6-methylene- $\Delta^4$ -cyclohexyl grouping in shonan acid.

CH. ABS. (r)

**Bark of *Terminalia arjuna*, Bedd.** I. Isolation of arjunin. R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 5, 50—54).— $\text{C}_6\text{H}_6$  extracts arjunin,  $\text{C}_{26}\text{H}_{40}\text{O}_{11}$ , m.p.  $192^\circ$  (decomp.) [ $\text{Pb}$ ,  $\text{Ag}$ , and  $\text{Na}$  salts;  $\text{Ac}_2$  and  $\text{Bz}_2$  derivatives, m.p.  $103^\circ$  and  $207^\circ$ , respectively; ( $\text{NO}_2$ )<sub>5</sub>-derivative, m.p.  $118^\circ$ ], from the bark. The substance is sol. in  $\text{NaHCO}_3$  and gives many colour reactions.

J. L. D.

**Lichen substances.** LXII.—See this vol., 314.

**Colouring matter of flowers of *Kerria japonica*, DC.** T. ITOUGH, H. SUGINOME, and K. UENO (J. Chem. Soc. Japan, 1934, 55, 1101—1105).—In the colouring wax the palmitate with smaller amounts of the oleate of lutein was the chief constituent.

CH. ABS. (p)

**Pigments of cotton flowers.** II. Uppam (*Gossypium herbaceum*). K. NEELAKANTAM, T. R. SESHADRI, and R. H. R. RAO (Proc. Indian Acad. Sci., 1935, 2, A, 490—496).—Petals of *G. herbaceum* from Coimbatore, South India, differ from those (from North India?) studied by A. G. Perkin (A., 1916, i, 280) in containing gossypitrin and quercetin (instead of isoquercetin), and a new flavonol monoglucoside, m.p.  $247^\circ$ — $249^\circ$ , with small quantities of gossypetin (cf. A., 1929, 326). E. W. W.

ation and respiration rates and in the starch and sugar contents of leaves are recorded. The influence of temp., light conditions, and  $H_2O$  supply is examined.

A. G. P.

**Gaseous exchange in aquatic plants during photosynthesis.** F. GÓRSKI (Bull. Acad. Polonaise, 1935, B, 177—198).—Factors affecting the results of the "bubble" method are examined. Most of the  $O_2$  produced (70%) diffuses in the  $H_2O$ , the balance escaping in bubbles. Relatively less N passes from the  $H_2O$  into the intercellular spaces at higher rates of assimilation, since the rate of diffusion is slow. The size of the plant has little influence on the relative amounts of gases evolved.

A. G. P.

**Kinetics of an intracellular system for respiration and bioelectric potential at fluxequilibrium.** G. MARSH (Plant Physiol., 1935, 10, 681—697).—Mathematical.

A. G. P.

**Absorption and accumulation of potassium bromide by *Elodea* as related to respiration.** R. S. ROSENFELS (Protoplasma, 1935, 23, 503—519).—In *Elodea* tissue immersed in aq. KBr, artificially induced changes in respiration rate were paralleled by similar changes in  $Br^-$  absorption. The mechanism of these effects is discussed.

A. G. P.

**Hormones in relation to root formation on stem cuttings.** W. C. COOPER (Plant Physiol., 1935, 10, 789—794).—Application of  $\beta$ -indolylacetic acid to leafy or leafless cuttings of lemon and other species stimulates root formation. The hormone is translocated in the phloem.

A. G. P.

**Chemical nature of some growth hormones as determined by the diffusion method.** A. N. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1935, 38, 1074—1081).—The growth hormone from root tips of *Vicia faba* is identical with auxin, and the latter is probably present in the regenerated tip of the coleoptile of *Avena*. The hormone obtained from the sporangiphore of *Phycomyces nitens* is probably  $\beta$ -indolylacetic acid.

J. N. A.

**Follicular and other hormones and plant growth.** M. A. H. TINCER and S. E. JACOBS (Ann. Appl. Biol., 1935, 22, 619—629).—Administration of ketoxyhydroxycastrin and theelol to plants, by the roots, by injection, or by application to cut surfaces failed to produce any growth response or acceleration of flowering. Auxin stimulated the growth of *Bacterium auxinophilum* (nov. sp.) isolated from gelatin cultures of greenhouse cuttings.

A. G. P.

**Influence of ovarian hormone on plant development.** G. TEODORO and R. ZAMPETTI (Arch. Ist. Biochim. Ital., 1935, 7, 425—440).—The cryst. hormone tends to inhibit germination of some plants, but stimulates the subsequent growth especially of the roots (e.g., with *Lens esculenta*). Variations occur with different plants and also with different culture media.

F. O. H.

**Effect of artificial wind on growth and transpiration in *Helianthus annuus*.** E. V. MARTIN and F. E. CLEMENTS (Plant Physiol., 1935, 10, 613—636).

A. G. P.

**Action of sulphurous mineral waters on germination and plant development.** P. TESTONI (Annali Chim. Appl., 1935, 25, 558—563).—Mineral  $H_2O$  (analyses given) of Tivoli and Telese produces more rapid germination and growth of wheat and lentil than does normal  $H_2O$ .

F. O. H.

**Growth and seasonal changes in composition of oak leaves.** A. W. SAMPSON and R. SAMISCH (Plant Physiol., 1935, 10, 739—751).—Protein (I) and fibre accumulate in the leaves at an early stage of growth. Assimilation of N ceases for a considerable period during active leaf expansion. Fibre production proceeds, only very slowly. Resorption of (I) of older leaves occurs in the late growth stage. The  $Et_2O$ -extractives increase steadily throughout growth. Accumulation of N-free extractives varies with the location. Rates of intake of Ca, Si, K, and P varied individually with advancing growth.

A. G. P.

**Formation of ethylene by plant tissues and its significance in the ripening of fruit.** R. GANE (J. Pomology, 1935, 13, 351—358).—Ripe apples generate gaseous products which produce epinastic effects on petioles and leaves of plants and abnormal growth of seedlings similar to those produced by  $C_2H_4$ . Esters evolved by ripe apples do not affect seedlings.  $C_2H_4$  is isolated from the "active substance" of apples (cf. A., 1935, 265).

A. G. P.

**Effects of ethylene on plant-growth hormone.** H. D. MICHENER (Science, 1935, 82, 551—552).—Experiments in which  $C_2H_4$  acts on plant growth in a manner different from heteroauxin are described. Action of  $C_2H_4$  on growth may be explained, not as direct effects of  $C_2H_4$  alone, but as effects of  $C_2H_4$  on a growth hormone.

L. S. T.

**Germination experiments with peas in heavy water.** J. BRUN and L. TRONSTAD (Kongl. Norske Vid. Selsk. Forh., 1935, 7, 171—173; Chem. Zentr., 1935, i, 3242).—Germination occurred in  $H_2O$  containing  $> 40\%$   $D_2O$ , but was inhibited at higher concns. Algal growth occurred up to 94%  $D_2O$ .

J. S. A.

**Effect of the pyrrole nucleus on the formation of chlorophyll.** G. POLACCI, B. ODDO, and M. GALLOTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 565—567).—Growth of algae and formation of chlorophyll are not opposed by Mg pyrrole-2-carboxylate.

R. N. C.

**Influence of sulphur deficiency on the metabolism of soya bean.** S. V. EATON (Bot. Gaz., 1935, 97, 68—100).—External symptoms of S deficiency resemble those of N, P, or K deficiency in many respects, and are probably the immediate effect of inferior assimilation of  $NO_3^-$  within the plant. Stem elongation is only slightly reduced by S deficiency, largely because of the ability of the soya bean to break down and re-utilise protein. Plants lacking S produce harder stems. Cell-wall thickness is more closely related to the accumulation of starch and hemicellulose (I) than to that of total carbohydrates. (I) probably acts as a reserve material. S-deficient plants contain much sol. org. N, but have a low sugar content. Proteolysis is active but resynthesis is incomplete through inadequacy of the S supply.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

APRIL, 1936.

### General, Physical, and Inorganic Chemistry.

Intensity variation in the fine structure of the Balmer lines  $H_\alpha$  and  $H_\beta$ . B. SVENSSON (Physica, 1936, 3, 91—104).—Data are recorded for the intensity ratio ( $I_k/I_l$ ) of short- and long-wave components, for pressures of 0.005—0.8 mm. at different c.d. With varying pressure, the transition from non-striated to striated discharge corresponds with a discontinuity in the  $I_k/I_l$  vals. L. J. J.

Comparison of theoretical and empirical values for Stark effect displacement of the components of  $H_\gamma$ ,  $\pi 18$ . K. BASU (Z. Physik, 1936, 98, 576—579). A. B. D. C.

Source of doubly ionised helium. O. LUHR (Physical Rev., 1936, [ii], 49, 317—319).—A magnetron type of low-voltage arc, giving about 2%  $He^{++}$  by multiple electron impact, is described. N. M. B.

Zeeman effect in helium. L. E. KINSLER and W. V. HOUSTON (Physical Rev., 1934, [ii], 46, 533—534).—The anomalous effect previously reported (A., 1935, 1437) is due to an experimental error. The val. of  $e/m$  obtained from Zeeman splitting of singlet lines of Zn, Cd, He, and Ne is  $1.7570 \pm 0.0007 \times 10^7$  e.m.u. per g. L. S. T.

Analysis of  $3d-4f$  for C II, N III, and N II. Intercombinations in C II and N III. B. EDLÉN (Z. Physik, 1936, 98, 561—568). A. B. D. C.

New members of the Lyman-Birge-Hopfield system [of  $N_2$ ]. J. KAPLAN and L. D. LEVANAS (Physical Rev., 1934, [ii], 46, 331).—A max. val. of 7.7 volts for  $D(N_2)$  is obtained. L. S. T.

New bands of the ionised nitrogen molecule. F. H. CRAWFORD and P. M. TSAI (Physical Rev., 1934, [ii], 46, 935).—400 new lines have been assigned in the  $2\Sigma-2\Sigma$  bands of  $N_2^+$ . L. S. T.

Zeeman effect in the atmospheric oxygen bands; production of a strong magnetic field over a length of 80 cm. R. SCHMID (Physical Rev., 1936, [ii], 49, 271).—A means of obtaining fields over the lengths necessary for the Zeeman effect is described. A qual. discussion of the observed effect is given. N. M. B.

Oxygen afterglow. E. M. STODDART (Proc. Roy. Soc., 1935, A, 153, 152—157).—A reply to Rayleigh's criticisms (A., 1935, 907). Experiments are described showing the effects on the  $O_2$  afterglow of  $H_2O$  vapour in the gas phase and adsorbed on the surfaces of the vessels, which are in agreement with the results of other investigators. L. L. B.

Zeeman effect in neon. L. E. KINSLER (Physical Rev., 1934, [ii], 46, 533).—Measurements of the

Zeeman splitting of the Ne lines 5852 and 6074 Å. indicate that the  $g$ -sum rule is valid to  $< 0.1\%$ ; assuming the validity of this rule,  $e/m$  is  $1.7580 \pm 0.0014 \times 10^7$  e.m.u. per g. L. S. T.

Series lines of magnesium in the solar spectrum. H. N. RUSSELL, H. D. BABCOCK, and C. E. MOORE (Physical Rev., 1934, [ii], 46, 826—827).—Members of the series  $3^1D-n^1F^0$  and  $3^3D-n^3F^0$  observed in the arc spectrum of Mg (A., 1932, 315), together with additional members, have been found in the infra-red solar spectrum. L. S. T.

Spectra of phosphorus. I. Spectra of neutral and singly-ionised phosphorus. H. A. ROBINSON (Physical Rev., 1936, [ii], 49, 297—305).—Using the discharge emitted by a Geissler tube containing P vapour, 22 new terms classifying 36 lines of P I were located; these lines also appear in a 25-amp. C arc containing  $Ca_3P_2$ . The revised ionisation potential is approx. 10.9 volts. 52 new terms classifying 194 lines in the Schumann and visible regions were located in P II. The singlet and triplet sequences are located from more than 20 inter-system combinations. Full data for classified lines of P I and P II are tabulated. The revised P II ionisation potential is 19.56 volts. N. M. B.

Band spectrum of sulphur and the statistics of the sulphur nucleus. R. M. BADGER (Physical Rev., 1934, [ii], 46, 1025—1026).—The analysis made by Naudé and Christy (A., 1931, 540) is criticised. Consts. of the S mol. are revised. L. S. T.

Nuclear mechanical and magnetic moments of  $K^{39}$ . D. A. JACKSON and H. KUHN (Nature, 1936, 137, 108; cf. A., 1935, 555).—Photometric measurements of the intensities of the hyperfine structure doublets of the resonance lines of K show that the shorter- $\lambda$  component is the stronger, thus establishing that the magnetic moment of the nucleus of  $K^{39}$  is negative. The val. calc. is  $-0.39$  nuclear magneton. L. S. T.

Hyperfine structure of some vanadium multiplets. H. KOFFERMANN and E. RASMUSSEN (Z. Physik, 1936, 98, 624—637).—The mechanical moment of the V nucleus is  $7/2$ . A. B. D. C.

Photographic photometry of iron multiplets in electric furnace spectra. R. B. KING (Physical Rev., 1934, [ii], 46, 327). L. S. T.

Band spectra of rubidium and of its combinations with other alkali metals. P. KUSCH (Physical Rev., 1936, [ii], 49, 218—222).—The magnetic rotation spectrum and absorption spectrum



of  $\text{Rb}_2$  in the region 6500—7100 Å. have been measured and correlated and a vibrational analysis is given. The vibrational frequency in the  $^1\Sigma$  ground state is 57.31  $\text{cm}^{-1}$ , and that in the excited  $^1\Pi$  state is 48.05  $\text{cm}^{-1}$ . The corresponding vals. in the magnetic rotation spectrum of NaRb are 106.6 and 61.5  $\text{cm}^{-1}$ . A band system due to RbCs has been identified.

N. M. B.

**Characteristics of the long and short spectral lines. II. Silver, zinc, and iron.** S. DATTA and K. M. CHATTERJEE (Indian J. Physics, 1936, 10, 65—73; cf. A., 1935, 908).—The long and short lines of Ag, Zn, and Fe have been classified. The fundamental generalisation previously given, with regard to the relative changes in orientation of the  $L$  and  $S$  vectors in the initial and final states for the long and short lines, appears to be verified. M. S. B.

**Regularities in the spectrum of trebly ionised iodine.** S. G. KRISHNAMURTI (Proc. Physical Soc., 1936, 48, 277—281).—The spectrum of a condensed discharge through I has been photographed in the range 6000—1900 Å. under varying conditions of excitation. Data for 68 lines ascribed to I IV and classifications of 34 lines are tabulated. Term vals. and assignments are given on analogy with the isoelectronic spectra Te III, Sb II, and Sn I.

N. M. B.

**Extinction coefficients of iodine and other halogens.** E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 540—546; cf. A., 1935, 586).—Extinction coeffs. of I vapour, measured at 20° in the range  $\lambda$  4300—6200 Å., are 2—6 times > the accepted vals. Small humps on the extinction curves, appearing both in vapour and solutions, are due to absorption by vibrating mols. The "limiting" extinction curve, obtained by diluting the vapour to a very low partial pressure with an inert gas, has a max. at 5200 Å., and resembles in shape the curve of a  $\text{CS}_2$  solution. The influence of the solvent on the extinction curves of solutions of  $\text{Cl}_2$ , Br, and I is investigated.

F. L. U.

**Band system of caesium.** P. KUSCH and F. W. LOOMIS (Physical Rev., 1936, [ii], 49, 217—218; cf. A., 1934, 1148).—A provisional analysis of the complex system at 6250 Å. is reported.

N. M. B.

**Magnetic moment of caesium determined from the hyperfine structure of the  $6p^2P_1$  state.** L. P. GRANATH and R. K. STRANATHAN (Physical Rev., 1934, [ii], 46, 317).—A  $g$  val. of 0.70 is obtained for Cs.

L. S. T.

**Spark spectrum of mercury, Hg II and Hg III.** T. S. SUBBARAYA (J. Mysore Univ., 1934, 7, 100—134; cf. A., 1934, 1280; 1935, 3).—Additional lines are classified. The ionisation potentials of Hg I and Hg II are 18.67 and 26.1 volts, respectively.

CH. ABS. (e)

**Second spark spectrum of mercury.** R. RICARD (Compt. rend., 1935, 201, 1342—1344).—30 new terms belonging to the Hg III spectrum have been identified in the visible and ultra-violet spectrum excited with an electrodeless discharge.

T. G. P.

**Anomalous Zeeman effect of single hyperfine structure components of the mercury resonance**

**line 2537 Å. II. The  $\sigma$  components.** A. ZVIRONAS (Helv. phys. Acta, 1934, 7, 684—708; Chem. Zentr., 1935, i, 3516; cf. A., 1935, 3).

H. J. E.

**Influence of pressure on the discharge-radiation in mercury vapour.** V. FABRIKANT, F. BUTAEVA, and J. CIRG (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 183—184; cf. A., 1934, 1280).—Absorption in Hg discharge at low pressures has been studied.

R. S.

**Fraunhofer's spectrum in the neighbourhood of 96,000 Å.** A. ADEL, V. M. SLIPHER, and O. FOUTS (Physical Rev., 1936, [ii], 49, 288—290; cf. A., 1935, 806).—The absorption of solar radiation by the atm. of the sun and earth, examined in the range 70,000—110,000 Å., is discussed in the vicinity of 96,000 Å. Fine-structure data for the  $\text{O}_3$  band with centre at 1043.7  $\text{cm}^{-1}$  are given, and the structure of the mol. is discussed.

N. M. B.

**Resistance to electric discharge in gas mixtures.** G. M. KOVALENKO (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 15—17).—The breakdown potential ( $V$ ) for spherical electrodes at various distances apart in mixtures of  $\text{NH}_3$  and  $\text{N}_2$  at approx. 1 atm. decreases with increasing % of  $\text{NH}_3$  to a min. at approx. 30%  $\text{NH}_3$ . With mixtures of  $\text{Et}_2\text{O}$  and  $\text{N}_2$  a min. occurs at 30%  $\text{Et}_2\text{O}$ . Since  $V$  for pure  $\text{Et}_2\text{O}$  and  $\text{NH}_3$  is >  $V$  for  $\text{N}_2$ , the decrease in  $V$  on adding  $\text{NH}_3$  and  $\text{Et}_2\text{O}$  to  $\text{N}_2$  is attributed to chemical action. With  $\text{NH}_3$   $V$  decreases at each discharge with successive discharges (ultimately becoming const.) owing to the formation of  $\text{H}_2$ , the presence of which in  $\text{N}_2$  at a total pressure of 100 mm. is shown to decrease  $V$ .

R. S. B.

**Electric discharge in gases and the Debye-Hückel theory.** V. T. CHIPLENKAR (Current Sci., 1936, 4, 481).—The Debye-Hückel electrolytic theory is applied to the phenomena in discharge tubes. In approx. agreement with experiment the length of the cathode fall is shown to vary as the log of the p.d. across it.

R. S. B.

**Ionisation steps and excitation energies of spectral lines according to the emission distribution in the arc light.** H. STEPHAN (Z. wiss. Phot., 1936, 35, 33—69).—The intensity of spark lines immediately in front of the cathode is dependent on cathode temp. The increase of intensity of arc lines just in front of the poles is due to higher v.d. The best conditions for observation of ionisation steps are obtained by the use of the smallest possible current through the arc. The arc and spark spectra of Mg, Ca, Cu, and Zn were separated by examining the emission distribution of arcs. The cause of the pole effect with arc lines (displacement of  $\lambda\lambda$  in the neighbourhood of the poles) is probably due to increased v.d.

A. J. M.

**Arcs in rare gases.** R. C. MASON (Physical Rev., 1934, [ii], 46, 630).

L. S. T.

**Determination of the temperature in the column of a discharge from the intensity measurement of rotational band spectra.** T. HAMADA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 50—57; cf. A., 1928, 930).—The radial



temp. distribution in a special  $N_2$  discharge tube of known volt-amp. characteristics has been studied by determination of the intensity of spectral lines. The axial (max.) temp. varies linearly with the product of pressure and current. R. S.

Effect of evaporated films on energy distribution in grating spectra. J. STRONG (Physical Rev., 1936, [ii], 49, 291—296).—Wood anomalies of intensity distribution can frequently be developed by coating the grating, especially if of fine ruling, with an evaporated film of Mg, Ag, or Al. The phenomenon is shown typically by a double band consisting of a dark band on the red side of a bright band; the dark band is characterised by a sharp boundary on the blue side, agreeing with the Rayleigh formula. N. M. B.

Ultra-rapid spectrograph at the Pic du Midi. H. GARRIGUE (Compt. rend., 1936, 202, 44—45).—An instrument operating at  $f$  0.55 is described. H. J. E.

Photographic method for determining the distribution of light intensity in interference rings. J. ROIG (Compt. rend., 1935, 201, 1346—1348). T. G. P.

Fixing scale of Röntgen wave-lengths in absolute measure. M. SÖDERMAN (Nova Acta Soc. Sci. Upsaliensis, 1935, [iv], 9, No. 8; Chem. Zentr., 1935, i, 2942—2943).—The  $\lambda$  of the Al K lines in the 9th and 10th orders are compared directly by a combination of the plane and concave grating methods with the Al spark lines at 50—90 Å., giving 1000 X (exp.) = 1.00212—1.00225 Å. The calcite lattice spacing is recalcd., and  $e$  calc. as  $4.806 \pm 0.003$  c.s.u. J. S. A.

Accuracy of determination of emission and absorption of monochromatic X-rays. H. KÜSTNER and E. ARENDS (Ann. Physik, 1936, [v], 25, 385—412).—An examination of the accuracy of methods previously employed (A., 1935, 556, 676). A. J. M.

Theory of X-ray absorption by molecular gases. III. H. PETERSEN (Z. Physik, 1936, 98, 569—575; cf. A., 1933, 332).—Calculations involved in Kronig's theory are simplified; applied to  $GeCl_4$  they agree with experiment. A. B. D. C.

Polarisation of X-rays from thin targets. D. S. PISTON (Physical Rev., 1936, [ii], 49, 275—279).—The polarisation of the portion of the continuous X-ray spectrum between the K limits of Ta and W, measured for targets of Al foil (0.7  $\mu$ ) and Ag foil (0.17  $\mu$ ), at voltages from the quantum limit up to 120 kv., is complete at the quantum limit, and decreases, more rapidly for Ag than for Al, as the tube voltage is raised above the quantum voltage for the spectrum band. N. M. B.

Wave-length measurements in the K-series of aluminium, sulphur, and chlorine, and in the L-series of zinc. J. SHEARER (Phil. Mag., 1936, [vii], 21, 501—505).—Vals. are tabulated for 9 lines arising from impurities in Ni during investigations previously reported (cf. A., 1935, 1293). N. M. B.

Ruled-grating wave-length of the copper  $K\alpha_1$  line. P. F. GOTTLING and J. A. BEARDEN (Physical Rev., 1934, [ii], 46, 435—436). L. S. T.

K spectrum of copper. Y. CAUCHOIS (Compt. rend., 1935, 201, 1359—1361).—Data for the K $\beta$  regions are recorded and discussed. T. G. P.

K radiation of elements from chromium to copper. M. PRIVAULT (Ann. Physique, 1936, [xi], 5, 280—324).—Three new lines in the K $\beta$  spectra are recorded. The effect of magnetisation of the anticathode on the K $\beta$  spectrum of Fe has been examined. Magnetisation to 75% saturation has no observable effect on the K $\beta_1$  and K $\beta_2$  lines. Temp. changes in the neighbourhood of the Curie and  $\gamma$  points are similarly without effect (for K $\beta_1$  and K $\beta_2$ ). The effect of combination on the K spectra has been examined by a fluorescence method.  $K_2Cr_2O_7$ ,  $MnO_2$ , and  $Fe_2O_3$  show a more general splitting of the lines than recorded by Yoshida (A., 1933, 656). L. J. J.

K spectra of molybdenum and rhodium. H. HULUBEI (Compt. rend., 1935, 201, 1356—1359; cf. A., 1935, 811).—Data for the K $\beta$  spectra are recorded and discussed. T. G. P.

Effects of chemical combination on the L absorption limits of tantalum, tungsten, gold, and lead. S. KAWATA (Proc. Phys.-Math. Soc. Japan, 1935, 17, 89—99).—The shifts of the  $L_{III}$  limits are (in volts):  $HTaO_3 + 2.0$ ;  $H_2WO_4 + 3.0$ ,  $Au_2O - 4.6$ ,  $Au_2O_3 - 3.4$ ;  $PbO + 3.4$ ,  $PbO_2 + 6.8$ . The assumption of a selection rule for X-ray absorption spectra is supported. The Au  $L_{III}$  absorption edge is double in  $Au_2O_3$ . CH. ABS. (c)

Probability of KL ionisation and X-ray satellites. R. D. RICHTMYER (Physical Rev., 1936, [ii], 49, 1—8).—A theory of multiple ionisation produced by a fast-cathode electron in the target of an X-ray tube is developed. The effective cross-section for  $1s2s$  ionisation of K, the distribution of energy and angular momentum, and the probability of  $1s2p$  ionisation are examined. N. M. B.

Ionisation potentials of the  $N_2$  molecule. J. SAVARD (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 1—7).—Using the method of electronic impact, 11 potentials in good agreement with calc. vals. are reported and the corresponding transformations are given. N. M. B.

Calculation of work of exit in the Richardson effect by a method of O. Scherzer. A. SOMMERFELD [with E. BARTELINK] (Helv. phys. Acta, 1934, 7, Suppl. II, 31—32; Chem. Zentr., 1935, i, 2953).—Theoretical. An expression is derived connecting the work of exit with the at. vol., which agrees with experimental data for the alkali metals. J. S. A.

Calculation of Townsend's  $\alpha$  for neon. M. J. DRUYVESTEYN (Physica, 1936, 3, 65—74).—Theoretical. The velocity distribution of electrons diffusing through an inert gas is calc., assuming elastic, exciting, and ionising collisions. Calc. and observed vals. of the ionisation coeff.  $\alpha$  agree for potential gradients of 5—30 volts per cm. per mm. gas pressure. L. J. J.



**Electrons and positrons.** C. H. DIX (Physical Rev., 1934, [ii], 46, 329—330).—Theoretical.

L. S. T.

**Production of positrons by  $\beta$ -rays.** D. SKO-BELTZYN and E. STEPANOVA (Nature, 1936, 137, 272; cf. A., 1935, 425).—Further evidence of the production of electron-positron pairs by the passage of fast  $\beta$ -rays through Pb and Al is presented. With Al, the predominating effect is the emission of a single positron accompanying the absorption of the primary  $\beta$ -particle. Production of positrons along the track of the  $\beta$ -particle in the gas ( $N_2$ ) was also confirmed. The effective cross-section in  $N_2$  is of the order  $5 \times 10^{-24}$  sq. cm.

L. S. T.

**Positron emission accompanying  $\beta$ -ray activity.** C. MÖLLER (Nature, 1936, 137, 314).—Theoretical.

L. S. T.

**Emission of positrons by a source of Th-B + C.** S. DE BENEDETTI (Compt. rend., 1936, 202, 50—52).—Counts of the positron emission are recorded, using Cellophane and Al screens of varying thickness.

H. J. E.

**Production of electron pairs.** J. C. JAEGER and H. R. HULME (Proc. Roy. Soc., 1936, A, 153, 443—447).—Mathematical. A method, which avoids the use of the Born approximation, for finding the no. of electron pairs created by a  $\gamma$ -ray traversing matter is described. The results are somewhat  $>$  those of Bethe and Heitler (A., 1934, 1150), but it is found that even for heavy elements the Born approximation may be expected to give good results for  $\gamma$ -rays of high energy.

L. L. B.

**Thomson's theory of condensation on ions.** E. HÜCKEL (Physikal. Z., 1936, 37, 137—138).—The assumption made by Thomson, that the charge of the drop is uniformly distributed over the surface of a sphere, does not hold in the case of single ions or electrons, where the charge is rather conc. at the centre of the sphere. An equation is derived on this assumption.

A. J. M.

**Emission of positive ions by platinum when heated in oxygen.** T. B. RYMER (Proc. Roy. Soc., 1936, A, 153, 422—442).—The variation with temp. of the positive ion emission from Pt heated in  $O_2$  has been examined, and the results are discussed in the light of the Saha equation. Satisfactory agreement with the theory is obtained, but a different val. from that determined experimentally must be assumed for the electronic work function, on account of the discontinuous nature of the emitting surface.

L. L. B.

**Absorption of high-energy protons by matter.** J. SOLOMON (Compt. rend., 1936, 202, 204—206).—The energy lost by protons and electrons by radiation and ionisation is considered theoretically.

T. G. P.

**Scattering of high-energy protons in hydrogen.** M. G. WHITE (Physical Rev., 1936, [ii], 49, 309—316).—Comparison of scattering frequency from 7340 photographs of high-energy proton tracks in  $H_2$  with Mott's wave-mechanical treatment showed strong anomalies for incident proton energies  $>$  600 kv. Since Mott assumes coulomb forces, the dis-

crepancies indicate a departure from the inverse square law for such energies. For a classical distance, therefore, of closest approach of about  $6 \times 10^{-13}$  cm. the two protons cannot be treated as point charges, but on classical grounds this is not so down to  $10^{-16}$  cm.

N. M. B.

**Formation of negative atomic ions of mercury.** F. L. ARNOT and J. C. MILLIGAN (Nature, 1936, 137, 150).—By means of the mass spectrograph negatively charged atoms but not negatively charged mols. of Hg have been detected. Their energies are  $>$  can be accounted for by the total potential across the tube or by the dissociation of excited mols.

L. S. T.

**Production of high-velocity particles in a cyclotron by the use of multiphase oscillators.** R. J. MOON and W. D. HARKINS (Physical Rev., 1936, [ii], 49, 273).

N. M. B.

**At. wt. of element 93.** H. J. WALKER (Phil. Mag., 1936, [vii], 21, 262—265).—By analogy with the relations between the isotopes of Ru, Rh, and Pd and between those of Th, Pa, and U, it is suggested that the  $\alpha$ -radioactive isotope of element 93 (eka-Re) has a mass no. 237. The mass nos. of the  $\alpha$ -radioactive isotopes of U and eka-Os are probably U, 232, 233, 234, 235, 236, and 238; eka-Os, 238, 239, 240, 241, 242, and 244. The lighter isotopes of eka-Os are probably short-lived, but eka-Os<sup>241</sup> is probably of long life and may exist terrestrially.

R. S. B.

**Masses of some light atoms measured by means of a new mass spectrograph.** F. W. ASTON (Nature, 1936, 137, 357—358).—Observations on the doublets linking H, D, He, C, and O give the following as the most probable vals. of the isotopic wts. on the physical scale: H  $1.00812 \pm 0.00004$ , D  $2.01471 \pm 0.00007$ , He  $4.00391 \pm 0.00016$ , and C  $12.0035 \pm 0.0003$ .

L. S. T.

**Abundance ratio of isotopes of potassium in mineral and plant sources.** A. K. BREWER (J. Amer. Chem. Soc., 1936, 58, 365—370).—Mass-spectrographic data for a large no. of K-containing minerals show only small differences in the isotope content. The ratio  $K^{39}/K^{41}$  is about 14.25. Greater variation is found in plant ashes, the  $K^{41}$  content differing by as much as 15%. Kelp shows a pronounced deviation from the average. The ratio varies with the variety, age, and section of the plant, and the type of soil.

E. S. H.

**Mass-spectrographic determination of the constancy of the at. wt. of potassium in ocean water.** A. K. BREWER (J. Amer. Chem. Soc., 1936, 58, 370—372).—The abundance ratio  $K^{39}/K^{41}$  for Pacific Ocean  $H_2O$  is 14.20 for samples obtained from different localities and at depths down to 2500 m. Variations in at. wt. are  $< \pm 0.00026$ . The derived at. wt. of K is 39.094.

E. S. H.

**Isotopic abundance ratios of carbon, nitrogen, argon, neon, and helium.** A. L. VAUGHAN, J. H. WILLIAMS, and J. T. TATE (Physical Rev., 1934, [ii], 46, 327).—Relative intensities of the peaks of mass-spectrograph curves give the following abundance ratios with the average deviations indicated:



$\text{C}^{12} : \text{C}^{13}$  91.6 (2.2),  $\text{N}^{14} : \text{N}^{15}$  265 (8),  $\text{A}^{40} : \text{A}^{36}$  304 (12),  $\text{Ne}^{20} : \text{Ne}^{21}$  337 (20),  $\text{Ne}^{20} : \text{Ne}^{22}$  9.25 (0.08), and  $\text{He}^4 : \text{He}^3 < 35,000$ .  
L. S. T.

**Isotopic constitution of rubidium, zinc, and argon.** A. O. NIER (Physical Rev., 1936, [ii], 49, 272).—The abundance ratio  $\text{Rb}^{85}/\text{Rb}^{87}$  is  $2.68 \pm 0.02$ . The upper limits of abundance relative to  $\text{Rb}^{85}$  computed for undetected hypothetical isotopes are,  $\text{Rb}^{80}$ , 81, 82, 89, 90,  $1 \times 10^{-5}$ ;  $\text{Rb}^{83}$ ,  $1/60,000$ ;  $\text{Rb}^{84}$ ,  $1/12,000$ ;  $\text{Rb}^{86}$ ,  $1/13,000$ ;  $\text{Rb}^{88}$ ,  $1/22,000$ .  $\text{Zn}^{61}$ , 66, 68, 67, 70 were found. The upper abundance limits relative to  $\text{Zn}^{70}$  of  $\text{Zn}^{65}$ , 63, 69 are  $1/200$ ,  $1/400$ , and  $1/300$ , respectively.  $\text{A}^{38}$  was confirmed.  $\text{A}^{40}/\text{A}^{36} = 325$ , and  $\text{A}^{36}/\text{A}^{38} = 5.1$ . The upper abundance limits of hypothetical isotopes relative to  $\text{A}^{40}$  are  $\text{A}^{41}$ ,  $39$   $1 \times 10^{-4}$ , and  $\text{A}^{42}$ ,  $37$   $0.5 \times 10^{-4}$ .  
N. M. B.

**Mass ratios of isotopes from band spectra.** W. W. WATSON (Physical Rev., 1934, [ii], 46, 319).—The effect of the perturbing interactions between the various energy states of a mol. on the  $B$  consts. should always be investigated in obtaining accurate mass ratios from band spectra. The corrections to be applied in the case of  $\text{CaH}$  and  $\text{CaD}$  are discussed.  
L. S. T.

**Chemical elements and natural atomic types from the viewpoint of the investigation of isotopes.** O. HAHN (Ber., 1936, 69, [A], 5—20).—A review of work published between the end of 1934 and of 1935.  
H. W.

**Properties of ions. I. Electronic homologues in the periodic system. II. Periodic system and the properties of ions.** B. V. NEKRASSOV (Bull. Soc. chim., 1936, [v], 3, 151—155, 155—159).—I. A new presentation of the periodic system, based on the electronic structures of the elements in their different states of valency, is given.

II. The properties of ions are discussed in the light of the above classification.  
E. S. H.

**System of masses of light atoms deduced from nuclear reactions alone. II.** L. ISAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 141—143; cf. this vol., 7).—Using the data of nuclear reactions, the at. wts. of the light elements up to Si have been determined and are compared with "chemical" and "physical" at. wts. When deviations of the at. mass vals. from the nearest integer val. are plotted against at. nos. between H and Al the curve is wave-shaped, the amplitudes of the waves rapidly diminishing until ultimately a straight line is obtained.  
W. R. A.

**Some properties of radioactive series.** E. LOPOUKHIN (Compt. rend., 1935, 201, 1361—1363).—The different phases of radioactive disintegration are discussed from the point of view of Perrin's nuclear model (A., 1932, 556).  
T. G. P.

**Continuous spectra of Ra-E and Ra-P<sup>30</sup>.** A. I. ALICHANOV, A. I. ALICHANIAN, and B. S. DZELEPOV (Nature, 1936, 137, 314—315).—The energy distribution curve of  $\beta$ -particles from Ra-E reveals the emission of a large no. of electrons with low energies. Comparison with the  $\beta$ -spectrum of radio-P, which has a max., shows a considerable

difference in the shape of the  $\beta$ -spectra of elements of low and high at. no.  
L. S. T.

**Absence of low-energy radiations from potassium and rubidium.** W. F. LIBBY (Physical Rev., 1934, [ii], 46, 745—746).—Geiger-Müller counter experiments indicate that no  $\alpha$ -particle of range much  $> 0.05$  cm. or  $\beta$ -particle with energy much  $> 500$  e.v. is emitted by K. The emission of any preliminary radiation is improbable. With Rb it is even less likely that a low-energy  $\alpha$ - or  $\beta$ -particle is initially emitted.  
L. S. T.

**Evidence of an excited state in the  $\alpha$ -particle.** C. C. LAURITSEN and H. R. CRANE (Physical Rev., 1934, [ii], 46, 537—538).—The 12 m.e.v.  $\gamma$ -ray component observed when Li is bombarded with protons (this vol., 402) is ascribed to the process  ${}^3\text{Li}^7 + {}^1\text{H}^1 \rightarrow {}^2\text{He}^4$ , in which the product of the reaction is presumably the only possible source of the  $\gamma$ -radiation. Analogous cases in which a  $\gamma$ -ray appears to be associated with an excitation level in one of the final products of the reaction are discussed.  
L. S. T.

**Does the  $\alpha$ -particle possess excited states?** E. FEENBERG (Physical Rev., 1936, [ii], 49, 328—331).—Evidence from recent experiments (cf. Crane, A., 1935, 1186) is supported by computations on three different nuclear models which indicate definitely a singlet  $2p$  level in the discrete eigenvalue spectrum of the  $\alpha$ -particle if the range of the intra-nuclear forces exceeds  $2.0 \times 10^{-13}$  cm.  
N. M. B.

**$\alpha$ -Particles from lithium ions striking hydrocarbon compounds.** J. ZELENY, C. J. BRASEFIELD, C. D. BOCK, and E. C. POLLARD (Physical Rev., 1934, [ii], 46, 318).—Bombardment of  $\text{NH}_4\text{Cl}$  and  $\text{Al}(\text{OH})_3$  with  $24 \times 10^4$  volt Li ions yields a small no. of  $\alpha$ -particles (approx. 12 and 9 per min. per microamp., respectively) resulting from the disintegration of Li, probably  $\text{Li}^7$ .  
L. S. T.

**Ranges of  $\alpha$ -particles in photographic emulsions.** H. J. TAYLOR and V. D. DABHOLKAR (Proc. Physical Soc., 1936, 48, 285—298; cf. A., 1935, 910).—From measurements on Ilford  $R$  plates of the tracks of a homogeneous group of  $\alpha$ -particles of range  $r$ , a distribution curve is drawn, from which  $L$ , the extrapolated length of the tracks, is calc. The ratio  $L/r$  is const.  $\pm 1\%$  for  $\alpha$ -particles of various ranges, and if  $L$  is measured  $r$  can be calc. This method, applied to the tracks produced by the disintegration of B and Li under slow-neutron bombardment, gives ranges  $1.14 \pm 0.02$  and  $6.64 \pm 0.06$  cm., respectively, in air. Sm emits  $\alpha$ -particles of range  $1.13 \pm 0.02$  cm. in air, and other particles of longer range.  
N. M. B.

**Scattering of fast  $\beta$ -particles by nitrogen nuclei.** F. C. CHAMPION (Proc. Roy. Soc., 1936, A, 153, 353—358).—The scattering of fast  $\beta$ -particles by N nuclei has been examined between  $20^\circ$  and  $180^\circ$ . Over the whole range, the most satisfactory agreement is with Mott's formula (A., 1929, 861). For the large-angle scattering the results support those of Neher (A., 1931, 1347), and for smaller angles those of Chadwick and Mercier (Phil. Mag., 1925, [vi], 50, 208).  
L. L. B.



**Anomalous absorption of  $\beta$ -rays.** D. SKO-BELZYN and (MISS) E. STEPANOVA (Nature, 1936, 137, 234). L. S. T.

**Energy of  $\gamma$ -rays excited by slow neutrons.** S. KIKUCHI, H. AOKI, and K. HUSIMI (Nature, 1936, 137, 186; cf. this vol., 266).—The energy of  $\gamma$ -rays accompanying the recombination of a proton with a slow neutron to form a deuteron is  $2.2 \times 10^6$  e.v. Curves showing the energies of  $\gamma$ -rays excited in Cd, Cl<sub>2</sub>, Cu, and Fe by slow neutrons are given. The  $\gamma$ -rays from Cd have at least two components, whilst those from Cl<sub>2</sub> appear to be homogeneous.

L. S. T.

**Absorption measurements of hard  $\gamma$ -rays from fluorine bombarded by protons.** E. McMILLAN (Physical Rev., 1934, [ii], 46, 325).— $\gamma$ -Rays from various targets bombarded by  $1.1 \times 10^6$  volt-protons and  $2.2 \times 10^6$  volt-deuterons have been investigated. With proton bombardment B, Be, Li, and F give strong  $\gamma$ -rays in increasing order of intensity. The F radiation is homogeneous and no neutrons are indicated. With deuteron bombardment F, C, B, Li, and Be give strong ionisation, part of which is due to neutrons.

L. S. T.

**Absorption of  $\gamma$ -rays excited in cadmium by slow neutrons.** H. HERSZFINKIEL and L. WERTENSTEIN (Nature, 1936, 137, 106–107).—The amount of  $\gamma$ -rays excited in Cd by neutron bombardment is practically independent of the thickness of Cd traversed between 0.1 and 1 mm. and decreases when thicker sheets are used. Further results obtained with screens of Pb, Fe, and Al indicate that the energy of these  $\gamma$ -rays must be of the order of  $10^7$  e.v.

L. S. T.

**$\gamma$ -Rays from boron bombarded with deuterons.** H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1934, [ii], 46, 1109–1110).—The spectrum of recoil electrons produced by the  $\gamma$ -rays from B bombarded with deuterons consists of components of  $\leq$  five different energies.

L. S. T.

**High-energy  $\gamma$ -rays from lithium and fluorine bombarded with protons.** H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1934, [ii], 46, 531–533; cf. A., 1935, 1186).

L. S. T.

**Nuclear photo-electric effect in deuterium.** G. ISING and M. HELDE (Nature, 1936, 137, 273).—The val. obtained for the mass of the neutron is 1.0080 (cf. A., 1935, 1293).

L. S. T.

**Existence of resonance levels for the capture of neutrons.** H. VON HALBAN, jun., and P. PREISWERK (Compt. rend., 1936, 202, 133–135).—Resonance levels seem to exist.

T. G. P.

**Energy distribution of neutrons slowed by elastic impacts.** E. U. CONDON and G. BREIT (Physical Rev., 1936, [ii], 49, 229–231).—Mathematical. The energy distribution of particles of mass  $m$ , initially of the same energy, which have made  $n$  impacts with particles of mass  $M$ , all initially at rest, is calc.

N. M. B.

**Effect of scattering neutrons on induced radioactivity.** J. ROTBLAT and M. ZYR (Nature, 1936,

137, 185–186).—The effect of screens or scatterers of various elements on the radioactivity induced in Ag by neutrons has been investigated. The component of 140 sec. half-period is increased in amount by Si, Fe, Cu, Zn, Ag, Cd, Sn, Hg, and Pb, but not by C or Al. The 22 sec. product is enhanced by C, Al, Cu, Cd, and Sn, and weakened by Hg or Ag.

L. S. T.

**Absorption of slow neutrons in carbon.** G. A. FRINK, J. R. DUNNING, and G. B. PEGRAM (Physical Rev., 1936, [ii], 49, 340).—In view of uncertainty as to whether C is responsible for some of the absorption of slow neutrons in paraffin (cf. A., 1935, 1186) data are given for neutrons detected per min. by a Li-lined ion chamber from a Rn-Be source surrounded by a paraffin sphere and a C cylinder. Results indicate that if C absorbs any slow neutrons this is  $>$  compensated for by neutrons slowed down in the C.

N. M. B.

**Capture of slow neutrons.** O. R. FRISCH and G. PLACZEK (Nature, 1936, 137, 357).—Cd is an efficient absorber for neutrons of thermal energies, but becomes almost transparent for neutrons of energy  $\geq$  1 volt. The capture probability in Cd has a max. between 1 and 0.03 volt.

L. S. T.

**Neutrons of thermal energies.** P. B. MOON and J. R. TILLMAN (Proc. Roy. Soc., 1936, A, 153, 476–492).—Experiment shows that a large proportion of the "slow" neutrons formed when fast neutrons pass through H<sub>2</sub>O or paraffin wax have thermal velocities. The cross-sections for the absorption of thermal neutrons by the nuclei Cu, V, Dy, Ag, Rh, I, and B increase when the temp. of the neutrons is reduced from room temp. to 90° abs., the increase depending on the geometrical conditions of the experiment. The apparent absorption of neutrons by I and by Ag is greatest when measured with the same element as detector.

L. L. B.

**Selective absorption of neutrons by gold.** O. R. FRISCH, G. HEVESY, and H. A. C. MCKAY (Nature, 1936, 137, 149–150).—Experiments on the activation of Au by neutrons slowed down by paraffin wax with a Cd filter indicate that there is a group of neutrons of narrow velocity range which are strongly absorbed by Au, but transmitted through Cd. The no. of strongly absorbed neutrons is apparently only a small fraction of the total no. transmitted by Cd.

L. S. T.

**Selective scattering of slow neutrons.** J. R. TILLMAN (Nature, 1936, 137, 107).—The  $\beta$ -ray activity induced in I, Ag, and Cu by neutrons slowed down by paraffin wax is increased by different amounts when the metals are backed with a further layer of paraffin wax.

L. S. T.

**Agreement between the balance of nuclear energy and the experimental masses of light elements.** L. CARTAN (Compt. rend., 1935, 201, 1363–1366).—The mass of the H atom (O=16) has been corr. to  $1.00810 \pm 0.00010$  from a study of the reactions  $B^{11} + H^1 = 3He^4$ ,  $Be^9 + H^1 = Li^6 + He^4$ ,  $B^{10} + D^2 = 3He^4$ , and  $B^{10} + D^2 = B^{11} + H^1$ , and vals. for D, He<sup>4</sup>, Li<sup>6</sup>, Li<sup>7</sup>, Be<sup>9</sup>, B<sup>10</sup>, B<sup>11</sup>, and C<sup>12</sup> calc. which agree with those of Oliphant *et al.* (A., 1935, 910), excepting



those of  $\text{Be}^9$  and  $\text{C}^{12}$ , which are  $9.0152$  and  $12.0037 \pm 0.0010$ , respectively.

T. G. P.

**Disintegration with the emission of protons induced by neutrons.** F. N. D. KURIE (Physical Rev., 1934, [ii], 46, 330).—Disintegration by neutrons from Be bombarded with  $3 \times 10^6$  volt-deuterons in which a proton or other particle of charge approx. 1 is emitted instead of the usual  $\alpha$ -particle is described. Possible reactions are  ${}^7\text{N}^{14} + {}^0n^1 \rightarrow {}^6\text{C}^{11} + {}^1\text{H}^1$  or  ${}^8\text{O}^{16} + {}^0n^1 \rightarrow {}^7\text{N}^{16} + {}^1\text{H}^1$ .

L. S. T.

**Disintegration of nitrogen by neutrons.** T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1936, [ii], 49, 223—229).—Disintegrations observed in a cloud-chamber filled with  $\text{N}_2$  at reduced pressure are attributed to one of the reactions:  ${}^7\text{N}^{14} + {}^0n^1 \rightarrow {}^5\text{B}^{11} + {}^2\text{He}^4$ ;  ${}^7\text{N}^{14} + {}^0n^1 \rightarrow {}^6\text{C}^{14} + {}^1\text{H}^1$ ;  ${}^7\text{N}^{14} + {}^0n^1 \rightarrow {}^2\text{He}^4 + {}^2\text{He}^4 + {}^3\text{Li}^7$ . The first is valid for slow and fast neutrons, the energy of disintegration for the reaction being  $2.33 \pm 0.26$  m.e.v. The second and third reactions are less frequent. Full data for 91 disintegration forks are tabulated.

N. M. B.

**Production of radioactive oxygen.** M. S. LIVINGSTON and E. McMILLAN (Physical Rev., 1934, [ii], 46, 437—438).—Bombardment of Pt and Cu targets by  $2 \times 10^6$  volt deuterons in a modified apparatus (A., 1935, 1441) produces a positron activity of  $126 \pm 5$  sec. half-life in  $\text{N}_2$  but not in  $\text{O}_2$ ,  $\text{H}_2$ , or A. This activity is due to activation of  $\text{N}_2$  (1 atom. per  $10^6$  incident deuterons), probably according to the reactions  ${}^7\text{N}^{14} + {}^1\text{H}^2 \rightarrow {}^8\text{O}^{15} + {}^0n^1$  and  ${}^8\text{O}^{15} \rightarrow {}^7\text{N}^{15} + {}^1e^+$ . The max. energy of the positrons from the second, radioactive process is approx.  $1.7 \times 10^6$  volts.

L. S. T.

**$\beta$ -Ray spectra of some induced radioactive elements resulting from neutron bombardment.** R. NAIDU and R. E. SIDAY (Proc. Physical Soc., 1936, 48, 332—336).—Preliminary determinations are given of the energies of the end-points, found from block diagrams, of the  $\beta$ -ray spectra of some unstable elements produced by neutron bombardment of F, Si, Rh, Ag, Eu, and Dy, a cloud chamber being used.

N. M. B.

**Action of slow neutrons on rare-earth elements.** G. HEVESY and H. LEVI (Nature, 1936, 137, 185).—The decay periods and relative intensities of the artificially radioactive rare-earth elements, as determined by various investigators, are summarised, together with new data for the absorption of slow neutrons by the rare-earth elements. Discrepancies in published data appear to be due mainly to the presence of small amounts of impurities.

L. S. T.

**Cosmic-ray particles of high penetrating power.** L. LEPRINCE-RINGUET (Nature, 1936, 137, 358).—New measurements agree with the assumption that the more penetrating cosmic rays consist of positive and negative electrons and of protons.

L. S. T.

**General interpretation of cosmic-ray effects.** R. A. MILLIKAN (Physical Rev., 1934, [ii], 46, 329; cf. A., 1935, 560).

L. S. T.

**Recovery time of Geiger-Müller counters.** W. E. DANFORTH (Physical Rev., 1934, [ii], 46, 1026—1027).

L. S. T.

**Artificial radioactivity and the conversion of kinetic into  $\gamma$ -ray energy associated with nuclear disintegration by neutrons.** W. D. HARKINS and D. M. GANS (Physical Rev., 1934, [ii], 46, 827—828).—A discussion. The at. nucleus is an efficient converter of large amounts of kinetic into  $\gamma$ -ray energy.

L. S. T.

**Transformation of energy.** (LORD) RUTHERFORD (Nature, 1936, 137, 135—137).—A lecture.

L. S. T.

**Neutron capture and nuclear constitution.** N. BOHR (Nature, 1936, 137, 344—348).—A lecture in which new views are presented.

L. S. T.

**Nuclear stability and isotope shift.** G. BREIT (Physical Rev., 1934, [ii], 46, 319).—Gamow's diagram (A., 1934, 939) is discussed in relation to the observed isotope shifts of Hg and Pb.

L. S. T.

**Neutrino theory of radiation and the emission of  $\beta$ -rays.** R. DE L. KRONIG (Nature, 1936, 137, 149).—A discussion.

L. S. T.

**Does conservation of energy hold in atomic processes?** P. A. M. DIRAC (Nature, 1936, 137, 298—299).

L. S. T.

**Negative protons in the nucleus?** J. H. BARTLETT, jun. (Physical Rev., 1934, [ii], 46, 435; cf. A., 1933, 1226).—Attention is directed to a certain regularity in the isotope pattern which may show how negative protons become incorporated in the nucleus. The case of Zn is discussed. Several elements, including In, Sb, and I, may be found to have 3 odd isotopes.

L. S. T.

**Heights of nuclear potential barriers.** E. D. EASTMAN (Physical Rev., 1934, [ii], 46, 744).—Barrier heights calc. from Heisenberg's theory are compared with other indications of their magnitude.

L. S. T.

**Nuclear moments.** S. FRISCH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 21—22).—The nuclear moments,  $I$ , of elements of odd at. no. are given by  $I = L \pm S$ , where  $L$  is the resultant moment of the proton orbit and the nuclear residue, and  $S$  is the proton spin. Vals. are tabulated.

H. J. E.

**Spin and magnetic moment of the potassium  $\text{K}^{39}$  nucleus.** S. MILLMAN, M. FOX, and I. I. RABI (Physical Rev., 1934, [ii], 46, 320).—Deflexion of a beam of neutral K atoms in a weak magnetic field gives  $3/2$  for the spin of  $\text{K}^{39}$ . The hyperfine structure separation calc. for the  ${}^2\text{S}_1$  normal state is  $0.0147 \text{ cm}^{-1}$ , giving 0.38 unit of the nuclear magneton  $\mu_0/1838$  for the nuclear magnetic moment.

L. S. T.

**Molecular orientation and the probability of excitation and dissociation of the hydrogen molecule by electron impact.** N. SASAKI and T. NAKAO (Proc. Imp. Acad. Tokyo, 1935, 11, 413—415; cf. A., 1935, 1185).—From quantum-mechanical calculations it is deduced that the probability of excitation of the  $\text{H}_2$  mol. to the  $1^3\Sigma$ -state is a max. when the mol. axis is parallel to the electron beam,



in accord with experimental data on the dissociation of  $H_2$  mols. J. W. S.

**Calculation of eigenfunction of metallic electrons.** H. BETHE (Helv. phys. Acta, 1934, 7, Suppl. II, 18—23; Chem. Zentr., 1935, i, 2954).—The method of calculation of Wigner and Seitz (A., 1934, 1283) is applied to the calculation of the eigenfunctions of electrons in metals and in free atoms, and to calculations arising therefrom of cohesion, excited electronic terms, and free electrons in alkali metals. J. S. A.

**Limits of elementary theory of metallic electrons.** L. NORDHEIM (Helv. phys. Acta, 1934, 7, Suppl. II, 3—17; Chem. Zentr., 1935, i, 2954).—The classical theory of Sommerfeld is restated in terms of quantum mechanics, and extended to cover effects at high temp. J. S. A.

**Statistical basis of electron theory of metals.** R. PEIERLS (Helv. phys. Acta, 1934, 7, Suppl. II, 24—30; Chem. Zentr., 1935, i, 2953—2954).—Theoretical. J. S. A.

**Sommerfeld's theory of metals.** K. F. NIESSEN (Ned. Tijdschr. Nat., 1935, 2, 71—89; Chem. Zentr., 1935, i, 3765).—An explanatory résumé of the chief features of the Sommerfeld theory. J. S. A.

**Errors of approximation in Jeffreys' phases.** F. L. ARNOT (Proc. Camb. Phil. Soc., 1936, 32, 161—178).—The errors involved in the use of an approximation method due to Jeffreys of solving the radial wave equation for the motion of an electron in the field of a spherically symmetrical atom are examined with reference to neutral Cl. A. J. M.

**Statistical theory of neutral atoms.** P. LAL and K. LAL (Indian J. Physics, 1936, 10, 1—6).—A simplified method is given for calculating the binding energy of an atom by making use of the Thomas-Fermi statistical model and neglecting the interaction between electrons. For the lighter atoms the results are in good agreement with those derived by other methods. An expression for the radius of a neutral atom has also been obtained. M. S. B.

**Dispersion of light in the region of magnetic dipole lines.** B. MILLANCUK (Bull. Acad. Polonaise, 1935, A, 438—444).—Theoretical. The Kramers-Heisenberg formula for dispersion holds for magnetic dipole lines if the corresponding transition probabilities are substituted. A. J. M.

**Magnetic dipole radiation.** B. MILLANCUK (Bull. Acad. Polonaise, 1935, A, 430—437).—Theoretical. The Zeeman separation and intensity ratios of spectral lines due to magnetic dipole radiation are calc. on Dirac's theory. A. J. M.

**Limit to the quantum theory and the avoidance of negative energy transitions.** H. T. FLINT (Nature, 1936, 137, 313—314).—The principle of min. proper time, according to which intervals of proper time  $< h/m_0c^2$  have no physical significance, eliminates the conception of an electron moving with a high velocity in a strong field of force and sets a boundary to the region to which such a conception may be applied and to the domain where the quantum theory is valid. L. S. T.

**Annihilation of positrons.** J. C. JAEGER and H. R. HULME (Proc. Camb. Phil. Soc., 1936, 32, 158—160).—Theoretical. A. J. M.

**Space quantisation.** I. I. RABI (Physical Rev., 1936, [ii], 49, 324—328).—A discussion of the effect of a rapidly varying weak magnetic field on an oriented atom having nuclear spin shows that on the basis of the Phipps-Frisch modification of the Stern-Gerlach experiment nuclear spin can be measured even when the hyperfine structure separation is very small. N. M. B.

**Interrelationships of  $e$ ,  $h/e$ , and  $e/m$ .** R. T. BIRGE (Nature, 1936, 137, 187).—A crit. survey. The existence of a major discrepancy between the grating val. of  $e$ ,  $(4.8029 \pm 0.0005) \times 10^{-10}$  e.s.u., and that obtained by various methods involving  $e/m$  and  $h/e$ ,  $(4.7824 \pm 0.0015) \times 10^{-10}$  e.s.u., indicates that either the Bohr formula for the Rydberg const. or the method of calculating  $e$  on the assumption of a geometrically perfect calcite crystal is incorrect. L. S. T.

**Intensity distribution in band spectra of diatomic molecules.** W. WEHRLI (Helv. phys. Acta, 1934, 7, 676—683; Chem. Zentr., 1935, i, 3515).—A discussion of anomalous data for GaI and InI (cf. A., 1934, 1286). H. J. E.

**Reversal of a branch in a non-electronic band.** A. ADEL (Physical Rev., 1936, [ii], 49, 340).—Attention is directed to the first recorded instances of this phenomenon. N. M. B.

**Chemical reactivity and light absorption.** N. R. DHAR and P. N. BHARGAVA (Indian J. Physics, 1936, 10, 43—47; cf. A., 1935, 144).—The increase in light absorption of a mixture of undried  $H_2$  and Br, above that of the separate constituents, is not observed when the gases are completely dry and therefore non-reactive. This is in accordance with the view that increased absorption is a measure of the reactivity of the system. M. S. B.

**Sodium resonance radiation and the polymerisation of ethylene.** J. C. JUNGERS and H. S. TAYLOR (J. Chem. Physics, 1936, 4, 94—96).— $C_2H_4$  quenches the resonance radiation of Na vapour between  $130^\circ$  and  $250^\circ$ , but no measurable polymerisation of  $C_2H_4$  takes place, contrary to the behaviour with the resonance radiation of excited Hg and Cd. Above  $250^\circ$ , however, the polymerisation of  $C_2H_4$  is catalysed by Na surfaces with an activation energy of 20 kg.-cal. Reasons for the apparently greater efficiency of thermal activation, as compared with photo-activation, are discussed. M. S. B.

**Spectrum emitted by a potassium bromide crystal under X-rays.** P. W. BURBIDGE and T. G. MOORCRAFT (Nature, 1936, 137, 278).—Bands with centres at 5310, 4520, and 3810 Å. have been photographed. L. S. T.

**Ultra-violet spectrum of ammonia.** II. Rotational structure of some bands in the Schumann region. A. B. F. DUNCAN and G. R. HARRISON (Physical Rev., 1936, [ii], 49, 211—214; cf. A., 1935, 912).—The seven (0, 2)—(0, 8) bands of the second electronic state above the normal, in the range



1620—1450 Å., have been photographed, and their structure is discussed. N. M. B.

**Ammonia bands in the near infra-red.** S. K. CHAKRAVORTI (Indian Phys. Math. J., 1934, 5, 25—33).—The fundamental frequencies of  $\text{NH}_3$  are calc. from wave mechanics, the mol. being regarded as a symmetrical pyramidal top, with N at the apex and H at each corner of the equilateral base. The calc. electric moment is 3.2 times the observed val. CH. ABS. (e)

**Band spectra of LiH, LiD, and NaD.** F. H. CRAWFORD and T. JORGENSEN, jun. (Physical Rev., 1934, [ii], 46, 939; cf. A., 1935, 561). L. S. T.

**Absorption spectrum of magnesium hydride in the ultra-violet.** B. GRUNDSTRÖM (Nature, 1936, 137, 108—109).—The absorption spectrum of  $\text{MgH}$  from Mg heated in  $\text{H}_2$  at  $1400^\circ$  shows, in addition to the band at 2430 Å. (A., 1929, 376), a band in the ultra-violet corresponding with a transition from the ground-level  $^2\Sigma$  to a hitherto unknown activated state in  $\text{MgH}$ . L. S. T.

**Intensities in the 3400 band of phosphorus hydride.** P. NOLAN and F. A. JENKINS (Physical Rev., 1934, [ii], 46, 327).—Line intensities in the rotational structure of the  $^3\Pi$ ,  $^3\Sigma$  band of PH have been measured. L. S. T.

**Absorption spectrum of nitrous oxide in Schumann region.** P. K. SEN-GUPTA (Bull. Acad. Sci. Agra and Oudh, 1934, 3, 197—202; Chem. Zentr., 1935, i, 2945).—Continuous absorption commences at 1850 Å., with a region of transmission between 1700 and 1580 Å. The absorption is attributed to the formation of excited N atoms according to  $\text{N}_2\text{O} + h\nu$  (1850) =  $\text{NO} + \text{N}(^2D)$ ;  $\text{N}_2\text{O} + h\nu$  (1580) =  $\text{NO} + \text{N}(^2P)$ , the calc. excitation potentials agreeing with experiment. J. S. A.

**Doublet separation in the normal state of nitric oxide and its thermodynamic quantities.** E. E. WITMER (Physical Rev., 1934, [ii], 46, 629). L. S. T.

**Pressure broadening in the  $\gamma$ -bands of nitric oxide.** O. R. WULF (Physical Rev., 1934, [ii], 46, 316).—An explanation of this effect is discussed. L. S. T.

**Spectrum of the first discharge through nitrogen peroxide.** L. GRILLET and M. DUFFIEUX (Compt. rend., 1935, 201, 1338—1340).—The emission spectrum of feebly excited  $\text{N}_2\text{O}_4$  streaming rapidly through a discharge tube consists of (a) the phosphorescent spectrum of  $\text{NO}_2$ , (b) O I bands, (c) N I bands, (d) the second positive group of  $\text{N}_2$ , (e) the 3 group of NO; three unknown spectra consisting of (f) a vibration-rotation band at  $5996\text{ cm}^{-1}$ , (g) 17 bands between  $5936$  and  $5227\text{ cm}^{-1}$ , (h) bands between  $5398$  and  $6547\text{ cm}^{-1}$  degraded towards the violet, between  $6405$  and  $6576\text{ cm}^{-1}$  degraded towards the red, and a band with a max. at  $6350\text{ cm}^{-1}$ , and (i) numerous unknown lines in the extreme red and infra-red. T. G. P.

**Quantitative data on the absorption spectrum of nitrogen peroxide.** M. LAMBREY and J. CORBIÈRE (Compt. rend., 1935, 201, 1334—1335; cf. A.,

1930, 1496).—The absorption coeffs. of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in the region  $3200$ — $4105\text{ Å.}$  have been measured. T. G. P.

**Absorption spectra of monoxides of alkaline-earth metals.** P. K. SEN-GUPTA (Bull. Acad. Sci. Agra and Oudh, 1934, 3, 203—208; Chem. Zentr., 1935, i, 2947).—The spectra of  $\text{CaO}$ ,  $\text{BaO}$ , and  $\text{SrO}$  show a limit of continuous absorption, corresponding with dissociation into neutral atoms. J. S. A.

**Absorption spectrum of sulphur trioxide.** E. FAJANS and C. F. GOODEVE (Trans. Faraday Soc., 1936, 32, 511—514).—The absorption spectrum of  $\text{SO}_3$  vapour between  $3000$  and  $2200\text{ Å.}$  consists of weak diffuse bands superimposed on a continuous background. The bands are of an unusual type and consist of flat max., with sharp min. separated by an approx. const. frequency distance =  $430\text{ cm}^{-1}$ . The bands cannot be measured with certainty above  $2500\text{ Å.}$  and are not due to  $\text{SO}_2$ . O. J. W.

**Absorption spectra of the tellurium oxides  $\text{TeO}_2$  and  $\text{TeO}$ .** C. S. PLAW (Compt. rend., 1936, 202, 127—128; cf. this vol., 134).—The absorption spectra of  $\text{TeO}_2$ , and of  $\text{TeO}$  which appears when  $\text{TeO}_2$  vapour is heated above  $1000^\circ$  at low pressures, have been studied. T. G. P.

**Band spectra of the lead halides,  $\text{PbF}$  and  $\text{PbCl}$ .** G. D. ROCHESTER (Proc. Roy. Soc., 1936, A, 153, 407—421).—The emission band spectra of  $\text{PbF}$  and  $\text{PbCl}$  are described. Their similarity to the corresponding spectra of the Bi halides is shown to be a consequence of the identity of the vibrational consts. Popov and Neujmin's analysis of  $\text{PbCl}$  (Physikal. Z., Sovietunion, 1932, 2, 394) is incorrect. No definite evidence of Pb isotope effects is obtained, but large Cl isotope effects are observed. The relations of the vibrational consts. of the Pb halides to those of other heavy mols. are considered. L. L. B.

**Absorption spectra the halides of fifth group elements.** H. TRIVEDI (Bull. Acad. Sci. Agra and Oudh, 1934, 3, 229—238; Chem. Zentr., 1935, i, 2946).—From the absorption spectra of  $\text{SbCl}_5$ ,  $\text{AsBr}_3$ ,  $\text{SbBr}_3$ ,  $\text{PI}_3$ , and  $\text{AsI}_3$  the heats of formation per atom of halogen have been calc. Vals. so found differ from accepted thermochemical data.  $\text{AsI}_3$  and  $\text{SbBr}_3$  show a second region of transmission. J. S. A.

**Absorption spectra of formaldehyde and hydrogen cyanide in the far ultra-violet.** W. C. PRICE (Physical Rev., 1934, [ii], 46, 529; cf. A., 1935, 805).—HCN shows bands extending from  $1450$  to below  $1000\text{ Å.}$  The bands at lower  $\lambda$  probably form an electronic series corresponding with an ionisation potential of HCN at  $14.8$  volts. Two types of absorption are indicated. L. S. T.

**Fluorescence and absorption bands of some derivatives of coumarin.** W. CZAPSKA-NARKIEWICZ (Bull. Acad. Polonaise, 1935, A, 445—447).—The fluorescence and absorption spectra of 7-hydroxy-coumarin-3-carboxylic acid (I), Et 7-hydroxy- (II) and 7:8-dihydroxy-coumarin-3-acetoacetate (III) have been investigated. The fluorescence max. are at  $4596$ ,  $4727$ , and  $4679\text{ Å.}$ , and the absorption max. at  $3300$ ,  $3414$ , and  $4517\text{ Å.}$ , for (I), (II), and (III), respectively. A. J. M.



**Absorption of ultra-violet light by some organic substances.** XL. L. MARCHLEWSKI and B. SKARZYŃSKI (Bull. Acad. Polonaise, 1935, A, 474—478).—The ultra-violet absorption spectrum of PhMe in EtOH solution was investigated. The mol. extinction curve has two max. at 2684 and 2720 Å., respectively. A similar curve was obtained for PhEt (max. at 2683 and 2620 Å., respectively).

A. J. M.

**Ergot alkaloids. Ultra-violet absorption spectra of lysergic acid and related substances.** W. A. JACOBS, L. C. CRAIG, and A. ROTHEN (Science, 1936, 83, 166—167).—Curves obtained for this acid and some of its derivatives are reproduced and discussed.

L. S. T.

**Emission spectra of cholesterol irradiated by sun- and ultra-violet light.** A. H. ROFFO and A. E. ROFFO, jun. (Compt. rend., 1935, 201, 1434—1435).—Emission bands at 353.3 and 357.2 mμ occur.

F. O. H.

**Carotene. X. Comparison of absorption spectra measurements on α- and β-carotene and lycopene.**—See this vol., 460.

**Infra-red absorption band of heavy-water vapour.** W. V. NORRIS, H. J. UNGER, and R. E. HOLMQUIST (Physical Rev., 1936, [ii], 49, 272).—Data for a band at 1.5291 μ are discussed.

N. M. B.

**Vibration-rotation bands of hydrogen fluoride.** E. O. SALANT and D. E. KIRKPATRICK (Physical Rev., 1934, [ii], 46, 318).—15 and 11 lines, respectively, of the (3←0) and (4←0) vibration-rotation bands of HF gas have been photographed at 8790 and 6744 Å.

L. S. T.

**Infra-red absorption spectra of quartz and fused silica from 1 to 7.5 μ. I. Experimental method. II. Results.** D. G. DRUMMOND (Proc. Roy. Soc., 1936, A, 153, 318—327, 328—339).—I. The apparatus is described. Sources of error and the accuracy attainable are discussed. The wave-no. error should be < 5 cm.<sup>-1</sup> throughout the range investigated.

II. Results of absorption measurements on a wide range of thicknesses of fused SiO<sub>2</sub> and quartz (ordinary and extraordinary rays) between 1 and 7.5 μ are given. The methods of calculating absorption coeffs. are indicated.

L. L. B.

**Infra-red absorption spectra of HCl in benzene.** E. K. PLYLER and D. WILLIAMS (Physical Rev., 1936, [ii], 49, 215—217).—Absorption curves are given for the range 2.5—4.2 μ. The C<sub>6</sub>H<sub>6</sub> band at 3.38 μ increased in intensity and shifted to longer λ in the solution; bands in the region 2—3 μ were unchanged. When the ratio of the absorption of the solution to the absorption of the C<sub>6</sub>H<sub>6</sub> is found, there appears a band with centre at about 3.49 μ. The relation of absorption to dipole moment is discussed.

N. M. B.

**Near infra-red absorption spectra of acid and basic solutions.** E. S. BARR and E. K. PLYLER (J. Chem. Physics, 1936, 4, 92—93; cf. A., 1934, 829, 1154).—Infra-red absorption spectra of H<sub>2</sub>O and aq. HCl, HBr, NaOH, KOH, ZnBr<sub>2</sub>, ZnCl<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub>

have been measured from 1.5 to 2.5 μ. The hydroxides have bands at 2.30 and 2.45 μ, the acids at 2.30 and 2.55 μ, and the salts at 2.30, 2.45, and 2.55 μ. The band at 2.30 μ is produced by hydration and at 2.45 μ by OH<sup>-</sup>.

M. S. B.

**Residual rays of magnesium oxide.** M. PARODI (Compt. rend., 1936, 202, 302—304).—Born's method of calculation for cubic crystals of the NaCl type is applied to MgO. The calc. λλ were 15.85 and 14.47 μ, corresponding with observed vals. of 15.3 and 14.8 μ, respectively.

H. J. E.

**Infra-red absorption spectra of liquefied gases. Methane.** C. CORIN and J. HERRY (Compt. rend., 1936, 202, 41—44).—Data are recorded for the absorption bands of liquid CH<sub>4</sub> and of its solutions in liquid N<sub>2</sub> (< 1 to 50%). Eleven bands were observed at λλ 0.8—2.7 μ, in positions agreeing with vals. for the gas. The data are compared with those for C<sub>6</sub>H<sub>14</sub>.

H. J. E.

**Effects of isomerism on infra-red absorption spectra.** W. GORDY and D. WILLIAMS (J. Chem. Physics, 1936, 4, 85—87; cf. this vol., 9).—The spectra of MeCN, EtCN, BuCN, PhCN, MeCNS, EtCNS, and their isomerides, and also of PhCNS, have been determined between 1.0 and 6.5 μ. The characteristic CN band near 4.6 μ is shifted to longer λλ by about 0.2 μ for NC, and its intensity is approx. doubled. This shift agrees with chemical data indicating C<sup>+</sup> and hence weaker binding forces in the NC compounds. The corresponding shift for the SCN isomerides is smaller, but the intensity difference is greater. No other bands in these compounds are appreciably modified by isomerism. This is a further indication of a simple type of binding between C and N atoms modified only slightly by associated groups in the mol. In the absorption spectra of aq. HCN there is an intense band at 4.75 μ and one less intense at 4.95 μ probably attributable to a small amount (2—4%) of HNC.

M. S. B.

**Constitution of oximes and their near infra-red absorption spectra.** (MME.) M. FREYMANN and R. FREYMANN (Compt. rend., 1936, 202, 312—314).—The two forms of oximes, CRAr·N·OH (I) and CRAr· $\begin{smallmatrix} \text{NH} \\ \diagup \text{O} \end{smallmatrix}$  (II), proposed by Ramart-Lucas (A., 1933, 159, 1278) are distinguishable by the infra-red absorption bands at 0.96 and 1.04 μ, associated, respectively, with (OH) and (NH). In the oximes from COEt<sub>2</sub>, COMePr, and COMeBu<sup>s</sup> the (OH) infra-red frequency is observed, and form (I) predominates. In the oximes of dimethylbutylacetophenone and dimethyltetralone both the (OH) and (NH) frequencies occur. The intensity of the (OH) band increases with rising temp., showing that at low temp. these oximes are associated.

H. J. E.

**Infra-red absorption spectra of anthracene hydrocarbons.** M. P. LAMBERT and M. J. LE COMTE (Ann. Office nat. Combust. liq., 1934, 9, 979—993; Chem. Zentr., 1935, i, 3532—3533; cf. A., 1933, 113).—The infra-red absorption spectra of anthracene, diethyl-, di-*n*-butyl-, diisobutyl-, diisomyl-, tetrahydro-, hexahydro-, decahydro-, and



perhydro-anthracene are described and discussed; they are quite different from those of the  $C_6H_6$ ,  $C_{10}H_8$ , and phenanthrene series. Infra-red spectra of 3 oil samples are discussed. H. N. R.

**Infra-red absorption spectra of nuclear halogenated hydrocarbons.** J. LECOMTE (Compt. rend., 1935, 201, 1340—1342; cf. A., 1934, 238).—The bands corresponding with the C-halogen linkings in nuclear monosubstituted benzenes and *m*- and *p*-toluenes have been identified. Their relationships with the Raman spectra are discussed. T. G. P.

**Raman spectrum of crystalline ammonium chloride.** F. T. HOLMES (J. Chem. Physics, 1936, 4, 88—90).—A method of growing cylindrical crystals of  $NH_4Cl$  stable at room temp. is described. The vibrational frequencies of this form are 3146, 3041, 2824, 2010, 1768, 1709, and 1407  $cm^{-1}$ , and subsidiary frequencies 3300 and 3232  $cm^{-1}$ . The high-temp. modification has frequencies 3102, 2801, 1931, 1655, and 1400  $cm^{-1}$ . The results indicate that the  $NH_4$  in cryst.  $NH_4Cl$  has not the geometrical structure of a tetrahedron of cubic symmetry unless it is strongly perturbed in a non-geometric sense. M. S. B.

**Acetylene linking frequency in heavy acetylene ( $C_2D_2$ ).** G. GLOCKLER and H. M. DAVIS (Physical Rev., 1934, [ii], 46, 535).—Raman scattering in  $C_2D_2$  at 2 atm. by 4358 Hg line gave one frequency at 1761  $cm^{-1}$ , which is ascribed to the triple linking vibration. L. S. T.

**Raman effect of neutral alkyl sulphates.** L. MÉDARD and R. MARCHAND (Compt. rend., 1936, 202, 320—321).—Data for  $Me_2SO_4$  and  $Et_2SO_4$  are recorded. The characteristic frequencies 391—433, 564, 1142, and 1370  $cm^{-1}$  of  $H_2SO_4$  are observed with small modifications in the spectra of  $Me_2SO_4$  and  $Et_2SO_4$ . The frequency 391—433  $cm^{-1}$  is associated with the  $:S(O)_2$  group. The alkyl sulphates have no frequency corresponding with the 917  $cm^{-1}$  frequency of  $H_2SO_4$ . The former have a strong frequency at approx. 775  $cm^{-1}$  which does not occur in  $H_2SO_4$ . H. J. E.

**Wing accompanying the Rayleigh line in liquid mixtures.** I. S. C. SIKKAR (Indian J. Physics, 1936, 10, 75—82; cf. this vol., 9).—The distribution of intensity in the wing accompanying the Rayleigh line in the Raman spectra of solutions of 40%  $C_6H_6$  in cyclohexane and 20%  $C_6H_6$  in MeOH has been compared with that due to pure  $C_6H_6$ . The results are discussed on the basis of existing theories. Differences in the distribution of intensity between liquid and gaseous  $C_6H_6$  can be explained by assuming that the wing originates partly in the rotational Raman effect and partly in the widening of the Rayleigh line, due to the fluctuation of the internal field caused by non-periodic and abrupt impacts of neighbouring mols. on the scattering centres. M. S. B.

**Comparison of the Raman spectra of  $\Delta^8$ -octen- $\alpha$ -ols and some of their *cis*- and *trans*-derivatives.** (MLLE.) B. GREDY (Compt. rend., 1936, 202, 322—323).—Data are recorded for amylvinylcarbinol, *trans*- $\alpha$ -bromo- $\Delta^8$ -octene, and for the *cis*-

and *trans*-forms of  $\Delta^8$ -octen- $\alpha$ -ol, Me  $\Delta^8$ -octenyl ether, and octyl acetate. H. J. E.

**Raman spectra and constitution of ozonides.** E. BRINER and E. PERROTTET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 283—287; cf. A., 1935, 1446).—Raman frequencies of methyleugenol, methylisoeugenol (I), alone and in  $CCl_4$ , methylvanillin, and (I) ozonide in  $CCl_4$  are tabulated. The lines associated with the  $\cdot CH:CHMe$  group disappear on ozonisation and become replaced by lines characteristic of ozonides. R. S.

**Raman spectra in the eugenol and estragol group.** B. SZUSZ and E. PERROTTET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 227—230; cf. A., 1935, 807).—The frequencies and intensities of the Raman lines of eugenol, isoeugenol, vanillin, estragol, and natural and synthetic anethole are given. R. S.

**Raman spectra of terpenes and camphors.** S. K. K. JATKAR and R. PADMANABHAN (Indian J. Physics, 1936, 10, 55—63).—Dipentene (I) gives a Raman spectrum showing all the characteristics of limonene (II) with that of another compound having a strong frequency at 1610  $cm^{-1}$ , probably due to  $\alpha$ -terpinene. It is suggested that both (I) and (II) contain mixtures of different amounts of the products of intramol. isomerisation. The shifts 1412—1450  $cm^{-1}$ , in the spectrum of camphor and not of fenchone, are due to the reactive  $\cdot CH_2 \cdot CO \cdot$  group present in the former only. M. S. B.

**Raman spectrum of rubber and related hydrocarbons.** S. D. GEHMAN and H. J. OSTERHOF (J. Amer. Chem. Soc., 1936, 58, 215—218; cf. A., 1935, 1054).—The most intense frequency in the spectra for rubber (I) (using a conc. solution in  $CS_2-CCl_4$ ) and balata (II) is at 1670  $cm^{-1}$  and is considered to be due to the double linking. Comparison of the frequencies for (I) and (II) with those for  $CHMe:CMMe_2$  (III), myrcene (IV), isoprene (V), and limonene shows that the primary linkings in (I) are similar to those in (III), thus supporting the view that (I) consists of a long chain of isopentene units. The differences in the spectra of (I) and (II) are consistent with *cis-trans* isomerism. The spectrum of (IV) is largely a superposition of those of (III) and (V). H. B.

**Raman spectra of quinoline, quinaldine, isoquinoline, and  $\alpha$ - and  $\beta$ -picolines.** S. K. K. JATKAR (Indian J. Physics, 1936, 10, 23—30).—A comparative study of the Raman spectra of the above compounds has been made. The structures are in harmony with the chemical evidence which indicates a variable stability of the  $C_6H_6$  and  $C_5H_5N$  rings according to whether they form fused-ring compounds containing both rings or one kind of ring only. M. S. B.

**Kinetics theory of liquids and diffusion of light.** J. YVON (Compt. rend., 1936, 202, 212—214).—Theoretical. T. G. P.

**Spectral region of the emission of chemical reactions.** R. AUDUBERT (Compt. rend., 1936, 202, 131—133; cf. A., 1933, 764).—With the aid of photon counters the ultra-violet emissions of the following reactions have been studied: (1) NaOH



+HNO<sub>3</sub>, (2) NaOH+H<sub>2</sub>SO<sub>4</sub>, (3) pyrogallol+O<sub>2</sub>, (4) glucose+KMnO<sub>4</sub>, (5) Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>+O<sub>2</sub>, (6) O<sub>2</sub>+K<sub>2</sub>SO<sub>3</sub>, (7) O<sub>2</sub>+Na<sub>2</sub>SO<sub>3</sub>, (8) Mg-Hg+H<sub>2</sub>O, (9) Na-Hg+H<sub>2</sub>O, (10) Al-Hg+H<sub>2</sub>O, (11) EtOH+H<sub>2</sub>CrO<sub>4</sub>, (12) 2Br+K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (13) 2Br+Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (14) 2I+Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Reactions (1)–(3), (5), (8)–(10) are shown by counters with cathodes of Al or CuI, (11)–(14) only by the former, and (4), (6), and (7) only by the latter.

T. G. P.

**Heterogeneity in crystals and phosphorescence.** M. CURIE (Compt. rend., 1935, 201, 1352–1353; cf. A., 1932, 560).—The rôle of impurities is discussed.

T. G. P.

**Fluorescent power and experimental study of fluorescent power as a function of concentration.** J. BOUCHARD (J. Chim. phys., 1936, 33, 51–71).—At const.  $p_H$  the fluorescent power of uranine solutions follows Perrin's law  $\Phi = \Phi_0 e^{-kc}$  ( $c$  = concn.). The const.  $k$ , measured by the light re-emitted in the direction of the exciting ray and laterally, decreases with increasing  $[H^+]$  and for  $p_H$  6–12,  $\log_{10} k \propto p_H$ . The results are related to the degree of ionisation of the fluorescent substance.

J. W. S.

**Becquerel effect and photochemical sensitivity of some fluorescent dyes.** (Mlle.) C. STORA (Compt. rend., 1936, 202, 48–50).—Vals. are recorded for the photo-potentials of uranine, eosin, and erythrosin. They are lowered by hydrosulphides, phenols, amines, or by TiCl<sub>3</sub>. The relation between the photo-potential, the fluorescence, and the effect of oxidising and reducing agents is discussed.

H. J. E.

**Photometric investigation and measurements of spectral intensity distribution of fluorescent screens, especially on irradiation with electron rays.** M. VON ARDENNE (Z. tech. Phys., 1935, 16, 61–67; Chem. Zentr., 1935, i, 3884).—The intensity and spectral distribution of light from a variety of fluorescent materials when excited by 4000 volt-electrons, X-rays, and ultra-violet light are recorded.

J. S. A.

**Connexion between illumination and strength of current in the barrier-layer photo-cell.** E. ELVEGÅRD (Physikal. Z., 1936, 37, 129–133).—An equation is given which expresses the variation of current obtainable from such cells with intensity of illumination, when connected with different external resistances. The equation can be used for the determination of light intensities.

A. J. M.

**Rectifying effect in chrome cast iron.** L. G. HALL (Physical Rev., 1934, [ii], 46, 1109).—Such an effect is described.

L. S. T.

**Molecular theory of the dielectric constant of non-polar liquids.** J. YVON (Compt. rend., 1936, 202, 35–37).—Mathematical.

H. J. E.

**Influence of a magnetic field on the dielectric constants of gaseous and liquid nitrogen and oxygen.** A. C. YOUNG (Canad. J. Res., 1935, 13, A, 111–119).—A balanced resonance method was used with gases and a special bridge with liquids. The only positive result was with gaseous O<sub>2</sub> at 100 atm. and room temp., when there was a change of  $1.1 \times 10^{-6}$  in the dielectric const. This can be accounted for

quantitatively by the increased pressure of the O<sub>2</sub> in the magnetic field.

E. E. A.

**Polarity of nitrogen tetroxide and nitrogen dioxide molecules.** J. W. WILLIAMS, C. H. SCHWINGEL, and C. H. WINNING (J. Amer. Chem. Soc., 1936, 58, 197–203).—The electric moments of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> mols. have been calc. from measurements of dielectric const. of their gaseous equilibrium mixtures at 298–398° abs. and 150–760 mm. The polarity of NO<sub>2</sub> decreases with rising temp., probably due to the passage of the mols. into more symmetrical higher vibrational states. The dipole moment of N<sub>2</sub>O<sub>4</sub> does not differ greatly from zero.

E. S. H.

**Permanent electric moment and structure of phosphorus pentachloride.** P. TRUNEL (Compt. rend., 1936, 202, 37–39).—Simons and Jessop's results are contradicted (A., 1931, 669). PCl<sub>5</sub> has a permanent dipole moment ( $\mu = 0.8$  at 25°) in CCl<sub>4</sub> or CS<sub>2</sub> solution. The mol. is unsymmetrical. The 5 Cl may not be all identical. Alternatively they are not co-planar.

H. J. E.

**Electrical moment of tantalum pentachloride and the structure of the compounds AX<sub>5</sub>.** H. MOUREU (Compt. rend., 1936, 202, 314–316).—TaCl<sub>5</sub> has a permanent moment of 1.2. The formulation of compounds of the type AX<sub>5</sub> is discussed. The formula cannot be symmetrical.

H. J. E.

**Dielectric constants of mercuric halides.** H. BRAUNE and R. LINKE (Z. physikal. Chem., 1935, B, 31, 12–17).—Measurements of the dielectric const. of HgI<sub>2</sub>, HgBr<sub>2</sub>, and HgCl<sub>2</sub> vapours at various temp. have shown zero dipole moments. The Hg-halogen linking moments are only  $\frac{1}{4}$ – $\frac{1}{3}$  of the val. corresponding with an ideal heteropolar linking.

R. C.

**Magnetic changes [ $\Delta\epsilon$ ] of the dielectric constant of liquids in a field of 20.4 k.-gauss.** A. PIEKARA (Compt. rend., 1936, 202, 206–207; cf. A., 1935, 1192).— $\Delta\epsilon$  has been measured for hexane, CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, and PhNO<sub>2</sub>, but no appreciable change was detected.

T. G. P.

**Polar properties of hydrogenation products of naphthalene.** M. PUCHALIK (Acta phys. polon., 1933, 2, 305–310; Chem. Zentr., 1935, i, 3914).—The following moments are recorded (in C<sub>6</sub>H<sub>6</sub> solution): *cis*- and *trans*-deca-, 0; tetra-hydronaphthalene,  $1.66 \times 10^{-18}$  e.s.u. The finite moment of the last is due to its unsymmetrical structure.

H. N. R.

**Dielectric polarisation of concentrated solutions.** A. JAGIELSKI and J. WESOŁOWSKI (Bull. Acad. Polonaise, 1935, A, 260–269).—Dipole moments of *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub>, *o*- and *p*-C<sub>6</sub>H<sub>4</sub>Cl·NO<sub>2</sub>, and Et<sub>2</sub>O, determined in C<sub>6</sub>H<sub>6</sub> solution, are 4.01, 4.22, 4.82, 3.12, and 0.74 ( $\times 10^{-18}$ ) e.s.u., respectively. The vals. differ from those recorded by other workers.

T. G. P.

**Dielectric polarisation.** XIV. Dipole moments of ethyl-, phenyl-, and  $\alpha$ - and  $\beta$ -naphthyl-carbimides. XV. Dipole moments of five-membered nitrogen ring compounds: indole, skatole, carbazole, isatin, phthalimide, and succinimide. E. G. COWLEY and J. R. PART-



INGTON. XVI. Dipole moments of some acid halides and of phosphorus oxychloride. G. T. O. MARTIN and J. R. PARTINGTON (J.C.S., 1936, 45—47, 47—50, 158—163).—XIV (cf. A., 1935, 916). The dipole moments ( $\mu$ ) in  $D$ , at  $20^\circ$ , in  $C_6H_6$  solution, of ethyl-, phenyl-,  $\alpha$ - and  $\beta$ -naphthylcarbimide are 2.81, 2.28, 2.30, and 2.34, respectively. These vals. agree with those for the corresponding thio-carbimides (A., 1933, 1230), allowing for  $\mu$  for  $:C:S$  being  $>$  for  $:C:O$ , and indicate similar linear structure for the  $:N:C:O$ , in agreement with the Raman spectra (Goubeau, A., 1935, 851). The possibility of resonance between three possible structures is discussed.

XV. Indole and skatole in  $C_6H_6$  at  $20^\circ$  give  $\mu$  2.05 and 2.08, respectively; carbazole, isatin, phthalimide (I), and succinimide (II), in dioxan, give  $\mu$  2.09, 5.72, 2.10, and 1.54, respectively.  $\mu$  for indole is  $>$  for pyrrole (A., 1933, 1230), the change in  $\mu$  being paralleled by the vals. for quinoline and  $C_5H_5N$ . In the case of isatin,  $\mu$  agrees with the diketonic formula. Since  $\mu$  for (II) is  $<$  for (I), the five-membered ring with N and two  $:CO$  must have a large polarising influence on the  $C_6H_4$  ring.

XVI.  $\mu$  for  $AcCl$  (in  $C_6H_6$  at  $20^\circ$ ) is 2.45, and for the series  $EtCOCl$ ,  $Pr^iCOCl$ ,  $Bu^iCOCl$ , and  $Bu^sCOCl$  is const. at 2.61—2.63. The large val. of  $\mu$  for  $AcCl$  (calc. 2.25) may be due to induction in the C-C linking. Vals. for  $AcBr$  (2.43) and  $AcI$  support this view.  $CH_3Cl \cdot COCl$  (in  $C_6H_6$  and  $CS_2$ ) and  $CCl_3 \cdot COCl$  (in  $C_6H_6$ ) give  $\mu$  2.22, 2.06, and 1.19, respectively. Free rotation about the C-C linking does not occur, and the  $\cdot COCl$  moment acts at  $16^\circ$  to the C-C axis. For  $POCl_3$ ,  $\mu$  is 2.40, giving 3.56 for the  $P \rightarrow O$  moment.

L. J. J.

Dielectric loss characteristics of a chlorinated diphenyl. W. JACKSON (Proc. Roy. Soc., 1935, A., 153, 158—166).—A study has been made of the dielectric behaviour of a chlorinated diphenyl from  $-20^\circ$  to  $80^\circ$  over the frequency range  $50$ — $10^7$  cycles per sec. The Debye power factor max. has been followed through this range from  $40^\circ$  to  $-5^\circ$ .

L. L. B.

Application of Debye's theory of polar molecules to solid dielectrics. B. J. O'KANE (Phil. Mag., 1936, [vii], 21, 369—383).—Curves are given for the variation of power factor and permittivity with temp. at const. frequency and with frequency at const. temp. for palmitic, oleic, and stearic acids and mixtures of these. If the expression for the viscosity ratio of liquids at different temp. is applied in the Debye expression for the power factor of a dielectric, in terms of the internal viscosity of the medium in which the dipole is assumed to move, the calc. and experimental power factor-temp. curves agree closely. Results indicate that the Debye theory of liquid dielectrics can be applied to solid dielectrics on the assumption that they possess some property analogous to the macroscopic viscosity of liquids and obeying the same temp. variation rules.

N. M. B.

Refractive index and molecular refraction of hydrogen selenide and deuterium selenide. O. E. FRIVOLD, O. HASSEL, and T. SKJULSTAD (Physikal. Z., 1936, 37, 134—136; cf. A., 1935,

148).—Vals. of  $(n_0 - 1) \times 10^6$  for  $H_2Se$  and  $D_2Se$ , respectively, at pressures about 20 mm. are for  $\lambda$  6562.8 Å., 798.3 and 795.1; for 5893.0 Å., 803.9 and 801.2; for 5460.7 Å., 809.8 and 807.6.

A. J. M.

Measurements of dispersion in the ultra-violet. M. BAYEN (Compt. rend., 1936, 202, 207—209).—A previous arrangement has been improved (Duclaux, J. Physique, 1921, 2, 346). Between 2250 and 5900 Å., for heptane at  $23^\circ$   $n^2 = 1.89729 + 0.8886 \times 10^6/\lambda^2 - 1,195,060$ ; for heptene at  $23^\circ$   $n^2 = 1.92364 + 1.0301 \times 10^6/\lambda^2 - 1,877,300$ ; for heptinene at  $22.5^\circ$   $n^2 = 1.95065 + 1.0556 \times 10^6/\lambda^2 - 1,583,500$ .

T. G. P.

Refractive dispersion of organic compounds. VII. Refractive indices of hexane and the refractivities of hydrogen and carbon. Significance of the dispersion constants. VIII. Isomerides of the formula  $C_4H_8O_2$ : dioxan, ethyl acetate, isobutyric acid, and acetoin. C. B. ALLSOPP and H. F. WILLIS (Proc. Roy. Soc., 1936, A, 153, 379—391, 392—406).—VII. The law of additivity of at. refractivities is discussed in the light of the first of the two fundamental observations on which it is based, viz., the constancy of the increment of mol. refraction in homologous series. The refractivity of a mol. may be expected to be the sum of the refractivities of its constituent atoms (or electrons) only when its refractive dispersion can be represented by an equation containing only one variable term with a characteristic frequency in the Schumann region of the spectrum. Vals. of  $n$  for hexane are recorded at 57  $\mu$  between 6708 and 2450 Å. and the at. refractivities of H and C over the same range are deduced with the help of data previously given for cyclohexane. Characteristic frequencies deduced by means of the Ketteler-Helmholtz equation are subject to errors of the order of 100 Å., and trustworthy vals. can be derived only from the Lorentz-Lorenz equation; the error from experimental inaccuracy is  $< 10$  Å.

VIII. Mol. extinction coeffs., refractive indices, and mol. refractivities over a wide range of visible and ultra-violet  $\lambda$  are recorded for dioxan,  $EtOAc$ ,  $Pr^iCO_2H$ , and  $CH_3AcMe \cdot OH$  (I), and at. refractivities are deduced for ethereal, carbonyl, and hydroxyl O. If allowance be made for the variations in the refractivity of O, according to the manner in which it is linked in the mol., the law for additivity of at. refractivities is valid at all  $\lambda$  for these compounds of which the refractive dispersions can be represented by equations containing only one variable term with a characteristic frequency in the Schumann region of the spectrum. The  $f$ -val. of the ketonic absorption band of (I) is almost identical with that of the corresponding band of cyclohexanone. The partial refractions of the absorption bands of org. mols. are not necessarily  $\propto$  the  $f$ -vals.

L. L. B.

Dispersion. K. F. HERZFELD and (Miss) M. G. MAYER (Physical Rev., 1936, [ii], 49, 332—339).—Mathematical. In interpreting measurements in the infra-red and the absorption of hot gases account must be taken of the fact that the measured absorption is the difference between absorption and forced



emission. For a gas, the paramagnetic part of the susceptibility depends on the frequency in the same way as the electric part, but is determined by the magnetic absorption lines; the diamagnetic part is almost independent of the frequency up to X-ray frequencies. N. M. B.

**Werner complexes. Optical activity and configuration of ions of the type  $MA_3$ .** J. P. MATHIEU (J. Chim. phys., 1936, 33, 78—96).—The optical absorption and rotation of  $[Co en_3]Br_3 \cdot 2H_2O$ ,  $[Rh en_3]I_3 \cdot H_2O$ ,  $[Ir en_3]Br_3 \cdot 2H_2O$ , and  $[Cr en_3]I_3 \cdot H_2O$  are compared with those of  $K_3[Cr(C_2O_4)_3] \cdot H_2O$ ,  $K_3[Rh(C_2O_4)_3] \cdot 2H_2O$ ,  $K_3[Ir(C_2O_4)_3] \cdot 2H_2O$ , and  $K_3[Co(C_2O_4)_3]$ . The oxalates have the higher optical activities, but compounds containing the same metal show close analogies. A parallelism exists between the factor of dissymmetry in the active bands and the chemical stability of the compounds. J. W. S.

**Optical activity dependent on co-ordinated bivalent ruthenium.**—See this vol., 485.

**Theory of optical activity. III. Regular tetrahedron twisted through a small angle about a binary axis.** B. Y. OKE (Proc. Roy. Soc., 1936, A, 153, 339—352; cf. A., 1935, 917).—A system of 4 identical vibrators, mutually interacting, at the corners of a tetrahedron gives 5 characteristic frequencies. If one pair of vibrators is rotated through a small angle about the line of centres, the distorted system becomes optically active. The rotatory power is calc. by a method of approximation; it is  $\propto$  the third power of the small angle of twist. L. L. B.

**Absolute configuration of lactic acid. Assumptions made in calculation of optical rotation.**—See this vol., 454.

**Magnetic rotatory power and dispersion of alkali mercuritetra-iodides.** R. LUCAS and F. GALLAIS (Compt. rend., 1936, 202, 129—131).—The exceptional rotatory properties of  $K_2HgI_4$ , which have been measured, are due to a broad absorption band. T. G. P.

**Electrical birefringence of compressed nitrogen.** H. BIZETTE (Compt. rend., 1936, 202, 304—305).—Measurements were made at 150 kg. per sq. cm. and with a field of 160,000 volts per cm. The val. of the Kerr const. found was approx. half that given by Bruce and Breazeale (cf. A., 1933, 1232; 1935, 1192). H. J. E.

**Electro-optic effect in zinc blende.** C. SCHRAMM (Ann. Physik, 1936, [v], 25, 309—336).—The double refraction and inhomogeneity of the crystals are due to cutting or polishing. Kerr consts. for Tl, Na, and K light are given and compared with the piezo-electric consts. ZnS has "light" voltage of 1240 or about one third the val. of  $PhNO_2$ . W. R. A.

**Constitution of thioether compounds of platinum. II.** K. A. JENSEN (Z. anorg. Chem., 1936, 226, 168—172).—An explanation of the results of Lifschitz *et al.* (A., 1935, 1335), different from that of the authors, is given. M. S. B.

**Planar configuration of quadricovalent compounds of bivalent copper and nickel.** E. G.

COX, E. SHARRATT, W. WARDLAW, and K. C. WEBSTER (J.C.S., 1936, 129—133).— $Cu(C_5H_5N)_2Cl_2$  (I) has been prepared under various experimental conditions with the object of identifying *cis*- and *trans*-isomerides. Only the *trans*-form was obtained, even by the action of  $C_5H_5N$  on *Cu alkylglyoxime dichlorides*, which must form *cis*-(I) initially. The cell dimensions of *cryst.* (I), determined by X-ray methods (*c*-axis 3.84 Å.), show that it can only have *trans*-planar configuration, in agreement with previous work (A., 1935, 920). *Cu* and *Ni bismethylethylglyoximes* are isomorphous, and occur in one form only. L. J. J.

**Significance of non-localised linkings ("p]-electron cloud") of aromatic hydrocarbons in formation of their molecular compounds with dipolar molecules.** G. BRIEGLEB (Z. physikal. Chem., 1935, B, 31, 58—78).—The secondary valency in the above mol. compounds depends chiefly on a dipole induction of the polar groups of the dipolar mol. on the polarisable charge of the unsaturated hydrocarbon. In mol. compounds of polar mols. with  $C_6H_6$  or condensed ring systems the polar groups of the dipoles induce moments in the localised  $\sigma$ -linkings of the hydrocarbon ( $\sigma$ -polarisation) and also perturb the charge distribution of the non-localised  $[p]$ -electrons ( $[p]$ -electron polarisation) (cf. A., 1932, 901). The induction effect changes the absorption spectrum of the hydrocarbon considerably, which is responsible for the characteristic colour of the mol. compound. Both polarisations can be estimated from spectroscopic data. Calc. heats of formation of compounds of unsaturated ring systems with  $NO_2$ -compounds agree satisfactorily with the observed vals. If a dipolar mol. forms a 1:1 compound with an unsaturated aromatic hydrocarbon with two Ph nuclei linked by saturated or unsaturated hydrocarbon chains, it adds itself to a Ph nucleus and an induction perturbation initially localised at that nucleus may be transmitted by the non-localised  $[p]$ -electrons to the other nucleus. Such spreading of the perturbation is stopped, however, by a  $CH_2$  group. R. C.

**Concepts of "resonance" and "intermediate stages" for organic substances with multiple linkings, and electronic formulæ.** F. ARNDT and B. EISTERT (Z. physikal. Chem., 1935, B, 31, 125—131).—The modern concept of "resonance between two mol. states" is equiv. to the authors' "intermediate stage" theory (A., 1925, i, 57; A., 1935, 324). Modifications in the representation of electronic formulæ are suggested. R. C.

**Formation of mercury molecules.** F. L. ARNOT and J. C. MILLIGAN (Proc. Roy. Soc., 1936, A, 153, 359—378).—Mainly a detailed account of work already noted (A., 1935, 1917). The ionisation potential of the mol. is 9.65 volts. A max. is observed in the mol. ionisation at 11.5 volts, due to triplet excitation, and a second max. at 40 volts, due mainly to singlet excitation of the atom which goes to form the mol. ion. L. L. B.

**Motions exhibited by anisotropic liquids under the influence of an electric field.** V. FREDERICKS and V. TZVETKOV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 4, 131—133).—The motions



of *p*-azoxyanisole in an electric field depend on the field strength and the thickness of the layer of liquid. The mol. axes of the turbulently streaming particles lie parallel to the force lines of the applied field.

W. R. A.

"Gas mists." V. NJEGOVAN (Z. Physik, 1935, 98, 415—416).—Correction of earlier work (this vol., 14).

A. B. D. C.

Association of liquids at the b.p. K. BILLIG (Ber., 1936, 69, [B], 434—436; cf. A., 1935, 815).—Mathematical relationships are developed between the association factor and surface tension at the b.p., sp. cohesion, and elevation of the b.p. by dissolved substances.

H. W.

Pressure effect on predissociation. W. LOCHTE-HOLTGREVEN (Nature, 1936, 137, 187—188).—The dependence of predissociation on pressure is discussed for S.

L. S. T.

Kinetics of dense fluids in two or three dimensions. E. FAHIR (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 8—13).—Mathematical. The electrostatic potential and field on a mol. partly immersed in an ideal fluid are examined.

N. M. B.

Dissociation of  $\text{SnCl}$  and  $\text{SnCl}_2$ . H. LESSHEIM and R. SAMUEL (Indian J. Physics, 1936, 10, 7—12).—The covalent character of the  $\text{SnCl}$  and  $\text{SnCl}_2$  linkings is reaffirmed (cf. A., 1933, 996; 1934, 477; cf. Trivedi, A., 1935, 913).

M. S. B.

Calculation of linking energies. W. LASAREFF (Physica, 1936, 3, 61—64).—From the dissociation energy of CO, vals. of 108 or 124 kg.-cal. are calc. for the transition  $\text{C}_{\text{diamond}} \rightarrow \text{C} (^3P)_{\text{gas}}$  at  $0^\circ$  abs., giving 51 or 59 kg.-cal., respectively, for the C-C linking in aliphatic hydrocarbons. A correction term to account for the discrepancy with the observed val. ( $> 70$  kg.-cal.) is suggested. Gershinowitz' criticism (A., 1935, 1448) is rejected.

L. J. J.

(A) Calculation of energy of  $\text{H}_3$  molecule. (B) Calculation of energy of  $\text{H}_3^+$  ion. J. HIRSCHFELDER, H. EYRING, and N. ROSEN (J. Chem. Physics, 1936, 4, 121—130, 130—133).—Mathematical.

M. S. B.

Zero point energy in determination of structure of solids. A. R. UBBELOHDE (Trans. Faraday Soc., 1936, 32, 525—529).—Substitution of one isotope for another in a solid compound will lead to differences in vibrational and rotational frequencies which, in certain cases, should be large enough to afford information on the structure of the solid.

F. L. U.

Constants of the methane molecule. T. NEUGEBAUER (Z. Physik, 1936, 98, 638—656).—Assuming the nucleus  $\text{C}^4$  and externally the Ne proper function, the polarisation energy in the inhomogeneous field of the four protons, the C-H separations, and vibration frequencies are calc.

A. B. D. C.

Normal vibration frequencies of the molecule  $\text{XYZ}_3$ . (Miss) J. E. ROSENTHAL and H. H. VOGEL (J. Chem. Physics, 1936, 4, 134—136).—A general expression is derived for the potential energy of the tetrahedral mol.  $\text{XYZ}_3$  and the normal vibration frequencies are given as functions of the consts.

The mode of application of these general formulæ to special types of potential energy functions is indicated.

M. S. B.

Potential functions of molecular groups and the vibrations of the halogen derivatives of methane. H. H. VOGEL and (Miss) J. E. ROSENTHAL (J. Chem. Physics, 1936, 4, 137—143).—Assuming that, in a series of mols.  $\text{YZ}_4$ ,  $\text{XYZ}_3$ ,  $\text{ZYX}_3$ , and  $\text{YX}_4$ , the potential energy of the  $\text{YZ}_3$  is the same whether it is attached to an X or to another Z and the force between Y and X is not changed by the nature of the other atoms in the mol., formulæ connecting the potential energy consts. of these mols. are given. Application to the series  $\text{CH}_4$ ,  $\text{MeCl}$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  gives satisfactory results. Frequencies calc. for  $\text{CHCl}_3$  and  $\text{CDCl}_3$  from those of  $\text{CH}_4$ ,  $\text{MeCl}$ , and  $\text{CCl}_4$  are in good agreement with observed data. Vals. for the frequencies of  $\text{CD}_3\text{Cl}$  are predicted. The  $\text{CH}_4$  consts. are discussed and it is shown that, although individual consts. may vary with the method of determination, certain linear combinations of them, to which a definite physical meaning can be attached, are practically invariant. The  $\text{C}_2\text{H}_6$  consts. calc. from the  $\text{CH}_4$  consts. are entirely different from those given by Sutherland *et al.* (A., 1935, 569), but account equally well for the observed frequencies.

M. S. B.

Dipole attraction and hydrogen bond formation in their relation to solubility. J. H. HILDEBRAND (Science, 1936, 83, 21—24).—An address.

L. S. T.

Rotation of dipoles in elastic and viscous media. N. L. YATES-FISH (Phil. Mag., 1936, [vii], 21, 226—233).—The couple acting on a rigid sphere when this is rotated through a small angle in a medium possessing relaxing elasticity has been calc. The result is applicable to the rotation of a dipole in a solid (cf. this vol., 21).

R. S. B.

Applications of astrophysics to physics and chemistry. W. NERNST (Oesterr. Chem.-Ztg., 1936, 39, 34—36).—A lecture.

Evaporation of small drops and the relationship between surface tension and curvature. J. L. SHERESHEFSKY and (Miss) S. STECKLER (J. Chem. Physics, 1936, 4, 108—115).—Rates of evaporation of  $o\text{-C}_6\text{H}_4(\text{CO}_2\text{Bu}^n)_2$  droplets of radius 3—0.5  $\mu$  have been determined for different v.p. in a Hoag type of Millikan's oil-drop apparatus. Two interpretations are given. According to one the surface tension of a droplet decreases with increasing curvature. The other assumes a vapour film surrounding the droplet and leads to Kelvin's equation.

M. S. B.

Parachor, surface tension, and density of substituted phenols and phenolic ethers. A. BURAWOY and I. MARKOWITSCH-BURAWOY (J.C.S., 1936, 36—39).—Data are recorded for the hydroxy- and methoxy-azobenzenes and -benzaldehydes, and compared with vals. for the nitro-phenols and -anisoles. For the *o*-OH-compounds, but not the *o*-ethers, the parachor is  $<$  both calc. val. and vals. for the *m*- and *p*-compounds. Surface tensions and  $d$  for each set of isomeric ethers agree among themselves, but the vals. for *o*-OH-compounds are  $<$  for *m*-



and *p*-isomerides. *m*- and *p*-Nitrophenol and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO are associated (as calc. from Ramsay-Shields const.), but the *o*-compounds and the Me ethers are normal. The anomalies of the *o*-compounds are probably due to interaction between the two *o*-substituents, which reduces their polarity, and those of *o*-hydroxyazobenzenes are not necessarily due to quinonoid structure. L. J. J.

**Parachor and ring structure. II. Spatial configuration of bridged-ring compounds.** S. K. RAY (J. Indian Chem. Soc., 1935, 12, 764—767; cf. A., 1934, 1058).—Data are given for cyclohexane, cyclohexanone, 3-methylcyclohexanone, cyclohexanol, cyclohexyl acetate, menthol, menthyl acetate, dipentene, camphoroxime, bromocamphor, camphene, bornyl acetate, fenchone, camphor benzoate, and  $\alpha$ -pinene. The structures are discussed. E. S. H.

**Parachor and chemical constitution. IV. Structure of aliphatic diazo-compounds.** S. K. RAY (J. Indian Chem. Soc., 1935, 12, 780—782; cf. A., 1935, 1306).—Data are given for the Me, Et, Pr<sup>n</sup>, and *n*-amyl diazoacetates between about 0° and 100°. The variation of parachor with temp. shows that these compounds are equilibrium mixtures of two forms. Low temp. favours the ring form, high temp. the open-chain structure. E. S. H.

**Constitution of formic acid and formates.** R. M. HALASYAM (J. Indian Chem. Soc., 1935, 12, 813—814).—Published work is discussed. Parachor determinations support the annexed formula as the most probable for the constitution of HCO<sub>2</sub>H. E. S. H.

**Interpolation equation for photo-densitometer charts of X-ray diffraction patterns.** W. SOLLER (Physical Rev., 1934, [ii], 46, 331). L. S. T.

**Influence of the slit on the distribution of intensities in the lines of a powder diagram.** A. ROGOZINSKI (Compt. rend., 1935, 201, 1354—1356).—Theoretical. T. G. P.

**Equation for X-ray crystal curves.** R. C. SPENCER (Physical Rev., 1934, [ii], 46, 1108—1109). L. S. T.

**X-Ray diffraction with calcite in several orders of reflexion.** L. G. PARRATT and F. MILLER (Physical Rev., 1936, [ii], 49, 280—288; cf. A., 1932, 1184).—Theoretical and experimental vals. of the four properties of reflexion, *i.e.*, width of the (*n*,  $-n$ ) rocking curve, % reflexion, coeff. of reflexion, and a factor determined by the shape of the (*n*,  $-n$ ) curve, are compared for calcite crystals in the  $\lambda$  ranges 0.71 <  $\lambda$  < 5.83 Å. in first order, 0.71 <  $\lambda$  < 2.75 Å. in second order, and at 0.71 and 1.54 Å. in third order, and 0.71 Å. in fourth and fifth orders. N. M. B.

**X-Ray examination of atomic vibrations in zinc and cadmium.** G. W. BRINDLEY (Nature, 1936, 137, 315—316).—The observed anomalous X-ray scattering of Zn and Cd is due to a greater lattice vibration along the *c* axis of the crystals than normal to it. L. S. T.

**Vacant positions in crystal lattice of ferriferous zinc blende.** H. BRAEKKEN (K. Norske Vid. Selsk. Forh., 1935, 7, 119—120; Chem. Zentr., 1935,

i, 3887).—Up to 25 at.-% of Fe, the ZnS lattice shows no expansion. From the observed X-ray intensities the presence of empty spaces in the lattice is inferred. J. S. A.

**Properties of graphite derived from the transformation of diamond.** P. CORRIEZ (Compt. rend., 1936, 202, 59—61).—Measurements of the X-ray spectrum, electrical resistance, and magnetic susceptibility are recorded for graphite prepared by heating diamond for 10 min. in vac. at 1900°. The X-ray spectrum differs from that of sugar C heated to 2000°. The differences are discussed. The resistance is < that of sugar C, but > that of natural graphite. The susceptibility was approx. the same. H. J. E.

**X-Ray interference in diamond as a wave-mechanical problem.** P. P. EWALD and H. HÖNL (Ann. Physik, 1936, [v], 25, 281—308).—Mathematical. The appearance of the forbidden diamond reflexions (222) is caused by a "zwischenladung" between the atoms which is inactive for higher interferences because of their considerable spread. W. R. A.

**(A) Changes of structure of crystals in an electric field. (B) Compensation apparatus and quantum fluctuation.** A. NÉMET (Helv. phys. Acta, 1935, 8, 97—116, 117—151; Chem. Zentr., 1935, i, 3517).—(A) X-Ray intensity measurements in electric fields are recorded for NaCl, calcite, quartz, mica, K Na and Na Rb tartrate, ice, (HCO<sub>2</sub>)<sub>2</sub>Ba, MgSO<sub>4</sub>, and tartar. The polarisability in various crystal directions is discussed.

(B) The experimental method is described. H. J. E.

**Electrolysis, dendritic growth, and discharge in alkali halide crystals.** A. VON HIPPEL (Z. Physik, 1936, 98, 580—596).—The movement of electrons and Cu ions through alkali halide crystals has been studied at 570°, and mobilities of the ions determined. Dendritic growths appear on reversal of the applied potential, and in NaCl the type of growth may change from the (100) to the (110) direction. A. B. D. C.

**Dendritic growth of crystals.** A. PAPAPETROU (Z. Krist., 1935, 92, 89—130).—Partly mathematical, partly a descriptive illustrated account under the following heads: part played by diffusion; effect of surface potential; observations on particular substances (especially inorg. halides); processes at the tip of the crystal; development near the tip and formation of branches; crystallisation from the melt. B. W. R.

**Growing and testing large single crystals of ice.** W. LEWIS (Physical Rev., 1934, [ii], 46, 328). L. S. T.

**Crystal structure of ice at low temperatures.** E. F. BURTON and W. F. OLIVER (Proc. Roy. Soc., 1935, A, 153, 166—172; cf. A., 1935, 686).—Details are given of the apparatus and method used. If the ice is formed above  $-80^\circ$ , the mols. have sufficient energy to arrange themselves into the highly organised state of a cryst. solid; at  $-90^\circ$ , the energy of the mols. is just enough to build up crystals along certain planes, whilst just below the crit. temp.,  $-110^\circ$ , there are sufficient mols. arranged in parallel planes



to give rise to two diffuse diffraction max., the size of the particles probably being of the order of  $10^{-7}$  cm.

L. L. B.

**Magnetic powder experiments on rolled nickel iron.** J. L. SNOEK (Physica, 1936, 3, 118—124).—Powder patterns (cf. Bitter, A., 1932, 1077) on isotropic and anisotropic samples are described. L. J. J.

**Crystal structure of cristobalite,  $\text{SiO}_2$ .** W. NIEUWENKAMP (Z. Krist., 1935, 92, 82—88).—The cell is pseudo-cubic,  $a_0$  7.02  $b_0$  6.92 Å., with 8 mols.  $\text{SiO}_2$ ,  $d$  (X-ray) 2.33, space-group  $P 4_2 2_1$ . Parameters are determined. B. W. R.

**Anomalous structures of fine crystalline silica.** N. A. SCHISCHAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 19—22).—Structures of  $\text{SiO}_2$  have been studied by the electron-diffraction method. Fused vitreous  $\text{SiO}_2$  is not amorphous, but consists of deformed crystals of cristobalite,  $a$  6.87 Å.,  $c/a$  1.06. Fine-grained sand ( $\alpha$ -quartz) also shows a deformation in its crystallites,  $a$  4.735,  $c$  5.210 (quartz  $a$  4.903,  $c$  5.393). Pumice gives  $a$  6.82,  $c$  7.23 Å. R. S. B.

**X-Ray investigation of the glassy state.** N. VALENKOF and E. PORAI-KOSCHITZ (Nature, 1936, 137, 273—274).—Photographs showing gradual changes in the X-ray pattern on transition from vitreous  $\text{SiO}_2$  to a mixture of cristobalite and tridymite are reproduced. Similar transition patterns are obtained when  $\text{Na}_2\text{O-SiO}_2$  glasses are subjected to a rising temp. and increased time of heating, leading to the gradual appearance of the cryst. pattern. The lack of a sharp boundary between the glassy and cryst. states and the gradual growth of crystallites are thus demonstrated. L. S. T.

**Crystal structure of boron carbide.** F. LAVES (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 57—58; Chem. Zentr., 1935, i, 2944).—The lattice is trigonal,  $a$  5.62,  $c$  12.12 Å., giving 2.19 mols. of  $\text{B}_6\text{C}$  per unit cell. It is considered that the compound must be  $\text{B}_4\text{C}$ . J. S. A.

**Structure of aluminium boride,  $\text{AlB}_2$ .** W. HOFMANN and W. JÄNICHE (Z. physikal. Chem., 1936, B, 31, 214—222).—A detailed account of work already noted (this vol., 143). R. C.

**Crystal structure of the high-temperature form of silver iodide,  $\alpha\text{-AgI}$ .** L. W. STROOK (Z. physikal. Chem., 1935, B, 31, 132—136).—In  $\alpha\text{-AgI}$  the  $\text{Ag}^+$  ions are "molten," i.e., are distributed at random over the gaps between the  $\text{I}^-$  ions, which form a body-centred cubic lattice. In  $\alpha\text{-Ag}_2\text{HgI}_4$  three cations occupy a four-fold point position (A., 1934, 1056). The intensities of the X-ray diagram of  $\alpha\text{-AgI}$  have been recalculated. R. C.

**Cubic high-temperature modifications of cuprous and silver sulphides, selenides, and tellurides.** P. RAHLFS (Z. physikal. Chem., 1936, B, 31, 157—194).— $\alpha\text{-Ag}_2\text{S}$  and  $\alpha\text{-Ag}_2\text{Se}$  have a body-centred cubic lattice with 2 mols. in the unit cell, whilst  $\alpha\text{-Ag}_2\text{Te}$ ,  $\alpha\text{-Cu}_{1.8}\text{S}$ , and  $\alpha\text{-CuSe}$  are face-centred cubic, with 4 mols. in the unit cell. The lattice structures of  $\alpha\text{-Ag}_2\text{S}$  and  $\alpha\text{-Ag}_2\text{Se}$  are similar, the  $\text{Ag}^+$  ions being statistically distributed among the gaps between the anions, which form a somewhat distended body-centred cubic packing. With  $\alpha\text{-Ag}_2\text{Se}$

more anions occupy large gaps than smaller gaps, but with  $\alpha\text{-Ag}_2\text{S}$  the anions are distributed uniformly over all the gaps. Cubic  $\alpha\text{-Cu}_2\text{S}$  is obtained only if there is a deficiency of Cu, corresponding with  $\sim\text{Cu}_{1.8}\text{S}$ . The lattice of  $\alpha\text{-Cu}_{1.8}\text{S}$  is apparently similar in structure to that of  $\alpha\text{-Cu}_2\text{Se}$ . In  $\alpha\text{-Ag}_2\text{Te}$  and  $\alpha\text{-Cu}_2\text{Se}$  4 cations per unit cell form with the anions a Zn blende structure, whilst the remaining 4 are statistically distributed in gaps. In the above compounds the lattice changes from body-centred to face-centred when the ratio of the radius of the cation to that of the anion changes from 0.637 to 0.57. R. C.

**Crystal structure of potassium, rubidium, caesium, and thallium silicofluorides and of  $\text{LiMnO}_4 \cdot 3\text{H}_2\text{O}$ .** J. A. A. KETELAAR (Z. Krist., 1935, 92, 155—156).—The silicofluorides are isomorphous with  $(\text{NH}_4)_2\text{SiF}_6$ ; their lattice consts. and parameter vals. are tabulated. Lattice consts. are also given for  $\text{LiMnO}_4 \cdot 3\text{H}_2\text{O}$ . B. W. R.

**Crystal structure of thallium fluoride.** J. A. A. KETELAAR (Z. Krist., 1935, 92, 30—38).—The cell is rhombic, space-group  $V_{2h}^{23}$ ,  $a_0$  5.18,  $b_0$  5.495,  $c_0$  6.080 Å., 4 mols. in cell,  $d$  (X-ray) 8.48. This is a new type of AB structure and may be regarded as a deformed NaCl lattice. The high polarisability of  $\text{Tl}^+$  is discussed. B. W. R.

**Anhydrous sulphates of the magnesium series.** F. HAMMEL (Compt. rend., 1936, 202, 57—59).—Comparative X-ray data are recorded for the anhyd. sulphates of Mg, Mn, Fe, Co, Ni, Cu, and Zn. H. J. E.

**Symmetry of tetragonal nickel sulphate.** A. SCHOER (Natuurwetensch. Tijds., 1936, 17, 233—242).—Corrosion figures obtained by etching the (111) and (001) faces of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  crystals indicate that they are holohedral, but those on the (112) and (101) faces correspond with a hemihedral structure.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  belongs to the enantiomorphic class of the tetragonal system, and single crystals are either dextro- or laevo-rotatory, with  $\alpha$  1.55° per mm. for  $\lambda$  5893 Å. (cf. A., 1932, 986). D. R. D.

**Crystal structure of tetramminocadmium perchlorate,  $\text{Cd}(\text{NH}_3)_4(\text{ReO}_4)_2$ .** K. S. PITZER (Z. Krist., 1935, 92, 131—135).—The cell is face-centred cubic,  $a_0$  10.53 Å., 4 mols. in cell, space-group  $T_h^h$ . Approximations to the parameters are made. B. W. R.

**Configuration of bisdimethylglyoximoammine cobaltic chloride.**—See this vol., 460.

**Crystal structure of tetrahydrated nickelous acetate.** R. B. HULL (Physical Rev., 1934, [ii], 46, 329).— $a : b : c = 0.7216 : 1 : 0.4143$  have been confirmed goniometrically, and  $\beta$  93° 25' by Laue photographs. Rotation photographs give  $a_0$  8.49  $\pm$  0.03,  $b_0$  11.77  $\pm$  0.05,  $c_0$  4.87  $\pm$  0.03 Å. The unit cell contains 2 mols. of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ;  $d^{20}$  is 1.717  $\pm$  0.001. L. S. T.

**Cell dimensions and space-group of calcium tartrate.** R. C. EVANS (Z. Krist., 1935, 92, 154—155).—The cell is orthorhombic,  $a_0$  9.20,  $b_0$  10.54,  $c_0$  9.62 Å., space-group  $P 2_1 2_1 2_1$ , 4 mols. in cell. B. W. R.



**Crystallised *p*-toluidine.** J. WYART (Bull. Soc. franç. Min., 1935, 58, 281—293).—The crystals,  $d$   $1.120 \pm 0.003$ , are orthorhombic with  $n_x$  1.68 and  $n_y$  1.58. X-Ray measurements give  $a$  5.95,  $b$  9.05, and  $c$  23.3 Å., with 8 mols. per unit cell. Details of mol. structure are given. L. S. T.

**Crystal structure of *p*-dinitrobenzene.** R. W. JAMES, G. KING, and H. HORROCKS (Proc. Roy. Soc., 1935, A, 153, 225—246).—The crystal structure of  $p$ -C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> has been determined by the method of double Fourier series. Projections of the electron density on the 3 axial planes have been made, and the 18 independent parameters of the structure measured. The unit cell has  $a$  11.05,  $b$  5.42,  $c$  6.56 Å., and contains 2 mols. Space-groups,  $P 2_1/n$ ;  $d_{\text{calc}}$  1.64. The C<sub>6</sub> ring, although nearly a regular hexagon of side 1.40 Å., is slightly distorted, the length of one of each of the pairs of sides adjacent to the C-N linking being shortened to 1.32 Å. The distortion is due to the displacement of the C linked to the NO<sub>2</sub>. The C-N linking lies nearly in the plane of the ring, but is inclined at about 25° to the plane of the NO<sub>2</sub>. The N-O distances are 1.10 and 1.25 Å., respectively, and the O-O distances 2.14 Å. L. L. B.

**X-Ray investigations of the molecular structure of chitin.** A. N. J. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 132—135, and Nature, 1936, 137, 277—278).—The lattice structure of chitin is based on an arrangement of cellulose chains along the  $b$  axis of the unit cell with protein side-chains along the  $a$  axis. The  $c$  axis agrees with the side distance of the protein chains. A. G. P.

**X-Ray analysis of the orthorhombic crystalline modification of 1 : 2 : 5 : 6-dibenzanthracene.** J. IBALL (Nature, 1936, 137, 361; cf. this vol., 17).—The unit cell has  $a$  8.22,  $b$  11.39,  $c$  15.14 Å., giving  $d$  1.295 assuming 4 mols. of C<sub>22</sub>H<sub>14</sub> per unit cell; space-group  $Q_1^{15}$ - $Pcab$ . L. S. T.

**Liquid crystals of some cholesterol compounds.**—See this vol., 467.

**X-Ray study of the absorption of cyclopentanone by cellulose trinitrate.** M. MATHIEU and (MLLE.) T. PETITPAS (Compt. rend., 1936, 202, 46—47).—Changes in the X-ray diagram of cellulose nitrate, due to treatment with cyclohexane and cyclohexanone, are recorded. The results for treatment with the liquids or vapours resemble those for COMe<sub>2</sub> (cf. B., 1935, 1039). H. J. E.

**Electrical orientation of wool cells.** H. J. WOODS (Proc. Leeds Phil. Soc., 1935—1936, 3, 132—134).—A method of obtaining films of oriented wool cells, 20—30  $\mu$  thick, by sedimentation from an aq. suspension in an alternating electric field is described. The X-ray fibre photograph from such films was identical with that of normal  $\alpha$ -keratin in the untreated fibres. H. J. E.

**Supercrystalline organic compounds.** D. VORLÄNDER (Naturwiss., 1936, 24, 113—117).—A supercryst. compound is one in which the crystal forces are so strong that it does not fuse to give an amorphous melt, but decomposes on heating. This indicates that the mols. are held more firmly in the

crystal lattice than the atoms are held within the mol. The connexion between mol. structure and supercrystallinity is discussed. Compounds possessing this property usually have long chains of atoms in the mol., but this is not necessarily the sole cause of the phenomenon. In aromatic compounds it is more probably due to the cryst. association of rod-like units of medium length. The supercrystallinity of starch, cellulose, and proteins is due to the existence of both long chains and cryst. association of mols.

A. J. M.  
**X-Ray investigations of liquid crystals.** V. K. HERRMANN (Z. Krist., 1935, 92, 49—81).—Nine substances are investigated for liquid crystal behaviour with rising and falling temp., optically and with X-rays, especially in the neighbourhood of the optical transition points. For several a new interference effect, the "wide sharp ring," is found, ascribed to a closest hexagonal packing of nearly cylindrical mols. The ring does not vanish abruptly; its disappearance is discussed. B. W. R.

"Extra" rings in graphite electron diffraction patterns. G. I. FINCH and H. WILMAN (Nature, 1936, 137, 271—272).—Prominent "extra" electron diffraction rings have been obtained with natural and artificial graphite powders of high C content. The rings are due to planes, the spacings of which have no counterpart in the X-ray structure assigned to graphite. The thin crystals contain certain Bragg spacings not exhibited by thicker graphite. The formation of the "extra" rings is illustrated diagrammatically. L. S. T.

**Electron distribution in (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O and the structure of the oxalate group.** S. B. HENDRICKS and M. E. JEFFERSON (J. Chem. Physics, 1936, 4, 102—107).—More accurate vals. of at. separations in the C<sub>2</sub>O<sub>4</sub> group of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O have been obtained from a Fourier analysis of the electron distribution on the (001) plane, using X-ray scattering data: C-C  $1.581 \pm 0.01$ , C-O  $1.25 \pm 0.02$ , and C-O  $1.23 \pm 0.02$  Å. with the angle O-C-O  $129 \pm 2^\circ$ . The O-C-O parts of the C<sub>2</sub>O<sub>4</sub> group are in planes at an angle of 28°, whilst in H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O,  $\alpha$ - and  $\beta$ -H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> the parts are coplanar. M. S. B.

**Study of the structure of chloroform by electron diffraction.** C. DEGARD (Bull. Soc. chim. Belg., 1936, 45, 15—20).—Electron diffraction measurements are in accord both with the tetrahedral model and with Urbain's model of the CHCl<sub>3</sub> mol. J. W. S.

**Contact difference of potential between barium and silver. External work function of silver.** P. A. ANDERSON (Physical Rev., 1936, [ii], 49, 320—323).—A method for measuring const. and reproducible contact p.d. between metal surfaces, in which both surfaces are prepared by thermal vaporisation in a "gettered" vac., is described. The contact p.d. at liquid air temp. between microcryst. Ba and Ag is  $1.94 \pm 0.02$  volts; this, with the val. 2.39 volts for the work function of Ba, gives  $4.33 \pm 0.05$  volts for the work function of microcryst. Ag. This val. is compared with results from thermionic and photo-electric studies. N. M. B.



**Ferrites. III.** R. S. HILPERT and R. SCHWEINHAGEN (Z. physikal. Chem., 1935, B, 31, 1—11; cf. A., 1933, 1234).—The graph of magnetisability,  $\sigma$ , against composition,  $x$ , for  $\text{CuO-Fe}_2\text{O}_3$  mixtures exhibits a max. corresponding with  $2\text{CuO} : 3\text{Fe}_2\text{O}_3$ . The  $d$ - $x$  curve of slowly cooled mixtures has min. at  $2\text{CuO}, 3\text{Fe}_2\text{O}_3$  and  $\text{CuO}, 3\text{Fe}_2\text{O}_3$ , and a max. at  $\text{CuO}, 2\text{Fe}_2\text{O}_3$ , but if the mixture has been quenched the first min. is absent. Zn ferrites have a max.  $\sigma$  and min.  $d$  at  $2\text{ZnO}, 3\text{Fe}_2\text{O}_3$ , but the min.  $d$  is absent in quenched mixtures. The  $d$  suggests the existence of three series of Zn ferrites having, however, the same X-ray diagram. The  $d$ - $x$  curves of Sr ferrites and  $\text{Fe}_2\text{O}_3\text{-PbO}, \text{Fe}_2\text{O}_3$  mixtures have no max. or min. For all these ferrites the property-composition curves show no indication of metaferrites. R. C.

**Mathematical expression of the [magnetic] hysteresis curve.** J. NEUFELD (Compt. rend., 1936, 202, 125—126).—Theoretical. T. G. P.

**Analysis of dynamic curves for the magnetic permeability and losses in iron.** V. ARKADIEV (Compt. rend., 1936, 202, 39—41). H. J. E.

**Non-orthogonality and ferromagnetism.** J. H. VAN VLECK (Physical Rev., 1936, [ii], 49, 232—240).—Mathematical. N. M. B.

**Curie point of nickel.** E. C. STONER (Proc. Leeds Phil. Soc., 1935—1936, 3, 127—131).—A discussion of the derivation of the Curie point from experimental data. H. J. E.

**Discontinuities of magneto-resistance.** C. W. HEAPS (Physical Rev., 1934, [ii], 46, 1108; cf. A., 1934, 480).—A reply to criticism (A., 1935, 287). L. S. T.

**Method of investigating the Hall effect.** H. S. HATFIELD (Proc. Physical Soc., 1936, 48, 267—276).—An improved method, avoiding thermo-electric and other disturbing effects, is described and checked approx. for Al, Cu, Pb, Ni, Ag, Zn, and Sn. N. M. B.

**Method for determining the optical constants of crystals and its application to certain organic compounds.** R. G. WOOD and S. H. AYLIFFE (Phil. Mag., 1936, [vii], 21, 321—336; cf. A., 1935, 434).—Using the immersion method with a polarising microscope and a special microscope stage-goniometer, measurements were made of the principal refractive indices and orientation of the indicatrix of red and yellow picryl-*p*-toluidine, picrylaniline,  $\text{Ph}_2\text{O}$ , and  $\text{Ph}_2\text{SO}_2$ . N. M. B.

**Superficial optical properties of spar.** R. DE MALLEMANN and F. SUHNER (Compt. rend., 1935, 201, 1344—1346).—The results of an examination of the optical properties of a beam of rectilinearly polarised monochromatic light after reflexion at a cleavage surface of spar indicate the existence of an isotropic surface layer 70 Å. thick. T. G. P.

**Crystallochemical relations between germanium and silicon.** W. SCHÜTZ (Z. physikal. Chem., 1936, B, 31, 292—308).—The pairs  $\text{Zn}_2\text{SiO}_4$  and  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Be}_2\text{SiO}_4$  and  $\text{Be}_2\text{GeO}_4$ , and  $\text{Cs}_2\text{SiF}_6$  and  $\text{Cs}_2\text{GeF}_6$  are probably isomorphous. The lattice consts. have been determined. In the heaviest

flint glass of the type *S* 231 the  $\text{SiO}_2$  may be replaced by an equal wt. of  $\text{GeO}_2$ , giving a glass corresponding approx. with  $\text{Pb}_2\text{GeO}_4$  and having  $d$  6.92,  $n_D$  2.100, and  $n_F - n_G = 0.073$ . The optical consts. of various  $\text{PbO-GeO}_2$  glasses have been measured (cf. B., 1927, 42). R. C.

**Rock-salt structure of  $\text{Li}_2\text{TiO}_3$  and its formation of mixed crystals with  $\text{MgO}$  and  $\text{Li}_2\text{Fe}_2\text{O}_4$ .** E. KORDES (Z. Krist., 1935, 92, 139—153).—Lattice consts.,  $d$ , and  $n$  of  $\text{Li}_2\text{TiO}_3$  are determined; the intensities indicate a statistical distribution of  $\text{Li}^+$  and  $\text{Ti}^{4+}$ . A continuous series of mixed crystals is formed with  $\text{MgO}$ , the lattice consts. and  $n$  of which alter continuously with the composition. A more complicated mixed crystal of  $\text{MgO}$ ,  $\text{Li}_2\text{Fe}_2\text{O}_4$ , and  $\text{Li}_2\text{TiO}_3$  is prepared and examined; its consts. can be deduced by an additive law. Possible applications to ceramics and refractories are discussed. B. W. R.

**Refractive indices of metallic films showing Newton's rings.** K. PROSAD and B. N. GHOSH (Indian J. Physics, 1936, 10, 49—53).—Previous work (*ibid.*, 1933—1934, 3, 425) on the coloured concentric rings, similar to Newton's rings, obtained on the Al cathode of a Hadding's X-ray tube with a Cu anti-cathode, has been extended to the examination of the rings obtained using a Pt anti-cathode. M. S. B.

**Rotation of the plane of polarisation by oblique crystalline refraction.** G. BRUNAT and L. WEIL (Bull. Soc. franç. Min., 1935, 58, 294—313).—Measurements on quartz and calc spar verify, for small angles of incidence, Potier's theory and MacCullagh's formula. L. S. T.

**Plastic deformation of cadmium single crystals.** R. ROSCOE (Phil. Mag., 1936, [vii], 21, 399—406).—Measurements were made on the bending of single-crystal wires of very pure Cd, and of Cd containing 0.11% Pb and 0.03% Zn. Results indicate that, when the stress over the glide-planes is not uniform, slip begins when the max. val. of the resolved shear stress reaches the crit. val. for deformation under uniform stresses. Surface oxidation produces, in resistance to plastic deformation, an increase that cannot be due to the cohesion of the oxide film, but probably arises from the healing of submicroscopic cracks in the film. N. M. B.

**Plasticity of deformed metals.** D. V. KONVISAROV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 139—140).—For Al, Cu, and Fe the plasticity diminishes as the torsional angles increase. W. R. A.

**Determinative elastic and deformation constants of crystals, with applications to isotropic substances.** P. BECHTEREV (Z. Krist., 1935, 92, 1—29).—Theoretical. A classification of elastic consts. on a suggested scale of "gradation." The terms hygro-, ortho-, plagio-, and sclero-morphic are given to extreme concepts of elastic behaviour; e.g., a fully hygomorphic substance has liquid fluidity, and a fully scleromorphic one resists changes of form without limit, but does not oppose vol. alteration. Published elasticity figures for many



substances (some isotropic) are summarised and classified on this "gradation" scale. B. W. R.

**Akulov's theory of coercivity.** V. S. MESSKIN and B. E. SOMIN (Z. Physik, 1936, 98, 610—623).—Experiment disproves Akulov's theory (A., 1931, 898). A. B. D. C.

**Abrasion hardness of dolomite.** H. TERTSCH (Z. Krist., 1935, 92, 39—48).—The amount of wear of a dolomite crystal by an abrasive plate is recorded for various directions and planes. The cleavage plane gives an asymmetric hardness figure; the basis plane gives threefold symmetry. B. W. R.

**Polymorphic transformation of simple ionic lattices. I. Transformation of caesium chloride into sodium chloride lattice by heating.** G. WAGNER and L. LIPPERT (Z. physikal. Chem., 1936, B, 31, 263—274).—At  $445 \pm 5^\circ$  the lattice of ordinary CsCl changes into a lattice of the NaCl type, with lattice const.  $7.02 \times 10^{-8}$  cm., the heat of transition being 1.8 kg.-cal. Between  $20^\circ$  and  $580^\circ$  CsBr, CsI, TlCl, TlBr, and TlI exhibit no transition points. R. C.

**Transition in aluminium at  $79^\circ$ .** W. BAND (Physical Rev., 1934, [ii], 46, 934—935).—The variety of hysteresses observed on heating an Al wire show that there is a transition of some kind at  $79 \pm 0.5^\circ$ . L. S. T.

**Distortion of  $\beta$ -brass and iron crystals.** (Miss) C. F. ELAM (Proc. Roy. Soc., 1936, A, 153, 273—301).—A comparison of the results obtained from experiments on the distortion in tension of the body-centred cubic metals, Fe and  $\beta$ -brass, indicates that there is no essential difference between them. Stress-strain curves of the crystals are given, and the fracture of  $\beta$ -brass crystals in tension and in rolling is described. The direction of slip is not always a crystal direction, and it is suggested that the deformation is brought about by movements of a complex nature, and not by slip on any definite crystal plane. L. L. B.

**Mott's theory of liquid metals, and the transition points of metals and other solids.** R. H. FOWLER (Helv. phys. Acta, 1934, 7, Suppl. II, 72—80; Chem. Zentr., 1935, i, 3386).—Mott's theory (A., 1934, 1300) is discussed in relation to the changes in state of metals, alloys,  $\text{NH}_3$  halides, and other substances. H. J. E.

**Hume-Rothery conception of the metallic state.** C. D. NIVEN (Phil. Mag., 1936, [vii], 21, 291—299).—The Hume-Rothery relation is restated for the periodic groups IIIB—VIIB in the form "in crystallising each atom has  $6-N$  near neighbours, where  $N$  is the no. of electrons in the  $p$  system." The bearing of the relation on conduction and superconductivity is discussed. R. S. B.

**Electrical resistance of aluminium at low temperatures.** H. A. BOORSE and H. NIEWODNICZAŃSKI (Proc. Roy. Soc., 1936, A, 153, 463—475; cf. A., 1935, 814).—The electrical resistances of 6 polycryst. Al wires were measured at  $0^\circ$  and liquid  $\text{N}_2$  and liquid  $\text{H}_2$  temp., and those of 4 wires drawn from 99.995% pure Al at the temp. of liquid

He. Reduced resistivities computed by means of the Mathiessen-Nernst formula were in agreement with these calc. from the Grüneisen formula (A., 1933, 452) for liquid  $\text{N}_2$  temp., but not for liquid  $\text{H}_2$  temp. L. L. B.

**Tension coefficients of resistance of the hexagonal crystals zinc and cadmium.** (Miss) M. ALLEN (Physical Rev., 1936, [ii], 49, 248—253; cf. A., 1933, 559).—The coeffs. have been measured, and are independent of secondary orientation. The curves correspond with those representing the points as functions of the primary orientation. Results are discussed in relation to the Bridgman-Cookson theory (cf. *ibid.*, 1935, [ii], 47, 194). N. M. B.

**Mean free electronic path in silver from electrical conductivity of very thin silver threads.** A. EUCKEN and F. FÖRSTER (Nachr. Ges. Wiss. Göttingen, 1934, [ii], 1, 129—137; Chem. Zentr., 1935, i, 2954).—A résumé of and additions to published work (A., 1935, 153). J. S. A.

**Variations in current in a conductor.** L. BRILLOUIN (Helv. phys. Acta, 1934, 7, Suppl. II, 47—67; Chem. Zentr., 1935, i, 2954).—Current variations are calc. from the distribution of electrons by a probability method. Magnetic interaction between the electrons is assumed. J. S. A.

**Temperature variation of the susceptibility of oxygen.** H. LÜES (Z. Physik, 1936, 98, 537—547).—The susceptibility of  $\text{O}_2$  shows increasing deviation from  $\chi T = \text{const.}$  with rise of temp. from  $286^\circ$  to  $600^\circ$  abs. A. B. D. C.

**Susceptibility measurements for oxygen and inert gases.** K. E. MANN (Z. Physik, 1936, 98, 548—560).—The susceptibility of  $\text{O}_2$  is independent of density and field strength from 90 to 750 mm. Hg, and from 1800 to 15,000 oersted. Vals. obtained for the inert gases are compared with theoretical vals. A. B. D. C.

**Magnetic studies on graphite and graphitic oxides.** N. GANGULI (Phil. Mag., 1936, [vii], 21, 355—369).—The principal susceptibilities of cryst. graphite along the vertical axis and along directions in the basal plane are  $-22 \times 10^{-6}$  and  $-0.5 \times 10^{-6}$  per g., respectively. By treating with conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  to form "blue graphite" the abnormal diamagnetism along the vertical axis is nearly destroyed, and that along the basal plane is almost unchanged; the anisotropy is of the same order of magnitude as in aromatic mols. containing several condensed  $\text{C}_6\text{H}_6$  nuclei:  $1.3 \times 10^{-6}$  per g. content of C. A diminution in the particle size of graphite has nearly the same effect as oxidation as above. These effects are attributed to a breaking up of the metallic linkings in graphite responsible for abnormal diamagnetism. N. M. B.

**Explosive antimony. III. Magnetic susceptibility.** C. C. COFFIN (Canad. J. Res., 1935, 13, A, 120—125; cf. A., 1934, 1297).—Explosive Sb is less diamagnetic than the ordinary polycryst. metal. magnetic susceptibilities being  $-0.38 \times 10^{-6}$  and  $-0.88 \times 10^{-6}$ , respectively. Explosive or amorphous Sb should be regarded as a true glass of supercooled liquid. E. E. A.



**Temperature variation of [magnetic] susceptibility of solid nitric oxide.** E. LIPS (Helv. phys. Acta, 1935, 8, 247—263; Chem. Zentr., 1935, ii, 189).— $\chi$  for solid NO between 63° and 90° abs. is const., and much < the theoretical val. The difference is attributed either to the formation of double mols., or to alterations in the electronic levels due to electric fields in the crystal lattice. J. S. A.

**Magnetic susceptibility of vapours of some organic substances.** J. SHUR and S. SIDOROV (Nature, 1936, 137, 317).—A redetermination of the magnetic susceptibility of CS<sub>2</sub> showed no change in the vals. for the vapour and liquid states (cf. A., 1935, 14).

L. S. T.

**Magnetic behaviour of alums of the iron group.** A. SIEGERT (Physica, 1926, 3, 85—90).—Theoretical. For Cr<sup>+++</sup>, Mn<sup>+++</sup>, and Fe<sup>+++</sup>, the Bose-Stoner relation can be explained on the basis of the known lattice structure. For Ti<sup>+++</sup> and V<sup>+++</sup>, deviations from cubic symmetry must be taken into account. L. J. J.

**Paramagnetic relaxation.** C. J. GORTER (Nature, 1936, 137, 190).—The relaxation time of the magnetic vector is approx. 10<sup>-10</sup> sec. for Fe<sup>+++</sup> alum.

L. S. T.

**Symmetry of the thermo-electric effects in single crystals.** H. P. STABLER (Physical Rev., 1934, [ii], 46, 938).

L. S. T.

**Variation with temperature of the absorption of ultrasonic waves by liquids.** E. BAUMGARDT (Compt. rend., 1936, 202, 203—204).—The absorption of ultrasonic waves  $\nu = 7.9578 \times 10^6$  by H<sub>2</sub>O at 18—40° has been measured. The coeff. of absorption  $\propto \eta \rho_0 V_0^3$ , where  $\eta$  is the coeff. of viscosity,  $\rho_0$  the density, and  $V_0$  the velocity of sound. T. G. P.

**Existence of diffusion of ultrasonic waves in liquids.** P. BIQUARD (Compt. rend., 1936, 202, 117—119).—The existence of diffusion in ultrasonic waves (Lucas, this vol., 148)  $\nu = 7.96 \times 10^6$  sec.<sup>-1</sup> in PhMe has been confirmed experimentally. T. G. P.

**Ultrasonic experiments.** H. SACK (Helv. phys. Acta, 1934, 7, 657—658; Chem. Zentr., 1935, i, 3767—3768).—Relative velocities of propagation of ultrasonic waves in H<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, and aq. ZnSO<sub>4</sub> are recorded. Measurements of absorption in solids show a greater absorption in imperfect NaCl crystals than in perfect crystals, and reveal considerable differences in the vol. absorption of different metals. J. S. A.

**Ultrasonic waves and chemical investigation.** G. SCHMID (Angew. Chem., 1936, 49, 117—127).—A review. A. J. M.

**Transition temperature.** R. PEIERLS (Helv. phys. Acta, 1934, 7, 81—83; Chem. Zentr., 1935, ii, 184).—Theoretical. The phenomena of transition and melting are considered from the viewpoint of displacements of mutually coupled, regularly arranged atoms, held by cohesive forces, the m.p. being that temp. above which the magnitude of the induced displacement increases with distance. J. S. A.

**Specific heat of solid helium and melting heat of helium.** W. H. KEESOM and (Miss) A. P. KEESOM (Physica, 1936, 3, 105—117).—Data for  $c_v$  of solid He are recorded in the region 1.2—3.0° abs. and  $d$  0.20—

0.22.  $c_v$  increases more rapidly with  $T$  than would follow from Debye's relation.  $\Theta_D$  is > the val. given by Kaischew and Simon (A., 1934, 589), and changes from 37 at 1.2° and  $d$  0.218 to 25 at 2.18° and  $d$  0.201, the  $\Theta$ - $T$  relation being linear. The heats of fusion at 2.5°, 3.0°, and 3.5° abs. are 0.835, 1.089, and 1.365 g.-cal. per g., respectively. Data for co-existing solid and liquid densities are also recorded. L. J. J.

**Effect of dissolved air on the specific heat of water over the range 15—20°.** E. O. HERCUS (Proc. Physical Soc., 1936, 48, 282—284; cf. *ibid.*, 1935, 47, 1003).—The effect is calc. thermodynamically from the solubility data for the case when no air is liberated. The sp. heat of H<sub>2</sub>O saturated with air at 20° and atm. pressure is > that of air-free H<sub>2</sub>O by  $6 \times 10^{-6}$  g.-cal. per g. N. M. B.

**Atomic heat of nickel at low temperatures.** K. CLUSIUS and J. GOLDMANN (Z. physikal. Chem., 1936, B, 31, 256—262; cf. A., 1935, 574).—Measurements at 10—30° abs. show an anomalous fall of sp. heat with temp., which is reconcilable with neither Bloch's  $T^{3/2}$  law for ferromagnetism nor Sommerfeld's  $T$  law for free electrons (cf. this vol., 148). R. C.

**Specific heat of Seignette salt. I. Anomaly at upper Curie point.** A. A. RUSTERHOLZ (Helv. phys. Acta, 1935, 8, 39—54; Chem. Zentr., 1935, i, 2957).—Work reported previously (A., 1935, 1454) is described in detail. Anomalies in the Curie point, calc. from  $C_p$  and from the dielectric const., and in the inner field are discussed. J. S. A.

**Heat capacity, entropy, and free energy of rubber hydrocarbon.** N. BEKKEDAH and H. MATHESON (J. Res. Nat. Bur. Stand., 1935, 15, 503—515).—Vals. of heat capacity at 14—320° abs. are given for the cryst. and amorphous forms of rubber, prepared by digesting latex with steam at 190° and extracting resins and hydrolysis products with EtOH and H<sub>2</sub>O. There was a transition temp. at approx. 199° abs. The cryst. form fuses at 284° abs. The entropy and standard free energy of formation were calc. H. J. E.

**Thermal properties of an incompletely degenerate Fermi gas.** N. F. MOTT (Proc. Camb. Phil. Soc., 1936, 32, 108—111).—Mathematical. The sp. heat and paramagnetic susceptibility of an electron gas obeying the Fermi-Dirac statistics are calc. for all temp. including those for which the gas is partly degenerate. A. J. M.

**Aggregative states. II. Ratio of the temperature interval of existence of substances in the solid and liquid states.** E. I. ACHUMOV (J. Gen. Chem. Russ., 1935, 5, 1445—1454; cf. this vol., 21).—Theoretical. The aggregative coeff.,  $\phi = (T_b - T_m)/T_m$ , where  $T_b$  is the b.p. and  $T_m$  the m.p. (abs.), is evaluated for a no. of elements and compounds, and certain regularities are pointed out. R. T.

**Density of liquid phosphorus.** S. DOBRIŃSKI (Bull. Acad. Polonaise, 1935, A, 253—259).—Data are recorded at 7—68°:  $d = 1.78685 - 0.0009386t$ . T. G. P.

**Density of mercury at 0°.** T. BATUECAS and E. L. CASADO (J. Chim. phys., 1936, 33, 41—50).—



$d_4^0$  for Hg cleaned chemically, doubly distilled, and fractionated is  $13.59539 \pm 0.00001$  g. per ml.

J. W. S.

**Carbon monoxide [rectilinear diameter] and helium.** E. MATHIAS and C. A. CROMMELIN (Ann. Physiq., 1936, [xi], 5, 137—166).—Densities of liquid and saturated vapour for CO between  $132.91^\circ$  ( $T_c$ ) and  $68.13^\circ$  abs. have been measured. The law of the rectilinear diameter is approx. obeyed, giving  $d_c$  0.3010 and crit. coeff. ( $K$ ) 3.394; earlier vals. for other gases are corr. The true diameter has a point of inflexion, and gives  $d_c$  0.3050 and  $K$  3.440. The difference between the true and rectilinear diameters is discussed. The temp. variations of  $p$ ,  $L$ , and internal and external heats of vaporisation are calc. by Clapeyron's equation. The density curve of He (cf. A., 1926, 774) is corr. Application of Clapeyron's equation as above shows that the sp. heat of the saturated vapour is negative, in agreement with theory.

L. J. J.

**Vapour pressure of silicon tetrachloride.** K. KEARBY (J. Amer. Chem. Soc., 1936, 58, 374—375).—Data for the range  $0$ — $60^\circ$  can be expressed by  $\log p = 7.6414 - 1572.3/T$ , from which it follows that the b.p. at 760 mm. is  $57.0^\circ$ .

E. S. H.

**Vapour pressures of metals.** A. EUCKEN (Metallwirts., 1936, 15, 27—31, 63—68).—A crit. survey of existing information on both experimental and theoretical aspects of the subject.

C. E. H.

**Free energies and vapour pressures of the alkali metals.** A. R. GORDON (J. Chem. Physics, 1936, 4, 100—102).—From spectroscopic data, the free energies of the diat. vapours of  $K_2$ ,  $Na_2$ , and  $Li_2$ , and the equilibrium consts. for dissociation into the monat. forms, have been calc. From these consts. and v.-p. data, equations for the partial pressures of atoms and mols. in the saturated vapour, for temp. up to the normal b.p., have been deduced. The entropies of solid Na and K have also been calc. from the v.-p. equation.

M. S. B.

**Isotherms of  $CO_2$ .** I. Between  $0^\circ$  and  $150^\circ$  and pressures from 16 to 250 atm. (Amagat densities 18—206). A. MICHELS and (Mrs.) C. MICHELS. II. Between 70 and 3000 atm. (Amagat densities 200—600). A. MICHELS, (Mrs.) C. MICHELS, and H. WOUTERS (Proc. Roy. Soc., 1935, A, 153, 201—214, 214—224).—I. The technique and results of isotherm measurements up to densities of 200 Amagat units are described. The vals. of  $[(pv)_t - (pv)_{75}]/(t - 75)$  are calc. and plotted against  $t$ , and from the slope of the curves it can be seen that the sp. heat  $c_p$  increases with increasing density  $d$ .

II. The method has been modified for higher densities (200—600 Amagat units).  $c_p$  increases with increasing  $d$  to a max. for  $d = 226.7$ , then decreases and passes through a min. for  $d$  390—460 Amagat units. The position of the max. coincides with the density of the crit. point.

L. L. B.

**Data of state of phosphine at low pressures and from  $190^\circ$  to  $300^\circ$  abs.** E. A. LONG and E. A. GULBRANSEN (J. Amer. Chem. Soc., 1936, 58, 203—205).—Apparatus and technique for comparing

directly the properties of a gas at low temp. and pressure with the known behaviour of He are described. Data have been determined for  $PH_3$ , and the second virial coeff.  $B$  calc. The dependence of  $B$  on temp. is well represented by a power series in  $1/T$ .

E. S. H.

**Internal pressure in gases. VII.** K. JABE CZYŃSKI (Rocz. Chem., 1935, 15, 450—459; cf. A., 1934, 952).—Van der Waals' equation is expressed as  $(p + P)(w - b) = RT$ , where  $p$  is the external pressure, and  $P$ , the internal pressure, is the resultant of the cohesive and repulsive forces between the mols., and  $= \{a - f(w)T\}/w^2$ . The vals. of  $P$  for various gases at different  $p$ ,  $T$ , and  $w$  have been evaluated, and it is shown that  $P$  rises abruptly with transition from the gaseous to the liquid state, showing that this process is not continuous.

R. T.

**Constants in the equation of state for the rare gases.** E. BRANDER and K. TAMMINEN (Soc. Sci. Fenn., Comm. phys.-math., 1935, 8, No. 5, 6 pp.; Chem. Zentr., 1935, i, 3519).—Vals. for van der Waals'  $a$  are calc., using the Wasastjerna equations (cf. A., 1935, 691).

H. J. E.

**Thermal expansions of alloyed bismuth crystals in the region of the eutectic m.p.** A. GOETZ, J. W. BUCHTA, and T. L. HO (Physical Rev., 1934, [ii], 46, 538; cf. A., 1935, 156).

L. S. T.

**Thermal conductivity of carbon dioxide.** T. L. IBBS (Phil. Mag., 1936, [vii], 21, 508—509).—An examination of Archer's conductivity-temp. curve for  $CO_2$  (cf. A., 1935, 691) appears to indicate an effect due to a change in the nature of the intermol. field at  $140^\circ$ .

N. M. B.

**Thermal conductivities of metals and alloys.** J. W. DONALDSON (Metallurgia, 1936, 13, 159—160).—A review of recent work.

**Method of determining the state of degeneration of a gas.** A. VAN ITTERBEEK (Nature, 1936, 137, 109).—The method consists in determining  $\eta$  at different temps. and then calculating the mean velocity of the mols. from Stokes' formula. With  $O_2$  at  $293^\circ$ ,  $90^\circ$ , and  $72^\circ$  abs. the val. obtained for the mean velocity agrees with that deduced from classical theory.

L. S. T.

**Influence of an electric field on the viscosity of liquids.** P. T. SOKOLOV and S. L. SOSINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 135—138).—The variation in the time of flow through the capillary of an Ostwald viscosimeter with and without an applied electric field has been investigated for  $COMe_2$ ,  $EtI$ ,  $MeOH$ ,  $Et_2O$ ,  $CHCl_3$ ,  $C_6H_{14}$ , and  $C_6H_6$  at different temp. Non-polar mols. are uninfluenced; polar mols. show the greatest variations at higher field strengths, the ratios of the times of flow with the applied field to the times of flow with no applied field increasing as the field strengths are increased. The higher is the dipole moment of the mol., the greater is the extent to which it is influenced.

W. R. A.

**Viscosity of liquid gallium over an extended range of temperature.** K. E. SPELLS (Proc. Physical Soc., 1936, 48, 299—311).—Using a special technique to overcome surface-film difficulties, measurements are given for  $\eta$  over the temp. range  $30$ —



1100°, and are compared with vals. calc. on Andrade's theory of variation with temp. At 1100° the decrease of  $\eta$  is 2% per 100°. N. M. B.

***p-v-T* relations of gaseous mixtures.** E. R. GILLILAND (Ind. Eng. Chem., 1936, 28, 212—215).—The isometric (*p-T* curve, *v* const.) for a pure gas approximates closely to a straight line at *T* > crit. temp. The slope of the isometric for a mixture can be obtained from the molal average of the slopes of the isometrics for the constituents, all measured at the same mol. concn. This fact, in addition to a simple method for obtaining the internal pressure from the isometrics, enables the *p-v-T* relationships for a mixture to be calc. more accurately than by the use of Dalton's or Amagat's laws. The theory is applied to  $A-C_2H_4$ ,  $H_2-CO$ , and  $CH_4-N_2$  mixtures. A. J. M.

**Viscosities of deuterium-hydrogen mixtures.** A. B. VAN CLEAVE and O. MAASS (Canad. J. Res., 1935, 13, B, 384—389; cf. A., 1935, 432, 691, 1455).—Further measurements at 22° have shown that the diameters of  $D_2$ , HD, and  $H_2$  mols. are identical. Variation of  $\eta$  with the temp. has been derived from measurements at -78.5° and -183.4°. Jeans' temp.-viscosity relation holds approx. for the mixtures. A comparison has been made of various equations which are said to express the dependence of  $\eta$  on the composition of mixtures. E. E. A.

**Description of binary solutions.** F. O. KOENIG (J. Amer. Chem. Soc., 1936, 58, 317—318).—Theoretical. The changes associated with different modes of description (*i.e.*, the formula assigned to each component) are discussed. E. S. H.

**Densities and refractive indices of bromoform-benzene mixtures.** J. L. WHITMAN and L. CLARDY (J. Amer. Chem. Soc., 1936, 58, 237—239).—Data at 30° are recorded. The *d*-composition relation conforms closely to that for an ideal system. E. S. H.

**Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration.** XII. T. ISHIKAWA and T. BABA (Bull. Chem. Soc. Japan, 1936, 11, 8—18).—The Ishikawa viscosity formula has been applied to the experimental data for binary mixtures such as  $C_6H_6$  with alcohols or AcOH, in which one component shows marked association. The calc. and observed vals. of  $\eta$  are in close agreement. A comparison is made with the Thiesen formula for gaseous mixtures (cf. A., 1929, 500). Where there is a max.,  $\eta$  calc. from the latter is not quite coincident with the observed  $\eta$ , but no such divergence occurs with the Ishikawa formula (cf. A., 1929, 387). M. S. B.

**Viscosities of liquid mixtures.** K. E. SPELLS (Trans. Faraday Soc., 1936, 32, 530—540).—Viscosities of mixtures of  $PrOH$ ,  $Bu^iOH$ ,  $CH_2Bu^iOH$ , and  $CH_3CH_2OH$  with  $C_6H_6$  have been measured at 22°. The results, together with other data, are used to test the validity of a single-const. expression connecting  $\eta$  with the composition. The curves for the two amyl alcohols show no anomalies corresponding with those shown by the dielectric const. F. L. U.

**Investigation of equilibrium between a boiling liquid and its vapour by thermal analysis.** L.

MEYER (Z. physikal. Chem., 1936, 175, 275—283).—The determination of the b.p. of a liquid mixture and the condensation point of a mixture of vapours by heating and cooling curves, respectively, is described. The apparatus is suitable for determining the proportion of condensable constituents in a gas mixture. R. C.

**Ferromagnetism and liquid mixtures.** C. ZENER (Physical Rev., 1934, [ii], 46, 824—825).—Analogies between the development of magnetisation below the Curie point and the separation of two phases from a homogeneous liquid mixture of two types of atoms are discussed. L. S. T.

**Crystal structure of beryllium alloys.** L. MISCH (Metallwirts., 1936, 15, 163—166).—Alloys of Be with several metals of the transition series have been examined, the majority being of the type  $AB_2$  ( $B=Be$ ). The results are discussed in relation to the Hume-Rothery rule (cf. A., 1935, 926). C. E. H.

**Solidification diagram of copper-tin alloys.** W. BRONIEWSKI, J. T. JABLONSKI, and S. MAJ (Compt. rend., 1936, 202, 305—307).—A complete fusion diagram is given. Formation of the compounds  $Cu_4Sn$ ,  $Cu_3Sn$ , and  $Cu_2Sn$  is indicated. H. J. E.

**Zinc-indium alloy system.** C. L. WILSON and E. A. PERETTI (Ind. Eng. Chem., 1936, 28, 204—205).—Thirty alloys have been examined, and the equilibrium diagram has been obtained. The eutectic contains 96% In and 4% Zn, and the eutectic temp. is 143.5°. The alloys become softer as the proportion of In is increased. A. J. M.

**Phase diagram of the system silver-gallium.** F. WEIBKE, K. MEISEL, and (FRL.) L. WIEGELS (Z. anorg. Chem., 1936, 226, 201—208).—Thermal, microscopic, and X-ray observations have been made. The data for the Ag-rich alloys agree with those of Hume-Rothery *et al.* (A., 1934, 725). Five series of mixed crystals are indicated. The system is compared with other systems containing Ag and Ga. The at. vol. of Ga in Ag, like that of Al, is > in Cu. M. S. B.

**Velocity of transformation in cadmium-magnesium alloys in the region of composition  $MgCd$ .** N. L. STEPANOV and S. A. BULACH (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 147—151).—The electrical conductivity of alloys tempered from above the transition points and also of annealed alloys has been measured at 25°, 50°, 75°, and 100°. The annealed alloys, stable at low temp., have the highest conductivity. Transition velocities have been determined at 100°. W. R. A.

**(A) Platinum-antimony alloys. (B) Platinum-rhodium alloys.** V. A. NEMILOV and N. M. VORONOV (Z. anorg. Chem., 1936, 226, 177—184, 185—191; cf. A., 1935, 440).—(A) The presence of a solid solution on the Pt side seems to be indicated.

(B) The thermoelectric power of systems of chemically pure Pt with different Pt-Rh alloys increases with the concn. of Rh, but more rapidly at low than at high concn. Pt-Rh alloys are not readily attacked by acids. By heating at 750° a slight surface oxidation takes place on alloys con-



taining  $>10\%$  Rh. At  $1150^\circ$  the oxide is dissociated leaving a bright metallic surface. M. S. B.

**Transformation in the copper-gold alloy  $\text{Cu}_3\text{Au}$ .** C. SYKES and H. EVANS (J. Inst. Metals, 1936, 58, Advance copy, 443–472).—From X-ray examination and from measurements of the electrical resistance and sp. heat of the Cu–Au alloy with 25 at.-% Au it is shown that the general character of the transformation is similar to that predicted by Bragg and Williams (A., 1934, 954); it takes place continuously from the crit. temp. to a very low temp. and the equilibrium is a dynamic one. The at. rearrangement proceeds first by the formation of nuclei having a relatively high degree of order and then, at const. temp., by the growth of these nuclei to a size approximating to that of the individual crystals, or, at gradually falling temp., by growth of the nuclei accompanied by an increase in their degree of order due to the fall in temp. Since nuclei formation is not taken into account in the statical theory of super-lattices it follows that the actual rate of relaxation into the equilibrium state differs considerably from that predicted by the theory. Very appreciable differences in the properties of the alloy can be effected by variations in the heat-treatment, but all are strictly reproducible, which confirms the conclusion that the transformation is an intra-cryst. phenomenon almost independent of grain-boundary effects. A. R. P.

**I. Paramagnetism of nickel alloys.** C. MANDERS. **II. Magnetic properties of the metallic state and energy of interaction between magnetic atoms.** L. NÉEL (Ann. Physique, 1936, [xi], 5, 167–231, 232–279).—I. Vals. for the sp. susceptibilities of dil. solid solutions of Ag, Au, Al, Ti, Zr, Si, Sn, Pb, V, As, Sb, Cr, Mo, W, Mn, Ru, Pd, and Pt are recorded for various temp. above the Curie point. The Curie point (0) and Curie const. (c) are calc. for each alloy. Deviations from the Curie–Weiss law are observed, due to a superimposed paramagnetism (a), which is independent of temp.

**II. Theoretical.** The variation of c with concn. of added metal, considered in relation to the results of Sadron (A., 1932, 679) for saturation magnetisation below 0, shows that in passing from the ferromagnetic to the paramagnetic state, there is no change in the no. of electrons (0.61 per Ni atom) responsible for the magnetic properties. The superimposed paramagnetism  $\alpha$  is due to the antiparallel arrangement of added atoms in the Ni lattice. The energy of interaction between magnetic atoms is discussed, and shown to depend only on the distance between their magnetic layers. L. J. J.

**Photo-electric effect of metallic alloys.** I. L. BELLADEN and G. GALLIANO (Annali Chim. Appl., 1936, 26, 30–34).—The photo-electric sensitivity (reciprocal of time required to produce unit charge on the electrometer, as compared with Cu) of Cu–Sn alloys has been measured in a new form of apparatus permitting the simultaneous examination of four samples; when plotted against Sn content the photo-electric sensitivity gives a graph with singular points at  $\text{Cu}_4\text{Sn}$ ,  $\text{Cu}_3\text{Sn}$ , and  $\text{Cu}_3\text{Sn}_2$ . E. W. W.

**Laws of valency electron concentration in binary intermetallic alloys.** H. PERLITZ (Acta Comm. Univ. Tartu., 1933, A, 24, No. 2, 16 pp.; cf. A., 1934, 22).—The Westgren and Hume-Rothery rule applies to  $\beta$ -,  $\gamma$ -, and  $\epsilon$ -alloys, the vals. of the ratio of the no. of valency electrons to the no. of atoms being 3:2, 21:13, and 7:4, respectively. A necessary condition for the existence of these structures is that one of the metals should contribute  $\leq 2$ , and the other  $\geq 1$ , valency electrons to the lattice structure. Various examples are discussed. CH. ABS. (e)

**Formation of spherical eutectic inclusions in alloys.** W. GELLER (Metallwirts., 1936, 15, 141–142).—Spherical eutectic inclusions have been observed in several Fe and Al alloys. The conditions for their formation are a narrow freezing range and rapid cooling just above the solidus. C. E. H.

**The system Mg–Cu–Al, particularly across the section  $\text{MgCu}_2$ – $\text{MgAl}_2$ .** F. LAYES and H. WITTE (Metallwirts., 1936, 15, 15–22).—Cu may be replaced by Al in  $\text{MgCu}_2$  without change of cryst. structure up to approx. 35%  $\text{MgAl}_2$ . With higher  $\text{MgAl}_2$  contents, hexagonal phases appear, but there are no definite limits of stability for the various structures. For the Al corner of the system previous results are not fully confirmed. Two compounds,  $\text{Mg}_2\text{Cu}_2\text{Al}_3$  and  $\text{Mg}_3\text{Cu}_7\text{Al}_{10}$ , are reported. C. E. H.

**System iron–aluminium–carbon.** R. VOGEL and H. MADER (Arch. Eisenhüttenw., 1935–1936, 9, 333–340).—The system contains six primary crystal phases:  $\alpha$ -Fe containing Al and Fe, ternary  $\gamma$ -Fe, graphite, ternary  $\epsilon$  ( $\text{FeAl}$ ) $_n$ , ternary  $\delta$  ( $\text{FeAl}_3$ ) $_n$ , and  $\text{Al}_4\text{C}_3$ . There are four 4-phase equilibria during solidification, viz., (1) liquid (Fe 83.1, Al 14.5%) +  $\alpha$  (Fe 85.1, Al 14.8%) +  $\gamma$  (Fe 91.7, Al 7.5%)  $\rightleftharpoons$   $\epsilon$  (Fe 85.2, Al 13%) at  $1335^\circ$ ; (2) liquid (Fe 83.35, Al 13.5%) +  $\gamma$  (Fe 90.3, Al 7.2%)  $\rightleftharpoons$   $\epsilon$  (Fe 83.5, Al 13%) + graphite at  $1132^\circ$ ; (3) liquid (Fe 56.7, Al 43%) +  $\delta$  (Fe 54.8, Al 45%)  $\rightleftharpoons$   $\epsilon$  (Fe 55.8, Al 44%) +  $\text{Al}_4\text{C}_3$  at  $1135^\circ$ ; (4) liquid (Fe 69.92, Al 29%)  $\rightleftharpoons$   $\epsilon$  (Fe 70.65, Al 29%) + graphite +  $\text{Al}_4\text{C}_3$  at  $1120^\circ$ . In the solid state three points of 4-phase equilibria exist, thus (5)  $\epsilon$  (Fe 71.7, Al 28%) +  $\text{Al}_4\text{C}_3$   $\rightleftharpoons$   $\delta$  (Fe 58.8, Al 41%) + graphite at  $1115^\circ$ ; (6)  $\epsilon$  (Fe 80, Al 17.5%) +  $\gamma$  (Fe 92.5, Al 6.9%)  $\rightleftharpoons$   $\alpha$  (Fe 92.3, Al 7.6%) + graphite at  $1111^\circ$ ; (7)  $\epsilon$  (Fe 72.85, Al 27%) + graphite  $\rightleftharpoons$   $\alpha$  (Fe 91.45, Al 8.5%) +  $\delta$  (Fe 71.3, Al 28.5%) at  $1100^\circ$ . Addition of Al to Fe–C alloys lowers the ledeburite eutectic temp., raises the pearlite transformation temp., extends the pearlite field, and favours the pptn. of graphite. A. R. P.

**System iron–cobalt–cobalt silicide–iron silicide.** R. VOGEL and K. ROSENTHAL (Arch. Eisenhüttenw., 1935–1936, 9, 293–299).—Microscopic and thermal examination of the system shows that FeSi and CoSi form a continuous series of solid solutions with one another and that a ternary compound  $\text{FeCoSi}$  exists below  $980^\circ$ . In the Fe–Co– $\text{Co}_2\text{Si}$ – $\text{FeCoSi}$ –FeSi section there are five planes of 4-phase equilibria, viz., liquid +  $\alpha$   $\rightleftharpoons$   $\gamma$  + FeSi at  $1185^\circ$ , liquid +  $\text{Co}_2\text{Si}$  solid solution  $\rightleftharpoons$  ternary  $\alpha$ -Fe + ternary  $\alpha$ - $\text{Co}_2\text{Si}$  at  $1180^\circ$ , liquid  $\rightleftharpoons$  ternary  $\alpha$ -Fe + ternary



$\gamma$ -Fe+Co-rich solid solution at 1165° and liquid  $\rightleftharpoons$  ternary  $\beta$ -Co<sub>2</sub>Si solid solution+ternary  $\gamma$ -FeSi at 1170°; at 985°  $\alpha$ -Fe reacts with FeSi to form Fe<sub>3</sub>Si<sub>2</sub> and  $\gamma$ -Fe. The compounds Co<sub>2</sub>Si and FeCoSi form a continuous series of solid solutions and hence the 3-phase equilibria in the system Co<sub>2</sub>Si-CoSi merge into those of FeSi-FeCoSi. Diagrams for const. Fe-Co ratios from 8:1 to 1:13 and for the equilibria at 20° and 1160° together with photomicrographs are given. A. R. P.

Diffusion of carbon, silicon, and manganese in solid and liquid iron. M. PASCHKE and A. HAUTTMANN (Arch. Eisenhüttenw., 1935—1936, 9, 305—309).—The diffusion of C in solid Fe is given by  $\log D = 4.6248 - 7.95 \times 10^3/T$ , where  $T$  is abs. temp. The rate of diffusion of Mn into Fe at 1400° appears to be about 0.01 times that of C. The diffusion coeff. of Mn in liquid Fe at 1530° is 9.1 and at 1570° 8.7 sq. cm. per 24 hr.; that of Si at 1540° is 3.3 sq. cm. per 24 hr. A. R. P.

Structure of solid solutions of Fe<sub>2</sub>O<sub>3</sub> in Mn<sub>2</sub>O<sub>4</sub>. E. J. W. VERVEY and M. G. van BRUGGEN (Z. Krist., 1935, 92, 136—138).—The system Mn<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> has been studied by powder photographs. B. W. R.

Piezometric researches. II. Mutual solubility of liquids. G. POPPE (Bull. Soc. chim. Belg., 1935, 44, 640—657; cf. A., 1935, 1314, 1457).—The crit. solution temp. and their variation with pressure have been determined for 36 binary mixtures, including 5 mixtures containing D<sub>2</sub>O. Replacement of H<sub>2</sub>O by D<sub>2</sub>O increases the range of incomplete miscibility. Glycerol and guaiacol are completely miscible, but small amounts of H<sub>2</sub>O cause separation. The salting-out action of KCl on  $\alpha$ -picoline-D<sub>2</sub>O mixtures is > with  $\alpha$ -picoline-H<sub>2</sub>O mixtures. J. W. S.

Comprehensive  $\log p-1/T$  diagram for binary system methylamine-water. W. MEHL [with FELSING and THOMAS] (Z. ges. Kälte-Ind., 1935, 42, 13—14; Chem. Zentr., 1935, i, 3021).—B.p.-concn.,  $\log p-1/T$ , and solubility-temp. data at 1 atm. are recorded. J. S. A.

Solubility relationships of 96% alcohol and glyceryl nitrate. D. A. COPEMAN (J. S. African Chem. Inst., 1936, 19, 17—18).—The miscibility has been studied between 15° and 40°. J. S. A.

Solubility of sulphur dioxide in sulphuric acid. J. MILBAUER (Bull. Soc. chim., 1936, [v], 3, 221—224).—Data are recorded for H<sub>2</sub>SO<sub>4</sub> ( $d$  1.824) at 23—237° and H<sub>2</sub>SO<sub>4</sub> ( $d$  1.53) at 25—100°. E. S. H.

Solubility and activity of the halogenates of some bivalent metals. Solubility and activity of (I) barium iodate and (II) lead iodate in water and in solutions of electrolytes. A. POLESSITSKI (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 193—196, 197—200).—The solubility of Ba(IO<sub>3</sub>)<sub>2</sub> and of Pb(IO<sub>3</sub>)<sub>2</sub> in H<sub>2</sub>O between 0° and 100°, and the solubility and activity coeffs. at 25° in solutions containing KNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and KIO<sub>3</sub>, have been determined. R. S.

Salts of higher alkylsulphonic acids. R. M. REED and H. V. TARTAR (J. Amer. Chem. Soc.,

1936, 58, 322—332).—The solubilities of Ca, Mg, and Na alkylsulphonates ( $n$ -octyl,  $n$ -decyl, lauryl, myristyl, cetyl, and  $n$ -octadecyl) in H<sub>2</sub>O have been determined at 25° and 60°. Data for surface tension, interfacial tension against C<sub>6</sub>H<sub>6</sub>, and electrical conductivity of these solutions are recorded. The interfacial tension changes with time. The conductivity relations are analogous to those of soap solutions. E. S. H.

Solubility of arsenious oxide in aqueous solutions of certain halides of alkali metals and ammonium. E. JOSEFOWICZ (Rocz. Chem., 1935, 15, 460—467).—Solubility data are recorded at 25° for solutions of Li, Na, K, and NH<sub>4</sub> chlorides and bromides, and of KI and NaI. The existence of mol. compounds is said to be indicated. R. T.

Influence of NH<sub>4</sub>Cl on the solubility of CoHg(SCN)<sub>4</sub>. B. V. J. CUVELIER (Z. anorg. Chem., 1936, 226, 197—200).—By a method previously described (A., 1934, 1323), the solubility has been determined at temp. up to 80° and concns. of aq. NH<sub>4</sub>Cl up to 3*N*. The solubility increases with temp., and more rapidly for higher [NH<sub>4</sub>Cl]. M. S. B.

Solubility of benzoic and salicylic acids in mixtures of organic solvents. P. G. DESAI and A. M. PATEL (J. Indian Chem. Soc., 1935, 12, 808—812).—In mixtures of non-polar solvents (C<sub>6</sub>H<sub>6</sub> with PhMe, xylene, or hexane) the solubility-composition curves are straight lines. The solubility in mixtures of polar and non-polar solvents (CHCl<sub>3</sub> or COMe<sub>2</sub> with aromatic hydrocarbons) gives a curve which is concave or convex to the composition axis; in mixtures of C<sub>6</sub>H<sub>6</sub> with MeOH, EtOH, Pr<sup>n</sup>OH, or Bu<sup>n</sup>OH the solubility curve passes through a max. E. S. H.

Fractionation of barium salts containing radium. (MME.) B. E. MARQUES (J. Chim. phys., 1936, 33, 1—40; cf. A., 1934, 22, 343, 726).—The distribution of Ra between solid and liquid phases (cf. A., 1925, ii, 381) is found to be the same whether the solid phase is obtained by crystallisation of supersaturated solutions, cooling of saturated solutions, or pptn., and whatever be the anion present (Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, or CO<sub>3</sub><sup>2-</sup>). J. W. S.

Adsorption isotherms. Critical conditions. R. H. FOWLER (Proc. Camb. Phil. Soc., 1936, 32, 144—151).—Mathematical. A. J. M.

Chemisorption on charcoal. VII. Adsorption of water vapour. C. G. LAWSON (Trans. Faraday Soc., 1936, 32, 473—478; cf. A., 1935, 27).—Earlier work has been repeated and extended using a sorption balance designed to measure adsorption of H<sub>2</sub>O on charcoal covered with various surface oxides, small quantities of desorbed gases being continuously removed. Isotherms are given for charcoals activated at different temp. The mean time of sojourn of H<sub>2</sub>O mols. on the surface is increased in the presence of the surface oxide formed at about 400°, but decreased by the oxide formed at high temp. The extent of hysteresis has been examined for two charcoals. Chemisorption is not observed with ash-free charcoal. Adsorption on graphite is of the same type and cannot be attributed to capillary condensation. O. J. W.



**Adsorption isotherm of heavy water on charcoal.** A. KING and C. G. LAWSON (Trans. Faraday Soc., 1936, 32, 478—481).—The isotherms of  $D_2O$  and of  $H_2O$  on outgassed charcoal at  $110^\circ$  are shown to be very similar. No special theoretical significance can be attached to the slightly greater adsorption of  $D_2O$ . O. J. W.

**Sorption of bromine and iodine by activated charcoal.** L. H. REYERSON and A. E. CAMERON (J. Physical Chem., 1936, 40, 233—237; cf. A., 1935, 696).—Equilibrium data for the sorption of Br by activated C at  $58^\circ$ ,  $98.1^\circ$ ,  $137.6^\circ$ , and  $178.4^\circ$  and of I at  $178.4^\circ$  and  $218.8^\circ$ , and also rates of adsorption and desorption of Br and I at  $137.6^\circ$ , are given. M. S. B.

**Dissociation equilibrium of hydrogen and its adsorption on tungsten.** J. K. ROBERTS (Proc. Camb. Phil. Soc., 1936, 32, 152—157).—The application of a formula derived from a kinetic treatment of the process of desorption in which a const. evaporation coeff. for desorbing particles is assumed (this vol., 155) leads to vals. for the rate of evaporation of H from W which do not agree with the dissociation equilibrium, if the results of Langmuir *et al.* (A., 1931, 782) are used. The nature of the surface reactions occurring is discussed. It would appear that measurements of the rate of removal of the adsorbed film of  $O_2$  on W do not afford a measure of the rate of evaporation of O atoms, or that it is not possible to obtain a general first approximation formula for the rate of evaporation of adsorbed atoms in terms of the heat of adsorption. A. J. M.

**Sorption of hydrogen and deuterium by copper and palladium.** I. Behaviour of copper and copper oxides. II. Sorption by palladium and diffusion through copper. H. W. MELVILLE and E. K. RIDEAL (Proc. Roy. Soc., 1935, A, 153, 77—88, 89—103).—I. CuO is reduced by at. H and D at  $20^\circ$  with the same velocity. It is more rapidly reduced by mol.  $H_2$  than  $D_2$  at  $156$ — $269^\circ$ , the difference in energy of activation being  $0.4$  kg.-cal.  $H_2$  and  $D_2$  are sorbed by, and desorbed from, Cu with the same velocity at  $71$ — $200^\circ$ ; at higher temp., however,  $H_2$  is sorbed slightly more rapidly. The results indicate that the process of activated diffusion of  $H_2$  into Cu is composite, including a true activated diffusion. There is also another process independent of the nature of the two gases which determines the rate at low temp.

II.  $H_2$  diffuses more rapidly than does  $D_2$  through Pd and through thin films of Cu and Ni supported on Pd, at temp. from  $150^\circ$  to  $350^\circ$  and pressures  $1$ — $200$  mm. In Cu it has been shown by using composite films, Cu-Pd-Cu and Pd-Cu-Pd, that the rate-determining step is not due to any process connected with the gas-metal interface.  $H_2$  is more sol. than  $D_2$  in Pd, the difference in diffusion velocities being due partly to this, and partly to the greater mobility of  $H_2$  in Pd. Potential barriers have been constructed from diffusion and solubility data. L. L. B.

**Active oxides. XCVIII. Changes in sorptive power of mixtures of calcium oxide with ferric oxide, and of calcium oxide and beryllium oxide with chromic oxide, during chemical combin-**

ation. J. HAMPEL (Z. anorg. Chem., 1936, 226, 132—140).—The oxide mixtures were prepared by the method previously described (A., 1934, 490; 1935, 440), heated at various temp. up to  $1000^\circ$ , and the sorptive power ( $s$ ) measured for Congo-red, acid fuchsin, and eosin (cf. A., 1935, 930). The  $s$ -temp. curves fall with rise in the temp. at which the preliminary heating takes place, but there are many irregularities resulting in max. and min. and points of inflexion. The curves are compared with those for the variation of other physical properties with temp. M. S. B.

**Sorption of gases and vapours by aerosol particles.** A. KRASSILCHIKOV (Kolloid-Z., 1936, 74, 138—147).—The concn. of a sorbable gas or vapour is determined in the presence or absence of aerosol particles by measuring its diffusion into a long narrow tube, the vol. of which is small compared with that of the experimental vessel with which it is connected. By this means the sorption of Br vapour by paraffin oil, resin, and  $NH_4Cl$  particles has been determined. The sorption isotherms for the oil indicate dissolution rather than adsorption. With resin, bromination occurs.  $NH_4Cl$  shows purely surface effects, and the adsorption can be expressed by Langmuir's equation. With increasing [Br] the adsorption per sq. cm. reaches a max. and thereafter decreases, apparently owing to rapid coagulation and desorption at high [Br]. F. L. U.

**Adsorption and diffusion in zeolite crystals.** A. TISELIUS (J. Physical Chem., 1936, 40, 223—232).—The adsorption of  $NH_3$  by analcite follows the Langmuir law and the heat of adsorption is const. over a wide range, indicating a lack of interaction between adsorbed mols. When  $NH_3$  is adsorbed by a Cu chabasite, prepared by cationic exchange in aq.  $CuSO_4$ , the crystal has the absorption spectrum of a solution containing  $CuNH_4$  ions, showing that co-ordination valencies play a part in adsorption. The diffusion const. of  $H_2O$  in a dehydrated heulandite crystal has been determined by following, with the polarising microscope, the changes in double refraction during adsorption of  $H_2O$ . The diffusion is anisotropic. It follows the ordinary diffusion laws of solutions for small concn. differences, but for larger is largely dependent on concn. Since concn. at the surface remains const. and equal to the saturation val., during adsorption, diffusion in the crystal must be the rate-determining factor. M. S. B.

**Adsorption of electrolytes on crystal surfaces.** (MISS) L. DE BROUCKÈRE (Chem. Weekblad, 1936, 33, 104—109).—A reply to criticism by Kolthoff (A., 1934, 727; cf. A., 1933, 457; 1934, 359). D. R. D.

**Adsorption at crystal-solution interfaces. IX. Concentration of foreign substances in solution relative to the quantity adsorbed by the host crystal.** W. G. FRANCE and (MISS) P. P. DAVIS (J. Physical Chem., 1936, 40, 177—185).—There is no relation between the no. of colloidal particles of dye in solution and the amount of dye adsorbed by a given host crystal. Crystals containing adsorbed impurities have the same lattice consts. as the pure crystals. The dichroism frequently observed in



crystals containing adsorbed dye appears to be due to orientation of the dye mols. with respect to the adsorbing surface. The colour effects observed, when crystals of  $\text{NH}_4$  alum containing Pontamine Sky Blue 6B are examined under a polarising microscope, indicate that the long axes of the adsorbed dye mols. are probably perpendicular to the cube faces of the crystals. The data for the adsorption of dye by alum and nitrate crystals are not in accordance with either the Langmuir or adsorption isotherm equations, but are reproduced over nearly the whole range by  $a = kc^{1/n} - k'c^{-1/n}$ , where  $a$  is the mol. ratio of impurity to host crystal and  $c$  the ratio in the solution. The cause of the failure of the adsorption curves to pass through the origin is discussed. M. S. B.

**Adsorption of anions by precipitated calcium oxalate.** T. P. CHAO, D. K. WU, W. P. CHIANG, and T. F. CHAO (J. Chinese Chem. Soc., 1936, 4, 6-19).—The adsorption of anions by  $\text{CaC}_2\text{O}_4$  occurs in the order  $\text{Fe}(\text{CN})_6''' > \text{NO}_3' > \text{Fe}(\text{CN})_6''' > \text{SO}_4''' > \text{NO}_2' > \text{ClO}_3' > \text{Cl}' > \text{Br}' > \text{CNS}'$ , i.e., except for  $\text{NO}_3'$  in the order of decreasing ionic charge. The order is slightly different from that with  $\text{BaSO}_4$  (cf. this vol., 154) and adsorption is much less. Adsorption is usually in the same order as the solubility of the Ca salts; the different behaviour of the univalent anions indicates that a sp. factor is involved. Special methods for the analysis of adsorbed ions are described. R. S. B.

[Theory of coprecipitation.] L. DE BROUCKÈRE (Bull. Soc. chim. Belg., 1935, 44, 625-636; cf. A., 1934, 359).—A reply to Kolthoff (*ibid.*, 727).

**Sorption of lime by cellulose and wood.** G. L. LABOQUE and O. MAASS (Canad. J. Res., 1935, 13, B, 380-383).—The adsorption of  $\text{CaO}$  is  $>$  that of  $\text{NaOH}$ . Considerable time is required for saturation adsorption to take place. The adsorption on similar woods is the same but much  $>$  that on cotton cellulose. E. E. A.

**"Apparent" and "true" adsorption functions.** K. S. G. DOSS and B. S. RAO (J. Mysore Univ., 1935, 8, 49-61).—Adsorption on  $\text{SiO}_2$  gel from  $\text{C}_5\text{H}_5\text{N}-\text{H}_2\text{O}$  and  $\text{CCl}_4-\text{H}_2\text{O}$  mixtures is discussed. C. W. G.

**Reversible adsorption in the surface of soap solutions.** J. W. MCBAIN and D. A. WILSON (J. Amer. Chem. Soc., 1936, 58, 379-380).—The fact that several hr. are required to complete the adsorption of solutes at the surface of their solutions throws doubt on many recorded surface tension measurements. E. S. H.

**Sorption of acid sodium oleate.** R. F. NICKERSON (J. Physical Chem., 1936, 40, 277-286).—The kinetics of the sorption at the interface between aq. Na oleate (I) and hydrocarbon oils—both aliphatic and aromatic—have been studied by a method previously employed (A., 1932, 803). Relative sorption potentials are tabulated. The results support the view that energy transfers in colloid systems involve chemical and electrochemical processes. In the case of the systems considered, free interfacial energy is stored as electrochemical potential through the ionisation of  $\text{H}_2\text{O}$  as a result of the hydrolysis of

(I) when acid (I) is adsorbed at the interface. The causes of the failure of Gibbs' adsorption equation are discussed. M. S. B.

**Direct measurement of absolute amount of adsorption in liquid surfaces.** T. F. FORD and J. W. MCBAIN (J. Amer. Chem. Soc., 1936, 58, 378).—An interferometer method is described. E. S. H.

**Kinetics of sorption.** A. V. LYKOV (Kolloid-Z., 1936, 74, 179-183).—The distribution of temp. in a sphere of cellulose during sorption of  $\text{H}_2\text{O}$  vapour has been determined. Curves showing change of  $\text{H}_2\text{O}$  content with time for different temp. are given. F. L. U.

**Adsorption and pyknometry.** P. G. NUTTING (J. Washington Acad. Sci., 1936, 26, 1-6).—A review of technique and errors in pyknetric determinations of  $d$  for highly adsorptive clays and similar materials. H. J. E.

**Adsorption by diatomaceous filters.** E. J. HOAGLAND and J. E. RUTZLER, jun. (J. Physical Chem., 1936, 40, 215-221).—A comparison of the adsorption of different liquids or solutions by Berkeley "N" diatomaceous candles has been made by comparing the rates of flow of air through candles wetted by the different liquids. Different filters of the same rating show great variations in behaviour, probably because of different degrees of crushing of the diatoms during manufacture. Salts are adsorbed to a variable extent and  $\text{MeOH}$ ,  $\text{EtOH}$ , and  $\text{CCl}_4$  are less readily adsorbed than  $\text{H}_2\text{O}$ . The significance of these results in the methods of pore size determination is discussed. M. S. B.

**Binding of water by inorganic materials.** I. R. BULL (Angew. Chem., 1936, 49, 145-153).—Bound  $\text{H}_2\text{O}$  is classified as discontinuous or continuous according as dehydration does or does not produce a new phase. Discontinuously bound  $\text{H}_2\text{O}$  may be determined by treating the solid with dioxan (I), the  $\text{H}_2\text{O}$  removed being calc. from the change in dielectric const. of (I). With varying amounts of material and (I), a stepped dehydration curve is obtained. Attainment of equilibrium in the removal of hydration  $\text{H}_2\text{O}$  is slow; mechanically held  $\text{H}_2\text{O}$  is rapidly extracted and may be so determined. Adsorbed  $\text{H}_2\text{O}$  is determined by extraction with a small proportion of moist (I). J. S. A.

**Surface tension of calcium amalgam.** L. CONVERS (Compt. rend., 1936, 202, 289-291; cf. this vol., 142).—Measurements in vac. by the drop-wt. method with amalgams containing 0-0.0033% of Ca are described. The measurements are affected by traces of  $\text{O}_2$ . H. J. E.

**"Pockeling" of freshly swept surfaces of solutions.** D. A. WILSON and T. F. FORD (Nature, 1936, 137, 235-236).—The sudden appearance and expansion of circular patches on fresh surfaces of dil. solutions of surface-active material are described and explained. Drastic sweeping eliminates this effect. L. S. T.

**Composition of fatty acid films on water containing calcium or barium salts.** I. LANGMUIR and V. J. SCHAEFER (J. Amer. Chem. Soc., 1936, 58, 284-287).—Technique for the removal and analysis of



unimol. films on  $H_2O$  is described. In presence of  $Ca^{++}$  or  $Ba^{++}$  (about  $10^{-4}M$ ) the films formed by stearic acid are nearly pure neutral soaps when the solution has  $p_H$  11, and free fatty acid films at  $p_H$  3; they are half converted into neutral soaps at  $p_H$  5.1 for  $Ca^{++}$  and  $p_H$  6.6 for  $Ba^{++}$ . The presence of  $Ca$  or  $Ba$  increases the rigidity of the films and affects the ease with which multimol. films can be formed on metal or glass.

E. S. H.

**Action of potassium *n*-amylxanthate on chalcocite.** A. M. GAUDIN and R. SCHUHMAN, jun. (J. Physical Chem., 1936, 40, 257—275).—The results show that the collecting action of xanthates in the flotation of chalcocite (I) is due to an oriented adsorbed film formed by the reaction of xanthate ions with impurities, produced by grinding, on the surface of the mineral, and subsequent reaction with the  $Cu$  of the (I) to give  $Cu^I$  xanthate. The film cannot be leached off by ordinary solvents until sufficient of the xanthates is formed to give a complete unimol. film. Only a relatively small fraction of a unimol. film of uncatchable product, however, is necessary for efficient flotation. Malachite (II) also abstracts xanthates from the aq.  $K$  *n*-amylxanthate, but the film is removed by leaching and the (II) is non-floatable. Adsorption-reaction curves, calc. on a kinetic basis, are in good agreement with the experimental results for (I).

M. S. B.

**Stream potentials and d.c. surface conductivities in small capillaries.** H. L. WHITE, (Miss) B. MONAGHAN, and F. URBAN (J. Physical Chem., 1936, 40, 207—214).—The streaming potential,  $E/P$ , of glass capillaries diminishes with decreasing capillary diameter, due mainly to increasing sp. conductance as a result of the relatively larger surface conductance.  $E/P$  also decreases with time, probably due to a decrease in  $\zeta$ . The normal d.c. sp. surface conductance of  $0.0001M$ - $KCl$  at a Pyrex surface is approx.  $1.5 \times 10^{-9}$  mho, and of  $0.0005M$ - $KCl$   $1.7 \times 10^{-9}$  mho (cf. A., 1932, 699). Variations in  $\zeta$  for a given capillary, as shown by variations in  $E/P$ , are also reflected in the sp. surface conductance.

M. S. B.

**Influence of size, symmetry, and concentration of ions and dipoles on the dielectric potential of the solution-dielectric interface.** B. KAMIENSKI (Bull. Acad. Polonaise, 1935, A, 309—318).—It is argued that (a) small ions have little effect on the dielectric potential at the interface solution-dielectric when the dielectric const. is small, (b)  $H_2O$  dipoles are preferentially adsorbed at the solution-air interface, and (c) large mols. and ions of weak electrolytes displace  $H_2O$  dipoles at the interface. These conclusions are supported by the dielectric potentials of quinine solutions in relation to  $p_H$ , and by previous data.

T. G. P.

**Simplified dynamical method of measuring dielectric potentials at the solution-air interface.** B. KAMIENSKI and W. GOSLAWSKI (Bull. Acad. Polonaise, 1935, A, 319—322).—The reference electrode is a vertical  $Cu$  tube moistened on the inside with aq.  $CuSO_4$ , through the centre of which the solution under investigation flows in a fine stream.

T. G. P.

**Influence of hydrogen ions on the dielectric potential of the stereoisomerides quinine and quinidine.** B. KAMIENSKI and W. GOSLAWSKI (Bull. Acad. Polonaise, 1935, A, 323—326).—Dielectric potentials at the solution-air interface of quinine and quinidine solutions have been measured at  $p_H$  2—9.  $0.01M$ -Quinidine is more sensitive to  $p_H$  than  $0.01M$ -quinine; at lower concn. the quinine solutions are the more sensitive.

T. G. P.

**Behaviour of water held in fine-pored media.** B. H. WILSDON, D. G. R. BONNELL, and (Miss) M. E. NOTTAGE (Trans. Faraday Soc., 1936, 32, 570).—Errors in a paper previously published (A., 1935, 1316) are corr.

F. L. U.

**Influence of an inert solid phase on the f.p. of water and dilute aqueous solutions. II. Starch-water.** A. V. RAKOVSKI, D. N. TARASENKOV, and A. V. KOMANDIN (J. Gen. Chem. Russ., 1935, 5, 1441—1444; cf. this vol., 156).— $H_2O$  adsorbed on starch (up to 33%) does not freeze at  $-180^\circ$ ;  $H_2O$  in excess of 33% freezes at  $0^\circ$  to  $-3.16^\circ$  according to the ratio of starch surface to excess of  $H_2O$ . The presence of low concns. of solutes does not specifically affect the results. The action of surface forces is not apparent at a distance of  $> 10,000$  mol. diameters of  $H_2O$ .

R. T.

**Microcataphoresis. I. Technique.** H. C. BROWN and J. C. BROOM (Proc. Roy. Soc., 1936, B, 119, 231—244).—An experimental cell and important details of technique are described. Komagata's correction of the calculation of the stationary layer in cells with a width/depth ratio of  $< 20$  is verified.

F. A. A.

**Rate of diffusion through membranes.** S. MIYAMOTO (Kolloid-Z., 1936, 74, 194—196; cf. A., 1933, 233).—Theoretical. Under certain conditions, which are specified, the expression deduced reduces to  $\lambda\sqrt{M} = \text{const.}$  ( $\lambda$ =dialysis const.,  $M$ =mol. wt. of solute).

F. L. U.

**Diffusion of water vapour through membranes of cellulose acetate and cellulose nitrate.** S. VOSNESSENSKI and L. M. DUBNIKOV (Kolloid-Z., 1936, 74, 183—194).—The rate of diffusion of  $H_2O$  vapour through membranes of cellulose acetate (Ac no. = 56) and nitrate has been measured under varying conditions of v.p., temp., thickness and character of membrane, and is related in a simple manner to the first three variables (expressions given). Membranes formed by evaporation of a solution in contact with a polished surface are less permeable when vapour enters at the "free" (matt) surface than for the reverse direction.

F. L. U.

**Ebullioscopic constants.** C. DUVAL (Compt. rend., 1936, 202, 660—662).—It is shown that Trouton's rule may be utilised in the calculation of ebullioscopic consts.

L. J. J.

**Refractions of electrolyte solutions. IV. Complete refraction curve of potassium chloride.** A. E. BRODSKI and N. S. FILIPPOVA (Z. physikal. Chem., 1936, B, 31, 227—236; cf. A., 1934, 131).—The refraction curve has been determined from  $0.001$  to  $1.4N$  and agrees with published data for



conc. solutions, and with the conclusions previously reached.

R. C.

**Dielectric constants of dilute solutions of strong electrolytes at various temperatures.** M. JEZEWSKI, M. WIERZBICKI, and J. KAMECKI (Bull. Acad. Polonaise, 1935, A, 417—429).—The dielectric consts. ( $\epsilon$ ) of solutions of NaCl, KCl,  $\text{MgSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{Ba}_2\text{Fe}(\text{CN})_6$  at  $0^\circ$ ,  $10^\circ$ ,  $18^\circ$ , and  $25^\circ$ , determined by a resonance method, agree with the Debye-Falkenhagen theory at low concns. but in the more conc. solutions  $\epsilon$  is  $<$  the theoretical val. This is probably due to orientation of dipoles in the strong ionic fields at higher concn. The relaxation times are also calc.

A. J. M.

**Dielectric constants of solutions of electrolytes.** G. FISCHER and W. D. SCHAEFFELD (Ann. Physik, 1936, [v], 25, 450—466; cf. Orthmann, A., 1931, 786).—The variation of dielectric const. ( $\epsilon$ ) with concn. ( $c$ ) in aq. solutions of NaCl, NaI,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{AgNO}_3$ , HCl,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  has been determined. There is a decrease in  $\epsilon$  with increasing  $c$ , expressed by a formula of the type,  $\epsilon = \epsilon_0(1 + ac^b - bc)$ , where  $a$  and  $b$  are consts. For NaI and NaCl,  $a = 0.095$ ,  $b = 1.45$ . For  $c < 0.01$  g.-mol. per litre, the results accord with the Debye-Falkenhagen theory,  $a$  being 0.047 and  $b$ , 1.0 over this concn. range. For  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$ ,  $a = 0.051$ ,  $b = 1.1$ . For HCl and  $\text{HNO}_3$  ( $c < 0.03N$ ),  $a = 0.55$ ,  $b = 8$ , and for  $\text{H}_2\text{SO}_4$ ,  $a = 0.2$ ,  $b = 5$ .

A. J. M.

**Optical behaviour of dissolved ions and its significance for the structure of solutions of electrolytes. II. Optical rotation of phenylbenzylmethylpropylammonium ion.** G. KORTUM (Z. physikal. Chem., 1935, B, 31, 137—151; cf. this vol., 285).—Some salts increase the sp. rotation of the above ion, whilst others depress it, but there is no simple relation between the magnitude and sign of the effect and the charge, size, or polarisability of the foreign anion. It is inferred that the optical properties of ions are affected by solvation forces far more than by Coulomb forces. In general the rotation is influenced by change in solvent much more than by the presence of salts. The results obtained agree with the view that in their aq. solutions at low and moderate concns. strong electrolytes are completely dissociated into fully solvated ions.

R. C.

**Faraday effect of strong electrolytes in aqueous solutions. III.** A. OKAZAKI (Mem. Ryojun Coll. Eng., 1935, 8, 1—29; cf. A., 1935, 1318).—Data at  $29^\circ$  are recorded for aq.  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{Pb}(\text{NO}_3)_2$  with  $\lambda$  3514 Å., and for aq.  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{CaBr}_2$ ,  $\text{BaBr}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$  with  $\lambda$  3441 Å. For most electrolytes  $[z]$  is independent of, or decreases with, increasing concn. For  $\text{H}_2\text{SO}_4$  and  $\text{Zn}(\text{NO}_3)_2$  it increases with concn.

CH. ABS. (e)

**Ionic susceptibilities of rubidium from its different salts in the solid and in the dissolved state.** S. S. BHATNAGAR, M. B. NEVGI, and M. L. KHANNA (J. Indian Chem. Soc., 1935, 12, 799—807).—Data for  $\text{RbCl}$ ,  $\text{RbBr}$ ,  $\text{RbI}$ , and  $\text{Rb}_2\text{SO}_4$  have been obtained at different temp. The ionic

diamagnetism of  $\text{Rb}^+$  is the same in the solid and dissolved states. The calc. ionic radius is  $1.875 \times 10^{-8}$  cm.

E. S. H.

**Crystalline structure and physicochemical properties in the colloidal state.** T. S. BHATNAGAR (Current Sci., 1936, 4, 570—571).—A review.

**Magnetic properties of colloidal powders of metallic elements.** S. R. RAO (Current Sci., 1936, 4, 572—576).—A review.

**Disperse gases. I. Thermodynamics and preparation.** R. AUERBACH (Kolloid-Z., 1936, 74, 129—138).—Relations between bubble size in gas-liquid systems, and surface tension, density, and external pressure are discussed. In preparing systems of varying dispersity gas is dispersed in a liquid by mechanical means while subject to a low total or partial pressure. Restoration of the system to atm. pressure then yields a dispersion of the required fineness.

F. L. U.

**Diffusion coefficients and velocities of fall in air of atmospheric condensation nuclei.** J. J. NOLAN and V. H. GUERRINI (Proc. Roy. Irish Acad., 1936, 43, A, 5—24).—Methods for the determination of the diffusion coeff.  $D$  and the velocity of fall in air  $V_f$  of atm. condensation nuclei are described. For Dublin air  $D = 18 \times 10^{-6}$  sq. cm. per sec. and  $V_f = 7.5 \times 10^{-5}$  cm. per sec. The mass calc. from these vals. is  $1.68 \times 10^{-16}$  g. and the radius  $2.85 \times 10^{-6}$  cm. In stored air there is a progressive increase in size, but the wt. of the nucleus decreases with time. Comparison of the nuclei in town and country air suggests that when nuclei are fresh from the place of production they are small and numerous, but as the source becomes more remote the concn. falls and the size increases whilst  $D$  diminishes. The relation between concn. and size of nuclei may help to explain the anomalies in the equilibrium between small ions and nuclei.

M. S. B.

**Emulsification by ultrasonic waves.** C. BONDY and K. SÖLLNER (Trans. Faraday Soc., 1936, 32, 556—567; cf. A., 1935, 820).—The influence of various experimental conditions on the extent of emulsification and the degree of dispersion of emulsions produced by ultrasonic waves has been investigated in the systems  $\text{H}_2\text{O}$ +org. liquid,  $\text{Hg}$ +aq. solution, and  $\text{Hg}$ +org. liquid. In the first group the concn. of the emulsion reached in a given time increases with increase of the energy of radiation. The degree of dispersion is the greater, the smaller is the energy and the shorter the time of radiation. Prolonged irradiation always leads to progressive coarsening of an emulsion already formed. The  $\text{Hg}$  systems behave differently, as is to be expected from the different mechanism involved in their emulsification.

F. L. U.

**Production of highly disperse states.** B. CLAUS (Z. tech. Physik, 1935, 16, 80—82; Chem. Zentr., 1935, i, 2958).—When the cathode is subjected to the action of supersonic radiation in the electrolysis of metallic salt solutions coherent deposition of metal is inhibited, and highly disperse metal sols are formed. Factors influencing the degree of dispersion have been investigated.

J. S. A.



**Perchlorates as solvents for cellulose and its derivatives.** (MME.) A. DOBRY (Bull. Soc. chim., 1936, [v], 3, 312—318).—Cellulose acetate dissolves in saturated aq. solutions of Ca, Mg, Cu, and Zn perchlorates in the cold, and in Li and Ag perchlorates and basic Pb perchlorate when hot.  $\text{Mg}(\text{ClO}_4)_2$  is the most active. The dissolution is not accompanied by chemical degradation. Cellulose nitrates and butyrate and benzylcellulose are insol. in these salt solutions. Cellulose dissolves practically unchanged in basic Be perchlorate solutions. E. S. H.

**Viscosity of suspensions and solutions. I. Viscosity of suspensions.** E. GUTH. **II. Theory of electro-viscosity.** W. KRASNY-ERGEN (Kolloid-Z., 1936, 74, 147—172, 172—178).—I. Introductory and mathematical.

**II. Mathematical.** Von Smoluchowski's formula is shown to be an approximation formula suitable for relatively good conductors. It is not valid for non-conducting liquids. F. L. U.

**Viscosity and lyotropic numbers.** J. H. C. MERCKEL (Rec. trav. chim., 1936, 55, 82—84).—A reply to Bruins (this vol., 285). D. C. J.

**Viscosity of organic colloids.** W. PHILIPPOFF and K. HESS (Z. physikal. Chem., 1936, B, 31, 237—255; cf. A., 1935, 31, 822).—The determination and variation of the consts. of the flow curve (cf. *ibid.*, 692) are described. For various solutions at consens.,  $c$ , of 0.01—30% the variation of  $\eta_0$  with  $c$  is given by  $\eta_{rel} = (1 + c/c_0)^8$ , where  $c_0$  is a const. for a given solvent and solute. For solutions of cellulose nitrate (I) in  $\text{BuOAc}$   $\eta_{\infty}$  is  $\propto c$ . Chemical and mechanical treatment of the solute, change of temp., and variation of the solvent and particle size distribution shift the  $\eta_0$ - $c$  curve along the  $c$  axis without altering its form, i.e., the above equation remains valid, with variation in  $c_0$ . With rise in temp.  $\eta_{rel}$  usually falls. For mixed solutions of several varieties of (I)  $\eta = (1 + \sum c_i/c_{0i})^8$ , where  $c_i$  are the consens. of the components in the mixture and  $c_{0i}$  the vals. of  $c_0$  for the components. It appears that  $\eta_0$  is a function of the space demand of the solute only in the sense that the flow of the solvent is impeded by the vol. of the solute. R. C.

**Lyophilic colloids. II. Interaction of agar fractions.** A. A. MOROZOV (J. Gen. Chem. Russ., 1935, 5, 1359—1372; cf. A., 1935, 932, 1320).—The fractions (I) of agar of smaller mol. wt. are extractable with cold  $\text{H}_2\text{O}$ , and are shown to exert a stabilising action on sols of the fractions (II) of higher mol. wt., and to augment imbibition of  $\text{H}_2\text{O}$  by gels of the latter, to an extent commensurate with difference in osmotic pressure between intra- and extra-micellar (I). \*The  $\eta$  of sols of (II) is  $<$  that of the original product, owing to their smaller structural  $\eta$ , and to the smaller vol. of the dispersed phase. R. T.

**Stability of colloids. II. Negative silver iodide colloid.** A. BASIŃSKI (Rocz. Chem., 1935, 15, 430—440; cf. A., 1935, 297).—The coagulating action of cations on dialysed negatively charged  $\text{AgI}$  sol diminishes in the series  $\text{Li} > \text{Na} > \text{K} > \text{NH}_4 > \text{H} > \text{Ag}$ ;  $\text{Cd} > \text{Mg} > \text{Mn}^{II} > \text{Co} > \text{Zn} > \text{Ni} > \text{Ca} > \text{Sr} > \text{Cu} > \text{Ba} > \text{Pb}^{II}$ ;  $\text{Fe}^{III} > \text{La}^{III} > \text{Ce}^{III} > \text{Al}$ ;  $\text{Zr}^{IV} > \text{Th}^{IV}$ .

The action of univalent cations is antagonistic to that of bi- and ter-valent ions; when uni- and quadri-valent ions are present together antagonism is observed only with  $\text{LiCl}$ . An interpretation of the above phenomena, based chiefly on considerations of exchange adsorption, is advanced. R. T.

**Zonal effect in the electrolytic coagulation of manganese dioxide.** S. S. JOSHI and S. J. RAO (Current Sci., 1936, 4, 481—482).—In  $> 80$  cases  $n$  during slow coagulation varies discontinuously with the time, in disagreement with Smoluchowski's theory. R. S. B.

**Coagulation of solvated sols by organic substances and salts. VI. Temperature-stable albumin sols which coagulate on cooling.** B. JIRGENSONS (Kolloid-Z., 1936, 74, 205—208; cf. A., 1933, 461).—Sols of ovalbumin containing 45—55 vol.-% of  $\text{Pr}^{\text{OH}}$  or  $\text{Pr}^{\text{OH}}$  and 0.05—0.5M with respect to  $\text{NaBr}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ , or  $\text{Ca}(\text{NO}_3)_2$ , are stable at room temp. or at  $40^\circ$ , and coagulate at  $-8^\circ$  to  $-10^\circ$ . The coagulum can be re-dispersed at  $65^\circ$ . An explanation is put forward. F. L. U.

**Ionic structure, solubility, and coagulation of proteins.** F. HAUROWITZ (Kolloid-Z., 1936, 74, 208—218; cf. A., 1935, 822).—Solubilities at different  $p_H$  have been determined for products formed by coupling albumin or globulin with diazotised  $m$ - $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ ,  $p$ - $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , or  $o$ - $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ . Data are recorded for the pptn. of various proteins by elupein (which ppts. only the protein anion), and by ovalbumin into which  $\text{SO}_3\text{H}$  have been introduced as above until the isoelectric point is at  $p_H < 1$ , whereby only the protein cations are pptd. The results are discussed theoretically. F. L. U.

**Mitogenetic radiations and Liesegang rings.** A. E. ROFFO (Rev. soc. argentina biol., 1934, 10, 297—305).—Small amounts of rat tissue supported close above a gelatin film cause an outward distortion and some thickening of  $\text{AgNO}_3 \cdot \text{K}_2\text{Cr}_2\text{O}_7$  rings formed on the film. The action of sarcoma tissue is  $>$  that of normal tissue. CH. ABS. (p)

**Thixotropy and rheopexy of  $\text{V}_2\text{O}_5$  sols.** F. JULIUSBURGER and A. PIRQUET (Trans. Faraday Soc., 1936, 32, 445—452).—The relation between thixotropy and rheopexy (cf. A., 1935, 933) has been investigated in more detail for  $\text{V}_2\text{O}_5$  sols. Freshly prepared  $\text{V}_2\text{O}_5$  sols with amiconic particles are only thixotropic, but as soon as large needle-shaped particles are formed the sols become rheoplectic. Rheoplectic sols can be made with Li salts or with acids, but not with K or  $\text{NH}_4$  salts, although the latter can produce thixotropic  $\text{V}_2\text{O}_5$  sols. Li salts and acids are weak coagulants for  $\text{V}_2\text{O}_5$  sols. Rheopexy appears to be an intermediate state between a stable sol and one coagulated by stirring, just as thixotropy is in many cases an intermediate state between a stable sol and one coagulated by electrolytes. O. J. W.

**Mechanism and kinetics of thixotropic solidification.** W. HELLER (Compt. rend., 1936, 202, 61—64).—Data are recorded for the rate of gel formation of  $\text{Fe}(\text{OH})_3$  sols containing  $\text{NaCl}$ , after centrifuging. This is determined by the rate at



which nuclei form, by the rate of growth of these nuclei, and by the rate of their association.

H. J. E.

**Structure and properties of thixotropic gels.** B. S. KANDELAKY (Kolloid-Z., 1936, 74, 200—205).—Sols of  $\text{Fe}_2\text{O}_3$  made by hydrolysis of  $\text{Fe}(\text{OEt})_3$  can set to thixotropic gels when containing as little as 6.3 g. of  $\text{Fe}_2\text{O}_3$  per litre. With increasing val. of  $\text{EtOH}/\text{H}_2\text{O}$  in the sol the particle size increases and the stability decreases. The time needed for the first setting is  $>$  for subsequent settings, owing to the incomplete breaking up of the aggregates on shaking. No thixotropic gels can be obtained from sols made from recryst.  $\text{Fe}(\text{OEt})_3$  and containing no excess electrolyte, whence it is inferred that at least some stabilising charge is necessary. Ultramicroscopic observations establish the existence of a network of aggregates in which the liquid is enmeshed. That the intracellular liquid does not "set" is shown by the appearance in it of small particles in Brownian movement when the system as a whole is gelatinised.

F. L. U.

**Sol-gel transformations. II. Dilatometric investigations on iron hydroxide, gelatin, methylcellulose, silicic acid, and viscose.** E. HEYMANN (Trans. Faraday Soc., 1936, 32, 462—473; cf. A., 1935, 822).—Changes associated with sol-gel transformations have been studied with a sensitive Hg dilatometer. With methylcellulose the vol. increases, with gelatin it decreases, whilst no vol. change occurs during the thixotropic sol-gel transformation of  $\text{Fe}(\text{OH})_3$  sol. It is suggested that a vol. increase corresponds with a decrease in hydration, since the bound  $\text{H}_2\text{O}$  has a smaller sp. vol. than that of the free  $\text{H}_2\text{O}$ . In the formation of silicic acid gels from Na silicate and HCl, the vol. increase is about 10—20 times as large. There is, moreover, a further increase in vol. which continues for many months. Chemical dehydration due to polymerisation may be the cause of these large vol. changes. The maturing of viscose solutions is also discussed.

O. J. W.

**Structures of precipitates. I. Influence of hydrogen, lithium, sodium, and potassium ions on peptisability of secondary particles of barium sulphate precipitates.** B. TEŽAK (Z. physikal. Chem., 1936, 175, 284—293).—The peptisability with  $\text{H}_2\text{O}$  of a  $\text{BaSO}_4$  ppt. varies with the cation of the pptg. sulphate according to the lyotropic series  $\text{Li}^+ > \text{Na}^+ \approx \text{H}^+ > \text{K}^+$ . It is inferred that the reversibility of the aggregation of the primary particles is determined by the hydration of the adsorbed foreign ions. There may be differences in magnitude and sign of charge between different fractions of a peptised system. For a  $\text{BaSO}_4$  dispersion the dispersity quotient falls linearly with increasing particle size.

R. C.

**Atomically divided silver.** A. TOPOREK (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 27—30).—The absorption spectra of Ag dispersed in KCl, KBr, and KI are recorded. The colloidal nature of the colour centres is discussed.

H. J. E.

**Swelling solution temperature of cassava starch.** A. J. OPHOF (Chem. Weekblad, 1936, 33,

91—93).—The percentage ( $P$ ) of cassava starch granules remaining undissolved in  $\text{H}_2\text{O}$  at any temp. has been determined microscopically with Congo-red as stain.  $P$  reaches an equilibrium val. in  $< 30$  min. which increases with temp., following an S-curve reaching 50% at  $61.07^\circ$  (by definition, the swelling solution temp.) and 95% at about  $65^\circ$ . The results are similar to those of Arzichovski (Bull. Acad. Sci. U.R.S.S., 1918, 12, 349) for potato starch. Samec's method (A., 1912, ii, 144) gives vals. of  $55.6$ — $59^\circ$  for cassava starch and  $59.1$ — $60.3^\circ$  for potato starch, but these depend on the concn.

D. R. D.

**Vapour pressure-water content relations for certain typical soil colloids.** L. T. ALEXANDER and M. M. HARRING (J. Physical Chem., 1936, 40, 195—205).—The colloids have been extracted from four different types of soil representing a wide range of progressive weathering, and the variations of v.p. with different  $\text{H}_2\text{O}$  content of the colloids have been determined. The curves are characteristically different for the different types of soil. The variation of free energy with  $\text{H}_2\text{O}$  content has been calc. and the free energy of wetting determined approx. The relation of v.p. to colloid composition is discussed. A theory of the nature of hygroscopic  $\text{H}_2\text{O}$  in soil colloids is given.

M. S. B.

**Equilibrium constants of the exchange reactions  $\text{HCl} + \text{HD} = \text{DCl} + \text{H}_2$  and  $\text{HBr} + \text{HD} = \text{DBr} + \text{H}_2$ .** K. WIRTZ (Z. physikal. Chem., 1936, B, 31, 309—318).—Assuming that the rotation of the mols. concerned is fully excited and the vibration unexcited the equilibrium consts. are calc. to be  $([\text{HD}][\text{HCl}])/([\text{H}_2][\text{DCl}]) = 2.362e^{-186.77/T}$  and  $([\text{HD}][\text{HBr}])/([\text{H}_2][\text{DBr}]) = 2.414e^{-128.11/T}$ . These agree with the observed equilibrium consts., using Pt to catalyse the exchange. In each case the partition ratio of  $D$  approximates to 1 and is practically independent of the temp. From these data and the equilibrium const. of  $\text{H}_2 + \text{D}_2 = 2\text{HD}$  (cf. A., 1934, 30) the equilibrium consts. of all the other exchange reactions possible in the systems H-D-halogen may be calc.

R. C.

**Equilibrium of exchange reactions with deuterium.** K. WIRTZ (Physikal. Z., 1936, 37, 165).—The exchange of D and H in HCl, HBr, and  $\text{NH}_3$  has been studied by determining the equilibrium isotopic ratio for mixtures of  $\text{D}_2$  and the above gases in presence of a Pt catalyst by the thermal conductivity method. The results are in good agreement with those calc. from spectroscopic data (cf. A., 1935, 1460).

A. J. M.

**Equilibria of the reactions between acetylene and heavy water at  $25^\circ$ .** L. H. REYERSON and B. GILLESPIE (J. Amer. Chem. Soc., 1936, 58, 282—284).—Equilibrium consts. for the reactions involving  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{D}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{HD}$ , and  $\text{C}_2\text{D}_2$  have been determined.

E. S. H.

**Concentration maximum of endothermic compounds at high temperatures. Application to ozone and nitric oxide.** E. BRINER, B. SUSZ, and E. ROD (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 198—200).—Previous results (A., 1931, 910) have been recalc. using recent experimental data.



The max. concn. of  $O_3$  in  $O_2$  at 1 atm. is  $2.2 \times 10^{-5}\%$  at  $3500^\circ$  abs. and that of  $NO$  in air at 1 atm. is  $4.7-7.5\%$  at  $3500^\circ$  abs. R. S.

**Relative values of the four butane-butene-hydrogen equilibrium constants.** L. S. KASSEL (J. Chem. Physics, 1936, 4, 144).—The method of Eidinoff *et al.* (A., 1935, 1064) has been developed and applied to calculate the vals. of the sum of the translational and the rotational entropies of the following compounds at  $25^\circ$ : *n*-butane 75.366, isobutane 71.249,  $\Delta^a$ -butene 72.98, *cis*- $\Delta^b$ -butene 68.225, *trans*- $\Delta^b$ -butene 67.800, isobutene 68.215. The possibility of determining vibrational entropy is discussed.

M. S. B.

**Activity of water in solutions of barium chloride.** R. F. NEWTON and E. A. TIPPETTS (J. Amer. Chem. Soc., 1936, 58, 280–282).—V.p. of  $BaCl_2$  solutions at  $25^\circ$  have been measured and the activity of  $H_2O$  has been calc.

E. S. H.

**Vapour pressures and activity coefficients of aqueous solutions of calcium and aluminium nitrate at  $25^\circ$ .** J. N. PEARCE (J. Amer. Chem. Soc., 1936, 58, 376–377).—Corr. data are given (cf. A., 1935, 302).

E. S. H.

**Calculation of activity coefficients and molal volumes.** O. REDLICH, P. ROSENFELD, and W. STRICKS (J. Amer. Chem. Soc., 1936, 58, 375–376).—A criticism (cf. Pearce and Blackman, A., 1935, 302).

E. S. H.

**Equilibrium and free energy relationships in the system acetone-diacetone alcohol.** G. L. DAVIS and G. H. BURROWS (J. Amer. Chem. Soc., 1936, 58, 311–312).—The partial pressures of  $COMe_2$  at  $25^\circ$  show that the mixture forms a perfect solution. The v.p. of diacetone alcohol (I) has been determined at  $25^\circ$ ,  $35^\circ$ , and  $45^\circ$ . The free energy change and heat of reaction of transformation of  $COMe_2$  into (I) have been calc.

E. S. H.

**Condition of iodic acid and iodates in aqueous solution.** N. R. DHAR and R. N. MITTRA (J. Indian Chem. Soc., 1935, 12, 771–773).—The coagulating power of aq.  $HIO_3$  and  $KIO_3$  on sols of  $Be(OH)_2$ ,  $Cr(OH)_3$ , and  $Th(OH)_4$ , and the variation of mol. conductivity of aq.  $KIO_3$  on dilution, indicate partial polymerisation. Evidence from Raman spectra is inconclusive.

E. S. H.

**Mannitoldimolybdic acid.**—See this vol., 453.

**Strength of isomeric bases of the type  $[Pt(NH_3)_2(OH)_2]$ .** A. A. GRÜNBERG and D. I. RJABTSCHIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 259–262).—Titration of the *cis*-compound with 0.1N-HCl at room temp. gives a colour change with Mc-red when 80% of the theoretical amount of acid has been added owing to the formation of the weak acid  $[Pt(NH_3)_2(H_2O)_2]^{++}$ . The change  $[Pt(NH_3)_2(H_2O)_2]Cl_2 \rightarrow [Pt(NH_3)_2Cl_2] + 2H_2O$  occurs on warming and the theoretical end-point may be attained. The *trans*-compound gives an end-point at room temp. corresponding with 50% of the theoretical amount of acid and this is attributed to the formation of  $[Pt(NH_3)_2(H_2O)(OH)]Cl$ . The final titration val. is obtained on warming.

R. S.

**Colorimetric researches on naphthazarin and dibromonaphthazarin.** L. BRÜLL and P. GIROTTI (Annali Chim. Appl., 1936, 26, 19–24).—The dissociation consts. of naphthazarin determined colorimetrically with  $KH_2PO_4$ -NaOH and  $H_3BO_3$ -KCl-NaOH buffers, and with NaOH, are  $K_1 = 6.3 \times 10^{-9}$ ,  $K_2 = 2.5 \times 10^{-11}$ ; those of *dibromonaphthazarin*, m.p.  $163^\circ$  ( $Ac_2$  derivative, m.p.  $212-213^\circ$ ), are  $K_1 = 3.2 \times 10^{-7}$ ,  $K_2 = 2.5 \times 10^{-10}$ . The possibility of using naphthazarin as indicator in the colorimetric determination of  $p_H$  from 7 to 12 is considered; the quantities of naphthazarin in 0.1N-HCl and 0.1N-NaOH required to match the colour of a given solution at each  $p_H$  are tabulated.

E. W. W.

**Application of the phase rule to systems containing distant phases.** F. J. TROMP (J. Chem. Met. Soc. S. Africa, 1935, 36, 143–145; cf. A., 1934, 1307).—When the phase rule is applied to systems such as  $H_2O$  vapour in contact with separate solutions of different salts, the no. of components must be taken as  $>$  the no. of constituents in the system and so the ordinary statement of the phase rule is inapplicable. The author's treatment can be extended to such systems without introduction of special assumptions.

J. W. S.

**Crystalline varieties of the hydrated nitrites of barium and strontium: the hydrate  $Sr(NO_2)_2 \cdot 4H_2O$ .** J. BUREAU (Compt. rend., 1936, 202, 307–309).— $Ba(NO_2)_2 \cdot H_2O$  exists in hexagonal and rhombic forms. The equilibrium diagram for  $Ba(NO_2)_2 \cdot H_2O$  is described.  $Sr(NO_2)_2$  forms the hydrate  $Sr(NO_2)_2 \cdot 4H_2O$  (cubic), which undergoes a peritectic transformation into the hexagonal monohydrate at  $15^\circ$ .

H. J. E.

**Decomposition pressures of the ammoniates of sodium and ammonium chlorides.** S. ABE, K. WATANABE, S. SIGETOMI, and R. HAVA (J. Soc. Chem. Ind. Japan, 1936, 39, 18–20B).—The compounds  $NaCl \cdot 5NH_3$  and  $NH_4Cl \cdot 3NH_3$  have been prepared. Apparatus and methods for studying the decomp. are described. Results are given for the change  $NaCl \cdot 5NH_3 \rightleftharpoons NaCl + 5NH_3$  over the temp. range  $-10^\circ$  to  $-30^\circ$  and for  $NH_4Cl \cdot 3NH_3 \rightleftharpoons NH_4Cl + 3NH_3$  over the range  $5^\circ$  to  $-53^\circ$ . Heats of formation are computed.

T. W. P.

**Volatilisation of lead oxide from lead oxide-silica mixtures.** E. PRESTON and W. E. S. TURNER (J. Soc. Glass Tech., 1935, 19, 296–311T).—Measurements at  $900-1200^\circ$  for mixtures containing 53.96–99.8% of  $PbO$  show that the rate of volatilisation exhibits discontinuities which are attributed to the presence of  $PbO \cdot SiO_2$ ,  $2PbO \cdot SiO_2$ , and  $4PbO \cdot SiO_2$ . The heats of decomp. and evaporation of these compounds are  $-56,000$ ,  $-49,000$ , and  $-30,000$  g.-cal. per mol., respectively. The v.p. of pure  $PbO$  at  $1100^\circ$  is 70 mm. of Hg. The general results confirm those previously obtained for the  $Na_2O-SiO_2$  and  $K_2O-SiO_2$  systems.

J. A. S.

**Fusion curve of the system *o*- and *p*-cresols.** S. TSURUTA (J. Chem. Soc. Japan, 1935, 56, 429–432).—Dawson and Mountford's results are confirmed (cf. J.C.S., 1918, 113, 923).

CH. ABS. (c)



The system: *p*-nitrotoluene-2-chloro-4-nitrotoluene-2 : 6-dichloro-4-nitrotoluene. O. J. MAGIDSON and V. A. SCHEVELEV (J. Appl. Chem. Russ., 1935, 8, 1431—1434).—The m.-p. diagrams afford no evidence of compound formation. R. T.

Equilibria in saturated solutions of salts occurring in sea-water. I. Ternary systems  $\text{MgCl}_2\text{-KCl-H}_2\text{O}$ ,  $\text{MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$ ,  $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ , and  $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$  at  $0^\circ$ . I. IGELSRUD [with T. G. THOMPSON] (J. Amer. Chem. Soc., 1936, 58, 318—322).—Equilibria have been determined at  $0^\circ$ . The KCl content of solutions saturated with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is very small. There is no evidence for double salt formation in the system  $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ . E. S. H.

Thermodynamic study of systems of the type  $\text{PbCl}_2\text{-RCl-H}_2\text{O}$  at  $25^\circ$ . V. E. HUNTER and A. J. ALLMAND (Trans. Faraday Soc., 1936, 32, 502—511; cf. A., 1933, 906).—The v.p. at  $25^\circ$  of solutions containing KCl and  $\text{PbCl}_2$  in equilibrium with various solid phases and also of certain unsaturated solutions have been determined. The results do not agree with vals. calc. from electrometric data, which are probably not sufficiently accurate. Over a narrow concn. region abnormally high v.p., approaching that of pure  $\text{H}_2\text{O}$ , are obtained. In the region of normal v.p. there is evidence of the presence of complexes in the solution. O. J. W.

Ternary system  $\text{NaCl-NaI-H}_2\text{O}$ . J. E. RICOI and N. S. YANICK (J. Amer. Chem. Soc., 1936, 58, 313—315).—Solubility data at  $10^\circ$ ,  $25^\circ$ ,  $50^\circ$ ,  $75^\circ$ , and  $100^\circ$  are recorded. Within this range neither double salts nor solid solutions are formed. E. S. H.

System mercuric iodide, caesium iodide, water. (JLLE.) M. PERNOT (Compt. rend., 1936, 202, 576—578).—The existence of  $3\text{HgI}_2 \cdot 2\text{CsI}$ ,  $\text{HgI}_2 \cdot 2\text{CsI}$ , and  $\text{HgI}_2 \cdot 3\text{CsI}$  has been confirmed. T. G. P.

System  $\text{CaO-SO}_2\text{-H}_2\text{O}$ . III. Precipitation temperatures. P. E. GISHLER and O. MAASS (Canad. J. Res., 1935, 13, B, 370—379).—A technique is described for measuring pptn. temp., and the results over a concn. range are tabulated. Colloidal matter causes supersaturation.  $[\text{H}^+]$  and  $[\text{HSO}_3^-]$  at the pptn. temp. have been calc.  $[\text{H}^+]$  probably plays an important part in pptn., and the increased pptn. with rising temp. above the pptn. temp. is explained.  $\text{HSO}_3^-$  concns. for a range of CaO and  $\text{SO}_2$  concns. from  $50^\circ$  to  $90^\circ$  are given. The system acts as a buffer in so far as  $\text{HSO}_3^-$  ions are concerned. E. E. A.

Fusion surface of the ternary system of organic compounds. I. T. ASAHINA and K. YOKOYAMA (J. Chem. Soc. Japan, 1935, 56, 415—428).—The system picric acid (I)- $\beta\text{-C}_{10}\text{H}_7\text{-OH}$  (II)-chalkone (III) has eutectic points at  $70^\circ$  [(I) 5.5, (II) 43, (III) 51.5%],  $84^\circ$  [(I) 25.5, (II) 16, (III) 58.5], and  $103^\circ$  [(I) 85, (II) 7.5, (III) 7.5%]. CH. ABS. (e)

Transformation of an incongruently fusing binary compound into a ternary eutectic. X. Carbamide-veronal-resorcinol. F. ADAMANIS (Rocz. Chem., 1935, 15, 546—553).—Thermal analysis indicates the existence of three 1 : 1 compounds, three ternary eutectics, and a peritectic. The system is

peculiar in that one of the compounds passes at the transition point into a ternary eutectic. R. T.

Specific heats of aqueous solutions of potassium chloride. C. J. B. CLEWS (Proc. Physical Soc., 1936, 48, 95—99).—Data for  $15\text{--}45^\circ$  and 0.1—2.5*N* are tabulated. The temp. coeff. decreases with concn. N. M. B.

Heat content of sodium chloride in extremely dilute aqueous solutions. T. F. YOUNG and W. L. GROENIER (J. Amer. Chem. Soc., 1936, 58, 187—191).—Theoretical. The chord-area method has been applied to published data for heats of dilution. E. S. H.

Sodium hydroxide solutions. Heat of dilution at  $20^\circ$ . J. W. BERTETTI and W. L. MCCABE (Ind. Eng. Chem., 1936, 28, 247—248).—The heat of dilution has been determined at  $20^\circ$  for the concn. ranges 13.59—26.14 and 17.16—48.14% NaOH. Results are slightly lower than those of Fricke (A., 1929, 1386) but agree with those of Tucker (A., 1915, ii, 674) after correcting for sp. heat. R. S. B.

Heat of hydrogenation of diisobutylene. B. L. CRAWFORD, jun., and G. S. PARKS (J. Amer. Chem. Soc., 1936, 58, 373).—Direct calorimetric measurements give  $\Delta H_{298}^\circ = -28,580 \pm 800$  g.-cal. for the reaction  $\text{C}_8\text{H}_{16}(l) + \text{H}_2(g) = \text{C}_8\text{H}_{18}(l)$ . E. S. H.

Electrolytic conductivity of calcium hydrogen sulphite solutions at  $20^\circ$ . (System  $\text{CaO-SO}_2\text{-H}_2\text{O}$ .) G. K. BERGMAN (Finnish Paper Timber J., 1935, Spec. Issue, 290—293).—Vals. for the conductivity of  $\text{CaO-SO}_2$  solutions are given. The  $[\text{CaO}]$  can be deduced from the conductivity and  $[\text{SO}_2]$ . CH. ABS. (e)

Properties of electrolytic solutions. XVII. Conductance of salts in benzene and dioxan. W. F. LUDER and P. B. KRAUS [with C. A. KRAUS and R. M. FUOSS] (J. Amer. Chem. Soc., 1936, 58, 255—258; cf. A., 1935, 705).—Data are given for tetraisoamylammonium iodide in  $\text{C}_6\text{H}_6$  at  $60^\circ$ , for  $\text{AgClO}_4$  in  $\text{C}_6\text{H}_6$  at  $25^\circ$ , and for  $\text{NBu}_4\text{-ClO}_4$  and  $\text{NBu}_4\text{-OAc}$  in  $\text{C}_6\text{H}_6$  and dioxan at  $25^\circ$ . The equiv. conductances show min. at low concns., below which they rise in accordance with the mass action law. A marked sp. effect of structure on conductance in solvents of very low dielectric const. is noted. E. S. H.

High- and low-frequency conductivities of solutions of electrolytes in glycerol and glycerol-water mixtures. J. HIEGEMANN (Ann. Physik, 1936, [v], 25, 337—358).—Published conductivity data for glycerol solutions agree with the square root law, but the slope is steeper than that required by the Debye-Onsager theory. Solutions of KCl and  $\text{MgSO}_4$  in glycerol and glycerol- $\text{H}_2\text{O}$  have been measured by the abs. method of Malsch, using a miniature thermostat (described). The results obtained are in close agreement with the requirements of the Debye theory for the solvents used. The ionic effects for both solutes are much  $>$  any previously reported. W. R. A.

New method of determining hydration of  $\text{SO}_4^{2-}$  from the electrolytic transport of water. J. BABOROVSKÝ (Chem. Listy, 1936, 30, 5—6).—The hydration of  $\text{SO}_4^{2-}$  cannot be determined directly, owing to the solubility of the depolarisers which



have to be used; an indirect method is proposed, based on measurement of the electrolytic transport of  $H_2O$  in a cell consisting of Ag-AgCl electrodes in  $N-KCl$ , separated by parchment-paper diaphragms from a central chamber containing an equiv. concn. of  $K_2SO_4$ . R. T.

**Electrochemical study of lithium, rubidium, and silver bromides in a solution of aluminium bromide in ethyl bromide.** V. A. PLOTNIKOV and E. J. GORENBEIN (J. Gen. Chem. Russ., 1935, 5, 1434—1440).—The val. of the max. sp. conductivity of the system  $MBr-AlBr_3-EtBr$  falls in the series  $Ag > Li > Cu > K > Rb$ . Except with  $AgBr$ ,  $Al$  is deposited at the cathode in all the systems, the decomp. potentials being:  $LiBr$  2,  $RbBr$  1.66,  $AgBr$  1.3 volts. R. T.

**Electrochemical study of solutions of acetamide in bromine.** V. A. PLOTNIKOV and S. I. JAKUBSON (J. Gen. Chem. Russ., 1935, 5, 1337—1341).—The conductivity max. corresponds with  $NH_2Ac_6Br$ ;  $Br$  is liberated at the anode, and  $NH_2Ac$  at the cathode. R. T.

**Metal-metal potential in the e.m.f. of electrochemical cells.** E. LANGE and K. NAGEL (Z. Elektrochem., 1936, 42, 50—65).—Theoretical. The source of the e.m.f. is discussed. E. S. H.

**Electrode potential of iron in relation to hydrogen-ion concentration.** J. W. SHIPLEY and J. H. SHIPLEY (Canad. J. Res., 1936, 14, B, 31—40).—The final electrode potentials observed when  $Fe$  has been immersed for several days in phosphate, borate, and citrate buffers show sharp falls of 0.74, 0.75, and 0.77 volts which occur at  $p_H$  3.1—4.0, 4.3—4.6, and 10.1—10.9, respectively, for the three series of buffer solutions. Bubbling  $H_2$  or  $O_2$  through the solutions has little effect, but the presence of  $Cl^-$  causes the breaks to be less marked and displaces them to higher vals. of  $p_H$ . Corrosion takes place when the  $p_H$  vals. are below those at which the breaks occur. It is suggested that the electrode potential is determined by the presence or absence of a non-conducting film on the  $Fe$ . L. A. O'N.

**Diffusion potentials and mobilities of ionised gelatin. II. Neutral and alkaline solutions.** E. B. R. PRIDEAUX (Trans. Faraday Soc., 1936, 32, 576—582; cf. A., 1935, 300).—Diffusion potentials of  $K$  gelatinate have been determined in dil. solutions at  $p_H$  6—10. The calc. mobility of the gelatin anion, nearly 40, agrees fairly with that found (A., 1932, 470) in much more conc. solutions. F. L. U.

**Decomposition and equilibrium reaction potentials of fused potassium chloride.** R. C. KIRK and W. E. BRADT (Trans. Electrochem. Soc., 1936, 69, Preprint, 75—88).—The decomp. voltage of fused  $KCl$  at  $800^\circ$  is 2.8 volts. By substituting a  $Cl_2$  anode and using a supplementary cathode the equilibrium potential of the cell  $K|KCl|Cl_2$  has been determined. The p.d. between anode and cathode increases almost linearly with increasing anodic c.d., and reaches a max. val. of 3.37 volts when the anodic c.d. is 1.0 amp. per sq. cm., which is in close agreement with the calc. val. of 3.32 volts for a cell with  $Cl_2$  at atm. pressure. With graphite electrodes depolarisation may reach 0.47 volt, and

is attributed either to anodic formation of  $CCl_4$  or to liberation of  $K$  carbide at the cathode.

J. W. C.

**Oxidation potential of the system potassium molybdocyane-potassium molybdicyanide, and the effect of neutral salts on the potential.** I. M. KOLTHOFF and W. J. TOMSICEK (J. Physical Chem., 1936, 40, 247—255; cf. A., 1935, 1462).—The normal potential of the system, extrapolated to zero ionic strength, is 0.7260 volt at  $25^\circ$ . Neutral salts increase the oxidation-reduction potential to a large extent. For univalent cations the effect decreases in the order  $K^+ = NH_4^+ > Na^+ > Li^+ > H^+$ . Bivalent cations at the same ionic strength have a much greater effect decreasing in the order  $Ba^{++} > Sr^{++} > Ca^{++}$ . The vals. of  $\log f_3/f_4$ , calc. from experimental data, are respectively  $<$  and  $>$  those calc. from the Debye-Hückel expression. M. S. B.

**Polarographic studies with the dropping mercury electrode. III. Cause of maxima on current-voltage curves.** D. ILKOVIČ (Coll. Czech. Chem. Comm., 1936, 8, 13—34).—Certain assumptions lead to the view that the intensity of the electric field is large close up to the dropping  $Hg$  electrode and falls rapidly towards the interior of the solution. This field attracts charged particles and dipoles much more strongly than the electrokinetic potential, and during the action of the "charging (non-faradic) current," the electrically adsorbable particles of the depolariser are drawn into and stored in this non-homogeneous field. If the applied e.m.f. is so large that the rate of exhaustion of the depolariser is  $>$  its rate of adsorption, polarisation starts at the electrode surface, destroying the non-homogeneous field in solution and leaving a very steep fall of potential very close to the interface. From this theory, conditions are derived mathematically, and confirmed by experiments with 0.002—0.01N- $KCl$  containing air, under which a large "adsorption current" and a small "diffusion current" with transition of the former into the latter appear on current-time curves during the charging in the formation of a single  $Hg$  drop at const. applied e.m.f. The current-voltage curve derived from these curves is confirmed experimentally. The theory explains the origin of the max. arising in current-voltage curves under various conditions with the dropping  $Hg$  cathode and predicts conditions under which similar max. may be realised with large stable  $Hg$  electrodes. J. G. A. G.

**Simultaneous discharge of cadmium and hydrogen ions from solutions of simple salts of cadmium.** O. ESSIN, T. BEKLEMISHEVA, and A. MATANTZEV (J. Gen. Chem. Russ., 1935, 5, 1383—1386).—An equation connecting the amount of  $Cd$  deposited per unit of current with the concn. of acid present (A., 1935, 310) has been verified for solutions of 0.25—1.0N- $CdSO_4$  in 0.1—10N- $H_2SO_4$ , for currents of 0.005—0.1 amp. per sq. cm., at  $25^\circ$ . R. T.

**Overvoltage and electrolytic separation of hydrogen isotopes.** J. HORIUTI and G. OKAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 231—242; cf. A., 1934, 153, 258).—Overvoltage



and current, and the velocity of exchange between H and D at an anodically polarised Ni-H electrode in 0.001*N*-H<sub>2</sub>SO<sub>4</sub>, and in contact with H<sub>2</sub> containing 3% of D<sub>2</sub>, have been determined. Parallel measurements of the electrolytic separation factor have been made. A theory of the electrode processes is put forward, and an explanation of Tafel's empirical equation is given. F. L. U.

**Polarisation discharges in multiple electrode systems.** H. HUNT, J. F. CHITTUM, and H. M. GRUBB (J. Physical Chem., 1936, 40, 239—245).—The conditions governing the production of currents between polarised exploring electrodes immersed in an electrolytic cell have been investigated. The phenomena observed originate in the polarisation at the ends of the electrodes and in the differential polarisation of each of the current electrodes at different points on the surface. The significance of these phenomena in electrolytic investigations is indicated. M. S. B.

**Anode process in electrolysis of aqueous alkali chloride solutions with impregnated and non-impregnated graphite electrodes. I. II. Liberation of chlorine and oxygen at the anode. III. Influence of impregnation of the graphite electrode on the anode process. V. S. JOFFE. IV. Electro-capillary phenomena. V. S. JOFFE and M. M. STROGANOV (Z. Elektrochem., 1936, 42, 71—76, 76—79, 79—82, 82—85).—I. The distribution of current between the outer surface of the porous electrode and the inner pore surface depends on the resistivity of the electrode and on the nature of the p.d.-c.d. relation. Discharge of ions occurs throughout the whole cross-section of the electrode, but is conc. mainly in the outer layer. When the pores are filled by impregnation with linseed oil, electrolysis occurs only at the outer surface.**

**II. The ratio O<sub>2</sub>:Cl<sub>2</sub> is greater in the anode gas liberated in the pores than in that liberated at the outer surface of the electrode, and passes through a min. at medium c.d.**

**III. The polarisation of the graphite anode in aq. NaCl has been studied. Under certain conditions of impregnation with oil, oxidation of C occurs and the anode suffers disruption.**

**IV. During anodic polarisation the electrolyte displaces air from the non-impregnated and oil from the impregnated graphite electrode. E. S. H.**

**Electrometallurgy of aluminium. P. DROSSBACH (Z. Elektrochem., 1936, 42, 65—70).—The equilibrium Na<sub>3</sub>AlF<sub>6</sub>-Li<sub>3</sub>AlF<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub> has been investigated at 750—1000°. Current efficiency and polarisation potential in the electrolysis of such mixtures have been determined. E. S. H.**

**Passivity of iron and steel in nitric acid solution. VIII. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 15—21; cf. A., 1934, 1463).—The ability of HNO<sub>3</sub> to render Fe passive is increased and the concn. at which the effect appears is lowered by the addition of nitrates, with the exception of Cu(NO<sub>3</sub>)<sub>2</sub>. HNO<sub>2</sub> and higher nitrates of the metals are formed. AgNO<sub>3</sub> is especially effective and causes passivity in relatively dil. solutions of HNO<sub>3</sub>. R. S. B.**

**Valency-linking shifting in cyclanes. J. BÖESEKEN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 28—30; cf. A., 1932, 269).—The influence of 1-hydroxycyclo-heptane-, -hexane-, -pentane-, -butane-, and -propane-1-carboxylic acids on the conductivity of 0.5*M*-H<sub>3</sub>BO<sub>3</sub> has been determined and compared with corresponding data for disubstituted glycollic acids. Saturated ring compounds with > 5 members increase the conductivity to the same extent as the open-chain compounds, but in the case of 3- and 4-C rings the effect is much less. It is inferred that the valency linkings in rings containing < 5 C are shifted by the ring-closure. R. S.**

**Explosive reactions and analytical geometry. W. P. JORISSEN (Chem. Weekblad, 1936, 33, 83—90).—The factors governing the form of the curves representing the explosion limits of ternary gaseous mixtures are discussed. D. R. D.**

**Pressure dependence of unimolecular reactions. E. A. STEWARDSON (Phil. Mag., 1936, [vii], 21, 233—248).—Theoretical. The chance that an activated mol. in a quasi-unimol. reaction will dissociate, and the ratio (*r*) of the velocity coeffs. (*k*) of the unimol. and bimol. reactions are calc. In agreement with experiment it is inferred that increases in temp. and pressure produce changes in *r* in opposite directions, and that the addition of a light gas will maintain the unimol. rate. Good agreement is obtained with the dissociation of N<sub>2</sub>O, except at low pressures, giving an average life of an activated complex (*τ*) of 10<sup>-11</sup> sec. With other reactions agreement is poor, but *τ* may be approx. estimated to be 10<sup>-6</sup>—10<sup>-8</sup> sec. *d*(log *k*)/*dT* is greater for the bimol. than for the unimol. reaction by  $\frac{1}{2}T$ . R. S. B.**

**Limits of inflammability of hydrogen and deuterium in oxygen and in air. W. PAYMAN and H. TITMAN (Nature, 1936, 137, 190).—The upper and lower limits of inflammability of D<sub>2</sub> in O<sub>2</sub> and in air at 1 atm. differ slightly from those of corresponding mixtures with H<sub>2</sub>. L. S. T.**

**Prevention of gas explosions by controlling oxygen concentration.—See B., 1936, 177.**

**Explosion limits. I. Influence of argon, nitrogen, helium, and carbon dioxide on explosion limits of hydrogen, carbon monoxide, methane, and butane in air. II. Occurrence of explosion limits, their dependence on the pressure, and the influence of dilution with an inert gas. J. VAN HEININGEN (Rec. trav. chim., 1936, 55, 65—75, 85—100).—I. The extinguishing action of the four gases is in all cases in the order CO<sub>2</sub> > He > N<sub>2</sub> > A (cf. Coward and Hartwell, A., 1926, 805). Addition of inert gas mainly affects the upper explosion limits, the lower limit depending little on the nature and amount of inert gas. The curves delimiting the explosion region of one particular combustible gas, obtained on the addition of the four inert gases, form a family having a common axis and intersecting only at the two explosion limits for 0% of inert gas.**

**II. A simple mathematical treatment of explosion limits is given without recourse to the theories of chain mechanisms. Assuming that the velocity of**



reaction of two gases  $A$  and  $B$  is bimol. obeying the relation  $s = kC_A C_B$ , where  $s$  is the velocity, the usual curve of the equation  $s = f(x)$ , where  $x$  is the no. of g.-mol. of  $A$  and  $1-x$  is the no. of g.-mol. of  $B$  present in  $v$  litres, is deduced. For certain vals. of  $s$  when reactions become explosive, two explosive limits occur at different concns. The effect of the change of thermal conductivity with concns. shows that the explosive limits are not given by the intersections of the parabola  $s = f(x)$  with a straight line parallel to the  $X$  axis. The conclusion is reached, with certain assumptions, that two explosive limits occur at high pressures and approach one another as the pressure is decreased. Dilution with an inert gas is considered and an equation deduced which covers certain of the experimental results. The sp. action of an inert gas can be explained if it is assumed to influence the reaction const. and an equation is derived for this effect, but if the changes in thermal conductivity are taken into account,  $A$ ,  $N_2$ ,  $He$ , or  $CO_2$  appear to have no appreciable influence on the reaction const.

D. C. J.

**Limits and speeds of detonation of some gaseous mixtures.** J. BRITON and P. LAFFITTE (Compt. rend., 1936, 202, 316—318; cf. A., 1934, 969).—Vals. are given for the upper and lower limits and velocity of detonation for the following mixtures:  $C_3H_8-O_2$ ,  $C_4H_{10}-O_2$ ,  $C_2H_2-O_2$ ,  $C_2H_2$ -air,  $NH_3-O_2$ ,  $Et_2O-O_2$ ,  $Et_2O$ -air, for the effect of pressure (1—8.7 atm.) on the limits for  $H_2-O_2$  and  $H_2$ -air explosions, and for the effect of small additions of  $H_2$  on the lower limit for  $CO-O_2$  mixtures.  $PbEt_4$  has no appreciable influence on the detonation limits.

H. J. E.

**Thermal study of the oxidation of hydrocarbons.** (MLLE.) S. ESTRADÈRE (Compt. rend., 1936, 202, 217—219).—A relationship is determined between inflammation temp. of hydrocarbons and the no. of C atoms; it is considered to run parallel with their octane nos.

T. G. P.

**Temperature and latent energy in flame gases.** W. T. DAVID (Phil. Mag., 1936, [vii], 21, 280—281; cf. A., 1935, 138, 598).—The temp. measured by a thin Pt-Rh wire in the flame gases on combustion at const. pressure of various gas mixtures for which the ideal calc. temp. is  $1900^\circ$  has been recorded. The measured temp. ranges from  $1390^\circ$  to  $1745^\circ$  and corresponds with latent energies of 28—8% of the heat of combustion. Similar data are given for mixtures which have the same measured temp., viz.,  $1550^\circ$ . The long-lived latent energy depends on the nature of the combustible gas and of the diluents, and on the pressure.

R. S. B.

**Thermal decomposition of ethane.** I. Probability of decomposition into two methyl radicals and into ethylene and hydrogen. II. Collision efficiency in activation and mean life in activated state. H. SACHSSE (Z. physikal. Chem., 1935, B, 31, 79—86, 87—104).—I. In the decomp. at  $560$ — $590^\circ$   $[H]$  is  $\sim$  twice as great as corresponds with the equilibrium  $H_2 \rightleftharpoons 2H$  in pure  $H_2$ , showing that part of the  $C_2H_6$  decomposes primarily into Me radicals, which form H atoms by chain reactions.  $[H]$  is, however, only about 0.001 of the val. calc. assuming,

according to the Rice-Herzfeld theory (A., 1934, 369), that all the  $C_2H_6$  decomposes by chain reactions initiated by the formation of Me. Hence only a small part of the  $C_2H_6$  decomposes primarily into radicals.

II. The effect of pressure on the reaction velocity at  $856$ — $910^\circ$  abs. leads to the equation  $\log k = 14.1 - 69,800/2.3RT$  for the velocity at infinite pressure. It appears that deactivation occurs in only 1 in  $\sim 10^{25}$  collisions between an active and a normal mol. The life of an active mol. is  $10^{-6}$  sec. The theory of "kinetically-effective degrees of freedom" (cf. A., 1927, 26) is criticised.

R. C.

**Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters.**

VIII. **Energies associated with induced polar effects in the hydrolysis of substituted benzoic esters.** C. K. INGOLD and W. S. NATHAN (J.C.S., 1936, 222—225).—The rate of alkaline hydrolysis of  $p-C_6H_4X \cdot CO_2Et$ , in which it is assumed that induced polar effects are isolated from local disturbances, has been determined in aq. 85 wt.-% EtOH at  $25^\circ$  and  $50^\circ$ . The velocity coeff.,  $k$ , varies with the substituent,  $X$ , thus,  $NH_2 < OMe < Me < H < Cl < I < Br < NO_2$  over a 5000-fold range. The activation energy,  $E$ , decreases from 20,000 to 15,000 g.-cal. thus,  $NH_2 > OMe > Me > H > \text{halogens} > NO_2$ . The linear relation between  $E$  and  $\log k$  corresponds with a const. val. of  $B$  in  $k = Be^{-E/RT}$ , and the similar relation, considered on the same scale, between existing data for the acid-catalysed bromination of substituted CPhMe (A., 1935, 1209) is not inconsistent with a const. val. of  $B$ .

J. G. A. G.

**Kinetic salt effect in saponification of ester ions.** R. F. NIELSEN (J. Amer. Chem. Soc., 1936, 58, 206—215).—A conductivity method has been used to study the hydrolysis of  $Et_1$  esters of malonic, succinic, and adipic acids, and a photometric comparison method for  $EtHC_2O_4$  and the betaine ester  $(NEt_3 \cdot CH_2 \cdot CO_2Et)ClO_4$  (I). No effect of the distance of the reacting group from the charge was observed for the four homologous ions. The kinetic salt effect for hydrolysis of (I) at ionic strengths down to 0.0001 is that given by the Brönsted-Debye equation for vals. of  $\sqrt{\mu} < 0.1$ .

E. S. H.

**Influence of heavy water on the rate of esterification of benzoic acid in ethyl-alcoholic hydrogen chloride.** A. KAILAN and H. HORNÝ (Ber., 1936, 69, [B], 437—440).—Under like mol. conditions the rate of esterification of  $BzOH$  by EtOH containing HCl is diminished less by  $D_2O$  than by  $H_2O$ .

H. W.

$\alpha\alpha$ -Dimethylacetoacetic acid. Hydrolysis of the ethyl ester. Ketonic decomposition. Reaction with iodine and bromine. Dissociation constant. K. J. PEDERSEN (J. Amer. Chem. Soc., 1936, 58, 240—246).—The rates of (a) hydrolysis of the Et ester at  $0^\circ$  and  $25^\circ$ , (b) ketonic decomp. of the acid in mixtures of HCl and NaCl at  $25^\circ$  and  $35^\circ$ , (c) ketonic decomp. of the ion at  $25^\circ$  and  $35^\circ$ , (d) reaction of the acid with I and Br at  $25^\circ$  have been studied. It is unlikely that the acid reacts directly with halogen; an intermediate enol form is probable. It appears that the  $CO_2$  cleavage of  $\beta$ -ketocarboxylic acids leads directly to the enol form of the reaction



product. This reacts instantaneously with free halogen; in absence of halogen it is transformed into the corresponding ketone. The dissociation const. of the acid in solutions containing NaCl has been determined at 25° and 35°.

E. S. H.

**Course of reaction in the alkaline hydrolysis of solutions of sodium chloroacetate.** H. M. DAWSON and E. R. PYCOCK (Proc. Leeds Phil. Soc., 1935–1936, 3, 135–140; cf. A., 1934, 847).—The alkaline hydrolysis of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$  (I) in presence of excess of alkali is a bimol. reaction. When excess of (I) is present the reaction of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$  with  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$ , and  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2'$  must also be considered.

H. J. E.

**Kinetics of thermal polymerisation of styrene.** H. MARK and R. RAFF (Z. physikal. Chem., 1936, B, 31, 275–291).—The rates of polymerisation of the solution in PhMe at 98.2° and of the pure liquid at 60–98° have been determined. Assuming that the polymerisation consists in (1) a bimol. thermal formation of doubly unsaturated nuclei followed by (2) a bimol. growth of the mol. chains, and applying the theory previously described (A., 1935, 1206), it is deduced that the ratio of the rate of (1) to that of (2) is  $\sim 8 \times 10^{-6}$ , the ratio of the steric factors is  $\sim 7.5 \times 10^{11}$ , and the energies of activation are  $\sim 30$  and  $\sim 8$  kg.-cal., respectively.

R. C.

**Appearance of radicals in thermal decomposition of organic molecules.** F. PATAT and H. SACUSSE (Z. physikal. Chem., 1935, B, 31, 105–124).—In the formation of Me by decomp. of such substances as  $\text{COMe}_2$ , a steady  $[\text{Me}]$  has a corresponding steady  $[\text{H}\cdot]$ , so that the former may be deduced from the latter. In the thermal decomp. of  $\text{MeCHO}$ ,  $\text{EtCHO}$ , and  $\text{COMe}_2$  free Me radicals are formed, but in amount far too small to account for the whole of the decomp. by a chain reaction (cf. A., 1934, 369). The smaller is the difference between the experimentally determined heat of activation and the heat of activation of the first step of the decomp. into radicals, i.e., the energy required to break the weakest linking, the more radicals are formed in a thermal decomp. The decomp. into radicals which involves the simplest spatial rearrangements occurs by preference.

R. C.

**Velocity of formation of compounds of higher order, with special reference to the streaming process for investigating very rapid reactions.** A. THIEL and A. LOGEMANN (Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg, 1934, 69, 50–188; Chem. Zentr., 1935, i, 2939).—Colorimetric study of the kinetics of the formation of  $[\text{Fe}(\text{phenanthroline})_3]\text{SO}_4$  indicate the initial formation of a 1:1 compound. A streaming method, using photoelectric registration, is described for the investigation of reactions proceeding to completion within  $5 \times 10^{-4}$  sec.

J. S. A.

**Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents.** VII. **Attack at a saturated carbon atom by a charged ion.** J. W. BAKER and W. S. NATHAN (J.C.S., 1936, 236–241).—The kinetics of the equilibrium  $\text{C}_6\text{H}_4\text{X}\cdot\text{CH}_2\text{Br} + \text{CH}_2\text{Ph}\cdot\text{NC}_5\text{H}_5\text{NO}_3 \rightleftharpoons \text{C}_6\text{H}_4\text{X}\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2 + \text{CH}_2\text{Ph}\cdot\text{NC}_5\text{H}_5\text{Br}$ , where X is H,

*p*-Me, *p*-Et, *p*-Bu', *p*-NO<sub>2</sub>, or  $\text{C}_6\text{H}_4\text{X}$  is 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2$ , have been investigated in  $\text{COMe}_2$  at 20° and 40°. The energy of activation (18.4–18.9 kg.-cal.) is independent of X and is identical for the forward and reverse reactions. In all cases the equilibrium is largely displaced towards the left, probably owing to an orientation effect when  $\text{NO}_3'$  attacks the C atom. The velocity coeff. varies with X thus:  $\text{H} < \text{Bu}' < \text{Et} < \text{Me} < \text{NO}_2 < 2:4\text{-(NO}_2)_2$ . The variations fall within a 20-fold range and are accounted for by changes in the probability factor which is of the order of unity (cf. A., 1935, 1208).

J. G. A. G.

**[Addition of bromine to] unsaturated acids.**—See this vol., 454.

**Mechanism of substitution at a saturated carbon atom. VI. Hydrolysis of isopropyl bromide.** E. D. HUGHES, C. K. INGOLD, and U. G. SHAPIRO (J.C.S., 1936, 225–236).—The rate of hydrolysis of  $\text{Pr}^i\text{Br}$  by  $\text{OH}'$  has been determined in aq. 60 and 80 vol.-%  $\text{EtOH}$  at 45–75°. At very low  $[\text{OH}']$ , the kinetically unimol. substitution,  $\text{S}_{\text{N}}1$ , occurs without elimination of  $\text{C}_3\text{H}_6$ , and at higher  $[\text{OH}']$  a bimol. substitution reaction,  $\text{S}_{\text{N}}2$ , supervenes concomitantly with the elimination of  $\text{C}_3\text{H}_6$  in a second-order reaction,  $\text{E}2$ . The temp. coeff. leads to the activation energies:  $\text{S}_{\text{N}}1$  22,690 g.-cal.,  $\text{S}_{\text{N}}2$  20,760,  $\text{E}2$  22,100, and  $\text{S}_{\text{N}}2 + \text{E}2$  21,490 in 60%  $\text{EtOH}$ , and slightly higher vals. in 80%  $\text{EtOH}$ . By adding  $\text{H}_2\text{O}$  to the solvent,  $\text{S}_{\text{N}}1$  is accelerated,  $\text{S}_{\text{N}}2$  is slightly retarded, and  $\text{E}2$  is more strongly retarded. These results accord with theory and the data are not invalidated by the formation of  $\text{EtOPr}^i$ , especially in 80%  $\text{EtOH}$ . The priority of Taylor's mechanism (A., 1935, 1465) is disputed.

J. G. A. G.

**Velocity of decomposition of diazo-compounds in water. XIX.** E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 15–17B).—*k* of decomp. of azobenzene-*p*-diazonium chloride (I) at 40–50°, and of azo-*o*-toluene-*p*-diazonium chloride (II) at 25–40° have been measured. Relative vals. of stability ( $1/k$ ) of 36 diazo-compounds are tabulated. If  $1/k$  for  $\text{PhN}_2\text{Cl}=1$ , that of (I) is 3.3, and that of (II) 6.2.

E. W. W.

**Influence of degree of acidity on velocity of diazotisation.**—See this vol., 465.

**Hydrolysis of nucleotides by acids.** H. ISHIKAWA (J. Biochem. Japan, 1935, 22, 385–395).—Rates of hydrolysis by dil.  $\text{H}_2\text{SO}_4$  of guanylic, xanthylic, inosinic, and adenylic acids, guanosine and xanthosine, and ribosephosphoric acid were determined.

F. O. H.

**Interaction of light and heavy water with aluminium carbide and calcium phosphide.** R. M. BARRER (Trans. Faraday Soc., 1936, 32, 486–490).—The decomp. of  $\text{Al}_4\text{C}_3$  by liquid  $\text{H}_2\text{O}$  has an apparent energy of activation of 14,200 kg.-cal. The reaction rates for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are in the ratio 3.9:1 at 273° abs., corresponding with a zero-point energy difference of 750 g.-cal. There is no evidence of a tunnelling mechanism at this temp. The decomp. of  $\text{Ca}_3\text{P}_2$  by  $\text{H}_2\text{O}$  vapour is governed by a diffusion



process. The rates of decomp. by  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  vapours are in the ratio of the v.p. of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ .

O. J. W.

**Rates of interaction of proto- and deuterio-hydrogen and methane with charcoal.** R. M. BARRER (Trans. Faraday Soc., 1936, 32, 481—486).—The rates of chemisorption of  $\text{H}_2$  and  $\text{D}_2$  and of  $\text{CH}_4$  and  $\text{CD}_4$  on charcoal have been measured. The differences in rate of sorption are due to zero-point energy differences, which are 770 and 750 g.-cal., respectively. The expression  $k_{\text{H}_2}/k_{\text{D}_2} = Ae^{-\Delta E/RT}$  gave a val. of  $A=1$ . No penetration of energy barriers could be detected. The ratio of the velocities decreased in both sorptions with rise in temp.

O. J. W.

**Oxidation of carbon.** J. D. LAMBERT (Trans. Faraday Soc., 1936, 32, 452—462).—The kinetics of the oxidation of several kinds of C have been investigated at 250—500° by a dynamic method, in order to distinguish between the two types of process which are possible, viz., (1) direct formation of  $\text{CO}_2$  by impact of  $\text{O}_2$  mols. on a clean C surface, and (2) primary formation of both  $\text{CO}_2$  and CO by the breakdown of surface oxide complexes. Pure graphite and diamond showed only process (1), activated coconut charcoal showed (1) with a trace of (2), and activated anthracite, containing much Fe, showed only (2). Treatment of coconut charcoal with  $\text{FeCl}_3$  under suitable conditions gave a product closely resembling anthracite in its behaviour on oxidation.

O. J. W.

**Kinetics of the oxidation of spherules and metallic powders.** G. VALENSI (Compt. rend., 1936, 202, 309—312; cf. A., 1935, 1466).—An expression is developed for the rate of oxidation of a solid, the grains of which are protected by oxide films. Measurements on the oxidation of powdered Ni support the theory. The oxidation of non-spherical particles may be considered in terms of an "equiv. sphere."

H. J. E.

**Velocity of corrosion of duralumin.**—See B., 1936, 200.

**Reactions in monolayers of drying oils. I. Oxidation of the maleic anhydride compound of  $\beta$ -elæostearin.** G. GEE and E. K. RIDEAL. II. **Polymerisation of the oxidised forms of the maleic anhydride compound of  $\beta$ -elæostearin.** G. GEE (Proc. Roy. Soc., 1935, A, 153, 116—128, 129—141).—I. The mechanism of "drying" of a monolayer of the maleic anhydride compound of  $\beta$ -elæostearin on dil. acid substrates has been examined by means of a determination of the surface pressure and phase boundary potentials. A primary unstable peroxide,  $\text{XO}_2'$ , is first formed, which can then form either a stable isomeride,  $\text{XO}_2$ , or be converted into a polymeride; the stable isomeride is also capable of forming the polymeride. At low temp. and high pressures the polymerisation of  $\text{XO}_2'$  occurs so rapidly that the whole reaction is pseudo-unimol. At higher temp. and pressures of the order of 5—6 dynes per cm. the two processes can be observed to proceed successively. The reactions  $\text{X} \rightarrow \text{XO}_2' \rightarrow \text{XO}_2$  are unimol. with energies of activation of 6500 and 19,000 g.-cal. per mol., respectively.

II. The kinetics of polymerisation are discussed; a steric factor alone is sufficient to account for the form of the curves obtained. Chain-breaking materials may be (a) inserted in the substrate like quinol, or (b) inserted in the film itself like Etmyristate. The polymerisations of the unstable peroxide and of its stable isomeride have energies of activation of the order of 5000 and 20,000 g.-cal. per mol., respectively.

L. L. B.

**Influence of constitution of the oxidised substances on the activity of catalysts for oxidation by concentrated sulphuric acid, and influence of temperature on the catalysts.** J. MILBAUER (Bull. Soc. chim., 1936, [v], 3, 218—221).—Tests with numerous catalysts for the Kjeldahl reaction show that the efficiency of the catalyst depends on the constitution of the substance to be oxidised, and on the temp.

E. S. H.

**Autoxidation. V. Induction period in autoxidation.** H. N. STEPHENS (J. Amer. Chem. Soc., 1936, 58, 219—224; cf. A., 1934, 607).—A study of the effect of purification and the influence of addenda shows that the induction period in the autoxidation of cyclohexene is due to the presence of inhibitors.

E. S. H.

**Oxidation of aqueous sulphite solutions in presence of pyridine. II. Autoxidation of aqueous sulphite solutions. Mechanism of sulphite autoxidation.** P. BAUMGARTEN (Ber., 1936, 69, [B], 229—242; cf. A., 1932, 1216).—Autoxidation of  $\text{SO}_3''$  in presence of  $\text{C}_5\text{H}_5\text{N}$  gives 1-pyridinium-sulphonic acid and small amounts of 2- and 3-pyridyl-pyridinium salts isolated as the perchlorates. In presence of sufficient  $\text{C}_5\text{H}_5\text{N}$  the yields diminish with increasing  $[\text{SO}_3'']$ , and reaction is best effected by passing a stream of air slightly laden with  $\text{SO}_2$  through a well-stirred solution of  $\text{C}_5\text{H}_5\text{N}$  in  $\text{H}_2\text{O}$ . The change does not occur in absence of air. Unlike  $\text{EtOH}$ ,  $\text{C}_5\text{H}_5\text{N}$  accelerates the autoxidation of  $\text{HSO}_3'$  owing to the increase of  $[\text{SO}_3'']$  which it causes. In the initial stages of the change autoxidation of  $\text{SO}_3''$  by  $\text{C}_5\text{H}_5\text{N}$  is not restricted, but subsequently such effect is obvious, due to increase of  $[\text{OH}']$ . Inhibition occurs only within narrow  $p_{\text{H}}$  range. The theories of  $\text{SO}_3''$  autoxidation are discussed.

H. W.

**Enzymic fission of glucosides in heavy water.**—See this vol., 520.

**Alcoholic fermentation in heavy water.**—See this vol., 522.

**Mechanism of reactions between solid phases and a gaseous phase.** M. BLUMENTHAL (Bull. Acad. Polonaise, 1935, A, 287—307).—The general properties of surface reactions are investigated theoretically.

T. G. P.

**Adsorption and heterogeneous catalysis. I.** KEMP (Chem. and Ind., 1936, 138).—Concerning terminology (cf. this vol., 298).

J. G. A. G.

**Conjugated catalytic phenomena. [Catalysis by binary and ternary mixtures.]** J. MILBAUER (Coll. Czech. Chem. Comm., 1936, 8, 1—12).—The catalysis of the oxidation of CO by 95.6%  $\text{H}_2\text{SO}_4$  at 237° has been investigated by a flow method. The final rate of oxidation catalysed by mixtures of



As and Se oxides is independent of As oxides and  $\propto [\text{SeO}_2]$ . Pd is a very strong catalyst, of which the action is enhanced by  $\text{HgSO}_4$  and raised to a max. by 10–30% of  $\text{Ag}_2\text{SO}_4$ , but is markedly depressed by Se. Sp. proportions of  $\text{HgSO}_4$  and  $\text{Ag}_2\text{SO}_4$ , separately, raise the catalytic activity of  $\text{SeO}_2$  to max. vals. Mixtures of  $\text{HgSO}_4$  and  $\text{Ag}_2\text{SO}_4$  are better catalysts than the single salts, whilst an approx. 1:4  $\text{CuSO}_4$ – $\text{HgSO}_4$  mixture has a max. catalytic activity. The effect on the reaction velocity of varying the composition of ternary catalysts is represented quantitatively by triangular diagrams. Catalysis by the systems Pd+Se+Ag, Hg+Se+Ag, Pd+Hg+Ag, Cu+Hg+Se was < the max. vals. obtained with the binary systems. J. G. A. G.

**Catalytic interaction of ammonia with deuterium.** A. FARKAS (Trans. Faraday Soc., 1936, 32, 416–427).—The exchange of H atoms between  $\text{D}_2$  and  $\text{NH}_3$  has been investigated on an Fe catalyst at 160–230°/30–400 mm. The rate of the exchange reaction is independent of  $\text{NH}_3$  pressure and increases with pressure of  $\text{D}_2$ . The apparent heat of activation is 15 kg.-cal. The *o-p* conversion of  $\text{H}_2$  and of  $\text{D}_2$  and the reaction  $\text{H}_2 + \text{D}_2 = 2\text{HD}$  are much faster than the exchange reaction. For the *o-p* conversions the activation energy is 8–9 kg.-cal. The conversion is inhibited by  $\text{NH}_3$ . The exchange reaction proceeds by the following reactions in the adsorption layer:  $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$ ,  $\text{D}_2 \rightarrow 2\text{D}$ ,  $\text{D} + \text{H} \rightarrow \text{HD}$ ,  $\text{D} + \text{NH}_2 \rightarrow \text{NH}_2\text{D}$ . The last of these is the slowest and rate-determining step. O. J. W.

**Thermal decomposition of light and heavy ammonia and phosphine on tungsten.** R. M. BARRER (Trans. Faraday Soc., 1936, 32, 490–501).—Velocity measurements have been made for the thermal catalytic decomp. on W filaments ( $\alpha$ ) of  $\text{NH}_3$  between  $6 \times 10^{-2}$  and  $6 \times 10^{-4}$  cm. and 950–1150° abs., and ( $\beta$ ) of  $\text{PH}_3$  between  $10^{-1}$  and  $2 \times 10^{-4}$  cm. and 800–970° abs. On various W catalysts and in the early stages of the reaction ( $\alpha$ ) was of zero order, but towards the end of decomp. or at the lowest *p* the velocity diminished as the  $\text{NH}_3$  pressure decreased. Reaction ( $\beta$ ) was of first order at  $p = 10^{-4}$  to  $5.0 \times 10^{-3}$  cm. and became of approx. zero order at about  $10^{-1}$  cm. The rate-determining step in both reactions involves a rearrangement of a H linking, since differences were found in zero-point energy of 800–900 g.-cal. for  $\text{NH}_3$  and  $\text{ND}_3$ , and 550 g.-cal. for  $\text{PH}_3$  and  $\text{PD}_3$ .  $\text{H}_2$  and  $\text{N}_2$  have no influence on the rate of catalytic decomp. of  $\text{NH}_3$ , but  $\text{O}_2$  produces a temporary poisoning of the catalyst. The energies of activation, measured by a compensating filament method, are 42,400 g.-cal. for the zero order  $\text{NH}_3$  decomp., 25,000 g.-cal. for the first order and 32,200 g.-cal. for the zero order  $\text{PH}_3$  decomp. O. J. W.

**Siderite as basic material for the catalytic synthesis of ammonia.**—See B., 1936, 190.

**Centrifugal transformation of a thin layer of copper sulphide under the influence of metallic copper; interruption of this transformation by a separation of 1 Å.** H. DEVAUX (Compt. rend., 1935, 201, 1305–1307).—A piece of Cu, Fe, Zn, Ni, Al, or Sn placed in contact with the thin layer of  $\text{CuS}$

deposited on the surface of aq.  $\text{CuSO}_4$  by  $\text{H}_2\text{S}$  induced a change which ultimately extended some distance around the metal. The reaction ceased when the film was so thin that the mols. were judged to be 0.6–1.0 Å. apart. The rate of the reaction  $\propto \sqrt{\text{temp.}}$  (approx.). T. G. P.

**Catalytic reduction of carbon dioxide to methane and higher hydrocarbons.**—See B., 1936, 180.

**[Catalytic] synthesis of *n*-heptane.**—See B., 1936, 181.

**Properties of the methyl alcohol catalyst copper-zinc oxide-chromic oxide.**—See B., 1936, 191.

**[Catalytic] synthesis of esters by dehydrogenation of alcohols.**—See B., 1936, 181.

**$\psi$ -Halogenes. XXXI. Detection of iodine-mixed halogens by measurements of the rate of reaction between cyclohexene and iodine in the presence of salts of the heavy metals.** L. BIRKENBACH, J. GOUBEAU, and H. G. KRALL (Ber., 1936, 69, [B], 476–484).—The reaction between I and cyclohexene in  $\text{PhMe}$ ,  $\text{CCl}_4$ , or  $\text{Et}_2\text{O}$  occurs very much more rapidly in the presence of  $\text{AgNO}_3$ ,  $\text{AgNCO}$ ,  $\text{AgClO}_4$ , or  $\text{PbCl}_2$  than in their absence. The dependence of the rate on the nature of the metallic salt is explicable on the basis of catalysis, which, however, does not account for the effect of the quantity of salt. The change is therefore attributed to the intermediate formation of mixed halogens:  $\text{I}_2 + \text{RHal}(\psi\text{-hal}) \rightarrow \text{IHal} \rightarrow (+>\text{C}:\text{C}<)>\text{Cl-CHal}<$ . H. W.

**Existence of a sharp temperature threshold for catalytic decomposition of molecules on a hot platinum surface, and the nature of this decomposition.** O. BEECK (Physical Rev., 1934, [ii], 46, 331–332).—Decomp. of mol. beams of hydrocarbons projected on to a Pt strip filament have been investigated. Decomp. of  $\text{C}_2\text{H}_6$  commences at approx. 800° and increases up to 1200° when all impinging mols. are dehydrogenated to  $\text{C}_2\text{H}_4$  and  $\text{H}_2$ .  $\text{C}_2\text{H}_4$  shows no decomp. below 830°, but at 850° every impinging mol. yields  $\text{C}_2\text{H}_2$  and  $\text{H}_2$ . L. S. T.

**Dehydrogenation and dehydration catalysed by nickel-aluminium oxide catalysts.** A. A. BALANDIN and A. M. RUBINSTEIN (Z. physikal. Chem., 1936, B, 31, 195–213; cf. A., 1935, 1348).—The parallel dehydrogenation and dehydration of isoamyl alcohol and the secondary decomp. of the aldehyde formed have been studied. Catalysts prepared by pptg. mixtures of Ni and Al salts with  $\text{NaOH}$  are more active than those pptd. with  $\text{Na}_2\text{CO}_3$ . Catalysts prepared from chlorides and sulphates may be as active as the most active catalysts prepared from nitrates. The ratio of the energy of activation of dehydrogenation to that of dehydration averages 0.51, the corresponding vals. for dehydrogenation: aldehyde decomp. and dehydration: aldehyde decomp. being 0.69 and 1.26, respectively. All three ratios vary little from one catalyst to another, but the heats of activation themselves vary considerably. The relation between the energy of activation and the coeff. *a* of Arrhenius' equation previously noted (A., 1933, 234) is valid for both dehydration and dehydro-



generation. It appears that the activity of a mixed catalyst is located at the lines of contact between its components. R. C.

**Asymmetric main valency catalysts.**—See this vol., 476.

**Hydrogenation of ketones.**—See this vol., 457.

**Catalytic reduction of aromatic carboxylic acid esters under high pressure and temperature.** K. MITSUI (Mem. Coll. Sci. Kyoto, 1935, A, 18, 329—336).—The reductions were effected by  $H_2$  at 100 atm. in the presence of reduced Ni. EtOBz reacts rapidly at 150—190° and the product contains 90 mol.-% of Et hexahydrobenzoate;  $CH_2Ph\cdot OH$  and BzOH were not produced. The product from  $CH_2Ph\cdot CO_2Et$  at >140° contains 90 mol.-% of Et cyclohexylacetate. The product from Et salicylate at >200° contains 75 mol.-% of cyclohexanol, cyclohexane, and EtOH.  $m\text{-OH}\cdot C_6H_4\cdot CO_2Et$  at 170—190° absorbs 3 mols. of  $H_2$  forming products containing 75 mol.-% of Et *m*-hydroxyhexahydrobenzoate, and  $p\text{-OH}\cdot C_6H_4\cdot CO_2Et$  at 180—200° absorbs 2 mols. of  $H_2$  forming products containing 40 mol.-% of Et *p*-hydroxyhexahydrobenzoate. J. G. A. G.

**Electrolytic separation of deuterium.** A. J. EDWARDS, H. F. WALTON, R. P. BELL, and J. H. WOLFENDEN (J.C.S., 1936, 286—287).—Vals. of the separation coeff.,  $\alpha$ , obtained by protracted electrolysis of aq. NaOH containing 0.5—1%  $D_2O$  under apparently identical conditions fluctuate widely. Vals. of  $\alpha$  for different cathode materials are recorded. J. G. A. G.

**Electrolytic formation of persulphate.** I. R. MATSUDA (Bull. Chem. Soc. Japan, 1936, 11, 1—7).—Aq.  $[NH_4]_2SO_4$  and  $H_2SO_4$ , in which the ratio of the normalities varied from 0:10 to 8:2, have been electrolysed at different c.d. and the variation of current efficiency for the formation of  $S_2O_8^{2-}$  examined. Current efficiency increases with c.d., the effect being greatest in the more acid solutions; it also increases as  $[H_2SO_4]$  diminishes and the effect at low c.d. is > at high. Increase in total concn. for a const. 5:1 ratio raises the efficiency, especially at higher c.d. The results indicate that increase in  $[OH^-]$  favours anodic oxidation. The effect of replacement of  $NH_4^+$  by other cations has been investigated. Current efficiency for  $K^+$ ,  $Na^+$ , and  $NH_4^+$ , which form acid sulphates, is > for the other cations, viz.,  $Mg^{2+}$ ,  $Li^+$ ,  $Al^{3+}$ ,  $Cd^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ; it is greatest for  $K^+$ , but the catalytic decomp. of  $S_2O_8^{2-}$  by cations is in the order  $Na^+ > K^+ > NH_4^+$ . M. S. B.

**Electrical synthesis of nitric oxide.** J. WILLEY (Nature, 1936, 137, 274—275).—With a 1:1 mixture of  $N_2$  and  $O_2$  the yield of NO at 5—10 mm. pressure with rapid gas circulation is practically independent of the electrical power supplied. A liquid air trap placed near the discharge condenses 7 to 10 times more  $NO_2$  than one placed at a distance from it, although the equiv. time interval is only 0.05 sec. This effect disappears when a plug of oxidised Cu is placed between the discharge and the trap, or when a large excess of  $O_2$  is used. It is apparently due to the simultaneous formation of active N which decomposes much of the NO formed. L. S. T.

**Simultaneous discharge of  $Cd^{2+}$  and  $H^+$  ions in solutions of simple salts of cadmium.** O. ESSIN, F. BEKLEMISHEVA, and A. MATANZEV (J. Chim. phys., 1936, 33, 72—77).—The yield of Cd obtained by electrolysis of aq.  $CdSO_4$  has been studied at 25° for  $[H_2SO_4]$  0.1N—10N and  $[CdSO_4]$  0.125N—1N and with c.d. 0.25—1 amp. per sq. dm. The results are in accord with the equation of simultaneous discharge calc. from Volmer's theory of overpotential. J. W. S.

**Electrolytic separation of bivalent europium.** A. BRUKL (Angew. Chem., 1936, 49, 159—161).—Eu can be readily separated by electrolytic reduction at a Hg cathode. For mixtures of rare earths containing < 2%  $Eu_2O_3$  it is necessary to co-ppt. the Eu (as  $EuSO_4$ ) with  $SrSO_4$  (cf. Selwood, A., 1935, 950), the  $SrSO_4$  being then removed by dissolution in hot 50% HCl, and further purification effected through pptn. with  $H_2C_2O_4$ . Sa mother-liquors containing 1—1.2%  $Eu_2O_3$  were electrolysed using c.d. of 0.1 amp. per sq. cm. (0.12 amp. per sq. cm. gave Sr-Hg), and after 8 electrolyses and subsequent separation of  $SrSO_4$ , the Eu content increased to 30%. Three further electrolyses without  $SrSO_4$  gave a product containing 99.40%  $Eu_2O_3$ , the impurities being Sa 0.5, Gd 0.03, and Yb 0.02%. The yield was 12 g. from 1.5 kg. of mother-liquor containing 1—1.2%  $Eu_2O_3$ . D. C. J.

**Mechanism of electrolytic processes. I. Anodic oxidation of some metals of the platinum group.** J. A. V. BUTLER and G. DREVER. II. **Electrolytic oxidation of sodium sulphite.** J. A. V. BUTLER and W. M. LESLIE (Trans. Faraday Soc., 1936, 32, 427—435, 435—444).—I. When electrodes of Pd, Rh, and Ir are anodically polarised in acid and alkaline solutions, an adsorbed layer of O is formed prior to the establishment of the O overvoltage, as in the case of Pt (cf. A., 1932, 1092; 1934, 154). With Pd and Rh the slow formation of peroxidic oxides has been observed as the second stage in the oxidation. These oxides are reduced cathodically at a more positive potential than the adsorbed O, and the conditions of their formation have been studied. A mechanism of the anodic oxidation of insol. metals is suggested.

II. The electrolytic oxidation of  $Na_2SO_3$  at Pt electrodes in buffer solutions of various  $p_H$  has been investigated. With  $p_H$  7 the oxidation takes place at a more negative potential than that at which adsorbed O is formed. Since no other primary process is observed in this region with the buffer solution alone, oxidation probably takes place in solutions of this  $p_H$  by direct transfer of electrons from the  $SO_3^{2-}$  ions to the electrode. With  $p_H$  9 oxidation occurs in the same region as that in which adsorbed O is formed, so that oxidation by adsorbed O is possible. The effect of adding various salts has been studied. With  $Mn^{2+}$  salts, which are the most effective, suppression of the initial stage of electrolysis is due to the formation of a film of  $MnO_2$ . The results do not agree with Glasstone and Hickling's theory (cf. A., 1933, 913) and an alternative mechanism is suggested. O. J. W.

**Effect of anode composition on zinc electrolysis.**—See B., 1936, 201.



**Electrolytic lead-plating.**—See B., 1936, 201.

**Electroplating bismuth on metals.**—See B., 1936, 201.

**Photochemical union of hydrogen and chlorine.**  
**IV. Reaction at low hydrogen pressures. Effects of wave-length, of temperature, and of traces of oxygen.** H. C. CRAGGS and A. J. ALLMAN (J.C.S., 1936, 241—252).—By irradiating O<sub>2</sub>-free mixtures of 0.1—0.6 mm. of H<sub>2</sub> and 1.7—166 mm. of Cl<sub>2</sub> with monochromatic light of  $\lambda$  546 m $\mu$ , HCl is formed, and the temp. coeff. leads to the activation energy 9.78 kg.-cal. (cf. 4.74—5.5 at  $\lambda$  436 m $\mu$ ). No HCl was obtained at  $\lambda$  579 m $\mu$ . The quantum efficiency,  $\gamma$ , relative to unity at 436 m $\mu$  is approx. 0.3 at 546 m $\mu$ . These results may be correlated with the continuous background of the banded spectrum region of Cl<sub>2</sub>. Thus, Cl<sub>2</sub> mols. in high vibration levels absorbing at  $\lambda$  546 m $\mu$  acquire sufficient additional energy to dissociate into atoms which initiate reaction chains. At approx. 2 mm. total pressure, ultra-violet light affords vals. of  $\gamma$  < with visible light, but at higher pressures this difference was not observed. Cl<sub>3</sub> formed by light of short  $\lambda$  would account for these results. 0.1 mm. of O<sub>2</sub> retards the reaction between Cl<sub>2</sub> and < 0.01 mm. H<sub>2</sub>, but has no effect when there is 0.5—0.01 mm. H<sub>2</sub>, although O<sub>2</sub> is consumed. These effects are discussed. J. G. A. G.

**Properties of illuminated iodine solutions.**  
**I. Photochemical dissociation of iodine molecules in solution.** E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 547—556).—Improvement of the apparatus previously described (A., 1935, 586) has permitted the detection and measurement of a reversible change in the extinction coeff. ( $\epsilon$ ) of I solutions under the influence of strong illumination. In CCl<sub>4</sub> and C<sub>6</sub>H<sub>14</sub>  $\epsilon$  decreases under illumination owing to dissociation of I<sub>2</sub> mols. into atoms. The velocity of recombination of the latter in solution is about 1000 times > that of Br atoms in He at atm. pressure, agreeing with the assumption that triple collisions are necessary in gas and that in solution every collision is effective. The quantum yield for dissociation of I<sub>2</sub> in solution is the same in the continuous spectral region as in the band region. Explanations of the results are offered. F. L. U.

**Detection of a latent image in thalious bromide.** W. J. G. FARRER (Nature, 1936, 137, 276).—Emulsions of TlBr in gelatin can receive a latent image, but direct reduction of the exposed bromide to Tl is not possible. By treatment with aq. AgNO<sub>3</sub> the Tl in the emulsion is replaced by Ag without destruction of the latent image, and after removal of the excess of sol. Ag the plate can be developed and fixed in the usual way. Replacement of the Tl by Ag occurs apparently without alteration in crystal shape or structure. TlBr emulsions can be colour-sensitised with dyes in the same way as Ag emulsions, but the same high degree of sensitivity has not yet been reached. L. S. T.

**Free *n*-propyl radical.**—See this vol., 451.

**Photodecomposition of iodoform and of alkyl and alkylene iodides.** K. E. GIBSON and T. IREDALE (Trans. Faraday Soc., 1936, 32, 571—576;

cf. A., 1933, 553).—The quantum yield in the photochemical production of I by C<sub>6</sub>H<sub>6</sub> solutions of MeI, CH<sub>2</sub>I<sub>2</sub>, Bu<sup>n</sup>I, CH<sub>3</sub>Bu<sup>n</sup>I, and C<sub>16</sub>H<sub>33</sub>I has been determined at room temp. and in absence of O<sub>2</sub>. For MeI and Bu<sup>n</sup>I the yield is approx. 1, and for the others 0.55—0.75. MeI in EtOH gives a val. > 1. The results are discussed. F. L. U.

**Photochemical decomposition of gaseous methyl iodide alone and in presence of hydrogen and nitrous oxide.** R. SPENCE and W. WILD (Proc. Leeds Phil. Soc., 1935—1936, 3, 141—144; cf. A., 1931, 1138).—Irradiation of MeI yielded CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and I. Increased yields of CH<sub>4</sub> were not obtained in presence of H<sub>2</sub>. The approx. quantum yield of CH<sub>4</sub> formation in terms of MeI disappearing was 0.06. There was no detectable reaction between Me and N<sub>2</sub>O. H. J. E.

**Photochemical formation of organic diradicals.**

**III. Anthracene, the fulgides, thiophosgene, and their derivatives.** A. SCHÖNBERG (Trans. Faraday Soc., 1936, 32, 514—521; cf. A., 1935, 986).—In order to explain the different chemical properties of irradiated solutions of certain anthracenes, fulgides, and CSeCl<sub>2</sub> in comparison with those of non-irradiated solutions, a photoequilibrium between the normal and diradical forms of the mol. is assumed, as was done in the case of rubrene (cf. A., 1934, 643). The phenomena of photo-oxidation, photoisomerisation, and photopolymerisation can be accounted for by this means. Objections to the theory are discussed. O. J. W.

**Behaviour of *dl*-serine, *dl*-phenylalanine, *dl*-alanine, *dl*-lactic acid, and propionic acid towards X-rays and ultra-violet light.** J. P. BECKER (Strahlenther., 1935, 52, 537—544; Chem. Zentr., 1935, ii, 203).—The decomp. of *dl*-serine (I) and *dl*-lactic acid (II) follows a different course from that of *dl*-alanine (III) and EtCO<sub>2</sub>H; this is ascribed to the presence of an  $\alpha$ -OH in (I) and (II). *dl*-Phenylalanine also differs from (III) in its mode of decomp. The physiological action of X-rays and ultra-violet light is, in part, attributed to such action. H. N. R.

**Comparison of the photochemical decomposition of *l*-aspartic acid, *l*-asparagine, and glycylglycine by X-rays and ultra-violet light.** J. P. BECKER (Strahlenther., 1935, 52, 531—536; Chem. Zentr., 1935, ii, 203).—Both *l*-aspartic acid and *l*-asparagine yield MeCHO on irradiation with X-rays or ultra-violet light; the decomp. products of glycylglycine are different. H. N. R.

**Photolysis of aliphatic aldehydes. III. Hydrogen from acetaldehyde.** F. E. BLACET and J. G. ROOF (J. Amer. Chem. Soc., 1936, 58, 278—280; cf. A., 1933, 930; 1934, 1188).—The fraction of mols. yielding H<sub>2</sub> increases linearly from 10% at  $\lambda$  3130 to 31% at  $\lambda$  2537. The mechanism of the primary process appears to be:  $\text{RHCO} + h\nu \rightarrow \text{R} + \text{HCO}$ . E. S. H.

**Photochemical reactions of cellulose. IV. Relation between wave-length and strength of light from a quartz mercury vapour lamp.** S. OGURI (J. Soc. Chem. Ind. Japan, 1936, 39, 35—



36B).—A table shows the deflexions of a thermopile galvanometer at  $\lambda$  of 2000—7000 Å. A. G.

**Concentrations of sodium vapour in the electric arc.** T. PECZALSKI and N. SZULC (Compt. rend., 1935, 201, 1335—1337; cf. A., 1935, 1046).—The concns. of Na within and around a C arc burning in the presence of NaCl have been determined spectroscopically. T. G. P.

**Significance of potassium carbonate for the corrosive action of potassium cyanide.** H. ELBEL (Z. ges. gerichtl. Med., 1934, 24, 25—29; Chem. Zentr., 1935, i, 3951—3952).—The corrosive action of KCN depends on its alkaline properties, and is weakened rather than strengthened by  $K_2CO_3$ . R. N. C.

**Rubidium and caesium fulminates.** L. HACKSPILL and W. SCHUMACHER (Compt. rend., 1936, 202, 69—71).—The fulminates were prepared by treating the alkali-metal amalgam, prepared in vac., with a suspension of Hg fulminate in anhyd. MeOH, and pptg. the salt with anhyd.  $Et_2O$ . Dissolution in MeOH and repptn. with  $Et_2O$  is necessary to remove traces of the double fulminate of Hg and Rb or Cs. The latter renders the product liable to detonate at  $< 50^\circ$ . H. J. E.

**Caesium mercury iodide.** F. GALLAIS (Compt. rend., 1936, 202, 54—56; cf. A., 1935, 592).—Measurements of electrical conductivity and of magnetic rotatory power are recorded for mixed solutions of CsI and  $HgCl_2$  in  $H_2O$  or EtOH. The formation of  $Cs_2HgI_4$  is indicated in 0.01—0.5M solutions. H. J. E.

**Basic copper sulphates.** O. BINDER (Ann. Chim., 1936, [xi], 5, 337—409).—A more detailed account of work previously described (this vol., 38, 172).  $4CuO \cdot SO_3 \cdot 4H_2O$  at  $150^\circ$  gives  $4CuO \cdot SO_3 \cdot 3H_2O$ , the X-ray photograph of which resembles that of  $4CuO \cdot SO_3 \cdot 4H_2O$ . The four basic sulphates are formulated  $[Cu\{(OH)_2Cu\}_3SO_4 \cdot H_2O]$ ;  $[Cu\{(OH)_2Cu\}_3SO_4]$ ;  $[Cu\{(OH)_2Cu\}_2SO_4]$ , and  $[Cu \cdot O \cdot Cu]SO_4$ . The first three are identified with langite, brochantite, and antlerite (stolznerite), respectively. F. R. G.

**Yellow cuprous oxide.** G. R. LEVI (Z. anorg. Chem., 1936, 226, 173—174).—A claim for priority over Straumanis *et al.* (A., 1935, 1332) with reference to the proof of the direct formation of  $Cu_2O$  by reduction in aq. solution. M. S. B.

**Organic cupri-tetrachlorides and -tetrabromides formed by secondary and tertiary amines and alkaloids.** J. AMIEL (Compt. rend., 1935, 201, 1383—1385; cf. this vol., 212).—The following compounds have been prepared and in some cases their *d* and solubilities determined:  $CuCl_4(NH_2Et)_2$ ,  $CuCl_4(NHEt)_2$ ,  $CuBr_4(NH_2Et)_2$ ,  $CuCl_4(NH_2PhMe)_2$ ,  $CuCl_4(NH_2PhEt)_2$ ,  $CuCl_4(NHPhMe)_2$ ,  $CuCl_4(NHPhEt)_2$ ,  $CuBr_4(NH_2PhMe)_2$ ,  $CuBr_4(NH_2PhEt)_2$ ,  $CuBr_4(NHPhMe)_2$ ,  $CuBr_4(NHPhEt)_2$ ; with nicotine, quinine, and strychnine  $CuCl_4(C_{10}H_{14}N_2H_2) \cdot H_2O$ ,  $CuCl_4(C_{10}H_{14}N_2H_2)$ ,  $CuCl_4(C_{20}H_{24}N_2O_2H_2)$ ,  $CuCl_4(C_{21}H_{24}N_2O_2H_2)$ ,  $CuBr_4(C_{10}H_{14}N_2H_2)$ ,  $CuBr_4(C_{20}H_{24}N_2O_2H_2)$ , and  $CuBr_4(C_{21}H_{24}N_2O_2H_2)_2$ ; and with brucine  $CuCl_4(C_{23}H_{26}N_2O_4H_2)$ . T. G. P.

**Silver solutions containing iodine.** (MLLE.) M. L. JOSIEN (Ann. Chim., 1936, [xi], 5, 147—265).—The action of aq. I on aq.  $AgNO_3$  comprises a rapid reaction between the HI produced by hydrolysis of the I and  $Ag^+$ , yielding insol.  $AgI$ , followed by decomp. of the  $HOI$  to give HI and  $HIO_3$ . The latter reaction is slow, being accelerated by increasing salt concn., by rise of temp., and by addition of acid. The reaction is most rapid when the Ag salt of a strong acid is used in the reaction. The reduction of  $IO_3^-$  by HCl and  $As_2O_3$  is attributed to a cyclic reaction, probably with intermediate production of I and oxidation of the  $As_2O_3$ , rather than to catalytic action. Sparingly sol. Ag salts react with I similarly to  $AgNO_3$ , but the first step is not instantaneous. The reaction between  $AgCl$  and I is not a direct substitution, but  $3I_2 + 5AgCl + 3H_2O = 5AgI + HIO_3 + 5HCl$ . It is concluded that there is no evidence of production of an intermediate product between  $OI^-$  and  $IO_3^-$  in the reaction between I and Ag salts or between I and alkali. J. W. S.

**Solid reactions at 1000—1200° between magnesium oxide or beryllium oxide and nickel, iron, chromium, manganese, and their oxides.** L. NAVIAS (J. Amer. Ceram. Soc., 1936, 19, 1—7).—The reactions were carried out with the mixtures as loose and pressed powders and with loose powder on a high-fired pressed slab of MgO or BeO. The degree of reaction was noted by the extent of discoloration at the interface. In an oxidising atm. at 1200° the reaction with MgO and BeO increased in the order NiO (with BeO, none),  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $MnO_2$ , in all cases reaction with MgO being the greater. The same sequence was found for the metallic elements in an oxidising atm., but the degree of reaction was  $>$  with the corresponding oxides. In a  $H_2$  atm. at 1200° only  $MnO_2$  showed any reaction, and of the metals, Cr and Mn oxidised with very slight reaction. Mixtures of oxides and of metals showed less reaction than the individuals. Wet air gave most reaction between MgO and Mn,  $MnO_2$ , or Cr powders. J. A. S.

**Double salt,  $K_2Mg(CO_3)_2 \cdot 4H_2O$ .** F. HALLA (Z. anorg. Chem., 1936, 226, 139—140).—On gradual addition of aq.  $K_2CO_3$  to aq.  $MgCl_2$ , of suitable concn., reaction takes place in two stages, a flocculent ppt. of  $MgCO_3 \cdot 3H_2O$  being first formed. This redissolves and, as the addition of aq.  $K_2CO_3$  continues, a cryst. ppt. of  $K_2Mg(CO_3)_2 \cdot 4H_2O$  is obtained. Solubility determinations have been made at  $17^\circ$  in aq. KCl of varying concn. to reduce hydrolysis. The temp. coeff. of solubility has also been determined. M. S. B.

**Production of calcium sulphate hemihydrate in the wet way, and the polymorphism of the anhydrous sulphate.** P. GAUBERT (Bull. Soc. franç. Min., 1934, 57, 252—267; Chem. Zentr., 1935, i, 3523).— $CaSO_4 \cdot 0.5H_2O$  was obtained as hexagonal prisms by evaporation of a hot  $HNO_3$  solution of  $CaSO_4$ . When dehydrated in air at  $130^\circ$ , or in a neutral liquid at  $170^\circ$ , they maintain their form and optical orientation, but *n* decreases, whilst the double refraction increases ( $\gamma$ -form). This is transformed at  $180^\circ$  into the  $\beta$ -form (*n*  $<$  that of natural anhydrite). At  $520^\circ$  the  $\beta$ -form gives the  $\alpha$ -form. H. J. E.



**Zinc, even impure but perfectly smooth and without external contamination, does not effervesce with dilute acids.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 206—213).—The technique described for Fe (A., 1935, 834; this vol., 174) has been applied to Zn with similar results. E. S. H.

**Barium arsenates. Characterisation of  $2\text{As}_2\text{O}_5 \cdot 3\text{BaO}$ .** H. GUÉRIN (Compt. rend., 1936, 202, 225—227; cf. this vol., 173).—The thermal decomp. of Ba meta-, ortho-, and pyroarsenates has been investigated.  $\text{BaO} \cdot \text{As}_2\text{O}_5$  when heated in a vac. at  $700^\circ$  yields the sesquiarsenate  $3\text{BaO} \cdot 2\text{As}_2\text{O}_5$ .

T. G. P.

**Purification of mercury.** B. PESCE (Annali Chim. Appl., 1935, 25, 654—657).—A pycnometer for determining the  $d$  of Hg is described. The presence of very small amounts of impurities in Hg can be detected most readily by  $d$  determinations. Hg cannot be purified completely by distillation only, but two preliminary distillations followed by the treatment suggested by Beutell (A., 1910, ii, 105) give a pure product.

A. M. P.

**Reactions of mercuric oxide.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 459—460).—The reactions of HgO with KCN, KCNS,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_2\text{Fe}(\text{CN})_6$ ,  $\text{NaBO}_2$ , Te, P, As, and Sb are described.

E. S. H.

**Action of mercuric oxide on solutions of sulphates and nitrates.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 193—196).—The products of reaction with Al,  $\text{Ti}^{IV}$ ,  $\text{Ce}^{III}$ ,  $\text{Fe}^{II}$ ,  $\text{Mn}^{II}$ , Zn, and  $\text{Cu}^{II}$  sulphates, and Bi, Zr,  $\text{Cu}^{II}$ , and  $\text{Ni}^{II}$  nitrates have been identified. HgO does not react with aq.  $\text{AgNO}_3$  or  $\text{UO}_2(\text{NO}_3)_2$ .

E. S. H.

**Mercuric chromates.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 460—462).—The conditions of formation of  $\text{HgCrO}_4$  and  $\text{HgSO}_4$  in the systems (1)  $\text{Hg}-\text{H}_2\text{SO}_4-\text{K}_2\text{CrO}_4$ , (2)  $\text{HgO}-\text{H}_2\text{SO}_4-\text{K}_2\text{CrO}_4$ , (3)  $\text{Hg}-\text{H}_2\text{SO}_4-\text{CrO}_3$ , (4)  $\text{HgO}-\text{H}_2\text{SO}_4-\text{CrO}_3$  at  $10-15^\circ$  have been determined.

E. S. H.

**Action of mercuric oxide on potassium dichromate.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 419—420).—With small amounts of HgO, the product is  $\text{HgCrO}_4$ ; further addition of HgO produces basic chromates.

E. S. H.

**Aluminium, even impure but perfectly smooth and without external contamination, does not effervesce with dilute acids.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 213—218).—The results obtained with Zn (see above) have also been observed with Al.

E. S. H.

**Decomposition of sodium aluminates.** V. D. DJATSCHKOV and O. S. KOSHUCHOVA (Kolloid-Z., 1936, 74, 196—200).—The stability of solutions of Na aluminate increases rapidly with increase of the ratio  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  above 1.4—1.5. The solutions exhibit min. stability at a concn. of 120—180 g.  $\text{Al}_2\text{O}_3$  per litre. Addition of  $\text{Na}_2\text{SiO}_3$  first stabilises the solutions, but at higher concns. causes coagulation, the pptd.  $\text{Al}_2\text{O}_3$  being contaminated with  $\text{SiO}_2$ . Addition of agar-agar increases the stability, whilst gelatin, methylene-blue, and Me-violet have no effect, and tannic acid very little.

F. L. U.

**Acid fluorides of univalent cations.** C. FINBAK and O. HASSEL (Z. anorg. Chem., 1936, 226, 175—176).—Determination of the lattice consts. of the TI compound, obtained by the concn. of the solution of  $\text{Ti}_2\text{O}$  or  $\text{Ti}_2\text{CO}_3$  in excess of HF, indicates that it is a silicofluoride and not an acid fluoride as supposed by other investigators. Similar conclusions have been reached previously with regard to other so-called "acid fluorides," and doubt is thrown on the possibility of the existence of acid fluorides in general.

M. S. B.

**Reactivity of red and yellow lead oxide with silica.** J. A. HEDVALL and A. ELDH (Z. anorg. Chem., 1936, 226, 192—196).—The amount of reaction occurring between red PbO and  $\text{SiO}_2$ , when an intimate mixture of the two is heated for 1 hr. at  $450-650^\circ$ , has been determined and compared with the rate of transition from red to yellow PbO at the same temp. Although the transition temp. is  $488.5^\circ$  both the rate of reaction with  $\text{SiO}_2$  and the rate of transition begin to be appreciable at approx.  $600^\circ$  only. Above this temp. both increase rapidly. The temp.-reactivity curve for red PbO with  $\text{SiO}_2$  is practically identical with that for yellow PbO, since the slight pressure used in mixing results in partial transformation into the stable red form.

M. S. B.

**Induced oxidation of nitrogen.** M. POLJAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 35—36).—A discussion of the formation of N oxides in gaseous explosions.

H. J. E.

**Structure of nitrogen peroxide deduced from its action on potassium iodide.** M. DODÉ (Compt. rend., 1935, 201, 1378—1380).—The reactions between  $\text{N}_2\text{O}_4$  and KI or aq. KI have been investigated; they indicate that  $\text{N}_2\text{O}_4$  exists in at least two forms in equilibrium.

T. G. P.

**Non-existence of the nitrosyl of Angeli.**—See this vol., 460.

**Nitrogen iodide.** E. ROEDERER (Z. anorg. Chem., 1936, 226, 145—167).—Attempts to employ  $\text{N}_2\text{H}_3\text{I}_3$  for the development of a new photographic process, depending on photochemical reactions with the highest possible quantum output, were unsuccessful.  $\text{N}_2\text{H}_3\text{I}_3$  shows a max. stability in aq. solution at  $p_H$  approx. 10. The requisite  $p_H$  is a little higher in the presence of aq.  $\text{NH}_3$  than in its absence. The equilibrium const. for the formation of  $\text{N}_2\text{H}_3\text{I}_3$  from aq.  $\text{NH}_3$  and I in aq. solution is  $K = [\text{NH}_4]^2[\text{OH}]^5[\text{I}]^3/[\text{I}']^3$  and is approx.  $10^{-29.23}$ . No  $\text{N}_2\text{H}_3\text{I}_3$  is formed by the interaction of  $\text{NH}_3$  and I in  $\text{CCl}_4$ . An additive product is mainly obtained, as in the reaction between gaseous  $\text{NH}_3$  and solid I, but there is also a small amount of oxidation of  $\text{NH}_3$ , probably to  $\text{N}_2$  and  $\text{H}_2$ , and simultaneous reduction of I to I' with formation of  $\text{NH}_4\text{I}$ . Similar behaviour is observed in  $\text{C}_6\text{H}_6$  solution. A reaction scheme is suggested. The distribution coeff. of  $\text{NH}_3$  between  $\text{CCl}_4$  and the gas phase is  $7.24 \pm 0.04$ .

M. S. B.

**Decomposition of nitrogen iodide.** W. E. GARNER and W. E. LACHEM (Trans. Faraday Soc., 1936, 32, 567—569).—See A., 1935, 828.

F. L. U.



**Constitution and mechanism of formation of the solid, yellow hydride of phosphorus.** P. ROYEN and K. HILL (*Naturwiss.*, 1936, 24, 108).—The hydride of P, generally regarded as  $P_{12}H_6$ , is not a definite compound, but arises from adsorption of  $PH_3$  on an amorphous, yellow P. X-Ray diagrams of  $P_{12}H_6$  and  $P_9H_2$  show no interference. More difficultly volatile mols., e.g.,  $NH_3$ , piperidine, and  $PEt_3$ , can cause partial or complete removal of the hydride as  $PH_3$ . The formation of red alkali-metal salts in aq.-EtOH solutions is probably due to peptisation, rather than to the existence of an acidic H in  $P_{12}H_6$ . The formula of the hydride is dependent on surface conditions, and varies from  $P_{12}H_{5.8}$  to  $P_{12}H_{7.2}$ . It is suggested that the reaction is  $3P_2H_4 = 4PH_3 + 2P$ , analogous to the reaction between  $PH_3$  and  $PEt_2Cl$ , in which an unstable intermediate compound,  $PH_2PEt_2$  is formed, and decomposes to give amorphous yellow P and  $PH_2Et$ ,  $PHEt_2$ , and  $PEt_3$ , some of these being adsorbed on the P. A. J. M.

**Phosphorus pernitride  $P_4N_6$ .** H. MOUREU and G. WETROFF (*Compt. rend.*, 1935, 201, 1381—1383).—The products of the reaction of  $PCl_3$  on liquid  $NH_3$ , heated in a vac. at  $550^\circ$ , yield  $P_4N_6$ , a white, insol., non-volatile substance spontaneously inflammable in air, and hydrolysed at  $215^\circ$  thus:  $P_4N_6 + 15H_2O = 2(NH_4)_2HPO_4 + NH_4H_2PO_4 + NH_4H_2PO_3$ . Under similar conditions  $P_3N_5 + 12H_2O = 2(NH_4)_2HPO_4 + NH_4H_2PO_4$ .  $P_4N_6$  heated above  $750^\circ$  in a vac. gives PN, which condenses out in a pure state. PN is completely hydrolysed only after 3 days at  $215^\circ$ . The primary reaction is  $PN + 3H_2O = NH_4H_2PO_3$ . T. G. P.

**Action of arsenic trichloride on the elements.** E. MONTIGNIE (*Bull. Soc. chim.*, 1936, [v], 3, 190—191).—At room temp. S, Bi, and Al are unattacked; with Se, Te, Pb, and Au, respectively, As is liberated and  $Se_2Cl_2$ ,  $TeCl_4$ ,  $PbCl_2$ , and  $AuCl_3$  formed; Ag forms  $AsCl_3Ag_3$ . E. S. H.

**Formulae of basic salts of bismuth.** M. PICON (*Bull. Soc. chim.*, 1936, [v], 3, 186—190).—The system advocated shows the ratio of acid radicals to metal atoms: e.g.,  $Bi_{20}O_{21}(NO_3)_{18} \cdot 6H_2O$  instead of  $10Bi_2O_3 \cdot 9N_2O_5 \cdot 6H_2O$ . E. S. H.

**Bivalent bismuth iodide.** E. MONTIGNIE (*Bull. Soc. chim.*, 1936, [v], 3, 191—193).—Unsuccessful attempts to prepare  $BiI_2$  are recorded. E. S. H.

**Preparation of bismuth iodosulphide by the wet method.** F. FRANÇOIS and M. L. DELWAULLE (*Bull. Soc. chim.*, 1936, [v], 3, 504—508).— $BiSI$  is formed by the action of  $H_2S$  or  $Bi_2S_3$  on solutions of  $BiI_3$  in HI, or by the action of HI on  $Bi_2S_3$ . Determinations of Bi as  $Bi_2S_3$  in solutions containing I are rendered invalid by pptn. of  $BiSI$ . E. S. H.

**Basic organic salts of bismuth.**—See this vol., 460.

**Occlusion of protoactinium by sulphides insoluble in hydrochloric acid.** CHENG DA-CHANG and L. HOANG (*Bull. Soc. chim.*, 1936, [v], 3, 326—328).—The co-pptn. of Pa with  $CuS$ ,  $Sb_2S_3$ ,  $HgS$ , and  $Bi_2S_3$  has been studied under different conditions of concn. and acidity. Pa sulphide is sol. in the aq. HCl, but is adsorbed incompletely by the ppt. E. S. H.

**Oxidation of inorganic reagents by ozone. I. Potassium iodide.** G. GUÉRON, M. PRETTE, and J. GUÉRON (*Bull. Soc. chim.*, 1936, [v], 3, 295—312).—Experiments in buffered, neutral solutions show that the normal reaction  $2I' + O_3 + H_2O = I_2 + O_2 + 2OH'$  is accompanied by an independent, heterogeneous reaction,  $I' + 3O_3 = IO_3' + 3O_2$ . The latter reaction preponderates in presence of a large glass surface. The influence of concn. has been studied. Preliminary observations have been made on the simultaneous oxidation of  $AsO_3'''$ . E. S. H.

**Constitution of sulphato-compounds.** A. VON KISS (*Z. anorg. Chem.*, 1936, 226, 141—144).—The dialysis method is not a conclusive test for the existence of true complex compounds, since a simple association of ions without change of the constitution of the co-ordination zone will produce the effect of increased ionic wt. The method must be combined with spectroscopic determinations. These do not confirm the formation of true complex sulphates reported by Brintzinger *et al.* (A., 1935, 181). M. S. B.

**Transformation from vitreous to metallic selenium.** K. TANAKA and H. Y. TIEN (*Mem. Coll. Sci. Kyoto*, 1935, A, 18, 309—310; cf. A., 1935, 920).—Between  $65^\circ$  and  $80^\circ$ , the wt.-% of metallic Se,  $p$ , in the specimen annealed for  $t$  hr. is  $p = P(1 - e^{-ct - t'})$ , where  $P$  is approx. 78.5%,  $t'$  decreases from 4 to 0.65 and  $c$  increases from 0.062 to 1.11 as the temp. is raised. J. G. A. G.

**Purification and preparation of very intense polonium sources.** M. HAISSINSKY (*J. Chim. phys.*, 1936, 33, 97—98).—Po can be separated from Te, Au, Hg, and Pt by reducing the latter with  $N_2H_4$ . Pptn. is preferably carried out in solution sufficiently acid to prevent adsorption of Po by the pptd. metal (20% HCl or AcOH). The Po can then be deposited by introduction of a polished Ag disc. J. W. S.

**Preparation of polonium sources from radon bulbs.** L. R. HAFSTAD (*J. Franklin Inst.*, 1936, 221, 191—213).—Details of the prep. of strong Po sources by an elaboration of the Curie method (A., 1926, 5) are given. R. S.

**Preparation of chemically pure hydrochloric acid.**—See B., 1936, 190.

**Existence of chlorous anhydride  $[Cl_2O_3]$ .** M. KANTZER (*Compt. rend.*, 1936, 202, 209—210).—The action of conc.  $H_2SO_4$  on  $KClO_3$  at  $-15^\circ$  in presence of undecenoic acid yields  $ClO_2$  and  $Cl_2O_3$ . The absorption spectrum of  $ClO_2$  consists of three groups of bands between 3895 and 4180 Å.  $Cl_2O_3$  absorbs continuously between 3500 and 4260 Å., and has 10 broad bands between 4260 and 4649 Å. T. G. P.

**Mechanism of permanganate reduction and the induced oxidation of chlorion.** H. BASSETT and I. SANDERSON (*J.C.S.*, 1936, 207—211).— $Mn'''$  is the first identifiable product when  $MnO_4'$  is reduced by  $Fe''$ . Induced oxidation of  $Cl'$  in permanganate reactions is attributed to  $Mn'''$  and especially  $Mn''$ , because the process  $Mn''' \rightarrow Mn''$  is probably simpler than  $MnO_4' \rightarrow Mn'''$ . The end-point of the titration  $FeCl_2-KMnO_4$  is most nearly stoichiometric when



Mn<sup>++</sup> or substances forming stable complexes with Mn<sup>+++</sup>, e.g., SO<sub>4</sub><sup>''</sup>, PO<sub>4</sub><sup>'''</sup>, F', and Cl', are added. Solutions 2–3*N* with respect to H<sub>2</sub>SO<sub>4</sub> are best (cf. this vol., 44) but the end-point is always unstable, possibly owing to the change 2Mn<sup>+++</sup> = Mn<sup>++</sup> + Mn<sup>++++</sup>. PO<sub>4</sub><sup>'''</sup> is almost completely pptd. as the Mn<sup>++</sup> salts of complex Mn<sup>IV</sup> phosphoric acids by digesting with conc. HNO<sub>3</sub> and Mn or Mn<sup>++</sup>. J. G. A. G.

Induced oxidation of potassium iodide by ozone. (MME.) G. GUÉRON, J. GUÉRON, and M. PRETTE (Compt. rend., 1935, 201, 1376–1378; cf. A., 1935, 945).—The heterogeneous oxidation of KI by O<sub>3</sub> in aq. solution is not an induced oxidation. With greatly diluted O<sub>3</sub> an induced oxidation accompanies, to a slight extent, the normal reaction O<sub>3</sub> + 2I' + H<sub>2</sub>O = O<sub>2</sub> + I<sub>2</sub> + 2OH'. T. G. P.

Iron of high purity. F. ADCOCK and C. A. BRISTOW (Proc. Roy. Soc., 1935, A, 153, 172–200).—Fe has been prepared (1) by the electrolysis of a solution of FeCl<sub>2</sub> and NaCl, using an "Arceo" Fe anode, and (2) by the decomp. of FeCl<sub>2</sub> by steam, in each case followed by treatment of the molten metal with a stream of pure H<sub>2</sub> and subsequent melting in vac. The work was controlled by chemical and X-ray analysis. Measurable differences existed in the physical properties of different batches. The α-γ transformation in some of the samples, indicated by dilatometric observations, does not take place at a const. temp. but over a definite temp. range. L. L. B.

Polished iron, even impure, does not oxidise in saturated moist air. P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 320–321).—A reply to criticism (cf. this vol., 174). E. S. H.

Active oxides. XCIII. Intermediate active states in the decomposition of needle iron ore into α-iron oxide and water vapour. G. F. HÜTTIG and E. STROTZER [with O. HNEVKOVSKY and H. KITTEL]. XCVII. A crystallised basic aluminium sulphite, Al<sub>2</sub>O<sub>3</sub>·2SO<sub>2</sub>·H<sub>2</sub>O. E. ROSENKRANZ and G. F. HÜTTIG (Z. anorg. Chem., 1936, 226, 97–125, 126–131).—XCIII. The changes in colour, bulk *d*, magnetic susceptibility, "apparent" mol. vol., and crystal structure, taking place during the dehydration of artificially prepared needle Fe ore, α-Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O, have been followed, and the results are discussed. There are no sharply defined intermediate active states, but the property-composition curves show points of inflexion.

XCVII. A basic compound, Al<sub>2</sub>O<sub>3</sub>·2SO<sub>2</sub>·H<sub>2</sub>O, has been separated from an aq. solution of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> by shaking at 78–80° until some of the SO<sub>2</sub> was driven off. The composition of the salt was confirmed by the isobaric decomp. curve and X-ray examination. M. S. B.

Ferric ammonium carbonate. V. AUGER and (MLLE.) M. GALLISSOT (Compt. rend., 1936, 202, 224–225).—Aq. FeCl<sub>3</sub> reacts with a large excess of saturated aq. NH<sub>4</sub>HCO<sub>3</sub> in presence of undissolved NH<sub>4</sub>HCO<sub>3</sub> and CO<sub>2</sub> to yield unstable yellow prisms, [Fe(OH)<sub>2</sub>NH<sub>3</sub>(H<sub>2</sub>O)]HCO<sub>3</sub>. T. G. P.

Two double salts of ferric fluoride. A. H. NIELSEN (Z. anorg. Chem., 1936, 226, 222–224).—

The salts Sr<sub>3</sub>Fe<sub>2</sub>F<sub>12</sub>·2H<sub>2</sub>O, *d* 3.71, and BaFeF<sub>5</sub>·H<sub>2</sub>O, *d* 3.94, have been prepared and their chemical and crystallographic properties determined. M. S. B.

Complex chemical behaviour of *o*-amino-phenol.—See this vol., 465.

Complex salts of α-phenylethylamine. Equivalence of the four co-valencies of bivalent platinum and palladium.—See this vol., 462.

Duration of analyses. RAUCH (Document. sci., 1935, 4, 4–10; Chem. Zentr., 1935, i, 3818).—The time taken for completion of various routine analyses has been determined. J. S. A.

Quantitative spectrum analysis. I, II. W. VAN TONGEREN (Chem. Weekblad, 1936, 33, 130–141, 151–159).—A historical review, with full experimental details of published methods. D. R. D.

Chromatographic analysis and its applications. H. WILLSTAEDT (Svensk Kem. Tidskr., 1936, 48, 32–48).—A lecture.

Adsorption analysis of aqueous solutions. W. KOSCHARA (Z. physiol. Chem., 1936, 239, 89–96).—The differences involved in the application of adsorption analyses in aq. and org. media are discussed. The use of natural or acid-treated fuller's earth, Brockmann's Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O and the dependence of efficiency on the *p*<sub>H</sub> of the solution are considered. H. W.

Influence of temperature on *p*<sub>H</sub> measurements in alkaline media. P. SZIGETI (Nature, 1936, 137, 276).—Alkaline *p*<sub>H</sub> vals. are valueless unless temp. is also recorded. L. S. T.

Analysis with fluorescent indicators. M. DÉRI-BÉRÉ (Ann. Chim. Analyt., 1936, [iii], 18, 37–39).—Acid-alkali titrations are performed in ultra-violet light, using the change of fluorescence colour at some characteristic *p*<sub>H</sub> to mark the end-point. Umbelliferone, β-methylumbelliferone, and uranyl salts (in the absence of halogens) are suitable for strong acid-strong base titrations; β-C<sub>10</sub>H<sub>7</sub>·OH or eosin BN for weak acids; and aesculin or fluorescein for weak bases. J. S. A.

Use of the micro-thermal conductivity method for the determination of heavy hydrogen. A. FARKAS, L. FARKAS, and E. K. RIDEAL (Nature, 1936, 137, 315).—The reliability and accuracy of the method is maintained (cf. this vol., 181). L. S. T.

Determination of bound water by means of the ultracentrifuge. J. W. McBAIN (J. Amer. Chem. Soc., 1936, 58, 315–317).—Theoretical. Formulae are derived to show the error caused by neglecting solvation in ultracentrifuge determinations. E. S. H.

Analysis of heavy water. A. FARKAS (Trans. Faraday Soc., 1936, 32, 413–415).—The micro-thermo-conductivity method for the analysis of H<sub>2</sub>-D<sub>2</sub> mixtures is applied to the analysis of H<sub>2</sub>O-D<sub>2</sub>O mixtures. The D content of the latter is calc. from the observed D<sub>2</sub> content of H<sub>2</sub>-D<sub>2</sub> gas brought into equilibrium with the water. The method is specially suitable for investigating the interchange of H and D atoms between water and other substances.



without the need of separating the water for each determination. O. J. W.

**Colour reactions of the chlorate ion.** A. SÁ (An. Farm. Bioquim., 1934, 5, 111—114; Chem. Zentr., 1935, i, 3573).—The same colours are given by  $\text{ClO}_3'$ ,  $\text{NO}_3'$ , and  $\text{NO}_3'$  with  $\text{NHPh}\cdot\text{C}_{10}\text{H}_7\text{-}\alpha$  and with  $\text{NH}(\text{C}_{10}\text{H}_7\text{-}\alpha)_2$ . Different colours (described) are given with  $\text{NHPh}\cdot\text{C}_{10}\text{H}_7\text{-}\beta$ ,  $\text{NH}(\text{C}_{10}\text{H}_7\text{-}\beta)_2$ , and phenyl-dihydrodibenzacridine. H. N. R.

**Determination of iodine in iodised salt.**—See B., 1936, 232.

**Determination of oxygen dissolved in 1 c.c. of water.**—See B., 1936, 254.

**Polarographic studies with the dropping mercury cathode. LVII. Determination of oxygen in gases and solutions.** V. VÍTEK (Coll. Czech. Chem. Comm., 1935, 7, 537—547).—The electroreduction of  $\text{O}_2$  causes two "waves" in the current-voltage curve corresponding with reduction first to  $\text{H}_2\text{O}_2$  and then to  $\text{H}_2\text{O}$ , and the magnitude of the saturation current of the total reduction of  $\text{O}_2 \propto [\text{O}_2]$  and permits  $[\text{O}_2]$  as low as 0.04 mg. per litre to be determined in a fraction of 1 c.c. 0.05—100% of  $\text{O}_2$  in gaseous mixtures is determined within  $\pm 2\%$  of the total  $[\text{O}_2]$  by bubbling through MeOH and determining the solubility of the  $\text{O}_2$  polarographically. J. G. A. G.

**Determination of sulphur in silicates.** A. F. FIOLETOVA (J. Appl. Chem. Russ., 1935, 8, 1461—1464).—Total S is best determined as  $\text{SO}_4''$  after fusion with  $\text{Na}_2\text{CO}_3\text{--KNO}_3$ .  $\text{SO}_4''$  is determined by extraction for 1 hr. with boiling 10% HCl in an inert atm.; atm.  $\text{O}_2$  leads to high vals., owing to oxidation of sulphide S to  $\text{SO}_4''$ . No satisfactory direct method of determination of sulphide S was found. R. T.

**Indirect colorimetric semi-micro-determination of the sulphate anion.** F. A. GOIN (An. Farm. Bioquim., 1934, 5, 61—68; Chem. Zentr., 1935, i, 3573).—The colour reaction between benzidine and  $\text{AcOH}\text{--NaNO}_2$  in EtOH is applied to the determination of  $\text{SO}_4''$  in urine. H. N. R.

**Determination of sulphate.** Conditions necessary for the precipitation of benzidine sulphate, with special reference to the determination of sulphates in urine. E. C. OWEN (Biochem. J., 1936, 30, 352—360).—The pptn. of  $\text{SO}_4''$  by benzidine (I) is optimal at  $p_H$  2—3;  $\text{HPO}_4''$  is pptd. by (I) at  $p_H > 2$  and may be removed before the  $\text{SO}_4''$  determination by the method of Fiske (A., 1921, ii, 556). The  $[\text{Cl}']$  in the urine is not sufficient to produce appreciable errors. H. D.

**Application of the systems water-ethyl alcohol-potassium carbonate and -ammonium sulphate to the rapid detection of certain anions.** A. G. KOBLJANSKI (J. Appl. Chem. Russ., 1935, 8, 1494—1497).—In the two-phase liquid system EtOH-saturated aq.  $\text{K}_2\text{CO}_3$ , the anions  $\text{SO}_4''$ ,  $\text{Cl}'$ ,  $\text{Fe}(\text{CN})_6'''$ , and  $\text{Fe}(\text{CN})_6'''$  are present chiefly in the aq. and  $\text{I}'$ ,  $\text{CNS}'$ , and  $\text{S}''$  in the EtOH, layer, whilst in EtOH-saturated aq.  $(\text{NH}_4)_2\text{SO}_4$   $\text{I}'$ ,  $\text{Br}'$ ,  $\text{Cl}'$ ,  $\text{CNS}'$ ,  $\text{Fe}(\text{CN})_6'''$  and  $\text{Fe}(\text{CN})_5\text{NO}''$  are found chiefly in the EtOH, and

$\text{Fe}(\text{CN})_6'''$  in the aq. layer. These findings are applied to the detection of the individual anions when present together. R. T.

**Gravimetric determination of selenates.** P. SPACU (Bull. Soc. chim., 1936, [v], 3, 159).—The slightly acid  $\text{SeO}_4''$  solution is treated with aq.  $\text{Pb}(\text{OAc})_2$  and the mixture boiled. The ppt. is collected, dried in vac., and weighed as  $\text{PbSeO}_4$ . E. S. H.

**Colorimetric determination of nitrates in water: influence of chlorides.**—See B., 1936, 254.

**Differentiation of constituents of nitrous vapours by formation of nitrogen compounds.** A. SANFOURCHE and J. BUREAU (Compt. rend., 1936, 202, 66—69).—Tests are described in which various mixtures of NO and  $\text{NO}_2$  were analysed (a) by absorption in  $\text{H}_2\text{SO}_4$  ( $d$  1.833), and (b) by absorption in a solution of  $\text{NH}_2\text{Ph}\cdot\text{HCl}$ . The latter method gave more trustworthy analytical results. H. J. E.

**Determination of nitrate- and nitrite-nitrogen with copper-zinc powder.** T. ARND and H. SEEBERG (Angew. Chem., 1936, 49, 166—167).—The vals. formerly obtained (B., 1932, 201; 1933, 118) were due mainly to the method of prep. of the Cu-Zn powder. Directions are given for this prep. and the method is recommended for fertilisers etc. D. C. J.

**Potentiometric titration of phosphates.** E. MICHALSKI (Rocz. Chem., 1935, 15, 468—480).—Excess of standard  $\text{AgNO}_3$  is added to the alkaline solution, 0.1N-NaOH is added to neutrality (orange coloration with phenol-red), a drop of  $N\text{-AcOH}$  is added, and Ag is determined in the filtrate; the results are 0.2% > the theoretical, owing to adsorption of Ag by the ppt. of  $\text{Ag}_3\text{PO}_4$ . Ca, Sr, Ba, and Mg do not interfere, but Cl, Br, I,  $\text{NH}_4$ , Al, and Fe should be absent. R. T.

**Sensitive reaction for phosphate.** A. STEIGMANN (Chem.-Ztg., 1936, 60, 129).—The sensitivity of the phosphomolybdate reaction is enhanced by adding a glycerol-gelatin solution, which is boiled until the protein no longer gives turbidity with  $(\text{NH}_4)_2\text{MoO}_4$ . J. S. A.

**Fluorine and ammonia as sources of error in determination of phosphate by the [hydroxy]-apatite method.** A. T. JENSEN (K. Veterin. Landsb. Aarskr., 1935, 41—50; Chem. Zentr., 1935, ii, 255).—Modifications of Damsgaard and Sørensen's method are described, eliminating errors due to the presence of  $\text{F}'$  or  $\text{NH}_3$  (cf. A., 1935, 718). J. S. A.

**Separate determination of arsine and phosphine in air.** V. G. GUREVITSCH and B. A. RASCHKOVAN (J. Gen. Chem. Russ., 1935, 5, 1317—1323).—1 c.c. of 12% KBr is added to the solution, containing 0.2 mg. of  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$ , the mixture is evaporated to dryness, 5 c.c. of 1—7N-HCl are added, and the solution is again evaporated to dryness (twice), the residue is dissolved in  $\text{H}_2\text{O}$ , and  $\text{H}_3\text{PO}_4$  is determined colorimetrically.  $\text{H}_3\text{AsO}_4$  is determined in presence of  $\text{H}_3\text{PO}_4$  by reducing with nascent H to  $\text{AsH}_3$  (0.001—0.05 mg.), absorbing the gaseous products in conc.  $\text{HNO}_3$ , evaporating the  $\text{HNO}_3$  to dryness, and determining  $\text{H}_3\text{AsO}_4$  in the residue by the



ordinary colorimetric procedure.  $\text{AsH}_3$  and  $\text{PH}_3$  in air are determined by absorption in conc.  $\text{HNO}_3$ , evaporation, and analysis of the residue by the above methods.

R. T.

**Risk of error in determining traces of arsenic in organic and inorganic materials.** W. A. DAVIS and J. G. MALBY (Analyst, 1936, 61, 96—100).—Before applying the Marsh or Gutzeit test  $\text{AsO}_4^{3-}$  must be reduced to  $\text{AsO}_3^{3-}$ , preferably by warming with aq.  $\text{H}_2\text{SO}_3$  or  $\text{NaHSO}_3$ , excess of which must be removed. During the actual test the Gutzeit flask should be heated at 40—60°.

E. C. S.

**Colorimetric determination of small quantities of silica in solutions, minerals, and technical products.** I. P. ALIMARIN and V. S. ZVEREV (Trans. Inst. Econ. Min. U.S.S.R., 1934, No. 63, 15 pp.).—A crit. survey. Dienert and Wandenbulcke's method, based on the formation of  $\text{H}_8[\text{Si}(\text{Mo}_2\text{O}_7)_6]$ , is best for 0.005—5%  $\text{SiO}_2$ . In presence of large amounts of mineral acids and their hydrolysable salts,  $\text{NaOAc}$  should be added. The effects of P and Fe are counteracted by adding excess of  $\text{H}_3\text{PO}_4$ . The phosphomolybdate colour can also be removed with tartaric or citric acid. The effect of F is avoided by adding  $\text{AlCl}_3$ , which forms  $\text{H}_3\text{AlF}_6$  from  $\text{H}_2\text{SiF}_6$ .

CH. ABS. (e)

**Rapid gravimetric determination of silicic acid.**—See B., 1936, 190.

**Quantitative spectrography of alkali metals.** P. URBAIN and M. WADA (Bull. Soc. chim., 1936, [7], 3, 163—169).—An electric arc between Cu electrodes is used. To reduce the rate of vaporisation of the alkali-metal compound, it is mixed with a refractory substance. Determination is by comparison of line intensities.

E. S. H.

**Determination of sodium chloride in salt.**—See B., 1936, 232.

**Reaction for calcium.** S. A. CELSI (An. Farm. Bioquim., 1934, 5, 85—89; Chem. Zentr., 1935, i, 3573).—A mixture of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{Cu}(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$  gives with  $\text{Ca}^{++}$  a sky-blue ppt.

H. N. R.

**Application of copper ferrocyanide ammoniate in testing for calcium.** J. V. DUBSKÝ and A. LANGER (Coll. Czech. Chem. Comm., 1936, 8, 47—56).—By the action of  $\text{K}_4\text{Fe}(\text{CN})_6$  on solutions of  $\text{CaCl}_2 + \text{CuCl}_2$  in presence of  $\text{NH}_3$ ,  $(\text{CH}_2\text{NH}_2)_2$  (en), or  $\text{C}_2\text{H}_5\text{N}$ , the following compounds have been obtained:  $\text{Cu}_2\text{Ca}(\text{NH}_4)_2[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{NH}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{Cu}_2\text{Ca}(\text{NH}_4)_2[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{CuCa}[\text{Fe}(\text{CN})_6]_2 \cdot 5$ , and  $6\text{NH}_3 \cdot 2\text{H}_2\text{O}$ ;  $\text{CuCa}[\text{Fe}(\text{CN})_6] \cdot 6\text{NH}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{Cu}_2[\text{Fe}(\text{CN})_6] \cdot \text{en}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{CuCa}[\text{Fe}(\text{CN})_6] \cdot \text{en}_2 \cdot 2\text{H}_2\text{O}$ ;  $\text{Cu}_2[\text{Fe}(\text{CN})_6] \cdot 4\text{C}_2\text{H}_5\text{N} \cdot 6\text{H}_2\text{O}$ ;  $\text{Cu}_2\text{Ca}[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{C}_2\text{H}_5\text{N} \cdot 30\text{H}_2\text{O}$ . Speculative coordination formulæ are advanced.

J. S. A.

**Potentiometric determination of calcium concentrations in solutions.** H. J. C. TENDELOO (J. Biol. Chem., 1936, 113, 333—339).—A method, using a  $\text{CaF}_2$  electrode, is described. Absorption of Ca by proteins decreases with increasing acidity.

H. G. R.

**Determination of radium in carnotite and pitchblende.**—See B., 1936, 232.

**Dithizone method for determination of lead.** P. A. CLIFFORD and H. J. WICHMANN (J. Assoc. Off. Agric. Chem., 1936, 19, 130—156).—The transmission spectra of solutions of dithizone (I) in  $\text{CHCl}_3$  and  $\text{CCl}_4$  show strong absorption at 600  $\text{m}\mu$ , and a weak band at 450  $\text{m}\mu$ . The quant. relation between Pb and (I) at  $p_{\text{H}}$  vals. between 5 and 12, and the principles and inherent errors of the different methods of extraction and colorimetric determination, are discussed. Procedures, based on the "mixed-colour" method (cf. B., 1934, 379) with the use of a photometer, are outlined for the determination of Pb in urine and bone etc.

E. C. S.

**Volumetric determination of lead and of molybdates with adsorption indicators.** C. CANDEA and I. G. MURGULESCU (Ann. Chim. Analyt., 1936, [iii], 18, 33—36).—Pb, present as  $\text{Pb}(\text{OAc})_2$  or  $\text{Pb}(\text{NO}_3)_2$ , is titrated against  $\text{MoO}_4^{2-}$  using eosin A as adsorption indicator.

J. S. A.

**Gravimetric determination of lead as lead chromate.** L. GUZELJ (Z. anal. Chem., 1936, 104, 107—119).—The accuracy of the method is not affected by the presence of  $\text{AcOH}$ ,  $\text{NH}_4\text{OAc}$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , or  $\text{NH}_4\text{NO}_3$ , but  $[\text{HNO}_3]$  should be  $> 0.1N$ . Addition of  $\text{NH}_3$  after pptn. may lead to the formation of basic Pb chromate, which is hindered by  $\text{NH}_4\text{OAc}$  or  $(\text{NH}_4)_2\text{CrO}_4$ .  $[\text{Pb}]$  should be as low as is practicable.

J. S. A.

**Determination of lead and antimony in pure metals and their alloys.** H. VDOVISZEWSKI (Z. anal. Chem., 1936, 104, 94—107).—The determination of Pb as  $\text{PbSO}_4$  by Treadwell's method, and of Sb as  $\text{Sb}_2\text{S}_3$  by Vortmann and Metzl's method, is critically reviewed, and modifications of procedure are advocated. The determination of Pb as  $\text{PbCrO}_4$  is rapid, but leads to slightly high results.

J. S. A.

**Gravimetric determination of certain metals [with thiolbenzthiazole].** III. Determination of lead, thallium, bismuth, and gold. G. SPACU and M. KURAS (Z. anal. Chem., 1936, 104, 88—93).—Pb is pptd. quantitatively by thiolbenzthiazole (I) from hot ammoniacal solutions as the basic salt,  $\text{C}_7\text{H}_4\text{NS}_2\text{PbOH}$  (II), which is dried at 110° and weighed as such. Any normal salt,  $(\text{C}_7\text{H}_4\text{NS}_2)_2\text{Pb}$ , is converted into (II) on boiling in presence of  $\text{NH}_3$ . Tl, Bi, and Au are similarly pptd. by (I).  $\text{C}_7\text{H}_4\text{NS}_2\text{Ti}$  is dried at 110°;  $(\text{C}_7\text{H}_4\text{NS}_2)_3\text{Bi}$  and  $(\text{C}_7\text{H}_4\text{NS}_2)_3\text{Au}$  are ignited to  $\text{Bi}_2\text{O}_3$  and Au, respectively.

J. S. A.

**Drop method for detection of cerium.** L. KULBERG (J. Appl. Chem. Russ., 1935, 8, 1452—1456).—Ag and  $\text{Ti}^{IV}$  are removed from 0.2 ml. of solution by pptn. as chlorides, 2—3 drops of saturated aq.  $\text{K}_4\text{Fe}(\text{CN})_6$ , 0.5 ml. of 10% KCN, and 3—4 drops of  $N\text{-NaOH}$  are added (to ppt. or neutralise the interfering effects of  $\text{Mn}^{II}$ ,  $\text{Co}^{II}$ , or  $\text{Th}^{III}$ ), and an  $\text{AcOH}$  solution of leuco-malachite-green is added, when a green coloration is obtained in presence of  $< 3 \times 10^{-8}$  g. of  $\text{Ce}^{III}$ .

R. T.

**Potentiometric determination of cerous salts with ferrocyanide.** P. SPACU (Z. anal. Chem., 1936, 104, 119—122).— $\text{Ce}^{III}$  is titrated potentiometrically against  $\text{K}_4\text{Fe}(\text{CN})_6$  in 30% aq. EtOH solution.



The Ce must be added to the  $K_4Fe(CN)_6$  to avoid adsorption errors. J. S. A.

**Colorimetric determination of aluminium in waters.**—See B., 1936, 222.

**Colorimetric determination of iron.** L. UR-BÁNYI (Mezőg. kutat., 1935, 8, 279—287).—The thiocyanic and sulphosalicylic acid reactions give inaccurate results. Comparison of the colours in the case of the Prussian-blue reaction is much easier. Best results were obtained when the acidity of the medium corresponded to 0.1N-HCl and the solution contained about 0.1—1.0 mg. of Fe per 10 ml.

NUTR. ABS. (m)

**Determination of ferric oxide.** A. F. FIOLETOVA and S. CHAIKINA (J. Appl. Chem. Russ., 1935, 8, 1467—1469).—Someya's Zn amalgam method is simpler and not less accurate than are the  $TiCl_3$  reduction, the iodometric, and the colorimetric methods. R. T.

**Determination of iron and manganese in water.**—See B., 1936, 254.

**Determination of cobalt by electrolysis at controlled potentials and using hydrazine hydrate and chloride as depolarisers.** A. JÍLEK and J. VŘEŠTAL (Coll. Czech. Chem. Comm., 1935, 7, 512—520).—The conditions for the quant. electrodeposition of Co have been investigated. < 100 mg. of Co are determined to within  $\pm 0.2$  mg. as a coherent, completely acid-sol. deposit by electrolysis at 4 volts and about 0.5 amp. with a rotating anode a solution of  $CoSO_4$  containing 0.5 g. of  $N_2H_4 \cdot HCl$ , 2 c.c. of conc.  $N_2H_4 \cdot H_2O$  (I), and 45 c.c. of conc. aq.  $NH_3$ , diluted to 100 c.c. After 1 hr., 1 c.c. of (I) is added and the electrolysis continued for 2 hr. Small quantities of Cl<sup>-</sup> have no effect, but the results are somewhat low with 1 g. of  $K_2SO_4$ , and with 1 g. of  $NH_4NO_3$ . Ni and Co-Ni mixtures can be determined under identical conditions. J. G. A. G.

**Volumetric determination of cobalticyanide ion.** R. UZEL and B. JEŽEK (Coll. Czech. Chem. Comm., 1935, 7, 497—511).—Electrometric titration of  $K_3Co(CN)_6$  with  $AgNO_3$  always gives results < stoichiometric owing to adsorption of  $Co(CN)_6^{3-}$  on colloidal  $Ag_3Co(CN)_6$ . Analogous results are obtained when  $Ag^+$  is replaced by  $Hg^+$ ,  $Hg^{2+}$ , and  $Cu^{2+}$ . With  $Cu^{2+}$ , the end-point becomes more vague as the at. wt. of the added univalent ion increases, but bi- and ter-valent ions do not interfere.  $K_2CrO_4$  indicates the stoichiometric end-point of the titration of  $Co(CN)_6^{3-}$  with  $AgNO_3$  even in the presence of  $Zn^{2+}$  and  $Mn^{2+}$  after boiling off excess of HCN in acid solution and neutralising. Ni, Fe, and other metals are eliminated earlier.  $Co(CN)_6^{3-}$  is formed from  $Co^{2+}$  by way of the intermediate brownish-red anion  $[Co^{III}(CN)_5OH]^{2-}$ . J. G. A. G.

**Volumetric determination of nickel in presence of cobalt.** G. CHARLOT (Bull. Soc. chim., 1936, [v], 3, 324—326).—The Ni and Co compounds are converted into  $K_4Ni(CN)_6$  and  $K_3Co(CN)_6$ , respectively, by the usual methods. By adding alkali, which ppt.  $Ni_2O_3$ , and then aq. HCl and  $H_2C_2O_4$ , the Ni complex is destroyed and  $NiCl_2$  obtained in solution, the Co complex being unchanged. Ni is then determined

volumetrically with KCN in aq.  $NH_3$  solution. The precision is 0.05—0.2 mg. of Ni. E. S. H.

**Oxidimetric determination of the oximes of nickel and copper.** J. MIRONOFF (Bull. Soc. chim. Belg., 1936, 45, 1—8).—The volumetric method described by Tougarnoff (A., 1935, 187) gives quant. results when small amounts of Cu and Ni are pptd. with phenylglyoxime (I), diacetylmonoxime (II), diphenylglyoxime (III), or benzoinoxime (IV). The same procedure as with dimethylglyoxime can be used for (I) and (II), but with (III) hydrolysis must be performed carefully on account of frothing. With (IV) the benzoin formed must be removed, or high results are obtained. J. W. S.

**Oxidation-reduction indicators. I. New indicators for the bromate titration of tin and antimony.** Z. RAICHINSCHTEIN (J. Appl. Chem. Russ., 1935, 8, 1470—1475).— $SnCl_2$  is titrated in 1.15N-HCl at 30—50° with 0.1N- $NaBrO_3$ , in presence of 0.1% benzopurpurin B.  $SbCl_3$  is titrated in 3.1—3.5N-HCl using benzopurpurin 4B as indicator. R. T.

**Precipitation of thorium by sebacic acid.** L. E. KAUFMAN (J. Appl. Chem. Russ., 1935, 8, 1520—1524).—3—10 ml. of 3% sebacic acid (I) in EtOH are added to 100 ml. of the boiling neutral solution, containing Th and Ce, the ppt. is collected, washed, dried at 100°, and warmed at 100° with fuming  $HNO_3$  to disappearance of  $NO_2$ , when the solution is evaporated to dryness, and dissolved in 100 ml. of  $H_2O$ . Th is then repptd. with (I), and the washed ppt. is calcined and weighed as  $ThO_2$ . R. T.

**Determination of oxides of vanadium in ores.**—See B., 1936, 191.

**Chemical differentiation of polished metallic minerals by the contact method. III, IV.** R. GALOPIN (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 252—257, 257—261; cf. A., 1935, 463).—Details are given for the detection of the minerals  $Sb_2S_3$ ,  $Bi_2S_3$ ,  $FeS$ ,  $Sb_2S_3$ ,  $3PbS$ ,  $Sb_2S_3$ ,  $2PbS$ ,  $Cu_2S$ ,  $Sb_2S_3$ ,  $NiS$ ,  $NiSb$ ,  $NiAs$ ,  $CuFeS_3$ ,  $Fe_3S_{n+1}$ , and  $(NiFe)S$ . R. S.

**Drop method of detection of bismuth.** N. A. TANANAIEV and A. V. TANANAIEVA (J. Appl. Chem. Russ., 1935, 8, 1457—1460).— $SnCl_2$  is added to the solution, when a brown coloration is given by  $\leq 2 \times 10^{-6}$  g. of Bi ( $Hg$  interferes). Alternatively, Ag and Pb are pptd. by saturated aq.  $NaCl-Na_2SO_4$  and  $SnCl_2$  and KI are added to the solution, when a yellow to orange ppt. is obtained in presence of  $\leq 10^{-5}$  g. of Bi. A third method consists in conversion into the chloride, followed by dilution, when  $BiOCl$  is pptd. ( $\leq 5 \times 10^{-5}$  g. of Bi). The limitations of the methods and their applications to special cases are discussed. R. T.

**Spectroscopic determination of adsorbed ions.** (Miss) M. ANNETTS and L. NEWMAN (J. Physical Chem., 1936, 40, 187—193).—The spectroscopic method for the determination of very small concns. of metal ions has been applied to the study of the action of NaOH and  $NaMnO_4$  as stabilising agents, and of  $AlCl_3$  as a coagulating agent, for Au sols, and also of  $MgCrO_4$  as a coagulating agent for Au and Cu sols. The limits of sensitivity are  $M/100,000$  for



Au and Mn,  $M/50,000$  for Mg, Cr, and Na, and  $M/1000$  for Al. M. S. B.

**Volumetric determination of palladium by means of oximes.** M. GAIHDE (Bull. Soc. chim. Belg., 1936, 45, 9—14; cf. this vol., 444).—Oximes of Pd cannot be hydrolysed and titrated directly like those of Cu and Ni. By pptn. with excess of standard salicylaldoxime in acid solution, filtering, and titrating the excess of oxime, 5—40 mg. Pd can be determined in presence of other metals. J. W. S.

**Use of overhead heating in analysis.** F. HEINRICH and F. PETZOLD (Chem.-Ztg., 1936, 60, 145—147).—Heating from above by electrical heating elements is recommended for rapid, quiet evaporation of liquids, drying of ppts., etc. R. S. C.

**Apparatus for measurement of thermal conductivity of metal foil.** A. EUCKEN and H. WARRENTUP (Z. tech. Physik, 1935, 16, 99—105; Chem. Zentr., 1935, ii, 191).—A centrally heated disc is used. Measurements on Cu and Al agree with previous data. J. S. A.

**Thermoregulator.** R. D. STEHLER (Science, 1936, 83, 40).—Increased precision is obtained by placing metal foil in the bulb of an ordinary PhMe regulator. L. S. T.

**Quantitative spectral analysis under variable discharge conditions.** V. NAEDLER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 23—26).—A discussion of errors in the use of a spark for excitation. H. J. E.

**Mercury-vapour lamp with very intense resonance radiation.** G. KORNFELD and F. MÜLLER-SKJOLD (Z. physikal. Chem., 1936, B, 31, 223—226).—A lamp is described which has an incandescent cathode of Konel metal and gives for 2537 Å. twelve times the intensity of the ordinary Hg-vapour lamp. R. C.

**Counter measurements and Röntgen unit.** H. WILHELM (Z. tech. Physik, 1935, 16, 2—8; Chem. Zentr., 1935, i, 3012—3013).—No general relationship between counter results and X-ray dose can be derived, but between limits of  $\lambda$ , and for homogeneous radiation, a fairly const. factor may be found. The use of counters for measurement of very weak X-ray doses is described. J. S. A.

**Photo-electric analysis with fluctuating light.** F. MÜLLER and W. DÜRICHEN (Chem. Fabr., 1935, 8, 267—269).—The insertion of a rotating perforated disc between the light source and the photo-electric cell gives rise to a fluctuating photo-electric current which may be amplified by means of thermionic valve circuits. The light intensity may be then reduced to give the max. sensitivity. Two barrier-layer cells may be used to provide a highly sensitive differential arrangement. J. S. A.

**Significance of ions in gas-filled photo-cells.** H. RICHTER (Z. tech. Physik, 1934, 15, 598—601; Chem. Zentr., 1935, i, 2951).—The relative importance of ionisation by collision, and of the formation of free electrons by bombardment of the cathode, has been investigated. By delaying the inception of the stable glow discharge, the performance of the cell may be improved. J. S. A.

H H

**Abnormalities in characteristic of vacuum photo-cells.** H. GEFFCKEN (Z. tech. Physik, 1934, 15, 595—598; Chem. Zentr., 1935, i, 2950—2951).—Vac. photo-cells in which the work of exit from the photosensitive layer is artificially lowered by suitable chemical treatment of that layer show irregular behaviour, the saturation current jumping reversibly from a lower to a higher val. The effect is not due to wall charges, but is attributed to changes in the cathodic space charge. Better compensation of space charges, and high sensitivity, may be attained by admission of traces of gas. J. S. A.

**Electrophotometer of barrier-layer [photo-] cells intended for practical opacimetry.** P. MEUNIER (Compt. rend., 1935, 201, 1371—1373). T. G. P.

**Photometric determination of m.p.** P. WOOG, J. GIVAUDON, R. SIGWALT, and J. LIENHART (Bull. Soc. chim., 1936, [v], 3, 439—442).—The fusion of the substance produces a "grease spot" on a paper screen, which is observed under unequal illumination from opposite sides, as in the Bunsen photometer. E. S. H.

**Shielded-filament X-ray tube for pure X-ray spectra.** E. DERSHEM (Rev. Sci. Instr., 1936, [ii], 7, 86—89).—The target is shielded from visible light and from spattered W from the filament. Fogging of plates by visible light is practically eliminated, the intensity of characteristic radiation remains const., the tube current is nearly const., and the life of the filament is increased. C. W. G.

**Apparatus for X-ray patterns of the high-pressure modifications of ice.** R. L. MCFARLAN (Rev. Sci. Instr., 1936, [ii], 7, 82—85).—Very rapid insertion and centring of the crystal, its rotation, and the evacuation of the diffraction chamber are possible. C. W. G.

**Influence of dispersion on the reading of the Haber-Löwe gas interferometer.** E. KARWAT (Z. Instrument., 1933, 53, 12—21, 70—78; Chem. Zentr., 1935, i, 3957). H. J. E.

**Simple comparator for absorption spectrograms.** F. ROSEBURY (Science, 1936, 83, 86). L. S. T.

$p_H$  measurements, dark-coloured substances, and indicator methods. F. ANSELM (Chem. Fabr., 1935, 8, 269—271).—The application of very thin colorimeter cells (up to 0.65 mm. thick) is described. J. S. A.

**Production of high-velocity lithium ions.** R. L. THORNTON and B. B. KINSEY (Physical Rev., 1934, [ii], 46, 324).—The arrangement described yields a current of 1.5 micro-amp. at  $5 \times 10^5$  volts. L. S. T.

**Superconducting galvanometer.** H. G. SMITH and F. G. A. TARR (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 23—35).—A moving-coil galvanometer, the coil of which is immersed in a liquid He cryostat, is described. H. J. E.

**Weston normal cell as standard for the international volt.** A. K. KOLOSOV (Vses. Nauch.-Issled. Inst. Metrol., 1932, No. 100, 131—137; cf. A., 1934, 625).—To avoid mixing of the components



during transport, the cathode limb has a constriction to hold the Hg in place. The saturated  $\text{CdSO}_4$  contains approx.  $0.004N\text{-H}_2\text{SO}_4$ . In washing the  $\text{Hg}_2\text{SO}_4$  with saturated aq.  $\text{CdSO}_4$  washing must cease when the concn. of acid in the washings is  $0.004N$ . High acid concns. lead to gas formation in the anode limb.

CH. ABS. (e)

**Resolving power in recording of coincidence by two counters arranged behind one another.** J. N. HUMMEL (Z. tech. Physik, 1934, 15, 573—575; Physikal. Z., 1934, 35, 997—999; Chem. Zentr., 1935, i, 2942).—Data concerning resolving power are given.

J. S. A.

**Sensitive counter tube arrangement.** E. B. ANDERSEN (Z. Physik, 1936, 98, 597—604).—A counter for weak radioactive measurements is surrounded by other tubes, and the amplifier registers those impulses present only in this tube.

A. B. D. C.

**Determination of the end-point of conductometric titrations by calculation.** J. H. BOULAD (Bull. Soc. chim., 1936, [v], 3, 408—412).—Mathematical procedure, replacing the graphical method, is described.

E. S. H.

**Easily constructed electrical relay.** G. F. KOEPF and J. F. MEZEN (Science, 1936, 83, 109—110).

L. S. T.

**Iron-free coil for production of maintained intense magnetic fields.** G. GERLOFF and E. LÖWE (Z. Physik, 1936, 98, 559—560).—The apparatus gives homogeneous fields up to 5000 oersted.

A. B. D. C.

**Pipette for measurement of aqueous solutions.** Y. P. LIU (J. Chinese Chem. Soc., 1936, 4, 20—21).—The pipette is provided with a two-way stopcock above the bulb.

R. S. B.

**Micro-burette.** W. SPATZ (Chem. Fabr., 1936, 9, 70).—A capillary connecting tube avoids the formation of air bubbles between the burette and the reservoir.

J. S. A.

**Apparatus for determination of gases.** M. L. JEAN (Bull. Soc. chim., 1936, [v], 3, 267—269).—The apparatus formerly described (A., 1935, 466) is modified.

E. S. H.

**Accessories for gas analysis.** W. ALLNER (Chem. Fabr., 1936, 9, 70—72).—A device for collecting gases at const. variable pressure, and a modified Jaeger  $\text{CuO}$  tube for the fractional combustion of  $\text{H}_2$  and hydrocarbons, are described.

J. S. A.

**Constant-volume gas analysis apparatus.** B. N. SINGH and P. B. MATHUR (Biochem. J., 1936, 30, 321—322).—The apparatus is used for determination of  $\text{O}_2$  and  $\text{CO}_2$  with an accuracy of  $\pm 0.1\%$ .

W. McC.

**Multiple-unit distilling apparatus for determination of fluorine by Willard and Winter's method.** D. S. REYNOLDS, I. B. KERSHAW, and K. D. JACOB (J. Assoc. Off. Agric. Chem., 1936, 19, 156—162; cf. A., 1933, 242, 654).

E. C. S.

**Preparation of glass helices for use in fractionating columns.** W. C. YOUNG and Z. JASAITIS (J. Amer. Chem. Soc., 1936, 58, 377).—Technique is recommended.

E. S. H.

**Determination of Poisson's elastic constants by means of ultrasonic waves.** R. BAR and A. WALTI (Helv. phys. Acta, 1934, 7, 658—661; Chem. Zentr., 1935, i, 3759).—The method is applied to the determination of the elastic moduli of glass.

J. S. A.

**Air-damped balances.** W. N. BOND (Analyst, 1936, 61, 85—90).—The theoretical and practical advantages of critically air-damped over oscillating balances are discussed.

E. C. S.

**Constant-level siphon.** R. LAUTIE (Bull. Soc. chim., 1936, [v], 3, 503—504).

E. S. H.

**Level control in funnels.** W. R. THOMPSON (Science, 1936, 83, 168).

L. S. T.

**Apparatus for catalytic hydrogenation at high pressure.** L. PALFRAY (Bull. Soc. chim., 1936, [v], 3, 508—511).—The apparatus consists of an autoclave and  $\text{H}_2$  compressor, with automatic recording of temp. and pressure. It is suitable for the range  $0\text{--}300\text{ kg.}$  and  $0\text{--}300^\circ$ .

E. S. H.

**Determination of density of grains.** W. F. DE JONG (Zentr. Min., 1935, A, 140—142; Chem. Zentr., 1935, ii, 252).—A flotation method, applicable to particles weighing about 1 mg., is described.

J. S. A.

**Improvised micro-manipulator.** P. H. SIMONS (J. S. African Chem. Inst., 1936, 19, 24—25).—The adjustments of a microscope sub-stage condenser may be used to manipulate needles, capillaries, etc. in the field of the microscope.

J. S. A.

**Determination of contact angles from measurements of the dimensions of small bubbles and drops.** I. Spheroidal segment method for acute angles. G. L. MACK. II. Sessile drop method for obtuse angles. G. L. MACK and (Miss) D. A. LEE (J. Physical Chem., 1936, 40, 159—167, 169—176).—I. Acute angles of contact may be determined as a function of the radius and vol. of a small spherical drop of liquid by a method which is practically independent of the solid surface concerned. An expression for the effect of gravity on the form of the drop is given.

II. Average obtuse contact angles may be determined from measurements of the vertical height, the horizontal radius, and the radius of curvature at the apex of sessile drops or bubbles under a plate. The third dimension required may be calc. from the capillary const. of the liquid by a simplified equation.

M. S. B.

**Apparatus for maintaining circulation of gases in laboratory apparatus.** V. I. KUZNETZOV (J. Appl. Chem. Russ., 1935, 8, 1516—1517).—A simple laboratory pump is described.

R. T.

**Safety tube for preventing bumping of liquids supersaturated with gas.** V. I. KUZNETZOV (J. Appl. Chem. Russ., 1935, 8, 1514—1515).—A U-tube, containing 1—2 drops of Hg, with one broad and one narrow limb, is fused to the lower part of the condenser tube of a Kjeldahl set. The tube, by allowing gases to enter, but not to leave, the apparatus, permits instant equalisation of pressure, thereby eliminating bumping.

R. T.



**Research applications of colloidal graphite.** B. H. PORTER (Rev. Sci. Instr., 1936, [ii], 7, 101—106).—Applications to vac. technique, electronic devices, electrical contacts, and other purposes are described. C. W. G.

**Determination of vapour pressure.** V. A. KIREEV and A. A. POPOV (J. Gen. Chem. Russ., 1935, 5, 1399—1401).—Apparatus is described, whereby the v.p. of  $\text{AcCl}$ ,  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , and propylene oxide have been measured at different temp., and empirical equations connecting temp. with v.p. have hence been derived. R. T.

**Glass apparatus for handling low-b.p. liquids.** S. F. BIRCH and P. DOCKSEY (Chem. and Ind., 1936, 169—170).—The construction of a simple apparatus which can be used also for the solvent extraction of liquids is described. S. M.

**Mixing arrangement for large quantities in the laboratory.** B. FLASCHENTRÄGER and P. FABER (Chem. Fabr., 1935, 8, 272).—A rotary shaking machine is described. J. S. A.

**Determination of surface tension by the drop-weight method.** K. C. BAILEY (Nature, 1936, 137, 323). L. S. T.

**Ripple method of measuring surface tension.** R. C. BROWN (Proc. Physical Soc., 1936, 48, 312—322).—An apparatus for the production, stroboscopic observation, and measurement of ripples for surface-tension determinations is described. Results for the fall of surface tension of a slowly adsorbed aq. solution of cetylpyridinium bromide are similar to those obtained by a static method, showing that the ripples do not retard attainment of surface equilibrium. N. M. B.

**Measurement of surface tension by means of stationary waves on a vertical jet.** J. SATTERLY and J. C. STRACHAN (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 105—112).—Measurements with  $\text{H}_2\text{O}$  and  $\text{Hg}$  are described, using a modification of Satterly and McPherson's method (*ibid.*, 1934, 28, 177). Sources of error are discussed. H. J. E.

**Determination of viscosity by the oscillation of a vessel enclosing a fluid.** I. E. N. DA C. ANDRADE and Y. S. CHONG. II. E. N. DA C. ANDRADE and L. ROTHERHAM (Proc. Physical Soc., 1936, 48, 247—260, 261—266).—I. An improved technique and method of calculation are described. Accurate results are obtained for  $\text{H}_2\text{O}$  over the temp. range 2.5—65.2°.

II. Instead of the energy of oscillation being dissipated by the viscous forces, energy is supplied at every oscillation, by the discharge of a condenser, to maintain a fixed amplitude;  $\eta$  is calc. from the amplitude and the energy supplied. The method is checked by measurements of  $\eta$  for hexane in terms of that of  $\text{H}_2\text{O}$ . N. M. B.

**Arrangement for measuring the viscosity of gases.** A. FORTIER (Compt. rend., 1935, 201, 1330—1332).—A method which depends on delivering a rigorously const. vol. of gas independent of the pressure and of the capillary is outlined. T. G. P.

**Measurement of absolute viscosity by the falling-sphere method.** L. R. BACON (J. Franklin Inst., 1936, 221, 251—273).—The vals. given by Stokes' formula are shown to depend on the ratio diameter of sphere/diameter of tube. Various correction formulæ have been tested, but only that due to Faxen yields vals. in agreement with capillary-tube determinations over the range 10—10,000 poises. R. S.

**Apparatus for automatically maintaining reduced pressure.** C. F. WINCHESTER (Science, 1936, 83, 64). L. S. T.

**Instruments for registration of vapour pressure [of water] and specific humidity.** F. WENK (Z. Instrument., 1935, 54, 15—19; Chem. Zentr., 1935, i, 3957).—Apparatus is described. J. S. A.

**Vacuum in laboratory and technique.** H. BAERMANN (Chem. Fabr., 1935, 8, 395—404).—A comprehensive review covering modern types of vac. pumps, measuring instruments, vac. sealing media, automatic regulators, and vac. evaporating and distilling technique. A. R. P.

## Geochemistry.

**Spectra of meteors.** P. M. MILLMAN (Ann. Ast. Obs. Harvard Coll., 1932, 82, 113—146).—9 spectra are discussed. Fe, Ca, Mg, Mn, Al, Cr, and Si were identified. CH. ABS. (e)

**Evolution of helium from the earth.** E. K. GERLING (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 41—43).—Analyses are recorded for the  $\text{He}+\text{Ne}$  content of air in contact with the earth in various districts. In none of the localities examined was the val. high. H. J. E.

**Lake Akanuma, a siderotrophic lake at the foot of volcano Bandai, Hukusima Prefecture, Japan.** S. YOSHIMURA (Proc. Imp. Acad. Tokyo, 1935, 11, 426—428).—The temp.,  $p_{\text{H}}$ ,  $[\text{O}_2]$ ,  $[\text{Mn}]$ ,  $[\text{Fe}]$ ,  $[\text{Cl}]$ , and sp. conductivity are recorded for samples of  $\text{H}_2\text{O}$  from the surface and from various

depths. The absence of dissolved  $\text{O}_2$  at 1 m. and below is due to reduction by  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ , which are present in high concn. The high conductivity is due to  $\text{CaSO}_4$ . J. W. S.

**Radioactive waters at Starobelsk.** E. S. BURKSER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 45—48).—Complete analytical data are given for samples from depths of 400—750 m. The Ra content was 0.80—6.1  $\times 10^{-11}\%$ . Th and mesothorium were absent. H. J. E.

**Mineral and medicinal springs of Switzerland.** ANON. (Mitt. Lebensm. Hyg., 1935, 26, 250—328).—Analyses of 62 springs are given and a system of classification is evolved based on mineral constituents, physical properties, and clinical effects. J. G.



**Characteristics of Pearl River water.** W. W. HUANG (J. Chem. Eng. China, 1935, 2, 139—147).—Seasonal variations in chemical composition of this H<sub>2</sub>O are recorded in detail. C. I.

**Corpus Christi structural basin postulated from salinity data.** W. A. PRICE (Bull. Amer. Assoc. Petrol. Geol., 1935, 19, 317—355).—Consideration of lines of isoalkalinity indicates that original oceanic H<sub>2</sub>O diluted with surface H<sub>2</sub>O entered at the outcrop and penetrated slowly down the dip.

CH. ABS. (p)

**Difference in the isotopic composition of the oxygen in air and water.** N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 36—38).—By preparing H<sub>2</sub>O from light H<sub>2</sub> and from O<sub>2</sub> obtained (1) from the air, (2) by the partial electrolysis (5%) of ordinary H<sub>2</sub>O, and (3) by the complete hydrolysis of H<sub>2</sub>O, and by comparing  $\delta$  for the three samples, it has been shown that air is richer in O<sup>18</sup> than ordinary H<sub>2</sub>O. The distribution coeff. of O<sup>18</sup> between air and H<sub>2</sub>O is approx. 1.04. M. S. B.

**Analyses of phosphorite from the culm formation of the Świetykrzyż mountains.** S. BISKUPSKI (Bull. Acad. Polonaise, 1935, A, 85—91).—Analytical data are recorded and discussed. The Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> content increases and that of CaCO<sub>3</sub> decreases with the age. The CaF<sub>2</sub> was almost const. in all the phosphorites. H. J. E.

**Origin of guano minerals in the Dominican Grotto, Slovakia.** J. V. KAŠPAR (Věstn. Stát. Geol. Úst. Českoslov. Repub., 1934, 10, 104—111; Chem. Zentr., 1935, i, 3527).—Analytical data are given. H. J. E.

**Symmetrical extinction angles of albite-twinned plagioclases.** S. TSUBOI (Proc. Imp. Acad. Tokyo, 1935, 11, 423—425).—The curve given by Wright (Amer. J. Sci., 1913, 36, Plate X) for the max. symmetrical extinction angles of albite-twinned plagioclases is shown to be incorrect and a revised curve is given. J. W. S.

**Relations of later gabbro to sulphides at the Horne Mine, Noranda, Quebec.** G. G. SUFFEL (Econ. Geol., 1935, 30, 905—915).—Sulphide ores at this mine are definitely later than all other formations except, possibly, the later gabbro dykes. All the chalcopryite, and probably the pyrrhotite and pyrite, are now shown to be post-dyke. L. S. T.

**Differentiation in traps and ore deposition.** A. C. LANE (Econ. Geol., 1935, 30, 924—927; of. A., 1935, 955).—A discussion. L. S. T.

**Mylonitic sphalerite from Friedensville, Pennsylvania.** R. D. BUTLER (Econ. Geol., 1935, 30, 890—904). L. S. T.

**Large quartz veins of Great Bear Lake, Canada.** G. M. FURNIVAL (Econ. Geol., 1935, 30, 843—859).—These have been formed by the deposition of quartz (I) from hydrothermal solutions at moderate temp. Minerals other than (I) are sparse and represent last-stage depositions. They are specular hematite, bornite, chalcopryite, covellite, chalcocite, pyrite, famatinite, and siderite. Pitchblende has also been found in a large vein on Hottah Lake. The extensive

alteration and replacement of the severely-fractured wall rocks by SiO<sub>2</sub> which accompanied the formation of the veins is described in detail. Analyses showing the chemical changes during alteration and a diagram showing gains and losses of oxides are given. The genetic relations of the veins are also discussed. L. S. T.

**Geologic problems of the Canadian Pre-Cambrian gold fields.** E. Y. DOUGHERTY (Econ. Geol., 1935, 30, 879—889).—Problems relevant to the science of ore deposits and to the practice of mining geology are discussed. L. S. T.

**Natural glasses of the insoluble residues of the Pennsylvanian limestones of Texas.** L. T. PATTON (Science, 1936, 83, 83—84). L. S. T.

**Origin of cyanite.** S. TABER (Econ. Geol., 1935, 30, 923—924; cf. A., 1935, 954). L. S. T.

**Synthetic emerald.** EPPLER (Deut. Goldschmiede-Ztg., 1935, 38, 144—146; Chem. Zentr., 1935, i, 3969).—Optical data are given for distinguishing natural from synthetic emeralds. J. S. A.

**Relations of amphibolites and peridotites at Sarrazac (Dordogne).** M. ROQUES (Compt. rend., 1936, 202, 332—334).—The rocks are described and their relationships are discussed. Analyses are given. H. J. E.

**Assimilation processes, formation of migmatites, and their signification in the origin of magmas.** F. K. DRESCHER-KADEN (Chem. Erde, 1936, 10, 271—310).—Cases of rock variation around granite and gabbro masses at various well-known localities, which have hitherto been ascribed to differentiation of the magma, are now asserted to be due to assimilation of the surrounding rocks into which the magma was intruded, with the production of migmatites or mixed rocks. The bearing of this on the origin of magmas and on petrological theory is discussed (cf. Reynolds, A., 1935, 1477). L. J. S.

**Copper-bearing spathic iron veins in the Bober-Katzbach Mtns., Silesia.** A. NEUHATS (Chem. Erde, 1936, 10, 247—270; Fortschr. Min. Krist. Petr., 1936, 20, 50—55).—These veins were discovered in 1922 and have been worked for Fe and Cu ores. The principal mineral is chalybite (containing 3% Mn), and the Cu ore is mainly chalcopryite with associated rarer Ni and Co minerals. A detailed description is given and the origin of the veins discussed. L. J. S.

**Geochemistry of barium.** W. VON ENGELHARDT (Chem. Erde, 1936, 10, 187—246).—Numerous igneous and sedimentary rocks, minerals, meteorites, and org. plant remains were examined spectroscopically for Ba. In igneous rocks Ba goes with K, ranging from 0.2% BaO in syenite to 0.0003% in peridotite, with an average of 0.048%. In sedimentary rocks it is adsorbed by clay, clay-slates containing BaO 0.05% and limestone 0.01%. The average for the whole lithosphere is 0.045%. The deposition of baryte under various conditions is discussed. L. J. S.

**Rocks from Cape Verde Islands.** H. ERMERT (Chem. Erde, 1936, 10, 155—186).—A collection of rocks from the islands of São Vicente and Sal is



described, with chemical analyses of foyaite, dioritic essexite, trachyandesite, gabbroid essexite-dolerite, and augite. These when tabulated and plotted with earlier analyses show a similarity to the rocks of the Canary Islands, and the two form a rock province characterised by the predominance of  $\text{Na}_2\text{O}$ . Mineral analyses are given of sands from the same islands.

L. J. S.

**Synthesis of montmorillonite.** W. NOLL (Chem. Erde, 1936, 10, 129—154; cf. A., 1935, 601).—In presence of little alkali both montmorillonite (I) and kaolin are formed; with still less or none (or in a slightly acid solution) only kaolin. With an excess of  $\text{NaOH}$  analcime is formed. Similar results are obtained in presence of  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . With excess of  $\text{Mg}(\text{OH})_2$  this enters into the composition of the (I) up to 15.3%  $\text{MgO}$ , which then corresponds with a fuller's earth. In the natural formation of clay minerals by the hydrothermal alteration of rocks, if alkalis accumulate, owing to feeble circulation, then (I) is formed, whilst if they are removed by an excess of  $\text{H}_2\text{O}$  kaolin is formed.

L. J. S.

**Rock-forming minerals from Belgian Congo.** A. VANDENDRIESSCHE (Natuurwetensch. Tijds., 1936, 17, 243—247).—The crystallography, physical properties, and chemical analyses of olivine and augite from near the Mikenov volcano, Kivu, are given. These minerals occur in soil derived from basaltic lavas.

D. R. D.

**Colour of corundum.** I. I. ISLAMOV and J. M. TOLMATSHEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 11—13).—Corundums have been analysed spectroscopically, the red form containing Cr 0.18, Ti 0.01, V 0.04, and Ga 0.005%, the blue, Cr 0.002, Ti 0.2, V trace, and Ga 0.005%, and the light grey, Cr trace, Ti 0.03, V trace, and Ga 0.002%. Fe is present in approx. the same amount in each. A qualitative analysis has been made for other elements in corundum, and on disthene. The cause of colour is discussed.

R. S. B.

**Optical diagram for magnesium-iron mica (phlogopite).** D. P. GRIGORIEV (Zentr. Min., 1935, A, 142—150; Chem. Zentr., 1935, ii, 198).—The variation of the optic axial angle and refractivity of phlogopite with the  $\text{FeO}$  content deviates widely from the theoretical curve. The cause is discussed.

J. S. A.

**Classification of the granites of the southern Katanga according to the planimetric study of thin sections.** M. GYSIN (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 243—246).—The granites can be divided into 8 classes, belonging to the granitic or dioritic groups of the calco-alkaline series.

R. S.

**Luminescence of calcite (with special reference to the Polish deposits).** S. KREUTZ (Bull. Acad. Polonaise, 1935, A, 486—500).—Specimens of calcite were heated to 300°, 330°, 360°, 530°, 680°, and red heat, and, on cooling, their luminescence was examined. Luminescence is lost on heating, this fact being connected with loss of  $\text{CO}_2$ . The blue luminescence of some samples changes to a bright yellow between 330° and 580°. Although the luminescence of specimens from different localities differs, there are

two main spectral ranges, one in the red, and the other in the blue and violet. The phosphorescence exhibited by some specimens of calcite was also investigated.

A. J. M.

**Origin of tektites. I. Tektites as fulgurites [formed in the atmosphere].** T. VOGT (Kong. Norske Vidensk. Selsk. Forh., 1935, 8, 9—12; Chem. Zentr., 1935, i, 3527).

H. J. E.

**Preservation of pyrite and marcasite.** F. A. BANNISTER (Museums J. London, 1933, 33, 72—75).—The decomp. of specimens of natural  $\text{FeS}_2$  can be arrested by cleaning with aq.  $\text{NH}_3$ , washing, drying at 70°, and coating with a 7% solution of vinyl acetate in 1:1  $\text{PhMe-COMe}_2$ .

CH. ABS. (e)

**Lovchorrite of the Chiba swamps.** I. K. CHAZANOVITSCH (Razved. Nedr, 1935, 4, No. 1, 28).—Lovchorrite contains approx. 16% of Ce and Ce earths, 1% of Th, and some U. It resembles glue plates. Chibinite is similar.

CH. ABS. (e)

**Lake Bosumtwi [volcanic glass].** N. R. JUNNER (Rep. Geol. Surv. Gold Coast, 1932—1933, 4—7).—The volcanic glass contained 64.01% of  $\text{SiO}_2$ .

CH. ABS. (e)

**Preliminary staining studies of the Lehigh Valley dolomitic limestone.** J. FULLER (Proc. Penna. Acad. Sci., 1934, 8, 83—87; Rev. géol., 14, 522).—Staining tests distinguish dolomitic from  $\text{MgO}$ -free limestones. Malachite-green and  $\text{K}_4\text{Fe}(\text{CN})_6$  with  $\text{HCl}$  are satisfactory. Lemberg's solution gives the best results.

CH. ABS. (e)

**Iron deposits of southern Anhui.** C. Y. HSIEH (Bull. Geol. Soc. China, 1931, 10, 317—347).—The Fe ores are genetically related to diorite intrusions, and are of the contact metamorphic and hydrothermal types. In the former, magnetite occurs with garnet and babingtonite.

CH. ABS. (e)

**Genesis of the Mivirando tin ores.** W. C. SIMMONS (Ann. Rep. Geol. Survey Uganda, 1932, 50—52; Rev. géol., 14, 290).—It is suggested that Sn came up as K stannate, which, on meeting  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , deposited cassiterite and muscovite. The alkali manganates, tungstates, titanates, etc. may transport the respective metals.

CH. ABS. (e)

**Occurrence and distribution of staurolite in Gangpur State, Bihar and Orissa.** M. S. KRISHNAN (Quart. J. Geol. Soc. India, 1933, 5, 67—73).—Staurolite occurs in mica-schists with quartz, biotite, muscovite, penninite, and garnet.

CH. ABS. (e)

**Correlation between specific gravity, chemical constitution, and condition of formation of minerals and rocks.** D. C. NAG (Quart. J. Geol. Soc. India, 1932, 4, 29—67).—The  $d$  has been calc. from analyses, assuming the mol. vol. of a compound equal to the sum of the mol. vols. of its constituents.

CH. ABS. (e)

**Geology of the Orkneys.** G. V. WILSON, W. EDWARDS, J. KNOX, R. C. B. JONES, J. V. STEPHENS, and J. S. FLETT (Mem. Geol. Survey Scotland, 1935, 205 pp.).—Deposits of galena associated with strombolite, and the petrography of numerous basic dikes, are described. Analyses are given.

CH. ABS. (e)



**Minerals in diamondiferous concentrates.** N. R. JUNNER (Rep. Geol. Survey Gold Coast, 1932—1933, 14—15).—Diamonds are often enclosed in pisolites of limonite with 0.15—1.19% of  $\text{Cr}_2\text{O}_3$ . This suggests their origin from ultra-basic igneous rocks. Analyses of garnets, ilmenite, and chrysoberyl are given. CH. ABS. (e)

**Arrangement of micro-crystals of silica in the onyx.** M. ICHINOSE (Mem. Coll. Sci. Kyoto., 1935, A, 18, 315—316).—X-Ray diffraction patterns show that micro-crystals of  $\text{SiO}_2$  in onyx have a fibrous arrangement, of which the common axis is [1120] and perpendicular to the surfaces of the banded layers in the mineral. J. G. A. G.

**Iron formations and associated rocks of the Eastern Bababudans, Kadur District, Mysore.** C. S. PICHAMUTHU (J. Mysore Univ., 1935, 8, 1—48).—Analyses are given, and the origin of the banded ferruginous quartzites is discussed. C. W. G.

**Viscosity of fused rocks.** M. VOLAROVITSCH (Compt. rend., 1936, 202, 78—80; cf. A., 1934, 751).—Analytical and  $\eta$  data (1110—1400°) are recorded for a series of rocks.  $\eta$  increases, in general, with the acidity of the rock. H. J. E.

**Violet fluorspars.** H. ARSANDAUX (Bull. Soc. franç. Min., 1935, 58, 268—277).—When slowly heated, strongly-coloured fluorspars emit a relatively prolonged thermoluminescence, which approx.  $\propto$  the intensity of pigmentation. They differ from most coloured fluorspars in emitting little or no fluorescence under the action of ultra-violet light until they have been decolorised by heat. The violet fluorspar from the Isle quarry, near Limoges, is described in detail. Mn may be responsible for the fluorescence in this case. L. S. T.

**Hydroxides of aluminium of the bauxitic clays of Ayrshire.** J. DE LAPPARENT (Bull. Soc. franç. Min., 1935, 58, 246—267).—These clays contain a large amount of boehmite (I) and a small quantity of diaspore (II). The origin of (I) and (II), which is formed after (I), is discussed. L. S. T.

**Elasticity and plasticity of rocks and artificial stone.** R. H. EVANS (Proc. Leeds Phil. Soc., 1935—1936, 3, 145—158).—Tests on numerous specimens in tension and compression are described and discussed. H. J. E.

**Andesites of the Trojaga District in the Mar-moros Carpathians.** M. KAMIENSKI (Bull. Acad. Polonaise, 1935, A, 399—407).—Microscopical and chemical investigations of the volcanic rocks of the Trojaga indicate that they belong to the calc-alkali series of the amphibole-andesites and amphibole-biotite-andesites which show the character of dacitoids. They were probably erupted in the second Mediterranean or the Samet epoch. T. G. P.

**Morphological studies of enargite.** S. KÔZU and S. WATANABÉ (Proc. Imp. Acad. Tokyo, 1935, 11, 418—420; cf. A., 1934, 244, 1060).—Examination of many crystals of enargite ( $\text{Cu}_3\text{AsS}_4$ ) leads to the conclusion that this crystal is hemimorphic. Its crystal habit and modes of twinning are discussed. J. W. S.

**Space-group and cell dimensions of enargite.** S. KÔZU and K. TAKANÉ (Proc. Imp. Acad. Tokyo, 1935, 11, 421—422; cf. preceding abstract).—Re-examination of the X-ray reflexions of enargite crystals indicates the cell dimensions  $a_0$  6.39,  $b_0$  7.35,  $c_0$  6.15 Å. with two  $\text{Cu}_3\text{AsS}_4$  mols. per unit cell. It is concluded that the space-group is  $C_{2v}^n$ . J. W. S.

**Chemical formula of malachite.** M. GUILLOT and G. GENESLAY (Compt. rend., 1936, 202, 136—137).—Artificial malachite ( $8\text{CuO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ ) identical with the natural product may be prepared by (a) the action of saturated aq.  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  on saturated aq.  $\text{CuSO}_4$  or (b) the hydrolysis of alkali cupricarbonates or  $\text{Cu}^{\text{II}}$  "carboxydiammine." T. G. P.

**Heavy mineral assemblage of white clay and ochres associated with the laterite of Sohawal State, central India.** N. L. SHARMA and S. PURKAYASTHA (Quart. J. Geol. Soc. India, 1934, 6, 49—54). CH. ABS. (e)

**Petrography of clay.** C. W. CORRENS (Naturwiss., 1936, 24, 117—124).—The distribution of nuclear size of clay particles in different specimens of clay, and the examination of the constituents of clay by microscopical and X-ray methods, are discussed. The effect of  $\text{HCl}$ ,  $\text{NaOH}$ , and  $\text{H}_2\text{O}_2$  of various concns. is reviewed.  $\text{H}_2\text{O}_2$  is without appreciable action. A. J. M.

**Transformation of absorbed anions in Ad-sharien red earth.** B. B. POLINOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 49—50).—Analytical data are given showing the displacement of adsorbed  $\text{Cl}'$  and  $\text{SO}_4''$  on treating samples of the soil with 0.1N- $\text{NaH}_2\text{PO}_4$ . H. J. E.

**Podolian loess.** I. Petrographical analysis of a loess profile from Grzybowice near Lwow. J. TOKARSKI (Bull. Acad. Polonaise, 1935, A, 374—398).—Microscopical and chemical investigations in 10 horizons indicate that the deposit belongs to the latest diluvial epoch. The loess exhibits only slight genetic relationship to the Tertiary sand of Lwow. T. G. P.

**Marine oil shale, source of oil in Playa del Rey field, California.** H. W. HOOTS, A. L. BLOUNT, and P. H. JONES (Bull. Amer. Assoc. Petrol. Geol., 1935, 19, 172—205).—The migration of oil in the field is discussed. CH. ABS. (e)

**Native hydrocarbons associated with oil shales of the Lothians.** H. R. J. CONACHER (Trans. Edinburgh Geol. Soc., 1934, 13, 89—97).—Chrimatite (m.p. 51°) occurs in cavities in igneous rocks. Zietrisikite (m.p. 84°) occurs in joints in sandstone. Wurtzilite (m.p. 130°) is found in oil shales and ironstone nodules, and resembles ixolite. CH. ABS. (e)

**Oil deposits in the Lena river basin and its tributaries (Siberia). Organic substance of the minerals from the river Tolba.** S. P. USPENSKI (Nef. Choz., 1935, 27, No. 2, 29—32).—Analyses are recorded and discussed. CH. ABS. (e)

**Migration of Hungarian hydrocarbons.** E. R. SCHMIDT (Föld. Közlöny, 1934, 64, 278; Chem. Zentr., 1935, i, 3527).—A discussion. H. J. E.



## Organic Chemistry.

Appearance of radicals in thermal decomposition of organic molecules.—See this vol., 433.

Thermal decomposition of ethane. I, II. See this vol., 432.

Free radicals and atoms in primary photochemical processes. Free *n*-propyl radical. T. G. PEARSON and R. H. PURCELL (J.C.S., 1936, 253–256).—Formation of  $\text{Pr}^\bullet$  by irradiation of  $\text{COPr}^\bullet$ , with ultra-violet light (A., 1935, 1221) is proved by removal of As, Sb, and Te mirrors and reaction with Hg (forms a liquid, which with  $\text{HgBr}_2$  gives  $\text{HgPr}^\bullet\text{Br}$ ); excitation of the Hg is avoided by filtration of the irradiating light through Hg vapour. The half-life period of  $\text{Pr}^\bullet$  is  $2.3 \times 10^{-3}$  sec. in  $\text{SiO}_2$  at room temp. R. S. C.

Preparation of isomeric hexanes. P. L. CRAMER and M. J. MULLIGAN (J. Amer. Chem. Soc., 1936, 58, 373–374).—*n*-Hexane, b.p. 68.74–68.78° ( $\text{CH}_3\text{EtPr}^\bullet\text{OH}$ ;  $\text{Al}_2\text{O}_3$  at 350°),  $\beta$ -methylpentane, b.p. 60.22–60.26° ( $\text{CMe}_2\text{Pr}^\bullet\text{OH}$ ; I at 122°),  $\gamma$ -methylpentane, b.p. 63.16–63.21° ( $\text{CMeEt}_2\text{OH}$ ; I at 120°),  $\beta$ -dimethylbutane, b.p. 49.8–49.82° ( $\text{CHMeBu}^\bullet\text{OAc}$  heated at 400°), and  $\beta$ - $\gamma$ -dimethylbutane, b.p. 57.82–58.02° ( $\text{OH}^\bullet\text{CMe}_2\text{CMe}_2\text{OH}$ ;  $\text{HBr}$  at 130–150°), are prepared by reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ) of the olefines formed by dehydration (methods quoted) of the alcohols quoted after the hydrocarbons. H. B.

Thermal study of oxidation of hydrocarbons.—See this vol., 432.

Polarisability of the ethylenic linking. G. WITTO (Ber., 1936, 69, [B], 471–475).—The additive capacity of the C:C linking in  $\text{CR}_2\text{:CR}_2$  depends on the nature of the addendum and on that of R. The displacability of the valency electrons on deformation of the state of union of the C:C group is much more pronounced than that of the C:C linking, and this reacts on R. Examples cited are the ability of  $\text{CHMe}^\bullet\text{CH}^\bullet\text{CHO}$  to undergo the aldol condensation, the fission of  $\text{CPh}_2\text{:CH}^\bullet\text{CH}_2^\bullet[\text{CH}_2\text{:CH}^\bullet\text{CPh}_2]$  by alkali metal, the pinacolin transformation of  $[\text{OH}^\bullet\text{CPhR}^\bullet\text{C}]_2$ , the action of NaOH on 2:6:3-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_2\text{Me}^\bullet\text{CHO}$ , and the dissimilarity in the behaviour of 2- and 4-pyrones. The conditions for the realisation of valency tautomerism are discussed. H. W.

Raman spectrum of rubber and related hydrocarbons. See this vol., 407.

Preparation of unsaturated hydrocarbons by elimination of halogen acids from corresponding halides. A. BELL and R. H. CLARK (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 61–68).—Quant. comparison of the prep. of unsaturated hydrocarbons from 25 halides by the use of  $\text{EtOH-KOH}$  (I), quinoline (II),  $\text{NH}_2\text{Ph}$ ,  $\text{NPhMe}_2$ ,  $\text{NPhEt}_2$ ,  $\text{C}_5\text{H}_5\text{N}$ , and piperidine indicates that (I) gives poor yields with *n*-halides owing to formation of ethers, but, together with the org. bases, is suitable for higher *sec.*, *tert.*, and *cyclo*-halides, whilst (II) is recommended for *n*- and lower *sec.*-halides. Bromides and iodides give better yields than chlorides. F. O. H.

Allylic rearrangements. II. Magnesium crotyl and methylvinylcarbinyl bromides. W. G. YOUNG, S. WINSTEIN, and A. N. PRATER (J. Amer. Chem. Soc., 1936, 58, 289–291; cf. A., 1932, 250).—The same mixture (method of analysis: Dillon *et al.*, A., 1930, 888) of  $56.4 \pm 2\%$  of  $\Delta^a$ - and  $26.5 \pm 1.4\%$  *cis*- and  $17.2 \pm 3\%$  *trans*- $\Delta^a$ -butene is obtained by hydrolysis (dil. HCl) of the Grignard reagents (A) from various mixtures of  $\text{CHMe}^\bullet\text{CH}^\bullet\text{CH}_2\text{Br}$  and  $\text{CH}_2^\bullet\text{CH}^\bullet\text{CHMeBr}$ . Rearrangement occurs during the formation of (A). H. B.

Thermal rearrangements of pentenes. C. D. HURD, G. H. GOODYEAR, and A. R. GOLDSBY (J. Amer. Chem. Soc., 1936, 58, 235–237).— $\Delta^a$ -Pentene (I) undergoes 56–58% decomp. at 580–600° (contact time 13–18 sec.; method essentially that of A., 1934, 1089) to give liquid (probably mainly *cycloalkenes* and aromatic hydrocarbons) and gaseous products ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and  $\Delta^a$ -butene in the mol. ratio 6:2:1:2:2; small amounts of  $\text{H}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\Delta^a$ -butene, and butadiene). A little of (I) rearranges to  $\Delta^b$ -pentene (II). The extent of decomp. of (II) at 580° and 600° is 23 and 54%, respectively. Essentially the same products are formed and a little of the (II) rearranges to (I). (I) prepared from  $\text{MgEtBr}$  and allyl bromide in  $\text{Bu}_2\text{O}$  contains a little  $\text{CH}_3^\bullet\text{CHPr}^\bullet$  (removable by distillation) [the statement (B., 1934, 228) that this is produced during pyrolysis of (I) is erroneous]. (II) (free from isomerides) is obtained by dehydration ( $\text{H}_2\text{SO}_4$ ) of  $\text{CHEt}_2\text{OH}$ . H. B.

Dimerisation of divinyl. J. M. SLOBODIN (J. Gen. Chem. Russ., 1935, 5, 1415–1420).—The condensate obtained as a by-product of the catalytic prep. of divinyl from  $\text{EtOH}$  by Lebedev's method consists of *p*-xylene 66, and 4-vinyl- $\Delta^1$ -cyclohexene +  $\text{PhMe} + \text{PhEt}$  33%; the probable intermediates are  $\text{CH}_2^\bullet\text{CH}^\bullet\text{CHMe}^\bullet\text{CH}^\bullet\text{CH}^\bullet\text{CH}_2^\bullet$ ,

$\text{CHMe}^\bullet\text{CH}^\bullet\text{CH}^\bullet\text{CH}^\bullet\text{CH}^\bullet\text{CHMe}^\bullet$ , and

$\text{CHMe}^\bullet\text{CH}^\bullet\text{CH}_2^\bullet\text{CH}_2^\bullet\text{CH}^\bullet\text{CH}_2^\bullet\text{CH}_2^\bullet\text{CH}^\bullet\text{CHMe}^\bullet$ . R. T.

Rôle of intermediate compounds in the process of catalytic polymerisation of acetylene. I. Reaction of acetylene with solutions of cuprous and ammonium chlorides, and a study of the complexes formed. L. G. TZIURICH and A. A. GINZBURG (J. Gen. Chem. Russ., 1935, 5, 1468–1478).—The cryst. product obtained by saturating a solution containing  $\text{CuCl}$  18 and  $\text{NH}_4\text{Cl}$  20% with  $\text{C}_2\text{H}_2$  has the composition  $6\text{CuCl}_3\text{NH}_4\text{Cl}_2\text{C}_2\text{H}_2$ ; it readily dissociates into its components, with which it is in equilibrium in the solution. R. T.

Hydrogenation of vinylacetylene. S. V. LEBEDEV, A. I. GULJAEVA, and A. A. VASSILIEV (J. Gen. Chem. Russ., 1935, 5, 1421–1433).—The  $\text{C}^\bullet\text{C}^\bullet$  and  $\text{C}^\bullet\text{C}^\bullet\text{C}^\bullet$  groups of  $\text{CH}_2^\bullet\text{CH}^\bullet\text{C}^\bullet\text{CH}$  (I) are hydrogenated simultaneously and with equal velocity in presence of Pt catalyst, whilst with Pd (on Ni or Na prot-albinate) addition takes place chiefly at the triple linking;  $\text{CHMe}^\bullet\text{CHMe}^\bullet$  is not found amongst the products of incomplete hydrogenation. (I) may be



quantitatively reduced to divinyl by nascent H (from Zn-Cu and H<sub>2</sub>O, or at a Pt-black cathode). R. T.

**Action of anhydrous alkaline earths on monohalogenated paraffins.** J. B. SENDERENS and J. ABOULENC (Compt. rend., 1936, 202, 104—106).—When dropped on heated CaO or BaO (reaction temp. in parentheses) C<sub>n</sub>H<sub>2n+1</sub>Cl decomposes cleanly to C<sub>n</sub>H<sub>2n</sub>+HCl (retained by catalyst). Thus Bu<sup>n</sup>Cl (275—285°) or Bu<sup>n</sup>Br (300—310°) gives C<sub>4</sub>H<sub>8</sub>; Pr<sup>n</sup>Cl (250°) or Pr<sup>n</sup>Br (265°) gives CHMe:CH<sub>2</sub>, and Bu<sup>n</sup>Cl (210°) gives CMe<sub>2</sub>:CH<sub>2</sub>. No C is deposited.

J. W. B.

**From iodoform to fluoroform.** O. RUFF [with O. BRETSCHNEIDER, W. LUCHSINGER, and G. MILTSCHUTZKY] (Ber., 1936, 69, [B], 299—308).—CHF<sub>3</sub> obtained by heating CHI<sub>3</sub>-AgF-SiO<sub>2</sub> is contaminated with CO and considerable amounts of SiF<sub>4</sub>. CaF<sub>2</sub> is a more suitable diluent, the best results being secured with AgF:CaF<sub>2</sub>=1:4 and HgF:CaF<sub>2</sub>=1:1.2. The prep. of CHF<sub>3</sub>, CHIF<sub>2</sub>, and CHI<sub>2</sub>F from HgF, CHI<sub>3</sub>, and CaF<sub>2</sub> (33.4:20:40) is described in detail. At >100° PbF<sub>2</sub>, ZnF<sub>2</sub>, CuF<sub>2</sub>, CoF<sub>2</sub>, and SbF<sub>3</sub> do not yield appreciable quantities of CHF<sub>3</sub>. Slow passage of CHCl<sub>3</sub> vapour over AgF-CaF<sub>2</sub> gives about 57% of CHCl<sub>2</sub>F at 100° and about 48% of CHClF<sub>2</sub> at 250°; at 340° about 10% of CHF<sub>3</sub> is obtained, but the mixture sinters and becomes ineffective at this temp. At about 500° PbF<sub>2</sub> gives a little CHCl<sub>2</sub>F among other products. CHF<sub>3</sub> has b.p. -84.4°/760 mm., m.p. -160°. It does not lose HF when heated alone or in presence of KF at 1150°. It is unchanged by HNO<sub>3</sub> alone or with conc. H<sub>2</sub>SO<sub>4</sub>, N<sub>2</sub>O<sub>3</sub>, or AgNO<sub>3</sub> at 140°; at >175° it is completely decomposed by N<sub>2</sub>O<sub>3</sub>. NOF leaves it partly unchanged after 3 hr. at 100° and Mn<sub>2</sub>O<sub>7</sub> is without action at 25°. Oxidising agents transform it into COF<sub>2</sub> and HF. It is unaffected by CaO at 365°. Iododifluoromethane, b.p. 21.6°/760 mm., is very sensitive to light and air, but in their absence it is stable indefinitely. It is only partly decomposed by Pt-asbestos at 700°. It reacts readily with AgNO<sub>3</sub>. Di-iododifluoromethane, b.p. 100.3±0.5°/760 mm., m.p. -34.5°±0.5°, is sensitive to light and air. It slowly separates I when warmed; at >250° it is almost completely decomposed with production of HF. It reacts with Mg only when irradiated. With liquid NH<sub>3</sub> it gives NH<sub>4</sub>F and NH<sub>4</sub>I. With Na<sub>2</sub>SO<sub>3</sub> in 50% EtOH at 80° complete separation of F from C is observed.

H. W.

**Hydrolysis of isopropyl bromide.**—See this vol., 433.

**Alcohol determination.** R. M. MAYER (Deut. Z. ges. gerichtl. Med., 18, 638—646; Chem. Zentr., 1935, i, 3961).—A modified Nicloux method is described.

H. N. R.

**Alcoholic fermentation in heavy water.**—See this vol., 522.

**Determination of small concentrations. II. Butyl and amyl alcohols.** M. V. ALEXEEVA (J. Gen. Chem. Russ., 1935, 5, 1324—1330).—7 ml. of 0.05N-KMnO<sub>4</sub> and 10 ml. of 5N-H<sub>2</sub>SO<sub>4</sub> are added to 10 ml. of solution, containing 0.1—1.5 mg. of BuOH or C<sub>5</sub>H<sub>11</sub>·OH, the mixture is kept in the dark for

35 min., when 10 ml. of 0.05N-Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> are added, the solution is warmed to 80—90°, and excess of oxalate is titrated with 0.05N-KMnO<sub>4</sub>. Esters to an amount of >25% of that of the alcohols present do not interfere, but EtOH should be absent.

R. T.

**Mechanism of conversion of Δ<sup>γ</sup>-butenol into Δ<sup>β</sup>-butenyl bromide.** L. W. J. NEWMAN and H. N. RYDON (J.C.S., 1936, 261—264).—Δ<sup>β</sup>- (I) and Δ<sup>γ</sup>-Butenol (II) are stable to boiling alone, hot 30% KOH, Ac<sub>2</sub>O, and AcOH; Δ<sup>β</sup>- (III) and Δ<sup>γ</sup>-butenyl bromides are similarly stable and hydrolysis of the acetates does not cause isomerisation. Change of (II) into (III) by hot H<sub>2</sub>SO<sub>4</sub>-HBr occurs by dehydration to butadiene and addition of HBr thereto, both the last reactions having been separately realised under the experimental conditions used. CH<sub>2</sub>:CMe·CH<sub>2</sub>·OH reacts with HBr as does (I) and its bromide is hydrolysed at the same rate as is (III). Mixtures of the Δ<sup>β</sup>- and Δ<sup>γ</sup>-isomerides are analysed by the much more rapid esterification by HBr or hydrolysis of the Δ<sup>β</sup>-isomeride at room temp.

R. S. C.

**Action of micro-organisms on the diastereomeric forms of hexane-γδ-diol.** H. VAN RISSEHEM (Bull. Soc. chim. Belg., 1936, 45, 21—35).—Griner's mixed [CH<sub>2</sub>:CH·CH(OH)·]<sub>2</sub> with H<sub>2</sub>-Pd-black in Et<sub>2</sub>O gives meso- (I), m.p. 90.1—90.2°, b.p. 115.1°/24 mm., and dl-hexane-γδ-diol (II), f.p. 20.9°, b.p. 108.65—108.75°/24 mm. (I) with *B. xylinum* or *M. aceti* gives d-hexan-γ-one-8-ol (III), b.p. 70.7—71°/22 mm., [α]<sub>D</sub><sup>20</sup> +88.16°, and a little (EtCO)<sub>2</sub> (II) with *B. xylinum* slowly or *M. aceti* rapidly gives the l-form of (III), whilst some l-(II) remains unattacked; d-(II) thus reacts preferentially. It is concluded that bacteria attack the d-C. Hydrogenation of d-(III) gives l-(II), b.p. 105.7—106.2°/20 mm., [α]<sub>D</sub><sup>20</sup> -12.24°.

R. S. C.

**Lycoxanthine and lycophyll, two natural derivatives of lycopene.** L. ZECHMEISTER and L. von CHOLNOKY (Ber., 1936, 69, [B], 422—429).—The fruits of *Solanum dulcamara* are ground with sand, washed with EtOH, and then extracted with Et<sub>2</sub>O. After removal of the solvent the residue is dissolved in C<sub>6</sub>H<sub>6</sub> and analysed chromatographically using Ca(OH)<sub>2</sub>. Alternatively, the dry residue is dissolved in benzene and the solution shaken with 90% MeOH; the final treatment is with Ca(OH)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>-benzene. Thus are obtained lycoxanthine (I), m.p. 168° (corr.) (acetate, m.p. 137°), lycophyll (II), C<sub>40</sub>H<sub>56</sub>O<sub>2</sub>, m.p. 179° (corr.) [dipalmitate, m.p. 76° (corr.)], and lycopene (III). The absorption spectra of (I), (II), and (III) are so remarkably similar that the presence of 11 conjugated and two isolated double linkings in each is regarded as established. On the assumption that the OH occupy the same positions as in other xanthophylls, the constitution

CMe<sub>2</sub>·CH·CH(OH)·CH<sub>2</sub>·[CMe·CH·CH:CH]<sub>3</sub>·[CH:CMe·CH:CH]<sub>2</sub>·CH:CH·CMe·CH<sub>2</sub>·CHR·CH:CMe<sub>2</sub> is assigned with R=H in (I) and R=OH in (II). The quant. separation of (II) from (I) and (III) is described, also the determination of (I) and (II) in the crude materials. (I) and (II) do not appear to be present in preserved tomatoes, but are detected in the



fresh fruit. The berries of *Tamus communis* contain (III) a little (I), but not (II). The carotenoids are unesterified. (I) and (II) are absent from *Rosa canina*, but present in traces in *Actinophleus Macarthurii*. (III) and its derivatives are not contained in *Coloneaster horizontalis*.  
H. W.

$\alpha$ -D-[ $\gamma$ -]Anhydromannitol. F. VALENTIN (Coll. Czech. Chem. Comm., 1936, 8, 35—42).— $\alpha$ -Methylmannopyranoside 6-bromide (freed from  $\text{NH}_2\text{Ac}$  by  $\text{EtOAc}$ ) with  $\text{Ba}(\text{OH})_2$  gives  $\alpha$ -methyl- $\gamma$ -anhydromannopyranoside, stable to  $\text{H}_2\text{S}$ , hydrolysed by 3%  $\text{HCl}$  to  $\gamma$ -anhydromannofuranose (I), which with 2.5%  $\text{Na-Hg}$  in slightly alkaline solution gives  $\alpha$ -anhydromannitol (50% yield), m.p.  $148^\circ$  (lit.  $138^\circ$ ),  $[\alpha]_D^{20} -23.75^\circ$  in  $\text{H}_2\text{O}$  (dibenzylidene derivative, m.p.  $125-126^\circ$ ,  $[\alpha]_D^{20} -48.8^\circ$  in  $\text{CHCl}_3$ ), which with  $\text{Br}$  reverts to (I).  $\text{CHPh}$  is determined by distillation with 60%  $\text{H}_2\text{SO}_4$  in  $\text{CO}_2$  and determination of the  $\text{PhCHO}$  in the distillate as phenylhydrazone.  
R. S. C.

Chloroalkoxylation of olefines by the action of chlorine in presence of alcoholic alkali. M. V. LICHOSCHERSTOV and A. A. PETROV (J. Gen. Chem. Russ., 1935, 5, 1348—1354).—Compounds of the type  $\text{OR}\cdot\text{CHMe}\cdot\text{CHMeCl}$  (I) ( $\text{R}=\text{alkyl}$ ) are obtained in 60—70% yield by adding a 30% excess of  $\text{NaOH}$  to the  $\text{ROH}$ , passing  $\text{Cl}_2$  continuously (25% excess), and introducing  $\text{CHMe}\cdot\text{CHMe}$  intermittently. When the mixture is diluted with  $\text{H}_2\text{O}$ , a 3:1 mixture of (I) and  $(\cdot\text{CHMeCl})_2$  separates.  
R. T.

Preparation of dimethylacetal by condensing methyl alcohol with acetylene. S. TAMARU and Y. TANAKA (J. Chem. Soc. Japan, 1935, 56, 486—504).— $\text{HgCl}_2$  or  $\text{H}_2\text{SO}_4$  may be used as catalysts, the optimum temp. being  $40^\circ$ ; the former is prevented from losing its activity by addition of  $\text{Fe}_2(\text{SO}_4)_3$ .  
CH. ABS. (r)

Mixed glycerides of salicylic acid and fatty acids. A. LUKASIAK (Rocz. Farm., 1934, 12, 1—26; Chem. Zentr., 1935, i, 3005—3006).—Resorption of salicylic acid (I) compounds is followed by determination of (I) in the urine. Results with  $\text{Et}$  and ethylene salicylates, the triglyceride of (I), salicylodichlorohydrin, and  $\alpha$ -distearo- $\beta$ -salicylin are described. The following are described:  $\beta$ -palmito-, m.p.  $32^\circ$ ,  $\beta$ -butyro-, b.p.  $102-103^\circ/12\text{ mm.}$ , and  $\beta$ -isovalero-, b.p.  $104-106^\circ/8\text{ mm.}$ , - $\alpha\gamma$ -dichlorohydrin;  $\alpha\beta$ -dibutyro- $\gamma$ -monochlorohydrin, b.p.  $133-136^\circ/8\text{ mm.}$ ; diisovalero- $\alpha$ -iodohydrin, b.p.  $153-155^\circ/4\text{ mm.}$ ;  $\alpha\gamma$ -diisovalerin, b.p.  $146-150^\circ/5\text{ mm.}$ ;  $\alpha\alpha$ -diisovalero- $\beta$ -salicylin, b.p.  $210-212^\circ/4\text{ mm.}$ ;  $\alpha$ -salicylo- $\gamma\gamma$ -dibutyryn, b.p.  $198-201^\circ/3\text{ mm.}$ ;  $\beta$ -palmito-, m.p.  $44^\circ$ ,  $\beta$ -butyro-, m.p.  $51^\circ$ , and  $\beta$ -isovalero- $\alpha\gamma$ -disalicylin, m.p.  $65^\circ$ .  
H. N. R.

Spectrophotometric determination of ethylene glycol dinitrate. J. H. FOULGER (J. Ind. Hyg., 1936, 18, 127—129).—The absorption of the coloured solution, formed by the action of  $\text{OH}\cdot\text{C}_6\text{H}_5(\text{SO}_3\text{H})_2$  on  $\text{C}_2\text{H}_4(\text{O}\cdot\text{NO}_2)_2$  (I), at  $4900\text{ \AA.}$  has been determined, and data obtained by which the concn. of (I) can be determined from (a) the sp. extinction val. (for concn.  $1.6-3.3\text{ mg. per }100\text{ c.c.}$ ) and (b) a table of differences of photometer readings (for concn.  $0.5-4.2\text{ mg. per }100\text{ c.c.}$ ).  
J. N. A.

Interpretation of differences in properties of alkyl chlorosulphites and chloroformates from the electronic viewpoint. P. CARRÉ (Compt. rend., 1936, 202, 298—300; cf. A., 1935, 606).—A discussion.

Reaction of complex sulphuric acid esters. L. LISON (Bull. Soc. Chim. biol., 1936, 18, 225—230).—The colour change produced by org. esters of  $\text{H}_2\text{SO}_4$  of high mol. wt. on metachromatic dyes such as toluidine-blue and cresyl-blue is sp. for such substances and might be used in their qual. investigation.  
A. L.

Polysaccharide hydrogen sulphates with heparin-like action. S. BERGSTRÖM (Z. physiol. Chem., 1936, 238, 163—168; cf. A., 1935, 1519).—Details are given of the prep. and activities of the esters [including that from pectic acid (I)]. Synthetic chondroitintrisulphuric acid, chitindisulphuric acid, and (I) polysulphate have activities  $\leftarrow$  that of the product (II) from cellulose. The activities of the other preps. are only 8—50% of that of (II).  
W. McC.

Mannitoldimolybdic acid. Variation of the  $p_H$  of molybdic acid caused by addition of sugar. (MME.) Z. SOUBAREV-CHATELAIN (Compt. rend., 1935, 201, 1390—1392).—The effect of sugars, e.g., mannitol, on the  $p_H$  of molybdic acid and its salts (A., 1933, 909) is explained by formation of mannitoldimolybdic acid (I),  $[\text{C}_6\text{H}_{14}\text{O}_6\cdot\text{HMo}_2\text{O}_7]\text{H}$ , thus: increase of  $p_H$ ,  $2\text{Na}_2\text{MoO}_4 + \text{C}_6\text{H}_{14}\text{O}_6 + 2\text{H}_2\text{O} \rightleftharpoons (\text{I}) + 3\text{NaOH}$ ; decrease of  $p_H$ ,  $2[\text{MoO}_3\text{Cl}_2]\text{H}_2 + \text{C}_6\text{H}_{14}\text{O}_6 + \text{H}_2\text{O} \rightleftharpoons (\text{I}) + 4\text{HCl}$ .  
R. S. C.

Aminoethyl phosphate from tumours.—See this vol., 364.

Specific reaction of dichlorodiethyl sulphide in presence of other chemical warfare gases. M. OBERMILLER (Angew. Chem., 1936, 49, 162—164).— $\text{S}(\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$  (I) in small concn. gives with aq. solutions of  $\text{AuCl}_3$  and  $\text{PdCl}_2$  a strong yellow colloidal turbidity. On filter-paper reddish-brown and yellow stains are given with  $\text{AuCl}_3$  and  $\text{PdCl}_2$ , respectively. Negative results were obtained with the other common war gases. A positive result was observed with 1.5 mg. of (I) in 20 c.c. of liquid. By means of a special apparatus (I) could be removed from a large vol. of air and (I) in concn. of 10 mg. per cu. m. detected in 4 min.  
D. C. J.

Mechanism of the sulphonation process. A. MICHAEL and N. WEINER (J. Amer. Chem. Soc., 1936, 58, 294—299).—Contrary to Wieland (cf. A., 1920, i, 280), the reaction between  $\text{C}_2\text{H}_4$  and oleum (I) does not involve addition of  $\text{H}_2\text{SO}_4$  (as  $\text{OH}+\text{SO}_3\text{H}$ ). The results now obtained [and the data of Plant and Sidgwick (A., 1921, i, 153)] show that  $\text{H}_2\text{S}_2\text{O}_7$  is the reactive entity and leads to ethionic acid (II) [ $\text{Ba}$  salt (+0.5 $\text{H}_2\text{O}$ )]; each mol. of  $\text{H}_2\text{S}_2\text{O}_7$  gives 1 mol. of (II):  $\text{CH}_2\cdot\text{CH}_2 + \text{OH}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH} \rightarrow \text{SO}_3\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ . When (I) contains more  $\text{SO}_3$  than is necessary to form  $\text{H}_2\text{S}_2\text{O}_7$ , carbyl sulphate (III),  $\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2$ , is also formed by the direct addition of  $\text{S}_2\text{O}_6$  to  $\text{C}_2\text{H}_4$ . (III) is also produced from  $\text{C}_2\text{H}_4$  (excess) and  $\text{SO}_3$  in the gaseous phase ( $\text{CO}_2$  used as diluent). Isethionic acid,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , is



converted into (II) by (a) 100%  $\text{H}_2\text{SO}_4$  (1 mol.), (b) 100%  $\text{H}_2\text{SO}_4$  (1 mol.) followed by  $\text{SO}_3$  (1 mol.), and (c)  $\text{SO}_3$  (1 mol.); 2 mols. of  $\text{SO}_3$  give (III).

Wieland's mechanism (*loc. cit.*) of aromatic substitution is held to be untenable. Sulphonation is considered to be an aldolisation (pseudo-substitution) reaction (cf. A., 1935, 1103). The formation of  $\text{Ph}_2\text{SO}_2$  from  $\text{C}_6\text{H}_6$  and (I) is explained:  $2\text{C}_6\text{H}_6 + \text{S}_2\text{O}_6 \rightarrow \text{SO}_2 \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{SPh}_2(\text{OH})_2 \rightarrow \text{Ph}_2\text{SO}_2 + \text{H}_2\text{SO}_4$ .

$\text{C}_6\text{H}_6$  could not be sulphonated by  $\text{Me}_2\text{SO}_4 + \text{AlCl}_3$ ; methylation occurs owing to the production of  $\text{MeCl}$ .

H. B.

[Addition of bromine to] unsaturated acids. C. E. SUN (J. Chinese Chem. Soc., 1936, 4, 1—5).—The activation energy for the addition of Br to  $\beta\gamma$ -unsaturated acids is probably the same as for olefines (22.4 kg.-cal.), whilst that for  $\alpha\beta$ -unsaturated acids is calc. to be 31.5 kg.-cal., in agreement with the more facile reaction in the former case.

R. S. C.

Exchange between organic compounds and heavy water. F. K. MÜNDBERG [with W. OBERST] (Z. physikal. Chem., 1935, B, 31, 18—22).—There is a small exchange of H for D in a solution of  $\text{HCO}_2\text{Na}$  in heavy  $\text{H}_2\text{O}$  at  $100^\circ$ , but not below. With solutions of  $\text{HCO}_2\text{H}$ ,  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ , and  $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$  at  $50^\circ$  only the H of  $\text{CO}_2\text{H}$  is exchangeable, whilst with  $\text{CH}_2(\text{CO}_2\text{H})_2$  all the H may be exchanged.

R. C.

Thermal decomposition of esters in presence of aluminium chloride. H. GAULT and E. BELOFF (Compt. rend., 1936, 202, 71—73).— $\text{Bu}^n\text{OAc}$  heated with  $\text{AlCl}_3$  to  $300$ – $330^\circ$  gives  $\text{Bu}^n\text{Cl}$  (50—55%), olefine (liquid at  $-70^\circ$ ), and a mixture of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{CH}_4$  with traces of  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and olefine. The amount of  $\text{BuOAc}$  decomposed  $\propto$  the wt. of  $\text{AlCl}_3$  used. Rise of temp. gives more gaseous products, but does not otherwise alter the course of the decomp.

H. B.

Electrolytic reduction of organic compounds. I. Analogies between cathodic reduction and the action of dissolving metals. Reduction of sorbic acid. E. ISAACS and C. L. WILSON (J.C.S., 1936, 202—207).—Evidence is reviewed showing that the course of electrolytic reduction depends on the solvent used.  $\text{H}_2$  overvoltage is important for reduction of ketones and aldehydes, but not for sorbic acid (I). Reduction of (I) gives the following % of  $\Delta^7$ -hexenoic acid in the product at Hg, Cd, and Cu cathodes: in  $N$ -NaOH, 40, 39, and 40; in 0.5*N*- $\text{NaHCO}_3$ , 41, —, —; in 70%  $\text{AcOH} + 0.5M$ - $\text{NaOAc}$ , 54, 50, and 50; in 2*N*- $\text{H}_2\text{SO}_4$ , 52, —, —, respectively; these are very similar to the results obtained with Na-Hg and Al-Hg (A., 1929, 1270). Hg as cathode or amalgam leads to much "pinacol," b.p.  $180$ – $183^\circ / <1$  mm. Anthracene gives the 9:10- $\text{H}_2$ -derivative with Na-Hg, Al-Hg, or Mg-Hg in EtOH or, better, dioxan, or at a Hg cathode in alcoholic NaOH,  $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_3$ , or  $\text{NMe}_4\text{OH}$ .

R. S. C.

Tricosanoic and tetracosanoic acids and their derivatives. R. ASHTON, R. ROBINSON, and J. C. SMITH (J.C.S., 1936, 283—285).—Lauryl chloride, b.p.  $134^\circ / 9$ –10 mm., is condensed with  $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et}$  and Na, and the product treated with Et  $\lambda$ -bromo-

undecolate, b.p.  $174^\circ / 10$  mm.; hydrolysis then leads to *v*-ketotetracosanoic acid, m.p.  $95^\circ$ , reduced (Clemmensen) to tetracosanoic acid (I), m.p. (a)  $83.5$ – $84.5^\circ$  (capillary), (b)  $83.8^\circ$  (thermometer in melt), f.p.  $83.5^\circ$ . Br yields  $\alpha$ -bromotetracosanoic acid, m.p.  $71.5$ – $72^\circ$  (lit.  $69.5$ – $70^\circ$ ), and thence is obtained  $\alpha$ -hydroxy-tetracosanoic acid, m.p.  $99.5$ – $100^\circ$  (lit.  $94$ – $95^\circ$ ). Undecoyl chloride leads similarly to tricosanoic acid (II), m.p. (a)  $79$ – $80.5^\circ$ , (b)  $78.86^\circ$ , f.p.  $78.75^\circ$ . (I) and (II) give continuous solid solutions with a max. depression of the m.p. of  $0.45^\circ$ . The product of oxidation of cerebronic acid may be impure (I).

R. S. C.

Preparation of unsaturated acids from stearic acid. E. M. PRIK (Plast. Massui, 1934, No. 6, 26—27).—Chlorination of stearic acid, followed by elimination of HCl (Zn dust, or heating in vac.), yields an unsaturated product, b.p.  $190$ – $214^\circ / 5$  mm.

CH. ABS. (r)

Reactions in monolayers of drying oils. I, II. —See this vol., 434.

Qualitative test for linolenic acid, its value and limitations. G. J. MARTIN (J. Amer. Chem. Soc., 1936, 58, 364—365).—Oils containing linolenic acid (I) give a deep blue colour when 1 c.c. is heated with 5 c.c. of arsenophosphotungstic acid (Benedict, A., 1931, 973) at  $100^\circ / 1$  hr. Approx. determinations of the amount of (I) present can be made; Me linolenate is used as standard. Other fatty acids containing 3 double linkings give the reaction.

H. B.

Fatty acids of phrenosin and kersin. A. C. CHIBNALL, S. H. PIPER, and E. F. WILLIAMS (Biochem. J., 1936, 30, 100—114).—Brain contains at least 3 phrenosins and 3 kersins, the components of which differ only in the chain-length of the fatty acids. A sample of phrenosinic (cerebronic) acid (I), m.p.  $102.3$ – $102.6^\circ$ ,  $[\alpha]_D^{25} + 3.33^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  (Ac derivative, m.p.  $66$ – $66.5^\circ$ ), obtained by hydrolysis of a highly purified specimen of phrenosin is shown to consist of a mixture of even-no.  $\alpha$ -OH-acids of mean mol. wt. corresponding closely with  $\text{C}_{24}$ , which on oxidation with  $\text{CrO}_3$  in  $\text{AcOH}$  give a mixture of odd-no. *n*-fatty acids, identified as 85%  $\text{C}_{23}$  and 15%  $\text{C}_{25}$ . (I) consists therefore of 85% of  $\alpha$ -hydroxy-*n*-tetracosanoic and 15% of  $\alpha$ -hydroxy-*n*-hexacosanoic acids. (I) of low m.p. contains also  $\alpha$ -hydroxy-*n*-docosanoic acid. Thudichum's neurostearic acid probably consists of 25—30% of (I), the rest being "lignoceric acid" (II). The acidic constituents of the kersins are *n*-docosanoic, *n*-tetracosanoic, and *n*-hexacosanoic acids; (II) is thus also a mixture and the name should be abandoned. Several binary mixtures of *n*-fatty acids of chain-length from  $\text{C}_{21}$  to  $\text{C}_{25}$  have been prepared and their m.p. and crystal spacings recorded.

P. W. C.

Absolute configuration of lactic acid. Assumptions made in calculation of optical rotation. W. KUHN (Z. physikal. Chem., 1935, B, 31, 23—57).—The sign of the rotation of  $\text{CHMcEt} \cdot \text{OH}$  has been calc. by means of a simplified model in which the Me, Et, and active C are each replaced by an isotropic resonator with the charge of the Et group > that at the centre of the Me or active C; the resonance interaction between the three, taken as having the



same natural frequency, is calc. by an exact method. If the optical vibration of the OH absorption band of longest  $\lambda$  is assumed to be non-isotropic the model will be optically active, whilst if the OH group is isotropic there will be no activity. From the light scattering and Kerr effects of OH-compounds it is probable that for the COH group the above absorption band vibrates in the plane defined by the C, O, and

H atom. This leads to  $\text{H}-\overset{\text{CO}_2\text{H}}{\underset{\text{Me}}{\text{C}}}-\text{OH}$  where the Me and

$\text{CO}_2\text{H}$  lie behind the plane of the paper, for the configuration of  $d(-)$ -lactic acid. Calculation shows that for  $\text{CHRR}'\text{OH}$  the direction of rotation is independent of the sp. nature of R and R'. On both theoretical and experimental grounds vibrations corresponding with optical absorption bands of a mol. must be regarded as non-isotropic. The direction of the optical vibrations of the absorption band of longest  $\lambda$  of a given mol. generally is that in which the polarisability, as measured by the Kerr effect and light scattering, is a max. In the most important cases optical activity appears to be an effect not of the third, but of the first, or at most second, order.

R. C.

**Mechanism of reactions of metal enolates of acetoacetic ester and related compounds. III. Copper enolates.** A. MICHAEL and G. H. CARLSON (J. Amer. Chem. Soc., 1936, 58, 353—364; cf. A., 1935, 474).—The  $\text{Cu}^{\text{II}}$  enolate (I) (1 mol.) of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  and Cl (1.5 mols.) in  $\text{CCl}_4$  at  $0^\circ$  or the b.p. give  $\text{Cu}_2\text{Cl}_2$  (1 mol.) and  $\text{CHClAc}\cdot\text{CO}_2\text{Et}$  (II) (2 mols.); the formation of  $\text{CuCl}_2$  (Schönbrodt, A., 1890, 27) is ascribed to the use of an excess of Cl. (I) and  $\text{Cu}_2\text{Cl}_2$  are also formed from (I) and  $\text{CuCl}_2$  in boiling  $\text{C}_6\text{H}_6$ . (I) and  $\text{AcCl}$  (1.5 mols.) in  $\text{C}_6\text{H}_6$  or  $\text{Et}_2\text{O}$  at room temp. afford  $\text{Cu}_2\text{Cl}_2$ , (II), and  $\text{OAc}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ ;  $\text{CHAc}_2\cdot\text{CO}_2\text{Et}$  (III) is not formed. The  $\text{Cu}^{\text{II}}$  enolate (IV) of (III) with  $\text{AcCl}$  similarly gives the *O*-Ac derivative of (III) and the (impure) enolate,  $\text{ClCu}\cdot\text{O}\cdot\text{CMe}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$ , which is converted by cold  $\text{H}_2\text{O}$  into (IV) and by  $\text{AcCl}$  in boiling  $\text{C}_6\text{H}_6$  into (III),  $\text{CuCl}_2$ , and  $\text{Cu}_2\text{Cl}_2$ . The  $\text{Cu}^{\text{II}}$  enolate (V) of  $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$  (VI) and  $\text{AcCl}$  (2 equivs.) in boiling  $\text{C}_6\text{H}_6$  afford the *O*-Ac derivative of (VI),  $\text{CuCl}_2$ , and some  $\text{Cu}_2\text{Cl}_2$ ; reaction is slow at room temp. and an intermediate enolate cannot be isolated. (I) and  $\text{ClCO}_2\text{Et}$  (2 equivs.) in boiling  $\text{C}_6\text{H}_6$  give (cf. Nef, A., 1892, 140)  $\text{Cu}_2\text{Cl}_2$ , some  $\text{CHAc}(\text{CO}_2\text{Et})_2$ , the enolate,  $\text{ClCu}\cdot\text{O}\cdot\text{CMe}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , and unidentified products; (V) and  $\text{ClCO}_2\text{Et}$  (1.5 mols.) similarly yield  $\text{Cu}_2\text{Cl}_2$ ,  $\text{CHBz}(\text{CO}_2\text{Et})_2$ , and a little of the enolate,  $\text{ClCu}\cdot\text{O}\cdot\text{CPh}\cdot\text{C}(\text{CO}_2\text{Et})_2$ . (I) and  $\text{BzCl}$  in boiling  $\text{C}_6\text{H}_6$  afford (cf. Nef, A., 1893, i, 628)  $\text{Cu}_2\text{Cl}_2$ , (VIII) (below),  $\text{CHBzAc}\cdot\text{CO}_2\text{Et}$ ,  $\text{CBz}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ , and  $\text{OBz}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  (VII), b.p.  $139^\circ/1.5$  mm., m.p.  $42^\circ$ , in varying proportions (according to amount of  $\text{BzCl}$  used). (I) and dry  $\text{HCl}$  (1 equiv.) in  $\text{Et}_2\text{O}$  and  $\text{N}_2$  furnish the unstable, impure enolate,  $\text{ClCu}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  [which is probably an intermediate in the reaction between (I) and  $\text{AcCl}$ ], converted by cold  $\text{H}_2\text{O}$  into (I) and  $\text{CuCl}_2$ , and by  $\text{BzCl}$  at room temp. into  $\text{Cu}_2\text{Cl}_2$ , (II), (VII), and the  $\text{Cu}^{\text{II}}$  enolate (VIII) of  $\text{CHBzAc}\cdot\text{CO}_2\text{Et}$ . (VIII) and  $\text{HCl}$  (1 equiv.) similarly give an impure  $\text{ClCu}$  enolate,

$\text{C}_{13}\text{H}_{13}\text{O}_4\text{ClCu}$ ; the  $\text{Cu}^{\text{II}}$  enolate of  $\text{COMe}\cdot\text{CH}_2\cdot\text{COPh}$  affords an impure enolate,  $\text{C}_{10}\text{H}_9\text{O}_2\text{ClCu}$ , whilst the  $\text{Cu}^{\text{II}}$  enolate of  $\text{COMe}\cdot\text{CH}_2\cdot\text{COMe}$  and (IV) yield the pure enolates,  $\text{ClCu}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COMe}$  and  $\text{ClCu}\cdot\text{O}\cdot\text{CMe}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$ , respectively, which with cold  $\text{H}_2\text{O}$  and aq.  $\text{HCl}$  give the original enolates and ketones, respectively. The results are interpreted by the theory (cf. *loc. cit.*) of the formation of polymols. and their subsequent decomp. Related reactions, e.g., the production of  $\text{CH}_2\cdot\text{CO}$  from  $\text{CH}_2\text{Br}\cdot\text{COBr}$  and  $\text{Zn}$ , are discussed briefly.

(VII) and its (liquid) isomeride (IX), b.p.  $139^\circ/1.5$  mm. (from  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  and  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$ ), absorb  $\text{H}_2$  and  $\text{Br}$  at about the same rate; (VII) reacts somewhat faster with  $\text{ONa}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  to give the Na enolate of  $\text{CHBzAc}\cdot\text{CO}_2\text{Et}$ . (VII) and (IX) could not be interconverted by heat or irradiation [whereby (IX) is destroyed and (VII) is unchanged]. It appears doubtful if (VII) and (IX) can be classed as ordinary stereoisomerides. H. B.

$\alpha\alpha$ -Dimethylacetoacetic acid.—See this vol., 432.

Monohydroxypalmitic acid in butter fat.—See this vol., 361.

**Chlorohydroxystearic acids from oleic and elaidic acids.** K. HASHI (J. Soc. Chem. Ind. Japan, 1936, 39, 18B).—Addition of  $\text{HOCl}$  to oleic acid, or of  $\text{HCl}$  to its oxide, yields only a *chlorohydrin*  $\alpha$ , m.p.  $38.0$ — $38.3^\circ$ ; that of  $\text{HCl}$  to elaidic acid oxide gives *chlorohydrins*  $\beta$  and  $\gamma$ , m.p.  $49.5$ — $51.0^\circ$ , and  $68.0$ — $69.5^\circ$ , with scarcely any  $\alpha$ , whereas that of  $\text{HOCl}$  to elaidic acid yields a mixture, half of which is a substance of m.p.  $51.0$ — $55.0^\circ$ . E. W. W.

**Action of alkali metals on dialkylmalonic esters.** F. KROLLFEIFFER and A. ROSENBERG (Ber., 1936, 69, [B], 465—470).—Na powder reacts vigorously with  $\text{CMe}_2(\text{CO}_2\text{Et})_2$  is anhyd.  $\text{Et}_2\text{O}$  giving  $\text{CO}$  (95.3% of amount calc. for elimination of 1  $\text{CO}_2\text{Et}$ ) and  $\text{Pr}^n\text{CO}_2\text{Et}$  (yield 35.8%); the deficit of the latter is attributed partly to volatility, partly to formation of further products; acidic substances are also produced, which are less in evidence when a more difficultly hydrolysable malonate is used. K and  $\text{CEt}_2(\text{CO}_2\text{Et})_2$  react violently giving  $\text{CO}$  (10.4%),  $\text{CHEt}_2\cdot\text{CO}_2\text{Et}$  (29.8%), and  $\text{CO}_2\text{H}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$  (31.5%); the more turbid action with Na affords  $\text{CO}$  (85.4%),  $\text{CHEt}_2\cdot\text{CO}_2\text{Et}$  (46.5%), and dicarbonyl compounds which could not be identified. K and  $\text{CPr}^n_2(\text{CO}_2\text{Et})_2$  yield  $\text{CO}$  (11.6%),  $\text{CHPr}^n_2\cdot\text{CO}_2\text{Et}$  (37.2%), and *Et H di-n-propylmalonate*, m.p.  $43$ — $44^\circ$ ; with Na the products are  $\text{CO}$  (83.2%),  $\text{CHPr}^n_2\cdot\text{CO}_2\text{Et}$  (61%), and minor amounts of acidic products.  $\alpha$ -*n*-Propylvaleranilide has m.p.  $102$ — $103^\circ$ .  $\text{C}(\text{CH}_2\text{Ph})_2(\text{CO}_2\text{Et})_2$  and K react slowly at  $15$ — $20^\circ$ , more vigorously at the b.p. of  $\text{Et}_2\text{O}$ , giving  $\text{CO}$  (4.6%) and  $\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{CO}_2\text{Et}$  (32.5%) with considerable amounts of acidic products; with Na the products are  $\text{CO}$  (58%),  $\text{CH}(\text{CH}_2\text{Ph})_2\cdot\text{CO}_2\text{Et}$  (38.1%), and very little acidic material. The mechanism of the change is not elucidated. H. W.

**Optically active anhydrides. I. Anhydride of  $d$ - $\alpha$ -methylglutaric acid.** E. BERNER and R. LEONARSEN (Kong. Norske Vidensk. Selsk. Forhandl., 1935, 7, 125—128; Chem. Zentr., 1935, i,



3781—3782).—Fractional crystallisation of the strychnine salt of *dl*- $\alpha$ -methylglutaric acid (I) yields *d*- $\alpha$ -methylglutaric acid, m.p. 81°,  $[\alpha]_D^{20} +20.05^\circ$  in  $H_2O$ ; with  $AcCl$  this affords *d*- $\alpha$ -methylglutaric anhydride, m.p. 50°,  $[\alpha]_D^{20} -38.8^\circ$  in  $H_2O$ . *l*- $\alpha$ -Methylglutaric acid may be obtained by crystallisation of the brucine salt of (I). H. N. R.

**Biochemistry of micro-organisms. XLVIII.** Penicillic acid, a metabolic product of *Penicillium puberulum*, Bainier, and *P. cyclopium*, Westling. J. H. BIRKINSHAW, A. E. OXFORD, and H. RAISTRICK (Biochem. J., 1936, 30, 394—411).—Penicillic acid (I),  $C_8H_{10}O_4$ , m.p. 87° (cryst. from  $H_2O$ ,  $C_8H_{12}O_5$ , m.p. 64—65°), a product of the metabolism of *P. puberulum*, Bainier, and in much larger yield of *P. cyclopium*, Westling, is optically inactive, monobasic, readily loses  $CO_2$ , contains 1 active H, 1 OMe, and gives a monoacetate,  $C_{10}H_{12}O_5$ , m.p. 72°, a condensation product with dimedon,  $C_{16}H_{22}O_6$ , m.p. 204° (decomp.), a  $Br_2$ -derivative,  $C_8H_{10}O_4Br_2$ , m.p. 154—155°, and a  $H_2$ -derivative (II), m.p. 86° (cryst. from  $H_2O$ ,  $C_8H_{14}O_5$ , m.p. 62—64°). On hydrolysis with  $2N-H_2SO_4$ , (I) gives  $CO_2$  (1 mol.) and a substance,  $C_{10}H_{16}O_4$  (bisdinitrophenylhydrazones, m.p. 254°), which probably resulted from the condensation of 2 mols. of  $AcCOEt$ , whilst (II) gives  $CO_2$  (1 mol.) and a substance  $C_6H_{10}O_2$ , probably acetylisobutyl (isolated as a mixture of a bisdinitrophenylhydrazones, m.p. 226—227°, with two monodinitrophenylhydrazones, m.p. 186—187° and 121°, respectively). On hydrolysis with  $0.25N-Ba(OH)_2$ , (I) gives the following:  $CO_2$ ; a substance,  $C_5H_{10}O_2$  (monodinitrophenylhydrazones, m.p. 193—194°);  $AcCOEt$  (bisdinitrophenylhydrazones, m.p. 272—274°); a substance,  $C_8H_{12}O$  (monodinitrophenylhydrazones, m.p. 152—154°); a substance,  $C_{10}H_{10}O_2$ , m.p. 98—102°, a lactonic condensation product;  $MeOH$ ;  $HCO_2H$ . (II) with  $CH_3N_2$  gives a neutral  $Me_1$  ester,  $C_9H_{14}O_4$ , an oil ( $N_2H_4$  derivative, m.p. 207—208°), whilst (I) yields a pyrazoline *Me* ester,  $C_{10}H_{14}O_4N_2$ , m.p. 74°, which with  $NH_2OH$  gives a pyridazone,  $C_9H_{12}O_2N_4$ , m.p. 181°, and with  $NHPh-NH_2$  a phenylpyridazone,  $C_{15}H_{16}O_4N_2$ , m.p. 198—199°. The ozonide of (I) on decomp. gives  $CH_2O$ , indicating the presence of a  $:CH_2$  group; (II) gives no  $CH_2O$ . Neither (I) nor (II) gives ketonic reactions in cold aq. solution, but (I) rapidly absorbs 1 mol., more slowly a second mol., of  $NH_2OH$ , whereas (II) does not absorb  $NH_2OH$ . On heating with  $NH_2OH$ , (I) gives a dioxime,  $C_6H_{10}O_2N_2$ , m.p. 210—212° (decomp.), decarboxylation and demethylation having occurred, whilst (II) gives an orthoxazine,  $C_8H_{11}O_3N$ , m.p. 54—56°. (I) with  $NHPh-NH_2$  gives a phenylpyrazolinephenylhydrazones (III),  $C_{18}H_{20}N_4$ , m.p. 176°, decarboxylation and demethylation occurring. (III) on oxidation with  $PbO_2-AcOH$  gives a phenylpyrazole (IV),  $C_{12}H_{12}ON_2$ , m.p. 72—74° (oxime,  $C_{12}H_{13}ON_3$ , m.p. 149°). (IV) on oxidation with  $NaOI$  gives a monocarboxylic acid (V),  $C_{11}H_{10}O_2N_2$ , m.p. 170°, which with alkaline  $KMnO_4$  gives 1-phenylpyrazole-3 : 4-dicarboxylic acid, m.p. 232° (*Me* ester, m.p. 89°). (V) on thermal decomp. gives 1-phenyl-4-methylpyrazole, m.p. 43°, oxidised with  $KMnO_4$  to 1-phenylpyrazole-4-carboxylic acid,  $C_{10}H_8O_2N_2$ , m.p. 219—221°. These reactions

show that the decarboxylated, demethylated product arising from (I) is  $\beta\gamma$ -diketo- $\delta$ -methylene-pentane (VI). (II) on heating with red  $P-HI$  gives  $\gamma$ -hydroxy- $\delta$ -methylhexoic acid (lactone, b.p. 227—230°; phenylhydrazide, m.p. 126°), thus fixing the point of attachment of the  $CO_2H$  to (VI). (II) with  $KMnO_4$  and with  $O_3$  gives *Me* dimethylpyruvate (monodinitrophenylhydrazones, m.p. 176—178°), which with  $N-NaOH$  gives the free acid (dinitrophenylhydrazones, m.p. 196—197°). The OMe is thus attached to the  $\beta$ -C in (VI). (I) is therefore  $\gamma$ -keto- $\beta$ -methoxy- $\delta$ -methylene- $\Delta^4$ -hexonoic acid and must exist in both keto and lactone forms:

$$CH_2:CMc \cdot CO \cdot C(OMe):CH \cdot CO_2H \rightleftharpoons CH_2:CMc \cdot C(OH) \cdot C(OMe):CH \cdot CO.$$

P. W. C.

**Reversible oxidation of ascorbic acid by norite charcoal.**—See this vol., 390.

**Colorimetric determination of aliphatic aldehydes.** K. FISCHBECK and L. NEUNDEUBEL (Z. anal. Chem., 1936, 104, 81—88).— $CH_2O$ ,  $MeCHO$ , and  $EtCHO$  are determined photometrically by means of the colour developed with 0.01% aq. fuchsin- $H_2SO_3$  (I) in acid solution, using filtered light of 470  $m\mu$ . (I) may be kept without change under  $H_2$ .  $CH_2O$  is warmed with (I) for 5 min. at 80°;  $MeCHO$  and  $EtCHO$  are mixed with (I) at room temp., and examined after a standardised time interval. A large excess of  $EtOH$  has no effect. J. S. A.

**Action of chloral on magnesium  $\beta$ -phenylethyl,  $\gamma$ -phenylpropyl, and  $\delta$ -phenylbutyl bromides.** P. M. DEAN and W. I. WOLF (J. Amer. Chem. Soc., 1936, 58, 332—333).—Chloral (I) (1 mol.) and  $CH_2Ph \cdot CH_2 \cdot MgBr$  (1 mol.) give  $CCl_3 \cdot CH_2 \cdot OH$  (II) ( $\alpha$ -naphthylcarbamate, m.p. 120°), styrene, and  $(CH_2Ph \cdot CH_2)_2$ . Similarly,  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot MgBr$  and (I) give (II),  $CH_2Ph \cdot CH_2 \cdot CH_2$ , and  $\alpha$ -diphenylhexane;  $CH_2Ph \cdot [CH_2]_3 \cdot MgBr$  affords (II),  $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CH_2$ , and  $\alpha$ -diphenyloctane. No  $CCl_3 \cdot CHR \cdot OH$  could be isolated. The main product is the olefine (usually isolated as dibromide). H. B.

**Micro-determination of acraldehyde.** I. M. KORENMAN (J. Appl. Chem. Russ., 1935, 8, 1476—1477).—3 ml. of 0.1*N*-I in KI and 1 ml. of 5%  $KOH$  are added to 5—10 ml. of dil. aq. acraldehyde, the solution is made acid with  $H_2SO_4$  after 30 min., and the liberated I is titrated with 0.1*N*- $Na_2S_2O_3$ . Alternatively, the solution is made strongly acid with  $H_2SO_4$ , excess of  $KMnO_4$  is added, the mixture is heated at 100° for 15 min., and  $Na_2C_2O_4$  is added, excess of which is titrated with  $KMnO_4$ . R. T.

**Constitution of Schiff's bases.** J. TURCAN (Bull. Soc. chim., 1936, [v], 3, 283—294).— $CHPr^a:NR$  ( $R=Pr^a$ ,  $C_5H_{11}$ ,  $CH_2Ph$ , and  $Ph$ ) and heptylideneaniline with  $Br$  give  $NH_2R$  (or its  $Br$ -derivatives) and  $CPr^aBr \cdot CHO$  (polymeride, m.p. 95—97°) or bromoheptaldehyde, respectively. Reaction occurs by addition to the  $CMe_2:CH \cdot NHR$  form.  $N_2O_4$ , however, reacts with Schiff's bases in the same way whether a *tert*-C is or is not present, i.e., with the enimine form. Equilibrium between the two forms is thus demonstrated. R. S. C.

**Constitution of oximes.** See this vol., 406.



Quadrivalent compounds of bivalent copper and nickel. See this vol., 410.

Hydrogenation of ketones in presence of nickel and platinised nickel. Influence of alkali. M. DELEPINE and A. HOREAU (Compt. rend., 1935, 201, 1301—1305).—The rate of hydrogenation of COMe<sub>2</sub>, COMeEt, COMe·C<sub>9</sub>H<sub>19</sub>, COMePh,  $\alpha$ -phenyl- $\beta$ -dimethylhexan- $\beta$ -one, cyclohexanone, CH<sub>3</sub>Ac·CO<sub>2</sub>Et, CHEtAc·CO<sub>2</sub>Et, lævulic acid, CHMe·CH·CHO, PhCHO, *o*- and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO, galactose, fructose, and  $\alpha$ -diethylaminopentan- $\delta$ -one to alcohols at room temp. and atm. pressure in presence of Raney Ni is greatly increased by addition of a little NaOH. Fixation of the second mol. of H<sub>2</sub> by mesityl oxide, methylheptenone, and CHPh·CH·COMe is similarly accelerated. The effect is not due to enolisation, as it occurs also with COPh<sub>2</sub> and Bz<sub>2</sub>. A similar, but smaller, acceleration is caused by platinising the Ni with a little dil. alkaline PtCl<sub>4</sub>. Pd, Rh, and Ru have slight similar effects. The effects of platinisation and alkali are additive.

R. S. C.

Action of magnesium *tert*-butyl chloride on methyl propyl ketone and ethyl laurate. A. D. PETROV, K. I. KARASEV, and M. A. TSCHELZOVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 31—33, and Bull. Soc. chim., 1936, [v], 3, 169—176).—With COMePr<sup>a</sup>, MgBu<sup>a</sup>Cl (I) affords some  $\beta$ -*tert*-butyl-pentan- $\beta$ -ol, b.p. 68.8—69.8°/16 mm. (chloride, b.p. 64.2—65.5°/12.5—13 mm.), together with large amounts of products formed by self-condensation of the ketone, but no *tert*-alcohol is obtained with dodecyl ketone (II) (reduced to carbinol, converted into the olefine through the xanthate) (Kipping, J.C.S., 1890, 57, 983). Et laurate and (I) in Et<sub>2</sub>O-xylene at 110—120° give only (II): 2R·CO<sub>2</sub>Et  $\rightarrow$  R<sub>2</sub>CO + CO(CO<sub>2</sub>Et)<sub>2</sub>  $\rightarrow$  CO<sub>2</sub> + Et<sub>2</sub>O (R = C<sub>11</sub>H<sub>23</sub>), but with MgBu<sup>a</sup>Cl it affords  $\epsilon$ -*n*-butylhexadecan- $\epsilon$ -ol (III), b.p. 180—182°/15 mm. (unstable bromide), with partial dehydration to  $\epsilon$ -*n*-butyl- $\Delta^8$ -hexadecene, b.p. 165—167.5°/15 mm., best obtained by dehydration of (III) with H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 140—180°. Similar results are obtained with Et palmitate. (I) is not decomposed by heating to 110°.

J. W. B.

Diacetyl. J. PIEN, J. BAISSÉ, and R. MARTIN (Lait, 1936, 16, 119—138).—The formation of a phenylhydrazone is recommended as a qual. test (photomicrographs of the crystals are given). A colorimetric determination (for dilutions down to 1 in 100,000) is described. The reagent used is *m*-tolylenediamine, which reacts to give a yellow colour.

E. B. H.

Nomenclature of methylated sugars. E. VETOČEK (Coll. Czech. Chem. Comm., 1936, 8, 43—45).—It is proposed to designate sugar Me ethers as methylglucose etc. and *C*-Me derivatives as methylglucose etc.

R. S. C.

Formation of osazones. J. KENNER and E. C. KNIGHT (Ber., 1936, 69, [B], 341—343).—The formation of osazones is ascribed to the oxidising action of salts of NHPH·NH<sub>2</sub>. The latter is stable below 300°, but mixtures of it and its hydrochloride commence to evolve gas at 120° and the reaction becomes very vigorous at 165°. From *o*-, *m*-, and

*p*-tolyl- and *p*-bromophenyl-hydrazine gas is rapidly evolved at about 100°, 100°, 115°, and 120°, respectively.

H. W.

Change in optical rotation of glucose in dilute solutions of boric acid. P. S. TANG and P. N. SUNG (Nature, 1936, 137, 275).—Contrary to previous observations (A., 1932, 120), changes occur in  $\alpha$  of glucose in H<sub>3</sub>BO<sub>3</sub> and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> at certain concns. For 10% solutions of glucose  $[\alpha]_D$  falls to a sharp min. with 0.13*M*-H<sub>3</sub>BO<sub>3</sub>.

L. S. T.

Simultaneous formation of two isomeric isopropylidene derivatives of 2-methyl- $\gamma$ -methylglucoside. D. J. BELL (J.C.S., 1936, 186—187).—The oily product from 2-methyl- $\gamma$ -methylglucoside, anhyd. CuSO<sub>4</sub>, and 1% H<sub>2</sub>SO<sub>4</sub>·COMe<sub>2</sub> is a mixture of 3:5- and 5:6-isopropylidene derivatives. By methylation (Purdie), hydrolysis (0.5% HCl at 100°), conversion into the  $\beta$ -glucoside, and then into the dinitrate, it yields 2:3-dimethyl- $\beta$ -methylglucoside 4:6-dinitrate, m.p. 99—100° (lit. 98—99°). The material from the mother-liquor with Zn and Fe in AcOH gives impure 2:6-dimethyl- $\beta$ -glucoside, characterised as 3:4-di-*p*-toluenesulphonate, m.p. 157—158°.

R. S. C.

Condensation products of acetoacetic ester.

IV. Two highly reactive compounds of glucose and acetoacetic ester. C. U. MOORE, R. J. ERLANGER, and E. S. WEST (J. Biol. Chem., 1936, 113, 43—47).—Et glucosycycloacetoacetate (I) (A., 1927, 1173) is oxidised by HgSO<sub>4</sub> at room temp. to a non-cryst. hygroscopic substance (II), C<sub>12</sub>H<sub>18</sub>O<sub>8</sub>, m.p. 65—72°,  $[\alpha]_D^{25}$  —70.9° in H<sub>2</sub>O (no mutarotation). (II) rapidly reduces cold Fehling's solution, and immediately becomes reddish-brown when treated with alkali. It gives unstable products with NHPH·NH<sub>2</sub> and NH<sub>2</sub>OH, and immediately affords CHI<sub>3</sub> with KOI. It contains 3 OH and 1 Ac. Treatment of it with BzCl in CHCl<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N affords a Bz<sub>2</sub> derivative, C<sub>26</sub>H<sub>26</sub>O<sub>10</sub>, m.p. 45—49°,  $[\alpha]_D^{25}$  —52.5° in abs. EtOH (no mutarotation). Oxidation of (I) with BzO<sub>2</sub>H in H<sub>2</sub>O-EtOAc containing BaCO<sub>3</sub> at 7° gives an isomeric product, C<sub>12</sub>H<sub>18</sub>O<sub>8</sub>, m.p. 57—60°,  $[\alpha]_D^{25}$  —33.4° in H<sub>2</sub>O, which closely resembles (II), but contains only 2 OH groups which are reactive towards Ac<sub>2</sub>O.

H. W.

Oxidation of  $\alpha$ -methyl-*d*-mannopyranoside.

E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1936, 58, 378—379).—Oxidation [aq. Ba(OBr)<sub>2</sub>] of  $\alpha$ -methyl-*d*-mannopyranoside (I) removes C<sub>3</sub> and gives the acid (II), CO<sub>2</sub>H·CH(OMe)·O·CH(CO<sub>2</sub>H)·CH<sub>2</sub>·OH (*Sr* salt,  $[\alpha]_D^{25}$  —53° in H<sub>2</sub>O), which does not reduce Fehling's solution. Hydrolysis (hot H<sub>2</sub>O) of (II) and subsequent oxidation (Br-H<sub>2</sub>O) affords H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and *d*-glyceric acid. (II) is also obtained by successive oxidation of (I) or  $\alpha$ -methyl-*d*-glucoside with HIO<sub>4</sub> and Br-H<sub>2</sub>O; (II) should be similarly produced from all the  $\alpha$ -methyl-*d*-aldohexopyranosides.

H. B.

Glucoside derivatives. E. JOLLES [in part with M. BOTRINI] (Gazzetta, 1935, 65, 1217—1221).—*Æseulin tetra*-, m.p. 270° (decomp.),  $[\alpha]_D^{18}$  +46.9° (all rotations in C<sub>5</sub>H<sub>5</sub>N), *amygdalin hexa*-, m.p. 267° (decomp.),  $[\alpha]_D^{18}$  —25.4°, *arbutin tetra*-, m.p. 224—225° (decomp.),  $[\alpha]_D^{18}$  +23.3°, and *salicin penta*-(*N*-phenyl-



carbamate), m.p.  $204^{\circ}$  (decomp.),  $[\alpha]_D^{18} -42.8^{\circ}$ , are obtained by action of PhNCO on the respective glucosides in  $C_5H_5N$ . E. W. W.

**Saponins from seeds of *Barringtonia asiatica*, Kurz.** Constituents of the sugar part of  $A_1$ -barrinin.—See this vol., 396.

**Saponin-like substance of radix clematidis.** See this vol., 396.

**Glycosides of the flowers of *Linaria vulgaris*, L.** Constitution of linarin and pectolinarin. K. W. MERZ and Y. H. WU (Arch. Pharm., 1936, 274, 126—148; cf. Schmid and Rumpel, A., 1931, 738; 1932, 621).—Extraction of the dried flowers with  $Et_2O$  removes fatty material from which hentriacontane is isolated. Further extraction with EtOH gives mannitol, the phenolic linarin (I),  $C_{28}H_{32}O_{14} \cdot H_2O$  (cf. Klobb, A., 1908, i, 903), m.p.  $256^{\circ}$  (decomp.) (rapid heating),  $[\alpha]_D^{18} -100.1^{\circ}$  in AcOH, and amorphous pectolinarin (II),  $C_{29}H_{34}O_{15}$ , m.p.  $240-250^{\circ}$  (decomp.). (I) gives a  $Ac_7$  derivative (III) ( $+2H_2O$ ), m.p.  $123-125^{\circ}$ , and is hydrolysed (conc. HCl) to glucose, rhamnose, and linareginin (IV),  $C_{16}H_{12}O_5$ , m.p.  $262^{\circ}$  (decomp.) [ $Ac_2$ , m.p.  $200^{\circ}$ ,  $Bz_2$ , m.p.  $200^{\circ}$ , and  $Br_2$ , m.p.  $257^{\circ}$  (decomp.), derivatives; *Me ether* ( $CH_2N_2$ ), m.p.  $170^{\circ}$ ; *Me ether acetate* (V), m.p.  $196^{\circ}$ ]. The  $Ac_1$  derivative obtained from (III) and AcOH-HBr in  $CHCl_3$  is methylated ( $CH_2N_2$ ) to (V). (IV) is degraded by conc. KOH in  $H_2$  to  $HCO_2H$ , anisic acid [also formed by oxidation (30%  $H_2O_2$  in 15% KOH) of (IV)], *s*- $C_6H_3(OH)_3$ , and *p*-OMe- $C_6H_4$ -COMe. (IV) is, therefore, 5:7-dihydroxy-4'-methoxyflavone; the disaccharide residue in (I) is at  $C_7$ . (IV) is identical with acacetin (Hattori, A., 1925, i, 1443), but (I) differs from acaciin (*loc. cit.*). (II) is hydrolysed (conc. HCl) to glucose, rhamnose, and pectolinarigenin (VI),  $C_{15}H_8O_4(OMe)_2$ , m.p.  $215-216^{\circ}$  [ $Ac_2$  derivative, m.p.  $151^{\circ}$ ; *Me ether* ( $CH_2N_2$ ), m.p.  $188^{\circ}$ ; *Me ether acetate* (VII), m.p.  $168^{\circ}$ ; *Me\_2 ether* ( $Me_2SO_4$ ), m.p.  $162^{\circ}$ , identical with 5:6:7:4'-tetramethoxyflavone (Robinson and Schwarzenbach, A., 1930, 735)]. The  $Ac_1$  derivative obtained from the  $Ac_7$  derivative, m.p.  $134-138^{\circ}$ , of (II) and AcOH-HBr in  $CHCl_3$  is methylated to (VII). Degradation (KOH) of (VI) gives  $HCO_2H$ , anisic acid, 2:4:6-(OH) $_3C_6H_2$ -OMe and *p*-OMe- $C_6H_4$ -COMe. (VI) is 5:7-dihydroxy-6:4'-dimethoxyflavone. (II) is the 6-OMe-derivative of (I). H. B.

**Cellulose of native composition from cotton wool.** II. E. SCHMIDT, W. JANDEBEUR, M. HECKER, R. SCHNEGG, and M. ATTERER [with W. HAHN and J. W. PEDLOW] (Ber., 1936, 69, [B], 366—374; cf. A., 1935, 610).—Cellulose from cotton wool and linters which has not been subjected to chemical treatment but has been purified by the  $ClO_2$  method contains 0.28% of  $CO_2H$ . This val. is unchanged by dissolution of the material in  $CuO-NH_3$  and repptn. by AcOH or  $(NH_4)_2SO_4$ , and is also observed in similarly treated specimens not purified with  $ClO_2$ . Since the latter specimens are free from all known impurity, it follows that cellulose is the sole carrier of 0.28%  $CO_2H$  and is a carboxylic acid. If 0.28% of  $CO_2H$  is present the material is unaffected by the action of  $CuO-NH_3$  and AcOH or  $(NH_4)_2SO_4$ , but a

variation from this % is accompanied by oxidation, frequently with marked increase in the % of  $CO_2H$ . Native cellulose (I) therefore consists of a chain of 96  $C_6$  units. The presence of 0.28% of  $CO_2H$  can be used as a criterion of the unaltered condition of (I), but natural conditions appear to exist which induce alteration in the crude material. (I) is changed by NaOH,  $NH_3$ ,  $CaCO_3$ , and many other substances at room temp.; possibly the fermentative degradation of (I) in the soil is preceded by the action of  $CaCO_3$ . The action of  $Cl_2$  in  $H_2O$  on (I) causes increase in the % of  $CO_2H$ , and even in very dil. solution the reagent is unsuitable for the scientific investigation of polymeric carbohydrates. The technical processes of purifying cotton wool and linters cause chemical alteration in (I). H. W.

**X-Ray studies of reactions of cellulose in non-aqueous systems. I. Interaction of cellulose and liquid ammonia.** A. J. BARRY, F. C. PETERSON, and A. J. KING (J. Amer. Chem. Soc., 1936, 58, 333—337).—Cellulose (ramie) (I) swells in liquid  $NH_3$  and gives  $NH_3$ -cellulose (II) (approx. 1 mol. of  $NH_3$  per  $C_6H_{10}O_5$ ), the X-ray diagram of which resembles that of  $N_2H_4$ -cellulose (Trogus and Hess, A., 1932, 149). (II) loses all its  $NH_3$  at  $105^{\circ}$  and passes into cellulose II [the X-ray diagram of which resembles that of hydrate cellulose (III)], which regenerates (II) when treated with liquid  $NH_3$ . (II) could not be obtained from (I) and dry  $NH_3$  or dil. or conc. aq.  $NH_3$ . (I) is recovered from (II) by treatment with  $H_2O$ , dil. AcOH, or dil. or conc. aq.  $NH_3$ . (III) and liquid  $NH_3$  give a product resembling (II). H. B.

**Perchlorates as solvents for cellulose and its derivatives.**—See this vol., 426.

**Carbonisation of ramie cellulose studied by means of X-rays and the "net density method."** C. PARK (Mem. Coll. Sci. Kyoto, 1935, A, 18, 311—313).—As the temp. of carbonisation,  $t$ , is raised from  $260^{\circ}$  to  $290^{\circ}$ , the X-ray pattern of the C changes from that of ramie cellulose to that of amorphous C, and  $d$  is a min. when  $t$  is approx.  $290^{\circ}$ . J. G. A. G.

**Organic cupritetra-chlorides and -bromides.**—See this vol., 438.

**McCrae's test [for salicylic acid]: special test for hexamethylenetetramine.** F. W. CHENG (J. Chem. Eng. China, 1935, 2, 137—138).—McCrae's test depends on the production of a pink colour with  $CH_2O$  and  $H_2SO_4$  disappearing on dilution with  $H_2O$ . It is more sensitive than the  $FeCl_3$  test and is applicable to derivatives without previous hydrolysis. The addition of  $H_2SO_4$  to  $(CH_2)_6N_4$  (I) liberates  $CH_2O$  so the test can be used for detection of (I). C. I.

**[Compounds of] copper ferrocyanide ammoniate.**—See this vol., 443.

**Synthesis of  $\alpha$ -amino- $\beta$ -hydroxypropane.** P. A. LEVENE [with M. KUNA] (J. Biol. Chem., 1936, 113, 153—156).— $CHMeBr \cdot CO_2H$  is added gradually to a solution of Li in  $CH_2Ph \cdot OH$  and the mixture is heated to  $150^{\circ}$ , whereby *r*- $\alpha$ -benzyloxypropionic acid (I), b.p.  $123-128^{\circ}/0.2$  mm., is obtained. It is slowly resolved by cinchonidine in  $COMe_2$ , the most sparingly sol. salt giving 1- $\alpha$ -benzyloxypropionic acid, b.p.  $125-$



128°/0.5 mm.,  $[\alpha]_D^{25} - 62.5^\circ$  in  $C_6H_6$ . *r*- $\alpha$ -Benzoyloxypropionyl chloride, b.p. 79—81°/0.5 mm., is converted by  $NH_3$  in MeOH at  $-10^\circ$  into *r*- $\alpha$ -benzyloxypropionamide, transformed by boiling  $SOCl_2$  into *r*- $\alpha$ -benzyloxypropionitrile (II), b.p. 91—93°/1 mm. Reduction (Raney) of (II) affords  $\alpha$ -amino- $\beta$ -benzyloxypropane (hydrochloride; platinichloride, m.p. 207°), whilst treatment with  $H_2$  in AcOH containing colloidal Pd gives *r*- $\alpha$ -amino- $\beta$ -hydroxypropane (platinichloride).

H. W.

Triethyl- $\beta$ -hydroxyethylammonium hydr-oxide.—See this vol., 510.

Synthesis of taurine. F. CORTESE (J. Amer. Chem. Soc., 1936, 58, 191—192).—Taurine, decomp. 300—305° (corr.) [*N*-phenylcarbamyl derivative, decomp. 195—200° (corr.)], is prepared in 80% yield from  $CH_2Br \cdot CH_2 \cdot NH_2 \cdot HBr$ , m.p. 174—175° (corr.) (modified prep.; cf. Gabriel, A., 1917, i, 541), and aq.  $Na_2SO_3$ .

H. B.

Alkaline hydrolysis of polypeptides [derived from] *l*-alanine. P. S. YANG (J. Chinese Chem. Soc., 1936, 4, 37—41).—The rate of hydrolysis of *l*-alanyl-, di-, tri-, and tetra-*l*-alanyl-*l*-alanine by 0.2*N*. and *N*-NaOH at 25° is independent of the nature of the peptide, but is much greater with the more conc. alkali. Racemisation occurs only at the beginning of the reaction; at least 3  $NH_2$ -acid units must be present for it to occur.

R. S. C.

Behaviour of *dl*-serine, *dl*-phenylalanine, *dl*-alanine, *dl*-lactic acid, and propionic acid towards X-rays and ultra-violet light.—See this vol., 437.

Photo-decomposition of *l*-aspartic acid, *l*-asparagine, and glycylglycine.—See this vol., 437.

Action of alkaline potassium hypobromite solutions on the amides of acylated amino-acids. S. J. KANEVSKAJA (Ber., 1936, 69, [B], 266—273).—The formation of cyclic compounds during the Hofmann reaction is characteristic only of amides of acylated  $\beta$ - $NH_2$ -acids; it is very probable that the change can be used for the determination of  $\beta$ - $NH_2$ -acids even when they are present in complex natural mixtures. Succinimide is converted by treatment with KOBr followed by KOH and BzCl into  $\beta$ -benzamidopropionic acid, m.p. 120° (yield 51%), transformed by successive treatment with  $SOCl_2$  and  $NH_3 \cdot CHCl_3$  into  $\beta$ -benzamidopropionamide (I), m.p. 170—171°. (I) is converted by KOBr- $H_2O$  at 80° into BzOH and tetrahydroglyoxal-2-one, m.p. 131°. Under similar conditions, hippuramide is converted into benzamidomethylamine (hydrochloride, m.p. 189—190°); occasionally, the reaction is accompanied by oxidation with production of  $NH_2Bz$ .  $NH_2 \cdot [CH_2]_3 \cdot CO_2H \cdot HCl$  is transformed by KOH and a slight excess of BzCl into  $\gamma$ -benzamidobutyric acid (II), m.p. 75° (yield 90%), the Me ester, m.p. 59—60°, of which yields  $\gamma$ -benzamidobutyramide (III), m.p. 122—123°, with  $NH_3 \cdot EtOH$ . (III) and KOBr afford benzamidotrimethyleneamine (hydrochloride, m.p. 150—160°). (II) is converted by  $SOCl_2$  or boiling  $Ac_2O$  into 1-benzoylpyrrolidone, m.p. 91—92°; if the change is effected at a very low temp. and the product

is treated with  $NH_3$  in  $CHCl_3$ ,  $\gamma$ -benzamidobutyramide, m.p. 122—123°, is isolated in about 10% yield.

H. W.

Reactions of maleimide. E. JOLLES (Gazzetta, 1935, 65, 1221—1225).—Maleimide in  $C_5H_5N$  and  $NHPh \cdot OH$  yield a substance,  $C_{10}H_{10}O_3N_2$ , m.p. 178°, regarded as phenylhydroxyaminosuccinimide, which is oxidised by  $FeCl_3$  to  $PhNO$ , and on prolonged heating in  $C_5H_5N$  loses  $H_2O$  to form anilinomaleimide, new m.p. 209°.  $NHPh \cdot OH$  with *o*- $C_6H_4(CO)_2O$  forms *o*- $C_6H_4(CO)_2NPh$ ; does not react with *o*- $C_6H_4(CO)_2NH$ ; and with succinimide or pyrrole gives resinous products.

E. W. W.

Colorimetric determination of carbamide; its determination in blood, cerebrospinal fluid, and tissues. J. A. SANCHEZ (J. Pharm. Chim., 1936, [viii], 23, 188—199).—0.5—4 c.c. of 0.01%  $CO(NH_2)_2$  solution and 1 c.c. of 0.02%  $NaNO_2$  solution are mixed and made up to 10 c.c. with  $H_2O$ ; 2 c.c. of pure liquid paraffin and then 30 drops of conc.  $H_2SO_4$  are added. The mixture is kept at 60° for 25 min. 1 c.c. of a solution of 0.5 g. of *p*- $NH_2 \cdot C_6H_4 \cdot SO_3H$  and 0.75 g. of  $PhOH$  in 100 c.c. of 2.5%  $H_2SO_4$  is added and the colour (due to azo-dye formed by the excess of  $HNO_2$ ) is measured after 5 min.  $CO(NH_2)_2$  is determined in defibrinated (Folin's reagent) whole blood, plasma, or serum by matching against standard solutions.

R. S. C.

Cupric and cuprous compounds of thiosemicarbazide and of its derivatives. V. HARLAY (Compt. rend., 1936, 202, 324—325).— $NH_2 \cdot NH \cdot CS \cdot NH_2$  with  $CuSO_4$ ,  $Cu(NO_3)_2$ , and  $CuCl_2$  gives the sulphate, nitrate, and chloride of Cu thiosemicarbazide in which the metal is linked to two org. residues through S. Acetonethiosemicarbazone in  $COMe_2 \cdot H_2O$  with  $Cu(NO_3)_2$  and  $NH_3$  gives the Cu derivative [hydrochloride and sulphate (each +1  $COMe_2$ ) when cryst. from  $COMe_2$ ], which when boiled with aq.  $COMe_2$  gives the  $Cu^I$  derivative (sulphate and hydrochloride are unstable to  $H_2O$ ).  $NH_2 \cdot NH \cdot CS \cdot NH_2 \cdot HCl$  with  $Cu_2O$  gives the  $Cu^I$  derivative,  $[CuS \cdot C(NH_2) \cdot N \cdot NH_2]HCl$ , easily oxidised in air.

J. L. D.

Theory of biuret reaction. P. S. YANG (J. Chinese Chem. Soc., 1936, 4, 27—36).—*l*-Asparagine and the amides of *dl*-leucine, *d*-alanine, and glycine form amorphous biuret compounds,  $CuX_2$ , m.p. 302—304° (decomp.), 248—250°, 229—231°, and 205—207°, respectively, in absence of alkali, the first two with  $CuSO_4$  or  $Cu(OAc)_2$ , the last two only with  $Cu(OH)_2$ . To form a biuret compound a substance must have a N carrying a replaceable H and a N which can co-ordinate with Cu, separated by  $\geq 3$  atoms; in some cases the two N are provided by different mols., in which case 4 mols. of the compound combine with 1 Cu.

R. S. C.

Rubidium and caesium fulminates.—See this vol., 438.

Preparation of hydroxamic acids. G. ODDO and E. DELEO (Ber., 1936, 69, [B], 287—294).—Hydroxamic acids are immediately formed when an aldehyde sol. in  $H_2O$  is treated with 1 mol. of  $NH_2OH$  in  $EtOH \cdot H_2O$  and then with 2 equivs. of 30%  $H_2O_2$ .



As the solubility of the aldehyde in  $H_2O$  diminishes reaction takes place less readily and to a limited extent and does not occur when the solubility is slight. MeOH or EtOH cannot be substituted for  $H_2O$ , since they are immediately oxidised to the corresponding aldehyde. No change takes place in  $COMe_2$ . If a suspension of the aldehyde in  $H_2O$  is used, a sudden reaction leads to resinous products. Since the reaction is confined to aldehydes sol. in  $H_2O$ , the possibility is excluded that it depends on a primary production of the oxime which is then oxidised by  $H_2O_2$  or that  $NH_2OH$  is oxidised by  $H_2O_2$  to  $NOH$  which is added to the aldehyde. The scheme,  $RCHO + NH_2OH = OH \cdot CHR \cdot NH \cdot OH$  (I), and  $(I) + H_2O_2 = 2H_2O + OH \cdot CR \cdot N \cdot OH$  is suggested. In support of this view it is shown that  $CCl_3 \cdot CH(OH)_2$  gives small amounts of the product  $CCl_3 \cdot CH(OH) \cdot NH \cdot OH$  and  $CHCl_2 \cdot CH(OH)_2$  yields the unstable adduct  $CHCl_2 \cdot CH(OH) \cdot NH \cdot OH$ , which immediately decomposes into chloroacetylhydroxamic acid (Cu salt) and  $OH \cdot CH \cdot N \cdot OH$ . Under defined conditions MeCHO and  $NH_2OH$  give the substance  $OH \cdot CHMe \cdot NH \cdot OH$ , immediately transformed by  $H_2O_2$  into  $OH \cdot CMe \cdot N \cdot OH$ . The prep. of  $OH \cdot CH \cdot N \cdot OH$ ,  $OH \cdot CMe \cdot N \cdot OH$ ,  $OH \cdot CEt \cdot N \cdot OH$  (Cu salt), and  $OH \cdot CPr^a \cdot N \cdot OH$  (Cu salt) is described in detail. H. W.

Additive products of aldehydes with the disodium salt of nitrohydroxylamine and with benzenesulphonhydroxamic acid; non-existence of the nitrosyl of A. Angeli. G. ODDO and E. DELEO (Ber., 1936, 69, [B], 294—298).—No evidence is obtained of the intermediate formation of nitrosyl  $NOH$ ,  $OHN$ , or  $HN(OH)_2$  by the action of the reagents on  $NH_2OH$  and its subsequent union with the aldehyde to the hydroxamic acid and Angeli's hypothesis should be discarded.  $CCl_3 \cdot CH(OH)_2$  and  $SO_2Ph \cdot NH \cdot OH$  at room temp. slowly yield the adduct,  $CCl_3 \cdot CH(OH) \cdot N(OH) \cdot SO_2Ph$ , which does not give the reactions of hydroxamic acids and is decomposed by warm alkali into  $PhSO_2K$ ,  $CCl_3 \cdot C(OH) \cdot N \cdot OK$ ,  $H_2O$ , and a colourless, cryst. compound probably of cyclic nature. Similarly,  $p-OMe \cdot C_6H_4 \cdot CHO$  and  $SO_2Ph \cdot NH \cdot OH$  afford the compound  $OMe \cdot C_6H_4 \cdot CH(OH) \cdot N(OH) \cdot SO_2Ph \cdot H_2O$ , m.p. 153—154°, also obtained in presence of  $KOH$  if heating is avoided. MeCHO and  $ONa \cdot N \cdot NO_2Na$  give the adduct,  $OH \cdot CHMe \cdot N(ONa) \cdot NO_2Na$ ,  $ONa \cdot N \cdot NO_2Na$ , whilst under similar conditions EtCHO yields the substance  $2OH \cdot CEt \cdot N(ONa) \cdot NO_2Na$ ,  $ONa \cdot N \cdot NO_2Na$ , each of which when dissolved in  $H_2O$  give the reactions of hydroxamic acids. H. W.

Formation of organo-metalloidal compounds by micro-organisms. IV. Dimethyl- and methylallyl-*n*-propylarsine. F. CHALLENGER and A. A. RAWLINGS (J.C.S., 1936, 264—267).—*P. brevicaulis* on bread crumbs with  $AsMePr^aO_2H$  or  $AsEtPr^aO_2H$  gives  $AsMe_2Pr^a$  and methylallyl-*n*-propylarsine (also obtained, b.p. 129—130°, from  $MgMeI$  and  $AsEtPr^aI$ ) [dimercurichloride, m.p. 171—172° (decomp. 188—189°); mercurichloride, m.p. 137—138°; benzylpicrate, m.p. 65—66°;  $HNO_3$  leads to methylallyl-*n*-propylhydroxyarsonium picrate, m.p. 108—109°], respectively. Phenyldimethylarsine mer-

curichloride, m.p. 193—194°, and phenylbenzylidimethylarsonium picrate, m.p. 125—126°, are described. R. S. C.

Basic organic salts of bismuth, soluble in organic solvents. M. PICON (Bull. Soc. chim., 1936, [v], 3, 176—185).—The prep. of bismuthyl cyclohexanolacetate,  $\alpha$ -carbethoxy- $\Delta^a$ -nonenoate,  $\alpha$ -carbethoxy- $\beta$ -phenyl-*n*-butyrate,  $\alpha$ -carbethoxycyclohexylacetate, camphorcarboxylate, and carboxymethylnonoate, by double decomp. between the Na salt and  $Bi(NO_3)_3$  in glycerol is described. These derivatives are sol. in org. solvents, especially  $CHCl_3$ ,  $C_6H_6$ ,  $CCl_4$ , and  $CS_2$ . E. S. H.

Preparation of tin alkyl and aryl trihalides. A. TOHAKIRIAN, M. LESBRE, and M. LEVINSOHN (Compt. rend., 1936 202, 138—140).— $KSnCl_3 \cdot H_2O$  (Rimbach *et al.*, A., 1916, ii, 332) reacts with the appropriate RI at 90—110° to give (%) yields in parentheses)  $SnMeI_3$  (43·7), *Sn Et tri-iodide*, b.p. 181—184·5°/19 mm. (37), *Sn Pr<sup>a</sup> tri-iodide*, b.p. 200°/16 mm. (<25), *Sn Ph tri-iodide*, decomp. > 220° (reaction temp. 210°), all formed thus:  $KSnCl_3 + RI \rightarrow KI + RSnCl_3 + 3KI \rightarrow 3KCl + RSnI_3$ ; and *Sn Pr<sup>3</sup> trichloride*, b.p. 75°/16 mm. (> 40). J. W. B.

Configuration of bisdimethylglyoximeammine cobaltic chloride. R. TSUCHIDA, M. KOBAYASHI, and A. NAKAMURA (Bull. Chem. Soc. Japan, 1936, 11, 38—40).—By a method for showing the optical activity of racemic substances by asymmetric adsorption on quartz when other methods are not available (J. Chem. Soc. Japan, 1935, 56, 1339), it has been found that the above compound is a *dl*-mixture, and is therefore a *cis*-compound, or has the dimethylglyoxime groups in the 1:2 instead of the 1:6 positions. M. S. B.

Substituted cyclohexyl nitrites. L. HUNTER and J. A. MARRIOTT (J.C.S., 1936, 285—286).—cycloHexyl nitrite, b.p. 31°/10 mm., rapidly decomposes yielding adipic acid. 2-Iodocyclohexyl nitrite, b.p. 110—117°/20—25 mm. (decomp.), is also unstable; 1-phenylcyclohexyl nitrite decomposes when distilled at 10 mm. 1-, b.p. 46°/12 mm., 2-, b.p. 42°/10 mm., 3-, b.p. 45°/12 mm., and 4-methyl-, b.p. 45°/14 mm., 1-ethyl-, b.p. 63°/15 mm., 2-bromo-, b.p. 87°/10 mm., and 2-chloro-cyclohexyl nitrite, b.p. 71°/12 mm., are, however, stable for > 6 months. 2-Bromocyclohexanol, b.p. 103—104°/18 mm., is unstable. R. S. C.

Bixin solutions as colorimetric standards for determination of carotene.—See this vol., 396.

Carotene. X. Comparison of absorption spectra measurements on  $\alpha$ - and  $\beta$ -carotene and lycopene. J. H. C. SMITH (J. Amer. Chem. Soc., 1936, 58, 247—255).—Curves are given for  $\alpha$ - (I) and  $\beta$ - (II) -carotenes and lycopene (III) using an improved photo-electric spectrophotometer (described in detail). The absorption coeffs. of solutions in EtOH-Et<sub>2</sub>O (20%) agree well with those found by Miller *et al.* (A., 1935, 1189); the curves for (I) and (II) are essentially the same as those previously found (A., 1934, 458) for solutions in 95% EtOH. The "pure carotene" of McNicholas (A., 1931, 1110) is (II). The coeffs. for solutions of (I), (II), and (III) in  $CS_2$  differ



considerably from those reported in the lit. (cf. Smakula, A., 1934, 1324). Variations in the positions of the absorption max. of (I) and (II), determined by spectrophotometric and spectroscopic methods (supplemented by a Cu-NH<sub>4</sub> filter), are probably due to superposition of the absorption of the filter on that of the pigment; the former should be the standard method.

H. B.

**Significance of non-localised linkings of aromatic hydrocarbons in formation of their molecular compounds with dipolar molecules.**—See this vol., 410.

**Beryllium bromide as a catalyst in the bromination of benzene.** M. F. TABOURY and R. PAJEAU (Compt. rend., 1936, 202, 328—330).—C<sub>6</sub>H<sub>6</sub> (86 g.) is readily brominated in presence of BeBr<sub>2</sub> (> 3 g.). Excess of Br converts C<sub>6</sub>H<sub>6</sub> or PhBr into *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> in good yield.

J. L. D.

**Purification and determination of the degree of purity of toluene.** W. SWIENTOSEWSKI and E. RAMOTOWSKI (Rocz. Chem., 1935, 15, 422—429).—Pure PhMe, b.p. 110.612/4°, is readily obtained by fractionation with a series of condensers, or with a special column ensuring slow distillation. Admixture of 1:1 C<sub>6</sub>H<sub>6</sub>-xylene does not affect the b.p., but increases the difference between the b.p. and the temp. of condensation of the vapour by 0.001° per 0.0024% of mixture present.

R. T.

**Mechanism of aromatic side-chain reactions.** VII.—See this vol., 433.

**Action of sulphinates on 2:4-dinitrophenylsulphones.** J. D. LOUDON (J.C.S., 1936, 218—221).—ArSO<sub>2</sub>Na reacts with *o*- and *p*-(NO<sub>2</sub>)<sub>2</sub>-compounds, replacing 1 NO<sub>2</sub>. The combination, 1-NO<sub>2</sub>-3-ArSO<sub>2</sub>, activates ArSO<sub>2</sub> or Cl in the 6 position, which can then be replaced by Cl, NH<sub>2</sub>, OH, or ArSO<sub>2</sub>, etc. Examples are given, in which Ar=Ph, *p*-C<sub>6</sub>H<sub>4</sub>Me, and *m*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>. The constitutions in the PhSO<sub>2</sub> series are rigidly proved; the others follow by analogy. 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·SO<sub>2</sub>Ph and PhSO<sub>2</sub>Na (I) in hot aq. dioxan or (CH<sub>2</sub>OH)<sub>2</sub> yield 1-nitro-2:5-diphenylsulphonylbenzene (II), m.p. 157—158°, which with hot piperidine gives 3-nitro-4-piperidinodiphenylsulphone, m.p. 133°, and with NaOH-EtOH gives 3-nitro-4-ethoxy-, m.p. 147°, and -hydroxy-diphenylsulphone, m.p. 137°. 1-Nitro-2:5-di-*p*-tolylsulphonylbenzene (III) (similarly prepared), m.p. 220—221°, gives similarly 3-nitro-4-piperidino-, forms, m.p. 96—97° and (stable) 107—108°, respectively, -hydroxy-, m.p. 157—158°, and -ethoxy-4'-methylidiphenylsulphone, m.p. 143—144°. The appropriate chloronitro- or (NO<sub>2</sub>)<sub>2</sub>-compounds with (I) or *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>Na in hot (CH<sub>2</sub>OH)<sub>2</sub> yield *o*-, m.p. 147°, and *p*-nitro-, m.p. 143°, and 2-, m.p. 156°, and 4-nitro-4'-methylidiphenylsulphone, m.p. 170°. Reduction by SnCl<sub>2</sub>-HCl-EtOH affords 2-, m.p. 120—121°, and 4-amino-4'-methylidiphenylsulphone (IV), m.p. 181°. *p*-Sulphonamidodiphenylsulphone (prep. in C<sub>2</sub>H<sub>5</sub>N), m.p. 190°, and hot HNO<sub>3</sub>-AcOH yield the 3-NO<sub>2</sub>-derivative, m.p. 171°, hydrolysed by warm conc. H<sub>2</sub>SO<sub>4</sub> to 3-nitro-4-aminodiphenylsulphone (V), m.p. 169—170°, which is also obtained from (II) and conc. aq. NH<sub>3</sub> at 130°. (IV) gives similarly its *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>

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derivative, m.p. 213—214°, which with hot HNO<sub>3</sub>-AcOH affords 3:5-dinitro-, m.p. 221°, and 3-nitro-4-*p*-toluenesulphonamido-4'-methylidiphenylsulphone, m.p. 129—130°, hydrolysed to 3:5-dinitro-, m.p. 216° after softening at 205°, and 3-nitro-4-amino-4'-methylidiphenylsulphone (VI), m.p. 184° [also obtained from (III) and NH<sub>3</sub>]. 4-Chloro-3-nitrobenzenesulphonyl chloride (modified prep.), m.p. 61—62° (lit. 40° and 60°), with AlCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> gives 4-chloro-3-nitrodiphenylsulphone, m.p. 127°, which is also obtained (diazo-reaction) from (V) and gives the same piperidino-, OH-, and NH<sub>2</sub>-derivatives as does (II). 4-Chloro-3-nitro-4'-methyl- [obtained from (VI)], m.p. 120°, and 2-chloro-5-nitro-diphenylsulphone (obtained from 2-chloro-5-nitrobenzenesulphonyl chloride), m.p. 174°, undergo similar reactions; 5-nitro-2-piperidinodiphenylsulphone has m.p. 178°. Nitration of 4-chlorodiphenylsulphone yields, according to the conditions, the 3'-NO<sub>2</sub>-, m.p. 139—140° (also obtained from *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>Cl, AlCl<sub>3</sub>, and PhCl), or 3:3'-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 146°, which latter leads to 3:3'-dinitro-4-piperidino-, m.p. 151—152°, and -4-amino-diphenylsulphone, m.p. 238°. 4-Chloro-4'-methylidiphenylsulphone gives similarly 4-chloro-3'-nitro-, m.p. 103°, and -3:3'-dinitro-, m.p. 152°, and 3:3'-dinitro-4-piperidino-, m.p. 149—150°, and -4-amino-4'-methylidiphenylsulphone, m.p. 231°. The requisite chloronitro-compound and Na arylsulphinate in aq. EtOH or dioxan yield (II), (III), 1-nitro-5-phenylsulphonyl-2-*p*-tolyl-, m.p. 180°, 1-nitro-2-phenylsulphonyl-5-*p*-tolyl-, m.p. 212°, 1-nitro-2-phenylsulphonyl-5-*m*-nitrophenyl-, m.p. 233°, and 1-nitro-5-*m*-nitrophenylsulphonyl-2-*p*-tolyl-sulphonylbenzene, m.p. 232°.

R. S. C.

**Naphthalene series. V. 8-Chloro-1-nitronaphthalene and 8-chloro- $\alpha$ -naphthol.** N. N. VOROSCHCOV and V. V. KOSLOV (Ber., 1936, 69, [B], 412—415).—Treatment of 1:8-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>3</sub>Na with HCl (*d* 1.19) and NaClO<sub>3</sub>-H<sub>2</sub>O in C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> at 96—98° and distillation of the product with steam affords the two forms of 8:1-C<sub>10</sub>H<sub>6</sub>Cl·NO<sub>2</sub>, m.p. 94—95° (I) and 125°, respectively, and some 8:1-C<sub>10</sub>H<sub>6</sub>Cl·OH, m.p. 67°, formed by hydrolysis. Chlorination of 1-C<sub>10</sub>H<sub>7</sub>·NO<sub>2</sub> in presence of FeCl<sub>3</sub> at 60—70° affords (I), 5:1-C<sub>10</sub>H<sub>6</sub>Cl·NO<sub>2</sub>, C<sub>10</sub>H<sub>7</sub>Cl, and 1:4:5-C<sub>10</sub>H<sub>5</sub>Cl<sub>3</sub>.

H. W.

**Preparation of halogenomethyl derivatives of naphthalene hydrocarbons. Synthesis of 1:2- and 1:4-dimethylnaphthalenes.** G. DARZENS and A. LÉVY (Compt. rend., 1936, 202, 73—75).—C<sub>10</sub>H<sub>8</sub> with a solution of trioxymethylene in AcOH-HCl at 60° gives 95% (on C<sub>10</sub>H<sub>8</sub> used) of 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>Cl, b.p. 148—150°/13 mm., m.p. 32°; the use of HBr leads to 1-C<sub>10</sub>H<sub>7</sub>·CH<sub>2</sub>Br, m.p. 56°. 1-C<sub>10</sub>H<sub>7</sub>·Me similarly gives 1:4-C<sub>10</sub>H<sub>6</sub>Me·CH<sub>2</sub>Cl, b.p. 124—125°/2 mm., m.p. 62° (picrate, m.p. 73—74°), oxidised (alkaline KMnO<sub>4</sub>) to 1:4-C<sub>10</sub>H<sub>6</sub>(CO<sub>2</sub>H)<sub>2</sub> and reduced (Al, EtOH-HCl) to 1:4-C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub>. 2-C<sub>10</sub>H<sub>7</sub>·Me affords 2:1-C<sub>10</sub>H<sub>6</sub>Me·CH<sub>2</sub>Cl, b.p. 125—126°/2 mm., m.p. 65° (picrate, m.p. 99°), similarly reduced to 1:2-C<sub>10</sub>H<sub>6</sub>Me<sub>2</sub>, b.p. 265°/770 mm., m.p. —3.5° (picrate, m.p. 130°). Small amounts of liquid products are also formed from the C<sub>10</sub>H<sub>7</sub>Me. H. B.



### Photochemical formation of organic diradicals III.—See this vol., 437.

**Dissociable anthracene oxides: effect of meso-tolyl groups.** A. WILLEMART (Compt. rend., 1936, 202, 140—141).—Reduction of the appropriate 9:10-dihydroxy-9:10-diaryldihydroanthracene with KI-AcOH affords 9:10-di-o-, m.p. 350°, di-m-, m.p. 221—222° (block) and di-p-tolylanthracene (Ingold *et al.*, A., 1927, 141), all giving dissociable oxides (evolve O<sub>2</sub> at 180—200°) when illuminated (sunlight) in solution in presence of air. The o-substituent is least effective in promoting reversible oxidation.

J. W. B.

**Dissociable organic oxides. Naphthacene formula of the rubenes.** Synthesis of 5:6:11:12-tetraphenyl-naphthacene; its identity with tetraphenylrubene (old rubrene). C. DUFRASSE and L. VELLUZ (Compt. rend., 1935, 201, 1394—1396).—6:11-Dihydroxynaphthacene-5:12-quinone and



MgPhBr give 5:12-diphenyl-naphthacene-6:11-quinone, m.p. 284°; with more MgPhBr this yields 6:11-dihydroxy-5:6:11:12-tetraphenyl-naphthacene, converted by loss of H<sub>2</sub>O into dehydro-rubrene (I) and by reduction into 5:6:11:12-tetraphenyl-naphthacene, identical with rubrene. Bis-2:2'-(1-hydroxy-3-ketoindenyl) gives substances not belonging to

the rubene series (cf. A., 1935, 1492). The formation of dissociable rubene oxides is due to the 5-, 6-, 11-, and 12-C (cf. CPh<sub>3</sub> and mesodiallylanthracenes).

R. S. C.

**m-Nitrobenzoylthiocarbimide as a reagent for the identification of amines.** W. L. TUNG, CHENG HENG KAO, CHUNG HSI KAO, and P. P. T. SAH (Sci. Rep. Tsing Hua Univ., 1935, 3, [4], 285—289).—m-Nitrobenzoylthiocarbimide, m.p. 94—95°, is obtained by heating NH<sub>4</sub>NCS in COMe<sub>2</sub> with m-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-COCl (I) in C<sub>6</sub>H<sub>6</sub>. For use as a reagent its isolation is unnecessary and the m-nitrobenzoylthiocarbamates of the following amines are prepared by slow addition of their solution in warm COMe<sub>2</sub> to a hot mixture of NH<sub>4</sub>NCS and (I) in COMe<sub>2</sub> and treatment of the product with cold H<sub>2</sub>O:NH<sub>2</sub>Ph, m.p. 153—154°; o-, m.p. 184—185°, m-, m.p. 194—195°, and p-, m.p. 178—179°, -NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>: α-, m.p. 180—181°, and β-, m.p. 194—195°, -C<sub>10</sub>H<sub>7</sub>-NH<sub>2</sub>: o-, m.p. 184—185°, m-, m.p. 126—127°, and p-, m.p. 158—159°, -C<sub>6</sub>H<sub>4</sub>Me-NH<sub>2</sub>: NHPh<sub>2</sub>, m.p. 150° (decomp.); p-C<sub>6</sub>H<sub>4</sub>Cl-NH<sub>2</sub>, m.p. 160—161°; p-C<sub>6</sub>H<sub>4</sub>Br-NH<sub>2</sub>, m.p. 175—176°; m-nitro-, m.p. 174—175°, and m-bromo-, m.p. 182—183°, p-toluidine; o-, m.p. 205° (decomp.), and p-, m.p. 221—222°, -NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H: NHPhMe, m.p. 135—136°.

H. W.

**Peroxidase action. I. Oxidation of aniline.** P. J. G. MANN and B. C. SAUNDERS (Proc. Roy. Soc., 1935, B, 119, 47—60).—NH<sub>2</sub>Ph (2% solution in dil. AcOH) is readily oxidised by the peroxidase (I) from horse-radish or turnips in presence of H<sub>2</sub>O<sub>2</sub> (concn. maintained at 10—20 mg.-%) at p<sub>H</sub> 4.5 and room temp.; benzoquinone-1-anil-4-p-aminoanilinoanil (II)

is considered to be an intermediate (causing a transient bluish-violet colour), whilst the substances isolated (by fractional extraction of the brown reaction product with various solvents) are 2:5-dianilinobenzoquinone-1-imine-4-anil (III) (Ac derivative, m.p. 212°), probably induline 3B (IV) (and a little induline 6B), ψ-mauveine (V), and ungreenable aniline-black (VI) [modified structure suggested (cf. Green and Wolff, A., 1913, i, 302)]. p-Benzoquinone and azobenzene are not isolated. The following reactions are considered to occur: (a) NH<sub>2</sub>Ph → NHPh-OH → p-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NHPh → NH-C<sub>6</sub>H<sub>4</sub>-NHPh → (II); (b) the conversion of (II) through emeraldine (VII) and nigraniline into (VI); (c) conversion of NH-C<sub>6</sub>H<sub>4</sub>-NHPh into (III) and thence through the dianil and a phenazine into (IV); (d) oxidative condensation of NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-N-C<sub>6</sub>H<sub>4</sub>-NHPh and NH<sub>2</sub>Ph to give (V). Schemes (a) and (b) are supported by the observed formation of (VII) from p-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NHPh and (I) (as above); (II) is again an intermediate. (VII) is also formed directly from NHPh-OH and (I), presumably by condensation of 8 mols. and subsequent oxidation. Oxidation (Fenton's reagent) of NH<sub>2</sub>Ph in dil. AcOH gives azobenzene and 2-amino-5-anilino- (VIII) and 2:5-dianilino-benzoquinone-1-anil, m.p. 202° [also formed from (VIII) and NH<sub>2</sub>Ph in AcOH].

H. B.

**Orthanilic acid (aniline-o-sulphonic acid).** E. WERTHEIM (Org. Syntheses, 1935, 15, 55—58).—o-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>Cl, prepared from (o-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-S<sub>2</sub>)<sub>2</sub>, HNO<sub>3</sub>, and Cl<sub>2</sub>, is hydrolysed and the sulphonic acid reduced with Fe in AcOH.

CH. ABS. (f)

**2:4-Dinitroaniline.** F. B. WELLS and C. F. B. ALLEN (Org. Syntheses, 1935, 15, 22—23).—1:2:4-C<sub>6</sub>H<sub>3</sub>Cl(NO<sub>2</sub>)<sub>2</sub> and AcO<sub>2</sub>NH<sub>4</sub> yield 2:4-(NO<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-NH<sub>2</sub>. The method cannot be applied to C<sub>6</sub>H<sub>4</sub>Cl-NO<sub>2</sub>.

CH. ABS. (r)

**Complex salts of α-phenylethylamine. Equivalence of the four co-valencies of bivalent platinum and palladium.** H. REIHLEN and E. FLOHR (Ber., 1936, 69, [B], 325—330).—Werner's hypothesis of the equivalence of covalencies is applicable without exception to hexacovalent compounds, and to quadricovalent substances with the exception of certain Pt and Pd compounds of which so many isomerides are known that their existence as stereoisomerides requires special *ad hoc* suppositions. Jørgenson's proof of the equivalence of the linkings in tetramminoplatinous dihalides is regarded as unconvincing. It is sought to obtain more suitable conditions by the use of chemically similar but readily differentiated amines [(+) and (-)-CHPhMe-NH<sub>2</sub>], which, with Pd, afford sufficiently labile derivatives. The replacement of amine linked to Pd by amine in solution, however, takes place so readily that the results throw no light on the problem. K<sub>2</sub>PtCl<sub>4</sub> and (+)-CHPhMe-NH<sub>2</sub> in H<sub>2</sub>O at 15—20° afford tetra-(+)-α-phenylethylaminoplatinous dichloride, [α]<sub>D</sub><sup>20</sup> +62.5° in 50% EtOH. Tetra-(+)-α-phenylethylaminopalladium dichloride, [α]<sub>D</sub><sup>20</sup> +69.0° in abs. EtOH, from PdCl<sub>2</sub> and amine in abs. EtOH at > 45°, and the corresponding 1-compound, [α]<sub>D</sub><sup>20</sup> -72° in H<sub>2</sub>O, -69.2° in abs. EtOH, are transformed by HCl at 60° into the trans-compounds



[Pd(CHPhMe·NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>], [ $\alpha$ ]<sub>D</sub> -65.5° (I) and +65.8° (II) in abs. EtOH, respectively. (I) and *r*-CHPhMe·NH<sub>2</sub> (2 mols.) in abs. EtOH at 35° afford *trans-di(-)di(r)-phenylethylaminopalladium dichloride*, [ $\alpha$ ]<sub>D</sub> -33° in abs. EtOH. Similarly (I) with (+)-CHPhMe·NH<sub>2</sub> (2 mols.) or (II) with (-)-CHPhMe·NH<sub>2</sub> (2 mols.) yields the optically inactive *tetra-r- $\alpha$ -phenylethylaminopalladium dichloride*. (II) and (-)-CHPhMe·NH<sub>2</sub> (6 mols.) afford *tri(-)-mono(+)- $\alpha$ -phenylethylaminopalladium dichloride*, [ $\alpha$ ]<sub>D</sub> -36° in abs. EtOH. H. W.

**Naphthalene series. VI. Transformation of diazotised 8-nitro- $\alpha$ -naphthylamine.** N. N. VOROSCHCOV and V. V. KOSLOV (Ber., 1936, 69, [B], 416—419).—1:8-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SO<sub>2</sub>H (I), m.p. 151—152° (Cu and Na salts), is readily obtained by adding a solution of diazotised 1:8-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> to H<sub>2</sub>SO<sub>3</sub> in presence of Cu powder. The nearly neutral diazo-solution and Na<sub>2</sub>S+S afford 1:1'-*di-nitrodinaphthyl 8:8'-disulphide* (II), m.p. 212—214°. Attempts to prepare 1:8-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·SH were unsuccessful. Mild reduction of (II) leads to the amino-mercaptan or naphthasultam (III), m.p. 174.5°. Reduction of (I) with glucose in EtOH also gives (III). 8-Nitro- $\alpha$ -naphthol, m.p. 212° (decomp.) (Ba and Pb salts), does not couple with diazo-compounds, but apparently gives diazo-oxides. H. W.

**Amide condensations. I. Preparation of acetoacetylphenylamide.** G. V. TSCHELINCEV and E. D. OSSETROVA (Ber., 1936, 69, [B], 374—377).—NEt<sub>2</sub>Ac is unchanged by Na in Et<sub>2</sub>O, whereas NPh<sub>2</sub>Ac and Na in C<sub>6</sub>H<sub>6</sub> at 100° afford *acetoacetylphenylamide* (I), m.p. 86—87°, and NHPH<sub>2</sub> in excellent yield. (I) gives a dark violet colour with FeCl<sub>3</sub> in EtOH and is hydrolysed by 18% HCl to COMe<sub>2</sub> and NHPH<sub>2</sub>·HCl. The analogy between the reaction and ester condensation is stressed. H. W.

**Derivatives of  $\alpha\beta$ -diphenylethane.** D. N. KUR-SANOV and A. S. KITSCHINA (J. Gen. Chem. Russ., 1935, 5, 1342—1347).—1-Benzamido-2- $\beta$ -chloroethylbenzene and C<sub>6</sub>H<sub>6</sub> in presence of AlCl<sub>3</sub> yield 2-benzamido- $\alpha\beta$ -diphenylethane, m.p. 157—158.8°, from which the amine, b.p. 138—143°/2 mm. (*hydrochloride*, decomp. at 171°), is obtained by hydrolysis with 10% KOH at 155—160° (5—6 hr.). 4-Nitro- $\alpha\beta$ -diphenylethane is obtained from [CH<sub>2</sub>Ph]<sub>2</sub> and BzNO<sub>2</sub> (3 hr. at room temp.). R. T.

**Aromatic lactams. (MLLE.)** G. GLOTZ (Bull. Soc. chim., 1936, [v], 3, 511—515).—The intensity of the ultra-violet absorption of *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>CO, and *ox-o-phenyleneamide*, sublimes at 330°, increases in the order quoted; one CO has a feeble bathochromic effect. The curve for *o*-C<sub>6</sub>H<sub>4</sub>(NHAc)<sub>2</sub> shows a slight inflexion at about 2650 Å.; *malon-o-phenyleneamide*, darkens at 328°, shows a max. at about 2900 Å., whilst *succin-o-phenyleneamide*, m.p. 232°, exhibits max. at 2800 and 2400 Å. and min. at 2600 and 2200 Å. The amides are prepared by Meyer's method (A., 1906, i, 765). H. B.

**Ortho- and meta-tellurates of benzidine.** M. PATRY (Compt. rend., 1936, 202, 64—66).—The compound Te(OH)<sub>6</sub>(C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>)<sub>2</sub> was prepared by

adding an EtOH solution of benzidine (> 30% EtOH) to aq. orthotelluric acid. The compound H<sub>2</sub>TeO<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>)<sub>2</sub> was prepared similarly, using an aq. or EtOH solution of polymetatelluric acid. Excess of base must be used in each case. Solubility data are given. H. J. E.

**Preparation of methyl-substituted azo- and azoxy-benzenes and rearrangement of the azoxy-benzenes.** T. PARSONS, jun., and J. C. BAILAR, jun. (J. Amer. Chem. Soc., 1936, 58, 268—271).—3-Methoxy- and 2- and 3-methyl-azobenzenes are prepared from PhNO and C<sub>6</sub>H<sub>4</sub>R·NH<sub>2</sub> in EtOH-AcOH. 4-Methyl- and 2:2', 3:3', and 4:2'-dimethyl-diazoaminobenzenes (the positions in the ring attached to NH are indicated, e.g., 2'), prepared by Mehner's method (A., 1902, i, 576), are rearranged by a modification of Goldschmidt's procedure (A., 1888, 685, 1283) to 4'-amino-4-methyl- and 2:3', -3:2', m.p. 85—86° (lit. 80°), and 4:3', m.p. 131—132° (lit. 128°), -dimethyl-azobenzene, respectively [*benzenesulphonyl* derivatives (A), m.p. 159°, 138—139°, 144°, and 152—153°, respectively], which are subsequently deaminated (diazo-method) to the methylazobenzenes. Reduction (Fe, dil. AcOH) of (A) gives the appropriate NH<sub>2</sub>Ar and *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·SO<sub>2</sub>Ph, 4:2-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·NH·SO<sub>2</sub>Ph (I), *benzenesulphon-4'-amino-3'-methylanilide*, m.p. 146° (also prepared by reduction of the 4'-NO<sub>2</sub>-derivative, m.p. 139°), and (I), respectively. The above azobenzenes are then oxidised (30% H<sub>2</sub>O<sub>2</sub> in AcOH) to the azoxybenzenes, which are rearranged by short treatment with 85% H<sub>2</sub>SO<sub>4</sub> at 88° to *p*-hydroxyazobenzenes (except when the 4 and 4' positions are substituted). 2- and 3-Methylazoxybenzenes give 4-hydroxy-2- and -3-methylazobenzene, respectively; the OH thus enters the substituted ring. 4-Methyl- and 3:3'-dimethyl-azoxybenzene afford 4-hydroxy-4'-methyl- (cf. Bigiani and Sabatelli, A., 1927, 1180) and -3:3'-dimethyl-azobenzene, respectively, whilst the 4:4'-Me<sub>2</sub> derivative gives (probably) 20% of 3-hydroxy-4:4'-dimethyl-, m.p. 210—212° (Et ether, m.p. 50°; benzyl ether, m.p. 123°; benzoate, m.p. 122—123°), and 75% of 4-methyl-4'-hydroxymethyl-azobenzene, m.p. 208—210° (decomp.) (benzoate, m.p. 121—122°), both of which are reduced (Fe, AcOH) to *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>. 2-Ethoxy-4:4'-dimethylazobenzene, m.p. 76°, is prepared from 4-amino-3-ethoxytoluene and *p*-C<sub>6</sub>H<sub>4</sub>Me·NO. H. B.

**Expulsion of the arylazo-group in *o*-amino-naphthaleneazo-derivatives.** G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1935, 65, 1250—1253).—4:2-C<sub>10</sub>H<sub>6</sub>Br·NH<sub>2</sub> (I) with PhN<sub>2</sub>Cl dissolved in isomyl alcohol forms 4-bromo-1-benzeneazo- $\beta$ -naphthylamine, m.p. 154°, which is degraded by *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O to 4-bromo-2-phthalimidonaphthalene, m.p. 125° [also obtained from (I)], and thus does not share the unusual stability of its isomeride, 4-bromo-2-benzeneazo- $\alpha$ -naphthylamine (A., 1935, 1490). E. W. W.

**Action of aliphatic carbimides on hydrazine derivatives.** C. C. P. FACILLY (Rec. trav. chim., 1936, 55, 101—121).—NR<sub>2</sub>:C=O with NR'R''·NH<sub>2</sub> in inert solvents yields NR'R''·NH·CO·NHR. The following new *semicarbazides* were prepared and the



regularities between their m.p. noted: 1-phenyl-4-n-propyl-, m.p. 135°, -4-isopropyl-, m.p. 147°; 1-o-tolyl-4-methyl-, m.p. 143°, -4-ethyl-, m.p. 130°; -4-n-propyl-, m.p. 113°, -4-isopropyl-, m.p. 110°; 1-m-tolyl-4-methyl-, m.p. 145°, -4-ethyl-, m.p. 127°; -4-n-propyl-, m.p. 104°, -4-isopropyl-, m.p. 126°; 1-p-tolyl-4-methyl-, decomp. 192°, -4-ethyl-, m.p. 174°, -4-n-propyl-, m.p. 123°, -4-isopropyl-, m.p. 161°; 1-p-bromophenyl-4-methyl-, m.p. 191°, -4-ethyl-, m.p. 162°, -4-n-propyl-, m.p. 144°, -4-isopropyl-, decomp. 179°; 1-o-nitrophenyl-4-methyl-, decomp. 224°, -4-ethyl-, decomp. 182°, -4-n-propyl-, decomp. 176°, -4-isopropyl-, decomp. 190°; 1-m-nitrophenyl-4-methyl-, decomp. 186°, -4-ethyl-, decomp. 199°, -4-n-propyl-, decomp. 127°, -4-isopropyl-, decomp. 166°; 1-p-nitrophenyl-4-methyl-, decomp. 224°, -4-ethyl-, decomp. 231°, -4-n-propyl-, decomp. 198°, -4-isopropyl-, decomp. 226°; 1-(5-chloro-2-nitro)-phenyl-4-methyl-, decomp. 240°, -4-ethyl-, decomp. 215°, -4-n-propyl-, decomp. 200°, -4-isopropyl-, decomp. 215°; 1-(5-bromo-2-nitro)phenyl-4-methyl-, decomp. 247°, -4-ethyl-, decomp. 223°, -4-n-propyl-, decomp. 212°, -4-isopropyl-, decomp. 234°; 1-(2:4-dinitro)phenyl-4-methyl-, decomp. 222°, -4-ethyl-, decomp. 218°, -4-n-propyl-, decomp. 187°, -4-isopropyl-, decomp. 206°; 1-benzoyl-4-methyl-, m.p. 181°, -4-ethyl-, m.p. 175°, -4-n-propyl-, m.p. 172°, -4-isopropyl-, m.p. 198°; 1-β-naphthyl-4-methyl-, decomp. 192°, -4-ethyl-, m.p. 136°, -4-n-propyl-, m.p. 133°, -4-isopropyl-, decomp. 185°; 1-phenyl-1:4-dimethyl-, m.p. 183°, -1-methyl-4-ethyl-, m.p. 97°, -1-methyl-4-n-propyl-, m.p. 63°, -1-methyl-4-isopropyl-, m.p. 124°; 1-phenyl-1-benzyl-4-methyl-, m.p. 161°, -4-ethyl-, m.p. 107°, -4-n-propyl-, m.p. 65°, -4-isopropyl-, m.p. 97°; 1-p-nitrophenyl-1:4-dimethyl-, decomp. 224°, -1-methyl-4-ethyl-, decomp. 229°, -1-methyl-4-n-propyl-, decomp. 187°; 1:4-diphenyl-4-methyl-, m.p. 192°, -4-ethyl-, m.p. 188°, -4-n-propyl-, m.p. 145°, -4-isopropyl-, m.p. 193°.

F. R. G.

**Action of aliphatic secondary bases on halogen derivatives of amines.** C. VASSILLADES (Bull. Soc. chim., 1936, [v], 3, 160—163).— $\text{NHEt}_2$  (2 mols.) and the appropriate *N*-chloro-amide or -imide (1 mol.) in dry  $\text{COMe}_2$  give benz-, m.p. 112—113°, *phthal*-, cryst., hygroscopic, and *succin*-*as*-diethylhydrazide, m.p. 105—106°, *acet*-, m.p. 168—169°, and *benz*-*as*-phenyl-diethylhydrazide, m.p. 152—153°, and *acet*-*as*-*p*-tolyl-diethylhydrazide, m.p. 140—145°.  $\text{NHAcBr}$ , however, brominates  $\text{NHEt}_2$ ;  $\text{NEt}_2\text{Cl}$  gives  $\text{NHEt}_2\text{HCl}$  and  $\text{NEt}:\text{CHMe}$ , which with  $\text{H}_2\text{O}$  affords probably  $\text{NH}_2\text{Et}$  and  $\text{MeCHO}$ .

R. S. C.

**Influence of nuclear substitution on [the formation and oxidation of] *as*-arylbenzylhydrazines.** M. BUSCH and K. LANG (J. pr. Chem., 1936, [ii], 144, 291—312).—*as*-Arylarylmethylhydrazines,  $\text{NH}_2\text{NAr}\cdot\text{CH}_2\text{Ar}'$  (I), are obtained from  $\text{NH}_2\text{NAr}$  and  $\text{CH}_2\text{Ar}'\text{Cl}$  (usually in  $\text{EtOH}$  at 100—125°), except when Ar is *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot$  or, occasionally, *o*- $\text{C}_6\text{H}_4\text{Me}$  and *o*- $\text{C}_6\text{H}_4\text{Br}$  (especially if Ar' is  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot$ ); in these cases  $\text{NHAr}\cdot\text{N}:\text{CHAR}'$  (II) are formed. Whether (II) result by rearrangement and oxidation of (I) or by dehydrogenation of  $\text{NHAr}\cdot\text{NH}\cdot\text{CH}_2\text{Ar}'$  is not clear. An *o*-substituent in Ar' renders reaction more difficult. Oxidation ( $\text{HgO}$  in  $\text{CHCl}_3$  at 0°) of (I)

usually results, especially when Ar is substituted, in the production of (II); in some cases, (II) and the tetrazene,  $(\text{N}:\text{NAr}\cdot\text{CH}_2\text{Ar}')_2$  (III), are produced. It is doubtful if (II) are formed by way of (III) (cf. Flaschner, A., 1905, i, 936). The following (II) are formed directly: *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CHPh}$  (80% yield in xylene at 135°; a little *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$  also produced); *o*-, m.p. 174° (65% yield), *m*-, m.p. 169°, and *p*-, m.p. 163°, -nitrobenzaldehyde-*o*-tolyl-hydrazones; *o*-nitrobenzaldehyde-*o*-bromophenylhydrazones, m.p. 158°; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{p}$ ; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{o}$  (in xylene at 140°). The following (I) are prepared: *as*-*o*-, *m*-, and *p*-tolylbenzylhydrazines (hydrochlorides, m.p. 176°, 166°, and 161°, respectively; *CHPh*: derivatives, m.p. 93°, 145°, and 138°, respectively, oxidised to  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$ ; *as*-*o*-chlorophenylbenzylhydrazine, m.p. 67° [hydrochloride, m.p. 219° (decomp.)]; *CHPh*: derivative, m.p. 95°, oxidised to *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$  and a little *di*-*o*-chlorophenyl-dibenzyltetrazene, m.p. 137°; *as*-phenyl-*o*-nitrobenzylhydrazine (*CHPh*:), m.p. 138°, and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : m.p. 147°, derivatives, oxidised at 0° to diphenyldi-*o*-nitrobenzyltetrazene (66%) (Flaschner, loc. cit.) and *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}:\text{NHPh}$  (34%) (at 25° and 55°, the % are 37, 63 and 0, 100, respectively); *as*-phenyl-*m*-nitrobenzylhydrazine (hydrochloride, decomp. 185—187°; *CHPh*:, m.p. 145°, and *o*-, m.p. 125°, *m*-, m.p. 132°, and *p*-, m.p. 189°, - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivatives), accompanied by a little *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}:\text{NHPh}$ ; *as*-phenyl-*p*-nitrobenzylhydrazine [*CHPh*:, m.p. 96°, *o*-, m.p. 111°, and *m*-, m.p. 150°, - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : m.p. 141° (lit. 132°), derivatives], oxidised to diphenyldi-*p*-nitrobenzyltetrazene (60%), red (stable) and yellow forms, both m.p. 163—164° (decomp.), and a little *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}:\text{NHPh}$ ; *as*-phenyl-*o*-chlorobenzylhydrazine [hydrochloride, m.p. 208° (decomp.)]; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivative, m.p. 122°, accompanied by a little *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{N}:\text{NHPh}$ ; *as*-*m*-tolyl-*o*- [hydrochloride, m.p. 195—197° (decomp.)]; *o*-, m.p. 136°, and *p*-, m.p. 174°, - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivatives], *m*- [hydrochloride, m.p. 188—190° (decomp.)], and *p*- [hydrochloride, decomp. 213—215°] -nitrobenzylhydrazines, oxidised to *o*-, m.p. 125°, *m*-, m.p. 124°, and *p*-, m.p. 113°, -nitrobenzaldehyde-*m*-tolyl-hydrazones, respectively; *as*-*p*-tolyl-*o*-, m.p. 96°, *m*- [hydrochloride, m.p. 180—182° (decomp.)], and *p*-, m.p. 77°, -nitrobenzylhydrazines (the last is accompanied by a little *p*-nitrobenzaldehyde-*p*-tolylhydrazones, m.p. 160°); *as*-*o*- [hydrochloride, m.p. 199—201° (decomp.)], *m*- [hydrochloride, m.p. 156—158° (decomp.)]; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivative, m.p. 129°, and *p*- [hydrochloride, m.p. 183° (decomp.)]; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivative, m.p. 168°] -tolyl-*o*-chlorobenzylhydrazines, all of which are oxidised to oily products; *as*-*o*-chlorophenyl-*o*-, m.p. 59° (hydrochloride, decomp. 160°; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivative, m.p. 176°, and *p*-, m.p. 89° [hydrochloride, m.p. 198° (decomp.)]; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}$ : derivative, m.p. 186°] -nitrobenzylhydrazines, oxidised to *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ; *as*-*o*-chlorophenyl-*o*-chlorobenzylhydrazine (hydrochloride, m.p. 166°; *CHPh*: derivative, m.p. 82°), oxidised to *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{o}$ .

H. B.



**Influence of degree of acidity on the velocity of the diazotisation reaction.** H. A. J. SCHOUTSEN (J. Amer. Chem. Soc., 1936, 58, 259—262; cf. A., 1921, ii, 34).—The velocity of diazotisation of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ ,  $o$ -,  $m$ -, and  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ , and  $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in presence of varying amounts of HCl is not inversely  $\propto$  the excess of HCl; reaction does not, therefore, occur between free  $\text{NH}_2\text{Ar}$  and  $\text{HNO}_2$ . The results with small concns. of HCl show that reaction takes place between  $[\text{NH}_3\text{Ar}]\text{Cl}$  and  $\text{HNO}_2$ . The velocity coeffs. (which do not agree with calc. vals.) increase with rise in concn. of HCl owing to decreased hydrolysis of the salt and a sp. action (being investigated further). H. B.

**Chemistry of diazoamino-compounds.** J. C. EARL (Chem. and Ind., 1936, 192—193).—A brief review.

**Mesohydry.** V. Acyltriazenes; particularly marked instance of mesohydric isomerism. G. ODDO and A. ALGERINO (Ber., 1936, 69, [B], 279—282; cf. A., 1932, 44).—Gradual addition of diazotised  $\text{NH}_2\text{Ph}$  to  $\text{NH}_2\text{Ac}$  in  $\text{H}_2\text{O}$  at  $0^\circ$  gives colourless *acetylphenyltriazene* (I), m.p.  $101\text{--}102^\circ$ , the  $A_g$  salt of which is not affected by  $\text{PhBr}$  or  $\text{MeI}$  in  $\text{MeOH}$ . When exposed to light (I) is rapidly transformed into a red *isomeride* (II), m.p.  $96^\circ$ , re-converted into (I) by dissolution in  $\text{NaOH}$  and pptn. with  $\text{HCl}$ . The absence of colour in (I) cannot be explained by any of the usual formulæ, and the mesohydric constitutions  $\text{AcN}\text{---}\text{N}\text{---}\text{NPh}$  and  $\text{O}\text{---}\text{N}\text{---}\text{NPh}$  are therefore assigned to (I) and (II), respectively. Similar but very unstable compounds appear to be derived from  $\text{HCO}\cdot\text{NH}_2$  and  $\text{PhN}_2\text{Cl}$ . H. W.

***p*-Iodophenol.** F. B. DAINS and F. EBERLY (Org. Syntheses, 1935, 15, 39—40).— $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  is diazotised and treated with  $\text{KI}$  and  $\text{Cu}$ .

CH. ABS. (r)

**2:6-Dibromo-4-nitrophenol.** W. W. HARTMAN and J. B. DICKEY (Org. Syntheses, 1935, 15, 6—7).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  is brominated in  $\text{AcOH}$ .

CH. ABS. (r)

**Photochemical decomposition of nitrated phenols.**—See this vol., 300.

**[Metal]complex chemical behaviour of *o*-aminophenol.** W. HIEBER and A. SCHNACKIG (Z. anorg. Chem., 1936, 226, 209—221).—The following compounds have been prepared with exclusion of air to prevent oxidation of *o*-aminophenol [ $\text{X}=\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ,  $\text{Y}=\text{O}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ]:  $\text{CoX}_2$ ,  $\text{NiX}_2$ ,  $\text{NiCl}_2\cdot\text{Y}_2$ ,  $\text{CuX}_2$ ,  $\text{ZnX}_2$ ,  $\text{CdCl}_2\cdot\text{Y}_2$ ,  $\text{CdBr}_2\cdot\text{Y}_2$ ,  $\text{CdI}_2\cdot\text{Y}_2$ ,  $\text{CdClX}$ ,  $\text{CdX}_2$ . The existence of  $\text{ZnCl}_2\cdot\text{Y}_2$  has been confirmed. Colour and stability show that the X compounds form internal complexes, metal being co-ordinated with N; the Y compounds, on the other hand, behave as additive compounds. On treatment of  $\text{ZnCl}_2\cdot\text{Y}_2$  and  $\text{CdCl}_2\cdot\text{Y}_2$  with gaseous  $\text{NH}_3$  almost the whole of Y is replaced. Direct absorption of  $\text{NH}_3$  by  $\text{NiX}_2$  also occurs. Reaction is favoured by the presence of a little moisture. Both types of compound will also take up 2 mols. of  $\text{HCl}$ , with the exception of  $\text{CdClX}$  which takes up 1 mol. Marked colour changes occur. M. S. B.

**Nitration of thymol methyl ether.** A. E. TSCHITSCHIBABIN and M. A. BESTUGEY (Bull. Soc. chim., 1936, [v], 3, 423—424).—1:4:3- $\text{C}_6\text{H}_3\text{MePr}^{\beta}\cdot\text{OMe}$  and 98%  $\text{HNO}_3$  in  $\text{Ac}_2\text{O}$  at  $-2^\circ$  to  $3^\circ$  give poor yields of 2:6-dinitro-3-methoxy-*p*-cymene (I), m.p.  $56^\circ$  (also prepared from the K salt of dinitrothymol and  $\text{KMeSO}_4$  in glycerol at  $180\text{--}200^\circ$ ), and 4:6-dinitro-*m*-cresol Me ether (by replacement of  $\text{Pr}^{\beta}$ ). The odour of (I) is less pleasant than that of “*musc-ambrette*.” H. B.

**[Application of the Friedel-Crafts reaction to methoxydiphenyl ether.]** O. VON SCHICKH (Ber., 1936, 69, [B], 242—244).—Gradual addition of  $\text{AcCl}$  and  $\text{Ph}_2\text{O}$  to sublimed  $\text{AlCl}_3$  gives 4:4'-dichloroacetyldiphenyl ether (I), m.p.  $102^\circ$ , in 43% yield; its constitution is established by its oxidation by  $\text{KMnO}_4$  to 4:4'-dicarboxydiphenyl ether, m.p.  $>285^\circ$ . [Di-*o*-tolyl ether, b.p.  $146\text{--}147^\circ/11\text{ mm.}$ , is oxidised to the corresponding dicarboxylic acid, m.p.  $210\text{--}217^\circ$ . 3:3'-Dicarboxydiphenyl ether has m.p.  $235\text{--}240^\circ$ .] The new group does not invariably occupy the 4 position (if free). The directive influence of OMe for example may override that of the O between the Ph groups. H. W.

**Polycyclic compounds related to the sterols.**

**V. Methoxy- and hydroxy-derivatives of phenanthrene.** G. A. R. KON and F. C. J. RUZICKA (J.C.S., 1936, 187—192).— $\beta$ -4-Methoxy-1-naphthylethyl alcohol, m.p.  $87^\circ$ , obtained from 1:4- $\text{C}_{10}\text{H}_8\text{Br}\cdot\text{OMe}$  and  $(\text{CH}_2)_2\text{O}$ , with  $\text{PBr}_3$  gives the bromide (I), b.p.  $161^\circ/1.2\text{ mm.}$ , which with *Et* cyclopentanone-2-carboxylate yields *Et* 2-( $\beta$ -4-methoxy-1-naphthylethyl)cyclopentanone-2-carboxylate, b.p.  $235\text{--}248^\circ/1.2\text{ mm.}$ , hydrolysed to  $\alpha$ -( $\beta$ -4-methoxy-1-naphthylethyl)adipic acid, m.p.  $178^\circ$ . The acid is pyrolysed to 4-methoxy-1-methylnaphthalene, b.p.  $121^\circ/0.8\text{ mm.}$ , and not to the pentanone. (I) and cyclopentene oxide yield  $\beta$ -4'-methoxy-1'-naphthylethylcyclopentene, b.p.  $150\text{--}160^\circ/0.02\text{ mm.}$  [ $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  complex, m.p.  $107\text{--}108^\circ$ ], and  $\alpha\delta$ -di-(4-methoxy-1-naphthyl)-butane, m.p.  $124^\circ$ . The pentene and  $\text{P}_2\text{O}_5$  give 9-methoxy-3:4-dihydro-1:2-cyclopentanophenanthrene, b.p.  $185\text{--}186^\circ/0.8\text{ mm.}$  [ $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  complex, m.p.  $166^\circ$ ]. (I) and 2-methylcyclopentanone afford 2-methyl-1- $\beta$ -4'-methoxy-1'-naphthylethylcyclopentanol, b.p.  $185\text{--}190^\circ/0.1\text{ mm.}$ , and another substance; the carbinol is cyclised to 9-methoxy-1-methyl-3:4-dihydro-1:2-cyclopentanophenanthrene, b.p.  $165\text{--}170^\circ/0.1\text{ mm.}$ , dehydrogenated (Se) to 9-methoxy-1:2-cyclopentanophenanthrene, m.p.  $129^\circ$  [picrate, m.p.  $124^\circ$ ;  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  complex, m.p.  $132^\circ$ ], trinitrotoluene complex, m.p.  $105\text{--}106^\circ$ ]. The following are similarly obtained: 2:5-dimethyl-1- $\beta$ -4'-methoxy-1'-naphthylethylcyclopentanol, b.p.  $195\text{--}200^\circ/0.2\text{ mm.}$ , 9-methoxy-1:3'-dimethyl-3:4-dihydro-1:2-cyclopentanophenanthrene, b.p.  $180\text{--}183^\circ/0.3\text{ mm.}$  [picrate, m.p.  $119\text{--}120^\circ$ ;  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  complex, m.p.  $140\text{--}141^\circ$ ], and 9-methoxy-3'-methyl-1:2-cyclopentanophenanthrene, m.p.  $111^\circ$  (picrate, m.p.  $147^\circ$ ). 1:5- $\text{C}_{10}\text{H}_8\text{Br}\cdot\text{OMe}$  and  $(\text{CH}_2)_2\text{O}$  give  $\beta$ -5-methoxy-1-naphthylethyl alcohol, m.p.  $53\text{--}54^\circ$  [with excess of  $(\text{CH}_2)_2\text{O}$ , a product,  $\text{C}_{13}\text{H}_{10}\text{O}_5$ , m.p.  $128^\circ$ , is obtained], converted ( $\text{PBr}_3$ ) into the bromide (II), b.p.  $180^\circ/1.7\text{ mm.}$  The bromide similarly gives 2-methyl-1-( $\beta$ -5-



*methoxy-1'-naphthylethyl*cyclopentanol, b.p. 190—195°/0.1 mm., and  $\alpha$ -di-(5-methoxy-1-naphthyl)butane, m.p. 176°. The carbinol is dehydrated to 8-methoxy-1-methyl-3:4-dihydro-1:2-cyclopentanophenanthrene, b.p. 185°/0.3 mm., dehydrogenated to 8-methoxy-1:2-cyclopentenophenanthrene, m.p. 153° [picrate, m.p. 160°;  $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$  complex, m.p. 194°]. (II), Et malonate, and K give an ester, hydrolysed to  $\beta$ -5-methoxy-1-naphthylethylmalonic acid, m.p. 182° (decomp.), decarboxylated to  $\gamma$ -5-methoxy-1-naphthylbutyric acid, m.p. 143°. Cyclisation of this acid with  $\text{SOCl}_2$  affords a compound,  $\text{C}_{15}\text{H}_{14}\text{O}_2$ , m.p. 88—89°, which does not form a semicarbazone and is demethylated to a substance,  $\text{C}_{14}\text{H}_{14}\text{O}_3$ , m.p. 155°; cyclisation with  $\text{SnCl}_4$  yields 1-keto-8-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 137°, demethylated to the hydroxy-ketone, m.p. 256°. (I), Et malonate, and Na yield an ester, b.p. 210°/3—5 mm., hydrolysed to  $\beta$ -4-methoxy-1-naphthylethylmalonic acid, m.p. 180° (decomp.), decarboxylated to  $\gamma$ -4-methoxy-1-naphthylbutyric acid, m.p. 131°. The acid is cyclised ( $\text{AlCl}_3$ ) to 1-keto-9-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 98°, demethylated to the hydroxy-ketone, m.p. 260°. F. R. S.

**2-Hydroxyphenanthrene in coal tar.** O. KRUBER (Ber., 1936, 69, [B], 246—247).—The isolation of 2-hydroxyphenanthrene, m.p. 168—169°, from a coal-tar fraction, b.p. 398—404°, is described. The "acid oil" content of the fraction is low in comparison with that of fractions of somewhat lower b.p.; pitch probably contains still less phenols.

H. W.

**Diastereoisomeric naphthalene-1:5-disulphonylacetic acids. Equivalence of the 1:5-positions in naphthalene.** F. GAJOWCZYK and J. SZUSZKO (Bull. Acad. Polonaise, 1935, A, 349—359).—Oxidation of Et naphthalene-1:5-dithioglycollate (I) (Corbellini *et al.*, A., 1931, 748) with  $\text{H}_2\text{O}_2$ -AcOH at room temp. affords *Et i-naphthalene-1:5-dithionylacetate*,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{SO}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m.p. 168° (decomp.) (less sol. in  $\text{C}_6\text{H}_6$ ), hydrolysed to the free *i-acid*, m.p. 235° (decomp.) [brucine, m.p. 179° (decomp.),  $[\alpha]_D^{20} -8.9^\circ$  in  $\text{CHCl}_3$ , quinine, m.p. 204° (decomp.),  $[\alpha]_D^{20} -139^\circ$  in  $\text{EtOH}\cdot\text{CHCl}_3$ , and cinchonine, decomp. 175°,  $[\alpha]_D^{20} -96.6^\circ$  in  $\text{EtOH}\cdot\text{CHCl}_3$ , salts], and, from the mother-liquor, the  $\text{C}_6\text{H}_6$ -sol. *Et dl-naphthalene-1:5-dithionylacetate*, m.p. 153° (decomp.), hydrolysed to the *dl-acid*, m.p. 125° (decomp.). This is resolved by fractional crystallisation of its quinine salt from  $\text{COME}_2$  into (+)-, m.p. 125—126° (decomp.),  $[\alpha]_D^{20} +511^\circ$  in 1% NaOH [quinine salt, m.p. 158° (decomp.),  $[\alpha]_D^{20} +61.2^\circ$  in  $\text{EtOH}\cdot\text{CHCl}_3$ ] and from the mother-liquor, or better by fractionation of the brucine salt, (—)-*naphthalene-1:5-dithionylacetic acid*, m.p. 124—125° (decomp.),  $[\alpha]_D^{20} -495.7^\circ$  in 1% NaOH [brucine salt, m.p. 187—188° (decomp.),  $[\alpha]_D^{20} -183.8^\circ$  in  $\text{EtOH}\cdot\text{CHCl}_3$ ]. The existence of a *dl*- and *i*-form proves the equivalence of the 1:5 positions in  $\text{C}_{10}\text{H}_8$ , which must possess a centre of symmetry. Oxidation of (I) with excess of  $\text{H}_2\text{O}_2$  at 70° affords the *Et* ester, m.p. 158°, of *naphthalene-1:5-disulphonylacetic acid*, m.p. about 300° (decomp.), which is obtained by hydrolysis. J. W. B.

**Salt-forming properties of halogens. Reaction of univalent positive halogen compounds with unsaturated hydrocarbons.** M. I. USCHAKOV, V. O. TSCHISTOV, and M. A. SCHLOSBERG (J. Gen. Chem. Russ., 1935, 5, 1391—1398).—Suspensions of Ag salts of different acids in  $\text{CCl}_4$  react with I or Br as follows:  $\text{R}\cdot\text{OAg} + \text{X}_2 = \text{R}\cdot\text{OX} + \text{AgX}$ . Substances possessing the  $\cdot\text{C}\cdot\text{C}\cdot$  group react with  $\text{R}\cdot\text{OX}$  to yield compounds of the general type  $\cdot\text{CX}\cdot\text{COR}$ . The following substances have been prepared in this way: from cyclohexene: iodo-cyclohexyl benzoate, m.p. 54.5—56°; bromo-, m.p. 64—64.5°, and chloro-, b.p. 168—195°/14 mm., -cyclohexylbenzoate; iodo-, m.p. 92.3°, and bromo-, m.p. 81.5°, -cyclohexyl *m*-nitrobenzoate; bromocyclohexyl acetate, b.p. 108—111°/17 mm., propionate, b.p. 118.5°/6 mm., *n*-butyrate, b.p. 138°/8 mm., and isovalerate, b.p. 141—142°/9 mm.; chlorocyclohexyl nitrate, b.p. 108—109°/13 mm.; from  $\text{C}_2\text{H}_4$ :  $\beta$ -bromoethyl acetate, b.p. 159—164°, and nitrate, b.p. 81.5°/43 mm.; from  $\text{CHMe}\cdot\text{CH}_2$ :  $\beta$ -bromoisopropyl acetate, b.p. 161—165°/750 mm., and benzoate, b.p. 152°/15 mm.; from styrene:  $\beta$ -chloro- $\alpha$ -phenylethyl nitrate, b.p. 107°/4 mm. R. T.

**Configurative relationship of methylcyclohexylcarbinol to methylhexylcarbinol.** P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1935, 113, 55—59).—Et (—)- $\alpha$ -methoxypropionate is transformed by  $\text{Mg}_2$  pentamethylene dibromide into (+)-1-*z*-methoxyethylcyclohexanol, b.p. 99—104°/22 mm.,  $[\alpha]_D^{20} +7.65^\circ$ , which is not decomposed at about 205° and yields ill-defined products when distilled with  $\text{KHSO}_4$ . When treated with K in anhyd.  $\text{Et}_2\text{O}$  followed by  $\text{CS}_2$  and MeI and then distilled it gives (—)-1-*z*-methoxyethyl- $\Delta^1$ -cyclohexene, b.p. 168—171°,  $[\alpha]_D^{20} -12.43^\circ$  readily hydrogenated (Adams) in AcOH but not in  $\text{C}_5\text{H}_{12}$  to (+)- $\alpha$ -methoxyethylcyclohexane (I), b.p. 168—171°,  $[\alpha]_D^{20} +2.93^\circ$ . Synthetic (I) has  $[\alpha]_D^{20}$  b.p. 170—171°,  $[\alpha]_D^{20} +7.90^\circ$ . The configurative relationship of *d*-methyl-*n*-hexylcarbinol to (I) is therefore established by chemical methods (cf. A., 1932, 1027—1028). H. W.

**Reduction of the  $\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$  grouping.** A. N. MELDRUM and A. S. DATAR (Proc. Indian Acad. Sci., 1935, 2, A, 580—583).—This grouping in compounds of type  $\text{NRR}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$  (obtained by condensing amines with  $\text{CCl}_3\cdot\text{CHO}$  at room temp. or at 50°) is reduced by  $\text{Zn}\cdot\text{AcOH}$  to  $\cdot\text{CH}_2\cdot\text{CHCl}_2$ . The following are prepared. *N*-Methyl- (I), m.p. 77° (Bz derivative, m.p. 130°), *N*-ethyl- (II), m.p. 73° (Bz derivative, m.p. 75°), *NN*-dimethyl-, m.p. 76° (picrate, m.p. 138°), *NN*-diethyl- (picrate, m.p. 140°), and *N*-benzyl-*N*-methyl- (picrate, m.p. 132°) [from  $\alpha$ -*p*-benzylmethylaminophenyl- $\beta\beta\beta$ -trichloroethyl alcohol, m.p. 85° (decomp.) (hydrochloride, decomp. 150°)] -*p*-( $\beta\beta$ -dichloroethyl)aniline. The *NO*-derivative of (I), m.p. 87°, is reduced by Zn in  $\text{EtOH}\cdot\text{AcOH}$  to  $\alpha$ -methyl- $\alpha$ -*p*-( $\beta\beta$ -dichloroethyl)phenylhydrazine hydrochloride (corresponding  $\text{PhCHO}$ , m.p. 150°, and glucose-, m.p. 165°, -phenylhydrazones); the *NO*-derivative of (II), m.p. 50°, gives the similar  $\alpha$ -ethyl-compound (corresponding  $\text{PhCHO}$ -phenylhydrazone, m.p. 110°). E. W. W.

***p*-Butylsaligenin.** R. V. RICE and W. C. HARDEN (J. Amer. Pharm. Assoc., 1936, 25, 7—9).— $\text{Pr}\cdot\text{CO}_2\text{H}$



treated with  $\text{SOCl}_2$  followed successively by  $\text{PhOH}$  and  $\text{AlCl}_3$  yields on fractional distillation  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COPr}^a$ , reduced ( $\text{Zn-HCl}$ ) to  $p\text{-C}_6\text{H}_4\text{Bu}^a\cdot\text{OH}$  (*phenylurethane*, m.p.  $113^\circ$ ), which affords (Reimer-Tiemann) 5-butylsalicylaldehyde, reduced (Adams) to *p-butylsaligenin*, m.p.  $81^\circ$ . F. O. H.

**Liquid crystals of some cholesterol compounds.** P. GAUBERT (Compt. rend., 202, 141—143).—The following compounds melted with cholesterol may give liquid crystals: resorcinol, pyrocatechol, phloroglucinol, pyrogallol, *p*-nitrophenol, saligenin, erythritol, phloridzin, saccharin, isosaccharin, rhamnose, nitrophthalic acid, and agaricic acid. The products are most easily obtained with equimol. proportions of the two components. Especially if quickly cooled, they may pass to a solid form preserving their optical anisotropy but gradually increasing in hardness. The melting of such hardened products is described.

B. W. R.

**Liebermann-Burchard reaction velocities of sterols.** I. Difference between free and ester cholesterol applied to the determination of cholesteryl esters. II. Test for coprostenol in plasma. J. G. REINHOLD (Amer. J. Med. Sci., 1935, 189, 302—303, 303).—I. Cholesteryl esters (I) and coprostenol (*allocholesterol*) develop colour with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  more rapidly than does cholesterol (II). The difference is more marked at low temp. and with dil.  $\text{H}_2\text{SO}_4$ , and disappears with high temp. and much acid. The Liebermann-Burchard reaction at  $0^\circ$  in presence of 0.025 c.c. of  $\text{H}_2\text{SO}_4$  determines (I), a small correction being necessary for free (II). At  $38^\circ$  the total (II) is recorded.

II. Coprostenol is determined as (I). None occurs in plasma.

CH. ABS. (p)

**Sexual hormones. XII. Amines of the androsterone series.** L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta, 1936, 19, 107—108).—Androsteroneoxime is reduced by Na and boiling  $\text{EtOH}$  to *cis*-17-amino-3-hydroxyandrostane, m.p.  $187\text{--}188^\circ$  (hydrochloride, m.p. about  $365^\circ$  after much decomp.). Similarly *trans*- $\Delta^{5:6}$ -dehydroandrosterone gives *trans*- $\Delta^{5:6}$ -17-amino-3-hydroxyandrostene, m.p.  $160\text{--}162^\circ$  [hydrochloride, m.p. about  $300^\circ$  (decomp.)]. Physiologically these compounds are much less active than the corresponding 17-OH-derivatives.

H. W.

**Combined oestriol in human pregnancy urine.**—See this vol., 503.

**Colourless compounds which accompany carotenoids in plants.**—See this vol., 533.

**Catalytic reduction of aromatic carboxylic esters.** See this vol., 436.

**Hydrolysis of substituted benzoic esters.**—See this vol., 432.

**Preparation of calcium or ammonium salts of iodoxybenzoic acid.** F. R. GREENBAUM (Amer. J. Pharm., 1936, 108, 17—22).—Very pure Ca *o*-iodoxybenzoate, free from the corresponding I- and IO-compounds and Cl, is obtained in excellent yield by oxidising *o*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{H}$  (prep. described) in dil.  $\text{H}_2\text{SO}_4$  suspension with  $\text{KBrO}_3$  at  $85^\circ$ . The crude acid is extracted with hot  $\text{EtOH}$ , dissolved in

$\text{NH}_3$  solution, decolorised with C, and pptd. as the Ca salt with  $\text{CaCl}_2$ . S. C.

**Halogenosulphobenzoic acids.** M. POLACZEK (Rocz. Chem., 1935, 15, 578—582).—The position of the  $\text{SO}_3\text{H}$  of 2-bromo- ( $\text{Ph}_2$  ester, m.p.  $125\text{--}126^\circ$ ) and 2-chloro- (I) ( $\text{Ph}_2$  ester) -5-sulphobenzoic acid has been established by conversion into 5-sulphosalicylic acid (II) by hydrolysis with 10% aq.  $\text{K}_2\text{CO}_3$  at  $170^\circ$ , and comparison of its  $\text{Ph}_2$  ester with that from synthetically prepared (II). (II) is obtained in 93% yield from *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$  and 20% oleum ( $100^\circ$ ; 3 hr.). R. T.

**Preparation of 2-chloro-4-nitrobenzoic acid.** A. ALBERT and W. H. LINNELL (J.S.C.I., 1936, 55, 54r).—In converting 4-nitro-*o*-toluidine (I) into *o*-chloro-*p*-nitrotoluene (II) by the Sandmeyer reaction, max. yields are realised only under carefully controlled experimental conditions. The by-products are 3:3'-dinitro-6:6'-dimethylazobenzene and 3:3'-dinitro-6:6'-dimethyldiphenyl. The oxidation of (II) to 2-chloro-4-nitrobenzoic acid (III) by  $\text{K}_2\text{Cr}_2\text{O}_7$  proceeds best with 1.3 equivs. of the latter. Several unrecorded properties of (III) are given. The yields by this process are compared with those obtained by acetylating (I), oxidising with  $\text{KMnO}_4$ , and then applying the Sandmeyer reaction. The identity of the 1:2:4-nitroanthranilic acid obtained as an intermediate with the so-called "1:2:5"-nitroanthranilic acid of Ullmann is shown, and a no. of unrecorded properties are given. The reactions (I)  $\rightarrow$  (III) gave lower yields in the case of the analogous Br-compounds.

**Organic reactions with boron fluoride. XII. Preparation of esters of aromatic acids.** F. J. SOWA and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 271—272).— $\text{C}_6\text{H}_4\text{R}\cdot\text{CO}_2\text{Alk}$  are formed when  $\text{C}_6\text{H}_4\text{R}\cdot\text{CO}_2\text{H}$  and  $\text{AlkOH}$  are heated with  $\text{BF}_3$  (amount for max. yield varies with R) or  $\text{BF}_3\cdot\text{Et}_2\text{O}$ ; in general, esterification occurs less readily than with  $\text{AlkCO}_2\text{H}$  (A., 1932, 728). The following are prepared: Me, Pr<sup>*β*</sup>, Bu<sup>*α*</sup>, Bu<sup>*β*</sup>, and *sec*-Bu benzoates; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ ; *o*- and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ ; *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{Me}$ ; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ ; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Bu}^\beta$ . Bu<sup>*γ*</sup>OBz is not preparable.

H. B.

**$\gamma$ -Phenylbutyric acid.** S. C. OVERBAUGH, C. F. H. ALLEN, E. L. MARTIN, and L. F. FIESER (Org. Syntheses, 1935, 15, 64—66).— $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is reduced with Zn and HCl. CH. ABS. (r)

**Asymmetric carbon atom CHDR'R". I. Constitution of a deuterio- $\beta$ -phenylpropionic acid from cinnamic acid and deuterium.** H. ERLMEYER and H. GÄRTNER (Helv. Chim. Acta, 1936, 19, 145—148).—Treatment of  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  with nascent D causes complete replacement of H by D.  $\text{Al}_2\text{S}_3$  and  $\text{D}_2\text{O}$  gives  $\text{D}_2\text{S}$ , transformed by I in  $\text{D}_2\text{O}$  into DI which, in presence of red P, converts  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  into  $\text{C}_6\text{H}_2_{18}\text{D}_{282}\cdot\text{C}_2\text{H}_{162}\text{D}_{238}\cdot\text{CO}_2\text{H}$  (I) which passes when treated with Br and subsequently heated into  $\text{C}_6\text{H}_2_{18}\text{D}_{282}\cdot\text{C}_2\text{H}_0_{74}\text{D}_{126}\cdot\text{CO}_2\text{H}$  and is oxidised by  $\text{KMnO}_4$  to  $\text{C}_6\text{H}_2_{18}\text{D}_{282}\cdot\text{CO}_2\text{H}$ . Attempts to resolve (I) into its optical antipodes have been unsuccessful. H. W.



**Condensation of esters of unsaturated acids with carbamide.** II. Z. JERZMANOWSKA-SIENKIEWICZOWA (Rocz. Chem., 1935, 15, 510—515).—CHPh·CH·CO<sub>2</sub>Et and CO(NH<sub>2</sub>)<sub>2</sub> (I) in EtOH in presence of NaOEt yield cinnamoylcarbamide (II) or cinnamamide (III), according to the conditions of the experiment. (II) affords cinnamic acid and (III) when heated with EtOH-NaOEt or MeOH-KOH, cyanuric acid and (III) when heated alone at 210—220°, and 6-phenyldihydrouracil when fused with (I) (180—185°; 2.5 hr.). Fumaric acid and (I) (135—140°; 2.5 hr.) yield biuret, triuret, and hydantoin-5-acetic acid. R. T.

**o-Phenylpentadecic and  $\chi$ -phenylbehenic acids.** G. M. HILLS and R. ROBINSON (J.C.S., 1936, 281—283).—Condensation of Et sodio- $\nu$ -keto- $\mu$ -carboethoxymyristate and CH<sub>2</sub>Ph·CH<sub>2</sub>Cl and subsequent hydrolysis by 5% H<sub>2</sub>SO<sub>4</sub> and then by 3.5% aq. KOH leads to  $\nu$ -ketomyristic acid (46%; Et ester, b.p. 145—160°/0.5 mm., m.p. 28—29°), and  $\nu$ -keto-o-phenylpentadecic acid (20%), m.p. 76—77° [semi-carbazone, m.p. 87—88°; Et ester (crude), m.p. 33—35°], reduced (Clemmensen) to o-phenylpentadecic acid, (I), m.p. 60—61°.  $\kappa$ -Phenyldecoyl chloride, b.p. 204°/14 mm. (decomp.) (anilide, m.p. 71—72°; gives the Et ester, b.p. 199°/13 mm.), leads similarly to  $\nu$ -keto- $\chi$ -phenylbehenic acid, m.p. 81°, reduced to  $\chi$ -phenylbehenic acid (II), m.p. 81° (Et ester, m.p. 53°). (I) and (II) cannot be injected and are unchanged when fed to rabbits. R. S. C.

**Chemical constitution and local anæsthetic action of alkamine esters of  $p$ -alkoxybenzoic acids.** C. ROHMANN and B. SCHEURLE (Arch. Pharm., 1936, 274, 110—126).—

$p$ -OR·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>Cl (I) (usually prepared from OR·C<sub>6</sub>H<sub>4</sub>·COCl and CH<sub>2</sub>Cl·CH<sub>2</sub>·OH) and NHET<sub>2</sub> at 110° give  $p$ -OR·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·NET<sub>2</sub> [isolated as the hydrochlorides (II)], which are local anæsthetics. The influence of R on the activity is Me < Et < H < Pr < Bu, isoamyl; Pr<sup>a</sup> and Bu<sup>a</sup> impart more activity than Pr<sup>b</sup> and Bu<sup>b</sup>. Introduction of NET<sub>2</sub> into R causes diminished activity. Increase in length of the alkamine group and introduction of Alk in the 3 position cause increased activity. The following are described: (I) R=H, m.p. 110°, Me, Et, m.p. 46°, Bu<sup>a</sup>, m.p. 32°; (II) R=H, m.p. 183°, Me, m.p. 146°, Et, m.p. 174°, Pr<sup>a</sup>, m.p. 137°, Pr<sup>b</sup>, m.p. 128°, Bu<sup>a</sup>, m.p. 147°, Bu<sup>b</sup>, m.p. 131°, isoamyl, m.p. 128°, allyl, m.p. 130° (lit. 193°) [from  $p$ -C<sub>3</sub>H<sub>5</sub>O·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H (1 mol.), NET<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>Cl (III) (1 mol.), and EtOH-NaOEt (2 mols.)], and  $\beta$ -diethylaminoethyl, m.p. 180° [from  $p$ -OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and (III) in EtOH-NaOEt].  $\gamma$ -Diethylaminopropyl  $p$ -ethoxybenzoate hydrochloride, m.p. 148°, is prepared from  $p$ -OEt·C<sub>6</sub>H<sub>4</sub>·COCl and Cl[CH<sub>2</sub>]<sub>3</sub>·OH followed by NHET<sub>2</sub>.  $\varepsilon$ -Diethylaminoamyl anisate,  $p$ -ethoxybenzoate, and  $p$ -butoxybenzoate hydrochlorides, m.p. 131°, 82—83°, and 56°, respectively, are obtained from  $p$ -OR·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Na and (CH<sub>2</sub>)<sub>5</sub>Br<sub>2</sub> followed by NHET<sub>2</sub>. Me  $p$ -allyloxybenzoate rearranges at 220—250° into Me 4-hydroxy-3-allylbenzoate, converted by Pr<sup>a</sup>Br and KOH in COMeEt followed by hydrolysis (10% NaOH) into 4-propoxy-3-allylbenzoic acid, m.p. 138°, which with

(III) in EtOH-NaOEt gives the  $\beta$ -diethylaminoethyl ester (hydrochloride, m.p. 103°). H. B.

**Aminohydroxy-acids and their degradation in the animal body.** F. KNOOP, F. DITT, W. HECKSTEDEN, J. MAIER, W. MERZ, and R. HÄRLE (Z. physiol. Chem., 1936, 239, 30—46).— $\alpha$ -Amino- $\beta$ -hydroxy-acids (I) are not degraded in the same manner as simple NH<sub>2</sub>-acids, but are transformed by  $\beta$ -oxidation into N-free acids containing fewer C.  $\alpha$ -Amino- $\beta$ -keto-acids, presumably intermediate products of the degradation of (I), have a very high redox potential, much > that of ascorbic acid. CH<sub>2</sub>Ph·CO·CH<sub>2</sub>·CO<sub>2</sub>Et is transformed by PhN<sub>2</sub>Cl and NaOAc in EtOH-H<sub>2</sub>O into the corresponding phenylhydrazone, C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 67°, which is converted by hydrogenation (Pd-C in 5% HCl-EtOH followed by Pt-Fe in H<sub>2</sub>O) and subsequent hydrolysis into  $\alpha$ -amino- $\beta$ -hydroxy- $\gamma$ -phenylbutyric acid, decomp. 259° (Bz<sub>1</sub> derivative, decomp. 181°); (?) 2:5-dibenzyl-3:6-dihydropyrazine, m.p. 75—76°, is formed as by-product. CH<sub>2</sub>Ph·CH<sub>2</sub>·CHO and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> are condensed in C<sub>5</sub>H<sub>5</sub>N at 90° and the Na salt of the resulting acid, m.p. 103—104°, is transformed by Br into  $\alpha$ -bromo- $\beta$ -hydroxy- $\delta$ -phenyl-n-valeric acid, m.p. 94—95°. The corresponding Et ester, b.p. 157—163°/0.5 mm., is transformed by NaN<sub>3</sub> in EtOH-H<sub>2</sub>O into the azido-ester, decomp. 100°/high vac., which is hydrolysed and then reduced (PtO<sub>2</sub> in anhyd. EtOAc) to  $\alpha$ -amino- $\beta$ -hydroxy- $\delta$ -phenyl-n-valeric acid, decomp. 246° (Bz<sub>1</sub> derivative, decomp. 196°). The Bz derivative, m.p. 175—176°, and the hydantoin, m.p. 191—193°, of hydroxyglutamic acid are described.  $\alpha$ -NH<sub>2</sub> and  $\alpha$ -OH-acids react with Pb(OAc)<sub>4</sub> in AcOH at 60—70° with loss of CO<sub>2</sub> and according to the principle of Criegee's glycol fission. Introduction of acyl into NH<sub>2</sub> or OH inhibits the reaction. Criegee's assumption that the method permits diagnosis of the groups ·NH·CH·CO<sub>2</sub>H is therefore too general. After acylation, therefore, serines and isoserines can be distinguished from one another by Criegee's method. H. W.

**Iodination of nitrotyrosine.** H. BAUER and E. STRAUSS (Ber., 1936, 69, [B], 245—246; cf. A., 1935, 1122).—Slow passage of ICl vapour into a solution of  $l$ -tyrosine in dil. HCl at 10° gives 3:5-diiodotyrosine, decomp. 194°. Nitrotyrosine hydrochloride is converted similarly into 5-iodo-3-nitrotyrosine. H. W.

**Synthesis of certain alkeines derived from mandelic and tropic acids.** E. PŁĄZEK and Z. RODEWALD (Rocz. Chem., 1935, 15, 481—490).—The cyanohydrin obtained from CPhMe in Et<sub>2</sub>O, AcOH, and KCN at 0° yields when heated with HCl (130°; 3 hr.) CH<sub>2</sub>Cl·CHPh·CO<sub>2</sub>H, the Me ester, b.p. 93°/0.4 mm., of which affords Me  $\beta$ -ethoxy- $\alpha$ -phenylpropionate (O-ethyltropate) (I), b.p. 98—100°/0.3 mm., when treated with NaOEt in EtOH. The acid has b.p. 132—134°/0.1 mm. (chloride, b.p. 88—89°/0.6 mm.; dimethylaminoethyl ester, b.p. 110—112°/0.1 mm.).  $\beta$ -Propoxy- $\alpha$ -phenylpropionic acid, b.p. 135—137°/0.15 mm. (chloride, b.p. 96—97°/0.3 mm.; Me ester, b.p. 108°/0.1 mm.; dimethylaminoethyl ester, b.p. 113°/0.1 mm.), is obtained analogously. Tropyl, b.p. 169—171°/0.4



mm. (picrate, m.p. 216—217°; picrolonate, m.p. 155—156°), and dimethylaminoethyl, b.p. 108—110°/0.2 mm. (picrolonate of methiodide, m.p. 139°),  $\alpha$ -ethoxy- $\alpha$ -phenylacetate (O-ethylmandelate) have been prepared from the appropriate alcohols and ethoxy-phenylacetyl chloride, b.p. 84—85°/0.4 mm.; tropyl, b.p. 170—172°/0.4 mm. (picrate, m.p. 106°; picrolonate, m.p. 164°), and dimethylaminoethyl, b.p. 110—112°/0.2 mm. (picrate of methiodide, m.p. 162°), O-propylmandelate were obtained similarly from propoxyphenylacetyl chloride, b.p. 85—86°/0.8 mm.

R. T.

Manufacture of arylamides of 2-hydroxydiphenyl-3-carboxylic acid and of azo-dyes therefrom.—See B., 1936, 229.

**Abnormal strength of 2:6-dihydroxybenzoic acids.** W. BAKER (Nature, 1936, 137, 236).—The increased acidity of salicylic acid and its derivatives over that of BzOH and other hydroxybenzoic acids is probably due to chelation of the anion, which would hinder return of the proton and hence increase dissociation. By analogy with 2-nitroresorcinol, it is suggested that an ionised  $\text{CO}_2\text{H}$  can chelate with two o-OH groups.

L. S. T.

**Decomposition of phenolic ethers. III.** Thermal decomposition of piperonylic acid in presence of sand, acid clay, or active carbon. K. ONO and M. IMOTO (J. Chem. Soc. Japan, 1935, 56, 347—352).—When heated with the above catalysts at 260—280°/130—135 mm., piperonylic acid yields o- $\text{C}_6\text{H}_4(\text{OH})_2$  and a little pyrocatechol Me ether.

CH. ABS. (r)

**Veratronitrile (3:4-dimethoxybenzonitrile).** J. S. BUCK and W. S. IDE (Org. Syntheses, 1935, 15, 85—86).—3:4-(OMe) $_2\text{C}_6\text{H}_3\cdot\text{CHO}$  is converted into the oxime, which is then dehydrated with  $\text{Ac}_2\text{O}$ .

CH. ABS. (r)

**Homoveratric acid.** H. R. SNYDER, J. S. BUCK, and W. S. IDE (Org. Syntheses, 1935, 15, 31—34).—The prep. is described in detail.

CH. ABS. (r)

**Stability of aqueous solutions of potassium hydrogen phthalate.** I. HOFFMAN (J. Res. Nat. Bur. Stand., 1935, 15, 583—584).—1% aq. K H phthalate solution is permanently stable under laboratory conditions.

J. S. A.

**Rabbits bile. I.  $\alpha$ - and  $\beta$ -Lagodeoxycholic acid and lithocholic acid.** S. KISHI (Z. physiol. Chem., 1936, 238, 210—220).—From the bile there have been isolated  $\alpha$ -lagodeoxycholic acid (I),  $\text{C}_{24}\text{H}_{40}\text{O}_4$ , m.p. 156—157°,  $[\alpha]_D^{25} + 80.21^\circ$  in 90% EtOH [Ba salt; Me ester, m.p. 107—108°,  $[\alpha]_D^{25} + 73.97^\circ$  in 90% EtOH; Et ester, m.p. 135°; formyl derivative (II), m.p. 202°; Me ester of (II), m.p. 103—104°; acetate (III), m.p. 188—189°; Me ester of (III), m.p. 144°],  $\beta$ -lagodeoxycholic acid (IV), m.p. 213°,  $[\alpha]_D^{25} + 37.43^\circ$  in 95% EtOH (Me ester, m.p. 175°; Et ester, m.p. 172°,  $[\alpha]_D^{25} + 34.05^\circ$  in 90% EtOH), and lithocholic acid. (I) gives dehydrodeoxycholic acid when oxidised with  $\text{CrO}_3$  in AcOH and deoxybiliary acid when oxidised with  $\text{HNO}_3$ . Heated at 320°/about 12 mm. and distilled in a high vac. (I) gives a choladienic acid, m.p. 135—137°, which with  $\text{H}_2\text{-PtO}_2$  gives cholanolic acid. (IV) with  $\text{CrO}_3$  in

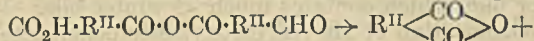
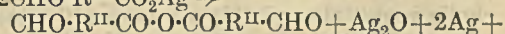
AcOH gives a dehydro-acid, m.p. 222—223°,  $[\alpha]_D^{25} + 87.21^\circ$  in 90% EtOH (Me ester, m.p. 136—138°).

W. McC.

**Fused rings. I.** P. C. MITTER and D. K. BANERJI (Ber., 1936, 69, [B], 456—458).—Et 2-methylcyclopentan-1-one-2-carboxylate,  $\text{CO}_2\text{Et}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , and Zn wool activated by I in anhyd.  $\text{C}_6\text{H}_6$  give a mixture of unsaturated and OH-ester transformed by  $\text{P}_2\text{O}_5$  in boiling  $\text{C}_6\text{H}_6$  into the unsaturated ester,  $\text{C}_{17}\text{H}_{26}\text{O}_6$ , b.p. 176—178°/3 mm., which is hydrogenated ( $\text{PtO}_2\text{-EtOH}$ ) to Et $_2$  2-carbethoxy-2-methylcyclopentylsuccinate (I), b.p. 173—175°/4 mm. (I) with Na in boiling  $\text{C}_6\text{H}_6$  affords Et $_2$  7-methyldicyclo-[0:3:3]-octan-1-one-2:3-dicarboxylate, b.p. 150—178°/3 mm. (slight decomp.) (semicarbazone, m.p. 195°), hydrolysed by KOH-EtOH to the corresponding non-cryst. acid, which slowly yields a semicarbazone, decomp. 198—200°.

H. W.

**Thermal decomposition of the silver salts of carboxylic acids. II. Experimental evidence of the reaction mechanism.** S. J. KANEVSKAJA, M. M. SCHEMJAKIN, and E. M. BANDASS-SCHEMJAKINA (Ber., 1936, 69, [B], 257—265; cf. A., 1934, 1219).—Isolation of intermediate products and their behaviour when heated with  $\text{Ag}_2\text{O}$  shows that thermal decomp. of the Ag salts of aldehydocarboxylic acids follows the course:  $2\text{CHO}\cdot\text{R}^{\text{II}}\cdot\text{CO}_2\text{Ag} \rightarrow$



$\text{R}^{\text{I}}\cdot\text{CHO} + \text{CO}_2$ . Cautious heating of Ag opianate affords opianic anhydride (I) and products among which hemipinic anhydride (II) is identified. Treatment of (I) at a higher temp. with excess of  $\text{Ag}_2\text{O}$  yields about 30% of (II) and 20% of veratraldehyde. About 21% of (I) remains unchanged and 5% of opianic acid is isolated. Similarly, Ag bromopianate yields about 16% of bromo-opianic anhydride, about 25% of bromoveratraldehyde, 0.2% of bromohemipinic anhydride, and 20% of bromohemipinic acid (probably a secondary product formed from traces of  $\text{H}_2\text{O}$  in the Ag salt and the anhydride); bromoveratric acid does not appear to be formed. Bromohemipinimide has m.p. 236—237°.

H. W.

**Choleic acid [complexes].** K. YAMASAKI (J. Biochem. Japan, 1935, 22, 243—249).—The mixed m.p. method (A., 1929, 925) indicates the formation of a 4:1 deoxycholic acid (I)- $\beta$ -carotene complex, m.p. 167°. Treatment of the unsaponifiable fraction of cod-liver oil with EtOH-(I) yields complexes of (I) with high alcohols (mainly selachyl). The fraction, m.p. 185°, converted into the xylene derivative and hydrogenated, affords batyl alcohol (II). M.-p. curves indicate a (I)-(II) (8:1) complex, m.p. 186.5°; such a complex, m.p. 186—187°,  $[\alpha]_D^{25} + 47.37^\circ$  in EtOH, crystallises from (I)+(II) in aq. EtOH.

F. O. H.

**Toad bile. III. Trihydroxyisosterocholenic acid,  $\text{C}_{28}\text{H}_{46}\text{O}_5$ , from winter bile. IV. Constitution of trihydroxybufosterocholenic acid.** T. SHIMIZU and T. KAZUNO (Z. physiol. Chem., 1936, 239, 67—73, 74—75; cf. A., 1934, 1219).—III. Exhaustive extraction of the bile with  $\text{Et}_2\text{O}$ , directly or after saturation with  $\text{CO}_2$ , and further acidification



with AcOH or mineral acid gives trihydroxybusterocholenic acid (I), which is removed as the cryst. Me ester; fractionation of the mother-liquors with 0.1*N*-NaOH affords trihydroxyisosterocholenic acid (II),  $C_{28}H_{46}O_5$ , m.p. 227°,  $[\alpha]_D^{20} +46.95^\circ$  in MeOH, which contains three *sec*.-OH and one double linking, adds Br, and decolorises  $KMnO_4$ . (II) gives a Me ester, m.p. 220°, and is oxidised by  $CrO_3$  in AcOH to triketoisosterocholenic acid (III),  $C_{28}H_{40}O_5$  (Me ester, m.p. 184–186°, and its trioxime, decomp. 231°). Reduction of (III) with Zn–Hg in AcOH–HCl gives isosterocholenic acid,  $C_{28}H_{46}O_5$ , m.p. 186.5–187° (Me ester, m.p. 117°), which adds Br, decolorises  $KMnO_4$ , does not give the Liebermann reaction, and is hydrogenated (PtO<sub>2</sub> in EtOH) to isosterocholenic acid, m.p. 149–149.5° (Na and K salts; Me ester, m.p. 90–90.5°). Reduction (PtO<sub>2</sub> in AcOH) of (II) affords trihydroxyisosterocholenic acid, m.p. 200° after marked softening at 133°,  $[\alpha]_D +38.96^\circ$  in MeOH (Me ester, m.p. 162°), which is oxidised by  $CrO_3$  in AcOH to triketoisosterocholenic acid, m.p. 234° (Me ester, m.p. 223–224°), also formed by hydrogenation (Pd-black in EtOH) of (III). Bromination of (II) in AcOH yields a Br-lactone,  $C_{28}H_{45}O_5Br$ , m.p. 202°, insol. in  $NH_3$ ; (II) therefore appears to contain the double linking in the side-chain and in the  $\delta$ -position to  $CO_2H$ . (II) does not give the Hammarsten reaction so that the three OH are not in the same position as in (I) or cholic acid. (I) and (II) can be readily isolated from summer bile, which contains much < winter bile.

IV. Ozonisation of Me trihydroxyisosterocholenate in cold AcOH or oxidation of it with  $CrO_3$  in warm solution gives products which do not depress the m.p. of  $\alpha$ -bisonorcholenic acid and its Me ester. The double linking of (I) is therefore in the  $\delta$ -position to the  $CO_2H$  of the side-chain.

H. W.

**Lichen substances. LXIII. Components of *Baomyces* varieties.** Y. ASAHINA, Y. TANASE, and I. YOSIOKA. **LXIV. Constitution of thamnolic acid.** IV. Y. ASAHINA and M. HIRATA. **LXV. Ramalinolic acid, a new depside.** Y. ASAHINA and T. KUSAKA (Ber., 1936, 69, [B], 125–127, 330–333, 450–455).—LXIII. Extraction of *B. placophyllus*, Ach., with Et<sub>2</sub>O followed by  $COMe_2$  affords stietic acid, m.p. 272° (decomp.) after softening at 230°. Similar treatment of *B. rosens*, Pers., yields baomycesic acid, (I) decomp. 222° [anil, m.p. 211° (decomp.)] (cf. Koller, *et al.*, A., 1935, 1432). Me baomycesate, m.p. 207°, is reduced (Pd–C in AcOH) to Me barbatate; since it is also formed by the partial methylation of atranorin, (I) is 4-3'-hydroxy-4'-aldehydo-5'-methoxy-*o*-toluoyl-2-hydroxy-3 : 6-dimethylbenzoic acid.

LXIV (cf. A., 1929, 818; 1932, 275). Examination of technical thamnolic acid (II), obtained by extraction of *Cladonia polydactyla* with  $COMe_2$ , discloses the presence of decarboxylthamnolic acid (III), m.p. 215° (decomp.) (anil; *p*-nitrophenylhydrazine, m.p. 219°), also obtained when (II) is heated in  $COMe_2$  at 120–130. (III) and  $CH_2N_2$  in  $COMe_2$  at 0° give the Me ester, m.p. 163°, whereas treatment of (III) with MeI and  $Ag_2CO_3$  in Et<sub>2</sub>O gives the Me ester  $Me_2$  ether, m.p. 183°. Exhaustive treatment of (III) with  $Ag_2O$  and MeI in boiling Et<sub>2</sub>O yields the Me ester  $Me_3$  ether, m.p.

154° transformed by boiling 95%  $HCO_2H$  into Me *H* orcinoldicarboxylate  $Me_2$  ether, m.p. 124° (converted at 200° into Me *p*-orsellinate  $Me_2$  ether, m.p. 84°), and thamnol  $Me_2$  ether, m.p. 104° (semicarbazone, m.p. 216°), which dissolves in KOH to a yellow solution, does not give a colour with  $FeCl_3$ , and is unaffected by  $H_2O_2$  in alkaline solution. (II) is therefore 6-4'-carboxy-3'-hydroxy-5'-methoxy-*o*-toluoyl-4-aldehydo-3 : 5-dihydroxy-*o*-toluic acid.

LXV. Exhaustive extraction of the thalli of *Ramalina farinacea*, Ach., var. *nervulosa*, Müll. Arg., with Et<sub>2</sub>O affords sekikaic acid, the mother-liquors of which contain ramalinolic acid (IV),  $C_{23}H_{28}O_8$ , m.p. 163–164°, which gives an intense blood-red colour with alkali in EtOH, a violet-red colour with  $FeCl_3$ , but no colour with  $CaOCl_2$ . It is hydrolysed by alkali to divaricic acid and an acid,  $C_{12}H_{16}O_5$ , m.p. 163°. Prolonged treatment of (IV) with  $CH_2N_2$  in Et<sub>2</sub>O yields the corresponding Me ester  $Me_3$  ether, m.p. 75°, hydrolysed by KOH–EtOH to divaricic acid Me ether, m.p. 63.5°, and Me amylpyrogallol-carboxylate  $Me_2$  ether (V), m.p. 72–73°. Et 3 : 4 : 5-trimethoxybenzoylacetate is converted by Na and Pr<sup>o</sup>I in EtOH into Et  $\alpha$ -3 : 4 : 5-trimethoxybenzoyl-*n*-valerate, b.p. 214–216° (trimethoxyphenylpropyl-pyrazolone, m.p. 223–224°), hydrolysed by 10% KOH–EtOH to 3 : 4 : 5-trimethoxyvalerophenone (VI), b.p. 190–192°/6 mm. (semicarbazone, m.p. 145–146°). Treatment of (VI) with conc.  $H_2SO_4$  at 38° leads to 4-hydroxy-3 : 5-dimethoxyvalerophenone, m.p. 89–90° (oxidised by  $K_2Cr_2O_7$  and 10%  $H_2SO_4$  to 2 : 6-dimethoxy-*p*-benzoquinone), which is reduced (Clemmensen) to 4-hydroxy-3 : 5-dimethoxy-1-*n*-amylbenzene (VII), b.p. 175°/7 mm. (Bz derivative, m.p. 89°). (VII) is converted by HCN–HCl– $AlCl_3$  into 3-hydroxy-2 : 4-dimethoxy-6-*n*-amylbenzaldehyde, m.p. 52°, which is treated with  $ClCO_2Et$  in  $C_5H_5N$  at –15° and then oxidised by  $KMnO_4$  in  $COMe_2$  whereby 3-carbethoxy-2 : 4-dimethoxy-6-*n*-amylbenzoic acid, m.p. 110–111°, is produced, transformed by  $CH_2N_2$  and subsequent hydrolysis into (V). (IV) is therefore 5-2'-hydroxy-4'-methoxy-6'-propylbenzoyl-4 : 6-dihydroxy-2-amylbenzoic acid.

H. W.

**Acids contained in the wood of *Libocedrus formosna*, Florin.**—See this vol., 395.

**Interaction of hydrogen sulphite derivatives of aromatic aldehydes with potassium cyanide.** S. SCHUSTER (J. Pharm. Chim., 1936, [viii], 23, 142–145).—The  $Na_2SO_3$  compound of PhCHO with KCN gives OH·CHPh·CN and a 12% yield of *N*-benzylidenemandelamide [*Ac* derivative, m.p. 121° (block)], converted by HCl in Et<sub>2</sub>O into a *Cl*-derivative.  $C_{15}H_{12}ONCl$ , m.p. 164°, converted by alkalis into 2 : 4-diphenyloxazole. Similarly the  $Na_2SO_3$  derivative of *p*-OMe· $C_6H_4$ ·CHO gives a substance,  $C_{25}H_{24}O_5N_2$ , m.p. 154° (block), and resinous products.

J. W. B.

**Action of acid chlorides on Schiff's bases. Additive products of these bases.** I. TANASESCU and A. SILBERG (Bull. Soc. chim., 1936, [v], 3, 224–239).—Schiff's bases, CHR·NPh, and acid chlorides, R'·COCl, in neutral solvents ppt. hydrochlorides, CHR·NPh}Cl (I) and  $NH_2Ph$ ·HCl in varying proportions, whilst the solution contains R·CHO,



$R'-CO_2H$ , and  $R'-CO-NHPh$ . Reaction does not occur in complete absence of  $H_2O$  and depends on hydrolysis first of  $R'-COCl$  and then of (I) (demonstrated on the isolated compound). Experiments are quoted in which  $R=Ph$ , *o*-, *m*-, and *p*- $NO_2-C_6H_4$ ,  $R'=Me$ ,  $Ph$ , *m*- $NO_2-C_6H_4$ . Addition to Schiff's bases occurs on the N; reaction with Br proceeds thus:  $CHR:NPhBr_2 \rightarrow HBr + [CHR:NPhBr]OH \rightarrow$

$OH \cdot CHR:NPhBr \rightarrow R \cdot CHO + H_2O + NHPhBr \rightarrow$   
 $NH_2 \cdot C_6H_4Br$  (II), followed possibly by bromination of  $R \cdot CHO$  or (II). *Hydrochlorides of benzyldene*, m.p. 176°, *m*-, m.p. 181° after previous sintering, *o*-, m.p. 156°, and *p*-nitrobenzyldene-aniline, m.p. 190—193°, are described. R. S. C.

**Hydrogen cyanide. VI. Mechanism of Gattermann's hydrogen cyanide aldehyde synthesis.** L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1936, 184—185).—Resorcinol (I), HCN, and HCl at room temp. give resorcyraldehyde (72%), and at 0°, the solid, m.p. 166—170° (decomp.), first formed, corresponds with a mixture of aldimine hydrochloride and dichloromethylformamide hydrochloride. Iminoformylcarbylamine, HCl, and (I) yield *resorcyldimethylformamide hydrochloride*, m.p. 135° (decomp.), decomposed by  $H_2O-HCl$  to the aldehyde, and also obtained from (I) and chloromethyleneformamide. This confirms the primary reaction as tendency to form iminoformyl chloride before derivatives of the dimeride. F. R. S.

**Phenylglyoxal.** H. L. RILEY and A. R. GRAY (Org. Syntheses, 1935, 15, 67—69).— $COPhMe$  is oxidised with  $SeO_2$ . CH. ABS. (r)

**Benzoin reaction. V. Effect of inhibitors on the reaction.** B. F. FERREIRA and T. S. WHEELER (Proc. Indian Acad. Sci., 1935, 2, A, 604—614).—The rate of reaction of  $PhCHO$  and solid KCN in presence of S (cf. A., 1935, 1329) and the inhibition caused by benzoquinone, I,  $PhCNS$ , and  $CS_2$  are studied. Inhibition is due to adsorption of inhibitors on the KCN.  $PhCHO$  (containing inhibitors) may be purified by keeping with a small quantity of KCN, under  $N_2$ , and filtering, after which it gives improved yields of benzoin; 0.1 g. of KCN purifies 50 g. of  $PhCHO$ . E. W. W.

**Kinetics of gaseous Diels-Alder reactions.**—See this vol., 297.

**Kinetics of the benzoin reaction in presence of organic solvents.**—See this vol., 297.

**Structure and absorption spectra of benzocycloalkanoneoximes.** (MME.) P. RAMART-LUCAS and J. HOCH (Compt. rend., 1935, 201, 1387—1390).—Absorption spectra indicate that the oximes of indan-1-one, 2:2-dimethylindan-1-one, and  $\alpha$ -tetralone have the  $C=N \cdot OH$  structure, but that of 2:2-dimethyl-1-tetralone has the *isooxime* structure,  $C \begin{smallmatrix} \text{NH} \\ \diagup \end{smallmatrix} \diagdown O$ . Benzocycloheptan-1-oneoxime exists mainly in the  $N \cdot OH$ , but its 2:2- $Me_2$  derivative mainly in the *isooxime*, form. The structure of the oxime is thus dependent on the influence of valency angles on the elimination of  $H_2O$  from  $OH \cdot CRR' \cdot NH \cdot OH$ , which is the primary product from a ketone and  $NH_2OH$ . R. S. C.

**$\alpha$ -Tetralone ( $\alpha$ -ketotetrahydronaphthalene).** E. L. MARTIN and L. F. FIESER (Org. Syntheses, 1935, 15, 77—79).— $Ph \cdot [CH_2]_3 \cdot COCl$  is treated with  $AlCl_3$  in  $CS_2$ . CH. ABS. (r)

**Ternary catalyst  $Cu-ZnO-Cr_2O_3$  as hydrogenation catalyst.**—See this vol., 298.

**Molecular conversion of ketones into [different] ketones by the action of zinc chloride at high temperatures.** M. A. FAVORSKI [with (MLLE.) T. E. ZALESSKAJA, D. I. ROSANOV, and G. V. TSHELINCEV] (Bull. Soc. chim., 1936, [v], 3, 239—248).—Ketones,  $CR_3 \cdot COPh$  ( $R$  is aliphatic), with  $ZnCl_2$  at about 320° give  $CPhR_2 \cdot COR$ , but ketones with no *tert*-C decompose. Isomerisation may proceed by way of an oxide or by direct interchange of position between O and two radicals.  $COPhEt$  with  $ZnCl_2$  at 320—330° gives  $CO$ ,  $CO_2$ ,  $BzOH$ ,  $EtCO_2H$ ,  $H_2O$ ,  $C_2H_4$ ,  $C_6H_6$ ,  $PhPr$ , and  $CHPh \cdot CHMe$ ; pyrolytic decomp., hydrolytic fission of the ketone, reduction to the hydrocarbon and alcohol, and dehydration of the alcohol must occur simultaneously. *cycloHexyl Ph ketone* (*semicarbazone*, m.p. 167°), obtained from *cyclohexylphenylcarbinol*, with  $ZnCl_2$  at 350—450° gives  $CO$  and *phenylcyclohexane*, b.p. 247—249°.  $MgBu^iBr$  and  $PhCHO$  give *phenyl-tert-butylcarbinol*, m.p. 44—45°, oxidised to *Ph Bu^i ketone*, b.p. 109°/22 mm. (*semicarbazone*, m.p. 159°), which with  $ZnCl_2$  at 320—330° gives  $\alpha$ -phenylisopropyl *Me ketone*, b.p. 97—98°/11 mm. (*semicarbazone*, m.p. 190—191°; oxidised by  $NaOBr$  to  $CPhMe_2 \cdot CO_2H$ ).  $CMe_2Et \cdot MgCl$  and  $PhCHO$  give *phenyl-tert-amylcarbinol*, b.p. 112—114°/8.5 mm., m.p. 22°, oxidised by  $CrO_3$  to *Ph tert-amyl ketone*, b.p. 112°/10 mm. (*semicarbazone*, m.p. 127—128°), which with  $ZnCl_2$  at 320—330° gives  $\beta$ -phenyl-sec-butyl *Me ketone*, b.p. 114—116°/13 mm. (*semicarbazone*, m.p. 177—178°; with  $NaOBr$  gives  $\alpha$ -phenyl- $\alpha$ -methylbutyric acid, m.p. 64°). R. S. C.

**Reactions of benzoyl chloride [fluoride].** C. L. TSENG and S. W. MAI (J. Chinese Chem. Soc., 1936, 4, 22—26).— $BzF$  (prep. from  $BzCl$  and  $KHF_2$  in a Cu retort in 67—80% yield) is unstable and attacks glass if slightly impure; with  $(NH_4)_2CO_3$  it gives  $NH_2Bz$  and with  $C_6H_6$  and freshly prepared  $AlCl_3$  in  $CS_2$  gives 64% of  $COPh_2$  more readily than does  $BzCl$ . R. S. C.

**5:5-Dimethyl-1:3-hexanedione (5:5-dimethyldihydroresorcinol).** R. L. SHRINER and H. R. TODD (Org. Syntheses, 1935, 15, 14—16).—A modified prep. from  $CMe_2 \cdot CHAc$  and  $CH_2(CO_2Et)_2$  is described. CH. ABS. (r)

**Action of selenium dioxide on some cyclanones.** M. GODCHOT and (MLLE.) G. CAUQUIL (Compt. rend., 1936, 202, 326—328; cf. A., 1932, 833).—*cyclo-Hex*-, *-hept*-, and *-oct*-anone with  $SeO_2$  in  $EtOH$  at 80° give 1:2-diones. The following are prepared similarly: 4-methyleyclohexane-1:2-dione, m.p. 37—38° [*dioxime*, m.p. 195—196° ( $Bz_2$  derivative, m.p. 218°); *diphenylhydrazone*, m.p. 148°; affords  $\beta$ -methyladipic acid with  $H_2O_2$ ]; 4-ethoxy-5-keto-2-methyl- $\Delta^6$ -cyclohexene, b.p. 118°/20 mm., is formed by a side reaction], and *cycloheptane-1:2-dione*, b.p. 107—109°/17 mm. [*diphenylhydrazone*, m.p. 135°; *dioxime*, m.p. 181—



182°; oxidised to pimelic acid). 2-Methylcyclohexanone affords 2:3-diketo-1-methyl- $\Delta^6$ -cyclohexene, b.p. 92—93°/16 mm. (diphenylhydrazone, m.p. 150°), which probably results from the dehydration of 3-hydroxy-3-methylcyclohexane-1:2-dione. cyclo-Octanone similarly affords 8-ethoxycyclooctane-1:2-dione, b.p. 133—135°/15 mm. J. L. D.

**Methyl  $\beta$ -m-nitrophenyl- $\beta$ -hydroxyethyl and m-nitrostyryl ketones.** W. KRASZEWSKI and B. WEICÓWNA (Rocz. Chem., 1935, 15, 506—509).—m-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO and COMe<sub>2</sub> in presence of 1% NaOH at room temp. yield a trimeride of m-nitrostyryl Me ketone, m.p. 232° (phenylhydrazone, m.p. 183°), also obtained, together with  $\beta$ -m-nitrophenyl- $\beta$ -hydroxyethyl Me ketone (I), m.p. 62° (benzoate, m.p. 107°; semicarbazone, m.p. 162°), which is the sole product at  $\pm$  5°. (I) yields m-nitrostyryl Me ketone, m.p. 90° (semicarbazone, m.p. 223°; Br-derivative, m.p. 112°), with Ac<sub>2</sub>O (1 hr. at the b.p.). R. T.

**Chrysene.** I. K. FUNKE and E. MÜLLER. II. K. FUNKE, E. MÜLLER, and L. VADASZ (J. pr. Chem., 1936, [ii], 144, 242—250, 265—272).—I. Chrysene (I), BzCl, and AlCl<sub>3</sub> in CS<sub>2</sub> give (probably) 2-benzoylchrysene (II), m.p. 191° [7:8-quinone, m.p. 249—250°, formed on oxidation (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH)], which is reduced (Clemmensen) to 2-benzylchrysene, m.p. 200°, and converted by AlCl<sub>3</sub> at 130° into (probably) a naphthobenzanthrone (not characterised). (I), AcCl, and AlCl<sub>3</sub> in CS<sub>2</sub> afford 1-, m.p. 254°, and 2- (III), m.p. 144°, -acetylchrysene, reduced (Clemmensen) to 1-, m.p. 236°, and 2-ethylchrysene, m.p. 126° (Br-derivative, m.p. 122°), respectively. (III) is oxidised (NaOCl) to chrysene-2-carboxylic acid, m.p. 308° (lit. 303°) [chloride (IV), m.p. 167°; Et ester, m.p. 124° (indef.)], also prepared by Liebermann and Zsuffa's method (A., 1911, i, 202). (IV), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> give (II).

II. BzCl (excess), (I), and AlCl<sub>3</sub> afford two dibenzoylchrysenes, A, m.p. 208° [also obtained from (II), BzCl, and AlCl<sub>3</sub> in CS<sub>2</sub>], and B, m.p. 252°. Dibromochrysene, m.p. 270° [from (I) and Br in CCl<sub>4</sub>], and Cu<sub>2</sub>(CN)<sub>2</sub> in quinoline give dicyanochrysene, m.p. >360°, hydrolysed (powdered KOH in MeOH at 200°) to chrysenedicarboxylic acid, m.p. >360° [chloride (V), m.p. >360°, best prepared using BzCl; Et ester, m.p. 169°; amide; anilide, m.p. >360°], which could not be converted into an anhydride. Bromo-2-benzoylchrysene, m.p. 176° [from (II) and Br in AcOH], is similarly converted into the nitrile, m.p. 207°, of 2-benzoylchrysenedicarboxylic acid, m.p. 286° (previous sintering), the chloride of which could not be prepared. (V), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub> give dibenzoylchrysene-C, m.p. 232°, reduced (Clemmensen) to dibenzylchrysene-C, m.p. 254°. (V) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O afford a compound, C<sub>40</sub>H<sub>30</sub>O<sub>4</sub>N<sub>6</sub>, m.p. >360°. The colours of most of the above compounds in conc. H<sub>2</sub>SO<sub>4</sub> are given. H. B.

**Synthesis of substances related to the sterols.** VIII. A ketomethoxymethylhexahydrophenanthrene. R. ROBINSON and J. WALKER (J.C.S., 1936, 192—195).—The Na compound of Me  $\gamma$ -acetyl- $\alpha$ -methylbutyrate, b.p. 110—112°/24 mm., and  $\gamma$ -methoxyphenylbutyryl chloride yield Me  $\gamma$ -methoxyphenylbutyrate and Me 5-keto-8-m-methoxy-

phenyloctane-2-carboxylate (I), b.p. 210°/1 mm. (I) and NaOEt give a dihydroresorcinol derivative, which with P<sub>2</sub>O<sub>5</sub> affords 1-keto-7-methoxy-2-methyl-1:2:3:4:9:10-hexahydrophenanthrene (II), m.p. 67—68° (2:4-dinitrophenylhydrazone, m.p. 221°), mixed with some 4-Me isomeride. (I) and H<sub>2</sub>SO<sub>4</sub> at -15° give Me  $\gamma$ -6-methoxy-3:4-dihydro-1-naphthyl- $\alpha$ -methylbutyrate, b.p. 181—183°/0.5 mm., the corresponding chloride being cyclised by Darzens' reaction. The ketone obtained is identical with (II); this method proves the constitution but the first method is to be preferred for prep. F. R. S.

**Sexual hormones and related substances.**

VII. Carboxylic derivatives of the follicle hormone. VIII. Catalytic hydrogenation of the follicle hormone and its acyl derivatives. W. DIRSCHERL (Z. physiol. Chem., 1936, 239, 49—52, 53—66).—VII. Follicle hormone (I) is largely unaffected by treatment with an equiv. amount of (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>COCl<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> but is quantitatively transformed by an excess of the reagent at 70—75° into the chloroformate (II), m.p. 101—102° (corr.). (II) is converted by EtOH at 80° into the corresponding Et carbonate, m.p. 115° (corr.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> +114° in dioxan, also obtained from (I) and ClCO<sub>2</sub>Et in C<sub>6</sub>H<sub>6</sub>-C<sub>5</sub>H<sub>5</sub>N at 70—75°. (II) is transformed by MeOH into the Me carbonate, m.p. 127° (corr.), and by NHET<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> into the diethylcarbamate, m.p. 194—195° (corr.). (I) and COCl<sub>2</sub> in alkaline solution afford the normal carbonate, m.p. 247° (corr.), and (II). (II) is about 10 times as active physiologically as (I), excelling all other hormone esters in this respect.

VIII. Hydrogenation of 17-keto-3-hydroxy- $\Delta^{1:3:5}$ -cestratriene (III) (PtO<sub>2</sub>-EtOH; room temp.) affords the dehydrohormone (IV), m.p. 174—175°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +82° in dioxan, which is 5—10 times as active as (III). Similar results are obtained at 70°, in EtOH-H<sub>2</sub>O at room or elevated temp. or when PtO<sub>2</sub> is reduced to Pt before hydrogenation, whereas hydrogenation does not occur with Pt-black under these conditions. Under like circumstances (IV) is also derived from the Bz, Ac, ClCO<sub>2</sub>, or EtCO<sub>2</sub>-derivative of (III). Hydrogenation (PtO<sub>2</sub>) of (I) in EtOH-HCl gives a small amount of (IV) and unchanged (III) but essentially affects the nucleus; the isolation of two octahydrohormones, m.p. 210—211° (corr.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> +7.2° in EtOH (V), and m.p. 154—155°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +31.4° in EtOH, respectively, and of two deoxohexahydrohormones, m.p. 104—105° after softening at 100°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +1.8° in EtOH, and m.p. 96—100°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +12.3° in EtOH, respectively, is described. Hydrogenation of (III) in AcOH affords (V) and lower-melting isomerides of it, deoxohexahydrohormones, and, apparently, a hexahydrohormone which yields a semicarbazone, m.p. 255°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +77.2° in CHCl<sub>3</sub>-EtOH (3:1). In 60% or 80% AcOH hydrogenation proceeds similarly but yields the products in different ratio. In 80% AcOH at 40° the main product is a mixture of ketones from which a hexahydrohormone-2:4-dinitrophenylhydrazone, m.p. 105—110°, and a semicarbazone, m.p. 255°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +46° in EtOH, are derived. H. W.

**Sexual hormones.** XI. Partial hydrolysis of cis-trans-androstane-3:17-diol and its partial esterification. Specificity of sexual hormone



action. L. RUZICKA and M. W. GOLDBERG (Helv. Chim. Acta, 1936, 19, 99—106).—Partial hydrolyses of *cis-trans*-androstan-3 : 17-diol diacetate with KOH—EtOH gives *cis-trans*-androstan-17-ol 3-acetate, m.p. 183—184°. Partial esterification of *cis-trans*-androstan-3 : 17-diol with 90% AcOH or Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N gives good yields of *cis-trans*-androstan-3-ol 17-acetate, m.p. 191—192° (corr.), oxidised by CrO<sub>3</sub> in AcOH to *androstan-3-one* 17-acetate, m.p. 158° (corr.), whence *trans-androstan-3-one*-17-ol (I), m.p. 180—181° (corr.), which is physiologically somewhat less active than testosterone (II). Comparison of the action of derivatives of (I) shows that 17-methyltestosterone, not observed naturally, is physiologically more active than (II) and that chemical structure has little specificity in the male hormone action. *cis*-Androstanediol 3-acetate is transformed by BzCl in C<sub>5</sub>H<sub>5</sub>N into *cis-trans-androstanediol-3-acetate* 17-benzoate, m.p. 198—199° (decomp.), which when partly hydrolysed by KOH—MeOH affords *cis-androstanediol* 17-benzoate, m.p. 203—204° (corr.) (the use of a difficultly hydrolysable acid residue at C-17 is particularly useful, but traces of the 3-acetate are observed), oxidised to *androstan-3-ol* 17-benzoate, m.p. 200—201° (corr.), hydrolysed to (I). H. W.

**17-Ethylandrostenediol and 17-ethyltestosterone.** A. BUTENANDT, H. COBLER, and J. SCHMIDT (Ber., 1936, 69, [B], 448—450).—Dehydroandrosterone is converted by MgEtI in Et<sub>2</sub>O into Δ<sup>5,6</sup>-17-ethylandrosten-3 : 17-diol, m.p. 198° (also +1H<sub>2</sub>O) (cf. Ruzicka *et al.*, this vol., 76), which is treated successively with Br and CrO<sub>3</sub> in AcOH and debrominated by Zn dust in MeOH thereby giving 17-ethyltestosterone, m.p. 149° after softening at 144°, [α]<sub>D</sub><sup>20</sup> −35.3° in abs. EtOH [semicarbazone, m.p. 210° (decomp.)]. H. W.

**Androsterone and related sterols.** R. E. MARKER, F. C. WHITMORE, O. KAMM, T. S. OAKWOOD, and J. M. BLATTERMAN (J. Amer. Chem. Soc., 1936, 58, 338—340).—Oxidation (CrO<sub>3</sub> in dil. AcOH at 70°) of 3-chloro-5 : 6-dibromocholestan-3-ol (from cholesteryl chloride and Br in Et<sub>2</sub>O—AcOH) and reduction (Zn dust, AcOH) of the product formed gives 3-chloro-Δ<sup>5</sup>-dehydrocholan-3-ol and 3-chloro-Δ<sup>5</sup>-dehydroandrosterone (I), m.p. 156—157° (Butenandt and Dannenbaum, A., 1935, 413). Reduction (H<sub>2</sub>, PtO<sub>2</sub>, Et<sub>2</sub>O) of (I) affords α-3-chloroandrosterone (II), m.p. 165—168°, converted by KOAc in valeric acid, subsequent hydrolysis (aq. EtOH—NaOH), and purification through the H succinate into androsterone, m.p. 178°. (II) is also obtained from isoandrosterone (III) (Ruzicka *et al.*, A., 1934, 1221) and SOCl<sub>2</sub>. Hydrolysis of (I) gives Δ<sup>5</sup>-dehydroisoandrosterone which is reduced to (III). Reduction (H<sub>2</sub>, PtO<sub>2</sub>, Et<sub>2</sub>O—AcOH) of cholesteryl bromide affords *cholesteryl bromide*, m.p. 115° [also prepared from epicholesterol (IV) and PBr<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>], which is hydrolysed [as for (II)] to (IV). H. B.

**Cortin, the hormone of the adrenal cortex.** I. T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 29—63).—There is no discrepancy between the Swingle—Piffner assay on dogs and the Everse—de Fremery test on rats if it is assumed that the same material is concerned in each method; per kg.

body-wt., rats require about 500 times as much hormone as dogs. Distribution of cortin extracts between pentane and 20% MeOH permits the isolation of all the physiologically active material in sufficient purity to allow further concn. to be effected without marked loss. The total hormone can be extracted from the concentrates by suitable ketonic reagents (NH<sub>2</sub>·CO·NH·NH<sub>2</sub> or Girard's reagent). The biologically active components from 1000 kg. of cortex can thus be reduced simply to about 5.4 g. without appreciable loss of activity. The preps. so obtained are essentially mixtures of OH-ketones and diketones. They are free from N, S, P, and halogen and contain about 3 rat units per mg. The following inter-related and closely allied to the active components, have been obtained partly from the active concentrates and partly from the inactive by-products; all are biologically inactive with the doses used. *Substance A*, C<sub>21</sub>H<sub>36</sub>O<sub>5</sub>±2H, m.p. 222—224° (decomp.) after becoming opaque at about 160°, [α]<sub>D</sub><sup>20</sup> +16° (±1°) in abs. EtOH; it contains 4 or 5 OH, gives a cryst. ppt. with digitonin in 50% MeOH, is not hydrogenated at 100—140°/100 atm. in presence of Ni—SiO<sub>2</sub>, yields a *tetra-* or *penta-acetate*, m.p. 150—151° (corr.), and a *monoisopropylidene* derivative, m.p. 209—210° (corr.), and yields CH<sub>2</sub>O when oxidised by Pb(OAc)<sub>4</sub> in AcOH. *Substance B*, C<sub>16</sub>H<sub>28</sub>O<sub>5</sub> or, more probably, C<sub>12</sub>H<sub>20</sub>O<sub>4</sub>, m.p. 253—255° in sealed capillary, is possibly a degradation product. *Substance C*, C<sub>21</sub>H<sub>34</sub>O<sub>5</sub>, m.p. 253—256° (corr.; decomp.), [α]<sub>D</sub><sup>20</sup> +69.8°±2.5° in abs. EtOH [monosemicarbazone, m.p. 265—267° (corr.; decomp.)]. *Substance D*, C<sub>21</sub>H<sub>36</sub>O<sub>5</sub> or C<sub>21</sub>H<sub>34</sub>O<sub>5</sub>, m.p. about 230—238° (corr.; decomp.) according to the rate of heating, [α]<sub>D</sub><sup>20</sup> +66°±1.5° in abs. EtOH [monosemicarbazone, m.p. 327—329° (corr.; decomp.)]. *Substance F*, probably C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>, m.p. 220—223° (corr.), [α]<sub>D</sub><sup>20</sup> +262° in abs. EtOH [disemicarbazone, gradual decomp. about 270°]. An *acid*, m.p. 223—226°, [α]<sub>D</sub><sup>20</sup> +166°±20° (determined as Na salt in H<sub>2</sub>O), and *substance E*, m.p. (indef.) 126—129° [semicarbazone, C<sub>25</sub>H<sub>37</sub>O<sub>5</sub>N<sub>3</sub>, m.p. (amorphous), 208—210°, m.p. (cryst.), 280—285° (corr.; decomp.)]. Hydrolysis of the fat insol. in pentane gives a substance, C<sub>4</sub>H<sub>10</sub>O<sub>3</sub>S, m.p. 113—114.5° (corr.), probably an aliphatic trihydroxy-sulphide or dihydroxysulphoxide, which is stable towards alkaline Ag solution but immediately decolorises KMnO<sub>4</sub> at 0°, glyceryl palmitate, and palmitic acid. H. W.

**1 : 2 : 3-Triketotetramethylcyclopentane :** a blue triketone. C. W. SHOPPEE (J.C.S., 1936, 269—274).—Francis and Willson (J.C.S., 1913, 103, 2238) state that 1 : 1-dibromo-2 : 2 : 3 : 3-tetramethylcyclopentanediol (I) and NaOAc give a colourless Br-free compound, m.p. 100°, regarded as a diacetate, and converted by KOH into a substance, m.p. 68°. (I) with NaOAc—MeOH yields 1 : 2 : 3-triketotetramethylcyclopentane hydrate (II), m.p. 95°, which forms a hydrate monosemicarbazone, m.p. 153° (decomp.), 2 : 4-dinitrophenylhydrazine, m.p. 219—220°, 2 : 4-dinitrophenyllosazone (? 1 : 3-bis-2' : 4'-dinitrophenylhydrazine), m.p. 268—270° (decomp.), and a quinoxaline, m.p. 108°, and a mol. compound of the



ketone (1 mol.) and its hydrate (1 mol.), m.p. 119—120°. (II) and KOH give the hydrate of the lactonic acid of  $\gamma$ -hydroxy- $\alpha\beta$ -tetramethylglutaric acid, m.p. 68°. (II) is dehydrated (80%) in vac. to the anhyd. triketone (III), m.p. 164°, bright blue prisms. (I) and AgOAc-MeOH afford 1:1-dimethoxy-2:2:3:3-tetramethylcyclopentanedione (IV), m.p. 68°, rose-red cubes [2:4-dinitrophenyllosazone, m.p. 266° (decomp.)], oxidised ( $H_2O_2$ ) to the lactone of  $\gamma$ -hydroxy- $\gamma$ -methoxy- $\alpha\beta$ -tetramethylglutaric acid, m.p. 58°, and tetramethylsuccinic acid. (IV) is hydrolysed (HCl) to (III) and 2:2-dimethoxytetramethylcyclopentane-1:3-dione, m.p. 62° (2:4-dinitrophenylhydrazone, m.p. 184°), also obtained from (I) and KOH-MeOH. The absorption spectra of (III) show that the blue colour is due to an absorption band with a max. at 685 m $\mu$  and the red colour of (IV) is due to an unsymmetrical band at 510 m $\mu$ ; the blue colour must be ascribed to the contiguous association of the three CO groups.

F. R. S.

**Chelation. III. Stabilisation of Kekulé forms in *o*-hydroxy-carbonyl compounds.** W. BAKER and (Miss) O. M. LOTHIAN (J.C.S., 1936, 274—281).—4-O-Allylresorpiophenone (I), b.p. 174°/14 mm. (Cu derivative, m.p. 158°), undergoes rearrangement by heating to 3-allylresorpiophenone, m.p. 124° (Me<sub>2</sub> ether, b.p. 180°/18 mm.), reduced to 3-n-propylresorpiophenone, m.p. 109—110°, also obtained from 2-n-propylresorcinol, EtCN, and ZnCl<sub>2</sub>. (I) is methylated (Me<sub>2</sub>SO<sub>4</sub>) to 2-O-methyl-4-O-allylresorpiophenone, m.p. 31°, rearranged on heating to 2-O-methyl-5-allylresorpiophenone, m.p. 132—133° (Me<sub>2</sub> ether, m.p. 67°). 4-O-Allyl- $\beta$ -resorcylaldehyde, b.p. 149—150°/3 mm., obtained from  $\beta$ -resorcylaldehyde and allyl bromide, is rearranged to 3-allyl- $\beta$ -resorcylaldehyde (II), m.p. 129—130°, which is methylated to 2-O-methyl-4-O-allyl- $\beta$ -resorcylaldehyde (III), m.p. 45°, and 2-methoxy-4-allyloxystyryl Me ketone, m.p. 39—40°. (III) is rearranged to 2-O-methyl-5-allyl- $\beta$ -resorcylaldehyde, m.p. 145—146°, methylated to 2:4-dimethoxy-5-allylstyryl Me ketone, m.p. 76—77°: the isomeric 2:4-dimethoxy-3-allylstyryl Me ketone, m.p. 45°, is obtained by methylation of (II). (II) is reduced ( $H_2$ -Pd) to 4-methyl-2-n-propylresorcinol, m.p. 96—97°, also obtained by reduction of 3-n-propyl- $\beta$ -resorcylaldehyde, m.p. 92—93°, prepared from the corresponding phenol.

2-Hydroxy-5-allyloxyacetophenone (IV), m.p. 59—60°, prepared from the (OH)<sub>2</sub>-compound and allyl bromide, is rearranged to 2:5-dihydroxy-6-allylacetophenone, m.p. 105—106°, methylated to the 2:5-(OMe)<sub>2</sub>-compound, b.p. 164—165°/14 mm., which with PhCHO gives 2:5-dimethoxy-6-allylphenyl styryl ketone, m.p. 75°. (IV) is methylated to 2-methoxy-5-allyloxyacetophenone, b.p. 166°/13 mm., rearranged to 5-hydroxy-2-methoxy-6-allylacetophenone, m.p. 104°, and -4-allylacetophenone. 2:4-Dimethoxy-3-allylacetophenone gives a semicarbazone, m.p. 159—160°. These experiments do not afford evidence of a stable Kekulé form in 2:5-dihydroxyacetophenone, but are in harmony with the view that such a stable form exists.

The rearrangement of the following allyl ethers does not take place smoothly: 4-ethylresorcinol diacetate,

b.p. 162°/14 mm., and diallyl ether, b.p. 146°/10 mm., Et 4-O-allyl- $\beta$ -resorcylate, m.p. 42°, and the acid, m.p. 155—156°; 4-nitroresorcinol 1-O-allyl ether, b.p. 157—158°/10 mm., rearranged (26%) to 4-nitro-6(or 2)-allylresorcinol, m.p. 85·5°; nitroquinol diallyl ether, m.p. 22°, and 2-nitroquinol 4-O-allyl ether, m.p. 48°.

F. R. S.

**Reactions of *o*-hydroxybenzylidenediace-phenones. VI. Diacetophenones derived from 3-methoxysalicylaldehyde.** G. H. BEAVEN and D. W. HILL (J.C.S., 1936, 256—258).—3-Methoxysalicylaldehyde, CPhMe, and NaOH give 3-methoxysalicylidenediacephenone (I), m.p. 145—146°, and 3-methoxychalcone; with the appropriate ketone the following are prepared: 3-methoxysalicylidenedi-(*p*-methoxyacetophenone) (II), m.p. 163—164°, and 3:4'-dimethoxychalcone, m.p. 142°; 3-methoxysalicylidenedi-(*p*-methylacetophenone) (III), m.p. 112°, and 3-methoxy-4'-methylchalcone, m.p. 131°. (I) in boiling AcOH for 1 hr. affords 8-methoxy-4-phenacylidene-flavene, m.p. 192° (8-methoxy-4-phenacylflavylum ferrichloride, m.p. 197—198°), and for 10 min. yields 8-methoxy-4-phenacylflavene, m.p. 136—137°, and with HCl-FeCl<sub>3</sub> it forms 8-methoxyflavylum ferrichloride, m.p. 162° (lit., 157°). (II) and AcOH afford 8:4'-dimethoxy-4-(*p*-methoxyphenacylidene)flavene, m.p. 195° (ferrichloride, m.p. 193°). (III) with AcOH gives 8-methoxy-4-(*p*-methylphenacylidene)-4'-methylflavene, m.p. 200° [ferrichloride, m.p. 192° (decomp.)], with Ac<sub>2</sub>O forms 2-acetoxy-3-methoxybenzylidenedi-(*p*-methylacetophenone), m.p. 120°, and with HCl-FeCl<sub>3</sub> affords 8-methoxy-4'-methylflavylum ferrichloride, m.p. 179° (decomp.).

F. R. S.

**4'-Hydroxy-2-*p*-hydroxybenzoylbenzophenone.** F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1936, 58, 273—276).— $\alpha$ -Di-*p*-chlorophenylphthalide (I), m.p. 157—158° [from *o*-C<sub>6</sub>H<sub>4</sub>(COCl)<sub>2</sub>, PhCl, and AlCl<sub>3</sub>], is reduced (Zn dust, aq. EtOH-NaOH) to 4':4'-dichlorotriphenylmethane-2-carboxylic acid, which with conc. H<sub>2</sub>SO<sub>4</sub> gives 3-chloro-9-*p*-chlorophenyl-10-anthrone (II), m.p. 143—144°. Oxidation (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH) of (II) affords 3-chloro-9-hydroxy-9-*p*-chlorophenyl-10-anthrone (III), m.p. 223—224° (Me ether, m.p. 165—166°), which with HCl in C<sub>6</sub>H<sub>6</sub>-AcCl gives 3:9-dichloro-9-*p*-chlorophenyl-10-anthrone, m.p. 121—122°, converted by mol. Ag in C<sub>6</sub>H<sub>6</sub> into the deep red free radical 3-chloro-9-*p*-chlorophenyl-10-anthranyl [peroxide, m.p. 255—265° (decomp.)]. Contrary to Baeyer (A., 1880, 650). (I) could not be obtained from phenolphthalein and PCl<sub>5</sub>; (III) is produced. 4'-Hydroxy-2-*p*-hydroxybenzoylbenzophenone (IV) (A., 1932, 617) [the supposed 3:9-dihydroxy-9-*p*-hydroxyphenyl-10-anthrone of Baeyer (*loc. cit.*) and PCl<sub>5</sub> at 120—125° give 4'-chloro-2-*p*-chlorobenzoylbenzophenone, m.p. 167—168° [the (III) of Baeyer] [bisphenylhydrazone, m.p. 202—203° (decomp.)], reduced (Zn dust, AcOH) to 2:5-di-*p*-chlorophenyl-3:4-benzofuran, m.p. 199—200° [the (II) of Baeyer]. Further reduction affords (probably) the 2:5-dihydrobenzofuran [the 3-chloro-10-hydroxy-9-*p*-chlorophenyl-9:10-dihydroanthracene of Baeyer (*loc. cit.*)]. Further proof of the structure of (IV) is given by the synthesis of its Me<sub>2</sub> ether (V), m.p. 157—159°, from *o*-CN·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et (VI) and



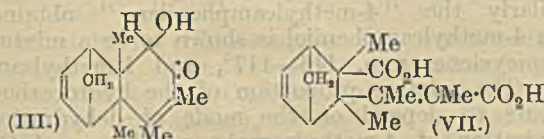
*p*-OMe·C<sub>6</sub>H<sub>4</sub>·MgI (VII). (V) is also prepared by oxidation (method: *loc. cit.*) of 2:5-dianisyl-3:4-benzofuran [from (VII) and anisylphthalide]. MgPhBr and (VI) afford *o*-benzoylbenzophenone. H. B.

**Phloracetophenone.** K. C. GULATI, S. R. SETH, and K. VENKATARAMAN (Org. Syntheses, 1935, 15, 70—71).—*s*-C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub> is treated with MeCN, ZnCl<sub>2</sub>, and HCl. CH. ABS. (r)

**2:6-Dibromobenzoquinone-4-chloroimide.** W. W. HARTMAN, J. B. DICKY, and J. G. STEMPFLI (Org. Syntheses, 1935, 15, 8—10).—Reduction of 2:6-dibromo-4-nitrophenol with Sn and HCl gives a quant. yield of 2:6-dibromo-4-aminophenol stannichloride, which is oxidised with NaOCl.

CH. ABS. (r)

**Diene reaction between tetramethyl-*o*-benzoquinone and cyclopentadiene.** L. I. SMITH and L. R. HAC (J. Amer. Chem. Soc., 1936, 58, 229—234).—Tetramethyl-*o*-benzoquinone (freshly prepared) and cyclopentadiene in boiling 95% EtOH give 3:4:9:10-tetramethyl-5:8-endomethylene-5:8:9:10-tetrahydronaphthalene-1:2-quinone (I), m.p. 181—182° [semicarbazone, m.p. 213—214° (decomp.)] (darkens at 207°); phenazine (II), m.p. 182—183° (from *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>), which is reduced (Zn dust, aq. AcOH) to 1-hydroxy-2-keto-3:4:9:10-tetramethyl-5:8-endomethylene-1:2:5:8:9:10-hexahydronaphthalene (III), m.p. 95.5—96° (acetate, m.p. 77—78°; oxime, m.p. 184—185°), oxidised (CrO<sub>3</sub>, aq. AcOH) to (I). (III) and *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in AcOH or EtOH afford (II). Clemmensen reduction of (I) gives



a little of a product (contains O), b.p. 101—103°/14 mm.; dehydrogenation (Se at 280—300°) of this or (I) affords indefinite products. Reduction (H<sub>2</sub>, PtO<sub>2</sub> or Pd-CaCO<sub>3</sub>, EtOH) of (I) or (III) gives 1-hydroxy-2-keto-3:4:9:10-tetramethyl-5:8-endomethylene-1:2:3:4:5:8:9:10-octahydronaphthalene (IV), m.p. 82—83° (acetate, m.p. 91°; oxime, m.p. 169—170°), oxidised (CrO<sub>3</sub>, aq. AcOH) to the 1:2-diketo-derivative (V), m.p. 141—141.5° [phenazine, m.p. 181—182°, also formed from (IV)]. Reduction [H<sub>2</sub> (1800 lb.), Raney Ni, 95% EtOH, 185°] of (I), (III), or (IV) affords 1:2-dihydroxy-3:4:9:10-tetramethyl-5:8-endomethylene-3:4:5:6:7:8:9:10-octahydronaphthalene (VI), m.p. 146—147° (diacetate, m.p. 81—82°), which could not be reduced further. (VI) does not give an oxime or a phenazine; on one occasion only it was oxidised (CrO<sub>3</sub>, aq. AcOH) to the 1:2-diketodecahydro-derivative, m.p. 96—97°, indicating that it can react as the 1-hydroxy-2-ketodecahydro-form. (I) is oxidised (15% H<sub>2</sub>O<sub>2</sub>, aq. MeOH-NaOH) to β-(2-carboxy-1:2-dimethyl-3:6-endomethylene-Δ<sup>4</sup>-cyclohexenyl)-α-methyl-Δ<sup>4</sup>-butenoic acid (VII), m.p. 239—240° (decomp.) [? 4:5-dibromide (VIII), m.p. 249—250° (decomp.)], which is reduced (H<sub>2</sub>, Pd-CaCO<sub>3</sub>, aq. Na<sub>2</sub>CO<sub>3</sub>) to the *butyric acid*, m.p. 229—230°, also formed by oxidation (H<sub>2</sub>O<sub>2</sub>) of (V). Ozonolysis of

(VIII) and subsequent reductive fission gives resinous products. H. B.

**Naphthazarin and dibromonaphthazarin.**—See this vol., 428.

**Manufacture of 1:4-dihalogenoanthraquinone-2-carboxylic acids.**—See B., 1936, 182.

**9:10-Dihydroxy-9:10-di-*n*-amyl-9:10-dihydrophenanthrene and 2:2'-di-*n*-hexoyldiphenyl.** T. W. JEZERSKI and M. MACIEJEWSKI (Rocz. Chem., 1935, 15, 543—545).—Phenanthraquinone and *n*-C<sub>5</sub>H<sub>11</sub>·MgBr in Et<sub>2</sub>O yield 9:10-dihydroxy-9:10-di-*n*-amyl-9:10-dihydrophenanthrene, m.p. 102.7—104°, converted by CrO<sub>3</sub> in aq. AcOH into 2:2'-di-*n*-hexoyldiphenyl, b.p. 206°/3.5 mm. R. T.

**Grignard reagent from pinene hydrochloride.** Action of phthalic acid. R. BOUSSET (Bull. Soc. chim., 1936, [v], 3, 318—319).—*o*-Carboxybenzoylcamphane (Ag salt) has [α]<sub>D</sub> +58.92°, the *Me* ester, m.p. 72—75°, [α]<sub>D</sub> +64.7°, and the *Et* and *Pr* esters, oils, [α]<sub>D</sub> +62.95° and +60.45°, respectively. With SOCl<sub>2</sub>, HCl-MeOH, or Me<sub>2</sub>SO<sub>4</sub> the acid gives phthaloylcamphane, m.p. 216° (corr.), [α]<sub>D</sub> +194°. Other optical data are given. R. S. C.

**Grignard reaction on α-pinene oxide.** J. J. RITTER and K. L. RUSSELL (J. Amer. Chem. Soc., 1936, 58, 291—293).—Contrary to Prileschaeff and Verschuk (A., 1929, 1076), α-pinene oxide (I) and MgMeI (first in Et<sub>2</sub>O and then in C<sub>6</sub>H<sub>6</sub>) give methylcampholenol (II),  $\begin{matrix} \text{CMe} \cdot \text{CMe}_2 \\ | \\ \text{CH} - \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$ , b.p. 82—83°/4 mm., 107—108°/12 mm., also prepared from campholenaldehyde (Arbuzov, A., 1935, 1246) and MgMeI. The formation of (II) involves a ring-fission and subsequent ring enlargement. (II) is oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, dil. H<sub>2</sub>SO<sub>4</sub>) to methylcampholenone, b.p. 73—74°/4 mm. [semicarbazone, m.p. 175—176° (corr.)]. Ethyl-, b.p. 88—89°/4 mm., *n*-propyl-, b.p. 100—101°/4 mm., *n*-butyl-, b.p. 110—112°/4 mm., isobutyl-, b.p. 106—107°/4 mm., and phenyl-, b.p. 140—142°/1.3 mm., *campholenols* are similarly formed from (I) and MgRX. Ethylcampholenone has b.p. 80—81°/2 mm. [semicarbazone, m.p. 148—149° (corr.)]. H. B.

**Norborneol and norbornylene.** G. KOMPPA and S. BECKMANN (Ann. Acad. Sci. fenn., 1934, A, 39, No. 7, 9 pp.; Chem. Zentr., 1935, i, 3940).—Mostly already reported (A., 1934, 658). 2-Carbamyl-dicyclo-[1:2:2]-heptane, m.p. 205—206°, prepared from the acid in the usual way affords norbornylamine with KOH-KOBr. H. N. R.

**Borneol-isoborneol question.** Y. ASAHINA, M. ISHIDATE, and T. SANO (Ber., 1936, 69, [B], 343—348; cf. A., 1935, 625; Lipp, *ibid.*, 983).—*d*-trans-π-apo-Borneol-7-carboxylic acid, obtained by vigorous reduction of isoketopinic acid with Na and EtOH (slow reduction causes some production of isoborneol derivatives), is quantitatively converted by AcCl in C<sub>5</sub>H<sub>5</sub>N into the corresponding acetate (I), m.p. 106—107°, which with SOCl<sub>2</sub> affords *d*-trans-π-apoacetylborneol-7-carboxyl chloride, b.p. 124°/6 mm., transformed by H<sub>2</sub> in boiling xylene containing Pd-C into *d*-trans-π-apoacetylborneol-7-aldehyde [reoxidised to



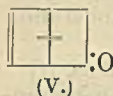
(I)], the *semicarbazone*, m.p. 195°, of which is converted by NaOEt-EtOH at 150—155° into *d*-borneol (II). Similarly, *trans*- $\pi$ -apoisoacetylborneol-7-carboxylic acid, from *apocamphenecarboxylic acid* (III) by hydration according to Bertram-Walbaum, is converted successively into the corresponding *chloride*, b.p. 120°/6 mm., *trans*- $\pi$ -apoisoacetylborneol-7-aldehyde (*semicarbazone*, m.p. 197°), and *isoborneol*. *trans*- $\pi$ -apoCamphor-7-carboxylic acid is therefore a substituted camphor which, like the latter, on energetic reduction gives mainly a borneol derivative, whereas (III) is a substituted camphene passing, when hydrated, mainly into an *isoborneol* compound. Reduction of *d*-ketodihydroteresantalic acid by Na and EtOH yields the antipode of the Semmler-Bartelt lactone, m.p. 196°, and *d*-cis- $\pi$ -apoborneol-7-carboxylic acid (IV), m.p. 278°. Treatment of (IV) with AcCl in C<sub>6</sub>H<sub>5</sub>N affords the corresponding *acetate*, b.p. 155—158°/5 mm., the *chloride*, b.p. 124°/6 mm., of which is converted *d*-cis- $\pi$ -apoacetylborneol-7-aldehyde, the *semicarbazone*, m.p. 224°, of which affords (II). *r*-isoBorneol is unchanged by NaOEt-EtOH at 155°, but passes at 170—180° into borneol. H. W.

**Oxidation of bornyl acetate.** Y. ASAHINA, M. ISHIDATE, and T. TUKAMOTO (Ber., 1936, 69, [B], 349—354).—Oxidation of *l*-bornyl acetate by CrO<sub>3</sub> in AcOH-Ac<sub>2</sub>O at 80° affords unchanged material, and fractions, b.p. 115—160°/15 mm. (I), and b.p. >160°/15 mm. (II), respectively. Treatment of (I) with 10% K<sub>2</sub>CO<sub>3</sub> gives small amounts of 1:5:5-trimethylcyclopentan-2-one-4-acetic acid (III) (*semicarbazone*, m.p. 240°), and the unattacked portion is oxidised by Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and dil. H<sub>2</sub>SO<sub>4</sub> to 3:6-diketocamphane, m.p. 212°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -105.5° in abs. EtOH (*disemicarbazone*, m.p. 295°), (III), and ketocampholenic acid (IV), m.p. 130° (*semicarbazone*, m.p. 218°). (IV) is also obtained by the action of KOH-EtOH on 6-bromo-2:5-diketocamphane or 2-bromo-3:6-diketocamphane, m.p. 145°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -152.7° in abs. EtOH, from 3:6-diketocamphane (V) and Br in CHCl<sub>3</sub>. *l*-p-Ketoborneol (VI) is oxidised by Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and dil. H<sub>2</sub>SO<sub>4</sub> at 100° to (IV) and (V); under like conditions, *l*-p-diketocamphane is largely unattacked. Catalytic hydrogenation (Pd-C in AcOH) of (IV) gives optically inactive 1:5:5-trimethylcyclopentan-3-one-4-acetic acid, m.p. 90° (*semicarbazone*, m.p. 229°). (II) when oxidised with H<sub>2</sub>O<sub>2</sub> in alkaline solution and then heated with alkali yields (VI) and *d*-2-hydroxycamphoric acid (VII), m.p. 165°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> +7.8° in abs. EtOH (*Me*<sub>3</sub> ester, b.p. 150—151°/11 mm., m.p. 46°). Synthesis of (VII) is effected by treating *l*-p-ketobornyl acetate, m.p. 78°, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -87.9° in abs. EtOH, with SeO<sub>2</sub> in Ac<sub>2</sub>O at 130—140°, thus yielding 6-acetoxycamphor-2:3-quinone, m.p. 109°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> -191.4° in abs. EtOH, which is oxidised by NaOH and H<sub>2</sub>O<sub>2</sub> to (VII). 2-Acetoxycamphor-5:6-quinone, m.p. 109°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> +188.5° in abs. EtOH, is oxidised to 1-2-hydroxycamphoric acid, m.p. 165°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> -8.0° in abs. EtOH. Oxidation of (VII) affords *d*-1:5:5-trimethylcyclopentan-2-one-4-carboxylic acid, m.p. 122°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> +163.74° in abs. EtOH (*semicarbazone*, m.p. 215°; *Me* ester, m.p. 41°); the corresponding *l*-acid has m.p. 122°, [ $\alpha$ ]<sub>D</sub><sup>23</sup> -166.8° in abs. EtOH (*semicarbazone*, m.p. 215°), and the *r*-acid has m.p. 117°. H. W.

**New camphor derivative, "ketobornylene."** Y. ASAHINA, M. ISHIDATE, and T. TUKAMOTO (Ber., 1936, 69, [B], 355—357).—6-Acetoxycamphorquinone with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in hot EtOH gives  $\alpha$ - (I), m.p. 175°, and  $\beta$ - (II), m.p. 99°, -6-acetoxycamphorquinone-3-monohydrazone. (I) with yellow HgO in boiling C<sub>6</sub>H<sub>6</sub> affords 3-diazo-6-acetoxycamphor, m.p. 120°, also obtained more slowly from (II); when distilled with Cu-bronze it yields 6-acetoxy- $\beta$ -pericyclocamphan-2-one (III), b.p. 145°/18 mm., hydrolysed to 6-hydroxy- $\beta$ -pericyclocamphan-2-one (IV), m.p. 234°. (III) or (IV) with HBr-AcOH at room temp. gives 5-bromo-6-hydroxycamphor, m.p. 123°, transformed by Zn dust and alkali into (IV) and by Zn dust and AcOH at 100° into *keto-bornylene* [dehydrocamphor] (V), m.p. 148°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -735° in abs. EtOH [*semicarbazone*, m.p. 234° (decomp.)], which immediately reduces cold KMnO<sub>4</sub> and slowly decolorises Br in AcOH. Catalytic hydrogenation (Pd-C in AcOH) of (V) gives *d*-camphor. H. W.

**Removal of water from camphenilol, 4-methylcamphenilol, and 4-methylborneol. Santene displacement and Nametkin transformation.** G. KOMPPA and G. A. NYMAN (Ber., 1936, 69, [B], 334—340).—Ozonisation of camphenilene obtained by heating camphenilol (I) with KHSO<sub>4</sub> leads to *apocyclene* (II) unattacked by O<sub>3</sub>, and santene diketone. Dehydration of (I) takes place partly by pinacolin transformation giving santene and partly by direct loss of H<sub>2</sub>O and subsequent ring-closure to (II). Similarly the "4-methylcamphenilene" obtained from 4-methylcamphenilol is shown to be a mixture of *epicyclene*, m.p. 116—117°, and 1-methylsantene. The relative proportion of the hydrocarbons appears to depend on the mode of dehydration. Ozonisation of 4-methylcamphene (III) in AcOH gives, as unattacked portion, 4-methyltricyclene (IV), m.p. 109—110° (also obtained by oxidation of 4-methylcamphorhydrazide with HgO); 4-methylcamphenilone, hydroxy-3-methylcamphenilonolactone, and trimethylnorcampholide are also isolated. These normal products are accompanied by considerable amounts of *dl*-fenchone (V); apparently (III) becomes partly hydrated, and the acetate thus produced suffers the Nametkin transformation and subsequent loss of AcOH. 1-Methylcamphene is thus produced, which is ozonised to (V). Elimination of H<sub>2</sub>O from 4-methylborneol occurs therefore in three directions. H. W.

**Organic catalysts. XII. Asymmetric main valency catalysis.** I. W. LANGENBECK and G. TRIEM (Ber., 1936, 69, [B], 248—250).—*d*-Camphoglyoxylic acid (I) has [ $\alpha$ ]<sub>D</sub><sup>20</sup> +255.1° in *N*-NaOH. *dl*-Camphoglyoxylic acid (II), m.p. 84—85° [oxime (+1H<sub>2</sub>O), m.p. 159°], is obtained from *dl*-camphor, Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and Na wire in ligroin. (I) and *dl*-alanine (III) at 150° afford small amounts of *d*-hydroxymethylenecamphor, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +183° in EtOH. (II) and (III) yield *dl*-hydroxymethylenecamphor, whereas (II) and *l*-alanine give a slightly levorotatory product. If *l*-leucine is used, the product appears to be optically

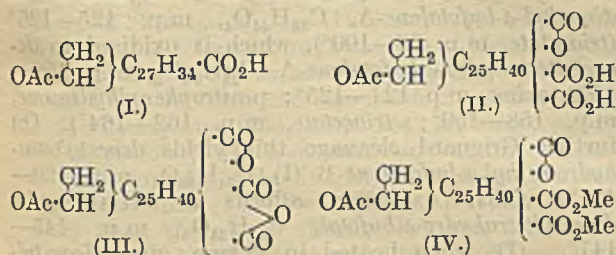




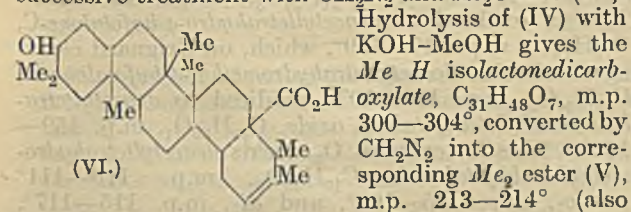
inactive. The stereochemical specificity of the carb-oxylase model is thus established. H. W.

**Chios turpentine.** E. EMMANUEL (Pharm. Acta Helv., 1935, 10, 12—22; Chem. Zentr., 1935, i, 3856).—The following are isolated from the resin of *Pistacia terebinthus*, L.: *terminthic acid*,  $C_{14}H_{20}O_2$ , m.p. 136—137°; *terminthinic acid*,  $C_{16}H_{24}O_4$ , m.p. 123.5—124.1°, monobasic (EtOH-insol. *Pb* salt); *termintholic acid*, m.p. 101.5—102.1°, monobasic (EtOH-sol. *Pb* salt); *termintholinic acid*,  $C_{22}H_{34}O_3$ , m.p. 127.5—128°, monobasic; an *etheral oil*,  $d_{15}^{20} 0.8695$ ,  $n_D^{20} 1.4668$ ,  $[\alpha] +33.5^\circ$ , separable into two fractions, b.p. 157—165° and 165°—190°; a *resin* and a *bitter principle*. H. N. R.

**Polyterpenes and polyterpenoids. C. Transformations in rings A and E of oleanolic acid. Carbon skeleton of pentacyclic triterpenes.** L. RUZICKA and K. HOFMANN (Helv. Chim. Acta, 1936, 19, 114—128).—Oxidation of acetyloleanolic acid (I) by  $CrO_3$  in  $AcOH-H_2SO_4$  gives the *substance* (II), m.p. 230°, which could not be obtained homogeneous; its formula and the function of the O atoms are



established by its conversion into the corresponding *anhydride* (III), m.p. 294—295°, (dehydrogenated by Se at 350° to 2:7- $C_{10}H_6Me_2$ ), its transformation by  $CH_2N_2$  or from the *Ag*<sub>2</sub> salt and MeI in  $Et_2O$  into the *Me*<sub>2</sub> ester (IV), m.p. 203—204°, or (+1MeOH) m.p. 178—179°, and its hydrolysis to the *lactone-carboxylic acid*,  $C_{30}H_{46}O_7$ , m.p. 270° (decomp.), converted by successive treatment with  $CH_2N_2$  and  $Ac_2O$  into (IV).



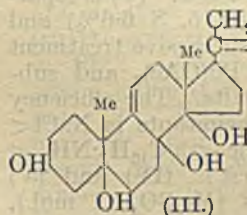
Hydrolysis of (IV) with  $KOH-MeOH$  gives the *Me H isolactonedicarboxylate*,  $C_{31}H_{48}O_7$ , m.p. 300—304°, converted by  $CH_2N_2$  into the corresponding *Me*<sub>2</sub> ester (V), m.p. 213—214° (also +1MeOH) (*Ac* derivative, m.p. 273—274°), which is very resistant to alkaline hydrolysis. Oxidation of (V) by  $CrO_3$  (=1.5O) in  $AcOH$  gives the *Me*<sub>2</sub> ester of the *ketoisolactonedicarboxylic acid*, m.p. 219—220° [*oxime*, m.p. 257—258° (decomp.); *OH·CH*: derivative]. *Me* oleanolate is oxidised by  $CrO_3$  to *Me oleanonate*, m.p. 156—157° [*oxime*, m.p. 218—219° (decomp.); *OH·CH*: derivative, m.p. 197—199°]. The above results and a review of the lit. suggest the structure (VI) for oleanolic acid. H. W.

**α-Tocopherol from wheat-germ oil.**—See this vol., 531.

**The crystalline acid of Canada balsam.** F. TROST (Annali Chim. Appl., 1936, 26, 38—42).—*Canadolic acid* (A., 1900, i, 678), new formula  $C_{20}H_{30}O_2$ ,  
K K

new m.p. 165—168°,  $[\alpha]_D^{20} -91^\circ$  in  $EtOH$ , is an isomeride of abietic acid. It is dehydrogenated (Se) to retene, gives a *compound*, m.p. 226°, with maleic anhydride, and is converted by  $AcOH$  at 100° into Steele's abietic acid (A., 1922, i, 739). E. W. W.

**Plant cardiac poisons. VIII. Convallatoxin.** R. TSCHESCHE and W. HAUPT (Ber., 1936, 69, [B], 459—464; cf. Karrer, A., 1929, 684).—Convallatoxin (I), m.p. 238—239°, or (hydrated) m.p. 225°, is  $C_{29}H_{42}O_{10}$ . It contains two double linkings, one of which is saturated with great difficulty. (I) is hydrolysed with difficulty by acids to *l*-rhamnose and monoanhydroconvallatoxinigenin, isolated as the *benzoate* (II), m.p. 279—281°,  $[\alpha]_D^{20} +22.2^\circ$  in  $CHCl_3$ . In addition to the three double linkings of the  $C_6H_6$  group, (II) contains three double linkings, one of which is very resistant towards saturation. Its absorption curve very closely resembles that of anhydrouzarigenin benzoate. (II) contains two, probably *tert.* OH (Zerevitinov). Convallatoxinigenin (III) therefore contains one *sec.* and two *tert.* OH. Like (II) it does not



react with ketonic reagents. The positive Legal test establishes the presence of an unsaturated side-chain which is opened by alkali, thus allowing the equiv. to be determined.

Acidification of the alkaline solution leads to α-, m.p. 256—258°, and β-, m.p. 289—290°, *isoconvallatoxin*. Assuming that (III) contains the same C skeleton as digitoxigenin, strophanthidin, and uzarigenin, the constitution shown explains satisfactorily the behaviour of (III). The disposition of the double linkings and OH is discussed in detail. H. W.

**Phytosterol and resin of *Fabiana denudata*.**—See this vol., 533.

**Punar-Nava (*Boerhaavia diffusa*).**—See this vol., 533.

**Two disputed properties of nitrolignin.** K. KÜRSCHNER (Zellstoff-Faser, 1935, 32, 17—19; Chem. Zentr., 1935, ii, 2987).—The non-cryst. nature and the presence of oximino-keto-compounds are refuted (cf. Nijhofs, B., 1934, 395). H. N. R.

**Action of benzaldehyde on lignin.** N. I. NIKITIN and I. M. ORLOVA (J. Appl. Chem. Russ., 1935, 8, 1402—1409).—The product pptd. by  $Et_2O$  or light petroleum from  $PhCHO$  solutions (prepared by heating at 150—160° for 7 hr.) of Willstätter lignin has a higher C and a lower OMe content than the original material. Since this undergoes similar changes when heated alone, it is not possible to decide whether the analytical data are interpretable on the basis of condensation with  $PhCHO$  or of thermal transformation; possibly both processes enter.

R. T.  
**Lignin and related compounds. XXIII. Preparation and methylation of spruce lignin-sulphonic acids. XXIV. Formation of vanillin from waste sulphite liquor. XXV. Mechanism**



of vanillin formation from spruce lignin-sulphonic acids in relation to lignin structure. G. H. TOMLINSON II and H. HIBBERT (J. Amer. Chem. Soc., 1936, **58**, 340—345, 345—348, 348—353).—XXIII. Spruce wood meal (extracted with EtOH- $C_6H_6$ ) (I) is heated with aq.  $Ca(HSO_3)_2 + SO_2$  at 125° and the liquor treated with  $CaCl_2$ , which salts out  $Ca$   $\alpha$ -ligninsulphonate (II);  $Ca$   $\beta$ -ligninsulphonate (III) (37% of total salt) (Ca 5, S 10.4, OMe 10.45%) is isolated from the mother-liquors through the Pb salt. (II) is separated by further salting out ( $CaCl_2$ ) into fractions (IIa) (19%) (Ca 3.5, S 9.4, OMe 11.2%) and (IIb) (44%) (Ca 3.8, S 9.6, OMe 11.35%). All the salts are purified by dialysis and subsequent pptn. from aq. EtOH by EtOH-Et<sub>2</sub>O. The liquor from (I) and aq.  $KHSO_3 + SO_2$  at 110° with quinoline hydrochloride gives (cf. Hägglund, B., 1933, 584; Freudenberg *et al.*, A., 1935, 861) a quinoline salt, subsequently converted into K ligninsulphonate (IV) (70%) (K 3.7, S 5.4%); a K salt (V) (30%) (K 2.7%) is isolated from the mother-liquors (A) through the Pb salt. (V) is separable into K salts (Va) (16%) (K 5, S 6.6%) and (Vb) (14%) (K 5.8, S 5.6%) by successive treatment of (A) with  $\beta$ - $C_{10}H_7$ -NH<sub>2</sub> and Pb(OAc)<sub>2</sub> and subsequent conversion into the K salts. The efficiency of the following reagents as precipitants is  $NaCl < CaCl_2 < quinoline, isoamylamine < \beta$ - $C_{10}H_7$ -NH<sub>2</sub> < Pb(OAc)<sub>2</sub> (cf. Hägglund, *loc. cit.*). (IV) and (V) (in aq. COMe<sub>2</sub>) are methylated [ $Me_2SO_4$  (1 mol.), 30% KOH (1.1 mols.), 20°] to fully methylated products (VI) and (VII), respectively, containing 30 and 31.6% OMe (calc. on K- and  $SO_3H$ -free basis), respectively, without loss of S.

XXIV. In agreement with Kürschner (cf. B., 1928, 292), vanillin (VIII) is obtained in yields of 3.44—7.27% (based on lignin content) when waste sulphite liquor is boiled with NaOH, KOH, or (less satisfactorily)  $Ba(OH)_2$ ; the mixture is acidified ( $H_2SO_4$ ), extracted with  $CHCl_3$ , and (VIII) is then isolated with  $NaHSO_3$  and subsequently determined as the *m*-nitrobenzoylhydrazone. The effect of the original cooking treatment on the yield of (VIII) is investigated; max. yields are obtained when sulphite liquors containing a relatively high proportion of "free"  $SO_2$  are used at 110—125° (prolonged heating at such temp. having little effect on the yield).

XXV. The yields of (VIII), calc. on metal- and  $SO_3H$ -free basis, obtained when the following salts (see Part XXIII) are boiled with 19.4% (wt.) NaOH in  $N_2$  for 12 hr. are: (IIa) 6.1, (IIb) 6.6, (III) 8.4, (IV) 6.4, (Va) 8.6, (Vb) 7.1. The other fission products contain less S but approx. the same OMe as the original compounds, indicating that a small non-methylated aliphatic fragment is also removed during the hydrolysis. Veratraldehyde (*m*-nitrobenzoylhydrazone, m.p. 221—223°) is formed in yields of 2.35 and 2.76%, respectively, from (VI) and (VII) with boiling 3.8% NaOH. The presence of the 4:3-(OH)(OMe) $C_6H_3$  group in spruce-lignin is thus proved. Unsulphonated lignin does not similarly yield (VIII). It is suggested that a group such as 4:3-(OH)(OMe) $C_6H_3$ -CH( $SO_3H$ )-CH<sub>2</sub> is hydrolysed ( $SO_3H$  replaced by OH), and that the resulting product gives (VIII) by a reversed aldol reaction;

evidence in support of this view (cf. Freudenberg *et al.*, *loc. cit.*) is given. H. B.

**Aesculus saponins and their sugar-free derivatives.** E. BUREŠ and K. BABOR, jun. (Časopis českoslov. Lék., 1935, **15**, 3—8, 25—34; Chem. Zentr., 1935, i, 3936).—Three saponins are isolated from chestnut seeds: *saponin B*, decomp. 80—120°; *saponin C*, m.p. 150° (decomp.), and *saponin A*, which, when purified by repeated pptn. from EtOH and by dialysis, has m.p. 190—194° (decomp.) and composition  $C_{24}H_{38}O_8(OH)_7$  (Br-derivative,  $C_{24}H_{45}O_{16}Br$ , decomp. 130°; *hepta-acetate*, m.p. 155—160°). The latter is hydrolysed to the prosapogenin, aescin, decomp. 211—225° [Br-derivative, m.p. 217° (decomp.); *penta-acetate*, m.p. 169—170°], which is further hydrolysed to aescigenin, m.p. 179—186°. H. N. R.

**Constituents of "Senso." IV. Grignard cleavage of methyl deacetyltetrahydro- $\psi$ -bufotalinate.** S. IKAWA (J. Pharm. Soc. Japan, 1935, **55**, 195—217).—Grignard cleavage of Me deacetyltetrahydro- $\psi$ -bufotalinate yields *deacetyltetrahydro-dimethyl- $\psi$ -bufotalene-A*,  $C_{26}H_{44}O_4$ , m.p. 125—126° (*triacetate*, m.p. 98—100°), which is oxidised to *deacetyltetrahydro- $\psi$ -bufotalone-A*,  $C_{23}H_{38}O_5$ , m.p. 158—159° (*oxime*, m.p. 124—125°; *p*-nitrophenylhydrazone, m.p. 158—159°; *triacetate*, m.p. 163—164°). On further Grignard cleavage this yields *deacetyltetrahydromethyl- $\psi$ -bufotalene-B* (I),  $C_{24}H_{40}O_4$ , m.p. 120—121°, whilst oxidation affords a OH-aldehyde, *deacetyltetrahydro- $\psi$ -bufotal*,  $C_{21}H_{34}O_5$ , m.p. 145—147°. (I), when heated in xylene, gives *deacetyltetrahydromethyl- $\psi$ -bufotalindiene*,  $C_{24}H_{38}O_3$ , m.p. 118—120°, oxidised to *deacetyltetrahydro- $\psi$ -bufotalene-B*,  $C_{20}H_{32}O_4$ , m.p. 127—129° (*p*-nitrophenylhydrazone, m.p. 172—175°; *diacetate*, m.p. 115—117°); with  $AcO_2H$  this yields a substance,  $C_{20}H_{32}O_5$ , m.p. 135—136° (*p*-nitrophenylhydrazone, decomp. 167—169°), whilst Grignard cleavage affords *deacetyltetrahydromethyl- $\psi$ -bufotalene-C*,  $C_{21}H_{34}O_3$ , m.p. 135—136°. This is oxidised to *deacetyltetrahydro- $\psi$ -bufotalone-C*,  $C_{18}H_{28}O_4$ , m.p. 117—119°, which, on Grignard cleavage, affords *deacetyltetrahydromethyl- $\psi$ -bufotalene-D*,  $C_{19}H_{30}O_3$ , m.p. 102—103°, oxidised to *deacetyltetrahydromethyl- $\psi$ -bufotalene oxide*,  $C_{19}H_{30}O_4$ , m.p. 159—160°. This latter, with  $O_3$ , yields *deacetyltetrahydromethyl- $\psi$ -bufotalonal*,  $C_{19}H_{30}O_5$ , m.p. 110—111° (*mono*-, m.p. 105—106°, and *di*-, m.p. 115—117°, *acetate*; *oxime*, decomp. 126—127°), which, with  $AcO_2H$ , affords *deacetyltetrahydromethyl- $\psi$ -bufotalonic peroxide*,  $C_{38}H_{60}O_{14}$ , decomp. 193—195°, yielding, with dil. NaOH, *deacetyltetrahydromethyl- $\psi$ -bufotalonic acid*,  $C_{19}H_{30}O_6$ , m.p. 184—185°. CH. ABS. (r)

**Identity of evodin, dictamnolactone, and obakulactone.** A. FUJITA, T. TAKU, and N. KUTANI (J. Pharm. Soc. Japan, 1935, **55**, 248—251).—The identity is indicated by m.p. and  $[\alpha]$ . CH. ABS. (r)

**Bilifuscin.**—See this vol., 501.

**Preparation of tetrahydrofurfuryl bromide and its reaction with magnesium.** R. ROBINSON and L. H. SMITH (J.C.S., 1936, 195—196).—Contrary to Paul (A., 1933, 954) the product of the interaction



of Mg with tetrahydrofurfuryl bromide (I) (improved prep.) in pure dry  $\text{Et}_2\text{O}$ , wet and commercial  $\text{Et}_2\text{O}$ , and in  $\text{Et}_2\text{O}$ - $\text{EtOH}$  (6:1) is always  $\Delta^8$ -penten- $\alpha$ -ol, only traces of tetrahydrofuran and of recovered (I) being obtained.

J. W. B.

**Hydroxyfurans. I. 3-Hydroxy-2:4:5-triphenylfuran.** E. P. KOHLER, F. H. WESTHEIMER, and M. TISHLER (J. Amer. Chem. Soc., 1936, 58, 264—267).—Successive treatment of 3-acetoxy-2:4:5-triphenylfuran (I) (Thiele, A., 1898, i, 469) with  $\text{MgMeI}$  and cold dil.  $\text{H}_2\text{SO}_4$  gives 3-hydroxy-2:4:5-triphenylfuran (II) (not isolable), which has no phenolic properties, but resembles an active open-chain enol. (II) (in  $\text{Et}_2\text{O}$ ) and  $\text{O}_2$  afford the 2:3-peroxide (III), decomp. about  $120^\circ$ . Hydrolysis (dil.  $\text{H}_2\text{SO}_4$  in  $\text{AcOH}$  and  $\text{N}_2$ ) of (I) gives 3-keto-2:4:5-triphenyl-2:3-dihydrofuran, m.p.  $112^\circ$  [the ketonic form of (II)], which is only slowly oxidised ( $\text{O}_2$ ) to (III). The deep yellow colour of (II) precludes direct titration with  $\text{Br}$ ; indirect titration is vitiated owing to the production of (III). Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOAc}$ ) of (III) gives 2-hydroxy-3-keto-2:4:5-triphenyl-2:3-dihydrofuran (IV), m.p.  $191^\circ$  [*Me ether* (V), m.p.  $138^\circ$ , formed by the action of  $\text{MeOH}$ - $\text{H}_2\text{SO}_4$ ; *Et ether*, m.p.  $111^\circ$ ; acetate (VI), m.p.  $138$ — $139^\circ$ ], converted by  $\text{Br}$  into 2-bromo-3-keto-2:4:5-triphenyl-2:3-dihydrofuran (VII), m.p.  $154^\circ$  [decomp. yielding (VIII) (below)], which is most conveniently prepared from (I) and  $\text{Br}$  in boiling  $\text{CCl}_4$ . (VII) is converted by  $\text{MeOH}$  into (V). Reduction of (III) by methods other than the above affords (IV) and 3:3'-diketo-2:4:5:2':4':5'-hexaphenyl-2:3:2':3'-tetrahydro-2:2'-difuryl (VIII),  $272$ — $274^\circ$  [also obtained from (VII) and Cu-bronze in  $\text{C}_6\text{H}_6$ ]. (IV) and  $\text{SOCl}_2$  give 2-chloro-3-keto-2:4:5-triphenyl-2:3-dihydrofuran, m.p.  $149$ — $150^\circ$ . (IV) and  $\text{Na}$  in  $\text{Et}_2\text{O}$  give a Na derivative, which with  $\text{CO}_2$ ,  $\text{AcCl}$ , and  $\text{MeI}$  (or  $\text{Me}_2\text{SO}_4$ ) affords (IV), (VI), and (V), respectively; treatment with  $\text{Br}$  gives  $\gamma$ -bromo- $\alpha\beta\delta$ -triketo- $\alpha\gamma\delta$ -triphenylbutane, m.p.  $111^\circ$ , which is reduced catalytically to (IV).

H. B.

#### Occurrence of furan derivatives in volatile oils.

**II.  $\alpha$ -Clausenan and di- $\alpha$ -clausenan.** B. S. RAO and K. S. SUBRAMANIAM (Proc. Indian Acad. Sci., 1935, 2, A, 574—579).— $\alpha$ -Clausenan (I) (A., 1935, 134) combines with maleic anhydride to give the anhydride  $\text{C}_{14}\text{H}_{14}\text{O}_4$ , m.p.  $85^\circ$ , of the acid  $\text{C}_{14}\text{H}_{16}\text{O}_5$ , m.p. ( $+9\text{H}_2\text{O}$ )  $98^\circ$ , (anhyd.)  $248^\circ$ . With  $\text{HgCl}_2$  (I) gives the substance  $\text{C}_{10}\text{H}_{10}\text{O}(\text{HgCl})_2$ . (I) is oxidised by  $\text{FeSO}_4$  to a mixture of  $\alpha$ -clausenyl alcohol,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , b.p.  $89$ — $90^\circ/30$  mm. (*Ac* derivative, b.p.  $98$ — $102^\circ/30$  mm.; phthaloyl derivative), a primary alcohol, with an isomeric tert.-alcohol, b.p.  $<93^\circ/30$  mm., dehydrated by  $\text{Na}$  to (I). With  $\text{KMnO}_4$ , (I) yields a ketone,  $\text{C}_9\text{H}_{10}\text{O}_2$ , b.p.  $95$ — $96^\circ/55$  mm. (*oxime*), with traces of an acid (*anilide*, m.p.  $154^\circ$ ).  $\text{HNO}_3$  (*d* 1.12) has little action on (I) at  $<30^\circ$ ; with fuming  $\text{HNO}_3$  in  $\text{AcOH}$ , a nitroketone,  $\text{C}_9\text{H}_9\text{O}_4\text{N}$ , charring at  $130^\circ$ , is formed.  $\text{HCO}_2\text{H}$  at  $0^\circ$  gives a resinous product, b.p.  $240^\circ/2$  mm., and no di- $\alpha$ -clausenan (II) (*loc. cit.*). (II) does not combine with maleic anhydride; with fuming  $\text{HNO}_3$  it yields a substance,  $\text{C}_{18}\text{H}_{18}\text{O}_8\text{N}_2$ , charring at  $140^\circ$ , and with  $\text{HgCl}_2$  the compound  $\text{C}_{20}\text{H}_{22}\text{O}_2(\text{HgCl})_2$ . Na

in  $\text{EtOH}$  reduces (II) to a compound, b.p.  $100$ — $101^\circ/4$  mm.

E. W. W.

**Passage from the sugar to the pyran and pyrrole series. Methylisopyromucic acid.** E. VOTOCEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1936, 8, 66—78).—Distillation of thamnono- (I), *d*-fucono-, and (probably) *d*-glucono-lactone, and  $\alpha\beta\alpha'\beta'$ -tetrahydroxy- $\alpha$ -methyladipilactone gives 3-hydroxy-6-methyl-1:2-pyrone ("methylisopyromucic lactone"), m.p.  $120$ — $121^\circ$ , which gives a green colour with  $\text{FeCl}_3$ , reduces Fehling's solution and  $\text{AgNO}_3$ , and gives a *Br*-, m.p.  $147^\circ$ , and *Bz* derivative, m.p.  $121$ — $122^\circ$ . Peligot's sugar decomposes when distilled. Ba fuconate gives an unidentified aldehyde. (I) is resinified by  $\text{HCl}$  at  $150^\circ$ . Distillation of  $(\text{NH}_4)_2\alpha\beta\alpha'\beta'$ -tetrahydroxy- $\alpha$ -methyladipate or  $\text{NH}_4$  rhamnionate with  $(\text{NH}_4)_2\text{CO}_3$ , best in glycerol under  $\text{NH}_3$ , gives 2-methylpyrrole.

R. S. C.

**Synthetical experiments in the chromone group. XVIII. Demethylation with aluminium chloride.** K. C. GULATI and K. VENKATARAMAN (J.C.S., 1936, 267—269).—Demethylation of 2:4:6-trimethoxyacetophenone (improved prep.) with  $\text{AlCl}_3$  in  $\text{PhCl}$  gives the 2:4-dihydroxy-6-methoxy-compound (Sonn *et al.*, A., 1925, i, 1267) (4-benzyl ether, m.p.  $72^\circ$ ). 2-Benzoyloxy-4:6-dimethoxyacetophenone, m.p.  $91^\circ$  (from  $\text{BzCl}$ - $\text{C}_2\text{H}_5\text{N}$  and the 2-OH-compound), with  $\text{NaNH}_2$  in  $\text{Et}_2\text{O}$  and treatment of the diketone with 20%  $\text{H}_2\text{SO}_4$ - $\text{EtOH}$ , affords chrysin  $\text{Me}_2$  ether (I), m.p.  $143^\circ$  (lit., m.p.  $115$ — $117^\circ$ ), also obtained from chrysin (II)- $\text{Me}_2\text{SO}_4$ - $\text{COMe}_2$ -20%  $\text{NaOH}$ , or by the action of 20%  $\text{H}_2\text{SO}_4$ - $\text{EtOH}$  on the product (containing 2-hydroxy-4:6-dimethoxy-dibenzoylmethane) of the action of  $\text{AlCl}_3$  on 2:4:6-trimethoxybenzoylacetophenone (III) in  $\text{PhNO}_2$ . (I) with  $\text{AlCl}_3$ - $\text{PhNO}_2$  at  $100^\circ$  affords tecto-chrysin (IV), but when heated with solid  $\text{AlCl}_3$ , (II) and (IV) are obtained. (III) with  $\text{HI}$  (*d* 1.7)- $\text{Ac}_2\text{O}$  also gives (II) and (IV). The crude product of interaction of phloracetophenone and  $\text{Bz}_2\text{O}$ , with  $\text{Me}_2\text{SO}_4$ - $\text{COMe}_2$ -10% aq.  $\text{NaOH}$  gave, in one experiment, (I) and its 3-*Bz* derivative, m.p.  $212^\circ$ , and, in another, (II) and 2-hydroxy-4:6-dibenzoyloxy- $\omega$ -benzoylacetophenone, m.p.  $157^\circ$ . (II) with either  $\text{CH}_2\text{PhCl}$ - $\text{COMe}_2$ - $\text{K}_2\text{CO}_3$  or  $\text{CH}_2\text{PhBr}$ -aq.  $\text{EtOH}$ - $\text{KOH}$  affords 5-hydroxy-7-benzoyloxy-6-benzylflavone, m.p.  $205^\circ$ .

J. W. B.

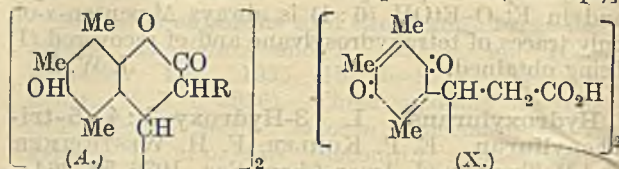
**Hydroxy-carbonyl compounds. X. Coumarins and chromones from *m*-4-xyleneol.** D. G. FLYNN and A. ROBERTSON (J.C.S., 1936, 215—217).—Condensation of *m*-4-xyleneol (I) with  $\text{CHRAc}\cdot\text{CO}_2\text{Et}$  gives (a) coumarins by Pechmann's method, and (b) chromones by that of Simonis, when  $\text{R}=\text{H}$ ,  $\text{Me}$ ,  $\text{Et}$ : when  $\text{R}=\text{CH}_2\text{Ph}$  or with  $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$  (b) fails to give condensation products. (I) and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  with 86%  $\text{H}_2\text{SO}_4$  give 4:6:8-trimethylcoumarin (II), converted (Canter *et al.*, A., 1931, 1069) into 2-methoxy- $\beta$ :3:5-trimethylcinnamic acid, m.p.  $139^\circ$ , oxidised to 2-methoxy-3:5-dimethylacetophenone, b.p.  $134$ — $135^\circ/21$  mm. (*semicarbazone*, m.p.  $193^\circ$ ), also obtained by methylation of the 2-OH-compound (III). 3:4:6:8-Tetramethyl- (IV), 4:6:8-trimethyl-3-ethyl-, m.p.  $112.5$ — $113^\circ$ , 4-phenyl-6:8-dimethyl-, m.p.  $111^\circ$ , and 3-benzyl-4:6:8-trimethyl-, m.p.  $112$ — $113^\circ$ , -coumarin are similarly obtained,



whence 2-methoxy- $\alpha$ : $\beta$ :3:5-tetramethyl-, m.p. 139.5—140°, and - $\beta$ :3:5-trimethyl- $\alpha$ -ethyl-, m.p. 112°, cinnamic acid are prepared. (III) with EtOAc-Na at 100° gives 2-hydroxy- $\omega$ -acetyl-3:5-dimethylacetophenone, m.p. 85°, cyclised (AcOH-HCl) to the chromone, m.p. 125° [also from (I)-CH<sub>2</sub>Ac-CO<sub>2</sub>Et-P<sub>2</sub>O<sub>5</sub>], condensed with piperonal to give 2-(3':4'-methylenedioxystyryl)-6:8-dimethylchromone, m.p. 195°. The propionate of (I) with AlCl<sub>3</sub> affords 2-hydroxy-3:5-dimethylpropiophenone, m.p. 52—53°, converted by Ac<sub>2</sub>O-NaOAc at 180° into 2:3:6:8-tetramethylchromone, m.p. 136—137° [also from (I) and CHMeAc-CO<sub>2</sub>Et], whence 2-(3':4'-methylenedioxystyryl)-3:6:8-trimethylchromone, m.p. 196° is obtained. 2-Hydroxy-3:5-dimethyl-n-butyrophenone, b.p. 145—150°/30 mm., m.p. 30° [from the butyrate, b.p. 132—133°/17.5 mm. of (I)], 2:6:8-trimethyl-(V), m.p. 112.5°, and 2-(3':4'-methylenedioxystyryl)-6:8-dimethyl-, m.p. 202—203°, 3-ethylchromone, are obtained similarly. (III) with Ac<sub>2</sub>O-NaOAc at 170° affords (V), its 3-Ac derivative (isolated at its oxime, m.p. 119°), and (II). (III) and (EtCO)<sub>2</sub>O-EtCO<sub>2</sub>Na give (IV) and 3-propionyl-6:8-dimethyl-2-ethylchromone (as its oxime, m.p. 93°); (III) with BzO-NaOBz affords 3-benzoyl-6:8-dimethylflavone, m.p. 191—192°. With EtCO<sub>2</sub>Et and Na (III) gives 6:8-dimethyl-2-ethylchromone, m.p. 109—110°. J. W. B.

**Reaction between duroquinone and sodio-malonic ester.** III. Reduction products. L. I. SMITH and R. O. DENYES (J. Amer. Chem. Soc., 1936, 58, 304—309).—The Et ester (I), m.p. 183—184°, of 6-hydroxy-5:7:8-trimethylcoumarin-3-carboxylic acid (II), m.p. 256—258° (decomp.) (A., 1926, 836), is reduced (H<sub>2</sub>, PtO<sub>2</sub>, EtOH) to Et 6-hydroxy-5:7:8-trimethyl-3:4-dihydrocoumarin-3-carboxylate (III), m.p. 104—105° [acetate, m.p. 116—117°, also prepared by reduction of the acetate of (I)], which is hydrolysed (20% HCl in COMe<sub>2</sub>) to 6-hydroxy-5:7:8-trimethyl-3:4-dihydrocoumarin (IV), m.p. 173—174° (acetate, m.p. 147—148°), also obtained by reduction (as above) of (II). (IV) and Me<sub>2</sub>SO<sub>4</sub> in MeOH-KOH afford  $\beta$ -2:5-dimethoxy-3:4:6-trimethylphenylpropionic acid, m.p. 132—133° (amide, m.p. 188—189°), whilst (IV) and aq. MeOH-NaOH in C<sub>6</sub>H<sub>6</sub> give trimethyl- $\beta$ -carboxyethyl-p-benzoquinone (V), m.p. 113—114°, which is reduced (Zn dust, aq. AcOH) to (IV). 2:4:5-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>:CH:CH-CO<sub>2</sub>H, m.p. 154—155°, best prepared from 2:4:5-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>:CHO, Ac<sub>2</sub>O, and NaOAc at 170—180° in N<sub>2</sub>, is reduced to 2:4:5-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>:CH<sub>2</sub>:CH<sub>2</sub>-CO<sub>2</sub>H [Me ester (VI), b.p. 125—127°/4 mm.], which with HNO<sub>3</sub> (d 1.52) in CHCl<sub>3</sub>+conc. H<sub>2</sub>SO<sub>4</sub> gives  $\beta$ -3:6-dinitro-2:4:5-trimethylphenylpropionic acid, m.p. 206—207° [amide, m.p. 215—216°; Me ester, m.p. 164.5—165°, also prepared by similar nitration of (VI)]. This is reduced (SnCl<sub>2</sub>, HCl, AcOH) to 6-amino-5:7:8-trimethyl-3:4-dihydrocarbostyryl, m.p. 223—224° (Ac derivative, m.p. 320°), which is oxidised (FeCl<sub>3</sub>, dil. HCl) to (V). Reduction (Zn, AcOH) of (I) gives (III), Et 6:6'-dihydroxy-5:7:8:5':7':8'-hexamethyl-3:4:3':4'-tetrahydro-4:4'-dicoumarinyl-3:3'-dicarboxylate (VII) (A., R=CO<sub>2</sub>Et), m.p. 212—213° (decomp.) (diacetate, m.p. 218—219°), and 6:6'-dihydroxy-5:7:8:5':7':8'-hexamethyl-3:4:3':4'-tetrahydro-

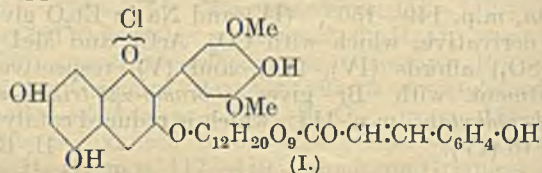
4:4'-dicoumarinyl (VIII) (A., R=H), m.p. 290—292° (decomp.) [diacetate, m.p. 298° (decomp.)].



Similar reduction of (II) affords (IV) and (VIII). (VII) is hydrolysed (50% H<sub>2</sub>SO<sub>4</sub>, EtOH) to (VIII) which with Me<sub>2</sub>SO<sub>4</sub> in MeOH-KOH affords  $\beta\beta'$ -di-(3:5-dimethoxy-3:4:6-trimethylphenyl)adipic acid (IX), m.p. 309° (decomp.) (Me<sub>2</sub> ester, m.p. 217—218°). Hydrolysis (3% NaOH) of (VIII) gives  $\beta\beta'$ -di-(3:4:6-trimethyl-2:5-benzoquinonyl)adipic acid (X), m.p. 256—258° (decomp.) (Me<sub>2</sub> ester, m.p. 293—294°), reduced (Zn, AcOH) to (VIII). A ketone could not be obtained from (IX) and Ac<sub>2</sub>O at 300° or by pyrolysis of the Th salt. No evidence has been obtained that (I) or (II) reacts in a tautomeric form. The prep. of duroquinone (*loc. cit.*) is improved. The reaction between a fully methylated quinone and Na enolates appears to be a general method of prep. of 3-substituted 6-hydroxypolymethylcoumarins.

H. B.

**Colouring matters of violet potatoes.** I. CHMIELEWSKA (Rocz. Chem., 1935, 15, 491—505).—Negretein (I) (picrate) and tuberlin chlorides (II) are pptd. by Et<sub>2</sub>O from the HCl-MeOH extract of Negress potatoes. (I) (+8, 4, or 1 H<sub>2</sub>O) yields negretin (III) (picrate; chloride) and p-hydroxycinnamic acid when hydrolysed with 10% aq. NaOH at 0°, and (III) affords malvidin chloride, glucose, and isorhodeose with 20% HCl at the b.p. (3 min.). This suggests the appended structure for (I).



(II) yields glucose and tuberidin chloride (IV) when hydrolysed with 20% HCl, and p-OH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H is obtained by the alkaline hydrolysis of (IV), so that (IV) is a Me<sub>1</sub> ether of 3:5:6:7:8:4'-hexahydroxyflavylium chloride, and (II) is its 3-glucoside.

R. T.

**Colour and constitution of dyes derived from fluorenone.** M. K. MUKHERJEE and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—1935, 5, 234—239; cf. A., 1931, 627).—Fluorenone (1 mol.) with a phenol or aminophenol (2 mols.) at 180—200° in presence of dry HCl affords fluorenylidene-xanthenes. The following are prepared: 3:6-dihydroxy-, m.p. 232° (Br<sub>2</sub>-, m.p. > 300°, Bz<sub>2</sub>-, m.p. 212°, and Na<sub>2</sub> derivatives) (from resorcinol); 4:5-dihydroxy-, m.p. 169° (Br<sub>2</sub>-, m.p. > 300°, Bz<sub>2</sub>-, m.p. 141°, and Na<sub>2</sub> derivatives) (from phloroglucinol); 3:4:5:6-tetrahydroxy-, m.p. 181° (Na<sub>2</sub> derivative) (from pyrogallol); 3:6-dihydroxy-1:8-dimethyl-, m.p. > 300° (from orcinol); 3:6-tetramethyldiamino-, m.p. 111° (from m-OH-C<sub>6</sub>H<sub>4</sub>-NMe<sub>2</sub>); and 3:6-tetramethyldiamino-9-fluorenylidene-xanthen, m.p. 127° (from



$m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}_2$ ). The absorption max. of these dyes are analogous to those of the phthaleins, but their colour (not due to a quinonoid form) and fluorescence are less intense. J. L. D.

#### Action of sulphuric acid on diarylphthalins.

I. F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1936, 58, 276—278).—Contrary to Baeyer (A., 1880, 650), tetrabromophenolphthalin [prepared from phenolphthalin (I) and Br in AcOH], m.p. 209—210° (lit. 205° and 208—209°) [ $\text{Ac}_2$  derivative, m.p. 186—187° (decomp.) (lit. 165—166°)], is converted by conc.  $\text{H}_2\text{SO}_4$  into 2:5-di-(3':5'-dibromo-4'-hydroxyphenyl)-3:4-benzofuran, m.p. 240—242° (decomp.) [ $\text{Ac}_2$  derivative, m.p. 264—266° (decomp.)], which is oxidised ( $\text{KMnO}_4$ , aq. NaOH) to 3:5-dibromo-4-hydroxy-2'-(3':5'-dibromo-4'-hydroxybenzoyl)benzophenone, m.p. 298—301° (decomp.), also prepared from 4'-hydroxy-2-*p*-hydroxybenzoylbenzophenone and Br in EtOH. Reduction (Zn dust, aq. NaOH) of tetrabromophenolphthalein gives (I) (cf. *loc. cit.*). *iso*Phenolphthalein, m.p. 201—202° (from 2-*o*-hydroxybenzoylbenzoic acid, PhOH, and  $\text{ZnCl}_2$  at 90—100°), is reduced to the phthalin, m.p. 193—194° (lit. 189—190°), which is methylated ( $\text{Me}_2\text{SO}_4$ , 10% NaOH) to 2':4''-dimethoxytriphenylmethane-2-carboxylic acid, m.p. 211—212°. This and conc.  $\text{H}_2\text{SO}_4$  give 2-*o*-anisyl-5-*p*-anisyl-3:4-benzofuran (also prepared from *o*-OMe· $\text{C}_6\text{H}_4\cdot\text{MgI}$  and  $\alpha$ -*p*-anisylphthalide), which is oxidised ( $\text{Na}_2\text{Cr}_2\text{O}_7$ , AcOH) to 4'-methoxy-2-*o*-methoxybenzoylbenzophenone, m.p. 109—110° [bis-*p*-bromophenylhydrazone, m.p. 163—165° (decomp.)]. Oxidation [ $\text{K}_2\text{Fe}(\text{CN})_6$ , 10% NaOH] of 2:5-di-*p*-hydroxyphenyl-3:4-benzofuran affords 4'-hydroxy-2-*p*-hydroxybenzoylbenzophenone. H. B.

#### Synthesis of rotenone and its derivatives.

VIII. Netoric acid and toxicaric acid. A. ROBERTSON and G. L. RUSBY (J.C.S., 1936, 212—214).—*Et* derrate, m.p. 64° (by esterification of the acid), is converted by Na in PhMe at 100° into *Et* 3-hydroxy-6:4-dimethoxy- $\Delta^3$ -chromene-4-carboxylate, m.p. 109—110° [ $\text{Ac}$  derivative (I), m.p. 84°], reduced (Adams) to *Et* 3-hydroxy-6:7-dimethoxychroman-4-carboxylate (*Et* hydroxynetorate), m.p. 106°, dehydrated (boiling  $\text{Ac}_2\text{O}$ ) and hydrolysed to 6:7-dimethoxy- $\Delta^3$ -chromene-4-carboxylic acid, m.p. 210—211° (decomp.), identical with toxicaric acid. Reduction of (I) (Adams) and subsequent hydrolysis with aq. KOH affords 6:7-dimethoxychroman-4-carboxylic acid +  $\text{H}_2\text{O}$ , m.p. 90—91° (rapid heating), and anhyd., m.p. 132—133°, identical with netoric acid. When boiled with  $\text{Ac}_2\text{O}$ -NaOAc, derric acid affords a substance, m.p. 85°, probably 3-acetoxy-6:7-dimethoxy- $\Delta^3$ -chromene, hydrolysed by aq. EtOH-NaOH at 25° to a substance, decomp. 203—204°, possessing ketonic properties. J. W. B.

Preparation of 1:4-dithiens. R. H. BAKER and C. BARKENBUS (J. Amer. Chem. Soc., 1936, 58, 262—264).— $\text{COAr}\cdot\text{CH}_2\cdot\text{S}_2\text{O}_3\text{Na}$  (from  $\text{COAr}\cdot\text{CH}_2\text{Cl}$  and  $\text{Na}_2\text{S}_2\text{O}_3$ ) are hydrolysed (dry or conc. HCl in EtOH) to  $\text{COAr}\cdot\text{CH}_2\cdot\text{SH}$ , which are immediately converted into 2:5-dihydroxy-2:5-diaryl-1:4-dithians and thence (by loss of  $2\text{H}_2\text{O}$ ) into 2:5-diaryl-1:4-dithiens (59—74% yield). Condensation occurs much

less readily with  $\text{COAr}\cdot\text{CHR}\cdot\text{SH}$ ; when R is Me and Ph the yields of dithien are 11% and 0, respectively. With  $\text{COMe}\cdot\text{CH}_2\cdot\text{SH}$ , a different condensation occurs; a compound (40.8% S), b.p. 77—78°/5 mm., is produced. The following are described: *Na phenacyl* (+ $\text{H}_2\text{O}$ ), *m-nitrophenacyl*,  $\beta$ -*naphthacyl*,  $\alpha$ -*methylphenacyl* (+ $\text{H}_2\text{O}$ ), *desyl* (I), and *acetonyl* (+ $3\text{H}_2\text{O}$ ) *thiosulphates*; 2:5-diphenyl-, m.p. 115—117°, 2:5-di-*m-nitrophenyl*-, m.p. 220—222°, 2:5-di- $\beta$ -*naphthyl*-, m.p. 198—200°, and 2:5-diphenyl-3:6-dimethyl-, m.p. 135—138°, 1:4-dithiens. Hydrolysis of (I) gives a trace of a compound (9.33% S), m.p. 184.5—185°. H. B.

Catalytic transformations of heterocyclic compounds. I. Transformations of furan into pyrrole and thiophen. J. K. JURIEV (Ber., 1936, 69, [B], 440—443).—Passage of furan (I) or furfuraldehyde and  $\text{NH}_3$  over non-ignited  $\text{Al}_2\text{O}_3$  at 450° gives pyrrole (II) in 30% yield. (I) and  $\text{H}_2$  similarly afford thiophen in 31% yield. The production of (II) from  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$  containing traces of  $\text{H}_2\text{O}$  in presence of  $\text{Al}_2\text{O}_3$  is probably due to intermediate formation of (I). H. W.

2:4-Dimethylpyrrole. H. FISCHER (Org. Syntheses, 1935, 15, 20—21).—The prep. from Et 2:4-dimethylpyrrole-3:5-dicarboxylate is described.

CH. ABS. (r)

Diethyl 2:4-dimethylpyrrole-3:5-dicarboxylate. H. FISCHER (Org. Syntheses, 1935, 15, 17—19).—The prep. from  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  is described in detail.

CH. ABS. (r)

Reactivity of bromine atoms in brominated pyridines. Preparation of some 2:6-disubstituted products of pyridine. H. J. DEN HERTOOG and J. P. WIBAUT (Rec. trav. chim., 1936, 55, 122—130).—The replacement of Hal. by  $\text{NH}_2$  in the 3 and 5 positions is described. 2:6- $\text{C}_5\text{H}_3\text{NBr}_2$  (cf. A., 1932, 522) when heated with NaOH in EtOH yields 6-bromo-2-ethoxypyridine (I), b.p. 218—219°, which when heated with NaOEt in EtOH in a sealed tube gives 2:6-diethoxypyridine, m.p. 21.5°. 6:2- $\text{C}_5\text{H}_3\text{NBr}\cdot\text{NH}_2$  (*loc. cit.*) similarly yields 2-amino-6-ethoxypyridine, b.p. 238° (*picrate*, m.p. 216—222°; *Ac* derivative, m.p. 136—137°), and with  $\text{NaNO}_2$  and  $\text{H}_2\text{SO}_4$  gives 6-bromo-2-hydroxypyridine, m.p. 123° (*Na* salt). 2:6- $\text{C}_5\text{H}_3\text{NBr}_2$  with  $\text{C}_5\text{H}_{11}\text{N}$  in  $\text{C}_5\text{H}_5\text{N}$  at 160° yields 6-bromo-2-piperidinopyridine, b.p. 120—125°/0.1 mm., which with  $\text{C}_5\text{H}_{11}\text{N}$  in  $\text{C}_5\text{H}_5\text{N}$  at 180° gives 2:6-dipiperidinopyridine, m.p. 39—40°. Similarly 6:2- $\text{C}_5\text{H}_3\text{NBr}\cdot\text{NH}_2$  and (I) give, respectively, 2-amino-6-piperidino-, b.p. 202°/30 mm., m.p. 38—39° (*Ac* derivative, m.p. 116—117°), and 6-piperidino-2-ethoxy-pyridine, b.p. 170°/22 mm. (*picrate*, two forms, m.p. 122° and 142°). 2- $\text{C}_6\text{H}_4\text{N}\cdot\text{Hal}$  does not react with Mg. The antiseptic properties of these compounds are described. F. R. G.

1-Methyl-2-pyridone. E. A. PRILL and S. M. McELVAIN (Org. Syntheses, 1935, 15, 41—44).—( $\text{C}_5\text{H}_5\text{NMe}$ ) $\text{MeSO}_4$  (from  $\text{C}_5\text{H}_5\text{N}$  and  $\text{Me}_2\text{SO}_4$ ) is oxidised with alkaline  $\text{K}_3\text{Fe}(\text{CN})_6$ . CH. ABS. (r)

Phenylhydrazone of *N*-phenylaminochelidamic ester. E. KOENIGS and H. GURLT (Ber., 1936, 69, [B], 358).— $\text{Et}_2$  acetonedioxalate and  $\text{NHPh}\cdot\text{NH}_2$  in boiling EtOH afford the phenyl-



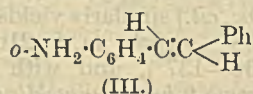
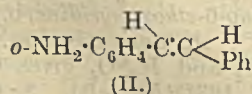
hydrazone of *Et*, 1-anilino-4-keto-1 : 4-dihydropyridine-2 : 6-dicarboxylate, m.p. 194°, which is not reduced to the corresponding  $\text{NH}_2$ -compound by  $\text{SnCl}_2$  and  $\text{HCl}$ . H. W.

**Indole compounds.** J. GNEZDA (Rad., 244, 13—15; Chem. Zentr., 1935, i, 3574).—Several colour reactions are described. H. N. R.

**Halogenated ketones. IIIa. Pyrrole. IVa. Skatole.** G. SANNA (Rend. Semin. Fac. Sci. Univ. Cagliari, 1934, 4, 59—61; Chem. Zentr., 1935, ii, 219; cf. A., 1933, 1169).—IIIa. Condensation of  $\text{CHMeBr}\cdot\text{COCl}$  with  $\text{Mg}$ -pyrrole affords 2- $\alpha$ -bromopropionylpyrrole, m.p. 106°, which gives a pyrrole-black with alkali.

IVa [with F. ATHENE]. Condensation of  $\text{Mg}$ -skatole with  $\text{CHCl}_2\cdot\text{COCl}$  or  $\text{CCl}_3\cdot\text{COCl}$  yields 1-di- or 1-tri-chloroacetyl-3-methylindole, which cannot readily be isolated as they break down into  $\text{CO}_2$ ,  $\text{CHCl}_3$ , and skatole; 2-substituted compounds are not obtained. H. N. R.

**Ring-closures of derivatives of 2-aminostyrene.** T. W. J. TAYLOR and (Miss) P. M. HOBSON (J.C.S., 1936, 181—184).—2-Acetamidostyrene (I) with  $\text{POCl}_3$  gives quinaldine, whilst adipodi-2-vinylanilide, m.p. 202°, obtained from 2-aminostyrene and adipyl chloride, similarly forms  $\alpha$ -di-(2-quinolyl)butane, m.p. 98°, and 2-n-hexamidostyrene, m.p. 61°, affords 2-n-amylquinoline (picrate, m.p. 104—105°; lit., 111—112°). (I) and  $\text{Br}$  yield (I) dibromide, m.p. 125°, which with  $\text{KOH}$  gives indole. *cis*-2-Nitrostilbene, obtained from 2-nitro- $\alpha$ -phenylcinnamic acid and  $\text{Cu}$  chromate, is reduced to the  $\text{NH}_2$ -compound, of which the *Ac* derivative, m.p. 112—113°, with  $\text{POCl}_3$ , yields 3-benzylidene-2-methylindolenine, also obtained from the corresponding *trans*-compound. Diazotisation of the *cis*- $\text{NH}_2$ -compound gives phenanthrene, but none is obtained from the *trans*-compound. The results indicate the structure (II) and (III) for *cis*- and *trans*-, (III) being the compound previously known.



Diazotisation of 4-aminophenylethyl alcohol affords  $\beta$ -4-bromophenylethyl alcohol, m.p. 36—38° (phenylurethane, m.p. 126°). F. R. S.

**Relation between chemical constitution and anaesthetic activity of 2-alkoxyquinoline derivatives.** H. WOJAHN (Arch. Pharm., 1936, 274, 83—106).—2-Chloro-4-quinoloyl chloride (I) (in  $\text{C}_6\text{H}_6$ ) and  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHAc}$  (in  $\text{H}_2\text{O}$ ) give 2-chloroquinoline-4-carboxyl- $\beta$ -acetamidoethylamide, m.p. 245°, converted by  $\text{EtOH}\cdot\text{NaOEt}$  into the 2-ethoxy-derivative, m.p. 209°. 2-Ethoxy-4-quinoloyl chloride (A., 1931, 1167) and  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COEt}$  similarly afford 2-ethoxyquinoline-4-carboxyl- $\beta$ -propionamidoethylamide, m.p. 204°; with  $\text{C}_2\text{H}_5(\text{NH}_2)_2$ ,  $\text{NN}'$ -di-2-ethoxy-4-quinolylethylenediamine, m.p. 280°, results. (I) (in  $\text{PhMe}$ ) and conc. aq.  $\text{NH}_3$  give 2-chloroquinoline-4-carboxylamide (II), m.p. 239—240°, converted by  $\text{NaOAlk}$  in  $\text{AlkOH}$  into 2-ethoxy-, m.p. 200—201°, and 2-butoxy-, m.p. 160°, -quinoline-4-carboxylamides.

2-Butoxyquinoline-4-carboxyldiethylamide\* (from the 2-Cl-derivative and  $\text{NaOBU}$ ) has b.p. 270°/20 mm., m.p. 62°. The above amides are converted by  $\text{NaOBr}$  into 2-chloro-4-amino-, m.p. 188° (hydrochloride, m.p. 250°), and 4-amino-2-ethoxy-, m.p. 128°, and -2-butoxy-, m.p. 85°, -quinoline, respectively. (II) is dehydrated by  $\text{SOCl}_2$  to 2-chloro-4-cyanoquinoline, m.p. 156°, which with  $\text{NaOAlk}$  gives 4-cyano-2-ethoxy-, m.p. 86°, and -2-butoxy-, b.p. 198°/18 mm., m.p. 31°, -quinoline, reduced ( $\text{H}_2$ ,  $\text{Pd}\cdot\text{BaSO}_4$ ,  $\text{AcOH}$ ) to 2-ethoxy-\* (III), b.p. 205°/20 mm., m.p. 53° [di-hydrochloride, m.p. 230° (decomp.)], and 2-butoxy-\* (IV), b.p. 225°/17 mm., m.p. 51° (dihydrochloride, m.p. >230°), -4-aminomethylquinoline, respectively. Catalytic reduction of the Schiff base from (III) and the appropriate  $\text{RCHO}$  or  $\text{CORR}'$  affords 2-ethoxy-4-propyl-, m.p. 207°, -4-benzyl-, m.p. 131°, and -4- $\beta$ -phenylethyl-, m.p. 250°, -aminomethylquinoline hydrochlorides, and 2-ethoxy-4-isobutyl-, m.p. 115°, and -4-phenylisopropyl-, m.p. 110°, -aminomethylquinoline dihydrochlorides. (IV) similarly gives 2-butoxy-4-propyl-, m.p. 213°, -4-benzyl-, m.p. 177°, -4- $\beta$ -phenylethyl-, m.p. 134°, and -4-phenylisopropyl-, m.p. 156°, -aminomethylquinoline hydrochlorides, and 2-butoxy-4-isobutyl-, m.p. 120°, and -4-phenylisopropyl-, m.p. 115°, -aminomethylquinoline dihydrochlorides. 2-Ethoxy-4- $\gamma$ -methylamino- (trihydrochloride, m.p. 121°), and -4- $\gamma$ -diethylamino- (trihydrochloride, m.p. 71°), - $\beta\beta$ -dimethylpropylaminomethylquinolines are similarly prepared from (III) and  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$  and  $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CHO}$ , respectively. (III) and  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NEt}_2\cdot\text{HCl}$  at 150—160° give 2-ethoxy-4- $\beta$ -diethylaminoethylaminomethylquinoline (trihydrochloride, m.p. 128°). 4-Cyano-2-ethoxyquinoline (V) and  $\text{MgMeI}$  ( $\pm 2$  mols.) in  $\text{PhOMe}$  afford 2-ethoxy-4-quinolyl *Me* ketone, m.p. 57° (hydrochloride, m.p. 108°; picrate, m.p. 101°), converted by  $\text{Br}$  in cold  $\text{CS}_2$  into the  $\text{CH}_2\text{Br}$  ketone hydrobromide, m.p. 80°, which with  $\text{EtOH}\cdot\text{NHET}_2$  affords 2-ethoxy-4-quinolyl diethylaminomethyl ketone, b.p. 175°/18 mm. (dihydrochloride, m.p. 65°), reduced ( $\text{H}_2$ ,  $\text{Pd}\cdot\text{BaSO}_4$ ,  $\text{EtOH}$ ) to 2-ethoxy-4- $\beta$ -diethylamino- $\alpha$ -hydroxyethylquinoline (hydrochloride, m.p. 157°). (V) and  $\text{MgEtI}$  similarly give 2-ethoxy-4-quinolyl *Et* ketone, b.p. 198—203°/20 mm. (hydrochloride, m.p. 90°; picrate, m.p. 158°), and thence the  $\alpha$ -bromoethyl (hydrobromide, m.p. 114°) and  $\alpha$ -diethylaminoethyl, b.p. 175—180°/18 mm. (dihydrochloride, m.p. 89°), ketones. 2-Ethoxy-4-quinolyl *Pr*, b.p. 190—200°/20 mm. (picrate, m.p. 150°),  $\alpha$ -bromopropyl (hydrobromide, m.p. 123°), and  $\alpha$ -diethylaminopropyl, b.p. 180°/20 mm. (dihydrochloride, m.p. 100°), ketones are similarly prepared. These  $\text{NEt}_2$ -ketones are vaso-constrictors. Of the various amines prepared, only those marked \* possess anaesthetic activity. These and previous results (*loc. cit.*) show that the 2-alkoxyquinolyl is the active group; the activity of percaïne [2-butoxyquinoline-4-carboxyl- $\beta$ -diethylaminoethylamide] is not due to the presence of the  $\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot$  grouping. The  $\text{CO}_2\text{H}$  (*cf. loc. cit.*) is not essential.

H. B.

$\alpha\beta$ -Diarylethylamines and their transformation into tetrahydroisoquinolines. I. B. REICHERT and W. HOFFMANN (Arch. Pharm., 1936,



274, 153—173).— $\alpha$ -Nitrostilbenes are hydrogenated (Pd-black) in  $C_6H_5N$  at 40—60° to deoxybenzoinoximes, which with 3% Na-Hg in EtOH-AcOH give the  $\alpha$ -diarylethylamines. These bases with hot aq.  $CH_2O$  give Schiff's bases, which are cyclised in excellent yield by hot 10% HCl to 3-aryltetrahydroisoquinolines if, but only if, Ar has OR in the *p*-position. A C-C chain could be attached to the *sec*.-N thus formed, but ring-closure with the 3-aryl nucleus could not be effected. The following are prepared by the above methods, the direction of ring-closure being proved by the reactions described.  $\beta$ -Nitro-3-methoxy- $\alpha$ - $\beta$ -diphenylethylene (from *m*-OMe- $C_6H_4$ ·CHO,  $CH_2Ph$ ·NO<sub>2</sub>, and a little  $NHMe_2$  kept in EtOH at room temp. for 4 days), m.p. 78°. Deoxybenzoinoxime, m.p. 94°; 3:4-methylenedioxy-, m.p. 138°, 3-methoxy-, m.p. 80°, 3:4-, m.p. 108°, and 2:4-dimethoxy-deoxybenzoinoxime, m.p. 91°.  $\alpha$ -Phenyl- $\beta$ -3:4-methylenedioxy-, m.p. 37—38°, b.p. 222—223°/17 mm. [acetate, m.p. 152—153°; hydrochloride, m.p. 258—259° (decomp.); Bz derivative, m.p. 180°], -4- (I), b.p. 202—203°/12 mm. (acetate, m.p. 135°; hydrochloride, m.p. 208—209°), and -3-methoxy-, b.p. 192°/11 mm. (hydrochloride, m.p. 205—207°), -3:4-, m.p. 67°, b.p. 233°/16 mm. (H oxalate, m.p. 176°; Bz derivative, m.p. 178°), and -2:4-dimethoxy-, b.p. 230—231°/18 mm. (hydrochloride, m.p. 214°; Bz derivative, m.p. 183—184°), and -4-hydroxyphenylethylamine [from (I) and 38% HCl at 150°], m.p. 159° (hydrochloride, m.p. 252° after sintering);  $\alpha$ -di-3:4-methylenedioxyphenylethylamine hydrochloride, m.p. 254° (lit. 245°). 6:7-Methylenedioxy (II), m.p. 82—83° [hydrochloride, m.p. 245—246° (decomp.); NO-derivative, m.p. 125°], 6:7-dimethoxy-, m.p. 96° [hydrochloride, m.p. 258° (decomp.); NO-derivative, m.p. 100°], and 6-methoxy-3-phenyl-1:2:3:4-tetrahydroisoquinoline (III), m.p. 72—73° (hydrochloride, m.p. about 263°); 6:7-methylenedioxy-3-3':4'-methylenedioxyphenyl-1:2:3:4-tetrahydroisoquinoline (IV), m.p. 124—125° (hydrochloride, m.p. 250—251°; NO-derivative, m.p. 149°). (II) and hot aq.  $KMnO_4$  afford 6:7-methylenedioxy-3-phenylisoquinoline (23% yield), m.p. 128° [hydrochloride, m.p. about 270°; methiodide, m.p. 239° (decomp.) after sintering], BzOH, and a small amount of a nitrogenous acid, m.p. 276°; (IV) and  $KMnO_4$  give similarly a small amount of 6:7-methylenedioxy-3-3':4'-methylenedioxyphenylisoquinoline, m.p. 210—211°. (II) and MeI yield 6:7-methylenedioxy-3-phenyl-2-methyl-1:2:3:4-tetrahydroisoquinoline methiodide, m.p. 268°, which (a) with Na-Hg in hot  $H_2O$  gives 4:5-methylenedioxy-2- $\beta$ -phenylethylbenzyl-dimethylamine (V), an oil (oxalate, m.p. 173°), the methiodide, m.p. 211°, of which with Na-Hg affords 4:5-methylenedioxy-2- $\beta$ -phenylethyltoluene, m.p. 49°, and (b) with hot conc. KOH gives 4:5-methylenedioxy-2-dimethylaminomethylstilbene, an oil (oxalate, m.p. 221—222°), hydrogenated (Pd-C) in warm  $H_2O$  to (V) and oxidised by hot aq.  $KMnO_4$  to BzOH and hydrastic acid. 6-Methoxy-3-phenyl-2-methyl-1:2:3:4-tetrahydroisoquinoline methiodide [from (III) and MeI], m.p. 255—258°, with hot conc. KOH gives 5-methoxy-2-dimethylaminomethylstilbene (oxalate, m.p. 181—182°), oxidised by  $KMnO_4$  to  $NHMe_2$ , BzOH, and 4-methoxyphthalic acid (anhydride, m.p. 92°).

(II) and (IV) with excess of  $CH_2Br$ · $CH_2$ ·OH give poor yields of 6:7-methylenedioxy-3-phenyl-, m.p. 92—93° (hydrochloride, m.p. 220—222°), and -3-3':4'-methylenedioxy-2- $\beta$ -hydroxyethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 49° (hydrochloride, m.p. 258°); attempts to dehydrate these OH-bases by  $NaOEt$ ,  $P_2O_5$  in PhMe, and long boiling in tetralin were unsuccessful;  $SOCl_2$  in  $CHCl_3$  led to mixtures. R. S. C.

**Synthesis of succinic acid-isoquinoliniumbetaines.** O. LUTZ and A. KRAUHLIS (Ber., 1936, 69, [B], 419—422).—isoQuinoline (I) and maleic acid (II) in abs.  $Et_2O$  at room temp. afford isoquinolinium *H* maleate, m.p. 103°, which passes when heated into succinic acid-isoquinoliniumbetaine (III),  $C_9H_7N$ — $\begin{matrix} \text{CH} \cdot \text{CO}_2\text{H} \\ \text{O} \cdot \text{CO} \cdot \text{CH}_2 \end{matrix}$ , m.p. (anhyd.) 151—152°, m.p. (+1H<sub>2</sub>O) 149—150°, better obtained by keeping (I) and (II) in MeOH or  $H_2O$  for some time at room temp. or by heating them in  $H_2O$  at 50—60°. (III) is also obtained similarly from (I) and fumaric acid and also appears to be produced from *l*-bromosuccinic acid. H. W.

**Carbon double linkings and nitrogen-carbon linkings. XIII. Degradation of quaternary ammonium compounds by catalytic hydrogenation.** H. EMDE and H. KULL (Arch. Pharm., 1936, 274, 173—184; cf. A., 1934, 515).—Many quaternary  $NH_4$  salts are hydrogenated to *tert*.-bases but the reaction differs in ease and often in course from the Na-Hg reduction.  $CH_2$ · $CH$ · $CH_2$ · $NMe_3I$  with  $H_2$ -Pt (not Pd) in AcOH or  $H_2O$  gives  $NMe_3$  (63%), a little  $C_3H_6$ , more  $C_3H_8$ , and much  $NMe_3Pr^+I$  (unaffected by hydrogenation).  $CHPh$ · $CH$ · $NMe_3Cl$  with  $H_2$ -Pt or -Pd gives  $PhPr^+$  (70%),  $NMe_3$ , and  $Ph$ · $[CH_2]_3$ · $NMe_3Cl$  (not degraded by hydrogenation, but slowly giving the cyclohexyl derivative).  $CH_2Ph$ · $NPhMe_2Cl$  with  $H_2$ -Pd gives PhMe and  $NPhMe_2$ , with  $H_2$ -Pt methylcyclohexane (I) and cyclohexyldimethylamine (platini-, m.p. 158°, and auri-chloride, m.p. 105°).  $CH_2$ · $CH$ · $CH_2$ · $NMeI$ · $CH_2Ph$ ,  $CH_2Ph$ · $NMe_3Cl$ , and  $CH_2Ph$ · $NMe_3I$  are unaffected by  $H_2$ -Pd, but the two last salts with  $H_2$ -Pt give  $NMe_3$  (96%) and PhMe [or by longer hydrogenation (I)].  $(CH_2Ph)_2NMe_2I$  with  $H_2$ -Pd in 50% AcOH or  $(CH_2Ph)_2NMe_2Cl$  with  $H_2$ -Pt in  $H_2O$  gives PhMe and  $NMe_3$ · $CH_2Ph$  very slowly.  $NPhMe_3Cl$  in AcOH with  $H_2$ -Pt (not Pd) gives slowly  $NMe_3$  and  $C_6H_6$  and then cyclohexane. 1-Methylpiperidine methiodide and methochloride, hygroscopic, cannot be hydrogenated. 1-Methyltetrahydroquinoline methiodide (methoaurichloride, m.p. 184°; methosulphate, m.p. 198°) with  $H_2$ -Pt (not Pd) in  $H_2O$  (not AcOH) gives  $Ph$ · $[CH_2]_3$ · $NMe_2$ , and 2-methyltetrahydroisoquinoline methiodide, m.p. 189°, or methochloride (methoaurichloride, m.p. 187°) yields similarly  $\beta$ -o-tolyethyl-dimethylamine, b.p. 223—224° [hydrochloride, m.p. 221°; platinichloride, m.p. 168° (decomp.); picrate, m.p. 126—127°; methoaurichloride, m.p. 156°, and -picrate, m.p. 152°]. Hydrogenation of  $o$ - $CH_2$ · $CH$ · $C_6H_4$ · $CH_2$ · $NMe_2$  affords *o*-ethylbenzyl-dimethylamine (auri-, m.p. 148°, and platini-chloride, m.p. 166—167°; picrate, m.p. 133—5°; methiodide, m.p. 226°; methoaurichloride, m.p. 187°). R. S. C.



**2:8-Dialkoxy-10-alkylacridinium derivatives** with various kinds of amino-group in the 5-position. X. Synthesis of 2:8-dialkoxy-5-*p*-aminoanilino-10-alkylacridinium derivatives and (2':8'-dialkoxy-10'-alkyl-10'-substituted-acridyl)-5:5'-*p*-phenylenediamino-2:8-dialkoxy-10-alkylacridinium derivatives. XI. Synthesis of 2:8-dialkoxy-5-piperazino-10-alkylacridinium and (2':8'-dialkoxy-10'-alkyl-10'-substituted-acridyl)-5:5'-piperazino-2:8-dialkoxy-10-alkylacridinium derivatives. K. ISHIIHARA (J. Chem. Soc. Japan, 1935, 56, 289—313, 457—485; cf. this vol., 343).—X. The following reactions are described for the 2:8-(OMe)<sub>2</sub>- and -(OEt)<sub>2</sub>-compounds, with OH and Cl as 10-acridinium anions: 5-chloro-2:8-dialkoxy-10-alkylacridinium chloride (I) and *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> give the hydrochloride (II) of the 5-*p*-aminoanilino-derivative (III) and the (acridinium) dialkoxide of NN'-bis-(2:8-dialkoxy-5-acridyl)-*p*-phenylenediamine, also obtained from (II) and (III).

XI. The (I) and piperazine (as above) give the hydrohalide (I as well as Cl) (IV) of the corresponding 5-piperazino-derivative and the (acridinium) dialkoxide (V) of NN'-bis-(2:8-dialkoxy-5-acridyl)-piperazine. (IV), with KOH·CHCl<sub>3</sub>, gives (V) and with H<sub>2</sub>O gives the 10-alkyl-5-acridone (VI), also formed by similarly treating either (V) or the (piperazinium or acridinium) dioxalate or the (acridinium) iodide or (piperazinium) oxalate corresponding with (IV). CH. ABS. (r)

**Sulphonation of acridone, and certain transformations of acridone-3-sulphonic acid.** M. POLACZEK (Rocz. Chem., 1935, 15, 565—577).—Acridone and conc. H<sub>2</sub>SO<sub>4</sub> at 100° yield acridone-3-sulphonic acid (I) [Ba and Pb salts; chloride; amide; Et ester, m.p. 232—233° (decomp.)], also synthesised by heating *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>K and K sulphanilate in H<sub>2</sub>O in presence of Cu (115—120°; 6 hr.), and condensing the K 4'-sulphodiphenylamine-2-carboxylate obtained in presence of POCl<sub>3</sub> at 115° (30 min.). When fused with KOH (I) yields 3-hydroxyacridone, m.p. 330—370° (benzoate, m.p. 285—287°), identical with the product obtained from 4'-ethoxydiphenylamine-2-carboxylic acid and H<sub>2</sub>SO<sub>4</sub> (100°; 15 min.). (I) in POCl<sub>3</sub> and NPhMe<sub>2</sub> (120°; 1 hr.) yield 3-*p*-dimethylaminobenzenesulphonyl-5-*p*-dimethylaminophenylacridone, m.p. 264—265°. (I) and 80% oleum at 100° afford acridone-3:7-disulphonic acid (Ba and Pb salts), also prepared from 2-chloro-5-sulphobenzoic acid and sulphanilic acid in presence of Cu and K<sub>2</sub>CO<sub>3</sub> (115—120°; 8 hr.), followed by condensation of the product with H<sub>2</sub>SO<sub>4</sub> at 100° R. T.

**Acridine compounds and their antimalarial action.** I. O. J. MAGIDSON and A. M. GRIGOROVSKI (Ber., 1936, 69, [B], 396—412).—Compounds of the type 8-chloro-5-diethylamino-R-amino-3-methoxyacridine have a very powerful antimalarial action which attains a max. when R=[CH<sub>2</sub>]<sub>4</sub>. Introduction of OH into the side-chain diminishes the therapeutic action if Cl is present, but increases it in the presence of NO<sub>2</sub>. Compounds without a substituent at 7 or 8 are therapeutically inactive. Increase in the size of 3-OAlk diminishes the therapeutic activity,

which vanishes if a second OMe is present. Protracted treatment of compounds of the above type with boiling H<sub>2</sub>O causes elimination of the 5-N-chain and production of acridones. With conc. HCl at 120—125° the 5-aminoacridone is formed, demethylation also occurring to some extent. The condensation of 5-chloroacridines with primary amines occurs only in presence of PhOH, since the 9-OPh-compounds readily react with amines under similar conditions, they appear to be intermediates.

α-Diethylaminobutan-γ-one is converted into the oxime, b.p. 141—142°/15 mm., which is reduced by Na powder in BuOH to γ-amino-α-diethylaminobutane, b.p. 72—74°/12 mm. NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub>, b.p. 145—149° atm. pressure, is obtained from *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·[CH<sub>2</sub>]<sub>2</sub>·Br and NEt<sub>2</sub> in boiling xylene followed by hydrolysis with 12*N*-HCl, and NH<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·NEt<sub>2</sub>, b.p. 55—58°/12 mm., is derived from *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·[CH<sub>2</sub>]<sub>3</sub>·Cl and NEt<sub>2</sub> or from *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK and NEt<sub>2</sub>·[CH<sub>2</sub>]<sub>3</sub>·Cl. ε-Diethylaminomethylamine, b.p. 205—208°, is obtained from NHBz·[CH<sub>2</sub>]<sub>5</sub>·Cl and NEt<sub>2</sub> at 100—120°, followed by hydrolysis with conc. HCl at 125°. NHBz·[CH<sub>2</sub>]<sub>5</sub>·Cl, PBr<sub>3</sub>, and Br give α-chloro-ε-bromopentane, b.p. 210—212°, transformed by the successive action of NaCN in MeOH and NEt<sub>2</sub> into ε-diethylaminohexonitrile, b.p. 92—97°/3.5 mm., reduced by powdered Na in abs. EtOH to α-amino-8-diethylaminohexane, b.p. 216—218° (aurichloride, m.p. 120—122°). *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H, K<sub>2</sub>CO<sub>3</sub>, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> in boiling amyl alcohol containing a trace of Cu powder give *N*-*p*-anisylanthranilic acid, m.p. 183—184°, transformed by boiling POCl<sub>3</sub> into 5-chloro-3-methoxyacridine, m.p. 152—153°. Nitration of *o*-C<sub>6</sub>H<sub>4</sub>Cl·CO<sub>2</sub>H and condensation of the product with *p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> affords 5-nitro-*N*-*p*-anisylanthranilic acid, m.p. 216—220°, transformed into 5-chloro-8-nitro-3-methoxyacridine, m.p. 220—221°. Aminoveratrole and 2:4-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CO<sub>2</sub>H afford 4-chloro-*N*-3':4'-dimethoxyphenylanthranilic acid, m.p. 190—191°, whence 5:7-dichloro-(?)2:3-dimethoxyacridine, m.p. 202—203°. Gradual addition of NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NEt<sub>2</sub> to a mixture of 5-chloro-3-ethoxyacridine and PhOH at 70—80° affords 5-β-diethylaminoethylamino-3-ethoxyacridine, m.p. 242—244°. The following acridines are obtained by similar methods: 7-nitro-5-β-diethylaminoethylamino-3-ethoxy-, m.p. 246—252°; 8-nitro-5-β-diethylaminoethyl-3-ethoxy-, m.p. 172—175° [dihydrochloride, m.p. 243—246° (decomp.)]; 7-nitro-5-γ-diethylaminopropylamino-3-ethoxy- [dihydrochloride (+H<sub>2</sub>O), m.p. 226—228°]; 7-chloro-5-γ-diethylaminopropylamino-3-methoxy- [dihydrochloride (+3H<sub>2</sub>O), m.p. 249—250°]; 8-nitro-5-γ-diethylamino-β-hydroxypropylamino-3-methoxy-, m.p. 124° (dihydrochloride, m.p. 213—214°); 7-chloro-5-β-hydroxy-γ-diethylaminopropylamino-3-methoxy-, m.p. 105—107° (dihydrochloride, m.p. 237—239°); 7-chloro-5-8-diethylaminobutylamino-3-methoxy-, m.p. 76—78° (dihydrochloride, m.p. 246—248°); 7-chloro-5-8-diethylamino-α-methylbutylamino-3-methoxy-, m.p. 86—88° (dihydrochloride, m.p. 246—248°); 5-γ-diethylaminopropylamino-3-methoxy- (dihydrochloride, m.p. 240—241°); 8-nitro-5-γ-diethylaminopropylamino-3-methoxy-, m.p. 122—123.5° (dihydrochloride, m.p. 229—230°); 7-chloro-5-γ-diethylaminopropyl-



amino-(?)2:3-dimethoxy- [dihydrochloride (+2H<sub>2</sub>O), m.p. 227—228°]; 7-chloro-5-di-( $\gamma$ -diethylaminopropyl)-amino-3-methoxy- (very unstable hydrochloride); 7-chloro-5-8-diethylamino- $\alpha$ -methylbutylamino-(?)2:3-dimethoxy- [dihydrochloride (+2H<sub>2</sub>O), m.p. 217—218°]; 7-chloro-5- $\gamma$ -diethylaminopropylamino-3-ethoxy- [dihydrochloride (+1H<sub>2</sub>O), m.p. 246—247°]; 7-chloro-5-8-diethylaminobutylamino-3-ethoxy- [dihydrochloride (+2H<sub>2</sub>O), m.p. 254—255.5°]; 7-chloro-5- $\gamma$ -diethylaminopropylamino-3-methyl- [dihydrochloride (+2H<sub>2</sub>O), m.p. 239—241°]; 7-chloro-5- $\epsilon$ -diethylaminoamylamino-3-methoxy- [dihydrochloride (+H<sub>2</sub>O), m.p. 266—268°]; 7-chloro-5- $\beta$ -diethylaminoethylamino-3-methoxy- (dihydrochloride, m.p. 258—259°); 7-chloro-5- $\gamma$ -diethylamino- $\alpha$ -diethylamino- $\alpha$ -methylpropylamino-3-methoxy- [dihydrochloride (+1H<sub>2</sub>O), m.p. 253—254°]; 7-chloro-5- $\epsilon$ -diethylaminoheptylamino-3-methoxy- (dihydrochloride, m.p. 232—235°). H. W.

Manufacture of acridine derivatives.—See B., 1936, 299.

Water-soluble salt of 3:6-diamino-10-methyl-acridinium.—See B., 1936, 220.

Optical activity dependent on co-ordinated bivalent ruthenium. F. H. BURSTALL (J.C.S., 1936, 173—175).—2:2'-Dipyridyl with RuCl<sub>3</sub> at 250° gives tris-2:2'-dipyridylruthenous chloride, from which the corresponding base, tris-2:2'-dipyridylruthenous bromide octahydrate, [Ru dipy<sub>3</sub>](OH)<sub>2</sub>·8H<sub>2</sub>O, and the bromide, iodide, perchlorate, nitrate, carbonate, and tartrate have been prepared. All these salts form hexahydrates, the carbonate also forming a decahydrate; they are more stable than the corresponding Fe<sup>++</sup> and Ni<sup>++</sup> salts. Resolution of the *d*- and *l*-tartrates gave *d*-, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +860°, [*M*] +7205°, and *l*-tris-2:2'-dipyridylruthenous bromide hexahydrate, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -815°, [*M*] -6828°, respectively. L. J. J.

Preparation of NN'-disubstituted barbituric and thiobarbituric acids. N. V. KOSCHKIN (J. Gen. Chem. Russ., 1935, 5, 1460—1467).—Disubstituted barbituric acids cannot be obtained from sodiomalonic ester and substituted carbamides and thiocarbamides, under various temp. conditions. NN'-Diphenylbarbituric acid, m.p. 238.5—239°, was obtained by heating a mixture of CO(NHPh)<sub>2</sub> (I) and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> with AcCl in dry CHCl<sub>3</sub> at the b.p. for 4 hr.; NN'-di-*o*-tolylbarbituric acid, m.p. 176.5—177°, and NN'-di-*o*-tolyl-, m.p. 216.5—217°, NN'-di- $\alpha$ -, m.p. 250—250.5° (decomp.), and NN'-di- $\beta$ -naphthylthiobarbituric acid, m.p. 247.5—248°, were obtained analogously. (I) and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> in xylene at the b.p. yield CH<sub>2</sub>(CO·NHPh)<sub>2</sub>. R. T.

[Glyoxalinecarboxylic esters.] W. JOHN (Ber., 1936, 69, [B], 484; cf. this vol., 211).—The ability of glyoxalinecarboxylic esters to lose CO<sub>2</sub> when heated is also shown by certain indazole- and pyrazolecarboxylic esters. H. W.

Synthesis of 1-phenyl-4- $\beta$ -hydroxyethylpiperazine. C. B. KREMER (J. Amer. Chem. Soc., 1936, 58, 379).—N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>3</sub>, NH<sub>2</sub>Ph, and conc. H<sub>2</sub>SO<sub>4</sub> give 1-phenyl-4- $\beta$ -hydroxyethylpiperazine, m.p. 84° (corr.) (lit. 83° and 91°). H. B.

Pyrimidines. CXLIX. Synthesis of aryl-substituted dihydrouacils and their conversion into uracils. T. B. JOHNSON and J. E. LIVAK (J. Amer. Chem. Soc., 1936, 58, 299—303).—Hydrobenzamide and CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> in cold EtOH give  $\beta$ -amino- $\beta$ -phenylethane- $\alpha\alpha$ -dicarboxylic acid, m.p. 153°; in the hot,  $\beta$ -amino- $\beta$ -phenylpropionic acid (I) results (cf. Rodionov *et al.*, A., 1929, 557; 1933, 1307). (I) is also prepared from CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, PhCHO, and EtOH·NH<sub>3</sub> or -NH<sub>4</sub>OAc.  $\beta$ -Amino- $\beta$ -anisylpropionic acid (II), m.p. 232° (decomp.), is similarly prepared using anishydramide. (I) and (II) with ArNCO give the  $\beta$ -arylcarbamido-acids, which are converted (usually by Ac<sub>2</sub>O) into 4-phenyl-1-aryl- (A) and 4-anisyl-1-aryl- (B) 4:5-dihydrouacils, respectively; ArNCS leads to the 2-thion analogues. Bromination of (A) in AcOH at 75—105° gives the 5-Br-derivative when aryl=Ph or *o*-tolyl; when aryl =  $\beta$ -C<sub>10</sub>H<sub>7</sub> or *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, bromination is retarded or inhibited. With (B), introduction of Br into the 3 position of the anisyl group first occurs; the resulting compounds then behave as (A). The following are described:  $\beta$ -carbamido-, m.p. 192° [from (I) and HNCO],  $\beta$ -phenylcarbamido-, m.p. 174°,  $\beta$ -*o*-tolylcarbamido-, m.p. 172°,  $\beta$ -2-naphthylcarbamido-, m.p. 201°,  $\beta$ -*p*-nitrophenylcarbamido-, m.p. 202—203°,  $\beta$ -1-naphthylcarbamido-, m.p. 184—186°, and  $\beta$ -phenylthiocarbamido-, m.p. 158°,  $\beta$ -phenylpropionic acids;  $\beta$ -carbamido-, m.p. 193°,  $\beta$ -phenylcarbamido-, m.p. 167—168°,  $\beta$ -*o*-tolylcarbamido-, m.p. 180—181°,  $\beta$ -1- and -2-naphthylcarbamido-, m.p. 178° and 191°, respectively,  $\beta$ -*p*-nitrophenylcarbamido-, m.p. 171—172°,  $\beta$ -methylcarbamido-, m.p. 168—169° [from (II) and MeNCO],  $\beta$ -phenylthiocarbamido-, m.p. 146°, and  $\beta$ -*o*-tolylthiocarbamido-, m.p. 163°,  $\beta$ -anisylpropionic acids; 4-phenyl-, m.p. 217° (5-Br-derivative, m.p. 214°), 4-anisyl-, m.p. 228° [3'-Br-, m.p. 232°, and 5:3'-Br<sub>2</sub>- (III), m.p. 193—194°, derivatives], 1:4-diphenyl-, m.p. 226° (5-Br-derivative, m.p. 220—223°), 1-phenyl-4-anisyl- (IV), m.p. 210°, 4-anisyl-1-*o*-tolyl- (V), m.p. 181°, 4-phenyl-1- $\beta$ -naphthyl-, m.p. 240—241°, 4-anisyl-1- $\beta$ -naphthyl- (VI), m.p. 256—257°, 4-phenyl-1-*p*-nitrophenyl-, m.p. 253—254°, 1-*p*-nitrophenyl-4-anisyl- (VII), m.p. 268—269°, 4-phenyl-1- $\alpha$ -naphthyl-, m.p. 192—193°, 4-anisyl-1- $\alpha$ -naphthyl-, m.p. 218—219°, 4-phenyl-1-methyl-, m.p. 149—151°, and 4-anisyl-1-methyl-, m.p. 138°, 4:5-dihydrouacils; 6-keto-2-thion-4-phenyl-, m.p. 238° (S-Me derivative, m.p. 163.5°), 4-anisyl-, m.p. 228°, 1:4-diphenyl-, m.p. 243°, 4-phenyl-1-*o*-tolyl-, m.p. 188°, 1-phenyl-4-anisyl-, m.p. 231—232°, and 4-anisyl-1-*o*-tolyl-, m.p. 188°, hexahydropyrimidines; 4-phenyl-, m.p. 267°, and 1:4-diphenyl-, m.p. 292—294°, -uracils, obtained by elimination of HBr from the appropriate 5-Br-derivative with C<sub>6</sub>H<sub>5</sub>N (general procedure); 4-3'-bromo-4'-methoxyphenyluracil, m.p. 304—305° [from (III)]. Bromination of (IV) gives 1-phenyl-4-3'-bromo-4'-methoxyphenyl-4:5-dihydrouacil, m.p. 210°, and then the 5-Br-derivative, m.p. 242°, which yields 1-phenyl-4-3'-bromo-4'-methoxyphenyluracil, m.p. 326—328°. 1-*o*-Tolyl-4-3'-bromo-4'-methoxyphenyluracil, m.p. 312°, and 4:5-dihydrouacil, m.p. 178° (5-Br-derivative, m.p. 201°), are similarly obtained from (V). (VI) gives 4-3'-bromo-4'-methoxyphenyl-1- $\beta$ -naphthyl-4:5-dihydrouacil,



m.p. 238—239°, which could not be brominated further; similarly, (VII) affords 1-*p*-nitrophenyl-4-3'-bromo-4'-methoxyphenyl-4 : 5-dihydrouracil, m.p. 194—196°.

H. B.

**Synthesis of 2-amino-4-ethylpyrimidine.** W. T. CALDWELL and W. M. ZIEGLER (J. Amer. Chem. Soc., 1936, 58, 287—288).—6-Chloro-2-ethylthiol-4-ethylpyrimidine, b.p. 110—112°/4—5 mm. (from the 6-OH-derivative and POCl<sub>3</sub>), is reduced (Zn dust, aq. EtOH) to 2-ethylthiol-4-ethylpyrimidine, b.p. 105—107°/4 mm., hydrolysed (conc. HCl) to 2-hydroxy-4-ethylpyrimidine hydrochloride, m.p. 211—213° (decomp.) (sinters about 200°). This and POCl<sub>3</sub> give 2-chloro-4-ethylpyrimidine, b.p. 89—91°/7 mm., converted by EtOH-NH<sub>3</sub> at 120—130° into 2-amino-4-ethylpyrimidine (I), b.p. 229°, m.p. 140—141° (picrate, m.p. 194·5—195·5°; aurichloride, m.p. 98—99°). 2-Amino-6-hydroxy-4-ethylpyrimidine, m.p. 243—245° (decomp.) (from guanidine carbonate and EtCO·CH<sub>2</sub>·CO<sub>2</sub>Et in EtOH), and POCl<sub>3</sub> give the 6-Cl-derivative, m.p. 129—130°, reduced (Zn dust, aq. EtOH) to (I). (I) differs from 6-amino-4-ethylpyrimidine (this vol., 344); the structure of the latter is thus established.

H. B.

**Piria reaction. III. Mechanism.** W. M. LAUER, M. M. SPRUNG, and C. M. LANGKAMMERER (J. Amer. Chem. Soc., 1936, 58, 225—228).—The isolation of 1 : 5-dimethylbenziminazole [tartrate, m.p. 185·2—185·8° (decomp.)] in 18·3% yield from the NaHSO<sub>3</sub>-reduction products of 3-nitro-4-dimethylaminotoluene indicates the intermediate formation of the NO-derivative. If NO-compounds are formed in this way, then the Piria reaction (A., 1931, 720) should occur with either the NO<sub>2</sub>- or NO-derivative. In agreement with this view, reduction (Na<sub>2</sub>SO<sub>3</sub>, NaHSO<sub>3</sub>, or mixtures) of *p*-C<sub>6</sub>H<sub>4</sub>Me·NO gives *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> (44—73%) and *p*-toluidine-3-sulphonic acid (I) (5·7—14·8%), i.e., the same products as are formed (*loc. cit.*) from *p*-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub> (II). Details are given for the isolation of Na<sub>2</sub> 3-sulpho-4-methylphenylsulphamate (+H<sub>2</sub>O) (III), from the NaHSO<sub>3</sub>-reduction products of (II); (III) is hydrolysed (dil. HCl) to (I) in quant. yield. (III) is also prepared from (I) and 1-pyridiniumsulphonic acid (Baumgarten, A., 1926, 1130) in aq. Na<sub>2</sub>CO<sub>3</sub> at 10°; Na<sub>2</sub> *m*- and *p*-sulphophenyl-, 4-sulpho-2-methylphenyl- (+2H<sub>2</sub>O), and 4-sulpho-1-naphthyl- (+2H<sub>2</sub>O) -sulphamates are similarly prepared. Reduction (alkaline Na metabisulphite) of *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH gives *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH and 4-aminophenol-2-sulphonic acid [since deamination (diazo-method) and subsequent bromination affords *s*-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·OH]. 5-Nitrosalicylic acid similarly yields 5-amino- and 5-amino-3-sulphosalicylic acid (deamination and bromination gives *s*-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·OH). In these cases, SO<sub>3</sub>H is introduced *meta* to NH<sub>2</sub>, presumably owing to 1 : 4-addition of NaHSO<sub>3</sub> to the ·N·C·C·C· of the intermediate nitroso-phenol (as quinoneoxime). The Piria reaction on (II) thus involves the following reactions: (a)  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2 \rightarrow p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO} \rightarrow p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{SO}_3\text{Na} \rightarrow p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ ; (b)  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO} \rightarrow 2 : 4\text{-SO}_3\text{Na}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{SO}_3\text{Na} \rightarrow \text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ .

H. B.

**Derivatives of quinazoline.** (Miss) T. M. REYNOLDS and R. ROBINSON (J.C.S., 1936, 196—199).—In part a reply to Späth (A., 1935, 873), and a detailed account of work already summarised (A., 1934, 1014). The following data are new: 3-allylquinazolinium iodide+0·33EtOH, m.p. 104—107° (picrate, m.p. 124°). When heated with MeNO<sub>2</sub> in EtOH, 4-hydroxy-3-allyl-3 : 4-dihydroquinazoline affords the 4-nitromethyl compound, isolated as its picrate, m.p. 152—153°, 4-nitromethyl-3-methyl-3 : 4-dihydroquinazoline, m.p. 137°, being obtained similarly. Passage of dry HCl into a mixture of HCO·NH<sub>2</sub>, 6-nitropiperonal, and C<sub>6</sub>H<sub>6</sub> at 60° affords 6-nitropiperonylidenediformamide, m.p. 248—250° (decomp.), converted by Zn dust-ice-AcOH into 6 : 7-methylenedioxyquinazoline, and, under certain conditions, into a non-diazotisable base, C<sub>9</sub>H<sub>6</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 260—261°. (I) when refluxed with MeI in EtOAc gives 6 : 7-methylenedioxy-3-methylquinazolinium iodide, m.p. 239—240° (picrate, softens 183°, m.p. 185—186°), converted by AgCl into the chloride, hydrolysed by aq. KOH at 2—10° to 4-hydroxy-6 : 7-methylenedioxy-3-methyl-3 : 4-dihydroquinazoline, softens 154°, m.p. 158—159°, converted by MeNO<sub>2</sub> into the 4-nitromethyl, m.p. 159—160°, by COMe<sub>2</sub>-aq. Na<sub>2</sub>CO<sub>3</sub> into the 4-acetonyl compound (picrate, sinters 184°, m.p. 187°), and by boiling 2% NaOH into 6-aminopiperonal.

J. W. B.

**Reaction between benzoyl chloride and aromatic amines, and their products, compounds of the quinazoline series.** K. DZIEWONSKI and L. STERNBACH (Bull. Acad. Polonaise, 1935, A, 333—348).—*p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> and BzCl with anhyd. ZnCl<sub>2</sub> at 180—200° afford 6-chloro-4-hydroxy-2 : 4-diphenyl-3-*p*-chlorophenyl-3 : 4-dihydro- (I), m.p. 159° (hydrochloride, m.p. 353°; picrate, m.p. 178°; Et ether, m.p. 225—226°), converted by heating at 250° into 6-chloro-2-hydroxy-2 : 4-diphenyl-3-*p*-chlorophenyl-2 : 3-dihydro-quinazoline (II), m.p. 199—201°. Hydrolysis of (I) or (II) with EtOH-HCl gives 5-chloro-2-benzamidobenzophenone (III), reconverted by SOCl<sub>2</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> into (II). Diazotisation of 5-chloro-2-aminobenzophenone (IV) [by EtOH-H<sub>2</sub>SO<sub>4</sub> hydrolysis of (III)] and coupling with β-C<sub>10</sub>H<sub>7</sub>·OH gives 4-chloro-2-benzoylbenzeneazo-β-naphthol, m.p. 184—185°. With NH<sub>3</sub>-EtOH at 140° (I) gives 6-chloro-2 : 4-diphenylquinazoline, m.p. 190·5°. With NH<sub>2</sub>·OH·HCl in boiling EtOH (I) affords the oxime anhydride, C<sub>6</sub>H<sub>3</sub>Cl<CPh:N>O (V), m.p. 186—187°, but (II) gives the oxime, m.p. 163°, of (III). With HNO<sub>3</sub> (d 1·52) *p*-C<sub>6</sub>H<sub>4</sub>Cl·NHBz gives its 2-NO<sub>2</sub>-derivative, m.p. 132—133°, reduced by Zn-AcOH to 6-chloro-2-phenylbenziminazole (Fischer *et al.* A., 1906, i, 895), also obtained from (V) and EtOH-HCl at 150°. Diazotisation of (IV) and treatment with Na<sub>2</sub>SO<sub>3</sub>-NaOH at < 10° gives 5-chloro-2-hydroxy-3-phenylindazole, m.p. 113—114°, reduced (SnCl<sub>2</sub>-HCl) to 5-chloro-3-phenylindazole, m.p. 125—127°. By similar methods from the appropriate amine and BzCl are obtained 4-hydroxy-2 : 4-diphenyl-3-*p*-tolyl-6-methyl- +COMe<sub>2</sub>, m.p. 141°, and solvent-free, m.p. 148—149° (hydrochloride, m.p. 320°; picrate, m.p. 143°; Et ether, m.p. 161°), and -6 : 8-dimethyl-3 : 4-



*dihydro-* (VI), m.p. 163—164° (*picrate*, m.p. 204°), converted into *2-hydroxy-2:4-diphenyl-3-p-tolyl-6-methyl-2:3-dihydro-*, m.p. 194—195°, *2:4-diphenyl-6-methyl-*, m.p. 176°, and *-6:8-dimethyl-*, m.p. 152°, *-quinazoline*, and the *-6-methyl-*, m.p. 190°, and *-6:8-dimethyl-*, m.p. 180°, *-oximeanhydride* [both as (V)]. From (VI) are obtained *2-amino-3:5-dimethylbenzophenone*, m.p. 128.5°, and its *Bz* derivative, m.p. 162°, and *6-benzoyl-2:4-dimethylbenzenazo-β-naphthol*, m.p. 130.5°. J. W. B.

**Quinazolines. XLII. Synthesis of 3:4-dihydroquinazoline derivatives from *p*-aminobenzoic acid, formaldehyde, and hydrochloric acid.** S. E. CAIRNCROSS and M. T. BOGERT (Coll. Czech. Chem. Comm., 1936, 8, 57—65; cf. A., 1935, 1134).—*p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et, CH<sub>2</sub>O, and (a) HCl at 25° or (b) HCl-H<sub>2</sub>SO<sub>4</sub> at 70° give *Et*<sub>2</sub> *methylenebis-p-aminobenzoate*, m.p. 192—193°, converted by HCl-EtOH into *Et 3-p-carbethoxyphenyl-3:4-dihydroquinazoline-6-carboxylate* (I), m.p. 186—187°, also obtained in small amount in (b) above or in fair yield by condensation of *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, CH<sub>2</sub>O, HCl, and H<sub>2</sub>SO<sub>4</sub> at 70° and subsequent esterification. (I) leads to the amorphous acid (*Na* salt), (CH<sub>2</sub>Cl·CH<sub>2</sub>)<sub>2</sub>, m.p. 173—174°, and *Me*<sub>3</sub> ester, m.p. 241—243°, which last with NEt<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·ONa in C<sub>6</sub>H<sub>6</sub> affords the (NEt<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub> ester, m.p. 114—115°, with anæsthetic properties. (I) and KMnO<sub>4</sub>-MgSO<sub>4</sub>-COMe<sub>2</sub> give *Et 3-p-carbethoxyphenyl-4-quinazoline-6-carboxylate*, m.p. 138.5—139.5°, also obtained from the 1-Et ester, m.p. 217—219° (lit. 216.5—218°), of 4:1:3-NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub> and *Et formamidobenzoate* (prep. by 40% HCO<sub>2</sub>H at 80°), m.p. 147—148°, at 140—150°, a *product*, m.p. 182—183°, being also formed in the latter reaction. M.p. are corr. R. S. C.

**Bromo-derivatives of 4-hydroxy-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline.** C. V. GHEORGHIU and (MLLE.) L. MANOLESCU (Bull. Soc. chim., 1936, [v], 3, 321—323).—5-Bromoisatin and PhNCS in NaOH-aq. EtOH give *6-bromo-4-hydroxy-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline-4-carboxylic acid*, m.p. 156—161° (decomp. from 142°), giving with EtOH *6-bromo-2-thion-4-ethoxy-3-phenyl-1:2:3:4-tetrahydroquinazoline*, m.p. 197—204°, which in HClO<sub>4</sub> yields *6-bromo-4-hydroxy-2-thion-3-phenyl-1:2:3:4-tetrahydroquinazoline perchlorate* (formulated as 4-carbonium salt), *cryst.*, red. R. S. C.

**Phenazine series. III. Isomeric octahydrophenazines.** G. R. CLEMO and H. McILWAIN (J.C.S., 1936, 258—261).—Reduction of 1:2:3:4-tetrahydrophenazine (I) with Na-EtOH affords the (?) *trans-1:2:3:4:9:10:11:12-H<sub>8</sub>-derivative* (II), m.p. 156° (A., 1935, 991, gives m.p. 150°), but with H<sub>2</sub>-Pd-C at room temp./100 lb. per sq. in., the (?) *cis-1:2:3:4:9:10:11:12-H<sub>8</sub>-derivative* (III), m.p. 147°, is obtained. Reduction of (I) with H<sub>2</sub>-catalyst B [Ni from Ni(OH)<sub>2</sub> at 370—380° by Rupe's method] at 180° gives mainly (II) and a little (III), but with catalyst A [Ni from Ni(NO<sub>3</sub>)<sub>2</sub> at 300—310° by Gattermann's method] at 180°, the product is the 1:2:3:4:5:6:7:8-H<sub>8</sub>-derivative (IV), m.p. 109° (Wallach *et al.*, A., 1924, i, 862). The geometrical

isomerism of (II) and (III) is proved since both have the properties of an *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and both give (NO)<sub>2</sub>-derivatives with H<sub>2</sub>SO<sub>4</sub>-NaNO<sub>2</sub>, (II) giving a (NO)<sub>2</sub>-derivative, m.p. 126°, and (III) an (NO)<sub>2</sub>-derivative, m.p. 109°, whereas (IV) gives no NO-derivative. (I), (II), (III), and (IV) are all dehydrogenated, by Pd-C at 200°, to phenazine. (II) is unchanged by treatment with Na-EtOH, H<sub>2</sub>-Pd-AcOH, or when passed over catalyst-B at 180°, but with catalyst-A it is converted into (IV). (III) is unchanged by treatment with Na-EtOH or H<sub>2</sub>-Pd-AcOH, but passage of its vapour over catalyst-A at 180° converts it into (IV), and, over catalyst-B at 180°, partial conversion into (II) occurs.

J. W. B.

**Hydroxy-compounds of the anthrapyrimidine series.**—See B., 1936, 182.

**Alkylated iminazoles of high mol. wt.**—See B., 1936, 183.

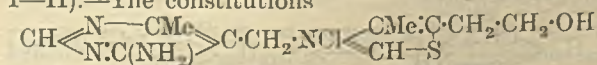
**New cleavage product of guanine.** G. HUNTER (Nature, 1936, 137, 405).—When guanine is auto-cleaved with an acid, approx. 20% is converted into C<sub>4</sub>H<sub>7</sub>N<sub>5</sub>, probably 4- (or 5-)guanidinoglyoxaline. Reactions are described. L. S. T.

**Function of halogens in hæmin.** K. LINDENFELD (Rocz. Chem., 1935, 15, 516—542).—The reaction between hæmin (HmCl) and MX (M=a cation, X=Br, I, CNS, HCO<sub>2</sub>) in C<sub>5</sub>H<sub>5</sub>N-AcOH is HmCl+X'=HmX+Cl'; C<sub>5</sub>H<sub>5</sub>N (or quinine) merely acts as a solvent, since diethylhæmin in CHCl<sub>3</sub>-AcOH undergoes the same changes in absence of the bases, and HmCl may be recovered unchanged from C<sub>5</sub>H<sub>5</sub>N solutions. The prep. and properties of *formylhæmin* are described; *acetylhæmin* cannot be obtained by the above reaction. It is concluded that the Cl linking is heteropolar. R. T.

**Preparation of cryptoxanthine from paprika.** L. VON CHOLNOKY (Magyar chem. Fol., 1934, 40, 85—89; Chem. Zentr., 1935, ii, 230; cf. A., 1934, 657).—A chromatographic separation is described. H. N. R.

**Abnormal reactions of hydroxylamine.** P. DREYFUSS (Rend. Semin. Fac. Sci. Univ. Cagliari, 1934, 4, 55—58; Chem. Zentr., 1935, ii, 46).—Formulae are proposed for the compound obtained from NH<sub>2</sub>OH and dibenzylidencyclohexanone (Poggi and Saltini, A., 1934, 773) and that from phorone and NH<sub>2</sub>OH (Vorländer and Gästner, A., 1899, i, 259). 4:5:4':5'-Tetramethoxy-2:2'-dibenzoylbenzophenone yields a compound with NH<sub>2</sub>OH (formula suggested). H. N. R.

**Chemistry of the antineuritic vitamin.** K. MAKINO and I. IMAI (Z. physiol. Chem., 1936, 239, I—II).—The constitutions



for the antineuritic vitamin (I) and

$\text{CH} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{N-CH(OH)} \end{array} \text{C}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{OEt}$  for the nitrate obtained therefrom (cf. Windaus *et al.*, this vol., 253) are suggested as alternative structures. The oxidation of (I) by K<sub>3</sub>Fe(CN)<sub>6</sub> and NaOH to thiochrome can then be explained by simple analogy. H. W.



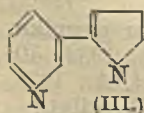
**Carbocyanine dyes.**—See B., 1936, 184.

**Nornicotine.** A. WENUSCH (Pharm. Zentr., 1936, 77, 141—143).—There is relatively little nornicotine (I) in the smoke from tobacco rich therein; oxidation of (I) either by  $\text{KMnO}_4$  or during smoking gives an alkaloid (picrate, m.p. 217—218°) resembling myosmine. (I) is less toxic than nicotine. R. S. C.

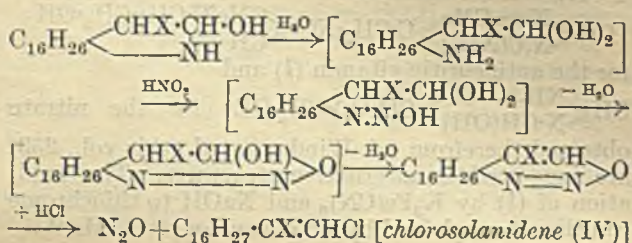
**d-Nornicotine.** E. SPATH, C. S. HICKS, and E. ZAJIC (Ber., 1936, 69, [B], 250—251).—Partly racemised *d*-nornicotine (A., 1935, 1136) is purified by conversion into the perchlorate, which is crystallised from  $\text{MeOH-Et}_2\text{O}$ . The most active portion has  $[\alpha]_D^{20} +86.3^\circ$ , whereas the optically pure substance has  $[\alpha]_D^{25} +88.8^\circ$ . H. W.

**Tobacco bases. IV. Syntheses of l-nornicotine.** E. SPATH, L. MARION, and E. ZAJIC. V. **Constitution of myosmine.** E. SPATH, A. WENUSCH, and E. ZAJIC (Ber., 1936, 69, [B], 251—255, 393—396).—IV. *l*-Nicotine (I) is cautiously oxidised with  $\text{KMnO}_4$  and the more strongly basic portions are removed from the product by fractional extraction with HCl. They are then distilled with steam in vac., whereby (I) is volatilised. The residue is transformed into the dipicrate, from which, after repeated crystallisation, *l*-nornicotine (II),  $[\alpha]_D^{20} -76.1^\circ$ , raised to  $-83.2^\circ$  after further purification through the perchlorate, is isolated. Treatment of (I) with  $\text{Ag}_2\text{O}$  and of the product dissolved in  $\text{Et}_2\text{O}$  with aq. NaCl containing HCl gives a most strongly basic fraction from which (II),  $[\alpha]_D^{20} -88.8^\circ$ , is isolated.

V. Myosmine (III), after purification through the picrate, m.p. 182—183° (vac.), has m.p. 42—43° (vac.), and is optically inactive in MeOH ( $c=20$ ). It is dehydrogenated by Pd sponge at 200° to 2-3'-pyridylpyrrole. Its composition, optical inactivity (assuming that it is not a racemate and hence does not contain an asymmetric C atom), and conversion by  $\text{Bz}_2\text{O}$  in abs.  $\text{Et}_2\text{O}$  with opening of the ring into (?) 3- $\gamma$ -benzamido butyrylpyridine, m.p. 118°, suggest formula (III). H. W.



**Constitution of solanidine from Solanum sodomaeum.** G. ODDO and G. CARONNA (Ber., 1936, 69, [B], 283—287).—The action of  $\text{HNO}_2$  on solanidine-*s* (I) gives azosolanidine (II), m.p. 260° (decomp.), which decolorises  $\text{Br-H}_2\text{O}$  and does not give the Liebermann reaction, and a quinhydrone  $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N} \cdot \text{C}_{18}\text{H}_{31}\text{ON}$ , m.p. 120°, decomposed by HCl into the hydrochloride of (I) and the quinone,  $\text{C}_{16}\text{H}_{25}\text{N}(\text{CO})_2$ . The reactions described by Oddo *et al.* (A., 1911, i, 671; 1914, i, 1174) are therefore interpreted thus:



$\text{C}_{16}\text{H}_{28} \cdot \text{CX}(\text{OH}) \cdot \text{CH}_2\text{Cl}$  (chlorohydroxysolanidane). The formation of (III) is established by the production of *tetra-acetylsolanidine*,  $\text{NAc}_2 \cdot \text{C}_{16}\text{H}_{26} \cdot \text{CHX} \cdot \text{CH}(\text{OAc})_2$ , m.p. 253° (acetate) by the action of  $\text{AcOH-Ac}_2\text{O-H}_2\text{SO}_4$  on (I). Attempts to remove Cl from (IV) by Zn and AcOH, Na and EtOH or amyl alcohol, or through the Mg compound were unsuccessful. (IV) is smoothly oxidised by  $\text{CrO}_3$  in AcOH or by  $\text{KMnO}_4$  in  $\text{COMe}_2$ ; with molten KOH it affords a monocarboxylic acid and a neutral substance, m.p. 145°. Since solanidine-*t* differs from (I) in the possession of  $\text{C}_7\text{H}_7$  and a *tert.* N, it is suggested that it may be *N*-benzylsolanidine-*s* and that (I) is therefore the parent of all the solanidines, which differ by the presence of alkyl or aryl attached to N or to the carbocyclic groups. H. W.

**Phenyl- $\psi$ -pelletierine.** B. K. BLOUNT (J.C.S., 1936, 287—288).—Dropwise addition of NaOMe-MeOH to a solution of  $\text{CH}_2\text{Ph} \cdot \text{CHO}$  and  $\text{CH}_3 \cdot \text{CH} \cdot \text{CHO}$  in MeOH at  $-18^\circ$  to  $0^\circ$  affords  $\text{CHO} \cdot [\text{CH}_2]_3 \cdot \text{CHPh} \cdot \text{CHO}$  in solution, condensed with  $\text{CO}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2 \cdot \text{CaCO}_3$ -aq. MeOH-33%  $\text{NH}_2\text{Me}$  to give 6-phenylgranatan-3-one (phenyl- $\psi$ -pelletierine), isolated as its 2:4-dipiperonylidene derivative, m.p. 210°. J. W. B.

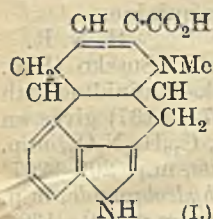
**Synthetic experiments on eserine. V. Synthesis of l-eserethole.** T. HOSHINO and T. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1935, 11, 416—417; cf. A., 1935, 1256, 1378).—*dl*-Eserethole and *d*-tartaric acid in EtOH give the *d*-tartrate, m.p. 173—174°,  $[\alpha]_D^{15} +115^\circ$  in  $\text{H}_2\text{O}$ , of the *d*-base and the mother-liquors with the *l*-acid give the *l*-tartrate, m.p. 173—174°,  $[\alpha]_D^{15} -115^\circ$  in  $\text{H}_2\text{O}$ , of the *l*-base. The active picrates melt at 135—136°, the *dl*-picrate at 151—152°. R. S. C.

**Synthesis of bicuculline.** I. P. W. G. GROENEWOLD and R. ROBINSON (J.C.S., 1936, 199—202).—Bromonormeconin when heated with methylene sulphate in aq.  $\text{COMe}_2\text{-NaOH}$  ( $\text{N}_2$  atm.) affords 6-bromo-3:4-methylenedioxyphthalide, m.p. 196°, reduced (Al-Hg in boiling EtOH, Zn dust-aq. NaOH, or  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O-Pd-SrCO}_3\text{-EtOH-KOH}$ ) to 3:4-methylenedioxyphthalide, converted by  $\text{HNO}_3$  ( $d$  1.42) at  $0^\circ$  into its 6- $\text{NO}_2$ -derivative (I), m.p. 222—223°, which with cotarnine in EtOH gives anhydrocotarnine-6-nitro-, m.p. 177—178°, reduced ( $\text{SnCl}_2\text{-HCl}$  at  $0^\circ$ ) to anhydrocotarnine-6-amino-3:4-methylenedioxyphthalide, m.p. 204—205° (decomp.). Local similarly condenses with (I) to give nitro-*x*-adlumine (anhydroloidal-6-nitro-3:4-methylenedioxyphthalide), m.p. 180—181° (decomp.), reduced to the  $\text{NH}_2$ -derivative, m.p. 218—219°. Hydrastinine and (I) afford nitro-*x*-bicuculline, sinters at 176°, blackens at 179°, reduced to the  $\text{NH}_2$ -compound, m.p. 203—204°. Diazotisation of this and treatment with aq. KI affords iodo-*x*-bicuculline, m.p. 208—209°, reduced (Al-Hg in boiling EtOH- $\text{C}_6\text{H}_6$ ) to *x*-bicuculline (anhydrohydrastinine-3:4-methylenedioxyphthalide), m.p. 215°, resolution of which gives the *d*-form, identical with the natural alkaloid (details later). J. W. B.

**Ergot alkaloids. Structure of lysergic acid.** W. A. JACOBS and L. C. CRAIG (Science, 1936, 83, 38—39).—The previous structure suggested for lysergic



acid (A., 1935, 1512) is revised to (I). The base,  $C_{11}H_{11}N$ , obtained by the alkali fusion of dihydrolysergic acid (II) is 1:5- $C_{10}H_6Me \cdot NH_2$ . The tribasic acid,  $C_{14}H_9O_8N$  (A., 1932, 1147), yields quinoline on distillation with soda-lime, and  $HNO_3$  oxidation of (I) yields picric acid. Catalytic hydrogenation of (I) produces (II) which, unlike (I), can no longer be titrated, indicating the proximity of the double linking and  $CO_2H$  in the ring containing NMe. Further hydrogenation appears to attack the indole ring system.



L. S. T.  
**Spectroscopic similarity between ergot (lysergic acid) and the yohimbine alkaloids.** M. S. KHARASCH, D. W. STANGER, M. A. BLOODGOOD, and R. R. LEGAULT (Science, 1936, 83, 36—38).—The marked similarity observed between the mol. absorption curves for ergotamine, ergotamine, and ergotocine (I) indicates a common structural skeleton, lysergic acid, responsible for their ultra-violet absorptions. Comparison of the curve for (I) with those of harmol, harmine, harmaline, and methyl- and tetrahydro-harmine indicates no structural relationship between (I) and the harmala alkaloids. The curve of yohimbine (II) is markedly similar to that of (I) in shape, but displaced toward shorter  $\lambda$ , whilst those of (II) and hydrogenated (I) are practically identical.

L. S. T.

**New ergot alkaloid.** M. S. KHARASCH, H. KING, A. STOLL, and M. R. THOMPSON (Nature, 1936, 137, 403, and Science, 1936, 83, 206—207).—Ergometrine, ergotocine, ergobasine, and ergostetrine are identical.

L. S. T.

**Peganine.** IX. Syntheses of  $\Delta^9$ -pegene and peganine. E. SPÄTH and N. PLATZER. X. *l*-Peganine (*l*-vasicine) from *Adhatoda vasica*, Nees. E. SPÄTH and F. KESZTLER. XI.  $\Delta^9$ -Pegen-1-one. E. SPÄTH and N. PLATZER (Ber., 1936, 69, [B], 255—257, 384—386, 387—393).—IX.  $o$ - $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$  and  $\gamma$ -butyrolactone (I) are heated at  $200^\circ$  in  $N_2$  with intermittent removal of the  $H_2O$  formed and the product is heated with  $POCl_3$ , whereby  $\Delta^9$ -pegene, m.p.  $99$ — $100^\circ$ , is obtained. It is transformed by the successive action of red P and Br and  $Ba(OH)_2$  into  $\alpha$ -hydroxybutyrolactone, b.p.  $128$ — $130^\circ/0.5$  mm., which affords peganine when heated with  $o$ - $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$  at  $200^\circ$ .

X. The dry leaves are extracted with EtOH at  $15$ — $20^\circ$ , the extracts are conc. in vac., acidified with 1% AcOH, freed from residual EtOH, rendered ammoniacal, and extracted with  $Et_2O$ . The crude base is treated with  $CHCl_3$ , in which peganine dissolves, leaving a small residue. Treatment of the alkaloid with AcOH followed by  $NH_3$  and crystallisation from  $Et_2O$  gives *l*-peganin (I) identical with the synthetic material. The natural alkaloid is therefore optically active, and its isolation in the inactive form is due to racemisation during extraction. (I) had  $[\alpha]_D^{25} -254^\circ$  in pure  $CHCl_3$ ,  $[\alpha]_D^{25} -61.5^\circ$  in abs. EtOH,  $[\alpha]_D^{25} +19.5^\circ$  as sulphate in  $H_2O$ . The optical activity in  $CHCl_3$  is strongly influenced by the presence of very small amounts of EtOH.

XI. Mainly corrections of the work of Juneja *et al.* (A., 1935, 765, 995).  $o$ - $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NH_2$  and  $(\cdot CH_2 \cdot CO)_2O$  in  $Et_2O$  and subsequently at  $100^\circ$  give succin-*o*-nitrobenzylamic acid (II), m.p.  $123$ — $124^\circ$ , which passes when distilled in a high vac. into succin-*o*-nitrobenzylimide (III), m.p.  $133^\circ$ . Reduction of (II) with  $FeSO_4 \cdot NH_3$  affords succin-*o*-amino-benzylamic acid, m.p.  $145^\circ$ , which passes when heated at  $180$ — $190^\circ/0.04$  mm., or with anhyd. NaOAc in  $H_2$  at  $140$ — $150^\circ$  into  $\Delta^9$ -pegen-1-one (IV), m.p.  $191^\circ$  (vac.). Alternatively, (III) is obtained from  $(\cdot CH_2 \cdot CO)_2NK$ ,  $o$ - $NO_2 \cdot C_6H_4 \cdot CH_2Cl$ , and NaCl at  $130^\circ$  and reduced by  $SnCl_2$  and HCl ( $d$  1.16) to (IV) and  $\beta$ -3:4-dihydro-2-quinazolypropionic acid, m.p.  $228$ — $230^\circ$ . Reduction of (III) with Zn turnings and 10%  $H_2SO_4$  at  $20$ — $25^\circ$  affords succin-*o*-aminobenzylimide, m.p.  $106$ — $107^\circ$ , which passes at  $230$ — $240^\circ/30$  mm. into (IV). Electrolytic reduction of (III) at a Pb cathode gives not pegane, but 1-*o*-aminobenzylpyrrolidine, m.p.  $30$ — $31^\circ$  (picrolonate, m.p.  $204$ — $206^\circ$ ). Pegane is obtained from (IV) by reduction with Na and boiling amyl alcohol.

H. W.

**Synthesis of papaverine derivatives.** II. **Synthesis of 1-(3':4':5'-trimethylphenyl)-6:7-diethoxyisoquinoline.** S. SUGASAWA (J. Pharm. Soc. Japan, 1935, 55, 224—233).—3:4-Dimethoxyhippuric acid and Cu chromite in quinoline afford  $\omega$ -benzamido-3:4-dimethoxystyrene, m.p.  $138^\circ$ , reduced catalytically to  $\beta$ -(3:4-dimethoxyphenyl)ethylbenzamide, m.p.  $90^\circ$  (also by benzoylation of 3:4-dimethoxy- $\beta$ -phenylethylamine). With  $POCl_3$ , this yields 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline, m.p.  $120$ — $121^\circ$ . Trimethylgalloyl chloride and aminoacetonitrile sulphate yield *Et* galloylglucynonitrile  $Me_3$  ether, m.p.  $186$ — $187^\circ$ , hydrolysed to galloylglucynonitrile  $Me_3$  ether, m.p.  $218^\circ$ . This with 3:4-diethoxybenzaldehyde gives 2-(3':4':5'-trimethoxyphenyl)-4-(3':4'-diethoxybenzylidene)oxazolone, m.p.  $163$ — $164^\circ$ . With NaOH this affords 3:4:5-trimethoxy-3':4'-diethoxybenzylidenehippuric acid, m.p.  $220$ — $221^\circ$ , which, with Cu chromite in quinoline, yields  $\omega$ -galloylamido-3:4-diethoxystyrene  $Me_3$  ether, m.p.  $157$ — $158^\circ$ , reduced catalytically to N-[ $\beta$ -(3:4-diethoxyphenyl)ethyl]galloylamine  $Me_3$  ether, m.p.  $130$ — $131^\circ$ . This, with  $POCl_3$ , affords 6:7-diethoxy-1-(3':4':5'-trimethoxyphenyl)-3:4-dihydroisoquinoline, m.p.  $163$ — $164^\circ$ , which, with Pd in xylene, yields 6:7-diethoxy-1-(3':4':5'-trimethoxyphenyl)isoquinoline, m.p.  $117$ — $118^\circ$ .

CH. ABS. (r)

**Synthesis of benzyltetrahydroisoquinoline bases under so-called physiological conditions.** E. SPÄTH, F. KUFFNER, and F. KESZTLER (Ber., 1936, 69, [B], 378—384).—Homopiperonylhomopiperonylamide is converted by successive treatment with  $POCl_3$  in PhMe and Zn and fuming HCl into 6:7:3':4'-dimethylenedioxybenzyl-1:2:3:4-tetrahydroisoquinoline (I), m.p.  $84$ — $85^\circ$  [hydrochloride, m.p.  $242$ — $243^\circ$  (vac.)], the presence of minute amounts of which can be detected by its transformation by  $CH_2O$  in MeOH into 2:3:12:13-dimethylenedioxyberbine (II), m.p.  $214^\circ$  (vac.). Homopiperonal (III) is obtained by the action of dry  $AgOBz$  and I in boiling  $C_6H_6$  on saffrole and treatment of the product with boiling NaOH-50% MeOH, whereby



safrole glycol is obtained, which is oxidised by  $\text{Pb}(\text{OAc})_4$ . When (III) is condensed with homopiperonylamine hydrochloride (Hahn *et al.*, A., 1935, 357) the products are: (I) homopiperonylamine, which cannot contain (I), since the compounds are readily separated from one another by distillation in a high vacuum, (2) 3':4'-methylenedioxybenzylidene- $\beta$ -3:4-phenylethylamine (IV), m.p. 115–117°, the formation of which is attributed to the presence of a trace of piperonal in (III), and (3) a non-cryst. material converted by  $\text{CH}_2\text{O}$  into norhydrohydrastinine unaccompanied by any trace of (II). It is therefore impossible that (I) is produced as reported by Hahn *et al.* (*loc. cit.*) and their product is very probably impure (IV). H. W.

**Hydrates of quinine.** G. MALQUORI and M. COVELLO (Annali Chim. Appl., 1935, 25, 647–654).—Neither the trihydrate nor the known higher hydrates can exist above 15°. Dehydration appears to be a discontinuous process, but definite hydrates do not result. Dehydration is complete at 50–60° and is "irreversible." A. M. P.

**Origin of  $\beta$ -isocupreidine.** R. LUDWICZAK and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 104–106).—A correction to previous work (A., 1935, 996) based on the observation that, when heated with  $\text{H}_2\text{SO}_4$ , hydrocupreidine is unchanged but cupreidine is partly converted (equilibrium) into  $\beta$ -isocupreidine. J. W. B.

**Hydriodoquinine and niquine.** J. REYMAN and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 360–373).—Hydriodoquinine-I (A)  $+\text{C}_6\text{H}_6$ , m.p. 93°, resolidifies and decomp. 130–140°,  $[\alpha]_D^{20} -18^\circ$  (Rosenmund *et al.*, A., 1924, i, 982) (methiodide, m.p. 112–114°,  $[\alpha]_D^{20} -82.5^\circ$ ), is decomposed in boiling  $\text{C}_6\text{H}_6$  to give  $\beta$ -isoquinine (B) (not isolated) and an insol. basic hydriodide,  $(\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}_2\text{I})_2\text{HI}$  (C), m.p. 178–204° (decomp.), reconverted into (A) by  $\text{NH}_3$ ; but (A) is unaltered by hot P-HI (*d* 1.7) and, contrary to Skrap (ref., *loc. cit.*) is converted into (B) by  $\text{AgNO}_3$ . Hydriodoquinine-II (D), decomp. 125–150°,  $[\alpha]_D^{20} -217^\circ$ , is similarly decomposed in boiling  $\text{C}_6\text{H}_6$  to the insol. basic hydriodide (E)  $+\text{CHCl}_3$ , m.p. 76–80°, and solvent-free, m.p. 175–192° (decomp.),  $[\alpha]_D^{20} -87^\circ$  [reconverted into (D) by cold  $\text{NH}_3$ ] and (from the mother-liquor) niquine (F):  $3\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}_2\text{I} \rightarrow (\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}_2\text{I})_2\text{HI} + \text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ . (E) is also obtained from (D) (3 mols.) and its dihydriodide, m.p. 223° (decomp.) (1 mol.). Although it could not be prepared by admixture of (A) and (D), decomp. of the mixed hydriodides of (A) and (D) with  $\text{NH}_3$  in presence of  $\text{C}_6\text{H}_6$  affords a mol. compound, m.p. 93°,  $[\alpha]_D^{20} -118^\circ$  [methiodide, m.p. 191–195° (decomp.)]. Thus (A) and (D) are only stereoisomerides, but (B) and (F) are structural isomerides, both of composition  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ . With  $\text{AcCl}-\text{C}_5\text{H}_5\text{N}$  (F) gives a  $\text{Ac}_5$  derivative, m.p. 142–143°  $[\alpha]_D^{20} +33^\circ$ , partly hydrolysed by 20% HCl at room temp. to the known  $\text{Ac}_1$  derivative: hence (F) contains a OH. Oxidation of (F) with  $\text{H}_2\text{O}_2$  at 100° gives quinic acid. All  $[\alpha]_D$  vals. are in 96% EtOH. J. W. B.

**Quinine-urethane solutions.** L. NOBILI (G. Farm. Chim., 1935, 84, 15–20; Chem. Zentr., 1935,

i, 3955).—The greenish-yellow colour is said to be due to the presence of a  $\text{CH}_2\text{OH}$  in quinine.

H. N. R.

**Niquidine.** T. DOMAŃSKI and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 457–464).—Quinidine with conc. HCl or HBr (cf. A., 1935, 874, 1137) gives an unsaturated alkaloid, *niquidine* (I),  $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2$ , m.p. 161°,  $[\alpha]_D^{20} +171^\circ$  in EtOH [dioxalate, m.p. 206–207° (decomp.),  $[\alpha]_D^{20} +189^\circ$  in  $\text{H}_2\text{O}$ ; dihydrobromide, m.p. 250° (decomp.); N-NO-derivative, m.p. 80–130°, decomp. 160–170°,  $[\alpha]_D^{20} -73^\circ$  in EtOH; dibromide, m.p. 170–171° (decomp.),  $[\alpha]_D^{20} +142^\circ$  in MeOH [dihydrobromide, m.p. 238° (decomp.),  $[\alpha]_D^{20} +152^\circ$  in MeOH and  $\text{H}_2\text{O}$ ; dinitrate, m.p. 186–187° (decomp.)]; N-Ac, m.p. 206–207°,  $[\alpha]_D^{20} +25^\circ$  in EtOH; and N-Ac<sub>2</sub>, m.p. 80–90°,  $[\alpha]_D^{20} -28^\circ$  in EtOH, derivatives. (I) with 25% AcOH in a sealed tube gives *nichotoxin* (*nichicin*) (II), m.p. 70°,  $[\alpha]_D^{20} -5^\circ$  (p-nitrophenylhydrazone, m.p. about 60°), and with  $\text{H}_2\text{O}_2$  yields quinic acid. (I) may be as shown

$$\begin{array}{c} \text{CH}_2\text{CH}(\text{CH}_2\text{CH}(\text{CH}_2)_2\text{CH}(\text{OH})\text{C}_5\text{H}_5\text{N}\cdot\text{OMe}) \\ | \\ \text{CH}_2\text{N}(\text{CH}_2)_2\text{CH}(\text{CH}_2\text{NH}_2)(\text{CH}_2\text{CO}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{OMe}) \end{array}$$

and (II)  $\text{C}_7\text{H}_{10}(\text{CH}_2\cdot\text{NH}_2)(\text{CH}_2\cdot\text{CO}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{OMe})$ .

F. R. G.

**Transformations of isoquinidines.** T. DOMAŃSKI and J. SUSZKO (Bull. Acad. Polonaise, 1935, A, 465–473).—Quinidine,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isoquinidine, nichidine, and the corresponding toxins (cf. preceding abstract) are interconvertible in presence of acids.

F. R. G.

**Addition of organomagnesium halides to  $\psi$ -codeine types.** I. Deoxycodine-C. L. SMALL and K. C. YUEN (J. Amer. Chem. Soc., 1936, 58, 192–196).—Deoxycodine-C (I) (*salicylate*, m.p. 195–196°) (A., 1931, 1077) and  $\text{MgMeI}$  give the phenolic methyl-dihydrodeoxycodine (II), m.p. 145–146°,  $[\alpha]_D^{20} +69.7^\circ$  in EtOH or  $\text{CHCl}_3$  (hydrobromide, m.p. 245–246°; hydriodide, m.p. 155–158°; methiodide, m.p. 239°), presumably formed by 1:2- or 1:4-addition involving the  $\cdot\text{O}$  linking. Zn dust distillation of (II) gives a hydrocarbon,  $\text{C}_{15}\text{H}_{12}$ , m.p. 103° (not sharp; sinters from 95°) [picrate, m.p. 95–98° (sinters from about 85°)], and oily hydrocarbon(s) (picrates, m.p. 118–119° and 138–141°, not identical with 2- and 4-methylphenanthrene picrates). Hydrogenation of (II) affords methyl-tetrahydrodeoxycodine, m.p. 128–129°,  $[\alpha]_D^{20} -47.8^\circ$  in EtOH [hydrochloride, m.p. 240.5°; hydrobromide, m.p. 248–249°; methiodide (+EtOH), m.p. 254–255°]. (I) and  $\text{MgEtI}$  give  $\alpha$ -ethyl-dihydrodeoxycodine (III), m.p. 156–164°,  $[\alpha]_D^{20} -184.2^\circ$  in  $\text{CHCl}_3$  (hydriodide, m.p. 205–210°; perchlorate, m.p. 187–200°; methiodide, m.p. 210–215°), and an oily product (A). (III) and (A) are reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , aq. MeOH, N-HCl) to  $\alpha$ -, m.p. 168.5–169°,  $[\alpha]_D^{20} -54.8^\circ$  in  $\text{CHCl}_3$  (hydriodide, m.p. 234°), and  $\beta$ -, m.p. 148–153°,  $[\alpha]_D^{20} -37.6^\circ$  in  $\text{CHCl}_3$ , -ethyl-tetrahydrodeoxycodines, respectively; (A) also gives an unidentified substance, m.p. 215–216°. The isomerism may be configurational or positional. (I) and  $\text{MgPhBr}$  afford  $\approx 83\%$  of phenyl-dihydrodeoxycodine (IV), m.p. 184.5–185.5°,  $[\alpha]_D^{20} +129.3^\circ$  in  $\text{CHCl}_3$  [picrate (+ $\text{H}_2\text{O}$ ), m.p. (anhyd.) 129–132°; benzoate, m.p. 203–204°; methiodide, m.p. 257.5–258°], and a little of an oil (B).



(IV) could not be reduced catalytically except with  $\text{PtO}_2$  in aq.  $\text{MeOH-HCl}$ ; a *hexahydrophenylltetrahydrodeoxycodeine* (V), m.p. 132—134°,  $[\alpha]_D^{24} -48.4^\circ$  in  $\text{CHCl}_3$  (perchlorate, m.p. 255—256°; *methiodide*, m.p. 250°), results. (B) is reduced to a *phenylltetrahydrodeoxycodeine*, m.p. 218—220°,  $[\alpha]_D^{26} +16.1^\circ$  in  $\text{CHCl}_3$ . *cyclohexyldihydrodeoxycodeine*, m.p. 131.5—132.5°,  $[\alpha]_D^{25} -51^\circ$  in  $\text{CHCl}_3$  (perchlorate, m.p. 250—251°), prepared from (I) and  $\text{Mg}$  cyclohexyl chloride in isoamyl ether (not obtained in  $\text{Et}_2\text{O}$ ) at 100°, is reduced [as for (IV)] to *cyclohexylltetrahydrodeoxycodeine*, m.p. 193—193.5°,  $[\alpha]_D^{25} -14.2^\circ$  in  $\text{CHCl}_3$  (*hydriodide*, m.p. 235—236°), which differs from (V).

H. B.

#### Alkaloids of *Sinomenium* and *Cocculus*. XL. Alkaloids of *Stephania cepharantha*, Hayata.

III. H. KONDO and I. KEMATSU (J. Pharm. Soc. Japan, 1935, 55, 234—241).—*isoTetrandrine* (I),  $\text{C}_{38}\text{H}_{42}\text{O}_6\text{N}_2$ , m.p. 181—182°,  $[\alpha]_D^{17} +146^\circ$  in  $\text{CHCl}_3$ , isolated from the above, yields a *methiodide*, decomp. 242°, an  $\alpha$ -, m.p. 171—172° [*methiodide* (II), decomp. 255°], and a  $\beta$ -, m.p. about 110°, *methine*. (II) with  $\text{MeOH-KOH}$  affords *de-N-isotetrandrine*, m.p. 220°, not depressed on admixture with *de-N-tetrandrine* or *de-N-berbamine* methylate.  $\text{KMnO}_4$  oxidises (II) to a *substance*, m.p. 305°, not depressed on admixture with  $\text{Et}_2$  6-methoxydiphenyl-3:4'-dicarboxylate. The partial formula  $\text{C}_{32}\text{H}_{24}(\text{O})_2(\text{OMe})_4(\text{NMe})_2$  is proposed for (I).

CH. ABS. (r)

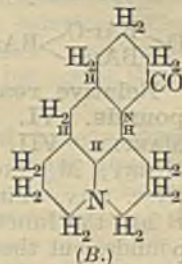
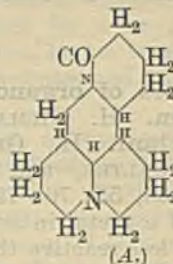
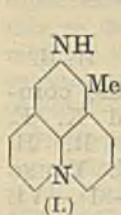
#### Alkaloids of *Sinomenium* and *Cocculus*. XLV. Stereochemical and biogenetic relationships of biscoclaurine alkaloids.

H. KONDO and M. TOMITA (Arch. Pharm., 1936, 274, 65—82).—The following alkaloids are considered to be derived from 2 mols. of coclaurine [7-hydroxy-6-methoxy-1-*p*-hydroxybenzyl-1:2:3:4-tetrahydroisoquinoline]: (a) oxidised to 2-methoxydiphenyl ether-5:4'-dicarboxylic acid (I): dauricine (II); oxyacanthine (III); berbamine; tetrandrine (IV) [optical isomeride of methylberbamine (=isotetrandrine)]; phæanthine [optical antipode of (IV)]; trilobamine; trilobine (V); isotrilobine (VI); menisarine (VII); normenisarine; cepharanthine; (b) not oxidised to (I): isochondodendrine (VIII); *l*-curine and its optical antipode *d*-bebeerine; insularine, probably  $\text{C}_{32}\text{H}_{23}(\text{O})_3(\text{OMe})_3(\text{NMe})_2$ , and not  $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$  as previously suggested (J. Pharm. Soc. Japan, 1927, 47, 815). Constitutional formulæ (and, in some cases, models) are given; those previously suggested (A., 1932, 1048) for (V) and (VI) are modified. Possible biological syntheses of (II), (III), (V), (VII), and (VIII) are discussed. The botanical sources of the alkaloids are given.

H. B.

**Constitution of matrine.** XVIII. K. TSUDA (Ber., 1936, 69, [B], 429—434; cf. A., 1935, 1514).—The constitutions assigned (*loc. cit.*) to dihydro-(I) and dehydro- $\alpha$ -matrinidine (II) lead to the conclusion that acetyl- $\alpha$ -matrinidine is a  $\delta$ -NHAc-ketone; this is confirmed by the isolation of its *semicarbazone*,  $\text{C}_{15}\text{H}_{27}\text{O}_2\text{N}_5$ , decomp. 203°. Treatment of (II) in  $\text{C}_6\text{H}_6$  with LiBu followed by EtBr gives *decarboxydehydromatrinane* (III), b.p. 200—210°/4 mm. (*hydriodide*, m.p. 193—194.5°), identical

with one of the products of the dehydrogenation of matrine by Pd-asbestos (A., 1935, 766). The chemical



behaviour of (I) and its relationship to the known leguminous alkaloids indicate for it the constitution (I). Against this view, (II) is not converted into its  $\text{NH}_2$ -derivative by  $\text{NaNH}_2$ , and its Bu compound is not formed from (III) and LiBu in  $\text{C}_6\text{H}_6$  at 100°. (Conyryne and LiBu in  $\text{C}_6\text{H}_6$  afford 2-propyl-6-butylpyridine, b.p. 228—230°.) Successive treatment of Me methylmatrate methiodide with  $\text{Ag}_2\text{O}$  and  $\text{KMnO}_4$  gives  $\text{H}_2\text{C}_2\text{O}_4$ ,  $(\text{CH}_2\text{CO}_2\text{H})_2$ , and glutaric acid but no  $\text{AcCO}_2\text{H}$ . A 3-methylpyrrolidone ring cannot therefore be present in matrine, and the only remaining possibility is a pyrrolidone ring, thus leading to a choice of constitutions (A) or (B) for the alkaloid.

H. W.

**South American curare.**—See this vol., 534.

**Alkaloids.** R. ROBINSON (Ann. Rev. Biochem., 1935, 4, 497—518).—A review of the lit. for 1933—1934.

CH. ABS. (r)

**Decomposition of aromatic arsines in the Friedel and Crafts reaction.** M. S. MALINOVSKI (J. Gen. Chem. Russ., 1935, 5, 1355—1358).—Aromatic arsines yield  $\text{AsCl}_3$  and  $\text{COPhMe}$  or its derivatives when treated with  $\text{AcCl}$  or  $\text{CH}_2\text{Cl}\cdot\text{COCl}$  in presence of  $\text{AlCl}_3$ . The reaction is useful in the identification and elucidation of the structure of arsines.

R. T.

**Arsenic-containing azo-dyes from 4-aminodiphenyl-4'-arsinic acid.** G. I. GERSCHON and R. P. LASTOVSKI (J. Appl. Chem. Russ., 1935, 8, 1435—1438).—4-Acetamido-4'-diazodiphenyl sulphate in aq. EtOH and  $\text{AsCl}_3$  at 100° in presence of  $\text{CuCl}$  yield 4-aminodiphenyl-4'-arsinic acid, the diazo-derivative of which yields a red-brown product with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ , and a violet dye with  $\text{H-acid}$ .

R. T.

**Phenylarsinic acid.** R. H. BULLARD and J. B. DICKEY (Org. Syntheses, 1935, 15, 59—61).—An improved prep. from  $\text{PhN}_2\text{Cl}$ ,  $\text{Na}_3\text{AsO}_3$ , and  $\text{CuSO}_4$  is described.

CH. ABS. (r)

**Mol. wts. of organoboric acids.** C. R. KINNEY and D. F. PONTZ (J. Amer. Chem. Soc., 1936, 58, 196).— $\text{ArB(OH)}_2$  ( $\text{Ar}=\text{Ph}$ , *p*- $\text{C}_6\text{H}_4\text{Me}$ , *m*- and *p*- $\text{C}_6\text{H}_4\text{Cl}$ , *p*- $\text{C}_6\text{H}_4\text{Br}$ , *o*- $\text{OEt-C}_6\text{H}_4$ , *p*- $\text{OPh-C}_6\text{H}_4$ , and  $\alpha$ - $\text{C}_{10}\text{H}_7$ ) are unimol. in  $\text{PhNO}_2$  (f.p. method).

H. B.

**Structure of organoboron oxides.** C. R. KINNEY and D. F. PONTZ (J. Amer. Chem. Soc., 1936, 58, 197).—The mol. wts. of phenyl-, *p*-tolyl-, *m*- and *p*-chlorophenyl-, *p*-bromophenyl-, and  $\alpha$ -naphthyl-boric oxides show considerable variation



in  $\text{PhNO}_2$  (f.-p. method) and indicate that the oxides are probably mixtures of  $\text{ArB} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{O} \text{Ar}$  and  $\text{O} \begin{smallmatrix} \text{Ar-O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{O} \text{Ar}$ .

H. B.

**Relative reactivities of organometallic compounds. VI. Boron.** H. GILMAN and K. E. MARPLE. **VII. Calcium.** H. GILMAN, R. H. KIRBY, M. LICHTENWALTER, and R. V. YOUNG (Rec. trav. chim., 1936, 55, 76—79, 79—81).—VI. B has the function of a metal in organoboron compounds, but these are less reactive than true organometallic compounds.  $\text{BPh}_3$  with  $\text{PhCHO}$  and  $\text{PhNCO}$  yields respectively  $\text{CHPh}_2\text{OH}$  and  $\text{NHBzPh}$ . The colour test (cf. A., 1925, ii, 1011) is given more rapidly by  $\text{BPr}_3$  than by  $\text{BPh}_3$ , but less rapidly than by organoaluminium compounds.

**VII.** Contrary to Gilman and Schulze (A., 1926, 1130)  $\text{CaPhI}$  is more reactive than  $\text{MgPhI}$ , as it converts  $\text{PhCN}$  into  $\text{COPh}_2$  5 times as rapidly, converts diphenylene oxide into its -1-carboxylic acid ( $\text{MgPhI}$  does not), and converts  $\text{NPh:CPh}_2$  into  $\text{NHPPh:CPh}_2$  (analogy with  $\text{LiPh}$ ). F. R. G.

**Mercuration of nipasol, a propyl ester of p-hydroxybenzoic acid.** A. M. SAMSON and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1935, 4, 149—154).— $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}$  with  $\text{Hg}(\text{OAc})_2$  in  $\text{AcOH-EtOH}$  affords a mixture (I) of  $\text{Pr } 3:5\text{-bis}(\text{acetoxymercuri})\text{-}$  and  $3\text{-(acetoxymercuri)-}4\text{-hydroxybenzoates}$ . (I) with  $\text{I-KI}$  yields a product of indefinite m.p., which affords  $3:5\text{-di-iodo-}$ , m.p. 236—237° (Me ester, m.p. 166—167°; Et ester, m.p. 123—124°), and  $3\text{-iodo-}$ , m.p. 190—200° (Me ester, m.p. 156—157°),  $4\text{-hydroxybenzoic acids}$  on hydrolysis with  $\text{EtOH-KOH}$ ; with  $\text{Br}$  (I) similarly affords  $3:5\text{-dibromo-}$ , m.p. 266—267° (Me ester, m.p. 125—126°), and  $3\text{-bromo-}$  (Me ester, m.p. 106—107°),  $4\text{-hydroxybenzoic acids}$ . CH. ABS. (r)

**Stereochemistry of some new complex thio-salts of mercury, cadmium, and zinc.** W. H. MILLS and R. E. D. CLARK (J.C.S., 1936, 175—181).— $1:3:4\text{-C}_6\text{H}_3\text{Me}(\text{SO}_2\text{Cl})_2$  is reduced ( $\text{Sn-HCl}$ ) to the  $3:4\text{-dithiol}$  (I), b.p.  $174^\circ/41\text{ mm.}$ , m.p.  $35^\circ$ .  $p\text{-C}_6\text{H}_4\text{Cl-NHAc}$  heated with conc.  $\text{H}_2\text{SO}_4$  affords  $p\text{-chloroanilinesulphonic acid}$ , converted through the diazonium xanthate and oxidation ( $\text{HNO}_3$ ,  $d$  1.4) into the  $3:4\text{-disulphonic acid}$  (Ba and Na salts), the sulphonyl chloride, m.p.  $82\text{--}83^\circ$ , of which is reduced to  $1\text{-chlorobenzene-}3:4\text{-dithiol}$  (II), b.p.  $165^\circ/32.5\text{ mm.}$ , m.p.  $31^\circ$ . When refluxed with yellow  $\text{HgO}$ , (I) in  $\text{KOEt-EtOH}$  affords  $\text{K}_2\text{ bis}(\text{toluene-}3:4\text{-dithiol})\text{-mercury}$ , +  $\text{EtOH}$  and solvent-free, of type  $[\text{Ar} \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \end{smallmatrix} \text{M}' \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Ar}] \text{M}'_2$  (III) ( $\text{M}' = \text{Hg}$ ,  $\text{M}' = \text{K}$ ); similar complexes are obtained with Cd and Zn. The corresponding alkaloid salts ( $\text{M}' = \text{alkaloid}$ , H) are obtained (i) from the  $\text{K}_2$  salt and the base sulphate or hydrochloride in  $\text{EtOH}$ , or (ii) by the action of  $\text{HgO}$  on a solution of the base and thiol in  $\text{CHCl}_3$ . Thus, from (II) is obtained *diquinine*  $\text{H}_2\text{ bis}(\text{1-chlorobenzene-}3:4\text{-dithiol})\text{mercury}$  as its  $\alpha\text{-form}$ , m.p.  $142^\circ$ ,  $[\alpha]_{\text{D}}^{20} +182^\circ$  in  $\text{COMe}_2$ ,  $[\alpha]_{\text{D}}^{20} -191^\circ$  in  $1:1\text{ CHCl}_3\text{-COMe}_2$ , which dissolves readily in  $\text{COMe}_2$ , the solution depositing crystals of the  $\beta\text{-form}$ , m.p.  $138^\circ$ ,  $[\alpha]_{\text{D}}^{17} -240^\circ$

in  $\text{CHCl}_3$ ,  $[\alpha]_{\text{D}}^{20} -188^\circ$  in  $1:1\text{ CHCl}_3\text{-COMe}_2$ . The solution of the  $\beta\text{-form}$  in cold  $\text{CHCl}_3$  sets to a jelly which slowly crystallises at  $40\text{--}60^\circ$  to the  $\alpha\text{-form}$ . Interconversion of  $\alpha\text{-}$  and  $\beta\text{-forms}$  can be repeated indefinitely by such methods, using various solvents. Assuming a tetrahedral arrangement of the 4 S in the complex anion, resolution should be possible, but, probably owing to very rapid autoracemisation, the  $\text{Na}_2$  salts were inactive and showed no mutarotation even at  $-35^\circ$ . One form is probably of type (III) and the other is assigned a 3 co-ordinated Hg structure. By similar methods are obtained the  $\alpha\text{-}$ , + $\alpha\text{CHCl}_3$  (effloresces), and  $\beta\text{-}$ , m.p.  $157^\circ$ , forms of *diquinine*  $\text{H}_2\text{ bis}(\text{1-chlorobenzene-}3:4\text{-dithiol})\text{cadmium}$  and, from (I), the  $\alpha\text{-}$ , m.p.  $155^\circ$ , and  $\beta\text{-}$ , sinters  $128^\circ$ , m.p.  $145^\circ$ , forms of *diquinine*  $\text{H}_2\text{ bis}(\text{toluene-}3:4\text{-dithiol})\text{zinc}$ , similarly interconvertible. An apparatus for rapid low-temp. polarimetry is described. J. W. B.

**Organic thallium compounds. III. Synthesis of organic thallium compounds with simple substituents in the aromatic radical.** S. S. NAMETKIN, N. N. MELNIKOV, and G. P. GRATSHEV (J. Gen. Chem. Russ., 1935, 5, 1455—1459).—The following substituted aryl Tl halides have been prepared by the reactions:  $\text{RB(OH)}_2$  (I) +  $\text{TlX}_3 + \text{H}_2\text{O} \rightarrow \text{RTlX}_2$  (II) +  $\text{HX} + \text{H}_3\text{BO}_3$ ; (I) + (II) +  $\text{H}_2\text{O} \rightarrow \text{R}_2\text{TlX} + \text{HX} + \text{H}_3\text{BO}_3$ :  $p\text{-C}_6\text{H}_4\text{Br-TlCl}_2$ , m.p.  $262^\circ$  (decomp.);  $p\text{-C}_6\text{H}_4\text{Br-TlBr}_2$ , decomp. at  $190\text{--}200^\circ$ ;  $p\text{-C}_6\text{H}_4\text{Cl-TlCl}_2$ , m.p.  $>250^\circ$ ;  $p\text{-C}_6\text{H}_4\text{Cl-TlBr}_2$ , m.p.  $>250^\circ$ ;  $\text{CH}_2\text{Ph-TlBr}_2$ , m.p.  $205^\circ$  (decomp.);  $(p\text{-C}_6\text{H}_4\text{Br})_2\text{TlCl}$ , m.p.  $>250^\circ$ ;  $(p\text{-C}_6\text{H}_4\text{Br})_2\text{TlBr}$ , m.p.  $>250^\circ$ ;  $(p\text{-OMe-C}_6\text{H}_4)_2\text{TlBr}$ , m.p.  $>250^\circ$ ;  $(p\text{-C}_6\text{H}_4\text{Cl})_2\text{TlCl}$ , m.p. not given;  $(p\text{-C}_6\text{H}_4\text{Cl})_2\text{TlBr}$ , decomp. at  $240^\circ$ . R. T.

**Proteins in liquid ammonia. III. Reaction of sodium in liquid ammonia with proteins and related substances.** R. G. ROBERTS and C. O. MILLER (J. Amer. Chem. Soc., 1936, 58, 309—310; cf. A., 1934, 638).—Dry proteins react with Na in liquid  $\text{NH}_3$  as acids,  $\text{H}_2$  being evolved; reaction is much slower than with  $\text{NH}_2\text{-acids}$  or dipeptides. Using a slight excess of Na, the vals. of the ratio mols.  $\text{H}_2$  evolved to g.-atoms N present for caseinogen, edestin, gelatin, and zein are 0.215, 0.285, 0.35, and 0.09, respectively; these vals. are generally  $>$  those calc. from the glutamic, aspartic, and hydroxyglutamic acid content. H. B.

**Physical chemistry of zein.** C. C. WATSON, S. ARRHENIUS, and J. W. WILLIAMS (Nature, 1936, 137, 322—323).—By the addition of  $\text{H}_2\text{O}$  to the  $\text{EtOH}$  solution, purified zein can be divided into 3 practically homogeneous fractions, which are now characterised by their sedimentation, diffusion, and dielectric consts., and by their electrophoretic mobilities. L. S. T.

**Crystalline ovalbumin. III. Fractionation of peptic hydrolysis products by dialysis.** H. O. CALVERY and E. D. SCHOCK. **IV. Rate of liberation of amino-nitrogen and cystine, tyrosine, and tryptophan.** Colorigenic values during peptic, acid, and alkaline hydrolysis of ovalbumin. H. O. CALVERY, W. D. BLOCK, and E. D. SCHOCK (J. Biol. Chem., 1936, 113, 15—19, 21—25).—III. Dialysis can be used to separate



peptic hydrolysis products into fractions of different composition. Free tyrosine has been isolated from a peptic hydrolysate of cryst. ovalbumin, thus supporting the view that free  $\text{NH}_2$ -acids are liberated when pepsin acts on protein.

IV. Uncoagulated cryst. ovalbumin is readily hydrolysed when the pepsin to protein ratio is 1:10 and the acid concn. is approx. 0.3%. During the digestion the  $\text{NH}_2\text{-N}$  val. rises gradually to a max. of 25.1% in 36 days whilst the chromogenic val. obtained by the Folin-Marenzi method for cystine increases gradually to a max. of 2.1% within 12 hr. and then falls to a const. val. between 1.6 and 1.7% during the next 35 days. This is much > the highest val. (1.3%) obtained by acid hydrolysis. The acid peak was reached after a gradual rise and did not follow the same curve as that obtained by Jones *et al.* (A., 1933, 1081) for the cystine content of caseinogen. The tyrosine and tryptophan colorogenic vals. rose gradually until they reached a max. during peptic and alkaline hydrolysis; the max. are not coincident.

H. W.

Dilatometric investigations on the heat-denaturation of proteins. I. E. HEYMANN (Biochem. J., 1936, 30, 127—131).—Solutions of serum-albumin and -globulin, ovalbumin, and zein all showed an increase in total vol. on heat-denaturation; when the latter was not accompanied by coagulation the vol. changes were smaller. The vol. increases were only 3—4% of the vol. decreases on dissolving in  $\text{H}_2\text{O}$ . A sensitive dilatometer is described.

H. D.

Chemistry of heat-denaturation of proteins. A. KIESEL and S. KUSMIN (Z. physiol. Chem., 1936, 238, 145—148).—The denaturation by heat ( $60^\circ$ ) of edestin (I) is accompanied by increases in the tyrosine and histidine (II) contents. Possibly ring-closure is the cause of the (II) increase. Elimination of  $\text{H}_2\text{O}$  occurs on methylation of (I), but not in denaturation by heat.

W. McC.

Ultrafiltration of proteins. II.—See this vol., 500.

Relation of protein coagulation to oxidation-reduction potential.—See this vol., 360.

Ionic structure solubility, and coagulation of proteins.—See this vol., 426.

Nitrogen determination by ter Meulen's method. P. MAES (Bull. Assoc. anc. Elèves Gand, 1935, 36, 39—41; Chem. Zentr., 1935, i, 3821).—A modified method is described.

H. N. R.

Determination of small amounts of arsenic in organic compounds. K. WINTERFELD, E. DÖRLE, and C. RAUCH (Arch. Pharm., 1936, 274, 214).—A correction (cf. this vol., 90).

Determination of methoxyl and ethoxyl groups. C. L. PALFRAY (Documentat. sci., 1935, 4, 1—3; Chem. Zentr., 1935, i, 3821).—A volumetric Zeisel method is described.

H. N. R.

Determination of semicarbazide and semicarbazones. V. HARLAY (J. Pharm. Chim., 1936,

L L

[viii], 23, 199—204).—Passage of steam for 8—10 hr. through a solution of semicarbazones in 20%  $\text{H}_2\text{SO}_4$  liberates semicarbazide which is decomposed to  $\text{N}_2\text{H}_4$ ; this is determined by I in AcOH solution. The method is applicable to semicarbazide and semicarbazones of aldehydes and ketones, but not to those of ketonic acids.

R. S. C.

Determination of carotene and xanthophyll by a single distribution between liquid phases. S. W. CLAUSEN and A. B. MCCOORD (J. Biol. Chem., 1936, 113, 89—104).—A general colorimetric method for the determination of two substances of the same colour by a single distribution between two immiscible liquids is described, and applied to mixtures of carotene and xanthophyll using hexane and aq. diacetone alcohol. The method is applicable to pigments in plasma and serum.

J. N. A.

Ehrlich diazo-reaction with urine.—See this vol., 502.

Decomposition of salts of acetylsalicylic acid. V. GERVAY (Magyar gyóg. Társ. Ért., 1935, 11, 241—245; Chem. Zentr., 1935, ii, 250).—Owing to this decomp. the determination of free salicylic acid can only be approx.

H. N. R.

Colour reaction of ammonia and glycine with hypobromite and phenolic substances. O. FÜRTH and F. GÖTZL (Biochem. Z., 1936, 283, 358—363).—The elementary compositions of a series of blue pigments obtained by interaction of  $\text{NaOBr}$  with  $\text{PhOH}$  (or thymol) and  $\text{NH}_2$ -acids (or  $\text{NH}_4$  salts) are summarised in the formula  $\text{C}_{15-84}\text{H}_{45-113}\text{NBr}_{1-5-3}$ .

P. W. C.

Determination of phytic acid.—See this vol., 535.

Gross and Smith colorimetric method for determination of rotenone and deguelin. L. D. GOODHUE (J. Assoc. Off. Agric. Chem., 1936, 19, 118—120; cf. A., 1934, 1017).— $\text{H}_2\text{SO}_4$  is substituted for  $\text{HNO}_3$ , the  $\text{KOH}$  in  $\text{EtOH}$  is diluted with  $\text{H}_2\text{O}$ , and the necessary  $\text{NO}_2$  added as  $\text{NaNO}_2$  to this solution. Fading is eliminated and the sensitivity increased 20-fold.

E. C. S.

Identification of alkaloids as picrates. A. IONESCO-MATIU and E. ILIESCO (J. Pharm. Chim., 1936, [viii], 23, 117—141).—Microchemical identification of alkaloids as picrates using (a) a cold saturated solution of picric acid (I) in 96%  $\text{EtOH}$  containing 5% of glycerol, or (b) picramic acid obtained by reduction of a 5% aq. solution of (I) with  $\text{Na}_2\text{CO}_3$ -glucose, is described. Using one drop of the alkaloid solution the picrates of the following are described, the sensitivity of the reaction, in mg. unless otherwise stated, being given in parentheses: atropine, m.p.  $165\text{—}166^\circ$  (b,  $10^{-2}$ ), hyoscyamine, m.p.  $162\text{—}163^\circ$  (a, 0.5), nicotine, darkens  $200^\circ$ , m.p.  $208^\circ$  (a,  $10^{-3}$ ), strychnine, decomp.  $200^\circ$  (a,  $2 \times 10^{-3}$ ; b,  $2 \times 10^{-4}$ ), brucine (a,  $5 \times 10^{-2}$ ), morphine (a, 0.5% solution), codeine (a, 0.2% solution), dionine (a, 0.1% solution), heroin (a, 0.01% solution), papaverine, shrinks  $150^\circ$ , m.p.  $154^\circ$  (a,  $10^{-2}$ ), sparteine, darkens  $195\text{—}196^\circ$ , m.p.  $199^\circ$  (a, 0.05), hydrastinine (a, 0.08% solution), cocaine, m.p.  $154\text{—}155^\circ$  (b,  $2 \times 10^{-3}$ ), ephedrine (a, > 0.8% solution), novo-



caine, reddens  $140^{\circ}$ , m.p.  $146-147^{\circ}$  ( $\alpha$ , 0.4% solution), stovaine, m.p.  $110-112^{\circ}$  ( $\alpha$ , 0.02%), antipyrine, m.p.  $180-182^{\circ}$  ( $\alpha$ ,  $10^{-2}$ ), and pyramidone, m.p.  $168-170^{\circ}$  ( $\alpha$ , 0.04% solution). Photomicrographs are given in each case. J. W. B.

**Recognition of papaverines by a colour reaction with acetic anhydride and sulphuric acid.** W. AWE (Pharm. Zentr., 1936, 77, 157-160; cf. A., 1923, i, 701).—Papaverine (5 mg.) in  $\text{Ac}_2\text{O}$  (3 c.c.) containing  $\text{H}_2\text{SO}_4$  (5 drops) at  $80^{\circ}$  affords a solution with a yellowish-green fluorescence in daylight. 0.05 mg. can be recognised by observing the fluorescence in ultra-violet light. When  $\text{AcCl-ZnCl}_2$  is used as condensing agent, the fluorescence in daylight is

obscured by the colour of the solution. Cryptopine (A., 1910, i, 502) does not interfere. J. L. D.

**Use of Zimmermann's reagent for detection of glycine and for determining its position in polypeptides.** E. ABDERHALDEN and A. NEUMANN (Z. physiol. Chem., 1936, 238, 177-182; cf. A., 1930, 897).—When free glycine (I) is present a ppt. is always produced. Of the other  $\text{NH}_2$ -acids (not mentioned by Zimmermann) of the protein mol. only tryptophan (which gives a brown ppt. and green solution) interferes. With polypeptides containing the (I) residue the reaction is positive only when this residue carries the  $\text{NH}_2$  (negative with silk fibroin, positive with silk peptone). W. McC.

## Biochemistry.

**Biochemistry and biophysics.** P. L. DU NOÛY (Bull. Soc. Chim. biol., 1936, 18, 138-156).—A lecture.

**Response of the chemical receptors of the carotid sinuses to the tension of carbon dioxide in the arterial blood in the cat.** A. SAMAAH and G. STELLA (J. Physiol., 1935, 85, 309-319).

R. N. C.

**Retention of carbonic acid in the dormouse (*Myoxus glis*) in course of carbon dioxide narcosis and rôle of the tissues in the maintenance of the alkaline reserve.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 447-449).—The anaesthetised animal retains considerable quantities of  $\text{CO}_2$ , suggesting the presence of an "alkaline reserve" in the tissues equiv. to that of the blood.

R. N. C.

**Nitrogen solubility in blood at increased air pressures.** J. A. HAWKINS and C. W. SHILLING (J. Biol. Chem., 1936, 113, 273-278).—The solubility coeff. of  $\text{N}_2$  (at atm. pressure) in dog's and ox blood is 0.0138-0.0148 and 0.0135-0.0140, respectively. With pressures of  $\text{N}_2$  of 1-6 atm., the val. follows Henry's law.

H. G. R.

**Regulation of the oxygen output of erythrocytes.** I. F. HIMMERICH. II. **Blood-glycolysis.** F. HIMMERICH and R. S. FEINBERG (Biochem. Z., 1936, 284, 146-151, 152-162).—I. An apparatus for measuring the output is described.

II. The glycolysis resulting from addition of glucose to human erythrocytes increases (up to 200%) their  $\text{O}_2$  output. Similarly, in defibrinated human and rabbits' blood the increased glycolysis due to an increase of 0.25-0.3 in  $p_{\text{H}}$  results in increases (up to > 300%) in the  $\text{O}_2$  output. Apparently all factors which stimulate glycolysis increase  $\text{O}_2$  output. Probably the glycolysis occurs at the surface of the erythrocytes and the accompanying production of acid and liberation of heat may play important parts in the process.

W. McC.

**Determination of colloid-osmotic pressure.** H. NAGAOKA (J. Biochem. Japan, 1935, 22, 351-366).—The colloid-osmotic pressure of horse serum, measured by a collodion membrane with a standard

membrane potential of 2-5 mv., attains equilibrium after 24 hr.; comparative measurements can be taken after 3-24 hr. Relationships between the pressure and concn. of colloid and temp. are determined.

F. O. H.

**Electrodialysis of serum.** A. V. MARKOVITSCH (J. Appl. Chem. Russ., 1935, 8, 1444-1451).—The  $p_{\text{H}}$  of serum falls during electrodialysis (parchment cathode and bakelite-paper anode membranes) from the original val. to 5.2. Max. pptn. of globulins takes place at  $p_{\text{H}}$  5.6-5.7, at low concn. of electrolytes.

R. T.

**Effect of continued passage of current through the external medium on the composition of blood in *Scyllium canicula*, the bronchial region being near the cathode.** E. A. PORA (Compt. rend. Soc. Biol., 1936, 121, 411-413).—The osmotic pressure and corpuscular vol. increase with the intensity of the current. Ca and proteins also increase, whilst K and alkaline reserve decrease progressively. Vals. afterwards tend to return to normal. Serum- $\text{H}_2\text{O}$  falls, but inorg. salts and org. substances both increase at the expense of the muscles, which take up  $\text{H}_2\text{O}$ .

R. N. C.

**Modifications of the blood of *Perca fluviatilis*, consecutive to deep-sea fishing.** L. BAUDIN (Compt. rend. Soc. Biol., 1936, 121, 437-439).

R. N. C.

**Determination of the alkaline reserve in small mammals.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 446-447).—The Van Slyke const.-vol. apparatus is used. Local anaesthetisation during the drawing of blood is necessary.

R. N. C.

**Effect of physical training on blood-volume, hæmoglobin, alkaline reserve, and osmotic resistance of erythrocytes.** J. E. DAVIS and N. BREWER (Amer. J. Physiol., 1935, 113, 586-591).—Blood-vol. and hæmoglobin per unit vol. (I) in the dog fall during the first week of training, and later rise, but (I) is never > normal. The alkaline reserve is increased. Erythrocyte osmotic resistance rises in swimming but falls in running animals.

R. N. C.

**Analysis of the constituents of suspensions of erythrocytes by the method of neutralisation**



curves. G. ACHARD (Compt. rend. Soc. Biol., 1936, 121, 478—481).—The buffering effect of erythrocyte suspensions, their excipients, and laked erythrocyte solutions is due to factors other than the inorg. salts present. R. N. C.

Alteration, with time, of the buffering power of suspensions of erythrocytes. G. ACHARD (Compt. rend. Soc. Biol., 1936, 121, 481—484).—After prolonged action of acids or alkalis on erythrocyte suspensions the neutralisation curves resemble those obtained in suspensions laked with  $H_2O$ . R. N. C.

Reduction of oxyhæmoglobin in the human skin. L. NICOLAI (Pflüger's Archiv, 1932, 230, 238—245; cf. A., 1932, 1270).—Reduction of oxyhæmoglobin in the skin follows the equation  $c=c_0e^{-kt}$ . The rate of reduction is unchanged in hyperæmia following anoxæmia. R. N. C.

Fate of hæmoglobin in the organism. K. BINGOLD (Klin. Woch., 1934, 13, 1451—1452).—A pigment (I) with a band at 535  $m\mu$  is formed by the action of alkaline  $Na_2S_2O_4$  on bilirubin-rich urine. It is found in old pleural exudates, but not in serum; its appearance in the urine is unaltered if the liver is choked. (I) is considered to be free from Fe and not bound to proteins, the colour being due to formation of a S derivative. Pigeons' blood or hæmin decolorised with  $H_2O_2$  and boiled with KOH gives a band at 535  $m\mu$ ;  $Na_2S_2O_4$  is often necessary for production of the spectrum. Cultures of *Pneumococci* on catalase-free blood-agar break down the blood to (I). R. N. C.

Effect of diet on the hæmoglobin concentration of the blood. L. N. ELLIS and O. A. BESSEY (Amer. J. Physiol., 1935, 113, 582—585).—Hæmoglobin in the rat at 1 month  $\propto$  the Fe content of the diet, but is independent at 1 year, when it falls into one of two ranges of vals., according to the sp. diet given. R. N. C.

Occurrence of several kinds of hæmoglobin in human blood. R. BRINKMAN and J. H. P. JONXIS (J. Physiol., 1935, 85, 117—127).—Fœtal hæmoglobin is replaced by a "less resistant" adult hæmoglobin after 7 months, and this in turn is replaced after 3 years by a hæmoglobin more resistant to alkaline denaturation. The three hæmoglobins differ in rate of alkaline denaturation and in isoelectric point, and so far have been detected only in human blood. R. N. C.

Relationship between specific gravity and protein content in plasma, serum, and transudate from dogs. A. A. WEECH, E. B. REEVES, and E. GOETTSCH (J. Biol. Chem., 1936, 113, 167—174).—The  $d$  of blood-plasma, -serum, or -transudate  $\propto$  the protein concn. H. D.

Serum electrolytes. X. Water of serum and factors for calculation of molality of a solute in serum from measurement of specific gravity. F. W. SUNDERMAN (J. Biol. Chem., 1936, 113, 111—115).—The  $d$  of serum bears to the total solids a linear relation (consts. given) from which concns. of a solid related to  $[H_2O]$  may be obtained. F. A. A.

Conductometric method for investigation of colloidal suspensions. A. SLAVINSKI (Bull. Soc. Chim. biol., 1936, 18, 195—202).—The author's method (A., 1934, 860) for determining the vol. of colloidal particles is applied to blood-plasma. Human and horse plasma contain about 9% of albumin associated with 4.5% of liquid, the tonicity of the plasma being that of 0.85% aq. NaCl. Measurements with hæmolyzed blood indicate that the corpuscles contain "hæmoglobules" occupying 55% of the vol. of the corpuscles and containing 52% of hæmoglobin and 48% of liquid. A. L.

Effect of hæmorrhage of varying degree on blood and plasma volume, on blood-sugar, and on arterial blood pressure. J. D. ROBERTSON (J. Physiol., 1935, 84, 393—409). R. N. C.

Effect of splenic extracts on the blood picture. T. IMAI (Tohoku J. Exp. Med., 1933, 22, 293—313). CH. ABS. (p)

Cyclic variations in the composition of fish blood. L. BAUDIN (Compt. rend. Soc. Biol., 1936, 121, 501—502). R. N. C.

Ultrafiltration studies with normal horse serum. W. J. ELFORD, P. GRABAR, and W. FISCHER (Biochem. J., 1936, 30, 92—99).—Analysis of the state of aggregation of horse serum-proteins by ultrafiltration through graded collodion membranes shows that the simplest protein units correspond in particle size with mol. serum-albumin (I) and pseudoglobulin in dil. solutions, and that a second fraction is present which is more readily retained by membranes and in particle size about twice that of (I). This fraction is essentially a globulin (II) aggregate and may correspond with the euglobulin of serum. The antibody of an aged sample of type I pneumococcus antiserum was retained by membranes simultaneously with the more complex (II) fraction. P. W. C.

Activity of the globulins of blood as alexins. M. DOLADILHE (Compt. rend., 1935, 201, 689—690).—The globulins (I) pptd. from diluted serum with  $CO_2$  are sol. in saline and are then separated by  $CO_2$  into an insol. (0.2036% P) and a sol. (0.0782% P) fraction, which may be components of a sol. complex. The sol. fraction exhibits the central-group properties of alexin, of the same intensity as does the saline solution of (I). J. L. D.

Total plasma-protein in normal and fasting rats. W. C. CUTTING and R. D. CUTTER (Amer. J. Physiol., 1935, 113, 150—158).—Total plasma-protein (I) is measured by determination of the blood vol. (for which a method is described) and protein concn. Decrease of (I) during fasting  $\propto$  time. Lymph- and plasma-proteins resemble each other in composition and participation in body functions. R. N. C.

Tyramine as a pressor substance in pallid hypertension. H. A. HEINSEN and H. J. WOLF (Klin. Woch., 1934, 13, 1688).—Blood fractions obtained by extraction of the deproteinised blood with  $C_2H_5OH$  and  $H_2SO_4$  give the color reaction with 1:2- $NO \cdot C_{10}H_6 \cdot OH$  and  $HNO_3$ , suggesting that tyramine is a cause of pallid hypertension. R. N. C.



**Pharmacological determination of adenosine and histamine in blood.** G. S. BARSOUM and J. H. GADDUM (*J. Physiol.*, 1935, 85, 1—14).—Tests described can detect  $2 \times 10^{-8}$  g. of histamine (I) and  $0.5 \times 10^{-6}$  g. of adenosine (II). (I) is present in normal human, rabbit's, guinea-pig's, dog's, and probably cat's blood. Corpuscular (I) and (II) are  $>$  plasma-(I) and -(II), respectively. Clotting of blood or shaking of citrated blood increases (II) without affecting (I). R. N. C.

**Appearance of histamine in venous blood during muscular contraction.** G. V. ANREP and G. S. BARSOUM (*J. Physiol.*, 1935, 85, 409—420).—The histamine (I) contents of the arterial and venous blood to and from resting muscle are the same. Venous (I) is increased by diminution of the blood supply and by muscular contraction. R. N. C.

**Presence of creatinine in blood.** I. S. DANIELSON (*J. Biol. Chem.*, 1936, 113, 181—195).—The major part of the chromogenic substance (in the Folin-Wu determination; A., 1919, ii, 308) in blood  $H_2WO_4$  filtrates and plasma ultra-filtrates is adsorbed by kaolin. The colour developed in a kaolin-treated filtrate heated with aq. NaOH is approx. the same as that obtained with an ordinary filtrate, whereas pure solutions of creatinine (I), or the material eluted from the kaolin, on treatment with NaOH give no colour with alkaline picrate. It is concluded that the chromogenic material in blood filtrates is (I). H. D.

**Variations of concentration of conjugated phenols in blood in passing different organs.** A. D. MARENZI (*An. Farm. Biochim.*, 1933, 4, 36—38; *Chem. Zentr.*, 1935, i, 3562).—The conjugated phenol content of portal blood is  $>$  that of the carotid and vena cava inferior. R. N. C.

**Lipochromes of human blood-serum.** E. VON DANIEL and T. BÉRES (*Z. physiol. Chem.*, 1936, 238, 160—162).—The material obtained from 3 litres of the serum by chromatographic adsorption on  $Ca(OH)_2$  (after pptg. with  $EtOH$ , etc.) consisted of 0.33 mg. of a yellowish-brown pigment (absorption max. at 502.5 and 472  $m\mu$ ), 0.15 mg. of lycopen, 0.08 mg. of a light yellow pigment (max. at 455 and 425  $m\mu$ ), and 0.28 mg. of carotene. The unidentified pigments may be biologically active. The proportions in which the pigments occur in the serum and the amounts of the individual pigments vary greatly. W. McC.

**Determination of fat in 0.1 c.c. of blood or serum.** J. SURÁNYI and P. VÉGHÉLYI (*Biochem. Z.*, 1936, 283, 415—421).—Blood (0.05 c.c. in each case) was extracted with  $EtOH$  and  $COMe_2$  at 100° and 75° and the filtered extracts were treated with  $HCl-H_2O-BuOH$ . The resulting turbidities were measured by the step-photometer. The total fat was thus obtained in the  $EtOH$  extract whilst lecithin was absent from the  $COMe_2$  extract. P. W. C.

**Spectrophotometric determination of blood-cholesterol by means of silica.** H. FOY and A. KONDI (*Brit. J. Exp. Path.*, 1935, 16, 349—357).—Variations in the state of hydration of plaster of Paris render the Myers and Wardell method unsatis-

factory. A modified method replacing this by  $SiO_2$  and using a photometer is described.

NUTR. ABS. (m)

**Effect of glucose ingestion on the cholesterol fractions of blood.** F. FITZ and M. BRUGER (*J. Biol. Chem.*, 1936, 113, 297—302).—The increase in total cholesterol when glucose is fed to fasting subjects is located in the cholesteryl ester fraction. H. G. R.

**Physiology of blood-glycogen.** I. G. GOLANDAS. II. H. STAUB and G. GOLANDAS (*Pflüger's Archiv*, 1935, 236, 230—238, 355—360).—I. The mean val. for fasting blood-glycogen (I) in the dog is slightly  $>$  that in man or rabbits. Plasma- and serum-glycogen are the same for all three; the greater part of (I) is contained in the corpuscles. (I) does not vary in the same subject; it diminishes in sterile blood stored at 37°, is scarcely altered at —8°, and is increased in unsterilised blood at 37° by bacterial action.

II. (I) rises in dogs and rabbits after fasting for 144—170 hr. Overcharging with carbohydrate generally increases (I) in man (mainly in the corpuscles) and rabbits. R. N. C.

**Mechanism of the origin of alimentary hyperglycaemia.** Y. HUKUI (*J. Biochem. Japan*, 1935, 22, 447—496).—Direct application of glucose (I) to the duodenum of rabbits produces no significant hyperglycaemia. Direct administration of (I), galactose, or fructose to the stomach or duodenum does not change the sugar content curves of blood from the portal, hepatic, or ear veins. Splanchnicotomy and/or vagotomy lower the alimentary hyperglycaemic curve. Administration of ergotamine or atropine also lowers the curve. Oral administration of fructose produces a hyperglycaemia due to blood-(I) and reduced by splanchnicotomy. The data support the absorption rather than the reflex-mechanism theory. F. O. H.

**True blood-sugar level in insulin shock and convulsions.** L. B. DOTTI and M. C. HRUBETZ (*J. Biol. Chem.*, 1936, 113, 141—143; cf. A., 1934, 565).—In rats, the true blood-sugar level falls during the course of insulin shock, and at the onset of convulsions is zero. F. A. A.

**Variations of blood-sugar in rabbits following subcutaneous injections of phenylhydrazine hydrochloride.** P. DERVILLÉE, L. LANSAC-FATTE, and R. CASTAGNOU (*Compt. rend. Soc. Biol.*, 1936, 121, 549—552).—Hyperglycaemia occurs in varying degree, but no hypoglycaemia. R. N. C.

**Lactacidæmia in fowls with avitaminosis-B.** I. I. NITZESCU and I. GONTZEA (*Compt. rend. Soc. Biol.*, 1936, 121, 562—563). R. N. C.

**Influence of preliminary training on the lactic acid content of blood after intense work.** A. V. PALLADIN and B. M. KOLDAEV (*Ukrain Biochem. J.*, 1934, 7, No. 1, 30—39).—Intense work causes accumulation of lactic acid in blood. Preliminary training lowers the rate of accumulation. CH. ABS. (p)

**Mendel and Goldscheider's method for determining lactic acid in blood.** R. MILTON (*Analyst*,



1936, 61, 91—96; cf. A., 1926, 212).—The effect of temp., time of heating, and concn. of  $\text{H}_2\text{SO}_4$  and veratrole on the intensity of the colour produced is investigated and modifications are suggested. The results obtained are slightly lower, but more consistent, than those given by Friedemann and Kendall's method (A., 1929, 677).  
E. C. S.

**Determination of sodium formaldehyde-sulphoxylate in blood-plasma.** E. HUG (Compt. rend. Soc. Biol., 1936, 121, 577—579).—Plasma is deproteinised with  $\text{UO}_2(\text{OAc})_2$ , and  $\text{NaHSO}_2\cdot\text{CH}_2\text{O}$  determined with I.  
R. N. C.

**Partition of calcium and inorganic phosphorus in equine serum.** P. B. PEARSON and H. R. CATCHPOLE (Proc. Amer. Soc. Animal Prod., 1935, Jan., 84—86).—Average vals. for total Ca and P in horses on a diet with adequate Ca and P were  $13.13 \pm 1.03$  and  $3.37 \pm 0.29$  mg. per 100 ml., respectively, and on a low-P diet vals. were  $13.60 \pm 0.70$  and  $2.61 \pm 0.21$  mg. The vals. for diffusible Ca and P were  $7.15 \pm 0.87$  and  $3.02 \pm 0.32$  mg. for the former and  $8.09 \pm 0.84$  and  $2.47 \pm 0.29$  mg. for the latter.  
NUTR. ABS. (m)

**Composition of the blood of dairy cattle. I. Effect of age and phosphorus intake on calcium and inorganic phosphorus content of whole blood of dairy heifers.** A. H. VAN LANDINGHAM, H. O. HENDERSON, and G. A. BOWLING (J. Dairy Sci., 1935, 18, 557—572).—Feeding of P-deficient rations lowers the blood-inorg. P to extents approx.  $\propto$  the deficiency. The P requirement of growing animals is not  $\propto$  the increase in body-wt. but depends on skeletal development as measured by the height of the withers. The requirement in proportion to body-wt. decreases as the animal approaches maturity. Age and level of P intake were without effect on blood-Ca.  
A. G. P.

**Blood-calcium in newborn infants.** N. P. COSTA, F. ESCARDO, and S. SCHERE (Rev. Soc. Argentina biol., 1934, 10, 273—279).—In newborn infants blood-Ca was slightly  $<$  that of the mother.  
CH. ABS. (p)

**Blood-magnesium in pregnant women.** N. ZAHARESCO-KARAMAN, M. ALEXIU, and I. URSU (Compt. rend. Soc. Biol., 1936, 121, 559—561).—Blood-Mg rises steadily to a max. in the 5th month, falls sharply in the 6th, rises again to the approx. val. of the first max. in the 7th, and then falls slightly until the end of pregnancy.  
R. N. C.

**Iodometric determination of iron in blood.** LASAUSSE and L. FROCRAIN (J. Pharm. Chim., 1936, [viii], 23, 82—84).—Aq.  $\text{NH}_3$  and milk of  $\text{MgO}$  are added and, after evaporating to dryness, incinerating at low temp., and igniting, the residue is freed from  $\text{HNO}_3$  by  $\text{HCl}$ , dissolved in  $\text{HCl}$ , and mixed with aq.  $\text{KI}$ . After 3 min. 3 drops of amidone solution are added and liberated I is titrated with 0.005N- $\text{Na}_2\text{S}_2\text{O}_3$ .  
W. McC.

**Effect of adrenalectomy on blood-chloride and -sodium.** C. I. URECHIA, G. BENETATO, and RETEZEANU (Bull. Acad. Méd. Roumanie, 1936, 1, 141—144).—Adrenalectomy in cats produces

a rise or fall in blood-Cl, but generally a fall in -Na.  
F. O. H.

**Blood-bromine.** C. I. URECHIA and RETEZEANU (Presse méd., 1935, 43, 701—703).—Low blood-Br was found only in manic-depressive psychoses. Injection of drugs and therapeutic preps. did not reduce it.  
NUTR. ABS. (m)

**Blood-iodine. V. Blood-iodine after total thyroidectomy in man.** G. M. CURTIS, L. E. BARRON, and F. J. PHILLIPS (J. Lab. Clin. Med., 1935, 20, 813—816; cf. A., 1934, 1024).—Thyroidectomy is followed by a rapid transient increase and a subsequent decline in blood-I to  $<$  normal. I then present in blood is probably absorbed from the alimentary tract.  
CH. ABS. (p)

**Polysaccharide hydrogen sulphates with heparin-like action.**—See this vol., 453.

**Effects of sodium citrate on the alkaline reserve and coagulability of the blood.** D. DE SOUZA and F. D. M. HOCKING (J. Physiol., 1935, 85, 168—172).—Alkaline reserve is increased; coagulability is increased with small, and reduced by larger, doses.  
R. N. C.

**Changes in the coagulability of the blood produced by citric acid and some of its decomposition products.** D. DE SOUZA and F. D. M. HOCKING (J. Physiol., 1935, 85, 173—178).—Citric acid or  $\text{NH}_4$  citrate (intramuscular) increases alkaline reserve and coagulability of cats' blood. Acetonedicarboxylic and aconitic acids may increase or diminish coagulability without affecting alkaline reserve, but their Na salts increase both;  $\text{COMe}_2$  affects neither.  
R. N. C.

**Blood coagulation.** H. DYCKERHOFF and H. F. KÜRZEN (Biochem. Z., 1936, 284, 111—132).—Thrombin (I) contains a very small amount of firmly bound Ca. The Ca-free material has no coagulating power, but very rapidly unites with Ca to produce active (I). Circulating blood contains  $>$  sufficient Ca to meet the requirements of (I). Under normal conditions  $\text{Ca}^{++}$  has no effect on coagulation. Pre-formed (I) probably occurs in circulating blood. Thrombokinase (II) activates (I) by removing inhibitors, in the absence of which (I) causes coagulation when  $\text{Ca}^{++}$  and (II) are not present.  
W. McC.

**Influence of novocaine anaesthesia on the fibrinogen content of the plasma and its coagulation.** W. L. DULIÈRE, A. HUSTIN, and P. BOSSAERT (Bull. Soc. Chim. biol., 1936, 18, 234—236).—Lumbar injection of novocaine causes a decrease in hæmatocrit, time of coagulation, and concn. of fibrinogen, followed by gradual return to normal.  
A. L.

**Technique for determination of fibrinogen in human blood: rate of coagulation of plasma.** W. L. DULIÈRE (Bull. Soc. Chim. biol., 1936, 18, 231—233)

**Test for coprosterol in plasma.**—See this vol., 467.

**Effect of spleen extract on the time of coagulation, thrombocytes, and erythrocytes of the**



blood. E. HAENLEIN and E. SCHLIEPHAKE (Klin. Woch., 1935, 14, 79—83). R. N. C.

Preparation of cobra-toxin for clinical purposes, particularly for alleviation of cancer pain. L. W. VAN ESVELD (Biochem. Z., 1936, 283, 343—357).—A method is described for separating from cobra-toxin the hæmolysin, hæmorrhagin, and non-toxic albumin contents without any considerable loss of the sp. neurotoxin. The purified prep., kept in the dark at  $p_H$  5.2, remained completely active for months while in clinical use. P. W. C.

Chemistry of immunity reactions. IV. Distribution of chemically distinguished antigens in the organism of normal and sensitised animals. F. HAUROWITZ and F. KRAUS (Z. physiol. Chem., 1936, 239, 76—82; cf. A., 1932, 542; 1933, 411).—Injection of arsanilazoprotein (I) into normal guinea-pigs is followed by accumulation of As in the organs of the reticulo-endothelial system, particularly in the liver. Similar results are obtained after injection of a suitable antiserum (*loc. cit.*). The gradual degradation of (I) in the organism has been studied. After injection of iodoglobulin the main portion of the antigen is found in the liver. H. W.

Recovery and stabilisation of the antibacterial agglutinin and anti-sheep hæmolysin of serum. H. GOLDIE (Compt. rend. Soc. Biol., 1936, 121, 761—764).—The agglutinin of *B. coli* and anti-sheep hæmolysin are recovered from their respective complexes by stabilisation with  $CH_2O$  and pptn. with 1:4:6:8- $NH_2 \cdot C_{10}H_4(SO_3Na)_3$  and citric acid. Both show the variation of  $p_H$  and isoelectric point and increase of thermostability on storage, exhibited by antitoxin recovered by flocculation with the toxin, and are not affected by heating to 85°, which denatures the associated globulins and reduces their anaphylactic activity. R. N. C.

Favourable effect of some lipins on the immunising action of antigens. G. RAMON (Compt. rend., 1935, 201, 687—689).—Tetanus toxin in oil containing cholesterol (I) when injected subcutaneously into horses is at least 7500 times as active in producing antibodies as when (I) is omitted. J. L. D.

Specific antigen and antibody in the urine of pregnant women. L. GRIMARD (Compt. rend. Soc. Biol., 1936, 121, 743—746). R. N. C.

Keten, a new reagent for detoxification of vaccine. J. T. TAMURA and M. J. BOYD (Science, 1936, 83, 61—62).—Acetylation of *B. dysenteriae*, Shiga, with keten for 30 min. detoxifies the antigen. L. S. T.

Characters of antitoxins purified by flocculation, stabilised by formaldehyde, and recovered with sodium naphthylaminetrisulphonate. H. GOLDIE (Compt. rend. Soc. Biol., 1936, 121, 649—652).—The recovered antitoxins become progressively acid during the first 2—3 months of storage, the isoelectric point is shifted, and the thermo-resistance increases. The antigenic power is not affected, but the anaphylactic action is reduced by heating to 80—85° to denature the attacked globulins; the antitoxin is unaffected by such heating. R. N. C.

Chemical specificity of heart muscle. B. KISCH (Klin. Woch., 1935, 14, 145—146).—A review. R. N. C.

Specific gravity and water content of the brains of vertebrate animals. I. Birds. L. P. KING and M. C. HSUNG (Bull. Nat. Acad. Peiping, 1935, 6, No. 1, 1—47). CH. ABS. (p)

Embryochemistry of *Hynobius*. M. TAKAMATSU (J. Biochem. Japan, 1935, 22, 203—211).—Data are given for the ash constituents and N distribution of the components of the eggs of *H. nebulosus* incubated for varying periods. The principal enzymes present are esterase, nucleinase, glycogenase, and glycerophosphatase. F. O. H.

Chemistry of blow-fly larvæ. M. TOMITA and T. KUMON (Z. physiol. Chem., 1936, 238, 101—104).—The amounts of various inorg. ions (mostly Na and  $PO_4$ ) and the nature of the proteins and enzymes in the larvæ are recorded. R. S. C.

Distribution of lead in human bones. S. L. TOMPSETT (Biochem. J., 1936, 30, 345—346; cf. A., 1935, 1160).—In bones from persons having had no special exposure to Pb the amounts of Pb per kg. of fresh material were: rib 4.0—17.5, vertebra 3.4—16.5, femur 18.2—108.3, and tibia 15.3—96.5 mg. W. McC.

Organic constituents of bone. T. INOUE (Tohoku J. Exp. Med., 1935, 26, 433—440).—Total C of the substantia compacta of the shaft of the rabbit femur, excluding preformed  $CO_2$ , ranged from 8910.5 to 11596.6 mg. (average 9744.6) and total N from 3119.6 to 3387.8 mg. (average 3269.4) per 100 g. of dry substance. The ratio total C: total N suggests that ossein forms the principal part of the org. ground substance. Residual C was 333.1—568.3 mg. (average 443.2) and the residual N 94.9—171.1 mg. (average 132.1). There was no definite sex difference. Calc. on org. ground substance, bones are richer in residual C and N than is blood. The results indicate that carbohydrates and fats are the most important substances metabolised in bone. NUTR. ABS. (m)

Copper content of some human and animal tissues. P. F. HAHN and E. FAIRMAN (J. Biol. Chem., 1936, 113, 161—165).—In the liver and spleen of dogs suffering from experimental anæmia, Cu tends to rise to high levels as Fe falls towards zero. In man, no marked change in Cu is found in various pathological conditions. Fœtal and infant livers are comparatively rich in Cu, so are the livers of patients with Mediterranean anæmia, although Fe (hæmosiderin) is high. F. A. A.

Phosphorus compounds in the nymph and butterfly of *Deilephilia euphorbiae*. J. HELLER (Compt. rend. Soc. Biol., 1936, 121, 414—416).—Analytical vals. for the butterflies and for the whole nymph and its organs are given. HCl-hydrolysable P (adenosinetriphosphoric acid) is high in the butterflies, especially in the male, but very low in the nymph. Intestinal P in the nymph is entirely inorg.; total P in the adipose tissue is as high as in the hæmolymph, muscles, and intestine. R. N. C.



**Calcium and magnesium content of the flesh of various animals.** M. TAKAMATSU (*Z. physiol. Chem.*, 1936, 238, 99—100).—Ca and Mg were determined in the muscle of 20 animals. Unusually high vals. are: adder, Ca 1.2524, Mg 2.5268; snail, Ca 1.3202, Mg 2.7673; clam, Ca 0.7819; crab, Ca 0.8424% (as oxides) of the dried muscle. R. S. C.

**Sodium content of mammalian muscle.** F. PODOLSKY and G. MALORNY (*Pflüger's Archiv*, 1935, 236, 339—347).—Na of the ash of mammalian muscle is slightly > that of the equiv. Cl, the excess representing Na of the fibres. The excess is of the same order of magnitude as in muscle of cold-blooded animals. Red and white muscles exhibit no important differences in Na content, but in heart-Na is slightly > that in skeletal muscle, particularly in pigs, rabbits, and man. R. N. C.

**am-Glucose in the animal organism.** H. K. BARRENSCHEEN and H. FANTA (*Biochem. Z.*, 1936, 283, 382—389).—When O<sub>2</sub> is bubbled through warm dil. glucose solutions, no oxidation occurs. On adding these solutions to blood, liver, or muscle the filtrates obtained by pptn. with EtOH-COMe<sub>2</sub> and treatment with colloidal Fe(OH)<sub>3</sub> show a decrease in total reducing power of 20—50%, according to the duration of the experiment and the organ used. This decrease is not due to oxidation, but concerns the fermentable portion of the sugar, 60—78% of which is now oxidisable with animal C. This oxidisable portion may be am-glucose. P. W. C.

**Comparative determination of hepatic glycogen by the cupric and iodometric methods.** H. BERRY, B. GOUZON, and C. MAGNAN (*Compt. rend. Soc. Biol.*, 1936, 121, 616—619).—The Cu method gives identical results whether or not the glycogen has previously been pptd. with EtOH; the results are also identical with those by the I method. The Cu-reducing power after Hg deproteinisation is due solely to an aldose. R. N. C.

**Micro-determination of liver-glycogen.** H. BERRY, B. GOUZON, and C. MAGNAN (*Compt. rend. Soc. Biol.*, 1936, 121, 614—616).—The liver is autoclaved with 30% KOH, and again after acidification with HCl. After deproteinising with Hg(NO<sub>3</sub>)<sub>2</sub>, and removing excess of Hg, the liberated glucose is determined by the micro-modification of Bertrand's method. R. N. C.

**Mixed glycerides of salicylic acid, and fatty acids.**—See this vol., 453.

**Fatty acids of phrenosin and kersin.**—See this vol., 454.

**Halibut-liver oils. Vitamin-A content of pilchard oil.**—See B., 1936, 242.

**Polyethenoid acids of the n-octadecane (C<sub>18</sub>) series in aquatic animal oils.**—See B., 1936, 204.

**Lipochromes of the frog (*Rana esculenta*).** L. ZECHMEISTER and P. TUZSON (*Z. physiol. Chem.*, 1936, 238, 197—203; cf. this vol., 97).—The liver contains carotene (I) ( $\alpha$ - and  $\beta$ -) (25% of total pigment), lutein (II), zeaxanthin (III), free and esterified xanthophyll (IV), and small amounts of other lipochromes; the skin and fat glands, chiefly esterified (IV) with

(I), (II), and (III); and the ovaries, (I), (II), and (III). W. McC.

**Colorimetric determination of cholesterol in liver oil.** K. HOTTA and M. KAWAJI (*Nagoya J. Med. Sci.*, 1935, 9, 23—24).—Volatile acids are removed by heating the oil with 0.9% aq. NaCl in a stream of air; after saponification with 25% aq. KOH at 150° for 30 min. cholesterol (0.34—0.54%) is determined by the Embden-Miyamori method.

NUTR. ABS. (m)

**Fate of carotene in the animal organism.** O. BAILLY (*Bull. Acad. méd.*, 1932, 108, 932—935).—The adrenal glands are by far the richest organs of the body in carotene (I), which is localised in the cortex in concns. of the same order as that in carrots. The (I) of bovine adrenals is  $\beta$ -carotene, similar to that found in the ovary. R. N. C.

**Carotenoid pigments in fishes. II. Effects of coloured backgrounds and of ingested carotenoids on the xanthophyll content of *Girella nigricans*.** F. B. SUMNER and D. L. FOX (*J. Exp. Zool.*, 1935, 71, 101—123).

NUTR. ABS. (m)

**Anti-anæmic principle of liver.** J. F. WILKINSON (*Lancet*, 1936, 230, 354—356).—The claim (A., 1935, 885) that Reinecke acid can be used further to purify and increase the potency of the anti-anæmic principle has been confirmed. L. S. T.

**Alleged occurrence of "Krampfstoffe" in acetone extracts of the mammalian brain.** E. HOLMES (*J. Physiol.*, 1935, 85, 400—408).—COMe<sub>2</sub> extracts of the brain contain no substances affecting the central nervous system, but a cardiac depressor.

R. N. C.

**Nitrogenous constituents of the stomach wall of dogs.** K. IKEYAMA (*J. Biochem. Japan*, 1935, 22, 397—407).—Total N and constituent NH<sub>2</sub>-acids (most of which were isolated) were determined in the mucosa and muscle layers of the fundus, cardiac, and pyloric regions. F. O. H.

**Significance of carnitine in muscle.** E. STRACK, P. WÖRDEHOFF, and H. SCHWANEBERG (*Z. physiol. Chem.*, 1936, 238, 183—196).—A simple process for isolating carnitine (I) (1.8% calc. as betaine) from meat extract is described. (I) and acetyl-carnitine (II) have little biological activity, but (I) is accompanied by very small amounts of a substance which persistently adheres to the Au salt of (I) and yields an active Ac derivative. Atropine counteracts the activity of this substance and phytostygmine increases it. (II) yields a sparingly sol. compound with AuCl<sub>3</sub>. W. McC.

**Part played by carnosine in muscles.** E. SAVRON (*Ukrain. Biochem. J.*, 1934, 7, No. 1, 53—61).—The carnosine content of muscle varies in different animals. Vals. for white are > those for red muscle. None occurs in pigeons, rats, guinea-pigs, or dogs. CH. ABS. (p)

**Micro-determination of creatine in muscle.** A. V. PALLADIN (*Ukrain. Biochem. J.*, 1934, 7, No. 1, 163—171).—Muscle is mixed with sand and boiled with aq. NaCl and AcOH. The filtered residue is re-extracted 8—10 times with H<sub>2</sub>O. The combined



extract is boiled with picric acid and the creatinine produced is determined colorimetrically.

CH. ABS. (p)

**Relation between functional requirements, acetylcholine reaction, and glutathione content of bird muscles.** L. CASSEL (Pflüger's Archiv, 1935, 236, 30—35).—The glutathione content of the wing muscles of flying birds is highest in birds that make long flights. Male birds contain > females. Ascorbic acid in the breast muscles is the same in good and bad flyers.

R. N. C.

**Muscle extractives of hibernating giant salamander (*Megalobatrachus japonicus*).** T. IWA-SAKI (J. Biochem. Japan, 1935, 22, 233—242).—From aq. extracts of the muscles were isolated creatine, creatinine, adenine, xanthine, hypoxanthine, histidine, methylguanidine, lysine, choline, and *D*-lactic acid.

F. O. H.

**Acetylcholine and choline in organ extracts.** F. PLATTNER and H. TSUDZIMURA (Pflüger's Archiv, 1935, 236, 175—180).—There is no evidence of a correlation between acetylcholine, choline, and esterase in the organs of the cat. Acetylcholine-like substances are not affected by thyroidectomy or adrenalectomy.

R. N. C.

**Composition of the protamines of sturgeon.** M. A. LISSITZIN and N. S. ALEXANDROVSKAJA (Z. physiol. Chem., 1936, 238, 54—58).—The protamines of the milt of *Acipenser huso*, *guldensstädtii*, and *stellatus* are probably identical, the sulphate being  $C_{35}H_{74}O_7N_{18} \cdot 3H_2SO_4$  (amount of  $H_2SO_4$  varies with method of prep.),  $[\alpha]$  about  $-55^\circ$  in  $H_2O$ , and  $NH_2$ -, arginine-, histidine-, and lysine-N being about 8, 72, 10.5, and 6% of the total N, respectively.

R. S. C.

**Preparation of *b*-thymonucleic acid by nucleogelase.** F. FEULGEN (Z. physiol. Chem., 1936, 238, 105—110).—*b*-Thymonucleic acid (free from *a*-isomeride) is prepared (a) from cell nuclei (e.g., heads of herring sperm) by digestion with slightly alkaline ( $Na_2CO_3$ ) 0.5% pancreatin solution, pptn. from alkaline (NaOH) solution by EtOH, acidification with AcOH, dehydration with EtOH, and desiccation, or (b) from natural organs (e.g., thymus glands) by liquefaction with about 5.5% NaOH (15 min. at  $65^\circ$ ), addition of  $NH_4Cl$ , pptn. with EtOH, and enzymic degradation of the ppt. as in (a) (cf. A., 1914, i, 888).

R. S. C.

**Form of proteins in blood-plasma and bone-marrow in the normal organism.** H. KEILHACK (Arch. exp. Path. Pharm., 1936, 180, 440—457).—Data are given for the contents of the various proteins in rabbit's plasma [7.0% total protein; approx. 0.30% fibrinogen (I)] and bone-marrow [average 3.2% total protein; 1.095% (I)]. The relation between the high (I) content of bone-marrow and the blood constituents is discussed.

F. O. H.

**Chemical constitution of liver-proteins.** F. F. URBAN (Biochem. Z., 1936, 283, 435—453).—The protein of cat's liver washed free from blood is investigated. About half of the protein is extractable by salt solutions, the globulin (I) : albumin (II) ratio in the extract being 7:3. The (II) fraction is P-free. The (I) fraction after repeated pptn. with

$(NH_4)_2SO_4$  contained 0.7% P. After pptn. also with urea, the P content fell to 0.3% and the purine-N to zero. The differences in total N, tyrosine, tryptophan, histidine, phenylalanine, cystine, arginine, lysine, etc. contents of the (I) and (II) fractions are small and considerably < the differences with serum-proteins.

P. W. C.

**Thiol and disulphide groups of proteins. II, III. Reducing groups of proteins.**—See this vol., 352.

**Ultrafiltration of proteins through graded collodion membranes. II. Haemocyanin (*Helix*), edestin, and ovalbumin.** W. J. ELFDON and J. D. FERRY (Biochem. J., 1936, 30, 84—91).—The influence of medium, of  $p_H$ , and of concn. of neutral salts on the filterability of the above proteins is investigated, the best results being obtained in Hartley's broth at  $p_H$  7—8. The filtration end-points for haemocyanin (*Helix*) of 55 m $\mu$  and for edestin of 18 m $\mu$  are established, indicating particle sizes of 18—28 m $\mu$  and 6—9 m $\mu$ , respectively. The results confirm the val. of the factor employed for deducing particle size from porosity of the membrane which just completely retains the disperse phase.

P. W. C.

**Action of radioactive substances on proteins.**—See this vol., 301.

**Electrical orientation of wool cells.**—See this vol., 414.

**Proteins of body-fluids. I. Quantitative and qualitative aspects. II. Application of physical data.** C. ACHARD (Bull. Acad. Méd. Roumanie, 1936, 1, 15—25, 26—30).—I. The nature and content of proteins in body-fluids in health and disease are discussed.

II. The Tyndall effect,  $\sigma$ , adsorption on C, fluorescence, and effect of dilution and flocculation with  $Fe(OH)_3$  of normal and pathological body-fluids are discussed.

F. O. H.

**Influence of high environmental temperature on the secretion and composition of milk.** S. BARTLETT (J. Dairy Res., 1935, 6, 283—288).—High temp. caused a lowering of the % of fat and solids-not-fat in milk. The depression in total yield was small.

A. G. P.

**Factors affecting milk and butter-fat secretion.**

I. Variations in fat weight, fat percentage, and the amount of fat in milk required to make a given weight of butter. II. Colour of the butter-fat. E. O. WHETHAM and J. HAMMOND (J. Dairy Res., 1935, 6, 320—339, 340—352).—I. The size of the fat globule is probably controlled by the rate of formation of fat in the cell and the rate of milk secretion. The influence of age, stage of lactation, and breed are examined. The ratio of the wt. of fat in milk required to make 1 lb. of butter is a measure of variations in the size of the fat globules.

II. Effects of genetic and dietary factors are examined.

A. G. P.

**Daily variations in butter-fat content of milk.** Z. CZUKÁS (Mezőg. kutat., 1935, 8, 270—278).—The daily average butter-fat % of cows' milk varied greatly,



(2.4–5.5). Morning milk contained 40% < evening milk and 30% < noon milk. These differences could not be eliminated by regulating the milking periods. NUTR. ABS. (m)

**Component fatty acids of goat milk fat.** R. W. RIEMENSCHNEIDER and N. R. ELLIS (J. Biol. Chem., 1936, 113, 219–233).—The fat of the milk of goats fed on a regulated diet contained undecolic, pentadecolic, palmitoleic, oleic, hexoic, octoic, decolic, myristic, palmitic, stearic, and arachidonic acid, and a mixture of saturated acids containing tetracosanoic and cerotic acids. H. D.

**Effect of type of feed on the solids-not-fat content of milk.** L. L. ROUX, G. N. MURRAY, and D. J. SCHUTTE (Onderstepoort J. Vet. Sci., 1935, 4, 167–197).—Rations containing identical amounts of protein and total digestible nutrients were fed to 3 groups of cows; group (1) received a high concentrate ration, group (2) high dry roughage, and group (3) high succulent rations. In group (1) solids-not-fat rose normally with advance of lactation, whilst groups (2) and (3) showed a fall. The milk production of group (1) did not decrease as rapidly as that of groups (2) and (3). NUTR. ABS. (m)

**Yield and composition of ewe's milk.** W. GODDEN and C. A. PUDDY (J. Dairy Res., 1935, 6, 307–312).—Analytical data are recorded. No appreciable difference in milk composition resulted from wide variations of Ca in the ration. A. G. P.

**Milk of a typical herd of Shorthorn cows.** III. Nitrogen distribution, chloride, lactose, copper, and iron contents over a period of two years. W. L. DAVIES (J. Dairy Res., 1935, 6, 362–368).—Analyses are recorded and discussed. A. G. P.

**Free lactic acid in fresh milk.** B. GROSS and C. OLIVEIRA (Rev. Quim. Farm., 1935, 1, 117–120).—Fresh milk, or its serum, had  $p_H$  6.65–6.85, whereas the val. calc. on the assumption that its acidity is due to lactic acid is about 2.8. Experiments described indicate that no free lactic acid or lactates are present. L. A. O'N.

**So-called normal lead of human milk.** M. KASAHARA and S. I. NOSU (Jahrb. Kinderheilk., 1935, 145, 78–80).—52 out of 87 samples of milk from women living in an area having a service  $H_2O$  supply contained Pb (trace to 0.18 mg. per litre). Out of 15 samples from women in rural districts only 3 contained Pb (0.04–0.11 mg. per litre). NUTR. ABS. (m)

**Excretion of drugs in milk.** N. T. KWIT and R. A. HATCHER (Amer. J. Dis. Children, 1935, 49, 900–904).—Morphine, codeine, and phenolphthalein are not secreted in human milk. Salicylic acid, I', and Br' appear in milk after administration. CH. ABS. (p)

**Plasma-protein determinations in lactating women.** S. C. PEACOCK and W. F. HINMAN (Amer. J. Physiol., 1935, 113, 235–237).—The excretion of caseinogen in the milk has no recognisable effect on the blood-proteins. R. N. C.

**Crystallisation of [sodium] chloride in presence of cerebrospinal fluid.** P. TOMESCO,

I. COSMULESCO, and F. SERBAN (Bull. Acad. Méd. Roumanie, 1936, 1, 133–140).—NaCl in presence of cerebrospinal fluid crystallises in various abnormal forms dependent on the composition of the fluid; the phenomenon is probably of diagnostic val.

F. O. H.

**Lymph-sugar.** J. W. HEIM, R. S. THOMSON, and F. C. BARTTER (Amer. J. Physiol., 1935, 113, 548–554).—Lymph- and plasma-sugar in the dog are almost identical under certain conditions; the glucose-tolerance curves are similar. Sugar administered *per os* or intravenously enters the lymphatic system readily, and is removed at about the same rate as from blood. R. N. C.

**Salivary secretion.** W. FELDBERG and J. A. GUIMARAIS (J. Physiol., 1935, 85, 15–36). R. N. C.

$p_H$  of normal resting saliva. I. Variations with age and sex. R. E. BRAWLEY (J. Dent. Res., 1935, 15, 55–77).—The average  $p_H$  was 6.75, there being no significant difference between the two sexes. NUTR. ABS. (m)

**Bile pigment metabolism.** I. Breakdown of blood pigments to protoporphyrin by the liver and other organs. Demonstration of a fermenting action. H. T. SCHREUS and C. CARRIÉ (Klin. Woch., 1934, 13, 1670–1673).—The liver is able to form protoporphyrin from hæmoglobin or hæmatin; the process is not associated with life or survival of the cells, but probably with the action of a hæmase. Within certain limits the amounts of fermented substances and of the products of reaction are proportional. Optimum conditions are 37–60° and  $p_H$  3–5; the action of the enzyme is restrained by EtOH, Et<sub>2</sub>O, CHCl<sub>3</sub>, CMe<sub>2</sub>, and glycerol, inhibited by cooling to 0°, and destroyed by boiling. R. N. C.

**Determination of bile salts in human bile.** R. GOIFFON, F. NEPVEUX, and CHALEIL (Compt. rend. Soc. Biol., 1936, 121, 425–427).—Proteins are pptd. from bile with the Folin-Wu reagent, and pigments with FeCl<sub>3</sub> and NH<sub>3</sub>. The bile salts are dissolved in aq. EtOH, evaporated alone and with AcOH, extracted with C<sub>6</sub>H<sub>6</sub> to remove fats, dissolved in 0.1N-NaOH, and pptd. with 0.1N-HCl saturated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, the homogeneous suspension being examined photometrically. R. N. C.

**Determination of free and combined cholesterol in bile.** C. RIEGEL and H. J. ROSE (J. Biol. Chem., 1936, 113, 117–124).—A modification of the Schoenheimer-Sperry (A., 1934, 1240) procedure for the determination of cholesterol in blood is used. F. A. A.

**Rabbits bile.** I.—See this vol., 469.

**Toad bile.** III, IV.—See this vol., 469.

**Bilifuscin.** E. WEINBERGER (Z. physiol. Chem., 1936, 238, 124–128).—Bilifuscin is C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>N. It is isolated impure from human biliary calculi (cf. A., 1901, i, 283). R. S. C.

**Effect of peptones and certain extracts of small intestine on the secretion of succus entericus.** E. S. NASSET and H. B. PIERCE (Amer. J. Physiol., 1935, 113, 568–577).—Witte's peptone contains a secretagogue which stimulates the jejunal glands when



administered *per os* or intravenously. It is extracted, free from depressor, by 70% EtOH, and is thermostable, but destroyed by erepsin or trypsin. It is not present in other peptones. Another secretagogue, which resists the digestive enzymes, but is destroyed by boiling in alkali, is extracted from the small intestines of pigs or dogs by acidified 70% EtOH.

R. N. C.

**Acidity of gastric juice and the diluting secretion of the stomach.** T. ENGSTRÖM (Acta med. scand., 1935, Suppl. 66, 73 pp.).—Gastric secretion in cats following administration of histamine (I) or EtOH is used to study regulation of gastric acidity. Intraglandular regulation by a diluting, HCl-free secretion is of primary importance. True hyperacidity,  $\approx$  about 170 millimol., exists. There was no parallel between blood-(I) and intensity of secretion. With continuous intravenous injection of (I), intensity of secretion increased steadily and appeared to tend towards a max. NUTR. ABS. (m)

**Histamine-like substance in the gastric juice.** C. L. BROWN and R. G. SMITH (Amer. J. Physiol., 1935, 113, 455—463).

R. N. C.

**Some physiological and physical aspects of the surface tension of urine.** P. W. PERRYMAN and C. F. SELOUS (J. Physiol., 1935, 85, 128—144).—A modification of the max. bubble pressure apparatus for determination of  $\sigma$  is described; it can be used to follow changes of  $\sigma$  with temp. and with time up to 2 hr. The  $\sigma$ -time curves for urine are logarithmic, in both normal and pathological urines; the changes are not due to proteins or absorption of CO<sub>2</sub>, but probably to slow adsorption of capillary-active substances. The  $\sigma$ -temp. curve is linear up to 54°, after which the decrease becomes more rapid. Variations of  $\sigma$  are not related to ingestion of food or liquid, but in females  $\sigma$  shows a cyclical variation corresponding with the menstrual cycle.  $\sigma$  is not related to *d*, or the presence of pathological constituents in the urine, and is not correlated with any sp. disease or group of diseases.

R. N. C.

**Chemical basis of the Ehrlich diazo-reaction with urine.** I. P. SACHS. II. P. SACHS and H. KLOSS (Z. klin. Med., 119, 381—402, 551—563; Chem. Zentr., 1935, i, 3019—3020).—I. A cryst. dichloroazobenzene dye, C<sub>31</sub>H<sub>24</sub>O<sub>7</sub>N<sub>6</sub>Cl<sub>4</sub> (Bz<sub>6</sub> and Bz<sub>7</sub> derivatives), is isolated.

II. By-products of high mol. wt. are formed in the reaction, the pathological significance of which is discussed.

H. N. R.

**Detection of histidine in urine as a reaction for pregnancy.** N. C. LOUROS (Klin. Woch., 1934, 13, 1156; Chem. Zentr., 1935, i, 3961).—The Kapeller-Adler reaction (A., 1933, 1094) is unsuitable, both for detecting histidine and as a reaction for pregnancy.

H. N. R.

**Elimination of xylose, creatinine, and urea by the perfused mammalian kidney.** A. HEMINGWAY (J. Physiol., 1935, 84, 458—468).—The average creatinine (I)/xylose (II) and urea/(II) clearance ratios in the isolated perfused kidney are 1.72 and 0.85, respectively, and are within the range of the vals. obtained from normal animals. Plasma concn.

decreases (I) elimination without affecting (II) and urea; (II) elimination  $\propto$  the glomerular filtration rate.

R. N. C.

**Excretion of inulin, creatinine, xylose, and urea in the normal rabbit.** B. I. KAPLAN and H. W. SMITH (Amer. J. Physiol., 1935, 113, 354—360).—Excretion of inulin (I), creatinine (II), xylose (III), and urea increases with urine flow. Simultaneous excretions of (I) and (II) are equal, regardless of urine flow or plasma-(II) level, and are  $>$  those of (III) and urea.

R. N. C.

**Excretion of kynurenic acid by the mammalian organism. Identification of small amounts of kynurenic acid.** W. G. GORDON, R. E. KAUFMAN, and R. W. JACKSON (J. Biol. Chem., 1936, 113, 125—134).—50—100 mg. of kynurenic acid (I) may be identified and determined as the Me ester. The rat, guinea-pig, and Dalmatian dog excrete (I) after administration of tryptophan. The cat does not excrete (I) under these conditions, but ingested (I) is excreted unchanged.

F. A. A.

**Properties of reducing material in certain fractions of normal urines. I. Nature of the free fermentable sugars and the fermentable sugars produced on hydrolysis in fasting urines.** V. J. HARDING, T. F. NICHOLSON, and R. M. ARCHIBALD. II. Effect of diet on hydrolysable sugar in urine. Nature of this sugar. V. J. HARDING, T. F. NICHOLSON, and S. H. JACKSON (Biochem. J., 1936, 30, 326—334, 335—341).—I. Conc. solutions of carbohydrate are obtained from human urine by successive treatment with basic Pb acetate (I), HgSO<sub>4</sub>-BaCO<sub>3</sub>, and CuSO<sub>4</sub>-Ca(OH)<sub>2</sub>. Differential fermentation of the solutions (e.g., with *Saccharomyces Marxianus*) shows the presence, before and after dil. acid hydrolysis, of glucose (II) and galactose (III) and, in some cases, of very small amounts of fructose and mannose. Probably most, if not all, of the fermentable sugar produced on hydrolysis is derived from the non-fermentable reducing fraction, not from a non-reducing precursor. Almost all the sugar of urine is N-free.

II (cf. A., 1931, 1443). Meals consisting chiefly of fat, fruit, and starch, respectively (but not those consisting chiefly of protein), cause increase in the amounts of substances giving rise to fermentable sugar on hydrolysis, excreted in the urine during 4 subsequent hr., the increase being almost entirely due to (II)-producing substances. A small amount of (II)-producing material, pptd. by (I) and HgSO<sub>4</sub>-BaCO<sub>3</sub> but not by Lloyd's reagent, occurs in fasting and non-fasting urines, but not after fat and fruit meals. About 33% of the hydrolysable material has reducing power, the reducing group being in the (II) mol. All (III) produced on hydrolysis exists combined through its reducing group, possibly as lactose.

W. McC.

**Reducing power of urine. II.** H. K. BARRENSCHEEN and H. PRINZ (Biochem. Z., 1936, 284, 99—107; cf. A., 1930, 806).—The reducing material is separated (60%) by adsorption on Al<sub>2</sub>O<sub>3</sub> (optimal at *p*<sub>H</sub> 7.73) and kaolin (optimal at *p*<sub>H</sub> 1.17). The part of the material which loses its reducing power on treatment with CH<sub>2</sub>O is preferentially adsorbed (max.



at  $p_H$  6.24 and 7.73) on kaolin, and is not removed by successive elution with aq.  $NH_3$  and dil.  $AcOH$ , which removes the other part. This part appears to consist of substances related to homogentisic acid.

W. McC.

**Isolation and identification of combined oestriol in human pregnancy urine.** S. L. COHEN and G. F. MARRIAN (Biochem. J., 1936, 30, 57—65).—A method is described for isolation from human pregnancy urine of a  $H_2O$ -sol.,  $Et_2O$ -insol., non-cryst. substance, m.p. 193—197° (decomp.), containing approx. 50 wt.-% of oestriol. The composition and the Ba content of the Ba salt agree with those required for an oestriolglycuronic acid,  $C_{24}H_{32}O_9$ . The substance gives strong naphthoresorcinol and Millon tests, but does not reduce Benedict's solution until after hydrolysis.

P. W. C.

**Excretion of oestrin by the kidneys of the pregnant mare.** S. KOBER (Acta Brev. neerl. Physiol., 1935, 5, 34—35; Chem. Zentr., 1935, ii, 238).—The folliculin content of mare's urine rises suddenly during the 5th and 6th months of pregnancy, and falls again during the last two months.

G. H. F.

**Bence-Jones protein.** H. TSUTSUI (J. Biochem. Japan, 1935, 22, 343—350).—Reactions for urine containing the protein (I) are given. The N distribution of isolated (I)  $\{[\alpha]_D - 95.78^\circ$  (1.305% solution in 0.1N-NaOH), isoelectric point  $p_H$  4.72} is tabulated. (I) is hydrolysed by gastric juice or trypsin. Its pathogenesis is discussed.

F. O. H.

**Colorimetric determination of urinary protein, plasma-protein, urinary and plasma-albumin. Salting out of these proteins.** H. BERGLUND and W. DE M. SCRIVER (Acta med. scand., 1935, 86, 82—87).—Methods with an accuracy of 3—5% are described.  $Na_2SO_4$ , essentially in the concns. used by Howe, is used for fractionation. N is determined by nesslerisation. The acid digestion of protein requires more heat than is required for determination of non-protein-N of blood.

NUTR. ABS. (m)

**Determination of sulphate in urine.**—See this vol., 442.

**Determination in series of the oxalic acid content of urine.** K. KOCH (Biochem. Z., 1936, 283, 422—432).—A method which requires 40 c.c. of urine and determines 0.04—0.1 mg. of  $H_2C_2O_4$  is described. 15—30 double determinations can be carried out per day.

P. W. C.

**Spectrographic determination of phenol added to urine.** G. BARAC (Compt. rend., 1935, 201, 1433).—The urine is treated successively with basic Pb acetate,  $Na_2HPO_4$ , and HCl, extracted with  $Et_2O$ , and the extract is examined (this vol., 126).

F. O. H.

**Determination of *p*-bromophenylmercapturic acid in the urine of the dog.** J. A. STEKOL (J. Biol. Chem., 1936, 113, 279—288).—A gravimetric (using the  $HgCl_2$  complex) and an iodometric titration method are described.

H. G. R.

**Strychnine and barbituric acids.** M. E. KER-GONOV (Bull. Trav. Soc. Pharm. Bordeaux, 1935, 73, 53—61; Chem. Zentr., 1935, i, 3822).—Extraction

methods for the determination of these substances in urine are described.

H. N. R.

**Spectrochemical study of aplysiopurpurin.** M. FONTAINE and A. RAFFY (Compt. rend. Soc. Biol., 1936, 121, 735—736).—Aplysiopurpurin in acid  $Zn(OAc)_2$  solution (cf. A., 1931, 1443) shows absorption bands at 501, 552, and 601  $m\mu$  and fluorescence bands at 518, 568, 617, and 644  $m\mu$ . When obtained in the solid state by pptn. with  $(NH_4)_2SO_4$ , it does not fluoresce; it is therefore related to mesobiliviolin, and is probably a breakdown product of chlorophyll and phycocchromoproteins absorbed by *Aplysia*.

R. N. C.

**Uroporphyrin in acute hæmatoporphyrinuria.** E. MERTENS (Z. physiol. Chem., 1936, 238, I—II).—The urine contained, in addition to a little coproporphyrin, a uroporphyrin (I) [ $Me_8$  ester (II), m.p. 258° (Cu compound, m.p. 304°)]. Decarboxylation of (I) with HCl under pressure gives coproporphyrin III and hence (I) is uroporphyrin III. The mother-liquor from (II) contained a  $MeOH$ -sol. ester, m.p. 240°.

W. McC.

**Urinary porphyrins in disease.** K. DOBRINER (J. Biol. Chem., 1936, 113, 1—10).—A method for separating and identifying porphyrins in urine is described. An increased excretion of coproporphyrin I is characteristic of most diseases, but pigment cirrhosis and liver tumour lead to excretion of coproporphyrin III. In two cases uroporphyrin I was isolated, and an unknown porphyrin ( $Me$  ester, m.p. 222°) was obtained. The formation of these porphyrins is discussed.

J. N. A.

**Acriflavine as a urinary antiseptic.** E. W. ASSINDER (Lancet, 1936, 230, 304—305).—Acriflavine is strongly antiseptic towards the gonococcus.

L. S. T.

**Phosphatase of the plasma and its variations in disease.** C. JIMÉNEZ DÍAZ, E. BASSADONE, and S. CLARIANA (Rev. españ. Enferm. Aparat. digest. Nutric., 1935, 1, 5—20).—Average vals. found were 0.142 Kay unit in adults and 0.26 in children. Increases in rickets, osteomalacia, bone diseases, degenerative rheumatism, and liver disease are noted.

NUTR. ABS. (m)

**Scurvy in Addison's disease and the value of the catalase index in adrenal insufficiency.** L. NORRHO (Deut. Arch. klin. Med., 1935, 177, 499—508; Chem. Zentr., 1935, ii, 245).—The blood-catalase index has no diagnostic significance in Addison's disease.

G. H. F.

**Adrenal disease in relation to hypoglycæmia and death.** J. C. NORRIS (Amer. J. Clin. Path., 1935, 5, 120—130).—Hypoglycæmia under these conditions indicates a relationship between liver and adrenals in glucose metabolism.

CH. ABS. (p)

**Correlation of hypertrophy of the adrenal cortex with bodily work and the vitamin-B content of the diet.** A. VON BEZNÁK and J. PERJÉS (Pflüger's Archiv, 1935, 236, 181—189).

R. N. C.

**Amidopyrine and granulopænia.** Reappearance of granulocytosis in a case of recurring agranulocytosis after large doses of amido-



pyrine. L. R. LIMARZI and I. G. MURPHY (J. Lab. Clin. Med., 1935, 20, 616—622). CH. ABS. (p)

Goat's milk anæmia. G. O. KOHLER, C. A. ELVEHJEM, and E. B. HART (Amer. J. Physiol., 1935, 113, 279—284). R. N. C.

Comparison of the anæmia produced by feeding young rats on human, cow's, and goat's milk. H. H. BEARD and T. S. BOGGESS (Amer. J. Physiol., 1935, 113, 642—646). R. N. C.

Blood regeneration in severe anæmia: fractions of kidney, spleen, and heart compared with standard fractions. F. S. ROBSCHT-ROBBINS, G. B. WALDEN, and G. H. WHIPPLE (Amer. J. Physiol., 1935, 113, 467—475). R. N. C.

Chlorophyll and regeneration of blood. Administration of chlorophyll derivatives in chronic hypochromic anæmia. A. J. PATEK, jun. (Arch. Int. Med., 1936, 57, 73—84).—Chlorophyll products when administered either parenterally or orally with comparable amounts of Fe produce blood regeneration. H. G. R.

Liver principle active in pernicious anæmia. C. C. UNGLEY (Nature, 1936, 137, 210—213).—A review. L. S. T.

Treatment of pernicious anæmia with Dakin and West's liver fraction (anahæmin). C. C. UNGLEY, L. S. P. DAVIDSON, and E. J. WAYNE (Lancet, 1936, 230, 349—354).—The prep. is highly active for blood regeneration in pernicious anæmia. L. S. T.

Pathological calcium deposits. D. R. MEEKER and H. D. KESTEN (J. Biol. Chem., 1936, 113, 289—296).—The average composition of calcified deposits in arterial sclerosis is: CaO 49.5, P<sub>2</sub>O<sub>5</sub> 36.1, MgO 0.90%. Calcification of implanted colloid material is increased by toxic doses of vitamin-D preps. and the deposit has the average composition: CaO 46.8, P<sub>2</sub>O<sub>5</sub> 32.7%. H. G. R.

Urinary sulphur in non-specific arthritis. B. D. SENTURIA (J. Lab. Clin. Med., 1935, 20, 855—861).—The total S excreted and the S partition in urine of affected patients are approx. normal. The N/S ratio is lowered in only a few cases. CH. ABS. (p)

Blood-urea in botulism of cattle. P. ROSSI (Compt. rend. Soc. Biol., 1936, 121, 526—527).—Botulism is accompanied by a rise of blood-urea and a fall in renal excretion of urea, both returning to normal on recovery. R. N. C.

Blood-urea and *Brucella* infection in horses. P. ROSSI (Compt. rend. Soc. Biol., 1936, 121, 611—612).—Blood-urea is not appreciably affected. R. N. C.

Carcinogenic chemical compounds. H. A. WEIDLICH (Chem.-Ztg., 1936, 60, 185—187).—A review.

Carcinogenic action of thorium dioxide in the white rat. G. ROUSSY, C. OBERLING, and M. GUÉRIN (Bull. Acad. méd., 1934, 112, 809—816). R. N. C.

Experimental production by œstrin of pituitary tumours with hypopituitarism and of mammary

cancer. W. CRAMER and E. S. HORNING (Lancet, 1936, 230, 247—249). L. S. T.

Cholesterol as a constituent of malignant cells. I. A. BRONSTEIN and D. V. WOLKENSOHN (Acta Cancerologica, 1935, 1, 205—214).—The cholesterol (I) content of the necrotic centre of the Jensen rat sarcoma is 2—2.5 times that of the developing periphery. X-Irradiation *in vivo* does not alter the (I) of the periphery. The (I) of culture media is not changed by growth of sarcoma cells. CH. ABS. (p)

Action of pituitary secretion on tumours. H. DRUCKREY (Arch. exp. Path. Pharm., 1936, 180, 367—380).—Following castration in female rats, the gonadotropic hormone (I) content of the pituitary increases 15—20-fold and, after approx. 7 months, decreases; the thyrotropic hormone content is unchanged. During the period of increased level of (I), development and growth of tumour implants are inhibited, the initially increased respiration decreasing to zero vals.; such non-respiring tumours are not re-implantable. Relations between hormonal influence and tumour growth are discussed. F. O. H.

Effect of cystine disulphoxide on spontaneous tumours of the mouse. F.S.H. FOR THE STAFF OF THE RESEARCH INSTITUTE OF THE LANKENAU HOSPITAL, PHILADELPHIA (Science, 1936, 83, 108—109).—Tumour growth and cell proliferation are retarded. L. S. T.

Variations of polypeptidæmia in cancerous patients treated by intravenous injections of complex salts derived from vitamin-C (ferri-scorbones). F. ARLOING, A. MOREL, A. JOSSERAND, M. CHAMBON, and S. CELLIÈRE (Compt. rend. Soc. Biol., 1936, 121, 683—685).—Polypeptides are increased. R. N. C.

Effect of hæmatoxylin on respiration and glycolysis of cancerous tissue and spleen of cancerous rats. R. IWATSURU and M. KAWAGUCHI (Biochem. Z., 1936, 284, 163—168).—The R.Q. is increased, in presence or absence of glucose, by addition of hæmatoxylin whereas that of spleen and liver of healthy rats is unchanged or slightly diminished; glycolysis in the diseased tissue and spleen is practically unchanged. W. McC.

Genetics, thiol, and cancer. F. S. HAMMETT (Science, 1936, 83, 57).—A discussion. L. S. T.

Cerebroside-containing cerebral cyst. C. TROPP and B. ECKARDT (Z. physiol. Chem., 1936, 238, 31—34).—The liquid from a cerebral cyst contained no inorg. Fe, cholesterol, or P, very little fat and hæmoglobin products, but mainly cerebrin and kerasin and some albumin. A small amount of solid deposit contained Fe and fat. R. S. C.

Gastric secretion in cœliac disease. J. W. OGILVIE (Arch. Dis. Childhood, 1935, 10, 93—98).—The disease is accompanied by lowered [HCl] in gastric juice without true achlorhydria. The increase in total Cl<sup>-</sup> probably results from the higher [Cl<sup>-</sup>] in blood. CH. ABS. (p)

Sulphur metabolism in cystinuria. J. C. ANDREWS and A. RANDALL (Amer. J. Med. Sci., 1935, 189, 301—302).—In a case described, the out-



put of cystine (I) was unaffected by doses of  $\text{NaHCO}_3$  and Na citrate sufficient to maintain urinary  $p_H$  at 7.0–7.5 and to keep (I) in solution, by equimol. proportions of glycine and glutamic acid, or by a high-egg diet. Orally administered (I) is completely oxidised to  $\text{SO}_4^{--}$ . 60–80% of *dl*-methionine is oxidised to  $\text{SO}_4^{--}$ , the remainder being excreted as unoxidised S without change in urinary (I). Cysteine (II) is excreted unoxidised. The (II) content of cystinuric urine increases 25–50% on keeping 24 hr.

CH. ABS. (p)

Sugar and glutathione contents of blood and skin in dermatitis produced by croton oil and by sunburn. C. MONCORPS, R. M. BOHNSTEDT, and R. SCHMID (Arch. Dermatol. Syphilis, 1933, 169, 67–75).—The changes are functions of the intensity of skin inflammation and time.

CH. ABS. (p)

"Soya water-bread" and the use of soya meal in the treatment of diabetes and corpulence. F. SCHELONG (Klin. Woch., 1935, 14, 487–490).—The composition of a comparatively carbohydrate-free "water-bread" prep. from oil-free soya-meal is given, and its therapeutic use is indicated. R. N. C.

Neuropathy in diabetes. Lipin constituents of the nerves correlated with the clinical data. W. R. JORDAN and L. O. RANDALL (Arch. Int. Med., 1936, 57, 414–421).—The phospholipins, cholesterol, and cerebroside of the nerves are reduced in diabetes, the greatest effect occurring in those from the lower part of the leg.

H. G. R.

Inorganic phosphorus in diphtheria. I. NATIN and C. DA RIN (Semana méd., 1935, I, 1148–1149).—Blood-inorg. P is not appreciably abnormal.

CH. ABS. (p)

Hyperglycæmia in diphtheria, carbohydrate metabolism, and treatment with glucose and insulin. I. NATIN and C. DA RIN (Semana méd., 1935, I, 1055–1058).—In diphtheria, deviation of glycæmia is small, but glucose tolerance is frequently disturbed by factors of hepatic origin.

CH. ABS. (p)

Experimental epilepsy. III. Alteration in the protective quality of serum in epileptiform convulsions produced by camphor. V. NEKLUDOV (Kolloid-Z., 1936, 74, 218–221).—During and between the convulsions produced in cats and dogs by injection of camphorated oil, the quantity of blood-serum needed to stabilise a sol of Congo-rubin is increased in severe attacks which end fatally, but is diminished in less severe, non-fatal attacks.

F. L. U.

Lipin diseases. IV. Lipin content of tissues in status epilepticus, toxic encephalopathy, and chronic leptomeningitis. D. M. COWIE and M. C. MAGEE (Amer. J. Dis. Children, 1935, 49, 884–893).—The ratio of phospholipins to cholesterol in liver, spleen, and skeletal muscle in status epilepticus is > in other diseases examined (cf. A., 1934, 550).

CH. ABS. (p)

Rôle of uric acid in gout. H. LUCKE (Deut. med. Woch., 1934, 60, 1783–1786).

R. N. C.

Serum-calcium, -inorganic phosphorus, and -phosphatase activity in hyperparathyroidism,

Paget's disease, multiple myeloma, and neoplastic disease of the bones. A. B. GUTMAN, T. L. TYSON, and E. B. GUTMAN (Arch. Int. Med., 1936, 57, 379–413).—Serum-phosphatase is augmented in the diseases studied. In hyperparathyroidism, multiple myeloma, and neoplastic disease of the bones hypercalcaemia is observed, inorg. P being low in hyperparathyroidism, but normal in other cases. In Paget's disease both serum-Ca and -inorg. P are normal.

H. G. R.

Blood-cholesterol in hypothyroidism. LESNÉ, BRISKAS, and LARDÉ (Bull. Soc. Pédiat. Paris, 1935, 33, 60–62).—The finding of high blood-cholesterol in hypothyroidism is confirmed. In infants, the val. is 2–4 and in children above 15 years 1.3–1.6 g. per litre.

NUTR. ABS. (m)

Blood-cholesterol in arterial hypertension. A. H. ELLIOT and F. R. NUZUM (Arch. Int. Med., 1936, 57, 63–72).—Hypercholesterolaemia was not observed in uncomplicated hypertension or in hypertension associated with vascular degeneration or renal impairment or a low metabolic rate unaccompanied by hypothyroidism. High vals. were generally associated with subnormal body-wt.

H. G. R.

Treatment of hyperinsulinism with insulin. H. J. JOHN (Endocrinol., 1935, 19, 689–694).

R. N. C.

Hypoglycæmic headache. P. A. GRAY and H. I. BURTNESS (Endocrinol., 1935, 19, 549–560).—Migraine and other headache conditions are often associated with low blood-sugar (I). The glucose tolerance curve is of the flat type. Reactivity to insulin (II) is measured by the (II) tolerance test; the fall of (I) below fasting level  $\propto$  the height above the fasting level before injection of (II).

R. N. C.

Van der Bergh reaction (ring test technique) and hæmoglobin-bilirubin interrelation in icterus neonatorum. N. W. ELTON (J. Lab. Clin. Med., 1935, 20, 817–826).—No relationship was apparent between the bilirubin content and changes in hæmoglobin content and no. of erythrocytes.

CH. ABS. (p)

Variations of oxalæmia in liver diseases. A. RODRIGUEZ-OLLEROS (Rev. españ. Enferm. Aparat. digest. Nutric., 1935, 1, 323–332).—Blood- $\text{H}_2\text{C}_2\text{O}_4$  in hepatic disease is > normal. No correlation was found between extent of bilirubinæmia and oxalæmia. Ingestion of 1 g. of  $\text{H}_2\text{C}_2\text{O}_4$  produces in liver patients in 2 hr. a 10–30% increase in oxalæmia, whereas there is no increase in non-hepatic patients. Diets poor or rich in  $\text{H}_2\text{C}_2\text{O}_4$  produce no const. variation in oxalæmia on the day following the diet.

NUTR. ABS. (m)

Carbohydrate exchange after carbohydrate charging and its disturbance in liver diseases. I. Insulin-glucose-water charging. R. MEIER and E. SCHMIEDT (Z. ges. exp. Med., 1935, 95, 277–287; Chem. Zentr., 1935, i, 3950–3951).—Injection of excess of insulin followed by ingestion of excess of glucose and  $\text{H}_2\text{O}$  by healthy man does not generally result in increased carbohydrate combustion, the R.Q. and  $\text{O}_2$  consumption showing little change. In cirrhosis of the liver, combustion is retarded and



continues longer than normally. Lactic acid formation is increased in jaundice. In normal rabbits glycogen is first synthesised, but is later oxidised; it disappears from the liver 3 hr. after ingestion, and is not deposited in the muscles. R. N. C.

**Glucose exchange in liver diseases. II.** E. SCHMIEDT (Z. ges. exp. Med., 1935, 95, 288—294; Chem. Zentr., 1935, i, 3951).—Charging with glucose is not suitable for the diagnosis of liver functional disturbance in man.  $O_2$  consumption shows no characteristic change, but R.Q. exhibits a late rise in cirrhotics. R. N. C.

**Biochemistry of blood of normal and malaria-infected monkeys.** R. C. WATS and B. M. DAS GUPTA (Indian J. Med. Res., 1934, 21, 475—481).—Blood-sugar, -non-protein-N, and -Ca were unchanged by infection, whilst the plasma-cholesterol decreased. Treatment with atebirin, quinine, etc. caused an unexplained increase in inorg.  $PO_4'''$ . CH. ABS. (p)

**Bromide content of blood determined by the method of Leipert and Watzlawek, in mental disease.** M. NAGY and J. STRAUB (Orvosi Hetilap., 1935, 79, 895—897).—In 70% of cases of recurrent psychosis blood-Br' was subnormal (normal 0.9—1.4 mg. per 100 ml.). In the remaining cases and in other mental diseases it was normal or high. NUTR. ABS. (m)

**Mineral metabolism in osteogenesis imperfecta.** W. W. SWANSON and L. V. IOB (Amer. J. Dis. Children, 1935, 49, 958—963).—In affected cases, retention of Na differs more from normal than that of other minerals. Vals. for Ca and P are < normal, and those for S, K, Cl, and N are in the normal range. The Ca and P of bones increase. Viosterol improves retention of Ca and P without affecting that of other minerals. CH. ABS. (p)

**Diagnostic value of pigmentation in paludism. Concentration [of pigment] in blood and urine.** M. CANCIULESCO and R. HIRSCH (Bull. Acad. Méd. Roumanie, 1936, 1, 31—34). F. O. H.

**Poikiloderma atrophicans vasculare (Jacobi).** A. MARCHIONINI and F. BÖHNING (Arch. Dermatol. Syphilis, 1934, 170, 112—122).—Changes in blood-sugar, serum-protein, -alkali reserve, -lactic acid, -cholesterol, -K, and -Ca during a sweat bath with a normal patient and with one almost devoid of sweat glands are examined. CH. ABS. (p)

**Rapid flocculation method for diagnosis of syphilis.** P. RYTZ (Amer. J. Clin. Path., 1935, 5, 159—161).—The reaction is made more rapid by coagulation of blood by heating for 2—3 min. at  $60^\circ$ , sensitisation of serum by  $(NH_4)_2SO_4$ , and use of a stable stock antigen. CH. ABS. (p)

**Calcium therapy in "staggers" in the bullock.** (A) J. R. SHEEHY. (B) J. R. GREIG (Vet. Rec., 1936, 16, 147—148; 202). R. N. C.

**Fistulous withers and poll-evil: calcium therapy.** W. W. LANG (Vet. Rec., 1936, 16, 238). R. N. C.

**Tetany in calves.** B. SJOLLEMA (Vet. J., 1935, 91, 133—137).—In tetany the mineral and, probably, the carbohydrate metabolism are disturbed. Blood-

Ca and -Mg vary irregularly. Tetany is not due to Mg deficiency but probably results from overfeeding with protein. CH. ABS. (p)

**Concentrated diet in childhood tuberculosis and malnutrition.** G. E. PRATT (Arch. Pediatr., 1934, 51, 529—533).—Supplementary milk feeding to increase the calorific val. of the diet and the intake of fat, protein, carbohydrate, Ca, P, vitamin-A and -B<sub>2</sub> increased the gain in wt. and general condition of tuberculous children. CH. ABS. (p)

**Effect of irradiated ergosterol on the phospholipins of the blood in pulmonary tuberculosis.** J. H. REICHART (Diss., Amsterdam, 1935, 64 pp.).—A photo-electric method of determining lipid P was found most accurate. The lipid P content of the blood in 34 normal subjects varied as much as 12% in 6—7 days. The vals. in tuberculous patients, treated with irradiated ergosterol or untreated, were not significantly different from one another or from normal vals. NUTR. ABS. (m)

**Blood-calcium in tuberculosis.** F. MEERSSE-MANN and H. SÉGUIN (Rev. Tuberc. Paris, 1935, [v], 1, 514—528).—Blood-C tends to be low. NUTR. ABS. (m)

**Variations in living matter controlled by chemical laws.** O. RAHN (Biochem. Z., 1936, 284, 40—62).—Vital processes (e.g., heat-inactivation of enzymes, fission processes in the cell, velocity of cell division, biological variation, death of cells) are considered from certain mathematical aspects. F. O. H.

**Basal heat production of the rhesus monkey (*Macaca mulatta*).** N. RAKIETEN (J. Nutrition, 1935, 10, 357—362).—The average basal heat production, 608 kg.-cal. per sq. m. per 24 hr., is the same for both sexes and is not affected by administration of Na amytal. A. G. P.

**Basal metabolism and iodine excretion during pregnancy.** L. ENRIGHT, V. V. COLE, and F. A. HITCHCOCK (Amer. J. Physiol., 1935, 113, 221—228).—Growth of the foetus and supplementary tissues is largely responsible for the increased metabolism accompanying pregnancy, but in adolescent girls there is another stimulatory factor absent in mature women. The increase is smaller if iodised salt is used during pregnancy. I excretion increases 3 weeks before birth, suggesting a possible change in thyroid function. R. N. C.

**Basal metabolism and urinary nitrogen excretion of Oriental women.** A. H. TURNER and F. G. BENEDICT (Amer. J. Physiol., 1935, 113, 291—295).—Basal metabolism is < the prediction standard and that of American women in the same environment. The urinary N excretion shows that proteins in the diet are not abnormally low, and that the fall of basal metabolism is not due to decreased protein metabolism. R. N. C.

**Interpretation of lowered basal metabolic level.** D. L. SEXTON (Endocrinol., 1935, 19, 579—586). R. N. C.

**Heat production in man. II. Output of carbon dioxide as a measure of heat production in basal metabolism.** T. W. ADAMS and E. P.



POULTON (Guy's Hosp. Rep., 1935, 85, 56—75).—Calculations and deductions support the view that, under basal conditions, carbohydrate and fat are burnt in a fixed ratio.  $\text{CO}_2$  production is a direct measure of the amount of combustion.

#### NUTR. ABS. (m)

Increase of the contents of reducing substances (glutathione and ascorbic acid) in the organs in training. K. WACHHOLDER and K. UHLENBROCK (Pflüger's Archiv, 1935, 236, 20—29).—I-reducing substances (I) are increased in the skeletal, heart, and stomach muscles, liver, lungs, and brain of the dog and the rabbit by regulated exercise, the increases being due to glutathione in the first instance, but in many cases to ascorbic acid as well. (I) are decreased in many organs in over-exerted rabbits. In a well-trained dog (I) are decreased in the thyroid and adrenals.

R. N. C.

Effect of muscular exercise on biological processes. E. TAKEDA (Japan. J. Exp. Med., 1935, 13, 471—509, 511—520, 521—527, 529—534, 535—541).—The following changes were observed in dogs as the result of work for 1 hr. on the treadmill: increases in no. of leucocytes and lymphocytes, blood-fat, and residual N, decreases in blood-sugar, no. of erythrocytes, haemoglobin content of the blood,  $\text{CO}_2$ -combining capacity of the plasma, and total urinary N. In dogs fed from infancy on meat diets all these changes were > in dogs fed on vegetable diets.

#### NUTR. ABS. (m)

Changes of volume of muscle as an expression of chemical processes. O. MEYERHOF and W. MOHLE (Biochem. Z., 1936, 284, 1—11).—The changes in vol. which occur in normal and poisoned [with  $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$  (I)] muscle on stimulation and in muscle with heat- or (I)-rigor are accompanied by an unexplained contraction, in Ringer's solution somewhat > that in paraffin oil, and especially pronounced during production of lactic acid (II). The dilations are only 40% (Ringer) and 50% (paraffin) of those observed during enzymic (II) production, and the contraction of muscle poisoned with (I) is > the expected val. When valeric acid penetrates muscle, slight contraction occurs.

W. McC.

Is the work of the kidney (due to excretion of urea) a factor in specific dynamic action? A. G. EATON, S. C. CORDILL, and J. L. GOUAUX [with V. CLAY] (J. Nutrition, 1935, 10, 429—436).—The work done by kidneys in the concn. of urine during rapid excretion of urea is not a material factor in the sp. dynamic action of proteins.

A. G. P.

Coefficient *K* of Nicloux in the gudgeon (A) living 24 hours in glucose solutions of increasing concentrations, (B) living in glucose solutions as a function of time. G. FONTÈS, J. BRUNER, and A. LINDENBERG (Compt. rend. Soc. Biol., 1936, 121, 452—455, 456—458).—(A) *K* diminishes as the concn. of glucose increases, the curve being linear. *K* becomes zero when the osmotic pressure becomes double the isotonic val.

(B) *K* shows little variation in a 1.25% solution of glucose, and becomes normal in 5 days. It falls rapidly in 5% solution, rises in 3 days, and then falls again.

R. N. C.

Behaviour of heavy water towards light water in the organism. F. BREUSCH and E. HOFER (Klin. Woch., 1934, 13, 1815—1816; Chem. Zentr., 1935, i, 3882—3883).—From determinations of *d* to  $\pm 5 \times 10^{-7}$  for  $\text{H}_2\text{O}$  mechanically and chemically held in various organs, no fractionation of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in the organism could be detected in normal cases, in sarcoma of the lung, in cirrhosis of the liver, or in blood from tuberculous or cancerous cases.

J. S. A.

Effect of ingestion of saline waters on the  $p_{\text{H}}$  of the intestinal tract, the nitrogen balance, and the coefficient of digestibility. V. G. HELLER, J. R. OWEN, and L. PORTWOOD (J. Nutrition, 1935, 10, 645—651).—Assimilation and digestibility of foods, if affected at all, are improved by dissolved salts provided serious disturbance of growth or reproduction does not occur. The  $p_{\text{H}}$  of the intestinal tract is not appreciably altered, but that of the stomach is somewhat affected.

A. G. P.

Respective variations of weight, water, and the constituents of the dry weight in the gudgeon as functions of the external glucose concentration. G. FONTÈS, J. BRUNER, and A. LINDENBERG (Compt. rend. Soc. Biol., 1936, 121, 459—462).— $\text{H}_2\text{O}$  and " $\text{H}_2\text{O}$  impermeable to EtOH" decrease, and non-protein substances increase, as the glucose (I) concn. increases. The dry wt. decreases, the curve being linear. In a 1.25% (I) solution conditions tend to return to normal after 5 days.

R. N. C.

Immediate effects of reduced cooling powers on the water balance and related effects in the human subject. D. H. K. LEE and A. G. MULDER (J. Physiol., 1935, 84, 410—432).

R. N. C.

Permeability and ion concentration in muscle excitation. V. S. ILJIN (Pflüger's Archiv, 1935, 236, 148).—A reply to Ernst and Fricker (cf. A., 1935, 239).

R. N. C.

Absorption of water from common salt and sugar solutions. E. J. McDOUGALL and F. VERZAR (Pflüger's Archiv, 1935, 236, 321—338).— $\text{H}_2\text{O}$  and hypotonic NaCl solutions are rapidly absorbed in the rat and cat; isotonic NaCl is absorbed well in the rat, but in the cat an increase in vol. of the solution sometimes occurs, as in the case of isotonic xylose (I) solutions in both species. The increase in vol. is not accompanied by a change of osmotic pressure, so that blood-crystalloids (II) diffuse into the intestine. Glucose (III) is absorbed from isotonic solution by the rat intestine after 15 min.; the absorption depends on the amount of (II) diffusing in, and is generally so intensive that the solution becomes hypotonic and  $\text{H}_2\text{O}$  is absorbed. Absorption is slower in the cat, no  $\text{H}_2\text{O}$  being resorbed from 5.4% (III). If (III) absorption in the rat is depressed by  $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ ,  $\text{H}_2\text{O}$  behaves as in the case of (I), and the solution becomes hypertonic through diffusion of (II) into the intestine. Increase of the hydrostatic pressure of the small intestine causes an increase in rate of absorption of isotonic NaCl  $\propto$  the increase in pressure.

R. N. C.

Relative significance of electrolyte concentration and tissue reaction in water meta-



**bolism.** H. A. DAVIS and L. R. DRAGSTEDT (Amer. J. Physiol., 1935, 113, 193—199).—Dogs dehydrated by simple H<sub>2</sub>O deprivation retain 0.9% NaCl and 5% glucose better than do normal dogs. Animals with gastric fistulae and consequent alkalosis retain H<sub>2</sub>O slightly better than those with pancreatic fistulae; the latter are extensively depleted of base, chiefly Na, through loss of pancreatic juice, but still cannot retain NaCl. R. N. C.

**Changes in the laid egg.** P. ULRIK and D. DAVIDSEN (Proc. 5th World's Poultry Congr. Rome, 1933, 2, 462—474).—The  $p_H$  of the egg increases from 8.2 when new laid to 9.2 after 12 hr., and to 9.8 in 9 days. Subsequent changes are insignificant. Titration with CH<sub>2</sub>O serves as an approx. index of egg age. CH. ABS. (p)

**Relation between metabolic processes and the ventricular electrogram.** A. S. DALE (J. Physiol., 1935, 84, 433—453). R. N. C.

**Mechanism of intracellular respiration.** D. KEILIN (Bull. Soc. Chim. biol., 1936, 18, 96—130).—A lecture.

**Accuracy of the Barcroft differential manometer in respiration studies.** A. S. CORBET and W. R. WOOLDRIDGE (Biochem. J., 1936, 30, 132—140).—The standard error in the determination of O<sub>2</sub> by the Barcroft technique depends on the duration and replication of the experiments. A statistical method for determining the significance of the difference between means is recommended. H. D.

**Effect of viosterol on oxygen consumption of frog's muscle.** S. GELFAN (Amer. J. Physiol., 1935, 113, 464—466).—O<sub>2</sub> consumption in isolated frog muscle is increased by daily injections of viosterol. R. N. C.

**Effect of thyroxine on tissue oxidation.** G. N. MARKOFF (Beitr. path. Anat., 1935, 94, 377—388; Chem. Zentr., 1935, i, 3561).—Thyroxine (I) augments tissue oxidation in the liver of the rat, but not in the spleen or brain. The increase does not occur until the regular effects of (I) are established. The increase in O<sub>2</sub> consumption in the liver is noticeable 3 days after the last injection of (I), whilst the increase of cellular oxidases is evident immediately after the last injection. R. N. C.

**Effect of liver feeding in relation to oxygen want.** H. B. PARRY (J. Physiol., 1935, 84, 454—457).—Exposure of rabbits to low O<sub>2</sub> tensions does not cause formation in the liver of any factor hæmopoietic to rats. R. N. C.

**Choline and liver respiration.** O. A. TROWELL (J. Physiol., 1935, 85, 356—374).—Choline (I) in concns. > 0.12% increases O<sub>2</sub> consumption by rat's liver- or kidney-tissue, decreases that of cardiac muscle and spleen, and does not affect that of brain. Added fatty acid or glucose does not affect the action of (I). Washed liver-pulp oxidises (I) with uptake of 1 atom of O per mol. (I) does not affect O<sub>2</sub> consumption by aq. liver extract, but in concns. > 0.01% it inhibits CH<sub>3</sub>Ac-CO<sub>2</sub>H production to a degree  $\propto$  the concn., inhibition being complete at 1%; fatty acid increases the inhibition. The effect of (I) on O<sub>2</sub> consumption by liver-tissue is probably the algebraic

sum of (I) oxidation by the liver and inhibition of normal fat oxidation; the increase in O<sub>2</sub> consumption due to the first process is > the decrease due to the second, at all (I) concns. R. N. C.

**Embryochemistry of amphibia. VIII. Oxidative processes in giant salamander's eggs.** F. YAMASAKI. IX. Urea and uric acid in incubated eggs of giant salamander. M. TAKAMATSU and T. KAMACHI (J. Biochem. Japan, 1935, 22, 181—184, 185—187).—VIII. Development of the eggs produces an increase in -SH and in indophenol-oxidase.

IX. The incubated eggs contain 0.0030—0.0047% of urea, but only traces of uric acid. F. O. H.

**Effect of frequency of contraction of the isolated mammalian heart on the consumption of oxygen.** A. E. COHN and J. M. STEELE (Amer. J. Physiol., 1935, 113, 654—658). R. N. C.

**Influence of muscular work on oxidative processes in the animal organism.** L. PAL-LADINA (Ukrain. Biochem. J., 1934, 7, No. 1, 23—30).—The oxidation of PhOH, injected into rabbits, diminishes after muscular work. CH. ABS. (p)

**Comparison of the rates of metabolic activity in the solitary and migratory phases of *Locusta migratoria*.** C. G. BUTLER and J. M. INNES (Proc. Roy. Soc., 1936, B, 119, 296—304).—*L. migratoria* may, according to the conditions, assume either a migratory or a solitary phase. The rate of O<sub>2</sub> uptake per unit area of body surface is higher for locusts in the migratory phase, in all instars after the first. The rate is higher for males than for females in all instars and both phases. The rate diminishes from the first to the third instars, and increases again from the fourth instar to the adult stage. F. A. A.

**Mechanical activity of gut muscle under anaërobic conditions.** B. N. PRASAD (J. Physiol., 1935, 85, 249—266).—The mechanical activity of gut muscle is arrested by asphyxia through exhaustion of its labile carbohydrates. Max. activity is maintained when both glucose and O<sub>2</sub> are supplied to the muscle. CH<sub>2</sub>I-CO<sub>2</sub>H limits considerably the anaërobic activity of the muscle, suggesting a low phosphagen content. R. N. C.

**Relation of rate of growth to diet. III. Comparison of stock rations.** L. B. MENDEL and R. B. HUBBELL [with F. FRANCIS] (J. Nutrition, 1935, 10, 557—563). A. G. P.

**Effect of cereal diets on the composition of body-fat of rats.** H. S. OLCOTT, W. E. ANDERSON, and L. B. MENDEL (J. Nutrition, 1935, 10, 517—523).—The I val. of the body-fat varied with the cereal food given. A. G. P.

**Alimentary value of (A) old, (B) new, maize.** G. NICHITA, N. TUSCHAK, and G. IFTIMESCO (Compt. rend. Soc. Biol., 1936, 121, 563—566, 567—570). R. N. C.

**Effect of differently de-fatted soya-bean meals on the blood picture of domestic animals.** I. ENVER (Diss., Tierärztl. Hochsch., Berlin, 1933; Bied. Zentr., 1935, 6, A, 1).—Effects of extraction with C<sub>2</sub>HCl<sub>3</sub> and with CCl<sub>4</sub> are compared by means



of rabbits and guinea-pigs. The blood picture is not appreciably altered by the use of these solvents.

A. G. P.

Are potato- and maize-starch nutritionally equivalent? F. FISCHLER (Münch. med. Woch., 1935, 82, 57—58; Chem. Zentr., 1935, ii, 243).—Equivalence is established.

G. H. F.

Comparative rachitogenic property of oats and maize. L. L. LACHAT and L. S. PALMER (J. Nutrition, 1935, 10, 565—577).—HCl extracts of oats when purified and freed from excess of NaCl showed rachitogenic properties when fed to rats receiving a mildly rachitogenic diet. With a severely rachitogenic diet the extracts produced no additional effect. Rolled oats and yellow maize are rachitogenic to rats and especially to chickens.

A. G. P.

Influence of diet on the glucose tolerance of the dog. E. M. GREISHEIMER and F. W. HOFFBAUER (J. Nutrition, 1935, 10, 525—534).—With low-carbohydrate diets an increase in the proportion of fat or protein lowers the glucose tolerance. Effects of other dietary variations are recorded.

A. G. P.

Effect of 1% of cod-liver oil on the rat with particular reference to the thyroid gland. C. B. FREUDENBERGER and F. W. CLAUSEN (J. Nutrition, 1935, 10, 549—555).

A. G. P.

Effect of choline on the weight of young rats. E. W. MCHENRY (J. Physiol., 1935, 85, 343—349).—Choline (I) and vitamin- $B_1$  exhibit a complementary effect on the gain in wt. of young rats. Rats not receiving (I) exhibit symptoms resembling those of vitamin- $B_1$  deficiency.

R. N. C.

Effect of deficient diets on the total ash, calcium, and phosphorus contents of bones. R. YEAGER and J. C. WINTERS (J. Nutrition, 1935, 10, 389—397).—In animals stunted (to maintain the same body-wt.) by calorie, protein, and lysine deficiency, the ash, Ca, and P of bones were > those of normal animals of the same wt. but < those of normal animals of the same age. Stunting by means of a low-salt diet caused very much lower bone vals. than in normal animals of the same wt. or age.

A. G. P.

Rats' milk and stomach contents of suckling rats. D. T. MAYER (J. Nutrition, 1935, 10, 343—350).—Recorded data indicate that suckling rats require a high-fat, low-carbohydrate diet. Although a large proportion of the calorific val. of rats' milk is derived from the fat, such a diet is not extremely ketogenic.

A. G. P.

Biological value of fresh milk and milk heated for short periods, in experiments on rat-feeding. H. HERTEL (Z. Immunitäts., 1935, 84, 321—327).—Milk heated for short periods is scarcely altered in its nutritional val. and vitamin content, whilst pasteurised milk differs considerably in biochemical composition. The short-period heated milk does not assure optimal or max. growth.

R. N. C.

Nutritive value of proteins for maintenance. S. MORRIS and N. C. WRIGHT (J. Dairy Res., 1935, 6, 289—302).—With maintenance rations containing min. proportions of protein a deficiency in lysine causes a decrease in urinary N characterised by an

MM

increase in  $\text{NH}_3$  and a decline in urea. Catabolism of body-tissue is high probably through excessive deamination with mild acidosis. Cystine deficiency has no effect.

A. G. P.

Utilisation of energy-producing nutriment and protein as affected by individual nutrient deficiencies. III. Effects of the plane of protein intake. E. B. FORBES, R. W. SWIFT, A. BLACK, and O. J. KAHLBURG (J. Nutrition, 1935, 10, 461—479).

A. G. P.

Effect of different percentages of protein in the diet on virgin rats. J. R. SLONAKER (Amer. J. Physiol., 1935, 113, 159—165).

R. N. C.

Replacement of protein [in cattle rations] by ammonium salts. S. V. FOMIN and V. I. DEMIN (Ukrain. Biochem. J., 1934, 7, No. 1, 133—143).—Replacement of proteins in the ration by urea and  $\text{NH}_4$  salts lowered the rate of growth.

CH. ABS. (p)

Proteins of foodstuffs. V. Contents of cystine and tryptophan. T. TOMIYAMA (J. Biochem. Japan, 1935, 22, 341—342).—The respective cystine, methionine (cf. A., 1934, 572), and tryptophan contents of the proteins from silk-worm pupæ (a), sardines (b), and soya beans (c) are: (a) 0.86, 2.97, 1.50; (b) 0.76, 3.14, 1.40; (c) 1.05, 1.96, 1.35%.

F. O. H.

Formation of histidine from arginine in incubating hens' eggs. T. KAMACHI (J. Biochem. Japan, 1935, 22, 199—202).—Injection of arginine (I) into incubating eggs is followed by an increase in the free histidine (II), whilst injection of (II) does not increase the level of (I).

F. O. H.

Origin of creatine from proteins and amino-acids. H. H. BEARD and T. S. BOGGESS (Amer. J. Physiol., 1935, 113, 647—653).—Creatine (I) in the muscles of rats fed on diets containing only 4% of protein is increased by re-feeding on a diet containing 25% of protein or 21% of glycine or glutamic acid. Total N, fat, and total solid in the muscles are scarcely changed. (I) is thus an exogenous catabolic product of proteins of  $\text{NH}_2$ -acids.

R. N. C.

Methionine content of food proteins. A. E. SCHARPENACK and G. P. JERJOMIN (Problems of Nutrition, Moscow, 1935, 4, No. 4, 11—16).—Casein has a very high methionine (I) but low cystine (II) content. Legume protein contains little (I), but some (II). Egg-yolk protein contains relatively large quantities of (I) and (II). Proteins of equal S content differ sharply in the character of their S compounds.

NUTR. ABS. (m)

Does bis- $\beta$ -aminoethyl disulphide (cystamine) promote growth in the rat limited to an inadequate intake of cystine and methionine? R. W. JACKSON and R. J. BLOCK (J. Biol. Chem., 1936, 113, 135—139; cf. A., 1933, 89; Mitchell, this vol., 102).—Cystamine does not promote growth of white rats maintained on a diet low in cystine and methionine.

F. A. A.

Availability of *dl*-amino-*N*-methylhistidine for growth. J. B. FISHMAN and A. WHITE (J. Biol. Chem., 1936, 113, 175—179).—*dl*- $\alpha$ -Chloro- $\beta$ -glyoxal-



inylpropionic acid was ineffective, and *dl*-amino-*N*-methylhistidine was effective, in producing a growth response in histidine-deficient rats. H. D.

**Influence of denervation on the carnosine content of muscles.** B. KOLDAEV and P. BUTKOV (Ukrain. Biochem. J., 1934, 7, No. 1, 63—67).—Section of the ischiatic nerve in one pad of a rabbit does not affect the carnosine (I) content of the gastrocnemius muscle. After rigor (I) probably decreases somewhat. CH. ABS. (p)

**Influence of fatigue on the glutathione content of muscle.** A. V. PALLADIN, S. BORSHKOVSKI, and L. PALLADINA (Ukrain. Biochem. J., 1934, 7, No. 1, 7—22).—Fatigued muscle shows an increase in oxidised glutathione (I). This is attributed to changed conditions of oxidation which lower the capacity of (I) to act as H acceptor. CH. ABS. (p)

**Aminohydroxy-acids and their degradation in the animal body.**—See this vol., 468.

**Formation of carbohydrate and fat from protein.** F. HÖLZL (Diss., München, 1933: Bied. Zentr., 1935, 6, A, 2).—A discussion. A. G. P.

**Effect of ingestion of cottonseed oil before and after hydrogenation on the composition of the body-fat of the rat.** J. M. SPADOLA and N. R. ELLIS (J. Biol. Chem., 1936, 113, 205—218).—The normal acids of rat adipose tissue were myristic, palmitic, stearic (I), palmitoleic (II), and oleic (III). Rats fed with a low-fat basal diet+ cottonseed oil deposited more (I) and (II) than those receiving partly hydrogenated oil or the basal diet alone. The deposition of linoleic acid  $\propto$  the amount fed and replaced (II) and (III). Small amounts of arachidonic acid were found in the fat after feeding with the oil. H. D.

**Digestion of fats from crude plant tissues: digestion of closed plant cells and their importance for physiology and pathology of digestion in man.** H. WEISS (Arch. Verdauungskr., 1935, 57, 42—45; Chem. Zentr., 1935, i, 3565).—The fat of the uninjured cells is digested by the intestinal lipases in the mouse. R. N. C.

**Carotenoids and oxidation of lipins.** J. VERNE (Compt. rend. Soc. Biol., 1936, 121, 609—610).—Only those lipins of skin or adrenal sections that do not give a positive Feulgen-Verne reaction can be stained with carotenoids (I); autoxidation renders the reaction positive, but prevents staining. (I) protect the lipins against autoxidation. R. N. C.

**Can intact monoglycerides be resorbed?** G. ROSENTHAL and H. TRAUTWEIN (Ber. Verh. sächs. Akad. Wiss., math.-phys. Kl., 1934, 86, 325—338).—The depancratised dog resorbs monoglycerides (I) better than triglycerides, probably because the (I) are absorbed without previous cleavage on account of their small solubility in  $H_2O$  or of their capacity to form emulsions; both these properties facilitate cleavage by intestinal lipases. Hydrolysis is further favoured by the surface activity of the (I), through which they are more readily adsorbed on the lipases and more quickly saponified. R. N. C.

**Fat metabolism. XVI. Biological degradation of fatty acids, esters, and fats to dicarboxylic acids.** B. FLASCHENTRÄGER and K. BERN-

HARD (Z. physiol. Chem., 1936, 238, 221—232; cf. A., 1935, 1151).—Coconut oil and cooking fat (20% butter), if given in sufficient amount, are degraded in the dog, yielding small amounts of sebacic (I) and suberic acid. The Me and Et esters of the  $C_9$ — $C_{12}$  monocarboxylic acids, given with fat, yield the corresponding dicarboxylic acids. Of the Na salts of the  $C_6$ — $C_{12}$  and  $C_{14}$ ,  $C_{16}$ , and  $C_{18}$  monocarboxylic acids only octoic, nonoic, and decoic acids yield dicarboxylic acids. The behaviour of the Me and Et esters of these monocarboxylic acids is analogous. (I), even when given in very small amounts, passes chiefly unchanged (partly  $\beta$ -oxidised) into the urine. The degradation of monocarboxylic acids probably proceeds more rapidly than does that of the dicarboxylic acids and consequently  $\beta$ - rather than  $\omega$ -oxidation predominates in the organism. W. McC.

**Fat metabolism in fowls: practical significance.** E. T. HALNAN and E. M. CRUICKSHANK (Proc. 5th World's Poultry Congr. Rome, 1933, 2, 612—619).—Pullets at 15 weeks of age commence to store more fat than cockerels, the difference increasing with advancing maturity. The  $Et_2O$ -sol. matter in the blood of laying hens is  $>$  that in the blood of cockerels. The I val. of depôt fat reflects that of food fat. Ingestion of unsaturated acids, e.g., hemp oil, causes an increase in unsaturated acids on egg-yolk fat. CH. ABS. (p)

**Deuterium as an indicator in fat metabolism.** B. CAVANAGH and H. S. RAPER (Nature, 1936, 137, 233—234).—By the use of linseed oil containing D for investigating the absorption of fatty acids in the rat, it is shown that lipins of the liver and kidney take up the D-containing fatty acids. L. S. T.

**Effect of liver feeding on the "fat" content of the liver.** A. W. BEESTON and H. WILKINSON. (Biochem. J., 1936, 30, 121—126).—Rats fed on a diet containing chiefly dried liver developed fatty livers (A., 1934, 104); cholesteryl esters (I) rose to 1.8% and glycerides (II) to 2%. 214 mg. of extra choline (III) added to the diet daily had no influence on the % of (I) but lowered that of (II). Using  $EtOH$ -extracted livers with added beef dripping gave vals. for (I) and (II) of 0.45 and 1.67%, respectively; addition of the extracted cholesterol (IV) to the diet raised the vals. to 3.62 and 3.19% so that the fatty liver production is due to (IV) in the diet.  $H_2O$ -extracted liver gave the same results as unextracted liver. Inclusion of extra (IV) in the diet produced increased fat deposition, whilst replacing the dried by raw liver or adding (III) had little effect. H. D.

**Dietary prevention of fatty livers. Triethyl- $\beta$ -hydroxyethylammonium hydroxide.** H. J. CHANNON and J. A. B. SMITH (Biochem. J., 1936, 30, 115—120).—Triethyl- $\beta$ -hydroxyethylammonium hydroxide (I) (aurichloride, m.p. 225°), prepared from  $NEt_3$  and  $CH_2Cl-CH_2-OH$ , when fed to rats on a fatty liver-producing diet caused an inhibition of fat accumulation rather  $<$  that of choline. Large individual variations in fat accumulation occurred which were not associated with food intake; the inhibitory action of (I) on does was  $>$  on bucks. H. D.



**Carbohydrate and fat metabolism during development of *Hynobius* eggs.** M. TAKAMATSU (Z. physiol. Chem., 1936, 238, 96—98).—The glycogen, fat, and cholesterol contents of the embryos of *H. nebulosus* eggs decrease with development. The fat is almost entirely sol. in both EtOH and Et<sub>2</sub>O.

R. S. C.

**Utilisation of inulin for growth by the young white rat.** A. BENDAÑA and H. B. LEWIS (J. Nutrition, 1935, 10, 507—515, 578).—With rats receiving a calorie-deficient diet utilisation of inulin was < that of sucrose or fructose. Inulin cannot serve as the sole source of carbohydrates for rats.

A. G. P.

**Do the phosphorus and glycogen contents of frog muscle run parallel?** A. MOSCHINI (Bull. Soc. Chim. biol., 1936, 18, 160—164).—The changes in the P and glycogen content of frog muscle caused by injection of glucose into normal animals and those with muscles atrophied by fasting, by section of the sciatic nerve, and by pancreatectomy do not run parallel. A lowering of the P content is always associated with functional disturbance.

A. L.

**Absorption and utilisation of carbohydrates [by animals].** H. B. PIERCE (J. Nutrition, 1935, 10, 689—716).—A review.

A. G. P.

**Fœtal carbohydrate metabolism following adrenalectomy, insulin, and glucose experiments on the mother.** E. L. COREY (Amer. J. Physiol., 1935, 113, 450—454).—Adrenalectomy and administration of insulin in the pregnant rat cause a fall of liver-glycogen in both mother and fœtus, whilst glucose (I) increases it. Cortical hormone is without effect. Placental and fœtal muscle-glycogen are relatively unaffected; the latter shows a slight rise with (I).

R. N. C.

**Carbohydrate metabolism of gut muscle.** B. N. PRASAD (J. Physiol., 1935, 85, 239—248).—The isolated muscle contains only about 0.25% of carbohydrate available for glycolysis; it oxidises about 1 mg. of carbohydrate per g. per hr. in presence of O<sub>2</sub>. In presence of glucose (I) it produces lactic acid under aerobic or anaërobic conditions; even in oxygenated Ringer's solution the deeper portions of the muscle probably receive an inadequate O<sub>2</sub> supply. Glycolysis under anaërobic conditions takes place at about 2 mg. of (I) per g. per hr.; it is inhibited by CH<sub>3</sub>I·CO<sub>2</sub>Na and increased by electric stimulation.

R. N. C.

**Utilisation of sugars and polyhydric alcohols by the adult blowfly.** G. FRAENKEL (Nature, 1936, 137, 237—238).—The utilisation by *Calliphora erythrocephala* of numerous carbohydrates and polyhydric alcohols is summarised. The results indicate the presence of several enzymes (enumerated) in the gut of the fly.

L. S. T.

**Animal calorimetry. XI. Specific dynamic action of carbohydrate.** Z. ASZÓDI and J. PÉLYI (Biochem. Z., 1936, 283, 393—414).—The sp. dynamic action of carbohydrate on administration of large amounts of sugar is > that of fat but with small amounts is not related quantitatively to the amount of sugar used. In presence of carbohydrate

reserves, these small amounts are not therefore immediately burnt. The elimination of heat on feeding carbohydrate does not synchronise with the O utilisation.

P. W. C.

**Acidosis, alkalosis, and carbohydrate metabolism. Influence of acid- and base-producing diets.** C. MORI (J. Biochem. Japan, 1935, 22, 437—446).—The assimilation of sugar by rabbits (as indicated by the change in blood-sugar after ingestion of glucose) on a diet producing acidosis is > that with a diet producing alkalosis.

F. O. H.

**Influence of calcium on intestinal absorption.** E. J. McDougall (J. Physiol., 1935, 85, 109—116).—Absorption of isotonic glucose, xylose, and sorbose solutions injected into the small intestine in rats is not affected by a diet producing low serum-Ca.

R. N. C.

**Mechanism of the suppression of ammonio-genesis in muscle by pyruvic acid.** J. K. PARNAS, B. SOBCEK, and W. MEJBAUM (Compt. rend. Soc. Biol., 1936, 121, 701—704).—NH<sub>3</sub> production is suppressed by AcCO<sub>2</sub>H (I) more rapidly in presence of hexose diphosphate, which accelerates NH<sub>3</sub> production *per se*. (I) probably reduces phosphoglyceraldehyde to phosphoglyceric acid, which is then transformed into phosphopyruvic acid. The latter reacts with NH<sub>3</sub> and adenylic acid to form adenosinetriphosphoric acid.

R. N. C.

**Transformation of adenosinetriphosphoric acid in muscle. II. Relation between dephosphorylation of the acid, production of ammonia, and degradation of creatinephosphoric acid during muscular activity.** D. FERDMANN and O. FEINSCHMIDT (Biochem. Z., 1936, 284, 63—71; cf. A., 1935, 778).—In the frog, muscular activity results in degradation of adenosinetriphosphoric (I) and creatinephosphoric acid (II) with production of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and H<sub>3</sub>PO<sub>4</sub>, respectively. During recovery of fatigued muscle, (I) and (II) are resynthesised with disappearance of H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and H<sub>3</sub>PO<sub>4</sub>, the extent of resynthesis depending on the length of the period of recovery and being almost complete in 15 min. The adenylic acid produced by dephosphorylation of (I) is deaminated during activity and reaminated during recovery.

W. McC.

**Effects of cod-liver oil and wheat germ on the retention of iron, nitrogen, phosphorus, calcium, and magnesium during human pregnancy.** C. M. COONS and R. R. COONS (J. Nutrition, 1935, 10, 289—310).—Addition of wheat germ to a basal diet improved the retention of Fe and N, the effect being due to the mineral rather than to the org. contents. Cod-liver oil enhanced the action of wheat germ. Increased retention of Ca, Mg, and P due to feeding cod-liver oil is small and irregular.

A. G. P.

**Spectrum analysis of hen-eggs and chick-tissues.** W. F. DREA (J. Nutrition, 1935, 10, 351—355).—Al, Ba, Ca, Cu, Fe, Mg, P, K, Rb (?), Si, Na, Sr, Ti, and V pass from food or H<sub>2</sub>O into the egg and thence into blood and tissues of the chick. Mn and Zn are absent from chicks' blood. Al, Ba, Cu, Si, Sr, Ti, and Zn are uniformly distributed among the tissues. Ba, Fe, Sr, and V are more conc. in hens'



blood and/or egg than in the food. B, F, and Ag are unnecessary or harmful to chicks. Cr, Pb, and Mo occur in hens' blood in amounts corresponding to those in the food but are not regularly present in eggs. When present in chicks, Mo accumulates in the liver, Pb in lungs, and Cr in brain and eye. Mn occurs in yolks but not in whites or shells, and in chicks accumulates in the liver. A. G. P.

**Chemistry of cephalopod embryos.** T. KAMACHI (Z. physiol. Chem., 1936, 238, 91—95).—The Ca, Mg,  $\text{SO}_4$ ,  $\text{NH}_2$ , and enzyme contents of the embryo increase at the expense of the residue during development of the eggs of *Loligo bleekeri*, Kefirstein, but the  $\text{PO}_4$  and Cu contents remain unchanged; the enzymes present resemble qualitatively those of other eggs. R. S. C.

**Toxicity and rate of disappearance of intracisternally injected calcium salts in the dog.** M. F. MASON, and H. RESNIK (J. Pharm. Exp. Ther., 1936, 56, 53—59).—Aq.  $\text{CaCl}_2$ , Ca gluconate and lactate containing 0.25 mg. of Ca per kg. body-wt. are injected into dogs without producing toxic action. Larger doses cause respiratory depression, 0.4 mg. of Ca per kg. being the lethal dose. Simultaneous injection of Mg does not increase the Ca tolerance. A. L.

**Influence of nutrition on metabolism during work. IV. Calcium.** F. BRUMAN and F. JENNY (Deut. Arch. klin. Med., 1935, 177, 527—543; Chem. Zentr., 1935, ii, 243).—The effects of Ca and K on metabolism were antagonistic. G. H. F.

**Calcium as a factor in the nutritional improvement of health.** H. C. SHERMAN (Proc. Nat. Acad. Sci., 1936, 22, 24—26).—A discussion of recent work. A. G. P.

**Effects of increasing the calcium content of a diet in which calcium is one of the limiting factors.** H. C. SHERMAN and H. L. CAMPBELL (J. Nutrition, 1935, 10, 363—371).—Addition of Ca to the diet improved food utilisation and the general development of rats. A. G. P.

**Calcium and phosphorus needs of pre-school children.** A. L. DANIELS, M. K. HUTTON, E. M. KNOTT, O. E. WRIGHT, and M. FORMAN (J. Nutrition, 1935, 10, 373—388).—The requirements are 45—50 mg. of Ca (with adequate vitamin-D) and 60—70 mg. of P per kg. A. G. P.

**Calcium and phosphorus metabolism in chick embryos.** T. KAMACHI (J. Biochem. Japan, 1935, 22, 189—197).—Injection of  $\text{CaCl}_2$ ,  $\text{Na}_2\text{HPO}_4$ , or org. Ca- $\text{PO}_4$  preps. (I) into incubating eggs diminishes the Ca content of the embryo but not that of the allantoic fluid; the effect is probably due to inhibition of Ca mobilisation from the shell. (I), but not  $\text{Na}_2\text{HPO}_4$ , increases the P content of the embryo. F. O. H.

**Calcium and phosphorus requirements of growing turkeys.** F. E. MUSSEHL and C. W. ACKERSON (Proc. 5th World's Poultry Congr. Rome, 1933, 2, 664—667).—A factor other than the Ca:P ratio of the diet influences Ca and P assimilation. The acid:base ratio of the entire ration probably has an important effect. In the absence of vitamin-D

and ultra-violet energy, poultts receiving the higher levels of Ca ( $\text{CaCO}_3$ ) were better able to adjust themselves to vitamin limitation. The Ca and P requirements vary with the growth rate, which is influenced by the quality and quantity of protein and the supply of vitamins other than -D.

CH. ABS. (p)

**Changes in lime content between various parts of the hen's egg during incubation.** A. CAZANIGA (Proc. 5th World's Poultry Congr. Rome, 1933, 2, 444—449).—The shell-Ca diminished rapidly from the 13th day of incubation. In the egg contents vals. increased subsequently. CH. ABS. (p)

**Experimental sodium chloride deficiency in man.** R. A. McCANCE (Proc. Roy. Soc., 1936, B, 119, 245—268).—In man, a severely limited intake of NaCl (about 40 mg. of Na, 200 mg. of Cl, daily), accompanied by sweating, but without limitation of  $\text{H}_2\text{O}$  intake, causes a loss of at least 25—30% of the extra-cellular Na and Cl. The N balance becomes negative, and the blood-urea rises. The body appears to react partly by allowing the total vol. of body fluids to fall, partly by allowing their osmotic pressure to fall. F. A. A.

**Acidosis as a factor of fatigue in dogs.** F. W. SCHLUTZ, M. MORSE, and A. B. HASTINGS (Amer. J. Physiol., 1935, 113, 595—601).—Alkalosis from  $\text{NaHCO}_3$  reduces, whilst acidosis from  $\text{NH}_4\text{Cl}$  favours, the capacity of dogs for exercise;  $\text{NaHCO}_3$  promotes lactic acid formation, whilst  $\text{NH}_4\text{Cl}$  depresses it. Acidosis accompanying exercise is not a causal factor of fatigue. R. N. C.

**Effect of sodium fluoride on the basal metabolism of the rat under several experimental conditions.** P. H. PHILLIPS, H. E. ENGLISH, and E. B. HART (Amer. J. Physiol., 1935, 113, 441—449).—Normal basal metabolism in rats is not affected by feeding with NaF, but when previously raised by thyroid it exhibits a sharp and rapid rise. KI alone causes a temporary reduction, which is unaffected by simultaneous administration of NaF. R. N. C.

**Metabolism in the rat of the naturally-occurring arsenic of the shrimp as compared with arsenic trioxide.** E. J. COULSON and R. E. REMINGTON and K. M. LYNCH (J. Nutrition, 1935, 10, 255—270).—In the shrimp As occurs in complex combination from which it cannot be liberated in the animal organism. Following the digestive process in rats shrimp-As appears in a sol. form and is eliminated through the kidneys; it is retained only to a very small extent. No evidence of toxicity was obtained. A. G. P.

**Physiological and clinical rôle of bromine metabolism.** L. A. JACOBSEN (Presse méd., 1935, 43, 452—454; Chem. Zentr., 1935, i, 3565).—A review. R. N. C.

**Human iodine balance.** V. V. COLE and G. M. CURTIS (J. Nutrition, 1935, 10, 493—506).—The combined urine- and stool-I may account for < 50% of the I intake in some cases. The output of I was fairly uniform for an individual on a monotonous diet. Increased faecal I occurred in cases of hyperthyroidism. A. G. P.



**Iron metabolism.** E. NOLTE (Arch. Pharm., 1936, 274, 107—110).—The liver, lung, and kidney of a goat kept during 5 months on a diet containing a liver-Fe-protein adsorbate (ferripan) ( $\approx 0.26$  g. Fe per diem) contain considerably more Fe than the same organs of a goat maintained on an Fe-free diet. The Fe content of the blood and milk is the same in both cases. H. B.

**Iron metabolism of pre-school children.** L. ASCHAM (J. Nutrition, 1935, 10, 337—342).—Retention of Fe by children of 4—6 years averaged 0.07 mg. with an intake of 0.59 mg. A. G. P.

**Iron requirements of normal adults.** G. E. FARRAR, jun., and S. M. GOLDBAMER (J. Nutrition, 1935, 10, 241—254).—The Fe requirement is normally  $> 5$  mg. daily. Normal urine contains 0.02 mg. of Fe per 100 c.c. A. G. P.

**Nitrogen metabolism in soya bean-feeding of horses.** U. I. LISTOVNISCHA and M. F. GULUII (Ukrain. Biochem. J., 1934, 7, No. 1, 153—161).—Feeding of soya beans increases N metabolism. Urinary N (daily excretion) increases and the urea: total N ratio declines through increase in other N constituents, especially  $\text{NH}_3$ . There is increased excretion of creatinine owing to higher endogenous protein metabolism. CH. ABS. (p)

**Metabolism of women during the reproductive cycle.** VI. Continuous nitrogen utilisation of a multipara during pregnancy, parturition, puerperium and lactation. H. A. HUNSCHER, F. C. HUMMELL, B. N. ERICKSON, and I. G. MACY (J. Nutrition, 1935, 10, 579—597).—N balances over a period of 8 months are recorded and discussed (cf. A., 1933, 304). A. G. P.

**Nitrogen and sulphur metabolism in supra-renalectomised rats.** M. SANDBERG and D. PERLA (J. Biol. Chem., 1936, 113, 35—41).—There was no change in the excretion of uric acid, faecal N and S, and in Cu and Fe metabolism. There was marked creatinuria and an increase in urea, urinary N and S, and neutral S. The % of  $\text{SO}_4^{--}$  decreased slightly. J. N. A.

**Effect of sulphur in the diet on the growth and wool production of sheep.** Nutritive value of some vegetable oils in N. China.—See B., 1936, 218.

**Food value of ethyl alcohol.** H. H. MITCHELL (J. Nutrition, 1935, 10, 311—335, 460).—The energy of ingested EtOH is largely available for physiological purposes. Added to a milk diet EtOH induces more rapid growth, a greater retention of N and fat, and improved digestibility of the basal diet. Sucrose (I) has a relatively greater growth-promoting action, more available energy, and no effect on the digestibility of the basal diet. (I) increases the faecal excretion of metabolic products, but EtOH has no action. A. G. P.

(A) Clearance, extraction percentage, and estimated filtration of sodium ferrocyanide in the mammalian kidney: comparison with inulin, creatinine, and urea. (B) Distribution of ferrocyanide, inulin, creatinine, and urea in

blood: effect on significance of their extraction percentages. D. D. VAN SLYKE, A. HILLER, and B. F. MILLER (Amer. J. Physiol., 1935, 113, 611—628, 629—641).—(A) The plasma clearances and extraction % of  $\text{Na}_4\text{Fe}(\text{CN})_6$  (I), inulin (II), and creatinine (III) in the dog are approx. equal; they are independent of plasma concn. The clearance of urea is about 57% of those of the above substances, and is also independent of plasma concn.

(B) (I) and (II) injected intravenously in the dog are not absorbed into the erythrocytes, but remain in the plasma. (III) enters the corpuscles very slowly, so that it is not withdrawn from them as the blood passes through the kidneys, whilst urea diffuses very readily into the cells, and is therefore withdrawn from them in the kidneys. R. N. C.

**Excretion of phenol-red by the dog.** J. A. SHANNON (Amer. J. Physiol., 1935, 113, 602—610).—Phenol-red (I) excretion is  $>$  insulin (II) excretion at low plasma-(I) levels, but the (I)/(II) excretion ratio falls as the level increases. The depression of (I) clearance as the level is raised is reversible. The ratio is unaffected by phloridzin. R. N. C.

**Metabolism of orally administered citric acid.** C. C. SHERMAN, L. B. MENDEL, and A. H. SMITH [with M. C. TOOTHILL] (J. Biol. Chem., 1936, 113, 265—271).—Only 0.7% of orally administered citric acid appeared in the urine of the dog, none appeared in the faeces, whilst the increased blood-content was maintained for 3—7 hr. The renal threshold was 2.2—6.0 mg. per 100 c.c. H. D.

**Citric acid formed in animal metabolism.** C. C. SHERMAN, L. B. MENDEL, and A. H. SMITH [with M. C. TOOTHILL] (J. Biol. Chem., 1936, 113, 247—263).—The quantity of citrate (I) excreted by men  $\propto$  urinary  $p_{\text{H}}$ ; addition of  $\text{NaHCO}_3$  to a low-citrate diet increases the excretion of (I); in dogs the increase is favoured by replacement of the dietary caseinogen by sucrose. Ingestion of the diet produced an increased excretion of (I) which was not due solely to a raised blood-(I) or diuresis. H. D.

**Curves of sodium formaldehydesulphoxylate in the blood after intravenous or intragastric administration.** E. HUG (Compt. rend. Soc. Biol., 1936, 121, 579—581).—The compound disappears rapidly from the plasma of the dog after intravenous injection, a large part being excreted by the kidneys. The relatively low plasma concn. after intragastric administration  $\propto$  the quantity given. The curve reaches its max. in 2—8 hr. R. N. C.

**Elimination of sodium formaldehydesulphoxylate by the digestive secretions.** T. C. MINNHAAR (Compt. rend. Soc. Biol., 1936, 121, 581—582).—In the dog the compound is eliminated in very small quantities in the saliva, bile, and pancreatic and intestinal juices. R. N. C.

**Degradation of mescaline and similar substances in the body.** K. H. SLOTTA and J. MÜLLER (Z. physiol. Chem., 1936, 238, 14—22).—Mescaline (I), given orally, is excreted mainly as  $(\text{OMe})_3\text{C}_6\text{H}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (II) in the urine of rabbits and dogs. Instead of (II), human urine gives a OMe-rich oil, a mixture of probably two substances,



which on hydrogenation ( $\text{PtO}_2$ ) absorbs  $3\text{H}_2$  and gives a substance,  $\text{C}_9\text{H}_{14}\text{O}_2\text{N}\cdot\text{OMe}$ , cryst. (no picrate, auri- or platini-chloride). (II) is recovered in good yield unchanged from the urine of dogs or rabbits to which it is fed, and has no physiological effect on these animals or man.  $3:4:5\text{-(OMe)}_3\text{C}_6\text{H}_2\cdot\text{CHO}$  is recovered from urine as the acid, but  $\beta\text{-}3:4:5\text{-trimethoxyphenylethyl alcohol}$  (III) yields a N-containing degradation product. (I) has very little effect on schizophrenic patients, who are, however, profoundly affected by  $2:3:4\text{-(OMe)}_3\text{C}_6\text{H}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$ , which is innocuous to healthy men.  $3:4:5\text{-(OMe)}_3\text{C}_6\text{H}_2\cdot\text{COCl}$  and  $\text{CH}_2\text{N}_2$  give  $3:4:5\text{-trimethoxy-}\omega\text{-diazoacetophenone}$ , m.p.  $103^\circ$  (and some Cl-ketone), which yields  $3:4:5\text{-trimethoxyphenylacetamide}$ , m.p.  $125^\circ$ , hydrolysed by hot  $\text{KOH}\cdot\text{MeOH}$  to (I), m.p.  $121^\circ$ . (I) and  $\text{HNO}_2$  afford (III), b.p.  $95\text{--}135^\circ/0\cdot01\text{ mm.}$  (*p*-nitrobenzoate, m.p.  $100^\circ$ ). R. S. C.

**Degradation of dimethylaniline and its oxide in the animal body.** F. HORN (Z. physiol. Chem., 1936, 238, 84—90).— $\text{NPhMe}_2$  is not converted by dogs into  $\text{NPhMe}_2\text{O}$ . Both compounds are converted, at least partly, into  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . The toxic symptoms of  $\text{NPhMe}_2$  include methæmoglobin formation. R. S. C.

**Tissue cultures exposed to the influence of a magnetic field.** R. PAYNE-SCOTT and W. H. LOVE (Nature, 1936, 137, 277).—Exposure to magnetic fields of 5000 gauss produced no observable change in the growth of cells from the heart of chick embryos cultivated *in vitro*. A slight tendency to protoplasmic disintegration in some of the resting cells was observed in certain exposed cultures. L. S. T.

**Changes in the blood-fluid of *Scyllium canicula* exposed to continuous current, when the branchial region is close to the anode.** E. A. PORÅ (Compt. rend. Soc. Biol., 1936, 121, 503—504).—The increases of blood-osmotic pressure and  $\text{-Ca} \propto I$ , but are  $<$  those obtained when the branchial region adjoins the cathode, as are also the variations of blood- and serum-Cl and  $\text{-Na}$ , whilst the increases of proteins and corpuscular Cl and the fall of the alkaline reserve are higher. The fall of  $\kappa$  is the same in both cases. The increases of inorg. salts and org. substances are  $>$  the corresponding losses in the muscles. R. N. C.

**Changes in the blood-fluid of the male *Scyllium canicula* produced by continuous electric current.** E. A. PORÅ (Compt. rend. Soc. Biol., 1936, 121, 507—508).—Passage of current for 12 hr. increases muscle- $\text{H}_2\text{O}$  at the expense of the blood. Inorg. salts in the muscles increase considerably, possibly through penetration of salts from the external medium, whilst org. substances fall in the muscles and rise in the serum. The alkaline reserve increases, whilst blood-Cl falls. R. N. C.

**Changes in the blood-fluid of the male *Scyllium canicula*, produced by an opposing continuous electric current in the external medium.** E. A. PORÅ (Compt. rend. Soc. Biol., 1936, 121, 660—662; cf. preceding abstract).—The blood loses  $\text{H}_2\text{O}$  without a corresponding gain in the muscles. Inorg. salts increase in both blood and muscles, but org.

substances pass from the muscles to the blood. Blood-, serum-, and corpuscular-Cl,  $\text{-Na}$ ,  $\text{-proteins}$ , the alkaline reserve, and  $\kappa$  are all increased, whilst  $\text{-Ca}$  falls. R. N. C.

**Effect of ultra-violet radiation on lens protein in the presence of salts and the relation of radiation to industrial and senile cataract.** J. H. CLARK (Amer. J. Physiol., 1935, 113, 538—547).—Ultra-violet irradiation of solutions of lens proteins in aq.  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$  at  $p_{\text{H}}$  6·0—7·2 and  $4^\circ$  denatures the proteins but produces no increase of opacity except when  $\text{CaCl}_2$  is present. No increase is found at  $p_{\text{H}}$  7·8, whilst the increase is general at  $p_{\text{H}}$  5·4. Opacity is not increased by heating to  $40^\circ$  at  $p_{\text{H}}$  7·2 without irradiation, but after irradiation it is increased considerably in all solutions containing  $\text{Ca}$ ;  $\text{Na}$ , but not  $\text{K}$ , exerts a restraining action. Light-coagulation probably consists of denaturation of the proteins followed by pptn. through  $\text{Ca}$ ; senile cataract may be due to accumulation of denatured protein in the lens together with increased blood- $\text{Ca}$ , whilst exposure to intense radiant heat is responsible for cataract in metal and glass workers. R. N. C.

**Factors concerned in the arrest of contraction in an ischemic myocardial area.** R. TENNANT (Amer. J. Physiol., 1935, 113, 677—682).— $\text{NaCN}$  and  $\text{KCl}$ , but not  $\text{CH}_3\text{I}\cdot\text{CO}_2\text{Na}$ , arrest contraction, which is also arrested by perfusion of a ventricular zone in the normal heart with  $\text{Na}$  lactate in buffered blood-Locke's solution. R. N. C.

**Adrenaline glycæmia in the dog submitted to slow continuous intravenous injections of alkaline mineral water.** E. CHABROL and J. SALLET (Compt. rend. Soc. Biol., 1936, 121, 733—735).—Large quantities of 0·7% aq.  $\text{NaHCO}_3$  reduce considerably the blood-sugar and its response to subsequent injection of adrenaline. R. N. C.

**Effect of buffered phosphate solutions on a thin layer of living vascular tissue, in moist chambers introduced into the rabbit's ear.** R. G. ABELL (Anat. Rec., 1935, 64, 51—73). R. N. C.

**Reversible loss of the all-or-none response in cold-blooded hearts treated with excess potassium.** G. H. ZWIKSTER and T. E. BOYD (Amer. J. Physiol., 1935, 113, 560—567). R. N. C.

**Deposition of strontium salts in hypertrophic cartilage *in vitro*.** R. ROBISON, K. A. O. LAW, and A. H. ROSENHEIM (Biochem. J., 1936, 30, 66—68).—The deposition *in vitro* of  $\text{Sr}$  salts in hypertrophic cartilage (dissected away from all calcified tissue) by immersion in solutions containing  $\text{Sr}^{++}$  (spectroscopically pure),  $\text{PO}_4^{---}$ , and  $\text{CO}_3^{--}$  is confirmed, the deposits being shown by spectrum analysis to consist largely of a  $\text{Sr}$  phosphate or carbonatophosphate. P. W. C.

**Function of fluorine in the human organism.** L. MICHAELIS (Klin. Woch., 1935, 14, 94—95).—Theoretical. R. N. C.

**Iodine injuries with particular reference to "complete salts" injuries.** I. MÜHE (Deut. Arch. klin. Med., 1935, 177, 345—367; Chem. Zentr., 1935, i, 3949). R. N. C.



**Action of iodine on basal exchange in intestinal closure.** J. GLATZEL (Wien. med. Woch., 1935, 85, 397—400; Chem. Zentr., 1935, i, 3565).—The high basal exchange in rectal cancer and artificial intestinal closure is reduced to normal in 7 days by Lugol's I solution. R. N. C.

**Selenium in [animal] nutrition.** H. A. SCHNEIDER (Science, 1936, 83, 32—34).—Growth effects are described for rats receiving up to 70 p.p.m. of Se as  $\text{Na}_2\text{SeO}_3$  with a normal diet. L. S. T.

**Effect of sulphur on the weight and adrenaline content of the adrenal capsule and on the vasoconstrictor action of blood-serum.** M. MITANI (Folia Endocrinol. Japon., 1933, 8, 104).—Intramuscular injection of large doses of S lowered the wt. and adrenaline content of the adrenals. Continuous small dosage of S produced a similar effect, but the wt. of the capsules increased.

CH. ABS. (*p*)

**Sulphur-mercury compounds and their action on the blood.** L. LIACI (Arch. Farm. speriment., 1933, 56, 372—381; Chem. Zentr., 1935, i, 3952).—Injection of a S-Hg compound in rabbits causes slight modifications of blood-sugar, increases of erythrocytes and leucocytes, and decrease of resistance of erythrocytes to hypotonic NaCl solutions. Blood-Ca and hæmoglobin are unaffected. R. N. C.

**Chemotherapeutic activity of compounds of arsenic with albumin breakdown products rich in sulphur.** W. A. COLLIER and M. KRAUSE (Z. Hyg., 1935, 117, 190—195). R. N. C.

**Physiological action of zinc in animals.** G. BERTRAND (Bull. Soc. Chim. biol., 1936, 18, 213—224).—A review. A. L.

**Pharmacology of ethyl alcohol.** I. Comparison of grain and synthetic alcohols. II. Correlation of the local irritant, anæsthetic, and toxic effects of three potable whiskies with their alcohol content. O. W. BARLOW [with A. J. BEAMS and H. GOLDBLATT] (J. Pharm. Exp. Ther., 1936, 56, 117—146).—The toxic and physiological effects of synthetic and grain EtOH are indistinguishable. The irritant and toxic effects of whisky are > those due to its EtOH content. Administration of synthetic or grain EtOH or whisky to rats in concns. equiv. to 7.5% of EtOH as the sole source of fluid had no effect on growth, but at concns. of 15% growth was retarded. Certain differences are observed in their actions on the stomach and intestine as between synthetic or grain EtOH and whisky. W. O. K.

[Action of] carbonyl chloride [on the blood].—See this vol., 301.

[Physiological] effect of acetic and substituted acetic esters of borneol. H. TSUJI (Tôhoku J. Exp. Med., 1934, 24, 374—379). CH. ABS. (*p*)

**Action of benzene in pregnancy.** G. BARZILAI (Boll. Soc. ital. Biol. speriment., 1933, 8, 1388—1392).—Pregnant female mice are less resistant to narcosis from  $\text{C}_6\text{H}_6$  in the inspired air. The effect is most noticeable at a concn. of 35.43 mg. of  $\text{C}_6\text{H}_6$  per litre of air; with < 26 mg. per litre acute narcosis does not occur. R. N. C.

**Anthelmintic studies on hydroxyalkylbenzenes.** VI. Alkyl polycyclic phenols. VII. Halogenated phenols. VIII. Phenolic ketones, ethers, and esters, and organic acids. P. D. LAMSON, R. W. STOUGHTON, and A. D. BASS (J. Pharm. Exp. Ther., 1936, 56, 50—52, 60—62, 63—68).—VI. The *in-vitro* ascaricidal properties of various polycyclic phenols are not significantly increased by introduction of alkyl groups.

VII. High activity is shown by *p*-chlorocarvacrol, 4-chloro-2-hexyl-phenol and -2-heptyl-phenol. 2:4:6-Tribromo-phenol and -resorcinol are, however, inactive.

VIII. Of > 100 phenolic ketones, ethers, esters, and acids, none shows marked *in vitro* ascaricidal activity. Some monoethers of dihydric phenols are active, but too toxic for use. A. L.

**Acid-base changes in the serum of the dog associated with the hyperthermia of dinitrophenol administration.** E. MUNTWYLER, V. C. MYERS, W. H. DANIELSON, and C. ZORN (Amer. J. Physiol., 1935, 113, 186—192).—Oral administration of sublethal doses of 2:4-dinitrophenol (I) frequently increases serum-Cl and decreases  $\text{HCO}_3^-$ . Total bases (II) are somewhat variable, depending on the quantity of (I) given;  $p_{\text{H}}$  remains within normal limits, but tends to fall slightly from the control level with large doses of (I). Subcutaneous injection of (I) lowers Cl and  $\text{HCO}_3^-$ ; (II) are decreased by sublethal and increased by lethal doses, the undetermined acid concn. being increased in both cases: the  $p_{\text{H}}$  remains fairly const. R. N. C.

**Mechanism of the stimulating action on metabolism of dinitro-compounds.** Acetaldehyde, dihydroxyacetone, and glutathione as antidotes. H. HANDOVSKY, H. CASIER, and C. SCHEPENS (Arch. int. Pharmacodyn., 1935, 50, 397—446).—Dinitrocyclopentylphenol (I) ("pentyl") is the most stimulating and least toxic of all the nitro-derivatives. An activator for dinitro-derivatives which varies in its ease of extractability exists in muscle. The stimulation of metabolism *in vitro* is attributed to a respiratory enzyme differing from the normal cellular respiratory enzymes in being cryolabile. (I) added to muscle diminishes its glutathione (II) content, and, in living pigeons, intravenously (II) prevents the hyperthermia which follows (I) injection. A similar inhibition is shown by dihydroxyacetone and MeCHO. *In vitro*, the destruction of MeCHO by muscular tissue is increased by addition of (I); hence MeCHO takes part in the oxido-reduction processes affected. NUTR. ABS. (*m*)

**Comparative actions of cardiazole and coramine on the respiratory centre of man.** I. Subcutaneous injection. H. STEININGER and E. GAUBATZ (Klin. Woch., 1935, 14, 159—160).—Cardiazole is the more active compound. R. N. C.

**Action of large quantities of glucose in prolonged intravenous infusion.** E. BAUER and H. KNÜPPER (Ber. Verh. sächs. Akad. Wiss. math.-phys. Kl., 1934, 86, 339—350).—The max. intravenous tolerance for glucose in the dog is normally about 1.4 g. per kg. per hr. Blood-lactic acid rises



some time before death, and the alkaline reserve falls. The abnormal glycogen content of the liver is not the cause of death. The relations between liver-glycogen and N, and the liver and body wts. are studied. R. N. C.

Effect of camphor on the adrenaline reaction. I. Blood pressure. J. SZELÖCZEY. II. Dilatation of pupil and increase of blood pressure. J. SZELÖCZEY. III. Permeability and adsorption. J. SZELÖCZEY and B. KOLONITS (Magyar orvosi Arch., 1935, 36, 37—50, 51—55, 56—62; Chem. Zentr., 1935, ii, 241). G. H. F.

Spectrographic and biological study of phloridzin derivatives. I. Phloridzin hepta-acetate. A. LAMBRECHTS (Bull. Soc. Chim. biol., 1936, 18, 237—238).—Phloridzin hepta-acetate (I) shows an absorption band with a max. at 275 m $\mu$  and an extinction coeff. of 675. Injection of a solution of 10 mg. of (I) in EtOH produces a glycosuria of 17%, but this may be due to the hydrolysis of (I) by the blood. A. L.

Nutrition of the euglenia, *Astasia chattoni*. A. LWOFF and H. DUSI (Compt. rend., 1936, 202, 248—250).—Addition of fatty acid to the media considerably increases the reproduction. H. G. R.

Point of attack of acetylcholine in the heart. Does nicotine inhibit the cardiac action of acetylcholine? F. PLATTNER (Pflüger's Archiv, 1935, 236, 226—229). R. N. C.

Acetylcholine and the normal striped muscle of mammals. A. SIMONART and E. F. SIMONART (Arch. int. Pharmacodyn., 1935, 49, 302—328; Chem. Zentr., 1935, i, 3003). G. H. F.

Influence of thyroparathyroidectomy and of bile acids on bile secretion. S. TUZIOKA (J. Biochem. Japan, 1935, 22, 367—374).—The vol. of bile and the total bile acids of dogs (with biliary fistulæ) are diminished and the bile- $p_H$  is increased. Administration of Na taurocholate produces a return to normal vals. F. O. H.

Influence of bile acids on calcium metabolism. XII. Tetany and blood-calcium in thyroparathyroidectomised dogs. T. HOSHIZIMA (J. Biochem. Japan, 1935, 22, 375—383). F. O. H.

Influence of changes induced by cholesterol on the calcification *in vitro* of rabbit aorta. K. A. O. LAW and R. ROBISON (Biochem. J., 1936, 30, 69—75).—The development of typical cholesterol (I) arteriosclerosis by feeding rabbits on a diet rich in (I) is not associated with any increased proneness to calcification of the aorta *in vitro*, nor did the deposits so obtained specially favour those portions of the vessel in which the (I) lesions occurred. P. W. C.

Cholesterol as a growth factor for flagellates. R. CAILLEAU (Compt. rend. Soc. Biol., 1936, 121, 424—425). R. N. C.

Action of muscle-adenylic acid and related substances on the blood-supply of the skeletal muscle. W. SCHOEDEL (Pflüger's Archiv, 1935, 236, 93—101).—Adenylic acid (I) from muscle increases the blood-supply to skeletal muscle by 100—

170%, as do acetylcholine, adenosine, and adenosine triphosphate. The effect of yeast-(I) is < than that of muscle-(I). Inosic acid (except in large quantities), adenine, hypoxanthine, and carnine are without effect. The NH<sub>2</sub>-compounds and carbohydrate of muscle-(I) are responsible for the action. R. N. C.

Influence of administration of tonsil extracts on sugar excretion in rabbits. C. TATEISHI (J. Biochem. Japan, 1935, 22, 251—261).—The sugar excretion threshold is lowered by administration of small, and increased by large, amounts of extracts of pig's tonsil; the diminished level returns to normal on administration of cholic acid. F. O. H.

Action of the oxidase of *Cynara scolimus* in decreasing the blood-sugar. A. RISI (Rass. ter. Pat. clin., 1933, 5, 297—298; Bied Zentr., 1935, 6, A, 7).—Injection of the artichoke oxidase modifies the carbohydrate metabolism and induces a marked hypoglycemia in rabbits. A. G. P.

Effect of yeast and yeast extracts on intestinal motion. H. WASTL (Biochem. Z., 1936, 284, 24—39). W. McC.

Ether anaesthesia. Changes in serum-potassium during and following anaesthesia. B. H. ROBBINS and H. A. PRATT (J. Pharm. Exp. Ther., 1936, 56, 205—208).—The normal serum-K is for dogs 20 mg. and for guinea-pigs 34 mg. per 100 c.c. During Et<sub>2</sub>O anaesthesia, serum-K falls in both animals, and returns to normal within 5 hr. W. O. K.

Chemical constitution and local anaesthetic action of alkamine esters of *p*-alkoxybenzoic acids.—See this vol., 468.

Adrenaline secretion and blood-sugar content in dogs anaesthetised with avertin. H. SATO, Y. SATOW, and T. DEGUCHI (Tohoku J. Exp. Med., 1934, 24, 485—494).—Anaesthesia did not affect adrenaline output but slightly decreased the blood-sugar. CH. ABS. (p)

Muscle contractions without production of lactic acid. E. MARTINI (Arch. ital. Biol., 1935, 88, 82—90; Chem. Zentr., 1935, ii, 248). G. H. F.

Emetine sulphocamphorate. I. IMAZ and M. F. PASTOR (Rev. Assoc. med. Argentina, 1935, 49, 99—104).—Effects of the sulphocamphorate are similar to those of the hydrochloride, but its toxicity is lower. CH. ABS. (p)

Effect of ergotamine on glycosuria and hyperglycemia produced by stimulation of the superior cervical sympathetic ganglion. D. A. CLEVELAND (Amer. J. Physiol., 1935, 113, 592—594).—Ergotamine inhibits the above effects. R. N. C.

Heart activity and vegetative poisons. I. Effect of intravenous injections of atropine on the heart action. G. W. PARADE and J. G. JÄGER. II. Effect of intravenous injections of adrenaline and pilocarpine on the heart action. G. W. PARADE and H. R. FOERSTER (Klin. Woch., 1934, 13, 1684—1686, 1709—1711). R. N. C.

Respiratory effects of morphine, codeine and related substances. V. Effect of  $\alpha$ -,  $\beta$ -, and



$\gamma$ -isomorphines and their dihydro-derivatives on the respiration of the rabbit. C. I. WRIGHT and F. A. BARBOUR (J. Pharm. Exp. Ther., 1936, 56, 39—49).—The min. subcutaneous doses of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomorphine and dihydro- $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomorphine required to depress the respiratory mechanism of the rabbit are 0.55, 8.0, 8.0, 0.4, 0.55, and 5.3 mg. per kg., respectively. A. L.

Effect of morphine on the human ureter. N. F. OCKERBLAD, H. E. CARLSON, and J. F. SIMON (J. Urol., 1935, 33, 356—362). CH. ABS. (p)

Effect of quinine on tissue respiration: relation between quinine and various hormones in this respect. I. Insulin or adrenaline. II. Genital glands. K. MIZUTANI (Folia Endocrinol. Japon., 1933, 8, 97—98, 98—99).—I. Injection of quinine (I) lowered the  $O_2$  consumption of liver, kidney, thyroid, spleen, and heart muscle to a small extent, and that of skeletal muscle markedly. Administration of insulin increased this effect on liver and thyroid and decreased it in all other organs. Adrenaline in all cases retarded the action of (I).

II. Feeding of dried testicle to male rats decreased these effects of (I) in all organs, especially thyroid. Interstitial tissue of the ovary had a similar, and corpus luteum a reverse, action in the case of female rats.

CH. ABS. (p)

Site and mode of action [of therapeutic substances] and intermediary metabolism. H. FREUND (Arch. exp. Path. Pharm., 1936, 180, 416—436).—Intermediary metabolism is dependent on the condition of the organ. The site and mode of action of a therapeutic substance are changed by changes in tissue metabolism. The relations between variation in metabolic processes and the action of drugs etc. are exemplified.

F. O. H.

Relation between the toxicities and the b.p. of related substances. J. FERGUSON (Nature, 1936, 137, 361—362).—An exact linear relationship exists between the b.p./1 atm. of a series of related compounds and the log of the molar lethal doses to insects for the most diverse cases. Data for the action of chlorinated ethylenes on *Sitophilus granarius* are given. In a homologous series or a series of substituted derivatives the effect of the substituent is probably purely physical, increasing the availability of the toxic grouping of the parent substance.

L. S. T.

Relation between toxicity, resistance, and time of survival. L. REINER (J. Gen. Physiol., 1936, 19, 419—422; cf. A., 1934, 323, 551).—Theoretical. A more general form of the equations is given, consistent with a limiting toxicity with increasing concn. of drug.

F. A. A.

Treatment of military gas poisoning. E. GILLERT (Therap. d. Gegenwart, 1934, 75, 529—537; Chem. Zentr., 1935, i, 3814).

H. N. R.

Chronic carbon monoxide poisoning. H. BURESCH (Z. Hyg., 1935, 117, 153—160).

R. N. C.

Action of alcohol and some other poisons on heart inhibition in the frog. C. G. SANTESSON (Skand. Arch. Physiol., 1934, 69, 255—292).

R. N. C.

Relative toxicity of acetone, methyl alcohol, and their mixtures. I. R. M. SKLIANSKAYA, F. E. URIEVA, and L. M. MASHBITZ. II. Action on white mice. L. M. MASHBITZ, R. M. SKLIANSKAYA, and F. E. URIEVA (J. Ind. Hyg., 1936, 18, 106—116, 117—122).—I.  $COMe_2$  depresses the activity of the isolated frog's heart more powerfully than MeOH, but recovery occurs more readily after  $COMe_2$ . Mixtures of  $COMe_2$  and MeOH show the predominant effect of  $COMe_2$ .

II. Measured by commencement of narcosis, the toxicity of  $COMe_2$  is  $>$  that of MeOH, but according to mortality, MeOH is more toxic than  $COMe_2$  or their mixtures. With mixtures of 40, 50, and 60% of  $COMe_2$ , the toxicity is  $<$  that of the separate compounds.

J. N. A.

Toxicity and potential dangers of ethylene glycol. F. H. WILEY, W. C. HUEPER, and W. F. VON OETTINGEN (J. Ind. Hyg., 1936, 18, 123—126).—A concn. of 300 mg. of  $(CH_2OH)_2$  per 1000 litres of air has no toxic effects on mice or rats, and probably none on man, even with continued exposure of 8 hr. per day for  $3\frac{1}{2}$  months.

J. N. A.

Simultaneous poisoning of frog's muscle with veratrine and iodoacetic acid. J. MÄRTENSSON (Skand. Arch. Physiol., 1935, 71, 229—237; Chem. Zentr., 1935, i, 3004).

G. H. F.

Antiseptic properties of wine. E. CERIOTTO (Semana méd., 1935, 42, 529—532; Chem. Zentr., 1935, ii, 290).—The antiseptic activity of wine *in vivo*, not *in vitro*, is ascribed to the presence of colloidal metals.

H. N. R.

Toxicity of potassium perrhenate. L. C. HURD, J. K. COLEHOOR, and P. P. COHEN (Proc. Soc. Exp. Biol. Med., 1933, 30, 926—928).—In contradistinction to  $KMnO_4$ ,  $KReO_4$  had low toxicity when injected intraperitoneally into rats or mice. In rabbits Re was conc. mainly in the urine with some distribution in the organs, but not in the brain.

CH. ABS. (p)

Relative toxicity of thiocyanate ions. P. BRUN (Compt. rend. Soc. Biol., 1936, 121, 543—546).—CNS' is equally toxic to germinating seeds, infusoria, and fish, but the toxicity is very feeble compared with that of  $CN'$ .

R. N. C.

Muscle metabolism in arsenic-treated rabbits. W. NONNENBRUCH, Z. STARY, A. BAREUTHER, and H. THELEN (Arch. exp. Path. Pharm., 1936, 180, 437—439).—The hexosemono- and adenylypyro-phosphoric acid contents of the muscle are diminished, due to a decrease in phosphorylation processes (cf. A., 1934, 1250).

F. O. H.

Halide distribution in body fluids in chronic bromide intoxication. M. F. MASON (J. Biol. Chem. 1936, 113, 61—74).—The distribution of  $Br'$  and  $Cl'$  in simultaneously taken samples of blood, spinal fluid, urine, gastric juice, and saliva from dogs and patients with chronic bromism has been determined. The distribution ratio for  $Br'$  between cells and serum is slightly  $>$  for  $Cl'$ , whilst that between serum and spinal fluid is much  $>$  for  $Cl'$ . The replacement of  $Cl'$  by  $Br'$  in urine is  $<$  in serum. In gastric juice the replacement is sometimes  $>$  and



sometimes < in serum. In dog's parotid saliva the replacement is approx. the same as in serum, whilst in human mixed saliva it is much greater.

J. N. A.

**Augmentation of the toxicity of fluorosis in the chick by feeding desiccated thyroid.** P. H. PHILLIPS, H. ENGLISH, and E. B. HART (J. Nutrition, 1935, 10, 399—407).

A. G. P.

**Experimental salt poisoning in ducks.** J. P. TORREY and R. GRAHAM (Cornell Vegetarian, 1935, 25, 50—53).

CH. ABS. (p)

**Pharmacology of the nitrite effect of bismuth subnitrate.** E. J. STIEGLITZ and A. E. PALMER (J. Pharm. Exp. Ther., 1936, 56, 216—222).— $\text{Bi}(\text{OH})_2\text{NO}_3$  or  $\text{NaNO}_3$ , added to cultures of *B. coli*, is partly reduced to nitrite (I). After oral administration of  $\text{Bi}(\text{OH})_2\text{NO}_3$  in therapeutic doses, the blood-(I) (normal,  $0.5\text{--}1.5 \times 10^{-6}$  g. per 100 c.c.) usually rises significantly, whilst the arterial blood pressure falls.

W. O. K.

**Lead in drinking-water.** F. WEYRAUCH and H. MÜLLER (Z. Hyg., 1935, 117, 196—201).—Traces of Pb in the drinking-water of German towns are probably responsible for the Pb present in human bones.

R. N. C.

**Treatment of plumbism.** I. GRAY (J. Amer. Med. Assoc., 1935, 104, 200—205).—A low-Ca, high-P (ratio 1:3—4) diet together with administration of  $\text{NH}_4\text{Cl}$  and  $\text{H}_3\text{PO}_4$  increased the elimination of Pb.

CH. ABS. (p)

**Biochemical behaviour of lead in the body.** J. C. AUB (J. Amer. Med. Assoc., 1935, 104, 87—90).—A review.

CH. ABS. (p)

**Acute poisoning from mercuric chloride.** T. SOLLMANN and N. E. SCHREIBER (Arch. Int. Med., 1936, 57, 46—62).—The average [Hg] in the organs of fatal cases of  $\text{HgCl}_2$  poisoning was: kidneys 3.8, liver 2.05, spleen 0.55, intestines 0.43, heart, skeletal muscle, and lungs 0.20—0.30, brain 0.14, blood 0.015—0.12 mg. per 100 g.

H. G. R.

**Selenium in proteins from toxic foodstuffs.** IV. Effect of feeding toxic proteins or toxic protein hydrolysates with and without removal of selenium. K. W. FRANKE and E. P. PAINTER (J. Nutrition, 1935, 10, 599—611).—Hydrolysates ( $\text{H}_2\text{SO}_4$ ) of toxic proteins retain the toxic factor, but become innocuous after pptn. of Se compounds by  $\text{HgCl}_2$ .

A. G. P.

**Toxicant occurring naturally in certain samples of plant foodstuffs.** XI. Effect of feeding toxic and control foodstuffs alternately. K. W. FRANKE (J. Nutrition, 1935, 10, 233; cf. this vol., 105).—Further data relating to the effects of "toxic" maize are given.

A. G. P.

**Acridine compounds.**—See this vol., 484.

**Succession of enzymic processes in muscular tissue.** J. K. PARNAS (Bull. Soc. Chim. biol., 1936, 18, 53—85).—A lecture.

**Mode of combination of an enzyme with an adsorbent and with a substrate.** K. G. STERN (Science, 1936, 83, 190—191).

L. S. T.

**Rôle of the concentration (A) of the co-enzyme, (B) of the substrate, in the rate of fermentation reactions.** L. AMBARD and S. TRAUTMANN (Compt. rend. Soc. Biol., 1936, 121, 470—472, 472—473).—(A) The variations in the fixation of the co-enzyme with univalent anionic concn. at const.  $p_{\text{H}}$  and in the concn. of the co-enzyme with  $[\text{H}^+]$  at const. univalent anionic concn. are confirmed.

(B) The rate of formation of the substrate-enzyme-co-enzyme complex in the inversion of sucrose (I) by invertase is inversely  $\propto$  the concn. of (I), but the rate of hydrolysis of the complex is independent of (I) concn.

R. N. C.

**How can water intervene in the calculation of enzymic reactions?** L. THIVOLLE (Compt. rend. Soc. Biol., 1936, 121, 476—477).—Theoretical.

R. N. C.

**Effect of ultra-violet light on enzymic reactions.** II. Pepsin. S. BANERJEE and H. K. SEN (J. Indian Chem. Soc., 1935, 12, 740—746; cf. A., 1935, 1415).—Ultra-violet light does not affect the action of pepsin on caseinogen at  $p_{\text{H}}$  1.8, when the peptic val. is a max. The influence of various org. and inorg. additions on the peptic val. is also investigated and the mechanism of the action is discussed.

R. S.

**Similarity between the mechanism of the rennin and pectase (pectin-methoxylase) reactions.** A. C. DAHLBERG and Z. I. KERTESZ (Science, 1936, 83, 56).

L. S. T.

**Lysozyme.** K. MEYER, R. THOMPSON, J. W. PALMER, and D. KHORAZO (J. Biol. Chem., 1936, 113, 303—309).—The method of prep. has been modified to include separation as the flavianate. Lysozyme is a basic polypeptide (15.3% N) active only in the reduced state.

H. G. R.

**Activation of villikin.** E. VON KOKAS and G. von LUDÁNY (Pflüger's Archiv, 1935, 236, 166—174).—Villikin is activated only by the HCl of the gastric juice; it is also activated by other acids, the activating powers of which vary, but not by NaOH, NaCl,  $\text{H}_2\text{O}$ , EtOH,  $\text{COMe}_2$ , urea, glycerol, or sucrose. When activated, it is sol. in  $\text{H}_2\text{O}$ , neutral salts, dil. alkali, and EtOH. It exists in the intestinal mucosa as an inactive heat-resistant precursor (provillikin).

R. N. C.

**Anhydrase activity in invertebrates.** M. FLORKIN (Arch. Int. Physiol., 1935, 40, 283—290; Chem. Zentr., 1935, i, 2997).—The occurrence of carbonic anhydrase of Meldrum and Roughton (A., 1933, 844) in many invertebrates is proved.

G. H. F.

**Influence of different diets on enzymes of the organism.** I. The problem. II. Starvation and blood enzymes. III. Insufficient consumption of proteins and the blood-enzymes. B. GOLDSTEIN (Ukrain. Biochem. J., 1934, 7, No. 1, 79—94, 95—107, 109—123).—I. A discussion.

II. Starvation caused no typical changes in blood-catalase (I), a slight initial increase followed by a decrease in -amylase (II), and a progressive and marked decline in -lipase (III). The (III) content



and the decomp. of albumin in the organism were unrelated.

III. Insufficient consumption of protein (such as to cause death in 30—40 days) effected no change in (I) or (II) but an increase in (III) which is paralleled by the decrease in wt. of the animal. Elimination of  $\text{NH}_2$ -acids (tryptophan, cystine, tyrosine) is of no importance in the formation of (III), which may serve as an index of protein sufficiency. CH. ABS. (p)

**Components of dehydrogenase systems. IX.** Cozymase and "codehydrogenase II." H. VON EULER and E. ADLER. **X.** Lactic acid dehydrogenase and malic acid dehydrogenase from heart muscle. E. ADLER and M. MICHAELIS. **XI.** Glucose dehydrogenase from liver. N. DAS (Z. physiol. Chem., 1936, 238, 233—260, 261—268, 269—274; cf. A., 1935, 1276).—IX. In addition to cozymase (I) yeast contains codehydrogenase II (II), (probably identical with the co-enzyme of red blood-cells), which is separated from (I) by chromatographic adsorption on  $\text{Al}_2\text{O}_3$  and is a necessary component of the dehydrogenase system of Robison's ester; (I) is a necessary component of the alcohol dehydrogenase system of yeast, (II) being inactive in the second system and (I) in the first. Both (I) and (II) act as H carriers.

X. The dehydrogenation of lactic acid (III) by the enzyme of heart muscle is activated by flavin enzyme (a necessary constituent), which is partly separated from (III) dehydrogenase by chromatographic adsorption on  $\text{Al}_2\text{O}_3$ . In the (III) and malic acid dehydrogenase systems (I) is the activating co-enzyme, (II) from yeast and red blood-cells having no effect.

XI. Both (I) and (II) activate the glucose dehydrogenase system of liver and (II) occurs in liver.

W. McC.

**Inhibiting action of hydrogen cyanide on biological oxidations.** E. J. BIGWOOD, J. THOMAS, and H. HERBO (Bull. Soc. Chim. biol., 1936, 18, 176—181).—Determinations of the amount of uric acid formed in the aerobic and anaerobic oxidation of hypoxanthine by xanthine-dehydrogenase from milk indicate that the aerobic oxidation is inhibited by HCN. This suggests that indophenol-oxidase is involved.

A. L.

**Histochemical investigation of oxidases by the indophenol-blue reaction. Application to lipins.** L. LISON (Bull. Soc. Chim. biol., 1936, 18, 185—189).—The indophenol-blue obtained on treating certain fatty substances with the Nadi reagent is produced by the oxidation of the reagent by the fatty substances and not by the preferential dissolution of the autoxidised reagent or by the presence of an oxidase. This view is supported by the fact that pure unsaturated lipins such as oleic acid, when kept exposed to the air, bring about the oxidation of benzidine by peroxidase.

A. L.

**Action of carbon monoxide on the indophenol-oxidase in milk.** E. J. BIGWOOD, J. THOMAS, and H. HERBO (Bull. Soc. chim. biol., 1936, 18, 182—184).—CO in the dark is without effect on the aerobic oxidation of hypoxanthine or the Nadi reagent by the xanthine-dehydrogenase from milk. The system

is therefore similar in behaviour to that of succino-dehydrogenase from muscle.

A. L.

**Action of neutral salts of the Hofmeister series on diastatic enzymes.** W. HAARMANN and O. FOLSCHKE (Biochem. Z., 1936, 283, 312—321).—In isotonic and unbuffered solutions, all neutral salts inhibit the conversion of starch into sugar by diastase (I). Animal (I) is particularly strongly inhibited by  $\text{OAc}'$ ,  $\text{PO}_4'''$ , and  $\text{I}'$  whilst  $\text{SO}_4''$ ,  $\text{Cl}'$ , and tartrate are only feebly inhibitory. Malt-(I) is strongly inhibited by all the salts, least by  $\text{I}'$ . In alkaline solution the activity of animal (I) is increased by neutral salts, particularly by  $\text{Cl}'$  and  $\text{SO}_4''$ , and that of malt-(I) is increased by  $\text{SO}_4''$ ,  $\text{OAc}'$ , and tartrate but not by  $\text{Cl}'$  and  $\text{I}'$ . The increase in alkaline solution does not occur at high concns. of the salts. In acid solution practically no activation occurs.

P. W. C.

**Influence of the chlorides of alkalis and of alkaline earths on the saccharification of starch by diastatic enzymes.** W. HAARMANN and K. BAERTSCHER (Biochem. Z., 1936, 283, 301—311).—In neutral and acid solution  $\text{Cl}'$  in low concn. accelerates by 20% and in higher concns. inhibits the activity of malt-diastase (I);  $\text{NaCl}$  and  $\text{MgCl}_2$  inhibit by 70% and other chlorides (except  $\text{LiCl}$ ) by 50%. Animal (I) under the same conditions is not or only slightly affected. In alkaline solution, the activity of animal (I) was considerably increased whereas that of plant (I) was inhibited. With increasing concn. the action of  $\text{Cl}'$  varies in a characteristic way for each cation, the accelerating action with animal (I) being gradually decreased and the inhibition of plant (I) increased.

P. W. C.

**Sisto- and eleuto-amylase.** R. DEPLANQUE (Z. Spiritusind., 1936, 59, 60, 62).—A lecture.

**Influence of heavy water on activity and stability of pancreatic amylase.** M. L. CALDWELL, S. E. DOEBBELING, and S. H. MANIAN (J. Amer. Chem. Soc., 1936, 58, 84—87).—The hydrolysis of starch by pancreatic amylase (I) is not influenced to any marked extent by  $\text{D}_2\text{O}$  (concn. up to 100%), provided deterioration of (I) is avoided. Inactivation of (I) occurs more rapidly and to a greater extent in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  at  $25^\circ$ .

H. B.

**Taka-amylase. VII. Purification by adsorption. VIII—X. Selectivity of different adsorption materials.** T. KITANO (J. Soc. Chem. Ind. Japan, 1936, 39, 22—24B, 24B, 25—26B, 26B; cf. A., 1935, 1535).—Separation of taka-amylase (I) from maltase (II) by adsorption is attempted. Adsorption is rapid, and greater at lower temp. Graphite has no adsorptive action. The relative adsorptive power, for (I) and (II), of various charcoals and earths, of kaolin, and of  $\text{Cu}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  is examined. By none of these is (I) obtained free from (II). The optimum action on starch and on maltose is at the same  $p_{\text{H}}$  (4.6). (I) may be a form of Ohlsson's saccharogenamylase ( $\beta$ -amylase).

E. W. W.

**Action of some oxidisers on amylolysis and alcoholic fermentation in flour paste.** R. GUILLEMET and C. SCHELL (Compt. rend. Soc. Biol., 1936,



121, 463—464).—Amylolysis in paste is increased by  $K_2S_2O_8 \propto$  the concn., and by  $KBrO_3$  and  $K_3BO_3$ , which show max. effect in min. concn. R. N. C.

**Determination of amylolytic activity of pancreatin.** A. DE CLERCQ (J. Pharm. Belg., 1935, 17, 95—98; Chem. Zentr., 1935, i, 2997).—The methods of the Belgian, American, French, and Spanish pharmacopœias are compared. The reaction on starch for  $< 1$  hr. at  $37^\circ$  is recommended. G. H. F.

**Hydrogen sulphide as a factor in the determination of free and bound amylase in ungerminated cereals.** T. CHRZASZCZ and J. JANICKI (Biochem. J., 1936, 30, 342—344; cf. this vol., 245).—More bound amylase is liberated in aq. extracts of barley, rye, and wheat by added  $H_2S$  than by added papain. The amount liberated when shaking is intermittent is  $>$  when it is continuous.

W. McC.

**Enzymic fission of glucosides in heavy water.** F. SALZER and K. F. BONHOEFFER (Z. physikal. Chem., 1936, 175, 304—321).—The results of investigations of the fission of  $\beta$ -glucosides by emulsin are examined in relation to the Michaelis-Menten theory of the velocity of enzymic reactions (A., 1913, i, 540). If the enzyme is almost saturated with substrate the rate of fission in  $D_2O$  solution is  $<$  in  $H_2O$ , showing that the hydrolytic decomp. of the enzyme-substrate complex is slower. If only a small part of the enzyme is combined with substrate fission is more rapid in  $D_2O$  than in  $H_2O$ , showing that the affinity of the enzyme for the substrate in  $D_2O$  is  $>$  in  $H_2O$ . Similar considerations are applicable to hydrolyses catalysed by  $H^+$ . The hydrolysis of salicin is more rapid in  $D_2O$  than in  $H_2O$ , indicating that the first step of the reaction is the formation of a complex of  $H^+$  and substrate at a speed which is high compared with that of the subsequent decomp. into  $H^+$  and products of hydrolysis. If, however, the first step is the slower, the rate of reaction may be higher in  $H_2O$  than in  $D_2O$ . The Michaelis consts. of *p*-cresol-glucoside and *n*-butylglucoside are 0.14 and 0.22, respectively, at  $30^\circ$ .

R. C.

**Action of emulsin. III. Sources of error in the polarimetric examination of enzymic hydrolysis of  $\beta$ -glucosides.** S. VEIBEL and F. ERIKSEN (Biochem. J., 1936, 30, 163—167).—Before the polarimetric determination the enzymic reaction is stopped by adding  $K_2CO_3$ , which raises the  $p_H$  of the solution from 4.4 to 10.5—10.6. The difference in rotation at these two  $p_H$  vals. is about 3—4%. Glucose solutions are unstable at  $p_H$  10.6; 0.1M solutions decrease in  $\alpha$  by  $0.0033^\circ$  per hr. Salicin is used as a standard glucoside; a concn. of 3.972% should be used (cf. Helferich, A., 1931, 873). PhMe should not be used as a bactericide as it accelerates the rate of enzymic hydrolysis by 25—35%.

E. A. H. R.

**Kinetics of ester hydrolysis by enzymes. VI. Relative specificity of esterases.** E. BAMANN and E. RENDLEN (Z. physiol. Chem., 1936, 238, 133—144; cf. A., 1934, 218).—The varying affinity of pig's liver esterase for  $Me_1$  and  $Me_2$  esters and  $Me$  ester amides of dicarboxylic acids (malonic to adipic) and the effects of altering  $[H^+]$  and substrate concn. con-

firm the view that the enzyme-binding power of the ester group of the substrate is controlled by the electrochemical nature of the adjacent groups. The predominating effect of the acid group in preventing production of the enzyme additive compound can be counteracted or restricted by increasing the distance between ester and  $CO_2H$  group, by esterifying  $CO_2H$  or converting it into  $CO-NH_2$ , and by reducing the degree of dissociation of  $CO_2H$ .

W. McC.

**Determination of activity of lipase and esterase.** H. PÉNAU and J. GUILBERT (J. Pharm. Chim., 1936, [viii], 23, 57—77).—The activity of the lipase (I) and esterase (II) of blood-serum is determined by measuring the extent of hydrolysis (at  $40^\circ$  with shaking) in 2 hr. of tributyrin [for (I)] and  $Pr^aCO_2Et$  [for (II)]. After the digestion  $NaPO_3$  and 0.1N- $H_2SO_4$  are added ( $p_H$  3.5), the mixture is centrifuged, and the liquor and washings are extracted 3 times with  $Et_2O$ . After addition of  $EtOH$  and  $H_2O$  the extract is titrated with 0.1N-NaOH (bromothymol-blue). In the dog there is little variation in the activities. Differences in the activities amongst animal species may be due to the presence of activators and inhibitors.

W. McC.

**Enzymic hydrolysis of tributyrin by pancreatic lipase.** A. I. VIRTANEN and E. LINDEBERG (Suomen Kem., 1936, 9, B, 2).—The hydrolysis proceeds in three stages: tributyrin  $\rightarrow$   $\alpha$ -dibutyryl  $\rightarrow$  monobutyryl  $\rightarrow$  glycerol. Each stage has a different reaction velocity.

J. N. A.

**Cathepsin and arginase in a melanoma of the horse.** A. PURR (Z. Krebsforsch., 1935, 41, 483—487; Chem. Zentr., 1935, i, 2998).—Melanomas of horse differ in their cathepsin (I) and arginase (II) contents from other malignant tumours; compared with rat sarcoma, the (I) content is much higher and the (II) content very low.

G. H. F.

**Determination of amino-acids in crystalline pepsin.** H. O. CALVERY, R. M. HERRIOTT and J. H. NORTHROP (J. Biol. Chem., 1936, 113, 11—14).—Cryst. pepsin has been analysed for total N,  $NH_2-N$  (before and after acid hydrolysis), humin-N, amide-N, tyrosine, tryptophan, cystine, arginine, histidine, lysine, aspartic and glutamic acid. The low basic N val. and the very high  $NH_2-N$  val. after acid hydrolysis are noteworthy. Coagulation by heat at  $p_H$  4 appears to cause partial destruction of the pepsin mol. and marked differences are shown by analyses of the coagulated and non-coagulable material.

H. W.

**Determination of peptic activity.** H. ESCHENBRENNER (Pharm. Ztg., 1936, 81, 229—231).—A direct measure of peptic activity cannot be obtained by a titration method or by the change in  $\eta$  on digestion. Preliminary observations are reported dealing with the possibility of using the ratio of  $\eta$  to titration vals. as a measure of the activity.

E. A. H. R.

**Fission of arginine during proteolytic hydrolysis.** S. KAMIYA (J. Biochem. Japan, 1935, 22, 263—277).—Liberation of arginine (I) during proteolytic hydrolysis of edestin, caseinogen, and gelatin was followed by treating aliquots of the hydrolysate at intervals with protease-free arginase preps. (from



pig's liver) and then determining (I) by the urease method; increase in  $\cdot\text{CO}_2\text{H}$  was followed by titration with 0.1N-KOH. Pepsin (II) (7—8 days) does not liberate (I) whilst  $\cdot\text{CO}_2\text{H}$  is increased by 8.5—27% of the total  $\cdot\text{CO}_2\text{H}$  liberation by (II)—trypsin (III)—erepsin (IV). Subsequent digestion by (III) (7—12 days) liberates 26.9—43.5% of the total (I) and increases  $\cdot\text{CO}_2\text{H}$  by 43.3—76.6%. Final digestion by (IV) (22 days) liberates 63.4—80.4% of (I). Liberation of (I) by (II)–(IV) hydrolysis is > that by (II)–(III)–(IV) hydrolysis.

F. O. H.

**Action of trypsin on substituted protein.** A. KIESEL and O. ROGANOVA (Z. physiol. Chem., 1936, 238, 149—159).—Substitution products of edestin (I) are less readily attacked by trypsin than is (I) itself, the effect being moderate or slight in the case of ethylated, sulphonated, and deaminated (I) and very great with benzoyl- (II), benzoylmethyl-, and benzoyl-deamino-destin (III). When the substituents are removed from (II) and (III) the product is nearly as readily attacked as is (I) itself. Probably the  $\text{NH}_2$  and OH groups (but not  $\text{CO}_2\text{H}$ ) play an important part in the process.

W. McC.

**Digestive enzymes in marine invertebrates.** I. **Proteolytic enzymes in *Polypus vulgaris* (Lamarck).** E. SAWANO (Sci. Rep. Tokyo Bunrika Daigaku, 1935, 2, B, 101—126).—The acidity of the digestive tract of *P. vulgaris* increases from the pharynx ( $p_{\text{H}}$  6.8) to the intestine ( $p_{\text{H}}$  5.5). The distribution of proteinase, amino- and carboxy-polypeptidase, and dipeptidase in the digestive tract, anterior and posterior salivary glands, liver, and pancreas is recorded. The  $p_{\text{H}}$  optima of these four enzymes appear to be unaffected by the nature of the tissues in which they occur. A cathepsin-like proteinase occurs in extracts of liver and pancreas.

E. A. H. R.

**Urinary phosphatase. II. Excretion by man.** H. WOLBERGS (Z. physiol. Chem., 1936, 238, 23—30; cf. Kutscher, A., 1935, 1279).—Details are given of work already reported (A., 1935, 1268). A difference (due to prostatic secretion) exists between the urines of the two sexes. Injection of insulin has the reverse action to, and inhibits, that of glucose administration.

F. O. H.

**Urinary phosphatase. III.** W. KUTSCHER and A. WÖRNER (Z. physiol. Chem., 1936, 238, 275—279; cf. Wolbergs, this vol., 111).—When urine is dialysed through parchment the activity of the phosphatase is increased. Subsequent electro dialysis, repeated with the solution obtained by dissolving in  $\text{H}_2\text{O}$  the active material which separates after 12—24 hr. on the first occasion, results in a high degree of purification accompanied by only slight loss of activity.

W. McC.

**Specificity of phosphatases.** W. SCHUCHARDT (Biochem. Z., 1936, 283, 433—434).—A sample of yeast when tested with dil. AcOH did not attack  $\alpha$ - and  $\beta$ -glycerophosphate between  $p_{\text{H}}$  6 and 9 and when treated with dil. aq.  $\text{NH}_3$  was inactive between  $p_{\text{H}}$  3.3 and 5.

P. W. C.

**Phosphatase action of emulsin.** H. BREDERECK and H. BEUCHELT (Naturwiss., 1936, 24, 107—108).—Active emulsin preps. from almonds bring about a

rapid cleavage of  $\text{H}_2\text{PO}_4$  from mononucleotides and yeast-nucleic acid. The glycosidic linking in purine nucleotides is not attacked.  $\text{H}_3\text{PO}_4$  is also liberated, although less rapidly, from glycerophosphoric acid.

E. A. H. R.

**Rôle of water in the activation of renal phosphatase.** L. THIVOLLE (Compt. rend. Soc. Biol., 1936, 121, 474—476).—The rate of fermentation by renal phosphatase (I) is increased by dilution, there being an optimum dilution depending on the amount of (I) present.

R. N. C.

**Chemical difference between protein-linked and free nucleic acid.** G. SCHMIDT (Science, 1936, 83, 15).—The observed difference in the rates of dephosphorylation of thymonucleic acid and thymonucleohistone by phosphatase is due to the linking of the nucleic acid component with the protein.

L. S. T.

**Anaërobic decomposition of hexosephosphoric acids by animal tissues. III. Hydrolysis by phosphatase.** T. TAKAHASHI (J. Biochem. Japan, 1935, 22, 303—321).—Production of hexose monophosphate and free sugar from hexose diphosphate by autolysed tissue is not invariably accompanied by formation of  $\text{AcCHO}$ .

F. O. H.

**Phosphodiesterase and hydrolysis of lecithin.** H. UDAGAWA (J. Biochem. Japan, 1935, 22, 323—340).—Diphosphatase preps. (from taka-phosphatase) free from monophosphatase hydrolyse lecithin (optimum  $p_{\text{H}}$  4—5) to the corresponding glyceride and cholinephosphoric acid, the latter being further hydrolysed only by monophosphatase.

F. O. H.

**Animal lipins. X. Cerebrosidase. Its relation to the splitting of polydiaminophosphatide by polydiaminophosphatase.** S. J. THANNHAUSER and M. REICHEL (J. Biol. Chem., 1936, 113, 311—317).—Cerebrosidase is inactive, its activators, which depress polydiaminophosphatase activity, being  $\text{H}_2\text{S}$ , cysteine, reduced glutathione, and *l*-ascorbic acid.

H. G. R.

**Hexokinase.** O. MEYERHOF (Naturwiss., 1935, 23, 850—851).—If glucose and adenylyl pyrophosphate are incubated with hexokinase (I), adenylic acid and hexose monophosphate are formed. If this mixture is boiled and added to fresh muscle extract lactic acid is rapidly formed. (I) probably acts by causing phosphorylation of sugars.

E. A. H. R.

**Fermentative enzymes. V. Phosphorylation systems of alcoholic fermentation.** A. SCHÄFFNER and H. BERL (Z. physiol. Chem., 1936, 238, 111—123; cf. A., 1935, 1026; this vol., 246).—Phosphorylation of hexose by macerated yeast is induced equally by hexose diphosphate (I) and adenosine triphosphate (II). Purification of the enzyme system results in induction by (I) [or by dihydroxyacetonephosphoric acid (III)] but not by (II); hence "phosphatase" is not identical with the "heterophosphatase" of Euler and Adler (A., 1935, 1276) and thus at least two phosphorylating systems exist in yeast extracts. A third system, whereby the monoester is converted into the diester, is probably also present, the mechanism being one of oxidation to a phosphohexonic acid and subsequent fission to



$\text{AcCO}_2\text{H}$  (decarboxylated to  $\text{MeCHO}$ ) and triose-phosphoric acid [2 mols. of which give 1 mol. of (I)]. Pyrophosphatase and Warburg's intermediary enzyme are also concerned in phosphorylation processes. A consideration of the rôle of (III) and of phosphoglyceric acid (IV) and of inhibition by  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  indicates that the reaction  $\text{glucose} + \text{phosphate} \rightarrow \text{hexose ester}$  is coupled with the oxidation-reduction process  $(\text{III}) + \text{MeCHO} \rightarrow (\text{IV}) + \text{EtOH}$ . Intra- and extra-cellular phosphorylation processes are compared.

F. O. H.

**Transformation of the pyrophosphate fraction in yeast cells.** M. M. LEVITOV (Biochem. Z., 1936, 284, 86—98).—Fresh yeast in aq. suspension loses very little of its pyrophosphate (I) content in 5 hr., but considerable loss of (I) and of orthophosphate (II) occurs when glucose (III) is added. No appreciable change in the (I) and (II) contents of fermenting (glucose) yeast occurs if fermentation is inhibited by  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$  and respiration by KCN but when fermentation is inhibited with NaF the (I) and (II) contents decrease. Addition of (III) checks the degradation of (I) which occurs on autolysis. Phosphoglyceric acid acts more powerfully than does (III), thus causing the diminished (I) content to increase. The (I) compound of yeast seems to act as a phosphate carrier in the same way as does adenosinetriphosphoric acid in animal cells.

W. McC.

**Inverse Pasteur reaction.** W. A. BELITZER (Biochem. Z., 1936, 283, 339—342).—Working with yeast, the inverse Pasteur reaction is observed only when the respiration system is saturated with a suitable H donor.

P. W. C.

**Sporulation of yeast.** II. H. STANTIAL (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 175—188).—Formation of ascospores by *S. cerevisiae* is increased by grapefruit juice, the active constituent of which is a carbohydrate [of 12 investigated, 8 (especially mannose and maltose) were active]. Aq. NaOAc or KOAc in presence of sugar is effective. Data for the influence of temp. and  $p_{\text{H}}$  on sporulation are given.

F. O. H.

**Wildier's bios.** W. L. MILLER (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 163—165).—Amino-hydroxybutyric acid (I) (from crotonic, isocrotonic, and phenoxyethylmalonic acid), aspartic (II) + amino-isobutyric acids, (II) +  $\alpha$ -aminobutyric acid or  $d$ -glutamic acid + alanine cannot replace the (I) isolated from tomato juice as a source of bios IIA in the growth of yeasts. Of 32  $\text{NH}_2$ -acids only  $l$ -leucine (III) had a significant effect; (III), however, also enhances the action of bios IIA. Wildier's bios appears to contain four constituents, viz., a (I), inositol, (III), and bios IIB (which is purified by the use of  $\text{COMe}_2$  and Cu and Hg acetates). Bios V is necessary for the growth of *S. hanseniospora valbyensis*.

F. O. H.

**Influence of inositol and bios IIA and IIB on the reproduction of twelve yeasts. New constituent of bios.** L. N. FARRELL (Trans. Roy. Soc. Canada, 1935, [iii], 29, III, 167—173).—*S.* and *Zyg. mandshuricus* are indifferent to inositol whilst *Zyg. mellis* is only slightly influenced. *S. hanseniospora valbyensis* and *S. galactosus* require an additional

factor (I). The remainder resemble Wildier's yeast. (I) (bios V; cf. preceding abstract) occurs in tomato and lemon juice and is not identical with ascorbic acid.

F. O. H.

**Balance of alcoholic fermentation by yeasts.** R. GUILLEMET (Compt. rend. Soc. Biol., 1936, 121, 465—467).—Anaërobic fermentation of sucrose, glucose, and fructose in aq. solution by yeasts reaches equilibrium in a few hr., with production of equimol. quantities of EtOH and  $\text{CO}_2$ . Maltose exhibits anomalies; some disappears without production of EtOH and  $\text{CO}_2$ , being probably broken down to intermediate products. Production of  $\text{CO}_2$  is independent of that of EtOH.

R. N. C.

**Rate of fermentation of sugars by different kinds of yeast.** R. GUILLEMET (Compt. rend. Soc. Biol., 1936, 121, 467—469).—The rates of fermentation of sucrose (I) and maltose (II) by "grain" yeasts are the same; yeasts grown on molasses ferment (I) more rapidly than do "grain" yeasts, but attack (II) irregularly and less rapidly than (I). The rate of fermentation of (I) does not vary with the age of the yeast, but that of (II) falls. Bakers' yeasts ferment (I) more rapidly than do brewers' yeasts.

R. N. C.

**Kinetics of alcoholic fermentation of sugars by brewer's yeast.** IV. Specificity. Rates of fermentation of  $\alpha$ - and  $\beta$ -glucose. R. H. HOPKINS and R. H. ROBERTS (Biochem. J., 1936, 30, 76—83).—The initial rates of fermentation attained by  $\alpha$ - (I),  $\beta$ - (II), and  $\alpha\beta$ -glucose (III) are the same except with initial consns. of < 1%, (I) with consns. of 0.5 and 0.25% attaining a max. rate > (II).  $K_m$  vals. for (I) and (II) are respectively 0.0099 and 0.0118. It is suggested that neither (I) nor (II) but an intermediate, probably open-chain, form of glucose is specifically fermented, (I) being converted more rapidly than (II) into this form. Mutarotation of partly fermented (III) may be explained on this hypothesis.

P. W. C.

**Alcoholic fermentation in heavy water.** O. REITZ (Z. physikal. Chem., 1936, 175, 257—274).—By the fermentation of sucrose (I) in pure  $\text{D}_2\text{O}$   $\text{CH}_2\text{D}\cdot\text{CD}_2\cdot\text{OD}$  is formed. With decrease in the D content of the solvent,  $\alpha$ , the proportion of it which is incorporated into the Me group of the alcohol formed, falls. Fermentation of (I) and  $d$ -glucose in pure  $\text{D}_2\text{O}$  is only half as rapid as in ordinary  $\text{H}_2\text{O}$  (cf. A., 1934, 327). The rate of decrease in the rate of fermentation with increase in  $\alpha$  increases with  $\alpha$ .

R. C.

**Metabolic systems involved in dissimilation of carbohydrate reserves in baker's yeast.** T. J. B. STIER and J. N. STANNARD (J. Gen. Physiol., 1936, 19, 479—494).—The endogenous respiration (dissimilation of carbohydrate reserves) of intact yeast cells is a purely respiratory process, fermentation not being involved. Anaërobic  $\text{CO}_2$  production and EtOH production are absent;  $R:Q=1$ , and is unaffected by cons.  $10^{-5}$  to  $10^{-1}M$  of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  or KCN. If the structure of the cells is destroyed, fermentation reactions occur.

F. A. A.

**Kinetic analysis of the endogenous metabolism of bakers' yeast.** T. J. B. STIER and



J. N. STANNARD (J. Gen. Physiol., 1936, 19, 461—477).—The endogenous metabolism of *Saccharomyces cerevisiae* placed in a non-nutrient medium shows two phases; (a) a const. rate of  $O_2$  consumption and  $CO_2$  production as long as the stored material is ample, (b) a first-order decline in rate, which  $\propto$  the concn. of some substrate, probably glycogen. R.Q.=1 in both phases; their relative duration depends on the age of the cultures. F. A. A.

**Absorption spectrum of reduced cytochrome from baker's and brewer's yeasts.** E. ELION (Bull. Soc. Chim. biol., 1936, 18, 165—172).—The method of Fink (A., 1932, 1167) for distinguishing between brewer's and baker's yeast is based on the finding that the absorption spectrum of the cytochrome of the former has two, that of the latter four, bands. There are exceptions to this, some brewer's yeasts having a four-banded, some baker's yeasts a two-banded, cytochrome spectrum. A. L.

**Effect of time and intensity of radium radiation on the inverting capacity of yeast.** G. HARKER (Nature, 1936, 137, 190—191).—Exposure of yeast to Ra emanations permanently reduces its sugar-inverting power. The effect reaches a saturation val. depending on the intensity of the radiation, and is due to some action on the living cells rather than on the enzyme itself. L. S. T.

**Polyose of yeast membrane. II.** L. ZECHMEISTER and G. TÓTH (Biochem. Z., 1936, 284, 133—138; cf. A., 1934, 810; Sevag *et al.*, A., 1935, 1280).—The polyose (I) occurs pre-formed in yeast and is obtained when it is degraded by enzymes. (I) is not attacked by  $H_2O$  at  $100^\circ$  but is hydrolysed by dil. acid and alkali. (I) in untreated yeast resists hydrolysis, being protected by impurities. W. McC.

**Isolation of adenosinetriphosphoric acid from yeast.** T. WAGNER-JAUREGG (Z. physiol. Chem., 1936, 238, 129—130).—100 g. of fresh yeast yield 60 mg. of adenosinetriphosphoric acid,  $[\alpha]_D -30.9^\circ$  (as Na salt in  $H_2O$ ), and some inosinepyrophosphoric acid (?). R. S. C.

**Mitogenetic radiations and Liesegang rings.**—See this vol., 426.

**Action of various growth-substances on the growth of certain fungi.** L. RONS DORF (Arch. Mikrobiol., 1935, 6, 309—325).—An apparent selectivity is shown in the response of various fungi to auxin, bios, and to Nielsen's growth-substance-A and -B. Auxin disappears from nutrient solutions whether added before or after sterilisation. Interrelationships between the various growth factors and vitamin-B are discussed. A. G. P.

**Auxogenic action of normal and pathological tissues on the growth of *Phycomyces*.** W. H. SCHOPFER (Compt. rend., 1936, 202, 236—238).—Rabbit liver contained a thermostable,  $H_2O$ - and EtOH-sol. growth-promoting substance, probably vitamin- $B_1$ , which was also present to a smaller extent in a tumour and the EtOH extract. H. G. R.

**Synthesis of vitamin- $B_1$  by *Phycomyces*.** W. H. SCHOPFER and A. JUNG (Arch. Mikrobiol.,

1935, 6, 345—349).—*Phycomyces* grown on a synthetic medium supplemented with vitamin- $B_1$  does not absorb an appreciable amount of the vitamin. Rat tests afford no evidence of the synthesis of - $B_1$  by the mould. *Phycomyces* produces a yeast-stimulating substance and an auxogenic factor. The action of - $B_1$  in stimulating the growth of *Phycomyces* is not a direct one. Its presence is necessary to enable the organism to produce its sp. growth factors. A. G. P.

**Growth factors and vitamins in plants. Effect of extracts of *Aspergillus* on the development of *Phycomyces*.** W. H. SCHOPFER and A. JUNG (Arch. Mikrobiol., 1935, 6, 334—344).—Extracts of several species of *Aspergillus* activate culture media of *Phycomyces*. The active agent is probably vitamin- $B_1$ , which is synthesised in very small quantities by the organism. A. G. P.

**Rôle of bios in the biology of fungi of the genus *Fusarium*.** A. R. WERNER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 61—64).—The presence of bios in the growth medium is essential for sporulation. Low viability and the physiological need of activators induce the fungus to invade living tissues. A. G. P.

**Availability of the nitrogen compounds eliminated by *Aspergillus niger*.** A. RIPPEL and G. BEHR (Arch. Mikrobiol., 1935, 6, 359—361).—N compounds appearing in the substrate of cultures of *A. niger* have little nutrient val. for the fungus. The substances are possibly related to the colouring matter and humin formed during autolysis. A. G. P.

**Absorption of oxalic acid by *Aspergillus repens*.** D. BACH and J. FOURNIER (Compt. rend., 1935, 201, 1416—1417).—In media containing or free from glucose, max. consumption of  $H_2C_2O_4$  occurs at  $p_H$  approx. 3.5 and is nil at  $p_H$  7, indicating utilisation of  $HC_2O_4'$  and not of  $C_2O_4''$ . F. O. H.

**Chemical sterilisation of humus for fungus cultures.** D. LHNELL (Arch. Mikrobiol., 1935, 6, 326—333).—Use of volatile antiseptics (Schweitzer 1932) gives only partial sterilisation. EtOH is the most effective of the substances examined, killing all fungus spores and reducing bacterial nos. to approx. 2%. A. G. P.

**Fungus fluorescence *in vitro*.** A. S. VON MALLINCKRODT-HAUPT and C. CARRIE (Arch. Dermatol. Syphilis, 1934, 169, 519—526).—Cultures of pathogenic skin fungi in sucrose-urea-mineral salt media showed fluorescence *in vitro* after 14 days. Colour changes followed variations in the  $p_H$  of the medium. Fluorescence nearly disappeared at neutrality. CH. ABS. (p)

**Action of micro-organisms on the diastereomeric forms of hexane- $\gamma$ -diol.**—See this vol., 452.

**Formation of organo-metalloidal compounds by micro-organisms. IV.**—See this vol., 460.

**Penicillic acid.**—See this vol., 456.

**Correlation of qualitative microchemical tests on the protozoan nucleus and the mode of nutrition.** M. S. LUCAS and C. A. EVANS (J. Roy. Microscop. Soc., 1935, [iii], 55, 261—264).—Certain



saprozoic protozoa contained no detectable thymonucleic acid or inorg. salts in their nuclei. H. D.

Why have some investigators been unable to grow *Chilomonas paramecium* in inorganic or simple organic solutions? S. O. MAST and D. M. PACE (Science, 1936, 83, 18—19).—Conflicting evidence is discussed (A., 1935, 1027). L. S. T.

Fixation of quinine by *Paramecia* as determined by its fluorescence. G. VALETTE (Compt. rend., 1935, 201, 681—683).—The cytological effect of the drug on *P. caudatum* is similar to that of neutral-red. J. L. D.

Glucose metabolism of trypanosomes (*T. equiperdum* and *T. Lewisi*). L. REINER, C. V. SMYTHE, and J. T. PEDLOW (J. Biol. Chem., 1936, 113, 75—88; cf. A., 1935, 125).—*T. equiperdum* decomposes 1 mol. of glucose anaerobically, forming 1 mol. each of glycerol and  $\text{AcCO}_2\text{H}$  (I). Under aerobic conditions 2 mols. of (I) are formed, together with small amounts of lactic acid and  $\text{CO}_2$ . Presence of serum or plasma does not alter the course of reaction, but increases the rate of the anaerobic process. *T. Lewisi* under anaerobic conditions forms succinic acid,  $\text{AcOH}$ , and  $\text{EtOH}$ , and in addition  $\text{HCO}_2\text{H}$  and  $\text{CO}_2$  under aerobic conditions. There is no evidence that phosphorylation is involved in the metabolism of either species. J. N. A.

Trypanocidal action of azo-dyes. A. ST. G. HUGGETT and S. F. SUFFOLK (J. Pharm. Exp. Ther., 1936, 56, 188—193).—Of the azo-dyes chlorazol-fast-pink B.K.S (I), chlorazol-sky-blue FFS and S.D. 2, all of which have an anticoagulant action, the most highly trypanocidal, as tested by its action on *T. equiperdum* infection in mice, is (I), which is only slightly less active than germanin. Its high toxicity, however, reduces its chemotherapeutic index to 3—7. W. O. K.

Physiology of pigments of purple bacteria. III. Carotenoids. E. SCHNEIDER (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, No. 2, 74—80; cf. A., 1934, 1265).—Two fractions were obtained. One is adsorbed by  $\text{Al}_2\text{O}_3$ ,  $\text{Ca(OH)}_2$ , or  $\text{CaCO}_3$ , and is probably a lipochrome containing O. The second fraction is adsorbed on  $\text{Al}_2\text{O}_3$  or  $\text{Ca(OH)}_2$ , and is probably related to, but is more autoxidisable than, lycopene. Both fractions are mixtures of very similar compounds, probably isomerides. E. P.

Carotenoids of purple bacteria.—See this vol., 340.

Formation of putrescine from *D*-arginine by bacterial action. K. HIRAI (Biochem. Z., 1936, 283, 390—392).—A strain of *B. coli* was used and the base isolated as aurichloride and platinichloride in good yield (7.5 g. of putrescine hydrochloride from 10 g. of arginine hydrochloride). P. W. C.

Lime-precipitating bacillus and an iron- and silica-accumulating coccus as stone formers. A. BRUSSOFF (Arch. Mikrobiol., 1935, 6, 471—474).—The rust-coloured layer found on the sides of conduits for hot spring  $\text{H}_2\text{O}$  in Aachen is formed by two types of bacteria. One ppts.  $\text{CaCO}_3$  and the other

accumulates Fe and  $\text{SiO}_2$ , which collect in a gelatinous condition between the calcareous concretions. A. G. P.

Bacterial proteases. III. Acidoproteolyte of Gorini. G. GORBACH and R. ULM (Arch. Mikrobiol., 1935, 6, 362—368).—Milk, and the casein-containing ppt. produced in skim-milk cultures of *Mammococcus Gorini*, contain a protease of the papain type exhibiting max. activity in neutral media. Proteolysis of casein increases and that of gelatin and peptone decreases with the age of the culture. A peptidase is also present (optimum  $p_{\text{H}}$  4.8) which tends to become less active with the ageing of the prep. A. G. P.

Reduction of methylene-blue by *B. abort. infectiosi*, Bang, and *B. melitense*. K. H. BAU and K. WANG (Z. Hyg., 1935, 117, 399—402).—The organisms reduce methylene-blue in presence of a no. of alcohols and carbohydrates, and also open-chain  $\text{NH}_2$ -acids; the action of *B. melitense* is the stronger. R. N. C.

Influence of dicyanodiamide, guanidine, and guanylurea on bacteria.—See B., 1936, 245.

Effect of metallic salts on lactic acid fermentation. A. ZLATAROV and D. KALTSHEVA (Biochem. Z., 1936, 284, 12—23).—Lactic acid fermentation of milk and whey by *Streptococcus lactis* is restricted by Mn, Co, Ni,  $\text{Fe}^{++}$ , and  $\text{Fe}^{+++}$  salts in concns. > approx. 0.01M ( $\text{Mn} < \text{Fe} < \text{Ni} < \text{Co}$ ), the extent of restriction depending on the concn. of salt. Lower concns. have a slight stimulatory effect. W. McC.

Biological activators of *Azotobacter*. A. R. WERNER (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 57—60).—Bios from yeast or from extracts of soil-grown green algae stimulates the fixation of N by *Azotobacter*. A. G. P.

Electrical method for killing bacteria in gaseous suspension. M. PAUTHENIER and H. VOLKRINGER (Compt. rend., 1936, 202, 250—252).—*B. prodigiosus* in air or  $\text{N}_2$  is killed by passage through an electric field maintained by an e.m.f. of the order of 3000 volts per cm. H. G. R.

Bactericidal action of ammonium persulphate. H. LEUNIG (Z. Hyg., 1935, 117, 257—262).—The bactericidal action of dil.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solutions is augmented considerably by small quantities of org. acids. R. N. C.

Chemistry of virulence. L. HALLAY (Wien. med. Woch., 1934, 84, 1254—1256; Chem. Zentr., 1935, i, 3800).—The virulence of pathogenic micro-organisms is generally increased by acidification of the inflamed regions, and reduced by restoration of the original  $[\text{H}^+]$  equiv., which can be effected by active hyperemia, sweat-production, antiketogenic diet, and surface inflammation with buffer solutions. R. N. C.

Cultivation of *B. diphtheriae* on telluric media. J. ZOPOTH (Compt. rend. Soc. Biol., 1936, 121, 785—788). R. N. C.

(A) Fibrinolysis by streptococci of human and animal origin. (B) Carbohydrate-fibrinolytic linking in *Streptococcus hemolyticus*. (C) Fibrinolytic streptococci from lower animals.



(D) Susceptibility of "hybrid" fibrins to *Streptococcus* fibrinolysins. R. R. MADISON (Proc. Soc. Exp. Biol. Med., 1934, 31, 1018—1019; 32, 49—50, 444—445, 641—644).—(A) Human plasma clots were liquefied by 94% of cultures of *S. haemolyticus* of internal human origin, by 17% of those from superficial human tissue, and by 7% of those of veterinary origin. Numerous strains of *S. viridans* were non-fibrinolytic.

(B) The Tillet-Garner sp. fibrinolytic titre of strains of *S. haemolyticus* was closely correlated with the Lamefield human-diagnostic "carbohydrate" titre.

(C) Strains of *S. haemolyticus* from horse and hog were sp. lytic for the fibrins of these animals.

(D) Heterogeneous fibrinogen (I)—thrombin (II) complexes vary in susceptibility according to the origin of the (I). Both (I) and (II) from man are carriers of susceptibility to antihuman streptococcus fibrinolytin. Similarly sp. phenomena occur in the horse and hog.

CH. ABS. (*p*)

Production of staphylococcal toxin and anatoxin. G. RAMON (Compt. rend. Soc. Biol., 1936, 121, 375—379).

R. N. C.

Determination of staphylococcal toxin. G. RAMON and R. RICHOU (Compt. rend. Soc. Biol., 1936, 121, 379—382).

R. N. C.

$p_H$  curve of certain smooth strains of tubercle bacilli. R. K. GOYAL (Compt. rend. Soc. Biol., 1936, 121, 390—392).—The curves for seven strains over a period of 10 weeks are described; they are affected by phenolsulphonaphthalein to different extents.

R. N. C.

Chemistry of the tubercle bacillus: lipid compounds. M. FRANCIOSI (R. Ist. lombardo Sci. Lettere, Rend., 1934, 67, No. 2, 737—740; Chem. Zentr., 1935, i, 3943).—Fractional extraction of the living bacilli in the cold yields fat, phosphatides, wax, and C-H-O compounds of high mol. wt. and m.p.

R. N. C.

Nuclear staining of myxobacteria and other species. P. F. MILOVIDOV (Arch. Mikrobiol., 1935, 6, 475—509).—A no. of species show nuclear staining after but not before hydrolysis with HCl. Application of the technique for ascertaining the distribution of nuclear material at various stages of development is described. Thymonucleic acid occurred generally in the organisms.

A. G. P.

Staining and microscopical demonstration of filterable viruses. A. C. COLES (J. Roy. Microscop. Soc., 1935, [iii], 55, 249—255).

H. D.

Isolation of crystalline tobacco mosaic virus protein from diseased tomato plants. W. M. STANLEY and H. S. LORING (Science, 1936, 83, 85).—An active cryst. protein has been obtained from tomato plants infected with tobacco mosaic virus (cf. A., 1935, 1181); it has the same cryst. form and properties as that isolated from tobacco plants.

L. S. T.

Irradiation of plant viruses and micro-organisms with monochromatic light. III. Resistance of the virus of typical tobacco mosaic and *E. coli* to radiations of 3000—3250 Å. A. HOLLAENDER and B. M. DUGGAR (Prac. Nat. Acad. Sci.,

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1936, 22, 19—24).—The amount of energy necessary to destroy 50% of the virus at 2250 Å. is 20% of that required at 2650 Å. To inactivate *E. coli* the energy requirement at 2250 Å. is > that at 2650 Å.

A. G. P.

Effect of food and of exhaustion on the pituitary, thyroid, adrenals, and thymus glands of the rat. D. H. ANDERSON (J. Physiol., 1935, 85, 162—167).

R. N. C.

Epiphysis problem. W. A. DEN H. JAGER and J. F. HEIL (Acta Brev. neerl. Physiol., 1935, 5, 32—34; Chem. Zentr., 1935, ii, 242).—Removal of the epiphysis or injection of epiphyseal extracts had no marked effects.

G. H. F.

Enteral absorption of insulin. F. LASCH and E. SCHÖNBRUNNER (Arch. exp. Path. Pharm., 1936, 180, 469—478).—Insulin (20 units) directly introduced into the small intestine of rats produces a significant hypoglycæmia in approx. 25% of the rats used. The % response is increased by admixture of insulin with glycerol, EtOH, serum, saponin, or Hg<sub>2</sub>Cl<sub>2</sub>. Acid but not basic dyes completely protect insulin from inactivation *in vitro* by peptic hydrolysis.

F. O. H.

Biological effects of pineal extract (Hanson). L. G. ROWNTREE, J. H. CLARK, A. STEINBERG, and A. M. HANSON (Science, 1936, 83, 164—165).

L. S. T.

Electrodialysis of oxytocin. N. DAS, B. N. GHOSH, and B. C. GUHA (Z. physiol. Chem., 1936, 238, 131—132).—When electrodialysed, oxytocin moves to the cathode at  $p_H$  9.6, but not at  $p_H$  10, and is, therefore, a base or adsorbed on a basic carrier.

R. S. C.

Action of adrenaline on the respiratory quotient. E. M. BRIDGE and H. R. NOLTIE (J. Physiol., 1935, 85, 334—342).—Continuous intravenous injection of adrenaline in unanæsthetised rabbits reduces the R.Q. to the protein-fat level; the low vals. of liver- and muscle-glycogen suggest a purely glycogenolytic action.

R. N. C.

Comparative variations of blood-sugar and bile secretion due to slow and continuous intravenous injection of adrenaline. E. CHABROL and J. SALLET (Compt. rend. Soc. Biol., 1936, 121, 538—540).—Increase of blood-sugar in dogs is accompanied by a fall in rate of bile secretion. Injection of atophan prior to that of adrenaline has no effect.

R. N. C.

Survival and increase of adrenaline in tissue cultures of adrenal glands from chick embryos. M. R. LEWIS and E. M. J. GELING (Amer. J. Physiol., 1935, 113, 529—533).

R. N. C.

Differential depression of vaso-motor mechanisms by adrenaline. L. C. WYMAN and C. TUM SUDEN (Amer. J. Physiol., 1935, 113, 271—278).

R. N. C.

Effect of adrenaline on the blood-sugar, -lactic acid, and -inorganic phosphorus of completely hypophysectomised dogs. I. L. CHAIKOFF, F. L. REICHERT, L. S. READ, and M. E. MATHES (Amer. J. Physiol., 1935, 113, 306—311).—The increases produced by adrenaline in completely hypophysectomised dogs are < those in normal and control animals.

R. N. C.



Comparison of the effects of sympathin and adrenaline on the iris. W. B. CANNON and A. ROSENBLUETH (Amer. J. Physiol., 1935, 113, 251—258). R. N. C.

Reflex liberation of circulating sympathin. A. C. LIU and A. ROSENBLUETH (Amer. J. Physiol., 1935, 113, 555—559). R. N. C.

Exhaustibility of the sympathin stores. J. A. DYE (Amer. J. Physiol., 1935, 113, 265—270).—The sympathin stores are relatively resistant to exhaustion. R. N. C.

Cortin. I.—See this vol., 473.

Sexual hormones. VII, VIII, XI, XII.—See this vol., 467, 472.

Effect of cortin on sensitivity to narcotics. I. SINDRAM (Acta Brev. neerl. Physiol., 1935, 5, 29—30; Chem. Zentr., 1935, ii, 240).—Adrenalectomised animals are very sensitive to narcotics; administration of cortical hormone restores normal sensitivity. G. H. F.

Action of cortical extracts of the adrenals (eucorton) on muscle-phosphagen in normal and adrenalectomised frogs. S. C. A. MOSCHINI (R. Ist. lombardo Sci. Lettere, Rend., 1934, 67, 695—707; Chem. Zentr., 1935, i, 3561).—Eucorton neither prevents the fall of muscle-phosphagen nor maintains life in adrenalectomised animals. R. N. C.

Relation of the adrenal cortical hormone to nitrogen metabolism in experimental hyperthyroidism. G. A. KOELSCH and E. C. KENDALL (Amer. J. Physiol., 1935, 113, 335—349).—The quantity of cortical hormone (I) administered is apparently the only factor that can modify the effect of thyroxine (II) on N metabolism in the dog. A negative N balance does not necessarily occur as a result of complete cortical excision, but may occur in an adrenalectomised dog given a low maintenance dose of (I); it is produced in such cases by (II). The action of (I) against the effect of (II) on N metabolism is a sparing action, and a negative N balance can be made positive by administration of sufficient (I). R. N. C.

Identity of the pigmenting and corticotropic hormones. A. JORES (Klin. Woch., 1935, 14, 132—133).—The pigmenting hormone of the posterior pituitary is not identical with the corticotropic hormone of the anterior pituitary, only the former being adsorbed by animal C. R. N. C.

Action of the melanophoric hormone on the darkness-adaptation of the human eye. W. BUSCHKE (Klin. Woch., 1934, 13, 1785—1786; Chem. Zentr., 1935, i, 3946).—The injected hormone has no action. A. G. P.

Melanophore hormone of the hypophysis cerebri. E. M. K. GEILING and M. R. LEWIS (Amer. J. Physiol., 1935, 113, 534—537).—The hormone is elaborated by the pars intermedia. R. N. C.

Conditions necessary for the continuous growth of hypophysectomised animals. H. M. EVANS, R. I. PENCHARZ, and M. E. SIMPSON (Endocrinol., 1935, 19, 509—514).—Growth of rats is maintained by aq. alkaline extract of pituitary, but not by extract purified with flavianic acid. R. N. C.

Effect of pitocin, pitressin, and antuitrin on fat tolerance tests. H. BLOTNER (Endocrinol., 1935, 19, 587—591).—Pitocin and pitressin (more active), but not antuitrin or antuitrin-S, prevent increases or cause decreases in plasma-cholesterol in patients following ingestion of a fat meal. R. N. C.

Anterior pituitary. IV. Effect of male hormone preparations on the anterior pituitaries of gonadectomised male and female rats. W. O. NELSON and T. F. GALLAGHER (Anat. Rec., 1935, 64, 129—145). R. N. C.

Effect of injection of pituitary extracts on blood-sugar and the residual chromic index of plasma. M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 121, 677—679).—Anterior pituitary extract does not appreciably affect the residual chromic index in normal or abnormal conditions. Posterior pituitary extract also has no effect in the normal subject, but raises blood-sugar (I) in diabetes, and both (I) and the residual chromic index in cancer. R. N. C.

Effect of pituitary (posterior lobe) extract on the urinary flow in non-anæsthetised dogs. A. SAMAAAN (J. Physiol., 1935, 85, 37—46). R. N. C.

Action of extracts of posterior lobe of pituitary on the heart of dogs under normal conditions of circulation. W. ANTOPOL and R. RÖSSLER (Z. ges. exp. Med., 1934, 94, 453—470; Chem. Zentr., 1935, i, 2998). G. H. F.

Effect of posterior pituitary preparations on the colloid osmotic pressure of serum-protein, water and mineral metabolism of dogs. K. YANAGI (J. Pharm. Exp. Ther., 1936, 56, 23—38).—Subcutaneous injections of 20—50 international units of pituitrin and pitressin to dogs cause marked hydræmia with a fall in hæmatocrit, and in *d*, *n*, and total protein of the serum, and an increase in plasma vol. During the period of hydræmia serum-K increases. A. L.

Action of parathormone. II. H. K. GOADBY and R. S. STACEY (Biochem. J., 1936, 30, 269—272; cf. A., 1935, 258).—Since in cases of grossly impaired renal function parathormone (I) does not produce the normal increased urinary P excretion, (I) probably acts directly on the kidneys. The effect on blood-Ca is normal. H. D.

Relation of the parathyroid hormone to the state of calcium in the blood. F. C. McLEAN, B. O. BARNES, and A. B. HASTINGS (Amer. J. Physiol., 1935, 113, 141—149).—The average serum-Ca (I) in normal cats is  $1.15 (\pm 0.07) \times 10^{-3} M$ , and ionisation follows the law of mass action. This relationship also holds over the entire range of (I) vals. from those associated with tetany to the max. (I) produced by parathyroid hormone (II). Plasma-Ca is maintained at normal levels by a regulatory mechanism associated with (II); Ca is reduced by parathyroidectomy and increased by (II). Tetany appears only when (I) falls to  $0.65 \times 10^{-3} M$ , and cannot be further correlated with (I). Hyperparathyroidism occurs when (I) is  $> 1.7 \times 10^{-3} M$ , and leads to death at  $1.17 \times 10^{-2} M$ . Na polyanethanolsulphonate used as



an anti-coagulant does not affect Ca ionisation, and plasma so obtained is not toxic to the frog's heart.

R. N. C.

**Effect of extirpation of the parathyroid and thymus of rats on the development of the gnawing teeth: influence of vitamin-D.** T. VON SPRETER (Z. ges. exp. Med., 1935, 96, 95—115; Chem. Zentr., 1935, i, 3002).—Thymectomy caused no deficiency symptoms in rats at puberty. Growth and Ca metabolism remained normal. Thymectomy with parathyroidectomy produced no defects in teeth. No antagonism between thymus and parathyroid in this respect is apparent.

A. G. P.

**Relationship between the parathyroid glands and sex hormones in tetany.** E. P. McCULLAGH and J. E. KEARNS (Endocrinol., 1935, 19, 532—542).

R. N. C.

**Effect of di-iodotyrosine on the thyroid of the rat.** P. DE FREMERY (Acta Brev. neerl. Physiol., 1935, 5, 35—36; Chem. Zentr., 1935, ii, 241—242).—Normal young rats are unsuitable for testing thyrotropic hormone as their thyroids appear to be exceptionally active. Injection of di-iodotyrosine inhibits this activity and renders the glands suitable for testing.

G. H. F.

**Influence of thyroidectomy on the effectiveness of gonad-stimulating hormones.** S. L. LEONARD and I. B. HANSEN (Anat. Rec., 1936, 64, 203—209).

R. N. C.

**Relationships in the sex hormone groups.** L. RUZICKA (Nature, 1936, 137, 260—262).—A summary.

L. S. T.

**Sex glands, particularly in connexion with the corpus luteum hormone.** K. EHRLHARDT (Münch. med. Woch., 1934, 81, 1838—1840).—A review.

R. N. C.

**Effect of sex hormones on the prostate of monkeys.** S. ZUCKERMAN and A. S. PARKES (Lancet, 1936, 230, 242—247).—Androsterone and androstanediol (I) produce rapid development of the prostate and seminal vesicles of immature rhesus monkeys. When administered in the ratio 50:1, (I), but not progesterone, suppresses the prostatic effects of œstrone.

L. S. T.

**Effect of some gonadotropic hormones on the chick.** W. R. BRENNEMAN (Anat. Rec., 1936, 64, 211—220).

R. N. C.

**Crystalline male hormone from urine.** K. DAVID and J. FREUD (Acta Brev. neerl. Physiol., 1935, 5, 31—32; Chem. Zentr., 1935, ii, 239—240).—Male hormone obtained from urine is probably not identical with that from testes. By reducing the cryst. hormone from urine a substance is formed which is thrice as active on capons as the original crystals.

G. H. F.

**Effect of male hormone on the protein and energy metabolism of castrate dogs.** C. D. KOCHAKIAN and J. R. MURLIN (J. Nutrition, 1935, 10, 437—459).—Injection of the hormone results in a temporary decrease followed by an increase in the amount of urea excreted. Other urinary N constituents are unaffected. Fat metabolism is increased,

that of protein decreased, and that of carbohydrate unaffected in thin but decreased in fat dogs.

A. G. P.

**Effect of the ovarian hormones, œstrin and progesterin, on the menstrual cycle of the monkey.** G. W. CORNER (Amer. J. Physiol., 1935, 113, 238—250).

R. N. C.

**Estimation of œstrin and of male hormone in oily solution.** E. BULBRING and J. H. BURN (J. Physiol., 1935, 85, 320—333).

R. N. C.

**Action of the ovarian hormones on the uterine muscle measured *in vivo* and *in vitro*.** J. M. ROBSON (J. Physiol., 1935, 85, 145—158).

R. N. C.

**Effects of œstrin on the urogenital tract of the male monkey.** G. VAN WAGENEN (Anat. Rec., 1935, 63, 387—403).

R. N. C.

**Excretion of theelin in the urine of guinea-pigs with irradiated ovaries.** I. G. SCHMIDT (Anat. Rec., 1936, 64, 255—266).—Theelin excretion is reduced in irradiated ovaries, which show a normal appearance but have very few follicles. It is excreted from irradiated ovaries in which the œstrous opening is prolonged, in amounts < in normal œstrous urine, but too high to be accounted for by the no. of follicles present; it is probably secreted also by the glandular tissue itself.

R. N. C.

**Hormonal control of œstrus, ovulation, and mating in the female rat.** E. WITSCHI and C. A. PFEIFFER (Anat. Rec., 1935, 64, 85—105).

R. N. C.

**Relation of lipins to œstrin and progesterin in the corpus luteum of the sow.** E. M. BOYD and C. A. ELDEN (Endocrinol., 1935, 19, 599—602).—œstrin in the corpus luteum  $\propto$  phospholipins, whilst progesterin is inversely  $\propto$  free cholesterol; other lipin fractions are not related to the hormone concns.

R. N. C.

**Hormones of the corpus luteum.** A. BUTENANDT and V. WESTPHAL (Ber., 1936, 69, [B], 443—447).—All the remaining ketone mixtures including those of m.p. > 100° and < 145—155° obtained from swine ovary (A., 1934, 1268) are dissolved in  $\text{CHCl}_3$ - $\text{C}_5\text{H}_5\text{N}$  and treated gradually at 0° with a cooled solution of  $\text{ClSO}_3\text{H}$  in  $\text{CHCl}_3$ . The alcohols are thereby converted into the H sulphates, which yield sparingly sol. Na salts; these are decomposed by  $\text{AcOH}$  or  $\text{EtOH}$ - $\text{H}_2\text{SO}_4$ . The material unattacked by  $\text{ClSO}_3\text{H}$  crystallises readily. All the crude crystallisates obtained from ovarian extracts through the semicarbazones are thus shown to be mixtures of *allopregnanolone* (Na sulphate, m.p. about 193°) and  $\alpha$ - or  $\beta$ -progesterone in varying proportion. Indications of the presence of other substances are not observed. Progesterone (I) and pregnenolone (II) can be separated similarly. (II),  $[\alpha]_D^{20} + 30^\circ$  in  $\text{EtOH}$  (oxime, m.p. 218—219°) (cf. A., 1934, 1268), is smoothly transformed into (I) by treatment with Br in  $\text{AcOH}$  at 0° and subsequently with  $\text{CrO}_3$ - $\text{AcOH}$  at 20° followed by Zn dust and  $\text{AcOH}$  at 100°. Treatment of various crystallisates with  $\text{ClSO}_3\text{H}$  shows the presence only of (I) and (II); transformation products are not observed.

H. W.



**Substances stimulating the uterus in the blood of pregnant and parturient women.** F. CAROCA and O. KOREF (*Endokrinol.*, 1935, 15, 244—250; *Chem. Zentr.*, 1935, ii, 238).—Whole blood or serum from men, or from women in the intermenstrual period, stimulates the contraction of the virgin guinea-pig uterus equally. Serum from pregnant, menstruating, and parturient women is one third as potent owing to counteraction by corpus luteum hormone, but whole blood from parturients is much more potent than its serum. The active substance is adsorbed on the fibrin during clotting. G. H. F.

**Action of hormones on the closed vagina.** E. DINGEMANSE and S. E. DE JONGH (*Acta Brev. neerl. Physiol.*, 1935, 5, 27; *Chem. Zentr.*, 1935, ii, 238).—Non-cryst. extracts of follicular fluids and of urines are relatively more effective in causing opening of the vagina of infantile rats than are cryst. preps. Probably the former contain another biologically active substance. G. H. F.

**Action of sex hormones on the prostate and its accessories in the mouse.** S. E. DE JONGH (*Acta Brev. neerl. Physiol.*, 1935, 5, 28; *Chem. Zentr.*, 1935, ii, 240).—Injection of folliculin (especially the benzoate) into young mice causes typical hypertrophy of the anterior lobe of the prostate. Injection of an equiv. amount of male hormone protects the mice against this stimulus; corpus luteum hormone gives no protection. G. H. F.

**Vitamin deficiency as a cause of disease and the vitamin requirements of man.** H. J. JUSATZ (*Z. Volksernähr.*, 1935, 10, 97—99; *Chem. Zentr.*, 1935, i, 3000).—A review. Daily requirements are given for -A, -B<sub>1</sub>, and -B<sub>2</sub> in adults, and -C and -D in infants and adults. G. H. F.

**Vitamin-A, -B, and -C content of raw, boiled, and pasteurised milk.** L. DE CARO and I. SPEIER (*Quad. Nutrizione*, 1935, 2, 171—188).—A daily dose of 3 ml. of raw milk (but not of the treated milks) or 6 ml. of either, provided sufficient vitamin-A for rats. For the -B complex, 10 ml. of all three milks sufficed, but 8 ml. of raw milk was not enough. The ascorbic acid content of raw milk was 4.8—14.5, of boiled milk 1.2—9.7, and of pasteurised milk 1.6—9.2 mg. per litre. NUTR. ABS. (m)

**Relation between vitamin-A and -D intake by the hen and the output in eggs.** W. C. RUSSELL and M. W. TAYLOR (*J. Nutrition*, 1935, 10, 613—623).—11—32% of ingested vitamin-A reappeared in eggs. The -A content of the liver varied inversely with egg production. 10% of ingested -D was transferred to eggs. Sunlight is more effective in increasing the -D content of eggs than is the amount of cod-liver oil given. A. G. P.

**Metabolism of vitamin-A.** A. PRZEŹDZIECKA (*Wiad. farm.*, 1935, 62, 201—203; *Chem. Zentr.*, 1935, ii, 244).—A colorimetric method for determining the vitamin in urine is described. G. H. F.

**Minimum vitamin-A requirements with particular reference to cattle.** H. R. GUILBERT and G. H. HART (*J. Nutrition*, 1935, 10, 409—427).—Vitamin-A requirement may be related to body-wt. rather than to energy requirement. Requirements

per unit body-wt. for chicken and turkeys are > those of mammals. A. G. P.

**Influence of breed and ration on carotene and vitamin-A content of milk.** W. M. BEESON (*Proc. Amer. Soc. Animal Prod.*, 1935, Jan., 54—56).—The carotene (I) content was highest in Guernsey and lowest in Holstein and Ayrshire butters, and the vitamin-A (II) content was highest in Holstein and lowest in Guernsey butters, so that the total (II) potency varied little with different breeds of cows. Large amounts of (I) in the diet increased the (I) and (II) contents of the butters. NUTR. ABS. (m)

**Application of the spectrophotometric method for the characterisation of photo-labile substances by their rate of decomposition.** A. CHEVALLIER and P. DUBOULOZ (*Bull. Soc. Chim. biol.*, 1936, 18, 190—194).—The method is applied to  $\beta$ -ionone and vitamin-A. A. L.

**Determination of vitamin-A.** A. PRZEŹDZIECKA (*Biol. Lekarska*, 1935, No. 6).—A modification of the SbCl<sub>3</sub> method is proposed. If the mixture is heated with guaiacol for 2 min. at 60° a rose or red colour is produced which is stable and may be compared with a standard solution of Sudan 3. NUTR. ABS. (m)

**Determination of vitamin-A.** E. M. HUME (*Nature*, 1936, 137, 277).—A defence of the decisions taken by the International Conference on vitamin standardisation (cf. this vol., 390). L. S. T.

**B-Avitaminosis and detoxication in rabbits.** T. KUMON (*J. Biochem. Japan*, 1935, 22, 213—224).—Conjugation of administered BzOH, CH<sub>3</sub>Ph·CO<sub>2</sub>H, and CH<sub>3</sub>Ph·CH<sub>2</sub>·CO<sub>2</sub>H with glycine is not affected by B-avitaminosis; excretion of BzOH following administration of BzOH of hippuric acid (I) is, however, diminished. The *in-vitro* hydrolysis of (I) by liver and kidney tissue is not affected. Other detoxication processes influenced include formation of ethereal sulphates by PhOH and indole and of indican and methylation of C<sub>5</sub>H<sub>5</sub>N, but not conjugation with glycuronic acid. F. O. H.

**Avian B-avitaminosis and enzyme action.** S. TSUNOO, M. TAKAMATSU, T. KAMACHI, and M. IMAIZUMI (*J. Biochem. Japan*, 1935, 22, 225—231).—The enzymic activities of normal pigeon and fowl tissues vary considerably in individual vals. No significant changes appear to be due to B-avitaminosis but the data indicate a diminished activity of kidney-phosphatase and increased activity of pancreatic esterase and hepatic amylase. F. O. H.

**Utilisation of sugars. Vitamin-B and alimentary equilibrium.** L. RANDOIN and F. MILHAUD (*Compt. rend.*, 1935, 201, 1426—1428).—Death of rats on a diet consisting only of glucose, fructose, sucrose, lactose (I), or especially galactose (II) is more rapid than that from actual starvation (H<sub>2</sub>O only). Compared with vitamin-B-free diets containing these sugars, life is prolonged to > 150 days by addition of -B except with (I) and (II). F. O. H.

**Effect of lack and excess of vitamin-B on the calcium and magnesium content of the tissues of pigeons.** S. MURZA-MURZICZ and H. BOHDANO-



WICZÓWNA (Biochem. Z., 1936, 284, 139—145).—The Ca contents of muscle, heart, and brain, but not liver, are decreased by overdoses of vitamin-B, whilst Mg remains unaffected or is slightly increased. Lack of -B causes increase in Ca and Mg. W. McC.

**Differentiation of the antidermatitis factor.** A. G. HOGAN and L. R. RICHARDSON (Science, 1936, 83, 17—18).—When vitamin-B carriers are exposed to ultra-violet irradiation, at least one member of the -B complex is destroyed, and the preps. cause a severe dermatitis and ultimate death of rats. This destructive action cannot be demonstrated when the diet contains significant amounts of maize starch. EtOH extracts of the starch heal the lesions, indicating that the preventive agent is not identical with -B<sub>2</sub>. L. S. T.

**Vitamins and tissue-diastase in relation to organ function.** F. MAIGNON (Ann. Physiol. Physiochim. biol., 1934, 10, 903—904; Chem. Zentr., 1935, i, 3000).—Diastase from various organs caused no improvement in pigeons suffering from B-avitaminosis or in scorbutic guinea-pigs. G. H. P.

**Vitamin-B complex in the root of the manioc.** F. A. DE MOURA CAMPOS (Ann. Fac. Med. Univ. São Paulo, 1935, 11, 27—31).—Manioc (cassava) meal is a fairly good source of the -B complex. NUTR. ABS. (m)

**Accumulation of the antineuritic vitamin-B in the animal organism.** N. L. JARUSOVA (Problems of Nutrition, Moscow, 1935, 4, No. 4, 98—106).—Tests on pigeons indicate a storage of -B<sub>1</sub>. NUTR. ABS. (m)

**Nitrogen metabolism of birds with vitamin-deficiency polyneuritis.** B. A. LAVROV and N. L. JARUSOVA (Problems of Nutrition, Moscow, 1935, 4, No. 4, 88—98).—Pigeons receiving a vitamin-B<sub>1</sub>-free diet lost more N than those receiving the same amounts of diet which contained the -B<sub>1</sub>. When birds were completely starved addition of 1 g. daily of a -B<sub>1</sub> concentrate did not result in increased N retention. NUTR. ABS. (m)

**Is the occurrence of methylglyoxal in the urine specific for avitaminosis-B?** J. LEHMANN (Skand. Arch. Physiol., 1935, 71, 157—165).—AcCHO is present in the urine of rats deficient in vitamin-B<sub>1</sub> or -B<sub>2</sub>, and also in control animals in small quantities; it is destroyed if the urine is kept for 12 hr. AcCHO in the urine is therefore not sp. for avitaminosis-B<sub>1</sub>. R. N. C.

**Antineuritic vitamin(-B<sub>1</sub>) contents of some oil-rich seeds.** V. ZAGAMI (Quad. Nutrizione, 1934, 1, 284—294; Chem. Zentr., 1935, i, 3949).—Vitamin-B<sub>1</sub> occurs in varying quantities in walnuts, hazelnuts, peanuts, pistachios, and sesame, pine, and sunflower seeds; almonds and olive oil contain none, or only traces. R. N. C.

**Antineuritic vitamin.**—See this vol., 487.

**Growth studies. III. Avitaminosis-B<sub>1</sub> and -B<sub>2</sub> in caecotomised rats. IV. Vitamin-B<sub>1</sub> and -B<sub>2</sub> contents of body tissues of normal and experimental rats.** W. H. GRIFFITH (J. Nutrition, 1935, 10, 667—674, 675—682).—III. Prolonged sur-

vival of rats on vitamin-B<sub>2</sub>-deficient diets is not due to a caecal supply of -B<sub>2</sub>.

**IV. Vitamin-B<sub>2</sub> is stored in the tissues, from which it is not readily lost during feeding of a deficient diet. -B<sub>2</sub> may function, in part, as a tissue constituent.** A. G. P.

**Vitamin-B<sub>2</sub> requirement of poultry.** L. C. NORRIS, G. F. HEUSER, A. T. RINGROSE, H. S. WILGUS, and V. HEIMAN (Proc. 5th World's Poultry Congr. Rome, 1933, 2, 510—520).—The factor essential for growth, hatchability, prevention of a pellagra-like syndrome and of leg and foot paralysis is probably vitamin-B<sub>2</sub>. The latter consists of at least two factors, one preventing paralysis and another necessary for growth. CH. ABS. (p)

**Behaviour of vitamin-B<sub>7</sub> towards various solvents.** E. MONTEVECOHI (Biochem. Terap. sperim., 1935, 22, 143—150; Chem. Zentr., 1935, ii, 244).—The vitamin is insol. in the usual fat solvents. It is extracted completely by 95% and partly by 70% EtOH. G. H. F.

**Influence of ascorbic acid on normal human carbohydrate metabolism.** S. STOICESCO and N. GINGOLD (Bull. Acad. Méd. Roumanie, 1936, 1, 130—132).—Intravenous or oral administration of ascorbic acid (0.24—0.50 g.) lowers the fasting blood-sugar and diminishes alimentary hyperglycaemia. F. O. H.

**Crystalline vitamin-C: its effects on the capillary fragility.** I. S. WRIGHT and A. LILLENFELD (Arch. Int. Med., 1936, 57, 241—274).—A capillary-fragility test for diagnosing human vitamin-C deficiency is described. The val. of ascorbic acid in various diseases is discussed. H. G. R.

**Effect of ascorbic acid on the proliferation of monocytes.** L. E. BAKER (Compt. rend. Soc. Biol., 1936, 121, 427—429). R. N. C.

**Cystine and vitamin-C deficiency.** L. DE CARO and W. BELTRAMI (Quad. Nutrizione, 1935, 2, 165—170).—Death of guinea-pigs on a scorbutic diet is greatly accelerated by cystine (I) or HCl. Ascorbic acid counteracts the effects of (I). NUTR. ABS. (m)

**Effect of diphtheria toxin on the vitamin-C content of guinea-pig tissues.** C. M. LYMAN and C. G. KING (J. Pharm. Exp. Ther., 1936, 56, 209—215).—Subcutaneous administration of diphtheria toxin to guinea-pigs rapidly lowers the vitamin content of the tissues, especially adrenals, kidney, and pancreas. W. O. K.

**Fixation of ascorbic acid in the adrenal and the liver of the scorbutic guinea-pig. Determination of the minimum curative dose of l-ascorbic acid.** V. DEMOLE and F. IPPEN (Compt. rend. Soc. Biol., 1936, 121, 687—689).—The daily min. dose is slightly < 0.5 mg. for an animal of 250 g. wt. The ingested ascorbic acid is stored in the adrenals, but not in the liver. R. N. C.

**Ascorbic acid in course of cadaverisation.** A. GIROUD, R. RATSIMAMANGA, M. RABINOWICZ, and E. HARTMANN (Compt. rend. Soc. Biol., 1936, 121, 739—740).—Ascorbic acid decreases slowly in the rat and the guinea-pig during cadaverisation; the rate of fall in the adrenals is > in the liver and kidney. R. N. C.



**Secretion of ascorbic acid by the healthy and diseased organism.** H. SCHROEDER (Klin. Woch., 1935, 14, 484—487; Chem. Zentr., 1935, i, 3001).—Ascorbic acid administered to healthy individuals, but not in various pathological conditions, is excreted in increased amounts in the urine, although the vitamin metabolism may be  $>$  normal. G. H. F.

**[Distribution of] ascorbic acid.** A. GIROUD and C. P. LEBLOND (Bull. Soc. Chim. biol., 1936, 18, 173—175).—By the use of acidified aq.  $\text{AgNO}_3$ , ascorbic acid is detected in the thymus, lymphatic ganglia, intestines, liver, sympathetic ganglia, suprarenal medulla and cortex, corpus luteum, ovaries, and pituitary. A. L.

**Vitamin-C in fresh-water fish and crabs.** G. VON LUDÁNY (Biochem. Z., 1936, 284, 108—110).—Data for various tissues are tabulated. In some cases the amounts exceed those found in warm-blooded animals. W. McC.

**Ascorbic acid in the lens of the eye.** H. VON EULER and M. MALMBERG (Arch. Augenheilk., 1935, 109, 225—234).—Indophenol titration of vitamin-C in the eye lens of animals revealed high vals. for sea fish, and -C was detected in the ox, rabbit, horse, and guinea-pig. While the animal received a -C-deficient diet, the -C content of the eye lens fell in guinea-pigs but not in rabbits. The -C content of the lens in rabbits was uninfluenced by high doses of -C. The reducing capacity of the lens in the rat was largely due to glutathione, the -C content being  $<$  in most cases investigated. No marked variation was detected in the -C content of the lens in rats fed on a -B<sub>2</sub>-deficient diet. The -C content of the human lens in cataract was  $<$  normal. Attempts to induce cataract in rabbits by  $\text{C}_{10}\text{H}_8$  poisoning were unsuccessful and the poisoning did not affect the -C content of the lens. Possibly part of the -C in the lens is synthesised there. NUTR. ABS. (m)

**Vitamin-C in the lens and aqueous humour in human cataract.** B. NAKAMURA and O. NAKAMURA (Arch. Ophthalmol., 1935, 134, 197—200).—A diminution was observed. NUTR. ABS. (m)

**Relative vitamin-C values of milk and curd.** A. R. GHOSH and B. C. GUHA (Indian Med. Gaz., 1935, 70, 382).—The vitamin-C content of curd was the same as that of the original milk, even though the curdling process was carried out for 24 hr. at 35°. In fresh milk stored at 0° for 24 hr., there was considerable loss of -C. There appeared to be no synthesis of -C by the lactic acid bacillus employed. NUTR. ABS. (m)

**Milk as a source of vitamin-C.** C. H. WHITNAH and W. H. RIDDELL (Science, 1936, 83, 162).—The milk of four major dairy breeds of cow gave an average val. of  $25.9 \pm 4.3$  mg. per litre. L. S. T.

**Vitamin-C in brain and cerebrospinal fluid.** Effect of diet on the vitamin-C content of the fluid: examination of the fluid in diagnosis of latent scurvy. F. PLAUT and M. BÜLOW (Z. ges. Neurol. Psychiat., 1935, 152, 84—97, 324—336).—The vitamin-C content of the brain in newly born or foetal rabbits and mice was 2—3 times  $>$  in the mother. In human cadavers the -C val. for the brain fell

steadily from foetus to 60—80 years of age. The same tendency was observed in the cerebrospinal fluid, but the concn. was always  $<$  in brain. The concn. in serum did not appear to decline with age. Daily treatment with 90 mg. of -C caused slow progressive rise in the -C content of the fluid of patients and a similar relationship between -C content of food and fluid was observed in rabbits.

NUTR. ABS. (m)

**Histochemistry. V. Vitamin-C concentration of the corpus luteum with reference to the stage of the oestrus cycle and pregnancy.** G. R. BISKIND and D. GLICK (J. Biol. Chem., 1936, 113, 27—33; cf. A., 1935, 1264).—The fully developed corpus luteum of the cow contained 1.4 mg. of vitamin-C per g. of tissue, which decreased to 0.3 mg. with regression. In gestation the content of -C remained at 1.5—2.2 mg. per g. for the first 7 months and decreased to 1.1 mg. in the 8th month. -C may be related to progesterone. J. N. A.

**Determination of vitamin-C and the influence of technological treatment on its preservation in cabbage.** S. G. VINOKUROV, M. M. EIDELMAN, and M. L. BUTOM (Kharkov State Med. Inst. Jubilee J., 1935, 142—161).—Food extracts should always be treated with  $\text{H}_2\text{S}$  before titration with indophenol in vitamin-C determinations. 40—70% of the -C content passed into  $\text{H}_2\text{O}$  when cabbage was cooked for 30 min. Cooking for longer periods involved heavy losses of -C. NUTR. ABS. (m)

**Provitamin-D of heat-treated cholesterol.** M. L. HATHAWAY and D. E. LOBB (J. Biol. Chem., 1936, 113, 105—110).—The provitamin of crude cholesterol (I) is destroyed by purification through the dibromide. When purified (I) is heated at 200° for 2 hr. its proantirachitic activity is increased. It is concluded that irradiation of heat-treated (I) produces a new form of vitamin-D which more closely resembles natural -D from cod-liver oil than -D of irradiated ergosterol. J. N. A.

**Evaluation of the antirachitic vitamin in comparison with the international standard.** M. PODZIMKOVÁ-RIEGLOVÁ (Trav. Inst. Hyg. publ. Tchecosl., 1935, 6, 20—30).—The degrees of calcification of the head of the radius produced by 0.4, 0.2, 0.1, and 0.05 international units of vitamin-D daily, and that observed in control rats receiving no -D are recorded. 0.4 unit was not always sufficient to produce normal calcification. After keeping for 13 months at -5° the activity of the international standard had not diminished. NUTR. ABS. (m)

**Size and structure of the thyroid gland of the cat after the administration of irradiated ergosterol.** A. M. LANDS and O. O. STOLAND (Endocrinol., 1935, 19, 701—704). R. N. C.

**Calcium, inorganic phosphorus, and serum-phosphatase in normal animals and in animals influenced by irradiated ergosterol.** S. FREEMAN and C. J. FARMER (Amer. J. Physiol., 1935, 113, 209—220).—Toxic doses of irradiated ergosterol (I) increase serum-Ca and/or -P, and proportionately decrease serum-phosphatase (II) in dogs and rabbits. (II) is decreased by bleeding and a high-protein diet,



and increased by a high-carbohydrate diet; the increase is enhanced by sub-toxic doses of (I). (II) activity is probably inversely  $\propto$  acid-sol. org. P of the whole blood. R. N. C.

Isolation from wheat-germ oil of an alcohol,  $\alpha$ -tocopherol, having the properties of vitamin-E. H. M. EVANS, O. H. EMERSON, and G. A. EMERSON (J. Biol. Chem., 1936, 113, 319—332).—The unsaponifiable matter yielded (?)  $\beta$ -amyirin allophanate, m.p. 250°, the allophanate, m.p. 138°, of an alcohol,  $C_{29}H_{50}O_2$ , and the allophanate, m.p. 158—160°, of  $\alpha$ -tocopherol (I),  $C_{29}H_{50}O_2$  (p-nitrophenylurethane, m.p. 129—131°). (I) has a characteristic absorption band at 298  $m\mu$ , and treatment with MeOH-AgNO<sub>3</sub> yields a substance with bands at 271 and 262  $m\mu$ . A single dose of 3 mg. of (I) enables vitamin-E-deficient rats to bear young. H. G. R.

Kinetics of penetration. XII. Hydrogen sulphide. A. G. JACQUES (J. Gen. Physiol., 1936, 19, 397—418).—The rate of entry of total sulphide ( $H_2S + S''$ ) into *Valonia macrophysa* is, during the first 5 min.,  $\propto$  external concn. of mol.  $H_2S$ .  $H_2S$  thus differs from  $NH_4^+$  and guanidine (cf. A., 1935, 671, 1179). The mode of entry appears to be diffusion of mol.  $H_2S$  through the cell wall; the rate deviates from a unimol. law. F. A. A.

Amylogenic capacity and organic matter of plastids. A. MAIGE (Compt. rend., 1935, 201, 1411—1414).—The relation of starch formation in potatoes, beans, etc. to the structure, constituents, and developments of starch plastids is discussed. F. O. H.

Transport in the cotton plant. III. Independence of solute movement in the phloem. T. G. MASON, E. J. MASKELL, and E. PHILLIS. IV. Simultaneous movement of solutes in opposite directions through the phloem. E. PHILLIS and T. G. MASON (Ann. Bot., 1936, 50, 23—58, 161—174; cf. A., 1934, 707).—III. Movements of carbohydrates (I), N, P, K, and Ca in petioles and stems of cotton plants, and the effects of ringing, are examined. Results are discussed in the light of current conceptions of the transport of solutes in plants.

IV. Examination of ringed and unringed plants grown in culture solutions shows that (I) and N may movesimultaneously and in opposite directions through the phloem. A. G. P.

Influence of light on the permeability of plant tissues to sugar. L. BRAUNER and M. BRAUNER (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, No. 2, 58—73; cf. A., 1935, 671).—The action of light probably causes a loss of electric charge in the electro-negative membrane cells, and a shrinking.  $H_2O$  or solutions of salts having a dipole moment find less resistance on passing the membranes, whilst compounds having no dipole moment are hindered. E. P.

Effect of light intensity on manganese content of plants. M. M. MCCOOL (Contr. Boyce Thompson Inst., 1935, 7, 427—437).—Visible injury to plants due to the addition of  $MnSO_4$  to soil decreased with the prevailing intensity of light. The % of Mn in leaves decreased, and, in some cases, that of stems increased, with declining light intensity. A. G. P.

Chemical restoration in *Nitella*. II. Restorative action of blood. W. J. V. OSTERHOUT (J. Gen. Physiol., 1936, 19, 423—425; cf. A., 1935, 1038, 1289).—The "K effect" in *Nitella* is restored by exposure to Ca-free blood-plasma (human, cat, calf, sheep). F. A. A.

Effect of potassium chloride on diurnal changes of carbohydrates of the potato leaf. D. J. WATSON (Ann. Bot., 1936, 50, 59—83).—Diurnal fluctuations in sucrose contents of leaflets were  $>$  those of reducing sugars. The rate of removal of dry matter (but not of carbohydrates) during darkness was increased by applications of KCl. KCl probably increases the efficiency of photosynthesis. The  $H_2O$  content per unit of dry matter was increased by KCl and the increase did not vary with time. A. G. P.

Action of radium emanation on the germination of grains. M. DE CARAMAN and C. CHAMPY (Compt. rend. Soc. Biol., 1936, 121, 750—752).—The % germination is increased, and early growth is accelerated. R. N. C.

Energy balance of carbonic acid assimilation [by plants]. K. WOHL (Z. physikal. Chem., 1935, B, 31, 152—156).—Energy considerations show that it is impossible that  $CH_2O + 2H_2O_2$  should be the intermediate product in the assimilation. The Franck-Willstätter-Stoll theory of the mechanism of  $CO_2$  assimilation (A., 1933, 326, 577; A., 1935, 794) is therefore untenable. R. C.

Amino-acid content of plants at different stages of growth. A. I. VIRTANEN and T. LAINE (Nature, 1936, 137, 237).—The tryptophan and aspartic acid contents of peas and clover vary considerably during different stages of growth, indicating that the ratio of various proteins changes during growth, or that in the growing plant the protein has no fixed composition, new  $NH_2$ -acid groups being continuously incorporated with the growing protein mol. L. S. T.

Nitrogen metabolism of the apple fruit. II. Course followed by certain nitrogen fractions during the development of the fruit on the tree. A. C. HULME (Biochem. J., 1936, 30, 258—268; cf. A., 1935, 422).—Non-protein-N was separated from the peel and pulp of apples by extraction with aq. EtOH and determined as total sol., free  $NH_3$ ,  $NH_2$ , and residual N. Titratable acid was also determined. The changes in these fractions during the course of development of two series of fruits was determined. The two series showed similar trends; an early stage of rapid increase in sol. N compounds was followed by a stage of relative equilibrium between protein and non-protein compounds. When mature a state of net synthesis of protein ensued. H. D.

Nitrogen-free aliphatic compounds as organic nutrients of algæ. H. MEYER (Biochem. Z., 1936, 283, 364—381).—The effect of 0.2% of 90 org. substances on the growth of *Chlorella luteoviridis*, as measured by increase in cellular vol. or dry wt. or intensity of division, in a medium containing  $MgSO_4$ ,  $CaCl_2$ ,  $FeCl_3$ ,  $(NH_4)_2HPO_4$ , and phosphate buffer is investigated. With saturated acids, alcohols, and



aldehydes, the first member of the series ( $\text{HCO}_2\text{H}$ ,  $\text{MeOH}$ ,  $\text{CH}_2\text{O}$ ) is toxic, the second member has the highest nutritive val. and the higher homologues are utilised to a decreasing content. *iso*-Acids and unsaturated acids are toxic.  $\beta$ -Hydroxybutyric acid and  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$  are readily utilised. Polybasic and sugar acids are indifferent. Hexoses form the best source of C, pentoses are not utilised, polysaccharides are used according to the ease of hydrolysis, whilst methylglucoside and glycerophosphoric acid are indifferent.

P. W. C.

**Fat metabolism in plants with special reference to sterols.** P. L. MACLACHLAN (J. Biol. Chem., 1936, 113, 197—204).—The sterol and fatty acid constituents of soya beans during germination in the light and dark were determined. A decrease in the fat content occurred during germination accompanied by a continuous synthesis and esterification of sterol. Small differences in the behaviour in the light and dark were observed.

H. D.

**Nitrogen fixation by the alder.** A. I. VIRTANEN and S. SAASTAMOINEN (Biochem. Z., 1936, 284, 72—85).—Since peas inoculated with N-fixing bacteria grow normally in an aerated N-free aq. medium it follows that there is no difference in this respect between leguminous plants and the alder. Inoculated alder seedlings grow better in N-free media than do non-inoculated in media containing  $\text{NH}_4\text{NO}_3$ ; the growth of the former is optimal at  $p_{\text{H}}$  6. Inoculated alder enables pine seedlings planted in the same N-free medium to grow normally and appears to give up N compounds to the medium.

W. McC.

**Interaction of factors in the growth of *Lemna*.** VII. Effect of potassium on growth and multiplication. H. L. WHITE (Ann. Bot., 1936, 50, 175—196).—Mathematical relationships between the [K] of the nutrient and the growth of *Lemna minor* are established. Deficiency of K is associated with high starch and dry matter contents per unit area, low rates of assimilation, and diminished amyolytic activity.

A. G. P.

**Supply of iron to plants in water cultures.** W. SCHROPP (Z. Pflanz. Dting, 1936, 42, A, 35—42).—In media containing  $\text{FeCl}_3$ , the accumulation of Fe by plants was inversely related to the reaction of the nutrient. When  $\text{Fe}^{\text{III}}$  citrate was used, growth was improved and the Fe intake was independent of  $p_{\text{H}}$ .

A. G. P.

**Skatole as a growth-promoting substance.** J. GLOVER (Nature, 1936, 137, 320—321).—Experiments with young oat shoots indicate that skatole (I) acts as a growth-promoting hormone. (I) and  $\beta$ -indolylacetic acid are both markedly light-sensitive.

L. S. T.

**Growth-promoting substance at the base of the oat coleoptile.** H. SÖDING (Ber. deut. Bot. Ges., 1935, 53, 843—846).—The growth hormone is present in the base of the coleoptile. No evidence was obtained of a "bound" or inactive form.

A. G. P.

**Absorption and movement of synthetic growth-substances from soil as indicated by responses of aerial parts [of plants].** A. E.

HITCHCOCK and P. W. ZIMMERMAN (Contr. Boyce Thompson Inst., 1935, 7, 447—476).—Application of heteroauxin, indolyl- or phenyl-propionic acids, naphthyl- or phenyl-acetic or indolylbutyric acid to soil induced responses in tomato and tobacco plants similar to those obtained by treatment of the aerial parts of the plants. The rate of absorption of active substances was influenced by the amount present in the soil and by the transpiration rates of the plants. The action of growth-substances (I) applied to aerial parts is not affected by transpiration rates. Within the plant translocation of (I) in living tissue was > in dead tissue and upward > downward movement. Strictly polar movement was not observed in either stems or leaves. Unilateral lighting favoured the bending-response of stems to (I) but light was not essential. Addition of (I) to soil hastened flowering without retarding vegetative growth. The optimum dosage for flowering was < that for root initiation.

A. G. P.

**Response of roots to "root-forming" substances.** P. W. ZIMMERMAN and A. E. HITCHCOCK (Contr. Boyce Thompson Inst., 1935, 7, 439—445).—Application of lanoline preps of  $\alpha$ -naphthyl-, indolyl-, and phenyl-acetic acids, indolyl-butyric, -propionic, and -valeric acids to aerial roots of *Cissus sicyoides*, L., var. *Jacquini*, caused the initiation of new root branches, inhibition of growth of the tip and/or swelling of the root. New rootlets ceased to grow when the main tip resumed elongation, but recommenced on a second treatment of the tip. The dominance of the tip disappeared when the treated area was immersed in  $\text{H}_2\text{O}$ . Results are discussed in relation to the movement of growth-substance in roots.

A. G. P.

**Selenium in native range plants occurring on soils derived from Permian or Triassic (?) sediments [of the Chugwater formation, Albany Co., Wyoming].** O. A. BEATH (Science, 1936, 83, 104).

L. S. T.

**Natural poisoning of hens by acid sorrel (*Rumex acetosella*): poisoning by oxalic acid and potassium hydrogen oxalate.** C. ORLANDINI (Boll. Soc. Eustach., 1933, 31, 217—229).—Poisoning by the sorrel is attributable to  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{KHC}_2\text{O}_4$ .

CH. ABS. (p)

**Compounds of hydroxylamine in fresh leaves of higher plants.** M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Compt. rend., 1935, 201, 1437—1439).—Distillation of the juice of fresh leaves of *Poa pratensis* yields  $\text{NH}_2\text{OH}$  (1—2 mg. per litre);  $\text{NH}_2\text{OH}$  probably participates in the N metabolism of higher plants.

F. O. H.

**Excretion of amino-acids from root nodules and their chemical nature.** A. I. VIRTANEN, T. LAINE, and S. VON HAUSEN (Suomen Kem., 1936, 9, B, 2).—The rate of excretion is greatest at an early stage of growth, before blooming. A cold- $\text{H}_2\text{O}$  extract of the sand on which peas had grown contained exclusively  $\text{NH}_2\text{-N}$ . About 50% of the total N was due to aspartic acid, while the remainder was probably lysine (I). Barley will grow with (I) as sole source of N.

J. N. A.



Glutamine and asparagine in tobacco leaves. H. B. VICKERY and G. W. PUCHER (J. Biol. Chem., 1936, 113, 157—160).—Glutamine (I) occurs, as well as asparagine (II), in the leaves of the tobacco plant, and may be extracted. Of the total amide-N, (II) appears to account for about  $\frac{2}{3}$ , (I) for about  $\frac{1}{3}$ , but other amide substances may be present. F. A. A.

Biologically active substances in the fruit of the tomato (*Solanum esculentum*) with histamine-like action. Therapeutic action of fresh vegetable juice. F. GLEICHMANN (Z. klin. Med., 1934, 127, 111—131; Chem. Zentr., 1934, ii, 3982).—The cryst. substance extracted from green or ripe tomatoes or conserve is stable to heat, pepsin, and HCl, and resembles histamine in its pharmacological action. R. N. C.

Chemical examination of Punar-Nava (*Bærrhaavia diffusa*, Linn.). R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. U.P. India, 1935, 4, 73—76).—Boiling EtOH extracts *bærrhaavic acid*,  $C_{10}H_{18}O_3$ , m.p. 108—109° (decomp.) (Pb salt;  $Br_3$ -derivative, m.p. 73°), tannins, phlobaphens, and glucose from the entire plant. J. L. D.

Chemical examination of the roots of *Citrullus colocynthis*, Schrader. R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. U.P. India, 1935, 4, 295—300; cf., J.C.S., 1910, 47, 99).—Boiling EtOH extracts  $\alpha$ -elaterin (0.2%); m.p. 229—230° [ $Ac_2$  derivative, m.p. 122—123° (cf. A., 1907, i, 230)], hentriacontane (?), saponins, and reducing sugars from the powdered roots. J. L. D.

2':6'-Dihydroxy-4'-methoxy- $\beta$ -phenylpropio-phenone from the essential oil of *Populus balsamifera*, L. A. GORIS and H. CANAL (Compt. rend., 1935, 201, 1435—1437).—The oil from the buds yields the above ketone, m.p. 168°. F. O. H.

Localisation of rotenone in derris root. P. A. VAN DER LAAN (Pharm. Weekblad, 1936, 73, 313—318).—Cells containing rotenone (I) are coloured green (transient) when treated with  $HNO_3$  and then with  $NH_3$ , and the colour produced on samples of derris root may be used as a rough measure of the (I) content. The (I) is localised in the parenchyma and pith cells present in both the wood and the bast. S. C.

Constituents of *Hamamelis virginica*. F. MERCIER and J. BALANSARD (Compt. rend. Soc. Biol., 1936, 121, 671—672).—The leaves contain choline, an acid saponin, and a sol. glucoside fraction. R. N. C.

Acid saponin of beetroot juice. K. SMOLEŃSKI (Rocz. Chem., 1935, 15, 554—564).—A review. R. T.

Sterols of *Achillea millefolium*. O. GISVOLD (J. Amer. Pharm. Assoc., 1935, 24, 1071).—The sterols consist of sitosterol and stigmasterol (cf. A., 1933, 1216). E. H. S.

Phytosterol and resin of *Fabiana denudata*, Miers. L. FLORIANI (Rev. Centr. Estud. Farm. Bioquim., 1934, 25, 60—62; Chem. Zentr., 1935, i, 3569).—A phytosterol,  $C_{27}H_{46}O$ , a resin, m.p. 44°, an  $\alpha$ -resin-acid, m.p. 37°, and a  $\beta$ -resin-acid, m.p. 39°, are isolated. H. N. R.

Sterols in the leaves and flowers of the lily. M. MIRANDE (Compt. rend., 1936, 202, 238—240).—The distribution of sterols in species of lily is examined. H. G. R.

Determination of carotene and xanthophyll.—See this vol., 493.

Lycoxanthine and lycophyll.—See this vol., 452.

Occurrence of carotenoids in plants. P. KARRER, F. RÜBEL, and F. M. STRONG (Helv. Chim. Acta, 1936, 19, 28—29).—Treatment of the seeds of *Passiflora coerulea* with EtOH followed by boiling  $CHCl_3$ , evaporation of the  $CHCl_3$ , and crystallisation of the residue from ligroin (b.p. 60—80°) gives lycopene in considerable amount.  $\beta$ -Carotene and zeaxanthin are obtained cryst. from *Halyserys polypodioides* but homogeneous fucoxanthin could not be isolated. H. W.

Colouring matters of violet potatoes.—See this vol., 480.

Colourless compounds which accompany carotenoids in plants. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1936, 238, 204—209; cf. Euler *et al.*, A., 1908, ii, 724; 1930, 1627; 1932, 785).—100 kg. of carrots yield 1.06 g. of daucosterol (I),  $C_{35}H_{60}O_6$ , decomp. at 305°,  $[\alpha]_D^{20}$  —49.6° in  $C_5H_5N$ , hydrolysed by acid to *d*-glucose and sitosterol. The sepals of the sunflower contain a dihydric sterol *helisterol*,  $C_{26}H_{44}O_2$ , m.p. 242°,  $[\alpha]_D^{20}$  +45.4° in  $CHCl_3$  (diacetate, m.p. 166—167° (corr.),  $[\alpha]_D^{20}$  +58.7°), a monohydric sterol, m.p. 217°,  $[\alpha]_D^{20}$  +42.8° in  $CHCl_3$ , a sterolin,  $C_{33}H_{56}O_6$ , m.p. 303°,  $[\alpha]_D^{20}$  —50.5° in  $C_5H_5N$ , which gives glucose and a sterol,  $C_{27}H_{46}O$ , m.p. 159°,  $[\alpha]_D^{20}$  —49.9° in  $CHCl_3$  on acid hydrolysis, an alcohol,  $C_{21}H_{50}O$ , m.p. 73° (corr.), and hentriacontane. W. McC.

Formation of anthocyanins in plants. R. ROBINSON (Nature, 1936, 137, 172—173).—A summary. L. S. T.

Glycosides of the flowers of *Linaria vulgaris*.—See this vol., 458.

Inulinogenesis in the *Compositæ*. H. COLIN (Compt. rend., 1935, 201, 1414—1416).—Data for the contents of reducing sugar, sucrose, and inulin (I) and for  $[\alpha]$  before and after hydrolysis are given to illustrate the discussed formation of (I) in the root, stem, leaf, and wood of various *Compositæ*. F. O. H.

Determination of starch in plant tissue, particularly apple fruit. C. S. HANES (Biochem. J., 1936, 30, 168—175).—After a preliminary extraction of the tissue with 70—80% EtOH the residue is boiled with dil. HCl-EtOH which renders the starch (I) sol. in hot  $H_2O$ . The  $H_2O$  extract is then hydrolysed by  $\beta$ -malt-amylase (II), which produces maltose (III) as almost the only reducing product. The degradation of (I) by (II) proceeds to a definite "hydrolysis limit" The amount of (III) formed is determined either by an alkaline  $Fe(CN)_6^{4-}$  or a Cu method. Apple-(I) is hydrolysed to the same extent by (II) throughout the season, with the production of 0.6 mg. of (III) per mg. of (I), much the same val. as for potato-(I). The (I) content of apples on storage falls nearly to zero in 10 days. If taka-diastase (IV) is used



instead of (II) the apparent (I) content is much higher and falls after 10 days to 1.5 mg. per g. This is due to non-(I) fractions hydrolysed by (IV) but not by (II), some of which are not metabolised, and so persist during storage. Methods are given for the prep. of (II) and control (I) from apples. E. A. H. R.

**Polysaccharides in sweet maize.** M. W. PARRKE (Plant Physiol., 1935, 10, 713—725).—Electrodialysis of the sol. polysaccharide fraction yields an anodic fraction and a further non-migratory fraction. With advancing maturity of the grain, the physical and chemical properties of the fractions approach more closely to those of  $\alpha$ - and  $\beta$ -amylose, and differ from those of dextrin. In maize the sol. polysaccharides may form the units from which starch grains are ultimately formed. A. G. P.

**Polysaccharides of *Iridaea laminarioides*.** II. T. TADOKORO, K. YOSHIMURA, and M. YANASE (J. Chem. Soc. Japan, 1935, 56, 188—191; cf. A., 1935, 268).—Hydrolysis of the product obtained by extraction with hot  $H_2O$  and pptn. with 70% EtOH yielded galactose and smaller amounts of glucose, fructose, and arabinose. The fraction not pptd. by EtOH contained an unidentified sugar having  $[\alpha]_D^{20} +31.4^\circ$ , and yielding a phenylosazone, m. p. 125—130°. CH. ABS. (p)

**Hai-jen-tsao (*Digenia simplex*, Ag).** C. F. HSÜ (Science [China], 1934, 18, 1418—1437).—This marine alga is used as a vermifuge. Alginic acid, extracted by 2%  $Na_2CO_3$ , contains uronic and either glycuronic or mannuronic acids. The boiling- $H_2O$  extract yields galactan, *d*-pararabin, and small amounts of alkaloid and fucoidin. The I content is 0.20%. CH. ABS. (p)

**Isolation of pectic substances from wood.** E. ANDERSON (J. Biol. Chem., 1936, 112, 531—539).—The sap-wood and cambium of *Robinia pseudacacia*, L., yield < 3% and < 13%, respectively, of pectic substances (yielding *d*-galacturonic acid but no methylpentoses), probably present largely as Ca pectate, protected by later deposition of other materials. R. S. C.

**Vegetable chitin.** J. M. DIEHL (Chem. Weekblad, 1936, 33, 36—38).—Analytical data, including determinations of Ac, show that animal and vegetable chitins from *Crangon vulgaris*, *Amanita muscaria*, and *Phycomyces Blakesleeanus* are identical. Like other chitins, that from *Lycoperdon gemmatum* gives AcOH and not  $HCO_2H$  on hydrolysis. S. C.

**Irritant principle in *Mimosoideae*.** A. SOLTYS and K. UMRATH (Biochem. Z., 1936, 284, 247—255).—Fractionation of aq. extracts of *Mimosa* or *Neptunia plena* leaves (4 kg.) by Hg and Pb acetates,  $C_5H_5N$ , EtOH, and  $Ba(OH)_2$  yields 10 mg. of a highly irritant (as indicated by plant movements) OH-acid of high O content, equiv. wt. 250, and mol. wt. 500. The activity is destroyed on acetylation but returns on subsequent hydrolysis. F. O. H.

**Digitalis.** I. New principles in evaluation. B. NIELSEN (Acta med. scand., 1935, 84, 315—354; Chem. Zentr., 1935, i, 3162—3163).—A biological method, employing the toxicity of digitalis preps. for mice, is described. H. N. R.

**Decomposition of nicotine by the fermentation of tobacco.** W. WEBER (Mitt. Lebensm. Hyg., 1935, 26, 214—249).—Aëration of moist tobacco or its  $H_2O$  extract leads to loss of nicotine (I) by decomp. as distinct from atm. oxidation or volatilisation. This is inhibited by antiseptics and occurs in sterile media after inoculation with bacteria from tobacco leaves. Bacterial decomp. of (I) takes place in artificial media, and there is evidence that oxidase, peroxidase, and catalase are produced.  $NH_3$  (but no  $C_5H_5N$ ) is produced, but unlike the  $NH_2Me$  found, it is not derived from (I) but from  $NH_2$ -compounds. A reagent suitable for determining (I) is best prepared by neutralising a mixture of 1 kg. of  $Na_2WO_4 \cdot 2H_2O$  and 117.1 g. of 26.3%  $Na_2SiO_3$  with  $H_2SO_4$ , filtration, extraction of the filtrate with  $Et_2O$  in the presence of 50%  $H_2SO_4$ , and slow evaporation of the  $Et_2O$ . J. G.

**Nornicotine.**—See this vol., 488.

**South American curare.** F. W. FREISE (Pharm. Ztg., 1936, 81, 241—243).—The characteristics and analyses of cork tissues of varying ages from 6 varieties of *Strychnos* are given. The isolation of two alkaloids,  $C_{23}H_{28}O_4N_2$  (similar to or identical with vellosine), and *ecurarine*,  $C_{20}H_{23}ON_2$ , m. p. 135—144°, decomp. 182° (toxic dose for frogs, 0.13 mg. per kg.), is described. E. H. S.

**New alkaloid of ergot.**—See this vol., 489.

**Alkaloids of *Sinomenium* and *Cocculus*.**—See this vol., 491.

**Barley proteins.** I. S. JAITSCHNIKOV and A. D. AVETISJAN (J. Appl. Chem. Russ., 1935, 8, 1439—1443).—The protein-N of barley from different localities of the U.S.S.R. varies from 2.16 to 3.07%; the distribution of the N amongst the albumin, globulin, glutenin, and prolamine fractions is recorded. Varying the order in which the various fractions are extracted (by  $H_2O$ , aq. NaCl, and aq. NaOH) affects the results. R. T.

**Distribution of nucleic acids and proteins in chromosomes.** T. CASPERSON (Naturwiss., 1936, 24, 108).—With the aid of a precipitant containing La, sp. for nucleic acids (I), ultra-violet photomicrographs of chromosomes (II) of extraordinarily fine structure are obtained. Distribution of (I) is identical in both halves of chromosomes. The non-absorbing segments have the properties of proteins. Digestion with proteolytic enzymes dissolves out one of the components, the chromosomes disintegrating into discs and granules of high (I) content. E. A. H. R.

**Highly polymerised compounds.** CIII. Application to biology of investigations on the constitution of highly polymerised compounds. H. STAUDINGER (Zangger-Festschr., 1934, 939—953; Chem. Zentr., 1935, i, 3528; cf. A., 1934, 1336).—The application of earlier work to biological problems, especially protein and rubber chemistry, is discussed. Terminal groups, present in relatively small amount, may be very important factors in determining the chemical properties of fibres. H. N. R.

**Biochemical apparatus.** E. McDONALD (J. Franklin Inst., 1936, 221, 103—138). W. McC.



**Spectrographic analysis of biological materials.** G. H. SCOTT and P. S. WILLIAMS (*Anat. Rec.*, 1935, 64, 107—127).—A method is described. Spectra of normal and pathological tissues are shown.

R. N. C.

**Nephelometric determinations using the photo-electric cell.** J. RENAUDIN (*Bull. Soc. Chim. biol.*, 1936, 18, 301—304).—Nephelometric biological determinations are liable to inherent faults in the apparatus and errors due to the difference in size of suspended particles, and to interfering constituents in the media.

A. L.

**Manometer for comparative study of physiological processes.** B. N. SINGH and P. B. MATHUR (*Biochem. J.*, 1936, 30, 323—325).—Direct reading of the scale suffices when the manometer is used for comparisons. When it is used for quant. determinations the degree of accuracy is  $\pm 1.25\%$ .

W. McC.

**$p_{H}$  determination in biological liquids with the Thompson electrode.** X. THIESSE, M. VERAINE, and A. ZIEGLER (*Bull. Soc. Chim. biol.*, 1936, 18, 203—207).—The glass electrode (A., 1933, 367) may be used.

A. L.

**Method for testing the sense of smell and for the establishment of olfactory values of odorous substances.** C. A. ELSBERG, I. LEVY, and E. D. BREWER (*Science*, 1936, 83, 211—212).

L. S. T.

**Mosaic collodion membranes as analogues of the plasma membrane.** S. C. BROOKS (*J. Exp. Biol.*, 1935, 12, 36—38).—"Anion-impermeable" and "cation-impermeable" membranes arranged in pairs on glass cells did not accumulate or exchange ions except traces of  $Cl^{-}$ .

CH. ABS. (p)

**Histochemical detection of phosphate conglomerates in tissue.** C. HEIDERMANNS and H. WURMBACH (*Z. wiss. Mikrosk.*, 1935, 51, 375—378; *Chem. Zentr.*, 1935, i, 3574).—The material is treated successively with uranyl sulphate,  $HNO_3$ , and  $K_4Fe(CN)_6$ , and observed microscopically.

H. N. R.

**Choice of counterstains.** H. D. MURRAY (*J. Roy. Microscop. Soc.*, 1935, [iii], 55, 233—237).—The absorption spectra of a no. of dyes are examined in relation to their suitability as stains.

H. D.

**Histological applications of tannic acid and ferric chloride.** H. T. NORTHERN (*Stain Tech.*, 1936, 11, 23—24).—The use of tannic acid or  $FeCl_3$  with a cellulose-wall stain (light-green or crystal-violet) and a nuclear lignin stain (safranin) gives clear preps. of plant stems superior to those stained by the usual safranin-crystal-violet and other combinations.

P. G. M.

**Comparative study of dehydration [of animal tissues].** T. T. BAIRD (*Stain Tech.*, 1936, 11, 13—22).—Whatever method of fixation is used, dioxan is the best of known dehydrating agents. The greatest distortion is produced by the  $EtOH-CHCl_3$  method.

P. G. M.

**Counterstains for Davenport reduced silver preparations of peripheral nerves.** J. O. FOLEY (*Stain Tech.*, 1936, 11, 3—8).

P. G. M.

**Lacto-phenol preparations.** W. E. MANEVAL (*Stain Tech.*, 1936, 11, 9—11).—Fungi, algæ, germin-

ating spores, etc. may be stained and mounted in Amann's lacto-phenol containing aniline-blue, cotton-blue, or acid fuchsin either singly or in combination, with or without addition of 20—25%  $AcOH$ . Detailed formulæ are given.

P. G. M.

**Determination of carbamide.**—See this vol., 459.

**Determination of alcohol in putrefied blood and tissues.** M. NICLOUX (*Compt. rend. Soc. Biol.*, 1935, 120, 1301—1303).—The blood or tissue is treated with  $AgNO_3$  and picric acid and distilled; the distillate is treated with  $KOCl$ ,  $Na_2CO_3$ , and  $AgNO_3-NH_3$ , and again distilled, the distillate being acidified and again distilled.  $EtOH$  is determined in the third distillate by any standard method. This process practically eliminates reducing substances, and  $> 99\%$  of  $EtOH$  added to the blood can be recovered.

R. N. C.

**Micro-determination of alcohol in putrefied blood and in corpses.** M. NICLOUX (*Bull. Soc. Chim. biol.*, 1936, 18, 318—351).—The material is first distilled with picric acid and  $AgNO_3$ , then with  $KOCl$  in aq.  $Na_2CO_3$  to remove reducing substances which interfere, the determination being made according to the author's method (A., 1931, 1327).  $EtOH$  administered to white mice previous to killing disappears from the bodies in a regular manner, the rate increasing with rise of temp. Considerable quantities (0.8 g. per kg.) of  $EtOH$  are formed during the putrefaction of corpses, this being accompanied in some cases by 15% of  $BuOH$ .

A. L.

**Micro-determination of alcohol in biological material.** R. N. HARGER (*J. Lab. Clin. Med.*, 1935, 20, 746—751).— $EtOH$  is removed from tissue, blood filtrates, urine, etc. by steam distillation. The distillate is oxidised by  $H_2SO_4-K_2Cr_2O_7$ , excess of the latter being titrated with a solution containing  $FeSO_4$  and Me-orange.

CH. ABS. (p)

**Determination of small amounts of citric acid in biological material.** G. W. PUCHER, C. C. SHERMAN, and H. B. VICKERY (*J. Biol. Chem.*, 1936, 113, 235—245).—Citric acid (I) (0.1—1.0 mg.) was determined in  $CCl_3CO_2H$  extracts by oxidation with  $KMnO_4$  and Br. The pentabromoacetone produced was extracted with light petroleum and treated with aq.  $Na_2S$ ; the colour in the aq. phase was stabilised with  $C_5H_5N$  and its intensity determined spectrophotometrically. Non-volatile ketones and keto-acids interfere if present in large amounts. Small quantities of (I) occur in saliva and erythrocytes.

H. D.

**Isolation from human tissues of easily volatile organic liquids and their identification.** A. O. GETTLER and H. SIEGEL (*Arch. Path.*, 1933, 19, 208—212).— $EtCl$ ,  $C_2H_4Cl_2$ ,  $C_3H_6Cl_2$ ,  $CCl_4$ ,  $CCl_2F_2$ ,  $CHCl_3$ ,  $CS_2$ ,  $C_6H_6$ , and  $Et_2O$  were identified.

CH. ABS. (p)

**Spectrographic determination of phenol in tissue.** G. BARAC and A. LAMBRECHTS (*Bull. Soc. Chim. biol.*, 1936, 18, 239—240).—The ultra-violet spectrum of the  $Et_2O$  extract of the material after defecation with  $CCl_3CO_2H$  is determined. Under these conditions  $PhOH$  gives a max. at 280.7  $m\mu$  with an extinction coeff. of 2400.

A. L.

**Diazo-coupling reaction for detection of o- and p-phenols in histological technique.** M. CLARA



(Z. wiss. Mikrosk., 1935, 51, 316—337; Chem. Zentr., 1935, i, 3574).—Commercial, stabilised diazo-compounds are used.  
H. N. R.

Detection of intravenously injected substances (especially 1-3:4-dihydroxyphenylalanine) inside epithelial cells. Detection of reducing sugar-like substances in the skin of men and animals, by means of silver nitrate. F. SCHAAF and W. BURCKHARDT (Arch. Derm. Syph., 165, 157—173; Chem. Zentr., 1935, ii, 3018).  
H. N. R.

Chemico-toxicological detection of physostigmine. I. MALANDRUCCO (Biochim. Terap. sperim., 18, 242—247; Chem. Zentr., 1935, i, 3020).—A colour reaction is described.  
H. N. R.

Colorimetric determination of morphine and its derivatives. G. RIZZOTTI (Arch. Farm. sperim., 1935, 60, 545—563).—Blood or tissue extracts are deproteinised by  $\text{Na}_2\text{WO}_4\text{--H}_2\text{SO}_4$ , the resulting clear fluid is treated with  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaCN}$  at  $100^\circ$ , cooled, and  $\text{Fe}_2(\text{SO}_4)_3$  added, and the Prussian-blue developed is compared with that from suitable glucose standards. The method is based on reduction of  $\text{K}_3\text{Fe}(\text{CN})_6$  by the phenolic OH of morphine and certain of its derivatives.  
F. O. H.

Extraction and determination of small amounts of morphine in organs. B. ZANELLA (Arch. Ital. Sci. farmacol., 1, 120—140; Chem. Zentr., 1935, i, 3020).—An improved isolation process is described.  
H. N. R.

Embsden's cholesterol determination. S. MIYAMORI (Nagoya J. Med. Sci., 1935, 8, 135—137).—The material (2 g.) is hydrolysed with 25% aq. KOH at  $100^\circ$ , the  $\text{Et}_2\text{O}$  extract of the product, dried and dissolved in  $\text{CHCl}_3$ , is treated with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ , and the colour measured. The vals. obtained agree with those from the digitonin method.  
NUTR. ABS. (m)

Colorimetric determination of small amounts of cholesterol in blood and other liquids of the organism. M. N. DEL AGUILA (Bol. Soc. quim. Peru, 1935, 1, No. 3, 73—74).—Blood is extracted with  $\text{Et}_2\text{O}$  after addition of  $\text{EtOH}$  (with or without  $\text{NaOH}$ ), and cholesterol is determined by Grigaut's  $\text{Ac}_2\text{O}$  method.  
CH. ABS. (p)

Determination of phytic acid. L. YOUNG (Biochem. J., 1936, 30, 252—257).—Phytic acid (I) is determined by addition of excess of  $\text{FeCl}_3$ , pptn. of Fe phytate at  $100^\circ$  in  $N/6\text{--HCl}$ , and determination of the excess of Fe colorimetrically with CNS'. In faeces extracts (I) is pptd. as before and the ppt. is separated and decomposed with  $\text{NaOH}$ , and after removal of  $\text{Fe}(\text{OH})_3$  the liberated (I) is determined as above.  
H. D.

Detection and determination of copper in organic matter by benzoinoxime. Z. GRUZEWSKA and G. ROUSSEL (Compt. rend. Soc. Biol., 1936, 121, 289—291; cf. this vol., 260).—Cu is accurately determined in rabbit liver by incineration and pptn. from the ash with benzoinoxime in slightly alkaline solution after removal of Fe. The ppt. is sol. in  $\text{CHCl}_3$ , forming a green solution which serves for the detection of Cu.  
R. N. C.

Colorimetric determination of copper in biological material. E. LASAUSSE and L. FROCRAIN (J. Pharm. Chim., 1936, [viii], 23, 77—82; cf. Fleury *et al.*, A., 1929, 784; Delépine, A., 1908, i, 511).—Org. matter is destroyed by ignition at low red heat after addition of  $\text{Mg}(\text{NO}_3)_2$ . The residue, dissolved in  $\text{HCl}$ , is freed from Fe and Ca by addition of aq.  $\text{NH}_3$  and aq.  $(\text{NH}_4)_2\text{CO}_3$ , and Cu is determined colorimetrically by Na dithiocarbamate.  
W. McC.

Modifications of the 2:2'-dipyridyl method for available iron. G. O. KOHLER, C. A. ELVEHJEM, and E. B. HART (J. Biol. Chem., 1936, 113, 49—53; cf. A., 1935, 115).—Chlorophyll and all interfering pigments are pptd. by  $\text{Pb}(\text{OAc})_2$ , and the method can be applied to green vegetables and other pigmented products, as well as to animal tissues. Wherever possible, a fresh and not a dried sample should be used.  
J. N. A.

Non-interference of sodium chloride in the determination of copper and iron in biological material. L. FROCRAIN and E. LASAUSSE (J. Pharm. Chim., 1936, [viii], 23, 84—85).—If  $\text{Mg}(\text{NO}_3)_2$  or  $\text{MgO}$  is present, no loss of Fe or Cu occurs when material is ignited in presence of very large excess of  $\text{NaCl}$ .  
W. McC.

Quantitative spectrographic analysis of biological material. I. Determination of lead in cerebrospinal fluid. J. S. FOSTER, G. O. LANGSTROTH, and D. R. MCRAE (Proc. Roy. Soc., 1935, A, 153, 141—152).—This micro-method is applicable to concns. of  $1 \times 10^{-8}$ — $2 \times 10^{-5}$  g. per c.c. with a precision of  $>15\%$ . It is based on the fact that when the atoms of a sample are excited by a d.-c. spark under suitable conditions, the intensity of a Pb line  $\propto [\text{Pb}]$ , if  $[\text{Pb}]$  is low.  
L. L. B.

Determination of small amounts of lead in biological material. H. CHEFFTEL and M. L. PIGEAUD (Ann. Falsif., 1936, 29, 76—92; cf. A., 1933, 621; B., 1933, 170).—The dithizone (I) method is substituted for the PbS colorimetric method (*loc. cit.*), which is not sufficiently sensitive. Cu etc. are removed by treatment with KCN. Fe is then liable to interfere by producing a brown colour with (I), but this is prevented by avoiding any excess of KCN. Sn does not interfere if present as  $\text{Sn}^{IV}$ .  
E. C. S.

Determination of lead.—See this vol., 443.

Micro-determination of ferrocyanide in muscle and urine. J. G. EDWARDS and W. D. LANGLEY (J. Biol. Chem., 1936, 112, 469—475).— $\text{Fe}(\text{CN})_6^{4-}$  (1—40 mg.) is determined in tissues by hydrolysis with  $\text{H}_2\text{SO}_4$ , absorption of the volatilised HCN in aq.  $\text{NaOH}$ , and titration with  $\text{AgNO}_3$ .  
H. D.

Determination of nitrate in animal tissues. M. WHELAN (J. Lab. Clin. Med., 1935, 20, 755—757).—The ground tissue is acidified ( $\text{H}_2\text{SO}_4$ ) and extracted first with  $\text{Et}_2\text{O}$  and then with hot  $\text{H}_2\text{O}$ .  $\text{Et}_2\text{O}$  is removed from the combined extract, which is then made alkaline, and diluted. An aliquot is treated with  $\text{HgCl}_2$  to remove interfering substances and  $\text{NO}_3^-$  is determined in the clear liquid.  
CH. ABS. (p)



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

MAY, 1936.



### General, Physical, and Inorganic Chemistry.

**Intensity distribution of the continuous spectrum of hydrogen in mixtures with helium and with neon.** N. D. SMITH (Physical Rev., 1936, [ii], 49, 345—350).—The intensity max. was shifted to longer  $\lambda$ . A study of the intensity distribution of the many-line spectrum in the presence of He showed that 20 cm. of He reduced the vibration in the excited states almost to zero, so that the continuous spectrum in presence of He must be due to transitions from the lowest vibrational level of its upper state. The  $\lambda$  distribution of energy in the continuous spectrum for 0.6 mm. H<sub>2</sub> and 21 cm. He, determined by comparison with the radiation emitted from the positive crater of the C arc, showed a max. intensity at about 3200 Å. compared with 2500 Å. under ordinary conditions.

N. M. B.

**Comparison between the continuous molecular spectra of hydrogen and deuterium.** (MILLE.) A. TOURNAIRE and E. VASSY (Compt. rend., 1936, 202, 562—564; cf. this vol., 127).—The distributions of intensity in the spectra have been measured at 1923—4990 Å. and 0.44—3 mm. pressure.

T. G. P.

**Nitrogen atom and the molecule.** L. S. MATHUR and P. K. SEN-GUPTA (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 187—226).—Recent measurements of the various band systems of N<sub>2</sub> are tabulated and discussed critically.

J. W. S.

**Fine structure of the metastable level of nitrogen.** B. STEPANOV (Physikal. Z. Sovietunion, 1935, 8, 352—353).—The N<sub>2</sub> lines 1742.74 and 1745.26 Å. have been resolved and the components found to have the separation 2.13 cm.<sup>-1</sup> Intensity distribution is discussed in relation to the scheme of Compton and Boyce (A., 1929, 365).

R. S.

**Glow discharge through oxygen.** F. D. GREEVES and J. E. McF. JOHNSTON (Phil. Mag., 1936, [vii], 21, 659—686).—A discharge tube fitted with probe tubes has been used for investigating the negative sections of the cold-cathode glow discharge in O<sub>2</sub>, and the range of conditions under which probes can be used without introducing errors determined. Data are given for the electron energy distributions and consens., and for the potential in the discharge.

J. W. S.

**Reversal of the neon lines 744, 736 Å.** T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 1—7).—When a strong condensed discharge is passed through a long tube of Ne at several mm. pressure the resonance lines 744 and 736 Å. are considerably broadened and the latter is much the more conspicuously reversed, with a

white gap in the core extending to about 0.3 Å. The contour of this line is quite asymmetric, with its wing extending towards the shorter  $\lambda$  side, and resembles that of the He resonance line 584 Å.

N. M. B.

**Perturbations of Ne I terms.** Y. ISHIDA and T. TAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 9—18).—Anomalies in certain sequences can be explained, assuming that the displacement const. of all the series is 780 cm.<sup>-1</sup> or 0, on the basis of Langer's perturbation theory.

N. M. B.

**Photo-electric measurement of the absorption of sodium resonance radiation.** F. FAIRBROTHER and J. L. TUCK (Trans. Faraday Soc., 1936, 32, 624—633; cf. A., 1935, 466).—A photo-electrometric method for measuring the intensity of a beam of Na resonance light with a precision of  $\pm 0.1\%$  is described, and measurements of absorption between 210° and 100° are recorded. The ratio (intensity of transmitted light)/(intensity of incident light) is a nearly linear function of the no. of Na atoms in the path of the beam up to 45% absorption. Beer's law is followed over 25% of the absorption.

F. L. U.

**Effect of a magnetic field on the absorption spectrum of diatomic sulphur molecules.** J. GENARD (Physica, 1936, 3, 125—130; cf. A., 1935, 1045).

N. M. B.

**Molecular spectrum of sulphur vapour.** M. DESIRANT and J. DUCHESNE (Bull. Acad. roy. Belg., 1935, [v], 21, 1062—1068).—Available data are critically reviewed. Investigations towards longer  $\lambda$  in the infra-red showed a new band system, degraded towards the violet, and extending to 7765 Å.; an expression is found for the band heads. The calc. heat of dissociation is  $4.41 \pm 0.02$  e.v.

N. M. B.

**Inter-system combination lines of A III.** J. C. BOYCE (Physical Rev., 1936, [ii], 49, 351).—Data and classifications for 6 of the lines found in the extreme ultra-violet are tabulated, and revised vals. for the singlet terms previously reported are given (cf. A., 1935, 1291).  $\lambda$  of the "forbidden" lines of A III are calc.; one of them agrees closely with a nebular line at  $\lambda$  7135.6.

N. M. B.

**Electron-optical investigations of the glow emission of nickel in caesium vapour.** D. SCHENK (Z. Physik, 1936, 98, 753—758).

A. B. D. C.

**First spark spectrum of copper.** A. G. SHENSTONE (Phil. Trans., 1936, A, 235, 195—243).—The spectrum of the Cu-cathode Schuler tube has been photographed in the range 10,000—600 Å. Tables



of predicted and identified terms, odd and even terms, and full data on  $\lambda$ , intensity, wave-no., and classification for 1350 lines are given. N. M. B.

**Extreme ultra-violet spectra of zinc and cadmium.** L. BLOCH and E. BLOCH (Ann. Physique, 1936, [xi], 5, 325—354).—Using normal and tangent grating spectrographs and an oscillating electrodeless discharge, complete  $\lambda$  and intensities are tabulated for the regions Cd 2322—221, and Zn 2349—227 Å. A fairly complete separation of the Cd II, III, IV, and Zn II, III, IV, spectra has been effected, and a classification of the fundamental multiplets of Cd IV and Zn IV is proposed. N. M. B.

**Intensity distribution of red cadmium lines excited by electron collisions in molecular rays.** R. MINKOWSKI (Z. Physik, 1936, 98, 791).—A printing error is corr. (cf. A., 1935, 1045). A. B. D. C.

**Anomalous dispersion of the first doublets of  $\text{Sr}^+$  and of  $\text{Ba}^+$ .** L. ALLEGRETTI (Atti R. Accad. Lincei, 1935, [vi], 22, 256—258).—The ratio of the anomalous dispersion coeffs.,  $N_1/N_2$ , for the first doublet of the principal series of  $\text{Sr}^+$  and  $\text{Ba}^+$  has the val. 2.07 and 2.16, respectively. O. J. W.

**Absorption of monochromatic light in iodine vapour.** J. HARDING (Phil. Mag., 1935, [vii], 21, 773—778).—The absorption of the 5461, 4358 Å. Hg lines by I vapour  $\propto$  the pressure up to 2.5 cm. The absorption of  $\lambda$  5461 Å. is increased by the presence of 1.8 cm. of He. For  $\lambda$  4358 Å. He has no effect. H. J. E.

**Spectrum of trebly ionised thorium.** R. J. LANG (Canad. J. Res., 1936, 14, A, 43—47).—The spectrum of Th IV has been analysed. The terms  $7P$ ,  $6D$ ,  $7D$ ,  $8D$ ,  $7S$ ,  $8S$ ,  $9S$ ,  $5F$ , and  $5G$  have been found. The ionisation potential of  $\text{Th}^{+++}$  is 29.38 volts. A. J. M.

**Stabilisation of a glow discharge in a homogeneous field in air at atmospheric pressure by means of electrolytically produced films of aluminium oxide.** T. RUMMEL (Naturwiss., 1936, 24, 158).—It was found possible to maintain a stable glow discharge between two plane, parallel Al electrodes covered electrolytically with a film of  $\text{Al}_2\text{O}_3$  (500  $\mu$ ). The stabilising effect of the  $\text{Al}_2\text{O}_3$  is due to the arrangement of pores in the film, which run from the surface to the base, and give a favourable ratio for the length- to cross-section-conductivity. A. J. M.

**Positive ionic current on the glow cathode in a gas discharge.** M. J. DRUYVESTYEN (Physikal. Z. Sovietunion, 1936, 8, 579—581).—The method employed by Gvozdozer (A., 1935, 1293) is criticised. A. J. M.

**Positive ionic current on the glow cathode in a gas discharge.** S. GVOZDOZER (Physikal. Z. Sovietunion, 1936, 8, 582—583).—A reply to Druyvesteyn (preceding abstract). A. J. M.

**Electrical properties of the interrupted arc.** K. GAULRAPP (Ann. Physik, 1936, [v], 25, 705—727).—Oscillograph records of current and voltage as the electrodes are separated have been obtained with a no. of metallic electrodes in air and  $\text{H}_2$  at various pressures. At low pressures the p.d. across a short

arc is independent of the current and length of the arc. Vals. are given for a no. of metals. Metals can be divided into three groups according to the type of trace left on the cathode. A const.-burning a.c. arc is described. L. J. J.

**Fine structure of sudden luminous discharges obtained by discharging a condenser across a gas tube.** M. LAPORTE and (Mlle.) PIERREJEAN (Compt. rend., 1936, 202, 643—645).—Arc and condensed spark spectra of A and Hg have been examined with a rotating mirror. In the cold Hg-A tube, arc and spark spectra of A are emitted; in the hot tube the arc spectrum of Hg is superimposed. L. J. J.

**"Tube" discharges.** R. SEELIGER and K. SOMMERMEYER (Z. Physik, 1936, 98, 733—739).—Constriction of electric discharges observed in electro-negative gases is explained by the electrons normally diffusing outwards, forming negative ions which return towards the discharge. A. B. D. C.

**Nebular red-shift.** R. J. KENNEDY and W. BARKAS (Physical Rev., 1936, [ii], 49, 449—452).—The possible effect of free electrons in a highly ionised gas on the frequency of light traversing it was investigated. Electrons to a density of about  $5 \times 10^{12}$  per c.c. were produced in a series of low-voltage arcs through which passed light of  $\lambda$  5461 Å. No frequency shift was observed with an interferometer in vac. sensitive to 2 parts in  $10^{10}$ . Results indicate that nebular red-shift is not due to interstellar electrons. N. M. B.

**Width of the  $K\alpha_1$  line of molybdenum.** J. WEIGLE (Compt. rend., 1936, 202, 564—566).—The width, measured with a curved mica crystal, is  $0.190 \pm 0.005$  X. T. G. P.

**Monochromatic cobalt  $K\alpha$  radiation (1.787 Å.).** E. I. SOVZ and V. L. CHEIFETZ (Rept. Centr. Inst. Met., 1934, No. 17, 234—236).—The  $K\alpha$  and  $K\beta$  Co radiations were separated by a filter composed of an electrolytic deposit of Fe on Al foil (0.01 mm. thick). CH. ABS. (e)

**Atomic scattering factors of aluminium, nickel, and copper for Cu  $K\alpha$  radiation and their relation to the theory of X-ray dispersion.** G. W. BRINDLEY (Phil. Mag., 1935, [vii], 21, 778—790; cf. this vol., 3).—Data for Ni and Cu were restandardised using Al powder, in place of KCl, as a basis for intensity measurements. H. J. E.

**X-Ray investigation of atomic vibrations in zinc.** G. W. BRINDLEY (Phil. Mag., 1936, [vii], 21, 790—808; cf. this vol., 412).—Reflecting planes making specially small angles with the basal plane of the structure give low scattering factors, whilst planes making angles of approx.  $90^\circ$  give high scattering factors. This anomaly is discussed in relation to Zener's results (this vol., 273). The lattice vibrations of Zn are calc. H. J. E.

**Al  $K\beta$  bands from Al-Cu alloys.** S. YOSHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 243—248).—The bands of the X-ray spectrum emitted when targets of pure Al and Al-Cu alloys were bombarded with electrons have been studied. With pure Al (single band) the results agree with the assumption of three free valency electrons. With the alloys the



band separates into two, and the intensity of the second band increases with the % of Cu. A theoretical interpretation is given. R. S. B.

**Intensity ratio  $E_{\alpha\alpha'}/E_{\beta\gamma}$  and yield coefficients  $u_{\alpha\alpha'}$  and  $u_{\beta\gamma}$  for the characteristic  $K$ -radiation from Co (27) to Te (52).** W. GROTHEY (Ann. Physik, 1936, [v], 25, 577—599).—An elaboration of the differential filter method of Küstner (A., 1931, 993) has been employed to determine  $E_{\alpha\alpha'}/E_{\beta\gamma}$ , with an accuracy of  $\pm 6\%$ , for 20 elements from Co to Te and their compounds with light atoms.  $E_{\alpha\alpha'}/E_{\beta\gamma}$  decreases with increasing at. no., and becomes const. after at. no. 47. L. J. J.

**Wave-length determinations for the  $L$  series of elements 29 copper to 26 iron.** F. TYRÉN (Z. Physik, 1936, 98, 768—774). A. B. D. C.

**X-Ray diffraction by a film of counted molecular layers.** C. HOLLEY and S. BERNSTEIN (Physical Rev., 1936, [ii], 49, 403).—Using a film of 301 mol. layers of Ba stearate on glass (cf. Blodgett, A., 1935, 931) and having a grating space of 48.8 Å., the thickness of two mol. layers, the first three orders of the  $L$  series and the  $M$  line of W were photographed. N. M. B.

**Photo-electric effect of aluminium films evaporated in vacuum.** E. GAVIOLA and J. STRONG (Physical Rev., 1936, [ii], 49, 441—443).—Sensitivity curves of Al films deposited by evaporation in vac. were determined. A new threshold val. of 2830 Å. and a selective max. around 2700 Å. were found. N. M. B.

**Photo-effect at thin adsorbed layers of alkali metals.** V. GEI and I. TRUTEN (Physikal. Z. Sovietunion, 1935, 8, 342—351).—The production of multimol. layers of alkali metals on  $\text{SiO}_2$  gel is described. Ohm's law is obeyed by the metal in this state when the e.m.f.  $< 5$  volts, and the photo-effect is normal, with long-wave limits for K 7800 Å. and Cs 9550 Å. R. S.

**Determination of the thermionic work function of nickel by a new method.** R. M. BOWIE (Iowa State Coll. J. Sci., 1934, 9, 131—132).—The electron emission from a cooling Ni sphere charged a condenser, which was discharged through a ballistic galvanometer. CH. ABS. (e)

**Changes of emission potentials of metals near the m.p.** H. KURZKE (Z. Physik, 1936, 98, 684—691).—Theoretical. These changes imply a change in binding energy of "free" electrons near the m.p. A. B. D. C.

**Ionisation probability of  $\text{He}^{++}$ .** W. BLEAKNEY and L. G. SMITH (Physical Rev., 1936, [ii], 49, 402; cf. *ibid.*, 1933, [ii], 43, 378).—The electron energy-ionisation current curve shows a sharp rise at 79 volts attributed to  $\text{He}^{++}$ . At 300 volts the current reaches a max. and is 1.1% of that ascribed to  $\text{He}^+$ , indicating that 0.55% of the ions are doubly charged. N. M. B.

**Effective cross-sections for ion collisions in the absence of resonance.** F. WOLF (Ann. Physik, 1936, [v], 25, 527—544).—Collisions of  $\text{He}^+$  with Ne and A,  $\text{Ne}^+$  with He, and  $\text{H}_2^+$  with He, Ne, and A, at 30—1030 volts, have been studied. With increas-

ing velocity ( $v$ ), the effective cross-section ( $\sigma$ ) falls steeply at low  $v$ , owing to the decrease in the angular scattering; at high  $v$ ,  $\sigma$  increases slowly, owing to transference of charge, which is marked only at high  $v$ , in contrast to the effect for strict resonance.  $\sigma$  is markedly  $<$  the kinetic theory vals. (e.g.,  $< 0.3$  of this val. for  $\text{Ne}^+$ -He collisions). For a given ion, the scattering decreases with increasing mass of the collision partner.  $\sigma$  due to transference of charge corresponds roughly with the resonance principle. L. J. J.

**Individual effects in ion collisions in the absence of resonance ( $\text{H}^+$ ,  $\text{H}_2^+$ ,  $\text{He}^+ \rightarrow \text{He}$ , Ne, A).** F. WOLF (Ann. Physik, 1936, [v], 25, 737—756).—The rôle of charge transference in the collisions  $\text{H}_2^+ \rightarrow \text{A}$ , Ne, He,  $\text{H}^+ \rightarrow \text{A}$ , and  $\text{He}^+ \rightarrow \text{A}$  has been investigated with velocities of 30—1030 volts. For  $\text{H}_2^+ \rightarrow \text{A}$ , as with other collisions, scattering decreases with increasing velocity, whilst ionisation is absent up to 1000 volts. The theoretical form of the charge transference cross-section ( $I$ )-velocity curve is realised only for  $\text{He}^+ \rightarrow \text{A}$  and  $\text{H}^+ \rightarrow \text{A}$ . For  $\text{H}_2^+ \rightarrow \text{A}$ ,  $I$  is large and approx. equal to the effective cross-section, increasing at both high and low velocities; the dissociation  $\text{H}_2^+ \rightarrow \text{H} + \text{H}^+$  is absent. For  $\text{H}_2^+ \rightarrow \text{Ne}$ ,  $I$  is extremely small at all velocities; dissociation is considerable. L. J. J.

**Collision of corpuscular rays with solids.** K. SOMMERMEYER (Ann. Physik, 1936, [v], 25, 481—511).—Mainly theoretical. Sputtering of metals cannot arise from impact of electrons even of high energy, nor by excitation energy of colliding mols. The theory of cathodic sputtering by local heating is developed. Sputtering takes place from locally vaporised collision areas immediately above the crit. temp., and should increase with decreasing  $t_c$ , and be inversely  $\propto$  the thermal conductivity of the cathode. Data for sputtering of KI by  $\text{A}^+$  rays are in agreement; the emission follows Knudsen's cosine law, and the degree of dissociation of the sputtered KI corresponds with a temp. about 3000° abs. The emission of secondary electrons is in agreement with the theory. L. J. J.

**Effect of the electric field on hydrogen atoms in atomic beam experiments.** H. SCHEFFERS and J. STARK (Physikal. Z., 1936, 37, 217—220; cf. A., 1934, 1053).—The deviation of a beam of H atoms in an inhomogeneous electric field gives the val.  $(3 \pm 1) \times 10^{-25}$  e.c. for the polarisability ( $\alpha$ ). A. J. M.

**Calculation in atomic beam experiments in the electric field.** H. SCHEFFERS (Physikal. Z., 1936, 37, 220—221).—Derivations of the formulæ used in computing results of at. beam experiments employing an electric field are given (cf. preceding abstract). A. J. M.

**Scattering of protons by protons.** M. A. TUVE, N. P. HEYDENBURG, and L. R. HAFSTAD (Physical Rev., 1936, [ii], 49, 402).—Data obtained for the angular range 15—45° and 320—980 kv. do not confirm White's results (cf. *ibid.*, 1935, [ii], 47, 573) for the variation of scattering with angle, but are of the order predicted by Mott's formula. N. M. B.

**Positive and neutral rays. III. Ionisation by atomic collision.** A. ROSTAGNI (Nuovo Cim.,



1934, [ii], 11, 621—634; Chem. Zentr., 1935, ii, 15).—The ionisation produced by neutral A atoms in A, or He atoms in He, increases with the velocity. The effective area of A is about 10 times that of He at the same velocity. J. S. A.

**Use of the magnetic field in the formation of ion-electron beams.** A. A. SLUTZKIN (Physikal. Z. Sovietunion, 1935, 8, 255—269).—The influence of the strength and direction of the magnetic field on the ion-electron beam generated in a magnetron system has been studied. R. S.

**Anomalous secondary electron emission.** L. MALTER (Physical Rev., 1936, [ii], 49, 478).—Al oxidised electrolytically in a bath of borax and  $\text{H}_3\text{BO}_3$  assumes a resistive surface film having a high emission coeff. for secondary electrons. Electron bombardment results in the establishment of an intense potential gradient through the resistive oxide film, and this gradient gives rise to anomalous secondary electron emission. N. M. B.

**Absolute values of the electron mobility in hydrogen.** N. E. BRADBURY and R. A. NIELSEN (Physical Rev., 1936, [ii], 49, 388—393).—A new electrical shutter method for measuring electron mobilities in gases is described. Results are compared with those of the Compton mobility equation. N. M. B.

**Scattering of high-speed electrons.** A. MATVEEV and F. VERGUNAS (Physikal. Z. Sovietunion, 1935, 8, 430—442).—The angular distribution of electrons of 200—240 kv. energy after nuclear scattering in Al, Pb, and Ag is investigated. The experimental results are compared with the theories of nuclear scattering and a difference is found in the magnitude of scattering with light and heavy nuclei. W. R. A.

**Motion of electrons in crossed electric and magnetic fields with space-charge.** L. TONKS (Physikal. Z. Sovietunion, 1935, 8, 572—578).—The conclusions of Braude (A., 1935, 1294) concerning the absence of a magnetic cut-off in the presence of a space-charge are criticised. A. J. M.

**"Cut-off" in the plane magnetron with space-charge.** S. J. BRAUDE (Physikal. Z. Sovietunion, 1935, 8, 584—586).—A reply to Tonks (preceding abstract). A. J. M.

**At. wt. of carbon.** G. P. BAXTER and A. H. HALE (J. Amer. Chem. Soc., 1936, 58, 510—515).—Gravimetric data obtained by combustion of pyrene, chrysene,  $\text{C}_6\text{H}_3\text{Ph}_3$ , and anthracene in  $\text{O}_2$  give the val. 12.009. E. S. H.

**Masses of light atoms.** M. L. OLIPHANT (Nature, 1936, 137, 396—397).—The masses of elements up to and including F are recalculated from transformation data and Aston's new data (this vol., 400). The high val. found for the mass of the neutron (1.0091) raises the question of its stability. Plotting the departure of the mass of an at. species from a whole no. in terms of  $^{16}\text{O}=16.0000$  against the mass no. gives a smooth curve showing repeated oscillations. Deductions concerning the stability of at. species are made, and the probable existence of He of mass 5.0125 is predicted. L. S. T.

**At. wt. of radiogenic lead.** F. HECHT and E. KROUPA (Z. anorg. Chem., 1936, 226, 248—256).—At. wts. of Pb determined by nephelometric titration with  $\text{AgNO}_3$  of  $\text{PbCl}_2$  obtained from various minerals are as follows: pitchblende from Great Bear Lake, 206.080; uraninite from Wilberforce, 206.183; pitchblende from Katanga, 206.044; ordinary galena, 207.216. The HCl-insol. part of the Katanga pitchblende was used. F. L. U.

**At. wt. of uranium.** O. HÖNIGSCHMID and F. WITTNER (Z. anorg. Chem., 1936, 226, 289—309).—The prep. and purification of  $\text{UCl}_4$  and  $\text{UBr}_4$  from four minerals of different origin and geological age are described. The mean at. wt. of U, determined argentometrically, from 18 analyses of  $\text{UCl}_4$ , is 238.073, and from 20 analyses of  $\text{UBr}_4$ , 238.076. The final val. is given as  $238.07 \pm 0.02$ . The differences in the vals. given by the four minerals are within the experimental error, and afford no support for the suggestion that minerals of different geological age contain metal of varying isotopic composition. F. L. U.

**Small chemical separation of the chlorine isotopes.** R. S. BRADLEY (Nature, 1936, 137, 403—404).—The slight increase in  $d$  observed for  $\text{CCl}_4$  after some of it has been decomposed by refluxing with Na amalgam is attributed to a small separation of the Cl isotopes, the light isotope reacting preferentially. No isotopic separation occurs on repeated distillation of  $\text{CCl}_4$  alone (cf. A., 1929, 484). L. S. T.

**Isotope separation for thallium by valency exchange?** J. ZIRKLER (Z. Physik, 1936, 98, 790).—Previous results (this vol., 282) suggest that valency exchange gives isotopic separation. A. B. D. C.

**Periodic system of the elements and its gaps.** I. NODDACK (Uspechi Chim., 1935, 4, 11—21).—Negative results were obtained in a search for elements of at. no. 61 and 87 in minerals which might contain them. CH. Abs. (e)

**Scattering of fast  $\beta$ -rays.** D. SKOBEŁTZYN and E. STEPANOVA (Nature, 1936, 137, 456).—The anomalous scattering of fast  $\beta$ -rays observed in  $\text{N}_2$  is probably due to an intranuclear effect. L. S. T.

**$\beta$ -Rays of high energy.** J. A. GRAY and W. J. HENDERSON (Physical Rev., 1936, [ii], 49, 477).—Intensity measurements show that there is no indication of the emission of  $\beta$ -rays of high energy beyond the main spectrum of Ra-E. N. M. B.

**$\beta$ -Activity induced by  $\gamma$ -rays.** W. RARITA (Physical Rev., 1936, [ii], 49, 475).—A nucleus which is not naturally  $\beta$ -active may be stimulated to emit a  $\beta^-$  or  $\beta^+$  particle under the influence of a  $\gamma$ -ray. The mechanism and emission cross-section are examined. N. M. B.

**Deviation of  $\beta$ -rays by nitrogen nuclei.** M. LECOIN (Compt. rend., 1936, 202, 839—840).—The ratio of the loss of energy to the initial energy of a  $\beta$ -ray in  $\text{N}_2$ , when deviated by  $> 10^\circ$ , has been determined for a no. of rays, and the effective sections of the nucleus for shocks corresponding with different energy losses have been calc. These are considerably  $>$  predicted by theory. M. S. B.



**Influence of pressure and temperature on the recombination coefficient and ionisation by  $\gamma$ -rays in air and carbon dioxide.** W. MÄCHLER (Physikal. Z., 1936, 37, 211—213).—The recombination coeff.  $\alpha$  was determined for  $\text{CO}_2$  up to 25 atm., and from 18° to 52°. Results agree closely with those of Langevin (Ann. Chim. Phys., 1903, 28, 433).  $\alpha$  for air decreases with rising temp., but for  $\text{CO}_2$  there is a very small increase. A. J. M.

**$\gamma$ -Rays of radium-*E*.** J. A. GRAY and J. F. HINDS (Physical Rev., 1936, [ii], 49, 477).—Absorption and intensity measurements show that the  $\gamma$ -rays of Ra-*E* are really X-rays produced by  $\beta$ -rays in escaping from the atoms in which they are produced. N. M. B.

**Scattered and secondary radiation of hard  $\gamma$ -rays.** W. BOTHE and W. GENTNER (Naturwiss., 1936, 24, 171—172; cf. A., 1934, 342, 713).—The dependence of the intensity of secondary radiation of hard  $\gamma$ -rays on the thickness of the radiator has been investigated for very thin layers of Pb (0.06 mm.) and Al (0.2 mm.). The thinness of the layers avoids the complications due to the multiple Compton scattering. A. J. M.

**Excitation of  $\gamma$ -rays by fast neutrons.** S. KIKUCHI, H. AOKI, and K. HUSIMI (Nature, 1936, 137, 398).—The relation between at. no. and the capture cross-sections for fast neutrons in various elements is tabulated. Discontinuities which may be connected with the internal structure of the nuclei of light elements are pointed out. L. S. T.

**Disintegration of the deuteron by  $\gamma$ -rays.** H. HALL (Physical Rev., 1936, [ii], 49, 401—402).—An upper limit to the range of the proton-neutron interaction is discussed in relation to the val. of the cross-section for photo-electric disintegration of a deuteron by  $\gamma$ -rays (cf. Bethe, A., 1935, 279). N. M. B.

**Position of the lowest energy term of the deuteron.** V. RAJEVSKI (Physikal. Z. Sovietunion, 1935, 8, 511—515).—The position of the 1's term of the deuteron can be obtained from the experimental val. of the scattering cross-section of slow neutrons in  $\text{H}_2$ . The term separation  ${}^3E-{}^1E$  thus derived is  $1.7 \times 10^6$  e.v. Consideration of the scattering of rapid neutrons in  $\text{H}_2$  leads to a val. for the radius of the deuteron rather  $> 3 \times 10^{-13}$  cm. A. J. M.

**Relative positions of the resonance levels for the capture of neutrons by silver and iodine.** P. PREISWERK and H. VON HALBAN, jun. (Compt. rend., 1936, 202, 840—842).—The energy of the resonance level of I is shown to be  $>$  that of the isotopes of Ag which form radio-Ag (period 22 sec.) by capturing a neutron. M. S. B.

**Neutron capture and the structure of the atomic nucleus.** N. BOHR (Naturwiss., 1936, 24, 241—245).—A lecture.

**Determination of the selective absorption regions of slow neutrons.** D. F. WEEKES, M. S. LIVINGSTON, and H. A. BETHE (Physical Rev., 1936, [ii], 49, 471—473).—A method is described for measuring energies of neutrons outside the thermal energy range (cf. Fink, this vol., 264), but in the

range deduced from the Wigner-Breit resonance theory of selective absorption. N. M. B.

**Absorption of neutrons detected by boron and lithium.** D. P. MITCHELL (Physical Rev., 1936, [ii], 49, 453—458).—Data are given for the neutron-nucleus collision cross-sections of H,  $\text{HgO}$ , Sm, Al, B, C, Fe, and Li for neutrons that are detectable by the B and by the Li neutron capture reaction and that are strongly absorbed by Cd. The vals. for the three first named differ considerably by the two detectors, and for the others are the same within 10%. Variation of the absorption coeff. of Cd, B, and Li with intensity, the effect of filtering through Ag, Cd, B, and Li, and through paraffin at 293° and 90° abs., and the velocity distribution were investigated. N. M. B.

**Absorption of neutrons in water, paraffin, and charcoal.** L. ARZIMOVITSCH, I. KURTSCHATOV, G. LATISCHEV, and V. CHROMOV (Physikal. Z. Sovietunion, 1935, 8, 472—486).—The  $\gamma$ -radiation, which results from the passage of neutrons through substances, is investigated and its intensity measured. The absorption coeffs. of neutrons for these substances are given and the effective cross-sections of neutrons compared with at. nuclei are ascertained. W. R. A.

**Scattering of slow neutrons.** A. C. G. MITCHELL, E. J. MURPHY, and L. M. LANGER (Physical Rev., 1936, [ii], 49, 400).—Investigations previously reported (cf. A., 1935, 1441) are extended to a determination of the % scattering curves and data for C, Mg, Al, S, Cr, Mn, Ni, Zn, Ag, Cd, and Bi. The respective relative cross-sections for scattering are 3.2, 2.8, 0.9, 0.8, 1.3, 2.0, 17.0, 3.4, 5.9, 1.2, and 9.5. Results are compared with those by the "absorption" method (cf. Dunning, *ibid.*, 1186). N. M. B.

**Selective scattering of slow neutrons.** A. C. G. MITCHELL, E. J. MURPHY, and M. D. WILTAKER (Physical Rev., 1936, [ii], 49, 401; cf. preceding abstract).—Using Ag, Rh, and In detectors, data are given for % scattering by Fe, Ni, Pb, Cu, Sn, Al, Bi, C, and Zn. Vals. differ widely for a given element with different detectors, and possible explanations are discussed. N. M. B.

**General theory of fluctuations in radioactive disintegration.** A. RUARK and L. DEVOL (Physical Rev., 1936, [ii], 49, 355—367; cf. this vol., 5).—Mathematical. N. M. B.

**Coincidence investigations on nuclear processes.** W. BOTHE and H. J. VON BAeyer (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 195—197; Chem. Zentr., 1935, ii, 646).—A concentric arrangement of eight counters around a central source and counter, with interposed absorbing screens, gave the expected coincidences between  $\beta$ - and  $\gamma$ -radiation from Rn. With artificially radioactive B, no coincidences between proton and  $\gamma$ -ray emission were found, in support of the views of Bothe and Becker (A., 1931, 1208). J. S. A.

**Capacity of the elements for disintegration.** T. SEXL (Physikal. Z., 1936, 37, 221—222).—A



formula used by Stetter (this vol., 265) is not applicable for elements with at. no. in the region of 5.

A. J. M.  
**Slowing down of neutrons.** S. GOUDSMIT (Physical Rev., 1936, [ii], 49, 406; cf. Wick, this vol., 264).—Mathematical.  
 N. M. B.

**Method for investigating artificially radioactive elements with very short periods.** K. S. KNOL and J. VELDKAMP (Physica, 1936, 3, 145—146).—A wheel, coated at the circumference with the element under investigation, rotates along the bombarding neutron source and is used with one or more counters. For  $\text{Li}_2\text{CO}_3$  bombarded with slow neutrons the resulting half-period is 0.7 sec., ascribed to the active isotope  ${}^3\text{Li}^8$ .  
 N. M. B.

**Efficiencies of production and the half-lives of radio-carbon and radio-nitrogen.** S. K. ALLISON (Proc. Camb. Phil. Soc., 1936, 32, 179—182).—The half-life of the activity produced by bombardment of a thick, solid target of  $\text{B}_2\text{O}_3$  by deuterons varies with time elapsing after the bombardment, the limits being 17.5 and 21.5 min. The low vals. are obtained immediately after bombardment, and are due to radio-N obtained from deuteron bombardment of C present as an impurity in the  $\text{B}_2\text{O}_3$ . Only radio-C is produced by the deuteron bombardment of  $\text{B}_2\text{O}_3$ , the mean half-life of radio-C removed from  $\text{B}_2\text{O}_3$  being  $21.0 \pm 0.6$  min. The half-life of radio-N obtained by bombardment of graphite by protons and deuterons, respectively, is the same ( $10.3 \pm 0.3$  min.). The efficiencies of production of radio-C and radio-N by various methods are compared.  
 A. J. M.

**Radiations emitted from artificially produced radioactive substances. I. Upper limits and shapes of the  $\beta$ -ray spectra from several elements.** F. N. D. KURIE, J. R. RICHARDSON, and H. C. PAXTON (Physical Rev., 1936, [ii], 49, 368—381).—The  $\beta$ -ray spectra of  $\text{N}^{13}$ ,  $\text{F}^{17}$ ,  $\text{Na}^{24}$ ,  $\text{Si}^{31}$ ,  $\text{P}^{32}$ ,  $\text{Cl}^{41}$ , and  $\text{K}^{42}$ , investigated by measuring the curvature of the tracks due to the  $\beta$ -rays in a cloud-chamber traversed by a known magnetic field, give results in good agreement with theory (cf. Konopinski, A., 1935, 1048), which, however, gives an upper limit  $>$  is found from the data. The upper limit of  $\text{N}^{13}$  is 1.5 mv.  
 N. M. B.

**Induced radioactivity of mercury.** E. B. ANDERSEN (Nature, 1936, 137, 457).—Bombardment of  $\text{HgO}$  by neutrons from a Rn-Be source yields an active product, probably  ${}^{80}\text{Hg}^{205}$ , decaying with a period of  $40 \pm 5$  hr.  $\text{CCl}_4$ , irradiated with neutrons, yields an active isotope of S decaying with a period  $> 2$  months. Irradiation of  $\text{Bi}_2\text{O}_3$  gives no measurable activity.  
 L. S. T.

**New transformation processes in the irradiation of uranium with neutrons.** L. MEITNER and O. HAHN (Naturwiss., 1936, 24, 158—159).—In addition to the elements of half-life 13 min., 100 min., and 3 days, respectively, previously discovered (A., 1935, 278, 1050), an element of half-life 12 hr. has been obtained by irradiation of U with neutrons. It is a higher homologue of the Pt group (eka-Os $^{237}$ ). For the investigation of the

processes by which these and other transformations with U occur, the activity produced in U by bombardment with rapid and with slow (through paraffin) neutrons, respectively, has been examined. Three concurrent processes take place. (1)  $\text{U}^{238} + n \rightarrow \text{Th}^{235} + \alpha$ ;  $\text{Th}^{235} \xrightarrow{\beta} \text{Pa}^{235} \xrightarrow{\beta} \text{U}^{235} \xrightarrow{\beta} \text{eka-Re}^{235} \rightarrow (?)$ . This occurs only when slow neutrons are used. (2)  $\text{U}^{238} + n \rightarrow \text{U}^{237} + 2n_1$ ;  $\text{U}^{237} \xrightarrow{\beta} \text{eka-Re}^{237} \xrightarrow{\beta} \text{eka-Os}^{237} \xrightarrow{\beta} \text{eka-Ir}^{237} (?)$ . This process is confirmed by the fact that the 13-min. element (eka-Re $^{237}$ ;  $Z=93$ ) is formed in smaller amount when the bombarding neutrons are slower. The process is brought about by rapid neutrons.  $\text{U}^{237}$  has half-life 40 sec.  $\text{U}^{238}$ , an  $\alpha$ -radiator of long life, and  $\text{U}^{237}$ , a  $\beta$ -radiator of short life, are analogous to  $\text{Th}^{232}$  and U-Y. (3)  $\text{U}^{238} + n_1 \rightarrow \text{U}^{239}$ ;  $\text{U}^{239} \xrightarrow{\beta} \text{eka-Re}^{239} \xrightarrow{\beta} \text{eka-Os}^{239} \xrightarrow{\beta} \text{eka-Ir}^{239}$ . This process occurs for bombardment with slow neutrons. Half-lives are eka-Re $^{239}$  2.2 min., eka-Os $^{239}$  59 min., eka-Ir $^{239}$  3 days.  
 A. J. M.

**Absorption of penetrating corpuscular radiation under different zeniths.** G. BERNARDINI and D. BOCCIARELLI (Ric. sci. Prog. tec., 1935, 6, 33—39; Chem. Zentr., 1935, ii, 12).—At three different inclinations, a superimposed soft and a hard radiation were detected, which were similarly distributed spatially.  
 J. S. A.

**Measurement of cosmic-ray showers by means of Geiger-Müller counters.** C. G. MONTGOMERY and D. D. MONTGOMERY (J. Franklin Inst., 1936, 221, 59—64).—Mathematical. A statistical basis for the formulation of experimental data is deduced.  
 L. J. J.

**Can protons represent the primary cosmic rays at sea level?** W. F. G. SWANN (Physical Rev., 1936, [ii], 49, 478; cf. A., 1935, 1442).—Difficulties in this view are discussed. The protons probably function through the production of secondary rays which are then observed by the counters.  
 N. M. B.

**Variations of properties of cosmic shower radiations with altitude.** J. C. STEARNS and D. K. FROMAN (Physical Rev., 1936, [ii], 49, 473—474, 591).—Curves for rates of shower detection in the determination of optimum thickness of Pb for shower production at altitudes of 120, 5300, 10,800, and 14,200 feet show no variation in shape or optimum Pb thickness with altitude, but the shape and max. vary with the method used. Curves for absorption measurements with Pb thickness are given.  
 N. M. B.

**Cloud chamber photographs of counter-selected cosmic-ray showers.** E. C. STEVENSON and J. C. STREET (Physical Rev., 1936, [ii], 49, 425—428).—Cosmic-ray showers from a Pb plate 1.3 cm. thick in a large cloud chamber controlled by three counters are described and discussed.  
 N. M. B.

**Direct photographic tracks of atomic cosmic-ray corpuscles.** T. R. WILKINS and H. ST. HELENS (Physical Rev., 1936, [ii], 49, 403).—A photograph obtained on a stratosphere flight shows a track interpreted as due to an  $\alpha$ -particle; at a point on the



path is the track of an ejected particle which is probably a proton. N. M. B.

Periods of natural and artificial radioactive bodies, the existence of shells, and the classification of atomic nuclei. B. KEVAL and (MLLE.) A. RIEDERBERGER (Compt. rend., 1936, 202, 566—567).—The existence of closed shells of protons suggests the possibility of a natural classification of at. nuclei. T. G. P.

Theory of the atomic nucleus. P. JORDAN (Naturwiss., 1936, 24, 209—216).—A review.

Structure of the electron and positron. U. KAKINUMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 249—270).—Theoretical. A wave equation for the electron similar to Schrödinger's is derived on the assumption of finite and continuous energy density. The radius of the electron is calc. to be approx.  $10^{-30}$  cm. The nature of the electron and positron and their bearing on cosmology are discussed. R. S. B.

Interaction between protons and neutrons. G. WATAGHIN (Compt. rend., 1936, 202, 833—835).—Theoretical. M. S. B.

Electron-neutron interaction. E. U. CONDON (Physical Rev., 1936, [ii], 49, 459—461).—Mathematical. N. M. B.

Polarisation effects in the positron theory. W. PAULI and M. E. ROSE (Physical Rev., 1936, [ii], 49, 462—465).—Mathematical. N. M. B.

Light quanta and neutrinos. P. JORDAN (Z. Physik, 1936, 98, 759—767).—Postulates two neutrinos corresponding with positive and negative electrons. A. B. D. C.

Consequences of Dirac's positron theory. W. HEISENBERG and H. EULER (Z. Physik, 1936, 98, 714—732).—Theoretical. Necessary modifications of Maxwell's equations are deduced. A. B. D. C.

Effects of exchange forces on the excitation function of  $\text{Li}^7$  under proton bombardment. M. OSTROFSKY, W. E. BLEICK, and G. BREIT (Physical Rev., 1936, [ii], 49, 352—354).—Van Vleck's recently reported effective potential due to Majorana exchange forces varies with proton or neutron velocity (cf. A., 1935, 1296). The effect of this variation on the shape of the excitation curve of Li under proton bombardment is negligible, but the position of stationary proton levels is largely affected. Agreement of calculations with the mass defect of  $\text{Be}^8$  is improved by using the exchange potential. N. M. B.

Depth distribution of energy absorbed from cathode rays by aluminium. K. GENTNER and W. ROLLWAGEN (Physikal. Z., 1936, 37, 214—215).—The experimental distribution curve agrees with theory. A. J. M.

Lower limit of the helium ground state calculated by Ritzsch's method. W. ROMBERG (Physikal. Z. Sovietunion, 1935, 8, 516—527).—Calculations of the lower limit of the ground state for He by the methods of Hylleraas (A., 1928, 698; 1929, 616), Ritzsch (Kellner, A., 1927, 912), and Weinstein (A., 1932, 787) are discussed. The method of Ritzsch gives good results. A. J. M.

Analytical wave-functions for beryllium-like atoms. V. FOCK and (Miss) M. PETRASHEN (Physikal. Z. Sovietunion, 1935, 8, 359—368). Analytical wave-functions of H-like type are constructed for atoms with four electrons and an arbitrary nuclear charge. Energy vals. are compared with those calc. by the method of self-consistent field with and without exchange, and with observed vals. for Be,  $\text{B}^{+1}$ ,  $\text{C}^{+2}$ ,  $\text{N}^{+3}$ ,  $\text{O}^{+4}$ . A semi-empirical formula for the energy in terms of the nuclear charge is deduced. W. R. A.

Deuteron theory. D. BLOCHINZEV (Physikal. Z. Sovietunion, 1935, 8, 270—274).—The theory of the deuteron is discussed from the relativistic viewpoint. R. S.

Atomic dimensions. M. PIERUCCI (Nuovo Cim., 1934, [ii], 11, 690—700; Chem. Zentr., 1935, ii, 322; cf. A., 1921, ii, 583).—At. radii are exact multiples of 0.0398 Å. This rule is consistent with wave mechanics. H. J. E.

Definition of electromagnetic field in terms of potentials; magnetic moment of the electron. A. PROCA (Compt. rend., 1936, 202, 641—643).—A complete description of an electromagnetic field must take into account the magnetic as well as the electric potential. The existence of the magnetic moment of the electron is implicit in the Maxwell-Lorentz equations. L. J. J.

Proper mass of the photon and the electromagnetic tensor. J. GÉHÉNIAU (Compt. rend., 1936, 202, 559—560).—Mathematical. T. G. P.

Franck-Condon principle. A. S. COOLIDGE, H. M. JAMES, and R. D. PRESENT (J. Chem. Physics, 1936, 4, 193—211).—Theoretical. M. S. B.

Interaction of "spinor"-particles. P. JORDAN (Z. Physik, 1936, 98, 709—713).—Theoretical. A. B. D. C.

Photon counters for visible and ultra-violet. Z. OLLANO (Nuovo Cim., 1934, [ii], 11, 603—620; Chem. Zentr., 1935, ii, 18).—The sp. sensitivity of a variety of photo-electrically active surfaces has been determined over the spectral range indicated. J. S. A.

Application of a simplified model of the Jamin polarisation interferometer to the study of absorption. P. BARCHWITZ (Compt. rend., 1936, 202, 300—301). H. J. E.

Absorption spectrum of solid oxygen. II. A. PRICHOTKO and M. RUHEMANN (Physikal. Z. Sovietunion, 1935, 8, 294—299; cf. A., 1935, 1291).—Five band groups similar to the first two series in the visible have been observed between 4000 and 3000 Å. with layers of  $\alpha\text{-O}$  of different thickness. Preliminary results for the region below 3000 Å. are given. R. S.

Continuous absorption spectra of diatomic molecules. H. TRIVEDI (Proc. Acad. Sci. Agra and Oudh, 1935, 5, 171—186).—Mathematical. J. W. S.

Far ultra-violet absorption spectra and ionisation potentials of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ . W. C. PRICE (J. Chem. Physics, 1936, 4, 147—153).—The absorption spectra of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  for  $\lambda\lambda < 1600$  Å. give



Rydberg series of which the limits indicate  $12.56 \pm 0.02$  and  $10.42 \pm 0.01$  volts, respectively, as the ionisation potentials of the two mols. The analysis agrees with Mulliken's prediction that the bands should be due to the excitation and removal of a non-bonding electron localised near O or S.

M. S. B.

Spin coupling in the  $^3\Sigma$ -state of phosphorus deuteride. R. W. B. PEARSE and M. ISHAQUE (Nature, 1936, 137, 457).

L. S. T.

Ultra-violet absorption in hydrogen fluoride. H. J. PLUMLEY (Physical Rev., 1936, [ii], 49, 405; cf. *ibid.*, 1935, [ii], 48, 105).—A correction.

N. M. B.

Optical properties of lithium fluoride in the extreme ultra-violet. E. G. SCHNEIDER (Physical Rev., 1936, [ii], 49, 341—345).—Variations similar to those for natural fluorite were found for the absorption coeff. of 50 laboratory-produced crystals of LiF in the extreme ultra-violet. Light lost at the surface from a transmitted beam and effects of surface cleaning and polishing were investigated. The refractive index (about 1.65 at 1200 Å.) was extended into the Schumann region by a modified min. deviation method.

N. M. B.

Influence of fluorides on the spectral absorption of coloured iron complexes. W. WEYL and H. RUDOW (Z. anorg. Chem., 1936, 226, 341—349).—Addition of F' to Fe(CNS)<sub>3</sub>, Fe salicylate, sulphosalicylate, or acetylacetonate leads to formation of the colourless FeF<sub>6</sub>'''', and thereby diminishes the intensity of coloration. Simultaneously the absorption bands are broadened and their max. shifted towards shorter  $\lambda$ , owing to loose addition of F'. The effect of added F' diminishes with rising temp., whilst simultaneous addition of H<sub>3</sub>BO<sub>3</sub>, which yields a complex with F', shifts the bands towards longer  $\lambda$ .

J. W. S.

Photochemistry of nitrites, nitrates, and nitro-compounds. H. W. THOMPSON and C. H. PURKIS (Trans. Faraday Soc., 1936, 32, 674—680).—Absorption spectra of Me and Et nitrites, MeNO<sub>3</sub>, EtNO<sub>3</sub>, nitro-methane and -ethane have been measured. The results are discussed. V.p. of the three Me compounds have been determined over a wide range and are expressed in formulæ.

F. L. U.

Intensities in the bands of the violet cyanogen system. N. R. TAWDE (Proc. Indian Acad. Sci., 1936, 3, A, 140—147).—Vibrational intensities in the  $2\Sigma \rightarrow 3\Sigma$  system of CN, emitted by a C arc in air, are estimated by the method of heterochromatic spectral photometry. The experimental distribution of intensities is compared with that derived by the application of the Franck-Condon principle of max. transitions from the potential energy functions of Morse and of Rydberg.

O. D. S.

Absorption spectra of chromium, molybdenum, and tungsten hexacarbonyls in vapour and dissolved states. G. MILAZZO and G. SCHEIBE (Z. physikal. Chem., 1936, B, 31, 431—438).—The absorption curves in the vapour state in the visible and down to about 1600 Å. consist of three continuous absorption regions at about 3800, 2800, and 2300 Å.,

respectively. It is inferred that light absorption in all three regions leads to dissociation; to what products of dissociation they are to be attributed is uncertain. The absorption curves of the EtOH and hexane solutions are practically the same as those of the vapours.

R. C.

Werner complexes. Absorption of hexacoordinated cobalt and chromium derivatives in aqueous solution. J. P. MATHIEU (Bull. Soc. chim., 1936, [v], 3, 463—475).—The absorption spectra of 24 complexes in aq. solution have been determined in the visible region. A wide absorption band is observed in each spectrum at a position varying with the chemical lability of the co-ordinated groups. In certain cases the wide band splits into two bands.

E. S. H.

[Optical absorption of substituted benzenes. VI.] H. CONRAD-BILLROTH (Z. physikal. Chem., 1936, B, 31, 475—476).—Corrections and comments on Steurer's paper (this vol., 8).

R. C.

Influence of physical state on absorption and fluorescence spectra of organic substances. P. K. SESHAN (Trans. Faraday Soc., 1936, 32, 689—694).—The positions of some absorption bands of fluorene, naphthacene, and perylene have been measured in the vapour, liquid, and solid state, and in liquid and solid solution. Corresponding with the change vapour  $\rightarrow$  solution  $\rightarrow$  liquid  $\rightarrow$  solid there is a progressive broadening of the absorption bands and a displacement of the whole band system towards the red. For solutions in different solvents, the shift towards the red is the greater, the higher is the refractive index of the solvent. For a given solvent the position of the bands is nearly independent of concn. when the solutions are dil. Similar results have been obtained for the fluorescence bands.

F. L. U.

Alterations in the spectra of solutions of diacenaphthylidene. I. Influence of solvent on fluorescence and absorption spectra. II. Influence of temperature on the fluorescence spectrum. B. TWAROWSKA (Acta phys. polon., 1933, 2, 267—272, 273—281; Chem. Zentr., 1935, ii, 346—347).—I. The fluorescence max. move towards the violet as the  $d$  of the solvent decreases. In xylene and isoamyl alcohol the fluorescence bands and, less markedly, the absorption bands tend to come together.

II. At lower temp. the fluorescence bands become smaller and sharper, and tend to split up into groups; the effect varies somewhat from solvent to solvent.

H. N. R.

Absorption spectra of some aromatic compounds. I. Hydrocarbons. II. Quinones and quinols. P. K. SESHAN (Proc. Indian Acad. Sci., 1936, 3, A, 148—171, 172—187).—I. An investigation of the variations produced in absorption spectra of aromatic compounds by the progressive addition of benzene rings to the mol. Absorption spectra have been determined from 7000 to 2300 Å. of C<sub>10</sub>H<sub>8</sub>, anthracene, naphthacene, phenanthrene, 1:2-benzphenanthrene, pyrene, and fluorene in solid and vapour states and in EtOH, of 1:2:5:6-dibenzanthracene in the solid state and EtOH solution, of



perylene, acenaphthene, fluorene,  $\text{CH}_2\text{Ph}_2$ , and  $\text{C}_2\text{H}_4\text{Ph}_2$  in the vapour state and in EtOH, and of  $\text{Ph}_2$ ,  $\text{C}_6\text{H}_4\text{Ph}_2$ ,  $\text{CHPh}_3$ ,  $s\text{-C}_6\text{H}_3\text{Ph}_3$ ,  $s\text{-C}_6\text{H}_2\text{Me}_4$ , and  $\text{C}_6\text{Me}_6$  in the vapour state. Characteristic vibrational and electronic frequencies are calc. The relation between the structure of the mol. and the nature of the absorption spectrum is discussed.

II. Absorption spectra have been determined between 7000 and 2200 Å. of *p*-benzoquinone (I) and quinol (II) in solid and vapour states and in EtOH solution, of 1:4-naphthoquinone (III), anthraquinone (IV), phenanthraquinone (V), 2-hydroxyanthraquinone in the vapour state and EtOH solution, and of naphthazarin, phloroglucinol, and quinhydrone (VI) in the vapour state. The spectra of (I) and (II) show rotational fine structure. Vibrational and electronic frequencies are calc. for (III), (IV), and (V). Vibrational fine structure is absent in the spectra of the quinols. The absorption of (VI), at  $t > 100^\circ$ , is a superposition of those of (I) and (II) which are probably present as dissociation products.

O. D. S.

Absorption spectra of pyocyanine, prodigiosine, and violaceine. O. EHRSIMANN and W. NOETHLING (Biochem. Z., 1936, 284, 376—382).—Max. absorption occurs at 264—300, 294 and 550, and 480 and  $< 250 \text{ m}\mu$ , respectively. F. O. H.

Optical absorption of porphyrins. IV. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1936, 175, 405—437; cf. this vol., 8).—The absorption of porphin (I), tetra- and hexa-substituted porphyrins, esters of porphyrins with higher alcohols, porphyrins having one or two groups containing CO,  $\beta\delta$ -di-iminocoproporphyrin  $\text{Me}_4$  ester, rhodin  $g_3$  Me ester, and 2-de-ethyldeoxyphyloerythrin has been determined. Alkyl substitution in (I) shifts all the band max. but one towards the red. If the absorption curve of a porphyrin is of the "rhodo" type a CO group is present in a nucleus of the (I) systems or conjugated with it. If the CO group is attached to a methine bridge of the (I) framework the absorption curve is not of the rhodo type. If there are two groups containing CO in two nuclei of the porphyrin, only those porphyrins which have the groups in the nuclei I and III or II and IV have curves of the rhodo type. The nucleus of the porphyrin system in which substitution with a group containing CO emphasises the "rhodo" character of the absorption curve has a pyrrole structure. In the formation of a monoxime of a porphyrin with two CO groups it is possible to determine from the absorption curve at which CO group the oxime has been formed. The application of these observations to the determination of configuration is discussed.

R. C.

[Absorption] spectra of solutions of chemical warfare materials. H. MOHLER and J. PÓLYA (Helv. Chim. Acta, 1936, 19, 283—287).—Preliminary. Extinction curves are given for  $\text{C}_6\text{H}_{14}$  solutions of nineteen compounds belonging to the four divisions of chemical warfare materials.

F. L. U.

Fine structure of the absorption band of water vapour at  $0.94 \mu$ . J. H. HSU (Chinese J. Physics, 1935, 1, 59—67).— $\lambda$  for 28 absorption lines are recorded, and agree with some absorption lines in

the solar spectrum. Doublet structure in agreement with a triangular  $\text{H}_2\text{O}$  mol. is indicated. L. J. J.

Hindered rotation in liquid  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . C. H. CARTWRIGHT (Physical Rev., 1936, [ii], 49, 470—471).—Assuming a tetrahedral quartz-like structure for the  $\text{H}_2\text{O}$  mol., the calc. intermol. field leads to the prediction of a characteristic frequency at  $60 \mu$  due to a mutual vibration between the mols., and a frequency at  $20 \mu$  due to hindered rotation. The observed characteristics and shifts of these bands, their variations in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , and a theoretical explanation are described and discussed. N. M. B.

Structure of the infra-red absorption of crystals. F. SEITZ (Physical Rev., 1936, [ii], 49, 405; cf. A., 1935, 1444).—A correction. N. M. B.

Infra-red absorption of hydrogen chloride in non-ionising solvents. W. WEST and R. T. EDWARDS (Physical Rev., 1936, [ii], 49, 405; cf. Plyler, this vol., 406).—Observations on the infra-red absorption for the harmonic at  $1.76 \mu$  are in general agreement with results obtained from Raman spectra (cf. A., 1934, 583). Information for solutions in  $\text{PCl}_3$ ,  $\text{POCl}_3$ ,  $\text{CCl}_4$ , and  $\text{SO}_2$  is outlined. N. M. B.

Infra-red absorption spectra of mixtures of acetone and water. D. WILLIAMS and E. K. PLYLER (J. Chem. Physics, 1936, 4, 154—157).—The infra-red absorption spectra of  $\text{COMe}_2\text{-H}_2\text{O}$  mixtures have a band indicating association near  $2.7 \mu$ . The intensity of the band increases with increasing  $\text{H}_2\text{O}$  content, but  $[\text{H}_2\text{O}]$  as low as 0.1% may be detected by the presence of the band. M. S. B.

Infra-red absorption spectra of deuteroxide solutions in deuterium oxide. E. K. PLYLER and D. WILLIAMS (J. Chem. Physics, 1936, 4, 157—160).—The infra-red absorption spectra of  $\text{D}_2\text{O}$  and solutions of  $\text{NaOD}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$  in  $\text{D}_2\text{O}$  have been measured for the range  $2.5\text{--}9 \mu$ . Intense bands are observed in  $\text{NaOD}$  solutions at  $3.1$ ,  $4.95$ , and  $7.1 \mu$ .  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in  $\text{D}_2\text{O}$  also give rise to bands in these regions, but with a shift in  $\lambda$  probably due to absorption by  $\text{CO}_3^{2-}$  and  $\text{D}_2\text{CO}_3$  formed in solution. The band at  $3.1 \mu$  is attributed to  $\text{OD}'$ , corresponding with the  $\text{OH}'$  band at  $2.3 \mu$ . The two bands at  $4.95 \mu$  and  $7.1 \mu$  are probably due to hydration and correspond with the bands at  $3.65 \mu$  and  $5.2 \mu$  in hydroxide solutions (cf. A., 1934, 1154). M. S. B.

Temperature dependence of the absorption spectra of alcohols in the near infra-red, up to and above the critical point. A. NAHERNIAC (Compt. rend., 1936, 202, 649—651).—For  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Pr}^\text{OH}$ ,  $\text{Pr}^\text{OH}$ , and  $\text{Bu}^\text{OH}$ , the intensity of the OH band at about  $10,000 \text{ Å}$ . increases continuously with rise of temp. The positions of the band for the liquid and vapour at const. vol. approach one another with rising temp., and coincide at the crit. temp. Thus the  $\lambda$ - $t$  curve resembles the density curve.

L. J. J.

Infra-red absorption spectrum of HDS and  $\text{D}_2\text{S}$ . A. H. NIELSEN and H. H. NIELSEN (J. Chem. Physics, 1936, 4, 229).— $\text{D}_2\text{S}$  has bands at  $3.65$ ,  $4.55$ , and  $10.8 \mu$  and HDS at  $2.1$ ,  $3.15$ ,  $4.1$ , and  $9.0 \mu$ . The  $\text{H}_2\text{S}$  bands are shifted towards longer  $\lambda$  in the anticipated manner.

M. S. B.



**Infra-red absorption spectra of chlorinated methanes.** C. CORIN (Compt. rend., 1936, 202, 747—749).—Data are recorded for 15, 15, and 18 bands in the infra-red absorption spectra of liquid  $\text{MeCl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ , respectively.  $\text{CCl}_4$  gave no bands in this region ( $0.7\text{--}2.6\ \mu$ ). The bands of  $\text{CHCl}_3$  were not observed in  $\text{CCl}_3\text{NO}_2$ , but 7 new bands, associated with the  $\text{C-NO}_2$  group and occurring for  $\text{C(NO}_2)_4$ , were observed. The intensity of absorption increases with the no. of C-H linkings in the mol. H. J. E.

**Vibration frequencies of chlorine derivatives [of some aliphatic compounds] deduced from infra-red absorption and Raman spectra.** H. C. CHENG and J. LECOMTE (Ann. Physique, 1936, [xi], 5, 427—443; cf. A., 1935, 1053).—Infra-red absorption spectra measurements in the frequency range  $640\text{--}1400\ \text{cm}^{-1}$  lead to interpretation of available Raman data and of C-Cl vibrational frequencies. The latter, in the case of  $\text{Cl}_3$ -derivatives, show marked divergence from theory, and anomalous bands are classified. N. M. B.

**Raman effect in chemistry.** G. DUPONT (Bull. Soc. chim. Belg., 1936, 45, 37—56).—A lecture.

**Raman effect and problems of constitution.**  
IX. **Stability of the aromatic C-X linking.**—See this vol., 599.

**Polarisation in the molecular diffusion spectrum of liquid carbon tetrachloride.** A. ROUSSET (Compt. rend., 1936, 202, 654—656).—Depolarisation factors  $\neq 0$  are recorded for the Rayleigh scattered radiation and the line of undisplaced  $\lambda$ , and are due, respectively, to depolarised rotational wings (Cabannes-Daure effect) and to the depolarised  $Q$  branch. This can be explained by anisotropy of the  $\text{CCl}_4$  mol., which is confirmed by the incomplete polarisation of the symmetrical vibration Raman line  $459\ \text{cm}^{-1}$  (isotopy effect of Cl), and the incomplete depolarisation and splitting of the Raman lines 219 and  $316\ \text{cm}^{-1}$ , due to dissymmetry of the C valencies. L. J. J.

**Polarisation of Raman radiation and constitution of molecules.** II. B. TRUMPY (Z. Physik, 1936, 98, 672—683).—Polarisation measurements show  $\text{Bu}^i\text{OH}$  to have  $C_{3v}$  symmetry, and give an allocation of Raman frequencies. Measurements on the Raman spectrum of  $\text{C}_2\text{H}_2\text{Br}_4$  show absence of free rotation, the *cis*- and *trans*-forms being equally probable.  $\text{C}_2\text{D}_2\text{Cl}_4$  and *cis*- and *trans*- $\text{C}_2\text{D}_2\text{Cl}_2$  have Raman spectra in agreement with their H equivs. (cf. A., 1935, 565). A. B. D. C.

**Raman effect in chemical dynamics.** W. F. BEZGHOLD and L. S. ORNSTEIN (Physica, 1936, 3, 154—172).—The Raman spectrum of transformer oil showed, after oxidation, a decrease in the intensity of the C-H oscillation lines. The photochemical chlorination of  $\text{CHCl}_3$  was followed completely by the Raman effect, the amount of  $\text{CCl}_4$  being estimated by the intensity of the lines; the reaction is independent of  $[\text{CHCl}_3]$ . A theoretical interpretation of the empirical reaction equation is given. Results are compared with those for the vapour state (cf. Schumacher, A., 1934, 740). A new method of illum-

ination and measurement by means of a photo-electric cell is described. N. M. B.

**Deformation frequencies in the Raman spectra of linear molecules: acetylene.** S. BHAGAVANTAM and A. V. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 135—139).—New bands at  $\Delta\nu$  589 and 646 have been recorded with long exposure. The negligible intensity of the  $Q$  branch and the observed separation support an interpretation as the max. of the unresolved  $O$ ,  $P$ ,  $R$ , and  $S$  branches of the total symmetric deformation vibration of the mol. The mean frequency shift is in good agreement with the val. deduced from infra-red absorption. N. M. B.

**Raman spectrum of some derivatives of pyrrole.** G. B. BONINO and R. MANZONI-ANSIDEI (Atti R. Accad. Lincei, 1935, [vi], 22, 349—354).—The Raman spectra of 1-ethyl-, 1-allyl-, 1-methyl-, 2:5-diethyl-, 2:5-dimethyl-1-ethyl-, and 2:5-dimethyl-3-ethyl-pyrrole have been measured. They all give the two pyrrole ring lines at  $1460\text{--}1520$  and  $1370\text{--}1390\ \text{cm}^{-1}$ . The interpretation of other lines found is discussed. O. J. W.

**Raman spectrum of pyrrole and some derivatives.** A. STERN and K. THALMAYER (Z. physikal. Chem., 1936, B, 31, 403—419).—In the Raman spectrum of pyrrole (I) frequencies due to the  $\text{CH}_2$  group and to the C'C, C'N, and aliphatic C-H linkings have been observed. Hence even in unsubstituted (I) there must be an equilibrium between the pyrrole and pyrrolene forms. The position of equilibrium between these forms and the supposed centric form is very much in favour of the latter. The model of (I) and interpretation of the Raman spectra of its derivatives proposed by Bonino (A., 1934, 830) are criticised. R. C.

**Comparison of Raman spectra of *cis*- and *trans*-cinnamyl derivatives.** (MLLE.) B. GREDY (Compt. rend., 1936, 202, 664—666).—In contrast to the corresponding *cis*- and *trans*- $\alpha$ -derivatives of  $\Delta^8$ -octene, the *cis*- and *trans*-cinnamyl derivatives (RH, ROH, ROME, ROAc, RBr) have only one or two lines in common in their Raman spectra, apart from the  $\text{C}_6\text{H}_6$  lines. Data are recorded. The *trans*- have higher b.p.,  $n$ , and  $d$  than *cis*-derivatives. L. J. J.

**Raman spectra of some organic liquids under high dispersion and resolving power.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 52—74).—Detailed data, including a no. of new faint lines, are recorded for  $\text{C}_6\text{H}_6$ , PhMe, PhOH, PhCl,  $\text{C}_5\text{H}_5\text{N}$ , and cyclohexane.  $\nu$  and relative intensities for the line  $992\ \text{cm}^{-1}$  of  $\text{C}_6\text{H}_6$  and its satellites are: 979 ( $\frac{1}{2}$ ), 984 (1), 992.5 (10), 998 (1), 1006 ( $\frac{1}{2}$ ). The corresponding line ( $802\ \text{cm}^{-1}$ ) in cyclohexane shows no fine structure; in  $\text{C}_5\text{H}_5\text{N}$  and mono-derivatives of  $\text{C}_6\text{H}_6$  it has a faint satellite,  $\nu$  and intensity of which, however, bear no simple relation to those of the main line. It is concluded that the satellite  $984\ \text{cm}^{-1}$  in  $\text{C}_6\text{H}_6$  is not due to the  $\text{C}^{13}$  isotope. The constitution of the  $\text{C}_6\text{H}_6$  ring is considered. L. J. J.

**Raman effect.** LIV. **cyclohexyl derivatives and symmetry of cyclohexane and dioxan.**



K. W. F. KOHLRAUSCH and W. STOCKMAIR (Z. physikal. Chem., 1936, B, 31, 382—401; cf. this vol., 137).—The spectra of monosubstituted cyclohexane (I) derivatives,  $C_6H_{11}X$  ( $X=NH_2$ , OH, Me, CN, Cl, Br, I) and of (I), dioxan (II), and piperidine have been determined. Substitution depresses the ring frequencies in (I) less than in  $C_6H_6$ .  $C_6H_{11}X$  show fewer Raman lines than would be anticipated, possibly owing to "accidental" degeneracy. The results are reconcilable with the "chair" configuration for the (I) ring, but not with the trough form, or a form intermediate between the trough and chair forms and having the C atoms 1, 2, 4, and 6 in one plane. For (II) also the trough and intermediate forms are excluded. R. C.

**Raman effect of organic sulphides.** P. DONZELLOT and M. CHAIX (Compt. rend., 1936, 202, 851—852).—The Raman spectra of  $(C_6H_5)_2O$  and  $(C_6H_5)_2S$  have been compared with those of  $Ph_2O$  and  $Ph_2S$  (A., 1935, 1301) in order to study the effect of a third closed ring connecting the two  $C_6$  rings. A marked displacement of the  $C_6H_6$  frequencies takes place, and, instead of two frequencies in the neighbourhood of 1000, as in  $Ph_2O$ ,  $Ph_2S$ , and some other  $C_6H_6$  derivatives, there is one only for  $(C_6H_5)_2O$  and  $(C_6H_5)_2S$ . Raman spectra of  $Et_2S$ ,  $Et_2S_2$ , and  $Et_2S_3$  indicate that the frequencies in the neighbourhood of 635, 655, 960, 1045, and 1150 are associated with the C-S linking, and that the frequency 179, associated with the S-S linking in  $Et_2S_2$ , is doubled, giving 151 and 204, in  $Et_2S_3$ . A frequency in the neighbourhood of 500 is probably associated with S-S in both compounds. M. S. B.

**Raman spectrum of tetraethylsilane. Vibrational resonance of tetra-alkyls.** T. F. ANDERSON (J. Chem. Physics, 1936, 4, 161—164).—The Raman spectrum of  $SiEt_4$  is given together with the data available for other tetra-alkyl compounds and assignments of frequencies are made. The presence of extra lines in the spectra is explained by resonance between vibrations. First-order perturbation calculations of the observed resonance effects are given. M. S. B.

**Molecular clustering in liquid fatty acids.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 126—134; cf. A., 1935, 11).—The intensity and depolarisation of light scattered transversely by dust-free samples of  $HCO_2H$ ,  $AcOH$ ,  $EtCO_2H$ , and  $Pr^iCO_2H$  are measured between  $20^\circ$  and  $90^\circ$ . The depolarisation of the horizontally polarised light is high for  $HCO_2H$  and  $AcOH$  and is greatest at room temp. In opposition to the theory of mol. scattering, the depolarisation decreases with rising temp. These anomalies show the presence in the liquids, at low temp., of mol. aggregates of a size comparable with the  $\lambda$  of light. Anomalies in the optical anisotropy of  $HCO_2H$  and  $AcOH$  in the liquid and vapour state observed by Ramanathan (Indian J. Physics, 1926, 1, 401) and Rao (A., 1928, 1311) are explained. No evidence is obtained of the presence of mol. clusters in  $EtCO_2H$  and  $PrCO_2H$ . O. D. S.

**Slightly modified scattered radiation of crystals and the characteristic vibrations of the molecules in the lattice.** M. VUKS (Compt. rend.

Acad. Sci. U.R.S.S., 1936, 1, 73—76; cf. A., 1935, 281, 564, 914).—The scattered spectra of the  $\alpha$  and  $\beta$  modifications of  $p-C_6H_4Cl_2$  show marked differences, whilst the usual Raman spectrum is found for both forms to be identical with that for the liquid substance. This is held to support the theory that the "wings" in the Raman spectra are produced by the linkings between mols. in the lattice, and give the characteristic vibrations of the mol. The Raman spectra of the isomorphous  $p-C_6H_4Cl_2$  and  $p-C_6H_4Br_2$  are compared. A. J. M.

**Selective light scattering in mercury vapour.** G. LANDSBERG and L. MANDELSTAM (Physikal. Z. Sovietunion, 1935, 8, 378—400).—The selective scattering at 2558 Å. of Hg is studied and a method is given for investigating the mol. and at. parts of the radiation. The intensity of the at. part agrees with the theoretical val. The mol. part is feebly polarised and the at. part almost completely polarised. The extinguishing effect of  $N_2$  is slight. W. R. A.

**Longitudinal scattering of light according to Plotnikov.** M. KATALINIĆ (Kolloid-Z., 1936, 74, 288—296).—A crit. discussion of published work. E. S. H.

**Raman effect of ammonia.** P. DAURE, A. KASTLER, and H. BERRY (Compt. rend., 1936, 202, 569—572).—The Raman spectra of gaseous, liquid, and aq.  $NH_3$  have been investigated and the polarisation has been determined. The spectrum in liquid  $NH_3$  is ascribed to association, which is destroyed by  $H_2O$ , probably in two stages. T. G. P.

**Raman spectra of sulphates at different concentrations.** S. M. MITRA (Z. Physik, 1936, 98, 740—741).—Variation of Raman displacements with concn. of  $Li_2SO_4$  and  $MgSO_4$  observed by Embrikos (A., 1930, 1499) could not be detected. A. B. D. C.

**Raman spectra of orthophosphoric acid and some phosphates.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1936, 3, A, 25—30).— $H_3PO_4$  at concns. 3—85% shows new lines indicating ionisation to  $H^+ + H_2PO_4^+$  and  $2H^+ + HPO_4^{++}$ , as well as weak lines due to OH vibrations. For  $MH_2PO_4$ ,  $M_2HPO_4$ , and  $M_3PO_4$  ( $M=Na$ ,  $K$ , and  $NH_4$ ), spectra due to  $H_2PO_4^+$ ,  $HPO_4^{++}$ , and  $PO_4^{+++}$  have been identified. Comparison with data for sulphates and selenates indicates tetrahedral structure for  $PO_4^{+++}$ . L. J. J.

**Raman spectra of organic borates.** M. S. JOGLEKAR and V. N. THATTE (Z. Physik, 1936, 98, 692—701).—Raman lines are given for Me, Et, Bu, amyl, isoamyl, and Ph borates. Some  $BO_3$  frequencies appear in the org. borate spectra, indicating similarity of  $BO_3^{+++}$  and  $B(OR)_3$ . A. B. D. C.

**Fluorescence of sodium salicylate.** G. DEJARDIN and L. HERMAN (Compt. rend., 1936, 202, 651—654).—The spectrum of the diffused light from cryst. Na salicylate irradiated with the continuous  $H_2$  spectrum is continuous, with weak intensity max. at  $\lambda\lambda$  2500, 2700, and 3300 Å., in addition to the fluorescence band in the blue-violet. With the Hg line 2482 Å., only the fluorescence band can be distinguished; the energy distribution in this band is independent of the incident  $\lambda$  for  $\lambda\lambda$  3130—2537 Å. L. J. J.



**Displacement of fluorescence and absorption spectra of tribenzyldecacyclene in relation to the solvent.** P. MARGULIES (*Acta phys. polon.*, 1934, 3, 373—384; *Chem. Zentr.*, 1935, ii, 31).—From measurements in 26 solvents connexions are traced between the displacement of the spectra and the properties of the solvent. H. N. R.

**Absorption and fluorescence spectra of a dicinnamoylmethane derivative and the carrier of this fluorescence.** E. RAKOWER (*Acta phys. polon.*, 1934, 3, 415—420; *Chem. Zentr.*, 1935, ii, 32).—The spectra of Me 3-cinnamoylacetyl coumarin-7-carboxylate, dicinnamoylmethane, and coumarin are described and discussed. H. N. R.

**Influence of viscosity and temperature on fluorescent power.** J. BOUCHARD (*J. Chim. phys.*, 1936, 33, 232—246).—The extinction coeff. ( $k$ ) of the fluorescence of a solution, corr. for its variation due to changes in the sp. inductive power of the medium, decreases with increasing viscosity ( $\eta$ ) of the medium. The  $k$ - $\eta$  curve is analogous to a velocity of diffusion  $\eta$  curve, in accord with the view relating the decay in fluorescence with the concn. and velocity of diffusion of fluorescent mols. Perrin's law represents satisfactorily the variation of fluorescent power ( $\Phi$ ) as a function of concn. at 2—80°. The extrapolated val. of  $\Phi$  for rhodamine-B decreases with rise of temp., but for uranine, eosin, erythrosin, and acridine-yellow it is approx. const.  $k$  increases with rise of temp. for solvents of low inductive power (alcohols,  $\text{COMe}_2$ , etc.), probably owing to the low association in these solvents and the increased probability of collision between dissolved mols. at higher temp. For aq. solutions  $k$  decreases with rising temp., probably because the extinction of fluorescence depends on the presence of associated mols., the concn. of which decreases with rising temp. J. W. S.

**Influence of specific inductive capacity on fluorescent power. I. Influence of the specific inductive capacity of the solvent on the decrease of fluorescent power as a function of the concentration of fluorescent material. Uranine. II. Fluorescent materials other than uranine.** J. BOUCHARD (*J. Chim. phys.*, 1936, 33, 127—149; cf. this vol., 408).—The fluorescence of uranine in aq. mixtures of MeOH, EtOH,  $\text{Pr}^n\text{OH}$ ,  $\text{Bu}^n\text{OH}$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{COMe}_2$  containing 0.1N-NaOH has been studied. The fluorescent power,  $\Phi$ , varies with concn.,  $c$ , and composition of the solvent according to Perrin's law,  $\Phi = \Phi_0 e^{-kc}$ , whilst the extrapolated fluorescent power,  $\Phi_0$ , is approx. const. Determinations of the dielectric consts. of the solvents lead to the relation  $k = 1/(A - B\epsilon)$  where  $A$  and  $B$  are consts. Eosin, acridine-yellow, rhodamine-B, -G, -S, -3B, and -6G behave similarly. In the case of rhodamine-B in EtOH- $\text{CCl}_4$  mixtures,  $k$  increases with  $[\text{CCl}_4]$  as if this acted only as a diluent. R. S.

**Theories of phosphorescence.** M. CURIE (*Compt. rend.*, 1936, 202, 751—753).—A discussion. H. J. E.

**Spectrum of the thermoluminescence of fluorite.** H. STEINMETZ and A. GISSER (*Naturwiss.*, 1936, 24, 172).—In contrast to the thermolumin-

escence spectra of most minerals, which are continuous, that of  $\text{CaF}_2$  is composed of several bands, the  $\lambda\lambda$  of which are given. A. J. M.

**Inner photo-effect with semi-conductors.** H. FRÖHLICH (*Physikal. Z. Sovietunion*, 1935, 8, 501—510).—The electron distribution function for a semi-conductor illuminated with monochromatic light is calc., and the result is confirmed by consideration of the Demer effect. A. J. M.

**Influence of temperature on the photo-electric effect of the metal-cuprous oxide interface.** J. ROULLEAU (*Compt. rend.*, 1936, 202, 749—751).—Anomalies in the temp. variation of the photopotential are explained by the simultaneous temp. variation of the contact resistance and of the photopotential. H. J. E.

**Photo-electric activity of iron and its oxides.** J. S. HUNTER (*Nature*, 1936, 137, 460; cf. A., 1935, 682).—The surface of  $\text{Fe}_2\text{O}_3$  is photo-electrically insensitive. The spectral distribution curve for FeO showed a max. at 2190 Å. with a photo-electric threshold at  $< 2500$  Å. The results support a theory of gas adsorption, in preference to instantaneous oxidation, as the initial change undergone by a clean metal surface on exposure to air. L. S. T.

**Electrical behaviour of cuprite crystals.** P. BRAUER (*Ann. Physik*, 1936, [v], 25, 609—624).—The resistance and Hall const. of  $\text{Cu}_2\text{O}$  crystals increase with the partial pressure of  $\text{H}_2\text{O}$  vapour in the surrounding atm., a surface effect due to variation in the concn. of conductivity electrons. The effect of  $\text{H}_2\text{O}$  vapour is not associated with any detectable change in the cryst. structure. L. J. J.

**Primary photo-electric current in NaCl crystals.** W. THIELE (*Ann. Physik*, 1936, [v], 25, 561—568).—Irradiation of rock-salt crystals containing absorption centres (free Na atoms) with  $\lambda\lambda$  405 and 436 m $\mu$  gives rise to a new absorption band in the infra-red. Subsequent irradiation with  $\lambda > 800$  m $\mu$  gives a photo-electric effect which decays with time. It is concluded that some of the electrons initially liberated from Na atoms combine with positive ions to form new loosely bound absorption centres. The half-life period of these centres diminishes as the temp. is raised. L. J. J.

**Destruction of an adsorbed rectifying film by pressure.** F. TREY (*Physikal. Z.*, 1936, 37, 213—214).—Pressure of 4000 kg.-per sq. cm. on a rectifying PbS pastille destroys its rectifying powers. A. J. M.

**True conductivity and back e.m.f. in layered dielectrics.** F. QUITTNER (*Physikal. Z. Sovietunion*, 1935, 8, 275—278; cf. A., 1930, 1504).—A model consisting of alternate thick and thin layers of good and bad conductivity is discussed in relation to previous experimental data on rock-salt. The simple form of model does not account for the results. R. S.

**Normal cathode fall at the m.p. of bismuth.** H. KURZKE (*Ann. Physik*, 1936, [v], 25, 688—696; cf. A., 1934, 1291).—Bi shows a decrease (2 volts with a normal cathode fall of 160 volts) in passing from solid to liquid, in contrast to Sn and Pb. This corre-



sponds with a change of 0.05 volt in the emission energy. L. J. J.

**Substances of low conductivity, and the Rebooul effect.** O. VIKTORIN (Chem. Listy, 1936, 30, 60—64).—A discussion. R. T.

**Abnormal electrical conductivity in powdered tellurium.** C. H. CARTWRIGHT (Physical Rev., 1936, [ii], 49, 443—448).—Under 1000 kg. per sq. cm. pressure Te powder had about 10 times greater conductivity than that of a single crystal under the same pressure. The anomaly was most marked in pure Te, disappearing, probably due to masking, in presence of impurities. Momentary passage of an electric current through the powder under pressure diminished its vol., and greatly decreased its conductivity. Under 20,000 kg. per sq. cm. hydrostatic pressure massive Te increases in conductivity > 100 times, and the rate of increase rises rapidly with pressure. The anomaly may be due to local pressures in excess of the measured average; other explanations are discussed.

N. M. B.

**Electrical conductivity of cuprous oxide in strong electric fields.** M. D. BORISSOV, I. I. KARA, and K. D. SNELENIKOV (Physikal. Z. Sovietunion, 1935, 8, 425—429).—Using different field strengths the increase in conductivity depends on the no. of conducting electrons. W. R. A.

**Mechanism of electrical conduction of solid ionic conductors.** A. SMEKAL (Physikal. Z., 1936, 37, 150—153).—The theory of Schottky (A., 1935, 1302, 1305) is discussed. The equation used by Schottky *et al.* for the polarisation effect is not applicable. According to the theory, in ionic conduction, an ion jumps from its place to a void in the lattice. The probability of this will depend on the properties of the ion and the frequency of the thermal vibrations of the lattice. When equal nos. of cationic and anionic voids are present, differences in mobilities of the ions must be due only to differences in properties of the ions. It is not necessary to assume any different mechanism for the conduction of AgCl and AgBr, where it is entirely cationic. Since lattice conduction is due to disorder phenomena, and these can be "frozen," it should be possible to observe unstable conditions of conduction at low temp. Reversible low-temp. decreases in conduction are therefore not always to be ascribed to electrolytic purification. This is probably the explanation of Kassel's experiments with rock-salt (A., 1934, 1163).

A. J. M.

**Breakdown with internal photo-electric effect.** I. M. GOLDMAN and B. M. VUL (Physikal. Z. Sovietunion, 1935, 8, 369—377).—For rock-salt crystals changes in electronic conductivity within a large range do not influence the dielectric strength. Stained crystals give lower breakdown potentials with d.c. and a.c. when subjected to light; this is due to secondary factors. W. R. A.

**Dielectric constant of wool fibre.** F. W. HOLL (Helv. Chim. Acta, 1936, 19, 281—283).—The dielectric const. of washed and fat-free Cape wool, determined by the bridge-condenser method, is  $4.56 \pm 10\%$ . F. L. U.

**Dielectric constant and electrostriction of amino-acids and peptides.** J. P. GREENSTEIN and J. WYMAN, jun. (J. Amer. Chem. Soc., 1936, 58, 463—465; cf. A., 1935, 694).—Data for *l*-asparagine, acetylhistidine, glycyl-leucine, alanyl-, *N*-methyl-leucyl-, glycyl-, and glycylphenyl-alanine, leucyl-, phenylalanyl-, and leucylglycyl-glycine are recorded. E. S. H.

**Determination of dielectric constants and dipole loss at high frequencies.** I. Introduction. M. WIEN. II. Dipole loss in liquids for long waves. C. SCHRECK. III. Determinations with sucrose and fructose solutions. W. DAHMS. IV. Determinations with different kinds of glass. W. HACKEL. V. Determination of losses in different liquids by the thermometer method. C. SCHMELZER (Physikal. Z., 1936, 37, 155—156, 156—158, 158—160, 160—162, 162—164).—I. Results previously obtained for the behaviour of liquids in powerful and high-frequency electric fields are summarised. The most important results of the Debye theory of dipole loss are collected.

II. Determinations of dipole loss were made using the barretter method with a non-polar liquid ( $C_6H_6$ ) and polar liquids (aq. solutions of sucrose and fructose,  $Bu^oOH$ ). The variation of dipole conductivity ( $\Delta\chi$ ) with  $\lambda$  was linear in the case of  $Bu^oOH$  and sucrose. For dil. solutions of fructose  $\Delta\chi \propto 1/\lambda^2$ , but for conc. solutions  $\Delta\chi \propto 1/\lambda$ . There was no loss in  $C_6H_6$ .

III. Aq. solutions of sucrose and fructose give qual. agreement with theory as regards variation of  $\Delta\chi$  with  $1/\lambda^2$  for short  $\lambda$ , but deviations occur with more conc. solutions. Similar results are obtained as for long  $\lambda$  (see above). There is a considerable decrease of dielectric const. ( $\epsilon$ ) of fructose solutions with increase of  $d$  of solution. This is not found for sucrose, contrary to theory. The deviations of the dipole effect from theory may be due to inhomogeneity, or to the possibility that the Debye theory is not accurate for very viscous solutions.

IV. A method for the simultaneous determination of  $\epsilon$  and conductivity ( $\chi$ ) of solids is described in which the solid is placed between the plates of a condenser filled with a liquid of which the  $\epsilon$  and  $\chi$  are varied until they are the same as those of the solid.  $\epsilon$  and  $\chi$  of the liquid are then determined. The method was used with various Jena (Schott) glasses over the  $\lambda$  range 12,000—10 m. The high-frequency  $\chi$  is strongly dependent on the kind of glass. At first  $\chi \propto 1/\lambda$  but with shorter  $\lambda$  it increases more slowly than this. The variation of  $\epsilon$  with  $\lambda$  is different for the different glasses, and although there are deviations from the Debye theory, the phenomena can still be explained as connected with dipole loss. The results are compared with those obtained for fructose solutions (see above).

V. The thermometer method of Harms and Malsch (A., 1932, 214) was used to determine the high-frequency  $\chi$  and dipole loss ( $\Delta\chi$ ) of various liquids. Non-polar substances (e.g., dioxan) show no loss. For  $Pr^oOH$   $\Delta\chi \propto 1/\lambda^2$ , although the slope of the curve between  $\Delta\chi$  and  $1/\lambda^2$  is > theory; this, however, is accounted for. Solutions of  $HgCl_2$  and  $AcOH$  in  $CO_2$  show a considerable increase in  $\chi$  at high frequency above that at low frequency. This is



due to formation of ion pairs of large dipole moment. A solution of  $\text{NBu}_4^+\text{Br}^-$  in  $\text{C}_6\text{H}_6$  behaves similarly.  $\Delta\chi$  in this case depends on field strength, which causes alteration in the no. of ion pairs. A. J. M.

**High-frequency loss of polar solutions.** G. MARTIN (Physikal. Z., 1936, 37, 164—165).—If dissolved mols. are regarded as spheres rotating in a viscous medium, an expression connecting relaxation time with coeff. of viscosity ( $\eta$ ) and size of mols. can be obtained on the basis of Stokes' law.  $\text{C}_6\text{H}_6$  solutions of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$  show a high-frequency loss  $\propto$  (dipole moment)<sup>2</sup>. The effect of size of mol. was investigated with  $\text{PrOH}$ , hexyl, octyl, and cetyl alcohols in dil.  $\text{C}_6\text{H}_6$  solutions. The loss, extrapolated to infinite dilution, increased linearly with the no. of C in the alcohol mol. The results agree with theory. The effect of  $\eta$  was investigated with solutions of *o*- $\text{C}_6\text{H}_4\text{Cl}_2$  in  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_6\text{H}_8$ ,  $\text{CCl}_4$ , and decalin. The relaxation time was not accurately  $\propto \eta$  as required by theory.

A. J. M.

**Dielectric losses at high frequency in liquids.** M. DIVILKOVSKI and M. FILIPPOV (Physikal. Z. Sovietunion, 1935, 8, 311—318).—The dielectric losses in  $\text{EtOH}$ ,  $\text{Pr}^n\text{OH}$ , and glycerol have been obtained by determination of the expansion of the liquid in a thermometer vessel when placed in a high-frequency electric field. No rise of temp. could be observed in the case of  $\text{C}_6\text{H}_6$ .

R. S.

**Electric moments of solute molecules.** E. A. GUGGENHEIM (Nature, 1936, 137, 459—460).—The new formula deduced is claimed to give vals. more accurate than the Clausius-Mosotti formula when applied to the experimental data of other investigators.

L. S. T.

**Calculation of various physical constants of heterogeneous substances. II. Dielectric constants and conductivities of polycrystals of non-regular systems.** D. A. G. BRUGGEMAN (Ann. Physik, 1936, [v], 25, 645—672).—The theory (this vol., 151) developed for mixtures of isotropic substances is extended to anisotropic aggregates. The new theory gives vals. in agreement with existing data for the dielectric const. of S and  $\text{CaCO}_3$  polycrystals and suspensions in liquids, and for  $\text{BaSO}_4$ -air and  $\text{PbCl}_2$ -air mixtures. The influence of texture in the case of Sb, Bi, Sn, Cd, and Zn polycrystals explains anomalies in existing conductivity data.

L. J. J.

**Minimum estimate of the dipole moments of two oxonium salts.** (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1936, 398—399).—2-Phenyl- and 2-phenyl-3-methyl-benzopyrylium perchlorates in  $\text{NPhMe}_3$  at  $25^\circ$  have dipole moments at least about 8 and 7, respectively. Four pyrylium ferriehlorides are sol. in  $\text{NPhMe}_3$  but have very high  $\kappa$ .

R. S. C.

**Dipole moment and solvent.** K. HIGASI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 284—309).—The polarising influence of an ellipsoidal dipole with an axis of symmetry ( $c$ ) on a non-polar solvent is considered. The dipole moment of the solute in solution,  $\mu'$ , is given by  $\mu + 4\pi n\alpha A\mu$ , where  $\mu$  is the moment in the gaseous phase,  $n$  is the no. of

solvent mols. per c.c.,  $\alpha$  is the polarisability of the solvent, and  $A$  is dependent only on the shape of the solute mol. If  $a$  is the axis perpendicular to the symmetry axis,  $\mu'$  is  $>$ ,  $=$ , or  $< \mu$  according as  $a$  is  $<$ ,  $=$ , or  $> c$ ; Müller's theory considers only the case  $\mu' < \mu$ . Examples agree with theory,  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ , and the alcohols (data of Higasi) in  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_{12}$  giving  $\mu' > \mu$ . The shape of the mols. is considered in relation to X-ray evidence, optical polarisabilities, and Kerr const.; in general negative vals. of the Kerr const. are correlated with  $\mu' > \mu$ .  $\mu'$  can be "corr." for solvent effect by plotting  $\mu'$  against  $(\epsilon - 1)/(\epsilon + 2)$  ( $\epsilon$  is dielectric const. of solvent), the slope of  $\mu'/\mu - 1$  against  $(\epsilon - 1)/(\epsilon + 2)$  being positive or negative, and extrapolating to  $\epsilon = 1$ . If extrapolation is not possible the solvent with the smallest  $\epsilon$  gives the best val. for  $\mu$ .

R. S. B.

**Steric configuration and the condition of strain of some ring compounds.** J. BÖESEKEN (Chem. Weekblad, 1936, 33, 206—214).—The importance of the study of dipole moments (in parentheses), the formation of *B*-compounds, and the velocity of the

reaction  $>\text{C}:\text{C} + \text{AcO}_2\text{H} \rightarrow \text{---}\text{C}\text{---}\text{C}\text{---}\text{O} + \text{AcOH}$ , for determining stereochemical configurations are discussed and applied to dioxan (0.3), tetra-, m.p.  $61-64^\circ$  (1.85), 99.5—101.5° (1.05), 143—144° (0), hexachlorodioxan (0), naphthodioxans, m.p.  $111^\circ$  (1.90),  $136^\circ$  (0.72), pyrocatechol dimethylene ether (1.40), and several cyclic hydrocarbons including terpenes. The mol. wt. of metaldehyde is twice that of paraldehyde.

S. C.

**Dipole moment and structure of organic compounds. XV. Electric moments of some chlorinated naphthalenes.** G. C. HAMPSON and A. WEISSBERGER (J.C.S., 1936, 393—398).—Data are recorded for the two  $\text{C}_{10}\text{H}_7\text{Cl}$  and the ten  $\text{C}_{10}\text{H}_6\text{Cl}_2$  in  $\text{C}_6\text{H}_6$  solution at  $25^\circ$ . The C-Cl moment in 2- $\text{C}_{10}\text{H}_7\text{Cl}$  (1.65D) is approx. the same as in  $\text{PhCl}$ , whilst in the 1-position it is less (1.51D).  $\mu$  is 0.48D for 1:4- $\text{C}_{10}\text{H}_6\text{Cl}_2$ , but zero for the 1:5- and 2:6-isomerides. There is no evidence of fixation of single and double linkings. The results indicate that each C-Cl is directed as from the centre of the ring, and induces in the rest of the mol. a moment corresponding with the calc. polarisability of the system, including an "ortho-effect" when two Cl are close together.

L. J. J.

**Structure of anisotropic liquids.** R. D. SCHULVAS-SOROKINA and M. V. POSNOVA (Physikal. Z. Sovietunion, 1935, 8, 319—325).—The dielectric const. of *p*-azoxyanisole is unaffected by electrical fields of frequencies  $10^3-35$  Hertz. The conductivity-temp. curve is inflected at  $116^\circ$  and  $136^\circ$  corresponding with the change from the supercooled state and the change anisotropic-isotropic state, respectively.

R. S.

**Molecular volume of normal liquids.** R. LAUTIE (Compt. rend., 1936, 202, 753—754; cf. A., 1935, 435, 814).—The val. of  $K$  in the expression  $(T_c/\theta) \log (240/V_c) = K$  is always  $< 3$  for the rare gases or for light mols. or mols. containing few atoms. For associated liquids it is  $> 3$ . Typical vals. are given.

H. J. E.



**Werner complexes.** Optical activity and configuration of ions containing the groups  $[\text{Me en}_2]$  or  $[\text{Me ox}_2]$ . J. P. MATHIEU (Bull. Soc. chim., 1936, [v], 3, 476—498).—The optical rotation and circular dichroism of 20 complexes of Co, Cr, and Ir have been studied in the visible region. The bearing of the results on the configuration of the ions is discussed. E. S. H.

**Heats of combustion and refractivity data of crotonic esters.** E. SCHJÄNBERG (Z. physikal. Chem., 1936, 175, 342—346).—The energy of cleavage of the C-C linking, calc. from the heats of combustion, shows slight constitutive variations. The refractive and dispersive increments of the linking are  $\gg$  the vals. calc. from Eisenlohr's at. refractions, and the increments for normal, *iso*-, and *sec*.-esters are all different. R. C.

**Magnetic rotatory power of nitric oxide.** H. BIZETTE and B. TSAI (Compt. rend., 1936, 202, 648—649).—The Verdet const. for NO is  $-0.0068'$  for the Hg green line at  $16^\circ$  and 90 kg. per sq. cm. Data for the variation of the magnetic rotation with  $\lambda$  are given. L. J. J.

**Absolute determination of the magnetic rotatory power of water.** R. DE MALLEMANN, P. GABIANO, and F. SUHNER (Compt. rend., 1936, 202, 837—838).—Verdet's const.,  $A$ , for  $\text{H}_2\text{O}$  for the green Hg line is  $(1.543' \pm 0.001) \times 10^{-2}$  at  $11.5^\circ$ . The val. of  $A$  calc. from this for the  $D$  line, using the known val. of the dispersion, is  $1.312 \times 10^{-2}$ , in agreement with the val. obtained by other investigators. M. S. B.

**Magneto-optical dispersion of acetylacetone.** L. SHUEQ-SHANN (Chinese J. Physics, 1935, 1, 54—58).—Data for magneto-optical dispersion and Verdet const., measured in a field of 6000 gauss, are recorded.  $M[\alpha]$ , and  $e/m$  calc. from the data, are compared with calc. and accepted vals., respectively. L. J. J.

**Optic moments of organic molecules in relation to crystalline and magnetic birefringence.** M. RAMANADHAM (Proc. Indian Acad. Sci., 1936, 3, A, 43—50; cf. A., 1935, 565).—Vals. of  $C_M$  are recorded for  $\text{C}_{10}\text{H}_8$ ,  $\text{Ph}_2$ , acenaphthene, benzil, salol,  $\text{COPh}_2$ , and phenanthrene, in  $\text{CCl}_4$  solution. For  $\text{C}_{10}\text{H}_8$ , observed vals. of  $C_M$  agree with vals. calc. from Salceanu's data for the fused state (A., 1932, 561). For  $\text{Ph}_2$ , the results of Groth for the positions of the optic axes, and of Hendricks and Jefferson (A., 1933, 1104) for  $n$ , are confirmed. The direction of max.  $n$  coincides with the length of the mol., making an angle  $20^\circ 42'$  with the crystallographic  $c$  axis. The optic moments  $b_1, b_2, b_3$  (length, breadth, and thickness of mol.), calc. from  $n$  in  $\text{CCl}_4$  solution, are 33.32, 23.06, and 12.13 ( $\times 10^{-24}$ ) c.g.s., respectively, for  $\text{Ph}_2$ , and 32.36, 23.74, and 14.36 ( $\times 10^{-24}$ ), respectively, for  $(\text{CH}_2\text{Ph})_2$ , in agreement with  $n$  for the liquids, and in the case of  $\text{Ph}_2$  with the observed  $C_M$ . L. J. J.

**Linking of magnesium oxide.** H. LESSHEIM and R. SAMUEL (Current Sci., 1936, 4, 584—586).—Mols. of  $\text{MgO}$ ,  $\text{CaO}$ , etc. crystallise with the NaCl type of lattice, yet do not show ionic properties. It is suggested that it is possible for a covalent non-ionic mol. to crystallise in this type. The infra-red absorp-

tion spectrum of  $\text{MgO}$  contains several main max. and in its gross structure appears to be much too complicated for a symmetrical cubic lattice, resembling more that of the hexagonal  $\text{BeO}$  lattice. It is therefore possible that the  $\text{MgO}$  crystal is a giant mol. with covalent linkings. The assumption that the NaCl lattice is a rigorously valid criterion of the electrovalent linking is criticised on the ground that many examples are known of substances crystallising in the same lattice type, yet possessing quite different linking forces. A. J. M.

**Symmetry of the benzene molecule.** P. TERPSTRA and W. J. VAN WEERDEN (Rec. trav. chim., 1936, 55, 161—169; cf. this vol., 274).—Consideration of available data leads to the conclusion that the symmetry of the  $\text{C}_6\text{H}_6$  mol. is either  $D_{3d}$  or  $D_{6h}$ , the former being the more probable. Models are suggested and discussed. F. L. U.

**Chemical constitution of planetary atmospheres.** K. WURM (Chem.-Ztg., 1936, 60, 266—268).—A review.

**Rearrangement of molecules in unimolecular films.** Polycyclic compounds of the five-ring series. W. D. HARKINS, H. E. RIES, jun., and E. F. CARMAN (J. Chem. Physics, 1936, 4, 228—229).—In unimol. films of certain compounds such as betulin, containing five  $\text{C}_6\text{H}_6$  rings, an increase in pressure is followed by a rapid rearrangement of the mols. resulting in an almost complete disappearance of the pressure increase. M. S. B.

**Distribution of molecules in a model liquid.** W. E. MORRELL and J. H. HILDEBRAND (J. Chem. Physics, 1936, 4, 224—227).—A three-dimensional model mol. assemblage has been constructed and employed to determine the relative frequency of occurrence of different intermol. distances. The model can also be made to simulate thermal expansion. The distribution is similar to that observed by Menke in liquid Hg by X-ray diffraction (A., 1932, 986). M. S. B.

**Virial theorem and the theory of fusion.** E. L. HILL (Physikal. Z. Sovietunion, 1935, 8, 401—406).—The force function used to describe the mutual interactions between mols. is discussed, and it is emphasised that this function contains a contribution from the kinetic energy terms of the electrons. From this fact, with further simplifying assumptions about the process of melting, a schematic explanation of the observed changes in kinetic and potential energies of the mols. along the melting curve is proposed. W. R. A.

**Some relationships between atomic lattices.** E. L. FEINBERG (Physikal. Z. Sovietunion, 1935, 8, 407—415).—An approximation of the metallic crystal by means of a space lattice formed by the ions, the inter-ion space being filled with the gas of free electrons, and the division of the crystal into the Wigner and Seitz spherically-symmetrical cells, permits determination of the interat. distance which corresponds with the stable state of the crystal expressed as the function of the valency  $z$  of the element. In this way the dependence of the valency on the at. vol. is obtained and Lothar Meyer's at. vol. curve is ex-



plained. Also, the dependence on the valency of the energy of the ionisation which deprives the atom of all its  $z$  valency electrons is obtained, in good agreement with experimental data. W. R. A.

**Theory of the accommodation coefficient.** L. LANDAU (Physikal. Z. Sovietunion, 1935, 8, 489—500; cf. Jackson *et al.*, A., 1932, 1074; 1934, 6).—Calculation of the accommodation coeff.  $\alpha$  on classical lines gives  $\alpha \propto T^{3/2}$  for  $T$  not too great and for  $(h/2\pi)\eta \ll kT$ , where  $\eta$  is collision frequency. Where  $(h/2\pi)\eta \gg kT$  a quantum treatment gives  $\alpha \propto T^3$ .

A. J. M.

**Possibility of applying the Thomas-Fermi method to the problem of metallic cohesion.** E. L. FEINBERG (Physikal. Z. Sovietunion, 1935, 8, 416—424).—Mathematical. The energy of the crystal calc. on the basis of the Thomas-Fermi method, when expressed as a function of the interat. distance, has no min. and confirms the calculations of the energy curve (Slater, Krutter). The Thomas-Fermi method does not explain the stability of the crystal lattice.

W. R. A.

**Heitler-London repulsive state of hydrogen.** H. M. JAMES, A. S. COOLIDGE, and R. D. PRESENT (J. Chem. Physics, 1936, 4, 187—193).—Theoretical.

M. S. B.

**American measurements on supercooled steam.** M. JAKOB (Z. tech. Physik, 1935, 16, 83—86; Chem. Zentr., 1935, ii, 22—23).—Yellott's curve for the spontaneous condensation of ion- and dust-free  $H_2O$  vapour indicates that condensation occurs on nuclei 1.5—2 times the radius of unassociated  $H_2O$  mols., in agreement with Wilson's theory that associated mols. are involved.

J. S. A.

**Calculation of surface tension from experiment.** II. [Capillary] rise in tubes of circular section of all widths. III. Height of the meniscus in wide or narrow tubes when the angle of contact is zero; or the determination of the capillary constant for sessile drops of all sizes. A. W. PORTER (Phil. Mag., 1936, [vii], 703—706, 706—708; cf. A., 1933, 250).—II. A satisfactory correction of Richards and Coombs' formula (A., 1915, ii, 522) can be obtained by using Bashford and Adams' tables and extending these by Rayleigh's formula for very wide tubes.

III. The treatment developed previously can be extended by Bashford and Adams' tables to include very narrow capillaries or very small sessile drops.

J. W. S.

**Parachor and chemical constitution. Structure of nitrobenzyl-dialkylamines.** B. SINGH and A. SARUP (J. Chim. phys., 1936, 33, 183—187).—The surface tensions,  $d$ , and parachors of *o*-, *m*-, and *p*-nitrobenzyl-dimethyl-, -dipropyl-, and -dibutylamine are given. The parachors of the *o*-compounds correspond to a non-co-ordinated mol. structure.

R. S.

**Double refraction of X-rays in crystals.** J. FRENKEL (Physikal. Z. Sovietunion, 1935, 8, 587—588).—The failure of Hertzrücken *et al.* (*ibid.*, 1933, 4, 50) to detect double refraction of X-rays in quartz is due to the fact that the  $\lambda$  of X-rays is  $<$  interat. distances. This, as well as some other optical effects

due to anisotropy of separate mols., cannot occur with X-rays, since the electrostatic interaction of the atoms vanishes compared with the radiative interaction, and the latter is unable to give rise to anisotropy.

A. J. M.

**Distribution of electron density and potential in a crystal lattice from X-ray data.** V. E. LASCHKAREV (Physikal. Z. Sovietunion, 1935, 8, 227—239; cf. A., 1935, 1308).—A new method of calculation is described.

R. S.

**Calculation of potential distribution in certain crystal lattices.** V. E. LASCHKAREV and A. S. TSCHABAN (Physikal. Z. Sovietunion, 1935, 8, 240—254; cf. preceding abstract).—The potential distributions in Li, Al, NaCl, and diamond have been calc.

R. S.

**Distribution of X-ray reflexions from a crystal lattice.** W. KOSSEL (Ann. Physik, 1936, [v], 25, 512—526; cf. A., 1935, 1306).—The directions of reflexion from a crystal for a given  $\lambda$  can be represented by the intersections with the surface of a sphere of a series of planes corresponding with the lattice planes. The development of such a system of reflexions with decreasing  $\lambda$  for a face-centred cubic lattice is illustrated.

L. J. J.

**Theoretical and experimental Laue patterns from bent sodium chloride crystals.** A. P. KOMAR (Nature, 1936, 137, 397—398).—A method of calculation and construction of Laue patterns from bent crystals of NaCl which gives good agreement with experimental patterns is proposed. The agreement shows that in the process of plastic deformation the crystal behaves as a mosaic aggregate of blocks which change their orientation practically independently.

L. S. T.

**Stability of closest packing of spheres.** R. NIINI (Ann. Acad. Sci. fenn., 1934, 39, A, No. 10; Chem. Zentr., 1935, ii, 13).—The hexagonal close-packed arrangement has the smallest potential energy.

J. S. A.

**Transition mechanism of cubic body-centred into hexagonal close-packed zirconium. Relation with the modifications of calcium.** W. G. BURGERS (Metallwirts., 1934, 13, 785—786; Chem. Zentr., 1935, ii, 318).—A cubic face-centred intermediate phase is assumed, but has not been detected. For Ca all three forms are known.

H. J. E.

**Kinetics of recrystallisation of tin, cadmium, and iron.** M. KORNFELD and F. SAVIZKI (Physikal. Z. Sovietunion, 1935, 8, 528—532).—In the recrystallisation of these metals, as with Al (Karnop, A., 1930, 530; B., 1930, 911) and rock-salt (Müller, A., 1934, 1058), there is an incubation period before the appearance of cryst. nuclei. The rate of growth of crystals is linear with time. Recovery from deformation is complete before the appearance of the first visible nucleus.

A. J. M.

**Formation of nuclei in recrystallisation. II. Nature of the incubation period.** M. KORNFELD (Physikal. Z. Sovietunion, 1935, 8, 533—535; cf. A., 1935, 1307).—The existence of the incubation period can be explained in two ways: (1) the formation of a



nucleus in a small vol. of the deformed material takes place suddenly owing to a single thermal fluctuation, and (2) a continuous irreversible process takes place in a definite part of the deformed material from the commencement of heating. The incubation period corresponds with the time taken for the completion of this process. The dependence of the no. of recrystallisation nuclei on the duration of heating is calc. on the basis of each of these explanations. The results of experiment favour the second explanation.

A. J. M.

**Effect of heat-treatment on the structure of gold- and silver-leaf.** G. D. PRESTON and L. L. BIRUMSHAW (Phil. Mag., 1935, [vii], 21, 713—727).—The contraction when Au-leaf is heated in air at 350—400° was shown by electron diffraction to be due to recrystallisation and reorientation. The new grains grow in a position favourable for reflexion from the (110) planes. The effect may be connected with transitory oxide formation, since it does not occur in H<sub>2</sub> or in vac. up to 700°. Similar, though less definite, results were obtained for Ag heated in air at 290°. Certain "extra" rings were attributed to the presence of Hg, but do not correspond with known phases in the Au-Hg and Ag-Hg systems. Phases present in thin films may have a different structure from those in the massive state.

H. J. E.

**Structure of solid  $\gamma$ -oxygen.** W. H. KEESOM and K. W. TACONIS (Physica, 1936, 3, 141—144).—Results obtained by the X-ray goniometer are identical with those of Vegard (cf. A., 1935, 1450).

N. M. B.

**Theoretical diffraction patterns corresponding with some simple types of molecular arrangement in liquids.** J. A. PRINS and H. PETERSEN (Physica, 1936, 3, 147—153).—Computations are made for the structures: (a) cubic and hexagonal close-packed, (b) body-centred cubic, (c) simple cubic, (e) diamond structure; the respective co-ordination numbers are 12, 8, 6, and 4. Results are confirmed experimentally by taking for (a) inert gases and Hg, (b) alkali metals, (c) Sb, (d) SiO<sub>2</sub> and H<sub>2</sub>O.

N. M. B.

**Structure of stannous sulphide and teallite.** W. HOFMANN (Fortschr. Min., 1935, 19, 30—31; Chem. Zentr., 1935, ii, 820).—Herzenbergite SnS (I), teallite PbSnS<sub>2</sub> (II), and synthetic ZnS have very similar deformed galena structures. (I) and (II) have  $a$  3.98, 4.04,  $b$  4.33, 4.28,  $c$  11.18, 11.33 Å., respectively.

J. S. A.

**X-Ray study of anhydrous ferric phosphates.** P. BRASSEUR (Compt. rend., 1936, 202, 761—762).—X-Ray diagrams showed the existence of only two forms of the metaphosphate Fe<sub>3</sub>(PO<sub>3</sub>)<sub>6</sub>. Characteristic diagrams were obtained from Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and from a pyrophosphate Fe<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>. No characteristic diagram was observed for Fe<sub>3</sub>O<sub>3</sub>(P<sub>2</sub>O<sub>5</sub>)<sub>2</sub>. An impure basic phosphate was identified.

H. J. E.

**Interpretation of X-ray diffraction pattern of liquid carbon tetrachloride.** I. NITTA and T. WATANABÉ (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 277—283).—It is inferred that under the influence of the van der Waals forces adjacent mols. orient themselves preferentially with

tetrahedral faces towards one another, giving a quasi-association. The distance between the centres of Cl atoms of adjacent mols. is 3.90 Å., i.e., the "envelope" around a Cl atom is 0.98 Å. thick.

R. S. B.

**Structure of cellulose nitrates.** I. Normal high nitrates. II. X-Ray patterns and structure of nitrates of various nitrogen contents. III. Density of nitrates and the properties of the recovered cellulose. IV. Existence of various space lattices of nitrates of the same nitrogen content. M. ISHIHARA (J. Soc. Chem. Ind. Japan, 1936, 39, 62—65B, 65—68B, 68—70B, 70—74B).—I. Details are given of the X-ray pattern of nitrated hemp (13.3% N); it is concluded that the lattice unit contains 20 glucopyranose nitrate units in four chains each five units long. No period corresponding with two units was observed.

II. The X-ray patterns of nitrates containing 3.95—13.54% N are described, and differences are observed between the classes 0—7, 10.01, 10.87, 12.80—13.2, 13.3—13.5, and 13.5% N.

III. Measurements of  $d$  of cellulose nitrates in H<sub>2</sub>O show that, with some exceptions,  $d$  increases with increasing N content, but not linearly.

IV. Nitrates with approx. the same N content (>13%) have different X-ray diagrams, and hence different lattices, according to their mode of prep. or subsequent treatment.

A. G.

**$\beta$ -Modification of the gutta-percha hydrocarbon.** G. W. PANKOW (Helv. Chim. Acta, 1936, 19, 221—222).—The stretched  $\beta$ -hydrocarbon shows interference in the X-ray diagram corresponding to a unit of length about 115 Å. along the length of the fibre.

R. S. C.

**X-Ray study of amorphous rubber.** G. L. SIMARD and B. E. WARREN (J. Amer. Chem. Soc., 1936, 58, 507—509).—The X-ray scattering curve for unstretched rubber has been submitted to a Fourier analysis. The distribution agrees with the view of a long-chain mol.

E. S. H.

**Electron microscope for filaments: emission and adsorption by tungsten single crystals.** R. P. JOHNSON and W. SHOCKLEY (Physical Rev., 1936, [ii], 49, 436—440).—A simple electron microscope for small cylindrical filaments is described. The activation of thoriated W was investigated. Electron emission from single crystals grown in drawn pure W filaments varies around the wire circumference and depends on crystallographic direction; the variation with this is more pronounced and complex for filaments self-activated in Cs or K vapour.

N. M. B.

**Surface structure of polished cleavage faces of calcite.** H. G. HOPKINS (Phil. Mag., 1936, [vii], 21, 820—830).—The polished cleavage face of calcite was shown, by electron diffraction, to be crystal. The action of very dil. acids is essentially one of pitting. Kikuchi lines were observed at a depth of 200 Å. The polishing action extends to a depth of 6000 Å., as a twinned layer was observed at this depth.

H. J. E.



**Experiments with models on the theory of the Kikuchi lines.** A. LICHTENFELD and K. SCHWARZ (Naturwiss., 1936, 24, 172—173).—The  $\lambda$  of electrons used in investigation of crystal structure is about 100 times  $<$  the distance between the lattice planes. It is suggested that besides diffraction phenomena, purely optical processes, such as shadow formation, will be encountered, and that the latter gives rise to the Kikuchi lines. Models of the NaCl lattice, with the lattice const. about 1000 times  $>$   $\lambda$  of visible light, give shadow effects with such light similar to the Kikuchi lines. A. J. M.

**Experiments with models on the theory of the Kikuchi lines.** M. VON LAUE (Naturwiss., 1936, 24, 218).—The model suggested by Lichtenfeld *et al.* (see above) for explaining the Kikuchi lines as a shadow effect is criticised on the ground that the shadows appear to be cast by the rods joining the spheres representing atoms in the model, instead of by the spheres themselves, and that the shadows fall in the direction of the incident light, whereas the position of the Kikuchi lines is determined only by the lattice. A. J. M.

**Theory of Kikuchi lines.** M. VON LAUE (Ann. Physik, 1936, [v], 25, 569—576; cf. A., 1935, 1306). L. J. J.

**Examination by electron beams of some aliphatic esters.** G. NATTA and R. RIGAMONTI (Atti R. Accad. Lincei, 1935, [vi], 22, 342—348).—Investigation of thin films of some aliphatic long-chain compounds (fatty acids, ethers, esters, and ketones) by means of electron diffraction shows that they all give two fundamental distances lying in the plane of the film and normal to the chain axis, viz., 7.46 and 4.98 Å. These are found also in the paraffins. It is suggested that these long-chain compounds show a two-dimensional isomorphism, which is independent of the active terminal groups and persists when  $\cdot\text{CH}_2\cdot$  groups are replaced at long intervals by  $\cdot\text{CO}\cdot$  or  $\cdot\text{O}\cdot$ . O. J. W.

**Supposed dependence on temperature of spontaneous magnetisation.** K. HONDA and T. NISHINA (Z. Physik, 1936, 98, 657—665).—Variation of remanent magnetisation with temp. has been measured for the three principal axes of single Fe crystals, and shows no dependence on temp. of spontaneous magnetisation. A. B. D. C.

**Volta potential, work function, and thermopotential.** I. G. MÖNCH (Erlanger Ber., 1934, 65, 191—201; Chem. Zentr., 1935, ii, 20).—A survey of the author's results as to (i) the relation between the Volta potential and the work function; (ii) the variation of the Volta potential of metals with temp. (no measurable variation up to 400°); (iii) the variation with temp. of the Volta potential of semiconductors.  $\text{Cu}_2\text{O}$  becomes more negative at high temp., probably due to alteration in the Volta potential; (iv) the connexion between Volta potential and thermopotential; (v) relationships between Volta potential, lattice dimensions, and at. vol. J. S. A.

**Connexion between work function and Volta potential.** II. G. MÖNCH (Erlanger Ber., 1934,

65, 202—207; Chem. Zentr., 1935, ii, 20).—For the metal pair W—Pt, the difference between the work functions is equal in magnitude to the difference in Volta potentials. J. S. A.

**Dependence of Volta potential on state of strain of a metal surface.** VI. G. MÖNCH (Erlanger Ber., 1934, 65, 211—214; Chem. Zentr., 1935, ii, 21).—The work function of a Ni surface, measured by the Volta potential, was not changed by the surface strains and lattice distortion resulting from flexion below the elastic limit. With  $\text{Cu}_2\text{O}$  a reproducible change occurred. J. S. A.

**Internal energy of ferromagnetics.** E. C. STONER (Phil. Trans., 1936, A, 235, 165—193).—Theoretical. A crit. analysis of the results obtained for the magnetisation, magneto-caloric effect, and sp. heat of Ni by various experimental methods is given. Discrepancies in  $-(1/\sigma)(dE/d\sigma)$  ( $E$ =internal energy,  $\sigma$ =sp. magnetisation) derived by different methods can be explained by supposing that a small amount of the Ni consists of domains of  $10^3$ — $10^4$  atoms. It is suggested that such domain-structure is not confined to ferromagnetics, but is practically equiv. to the mosaic structure met with in metals in general, due to distortion arising from impurity atoms. A. J. M.

**Refraction and dispersion in crystals and solids.** XII. Molecular refractivities and molecular volumes in the glasses  $\text{B}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3, x\text{Na}_2\text{O}$ , and  $\text{B}_2\text{O}_3, x\text{Na}_2\text{O}, y\text{NaCl}$ . P. WULFF and S. K. MAJUMDAR (Z. physikal. Chem., 1936, B, 31, 319—342).—The  $d$  of anhyd.  $\text{B}_2\text{O}_3$  is  $<$  that of  $\text{B}_2\text{O}_3$  containing a small amount of  $\text{H}_2\text{O}$ , whilst the mol. refractivity,  $R$ , is larger; apparently  $d$  passes through a max. at a very small  $\text{H}_2\text{O}$  content. The apparent mol. vol.,  $\Phi$ , and  $R$  of  $\text{Na}_2\text{O}$  in  $\text{Na}_2\text{O}$ — $\text{B}_2\text{O}_3$  glass rise with the  $\text{Na}_2\text{O}$  content, but approach a limit at  $\text{Na}_2\text{O}:\text{B}_2\text{O}_3=1:2$ . For  $\text{B}_2\text{O}_3$   $\Phi$  is approx. const. in presence of varying amounts of  $\text{Na}_2\text{B}_4\text{O}_7$ , but is  $<$  the val. for pure  $\text{B}_2\text{O}_3$  glass. For  $\text{Na}_2\text{B}_4\text{O}_7$   $R$  and  $\Phi$  fall with increase in the ratio  $\text{B}_2\text{O}_3:\text{Na}_2\text{B}_4\text{O}_7$ , the effect being large compared with those observed with aq. solutions. These variations are ascribed to the effect of the  $\text{Na}^+$  ions and dipole mols. on the  $\text{B}_2\text{O}_3$  glass, acting as solvent of small dielectric const. The  $R$  and  $\Phi$  of NaCl dissolved in  $\text{Na}_2\text{O}$ — $\text{B}_2\text{O}_3$  glass are rather  $<$  those of cryst. NaCl, corresponding with the view that a one-sided deformation of ions in the formation of mols. has a greater effect on refractivity than a deformation on all sides, as in a crystal lattice. R. C.

**[Optical] dispersion of crystalline and vitreous quartz.** J. ENGL (Ann. Physik, 1936, [v], 25, 600—608).—Theoretical. A formula is given for the refractive power of  $\text{SiO}_2$  as a function of  $\lambda$ . The relation between the dispersive power and the absorption coeff. with varying  $\lambda$  is discussed. L. J. J.

**Theory of elastic after-effect in un-ordered mixed crystals.** V. S. GORSKI (Physikal. Z. Sovietunion, 1935, 8, 457—471).—Mathematical. The after-effect in polycryst. metals and alloys is discussed in relation to diffusion and a theory is developed. W. R. A.



**Metallic crystals.** E. SCHMID (Rev. Mét., 1935, 32, 638—648).—A survey is given of the properties of single crystals in which attention is given to lattice types and the mechanism of transformation from type to type. Properties discussed are anisotropy of physical properties, mode of plastic deformation, pptn. from supersaturated solid solution, and the relationship between the polycryst. aggregates and single crystals. E. H. B.

**Electrical and optical investigations of the conversion of non-metallic into metallic antimony.** R. SUHRMANN and W. BERNDT (Physikal. Z., 1936, 37, 146—149).—Sb vapour was condensed in vac. on a quartz surface cooled by liquid  $N_2$ , and the absorption spectrum of the substance immediately after condensation compared with that shown by the film after it had warmed to a temp.  $>$  transition temp. at which the film becomes metallic in character. Well-defined absorption lines were found at low temp. but they disappeared on warming to  $373^\circ$  abs., indicating a transition from the non-metallic to the metallic state. The transition temp. varied with the thickness of the film, three vals. obtained being  $325^\circ$  (15  $m\mu$ ),  $280^\circ$  (35  $m\mu$ ), and  $270^\circ$  abs. (109  $m\mu$ ). The higher val. obtained by Kramer *et al.* (A., 1932, 1192) is possibly due to the film containing gas. A. J. M.

[Allotropy of] potassium metaphosphate prepared by dehydration of potassium dihydrogen orthophosphate. A. BOULLÉ (Compt. rend., 1936, 202, 662—664).—Thermal analysis of  $KPO_3$  obtained by dehydration of  $KH_2PO_4$  at  $225^\circ$  indicates reversible transformations at  $460^\circ$  and  $650^\circ$ . The X-ray spectrum and the m.p. ( $810^\circ$ ) are unaffected by washing the product. The same X-ray spectrum is given by the initial dehydration product, the product of slow cooling from fusion, and specimens cooled rapidly from  $300^\circ$ ,  $550^\circ$ ,  $615^\circ$ ,  $700^\circ$ , and  $800^\circ$ , which give different viscosities in 0.1N- $Na_4P_2O_7$  solution. It is concluded that only the amorphous form and a single cryst. form can exist at room temp. L. J. J.

**Transition of solid ammonium bromide at about  $-39^\circ$ .** A. SMITS, J. A. A. KETELAAR, and G. J. MÜLLER (Z. physikal. Chem., 1936, 175, 359—376).—The results of the study of the transition of  $NH_4Cl$  (A., 1933, 1119) are examined thermodynamically in relation to Smits' theory of allotropy. Dilatometric studies have shown that at about  $-39^\circ$   $NH_4Br$  undergoes a heterogeneous transition, arising from a homogeneous transformation above or below the transition region. There is a region of heterogeneous hysteresis extending over  $0.06^\circ$ . It is suggested that one pseudo-component of the system  $NH_4Br$  contains oscillating, the other rotating,  $NH_4$  groups. R. C.

**Sodium benzyldisulphonate: dimorphism.** F. D. DODGE (J. Amer. Chem. Soc., 1936, 58, 437—438).—The conditions of formation of an unstable orthorhombic and a stable mono- (or tri-)clinic modification are described. Peculiar optical properties of the latter form may be due to twinning of the crystals. E. S. H.

**Dispersion of sound and stereochemistry of nitrogen atom.** O. STEEL (Z. physikal. Chem., 1936, B, 31, 343—360).—By means of an acoustic interferometer capable of measurements up to  $150^\circ$  the velocity of sound,  $v$ , in  $NH_3$  at room temp. has been measured. Between 300 and 1000 kilohertz there is anomalous dispersion of  $v$ , which is probably connected with the N atom moving through the  $H_3$  plane so as to turn the pyramidal mol. inside out. A relation between  $v$  and frequency is deduced. R. C.

**Velocity of ultrasonic waves at low pressures.** E. J. PUMPER (Physikal. Z. Sovietunion, 1935, 8, 300—310).—The influence of pressure on the velocity of ultrasonic waves in air and in  $CO_2$  at low pressures has been studied, and the reasons for the observed deviations from classical laws are discussed. R. S.

**Absorption of ultrasonic waves in certain liquids.** P. BASHULIN (Physikal. Z. Sovietunion, 1935, 8, 354—358).—The absorption coeffs.  $\alpha$  of ultrasonic waves in vaseline-petroleum mixtures and in  $CCl_4$  have been determined by two methods depending on the diffraction of light. Agreement with the hydrodynamic theory is only partial.  $\alpha$  is unaffected by rise of temp. R. S.

**Diffraction of light by high-frequency sound waves. III. Doppler effect and coherence phenomena.** C. V. RAMAN and N. S. N. NATH (Proc. Indian Acad. Sci., 1936, 3, A, 75—84; cf. this vol., 148).—Theoretical. The variation of the refractive index of the medium with time is taken into account. L. J. J.

**Diffraction of light by high-frequency sound waves. IV. Generalised theory.** C. V. RAMAN and N. S. N. NATH (Proc. Indian Acad. Sci., 1936, 3, A, 119—125).—Mathematical. O. D. S.

**Theory of volume anomalies for ferromagnetic substances.** L. NÉEL (Compt. rend., 1936, 202, 742—744).—Theoretical. H. J. E.

**Magnetic atomic moments of manganese dissolved in copper, silver, and gold.** G. GUSTAFSSON (Ann. Physik, 1936, [v], 25, 545—560).—A method of measuring para- and dia-magnetic susceptibilities of samples in the form of wire at  $20$ — $450^\circ$  is described. Data are recorded for the at. susceptibility ( $\chi_A$ ) and at. moment of Mn for a no. of dil. solid solutions in Cu, Ag, and Au. There is a linear relation between  $\chi_A$  and  $1/T$ . L. J. J.

**Magnetic susceptibility of single crystals of lead, thallium, and tin.** S. R. RAO and K. R. SUBRAMANIAM (Phil. Mag., 1936, [vii], 21, 609—624).—No change in the magnetic susceptibility ( $\chi$ ) of single Pb or Sn crystals is noted as they are rotated about the cylindrical axis. For  $\alpha$ -Tl,  $\chi$  parallel to and perpendicular to the hexagonal axis is  $0.412$  and  $0.165 (\times 10^{-6})$ , respectively, indicating a magnetic anisotropy ( $2.5$ )  $>$  for other similar metals. The average val. for polycryst.  $\alpha$ -Tl is  $0.247$ . The mean val. of  $\chi$  for  $\beta$ -Tl (cubic) is  $0.158 \times 10^{-6}$ , becoming  $0.131 \times 10^{-6}$  after melting. It is suggested that two of the three valency electrons in  $\alpha$ -Tl have orbits in the hexagonal planes and that their linking is



homopolar, whilst the third electron is free. In  $\beta$ -Ti there are probably only Ti<sup>+</sup> ions, with the remaining electron free. J. W. S.

**Magnetochemical investigations. XX. Magnetic behaviour of simple vanadium compounds.** W. KLEMM and E. HOSCHKE (Z. anorg. chem., 1936, 226, 359—369).—The magnetic susceptibilities ( $\chi$ ) of V<sub>2</sub>O<sub>5</sub>, VCl<sub>4</sub>, VO<sub>2</sub>, VCl<sub>3</sub>, VBr<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>S<sub>3</sub>, VCl<sub>2</sub>, and VBr<sub>2</sub> have been measured at 20°, -78°, and -183°.  $\chi$  for VCl<sub>4</sub>, VCl<sub>3</sub>, and VBr<sub>3</sub> is in accord with theory, but for VCl<sub>2</sub> and VBr<sub>2</sub> divergencies are obtained, especially at low temp.  $\chi$  for V<sub>2</sub>O<sub>5</sub> is in accord with theory; VO<sub>2</sub> in spite of its odd no. of electrons is almost non-magnetic. V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>S<sub>3</sub> show deviations from the vals. expected for ionic compounds, of the magnitude observed with other analogous compounds. V<sub>2</sub>S<sub>5</sub> does not exist, and heating of V<sub>2</sub>S<sub>3</sub> with S yields only a polysulphide of composition between VS<sub>3.8</sub> and VS<sub>4</sub>. J. W. S.

**New types of complex paramagnetic salts of the iron series.** L. CAMBI and A. CAGNASSO (R. Ist. lomb. Sci. Lett., 1934, [ii], 67, 741—747; Chem. Zentr., 1935, ii, 331; cf. A., 1934, 1057).—The vals. of  $\chi$  for complex salts of Fe(CNS)<sub>2</sub> and Co(CN)<sub>2</sub> with *o*-phenanthroline and 2:2'-dipyridyl point to the existence of forms derived from the homopolar valency 3d4sp<sup>2</sup>, as predicted by Pauling (A., 1931, 670, 1356). H. J. E.

**Determination of magnetic susceptibilities of some diamagnetic compounds. Calculation of ionic susceptibilities.** O. E. FRIVOLD (Avh. norsk. Vidensk.-Akad. Oslo, Mat.-nat. Kl., 1933, No. 9, 21 pp.; Chem. Zentr., 1935, ii, 331).—The vals. for  $\chi_m \times 10^6$  in aq. solution at 20° were: HCl 21.0, HBr 32.5, LiCl 24.2, LiBr 36.0, KBr 50.3, KF 24.1, CaCl<sub>2</sub> 56.7, CaBr<sub>2</sub> 78.5, SrCl<sub>2</sub> 65.3, SrBr<sub>2</sub> 87.9, BaCl<sub>2</sub> 76.3, CdBr<sub>2</sub> 92.1, K<sub>4</sub>Fe(CN)<sub>6</sub> 134.1, ZnCl<sub>2</sub> 60.1. Vals. of the ionic  $\chi$  were calc. H. J. E.

**Measurement of the coefficient of magnetisation of organic liquids.** C. COURTY (Bull. Soc. chim., 1936, [v], 3, 420—422).—The mol. susceptibilities of pyrrole and nicotine are  $46.029 \times 10^{-6}$  and  $116.316 \times 10^{-6}$ , respectively. E. S. H.

**Thermomagnetism of rare earth salts in solution.** G. DUPOUX (Compt. rend., 1936, 202, 646—648).—Data are recorded for the paramagnetic ions Pr<sup>+++</sup>, Nd<sup>+++</sup>, Sm<sup>+++</sup>, Eu<sup>+++</sup>, and Gd<sup>+++</sup>, for which the magnetic moment and Curie temp. are calc. Weiss' law is obeyed by all the solutions studied. The existence of different magnetic states is indicated. L. J. J.

**Magnetic effects and current-sensitivity of superconducting films.** A. D. MISENER (Canad. J. Res., 1936, 14, A, 25—37).—The extent to which an external magnetic field will penetrate a thin superconducting film of Sn, mounted on a German-silver tube, has been studied for films of various thicknesses (12.2—0.3  $\mu$ ) at different temp. < transition point. There is a crit. field which will penetrate the film, this field being < that required to restore the resistance of the film at the same temp. The current-sensitivity of the films is due to a surface increase of c.d. The restoration of resistance is caused by the

magnetic field associated with the current, but this field is < that which has to be applied externally to produce the same result. Thin films of Sn are anomalous superconductors. A. J. M.

**Superconductive tantalum.** K. MENDELSSOHN and (Miss) J. R. MOORE (Phil. Mag., 1936, [vii], 21, 532—544).—A discrepancy exists between the magnetic threshold curve and the penetration curve for superconducting Ta, similar to that observed for alloys (A., 1934, 480; 1935, 20). This is attributed to the formation of a non-homogeneous sponge-like structure, since thermodynamically if the same free energy difference occurs between superconductive and normal Ta, much higher magnetic threshold vals. would be expected for small regions than for solid material. J. W. S.

**Relaxation phenomena in the transition from the superconductive to the non-superconductive state.** W. H. KEESOM and P. H. VAN LAER (Physica, 1936, 3, 173—181).—The transition in the case of Sn, if caused by a rise of temp. with const. magnetic field, takes place with a relaxation of several sec.; if caused by an increase of external magnetic field no appreciable relaxation is found. These results agree with the view that, the threshold val. curve being reached, there is a weak coupling between the at. lattice and the system of superconductive electrons, and a strong coupling between the latter and the external magnetic field and between the non-superconductive electrons and the at. lattice. N. M. B.

**Transition of a monocrystalline tin sphere from the superconductive to the non-superconductive state.** W. J. DE HAAS and O. A. GUINAU (Physica, 1936, 3, 182—192).—Transition is investigated at const. temp. with increasing magnetic field and at const. external field and rising temp. Relations between permeability, applied field, and crit. field are determined. N. M. B.

**Energetic theory of thermo-electric phenomena.** F. MICHAUD (J. Chim. phys., 1936, 33, 161—179).—The classical theory is criticised. It is shown that thermo-electric phenomena are partly irreversible in nature, and an appropriate equation has been deduced. R. S.

**Thermo-electric and voltaic properties of normal and abnormal metallic films.** R. DEAGLIO (Compt. rend., 1936, 202, 831—832).—The electrical properties of Au films vary with variation in colour by transmitted light. An e.m.f. of 0.6 volt may be obtained from the system: red or blue Au film|H<sub>2</sub>O|massive Au, but, after replacement of the red by a green film, the voltage is < 0.005. By combining the green film with massive Au in a hot and cold junction, however, a definite e.m.f. is obtained. The results may be explained by Perucca's theory (A., 1930, 280) of a difference between the surface and bulk concn. of electrons in a metal. In the first case the surface concn. is involved and in the second the bulk concn. M. S. B.

**Atomic heats and heats of fusion of neon, argon, and krypton.** K. CLUSIUS (Z. physikal. Chem., 1936, B, 31, 459—474).—The at. heats have been determined between 10° abs. and the normal



b.p. The Debye  $\theta$  vals. and latent heats of fusion are: Ne, 64°, 80.1; A, 80°, 280.8; Kr, 63°, 390.7 g.-cal. per mol.; Xe, 55°. For A, Kr, and Xe the observed  $\theta$  vals. agree with those calc. from Lindemann's formula with a modified numerical factor:  $0 = 163 \sqrt{(T_e/A v^{2/3})}$  ( $T_e = \text{m.p.}$ ,  $A = \text{at. wt.}$ ). The calc. (approx.) compressibilities and the relative space demands of the individual atoms in the solid decrease with increasing at. wt. With He the zero point energy has a decisive influence on the thermal behaviour, and with Ne the effect is still appreciable, but from A onwards it is negligible. In applying the principle of corresponding states to the thermal data the zero point energy must be allowed for. R. C.

**Specific heats of liquid carbon tetrachloride at high temperatures.** G. DAMKÖHLER (Z. physikal. Chem., 1936, B, 31, 439—453).—The isentropic cooling on adiabatic expansion, the coeff. of expansion, and the isothermal compressibilities have been determined at room temp. to 200°, and from them  $C_p$  and  $C_v$  under 26 atm. calc. The difference between  $C_p$  and that part of it due to at. vibrations within the mol. is const. at 10.4 g.-cal. up to 100°, then slowly rises with the temp. and approaches  $6R$ . It is inferred that the rotation of the mols. in the liquid is not completely free, neither is there pure rotation-vibration. R. C.

**Determination of molecular heat of gases at low temperatures by thermal conductivity method.** A. EUCKEN and A. BERTRAM (Z. physikal. Chem., 1936, B, 31, 361—381).—The method previously described (A., 1934, 20) has been developed further and used to determine the mol. heat of Kr, N<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, SF<sub>6</sub>, SeF<sub>6</sub>, TeF<sub>6</sub>, CF<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>N<sub>2</sub>, and CF<sub>4</sub> at 150—280° abs. From the results the following fundamental frequencies have been deduced: CF<sub>2</sub>Cl<sub>2</sub>,  $\nu_{\text{rotation}} = 408$ ; C<sub>2</sub>N<sub>2</sub>,  $\delta(a) = 740$ ; CF<sub>4</sub>,  $\nu_3 = 503$ ,  $\nu_4 = 1000$  ( $\pm 100$ ) cm.<sup>-1</sup>. At temp. equal to about  $\frac{3}{2}T_b$ , where  $T_b$  is the b.p. abs., the accommodation coeffs. of the above gases and A on an oxidised Ni wire in respect of translational degrees of freedom are  $\sim 1$ . For the variation with temp.,  $T$ , of the accommodation coeff. in respect of rotational and vibrational degrees of freedom,  $\alpha'$ , the equation  $\log_e (1/\alpha' - 1) = -A/T + B$  has been deduced theoretically and agrees with the experimental data. In general,  $A$  increases with  $T_b$ . R. C.

**Thermal data on organic compounds. XVI.** Heat capacity, entropy, and free energy data for typical benzene derivatives and heterocyclic compounds. G. S. PARKS, S. S. TODD, and W. A. MOORE (J. Amer. Chem. Soc., 1936, 58, 398—401; cf. this vol., 278).—Data for C<sub>6</sub>H<sub>3</sub>Ph<sub>3</sub>, PhNO<sub>2</sub>, PhSH, CH<sub>2</sub>Ph.OH, *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O, C<sub>5</sub>H<sub>5</sub>N, and quinoline are recorded. E. S. H.

[Boiling points of elements.] J. J. VAN LAAR (Chem. Weekblad, 1936, 33, 215—216).—A criticism. The following b.p. are recorded: Zn 907°, Cd 767°, Hg 356.71°, Sc 2400°, Cu 2369°, Pb 1730°. S. C.

**Critical temperatures of simple deuterium compounds.** H. KOPFER (Z. physikal. Chem., 1936, 175, 469—472).—The crit. temp. for various D

compounds have been determined. They are  $<$  those of the corresponding H compounds. R. C.

**Fusion.** E. L. HILL (Physical Rev., 1936, [ii], 49, 406).—A discussion of Herzfeld's theory of the fusion of solid A and He (cf. A., 1935, 157).

N. M. B.

**X-Ray measurement of the thermal expansion of pure nickel.** E. A. OWEN and E. L. YATES (Phil. Mag., 1936, [vii], 21, 809—819).—The parameter of Ni at 18° was 3.5172<sub>4</sub> Å. Its structure was face-centred cubic (12—600°). In the region of magnetic transformation (320—390°) there was an abnormally high rate of expansion (max. at 370°), followed by a rapid decrease. The ferromagnetic change in length per unit length for 99.98% pure Ni was  $2.4 \times 10^{-4}$ .

H. J. E.

**Vapour density of water.** R. SCHARF (Z. phys. chem. Unter., 1935, 48, 108—110; Chem. Zentr., 1935, ii, 87).—A modification of the Victor Meyer method is described, using apparatus filled with H<sub>2</sub>.

J. S. A.

**Temperature dependence of the vapour pressure of metals.** W. LEITGEBEL (Metallwirts., 1935, 14, 267—270; Chem. Zentr., 1935, ii, 334).—A summary and crit. discussion of available data.

H. J. E.

**Vapour pressure of caesium.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1936, 55, 157—160).—Formulæ for the v.p. of liquid and solid Cs, based on the most accurate published data, are given.

F. L. U.

**Vapour pressure abnormalities of capillary-active amalgams.** H. H. VON HALBAN (Helv. phys. Acta, 1935, 8, 65—79; Chem. Zentr., 1935, ii, 334).—Na, K, and Zn amalgams have abnormally low Hg v.p. unless the surface is fresh. The hypothesis of surface enrichment of the dissolved metal is not entirely satisfactory. An adsorbed film of C<sub>6</sub>H<sub>6</sub> does not alter the v.p. of Hg.

H. J. E.

**Methods and apparatus in use at the Bureau des Etalons Physico-Chimiques. IX.** Variation of the density as a function of temperature for a series of ten hydrocarbons. L. MASSART (Bull. Soc. chim. Belg., 1936, 45, 76—94).—Liquid and v.d. of C<sub>6</sub>H<sub>6</sub>, PhMe, *o*-, *m*-, and *p*-xylene, PhEt, PhPr<sup>2</sup>, PhBu<sup>2</sup>, cyclohexane, and methylcyclohexane have been determined dilatometrically from the m.p. to  $>$  b.p.

R. S.

**Vapour pressures and association of metallic and non-metallic alkyls.** H. W. THOMPSON and J. W. LINNETT (Trans. Faraday Soc., 1936, 32, 681—685).—V.p. of the following have been measured: ZnMe<sub>2</sub>, ZnEt<sub>2</sub>, HgMe<sub>2</sub>, HgEt<sub>2</sub>, SnMe<sub>4</sub>, PEt<sub>3</sub>, NMe<sub>3</sub>, NEt<sub>3</sub>, MeI. The Trouton consts. are calc., and indicate little or no association. The results are compared with those for other similar compounds.

F. L. U.

**Formation of drops in supersaturated D<sub>2</sub>O vapour.** Surface tension of D<sub>2</sub>O. H. FLOOD and L. TRONSTAD (Z. physikal. Chem., 1936, 175, 347—352).—The adiabatic expansion required for drop formation in D<sub>2</sub>O vapour is  $\ll$  than that necessary with H<sub>2</sub>O. This is explained on Volmer's theory (A., 1935, 25) by the variation of the metastable limit with temp.



The difference in the crit. supersaturations, however, is small, because the supersaturation of  $D_2O$  increases with the degree of supercooling more rapidly than that of  $H_2O$ . At 12–50° the surface tension of 99%  $D_2O$  is the same as that of  $H_2O$  (cf. *ibid.*, 1059). R. C.

**Application of kinetic theory to the problems of evaporation and sublimation of monatomic gases.** P. D. CROUT (J. Math. Phys. Mass. Inst. Tech., 1936, 15, 1–54).—The complete relationship between surface pressure and rate of evaporation for all rates of evaporation is derived. At the boundary of the liquid surface where isotropy has not been attained, it is necessary to assume two temp. corresponding with mol. motions parallel and normal to the liquid surface. It is assumed that velocity distribution of the emitted mols. is unaffected by that of the incident mols. It follows that the rate of evaporation cannot exceed that corresponding with a drift velocity equal to the velocity of sound in the isotropic gas. The anisotropic region has a depth of the order of several mean free paths. The theory is illustrated by data on the evaporation of Hg. C. R. H.

**Theoretically interesting aspects of high-pressure phenomena.** P. W. BRIDGMAN (Rev. Modern Phys., 1935, 7, 1–33). CH. ABS. (e)

**Extreme values of the Joule-Thompson effect. Inversion points of the second order.** V. JACZYNA (Z. Physik, 1936, 98, 775–789).—Theoretical.

A. B. D. C.

**Glass. XIV. Compressibility of glucose glass.** J. C. LYMAN and G. S. PARKS (J. Chem. Physics, 1936, 4, 218–219).—The coeff. of cubic compressibility of glucose glass (I) at 24° is  $18.8 \times 10^{-4}$  atm.<sup>-1</sup> at 7–25 atm. Liquid glycerol and (I) have a smaller compressibility and thermal expansion than org. substances such as EtOH and  $C_6H_6$  (liquid and cryst.), indicating that the intermol. forces in polyhydroxy-compounds are considerably > in ordinary liquids, or even in a typical non-polar crystal. This is probably a factor governing the formation of a stable glass. M. S. B.

**Gas-kinetics properties of light and heavy hydrogen.** O. HALPERN and E. GWATHMEY (J. Chem. Physics, 1936, 4, 229).—The effect of statistical wts. of mols. on the difference between the viscosity of ordinary and para-H at different temp. has been calc. The difference is thus shown to be vanishingly small for D. M. S. B.

**Viscosity of "ice sol" as dependent on temperature and concentration.** E. EMBLIK (Z. ges. Kalte-Ind., 1935, 42, 71–74; Chem. Zentr., 1935, ii, 23).—Data for the dynamic and kinematic viscosity are given. J. S. A.

**Viscosity of methyl alcohol and acetone above their b.p.** P. C. BLOKKER (Rec. trav. chim., 1936, 55, 170–172; cf. this vol., 291).—Viscosities of MeOH and  $CO_2$  at temp. up to 218° have been measured. The vals. for  $CO_2$  up to 140° agree with Batschinsky's formula. Deviations observed at higher temp. are discussed. F. L. U.

**Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration.** T. ISHIKAWA and T. BABA

(Bull. Chem. Soc. Japan., 1936, 11, 64–101).—Viscosity formulæ are applied to the published results of other observers. The characteristic consts. for various binary mixtures are tabulated. C. R. H.

**Interpretation of diffusion and viscosity curves in binary mixtures.** H. LEMONDE (Compt. rend., 1936, 202, 731–733).—The interpretation of curves connecting the diffusion coeff. (*D*), the viscosity ( $\eta$ ), and the product *D* $\eta$  with the composition of EtOH- $H_2O$  mixtures at 10° and 18° is discussed. The *D*- $\eta$  curve leads to the same conclusions about association as the b.-p. curve. H. J. E.

**Viscosity of solutions of phenol and of camphor.** A. CASTIGLIONI (Gazzetta, 1935, 65, 1214–1217; cf. A., 1934, 1166).—PhOH, like camphor (I), lowers the viscosity of oils. Data are recorded for mixtures of olive oil and a second liquid ( $CHCl_3$ ,  $C_6H_6$ , PhMe, xylene) and for mixtures of vaseline and PhMe, before and after the addition of 10% of (I). For certain mixtures, the viscosity is not affected by the addition of (I). O. J. W.

**Viscosity of the critical mixture for the ternary system benzene-alcohol-water.** O. KIMURA (Bull. Chem. Soc. Japan., 1936, 11, 57–63).—Viscosity data for mixtures in the crit. region indicate that increase of viscosity, accompanied by opalescence, is due to the presence of colloid particles, supposed to be  $C_6H_6$  droplets covered with a thin EtOH film. The concn. of the colloid particles is of the order of 0.0001 near the crit. point. C. R. H.

**Magnetic susceptibility and other properties of binary mixtures of organic liquids.** V. C. G. TREW and J. F. SPENCER (Trans. Faraday Soc., 1936, 32, 701–708; cf. A., 1934, 137).—The density,  $n$ , heat of mixing, sp. heat, and magnetic mass susceptibility have been determined for mixtures of  $C_6H_6$  with PhMe, *m*-xylene with  $C_6H_6$ , PhMe,  $PhNO_2$ , and  $NH_2Ph$ , and  $PhNO_2$  with  $NH_2Ph$ . Deviations from the mixture law are shown by all the pairs and for all the properties considered. The mol. magnetic susceptibility is a more nearly additive property than the others studied. F. L. U.

**Diamagnetic susceptibility of sulphuric acid-water mixtures.** B. N. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 188–192).—Deviations from additivity are attributed to the formation of  $H_2SO_4 \cdot 2H_2O$ . O. D. S.

**Condensation and b.p. curves of nitrogen-carbon monoxide mixtures up to 17 atmospheres.** F. STECKEL (Physikal. Z. Sovietunion, 1935, 8, 337–341).—The data are tabulated and show good agreement with the theory of Roozeboom. R. S.

**Heats of vaporisation of ternary mixtures.** V. FISCHER (Ann. Physik, 1936, [v], 25, 728–736).—Theoretical. Expressions are deduced for heats of vaporisation at const. pressure and temp., and these are used to calculate heats of mixing and entropy changes. L. J. J.

**Rectification of ternary mixtures, especially oxygen-nitrogen-argon mixtures.** H. HAUSEN (Forsch. Ingenieurw., 1935, 6, A, 9–22; Chem. Zentr., 1935, ii, 730).—Equilibrium diagrams between



1 and 5 atm. are given and methods for calculating the composition of the products of rectification under various conditions are discussed. J. S. A.

**Classification of binary, ternary, and quaternary alloys.** E. JANECKE (Z. Elektrochem., 1936, 42, 128—138).—A lecture. F. L. U.

**Binary systems of alkali metals. II.** G. GORIA (Gazzetta, 1935, 65, 1226—1230; cf. this vol., 23).—Thermal diagrams for the systems Na-Cs, K-Cs, and Rb-Cs are recorded. The first shows the formation of the compound Na<sub>2</sub>Cs, a eutectic at -28° with 7.0 wt.-% Na, and no solid solution formation. The second suggests the formation of the compound KCs. In the third system there is a eutectic at -39° (13 wt.-% Rb) but neither compound nor solid solution formation is indicated. O. J. W.

**Structure of some alloys of copper.** W. BRONIEWSKI (Rev. Mét., 1935, 32, 649—657).—The constitution and properties of binary alloys of Cu with Ni, Ag, Al, Zn, Sn, and Au are reviewed. E. H. B.

**Elastic after-effect in the ordered Cu-Au alloys. (Elastic after-effect of the first kind.)** V. S. GORSKI (Physikal. Z. Sovietunion, 1935, 8, 562—571; cf. A., 1935, 439).—An after-effect amounting to 60—100% of the elastic deformation is shown by polycryst. alloys; for single crystals the corresponding magnitude of the after-effect is 10—60%. The influence of temp. on the time factor involved has been examined in both polycryst. material and single crystals. Results are in agreement with theory. A. J. M.

**Transitions in alloys. IV. Theory of arrangement processes and diffusion in mixed crystals of AuCu.** V. S. GORSKI (Physikal. Z. Sovietunion, 1935, 8, 443—356).—Mathematical. The temporary change in the degree of orderliness and the diffusion coeff. for an ordered CuAu lattice has been calc. by three methods: atom migration in the inter-lattice plates, migration of empty lattice plates, and direct atom plate alternation. Experimental data disagree with the vals. given by each of these methods. W. R. A.

**Gold-copper alloys.** W. BRONIEWSKI and K. WESOŁOWSKI (Ann. Physik, 1936, [v], 25, 757—758).—Polemical, against Le Blanc and Wehner (A., 1935, 1198). L. J. J.

[Gold-copper alloys.] M. LE BLANC and G. WEHNER (Ann. Physik, 1936, [v], 25, 759—760).—A reply to the above. L. J. J.

**Electrical conductivity and equilibrium diagram for binary alloys. XVIII. System palladium-cobalt.** G. GRUBE and H. KÄSTNER (Z. Elektrochem., 1936, 42, 156—160; cf. A., 1935, 291).—Data for the f.p. and m.p., variation of sp. resistance with temp., and Curie temp. of alloys of Pd and Co have been determined. The phase-equilibrium diagram is given. F. L. U.

**Equilibrium diagram of the magnesium-rich magnesium-aluminium-silicon ternary system.** H. SAWAMOTO (Suiyo-Shi, 1935, 8, 713—727).—The

ternary eutectic temp. coincides with that of the Mg-Al binary system at 437° (Al 32.7, Mg 67.3%).

CH. ABS. (e)

**Effect of nickel on the limits of the  $\alpha$ -phase of copper-aluminium alloys.** V. GRIDNEV and G. KURDJUMOV (Metallwirts., 1936, 15, 229—231, 256—259).—Additions of 2% and 4% Ni reduce the limit of the  $\alpha$ -range from 9.8 to 8.6% Al at the eutectoid temp., and raise the latter from 570° to 605°. Below this temp. the  $\alpha$ -range is const. in alloys containing 2% Ni, but narrows slightly with falling temp. when 4% Ni is added. The eutectoid point is displaced to higher Al contents. C. E. H.

**Spectrographic study of modifications undergone by the surface of light alloys; application to duralumin.** H. TRICHÉ (Compt. rend., 1936, 202, 745—747).—The spectrum obtained with a high-frequency spark between a Au wire and a duralumin electrode has been examined. After electrolysis in conc. aq. H<sub>2</sub>CrO<sub>4</sub> the intensity of the lines of Cu, Si, and Ca became much feebler, or even disappeared. The spectrum was unaltered after electrolysis in H<sub>2</sub>SO<sub>4</sub>. After short treatment with H<sub>2</sub>CrO<sub>4</sub>, electrolysis in H<sub>2</sub>SO<sub>4</sub> restores the surface to its initial state (as judged by the spark spectrum), but after prolonged treatment with H<sub>2</sub>CrO<sub>4</sub> the H<sub>2</sub>SO<sub>4</sub> electrolysis merely increases the thickness of the surface film. H. J. E.

**Special magnetic behaviour of cold-rolled iron-nickel alloys. (Development of isoperms.)** O. DAHL and J. PFAFFENBERGER (Metallwirts., 1935, 14, 25—28; Chem. Zentr., 1935, ii, 659).—Binary Fe-Ni alloys, like those containing Cu, show isperm properties, but these can be made use of only if the hysteresis is depressed. X-Ray investigation shows a well-developed cubic macrostructure. J. S. A.

**Compensation of nickel-beryllium alloys.** W. GERLACH (Naturwiss., 1936, 24, 218).—An alloy containing 2% Be is weakly magnetic after heating to 1200° and quenching. After annealing at 500° with mechanical compensation, the magnetisation increases by 50%, and the coercive force, residual magnetism, and Curie point also show a rise. The phenomenon is due to the separation during the annealing of Be from the Ni-Be mixed crystals, which are supersaturated at low temp. A mixed crystal with higher Curie point results. There is also considerable distortion of the Ni lattice. The distorted lattice is very stable, and the magnetic properties are not changed by long heating at 300°. A. J. M.

**Critical solution temperatures of aliphatic acids with nitromethane.** G. BROUGHTON and D. C. JONES (Trans. Faraday Soc., 1936, 32, 685—689; cf. A., 1934, 477).—Crit. solution temp. of mixtures of MeNO<sub>2</sub> with normal saturated fatty acids are as follows: C<sub>6</sub> (hexoic) -3.4°, C<sub>8</sub> 34.85°, C<sub>9</sub> 48.60°, C<sub>12</sub> 78.90°, C<sub>16</sub> 104.55°, C<sub>18</sub> 114.0°. F. L. U.

**Calculation of the solubility of a mixture of hydrogen and nitrogen in water at 25° in the pressure range 50—1000 atmospheres.** J. KIEL-



LAND (J. Amer. Chem. Soc., 1936, 58, 426—427).—Theoretical. E. S. H.

**Solubility of nickel sulphate in mixtures of sulphuric acid and water.** A. V. BABAEVA and E. I. DANILUSCHKINA (Z. anorg. Chem., 1936, 226, 338—340).—The solubility of  $\text{NiSO}_4$  in  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  mixtures has been measured at 0°, 20°, 40°, and 80°. Besides the known hydrates  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (blue),  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (green), and  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ , the hydrate  $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$  (green) has been found to occur at 40° in presence of higher  $[\text{H}_2\text{SO}_4]$ . J. W. S.

**Solubility of monometric  $\text{As}_2\text{O}_3$  in acids and compounds  $\text{AsXO}_4$ .** D. GHIRON and G. MANGILI (Gazzetta, 1935, 65, 1244—1249).—The solubility in dil. acid solutions ( $< 1.0M$ ) is approx. the same as in  $\text{H}_2\text{O}$ , but the rate of dissolution is  $>$  in the acid solutions. In more conc. acid solutions the solubility depends on the basicity rather than on the strength of the acid, and is greatly increased in  $\text{H}_3\text{AsO}_4$  and in  $\text{H}_3\text{PO}_4$ . The existence of the compounds  $\text{AsAsO}_4$  and  $\text{AsPO}_4$  is confirmed. O. J. W.

**Solubility of potassium silicofluoride under different conditions.** A. A. VASILIEV and N. N. MARTJANOVA (J. Appl. Chem. Russ., 1936, 9, 152—154).—At 17° the solubility in  $\text{H}_2\text{O}$  is 0.1147, in 50%  $\text{EtOH}$  0.0042, in saturated aq.  $\text{KNO}_3$  and  $\text{KCl}$  0.0055 and 0.0054, respectively, and in 50%  $\text{EtOH}$  (containing 2%  $\text{KCl}$ ) 0.0022 g. per 100 ml. When used for washing the ppt., 100 ml. of the last named solution dissolve 0.9 mg. of  $\text{K}_2\text{SiF}_6$ . R. T.

**Solubility of sodium naphthalene-1:6-disulphonate in aqueous sodium chloride at 15°.** N. A. TOLMATSHEV (Anilinokras. Prom., 1935, 5, 219—220).—The solubility falls from 18% in  $\text{H}_2\text{O}$  to 1% in 25%  $\text{NaCl}$ . R. T.

**Congruent solubility of dolomite.** F. HALLA (Z. physikal. Chem., 1936, 175, 396—399).—Whether a double carbonate dissolves in  $\text{H}_2\text{O}$  congruently or incongruently is independent of the pressure of  $\text{CO}_2$  above the solution. R. C.

**Influence of foreign ions on the double [zinc] mercuric thiocyanate reaction.** B. V. J. CUVELIER and F. BOSCH (Natuurwetensch. Tijds., 1936, 18, 9—11).—The solubility of  $\text{ZnHg}(\text{SCN})_4$  in various salt solutions increases in the order  $\text{NaNO}_3 < \text{Na}_2\text{SO}_4 < \text{NaCl} < \text{NaBr} < \text{NaI}$ . The solubility in aq.  $\text{NaNO}_3$  is  $\times$  in  $\text{H}_2\text{O}$ , and for its determination Zn should therefore be in the form of nitrate (cf. A., 1935, 441, 721, 1068). D. R. D.

**Simultaneous solubility of sulphur and iodine in carbon tetrachloride.** A. A. JAKOVKIN and P. A. ARCHANGELSKI (Z. anorg. Chem., 1936, 226, 350—352).—At 0° the solubility of S in  $\text{CCl}_4$  is almost unaltered in presence of I, whilst the solubility of I is slightly increased. At 25° the solubility of each solute is increased in presence of the other, equilibrium being reached with 0.178 g. of I and 0.137 g. of S per 100 c.c. of solution. The results can be explained by the formation of a small amount of an unstable compound between the solutes. J. W. S.

**Liquid ammonia as a solvent for inorganic compounds. III. Vapour pressure measure-**

**ments.** M. LINHARD (Z. physikal. Chem., 1936, 175, 438—458; cf. A., 1934, 138).—The v.p. of solutions of alkali chlorides, bromides, and iodides, and of alkali and alkaline-earth nitrates have been determined at 0° from 0.2N to saturation. The ionisation in liquid  $\text{NH}_3$  solution is much  $<$  in aq. solution at the same concn. With  $\text{NH}_4\text{Cl}$ ,  $\text{AgI}$ , and alkaline-earth nitrates there is appreciable association even at small concns. The solvation of the ions and the tendency to association in conc. solution and in the ammoniated cryst. salts largely run parallel. Solvation increases from the chlorides to the iodides and from the Cs to the Na salts. The solubility increases, in general, in the same order, and for a series of salts with a common ion increases as the solvation increases and the lattice energy of the salt diminishes. With the alkaline-earth nitrates solvation is especially high, owing to the double charge of the cation, and the solubility falls with increasing at. vol. of the metal. The Raman spectrum of  $\text{NH}_3$  solutions of  $\text{AgI}$  indicates the presence of polymerised mols. R. C.

**Supersaturation.** R. E. LIESEGANG (Scientia, 1935, 57, 345—353; Chem. Zentr., 1935, ii, 476).—A discussion. H. J. E.

**Growth of crystals. VIII. Stabilising action of cations which accelerate the crystal growth on the supersaturated solution.** T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 183—200).—Data for the supersaturation, crystallisation temp., and supersolubility of  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{KCl}$  in presence of  $\text{Pb}^{++}$ , and of  $\text{NH}_4\text{Cl}$  in presence of  $\text{Mn}^{++}$ , are given and discussed. N. M. B.

**Distribution of radium in crystals of radium-containing barium salts.** (MME.) B. E. MARQUES (J. Chim. phys., 1936, 33, 219—225).—A comparison of the effects produced on a photographic plate by outer and inner crystal faces has shown that  $\text{BaBr}_2$  crystals which contain  $\text{RaBr}_2$  have a higher  $[\text{Ra}]$  near the centre than in the outer layers. Doerner and Hoskins' formula holds for the distribution in a single crystal as well as for the distribution between solid and liquid phases. J. W. S.

**Calorimetric investigation of adsorption of light and heavy hydrogen on active nickel.** A. MAGNUS and G. SARTORI (Z. physikal. Chem., 1936, 175, 329—341).—The rate of absorption at 0° and 25° and initial pressures of 0.25—1.25 mm. has been studied by observations on the heat evolved and the change in pressure. The results agree with the view that the sorption consists in an almost instantaneous physical adsorption of a small amount of H which undergoes adsorption at a high but measurable rate on the active centres; the sorbed H then slowly changes into another state, perhaps the dissolved state, the heat effect accompanying this process being too small to be detectable calorimetrically. H is adsorbed much more rapidly than D, the heat of activation being  $\sim 1.0$  as compared with  $\sim 1.7$  kg.-cal. The heats of adsorption vary little with temp. R. C.

**Absorption of gases on sodium chloride.** F. C. TOMPKINS (Trans. Faraday Soc., 1936, 32, 643—653).—Adsorption isotherms for  $\text{NO}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,



A, and  $O_2$  at  $-183^\circ$ , and for  $(CN)_2$ ,  $CO_2$ ,  $N_2O$ , and  $C_2H_4$  at  $-78.2^\circ$  on cryst. NaCl have been determined at pressures  $> 0.4$  mm. The dipole gases are highly adsorbed according to the val. of their electric moment. Adsorption of non-polar gases increases with their polarisability. The shape of the isotherms is explained. No lateral diffusion of adsorbed mols. occurs at  $-192^\circ$  or  $-183^\circ$ , but slow secondary absorption is observed at  $-78.2^\circ$ . Heats of adsorption of A,  $CH_4$ , and CO in the range  $-183^\circ$  to  $-192^\circ$  are  $<$  those theoretically expected. F. L. U.

**Adsorption isotherm for lead chloride as an adsorbent.** F. DURAU and G. TSCHOEPE (Naturwiss., 1936, 24, 156—157).—The adsorption of  $C_6H_6$ ,  $C_6H_{14}$ , and  $COMe_2$  on purified  $PbCl_2$  has been examined by a method based on measurements of vol. The adsorption-pressure curves for dry  $C_6H_6$  and  $C_6H_{14}$  are linear at low pressures, but that for  $COMe_2$  dried over  $CaCl_2$  shows some deviations due to  $H_2O$  vapour not removed by  $CaCl_2$ . The curves deviate from the linear as the saturation pressure is approached and do not agree with Langmuir's theory. A. J. M.

**Mathematical formula for determination of the total adsorbable substance of an adsorption system by means of repeated extractions.** J. VOICU (Kolloid-Z., 1936, 74, 316—328).—Mathematical. E. S. H.

**Structural changes taking place during the ageing of precipitates. IX. Mechanism of adsorption of lead on aged barium sulphate.** I. M. KOLTHOFF and W. M. MACNEVIN (J. Amer. Chem. Soc., 1936, 58, 499—504; cf. this vol., 284).—Th-B is removed from aq. solution when shaken with pptd.  $BaSO_4$  (a) by rapid exchange of the ions with  $Ba^{++}$  in the surface, (b) by incorporation of exchanged Th-B in the  $BaSO_4$  lattice as a result of recrystallisation. The rate of recrystallisation depends on the degree of perfection of  $BaSO_4$ , the temp. and composition of the solution; it is reduced markedly by addition of 50% EtOH. Th-B can be desorbed by adding a large excess of Ba salt. E. S. H.

**Separation of amino-acids. I, II. Adsorption of diamino-acids on Japanese acid clay.** M. MASHINO and N. SHIKAZONO (J. Soc. Chem. Ind. Japan, 1936, 39, 54—55B).—Japanese acid clay, especially when activated by treatment with HCl, is a powerful absorbent for the  $(NH_2)_2$ -acids from hydrolysed soya-bean protein. Adsorption is a max. at  $pH$  5—7 and falls rapidly in alkaline media. The following amounts % of  $NH_2$ -acids were absorbed from 0.5% solutions: glycine 8.45, alanine 9.38, leucine 6.5, phenylalanine 11.14, aspartic acid 3.55, glutamic acid 4.18, arginine 86.80, histidine-HCl 84.80, lysine-2HCl 62.92%. Active C adsorbs  $NH_2$ - and  $(NH_2)_2$ -acids equally;  $SiO_2$  gel is much less effective. S. C.

**Application of Bangham and Sever's formula of sorption velocity.** I. HIGUTI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 96—108).—Bangham and Sever's formula  $\log[S/(S-x)] = kt^n$ , where  $S$  is the saturation val.,  $x$  the quantity adsorbed at time  $t$ , and  $k$  and  $n$  are consts., has been found to

hold for a wide range of published results.  $k$  and  $n$  change abruptly near the saturation point. The formula holds for chemisorption as well as occlusion, but when several compounds are formed, as with  $NH_3$  and  $AgCl$ ,  $n$  and  $k$  are sp. for each compound. R. S. B.

**Surface tension of soap solutions.** N. K. ADAM (Trans. Faraday Soc., 1936, 32, 653—656).—Increase in the surface tension of soap solutions caused by adding small amounts of alkali is due to suppression of hydrolysis, which is greatly magnified in the surface layer because the surface activity of the acid, or acid soap,  $>$  that of neutral soap. The adsorption of neutral K dodecoate is calc. from published data. The adsorbed film is gaseous. F. L. U.

**Transport numbers of ions through membranes, as a characteristic of their electro-osmotic properties.** I. I. I. SHUKOV and A. I. JURSHENKO (J. Appl. Chem. Russ., 1936, 9, 9—22).—The  $\zeta$ -potentials of membranes (porcelain, gelatin, cellulose, bakelite paper, leather) interposed between the anode and cathode in the electrolysis of aq. KCl-HCl, at different  $p_H$ , do not run parallel with the transport nos. of the ions within the membranes. In the case of leather different results are obtained according to which side is directed towards the anode or cathode. R. T.

**Cryoscopy of solutions in formamide.** I. F. H. GETMAN (Rec. trav. chim., 1936, 55, 231—243).—From measurement of the surface tension between  $4^\circ$  and  $78^\circ$  the association factor for  $HCO \cdot NH_2$  is calc. to be about 6 at room temp. The f.p. const. is 3.50, and  $n_D^{25} = 1.44682$ . The mol. wts. of  $HCO \cdot NH_2$  and  $H_2O$ , each dissolved in the other, are those of non-associated mols. A modification of the Beckmann f.-p. method is described. F. L. U.

**Electrolytic solutions. XVIII. Molecular polarisations and polar moments of electrolytes in benzene solutions.** J. A. GEDDES and C. A. KRAUS. XIX. Conductance of mixed electrolytes in ethylene chloride. Tetrabutyl- and tetramethyl-ammonium picrates. D. J. MEAD, R. M. FUOSS, and C. A. KRAUS (Trans. Faraday Soc., 1936, 32, 585—593, 594—606).—XVIII. Dielectric consts. of  $C_6H_6$  solutions of various alkyl-ammonium salts have been determined at  $25^\circ$  at concns. down to  $4 \times 10^{-5} N$ . Polar moments ranging from 7 to  $20 \times 10^{-18}$  indicate the existence of electrical dipoles. Polarisation-concn. curves of three types are obtained, the form being related to the structure of the ions concerned, and determined by the association of dipoles. The results agree with f.p. and conductance measurements in  $C_6H_6$  (A., 1933, 1120; 1934, 1304).

XIX. Conductances of solutions of  $NMe_4$  and  $NBu_4$  picrates, and of mixtures of the two, in  $C_6H_6$ , have been determined at  $25^\circ$  between  $10^{-5}$  and  $10^{-3} N$ . Up to about  $10^{-4} N$ , conductances of the mixtures calc. theoretically agree within 0.1% with the observed vals. Improved technique for making dilutions with a volatile solvent is described. F. L. U.



**Polar structure of betaines.** II. G. DEVOTO and M. ARDISONE (*Gazzetta*, 1935, 65, 1235—1239; cf. A., 1934, 1100).—Further measurements of the dielectric const. of aq. solutions of betaines of varying concn. show that the latter all have a polar amphoteric structure. O. J. W.

**Highly polymerised compounds.** CXXXV. [Viscosity of solutions of aliphatic hydrocarbons.] H. STAUDINGER (*Helv. Chim. Acta*, 1936, 19, 204—218).—Criticism of a paper by Meyer and van der Wyk (A., 1935, 1318). F. L. U.

[Viscosity of solutions of aliphatic hydrocarbons.] K. H. MEYER and A. VAN DER WYK (*Helv. Chim. Acta*, 1936, 19, 218—221).—A reply to the above. F. L. U.

**Constitution of ferric oxide sols.** W. HELLER, O. KRATKY, and H. NOWOTNY (*Compt. rend.*, 1935, 202, 1171—1173).—By magneto-optical and X-ray observations of the sols over several years it has been shown that the normal course of the ageing process is  $\text{FeOCl} \rightarrow \beta\text{-FeO}\cdot\text{OH} \rightarrow \alpha\text{-FeO}\cdot\text{OH}$ . The time required varies with the method of prep. of the sol. M. S. B.

**Viscosity of aqueous suspensions.** R. HERMANN (*Forsch. Ingenieurw.*, 1935, A, 6, 1—8; *Chem. Zentr.*, 1935, ii, 815).—Aq. suspensions possess no true viscosity. The  $\eta$  val. derived from the Hagen-Poiseuille law is a function of the tangential stress at the wall and decreases to a const. val. at high tangential stress.  $\eta$  increases on ageing. Aq. suspensions exhibit no external friction. J. S. A.

**Viscosity of suspensions and solutions.** III. **Viscosity of sphere suspensions.** (Calculation of wall effect and reciprocal influence in viscosity, with rotating spheres.) E. GUTH and R. SIMHA (*Kolloid-Z.*, 1936, 74, 266—275; cf. this vol., 426).—Mathematical. E. S. H.

**Viscosity of suspensions and solutions.** IV. **Viscosity of sphere suspensions.** F. EIRICH, M. BUNZL, and H. MARGARETHA (*Kolloid-Z.*, 1936, 74, 276—285).—Measurements made with the Couette, falling-sphere, and capillary viscosimeters agree with Einstein's relation between  $\eta$  and the vol. of disperse phase. E. S. H.

**Tyndall light of milk.** T. KATSURAI (*Kolloid-Z.*, 1936, 74, 287—288).—The turbidity-concn. relations of whole and skimmed milk have been determined in the region of visible  $\lambda$ , and the theoretical aspects are discussed. E. S. H.

**Stability of emulsions.** H. M. CASSEL (*Nature*, 1936, 137, 405).—Theoretical. L. S. T.

**Emulsions.** V. **Heterogeneous regions of the sodium oleate-phenol-xylene-water system and the corresponding binary and ternary systems.** J. WEICHERTZ and N. PLETENJEVA (*Kolloid-Z.*, 1936, 74, 330—343; cf. A., 1932, 994, 1086).—Equilibria in the above systems have been determined at 25°. E. S. H.

**Observations of the coagulation of cellulose acetate under the ultramicroscope.** K. ATSUKI and S. OKAJIMA (*J. Soc. Chem. Ind. Japan*, 1936, 39, 57—58B).—When cellulose acetate in  $\text{CHCl}_3$  is

coagulated by EtOH the behaviour is similar to that observed when suspensoids are coagulated by electrolytes; the particles are probably rod-shaped. The rate of coagulation is expressed by Smoluchowski's equation  $1/n = 1/n_0 + kt$ , in which  $n$  is the no. of particles. A. G.

**$\zeta$ -Potential and stability of cellulose [nitrate and] ethers.** S. GLIKMAN and E. MEDVEDKOV (*J. Chim. phys.*, 1936, 33, 150—160; cf. A., 1934, 1069).— $\zeta$ -Potentials have been determined by the method of electrophoresis under the ultramicroscope using (a) lyophobes present as impurity in the sol, and (b) added lyophobes such as AgI. The  $\zeta$ -potential decreases with the cellulose nitrate concn. to a limiting val. corresponding to the adsorption max. This is the same for different cellulose nitrate fractions.  $\zeta$ -Potentials of benzyl- and ethyl-cellulose in various solvents have also been derived. Increasing concn. of salts lowers the potential and in the case of  $\text{CaCl}_2$  the charge may be reversed, whilst in different  $\text{COMe}_2\text{-H}_2\text{O}$  mixtures there is a sharp increase corresponding with the change lyophile  $\rightarrow$  lyophobe (16—18%  $\text{H}_2\text{O}$ ). It is inferred that the  $\zeta$ -potential is not the essential factor determining the stability of colloids. R. S.

**Mechanism of coagulation by ultrasonic waves.** K. SÖLLNER and C. BONDY (*Trans. Faraday Soc.*, 1936, 32, 616—623; cf. A., 1935, 820).—Coagulation of emulsions or suspensions by ultrasonic waves is primarily due to a "radiation pressure," caused by diffraction of sound energy by the individual particles, imparting to the latter a movement which results in a kind of orthokinetic coagulation. When stationary waves are produced the coagulating effect is accentuated by the increased concn. of the disperse phase through accumulation of particles at the nodes, if the particles are less dense than the dispersion medium, or at the antinodes if they are denser. This effect is most marked with large ( $> 1\mu$ ) particles, and hardly observable with those of truly colloidal size. The limiting concn. of an emulsion formed by ultrasonic radiation is the resultant of the formative and destructive actions which proceed simultaneously. If the energy supplied is  $<$  the crit. val., or if cavitation is prevented by applying external pressure, coagulation only takes place. F. L. U.

**Physical chemistry of amino-acids, peptides, and related substances.** VI. **Densities and viscosities of aqueous solutions of amino-acids.** J. DANIEL and E. J. COHN (*J. Amer. Chem. Soc.*, 1936, 58, 415—423; cf. A., 1935, 1467).—The increase of apparent mol. vol. of the free  $\text{NH}_2$ -acids with concn. is greater with increasing dipole moment and diminishing hydrocarbon chain. The increase of  $\eta$  with length of hydrocarbon chain is given by  $(\eta/\eta_0) - 1 = (0.052 + 0.10 \times n_{\text{OH}})C = 2.5k\varphi$ , where  $\varphi$  is the vol. fraction occupied by the solute,  $C$  its concn., and  $V$  its mol. vol. Solutions of the Na salts are more viscous than those of the free acids. E. S. H.

**Gans effect, streaming double refraction, and particle shape in protein solutions.** E. WÖHLISCH and B. BELONOSCHKIN (*Biochem. Z.*, 1936, 284, 353—364).—The polarisation of Tyndall light and the presence of streaming double refraction have been examined in sols of ovalbumin, caseinogen, serum-



and ovo-globulin, fibrin, fibrinogen, and myosin. The behaviour is compared with that of inorg. sols and discussed with reference to particle shape. F. O. H.

**Determination of diffusion constants of proteins by a refractometric method.** O. LAMM and A. POLSON (Biochem. J., 1936, 30, 528—541).—A refractometric method for measuring diffusion consts. of proteins is described and several methods for calculating the diffusion consts. from the curves are discussed. The consts. of ovalbumin (I), human CO-haemoglobin (II), serum-albumin (III), gliadin, erythrocrucorin, and lactoglobulin are determined and it is shown that the consts. for (I), (II), and (III) increase greatly on dilution below 0.5%. In monodisperse systems the diffusion follows closely the ideal dispersion law, but in polydisperse systems deviations from normal curves are obtained. The refractive indices are calc. from the areas included by the diffusion curves and the mol. wts. from the diffusion and sedimentation consts. P. W. C.

**Hæmocyanin in heavy water.** T. SVEDBERG and I. B. ERIKSSON-QUENSEL (Nature, 1936, 137, 400—401).—Determinations of the sedimentation const. for solutions of hæmocyanin (I) containing different amounts of D<sub>2</sub>O indicate that the mol. of (I) has the same wt. and shape in D<sub>2</sub>O as in H<sub>2</sub>O. The  $p_H$  vals. at which dissociation occurs in buffered 94.5% D<sub>2</sub>O and in buffered H<sub>2</sub>O are the same, but since [D'] is different from [H'] the dissociation points actually alter. E.m.f. measurements indicate that the buffers in D<sub>2</sub>O are 0.5  $p_H$  more alkaline than the corresponding buffers in H<sub>2</sub>O. The isoelectric point and the stability curve of (I) in D<sub>2</sub>O probably change by the same amount. L. S. T.

**Preparation of thorium gels.** S. M. MEHTA, M. U. PARMAR, and M. PRASAD (J. Indian Chem. Soc., 1936, 13, 69—71).—Clear, firm gels may be prepared from Th(NO<sub>3</sub>)<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> and these exhibit the sol-gel transformation. E. E. A.

**Thorium phosphate gels.** M. U. PARMAR, S. M. MEHTA, and M. PRASAD (Proc. Indian Acad. Sci., 1936, 3, A, 107—118; see preceding abstract).—The time of setting ( $t$ ) of Th phosphate gels is diminished by increasing [H<sub>3</sub>PO<sub>4</sub>], by rise in temp., and by addition of electrolytes. It is increased by increase in [Th(NO<sub>3</sub>)<sub>4</sub>] and by the addition of NaOH, MeOH, EtOH, PrOH, and glycerol. The effect produced by HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> varies with the concn. of the acid. O. D. S.

**Gelation of albumin in aqueous propyl alcohol containing salts. Thixotropy and syneresis of albumin-propyl alcohol gel.** B. JIRGENSONS (Kolloid-Z., 1936, 74, 300—305).—Sols of 2.5% albumin in 40—60 vol.-% PrOH, containing 0.5 mol. per litre of K or Na salt, set to a reversible gel at 60—70°. Anions accelerate the gelation in the order SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> > CNS<sup>-</sup>. The gels are thixotropic and undergo syneresis. E. S. H.

**Mesomorphic state of soaps and washing materials.** W. SECK [with G. ŠKRILECZ] (Angew. Chem., 1936, 49, 203—206).—The Na salts of stearic, hydroxystearic, hydroxystearin- and stearyl-sulphonic (I) acids, cryst. directly from solution, are shown

(X-ray) to form single mols. inclined at 39—41° to the basal plane. The formation of double mols. observed previously by other workers is attributed to orienting polar effects due to crystallisation at a foreign solid surface. The take-up of H<sub>2</sub>O by the anhyd. soaps leads to two-dimensional swelling; the spacing which corresponds with the breadth of the mols. persists in the case of (I) down to 10% solutions. The formation of nematic hydrogels on dissolution of the dry soaps is indicated. The effect of interfaces in promoting the transition between the nematic and smectic states is discussed, and related to the detergent action of soaps. J. S. A.

**Rôle of coacervation in the resorption of fats.** A. DE KUTHY (J. Chim. phys., 1936, 33, 247—249; cf. A., 1929, 466).—When 15 c.c. of a 5% EtOH solution of oleic acid are added to 50 c.c. of M/30-phosphate buffer solution of  $p_H$  6.5 and the mixture is then warmed to expel EtOH and mixed with 50 c.c. of 10% Na taurocholate solution, a clear solution is obtained which yields drops of coacervate when mixed with 0.4% hæmoglobin solution in the same buffer. Addition of acid to the solution produces coacervation only at  $p_H$  3.5—4.0, a condition never present in organisms. These observations are applied to explain the fact that fat particles are formed only after passage of the fatty acids through the membranes of the intestines. J. W. S.

**Influence of light intensity on the periodic formation of Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> precipitates in gelatin.** V. K. NIKIFOROV and M. R. LEMECH (J. Chim. phys., 1936, 33, 250—256).—The "pressure" of rings produced by AgNO<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> diffusing in gelatin varies with the intensity of illumination ( $I$ ) according to the law  $\lambda_n I^k = a_n$ , where  $\lambda_n$  is the distance between the rings,  $a_n$  is a const., for any frequency, and  $k$  is a const. independent of frequency. The greater is the energy of the light quanta, the greater is the energy which is associated with the formation of rings. The results are explained on the wave theory of periodic reactions. J. W. S.

**Liesegang phenomena.** T. OKAYA (Proc. Phys.-Math. Soc. Japan, 1935, 17, 101—118).—The calc. energy of pptn. of Ag<sup>+</sup> in the formation of Liesegang rings is approx. 17.8 g.-cal. per mol. An expression is given for the diffusion coeff. of Ag<sup>+</sup> in gelatin. CH. ABS. (e)

**Dissociation of products of combustion.** W. L. DE BAUFRE (Combustion, 1935, 6, No. 11, 23—31).—The dissociation of H<sub>2</sub> and CO<sub>2</sub> is discussed. CH. ABS. (e)

**Thermodynamics of ammonia-water mixtures.** V. FISCHER (Forsch. Ingenieurw., 1935, A, 6, 57—66; Chem. Zentr., 1935, ii, 23).—Equilibrium data for the NH<sub>3</sub>-H<sub>2</sub>O system at 1 atm. and 10 atm. calc. from the heats of mixing and the contractions agree with experimental vals. J. S. A.

**Practical application of electrostatic valency. Strength of acids.** A. E. VAN ARKEL and G. CARRIÈRE (Chem. Weekblad, 1936, 33, 182—184).—Data relating to the strengths of inorg. acids and of bases of the NH<sub>3</sub> type are reviewed and the causes of the differences are discussed. D. R. D.



**Ionisation of lactic acid.** L. F. NINS and P. K. SMITH (J. Biol. Chem., 1936, 113, 145—152).—E.m.f. data between 0° and 50° for cells, without liquid junction, containing the lactates of Li, Ca, Sr, Ba, and Zn, show that the ionisation of lactic acid is greatest at 23.5°; the val. of  $pK$  at 25° is 3.862, at 37.5° is 3.872. F. A. A.

**Anomalies in the dissociation constant of some halogenated organic acids. II.** M. BETTI and M. MANZONI (Atti R. Accad. Lincei, 1935, [vi], 22, 284—287).—For the Cl- and Br-substituted acids  $o\text{-C}_6\text{H}_4\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$   $K=1.35\times 10^{-4}$  and  $1.92\times 10^{-4}$ , respectively. O. J. W.

**Calculation of intramolecular atomic distances from dissociation constants of dibasic acids. IV. Acidity of aliphatic dithiols.** G. SCHWARZENBACH and A. EPPRECHT. **V. Dissociation constants of hydrazine.** G. SCHWARZENBACH (Helv. Chim. Acta, 1936, 19, 169—178, 178—182; cf. A., 1933, 665).—IV. Normal acidity potentials of  $\text{SH}\cdot[\text{CH}_2]_n\cdot\text{SH}$  ( $n=2-5$ ) in aq. EtOH are calc. from results of H electrode potential measurements at 20°. The dithiols are all extremely weak acids. The acidity increases as  $n$  decreases, owing to the influence of the second  $\cdot\text{SH}$ . The results are compared with those obtained for the corresponding dicarboxylic acids and diammonium ions.

V. H electrode potential measurements in  $\text{N}_2\text{H}_4$  give for  $K_1$   $8.5\times 10^{-7}$ . Colorimetric determination of the second stage gives  $K_2=8.9\times 10^{-16}$ . F. L. U.

**Chemical union of acids with one another.** J. A. CRANSTON and H. F. BROWN (J. Roy. Tech. Coll., 1936, 3, 569—575).—An acid may act as proton acceptor in presence of stronger acid and therefore come under definition of a base. Other factors, e.g., the symmetry of the ion produced, may favour this complex ion formation.  $[\text{H}^+]$  of aq. HCl shows an increase in the order  $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HClO}_4$ , when these acids are substituted for an equal vol. of  $\text{H}_2\text{O}$  in aq. HCl. Formation of complex ions, e.g.,  $\text{H}_4\text{PO}_4^+$ , accounts for this, and an explanation is given for the concomitant reduction in sp. conductivity of these mixed solutions (cf. A., 1928, 369). The behaviour of solutions obtained by absorption of dry HCl by  $\text{H}_3\text{PO}_4$  is ascribed to the initial formation of  $\text{H}_4\text{PO}_4\text{Cl}$ . D. C. J.

**Determination of basic dissociation constants and ionic products of solvents in acetic acid. I. Equations.** S. KILPI (Suomen Kem., 1936, 9, B, 7—8).—Equations are developed for calculating the consts. from the buffer capacity of the solutions in the initial stages of acid-base titrations. J. S. A.

**Determination of basic dissociation constants and the ionic product of the solvent in acetic acid. II. Experimental results.** S. KILPI (Suomen Kem., 1936, 9, B, 9).— $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  has been titrated with  $\text{HClO}_4$  in AcOH (0.9% of  $\text{H}_2\text{O}$ ) and  $K_B$  and  $K_I$  calc. R. S.

**Dissociation constants of alkylamines.** G. SCHWARZENBACH (Helv. Chim. Acta, 1936, 19, 182—183).—Normal acidity potentials at 20° have been determined for  $\text{NH}_2\text{Me}$ ,  $\text{NH}_2\text{Pr}$ ,  $\text{NH}_2\text{Bu}$ , and  $n\text{-amylamine}$ . F. L. U.

**Activity coefficients of strong electrolytes.** S. KANEKO (J. Chem. Soc. Japan, 1935, 56, 411—414).—Mathematical. A simpler differential equation for strong electrolytes is given, and its solution is discussed. CH. Abs. (e)

**Theory of strong electrolytes and activity of cadmium chloride.** (MLLE.) M. QUINTIN (J. Chim. phys., 1936, 33, 111—126; cf. A., 1934, 492).—The e.m.f. of the cell  $\text{Cd (amalgam two phases)}|\text{CdCl}_2(c)|\text{AgCl}|\text{Ag}$  has been measured at different temp. When  $c>0.005M$  the plot of  $e$  against temp. gives two intersecting straight lines. This is attributed to the formation of a compound between AgCl and  $\text{CdCl}_2$ .  $E_0$  has been calc. using the method of Gronwall *et al.* (A., 1931, 1127), and the activity coeffs. at different temp. are given. The ionic radius is 3.8 Å. at 25° and it is inferred that the association of the ions is negligible. The method used is applicable up to concns. of 0.005M. R. S.

**Phase diagrams of low-melting mixtures. II. M.p. diagram of oxygen-nitrogen and the phase diagram of nitrogen-carbon monoxide.** M. RUHEMANN, A. LICHTER, and P. KOMAROV (Physikal. Z. Sovietunion, 1935, 8, 326—336; cf. A., 1935, 447).—Variation of sp. heat with temp. has been studied in a special calorimeter and the results applied to the derivation of phase diagrams.  $\text{N}_2$  and CO form two complete series of mixed crystals whilst the diagram for  $\text{N}_2+\text{O}_2$  shows a eutectic at 23%  $\text{N}_2$  and 50.1° abs. The latent heat of fusion of  $\text{O}_2\text{-N}_2$  is a min. at 69%  $\text{O}_2$ . R. S.

**Thermal diagram for system ferrous sulphide-cuprous sulphide. Determination of dissociation pressures of iron sulphides.** D. D. HOWAT (J. Roy. Tech. Coll., 1936, 3, 587—598).— $\text{Cu}_2\text{S}$  is sol. in FeS up to 20% and FeS in  $\text{Cu}_2\text{S}$  up to 40%; the eutectic at 970° corresponds with 61% FeS. The cooling curves for all melts containing from 95% to 55% FeS show a lower arrest point at 890—910°, and it is suggested that this may be due to dissociation of FeS. A method is described for the measurement of dissociation pressures of Fe sulphide mixtures which depends on the reducing action of  $\text{H}_2$ . D. C. J.

**Equilibrium between the sulphates of cobaltic chloropentammine and their sulphuric acid solutions.** L. O. TAO and W. S. MO (Compt. rend. 1936, 202, 846—848).—Equilibrium data for the system  $\text{Co}^{\text{III}}$  chloropentammine sulphate- $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  suggest the formation of  $[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4\cdot 0.33\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ , which is not in agreement with any of the formulæ previously proposed. The establishment of equilibrium is very slow at room temp. and measurements were made at 35—50°. M. S. B.

**System naphthalene-hexachloroethane.** S. PARIJS (Z. anorg. Chem., 1936, 226, 425—428).—The m.-p. diagram of the system  $\text{C}_{10}\text{H}_8\text{-C}_2\text{Cl}_6$  shows a eutectic at 56.6° and a transition point at 71° corresponding with the change of  $\text{C}_2\text{Cl}_6$  from the triclinic to the cubic form. No transition point was observed at 125° (cf. A., 1912, i, 330). The heats of



fusion of  $C_{10}H_8$  and of the two forms of  $C_2Cl_6$  are 4.56, 4.5, and 2.01 kg.-cal. per mol., respectively.

J. W. S.

**Equilibrium of the light and heavy isotopes of hydrogen with crystalline cuprous chloride.**

A. F. KAPUSTINSKY (J. Amer. Chem. Soc., 1936, 58, 460—463).—The equilibrium has been studied at 320—400°. The entropy, free energy, and heat of formation of  $CuCl$ , and the equilibrium const. for reduction of  $HCl$  by  $D_2$  have been calc. E. S. H.

**$CaO, TiO_2, SiO_2-CaO, SiO_2-CaO, Al_2O_3, 2SiO_2$  system. I. Equilibrium diagram of the system  $CaO, SiO_2-CaO, Al_2O_3, 2SiO_2$ .** U. NISHIOKA (Kinz.-no-Kenk., 1935, 12, 168—171).—The diagram shows a eutectic at 1283° (57 wt.-%  $CaO, SiO_2$ ). CH. Abs. (e)

**Geometrical theory of heterogeneous equilibria.** E. SCHEIL (Z. Elektrochem., 1936, 42, 153—155).—The elements of a geometrical treatment of the phase rule, based on the principle that the boundary between two  $n$ -dimensional figures has  $n-1$  dimensions, is developed. F. L. U.

**Specific heat of concentrated aqueous lithium, sodium, and potassium chlorides.** A. J. BOGORODSKI and G. P. DEZIDERIEV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 29—40).—Data are recorded for 11.4—36.68%  $LiCl$ , 7.42—26%  $NaCl$ , and 6.95—24.8%  $KCl$ , for the range 16—34°. R. T.

**Specific heats of sodium hydroxide solutions.** J. W. BERTETTI and W. L. MCCABE (Ind. Eng. Chem., 1936, 28, 375—378).—The sp. heats of  $NaOH$  solutions (4—51 wt.-%) have been determined at 37—191° F. using the adiabatic method. The results agree with those of Richards and Gucker (A., 1929, 652) but the work of Tucker (A., 1915, ii, 674) seems to involve a const. error. R. S. B.

**Correction in calculation of the heat of formation of sodium ferrite.** M. MATSUI (J. Soc. Chem. Ind. Japan, 1936, 39, 55—56B; cf. A., 1934, 1174).—The heat of formation of  $Na_2Fe_2O_4$  is given as 34,714 g.-cal. M. S. B.

**Heat of formation of iron nitrides.** S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 28, 271—276).—The heats of formation of  $Fe_4N$  and  $Fe_2N$  derived from the Nernst heat theorem and the equilibrium data of the systems  $Fe-NH_3-Fe_4N-H_2$  and  $Fe_4N-NH_3-Fe_2N-H_2$  are 4322 and 3090 g.-cal., respectively. The calorimetric vals. are 4460 and 3040 g.-cal., respectively. R. S. B.

**Heat of formation and specific heat of aluminium nitride.** S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 19—30).—The mean sp. heats of  $Al$  and of a specimen of  $AlN$  containing 10.18%  $Al$  were measured by the ice calorimeter in the intervals 0—100°, 0—420°, and 0—598°. The corresponding corr. vals. of the sp. heat of pure  $AlN$  are 0.193, 0.226, and 0.239, respectively. An equation for the true sp. heat is found, and using this, the heat of formation, computed from the equilibrium data of the reaction  $Al_2O_3+3C+N_2=2AlN+3CO$  at high temp., gives the result:  $Al+N=AlN+74,700$  g.-cal. N. M. B.

**Gallium and indium compounds. XI. Heat of formation of gallous oxide.** W. KLEMM and I. SCHNICK (Z. anorg. Chem., 1936, 226, 353—358).—By sublimation of mixtures of  $Ga_2O_3$  and  $Ga$ , products of composition between  $GaO$  and  $Ga_2O$  are obtained. Repetition of the sublimation with addition of  $Ga$  increases the  $Ga_2O$  content to about 84%. From the heat of combustion of this mixture  $Ga_2O+O_2 \rightarrow Ga_2O_3=175 \pm 2$  kg.-cal. per mol., whence the heat of formation of  $Ga_2O$  is  $82 \pm 2$  kg.-cal. and its heat of decomp. into  $Ga_2O_3$  and  $Ga$  is  $3.7 \pm 2$  kg.-cal. J. W. S.

**Free energy of ethylene hydration.** E. R. GILLILAND, R. C. GUNNESS, and V. O. BOWLES (Ind. Eng. Chem., 1936, 28, 370—372).—From equilibrium data for  $C_2H_4+H_2O \rightleftharpoons EtOH$  at 176—307°, with  $H_2SO_4$  as catalyst, the free energy of hydration in the gaseous phase is found to be  $26.9T-8300 \pm 500$  g.-cal. The val. 326,610 g.-cal. for the heat of combustion of  $C_2H_4$ , due to Rossini, is confirmed. R. S. B.

**Conductance of non-aqueous solutions. II. Temperature coefficient of conductivity.** A. S. COOLIDGE and H. E. BENT (J. Amer. Chem. Soc., 1936, 58, 505—506; cf. A., 1935, 1462).—Theoretical. The negative temp. coeff. is discussed and the rôle of the solvent in determining  $\Delta H$  and  $\Delta S$  emphasised. The calc. entropy of ionisation of  $Na$  triphenylboron is —60 entropy units. E. S. H.

**Measurement of absolute rates of migration of ions by the method of moving boundaries. II.** J. MUKHERJEE, R. MITRA, and N. SEN-GUPTA (J. Indian Chem. Soc., 1936, 13, 42—68; cf. A., 1935, 825).—Rising boundaries between  $HCl$  and picric acid,  $KCl$  and  $K$  picrate,  $NaCl$  and  $Na$  picrate,  $KCl$  and  $K$  compound of tetraiodoococin and also boundaries between mixtures of these electrolytes have been investigated. The variations of p.d. between two fixed planes with the linear displacement of the boundary have been directly measured and the abs. rates of migration of the "leading" and "indicator" ions have been calc. from such variations and the observed rate of motion of the boundary. Simultaneous measurements of the transference nos. of the leading ion have been made from observations of the vol. displacement of the boundary. The effects of the area of cross-section of the tube, the current strength, and the addition of small quantities of the leading solution to an approx. adjusted solution of the indicator electrolyte, have been studied. Light is thrown on the mechanism of concn. adjustments at and near the boundary, whilst the need of securing the condition of adjustment for obtaining correct and reproducible results is emphasised. The method gives vals. of abs. rates of migration of ions and may be applied to ascertain the changes taking place in different layers of the solutions at the boundary. As in the MacInnes method (A., 1929, 1390) the transference nos. can be obtained simultaneously. E. E. A.

**Breakdown and conductivity of anodically oxidised aluminium.** J. W. HOLST (Z. Elektrochem., 1936, 42, 138—143).—The breakdown potentials of the dried oxide layer in anodically oxidised



Al are found, in conformity with the results of Just and Betz (A., 1933, 555, 667), to differ widely according to the direction of the applied p.d. An explanation is afforded by the observation that the conductivity ( $\kappa$ ) of the oxide layer in the negative ( $\text{Al}^-$ ) direction  $>$  in the positive ( $\text{Al}^+$ ). Comparison of oxide layers when dry and when immersed in electrolyte solutions shows that  $\kappa$  does not depend on the electron concn. in the adjacent layers of Al and electrolyte. The experiments indicate that  $\kappa$  is determined by the migration of  $\text{H}^+$  and  $\text{OH}^-$  within the oxide layer. F. L. U.

**Oxido-reduction potential of reductone.** R. WURMSER, N. MAYER, and O. CRÉPY (J. Chim. phys., 1936, 33, 101—110; cf. A., 1934, 1072).—It has been shown spectrographically that reductone (I) forms a reversible oxidation-reduction system. The absorption max. shifts from 2650 to 2900 Å. when the  $p_{\text{H}}$  changes from 4 to 6 and (I) regenerated by reversible oxidation behaves identically. (I) is more stable in alkaline solutions whilst the product of oxidation is more stable in acid solutions. The normal potential of the system at different  $p_{\text{H}}$  vals. has been determined. R. S.

**Displacement of the oxidation-reduction potential on illumination of methylene-blue solutions containing iron.** H. HELLSTRÖM (Naturwiss., 1936, 24, 217; cf. A., 1935, 1087; this vol., 270).—The reduction-oxidation potential of the methylene-blue (I)— $\text{Fe}^{2+}$  system decreases reversibly when the system is illuminated. The potential depends on  $p_{\text{H}}$  in a manner similar to the fluorescence. In the system (I)—leuco-base in equal concns. no change of potential occurred on illumination. Addition of  $\text{K}_4\text{Fe}(\text{CN})_6$  in place of  $\text{Fe}^{2+}$  was ineffective. This further supports the view that there is combination between (I) and Fe, (I) being probably activated in the compound. A. J. M.

**Diffusion potential.** Y. KAUKO and V. MANTERE (Suomen Kem., 1936, 9, B, 9—12).—The e.m.f. of the electrode  $\text{H}_2|0.1\text{N-HCl}|0.1\text{N-KCl}$  in combination with the  $\text{Hg}_2\text{Cl}_2$  electrode is unaffected by movement of the  $0.1\text{N-HCl}$  into the  $0.1\text{N-KCl}$  or by stirring of the latter. Investigation of the diffusion potentials of a series of cells shows that in previous work (A., 1935, 1321) the error from this source is small and can be calc. At greater ionic concns. the calculation is uncertain. R. S.

**Preparation and investigation of oxide cathodes of colloid structure.** E. PATAI and Z. TOMASCHEK (Kolloid-Z., 1936, 74, 253—265).—Alkaline-earth oxide cathodes have been prepared by electrophoretic deposition from colloidal hydrosols of the corresponding carbonates under controlled conditions. The influence of composition, concn., c.d., temp., and cathode material on the structure and emissive properties of the cathodes has been investigated. E. S. H.

**Influence of colloids on electrode processes.** V. J. VOLKOV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 57—79).—Anode polarisation is absent in the electrolysis of  $0.5\text{—}1\text{N-ZnSO}_4$  in presence of gelatin, ovalbumin, or agar, whilst

cathode polarisation rises to a max., and then falls with increasing concn. of these colloids. The rise is ascribed to the binding of Zn by the colloids, with consequent diminution in its ionic concn., whilst the subsequent fall is due to increase in  $[\text{Zn}^{2+}]$ , owing to binding of  $\text{H}_2\text{O}$  by the colloids. R. T.

**Mineral electrodes. III. Adsorption of calcium by gum arabic.** H. J. C. TENDELOO (Rec. trav. chim., 1936, 55, 227—230; cf. A., 1935, 706).— $\text{CaF}_2$  (fluorite) electrodes can, with suitable precautions, be used to measure  $p_{\text{Ca}}$ . The potential is not affected by changes of acidity. Measurement of the  $p_{\text{Ca}}$  of solutions of gum arabic containing varying amounts of Ca shows that a part of the Ca is adsorbed, the solution behaving as a Ca buffer. F. L. U.

**Cathode effect in electrolysis of cadmium salts.** O. KUDRA (Z. physikal. Chem., 1936, 175, 377—382; cf. B., 1935, 857).—If the c.d. at the cathode,  $\sigma$ , is kept const. the deposit of Cd, which is initially smooth and white, suddenly becomes black and spongy when electrolysis has proceeded for a time  $\tau$ , which depends on the concn. of the solution,  $c$ , according to  $\log c = \alpha \log \sigma + \beta \log \tau + \gamma$ , where  $\alpha$ ,  $\beta$ , and  $\gamma$  are consts. which depend on the salt being electrolysed. Probably the formation of a spongy deposit is promoted by the presence in it of oxide, which agrees with the observation that the effect is the more marked the greater is the oxidising power of the salt anion. R. C.

**Polarisation phenomena at the ferric-ferrous electrode.** W. L. H. MOLL (Z. physikal. Chem., 1936, 175, 353—358).—In the electrolysis of a mixed solution of a  $\text{Fe}^{\text{II}}$  and a  $\text{Fe}^{\text{III}}$  salt with a fresh electrode of Pt or Au there is no overvoltage, showing that the change in ionic charge occurs without any considerable hindrance. If the electrode has been in contact with the solution for some time, however, it exhibits a continually increasing chemical polarisation, which can be eliminated by polarising the electrode cathodically or anodically so far that gas is evolved. R. C.

**Production of aluminium by electrolysis of fused cryolite and aluminium oxide.** P. DROSSBACH (Z. Elektrochem., 1936, 42, 144—147).—Decomp. potentials of  $\text{NaF}$  and  $\text{AlF}_3$  (cf. A., 1934, 1078) are recalcd. The vals. at  $950^\circ$  are:  $\text{NaF}$  4.4—4.6,  $\text{AlF}_3$  3.4—3.7 volts. F. L. U.

**Neutralisation of aqueous solutions of metaphosphimic and di-imidotriphosphoric acids.** A. M. DE FICQUELMONT (Compt. rend., 1936, 202, 848—850).—Variations of conductance during titration by  $\text{NaOH}$  have been determined for  $N/3000$  solutions of di-imidotriphosphoric (I), tri- (II) and tetra-metaphosphimic (III) acids. (I) and (II) are tribasic, but (III) has a fourth ionisable H with an ionisation const. which is much  $<$  that of the other three, but of the same order as that of the second  $\text{H}^+$  of  $\text{H}_3\text{PO}_4$ . M. S. B.

**Devaux's observation of the modification of a film of copper sulphide by means of copper.** J. CAYREL (Compt. rend., 1936, 202, 926—929; cf. this vol., 435).—When a piece of Cu is placed in con-



tact with the film and with a  $\text{CuSO}_4$  solution Cu is deposited. The e.m.f. of the cell  $\text{CuS}|10\% \text{ aq. CuSO}_4|\text{Cu}$  is 0.2 volt ( $15^\circ$ ). The thickness of the Cu film is independent of the current, extent of the film, and  $[\text{CuSO}_4]$ . H. J. E.

Recent theoretical and experimental researches on unimolecular reactions. A. LALLANDE (Bull. Soc. chim., 1936, [v], 3, 521—537).—A lecture.

Chemical reaction in ionised gases. K. G. EMELEUS and R. W. LUNT (Nature, 1936, 137, 404).—The assumption that, in the reactions in ionised gases, one or more of the reacting atoms or mols. react while ionised is unnecessary. The kinetics of reactions in discharges can be accounted for on the assumption that the reacting particles are all neutral. Reactions appear to be related only incidentally to the conductivity of the gas. L. S. T.

Ignition of hydrogen-chlorine gas [mixtures] by high-velocity electrons. A. E. MALINOVSKI and K. A. SKRINNIKOV (Physikal. Z. Sovietunion, 1935, 8, 289—293; cf. A., 1935, 1212).— $\text{H}_2\text{—Cl}_2$  mixtures are not exploded by high-velocity electrons in concns. up to  $0.6 \times 10^5$  per c.c. R. S.

Rate of reaction of deuterium with hydrogen chloride. P. GROSS and H. STEINER (J. Chem. Physics, 1936, 4, 165—169).—The reaction  $\text{D}_2 + \text{HCl} = \text{HD} + \text{DCl}$  between  $765^\circ$  and  $843^\circ$  abs. is bimol. and mainly homogeneous over a range of  $\text{D}_2$  and HCl partial pressures of 80—300 mm. Conditions appear to change at pressures below 50 mm. Measurements made in packed vessels indicate that a wall reaction takes place also, but to an extent of  $> 15\%$  at the lowest temp. The activation energy is  $52.1 \text{ kg.-cal.}$  and the homogeneous bimol. const. is  $k = 6.27 \times 10^{13} T^{0.5} e^{-26,200/T} \text{ mole}^{-1} \text{ c.c. sec}^{-1}$ . Deviations observed at the highest temp.,  $843^\circ$  abs., are probably due to at. reactions. M. S. B.

Reactions involving hydrogen molecules and atoms. J. HIRSCHFELDER, H. EYRING, and B. TOPLEY (J. Chem. Physics, 1936, 4, 170—177).—The best potential energy surface for three H atoms has been constructed, and from it the rates of all the possible reactions between H and D have been calc. by means of the general theory of abs. rates. The agreement with experimental data is satisfactory. M. S. B.

Absolute rates of reaction of hydrogen with the halogens. A. WHEELER, B. TOPLEY, and H. EYRING (J. Chem. Physics, 1936, 4, 178—187).—The statistical-mechanical method is applied to the calculation of the abs. rates of reaction of I,  $\text{Cl}_2$ , and Br with  $\text{H}_2$ , HD, and  $\text{D}_2$ . The correct relative rates are obtained and, in agreement with experiment, the potential surfaces indicate that H is much more reactive than D. M. S. B.

Rate of elementary reactions of hydrogen and deuterium. L. FARKAS and E. WIGNER (Trans. Faraday Soc., 1936, 32, 708—723; cf. this vol., 32).—Velocity coeffs. of the following reactions are calc. on the basis of recent theory (A., 1932, 343; 1933, 30):  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ ;  $\text{D} + \text{D}_2 \rightarrow \text{D}_2 + \text{D}$ ;  $\text{D} + \text{H}_2 \rightarrow \text{DH}$

$+ \text{H}$ ;  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ . The vals. obtained are discussed in relation to available experimental data. F. L. U.

Para-hydrogen conversion on glass. A. M. MAGID and S. Z. ROGINSKI (J. Phys. Chem., U.S.S.R., 1934, 5, 1278—1282).—The para-ortho conversion of H on soda-glass at  $160\text{—}320^\circ/20\text{—}200 \text{ mm.}$  is a first-order reaction (energy of activation 17000 g.-cal. per mole). Only about 1% of the sufficiently activated mols. striking the walls undergo conversion. On Pyrex and Mo-glass the reaction is much more rapid. On the latter it is rapid at  $< 200^\circ$ . CH. ABS. (e)

Kinetics of the thermal chain reaction in mixtures of hydrogen and oxygen. M. PRETTRE (J. Chim. phys., 1936, 33, 189—218; cf. this vol., 32).—At  $500\text{—}600^\circ$  glass walls adsorb considerable amounts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  with a low velocity which increases with rise of temp., and these adsorbed gases, respectively, decrease and increase the velocity of reaction between  $\text{H}_2$  and  $\text{O}_2$ . The  $\text{H}_2$  probably increases the no. of centres of chain formation, but also breaks the chains, whereas  $\text{H}_2\text{O}$  promotes their branching. A KCl surface, which is less adsorbent than glass, diminishes the no. of centres of chain formation, and also breaks the chain more than a glass surface. Near ignition conditions at  $400\text{—}700 \text{ mm.}$ , the velocity of reaction no longer obeys Arrhenius' law and rises increasingly rapidly with rise of temp., indicating the occurrence of a homogeneous reaction with frequently branched chains, which is responsible for ignition. J. W. S.

Theory of the chamber process. Mechanism and kinetics of oxidation of  $\text{SO}_2$  by nitrogen dioxide in the gas phase. I. N. KUZMINICH, E. J. TURCHAN, and M. S. ARCHIPOVA (Z. anorg. Chem., 1936, 226, 310—320; cf. A., 1935, 308).— $\text{SO}_2$  is oxidised by  $\text{NO}_2$  in the gas phase at  $80^\circ$  in the absence of liquid. Increasing the amount of  $\text{H}_2\text{O}$  vapour above 0.1 vol.-% does not increase the speed of reaction, whilst drying with  $\text{P}_2\text{O}_5$  diminishes it to about  $\frac{1}{3}$  of the normal val. The reaction is bimol. Velocity coeffs. are given for the range  $65\text{—}150^\circ$ . The velocity depends on the shape of the reaction vessel and decreases with decreasing rate of flow in a manner consistent with a chain mechanism.  $\text{H}_2\text{O}$  acts as a homogeneous catalyst. F. L. U.

Reaction of nitric oxide with hydrogen and with deuterium. C. N. HINSHELWOOD and J. W. MITCHELL (J.C.S., 1936, 378—384).—A reinvestigation at  $801^\circ$  of the reaction between  $< 900 \text{ mm.}$  of  $\text{H}_2$  and  $< 500 \text{ mm.}$  of NO in  $\text{SiO}_2$  bulbs affords no evidence of long reaction chains and shows that the proportion of heterogeneous reaction is much  $<$  was previously supposed (A., 1926, 579). When  $[\text{H}_2]$  is  $< 100 \text{ mm.}$ , the initial rate of reaction decreases more rapidly than corresponds with the linear relation, at const.  $[\text{NO}]$ , between velocity and  $[\text{H}_2]$ . The reaction, although homogeneous and essentially termol., probably involves binary collision complexes of different lives. The hypothesis leads to an equation which accords with the data. With  $\text{H}_2$ , the rate of change of pressure (mm. per 100 sec.) is  $[\text{NO}]^2[\text{H}_2]\{1.0 + 30/(1 + 8.0[\text{NO}]) + 11/(1 + 3.4[\text{H}_2])\}$  and with  $\text{D}_2$ ,  $[\text{NO}]^2[\text{D}_2]\{0.7 + 12.5/(1 + 8.0[\text{NO}]) + 7.7/(1 + 2.4[\text{D}_2])\}$



(concn. unit, 100 mm.); the differences between the velocities are ascribed chiefly to the different mol. speeds. The temp. coeff. of the  $H_2$  reaction at 700—825° leads to the activation energy 47 kg.-cal.

J. G. A. G.

**Reactions between sodium vapour and volatile polyhalides. Velocities and luminescences.** W. HELLER and M. POLANYI (Trans. Faraday Soc., 1936, 32, 633—642).—See A., 1935, 150. F. L. U.

**Pressure and ionisation in the front of the explosion wave in the pre-detonation period.** A. E. MALINOVSKI, B. I. NAUGOLNIKOV, and K. T. TRATSCHENKO (Physikal. Z. Sovietunion, 1935, 8, 536—540).—A method for registering simultaneously the flame velocity, the spreading of the compression wave, and the ionisation at the front of the wave when a mixture of  $C_2H_2$  and air was exploded, is described. The conductivity at the explosion wave-front was determined by a method similar to that of Kirkby (A., 1931, 688) and the pressure changes by Töppler's method. A. J. M.

**Kinetics of the decomposition of ethyl ether at high pressures.** E. W. R. STEACIE, W. H. HATCHER, and S. ROSENBERG (J. Chem. Physics, 1936, 4, 220—223).—A more accurate investigation of the decomp. of  $Et_2O$  at 426° and pressures up to 260 atm. confirms previous approx. data (A., 1934, 1179). The rate of reaction increases with pressure throughout the range in which it was examined. The results are explicable, qualitatively, on the basis of the Rice-Herzfeld free radical mechanism, but the reaction is too complicated for quant. comparison with theory. M. S. B.

**Decomposition of ethylamine and diethylhydrazine.** H. A. TAYLOR and J. G. DITMAN (J. Chem. Physics, 1936, 4, 212—218).—The decomp. of  $NH_2Et$  has been reinvestigated (cf. A., 1931, 175). The reaction is now shown to be bimol., giving  $(NH_2Et)_2$  (I) and  $H_2$  without vol. change. (I) subsequently decomposes by a first-order chain reaction at a rate < that of the first reaction. This mechanism accounts for the induction period and its rapid variation with temp. and pressure. M. S. B.

**Decomposition of methyl nitrite at high pressures.** E. W. R. STEACIE and S. ROSENBERG (J. Chem. Physics, 1936, 4, 223).—Measurements of the decomp. of  $MeO\cdot NO$  at high pressures indicate that, within a rather large experimental error, there is no appreciable increase in the rate of decomp. on changing the pressure from 65 cm. to 35 atm. The previous conclusion that the reaction is unimol. (A., 1935, 938) is confirmed. M. S. B.

**Homogeneous unimolecular decomposition of gaseous alkyl nitrites. V. Decomposition of methyl nitrite at low pressures.** E. W. R. STEACIE and D. S. CALDER (J. Chem. Physics, 1936, 4, 96—99).—Measurements of the rate of decomp. of  $MeO\cdot NO$  at pressures of 0.005—5.0 cm. and 210—240° have been made in packed and empty vessels. The reaction is about 5% heterogeneous at 1.5 cm. initial pressure and about 15% at 0.05 cm. The average val. of the activation energy is 36,100 g.-cal. The results are in good agreement with previous data at high

pressures (A., 1934, 1312). The fall in rate with diminishing pressure can be accounted for by Rice and Ramsperger's theory on the assumption of a mol. diameter of  $5.0 \times 10^{-8}$  cm. and 13 degrees of freedom. M. S. B.

**Thermal decomposition of divinyl ether.** H. A. TAYLOR (J. Chem. Physics, 1936, 4, 116—120).—The thermal decomp. of divinyl ether has been studied at 460—500°/30—1000 mm. The reduction in velocity at low pressures by increasing the surface of the reaction vessel, or at high pressures by adding  $N_2$ , the variation of temp. coeff. with pressure, and the induced decomp. with azomethane indicate a chain reaction in which the chains are broken on the walls at low and in the gas phase at high pressures. The overall order of the reaction at high pressures is 1.5. M. S. B.

**Influence of pressure of the surrounding gas on the luminosity accompanying the detonation of explosives.** A. MICHEL-LÉVY and H. MURAOUR (Compt. rend., 1936, 202, 755—757).—The transmission of detonation from one  $PbN_6$  granule to the next becomes increasingly difficult as the pressure ( $p$ ) of the surrounding gas is increased. At the same  $p$  it occurs more readily in A than in  $CO_2$ . With increasing  $p$  the deposit of Pb became more localised. At vals. of  $p > 20$  mm. a diffuse luminosity was observed at distances  $> 40$  cm. from the explosive. This was attributed to a shock wave. H. J. E.

**Practical rule permitting the interpretation of certain reactions of organic chemistry from the electronic point of view.** P. CARRÉ (Compt. rend., 1936, 202, 740—742; cf. this vol., 453).—The difference in reactivity of directly bound elements corresponds with a difference in polarity, which increases with the electronic displacement. Examples are discussed. H. J. E.

**Bimolecular reactions in solution.** C. N. HINSHELWOOD and C. A. WINKLER (J.C.S., 1936, 371—377).—Theoretical. The transition-state method does not supersede the collision method for treating bimol. reactions. Existing data for series of bimol. reactions in solution lead to vals. of the probability factor between  $P=1$  and  $P=10^{-8}$ , where (no. of mols. reacting) =  $PZe^{-E/RT}$  and  $Z$  is the no. of collisions. The factors affecting  $P$  are discussed, and it is shown, by assigning plausible magnitudes to each effect, that the whole range of observed behaviour can be explained, at least qualitatively, in terms of (i) the orientation of the mols. at collision, (ii) the phase of vibration at which the linkings rupture, (iii) steric hindrance, and (iv) solvent effects. J. G. A. G.

**Kinetics of the oxidation of nitrites with nitric acid.** A. F. POROVITSCH (Chimstr., 1935, 7, 202—205).—The reaction is bimol. in aq. solution, the temp. coeff. at 20—80° being given by  $\log k = 11.77 - 3767/T'$ . CH. ABS. (c)

**Kinetics and mechanism of reaction of ferrous ion with nitrous and nitric acids.** E. SCHRÖER (Z. physikal. Chem., 1936, 176, 20—47).— $Fe^{++}$  does not react with  $NO_2$  or  $HNO_3$ , but only with  $NO$ , the rate being given by  $d[Fe^{++}]/dt = k'[HNO_2]^2[Fe^{++}]/[NO]$ . Here  $k'$  is the product of a velocity coeff. by  $\sqrt{(K_1K_2)}$ .



where  $K_1$  and  $K_2$  are the equilibrium consts. of  $4\text{HNO}_2 \rightleftharpoons \text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O}$  and  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , respectively. The reaction mechanism is  $2\text{HNO}_2 \rightleftharpoons \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$ ,  $\text{Fe}^{++} + \text{NO}_2 \rightarrow \text{Fe}^{+++} + \text{NO}_2'$ ,  $\text{NO}_2' + \text{H}^+ \rightleftharpoons \text{HNO}_2$ . The energy of activation of the second of these is small or zero. Reaction begins normally, but after a time the velocity increases considerably and falls only towards the end. The explanation is that the NO formed retards the reaction because it depresses  $[\text{NO}_2]$  and at first the NO remains almost entirely in solution combined with the  $\text{Fe}^{++}$  salt, but as  $[\text{Fe}^{++}]$  falls the distribution ratio of the NO changes in favour of the gaseous phase. The velocity is independent of  $[\text{Fe}^{+++}]$ , and is influenced by  $[\text{H}^+]$  only in so far as this affects the dissociation of the  $\text{HNO}_2$ . The velocity-time relations for the reaction between  $\text{Fe}^{++}$  and  $\text{HNO}_3$  catalysed by  $\text{HNO}_2$  are similar to the above, but here the NO is removed by  $\text{NO}_2 + \text{NO} + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$ ; the amount of  $\text{HNO}_2$  which must be added to effect complete reactions decreases with rising temp. and is zero above  $65^\circ$  (cf. A., 1932, 242).

R. C.

**Hydrolysis of starch by hydrogen peroxide and ferrous sulphate.**—See this vol., 594.

**Kinetic study of addition of methyl hypobromite to stilbene.**—See this vol., 600.

**Rates of alcoholysis of triarylmethyl chlorides.** A. C. NIXON and G. E. K. BRANCH (J. Amer. Chem. Soc., 1936, 58, 492—498).—The kinetics of reaction of *p*-monosubstituted  $\text{CPh}_3$  chlorides with  $\text{EtOH}$  in  $\text{Et}_2\text{O}$  solution at  $25^\circ$  has been studied by electrical conductivity determinations. The heats of activation of all the reactions have been determined. The influence of substituent groups is discussed.

E. S. H.

**Heats of activation of the related reactions involved when *l*-bromosuccinic acid is treated with chloride ion.** A. R. OLSON and F. A. LONG (J. Amer. Chem. Soc., 1936, 58, 393—398).—The heats of activation and the collision factors for the 6 related reactions (cf. A., 1934, 847) have been determined at  $25$ – $88^\circ$ . The collision factors of the four binol. reactions are of the same order of magnitude as those calc. from kinetic theory.

E. S. H.

**Oxidation of cyclic compounds by potassium permanganate.** C. N. HINSHELWOOD and C. A. WINKLER (J.C.S., 1936, 368—370).—The velocity coeffs. at  $0$ – $80^\circ$  lead to the following activation energies of the oxidations using  $0.1N\text{-KMnO}_4$  and  $0.02N\text{-H}_2\text{SO}_4$ : picric acid (I) 12,200 g.-cal.,  $\text{BzOH}$  (II) 12,700, 2:4:6-trinitro-3-methylnitroaminophenol (III) 13,100, trinitro-*m*-cresol (IV) 14,600, 2:4-dinitrophenol (V) 15,300, 2:6-dinitrophenol (VI) 15,600, and  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$  (VII) 17,300. The primary ring-breaking step is an interaction of  $\text{MnO}_4^-$  with a mol. (or ion) of the org. compound. (I), (III), and (IV) react as ions, (II), (V), and (VII) react as mols., and (VI) reacts chiefly as mols. The structure of the mols. has very sp. effects on the probability factor.

J. G. A. G.

**Velocity of the exchange reaction of the hydrogen atom between sugar and water.** M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 55—56).—By adding  $\text{D}_2\text{O}$  to neutral, acid, or alkaline aq.

q q

solutions of glucose and distilling portions at intervals, it is concluded from the absence of any difference in the  $d$  of the distillates that the exchange of H between glucose and  $\text{H}_2\text{O}$  is rapid and that equilibrium is attained in  $< 1$  min.

C. R. H.

**Mutarotation of glucose in  $\text{H}_2\text{O}$ – $\text{D}_2\text{O}$  mixtures.** W. H. HAMILL and V. K. LA MER (J. Chem. Physics, 1936, 4, 144—145).—If the changes in velocity with  $\alpha$ -*D*-glucose (I) in heavy  $\text{H}_2\text{O}$  are ascribed solely to the replacement of H by D in that position in the (I) mol. involved in the mutarotation, viz., in the OH on the terminal C, and not, as before (A., 1935, 309), to the relative concns. of  $\text{H}_2\text{O}$ ,  $\text{HDO}$ , and  $\text{D}_2\text{O}$ , an exchange const.,  $K = [\text{D} - (\text{I})] \cdot [\text{H}_2\text{O}] / [\text{H} - (\text{I})] \cdot [\text{HOD}]$  may be determined from previous experimental data. The average val. of  $K$  is 0.83, in exact agreement with that for tetramethyl- $\alpha$ -*D*-glucose found directly from exchange experiments (A., 1935, 1212), but not with that for (I), 0.69, which is, however, an average val. for the 5 possible variations due to the 5 exchangeable H in the (I) mol. The correct explanation may be between the two extreme views advanced.

M. S. B.

**Reaction rates of propionic and acetic propionic anhydrides.** E. S. BARR and E. K. PLYLER (J. Chem. Physics, 1936, 4, 90—92).—The velocities of hydrolysis of propionic (I) and acetic propionic (II) anhydrides in  $\text{H}_2\text{O}$  have been determined at  $27^\circ$  by the rate of change in intensity of the infra-red spectra (cf. this vol., 34). The reactions are apparently unimol., but the val. of the coeff. is influenced by the concn. of the anhydride and  $\propto [\text{H}_2\text{O}]$ , approx. The val. for (II) is about double that for (I).

M. S. B.

**Mechanism of aromatic side-chain reactions, etc. IV. (Addendum.) Velocity of the reaction between *o*-nitrobenzyl bromide and pyridine.** J. W. BAKER (J.C.S., 1936, 399—400; cf. this vol., 195).—The data indicate that the enhanced reaction rate observed with 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Br}$  results from augmented electron attraction due to two  $\cdot\text{NO}_2$  radicals suitably oriented to the side-chain (cf. Bennett, Chem. and Ind., 1935, 1008).

J. G. A. G.

**Adsorption velocity of active carbon.** M. TARLÉ (Bull. Mukden Arsenal, No. 8, 11 pp.).—The adsorption of  $0.1N\text{-KMnO}_4$  by active C is a unimol. surface reaction, the active area of the C being inversely  $\propto$  the  $\text{KMnO}_4$  removed by adsorption at any given time.

Ch. Abs. (e)

**Oxidation of metals. III. Kinetics of the oxidation of molten tin.** L. L. BIRCHUMSHAW and G. D. PRESTON (Phil. Mag., 1936, [vii], 21, 686—697).—The rate of oxidation ( $v$ ) of molten Sn rises rapidly at  $400$ – $800^\circ$ , but at any given temp.  $v$  is found to vary even with similar samples. The parabolic law is not obeyed, especially at high and low  $\text{O}_2$  pressures, so  $v$  is controlled by a factor other than progressive increase in film thickness. It is suggested that the orientation of the crystals in the oxide film is a controlling influence in determining the rate of oxidation.

J. W. S.

**Oxidation of metallic magnesium at high temperature.** Y. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 147—165).—The increase in wt.



of Mg at about 560° in air, plotted by means of a thermobalance, was a linear function of time. The initial atm. corrosion film and the oxide film produced had no measurable resistance to the reaction. Only a trace of nitride was detected. N. M. B.

**Dust explosions.** W. P. M. MATLA (Rec. trav. chim., 1936, 55, 173—191; cf. B., 1935, 1024).—The reaction regions of mixtures of air with dusts of Al, dextrin, Ph<sub>2</sub>, anthracene, and picric acid have been determined, using spark ignition. The quenching effect of added shale, stone, fuller's earth, bone C, Fe<sub>2</sub>O<sub>3</sub>, C<sub>2</sub>Cl<sub>6</sub>, MnO<sub>2</sub>, hopcalite, and various inorg. K and Na salts depends partly on the nature of the combustible dust. With anthracene the order of effectiveness is: KF > KNO<sub>3</sub> > KI > KBr > KCl; NaF > NaI > NaNO<sub>3</sub> > NaBr > NaCl; KCl > C<sub>2</sub>Cl<sub>6</sub> > NaCl. With dextrin, KClO<sub>3</sub> > MnO<sub>2</sub> > Fe<sub>2</sub>O<sub>3</sub> > hopcalite. Fe<sub>2</sub>O<sub>3</sub> is more effective than KClO<sub>3</sub> with Al, whilst the reverse is true for picric acid. K salts are invariably more effective than the corresponding Na salts. The quenching effect of Fe<sub>2</sub>O<sub>3</sub> on different combustible dusts is in the order Al > dextrin > picric acid > Ph<sub>2</sub>. There is no parallelism between the quenching power and the sp. heat of the quenching material, and the cause of the effect is at present obscure. F. L. U.

**Reduction of iron oxides by gaseous reducing agents.** II. **Rate of reduction of magnetic iron oxide by hydrogen.** G. I. TSCHUFAROV and B. D. AVERBUCH (J. Phys. Chem. U.S.S.R., 1934, 5, 1292—1298; cf. this vol., 166).—Natural samples and those prepared from piano wire show autocatalytic effects on reduction. The initial rate of reduction increased with the temp. (350—900°), but above 600° the rate decreases quickly with time, and the curve for 800° crosses those for 400° and 600° at approx. 70% reduction. Above 800° this effect is less marked. FeO is formed as an intermediate. The max. rates were observed at 600°. CH. ABS. (e)

**Oxidation of aromatic hydrocarbons at high pressures.** I—III.—See this vol., 599.

**Hydrolysis in the vapour phase.** S. YAMASAKI (Bull. Chem. Soc. Japan., 1936, 11, 43—44).—Using HCl or I as a catalyst, EtOAc is only slightly hydrolysed at 200°. The catalytic effect of gas ions, obtained by exposing the reaction mixture to X-rays, is also negligible. C. R. H.

**Thermal decomposition of ethylene oxide and an induced acetaldehyde decomposition.** C. J. M. FLETCHER (J. Amer. Chem. Soc., 1936, 58, 534—535).—The production of free radicals and aldehydes at 400°, followed by decomp. of the aldehydes, is suggested as a mechanism of reaction. E. S. H.

**Kinetics of polymerisation processes.** II. G. GEE. III. **Effects of catalysts and inhibitors.** G. GEE and E. K. RIDEAL (Trans. Faraday Soc., 1936, 32, 656—666, 666—674; cf. A., 1935, 1080).—II. Theoretical. In polymerisations in which chain-breaking occurs through spontaneous deactivation or deactivation by a special type of collision with the monomer, the fraction polymerised before the max. velocity is attained varies from 0 with strong deactivation to  $\frac{1}{2}$  with no deactivation and zero steric

factor, and finally approaches 0.5 for large steric factors. The theory is applied to actual examples.

III. All experimental observations can be explained by assuming that the action of a catalyst depends on its forming a reactive complex. The assumption that the effect of an inhibitor is to diminish the velocity of a polymerisation process and the chain length of the polymeride in the same ratio is approx. valid only in the early stages of the reaction. F. L. U.

**Ozone as oxidising catalyst.** X. **Ozonisation of ferrous ammonium sulphate and of stannous chloride.** E. BRINER and (MLLE.) B. BEVER (Helv. Chim. Acta, 1936, 19, 367—369; cf. A., 1935, 1328).—Ozonised O<sub>3</sub> acts on aq. Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, thus:  $2\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 + \text{O}_3 + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} + \text{O}_2$ . The autoxidation is  $\approx 1-2\%$ . Aq. SnCl<sub>2</sub> containing 10% of HCl reacts thus:  $3\text{SnCl}_2 + 6\text{HCl} + \text{O}_3 = 3\text{SnCl}_4 + 3\text{H}_2\text{O}$ . The action of O<sub>3</sub> is indirect, i.e., it oxidises the HCl in presence of SnCl<sub>2</sub>, although it has no effect in its absence. Autoxidation amounts to 8—12%. F. L. U.

**Interpretation of the immeasurably fast reaction in a solution containing oxalic acid, permanganate ion, and manganous ion.** M. J. POLISSAR (J. Chem. Educ., 1936, 13, 40—42).—The reduction of MnO<sub>4</sub>' with Mn<sup>++</sup> in acid solution is autocatalytic. The reaction is catalysed by MnO<sub>2</sub>. Skrabal's mechanism for the reaction between MnO<sub>4</sub>', Mn<sup>++</sup>, and C<sub>2</sub>O<sub>4</sub>' in acid solution needs modification. The assumption of a rapid equilibrium between MnO<sub>4</sub>', Mn<sup>++</sup>, Mn<sup>+++</sup>, and Mn<sup>++++</sup> explains this reaction, and also the accelerating effect of other complex-forming ions on the Mn<sup>++</sup>-MnO<sub>4</sub>' reaction. L. S. T.

**Organic catalysts.** XIII.—See this vol., 589.

**Catalytic action of copper oxide on the combustion of hydrogen.** [New catalysts.] G. TERESCHI (Gazzetta, 1936, 66, 57—64).—If the catalytic action of CuO on the combustion of H<sub>2</sub> is due to the reactions:  $\text{CuO} + \text{H}_2 = \text{H}_2\text{O} + \text{Cu}$ , and  $2\text{Cu} + \text{O}_2 = 2\text{CuO}$ , and if O<sub>2</sub> is in great excess,  $-d[\text{H}_2]/dt = k_1[\text{H}_2]$ . If O<sub>2</sub> is not in great excess, but  $[\text{H}_2] \gg 2[\text{O}_2]$ , the catalyst will be partly reduced, and  $-d[\text{H}_2]/dt = k_1'[\text{H}_2]$ , where  $k_1' < k_1$ . The first approximation  $k_1' = k_1 - a[\text{H}_2]/[\text{O}_2]$  has been tested experimentally at 151° for  $[\text{H}_2]/[\text{O}_2] = 0.18, 1, \text{ and } 2$ , and graphs obtained agreeing with the integrated equations and the val.  $k_1 = 6.10 \times 10^{-4}$ ,  $a = 5.14 \times 10^{-5}$ .

$\text{CuO} + \text{Al}_2\text{O}_3$ , prepared by simultaneous pptn., is an unsatisfactory catalyst.  $\text{CuO} + \text{MgO}$ , obtained from MgO and CuSO<sub>4</sub>, has increased activity if MgSO<sub>4</sub> is well washed out.  $\text{CuO} + \text{CaO}$ , and  $\text{CuO} + \text{BaO}$ , obtained similarly, and dried at 90—100°, are very much more active as catalysts than the CuO ordinarily used. E. W. W.

**Influence of different metals and metallic oxides on the decomposition of carbon monoxide.** W. BAUKLOH and G. HIEBER (Z. anorg. Chem., 1936, 226, 321—332).—The catalytic effects of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe, Co<sub>3</sub>O<sub>4</sub>, Co, Ni<sub>2</sub>O<sub>3</sub>, NiO, Ni, Cr<sub>2</sub>O<sub>3</sub>, Cr, Mn<sub>3</sub>O<sub>4</sub>, Mn, Al<sub>2</sub>O<sub>3</sub>, Al, ZnO, Zn, and CuO on the decomp. of CO have been studied at 350—850°. The results indicate that the decomp. is cata-



lysed by reduced metal, and not by the oxides, the activity of easily reducible oxides being  $>$  that of the metal, but decreasing as the active centres become coated with C. Oxides which are difficult to reduce show little or no activity. J. W. S.

**Vanadium catalysts for the manufacture of sulphuric acid.**—See B., 1936, 315, 316.

**Platinised nickel gauze for contact oxidation of ammonia.**—See B., 1936, 316.

**Effect of magnesia on the synthesis of tricalcium silicate.** S. KONDO and M. HIGUCHI (J. Japan. Ceram. Assoc., 1935, 43, 273—280).—Mixtures of 100 parts of  $3\text{CaO} + \text{SiO}_2$  and 0—6 parts of  $\text{MgO}$  were heated for 90 min. at  $1500^\circ$ . Formation of  $\text{Ca}_3$  silicate was accelerated by  $\text{MgO}$ . Pulverisation and reheating also favoured its formation.

CH. ABS. (e)

**Catalytic decomposition of bleaching powder liquor.**—See B., 1936, 368.

**Effect of water vapour on the rate of interaction between iodine and metals (iron and copper).** A. V. SOLOVIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 185—188; cf. A., 1931, 698).—The interaction between I and Fe or Cu in presence of different  $[\text{H}_2\text{O}]$  has been studied. The rate decreases with time, but not always according to a parabolic law. R. S.

**Interaction between aluminium and iodine in an air atmosphere of different humidities.** A. V. SOLOVIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 189—191).—The rate of reaction between I and Al is a max. at 6.18 and at 12.7 mm. of  $\text{H}_2\text{O}$  at  $15^\circ$ . Absorption of  $\text{H}_2\text{O}$  occurs as the reaction proceeds, resulting in an increase in the rate owing to electrochemical and chemical action. R. S.

**Properties and industrial application of catalysts.** O. KOSZTELITZ (Tech. Kurir, 1936, No. 3, 1—3; No. 4, 2—5).—A review. E. P.

**Catalytic combustion of methane.** I. W. DAVIES (Phil. Mag., 1936, [vii], 21, 513—531; cf. A., 1935, 455).—The temp. at which reaction between  $\text{CH}_4$  and  $\text{O}_2$  is initiated on a Pt wire is nearly  $1000^\circ$  at low  $[\text{CH}_4]$ , but the rate of heating of the wire is then rapid, whereas at high  $[\text{CH}_4]$  combustion begins at  $400^\circ$ , but the catalytic activity of the wire decreases rapidly with further rise of temp. With small quantities of  $\text{CH}_4$  and  $\text{H}_2$  in  $\text{O}_2$ , combustion of the  $\text{H}_2$  begins at  $200^\circ$ , whilst the  $\text{CH}_4$  remains inert up to about  $900^\circ$ . Hence the wire acts as a preferential catalyst for the combustion of  $\text{H}_2$  between  $200^\circ$  and  $900^\circ$ . These limits are reduced as the ratio  $[\text{CH}_4] : [\text{O}_2]$  is increased. The reaction between  $\text{CH}_4$  and  $\text{O}_2$  probably involves adsorption of both reactants, whereas that between  $\text{H}_2$  and  $\text{O}_2$  involves adsorbed  $\text{O}_2$  and  $\text{H}_2$  from the gas phase. J. W. S.

**Preparation and catalytic oxidation of pure amorphous carbon.**—See B., 1936, 305.

**Phosphoric acid as catalyst for alkylation of aromatic hydrocarbons.**—See B., 1936, 309.

**Properties of zinc-chromium catalyst for methyl alcohol synthesis.**—See B., 1936, 309.

**Catalytic decomposition of alcohols.** P. J. IVANNIKOV and E. J. GAVRILOVA (J. Chem. Ind. Russ., 1935, 12, 1256—1260).—The process of catalytic ( $\text{CuO} + 0.1\% \text{ThO}_2$ ) conversion of  $\text{EtOH}$  (I) into  $\text{EtOAc}$  (II) at  $220$ — $450^\circ$  (optimum  $350^\circ$ ) consists of the reactions  $(\text{I}) \rightarrow \text{MeCHO}$  (III) +  $\text{H}_2$ ;  $2(\text{III}) \rightarrow (\text{II})$ ;  $(\text{III}) + 2(\text{I}) \rightarrow \text{CHMe}(\text{OEt})_2$  (IV) +  $\text{H}_2\text{O}$ ;  $(\text{II}) + \text{H}_2\text{O} \rightleftharpoons (\text{I}) + \text{AcOH}$  (V);  $(\text{III}) + \text{H}_2\text{O} \rightarrow (\text{V}) + \text{H}_2$ ;  $(\text{IV}) + (\text{V}) \rightarrow (\text{II}) + (\text{I}) + (\text{III})$ . Production of (II) through the intermediary of (IV) is the dominant reaction at  $300$ — $350^\circ$ . The reactions take place at the catalytic surface, and not in the vapour phase. R. T.

**Electrolysis of phosphate melts. II. New tungsten phosphide  $\text{W}_4\text{P}$ .** H. HARTMANN and J. ORBAN (Z. anorg. Chem., 1936, 226, 257—264; cf. A., 1931, 805).—The mixture of  $\text{PH}_3$  and  $\text{H}_2$  produced at the cathode during electrolysis of fused  $\text{NaPO}_3 + \text{LiPO}_3$  containing  $\text{WO}_3$  reacts with the latter at temp. below  $520^\circ$  and at c.d.  $> 0.0085$  and  $< 0.04$  amp. per sq. cm. to give the compound,  $\text{W}_4\text{P}$ , d 16.03. Chemical properties are described. At  $500$ — $550^\circ$   $\text{W}_4\text{P}$  decomposes irreversibly into  $\text{W}_2\text{P}$  and  $\alpha\text{-W}$ . The substance is amorphous. X-Ray examination of  $\text{W}_2\text{P}$  shows it to be hexagonal, with  $a$  6.18,  $c$  6.78 Å. F. L. U.

**Electrolytic polishing of copper, lead, tin, and their alloys, and its applications to metallography.** P. JACQUET (Bull. Soc. chim., 1936, [v], 3, 705—723).—A procedure for polishing metal and alloy specimens for micrographical examination consists in anodic treatment in a suitable acid between certain limiting c.d. The treatment of Cu surfaces in aq.  $\text{H}_3\text{PO}_4$ , and of Pb, Sn, and Pb-Sn alloys in aq.  $\text{HClO}_4$ -AcOH is described. The structures thus revealed are different from those obtained by mechanical polishing, as distortion does not occur. The mechanism of the electrolytic process is discussed. E. S. H.

**"Electrolysis" of a solid gold-copper alloy.** G. NEHLEP, W. JOST, and R. LINKE (Z. Elektrochem., 1936, 42, 150—153; cf. A., 1935, 936).—Passage of a current of 3.2 amp. for 3 months at  $1000^\circ$  through wires of a Cu-Au alloy with Au 65.7% produced an accumulation of Au at the anode. The transport no. for Cu was  $5$ — $10 \times 10^{-11}$ . F. L. U.

**Protection and decoration of aluminium and its alloys.**—See B., 1936, 278.

**Electrolysis of alkali zincate solution.**—See B., 1936, 332.

**Platinum plating.**—See B., 1936, 329.

**Chemical action of electric discharges. VIII. Production of nitric oxide by the electric arc at different frequencies.** B. SIEGRIST, C. H. WAKKER, and E. BRINER. **IX. Effect of addition of alkali and alkaline-earth metals to the electrodes on the yield of nitric oxide in industrial furnaces.** E. BRINER, C. H. WAKKER, H. PAILLARD, and G. CARRISSON. **X. Effect of increase of frequency conjoined with addition of lithium to the electrodes and enrichment of the air with oxygen on the yield of nitric oxide.** C. H. WAKKER and E. BRINER (Helv. Chim. Acta, 1936, 19, 287—308, 308—320, 320—322; cf. A., 1932, 820).—VIII. Yields of NO have been determined, using arcs



supplied with d.c., and a.c. at 50, 1410,  $10^6$ , and  $10^7$  cycles. For the same power consumption, the yield given by d.c. is  $>$  that given by a.c. at 50 or 1410 cycles, above which the yield increases with frequency. For any given type of discharge the yield increases with decreasing power consumption. The best yield, 128.5 g.  $\text{HNO}_3$  per kw.-hr., was obtained with a.c. 12 watts at  $10^7$  cycles.

IX. Using a 15-kw. Schönherr furnace, the effect of adding Li, Na, K, Be, Ca, and Ba to the Cu electrodes has been studied. The best result is obtained by the addition of 4.25% of Li, which increases the yield by 35%. The improvement is attributed to the Li facilitating ionisation and contributing to cooling of the arc. By combining the use of Cu-Li electrodes with addition of  $\text{O}_2$  to give an equimol. mixture of  $\text{N}_2$  and  $\text{O}_2$  the yield has been increased by 61%.

X. Improvement of the yield by 115% is obtained by combining Cu-Li electrodes and addition of  $\text{O}_2$  with the use of an a.c. arc at 1800 cycles. F. L. U.

**Control experiments on graphite oxidation by high-tension alternating current.** V. SIHVONEN and R. NASANEN (Suomen Kem., 1936, 9, B, 5—6).—In accordance with earlier views (A., 1933, 1019, 1020), the discharge of negative O ions at a graphite surface passes over at high voltage from passive discharge at the crystal face to an oxidative action on the edge atoms. The reaction due to the anodic component increases with increasing asymmetry of the discharge. J. S. A.

**Spectral analysis of the flame of an acetylene-air mixture in an electric field.** A. E. MALINOVSKI and V. S. ROSSICHIN (Physikal. Z. Sovietunion, 1935, 8, 541—546).—The spectra of the inner and outer cones of the stationary flame of a mixture of  $\text{C}_2\text{H}_2$  and air were examined with and without the application of an electric field (800—1300 volts per cm.). No difference in the structure or intensity of the lines in the bands due to C-C and C-H could be detected with the application of the field (direct and alternating). The continuous spectrum of both the inner and outer cones, however, decreases in intensity on application of the field. A. J. M.

**Decomposing action of X-rays on potassium iodide.** T. TOYOMA (Tōhoku J. Exp. Med., 1935, 24, 405—409).—The I-eliminating activity of the rays varies inversely with  $\lambda$ , and increases with the temp. CH. ABS. (c)

**Mercury-photosensitised decomposition of arsine.** N. L. SIMMONS and A. O. BECKMAN (J. Amer. Chem. Soc., 1936, 58, 454—459).—The rate of decomp. into As and  $\text{H}_2$   $\propto$  the intensity of radiation and is independent of  $\text{AsH}_3$  pressure at high pressures; at low pressures the rate is decreased on account of the fluorescence of activated Hg atoms. The decomp. is inhibited slightly by  $\text{H}_2$ . The quantum yield is  $1.03 \pm 0.05$  mols. of  $\text{AsH}_3$  per quantum of  $\lambda 2537 \text{ \AA}$ . The mechanism of decomp. is discussed. E. S. H.

**Law of blackening of photographic plates by ultrasonic rays.** N. MARINESCO (Compt. rend., 1936, 202, 757—759).—The blackening produced on a photographic plate by ultrasonic radiation of  $\nu = 625,000$  cycles per sec. follows the Hurter and Driffeld

law. The latter also governs the blackening of plates by ordinary light. H. J. E.

**Evolution of the latent photographic image.** C. JAUSSEAN (Ann. Physique, 1936, [xi], 5, 355—426; cf. A., 1935, 943).—An investigation of the modifications undergone spontaneously by the latent image in the time interval between exposure and development shows that the density of the developed image increases with the log of the age of the impression. The increase depends on the illumination of the plate, showing a max. for normal exposure, and on the nature and duration of action of the developer, and is attributed to a definite property of the latent image on Ag gelatinobromide. The properties of the real image and its susceptibility to chemical weakening are modified by the evolution of the latent image. It is concluded that the latent image and the developed image are not defined by the density val. of the latter. N. M. B.

**Photo-oxidation of methylene iodide.** R. A. GREGORY and D. W. G. STYLE (Trans. Faraday Soc., 1936, 32, 724—736).—The photo-oxidation of  $\text{CH}_2\text{I}_2$  in the vapour phase has been studied at  $20^\circ$ ,  $30^\circ$ ,  $35^\circ$ , and  $45^\circ$ , and at different low partial and total pressures ( $< 24$  mm.). The products are  $\text{H}_2$ , CO,  $\text{CH}_2\text{O}$ ,  $\text{HCO}_2\text{H}$ , and  $(\text{CH}_2\cdot\text{OH})_2$ . A mechanism is proposed, in which it is assumed that  $\text{CH}_2$  and the peroxidic substances  $\text{CH}_2\text{O}_2$  and  $(\text{CH}_2\text{O})_2$  are first formed, the latter two changing spontaneously into  $\text{HCO}_2\text{H}$  and  $\text{CH}_2\text{O}$  respectively. F. L. U.

**Oxidation of monochloroacetic acid by potassium permanganate at wave-lengths  $366 m\mu$  and  $436 m\mu$  with uranyl salt as photosensitiser.** J. C. GHOSH and B. B. RAY (J. Indian Chem. Soc., 1936, 13, 1—10).—The velocity of the reaction is zero-mol. with respect to  $\text{KMnO}_4$ ,  $\propto$  intensity of incident radiation, and is influenced by change in  $[\text{UO}_2\text{SO}_4]$ , whilst  $1/\text{velocity}$  plotted against  $1/[\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}]$  gives a straight line. A reaction mechanism is suggested. E. E. A.

**Sensitised photolysis of glycollic acid and glyoxylic acid.** E. BAUR (Helv. Chim. Acta, 1936, 19, 234—246; cf. A., 1913, i, 443).—Aq.  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  is decomposed by light in presence of fluorescein, eosin, erythrosin, chlorophyll,  $\text{FeCl}_3$ , or  $\text{UO}_2\text{SO}_4$ , giving  $\text{CH}_2\text{O}$  and  $\text{CO}_2$ , whilst  $\text{HgCl}_2$  used as a depolariser is reduced to  $\text{Hg}_2\text{Cl}_2$ .  $\text{O}_2$  plays no direct part in the photolysis, but in presence of  $\text{FeCl}_3$  it re-oxidises the  $\text{Fe}^{2+}$  produced. Under similar conditions  $\text{CHO}\cdot\text{CO}_2\text{H}$  yields only  $\text{CO}_2$ . The Na salts are changed more rapidly than the acids themselves. In all cases a stationary state is reached, in agreement with the author's theory. F. L. U.

**Decomposition of fructose in ultra-violet light.**—See this vol., 594.

**Comparative velocities of hydrolysis of certain glucosides under the influence of ultra-violet rays, acids, and enzymes.** G. TANRET (Compt. rend., 1936, 202, 881—883).—Nine glucosides have been examined. The order of velocity of hydrolysis is different for the different hydrolytic agents employed, the order for acids differing most markedly from that of the other two, for which a certain degree of similarity



may be observed. Glucosides with reducing properties are most readily hydrolysed by enzymes. M. S. B.

**Photochemical decomposition of oxalyl chloride vapour.** K. B. KRAUSKOPF and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1936, 58, 443—448).— $(\text{COCl})_2$  is slowly decomposed by light of  $\lambda < 3800 \text{ \AA}$ . The reaction is unimol. and has a low quantum yield. The final products are  $\text{COCl}_2$  and  $\text{CO}$ , although  $\text{Cl}_2$  and  $\text{CO}$  are probably formed initially. It is probable that light of short  $\lambda$  breaks the mol. at the C-C linking, and that of long  $\lambda$  at the C-Cl linkings. The absorption coeffs. of  $(\text{COCl})_2$  at 3700—2400  $\text{\AA}$ . have been measured. E. S. H.

**Photolysis of lead tetramethyl and lead tetraphenyl.** P. A. LEIGHTON and R. A. MORTENSEN (J. Amer. Chem. Soc., 1936, 58, 448—454).—The pure liquid or vaporised compounds, or solutions in octane, absorb light in the ultra-violet region, decomp. thus:  $\text{PbR}_4 \rightarrow \text{Pb} + 2\text{R}_2$ . The method of radioactive indicators has been applied to determine quantum yields. The formation of Me radicals has been demonstrated. E. S. H.

**Effect of simultaneous irradiation with several wave-lengths on oxidation of mandelic acid by bromine.** J. C. GHOSH and S. K. BHATTACHARYYA (Z. physikal. Chem., 1936, B, 31, 420—430).—The photochemical oxidation in aq. solution in presence of KBr in light of  $\lambda$  366, 436, and 546 m $\mu$  is a reaction of zero order. The effect of simultaneous irradiation with two of these  $\lambda$  is  $<$  the sum of the effects produced by the two separately. In monochromatic light the velocity coeff.  $\propto$  the square root of the energy absorbed. The reaction mechanism is:  $\text{Br} + \text{AH}_2 \rightarrow \text{HBr} + \text{AH}^\cdot$ ,  $\text{AH}^\cdot + \text{Br}_2 \rightarrow \text{HBr} + \text{A}^\cdot + \text{Br}$ . Quantum efficiencies have been determined. R. C.

**Concentration of artificially produced radioelements by means of an electric field.** J. W. J. FAY and F. A. PANETH (J.C.S., 1936, 384—390; cf. A., 1935, 802).—The effects of bombardment by slow neutrons on  $\text{AsH}_3$  and org. bromides and iodides have been investigated. The active isotope  $^{33}\text{As}^{76}$  does not retain any characteristic charge which may be given to it at the moment of formation, but picks up positive and negative ions in the gas and can be deposited on electrodes of either sign. With EtI, I atoms which are activated and detached from the Et groups acquire, by exchange processes, the negative charge of I ions which are usually present in the liquid or are supplied by adding  $\text{SO}_2$  etc. The active isotope,  $^{53}\text{I}^{128}$ , is collected on Cu and Ag anodes, but not Pt, by electrolysis. Similarly, active I is collected from MeI and BuI, and active Br from EtBr, BuBr,  $\text{CH}_2\text{Br}_2$ , and  $(\text{CH}_2\text{Br})_2$ . The method is not effective in some cases, which are discussed. Practically pure radioactive isotopes are obtained in certain cases by the electric field method and concn. factors as high as 19,000 are recorded. J. G. A. G.

**Direct production of organic compounds containing artificial radio-elements.**—See this vol., 588.

**Heavy hydrogen : its importance for the study of chemical and biological problems.** W. BRANDT (Chem.-Ztg., 1936, 60, 285—288).—A review.

**Para-ortho composition of hydrogen gas produced from hydrogen atoms.** N. SASAKI and O. MABUCHI (Proc. Imp. Acad. Tokyo, 1936, 12, 39—41).—The composition of the  $\text{H}_2$  formed in the reaction  $\text{H} + \text{HI} = \text{H}_2 + \text{I}$  was investigated, the H atoms being obtained by the photochemical decomp. of HI. The product, examined by the thermal conductivity method, contained 25% *p*- $\text{H}_2$ . A. J. M.

**Deuterohydrates of krypton and xenon.** M. GODCHOT, (MLLE.) G. CAUQUIL, and R. CALAS (Compt. rend., 1936, 202, 759—760).—The unstable compounds  $\text{Kr}, 6\text{D}_2\text{O}$  and  $\text{Xe}, 6\text{D}_2\text{O}$  have been prepared and their dissociation pressures measured. They resemble the corresponding hydrates very closely. H. J. E.

**Production of large single crystals of lithium fluoride.** D. C. STOCKBARGER (Rev. Sci. Instr., 1936, [ii], 7, 133—136).—The molten salt is cooled in a Pt crucible under carefully controlled conditions. C. W. G.

**Preparation of single crystals of sodium nitrate from the molten salt.** E. V. TZECHNOVITZER (J. Phys. Chem. U.S.S.R., 1934, 5, 1452—1458).— $\text{NaNO}_3$  crystals of dimensions up to  $24 \times 20 \times 12$  mm. were prepared from  $\text{NaNO}_3$ , containing  $\text{KNO}_3$  0.03 and  $\text{Fe}_2\text{O}_3$  0.05%, by heating in a Ni crucible to  $\approx 350^\circ$ , and cooling at a uniform rate to room temp. (40 hr.) so that crystallisation started at the bottom of the crucible. CH. ABS. (e)

**Production of potassium and sodium hydroxides from the sulphates.**—See B., 1936, 273.

**Ammoniates of simple salts. I. Ammoniates of copper salts.** G. SPACU and P. VOICHESCU (Z. anorg. Chem., 1936, 226, 273—288; cf. A., 1934, 613).—Isobars of systems consisting of  $\text{NH}_3$  and the cupric salts of  $\text{H}_2\text{CrO}_4$ ,  $\text{HCNS}$ ,  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ ,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ ,  $[\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}]_2$ ,  $\text{BzOH}$ , *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , and sulphosalicylic acid have been determined between  $-80^\circ$  and  $140^\circ$ . The capacity for co-ordinating  $\text{NH}_3$  mols., and the stability of the ammoniates formed, increases with increasing strength of the acid. F. L. U.

**Dissolution of metals in potassium cyanide solution.** R. HAY (J. Roy. Tech. Coll., 1936, 3, 576—586).—Results of experiments on the dissolution of Cu, Al, Ag, Zn, Pb, and Zn-Pb in aq. KCN are discussed.  $\text{H}_2$  is evolved under certain conditions, and  $\text{O}_2$  functions as a depolariser. The composition of the deposits on partly immersed metals in air has been determined, and the cause of their formation investigated. The influence of  $\text{OH}^\cdot$  on  $[\text{H}^\cdot]$  of aq. KCN and on the rate of dissolution of Ag in KCN solution has been determined. Addition of CaO to aq. cyanide does not depend for beneficial results on the  $\text{OH}^\cdot$  radical introduced; presence of  $\text{OH}$  reduces the rate of dissolution of Ag and probably that of Au. D. C. J.

**Factors influencing reduction of alkaline copper reagents by glucose.** W. H. FORBES and A. ANDREEN-SVEDBERG (Skand. Arch. Physiol., 1934, 70, 168—185; Chem. Zentr., 1935, ii, 1067—1068).—*p*<sub>H</sub> is without effect,  $< 1\%$  of NaCl or  $\text{Na}_2\text{SO}_4$  is without



action, but  $\text{ZnSO}_4$ ,  $\text{NaHSO}_4$ , and  $\text{NaCN}$  have a disturbing influence; the influence of sugar concn. is small.

H. N. R.

**Hydration of dicalcium silicate and tricalcium silicate.** N. B. KEEVIL and T. THORVALDSON (Canad. J. Res., 1936, 14, B, 20—30).— $\beta$ - and  $\gamma$ - $\text{Ca}_2\text{SiO}_4$  silicates, exposed to saturated steam between  $110^\circ$  and  $350^\circ$ , formed three cryst. products. X-Ray diffraction patterns and optical properties showed two of these to be identical with products previously described (A., 1935, 50), whilst the third (I) had distinctive structure but variable  $\text{H}_2\text{O}$  content with limiting composition  $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ . When conditions did not favour hydrolysis,  $\text{Ca}_3\text{Si}_2\text{O}_7$  silicate hydrated to a cryst. product (II) with probable limiting composition  $3\text{CaO}\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$ . Hillebrandite (III), heated at  $160^\circ$ , remained unchanged, but dehydrated (III) gave a product similar to (I). (I) could be dehydrated but (II) liberated  $\text{CaO}$ . When treated with a large excess of  $\text{H}_2\text{O}$  the hydrated silicates hydrolysed to the same extent as, but more rapidly than, the anhyd. silicates.

L. A. O'N.

**Hydration of  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ .** Y. SANADA (J. Soc. Chem. Ind. Japan, 1936, 39, 46B).—The compound brownmillerite,  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ , was prepared by heating together  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  in the required proportions at  $1400^\circ$  for 3 hr. 0.5 g. of the finely ground product, when treated with 50 c.c. of  $\text{CO}_2$ -free  $\text{H}_2\text{O}$ , gave  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{aq.}$  and  $\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot\text{aq.}$  Under the microscope the product was observed to form cryst. needles, hexagonal plates, and, with excess of  $\text{H}_2\text{O}$ , rhombic dodecahedra.

M. S. B.

**Formation of mercuriammonium salts from mercuriammonium nitrate by double decomposition. II. Mercuriammonium chlorate.** S. AUGUSTI (Boll. Chim. Farm., 1936, 75, 129—135).—A yellowish-white ppt. of mercuriammonium chlorate,  $\text{Hg}_2\text{NClO}_3$ , is obtained on adding aq.  $\text{KClO}_3$  to aq. ammoniacal  $\text{Hg}_2\text{NNO}_3$ . The following quant. reactions are shown to occur:  $\text{Hg}_2\text{NClO}_3 + 8\text{KI} + 4\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{HgI}_4 + \text{NH}_4\text{ClO}_3 + 4\text{KOH}$  at room temp.;  $\text{Hg}_2\text{NClO}_3 + 8\text{KI} + 3\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{HgI}_4 + \text{NH}_3 + \text{KClO}_3 + 3\text{KOH}$  at the b.p.;  $\text{Hg}_2\text{NClO}_3 + 2\text{Na}_2\text{S} + 3\text{H}_2\text{O} \rightarrow 2\text{HgS} + \text{NH}_3 + 3\text{NaOH} + \text{NaClO}_3$  at the b.p.;  $\text{Hg}_2\text{NClO}_3 + 4\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{Hg}(\text{S}_2\text{O}_3)_2 + 4\text{NaOH} + \text{NH}_4\text{ClO}_3$  at room temp.;  $\text{Hg}_2\text{NClO}_3 + 4\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{Hg}(\text{S}_2\text{O}_3)_2 + 3\text{NaOH} + \text{NaClO}_3 + \text{NH}_3$  at the b.p.;  $\text{Hg}_2\text{NClO}_3 + 8\text{KCN} + 4\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{Hg}(\text{CN})_4 + 4\text{KOH} + \text{NH}_4\text{ClO}_3$  at room temp. Thermal decomp. produces  $\text{HgO}$ .

D. R. D.

**Potassium and sodium mercury sulphites. Potentiometric investigation. II.** G. SPACU and C. DRĂGULESCU (Z. anorg. Chem., 1936, 226, 416—424; cf. A., 1935, 1469).—Potentiometric methods indicate the existence only of the following mercuri-sulphites:  $\text{K}[\text{HgClSO}_3]$ ,  $\text{K}_2[\text{Hg}(\text{SO}_3)_2]$ , and  $\text{Na}_2[\text{Hg}(\text{SO}_3)_2]$ , no evidence of  $\text{HgSO}_3\cdot\text{NaCl}$  or of  $\text{Na}_2\text{SO}_3\cdot 2\text{HgSO}_3$  being obtained. The formation of the complex ion  $[\text{Hg}(\text{SO}_3)_2]^{2-}$  provides a method for determination of  $\text{SO}_3^{2-}$ .

J. W. S.

**Mercurous salts and their amino-compounds. I.** E. GLEDITSCH and T. F. EGDIVUS (Z. anorg. Chem., 1936, 226, 265—272, and Compt. rend., 1936, 202, 574—576).—The primary product of reaction

between aq.  $\text{NH}_3$  and  $\text{Hg}_2\text{X}_2$  ( $\text{X}=\text{Cl}$  or  $\text{NO}_3$ ) is  $\text{NH}_2\cdot\text{Hg}_2\cdot\text{X}$  (I), which decomposes reversibly into  $\text{NH}_2\cdot\text{Hg}\cdot\text{X}$  (II) and  $\text{Hg}$ . Comparison of the X-ray diagrams of (I) and (II) shows the former to be a distinct compound.

F. L. U.

**Reducing action of mercury. I. Formation of hydrogen peroxide in the interaction of mercury with hydrochloric acid in presence of oxygen.** N. H. FURMAN and W. M. MURRAY, jun. (J. Amer. Chem. Soc., 1936, 58, 429—433).—The reaction may be represented stoichiometrically as (1)  $2\text{Hg} + 2\text{HCl} + \text{O}_2 = \text{Hg}_2\text{Cl}_2 + \text{H}_2\text{O}_2$ , (2)  $2\text{Hg} + 2\text{HCl} + \text{H}_2\text{O}_2 = \text{Hg}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ . The mechanism is discussed.

E. S. H.

**Halides of boron, and their m.p.** A. M. VASILIEV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 93—95).—The m.p. is  $2507^\circ$ , as calc. by Flavitski's formula (A., 1906, ii, 152) from the physical consts. of  $\text{BBr}_3$ , and  $2593^\circ$  from those of  $\text{BI}_3$ .

R. T.

**Borovanadates.** D. GHIRON (Atti R. Accad. Lincei, 1935, [vi], 22, 259—264).—The existence of two series of borovanadates has been shown, viz.,  $2\text{M}^{11}\text{O}\cdot\text{V}_2\text{O}_5\cdot 3\text{B}_2\text{O}_3$  ( $\text{M}=\text{Pb}$ ,  $\text{Cd}$ ) and  $\text{M}^{11}\text{O}\cdot\text{V}_2\text{O}_5\cdot\text{B}_2\text{O}_3$  ( $\text{M}=\text{Pb}$ ,  $\text{Cd}$ ,  $\text{Zn}$ ).

O. J. W.

**Fused "onium" salts as acids. Reactions in fused pyridinium hydrochloride.** L. F. AUDRIETH, A. LONG, and R. E. EDWARDS (J. Amer. Chem. Soc., 1936, 58, 428—429).—Al, Cd, Ca, Mg, Zn, and Cu react rapidly and Mn, Ni, Sn, Pb, and Fe slowly with fused  $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$  (I), yielding  $\text{H}_2$  and the corresponding chlorides. Many metallic oxides dissolve in (I), forming chlorides. Solutions of metallic chlorides in (I) are electrolytically conducting; Sn, Pb, As, Sb, and Bi can be electrodeposited therefrom.

E. S. H.

**Action of dilute acids on aluminium.**—See B., 1936, 327.

**Enrichment of carbon in the heavier isotope by diffusion.** D. E. WOOLDRIDGE and F. A. JENKINS (Physical Rev., 1936, [ii], 49, 404).—Using an apparatus containing 35 separation members for the separation of gaseous isotopes by diffusion, gaseous  $\text{CH}_4$  of increased abundance in  $\text{C}^{13}$  was obtained. Spectroscopic observations showed the  $\text{C}^{12}\text{C}^{13}$  band head at  $4744 \text{ \AA.}$ , the relative intensity indicating an abundance of 6.6 at.-% of  $\text{C}^{13}$ , or an enrichment factor  $\approx 7$ . A faint head corresponding with  $\text{C}^{13}\text{C}^{13}$  was observed.

N. M. B.

**Reactions in the solid state at high temperatures. XIII. Course of reaction in formation of magnesium, strontium, and barium silicates.** W. JANDER and J. WUHRER (Z. anorg. Chem., 1936, 226, 225—247; cf. A., 1935, 944).—Mixtures of  $\text{SiO}_2$  with  $\text{MgO}$  at  $1170^\circ$ , with  $\text{SrCO}_3$  at  $920^\circ$ , and with  $\text{BaCO}_3$  at  $1010^\circ$  give rise primarily to the ortho-silicates (I), even when  $\text{SiO}_2$  is in excess, in which latter case metasilicate is formed in a subsequent reaction between  $\text{SiO}_2$  and (I). The result is in part explained by the greater readiness of (I) to crystallise, as is to be expected from the structures of the two substances.

F. L. U.



**Titanium chlorosulphonato-chloride.** G. P. LUTSCHINSKI with A. I. LICHATSHEVA (Z. anorg. Chem., 1936, 226, 338—337).—Interaction of  $\text{TiCl}_4$  (1 mol.) and  $\text{SO}_3$  (2 mols.) in  $\text{CHCl}_3$  or  $\text{SO}_2\text{Cl}_2$  solution yields the compound  $\text{Ti}(\text{SO}_3\text{Cl})_2\text{Cl}_2$  (I), a yellow cryst. substance,  $d^{20}_4$  2.012, fuming in moist air and turning white. It is insol. in  $\text{CHCl}_3$  and  $\text{SO}_2\text{Cl}_2$ . When heated it darkens and vaporises, being completely sublimed on vigorous heating, with production of  $\text{TiCl}_4$  and  $\text{SO}_3$ . Action of  $\text{SO}_3$  converts it into the compound  $\text{Ti}(\text{SO}_3\text{Cl})_3\text{Cl}$ . When  $\text{SO}_2\text{Cl}_2$  vapour is passed over heated  $\text{TiO}_2$  (I) is obtained only when the  $\text{TiCl}_4$  and  $\text{SO}_3$  produced condense together.

J. W. S.

**Allotropic modifications of lead monoxide.** E. RENCKER and M. BASSIÈRE (Compt. rend., 1936, 202, 765—767).—The  $\alpha$ -modification of  $\text{PbO}$  is transformed into  $\beta$ - $\text{PbO}$  at  $530^\circ$ . These two forms give distinct X-ray diagrams. The reverse transformation was not observed. Methods of preparing these forms are discussed. The action of conc. aq.  $\text{NaOH}$  on  $\text{Pb}(\text{OH})_2$  at  $20^\circ$  yields  $\beta$ - $\text{PbO}$ , which is transformed on keeping in contact with the solution into red  $\alpha$ - $\text{PbO}$ .  $\beta$ - $\text{PbO}$  prepared at a high temp. is also converted by conc. aq.  $\text{NaOH}$  into  $\alpha$ - $\text{PbO}$ .

H. J. E.

**Raschig's hydrazine synthesis.** M. MØLLER (Kong. dansk. Vidensk. Selsk., 1934, 12, No. 16, 59 pp.; Chem. Zentr., 1935, ii, 985—986).—With pure reagents, a 40% yield of  $\text{N}_2\text{H}_4$  can be obtained in the absence of gelatin (I).  $\text{Cu}$  in  $1.66 \times 10^{-6} M$  solution practically inhibits formation of  $\text{N}_2\text{H}_4$ .  $\text{Fe}^{\text{III}}$  to some extent, but not  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Mn}$ , or  $\text{Pb}$ , behaves like  $\text{Cu}$ . (I) or mannitol suppresses the inhibiting action. Electrolysis of  $\text{NaCl}$ - $\text{NaOH}$ - $\text{NH}_3$  (I) solutions, or use of  $\text{NaOBr}$ , affords only traces of  $\text{N}_2\text{H}_4$ .

J. S. A.

**Proof of the existence of free  $\text{NH}$  (imine) in the thermal decomposition of ammonia.** H. H. FRANCK and H. REICHARDT (Naturwiss., 1936, 24, 171).—The existence of  $\text{NH}$  in the thermal decomp. of  $\text{NH}_3$  at atm. pressure and  $2000^\circ$  is shown by the presence of the  $\text{NH}$  absorption band at  $3360 \text{ \AA}$ . The stationary  $[\text{NH}]$  is estimated at 0.1—1%. That the radical is produced by decomp. of  $\text{NH}_3$  and not by combination of  $\text{N}$  and  $\text{H}$  is shown by the fact that the band could not be obtained when  $\text{N}_2$  and  $\text{H}_2$  were heated together at  $2500^\circ$ .

A. J. M.

**Causes of spontaneous inflammation of red phosphorus prepared by the dry method.** I. I. KUKUSCHKIN and A. A. KORINFSKI (J. Chem. Ind. Russ., 1935, 12, 1240—1249).—Spontaneous inflammation takes place when the product contains > 10% of a bright red, active form of  $\text{P}$ , distinguished from ordinary red  $\text{P}$  by its smaller  $d$ , and by its ability to ppt.  $\text{Cu}$  from its solutions; contamination with white  $\text{P}$ ,  $\text{P}_2\text{O}_5$ , or  $\text{SiO}_2$  does not affect the flash point of red  $\text{P}$ . The content of active  $\text{P}$  in red  $\text{P}$  may be reduced from 11 to 2% by heating for several hr. in a steel autoclave at  $340$ — $350^\circ$ .

R. T.

**Vanadium oxychloride as a solvent.** II. F. E. BROWN and F. A. GRIFFITHS (Iowa State Coll. J. Sci., 1934, 9, 89—93; cf. A., 1931, 1405).— $\text{Cs}$ ,  $\text{Rb}$ ,  $\text{K}$ , and  $\text{Na}$  react violently with  $\text{VOCl}_3$  at  $30^\circ$ ,

$60^\circ$ ,  $100^\circ$ , and  $180^\circ$ , respectively.  $\text{Li}$  also reacts.  $\text{Ca}$  and  $\text{In}$  react slightly, and  $\text{Ga}$  forms a blue ppt.  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{I}$ ,  $\text{Hg}$ ,  $\text{Se}$ ,  $\text{S}$ , and  $\text{V}$  have little reaction with  $\text{VOCl}_3$  at room temp.  $\text{S}$  reacts at high temp. The reaction of  $\text{P}$  is explosive at  $100^\circ$ .  $\text{As}$  and  $\text{Sb}$  are less vigorous and  $\text{Bi}$  is inert. Liquid  $\text{SO}_2$  and  $\text{VOCl}_3$  are immiscible. Liquid  $\text{H}_2\text{S}$  reacts, forming ppts. varying in composition between  $\text{VSCl}_3$  and  $\text{V}(\text{OH})(\text{SH})\text{Cl}$ . No stable compound was formed with  $\text{MgPhBr}$ .

CH. ABS. (e)

**Constitution of vanadium carbide.** A. MORETTE (Compt. rend., 1936, 202, 572—573; cf. A., 1935, 313).— $\text{V}_2\text{O}_5$  and excess of  $\text{C}$  heated at  $> 1800^\circ$  yield  $\text{V}_4\text{C}_3$ .

T. G. P.

**Behaviour of zinc and lead arsenites and arsenates at high temperatures.** I. M. DUBROVIN (J. Appl. Chem. Russ., 1936, 9, 40—60).— $\text{Zn}_3(\text{AsO}_3)_2$  (I) yields  $\text{ZnO}$  and  $\text{As}_2\text{O}_3$  when heated at  $400$ — $500^\circ$ ; at  $500$ — $550^\circ$  oxidation-reduction reactions take place, associated with sublimation of  $\text{As}$ , leaving a residue of  $\text{Zn}_3(\text{AsO}_4)_2$  (II) and  $\text{ZnO}$ . At  $550$ — $675^\circ$  loss of  $\text{As}$  is small, the reaction consisting chiefly of  $(\text{I}) + \text{O}_2 \rightarrow (\text{II})$ , whilst at  $> 675^\circ$  (II) dissociates as follows:  $(\text{II}) \rightarrow \text{ZnO} + \text{As}_2\text{O}_3 + \text{O}_2$ . Decomp. of  $\text{Pb}_3(\text{AsO}_3)_2$  commences at  $250^\circ$ , and is associated with oxidation by atm.  $\text{O}_2$ ; at  $700$ — $850^\circ$  the reaction consists almost exclusively of oxidation to arsenate, which undergoes thermal decomp. at  $1000^\circ$ .

R. T.

**Dehydration of sodium niobates.** P. SUE (Compt. rend., 1936, 202, 762—764).—In the dehydration of  $6\text{Nb}_2\text{O}_5 \cdot 7\text{Na}_2\text{O} \cdot 32\text{H}_2\text{O}$  intermediate di- and tetra-hydrates were formed. Dehydration commenced at  $80^\circ$ . The tetrahydrate was stable at  $110^\circ$ .  $\text{Nb}_2\text{O}_5 \cdot \text{Na}_2\text{O} \cdot 7\text{H}_2\text{O}$  was stable up to  $40^\circ$ . It yielded a monohydrate, stable to  $110^\circ$ .

H. J. E.

**Existence of perchromic acid,  $\text{H}_3\text{CrO}_8 \cdot 2\text{H}_2\text{O}$ .** R. SCHWARZ and G. ELSTNER (Ber., 1936, 69, [B], 575—579).—The product of the interaction of  $\text{CrO}_3$  and conc.  $\text{H}_2\text{O}_2$  in  $\text{Me}_2\text{O}$  is the etherate  $\text{CrO}_5 \cdot \text{Me}_2\text{O}$ , which is stable at low temp. and does not possess appreciable vapour tension, but explodes with great violence at  $> -30^\circ$ . The compound  $\text{H}_3\text{CrO}_8 \cdot 2\text{H}_2\text{O}$  (Riesenfeld *et al.*, A., 1914, ii, 279) does not exist. The reaction between  $\text{CrO}_2\text{Cl}_2$  and  $\text{H}_2\text{O}_2$  does not lead to a definite product, an equilibrium, formulated  $\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O}_2 \rightleftharpoons \text{CrO}_5 + 2\text{HCl} + \text{H}_2\text{O}$ , being reached.

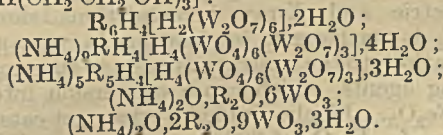
H. W.

**Reinecke's salt,  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4] \cdot \text{H}_2\text{O}$ .** H. D. DAKIN (Org. Syntheses, 1935, 15, 74—76).—The prep. from  $\text{NH}_4\text{SCN}$  and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is described.

CH. ABS. (r)

**Reaction of tris- $\beta$ -hydroxyethylamine with tungstic acid.** F. GARELLI and A. TETTAMANZI (Gazzetta, 1935, 65, 1239—1243).—The prep. of the following compounds is described

$[\text{R}=\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_3]:$



O. J. W.



**Phospho- and silico-tungstates.**—See this vol., 620.

**Hydrogen bromide (anhydrous).** J. R. RUHOFF, R. E. BURNETT, and E. E. REID (Org. Syntheses, 1935, 15, 35—38).—Prep. from  $H_2$  and Br is described.

CH. ABS. (p)

**Preparation and properties of bromine oxide  $Br_2O$ .** W. BRENSCHÉDE and H. J. SCHUMACHER (Z. anorg. Chem., 1936, 226, 370—384; cf. A., 1935, 1334).—No  $Br_2O$  could be isolated after heating Br in presence of  $HgO$ , or after passing Br vapour over heated  $HgO$ . It was obtained in concn.  $> 50\%$  of the total [Br] by action of  $HgO$  on Br in  $CCl_4$ . The reaction probably occurs thus:  $HgO + Br_2 = HgOBr_2$ ;  $HgOBr_2 + Br_2 = HgBr_2 + Br_2O$ . The absorption spectrum of the  $Br_2O$  solution in the visible region has been measured.

J. W. S.

**Exchange reactions of iodine by the method of radioactive indicators.** D. E. HULL, C. H. SHIFFLETT, and S. C. LIND (J. Amer. Chem. Soc., 1936, 58, 535).—Preliminary results, indicating exchange between I and radio-I, are reported.

E. S. H.

**Action of nascent iodine and hydriodic acid on oxides.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 704—705).—I and HI, liberated from  $CHI_3$  by photochemical decomp., can react with the oxides of alkali and alkaline-earth metals,  $Ag_2O$ ,  $HgO$ ,  $Ni(OH)_2$ , and  $Cu(OH)_2$  to form iodides.

E. S. H.

**Preparation and properties of pure iron.** J. G. THOMPSON and H. E. CLEAVES (J. Res. Nat. Bur. Stand., 1936, 16, 105—130).—A crit. review of available information.

E. S. H.

**Modern theories of corrosion. I. Water-line corrosion.** J. E. O. MAYNE (J.C.S., 1936, 366—368).—A steel plate partly immersed in de-aerated 0.01—0.1N-KCl in vac. corrodes at the water-line and  $Fe(OH)_2$  is formed. This reaction, which does not occur when the plate is completely immersed, may be due to the potential existing at the surface of the solution. Corrosion is retarded by adding EtOH, possibly owing to negative adsorption of the solute at the surface of the solvent. Similarly, water-line corrosion is caused by KBr, KI,  $KNO_3$ , and  $K_2SO_4$ , but not by  $KClO_3$ , KOH,  $K_2CrO_4$ ,  $K_2CO_3$ , and  $Na_2HPO_4$ .

J. G. A. G.

**Fundamental theories of metal corrosion. I.** ITAKA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 131—146).—Necessary and abs. factors to promote corrosion of the following metals are shown in parentheses: Fe ( $H_2O$ ,  $O_2$ ), Al ( $H_2O$ ,  $O_2$ ,  $Cl'$ ), Mg ( $H_2O$ ,  $Cl'$ ), Cu ( $H_2O$ ,  $Cl'$ ), Zn ( $H_2O$ ),  $\alpha$ -brass ( $H_2O$ ,  $Cl'$ ),  $\alpha + \beta$ -brass ( $H_2O$ ,  $Cl'$ ,  $O_2$ ). Equations for the mechanism of corrosion are given.

N. M. B.

**Oxides. VII. Thermal dissociation of  $\gamma$ - $Fe_2O_3$ .** A. SIMON and A. LANDGRAF (Kolloid-Z., 1936, 74, 296—300; cf. A., 1932, 468).—Tensiometric and X-ray investigations show that  $\gamma$ - $Fe_2O_3$  is unchanged by heating in vac. at  $300^\circ$ . Observations to the contrary are due to the presence of reducing agents, which cause conversion into  $Fe_3O_4$  and  $\alpha$ - $Fe_2O_3$ . Finely-divided Pt does not catalyse the decomp. of  $\gamma$ - $Fe_2O_3$  at  $300^\circ$ .

E. S. H.

**Ferric oxalate.** C. DUVAL (Compt. rend., 1936, 202, 845—846).—The absorption spectrum of aq.  $Fe^{III}$  oxalate is identical with that of K ferrioxalate and, under the influence of an electric current,  $Fe^{III}$  migrates to both anode and cathode. These results apparently confirm the formula  $Fe[Fe(C_2O_4)_3] \cdot 4H_2O$ . Since, however, there is no reaction with KSCN, the cationic Fe is apparently not free and a probable formula is  $[Fe(H_2O)_4][Fe(C_2O_4)_3]$ . An examination of the ionic migration in abs. EtOH supports this formula, since  $H_2O$  is detected at the cathode only, by the use of a very hygroscopic complex Co chloride.

M. S. B.

**Preparation of alkali ferrates. II. Basicity and chemical properties of ferrates.** A. D. DEL BOCA (An. Farm. Bioquim., 1934, 5, 120—126; Chem. Zentr., 1935, ii, 817).— $FeO_2$  is considered to be  $O \cdot Fe \cdot O$ , giving rise to salts  $M_2FeO_3$  without peroxidic properties. With acids, autoxidation occurs,  $H_2FeO_4$  and its salts being formed.  $H_2O_2$  initially yields  $H_2FeO_4$ , finally giving  $H_2O_2$ .  $HMnO_4$  yields  $Mn^{II}$ ,  $Fe^{III}$ , and  $O_2$ .

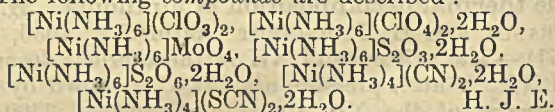
J. S. A.

**Bisdimethylglyoxime diamine cobaltic salts and their configuration.**—See this vol., 598.

**Formation and decomposition of nickel ferrites.** A. D. POGORELUI (Tsvet. Metal, 1935, No. 2, 79—96).— $NiO \cdot Fe_2O_3$  was prepared by heating NiO and  $Fe_2O_3$  at  $600$ — $1000^\circ$ . The products dissolved more slowly in aq. HCl and  $H_2SO_4$  than did NiO, and were less readily reduced by CO and  $H_2$ . Reaction with CaS proceeded equally readily in both cases. That with  $SO_2$  or  $SO_3$  at  $550^\circ$  proceeded more readily with  $NiO \cdot Fe_2O_3$  than with NiO.

CH. ABS. (e)

**Nickel ammine complexes. IV. Nickel hexammine and tetrammine compounds with water of crystallisation.** E. J. KOCIS (Magyar chem. Fol., 1934, 40, 147—150; Chem. Zentr., 1935, ii, 494).—The following compounds are described:



H. J. L.

**Ruthenium carbonyls and nitrosyls.** W. MANCHOT and W. J. MANCHOT (Z. anorg. Chem., 1936, 226, 385—415).—Action of CO at  $180^\circ/200$  atm. on Ru yields the compound  $Ru(CO)_5$  (I), m.p.  $-22^\circ$ . (I) decomposes in light or on warming, yielding orange-yellow crystals of the compound,  $Ru_2(CO)_9$  (II), which is best prepared by heating a solution of (I) in  $C_6H_6$ . (II) is stable in light and air, in org. solvents, and in conc. HCl. Decomp. begins at  $150^\circ$  in air and at  $200^\circ$  in absence of  $O_2$ . Another carbonyl, of unknown composition, is obtained as a green amorphous powder in the decomp. of (I) and by the action of dil. alkali on (II). Compounds  $RuX_2(CO)_2$  are obtained by action of halogens on (II). When heated with Ag in a current of CO these yield (I). The action of NO on (II) yields a nitrosyl compound,  $Ru(NO)_4$  or  $Ru(NO)_5$ . These compounds are compared with the corresponding Fe compounds.

J. W. S.

**Collision effects in mechanical analysis by Odén's method.** A. ROMWALTER (Mitt. berg-hüttenm. Abt. Univ. Sopron., 1934, 6, 52—57; Chem.



Zentr., 1935, ii, 886).—The method eliminates possible errors in sedimentation analysis due to collision effects.

J. S. A.

**Capillary analysis and its applications.** R. DUBRISAY (Bull. Soc. chim., 1936, [v], 3, 631–640).—The change of surface tension produced by addition of alkali or acid can be used as a means of tracing titration curves. Examples of the application of this principle to acid-alkali and similar reactions are given.

E. S. H.

**Analytical notes.** H. TRAPP (Z. anal. Chem., 1936, 104, 255–257).—(a) Approx. formulae are given for calculating the composition of gas mixtures by the displacement of one gas from a known vol. by another gas at a measured streaming rate. (b)  $\text{SnCl}_4$  is reduced by Sn to  $\text{SnCl}_2$ .

J. S. A.

**Difficulties in colorimetric determination of  $p_H$  values.** A. B. COX (Soc. Chem. Ind. Victoria, 1935, 35, 1001–1005).—Sources of error in colorimetric  $p_H$  determinations on biological solutions due to (a) reaction of  $\text{NH}_2$ -acids with certain indicators (e.g., bromocresol-purple), (b) formation of coloured lakes by Cu and other metals, (c) colour matching by light of composition differing from sunlight are discussed.

J. S. A.

**Determination of  $p_H$ .** A. VAN VIANEN (Pharm. Weekblad, 1936, 73, 350–352).—The accuracy of  $p_H$  determinations using a commercial comparator consisting of a mixed indicator and a series of comparison tubes was determined by comparing the results obtained by 17 observers for the same standard buffer solutions. An accuracy of  $\pm 0.2$ – $0.5$  was obtained.

D. R. D.

**Absolute colorimetry. XIII. Azobilirubin as an indicator.** A. THIEL and H. LOGEMANN (Biochem. Z., 1936, 284, 347–352; cf. this vol., 44).—The light extinction curves of azobilirubin (prepared from bilirubin by diazotisation in  $\text{EtOH-CHCl}_3$  and extraction with  $\text{Et}_2\text{O}$ ) are given for the  $p_H$  range of 1.54–3.10 (red–blue) (cf. A., 1934, 912; 1935, 1290). Anomalous colour changes occur in the presence of certain buffer salts.

F. O. H.

**Titration of hydrogen peroxide in presence of oxalic acid (alkali oxalates).** A. SIMON and T. REETZ (Z. anal. Chem., 1936, 104, 249–255).—Total  $\text{H}_2\text{O}_2 + \text{C}_2\text{O}_4^{2-}$  is titrated with  $\text{KMnO}_4$ , first at room temp. ( $\text{H}_2\text{O}_2$ ) and then in hot solution. To a second portion an excess of  $M\text{-Ca}(\text{NO}_3)_2$  in 10% aq.  $\text{NH}_3$  is added,  $+\text{FeCl}_3$  as catalyst, and the  $\text{H}_2\text{O}_2$  is then destroyed by boiling. The solution is finally acidified with  $\text{H}_2\text{SO}_4$ , and  $\text{C}_2\text{O}_4^{2-}$  is titrated with  $\text{KMnO}_4$ .

J. S. A.

**Mercurimetry. Titration of halogens.** M. SCHTSCHIGOL (Ann. Chim. Analyt., 1936, [iii], 18, 61–64).—The solution of  $\text{Cl}^-$  or  $\text{Br}^-$  + a mixture of 0.05N- $\text{NH}_4\text{CNS}$  and  $\text{Fe}(\text{NO}_3)_3$  is titrated with 0.1N- $\text{Hg}_2(\text{NO}_3)_2$  until colourless.  $\text{I}^-$  is treated with an excess of  $\text{Hg}_2(\text{NO}_3)_2$ , and the ppt. of  $\text{Hg}_2\text{I}_2 + \text{HgI}_2 + \text{Hg}$  is filtered off. Excess of  $\text{Hg}$  in the filtrate is oxidised with  $\text{KMnO}_4$ , and is then titrated back with  $\text{NH}_4\text{CNS}$ .

J. S. A.

(A) Determination of chlorates, bromates, and iodates by the use of liquid amalgams. (B) Ap-

plication of Wood's alloy as a reducing reagent. P. G. POPOV (Ukrain. Chem. J., 1935, 10, 413–416, 428–430).—(A)  $\text{ClO}_3^-$  is determined by adding 10 ml. of 50%  $\text{H}_2\text{SO}_4$  to 10 ml. of the solution, and shaking for 10 min. with Zn-Hg, after which  $\text{Cl}^-$  is determined by Volhard's method.  $\text{BrO}_3^-$  and  $\text{IO}_3^-$  are determined similarly, except that 7N- $\text{H}_2\text{SO}_4$  is used, and the titration is performed after 3 min.

(B) Wood's alloy may be substituted for Zn-Hg in the above procedure (at  $90^\circ$ ).

R. T.

**Sensitive reaction for chlorates, bromates, and sulphites.** I. M. KORENMAN (J. Appl. Chem. Russ., 1936, 9, 157–158).—A mixture of 1 drop of solution, 1 drop of 0.02% indigo-carmin, 1 drop of saturated aq.  $\text{Na}_2\text{SO}_3$ , and 1 drop of 3N-HCl is decolorised in presence of  $< 0.2 \times 10^{-6}$  g. of  $\text{KClO}_3$ , or  $0.24 \times 10^{-6}$  g. of  $\text{KBrO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ ;  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{IO}_3^-$  do not interfere. The reaction is given by  $\text{MnO}_4^-$  and  $\text{OCl}^-$  in absence of  $\text{Na}_2\text{SO}_3$ .  $\text{SO}_3^{2-}$  ( $< 1.6$  in  $10^6$ ) can be detected by the above reaction with  $\text{KClO}_3$ , but without  $\text{Na}_2\text{SO}_3$ ;  $\text{S}^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  interfere.

R. T.

**Determination of iodine in air.** H. CAUER (Z. anal. Chem., 1936, 104, 161–169).—A measured vol. of air is washed intensively through 13% aq.  $\text{K}_2\text{CO}_3$ , using the apparatus described previously (this vol., 47). For work at low temp., saturated aq.  $\text{K}_2\text{CO}_3$  may be used. The  $\text{K}_2\text{CO}_3$  solution is evaporated down, and  $\text{K}_2\text{CO}_3$  is pptd. by addition of  $\text{EtOH}$ . The  $\text{EtOH}$  containing KI is decanted, evaporated, and the separation from  $\text{K}_2\text{CO}_3$  repeated. The residue so obtained, freed from org. matter by cautious heating, is dissolved in 0.3 c.c. of  $\text{H}_2\text{O}$ . 0.02 c.c. of  $\text{CHCl}_3$  is added, and I is liberated by addition of 0.05 c.c. of 3N- $\text{H}_2\text{SO}_4$  containing  $\text{NaNO}_2$ . The colour of the  $\text{CHCl}_3$  drop is matched against solutions of known I content. Alternatively, I may be oxidised to  $\text{IO}_3^-$  with  $\text{Cl-H}_2\text{O}$ . KI is added, and the I liberated is titrated with 0.004N- $\text{Na}_2\text{S}_2\text{O}_3$ .

J. S. A.

**Titration with 0.001N-iodine.** A. B. COX (Soc. Chem. Ind. Victoria, 1935, 35, 996–1000).—The indicator correction may be reduced by adding 0.25 ml. of 0.2N-KI per 20 ml. of solution. Titration of I with 0.001N- $\text{Na}_2\text{S}_2\text{O}_3$  is not practicable.

J. S. A.

**Standard iodine solutions.** A. H. SCOTT (J. Biol. Chem., 1936, 113, 511–513).—I solutions diluted with  $\text{H}_2\text{O}$  show an apparent loss of I; titrations should be made in 0.3M-KI.

F. A. A.

**Hydrochemical analysis. I. [Determination of hydrogen sulphide.]** W. OHLE (Angew. Chem., 1936, 49, 206–208).— $\text{H}_2\text{S}$  in  $\text{H}_2\text{O}$  is pptd. as CdS immediately after sampling by the addition of slightly acid 50% aq.  $\text{CdSO}_4$ . The ppt. is collected and treated with acidified 0.01N-I. The excess of I is titrated back with 0.02N- $\text{Na}_2\text{S}_2\text{O}_3$ .

J. S. A.

**Reversible indicator for detection of small quantities of hydrogen sulphide in the atmosphere.**—See B., 1936, 349.

**Direct titration of sulphates. Tetrahydroxybenzoquinone as internal indicator.** R. T. SHEEN and H. L. KAHLER (Ind. Eng. Chem. [Anal.], 1936, 8, 127–130).—The procedure of Schroeder (A., 1934, 46) is modified so as to extend the range of  $[\text{SO}_4^{2-}]$ .



$\text{PO}_4'''$  interferes, but when  $\geq 60$  p.p.m. are present can be eliminated by  $p_{\text{H}}$  control. EtOH may be replaced by  $\text{Pr}^{\text{e}}\text{OH}$ . The end-point may be sharpened by adding NaCl. E. S. H.

**Determination of sulphate by titration with lead nitrate, using eosin as indicator.** J. E. RICCI (Ind. Eng. Chem. [Anal.], 1936, 8, 130—132).—0.10—0.25 g. of  $\text{Na}_2\text{SO}_4$  may be determined by titration with 0.1M- $\text{Pb}(\text{NO}_3)_2$ , using 0.5% eosin as indicator, with an accuracy of about 0.0005 g. of  $\text{Na}_2\text{SO}_4$ . E. S. H.

**Determination of selenocyanides in presence of cyanides.** R. RIPAN-TILICI (Z. anal. Chem., 1936, 104, 189—192).—The potential curve shows discontinuities corresponding with formation of  $[\text{Ag}(\text{CN})_2]'$  (a); pptn. of  $\text{AgSeCN}$  (b); and pptn. of  $\text{AgCN}$  (c). Then  $\text{SeCN}' = (a) - (b)$ . J. S. A.

**Semi-micro-method of analysis for nitrogen.** A. R. RONZIO (Ind. Eng. Chem. [Anal.], 1936, 8, 122—123).—The main difficulties in the Dumas method are avoided by placing at the end of the combustion tube a heated section containing  $\text{I}_2\text{O}_5$ . A modified nitrometer is recommended. E. S. H.

**Determination of small amounts of nitric acid in sulphuric acid.**—See B., 1936, 316.

**Determination of total oxidising power, nitrite, ozone, and total chlorine in air.** II.—See B., 1936, 349.

**Colour reaction for nitric acid.** A. S. VASILIEV (J. Appl. Chem. Russ., 1936, 9, 155—156).—3 drops of 0.1%  $\beta$ -methylumbelliferone in conc.  $\text{H}_2\text{SO}_4$  are added to 2 drops of the solution, and 2 litres of  $\text{H}_2\text{O}$  are added; a lemon-yellow coloration is obtained in presence of  $0.5 \times 10^{-6}$  g. of  $\text{HNO}_3$ . R. T.

**Determination of nitrate, nitrite, and ammonia in water and effluents.**—See B., 1936, 398.

**Determination of ortho- in presence of pyrophosphate by Copaux' method.** J. COURTOIS (J. Pharm. Chim., 1936, [viii], 23, 232—238).—Conditions for accuracy have been determined (A., 1921, ii, 707).  $\text{P}_2\text{O}_7'''$  is also pptd. by  $\text{NH}_4$  Mg reagent by heating in dil. AcOH,  $\text{PO}_4'''$  being pptd. from the filtrate on adding alkali. F. O. H.

**Acidimetric determination of water-soluble and total phosphoric acid in superphosphate.**—See B., 1936, 368.

**Spectral-analytical determination of arsenic, phosphorus, and sulphur in metals, particularly platinum.**—See B., 1936, 375.

**Application of Copaux' technique to determination of arsenic acid.** J. COURTOIS (J. Pharm. Chim., 1936, [viii], 23, 269—283).—Acid solutions containing  $\text{AsO}_4'''$ , treated with  $\text{Na}_2\text{MoO}_4$  in presence of  $\text{Et}_2\text{O}$ , ppt. an oil of very indefinite composition, considered to be  $\text{AsO}_4 \cdot 12\text{MoO}_3 \cdot 24\text{—}27\text{Et}_2\text{O} \cdot 24\text{—}33\text{H}_2\text{O}$ , which may be separated and measured. The method is proposed for the determination of  $\text{AsO}_4'''$  in presence of  $\text{AsO}_3'''$ , HCl solutions giving the least unsatisfactory results. J. S. A.

**Determination of arsenic in steel.**—See B., 1936, 323.

**Ignition of silicic acid.** K. A. KRIEGER and H. S. LUKENS (Ind. Eng. Chem. [Anal.], 1936, 8, 118).— $\text{SiC}$  may be produced when  $\text{SiO}_2$  ppts. are ignited in contact with a moist filter-paper.

E. S. H.

**Determination of silica in presence of fluorine.** S. S. KOROL and V. M. KALUSHSKAJA (J. Appl. Chem. Russ., 1936, 9, 148—151).—The methods of Tischtschenko *et al.* (cf. A., 1932, 488) and of Millner *et al.* (A., 1933, 41) are equally trustworthy for determining  $\text{SiO}_2$  in presence of F compounds; that of Tananaev and Babko (B., 1930, 863, 1110) is preferred for silicofluorides. Siegel's method (A., 1929, 1158) is applicable to all cases. R. T.

**Detection and determination of carbon monoxide and dioxide in air.**—See B., 1936, 396.

**Colorimetric micro-determination of cyanides.** Application to officinal preparations, especially to mercuric cyanide. A. D. MARENZI and A. J. BANDONI (An. Farm. Biochim., 1934, 5, 135—140; Chem. Zentr., 1935, ii, 883).— $\text{CN}'$  is converted into  $\text{CNS}'$  and determined as such. H. N. R.

**Analysis of alkali metals. I. Separation of alkali metals. II. Determination of alkali metals.** T. KATÔ (J. Chem. Soc. Japan, 1935, 56, 373—397, 398—410).—I.  $\text{MeOAc}$  is recommended instead of EtOH for dissolving  $\text{Na}_2\text{PtCl}_6$  and  $\text{Li}_2\text{PtCl}_6$ .

II. The determinations of Li and Na by treating the platinichlorides with  $\text{MeOAc}$ , of Rb as  $\text{Rb}_4\text{P}_2\text{O}_7 \cdot 24\text{WO}_3$ , of Cs as  $\text{CsP}_2\text{O}_7 \cdot 24\text{WO}_3$ , and of Li as  $\text{Li}_2\text{SO}_4$  are described. CH. ABS. (e)

**Analysis of the system  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_2$ ,  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{Na}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ , and adsorbed  $\text{NH}_3$ .** I. L. SCHERESCHEVSKI (J. Appl. Chem. Russ., 1936, 9, 166—170).—A scheme for the analysis of mixtures of the above substances is given. R. T.

**Drop reaction for caesium, and its adaptation to drop colorimetry.** E. S. BURKSER and M. L. KUTSCHMENT (J. Appl. Chem. Russ., 1936, 9, 145—147).—A drop of the solution is placed on a drop of conc. aq.  $\text{AuBr}_3\text{—PtBr}_4$  on filter-paper, when a black stain due to the compound  $\text{Cs}_3\text{Au}_2\text{PtBr}_{12}$  (decomp.  $175\text{—}180^\circ$ ) is formed in presence of  $\leq 0.25 \times 10^{-6}$  g. of Cs.  $\text{NH}_4$ , K, Na, and Li do not interfere, but Rb gives a similar reaction when present in considerable amount. The amount of Cs may be determined by comparing the intensity of the stain obtained with a series of standards. R. T.

**Precipitation of silver chloride. II. From silver nitrate and hydrochloric acid.** C. H. GREENE and L. D. FRIZZELL (J. Amer. Chem. Soc., 1936, 58, 516—522; cf. A., 1934, 860).—Nephelometric investigations reveal two distinct stages: an initial, rapid growth in opalescence, followed by a period of slow development to a max. and subsequent fall. The rate of development depends mainly on the concn. of the reagent in excess. Centrifugal, ultra-microscopical, and coagulation experiments support the view that there is a progressive diminution of particle size with the increasing supersaturation that results from increased concn. of pptg. reagent.

E. S. H.



**Analysis of groups I, II, and III cations in presence of phosphoric acid.** C. N. POTSCHNIK (J. Appl. Chem. Russ., 1936, 9, 140—144).—Group I metals are detected by the usual procedure, as are group II and III cations after elimination of  $\text{PO}_4^{3-}$  as  $\text{AlPO}_4$ . R. T.

**Precipitation of barium sulphate in presence of hydrochloric and nitric acids, in the cold.** L. A. VASILIEVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 97—105).—The wt. of the ppt. obtained rises with increasing  $[\text{HNO}_3]$  to a max. when  $\text{H}_2\text{SO}_4 : \text{HNO}_3 = 1 : 60$ , and then falls to the theoretical val. when the ratio is  $1 : 150$ ; the variations obtained in presence of HCl are similar, although less marked. The phenomena are ascribed to co-pptn. of  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$ , together with diminishing  $[\text{Ba}^{2+}]$  and  $[\text{SO}_4^{2-}]$  due to reversal of dissociation. R. T.

**Precipitation of barium sulphate.** N. A. RUDNEV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 107—109).—The amount of precipitant pptd. together with  $\text{BaSO}_4$  when different salts of Ba are added to aq.  $\text{H}_2\text{SO}_4$  varies inversely with the solubility of the precipitant, and directly with the concn. of its anion; hence  $\text{Ba}(\text{NO}_3)_2$  is co-pptd. even in absence of  $\text{HNO}_3$ ,  $\text{BaCl}_2$  in presence of HCl, and  $\text{BaBr}_2$  only when  $\text{H}_2\text{SO}_4 : \text{HBr} = 1 : 240$ . R. T.

**Determination of magnesium metal, magnesium, and magnesium fluoride in the products of electrolytic recovery of metallic magnesium.**—See B., 1936, 329.

**Determination of zinc in sea-water using sodium diethyldithiocarbamate.** W. R. G. ATKINS (J. Marine Biol. Assoc., 1936, 20, 625).—The approx. concn. is determined by adding 10 c.c. of a 0.1% solution of the reagent to Nessler tubes containing the test sample and various concns. of Zn in neutral solution, respectively. The comparison is completed in Nessler tubes. The colour due to Cu obtained with conc. sea-water can be compared with the white standards if a Schott No. OG2 filter is used in conjunction with the latter. English Channel water contains < 8 mg. per cu.m., the limit of detection. J. W. S.

**[Detection and determination of] cadmium.** K. HELLER and F. MACHEK (Mikrochem., 1936, 19, 147—161).—A review.

**Volumetric determination of lead by Fajans' method.** S. N. ROY (J. Indian Chem. Soc., 1936, 13, 40—41).— $\text{Na}_2\text{CO}_3$  with a Na fluoresceinate indicator has been employed. E. E. A.

**Rational analysis of lead compounds in oxide and semi-sulphide lead ores.**—See B., 1936, 317.

**Polarometric titrations.** V. MAJER (Z. Elektrochem., 1936, 42, 120—123).—By measuring the current between two electrodes to which a const. p.d. is applied, one of the electrodes having a large surface of Hg at rest (and therefore unpolarisable for sufficiently small currents) and the other being a dropping Hg electrode, "polarometric" titrations involving pptn., neutralisation, or complex formation, as well as oxidation and reduction, can be carried out. The principles of the use of a dropping Hg cathode are discussed. F. L. U.

**Polarometric precipitation titrations with dropping mercury cathode.** V. MAJER (Z. Elektrochem., 1936, 42, 123—127; cf. preceding abstract).—Results of polarometric titrations of  $\text{Pb}(\text{NO}_3)_2$  with  $\text{H}_2\text{SO}_4$  and of  $\text{BaCl}_2$  with  $\text{K}_2\text{SO}_4$  (all 0.1N) are given and discussed. F. L. U.

**Determination of copper in presence of interfering elements. Modified iodometric method.** H. W. FOOTE and J. E. VANCE (Ind. Eng. Chem. [Anal.], 1936, 8, 119—121).—The modified iodometric procedure (A., 1935, 837), with controlled  $p_{\text{H}}$ , may be used to determine Cu accurately in presence of  $\text{Sb}^{\text{V}}$  or  $\text{As}^{\text{V}}$ . Addition of NaF prevents the interference of  $\text{Fe}^{\text{III}}$ . E. S. H.

**Objective colorimetric determination of copper.** C. A. GOETHALS (Z. anal. Chem., 1936, 104, 170—182).—Using a photo-electric colorimeter and filtered light, Cu may be determined colorimetrically by the following methods, at concns. down to the limit indicated. (a) As  $\text{CuSO}_4$  in acid solution; limit  $2 \times 10^{-3}$  mol. per litre. (b) As  $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4]^{2+}$  in presence of 0.5M- $\text{C}_5\text{H}_5\text{N} + 0.003\text{M-H}_2\text{SO}_4$ ; limit  $3 \times 10^{-4}$  mol. per litre. (c) As  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  in presence of 10 c.c. of 28% aq.  $\text{NH}_3 + 20$  g. of  $\text{NH}_4\text{Cl}$  in 300 c.c. of solution; limit  $5 \times 10^{-4}$  mol. per litre. (d) In neutral solution in the absence of Fe, Zn, or an excess of other electrolytes, from the colour of colloidal suspensions of  $\text{Cu}_2\text{Fe}(\text{CN})_6$ ; limit  $3 \times 10^{-5}$  mol. per litre. (e) From the colour given by Cu with oxidised dimethylglyoxime (I). To the slightly acid solution,  $\text{C}_5\text{H}_5\text{N}$  is added, and then (I) +  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 5$  c.c. of 0.01M- $\text{AgNO}_3$  as catalyst. An unstable reddish violet colour is developed; limit  $2 \times 10^{-6}$  mol. of Cu per litre. (f) From the catalytic accelerating effect of  $\text{Cu}^{2+}$  on the  $\text{Fe-Na}_2\text{S}_2\text{O}_3$  reaction, in presence of  $\text{NH}_4\text{CNS}$  as indicator; limit  $2 \times 10^{-6}$  mol. per litre. By adding to an Ag solution 2 c.c. of 0.01M- $\text{CuSO}_4$ , method (e) may be applied to the determination of  $10^{-5}$  mol. of Ag per litre. J. S. A.

**Iodometric determination of copper in sugar and other liquids containing organic substances.**—See B., 1936, 388.

**Permanganate method of determining reduced copper in the determination of reducing sugars.**—See B., 1936, 388.

**Inorganic complex compounds in analytical chemistry. IV. Detection and determination of mercury.** C. MAHR (Z. anal. Chem., 1936, 104, 241—245; cf. this vol., 179).—Hg is pptd. by aq.  $\text{NH}_3[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2]$  from acid (0.1N-HCl) solution as the very insol. salt  $\text{Hg}[\text{Cr}(\text{CNS})_4(\text{NH}_3)_2]_2$  (I).  $2.5 \times 10^{-6}$  g. of Hg may be so detected in presence of 20,000 parts of Cu or Pb, or 5000 parts of Cd. (I) is quantitatively pptd. from hot HCl solution, and may be dried at  $105^\circ$ , or ignited to  $\text{Cr}_2\text{O}_3$ . Alternatively, (I) may be dissolved in aq.  $\text{KCN} + \text{HCl}$ . Cr is then oxidised to  $\text{CrO}_4^{2-}$  by means of  $\text{KBrO}_3$ , and determined iodometrically. J. S. A.

**Volumetric determination of mercuric chloride.** C. CHINES (Ann. merc. Siciliana, 1934, 2, 282—286).—To 50 c.c. of boiling Fehling's  $\text{CuSO}_4$  solution are added 10 c.c. of a solution of approx. 0.5 g. of  $\text{HgCl}_2$  and 6 g. of KI in 100 c.c. of  $\text{H}_2\text{O}$ . On cooling



and keeping,  $\text{Cu}(\text{NH}_3)_4\text{HgI}_4$  is pptd. It is filtered off, and excess of I is determined in the filtrate after acidifying with  $\text{AcOH}$ . CH. ABS. (e)

**Determination of aluminium in presence of iron.** W. DAUBNER (*Angew. Chem.*, 1936, 49, 137—138).—Fe is determined by reduction of  $\text{FeCl}_3$  to  $\text{FeCl}_2$  by HI (Mohr's method); the HI is added dropwise to the heated and agitated solution, any volatilised I being trapped. Another portion of the solution is treated, in presence of  $\text{AcOH}$ , with  $(\text{NH}_4)_3\text{AsO}_4$ , and the ppt.  $[\text{AlAsO}_4 + \text{Fe}_2(\text{HAsO}_4)_3]$  is washed with 90%  $\text{EtOH}$  and dissolved in  $\text{HCl}$ . The  $\text{H}_3\text{AsO}_4$  in this solution is determined in known manner by reduction with HI; by subtracting the amount equiv. to the Fe present that equiv. to the Al is obtained, whence the Al present can be calc.

A. B. M.

**Analysis of aluminium alloys.**—See B., 1936, 327.

**Determination of gallium in aluminium.**—See B., 1936, 327.

**Detection of rhenium in the sodium carbonate bead.** H. YAGODA (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 133—134).—With 0.015 mg. of Re a transitory yellow is formed in the oxidising or reducing flame. Tungstates and molybdates do not interfere.

E. S. H.

**Determination of rhenium. II. Geilmann reaction.** L. C. HURD and B. J. BABLER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 112—114; cf. A., 1932, 1224).—The conditions under which the Geilmann reaction gives quant. results have been determined.

E. S. H.

**Determination of iron in sea-water.** N. W. RAKESTRAW, H. E. MAHNCKE, and E. F. BEACH (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 136—138).—Mg and Fe are co-pptd. by boiling with  $\text{NH}_4\text{HS}$ .  $\text{FeS}$  is dissolved in dil.  $\text{HCl}$ , oxidised with Br, and pptd. as  $\text{Fe}(\text{OH})_3$  by aq.  $\text{NH}_3$ . The ppt. is redissolved in  $\text{HCl}$ , oxidised, and Fe is determined colorimetrically by KCNS. The colour is stabilised by the addition of  $\text{OH} \cdot [\text{CH}_2]_2 \cdot \text{OBu}$ .

E. S. H.

**Brucine sulphate as internal indicator in titrations with standard dichromate solution.** D. S. NARAYANAMURTHI and T. R. SESHADRI (*Proc. Indian Acad. Sci.*, 1936, 3, A, 38—42; cf. A., 1933, 800).—With a 1% solution of brucine in  $3N\text{-H}_2\text{SO}_4$  as indicator, and total acidity  $\leq 2N$ , the colour change (green to red) is more distinct than that of  $\text{NHPh}_2$ , and its distinctness is unaffected by  $\text{Fe}^{++}$  (in large excess),  $\text{Hg}^{++}$ ,  $\text{Hg}_2^{++}$ , or  $\text{Sn}^{++++}$ . It can also be used in titration of  $\text{Fe}^{++}$  with  $\text{KMnO}_4$  in presence of  $\text{HCl}$ .

L. J. J.

**Diphenylcarbazide.** An internal indicator for use in the titration of iron with dichromate. H. E. CROSSLEY (*Analyst*, 1936, 61, 164—169).—A standardised method is described. The end-point, from violet to colourless, is very sharp and the titration is not affected by the previous use of  $\text{SnCl}_2$  and  $\text{HgCl}_2$  or Zn for reduction. A correction is necessary for the amount of indicator oxidised, but the method is of general application and gives accurate results.

E. H. S.

**Determination of iron by titanium titration and by 2:2'-dipyridyl colorimetry.** W. D. MCFARLANE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 124—126).—A horizontal micro-burette for titration with dil.  $\text{TiCl}_3$  solutions is described. Modified colorimetric procedure is recommended.

E. S. H.

**Spectral determination of chromium [alloyed with aluminium].**—See B., 1936, 375.

**Tests for molybdenum, lead, and cobalt in minerals and rocks.** H. LEITMEIER and F. FEIGL (*Tsch. Min. Petr. Mitt.*, 1936, 47, 313—327).—The following are delicate colour reactions for detecting the presence of minute quantities. Ca xanthate gives a reddish-violet colour with Mo. In  $\text{AcOH}$  solution benzidine gives a deep blue with  $\text{PbO}$  (in the absence of Mn). Alkali thiocyanates form double salts with Co (even in presence of much Fe and Ni) which are sol. in a mixture of  $\text{Et}_2\text{O}$  and  $\text{EtOH}$  giving a blue colour.

L. J. S.

**New indicators for direct titration of tungstate with lead nitrate.** Z. RAICHINSTEIN and N. KOROBV (*Z. anal. Chem.*, 1936, 104, 192—198; cf. A., 1935, 951).—Diamine-scarlet and diamineazo-scarlet may be used as adsorption indicators. The presence of  $\text{NH}_4\text{NO}_3$  interferes.

J. S. A.

**Separation of stannic oxide from various oxides by ignition with ammonium iodide. Application to analytical purification of ignited stannic oxide.** E. R. CALEY and M. G. BURFORD (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 114—118).— $\text{SnO}_2$  is quantitatively volatilised as  $\text{SnI}_4$  when heated at 400—500° with excess of  $\text{NH}_4\text{I}$ . Separation from most other oxides may thus be effected. In the determination of Sn in alloys as  $\text{SnO}_2$ , the method may be used advantageously for purification of  $\text{SnO}_2$ .

E. S. H.

**Precipitation of tin and antimony salts by organic bases in presence of potassium iodide: application to analytical characterisation of these metals.** J. A. GAUTIER (*J. Pharm. Chim.*, 1936, [viii], 23, 283—290).—Antipyrine (I) gives with solutions of Sb in presence of KI a yellow-orange ppt.; Sn similarly gives a less sensitive white ppt. The reaction is applied to the solution, containing Sb but little Sn, obtained by digesting the Sb, Sn, and As sulphides with  $\text{HCl}$  at 80°. Other org. bases give reactions similar to, but less sensitive than, that of (I).

J. S. A.

**Determination of tin in minerals and metallurgical residues by 0.1N-potassium bromate.**—See B., 1936, 278.

**Colour reaction of titanium with ascorbic acid and other molecules containing the group  $\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot$ .** J. ETTORI (*Compt. rend.*, 1936, 202, 852—854).—When a very dil. solution of  $\text{Ti}(\text{SO}_4)_2$  is added to ascorbic acid no coloration is observed at  $p_H < 3$ . At  $p_H 3$  there is a light yellow coloration which gradually changes until it becomes an intense reddish-brown at  $p_H 4.6$ . This diminishes with diminishing acidity and disappears at  $p_H 5.2$ . In alkaline solution the colour is pale rose. With too large a proportion of  $\text{Ti}(\text{SO}_4)_2$  pptn. of  $\text{Ti}(\text{OH})_4$  may take place with decolorisation of the solution.



All other compounds found to give the same type of reaction, *e.g.*, dihydroxymaleic acid, pyrocatechol, gallic acid, etc., contain the group  $\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})$ .

M. S. B.

**Determination of gold with avoidance of the cupellation process.** J. DONAU (Z. anal. Chem., 1936, 104, 257—270).—A method described previously (cf. A., 1935, 1096) is improved. A Cd (87%)—Zn alloy is used for inquartation, permitting the use of glass ignition tubes. In presence of Pd repeated treatment of the inquartation mass with  $\text{HNO}_3$  is necessary: with >20% of Pd repeated inquartation may be required. In the presence of Sn, the Au+ $\text{SnO}_2$  resulting from the  $\text{HNO}_3$  treatment of the inquartation mass is heated with an excess of  $\text{NH}_4\text{Cl}$ , whereby Sn is quantitatively removed as  $\text{SnCl}_4$ .

J. S. A.

**Apparatus for extraction on a very small scale.** K. SCHMALFUSS (Chem. Fabr., 1936, 9, 161—162).—A modified Soxhlet apparatus has the advantage of using only small amounts of substance and of solvent (*e.g.*, 0.5 g. and 40 c.c., respectively). Fewer extractions, of only 1.5 hr., are necessary.

D. R. H.

**Calibration of platinum thermometers at the b.p. of sulphur.** C. D. NIVEN (Canad. J. Res., 1936, 14, A, 1—15).—Experimental technique, errors, and calculation are discussed. The accuracy of determination of  $\delta$  is considered to be limited to the third decimal place.

L. A. O'N.

**Recent revisions of high temperatures.** H. T. WENSEL (J. Amer. Ceram. Soc., 1936, 19, 81—86).—The correct method of converting temp. vals. based on Wien's law to those based on the International Scale is described. In giving corrections to be applied to quoted temp. such corrections must have been calc. from the consts. used in the original temp. scale. The implication that a recent correction table (B., 1936, 21) can be universally used is erroneous.

J. A. S.

**Determination of surface temperatures.** T. YOSHII (J. Japan. Ceram. Assoc., 1935, 43, 352—357).—Methods depending on fusion, ignition, or colour changes of suitable substances applied to the surface are proposed.

CH. ABS. (e)

**Low-temperature thermostat.** G. B. HEISIG (Ind. Eng. Chem. [Anal.], 1936, 8, 149).—A const. temp. between 25° and -75° can be maintained by means of solid  $\text{CO}_2$ , using the apparatus described. The bath contains  $\text{COMe}_2$ , EtOH, or kerosene, according to the temp. required.

E. S. H.

**Electrically heated thermostat.** G. VAN DE VOORDE (Natuurwetensch. Tijds., 1936, 18, 21—22).

D. R. D.

**Photo-electric photometer.** L. E. HOWLETT (Canad. J. Res., 1936, 14, A, 38—42).—Apparatus for measuring light transmitted by glasses and solutions is described. It has been used for the determination of the amounts of dyes removed from solution by adsorbents, and the concn. and purity of substances in solution.

A. J. M.

**Photometry of different coloured light sources.** M. PIRANI and R. ROMPE (Naturwiss., 1936, 24, 142).

—It is suggested that a phosphor or fluorescent liquid should be used as a frequency transformer for light, thus enabling the intensities of different coloured lights to be compared by comparison of the intensity of phosphorescence or fluorescence. The process is especially simple if a fluorescent liquid is used in such concn. that the incident light is completely absorbed by a thin layer of the liquid, since in this case a knowledge of the absorption curve of the liquid is not necessary, and the intensity of the fluorescence  $\propto$  the no. of incident light quanta. The method gave the val. 250:1 for the intensity ratio of the Hg lines (5770+5791 Å.) and 4916 Å. The errors of the method are discussed. Suitable fluorescent liquids for ultra-violet light are an EtOH solution of resculin, and an EtOH solution of Et dihydrocollidinedicarboxylate.

A. J. M.

**Photomagnetron and its applications in measuring low light intensities.** A. DAUVILLIER (Compt. rend., 1936, 202, 738—740).—A photo-electric method, with a photo-electric device for varying the light flux, is described.

H. J. E.

**Microscopical determination of indices of refraction of resinous substances and minerals of high refringence.** N. VEDENEJEVA, S. GRUM-GRSHMAILLO, and A. VOLKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 207—210).—An interferometric method, in which a plano-convex lens is utilised, is described. The dispersions of 16 samples of piperine containing 24—84% of LiI, NaI, etc. have been determined.

R. S.

**Rotating sector for quantitative analytical spectrography.** M. F. HASLER and R. W. LINDHURST (Rev. Sci. Instr., 1936, [ii], 7, 137—139).—A half-cylindrical shutter is mounted in front of the film.

C. W. G.

**Recent results and methods of vacuum spectroscopy.** H. BOMKE (Physikal. Z., 1936, 37, 222—260).—A review.

**Arrangement for converting a spectrograph into a monochromator.** A. CHEVALLIER and P. DUBOULOZ (Bull. Soc. Chim. biol., 1936, 18, 428—430).

A. L.

**Standard source of ultra-violet radiation for calibrating photo-electric dosage intensity meters.** W. W. COBLENTZ and R. STAIR (J. Res. Nat. Bur. Stand., 1936, 16, 83—92).—The quartz Hg-arc lamp is well adapted for the purpose by reason of the high intensity and favourable distribution of the ultra-violet emission lines at 2967—3132 Å. Methods of calibration of ultra-violet output in abs. units are described.

E. S. H.

**Refractometer and other refractive index methods.** B. W. ANDERSON (Gemmologist, London, 1934, 3, 216—222).— $\text{C}_2\text{I}_4$  and S dissolved in  $\text{C}_2\text{H}_2\text{I}_2$  give a stable liquid of  $n_D$  1.81.  $\text{AsPhI}_2$  has  $n_D$  1.843.  $\text{Se}_2\text{Br}_2$  has  $n_{D,1}$  1.96. The use of a hemisphere of Zn blende ( $n_D$  2.37) is suggested for measuring liquids.

CH. ABS. (e)

**Colorimetric analysis by the photo-electric cell.** N. STRAFFORD (Analyst, 1936, 61, 170—177).—A photo-electric colorimeter for the measurement of relative colour intensities by use of absorption density



determinations is described. Measurements are independent of the human eye, and the calibration curve, which is virtually a straight line, is always available. Notes on the choice of working conditions and on the applications are given. E. H. S.

**X-Ray powder camera.** M. J. BUERGER (Amer. Min., 1936, 21, 11—17). L. S. T.

**Precision lattice constants from X-ray powder photographs.** M. U. COHEN (Rev. Sci. Instr., 1936, [ii], 7, 155).—Corrections (cf. A., 1935, 598). C. W. G.

**General-utility vacuum chamber for X-ray fine structure photographs.** E. FRANKE (Z. physikal. Chem., 1936, B, 31, 454—458).—A convenient high-precision apparatus is described. R. C.

**Measurement of the angle between the optical axes and determination of the optical sign (of crystals) by means of the refractometer.** H. BUTTGENBACH (Bull. Acad. roy. Belg., 1936, [v], 22, 125—133). A. J. M.

**Guarded-field X-ray ionisation chamber.** L. S. TAYLOR and G. SINGER (J. Res. Nat. Bur. Stand., 1936, 16, 165—169).—Modified apparatus is described (cf. A., 1930, 1502). E. S. H.

**Electrophysical methods in analytical chemistry.** J. KRÖNERT (Chem. Fabr., 1936, 9, 133—138).—The applications of  $p_H$ , conductivity, electro-optical, and magnetic measurements to technical problems are reviewed. J. S. A.

**Ionisation gauge for atomic beam measurements.** R. D. HUNTOON and A. ELLETT (Physical Rev., 1936, [ii], 49, 381—387).—Various factors influencing the design of a gauge are discussed, and an arrangement to fulfil the necessary requirements is described. Beam pressure changes as low as  $3 \times 10^{11}$  mm. Hg, or approx.  $3 \times 10^9$  Hg atoms per sq. cm. per sec., can be measured. N. M. B.

**Single sparks and interrupted alternating-current arcs and their application to quantitative spectroscopic analysis.** T. KOSBAHN (Ann. Physik, 1936, [v], 25, 625—644).—The optical and electrical conditions necessary for obtaining light sources of max. reproducibility have been investigated. Electrically and spectroscopically reproducible single sparks can be produced in non-inductive circuits. An arrangement for producing intense interrupted a.c. arcs, and the effect of discharge conditions on their spectral character, are described. L. J. J.

**Apparatus for the conductometric determination of carbon monoxide and dioxide (and benzene vapour) in air.**—See B., 1936, 349.

**Differential electrometric titration apparatus.** S. SAITO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 109—123).—A differential electrode and galvanometer are used, and polarisation is reduced. Al may be determined volumetrically, using  $H_2C_2O_4$ , with a sharp end-point. The addition of a little  $H_2SO_4$  increases the sharpness of the end-point in the titration of  $Cl'$  and  $Br'$ , and 0.1 mg. of  $Br'$  in presence of 6 mg. of  $Cl'$  is titratable. R. S. B.

**Glass electrode with galvanometer reading.** L. MICHAELIS (Science, 1936, 83, 213—214). L. S. T.

**Glass electrode for measurement of  $p_H$  of unbuffered solutions in simple compensation circuit.** K. SCHWABE (Z. Elektrochem., 1936, 42, 147—150; cf. A., 1935, 1341).—A spherical glass electrode permanently housed in an outer tube, with provision for a continuous renewal of the liquid in which it is immersed, is suitable for measuring the  $p_H$  of unbuffered solutions, using the ordinary compensation method. A full description is given. F. L. U.

**Permanent glass electrode for measurement of  $p_H$  values.** G. PARSY (J. Soc. Leather Trades Chem., 1936, 20, 188—195).—In a new form of glass electrode a piece of Pt foil is suspended in aq.  $PtCl_4$  in a Haber glass bulb, mounted in a glass vessel filled with the solution under test. The apparatus is always ready for immediate use and results are quickly obtained. D. W.

**Potentiometric volumetric analysis with three electrode pairs connected in series.** L. SZEBELÉDY and J. JÓNÁS (Z. anal. Chem., 1936, 104, 271—278).—The titration vessel has three pairs of electrodes recessed in its side, which are brought into action without short-circuiting each other when the vessel is tilted. A threefold increase in sensitivity is thus obtained. J. S. A.

**Thermionic titrimeter without batteries.** H. H. WILLARD and O. B. HAGER, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 144—145).—An a.c. voltmeter for potentiometric titrations is described. E. S. H.

**Electrostatic dust count sampler.** E. C. BARNES and G. W. PENNEY (J. Ind. Hyg., 1936, 18, 167—172).—Of the three methods of collecting dust particles from samples of air, centrifugal, thermal, and electrostatic pptn., the last has definite advantages. An apparatus for carrying it out is described. W. O. K.

**Continuous-reading electron-tube conductance meter.** R. L. GARMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 146—147).—The apparatus combines an audio oscillator bridge and a detector meter system. Its application to conductometric titration is described. E. S. H.

**Investigation of piezo-electric substances in powder form.** J. ENGL and I. LEVENTER (Naturwiss., 1936, 24, 217—218).—The powder is suspended in a liquid of no dielectric loss (e.g.,  $C_6H_6$ ) in a high-frequency field (400 volts per cm.), the mixture being placed in a condenser vessel for determination of dielectric loss. The measured expansion is supposed  $\propto$  temp. change, and the loss (product of temp. change and  $\lambda$ ) plotted against  $\lambda$ . For quartz powder there is a resonance at 103 m., agreeing with the val. for quartz plates. The max. heating at resonance  $\propto$  (field strength)<sup>2</sup>. A. J. M.

**Visual conductometry.** II. L. WOLF (Chem. Fabr., 1936, 9, 139—140; cf. this vol., 305).—An improved a.c. circuit for conductometric titrations is given. J. S. A.



**Apparatus for direct determination of radon in water and in air.** F. BEHOUNEK (Physikal. Z., 1936, 37, 203—208).—The first apparatus will measure the radioactivity of  $H_2O$  to 2 Mache units. The second is portable, and is adapted for the determination of the activity of air. In both methods the strength of the activity is read directly on a scale.

A. J. M.

**Modified Nessler tube set.** G. W. CORNELL (Soc. Chem. Ind. Victoria, 1935, 35, 1008—1010).

J. S. A.

**Burette for alkali titrations.** L. S. KEYSER (Ind. Eng. Chem. [Anal.], 1936, 8, 121).

E. S. H.

**Burette for potentiometric titrations.** L. S. KEYSER (Ind. Eng. Chem. [Anal.], 1936, 8, 82).

E. S. H.

**Emulsifier.** R. AUERBACH (Kolloid-Z., 1936, 74, 285—287).—Apparatus and technique are described.

E. S. H.

**Accuracy attainable with the Chattock tilting manometer.** W. F. COPE and R. HOUGHTON (J. Sci. Instr., 1936, 13, 83—88).—An accuracy of 0.1% can be obtained by the application of corrections.

C. W. G.

**Micromanometer.** H. W. SMITH (Rev. Sci. Instr., 1936, [ii], 7, 157—158).—Liquid in an inclined tube is brought to a predetermined mark by means of a micrometer screw.

C. W. G.

**Measurement of the coefficients of absorption of ultrasonic waves in gases.** L. BELAVSKAJA (Bull. Acad. Sci. U.R.S.S., 1935, 917—925).—The piezo-electric properties of quartz are utilised.

C. W. G.

**Bacteria-proof filter.** F. WOKES (Pharm. J., 1936, 136, 313).—Pressure generated by a cycle pump forces the liquid through a Seitz filter.

C. W. G.

**Laboratory sublimation apparatus.** S. T. BOWDEN (J. Sci. Instr., 1936, 13, 97—98).—Sublimation may be carried out in vac. or in a current of inert gas.

C. W. G.

**Surface-tension measurements of viscous liquids.** A. H. PFUND and E. W. GREENFIELD (Ind. Eng. Chem. [Anal.], 1936, 8, 81—82).—The depth of the small depression, produced when an air jet impinges on the surface of a viscous liquid, is an inverse function of the surface tension of the liquid. Apparatus and technique for application of the method are described.

E. S. H.

**Application of viscosimetry and plastometry to problems of applied mineralogy.** M. P. VOLAROVITSCH (Trans. Inst. Econ. Min. U.S.S.R., 1934, No. 66, 56 pp.).—A high-temp. viscosimeter consisting of two coaxial Pt-Ir cylinders, the outer of which rotates, is described. Measurements with various

slags, glasses, and minerals are described and discussed.

CH. ABS. (e)

**Extraction apparatus.** F. C. OPPEN (Ind. Eng. Chem. [Anal.], 1936, 8, 110—111).—A modified Soxhlet-type apparatus is described.

E. S. H.

**[Efficiency of] desiccators.** H. S. BOOTH and L. MCINTYRE (Ind. Eng. Chem. [Anal.], 1936, 8, 148—149).—A considerable time must elapse before the air inside a desiccator is reasonably dry, after the cover has been removed momentarily.  $BaO$  is a useful desiccant.

E. S. H.

**Laboratory desiccants: silica gel.** F. G. LENOX (Soc. Chem. Ind. Victoria, 1935, 35, 988—996).—The use of  $SiO_2$  gel as a laboratory desiccant is described.

J. S. A.

**Apparatus for isolation of fluorine.** Willard and Winter method. W. K. GILKEY, H. L. ROHS, and H. V. HANSEN (Ind. Eng. Chem. [Anal.], 1936, 8, 150—151).—Modified distillation procedure is recommended (cf. A., 1933, 242).

E. S. H.

**Device for determining rate of siphoning in metal extraction systems.** R. S. ASBURY (Ind. Eng. Chem. [Anal.], 1936, 8, 152).—An electrical device for registering siphoning in a steel Soxhlet apparatus is described.

E. S. H.

**Rapid mixer.** D. H. NELSON (Ind. Eng. Chem. [Anal.], 1936, 8, 111).—A spiral bit is recommended for preparing analysis samples of emulsions and plastics.

E. S. H.

**Control of high lights in reading microbalance swings.** P. H. M. P. BRINTON (Ind. Eng. Chem. [Anal.], 1936, 8, 104).—Observation is facilitated by using a dark cardboard screen, provided with a circular hole, in front of the lens.

E. S. H.

**Control of pressure during vacuum distillation.** G. GOETHALS (Natuurwetensch. Tijds., 1936, 18, 18—20).— $P$  may be maintained const. within  $\pm 0.04$  mm. by means of Jacobs' apparatus (A., 1935, 321).

D. R. D.

**Formation of metallic blacks on thin foils by evaporation.** R. V. JONES and B. V. ROLLIN (J. Sci. Instr., 1936, 13, 130—131).—In  $H_2$  or He at 0.1—3 mm. there is no difficulty in condensing metals evaporated from hot filaments.

C. W. G.

**Ozoniser.** R. P. JACQUEMAIN and G. BALLOUÉ (Bull. Soc. chim., 1936, [v], 3, 701—704).—The simple apparatus described gives a higher yield of  $O_3$  than is obtained with the Berthelot ozoniser.

E. S. H.

**Guide for crystal drawing.** W. M. McNABB and J. W. McNABB (J. Franklin Inst., 1936, 221, 539—546).—Directions for drawing crystals from gnomonic projections are given.

C. W. G.

## Geochemistry.

**Ozone measurements and the possible connexion of ozone with the sunspot cycle.** F. E. FOWLE (Trans. Amer. Geophys. Union, 1934, 160—162; cf. A., 1935, 59).—New data show an even higher mean val. of  $O_3$ , despite the min. for sunspots.

CH. ABS. (e)

**Determination of the ozone content of the air layer near the ground by a photo-electric counter.** R. STOLL (Helv. phys. Acta, 1935, 8, 3—38; Chem. Zentr., 1935, ii, 343).—Measurements were made with a photo-electric counter at distances of 405—1555 m. from a Hg arc. The atm. [ $O_3$ ] was



deduced from light intensity measurements in the region 2600—3100 Å. An average  $O_3$  layer of  $27 \times 10^{-4}$  cm. per km. (Arosa) and  $10 \times 10^{-4}$  cm. per km. (Zurich) was found. H. J. E.

**Isotopes in snow and rain water.** W. A. ALEXANDER and L. A. MUNRO (Canad. J. Res., 1936, 14, B, 47).—April snow  $H_2O$ , investigated by the balanced float method, showed a decrease in  $d$  of  $3.9 \times 10^{-6}$  g. per c.c. Appreciable fractionation of  $H_2O$  into its isotopic forms occurs in April. L. A. O'N.

**Radioactivity of spring water.** Y. DEUX (Petit J. Brasseur, 1935, 43, 507, 510; Chem. Zentr., 1935, ii, 734).—The determination of the radioactivity of natural  $H_2O$  is described. J. S. A.

**Radioactivity of mineral springs of the group Cachat d'Evian.** R. CASTAGNÉ and (MILLÉ.) D. OSBORNE (Compt. rend., 1936, 202, 567—569).—Data are recorded. T. G. P.

**Oceanographic research at the Scripps Institute of Oceanography.** T. W. VAUGHAN (Trans. Amer. Geophys. Union, 1934, 222—225).—Salinity data for the region between the Californian coast and the Philippines are recorded and discussed. CH. ABS. (e)

**Temperature-salinity correlation with the Florida Current.** C. O'D. ISELIN (Trans. Amer. Geophys. Union, 1934, 208—209). CH. ABS. (e)

**German calcium chloride springs.** H. HARRASSOWITZ (Kali, 1935, 29, 75—80; Chem. Zentr., 1935, ii, 820).—Analyses are given of German mineral springs of secondary origin with  $Ca : Cl = 1 : 2$ . J. S. A.

**Morven meteorite, New Zealand.** C. O. HUTTON (Min. Mag., 1936, 24, 265—275).—This stone, weighing 7100 g., was found in 1925 near Morven in South Canterbury. The microscopical characters are described and detailed chemical analyses were made of the magnetic and non-magnetic portions sol. and insol. in aqua regia. The mineral (modal) composition is olivine 40.74, bronzite 20.93, diopside 3.68, feldspars 10.34, metallic Ni-Fe 13.19, troilite 5.67% etc.  $Fe + Co : Ni$  in the metal 9.58;  $MgO : FeO$  in silicates 2.45. The stone is classed as a veined and brecciated grey bronzite-olivine-chondrite. This is the fourth meteorite to be recorded from New Zealand. L. J. S.

**The Bruno meteorite.** H. H. NININGER (Amer. J. Sci., 1936, [v], 31, 208—222).—Analyses are given. C. W. G.

**Diabase-porphyrite and glaucophane rocks in the North Calabrian trias.** H. W. QUITZOW (Nachr. Ges. Wiss. Göttingen, 1935, [iv], 1, 83—118; Chem. Zentr., 1935, ii, 342). H. J. E.

**Maxixe beryl. II. Analysis and separation of beryllium and aluminium and alkalis.** W. ROEBLING and H. W. TROMNAU (Zentr. Min., A, 1935, 134—139; Chem. Zentr., 1935, ii, 495; cf. this vol., 49).—Analysis gave  $SiO_2$  62.52,  $Al_2O_3$  18.08,  $Fe_2O_3$  0.03,  $BeO$  11.30,  $CaO$  0.22,  $MgO$  0.25,  $CuO$  trace,  $Li_2O$  0.98,  $Na_2O$  1.28,  $Cs_2O$  2.80,  $B_2O_3$  0.39, and loss on ignition 2.20%. Al and Be were separated by the hydroxyquinoline or guanidine

carbonate methods, after repeated pptn. with aq.  $NH_3$  to remove alkalis. H. J. E.

**Alteration of the rocks of the Eibenstock-Neudek [Saxony-Bohemia] granite massif.** E. O. TEUSCHER (Tsch. Min. Petr. Mitt., 1936, 47, 273—312).—Later pneumatolytic and hydrothermal processes have given rise to greisenisation, kaolinisation, silicification, chloritisation, etc. in the various granitic rocks, with the production also of tourmaline, topaz, and deposits of Sn ore. L. J. S.

**Lead-uranium ratio of siliceous pitchblende from Great Bear Lake, N.W.T., Canada, and its possible age.** J. P. MARBLE (J. Amer. Chem. Soc., 1936, 58, 434—437).—A sample yields a "corr." Pb ratio of 0.193, corresponding with an age of  $1323 \times 10^6$  years. E. S. H.

**Hydrothermal synthetic investigations on  $Al_2O_3$ - $SiO_2$ - $H_2O$  system.** W. NOLL (Fortschr. Min., 1935, 19, 46—47; Chem. Zentr., 1935, ii, 819).—Under the conditions of hydrothermal epimagmatic and metamorphic mineral formation, up to  $400^\circ$  with  $SiO_2 : Al_2O_3 > 2 : 1$ , kaolin is formed, and at  $400$ — $500^\circ$  a pyrophyllite mineral. With excess of  $Al_2O_3$ , böhmite is formed up to  $400^\circ$ ; corundum is formed at  $500^\circ$  from pure  $Al_2O_3$ . J. S. A.

**Stability of an argillite inclusion in basalt.** H. VON WARTENBERG (Nachr. Ges. Wiss. Göttingen, 1935, [iv], 1, 119—121; Chem. Zentr., 1935, ii, 342).—The inclusion was fused only on the outside. The basalt was probably near its m.p. when the inclusion was formed. H. J. E.

**Alkaline trachite from Dschebel Auenât in the Lybian desert.** P. GALLITELLI (R. Ist. lomb. Sci. Lett., 1934, [ii], 67, 731—736; Chem. Zentr., 1935, ii, 342).—The chief constituent was sanidine, together with pyroxene, agirine, nepheline, and sodalite. H. J. E.

**Geological-petrographical investigation of potash deposits in the Werra region.** F. BESSERT (Kali, 1935, 29, 27—30, 40—43, 53—58, 63—66, 73—75; Chem. Zentr., 1935, ii, 343). H. J. E.

**Crystallisation of hornblende and mica from artificial silicate melts.** D. P. GRIGORIEV (Zentr. Min., 1935, A, 117—123; Chem. Zentr., 1935, ii, 341—342).—Hornblende was synthesised from a melt containing (in parts by wt.):  $K_2O$  1,  $Al_2O_3$  0.4—0.5,  $MgO$  6,  $SiO_2$  6,  $CaF_2$  1. Optical data are given. H. J. E.

**Mineralogy of asbestos. Ishkyldite, a new structural variety of chrysotile.** F. V. SIROMIATNIKOV (Amer. Min., 1936, 21, 48—54).—*Ishkyldite* (I),  $H_2Mg_{15}Si_{11}O_{47}$ ,  $d$  2.62,  $n_g$  1.573,  $n_p$  1.566, from Ishkyldino, Middle Volga District, has  $SiO_2$  42.49,  $Al_2O_3$  1.27,  $Fe_2O_3$  2.01,  $FeO$  2.73,  $MgO$  38.28,  $CaO$  none,  $Na_2O + K_2O$  0.02,  $H_2O$ —0.79,  $H_2O +$  11.88,  $CO_2$  0.35,  $TiO_2$  trace,  $MnO$  0.06,  $Cr_2O_3$  trace,  $NiO$  0.38, volatiles 0.04, total 100.30%. It resembles actinolite-asbestos in appearance, chrysotile-asbestos (II) in composition, and antigorite in optical properties. X-Ray analysis reveals a peculiar at. arrangement. The dehydration curve shows distinct peaks. (I) is probably an earlier mineral than (II) and grew under conditions of stress. L. S. T.



**Cubanite from [the Frood Mine,] Sudbury, Ontario.** M. A. PEACOCK and G. M. YATSEVITCH (Amer. Min., 1936, 21, 55—62).—The orthorhombic, dipyrarnidal crystals,  $d^{27}$  4.101, hardness 3.5, contain Cu 22.88, Fe 41.41, S 35.35, total 99.64%, in agreement with  $\text{CuFe}_2\text{S}_3$ . The identity of cubanite and chalmersite is confirmed. L. S. T.

**Ganophyllite and zincian amphibole from Franklin Furnace, New Jersey.** W. F. FOSHAG (Amer. Min., 1936, 21, 63—67).—Ganophyllite (I) from this locality has  $\text{SiO}_2$  44.36,  $\text{Al}_2\text{O}_3$  11.40,  $\text{Fe}_2\text{O}_3$  none, FeO 0.09, CaO 2.64, MgO 3.82, MnO 24.24,  $\text{Na}_2\text{O}$  2.86,  $\text{K}_2\text{O}$  0.26,  $\text{H}_2\text{O}$  10.72, total 100.39%, corresponding approx. with  $5\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ ;  $d$  2.878, hardness 3.5,  $n_\alpha$  1.545,  $n_\beta$  1.586,  $n_\gamma$  1.589. Comparison with Swedish (I) shows that the chemical composition is variable. The zincian amphibole closely associated with (I) has  $\text{SiO}_2$  53.20,  $\text{Al}_2\text{O}_3$  5.37,  $\text{Fe}_2\text{O}_3$  8.03, FeO 4.46, MgO 11.12,  $\text{TiO}_2$  0.12, ZnO 4.70, MnO 2.97, CaO 3.36,  $\text{Na}_2\text{O}$  4.35,  $\text{K}_2\text{O}$  0.21,  $\text{H}_2\text{O}$  1.79, total 99.68% corresponding with  $(\text{Na}, \text{Ca}, \text{Zn}, \text{Mn})_3(\text{Mg}, \text{Fe}^{++})_3(\text{Al}, \text{Fe}^{+++})\text{Si}_8\text{O}_{22}(\text{O}, \text{OH})_2$ . L. S. T.

**Felspar twinning in a differentiated sill.** W. M. CHAPMAN (Amer. Min., 1936, 21, 33—47).—A statistical increase in the no. of twins occurs with an increase in basicity, or anorthite content, of the sill. There is apparently no control of, or change in, the type of twinning with the composition of the rock as it appears after crystallisation. An unknown factor and not composition must be responsible for the variation in twinning in different types of rocks. L. S. T.

**Silica-fluorite pseudomorphs.** J. MURDOCH (Amer. Min., 1936, 21, 18—32).— $\text{SiO}_2$ -fluorite pseudomorphs, closely related to intrusions of basalt, occur in Los Angeles County, California. They consist mainly of finely fibrous  $\text{SiO}_2$  and partly of normal quartz (I) grains which may be largely replaced by later fibres. Optical and X-ray examinations show that the apparently different fibrous forms of  $\text{SiO}_2$  are probably due to variant orientations of microcryst. (I). Formation of the pseudomorphs is due to replacement of fluorite from outside, the character of the resultant  $\text{SiO}_2$  depending on the conditions of temp. and concn. at the time of deposition. L. S. T.

**Vesuvianite [and grossularite] from Georgetown, California.** A. PABST (Amer. Min., 1936, 21, 1—10).—Veins of vesuvianite (I) occurring in a serpentine belt along Traverse Creek are described. (I) has  $\text{SiO}_2$  36.60,  $\text{Al}_2\text{O}_3$  19.75,  $\text{Fe}_2\text{O}_3$  0.80, FeO 1.64, MgO 2.58, CaO 37.80,  $\text{H}_2\text{O}$ —0.20,  $\text{H}_2\text{O} +$  0.40,  $\text{TiO}_2$  trace,  $\text{Cr}_2\text{O}_3$  0.18, MnO trace, F,  $\text{CO}_2$ , and Ni none, total 99.95%,  $d_{25}^{25}$  3.326. Spectroscopic traces of Na, B, and V are present. An analysis of grossularite,  $d$  3.5062, is also given. L. S. T.

**Uranium-rich xenotime from Yu, Japan.** S. HATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 37—40).—The specimens showed 5—10 times the normal activity. Physical data and those of a gravimetric analysis are given. The total Ra and  $\text{UO}_2$  content, determined by the emanation method, was Ra ( $10^{-10}$  g.) 9.54,  $\text{UO}_2$  5.28%. A new

method of separating U and Zr consists in dissolving their mixed phosphates in 10%  $\text{H}_2\text{SO}_4$ , the dissolved part being regarded as U, and the remainder as Zr; the correctness of this was confirmed by the emanation data. N. M. B.

**Emanation capacity of ores and rocks of the Taboshar uranium-radium deposit.** A. P. KIRIKOV, T. BOGOSLOVSKAJA, and G. GORSCHKOV (Bull. United Geol. Prospecting Serv. U.S.S.R., 1932, 41, 1293—1299).—The Rn capacity of ores containing yellow U phosphates was considerably > that of torbernite ores. The capacity was greater in  $\text{H}_2\text{O}$  than in air, and increased with fineness of particles. CH. ABS. (e)

**Geological age of bauxite and manganese ore formation in Dunántul (Hungary).** E. VADÁSZ (Bányászati kohászati Lapok, 1935, 68, 163—168, 193—196; Chem. Zentr., 1935, ii, 987).—Both ores are of Lower Cretaceous age. J. S. A.

**Mineral structure of the Ivdel (Ural) bauxite.** F. V. SIROMIATNIKOV (Bull. Soc. nat. Moscow, Sect. geol., 1933, 11, 437—442).—The main components are chamoisite and diasporc, with a small admixture of limonite. The val. as an Al ore is not high. CH. ABS. (e)

**Bababudanite, a soda-amphibole from the banded ferruginous quartzites on Mysore, India.** C. S. PICHAMUTHU (Geol. Mag., 1936, 73, 39—45).—Bababudanite from the Bababudan Hills, Mysore, has  $\text{SiO}_2$  49.80,  $\text{Al}_2\text{O}_3$  1.56,  $\text{Fe}_2\text{O}_3$  18.62, FeO 10.59, MgO 9.30, CaO 0.45,  $\text{Na}_2\text{O}$  8.80,  $\text{K}_2\text{O}$  trace,  $\text{H}_2\text{O}$  0.65, total 99.77%, corresponding with  $4\text{NaFe}^{III}(\text{SiO}_3)_2 \cdot 2\text{FeSiO}_3 \cdot 3\text{MgSiO}_3$  or  $2\text{Na}_2\text{Fe}_2\text{Si}_4\text{O}_{12} \cdot 5(\text{Mg}, \text{Fe}, \text{H}_2, \text{Ca})\text{SiO}_3$ . In chemical and optical properties it is allied to rhodusite. (I) is of contact metamorphic and not primary origin, and is not connected with the origin of the Bababudan iron-stones. L. S. T.

**Geology of an area in the Kavirondo District, Kenya Colony.** W. PULFREY (Geol. Mag., 1936, 73, 26—38).—The greater part of the area is occupied by arenaceous and argillaceous sediments of Muva-Ankolean age. Au occurs in the area as a metasomatic phase of the end stages of the granite intrusion. L. S. T.

**Sulphur deposits of the Sierra de Gádor, Province of Almeria, Spain.** D. WILLIAMS (Bull. Inst. Min. Met., 1936, No. 378, 29 pp.).—Analyses and geology of the S deposits are given and the mode of formation is discussed. D. K. M.

**Gold and silver in crystalline rocks of the Malvern Hills.** A. BRAMMALL and D. L. DOWIE (Min. Mag., 1936, 24, 260—264).—Numerous assays were made of various types of rocks. Appreciable amounts of Au (trace up to 72 grains per ton) and Ag (to 42.4 dwt. per ton) were found only in red granite. L. J. S.

**Silver ores of Freiberg [Saxony].** E. ZIMMER (Tsch. Min. Petr. Mitt., 1936, 47, 328—370).—Polished sections of ores examined by the metallographic method show an intimate intergrowth of various minerals. Argentiferous galena, Zn blende, and pyrite contain minute enclosures of pyrargyrite and



tetrahedrite. A "Weissgiltigerz" containing Ag 4—6% replacing Pb is identified with jamesonite.

L. J. S.

**Microscopic analysis of opaque minerals.** F. L. STILLWELL (Soc. Chem. Ind. Victoria, 1935, 35, 983—987).—Procedure is described.

J. S. A.

**"Chloropal" nontronite ferrosilicates of Satschkovie Chutory.** I. J. MIKEI (Ukrain. Chem. J., 1935, 10, 467—472).—Analytical and other data are recorded.

R. T.

**Dielectric constants of rocks and their dependence on moisture.** N. K. SCHTSCHODRO and N. M. MASLOV (Bull. Acad. Sci. U.R.S.S., 1935, 933—950).—Results are tabulated.

C. W. G.

**Variable composition of cordierite in the Dartmoor granite.** A. BRAMMALL and B. R. RAO (Min. Mag., 1936, 24, 257—259).—The range in optic axial angles ( $2V$  56—82°) shown by different crystals of cordierite suggested a variation in chemical composition. Partial analyses of material fractionated in heavy liquid from the crushed rock gave FeO 4.00—9.10%, MgO 2.07—9.3% (but this variation is not correlated with  $2V$  and  $d$ ).

L. J. S.

**Variability of garnet in granites.** A. BRAMMALL and S. BRACEWELL (Min. Mag., 1936, 24, 254—256).—Two detailed and several partial analyses of manganiferous garnet from the granite of Dartmoor show MnO 3.37—22.00%,  $d$  3.7—4.2. Garnet from the granite of Eskdale, Cumberland, shows MnO 4.15—7.08%,  $d$  < 4.15 to > 4.2.

L. J. S.

**Zeolites. IX. Scolecite and metascolecite.** M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1936, 24, 227—253; cf. A., 1935, 1345).—Two new chemical analyses with detailed crystallographic, optical, and X-ray data are given of scolecite from India and Iceland. Discussed with the best analyses from the lit. these confirm the unit-cell formula  $\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot 24\text{H}_2\text{O}$ , the dimensions of the unit cell being  $a$  18.48,  $b$  18.95,  $c$  6.54 Å.,  $\beta$  89° 21', and the space-group  $S^4$ . Ca may be replaced by  $\text{Na}_2$  to the

extent of 1 atom of Na per unit cell, and by  $\text{K}_2$  about 0.1 atom. The base-exchange products, introducing Na, K, Li,  $\text{NH}_4$ , Ag, and Tl in place of Ca, are in several cases natrolites, confirming the view that natrolite and scolecite are isostructural. V.-p. measurements show that on partial dehydration a transition to metascolecite occurs at a degree of hydration dependent on the temp. and usually before the composition  $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$  is reached. In both scolecite and metascolecite the  $\text{H}_2\text{O}$  consists of two distinct groups, in the former a more volatile 16 mols. and a less volatile 8 mols.; and in the latter, a group of 8 mols. is more volatile.

L. J. S.

**Mineralogical composition of the volcanic rocks of Easter Island.** A. LACROIX (Compt. rend., 1936, 202, 527—530).—The rocks are described. Attention is directed to the existence of rhyolites and obsidians.

T. G. P.

**Composition of Easter Island lavas.** A. LACROIX (Compt. rend., 1936, 202, 601—605).—Analyses of plagioclasic rocks are recorded. Basalts and leucocratic types are associated, Na predominating over K even in the most siliceous members (rhyolites and dacitoids). Easter Island therefore belongs to the nepheline-free series of lavas in the author's classification.

L. J. J.

**Volcanic rocks of Pitcairn Island.** A. LACROIX (Compt. rend., 1936, 202, 788—791).—The volcanic rocks of Pitcairn Island are andesites and trachytes and not, as in the neighbouring islands, basalts and oceanites. Analyses of 7 different rocks are given.

M. S. B.

**Mineralisation of the Precambrian of the Anti-Atlas.** F. BLONDEL and J. BONDON (Compt. rend., 1936, 202, 673—674).—The association of Co with Au in this formation has been investigated. Co and Au are distributed independently, Co having been introduced subsequently to the Au, which is associated with intact or dolomitised quartz.

L. J. J.

**Transformation of fatty acids in the course of geological periods.** See this vol., 589.

## Organic Chemistry.

**Electronic theory and organic chemistry. IV. Structure of saturated and unsaturated molecular systems.** V. RASUMOVSKI (Bull. Soc. chim., 1935, [v], 3, 568—580; cf. A., 1935, 431, 843).—The theory developed previously (*loc. cit.*) is applied to open-chain compounds containing contiguous and conjugated ethylenic linkings. It explains the difference in the capacity for reaction of the groups  $\text{Me}$ ,  $\text{CH}_2$ , and  $\text{CH}$  and, in normal, saturated hydrocarbons, the enhanced reactivity of  $\text{CH}_2$  placed towards the end of the chain.

H. W.

**Catalytic production of optically active substances and chemical necessity of a unidirectional course in biochemical processes.** W. KUHN (Angew. Chem., 1936, 49, 215—219).—A lecture.

E. W. W.

**Isomerism and structural theory.** Y. I. GOLDFARB and L. M. SMORGONSKY (J. Chem. Educ., 1936, 13, 22—27).

L. S. T.

[Viscosity of solutions of aliphatic hydrocarbons.] K. H. MEYER and A. VAN DER WYK (Ber., 1936, 69, [B], 545—548; cf. A., 1935, 1318).—A reply to Staudinger (this vol., 309).

H. W.

**Mechanism of oxidation of paraffin hydrocarbons.** A. K. PLISSOV (Bull. Soc. chim., 1936, [v], 3, 425—429).—During atm. oxidation of Grozni paraffin, m.p. 52°, at 120° or 150°, the amount of peroxides (I) formed increases slowly to a max. after 3 hr. and then decreases; after 5—6 hr. (I) are not detectable. (I) are thus not the principal reaction products. In presence of catalysts (Na and Ca salts of naphthenic and higher fatty acids) the concn. of



(I) does not pass through a max. but diminishes steadily and after 4–5 hr. is zero; the catalysts do not, therefore, activate  $O_2$ . (I) are determined by a slight modification of Yule and Wilson's method (B., 1932, 7).

H. B.

**Hexadecane.** P. A. LEVENE (Org. Syntheses, 1935, 15, 27–28).— $C_{16}H_{33}I$  is reduced with Zn and HCl.

CH. ABS. (r)

**Chlorination of paraffins.** H. B. HASS, E. T. MCBEE, and P. WEBER (Ind. Eng. Chem., 1936, 28, 333–339).—The following rules are deduced for the reaction between paraffins and  $Cl_2$ . (1) At  $300^\circ$  in the vapour phase H atoms attached to primary, *sec.*, and *tert.* C are replaced at the relative rates 1.00:3.25:4.43. (2) At rising temp. the relative rates approach unity in both the liquid- and vapour-phase reactions. (3) Liquid-phase chlorination gives relative rates of primary, *sec.*, and *tert.* substitution obtainable only at much higher temp. in the vapour phase. (4) Presence or absence of moisture, C, or light does not appreciably affect the relative rates of substitution. (5) Excessive temp. and/or reaction time results in appreciable pyrolysis of the chloroparaffins in the order primary < *sec.* < *tert.* (6) With a mol. excess of paraffin and const. conditions the yield of monochlorides against polychlorides may be obtained from an equation. (7) Dichlorination proceeds by (a) loss of HCl followed by addition of  $Cl_2$ , and (b) progressive substitution; (a) is favoured by slow, thermal reaction, (b) by rapid liquid- or vapour-phase, single-pass thermal reaction, or low-temp. photochemical conditions. (8) In vapour-phase chlorination the presence of Cl attached to C tends to hinder further substitution on that atom. Herzfelder's rule (cf. A., 1893, i, 449) does not apply to chlorinations. The above rules are illustrated by the calculation of the proportions of isomerides formed by chlorinating  $C_3H_8$ , *n*- and *iso*- $C_4H_{10}$ , *n*- and *iso*- $C_5H_{12}$ .

P. G. C.

**Photo-oxidation of methylene iodide.**—See this vol., 572.

**Dodecyl bromide (lauryl bromide).** E. E. REID, J. R. RUHOFF, and R. E. BURNETT (Org. Syntheses, 1935, 15, 24–26).—The prep. from the alcohol and HBr is described; cyclohexyl, heptyl, tetradecyl, and octadecyl bromides are prepared similarly.

CH. ABS. (r)

**Hexadecyl iodide.** W. W. HARTMAN, J. R. BYERS, and J. B. DICKEY (Org. Syntheses, 1935, 15, 29–30).—The prep. from the alcohol with I and red P is described.

CH. ABS. (r)

**Use of wetting and emulsifying agents [in facilitating reactions].** J. COLONGE (Bull. Soc. chim., 1936, [v], 3, 501–503).—Hydrolysis ( $H_2O$ ) of  $CMc_2Br \cdot CHMeBr$  to  $COMePr^s$  (yield 80%) (cf. Evers *et al.*, A., 1933, 485) occurs much more readily in presence of a little of Twitchell's reagent (I) or Gardinol R (II). (I) also accelerates hydrolysis of  $CH_2[CH(CO_2Et)_2]_2$  to  $CH_2(CH_2 \cdot CO_2H)_2$ . Reduction of  $PhNO_2$  to azoxybenzene is conveniently carried out in presence of (II); the emulsion formed renders shaking unnecessary.

H. B.

**Nitration of gaseous paraffins.** H. B. HASS, E. B. HODGE, and B. M. VANDERBILT (Ind. Eng. Chem., 1936, 28, 339–344).—Nitration was effected in the vapour phase at  $420^\circ$ ;  $CH_4$  is not affected under the conditions used. Some oxidation occurs and probably leads to nitroparaffins of lower C content. The following products are obtained. From  $C_2H_6$ :  $MeNO_2$  (10–20),  $EtNO_2$  (80–90) (total yield, 9%). From  $C_3H_8$ :  $MeNO_2$  (9),  $EtNO_2$  (26?),  $\alpha$ -nitropropane, (I), b.p.  $131^\circ$  (32),  $\beta$ -nitropropane (II), b.p.  $118^\circ$  (33) (total yield, 21%). From *n*- $C_4H_{10}$ :  $MeNO_2$  (6),  $EtNO_2$  (12), (I) (5),  $\alpha$ -nitrobutane, b.p.  $151^\circ$  (27),  $\beta$ -nitrobutane, b.p.  $139^\circ$  (50) (total yield, 28%). From *iso*- $C_4H_{10}$ :  $MeNO_2$  (3), (II) (20),  $\alpha$ -nitroisobutane, b.p.  $140.5^\circ$  (65),  $\beta$ -nitroisobutane (III), b.p.  $126.4^\circ$ , m.p.  $25.6^\circ$  (7),  $COMe_2$  (5) (total yield, 25%). At  $150^\circ$  in sealed tubes *iso*- $C_4H_{10}$  affords 22% of (III). Total yields are practically const. from  $150^\circ$  to  $420^\circ$  if the optimum reaction rate for each temp. is used, but the ratios of isomerides vary, increase of temp. favouring production of primary isomerides. Presence of  $O_2$  results in increased oxidation. Increase of pressure increases reaction rate and yields (slightly). With the exception of  $MeNO_2$ , the nitroparaffins could not be exploded; they are stable, non-toxic, good solvents for gums and resins, and can be used in admixture with alcohols as solvents for cellulose nitrate.

P. G. C.

**Determination of the terminal methylene group.** J. DŒUVRE (Bull. Soc. chim., 1936, [v], 3, 612–620).—A very dil. solution of the substance in  $EtOAc$ – $AcOH$  (3:2) is treated with  $O_3$  (about 5%) at  $-15^\circ$  to  $-20^\circ$ , excess of  $O_3$  being avoided. The ozonide is reduced by  $SO_2$  and  $CH_2O$  determined colorimetrically (Denigès). Substances containing the groups  $CH_2 \cdot CMe$ ,  $CH_2 \cdot CH \cdot CH_2$ , and  $CH_2 \cdot CH$  give, respectively, 90–95%, 75–90%, and about 50% of the expected amounts of  $CH_2O$ . Two conjugated  $CH_2$  groups behave as a single group. Unsaturated compounds devoid of  $\cdot CH_2$  give only negligible amounts of  $CH_2O$ . *Acraldehyde-2:4-dinitrophenylhydrazones* has m.p.  $184^\circ$ .

H. W.

**Olefine formation.** W. TAYLOR (Chem. and Ind., 1936, 275–276).—Polemical against Ingold *et al.* (this vol., 433). The author claims that his results (A., 1935, 1465; cf. Olivier, *ibid.* 62) first made possible a general theory of olefine formation.

J. W. B.

**Ring tension of cyclenes.** J. BÖSEKEN and J. STUURMAN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 2–9; cf. A., 1935, 1103).—Vals. of *E* and *B* obtained from  $\log_e k = -E/RT + B$  are given for the interaction of  $C_2H_4$ ,  $C_3H_6$ ,  $CHPr^s \cdot CH_2$ ,  $CHBu^s \cdot CH_2$ ,  $CH_2Ph \cdot CH \cdot CH_2$ ,  $CMc_2 \cdot CH_2$ ,  $CHEt \cdot CHMe$ ,  $CHPr^s \cdot CHMe$ ,  $CHEt \cdot CHEt$ ,  $CHPh \cdot CHMe$ ,  $CPh_2 \cdot CH_2$ ,  $CHPh \cdot CHPh$ ,  $CMc_2 \cdot CHMe$ ,  $CPh_2 \cdot CHPh$ ,  $CHPh \cdot CH_2$ , cyclohexene, cyclopentene, cyclobutene, indene, 1:2- and 1:4-dihydronaphthalene, and methylcyclopentene, respectively, with  $AcO_2H$ .

R. S.

**Gutta-percha hydrocarbon.** Amorphous rubber.—See this vol., 553.

**Preparation and properties of an  $\alpha\gamma$ -disubstituted allene:  $\Delta^{\beta\gamma}$ -hexadiene.** H. VAN RIS-



SEGHEM (Bull. Soc. chim. Belg., 1936, 45, 95—96; cf. this vol., 187).—Corrigenda. The hydrocarbon, b.p. 67·75—68·25°, as shown by its Raman spectrum, is not an allene, but a mixture of *cis*- and *trans*-isomerides of a disubstituted ethylene. The Br-compound, b.p. 49·0—49·2°/26 mm., is fully saturated and does not absorb Br or H<sub>2</sub>. J. L. D.

**Dehydration of methyl ditert.-butylcarbinol. Fission and isomerisation of ditert.-butylethylene.** N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 79—82; cf. A., 1933, 1271).—CMeBu<sup>t</sup><sub>2</sub>·OH when distilled with I gives CBut<sup>t</sup><sub>2</sub>:CH<sub>2</sub> (cf. A., 1933, 1140), which when distilled with 1:4-C<sub>10</sub>H<sub>6</sub>Br·SO<sub>3</sub>H (A., 1935, 62) gives CMe<sub>2</sub>:CH<sub>2</sub> along with CMe<sub>2</sub>:CMe<sub>2</sub>, CMePr<sup>β</sup>:CH<sub>2</sub>, and CHBu<sup>t</sup>:CH<sub>2</sub>. The origin of these products is discussed. J. L. D.

**Direct production of organic compounds containing artificial radio-elements.** E. GLÜCKAUF and J. W. J. FAX (J.C.S., 1936, 390—393).—When org. halogen compounds are irradiated with slow neutrons, all the halogen atoms activated are ejected and then enter other mols., replacing other halogens, OH, NH<sub>2</sub>, CO<sub>2</sub>H, or CH<sub>2</sub>·OH. Some of the newly formed compounds can be separated with high activity. In the following experiments the figure in parentheses is the % of the total activity which is found in the reaction product named. MeI gives CH<sub>3</sub>I<sub>2</sub> (11). CH<sub>3</sub>Br<sub>2</sub> gives CHBr<sub>3</sub> (14). CHBr<sub>3</sub> gives CBr<sub>4</sub> (19). PhCl gives C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (15). CH<sub>3</sub>Br·CO<sub>2</sub>H gives CH<sub>2</sub>Br<sub>2</sub> (22). EtOH—I (saturated) gives MeI (6) and EtI (4). AcOH—I (saturated) gives MeI (10). C<sub>6</sub>H<sub>6</sub>·CCl<sub>4</sub> (1:1) gives PhCl (10). C<sub>6</sub>H<sub>6</sub>·CBr<sub>4</sub> (1:1) gives PhBr (15). PhOH·MeBr (1:1) gives MeBr (6), PhBr (2), and C<sub>6</sub>H<sub>4</sub>Br·OH (2). NH<sub>2</sub>Ph·HBr gives PhBr (1) and C<sub>6</sub>H<sub>4</sub>Br·OH (2). C<sub>6</sub>H<sub>6</sub>·MeI (10:1) gives PhI (15). Since often relatively small amounts of the products are isolated, the degree of activity contained in them is often very high. MeI gives the same result at -175° as at room temp., so that exchange of atoms is not due to ordinary chemical action; moreover, large dilution with an inert material (e.g., CHBr<sub>3</sub> with CS<sub>2</sub>) prevents formation of the active product (e.g., CBr<sub>4</sub>), because no mols. are available for collision. If air saturated with MeI is passed through KI-80% AcOH which is irradiated, highly active MeI is collected from the issuing air in a liquid air trap; no material is used up in this transformation, which can proceed indefinitely. An experiment under modified conditions shows that < 80% of the activity is due to slow neutrons.

R. S. C.

**Allylic rearrangements. III. Action of zinc on crotyl and methylvinylcarbinyl bromides.** W. G. YOUNG and S. WINSTEIN (J. Amer. Chem. Soc., 1936, 58, 441—443).—Reduction (Zn dust, boiling aq. EtOH) of various mixtures of CHMe:CH·CH<sub>2</sub>Br and CH<sub>3</sub>:CH·CHMeBr gives the same mixture of Δ<sup>a</sup>- (62·1±1·9%) and Δ<sup>β</sup>- (30·5±0·5% *cis* and 7·5±2·4% *trans*) -butene, the composition of which differs somewhat from that of the mixture obtained (this vol., 451) from the Grignard reagent.

H. B.

**Electron in organic chemistry. IV. Monohydroxy-compounds.** M. S. KHARASCH, O. REIN-

MUTH, and F. R. MAYO (J. Chem. Educ., 1936, 13, 7—19; cf. *ibid.*, 1934, 11, 82). L. S. T.

**Catalytic decomposition of alcohols.**—See this vol., 571.

**Thermal decomposition of ethylene oxide and an induced acetaldehyde decomposition.**—See this vol., 570.

**Preparation and properties of keten diethyl acetal.** F. BEYERSTEDT and S. M. McELVAIN (J. Amer. Chem. Soc., 1936, 58, 529—531; cf. A., 1933, 258, 259).—Attempts to prepare keten Et<sub>2</sub> acetal (I) by Scheibler's modified procedure (A., 1933, 377) were unsuccessful. (I), b.p. 124—126°, is now prepared in 52% yield from CH<sub>2</sub>I·CH(OEt)<sub>2</sub> (II), b.p. 69—70°/8 mm. [from CH<sub>2</sub>Br·CH(OEt)<sub>2</sub> (III) and NaI in COMe<sub>2</sub> at 110°], and boiling Bu<sup>t</sup>OH·KOBu<sup>t</sup>. (I) reacts rapidly and exothermically with H<sub>2</sub>O and EtOH at room temp. yielding EtOAc and CMe(OEt)<sub>3</sub>, respectively. Polymerisation of (I) occurs slowly at room temp. and is accelerated by heat. Reduction [H<sub>2</sub> (2000 lb.), Raney Ni, Et<sub>2</sub>O, 100°] of (I) occurs rapidly and gives CHMe(OEt)<sub>2</sub> (35%); much polymerised (I), which inactivates the catalyst, is also formed. CH<sub>2</sub>Cl·CH(OEt)<sub>2</sub> and EtOH·KOH (10% excess) at 150° give 95% of OH·CH<sub>2</sub>·CH(OEt)<sub>2</sub> (IV); (III) similarly affords (at 130°) (IV) (70%) and EtOAc (24%), whilst (II) yields (IV) (30%), EtOAc (23%), and CMe(OEt)<sub>3</sub> (42%). (II) and EtOH·NaOEt give OEt·CH<sub>2</sub>·CH(OEt)<sub>2</sub> (30%), EtOAc (21%), and CMe(OEt)<sub>3</sub> (46%). (I) is undoubtedly formed in these reactions with (II) but it then reacts with H<sub>2</sub>O and EtOH. H. B.

**Trichloroethyl alcohol.** W. CHALMERS (Org. Syntheses, 1935, 15, 80—84).—Al(OEt)<sub>3</sub> and CCl<sub>3</sub>·CHO afford Al(O·CH<sub>2</sub>·CCl<sub>3</sub>)<sub>3</sub>, which is hydrolysed to CCl<sub>3</sub>·CH<sub>2</sub>·OH. CH. ABS. (r)

**Biochemical hydrogenations. III. Hydrogenation of conjugated double linkings by fermenting yeast.** F. G. FISCHER and O. WIEDEMANN (Annalen, 1936, 522, 1—16).—The hydrogenation (method: A., 1935, 123) of conjugated systems containing ·CH:CH·CO· or ·CH:CH·CH<sub>2</sub>·OH results in α-β-addition and differs (cf. below) from reduction with Na or Na-Hg. Thus, the hexenol (I) obtained (*loc. cit.*) from Δ<sup>αγ</sup>-hexadienal (II) or Δ<sup>βδ</sup>-hexadien-α-ol (III) is essentially Δ<sup>δ</sup>-hexen-α-ol (IV), since careful ozonolysis in cold EtCl and subsequent reductive fission (Zn, AcOH) gives MeCHO (0·72—0·84 mol.) and (after oxidation of non-volatile residue with KMnO<sub>4</sub> in aq. Na<sub>2</sub>CO<sub>3</sub>) succinic acid (V) (0·76—0·82 mol.). Oxidation (KMnO<sub>4</sub>, aq. Na<sub>2</sub>CO<sub>3</sub>) of (I) affords AcOH (≠ 0·6 mol.) and (V) (≠ 50%). The octadienol previously described (*loc. cit.*) is Δ<sup>αδ</sup>-octadien-α-ol since it is oxidised (KMnO<sub>4</sub>, COMe<sub>2</sub>) to (V) (66—77%). CHMe:CH·CH:CH·COMe (VI) is hydrogenated (cf. *ibid.*, 1367) to Δ<sup>α</sup>-hepten-β-one (ozonolysis products, MeCHO and levulaldehyde) and -β-ol (ozonolysis products, MeCHO and γ-hydroxyvaleraldehyde), whilst CHPh:CH·CH:CH·COMe (VII) similarly gives (cf. *loc. cit.*) ζ-phenyl-Δ<sup>α</sup>-hexen-β-one and -β-ol, which are oxidised (O<sub>3</sub> followed by H<sub>2</sub>O<sub>2</sub>) to BzOH and levulic acid.

Reduction (Na, MeOH) of (III) gives approx. 33% of



(IV) and 66% of  $\Delta^2$ -hexen- $\alpha$ -ol; undistillable products are obtained from (II) and Na- or Al-Hg. (VI) is reduced (3% Na-Hg, EtOH) to mainly  $\Delta^8$ -hepten- $\beta$ -one (ozonolysis products, EtCHO and  $\text{CH}_3\text{Ac}\cdot\text{CHO}$ ), whilst (VII) and Na-Hg in EtOH-AcOH afford  $\zeta$ -phenyl- $\Delta^8$ -hexen- $\beta$ -one (ozonolysis products,  $\text{CH}_2\text{Ph}\cdot\text{CHO}$  and  $\text{CH}_3\text{Ac}\cdot\text{CHO}$ ) and products of higher mol. wt.

H. B.

**Dibutylcarbinol.** G. H. COLEMAN and D. CRAIG (Org. Syntheses, 1935, 15, 11-13).—The prep. from  $\text{MgBuBr}$  and  $\text{HCO}_2\text{Et}$  is described.

CH. ABS. (r)

**Oleyl alcohol** ( $\Delta^9$ -octadecenol). E. E. REID, F. O. COCKERILLE, J. D. MEYER, W. M. COX, jun., and J. R. RUHOFF (Org. Syntheses, 1935, 15, 51-54).—The reduction of  $\text{C}_{17}\text{H}_{33}\cdot\text{CO}_2\text{Bu}$  with  $\text{NaOBu}$  is described.

CH. ABS. (r)

**General method for preparation of  $\alpha\alpha'$ -diethyl- $\epsilon$ -nic glycols,  $\text{OH}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{OH}$ .** Conversion of some of these glycols into sugars. J. WIEMANN (Ann. Chim., 1936, [xi], 5, 267-336).—By the method previously described (A., 1935, 608, 963) the following were obtained:  $\Delta^{\alpha\epsilon}$ -heptadiene- $\gamma\delta$ -diol (two phenylurethanes, m.p. 151.5-152° and 160°);  $\epsilon$ -phenyl- $\Delta^{\beta\epsilon}$ -pentene- $\delta\epsilon$ -diol, b.p. 139°/2 mm.;  $\gamma\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -octadiene- $\delta\epsilon$ -diols, b.p. 133-135°/12 mm., m.p. 36-38°, and b.p. 133-135°/12 mm.;  $\delta\eta$ -dimethyl- $\Delta^{\gamma\epsilon}$ -decadiene- $\epsilon\zeta$ -diols, m.p. 72-73° and b.p. 148-149°/12 mm. [not identical with the compound, m.p. 89.5°, described by von Lenz (A., 1903, i, 460)];  $\epsilon$ -methyl- $\Delta^{\alpha\epsilon}$ -heptadiene- $\gamma\delta$ -diol, b.p. 116-117°/12 mm.;  $\zeta$ -methyl- $\Delta^{\beta\epsilon}$ -octadiene- $\delta\epsilon$ -diol, b.p. 124-125°/12 mm.;  $\zeta$ -methyl- $\Delta^{\beta\epsilon}$ -nonadiene- $\delta\epsilon$ -diol, b.p. 130-131°/12 mm.;  $\gamma\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -nonadiene- $\delta\epsilon$ -diol, b.p. 140-141.5°/12 mm. A mixture of two isomeric  $\Delta^{\beta\epsilon}$ -octadiene- $\delta\epsilon$ -diols (Charon, A., 1899, i, 848) was separated by fractional crystallisation of phenylurethanes from EtOH into *dl*- and *meso*-forms, m.p. 23-24° (phenylurethane, m.p. 168°) and 48° (phenylurethane, m.p. 190°), respectively. The *dl*- and *meso*-forms of  $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma\delta$ -diol previously separated by Romburgh *et al.* (A., 1932, 718) have m.p. 14° (phenylurethane, m.p. 124°) and 17-18° (phenylurethane, m.p. 181°). A more detailed account is also given of the oxidation of these glycols (A., 1932, 718; 1933, 47; 1935, 605, 1104). *d* and *n*<sub>D</sub> for the above compounds are recorded.

F. R. G.

**Hexose monophosphates. Glucose 4-phosphate.** A. L. RAYMOND (J. Biol. Chem., 1936, 113, 375-382).—Benzylideneglucose when heated with  $\text{AcOH}\cdot\text{NaOAc}$  affords  $\alpha$ - (sol. in 95% EtOH) and  $\beta$ -4 : 6-benzylideneglucose triacetate (insol.), converted by hydrolysis ( $\text{HCl}$ -aq.  $\text{COMe}_3$ ) and subsequent acetylation ( $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  in  $\text{CHCl}_3$ ) into  $\beta$ -glucose 1 : 2 : 3 : 6-tetra-acetate (Helfferich *et al.*, A., 1927, 135), which with  $\text{POCl}_3\cdot\text{C}_5\text{H}_5\text{N}$  in dry  $\text{CHCl}_3$  at -30° to 0° followed by hydrolysis with  $\text{Ba(OH)}_2$  gives glucose 4-phosphate (I) (*Ba* salt), isolated as its *dibrucine* salt, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -45.3° in  $\text{C}_5\text{H}_5\text{N}$ . (I) behaves differently from the 3- and 6-phosphates: it gives no osazone, but its *Ba* H salt gives an *osazone*: the course of glucoside formation (at room temp. and at 76°) differs from that of the 3- and 6-phosphates (Levene *et al.*, A.,

1929, 423), but is related to that of tetramethyl-glucopyranose. At low concns. (0.005, 0.02*M*) the rate of fermentation of the Na salt of (I) with zymine (*p*<sub>H</sub> 6.4) is negligible, and both in the presence and absence of glucose and of hexose diphosphate, no reduction in the induction period occurs. At higher concn. (0.06*M*) (I) has an inhibiting effect on fermentation.

J. W. B.

**Alkane- $\alpha\omega$ -disulphonates.** G. C. H. STONE (J. Amer. Chem. Soc., 1936, 58, 488-489).—

$(\text{CH}_2)_n(\text{SO}_3\text{Na})_2$  are prepared in 30-50% yield from  $(\text{CH}_2)_n\text{Br}_2$  (1 mol.) and saturated aq.  $\text{Na}_2\text{SO}_3$  (2.5 mols.) at 100° (bath). *Na ethylene-* and *tri-, tetra-, penta-, hexa-, and deca-methylene-disulphonates* are described. Titration curves of  $(\text{CH}_2)_n(\text{SO}_3\text{H})_2$  are identical with that of  $\text{H}_2\text{SO}_4$ . *Decamethylene dibromide* has b.p. 161-162°/10 mm., f.p. 25-26°.

H. B.

**Tautomerism of butadiene sulphone.** J. BÖSEKEN and E. DE ROY VAN ZUYDEWIJN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 31; cf. A., 1935, 326).—Treatment of butadiene sulphone

with KOH gives  $\text{HO}\cdot\text{CH}\cdot\text{CH}_2\text{CH}_2\cdot\text{SO}_2$  (I), m.p. 35° (*Ac* derivative, m.p. 74-75.5°). Irradiation of (I) in presence of aq. KOH does not yield  $\alpha$ - or  $\beta$ -butadiene sulphone (cf. Backer *et al.*, A., 1935, 1105). R. S.

**Organic catalysts. XIII. Esterase models.** W. LANGENBECK and F. BAEHREN (Ber., 1936, 69, [B], 514-520; cf. this vol., 476).—Measurements of the rate of hydrolysis of  $\text{Pr}^c\text{CO}_2\text{Me}$  alone and in presence of  $\text{CH}_2\text{Bz}\cdot\text{OH}$ , 1- or 2- $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ ,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , and 1- or 2- $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$  by a modified technique are recorded whereby the last-named substance is shown to be the most active catalyst. The previous hypothesis that hydrolysis is preceded by alkyl exchange,  $\text{Pr}^c\text{CO}_2\text{Me} + \text{CH}_2\text{Bz}\cdot\text{OH} \rightarrow \text{Pr}^c\text{CO}_2\text{CH}_2\text{Bz}$  (I) +  $\text{MeOH}$  and (I) +  $\text{H}_2\text{O} \rightarrow \text{Pr}^c\text{CO}_2\text{H} + \text{CH}_2\text{Bz}\cdot\text{OH}$ , is supported by the observed rate of hydrolysis of esters (I), so that it appears that the alkyl exchange is the slowest part of the total reaction. Gradual addition of 3 : 2- $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$  in anhyd.  $\text{Et}_2\text{O}$  to  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  at 0° affords 3-acetoxy-2-naphthyl diazomethyl ketone, m.p. 120-121°, converted by  $\text{HCl}$  in  $\text{Et}_2\text{O}$  into 3-acetoxy-2-naphthyl  $\text{CH}_2\text{Cl}$  ketone, m.p. 90-91°, by warm  $\text{AcOH}$  into 3-acetoxy-2-naphthoylecarbinyl acetate, m.p. 127°, and by boiling 50%  $\text{AcOH}$  into 3-acetoxy-2-naphthoylecarbinol, m.p. 117°. 6 : 2- $\text{OAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  and  $\text{PCl}_5$  in ligroin afford 6-acetoxy-2-naphthoyle chloride, m.p. 124°, whence 6-acetoxy-2-naphthyl diazomethyl ketone, m.p. 123°, 6-acetoxy-2-naphthyl  $\text{CH}_2\text{Cl}$  ketone, m.p. 112°, and 6-acetoxy-2-naphthoylecarbinyl acetate, m.p. 112°. 1 : 2- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  does not appear to be affected by  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  and is resinified by  $\text{Ac}_2\text{O}$  containing a little conc.  $\text{H}_2\text{SO}_4$ . H. W.

**Transformation of fatty acids in the course of geological periods.** G. STADNIKOV and O. EGOROVA (Brennstoff-Chem., 1936, 17, 48-49; cf. A., 1933, 928).—The residue obtained after extraction of baltashite with org. solvents was dissolved by heating with 2% aq.  $\text{NaOH}$ /25 atm. On acidifying the solution the acids separated as a clear yellow liquid, which rapidly changed into a viscous dark brown



mass insol. in org. solvents. On acidifying the solution in presence of  $\text{Et}_2\text{O}$  the acids dissolved therein, but subsequently changed into the insol. form. This tendency to change was diminished by heating the balkashite residue with the aq.  $\text{NaOH}$  under high  $\text{H}_2$  pressure. It is concluded that the conversion into a viscous or rubber-like form is not a polymerisation, but a colloid-chemical process similar to the conversion of humic acids into the insol. form by ageing.

A. B. M.

**Interaction of carbon monoxide and alcohols.**

**II. Synthesis of propionic and isobutyric acids.**  
**III. Synthesis of methylethylacetic and pivalic acids.** D. V. N. HARDY (J.C.S., 1936, 358—362, 362—364; cf. A., 1934, 1200).—II. In presence of  $\text{H}_3\text{PO}_4\text{-Cu}_3(\text{PO}_4)_2$ ,  $\text{EtOH}$  and  $\text{CO}$  at  $250\text{--}370^\circ$  give 3.7% of  $\text{EtCO}_2\text{H}$ , 2% of  $\text{EtCO}_2\text{Et}$ , and 8—24% of polymerised  $\text{C}_2\text{H}_4$ , the % of polymerides rising rapidly with rising temp.  $\text{Pr}^\alpha\text{OH}$  and  $\text{Pr}^\beta\text{OH}$  react at  $150\text{--}300^\circ$  to give  $\text{Pr}^\beta\text{CO}_2\text{H}$  (max. about 30—33% at  $210^\circ$ ) (no  $\text{Pr}^\alpha\text{CO}_2\text{H}$ ), small amounts of esters, much higher acids (mainly  $\text{C}_{3n}\text{H}_{6n+1}\cdot\text{CO}_2\text{H}$ ), and polymerised hydrocarbons,  $\text{C}_3\text{H}_6$ , and some  $\text{COMeBu}^\beta$  and  $\text{COPr}^\beta$ . It is concluded that reaction occurs by preliminary dehydration of the alcohol, and, in conformity with this view,  $\text{Pr}^\beta\text{OH}$ , being more readily dehydrated, reacts more completely than does  $\text{Pr}^\alpha\text{OH}$ . The ketones are formed by two routes, (i) condensation of alcohol or olefine to higher alcohol and dehydrogenation, and (ii) loss of  $\text{CO}_2$  from acids formed.

**III.** In presence of  $\text{H}_3\text{PO}_4$  with or without  $\text{Cu}_3(\text{PO}_4)_2$  at  $200\text{--}210^\circ$   $\text{Bu}^\alpha\text{OH}$  or  $\text{Bu}^\beta\text{OH}$  and  $\text{CO}$  give much  $\text{Bu}^\gamma\text{CO}_2\text{H}$ , a little  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ , large amounts of a mixture,  $\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$ , and polymerised hydrocarbons.  $\text{CHMeEt}\cdot\text{OH}$  gives similar products, except that only traces of  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$  are formed. Reaction occurs only by way of the butylenes, which are interconvertible under the conditions used.

R. S. C.

**Interaction of olefines, carbon monoxide, and steam.** D. V. N. HARDY (J.C.S., 1936, 364—365).—At  $290\text{--}300^\circ/150$  atm. in presence of  $\text{H}_3\text{PO}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  give  $\text{EtCO}_2\text{H}$  (1 mol.),  $\text{EtOH}$  (3 mols.), and polymerised hydrocarbons (2 mols.). At  $200^\circ/200$  atm.  $\text{C}_3\text{H}_6$  gives similarly much  $\text{Pr}^\gamma\text{CO}_2\text{H}$  and homologues; and  $(\text{CHMe})_2$  gives  $\text{Bu}^\gamma\text{CO}_2\text{H}$  and other acids and some  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$ . These reactions exactly resemble those with alcohols (preceding abstract) and confirm the mechanism suggested. For reaction the olefine must be activated; in presence of  $\text{H}_3\text{PO}_4$  activation occurs by formation and decomp. of alkyl phosphates.

R. S. C.

**Elaidinisation of oleic acid and cis-trans isomerism.** J. STUURMAN (Chem. Weekblad, 1936, 33, 201, 255).—Polemical against Bertram (this vol., 189, and below).

D. R. D.

**Elaidinisation of oleic acid and cis-trans isomerism.** S. H. BERTRAM (Chem. Weekblad, 1936, 33, 216, 255).—Replies to Stuurman (preceding abstract).

S. C.

**Telfairic acid.** G. D. GOODALL and R. D. HAWORTH (J.C.S., 1936, 399).—Telfairic acid (A., 1900, i, 473) from the seeds of *Telfairia pedata* is really linoleic acid.

R. S. C.

**Ketolic condensations of ethyl acetoacetate with acetaldehyde.** H. GAULT and T. WENDLING (Bull. Soc. chim., 1936, [v], 3, 369—388).—Partly a more detailed account of work previously reviewed (A., 1935, 65). The following appears to be new. **Et di- $\alpha'$ -hydroxyethylacetoacetate (I)** is decomposed by  $\text{PhNCO}$ ; **Et ethylideneacetoacetate (II)** and resinous products are formed. (I) and  $\text{AcCl}$  give an unstable  $\text{Cl}$ -containing compound, b.p.  $104\text{--}105^\circ/14$  mm.; in presence of  $\text{C}_5\text{H}_5\text{N}$ , (II) results. Decomp. of (I) also occurs with  $\text{BzCl}$  (in  $\text{C}_5\text{H}_5\text{N}$ ) or  $\text{Ac}_2\text{O}$ ;  $\text{EtOH}\cdot\text{NH}_3$  leads to  $\text{MeCHO}\cdot\text{NH}_3$  and resin. Attempted prep. of a pyrazolone and phenylhydrazone from (I) gives the corresponding derivatives (*loc. cit.*) of **Et  $\alpha'$ -hydroxyethylacetoacetate (III)**. The stability of (III), alone and in various solvents, is studied. (III) is dehydrated ( $\text{H}_3\text{PO}_4$ ) to (II).

H. B.

**Ketolic condensations of ethyl acetoacetate with acetaldehyde.** H. GAULT and T. WENDLING (Bull. Soc. chim., 1936, [v], 3, 549—568; cf. preceding abstract).— $\text{OH}\cdot\text{CHMe}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$  (I) appears to be dehydrated and resinified by  $\text{PhNCO}$  in  $\text{Et}_2\text{O}$ . With  $\text{AcCl}$  it affords an unstable compound, probably  $\text{CEtAcCl}\cdot\text{CO}_2\text{Et}$ , b.p.  $109\text{--}112^\circ/17$  mm., whereas it is dehydrated by  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  to **Et ethylideneacetoacetate**. With  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{EtOH}$  (I) yields **3-methyl-4- $\alpha$ -hydroxyethylpyrazol-5-one**, m.p.  $275^\circ$ , whilst with  $\text{NHPh}\cdot\text{NH}_2$  in  $\text{EtOH}$  it gives the **phenylhydrazone**, m.p.  $92^\circ$ , which loses  $\text{MeCHO}$  and resinifies when heated. (I) is resinified by  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}_2\cdot\text{NH}_2$ . Alkaline or acidic hydrolysis of (I) does not give well-defined results, whilst  $\text{EtOH}\cdot\text{NH}_3$  gives  $\text{MeCHO}\cdot\text{NH}_3$ . (I) with  $\text{CH}_2\text{O}$  in presence of  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{O}$  gives a mixture of products from which **Et<sub>2</sub>  $\alpha,\epsilon$ -dihydroxy- $\beta\delta$ -diacetylpentane- $\beta\delta$ -dicarboxylate**, m.p.  $97^\circ$ , is isolated; with  $\text{MeCHO}$  **Et di- $\alpha'$ -hydroxyethylacetoacetate** is produced. (I) and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  in presence of  $\text{NHEt}_2\cdot\text{EtOH}$  afford **Et<sub>2</sub> 2-hydroxy-2 : 6-dimethylcyclohexan-4-one-1 : 6-dicarboxylate**, m.p.  $78\text{--}79^\circ$ . (I) and  $\text{NHEt}_2$  at  $-10^\circ$  give crude **Et<sub>2</sub>  $\epsilon$ -hydroxy- $\gamma$ -diacetyl- $\beta$ -methylpentane- $\alpha\gamma$ -dicarboxylate**, identified by conversion into the **dipyrazolone**,  

$$\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{N}=\text{CMe} \end{array} \text{CH}\cdot\text{CHMe}\cdot\text{C}(\text{CHMe}\cdot\text{OH}) \begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{CMe}\cdot\text{N} \end{array}$$
 m.p.  $267\text{--}268^\circ$ .

H. W.

**Ferric oxalate.**—See this vol., 576.

**Polymembered heterocyclic compounds. IX. Polymembered cyclic esters from dihydric alcohols and dicarboxylic acids.** M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1936, 19, 253—261; cf. A., 1935, 1351).—The relative ease of formation of various polymembered cyclic lactones, di- and tri-lactones is in harmony with probability considerations if the effect of change of mol. concn. is taken into account.  $\text{OH}\cdot[\text{CH}_2]_9\cdot\text{OH}$  and  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$  in 0.005*M* solution give **di-** (I),  $\text{CO} < \begin{array}{c} \text{O} \\ | \\ [\text{CH}_2]_9 \end{array} > \text{CO}$ , m.p.  $10\text{--}12^\circ$ , b.p.  $147\text{--}148^\circ/0.01$  mm., and **tetra-lactone** (II),  $\text{CO} < \begin{array}{c} \text{O} \\ | \\ [\text{CH}_2]_9 \end{array} \text{O}\cdot\text{CO} < \begin{array}{c} \text{O} \\ | \\ [\text{CH}_2]_7 \end{array} > \text{CO}$ , m.p.  $65\text{--}68^\circ$ ; the ratio, (I) : (II) = 46 : 54, is < expected from the lactonisation of  $\text{OH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ ; this is attributed to formation of more highly complex esters.



$\text{OH} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ ,  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ , and anhyd.  $\text{PhSO}_3\text{H}$  give the *di*-,  $\text{CO} \cdot \text{O} \cdot \text{O} \cdot [\text{CH}_2]_3 \cdot \text{CO}$ , m.p. 14–17°, b.p. 100–102°/0.02 mm., and *tetra-lactone*,  $\text{CO} \cdot \text{O} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{CO} \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{CO}$ , m.p. 113–113.5°, but 70% of the material is converted by primary esterification of the  $\text{PhSO}_3\text{H}$  into the *esters*,  $\text{SO}_3\text{Ph} \cdot \text{O} \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{CO} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot [\text{CH}_2]_3 \cdot \text{OH}$ , an oil, and  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{CO} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2 \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{SO}_2\text{Ph}$  (not obtained pure), a glass. R. S. C.

Two crystalline *d*-talomucolactones. (FRL.) M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 195–203).—*d*-Talomucic acid (modified prep. from *d*-talonic acid), m.p. 155–158°,  $[\alpha]_D^{25} + 29^\circ \rightarrow [\alpha]_D^{25} + 6.7^\circ$  in  $\text{H}_2\text{O}$  in 61 days, when boiled with  $\text{H}_2\text{O}$ , gives a mixture of  $\alpha\delta$ -(I), m.p. 187–189° (decomp.; corr.),  $[\alpha]_D^{25} - 49.1^\circ \rightarrow [\alpha]_D^{25} + 8^\circ$  in  $\text{H}_2\text{O}$  in 62 days, and  $\gamma$ -*lactone* (II),  $+\text{H}_2\text{O}$ , double m.p. about 66–70° and 133° (corr.),  $[\alpha]_D^{25} + 32.5^\circ \rightarrow [\alpha]_D^{25} + 10.6^\circ$  in  $\text{H}_2\text{O}$  in 60 days. Na-Hg reduction of (I) gives *d*-altronic acid, that of (II) *d*-talonic acid. R. S. C.

Hydrazine compounds of *d*-galacturonic acid and the isolation of crystalline *d*-galacturonic acid from tobacco. H. COLLATZ (Ber., 1936, 69, [B], 485–492; cf. Neuberg *et al.*, A., 1932, 202).—Conditions are precisely defined for the conversion of *d*-galacturonic acid (I) into its phenylhydrazone, m.p. 134° (corr.; decomp.), *p*-bromophenylhydrazone, m.p. 152–153° (corr.; decomp.), *p*-nitrophenylhydrazone, m.p. about 170–175° (decomp.) according to the rate of heating; 2 : 4-dinitrophenylhydrazone (II), m.p. 152° (corr.; decomp.), and thiosemicarbazide derivative,  $\text{C}_7\text{H}_{15}\text{O}_7\text{N}_3\text{S} \cdot \text{H}_2\text{O}$ , m.p. 147° (corr.; decomp.). Tobacco leaves are repeatedly extracted with  $\text{H}_2\text{O}$ , and the dry residue is hydrolysed with boiling 2.5%  $\text{H}_2\text{SO}_4$ . The mixture is treated with  $\text{BaCO}_3$  and filtered. The filtrate is conc. at 50°/vac. and the mixture (III) of Ba and Ca galacturonate (IV) is pptd. by EtOH. From (III) the free uronic acid is obtained by treatment with  $\text{H}_2\text{SO}_4$  in amount equiv. to Ba and from (IV) by means of  $\text{H}_2\text{C}_2\text{O}_4$ . The solutions are conc. to a syrup, which is dissolved in EtOH. Treatment of the solution with 2 : 4- $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{NH}_2$  affords (II), converted by MeCHO into (I),  $[\alpha]_D^{25} + 50.74^\circ$  in  $\text{H}_2\text{O}$  (equilibrium val.). H. W.

*d*-Saccharodilactone. K. REHORST and H. SCHOLZ (Ber., 1936, 69, [B], 520–526).—Potato starch (200 g.) is mixed with  $\text{H}_2\text{O}$  (200 c.c.) and  $\text{HNO}_3$  (d 1.20, 800 c.c.) and then evaporated at 100° to incipient discoloration. Treatment of the product with a slight excess of  $\text{K}_2\text{CO}_3$  followed by AcOH gives pure KH *d*-saccharate, converted through the Ca salt into *d*-saccharomonolactone. Since for further work the purity of the product is essential it is recryst. from  $\text{Et}_2\text{O}$  in a continuous extraction apparatus, thus giving a material of m.p. 133°,  $[\alpha]_D^{25} + 40.2^\circ$  in  $\text{H}_2\text{O}$ . It suffers partial hydration during titration with 0.1N-NaOH. When heated over  $\text{P}_2\text{O}_5$  at 100°/vac. it is transformed into *d*-saccharodilactone (I), m.p. 134–135° after softening at 132°,  $[\alpha]_D^{25} + 164.6^\circ$  to  $+33.5^\circ$  in  $\text{H}_2\text{O}$  in 10 days. The presence

of the  $\delta$ -lactone ring is shown by the immediate and rapid mutarotation and the immediate neutralisation of alkali in presence of phenolphthalein. The total consumption of alkali exceeds that required for the opening of the two lactone rings. Chemically (I) resembles mannosaccharodilactone, since it is resinified by alkali and reduces Fehling's solution and  $\text{Ag}_2\text{O} \cdot \text{NH}_3$ ; with I-KOH it affords  $\text{CHI}_3$ . H. W.

Attempts to reduce carbon monoxide electrocatalytically. G. FESTER and M. SCHIVAZAPPA (Rev. fac. quim. ind. agr., 1930, 1, 53–57).—The combination of catalytic and cathodic reduction of CO in solution gave determinable amounts of  $\text{CH}_2\text{O}$ , and small amounts of  $\text{HCO}_2\text{H}$  and MeOH.

Polymeride of acetaldehyde. M. LETORT (Compt. rend., 1936, 202, 767–768; cf. this vol., 316).—Pure MeCHO (prep. described) when distilled from a vessel at  $-15^\circ$  to one at  $-185^\circ$  at  $10^{-3}$  to  $10^{-5}$  mm. affords a spongy polymeride, which is slowly reconverted at room temp. into MeCHO, and reacts violently with fuming  $\text{HNO}_3$  to give  $\text{PhNO}_2$ . J. L. D.

Methylglyoxal. T. BERSIN (Ber., 1936, 69, [B], 560–562; cf. Schubert, this vol., 55).—The bimol. form of AcCHO (in  $\text{H}_2\text{O}$ ) is the hydrate  $\text{OH} \cdot \text{CHAc} \cdot \text{O} \cdot \text{CMe}(\text{OH}) \cdot \text{CH}(\text{OH})_2$  or  $\text{O} \cdot \text{CMe}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CMe}(\text{OH}) \cdot \text{O}$ , b.p. 25–27°/14–17 mm., 104–105°/743 mm.; in AcOH it suffers partial decomp. into AcCHO and  $\text{H}_2\text{O}$ . Reversible dissociation with production of yellow colour occurs during distillation under atm., but not under diminished pressure. Schubert's semi-mercaptal from AcCHO and  $\text{SH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$  or glutathione is unimol. in  $\text{H}_2\text{O}$  and has the structure  $\text{OH} \cdot \text{CHAc} \cdot \text{SR}$ . The substrate of methylglyoxalase has the constitution  $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CHAc} \cdot \text{OH}$ . Under the influence of the flavin enzyme (I) gives an acid, probably  $\text{OH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ . H. W.

Photo-activation of the carbonyl group in prototropic reactions. W. S. NATHAN (Nature, 1936, 137, 460). L. S. T.

Acetonecyanohydrin. R. F. B. COX and R. T. STORMONT (Org. Syntheses, 1935, 15, 1–2).—An improved prep. from  $\text{COMe}_2$ , NaCN, and  $\text{H}_2\text{SO}_4$  is recorded. CH. ABS. (7)

Action of mixed organomagnesium compounds on aliphatic  $\alpha$ -ethylenic ketones. II. J. COLONGE (Bull. Soc. chim., 1936, [v], 3, 413–418; cf. A., 1935, 847).— $\text{COMe} \cdot \text{CPr}_2 \cdot \text{OH}$  is dehydrated (99.5%  $\text{H}_2\text{SO}_4$ ) to  $\text{CHEt} \cdot \text{CPr} \cdot \text{COMe}$ , b.p. 66–74°/9 mm., separated (method: Locquin and Heilmann, A., 1928, 509) into *cis*-, b.p. 72°/9 mm., and *trans*-, b.p. 71–75°/9 mm., forms, both of which with  $\text{MgEtBr}$  at 15–20° give approx. equal amounts of *Me*  $\beta$ -ethyl- $\alpha$ -propylbutyl ketone, b.p. 199–200°/747 mm. (semicarbazone, m.p. 125°), and  $\gamma$ -methyl- $\delta$ -propyl- $\Delta^2$ -hepten- $\gamma$ -ol (not obtained pure).  $\text{COMe} \cdot \text{CH}_2 \cdot \text{CHPr} \cdot \text{OH}$



is dehydrated (trace of I) to *trans*-CHPr:CH·COMe, b.p. 58—59°/13 mm., 158—159°/750 mm., whilst the *cis*-form, b.p. 61.5—63°/13 mm., is prepared (cf. Eccott and Linstead, A., 1930, 893) from PrCHO, COMe<sub>2</sub>, and 15% NaOH; both forms with MgEtBr give 40% of *Me β-ethylamyl ketone*, b.p. 72°/12 mm. (*semicarbazone*, m.p. 115°), and 60% of *γ-methyl-Δ<sup>8</sup>-octen-γ-ol*, b.p. 69—70°/10 mm. (cf. Grignard and Dubien, A., 1925, i, 111). H. B.

**Reducibility of bromo-ketones by hydrogen bromide and consequences thereof.** F. KRÖHNKE and H. T. TRIMLER (Ber., 1936, 69, [B], 614—621).—In principle, all Br-ketones and related compounds are reducible by HBr, the ease depending on their constitution. Simple Br-ketones such as CPh·CH<sub>2</sub>Br in which no activating group except CO is present require a Br acceptor. The ready reducibility of others is shown by the ease with which in EtOH or COMe<sub>2</sub> they liberate I from aq. KI. CO<sub>2</sub>H or CO<sub>2</sub>Et are feebly activating, but 2 CO<sub>2</sub>Et facilitate elimination of Br as in CHBr(CO<sub>2</sub>Et)<sub>2</sub>, which gives a marked "I reaction." CHPhBzBr, CPh·CHBr<sub>2</sub>, CBr<sub>3</sub>·CHO, and CHBr<sub>2</sub>·CO·CO<sub>2</sub>H react in order of increasing ease. The difficulty of introducing 2 Br at the same C atom is due to the counteraction of HBr. Thus the direct conversion of CPhEt into CPh·C<sub>2</sub>H<sub>5</sub>Br<sub>2</sub> appears impossible, but the *compound*, m.p. 31°, is formed if HBr is removed after formation of CPh·C<sub>2</sub>H<sub>5</sub>Br and bromination is then repeated. CHBr<sub>2</sub>·CO<sub>2</sub>H is resistant towards HBr, but CBr<sub>3</sub>·CO<sub>2</sub>H is somewhat affected. CH<sub>2</sub>Bz<sub>2</sub> + Br<sub>2</sub> ⇌ CHBz<sub>2</sub>Br + HBr is established unless HBr is removed. With CH<sub>2</sub>Ac·CO<sub>2</sub>Et the initial product is CHAcBr·CO<sub>2</sub>Et; Br removed therefrom by HBr re-enters in the *γ*-position, giving thus CH<sub>2</sub>Br·CO·CH<sub>2</sub>·CO<sub>2</sub>Et as final product. Treatment of CH<sub>2</sub>AcBz with NaOBr gives CHAcBzBr, transformed by C<sub>5</sub>H<sub>5</sub>N through a non-isolated enolbetaine into AcOH and phenacylpyridinium bromide; with HBr·AcOH the Br of CHAcBzBr wanders with production of CH<sub>2</sub>Bz·CO·CH<sub>2</sub>Br, converted by C<sub>5</sub>H<sub>5</sub>N into *benzoylacetonylpyridinium bromide*, m.p. 181° (decomp.) (corresponding *perchlorate*, m.p. 169°), which with alkali yields BzOH, AcOH, and methylpyridinium salt. Since NO<sub>2</sub> is more strongly activating than CO, Br can be readily removed from aliphatic Br·NO<sub>2</sub>-compounds such as CH<sub>2</sub>Br·NO<sub>2</sub> and NO<sub>2</sub>·CBr(CO<sub>2</sub>Et)<sub>2</sub>; N<sup>+</sup> in quaternary salts also activates if CO also is present. Determination of otherwise stable Br-ketones can be effected if a suitable acceptor, such as β-C<sub>10</sub>H<sub>7</sub>·OH, is present. The bearing of the observation on the indirect enol titration is discussed. The suggested mechanism of debromination is ·CO·CHBr· + HBr → ·(OH)CBr·CHBr· → ·(OH)C·CH· + Br<sub>2</sub> → ·CO·CH<sub>2</sub>·.

H. W.

**Reaction of sulphur and keto-alcohols in glycerol containing iron.** E. ZMACZYNSKI (Compt. rend., 1936, 202, 668—669).—Benzoin, fructose (I), or CO(CH<sub>2</sub>·OH)<sub>2</sub> heated with S in glycerol (II) containing combined Fe gives a black coloration and then a ppt.; the change does not occur in pure (II). The reaction appears to be sp. for the OH·CH·CO· group;

0.1 mg. of S in 1 c.c. of (II) is also detectable and (I) can be distinguished from glucose or sucrose.

H. B.

***d*-Psicose.** (FRL.) M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 184—189).—*d*-Ribose, HCN, and Ba(OH)<sub>2</sub> give *d*-altronic acid (Cd salt, cryst.) and *d*-allonolactone (*diisopropylidene* derivative, b.p. about 130°/1 mm.); the lactone with Na-Hg gives *d*-allose (I), m.p. 128—130° (corr.), which is isomerised by hot C<sub>5</sub>H<sub>5</sub>N to a mixture, whence is obtained a poor yield of *d*-*psicose* (II), an oil, [α]<sub>D</sub><sup>20</sup> +3.1° in H<sub>2</sub>O, stable to yeast and best isolated as *diisopropylidene* derivative, b.p. 104—105°/0.3 mm., m.p. 57—58.5°, [α]<sub>D</sub><sup>20</sup> —98.2° in COMe<sub>2</sub>. *l*-Psicose (III) gives an oily *dicyclohexylidene* derivative. Hydrogenation (Ni-kieselguhr) in EtOH at 140°/120 atm. gives *allodulcitol*, m.p. 150—151° (corr.). *d*-Allosazone, m.p. 173—174° (decomp.), [α]<sub>D</sub><sup>20</sup> —19.2° ± 4° in EtOH, variable in C<sub>5</sub>H<sub>5</sub>N, is obtained from (I) and (II), and the *l*-isomeride from (III); the *dl*-form has m.p. 204° (decomp.).

R. S. C.

**Preparation of *d*-ribose.** (FRL.) M. STEIGER (Helv. Chim. Acta, 1936, 19, 189—195).—*d*-Ribose is prepared in 17% over-all yield from arabinose by electrolytic oxidation to Ca *d*-arabonate, isomerisation by boiling C<sub>5</sub>H<sub>5</sub>N to *d*-ribonolactone, and controlled reduction of this by 2.5% Na-Hg; it is isolated as *p*-bromophenylhydrazine, m.p. 166—167°, from which it is obtained by PhCHO. R. S. C.

**Determination of *O*- and *N*-acetyl and structure of osazone acetates.** M. L. WOLFROM, M. KONIGSBERG, and S. SOLTZBERG (J. Amer. Chem. Soc., 1936, 58, 490—491).—Freudenberg and Harder's method (A., 1923, ii, 884) of determination of Ac gives *O*-+*N*-Ac, whilst Kunz and Hudson's method (A., 1926, 941) gives *O*-Ac only. It is thus possible to distinguish, e.g., *aldehydo*- and *β*-*d*-glucoseoxime hexa-acetates, since the latter contains 1 *N*-Ac. *d*-Glucose-, m.p. 115—117°, [α]<sub>D</sub><sup>25</sup> (in CHCl<sub>3</sub>) —55° → —45° (cf. Maurer and Schiedt, this vol., 193), and *d*-galactose-phenylosazone tetra-acetate, m.p. 178—179° (decomp.), [α]<sub>D</sub><sup>25</sup> +87° in CHCl<sub>3</sub> (from the osazone and Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N at room temp.), contain 4 *O*-Ac groups, indicating open-chain structures.

H. B.

**Carbohydrates. VII. Xanthate reaction of glucose.** T. LIESER and R. THIEL (Annalen, 1936, 522, 48—55).—The solution (A) from α-methylglucoside (I), 2*N*-NaOH, and CS<sub>2</sub>, with CO<sub>2</sub> followed by CuOAc, gives Cu<sub>2</sub> α-methylglucosidyl dioxanthate. (A) with AcOH (slight excess), followed by CO<sub>2</sub> and Cd(OAc)<sub>2</sub>, yields the Cd dioxanthate (II); with CO<sub>2</sub> and 0.1*N*-I the (impure) dioxanthogen, C<sub>9</sub>H<sub>12</sub>O<sub>6</sub>S<sub>4</sub>, is obtained. β-Phenylglucoside (III) similarly leads to Cd β-phenylglucosidyl dioxanthate and a polyxanthogen (shown by fractionation to be mainly di- with small amounts of mono-, tri-, and tetra-xanthogens). A small amount of dioxanthate is also obtained (cf. A., 1935, 1354) from (I), 0.36*N*-Ba(OH)<sub>2</sub>, and CS<sub>2</sub>; the purified solution (B) and Cd(OAc)<sub>2</sub> give a little (II). (B) with MeI or Me<sub>2</sub>SO<sub>4</sub> affords the H<sub>2</sub>O-sol. Me α-methylglucosidyl xanthate (*loc. cit.*) and a little of the non-cryst., H<sub>2</sub>O-insol. Me<sub>2</sub> α-



*methylglucosidyl dioxanthate* [also obtained from the previously described (*loc. cit.*) Ag salt and MeI]. Ba  $\beta$ -phenylglucosidyl xanthate (*loc. cit.*) with  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NEt}_2$  and MeI gives 52.6% of  $\text{NEt}_2\cdot\text{CO}\cdot\text{CH}_2$ , m.p. 133—135° (corr.), and 66% of Me, m.p. 173—174°,  $\beta$ -phenylglucosidyl xanthate, respectively. (III) with 3.5N- $\text{NEt}_2\cdot\text{OH}$  and  $\text{CS}_2$ , followed by MeI (or  $\text{Me}_2\text{SO}_4$ ) or I (slight excess), yields  $\text{Me}_4$   $\beta$ -phenylglucosidyl tetraaxanthate (26%), m.p. 135° (corr.) or the *trixanthogen*, respectively. Homogeneous cryst. di- and tri-xanthates could not be prepared from glucose. H. B.

**Position of the equilibrium and specificity of the  $\beta$ -glucosidase action.** C. N. IONESCU (Ber., 1936, 69, [B], 588—591).—Further evidence (cf. A., 1934, 927) is adduced in favour of the view that the law of mass action is unreservedly applicable to reactions catalysed by  $\beta$ -glucosidase if the concn. of  $\beta$ -glucose instead of total glucose is considered. The apparent deviations caused by increasing  $[\text{EtOH}]$  are not due to inactivation of the enzyme but to displacement of the equilibrium  $\beta \rightleftharpoons \alpha$ -glucose towards the  $\alpha$ -form. H. W.

**Kinetics of  $\beta$ -glucosidase action.** C. N. IONESCU and A. KIZYK (Ber., 1936, 69, [B], 592—597).—The experiments of Bourquelot and present experiments with  $\beta$ -methyl- (I) and  $\beta$ -ethoxyethylglucoside show no deviation from the law of mass action. If, separately, the hydrolysis of a definite amount of (I) and parallel to it the syntheses of the same glucoside are effected whereby equiv. amounts of glucose and (I) are involved, it is possible to calculate four velocity coeffs. The hydrolysis experiment gives a velocity coeff. for the hydrolysis  $k_2$  and for the synthesis  $k_1$  by reason of the reversible process. Analogously from the synthetic experiment velocity coeffs. for the synthesis  $k_1$  and for the opposed hydrolysis  $k_2$  are derived. The ratio of any velocity coeff. of hydrolysis to any velocity coeff. of synthesis is the same and is identical with the equilibrium const. from the concns. at the completion of the reaction. von Euler's hypothesis is not applicable to the synthesis of  $\beta$ -glucosides even in those cases in which the affinity of the glucoside for  $\beta$ -glucosidase may be assumed to differ appreciably from that of glucose. H. W.

**Photochemical reactions of *o*-nitrobenzylidenacetals.** IX. *o*-Nitrobenzylidenacetals of the oses. I. TANASESCU and E. CRACIUNESCU (Bull. Soc. chim., 1936, [v], 3, 581—598; cf. A., 1933, 275, 393; 1934, 169).—Treatment of galactose with  $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in presence of  $\text{P}_2\text{O}_5$  or, preferably, anhyd.  $\text{Na}_2\text{SO}_4$  at 40—45° for 5—6 hr. gives 1:2(? 1:3)-4:6-*di-o-nitrobenzylidenegalactose* (I), m.p. 135° after softening,  $[\alpha] \pm 0^\circ$  in  $\text{CHCl}_3$  or  $\text{C}_5\text{H}_5\text{N}$ . It is very resistant to acid hydrolysis, which, however, can be effected by  $\text{HNO}_3$  (1:1). It does not react with  $\text{AcCl}$  or  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  or in presence of alkali, and is indifferent towards  $\text{PhSO}_2\text{Cl}$  or  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ . It does not give a phenylhydrazone or reduce  $\text{Ag}_2\text{O}\cdot\text{NH}_3$ . Reduction of (I) with Zn dust in boiling  $\text{COMe}_2$  containing  $\text{CaCl}_2$  gives a very unstable basic substance, m.p. 118°. Insolation of (I) in  $\text{CHCl}_3$  affords 1:2(? 1:3)-*o-nitrobenzylidenegalactose* 4-*o*-

*nitrosobenzoate*, m.p. 147° after shrinking,  $[\alpha] \pm 0^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , the constitution of which is deduced from the isolation of the corresponding 6-*benzoate*, m.p. 165° (decomp.) after softening, 6-*acetate*, m.p. about 135° after softening, and 6-*benzenesulphonate*, m.p. 162° after softening, and its condensation with 1 mol. of  $\text{NH}_2\text{Ph}$  in glacial  $\text{AcOH}$  to 1:2(? 1:3)-*o-nitrobenzylidenegalactose* 4-*o-phenylazobenzoate*, m.p. 154° after shrinking. 1:2(? 1:3)-4:6-*Di-m-nitrobenzylidenegalactose*, m.p. 122° after softening, is obtained similarly but in poorer yield, and is similarly reduced to an unstable base.  $\alpha$ -Methylgalactoside and  $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in presence of  $\text{P}_2\text{O}_5$  (but not of anhyd.  $\text{Na}_2\text{SO}_4$ ) at 45° afford 2:3-4:6-*di-o-nitrobenzylidene- $\alpha$ -methylgalactoside*, m.p. 105° after softening, rapidly isomerised by insolation in  $\text{CHCl}_3$  to the substance  $\text{C}_{21}\text{H}_{20}\text{O}_{10}\text{N}_2$ , m.p. 155° after softening. 1:2(? 1:3)-4:6-*Di-o-nitrobenzylidenemannose*, m.p. 120° after softening, readily obtained at  $\geq 50^\circ$ , is hydrolysed by  $\text{HNO}_3$  (1:1), cannot be acylated, and does not give a phenylhydrazone; insolation of it affords 1:2(? 1:3)-*o-nitrobenzylidenemannose* 4-*o-nitrosobenzoate*, m.p. 145° after softening,  $[\alpha] \pm 0^\circ$ , which yields a 4-*benzoate*, m.p. 165° after softening, and 4-*benzenesulphonate*, m.p. 160° after softening, and is transformed by  $\text{NH}_2\text{Ph}$  into 1:2(? 1:3)-*o-nitrobenzylidenemannose* 4-*o-phenylazobenzoate*, m.p. 154° after softening. 1:2(? 1:3)-*Di-m-nitrobenzylidenemannose*, m.p. 110° after softening, is reduced to a very unstable base. In presence of  $\text{P}_2\text{O}_5$  at 40°, rhamnose is rapidly condensed to 1:2-3:4-*di-o-nitrobenzylidenerrhamnose*, m.p. about 105° (decomp.), which cannot be acylated and is isomerised to the compound  $\text{C}_{20}\text{H}_{19}\text{O}_9\text{N}_2\cdot\text{H}_2\text{O}$ , m.p. about 150° after softening, 2:3-4:6-*Di-o-nitrobenzylidenefructose*, m.p. 112° after softening,  $[\alpha] \pm 0^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , gives a phenylhydrazone, m.p. 126°, after softening. Lactose in presence of  $\text{P}_2\text{O}_5$  and  $\text{Na}_2\text{SO}_4$  at 70° slowly affords *tri-o-nitrobenzylidenelactose*, m.p. about 220° after softening, isomerised by light to the compound  $\text{C}_{33}\text{H}_{31}\text{O}_{17}\text{N}_3$ , m.p.  $> 300^\circ$ . Sucrose more readily yields *di-o-nitrobenzylidenesucrose*, m.p. 135° after softening, converted by insolation into the substance  $\text{C}_{26}\text{H}_{28}\text{O}_{13}\text{N}_2$ , m.p. 185° after softening. H. W.

**Hyperacetylation of aldoses.** N. W. PIRIE (Biochem. J., 1936, 30, 374—376).—The *hepta-acetates* of *d*-galactose, m.p. 106°,  $[\alpha]_D + 4.0^\circ$ , *d*-mannose, m.p. 122°,  $[\alpha]_D + 0.4^\circ$ , *d*-glucose, m.p. 121—122°,  $[\alpha]_D^{20} + 7.9^\circ$ , and the *hexa-acetates* of *l*-arabinose, m.p. 91°,  $[\alpha]_D^{20} - 27.7^\circ$  (all in  $\text{CHCl}_3$ ), *l*-rhamnose, m.p. 72—73°,  $[\alpha]_D^{20} - 7.5^\circ$  in  $\text{MeOH}$ , and *d*-xylose,  $[\alpha]_D^{17} + 4.0^\circ$  in  $\text{CHCl}_3$ , were prepared from the appropriate aldose penta- and tetra-acetate  $\text{Et}_2$  mercaptals. *d*-Mannose penta-acetate, m.p. 51—52°,  $[\alpha]_D^{17} + 31.2^\circ$  in  $\text{CHCl}_3$ , and *l*-rhamnose tetra-acetate  $\text{Et}_2$  mercaptal, m.p. 60°,  $[\alpha]_D^{15} + 39.5^\circ$  in  $\text{CHCl}_3$ , are described. H. D.

**Preparation of *dl*-galactose hepta-acetate by the acetolysis of agar.** N. W. PIRIE (Biochem. J., 1936, 30, 369—373).—*dl*-Galactose hepta-acetate (I) is prepared by treatment of agar with  $\text{Ac}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ . After slight hydrolysis of agar with 0.1N- $\text{H}_2\text{SO}_4$  for 40 min.,  $\text{Ac}_2\text{O}$  gave the usual yield of (I); completely hydrolysed agar gave no (I) but *dl*- and *d*-galactose penta-acetate were isolated. H. D.



**Oxidation of mannose to mannonic acid by *B. gluconicum*.**—See this vol., 640.

(A) Delay and "prolongation" of reaction during the decomposition of fructose in ultra-violet light. Light-induced [light-activated] fructose. (B) Effect of sodium chloride and other metal halides on [the decomposition of] fructose in ultra-violet light. R. CANTIENI (Helv. Chim. Acta, 1936, 19, 270—276, 276—280).—(A) 10% aq. fructose solution decomposes in ultra-violet light to give CO with a little CO<sub>2</sub> and (in light of short  $\lambda$ ) H<sub>2</sub> (cf. A., 1932, 237). Reaction commences only after irradiation for about 45 min., then increases to a fixed val. ("delay of reaction"), and continues at a decreasing rate for many hr. after irradiation has ceased ("prolongation of reaction"). The vol. of gas liberated after cessation of irradiation about equals the decrement due to the delay of the reaction. It is assumed that a "light-induced" (light-activated) fructose mol. is formed by absorption of a light quantum, that this mol. has a moderate stability, and decomposes at a rate  $\propto$  its concn. partly into ordinary fructose and partly into CO and C<sub>5</sub>H<sub>12</sub>O<sub>5</sub>. In accordance with this view, (a) the activated mol. is less stable at 100° than at room temp. (since the "prolongation" is very slight at 100°), and (b) light of short  $\lambda$  gives a less stable activated mol. (less "prolongation") than does light of long  $\lambda$ . Increase of pressure increases both the delay and prolongation of the reaction, indicating increased stability of the activated mol.

(B) Addition of 25% of NaCl to a 10% fructose solution irradiated by ultra-violet light of long  $\lambda$  decreases the delay and prolongation of the reaction, without affecting the total vol. of gas liberated. The stability of the activated mol. is reduced by about 50%; the time required to give sufficient CO to be detected by hæmoglobin is reduced from 255 to 97.5 sec. KBr and, more so, KI reduce the total vol. of gas liberated, presumably by favouring decomp. of the activated mol. to ordinary fructose. R. S. C.

**Velocities of hydrolysis of glucosides.**—See this vol., 572.

**Digitalis glucosides. VI. Existence of two anhydrodigoxigenins.** S. SMITH (J.C.S., 1936, 354—355; cf. A., 1935, 1355).—Digoxigenin and conc. HCl at 10—0° give an unstable Cl-compound, m.p. 185° after decomp. at 120°, converted by hot aq. MeOH into  $\alpha$ -anhydrodigoxigenin, m.p. 192°,  $[\alpha]_{D}^{20} +46^\circ$  in MeOH (diacetate, m.p. 155°,  $[\alpha]_{D}^{20} +68^\circ$  in MeOH), oxidised by CrO<sub>3</sub> to  $\alpha$ -anhydrodigoxigenone, m.p. 178°,  $[\alpha]_{D}^{20} +136^\circ$  in MeOH [semicarbazone, m.p. 235° (decomp.); dioxime, an oil], and a substance, m.p. 215°. The similarity of this anhydro-compound and its known isomeride (now called  $\beta$ -), m.p. 182°,  $[\alpha]_{D}^{20} -16.3^\circ$ , to  $\alpha$ - and  $\beta$ - ( $[\alpha]_{D}^{20} -17.3^\circ$ ) -anhydrodigitoxigenin, respectively, is noted. R. S. C.

**Determination of particle size of polysaccharides by osmotic pressure measurements.** S. R. CARTER and B. R. RECORD (Chem. and Ind., 1936, 218—219).—Preliminary results obtained with methylated and acetylated inulin or glycogen, and methylated starch or dextrin, point to the association of the chemical units of the polysaccharide mols. into larger

aggregates and confirm the structural views of Haworth and collaborators. E. S. H.

**Colloid-chemical aspects of starch.** J. ALEXANDER (Chem. and Ind., 1936, 206—209).—Starch from maize, potato, tapioca, wheat, or rice swells and ultimately disperses in cold, conc. HCO<sub>2</sub>H. The optical properties and behaviour on dilution with H<sub>2</sub>O of such solutions are described. The rôle of colloidal protection in the behaviour of starches is discussed. E. S. H.

**Hydrolysis of starch by hydrogen peroxide and ferrous sulphate.** W. R. BROWN (J. Biol. Chem., 1936, 113, 417—425; cf. Omori, A., 1932, 346).—The reaction is one of hydrolysis and appears to be a true catalysis, producing dextrans, sugars of high mol. wt., and simple sugars. It is analogous to that of amylase except that the simple sugars are further hydrolysed and oxidised to aldehydes and acids. It is assumed that the Fe transfers energy from the H<sub>2</sub>O<sub>2</sub> breakdown to the starch, causing it to be reactive. J. N. A.

**Starch nitrate.** G. CENTOLA (Gazzetta, 1936, 66, 8—15).—Rice starch with HNO<sub>3</sub> of varying concn. yields nitrates with 8.5—12.4% N. The last, the trinitrate, gives an X-ray spectrogram corresponding with a lattice distance of 7.15 Å., and similar to that given by collodion cotton of 12% N; it thus has the same structure as unstable cellulose trinitrate. Products of lower N content give diffraction lines in the same position, but wider and less distinct; the trinitrate is mixed with unchanged starch. Reaction is much more rapid than that of cellulose, owing to ease of penetration of starch grains. HNO<sub>3</sub>—H<sub>2</sub>SO<sub>4</sub>—H<sub>2</sub>O mixtures containing H<sub>2</sub>O > 20% or H<sub>2</sub>SO<sub>4</sub> > 73% give very poor yields, owing to hydrolysis and oxidation. The product obtained when H<sub>2</sub>SO<sub>4</sub> is present can be fractionated into amylose nitrate, sol. in MeOH, and amylopectin nitrate, insol.; these are hydrolysed to amylose and to amylopectin. Differences in X-ray spectra of starches of groups A, B, and C (A., 1933, 464) disappear when the latter are converted into nitrates, which thus have the same structure. E. W. W.

**Behaviour of cellulose in solutions of mineral acids. I. Determination of its mol. wt. in phosphoric acid solution. II. Kinetics of the degradation of cellulose in acid solutions.** A. AF EKENSTAM (Ber., 1936, 69, [B], 549—552, 553—559).—I. The process of dissolution of cellulose (I) in acids involves swelling. The initial process consists in the formation of oxonium compounds such as (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, 2H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>)<sub>n</sub>, (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, 4H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>)<sub>n</sub>, and (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, H<sub>2</sub>O, HNO<sub>3</sub>)<sub>n</sub>. These compounds, if obtained from hemicolloidal (I), are sol. in very dil. acid, but if derived from highly polymerised (I) require acid of increasing concn. as the mol. wt. increases. At low temp. they are dissolved by a more dil. acid than at a higher temp. From the clear solutions ppts. in more or less swollen form are obtained by addition of H<sub>2</sub>O or dil. acid (provided the material is moderately complex), and these yield (I) free from acid if sufficiently washed with H<sub>2</sub>O. Except with HNO<sub>3</sub> esterification does not take place. H<sub>3</sub>PO<sub>4</sub> is preferable to H<sub>2</sub>SO<sub>4</sub> as solvent for (I), since it is less degrading;



the solutions can be kept unchanged for several hr., particularly at low temp., and are not sensitive to air, so that, in this respect,  $H_3PO_4$  is preferable to Schweitzer's reagent as solvent. Viscosimetric determinations of the mol. wt. of (I) in  $H_3PO_4$  are recorded. The highest val. (157,000) is observed for Swedish filter-paper, which contains very little native (I). The vals. for native (I) such as cotton are very uncertain and are greater in  $H_3PO_4$  than in Schweitzer's reagent. Pure hydrocellulose (II) gives concordant results in each solvent.

II. Correlation of viscosity with age of the solution shows that (II) in  $H_3PO_4$  is degraded initially at a const. rate which alters when the mol. wt. has declined to a few thousand. Native (I) is very rapidly degraded shortly after its dissolution, but the rate soon declines and gradually approaches that of (II). The relationships in  $H_2SO_4$  are similar but the initial rates are not so obvious as with  $H_3PO_4$ . A const. initial rate of degradation of (II) is not observed, the val. declining steadily. With native (I) the initial rate is somewhat  $>$  with (II), but the rates for (I) and (II) gradually become identical. It appears therefore that (II) of high mol. wt. contains a single type of linking affected by acid, whereas native (I) usually contains much larger mols. than (II) and has, in addition to the ordinary glucosidic linking, a type of union much more rapidly hydrolysed by acid.

H. W.

**Constitution of cellulose xanthates.** IV. T. LIESER and E. LECKZYCK (Annalen, 1936, 522, 56—65).—Cellulose (I) undergoes pronounced swelling in 2*N*. but dissolves in 2·27—4*N*- $NEt_4$ ·OH. (I) swells in 2*N*-, dissolves in 2·1—3·6*N*-, and is insol. in 3·8*N*-*p*-tolyltrimethylammonium hydroxide (II); the corresponding *N* for  $NEtBu_3$ ·OH are 1·5, 1·7—2·4, and 2·6. The min. concn. for complete solubility thus decreases with increased mol. wt. of the base. (I) reacts rapidly with  $CS_2$  in 3·7*N*- $NEt_4$ ·OH at 0° to give  $(NEt_4)_3$  cellulose trixanthate (III), which is oxidised by 0·1*N*-I in MeOH to the nearly pure trixanthogen,  $[C_6H_7O_5(CS_2)_3]_2$ . (III) is sol. in MeOH (pptd. by  $Et_2O$ ) or  $COMe_2$ , but is insol. in EtOH. When solutions of (III) in  $H_2O$  or MeOH are kept for 3 days at room temp. and then oxidised by I, the xanthogen formed contains 18—20% S; the "ripening" is much slower in MeOH at 0°. The dixanthogen,  $[C_6H_8O_5(CS_2)_2]_2$ , is the main product from (I),  $CS_2$ , and 2·5*N*- $NPr_4$ ·OH, 2·35*N*- $NEtBu_3$ ·OH, or 3·6*N*-(II), followed by oxidation. (I) is insol. in CsOH (all concns.).

H. B.

**Degradation of simple amines during "kjeldahlisation."** E. KAHANE and J. G. CARRERO (Bull. Soc. chim., 1936, [v], 3, 397—408).— $NH_2Me$  is produced rapidly from  $NHMe_2$ , and slowly from  $NMe_3$ , during the action of boiling conc.  $H_2SO_4$ ; slow conversion into  $NH_3$  then occurs. The analogous changes with  $NHEt_2$  and  $NEt_3$  take place more readily. Catalysts, in increasing order of efficiency, are  $K_2SO_4 + CuSO_4$  (A),  $HClO_4$ ,  $SeO_2$ ;  $NH_2Et$  is thus completely converted into  $NH_3$ .  $NH_3$  is formed to the extent of 87—97% during "kjeldahlisation" [catalyst (A)] of  $(CH_2)_6N_4$ ,  $NHPhMe$ ,  $NPhMe_2$ , and novocaine; ephedrine, adrenaline, and hordenine

similarly give (mainly)  $NH_3 + NH_2Me$ , whilst betaine affords  $NH_2Me + NHMe_2$ . The amine mixtures are determined by Weber and Wilson's method (A., 1918, ii, 377).

H. B.

**Decomposition of ethylamine and diethylhydrazine.**—See this vol., 568.

**Action of ammonia on esters.** F. D. CHATTAWAY (J.C.S., 1936, 355—358).—The normal action of  $NH_3$ ,  $NH_2R$ , or  $NH_2\cdot NHR$  on esters,  $R'\cdot CO_2R''$  ( $\rightarrow R'\cdot OH + R'\cdot CO\cdot NH_2$  etc.), is due to the cationoid nature of the C of the  $CO$ . If, however, the alkyl carries a sufficiently powerful cationoid centre, the N will become attached to  $R''$ , yielding  $R'\cdot CO_2H$  and  $NH_2R''$  etc., as in the following cases. With the appropriate basic reagents under the usual conditions  $CCl_3\cdot CH(CH_2\cdot NO_2)\cdot OAc$  yields  $\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -aminopropane, b.p.  $108^\circ/2$  mm. (hydrochloride, cryst.; Ac derivative, m.p.  $137^\circ$ ), and the corresponding  $\beta$ -*p*-toluidino-, m.p.  $61^\circ$ ,  $\beta$ -phenyl-, m.p. about  $120^\circ$  (decomp.) [ $Ac_2$  derivative, m.p.  $199$ — $200^\circ$  (decomp.)],  $\beta$ -*p*-tolyl-, m.p.  $115^\circ$  ( $Ac_2$  derivative, m.p.  $157$ — $158^\circ$ ),  $\beta$ -chlorophenyl-, m.p.  $118^\circ$  ( $Ac_2$  derivative, m.p.  $152^\circ$ ), 2:4-dichlorophenyl-, m.p.  $79^\circ$  ( $Ac_2$  derivative, m.p.  $125^\circ$ ), and  $\beta$ -*m*-nitrophenyl-hydrazino-compounds, m.p.  $112$ — $113^\circ$ .  $CHMeCl\cdot CCl_2\cdot CH(CH_2\cdot NO_2)\cdot OAc$  gives similarly  $\gamma\gamma\delta$ -trichloro- $\alpha$ -nitro- $\beta$ -amino-, m.p.  $54$ — $55^\circ$  (hydrochloride, cryst.; Ac derivative, m.p.  $104^\circ$ ),  $\beta$ -*p*-toluidino-, m.p.  $110^\circ$ , and  $\beta$ -phenylhydrazino-pentane, m.p.  $129^\circ$  (Ac, m.p.  $111^\circ$ , and  $Ac_2$  derivative, m.p.  $158$ — $159^\circ$ ).

R. S. C.

**Reaction of tris- $\beta$ -hydroxyethylamine with tungstic acid.**—See this vol., 575.

**Oxidation of amino-acids by hypochlorite.** I. Glycine. M. F. NORMAN (Biochem. J., 1936, 30, 484—496).—For complete oxidation of glycine (I) by  $NaOCl$ , 1 mg. of (I) requires 4·26 mg. of Cl, the observed increase in Cl' being equiv. to one half of the Cl used. The reaction is complete in 2 hr. between concns. of 0·05 millimol. per 100 ml. of acid or alkali, but is retarded at a higher concn. During the reaction the  $p_H$  falls, oxidation being most rapid between  $p_H$  7 and 9. In the first stage  $HCN$ ,  $CO_2$ , and  $H_2O$  are formed;  $HCN$  then gives  $HCO_2H$  and  $NH_3$  and finally  $CO_2$ ,  $H_2O$ , and  $N_2$ , thus accounting for  $4\frac{1}{2}$  atoms of O per mol. of (I).

H. G. R.

**Effect of heat on betaine.** H. T. STRAW and H. T. CRANFIELD (J.S.C.I., 1936, 55, 40—41t).—Betaine as the free base was prepared by neutralising betaine hydrochloride dissolved in MeOH with 25%  $NaOH$ -MeOH, pptd.  $NaCl$  being removed by filtration. On heating the recryst. and dried betaine in a current of air no decomp. occurred below  $200^\circ$ , but at  $260^\circ$  a pale yellow oil began to distil over, the rate of evolution increasing up to  $295^\circ$  and decomp. being complete at  $300^\circ$ . The products isolated were  $NMe_2\cdot CH_2\cdot CO_2Me$  (max. yield 30%),  $NMe_3$ ,  $NHMe_2$ ,  $NH_2Me$ ,  $N_2$ ,  $CH_3O$ , pyrrole, and a carbonaceous residue containing N. The distribution of N in the main decomp. products was 7·2% as  $NHMe_2$ , 29·7% as  $NMe_3$ , 19·9% as  $N_2$ , 32·6% as oil, and 10·6% as residues.

**Stepwise degradation of polypeptides.** M. BERGMANN, L. ZERVAS, and (in part) F. SCHNEIDER



(J. Biol. Chem., 1936, 113, 341—357; cf. A., 1934, 802).—Stepwise degradation of polypeptides is effected thus:  $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{NHBz}\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{CON}_3\cdot\text{CH}_2\text{Ph}\cdot\text{OH} \rightarrow \text{NHBz}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{Ph} + \text{H}_2 \xrightarrow{\text{Pd}} \text{NHBz}\cdot\text{CHR}\cdot\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{R}\cdot\text{CHO}$  (characterised). Thus *N*-benzoyl-*l*-leucine *Me* ester, m.p. 104° (from *l*-leucine-HCl-MeOH-BzCl), with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ -EtOH gives the *hydrazide*, m.p. 153°, converted by  $\text{NaNO}_2\cdot 5\text{N}\cdot\text{HCl}$ -50% AcOH at 0°, and  $\text{CH}_2\text{Ph}\cdot\text{OH}$  into  $\alpha$ -benzamido- $\alpha$ -carbobenzyloxyamido-, m.p. 178°, reduced ( $\text{H}_2$ -Pd-5N-HCl) to  $\alpha$ -amino- $\alpha$ -benzamido- $\gamma$ -methyl-*n*-butane hydrochloride,  $[\alpha]_D^{25} -47^\circ$  in MeOH [converted by boiling MeOH into a (*NHBz*)<sub>2</sub> derivative, m.p. 210°, of  $\text{Bu}^t\text{CHO}$ ], converted by distillation with  $\text{H}_2\text{O}$  into  $\text{Bu}^t\text{CHO}$ , isolated as its *p*-nitrophenyllhydrazone. Similar degradation of benzyl-dl-phenylalanine *Me* ester, m.p. 90°, affords, successively, its *hydrazide*, m.p. 192°,  $\alpha$ -benzamido- $\alpha$ -carbobenzyloxyamido-, m.p. 196°, and  $\alpha$ -amino- $\alpha$ -benzamido- $\beta$ -phenylethane, m.p. 156°, previous sintering (converted by  $\text{HNO}_2$  into a substance, m.p. 128°), the hydrochloride of which gives  $\text{NH}_2\text{Bz}$  and  $\text{CH}_3\text{Ph}\cdot\text{CHO}$  (as oxime). Similarly *Me* benzoyl-*l*-glutamate, m.p. 83°, gives its dihydrazide, m.p. 216°, diazide, decomp. 75°,  $\alpha$ -benzamido- $\alpha$ - $\gamma$ -biscarbobenzyloxyamidopropane, m.p. 174°, hydrogenated to the dihydrochloride, m.p. 158°,  $[\alpha]_D^{25} -50\cdot7^\circ$  in  $\text{H}_2\text{O}$  (dipicrate, + $\text{H}_2\text{O}$ , decomp. 100°), hydrolysed to  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$  (I) (dimedon compound, m.p. 208—209°). The Et ester of *l*-alanine and  $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COCl}$  with 10%  $\text{Na}_2\text{CO}_3$  in EtOAc gives the Et ester, m.p. 59°, of carbobenzyloxyglycyl-*l*-alanine, converted into the *hydrazide*, m.p. 133°, and the *azide*, which with *l*-leucine *Me* ester gives the *Me* ester, m.p. 112°, of carbobenzyloxyglycyl-*l*-alanyl-*l*-leucine, converted through the *hydrazide*, m.p. 186°, into *Me* carbobenzyloxyglycyl-*l*-alanyl-*l*-leucyl-*l*-glutamate, m.p. 149°, hydrolysed to glycyl-*l*-alanyl-*l*-leucyl-*l*-glutamic acid + $1\cdot5\text{H}_2\text{O}$  {Bz derivative, m.p. 215° [*Me*<sub>2</sub> ester (II), m.p. 178°]}. Degradation of (II) is effected through its dihydrazide, m.p. 253°, diazide, the dicarbobenzyloxy-derivative, m.p. 201°, hydrogenated to (I) and benzoylglycyl-*l*-alanyl-*l*-leucylamide, m.p. 186°, the *hydrazide*, m.p. 230°, of which similarly affords the benzoylglycyl-*l*-alanyl derivative, m.p. 212°, of  $\alpha$ -amino- $\alpha$ -carbobenzyloxyamido- $\gamma$ -methylbutane, hydrogenated to  $\text{Bu}^t\text{CHO}$  and benzoylglycyl-*l*-alanyl-*l*-leucylamide, m.p. 192°, the *hydrazide*, m.p. 212°, of which is degraded to the benzoylglycyl derivative, m.p. 207°, of  $\alpha$ -amino- $\alpha$ -carbobenzyloxyamidoethane, hydrogenated to MeCHO and hippuramide.

J. W. B.

**Occurrence of prolinase.** E. ABDERHALDEN and R. MERKEL (Fermentforsch., 1936, 15, 1—23; cf. A., 1933, 615).—Attempts have been made to isolate the enzyme following observations of the effects of enzyme complexes on prolyl peptides. Of the peptides tested only those containing tyrosyl directly united to  $\text{CO}_2\text{H}$  are hydrolysed by trypsin (I). (I) attacks glycyl-*l*-prolyl-*l*-phenylalanine (II) slightly, *l*-leucyl-*l*-prolyl-*l*-tyrosine (III) strongly, and dl-alanyl-*l*-prolyl-*l*-phenylalanine (IV), *l*-prolylglycine (V), *l*-prolyl-*l*-alanine (VI), *l*-prolyl-*l*-serine (VII), dl-leucyl-*l*-prolylglycine (VIII), and dl-leucyl-*l*-prolyl-*l*-alanine (IX) not at all. (I) [but not erepsin (X)] hydrolyses

chloroacetyl-*l*-prolyl-*l*-phenylalanine, dl- $\alpha$ -bromopropionyl-*l*-prolyl-*l*-phenylalanine, and dl- $\alpha$ -bromoisohexoyl-*l*-prolyl-*l*-alanine. (X) attacked all the prolyl di- and tri-peptides.  $\text{H}_2\text{S}$  inactivated prolinase (XI) and dipeptidase (XII) and diminished the activity of aminopolypeptidase (XIII). Ag<sup>+</sup> and HCN diminished, in different degrees, the activity of (XI), (XII), and (XIII). The activity of (XI) and (XIII) is greatly and that of (XII) is slightly diminished by shaking (15—35 hr.). (XI) could not be isolated from solutions containing also (XII) and (XIII) by adsorption on Fe oxide and  $\text{Al}_2\text{O}_3$  but partial separation was effected. *l*-Prolyl-*l*-tyrosine (XIV) has m.p. 228°,  $[\alpha]_D^{20} -7\cdot56^\circ$ . *l*-Prolyl-*l*-phenylalanine (XV) is obtained from the product of interaction of *N*-carbobenzyloxy-*l*-proline (XVI) and  $\text{PCl}_5$  by treatment with *l*-phenylalanine Et ester and subsequent hydrolysis. The *N*-carbobenzyloxy-*l*-prolyl-*l*-phenylalanine produced gives (XV) with Pd- $\text{H}_2$ . The product of interaction of *l*-serine and (XVI) chloride gives, with Pd- $\text{H}_2$ , (VII), m.p. 215—216°,  $[\alpha]_D^{20} -47\cdot9^\circ$  in  $\text{H}_2\text{O}$ . *N*-Carbobenzyloxy- (V) has m.p. 127°. Alanine with (XVI) chloride gives *N*-carbobenzyloxy-*l*-prolyl-*l*-alanine, m.p. 153°, which, with Pd- $\text{H}_2$  yields (VI), m.p. 232°,  $[\alpha]_D^{20} -66\cdot33^\circ$  in  $\text{H}_2\text{O}$ . (XV) with AcCl gives the chloroacetyl derivative, m.p. about 78°, which yields (II), m.p. 200—202°, on amination and with dl- $\alpha$ -bromopropionyl chloride it gives  $\alpha$ -bromopropionylprolylphenylalanine, m.p. 153—154°, which with  $\text{NH}_3$  gives (IV), m.p. 176°,  $[\alpha]_D^{20} -58\cdot3^\circ$  in  $\text{H}_2\text{O}$ . (XIV) with d- $\alpha$ -bromoisohexoyl chloride gives  $\alpha$ -bromoisohexoylprolyltyrosine, m.p. about 108°, which with  $\text{NH}_3$  yields (III), m.p. about 222°,  $[\alpha]_D^{25} -7\cdot46^\circ$  in  $\text{H}_2\text{O}$ . In the same way (V) gives dl- $\alpha$ -bromoisohexoylprolylglycine, m.p. 89—91°, which yields (VIII), m.p. 224°,  $[\alpha]_D^{24} -9\cdot71^\circ$  in  $\text{H}_2\text{O}$ , and (VI) gives  $\alpha$ -bromoisohexoylprolylalanine, m.p. 107—109°,  $[\alpha]_D^{25} -67^\circ$  in EtOH, which yields (IX), m.p. 221°,  $[\alpha]_D^{25} -37\cdot36^\circ$  in  $\text{H}_2\text{O}$ . W. McC.

#### Oxidation of cystine in non-aqueous media.

**V. Isolation of a disulphoxide of *l*-cystine.** G. T. TOENNIES and T. F. LAVINE. **VI. Reactions of the disulphoxide of *l*-cystine, especially its dismutative decompositions.** T. F. LAVINE (J. Biol. Chem., 1936, 113, 571—582, 582—597).—V. Two improved techniques for the oxidation of *l*-cystine perchlorate by  $\text{BzO}_2\text{H}$  in MeCN (A., 1934, 284) to give a 75% yield of *l*-cystine disulphoxide (I), m.p. 179—182° (decomp.) (corr.),  $[\alpha]_D^{25} -30\cdot2^\circ$  in *N*-HCl, isolated by virtue of its slight  $\text{H}_2\text{O}$ -solubility, obtained cryst. by dilution of its saturated solution in *N*-HCl, are described. Rise of temp. from  $-10^\circ$  to  $25^\circ$  favours this reaction at the expense of the formation of higher oxidation products, only a slight excess of  $\text{BzO}_2\text{H}$  being necessary to ensure complete removal of cystine (essential).  $\text{O}_2$  consumption in the non-aq. solution is controlled by titration of the I liberated from *N*-KI-0.05N- $\text{H}_2\text{SO}_4$ , and cystine removal by colorimetric determination (cyanide-nitroprusside). The effects of varying the cystine/ $\text{BzO}_2\text{H}$  ratio, total concn., and temp. are tabulated. Oxidation of (I) by I:  $\text{R}\cdot[\text{SO}]_2\cdot\text{R} + 3\text{I}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{R}\cdot\text{SO}_2\text{H} + 6\text{HI}$  (a), and reduction by KI-HCl:  $(\text{I}) + 4\text{HI} \rightarrow (\cdot\text{SR})_2 + 2\text{I}_2 + 2\text{H}_2\text{O}$ , are almost quant. The isoelectric point of (I) is at  $p_H$  3.



VI. Various decomp. of (I) are studied by determination of the intermediate oxidising val. by use of reaction (a) (complete in 1—2 hr. with 1—2*N*-HCl-KI), and by determination of cystine (above). Aq. solutions of (I) undergo dismutative decomp. with formation of cystine (to an equilibrium val. of 33 mol. %), and acid derivatives, the rate of decomp. increasing with increasing  $p_H$  and rise of temp. In alkaline solution decomp. occurs thus:  $3(I) + 4NaOH \rightarrow (\cdot SR)_2 + 4R \cdot SO_2Na$ , isolation of the sulphinic acid, decomp. 152—153° (corr.),  $[\alpha]_{D}^{25} + 33.4^\circ$  in *N*-HCl, +11° in  $H_2O$ , -23.8° as its Na salt, being described. In acid solution, decrease in available intermediate O occurs, but the equation  $3(I) + 2H_2O \rightarrow (\cdot SR)_2 + 2R \cdot SO_2H + R \cdot SH \cdot O + R \cdot SO_3H$ , approx. represents the data. With cysteine, in either acid or alkaline solution, (I) reacts almost instantaneously:  $(I) + RSH \rightarrow (\cdot SR)_2 + R \cdot SO_2H$ , the sulphinic acid then reacting slowly with cysteine:  $R \cdot SO_2H + 3RSH \rightarrow 2(\cdot SR)_2 + 2H_2O$ . Similar reaction occurs with  $H_2S$ , thioglycolic acid, and *p*-thiocresol [ $(\cdot S \cdot C_6H_4Me \cdot p)_2$  isolated].  $2(I) + 2ArSH \rightarrow (\cdot SR)_2 + (\cdot SAr)_2 + 2R \cdot SO_2H$ . With NaCN the reaction is  $(I) + NaCN \rightarrow R \cdot SCN + R \cdot SO_2Na$ , and with phosphorus acid a blue colour develops at  $p_H$  5.2, probably due to formation of cysteine:  $2(I) + H_2O \rightarrow 2RS \cdot OH + 2R \cdot SO_2H$ ;  $2RS \cdot OH \rightarrow RSH + R \cdot SO_2H$ , which is thus prevented from further reaction with (I).

J. W. B.

Reduction of cystine by sodium sulphite. T. CHEN (Chinese J. Physiol., 1936, 10, 187—189).—One mol. of cystine yields only one mol. of cysteine (I) on reduction by  $Na_2SO_3$ , whilst by electrolysis 2 mols. of (I) are produced.

J. N. A.

Nickel nitroprusside reaction for reduced glutathione. D. ZIMMET (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 225—226).—The use of a reagent containing 5 g. of  $NiCl_2$  and 5 c.c. of a 10% solution of  $Na_2Fe(NO)(CN)_5$  made up to 100 c.c., for the detection of reduced glutathione (I) is described. In the presence of (I) the colour of the reagent changes from pale green to pale pink. 1 p.p.m. of (I) can thus be detected. The necessity of adding a base as in the nitroprusside test for (I) is avoided. Advantages of the new method are the greater persistence of the colour and the absence of any colour reaction with  $COMe_2$ .

E. A. H. R.

Synthesis of cyanamide by oxidation of formaldehyde and ammonia. R. FOSSE and P. DE GRAEVE (Compt. rend., 1936, 202, 799—803).—Oxidation of  $(CH_2O)_n$  in aq.  $NH_3$  with  $CaMn_2O_8$  gave a small yield of  $CN \cdot NH_2$ , which could be oxidised to  $HCNO$  and  $HCN$ .

J. N. A.

Sensitive colour reaction of carbamide. J. A. SANCHEZ (Ann. Chim. Analyt., 1936, [iii], 18, 65—66).—A solution of  $CO(NH_2)_2$  is evaporated down with aq.  $NHPh \cdot NH_2 \cdot HCl$  and heated at 160—170° for 5 min. The product is heated at 100° with a 0.5% solution of vanillin in conc. HCl. In presence of  $CO(NH_2)_2$ , urethanes, or carbazides a cerise coloration is obtained.

J. S. A.

Nitrosomethylcarbamide. F. ARNDT (Org. Syntheses, 1935, 15, 48—50).—Improved preps. from  $NH_2Me \cdot HCl$  and from  $Me_2SO_4$  are described.

CH. ABS. (r)

Transformation products of some hydrazides of organic acids. III. (SIGNA.) M. FRERI (Gazzetta, 1936, 66, 23—30; cf. A., 1934, 1372).—Me isocrotonate or chloroisocrotonate and  $N_2H_4 \cdot H_2O$  yield 5-methylpyrazolone.  $Me_2$  itaconate, b.p. 105°/12 mm. (new prep. using  $Me_2SO_4$ ), forms the dihydrazide, m.p. 150° (dibenzylidene derivative, m.p. 220°), which gives the diazide, m.p. 50° (decomp.). Mesocon-dihydrazide, m.p. 215° (decomp.), and -diazide, m.p. 111° (decomp.), are similarly obtained. Citracondihydrazide, m.p. 177° (dibenzylidene derivative, m.p. 222°), in dil. solution is converted by  $HNO_3$  in HCl into the diazide, m.p. 114° (decomp.), and in AcOH into 3:6-diketo-4-methyltetrahydropyridazine, m.p. 277°, whilst in conc. solution in HCl it gives 4-oximino-3-methyl-5-pyrazolone, m.p. 232° (decomp.) (K and Ag salts; Bz, m.p. 177°, and *p*-nitrobenzoyl, m.p. 188°, derivatives). The last is oxidised by  $O_2 + O_3$  in KOH to nitromethylpyrazolone, m.p. 276°, and is reduced ( $SnCl_2$ ) to the hydrochloride, m.p. 225°, of aminomethylpyrazolone [*p*-nitrobenzylidene, m.p. 257° (decomp.), anisylidene, m.p. 202—203°, and piperonylidene, m.p. 245°, derivatives]. The hydrochloride is oxidised by  $H_2O_2$  to a "rubazonic acid,"  $Me \cdot C_3H_2ON_2 \cdot N \cdot C_3HON_2 \cdot Me$ , m.p. 282—283° (decomp.); this is reduced ( $SnCl_2$ ) to 5:5'-diketo-3:3'-dimethyl-4:4'-dipyrazolylammonium chloride, m.p. 247° (decomp.), which is easily re-oxidised.

E. W. W.

Fluorination of silver cyanide. I. O. RUFF and M. GIESE (Ber., 1936, 69, [B], 598—603).— $Hg(CN)_2$  burns in  $F_2$  after being gently heated at one point in a  $SiO_2$  tube, giving essentially  $CF_4$ ,  $N_2$ , and  $HgF_2$ ;  $SiF_4$  and  $CO_2$  from the tube and  $C_2N_2$  from the original material are also obtained. A violent explosion ensues when  $AgCN$  and  $F_2$  come in contact at room temp., but the reaction can be controlled if  $AgCN$  is mixed with  $CaF_2$  and  $F_2$  is used under diminished pressure.  $AgF$  remains and is ultimately converted into  $AgF_2$ . The volatile products contain  $N_2$ ,  $CF_4$ , trifluoronitrosomethane, b.p.  $\sim -80^\circ/760$  mm., m.p.  $\sim -150^\circ$ ,  $CF_3 \cdot NF_2$ ,  $SiF_4$ ,  $COF_2$ ,  $CO_2$ ,  $N_2O$ ,  $C_2F_6$ , a mixture of isomerides  $(CNF_3)_2$ , and a mixture  $(CNF_4)_2$ . The course of the change is represented:  $Ag \cdot N \cdot C + F_2 \rightarrow Ag \cdot N \cdot CF_2$  (I);  $(I) + F_2 \rightarrow AgF + NF \cdot CF_2$  (II). (II) is exceedingly unstable by reason of the double linking and polymerises in many directions, mainly towards  $(CNF_3)_2$  with some production of  $(CN_3F)_3$  and production of combined polymerised substances. Further fluorination of  $CNF_3$  gives  $(CNF_4)_2$ ,  $CNF_5(NF_2 \cdot CF_3)$ , and  $C_3F_6$ . The presence of O in the  $AgCN$  gives rise to  $CF_3 \cdot NO$  and  $N_2O$  whilst  $SiO_2$  is the source of  $SiF_4$ ,  $COF_2$ , and  $CO_2$ .

H. W.

Isomerism of dicyanohexafluoride,  $C_2N_2F_6$ . II. O. RUFF and M. GIESE (Ber., 1936, 69, [B], 604—607).—The crude  $C_2N_2F_6$  is treated first with  $NH_3$  and then with  $Hg$  whilst a second portion is treated with the reagents in the reverse order, and the products are analysed. In evaluating the results



the following considerations are involved.  $\text{NH}_3$  reacts particularly on the  $\text{CF}_2\text{:N}\cdot$  and  $\cdot\text{CF:N}$  double linkings, Hg only on mobile F attached to N in  $\cdot\text{NF}$ . This is shown by the instability of unimol.  $\text{CF}_2\text{:NF}$  (which is not present among the products of the action of F on  $\text{AgCN}$ ) and by the observation that  $\cdot\text{NF}$  is far less stable than  $\cdot\text{NF}_2$  ( $\text{CF}_3\cdot\text{NF}_2$  is remarkably stable) whilst F is not removed from CF by Hg.  $\text{NH}_3$  is added to fluorinated N:C linkings and causes their fission with elimination of N. In presence of  $\text{NH}_3$  H cannot exist in union with a fluorinated C atom to which a fluorinated N is attached;  $\text{NH}_4\text{F}$  is produced with brown substances containing  $\text{C:N:F}=2:1:1$ . The chemically less active forms are regarded as *trans* varieties, increasing reactivity being shown by the *cis*- and *as*-forms. On this basis the isomerides  $\text{CF}_3\text{:N:N}\cdot\text{CF}_3$  (*cis*- and *trans*-),  $\text{CF}_3\text{:N}\cdot\text{CF}\cdot\text{NF}_2$  (*cis*- and *trans*-),  $\text{CF}_2\text{:N}\cdot\text{CF}_2\cdot\text{NF}_2$ , and  $\text{CF}_2\text{<}\begin{smallmatrix} \text{NF} \\ \text{NF} \end{smallmatrix}\text{>CF}_2$  or  $\text{CF}_2\text{<}\begin{smallmatrix} \text{CF}_2 \\ \text{NF} \end{smallmatrix}\text{>NF}$  are shown to be present. H. W.

**Action of thiocyanogen on unsaturated hydrocarbons.** A. KRASSILCHIK (Ann. Off. nat. Combust. liq., 1935, 10, 923—987).—The CNS method of determining unsaturation is more trustworthy than the Winkler-Dubowitz Br method. The prep. and use of the reagent are described. With 300% excess of CNS the reaction is bimol. and is practically complete in 10—40 hr. with absorption 60—95% of theoretical depending on the hydrocarbon. Certain hydrocarbons like stilbene do not react. Addition of I in AcOH is not as regular as that of CNS and is greatly influenced by traces of Cl or Br. Differences in the rate of addition of CNS may be used to fractionate mixtures of olefines, e.g., a mixture of  $\Delta^a$ - and  $\Delta^b$ -octene. R. B. C.

**Diazomethane.** F. ARNDT (Org. Syntheses, 1935, 15, 3—5).—An improved prep. from  $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}$  is described. CH. ABS. (r)

**Quantitative studies of organometallic compounds.** E. A. ZOELLNER (Iowa State Coll. J. Sci., 1934, 9, 213—214).—The yields of  $\text{MgRHal}$  obtained from a large no. of alkyl halides under various conditions are given; the practical significance of the results is discussed. CH. ABS. (r)

**Organic magnesium compounds. II. Reactions of aryl *p*-toluenesulphonates with Grignard reagents.** K. MINE (J. Chem. Soc. Japan, 1934, 55, 1087—1090; cf. A., 1935, 739).—Two reactions occur: (i)  $\text{R}\cdot\text{SO}_3\text{R}' + \text{MgXR}'' \rightarrow \text{R}\cdot\text{SO}_2\cdot\text{R}' + \text{OR}'\cdot\text{MgX}$  and (ii)  $\text{R}\cdot\text{SO}_3\text{R}' + \text{MgXR}'' \rightarrow \text{R}\cdot\text{SO}_2\cdot\text{OMgX} + \text{R}' + \text{R}''$ ; when  $\text{R}' = \text{aryl}$  (i) is the main reaction, but is replaced by (ii) when  $\text{R}' = \text{alkyl}$ . CH. ABS. (r)

**Photolysis of lead tetramethyl and lead tetraphenyl.**—See this vol., 573.

**Bisdimethylglyoxime diamine cobaltic salts and their configuration.** Y. NAKATSUKA and H. INUMA (Bull. Chem. Soc. Japan, 1936, 11, 48—54; cf. A., 1935, 51).—An EtOH solution of  $\text{CoCl}_3$  and of  $\text{OH}\cdot\text{N}:\text{CMe}\cdot\text{CMe}:\text{N}\cdot\text{OH}$  ( $\Delta\text{H}_2$ ) treated with aq.  $\text{NH}_3$  or with an org. base (*B*) and allowed to oxidise in the air gives compounds of type  $[\text{CoB}_2(\Delta\text{H})_2]\text{Cl}$ , from which

other salts are obtainable. In this way the *chlorides* in which  $B = \text{NH}_3$ ,  $\text{NH}_2\text{Ph}$ , *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ , *m*-4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}_2$ , and  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ , are prepared, and in most cases converted into the *bromides*, *iodides*, *thiocyanates*, *nitrates*, *sulphates*, and *H sulphates*; the *bases*

$[\text{Co}(p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2)_2(\Delta\text{H})_2]\text{OH}\cdot 2\text{H}_2\text{O}$  and  $[\text{Co}(\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2)_2(\Delta\text{H})_2]\text{OH}\cdot 2\text{H}_2\text{O}$  are also prepared. Since *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  gives the *chloride*  $[\text{Co}(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\Delta\text{H})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$ , and not one containing 1 mol. of *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  with both  $\text{NH}_2$  coordinated, the groups of the bases must be in *trans* configuration, and those of ( $\Delta\text{H}$ ) must lie in the same plane. In presence of NaOH, a compound  $[\text{Co}(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\Delta\text{H})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$ , containing non-ionisable Cl, is obtained.  $[\text{Co}(\Delta\text{H}_2)_2]\text{Cl}_2$  treated in  $\text{COMe}_2$  with  $\text{NH}_3$  or  $\text{NH}_2\text{Ph}$  gives the same compound, and not one of type  $[\text{CoB}_2(\Delta\text{H})_2]\text{Cl}$ ; if, however, *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  is used, the compound  $[\text{Co}(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\Delta\text{H}_2)_2(\text{H}_2\text{O})]\text{Cl}_2\cdot \text{COMe}_2$  is obtained, from which  $\text{H}_2\text{O}$  is not lost at  $110^\circ$  or over  $\text{H}_2\text{SO}_4$ , and which in  $\text{H}_2\text{O}$  has an acid reaction, owing apparently to the formation of  $[\text{Co}(o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2(\Delta\text{H}_2)_2(\text{OH})]\text{Cl} + \text{HCl}$ . E. W. W.

**Phosphoric oxide, catalyst for polymerisation of unsaturated hydrocarbons.** Decahydrodiphenyl obtained by dimerisation of *cyclohexene*. R. TRUFFAULT (Bull. Soc. chim., 1936, [v], 3, 442—459).—1-*cyclohexyl*- $\Delta^1$ -*cyclohexene* (I), b.p.  $103\text{—}105^\circ/12\text{ mm.}$ ,  $238\text{—}239^\circ/760\text{ mm.}$ , m.p. about  $-45^\circ$ , is obtained in 80—90% yield when *cyclohexene* (II) is condensed on  $\text{P}_2\text{O}_5$  (using a Soxhlet apparatus). (I) is reduced ( $\text{H}_2$ , Ni—Cr, hexane, room temp.) at nearly the same rate as (II), and is oxidised ( $\text{CrO}_3$ , AcOH) to adipic and  $\epsilon$ -keto- $\epsilon$ -*cyclohexylhexoic* acids. (I) and  $\text{HHal}$  in  $\text{CHCl}_3$  at  $0^\circ$  give 1-*chloro*-, m.p.  $40^\circ$  (similarly obtained from 1-*cyclohexylcyclohexanol*), 1-*bromo*-, m.p.  $46^\circ$  [converted by boiling  $\text{H}_2\text{O}$  or  $\text{AgOH}$  into (I)], and 1-*iodo*-, m.p.  $52^\circ$ , -*dicyclohexyl*. (I) and Br in  $\text{CHCl}_3$  at  $0^\circ$  afford 25% of (probably) 1:2:1'-*tribromodicyclohexyl*, m.p.  $127^\circ$ . (I) is also obtained in much smaller yield from (II) and  $\text{H}_3\text{PO}_4$ ;  $\text{HPO}_3$  is not a catalyst. (II) and 85%  $\text{H}_2\text{SO}_4$  give (cf. Brooks and Humphrey, A., 1918, i, 286; Nametkin and Abakumovskaja, A., 1933, 152, 385) 23% of *cyclohexanol* and 48% of *cyclohexyl H sulphate* or *cyclohexanesulphonic acid*.  $\text{P}_2\text{O}_5$  is a good catalyst for the prep. of diamylene (from  $\text{C}_5\text{H}_{10}$ ) and a hydrocarbon,  $\text{C}_{20}\text{H}_{32}$  (from limonene). H. B.

$\Delta^{1:3}$ -*cyclohexadiene* and structure of its monoxide. P. BEDOS and A. RUYER (Compt. rend., 1936, 202, 671—673; cf. A., 1933, 500).—Successive treatment of the dibromide (I), m.p.  $108^\circ$ , of  $\Delta^{1:3}$ -*cyclohexadiene* (II) with  $\text{AgOAc}$  and dry KOH in  $\text{Et}_2\text{O}$  gives the oxide (III) of (II). (III) and  $\text{H}_2\text{O}$  at  $0^\circ$  afford the *cyclohexenediols* previously described (*loc. cit.*). (III) and  $\text{PBr}_5$  in  $\text{Et}_2\text{O}$  give (I) and a liquid isomeride (cf. Farmer and Scott, A., 1929, 304). (III) does not immediately decolorise Br in  $\text{CCl}_4$  unless a little  $\text{H}_2\text{O}$  is present; it reacts slowly with  $\text{BzO}_2\text{H}$  to give the dioxide (*loc. cit.*). It is unlikely that (III) is a mixture (cf. *loc. cit.*); the activity of the double linking present is reduced whilst the oxide reactions



are enhanced. The Raman spectra of (II) and (III) are given; (III) shows the frequency characteristic of the double linking, whilst that at  $1581\text{ cm}^{-1}$  for (II) is considered to be due to the conjugated double linkings. H. B.

**Orienting rule of Svirebely and Warner.** K. GANAPATHI (Current Sci., 1936, 4, 482).—Various derivatives with electric moments  $> 2.07 D$  yield *o*- and *p*-products, and not *m*- as required by this rule (A., 1935, 684), which further fails to explain why a *m*-directing group R, of high moment, becomes *o*- and *p*-directing when in the group  $\cdot\text{CH}_2\text{R}$  or  $\cdot\text{CH}_2\cdot\text{CH}_2\text{R}$ , of similar moment. E. W. W.

**Aromatic hydrocarbons. XX. Simple principle of the structure of aromatic hydrocarbons and their absorption spectra.** E. CLAR (Ber., 1936, 69, [B], 607—614).—Examination of the absorption spectra of  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ , anthracene, benzanthracene, and dibenzanthracene shows that the square roots of the absorption frequencies are inversely to 6, 7, 8, 9, and 10. Similar comparison of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_6\text{H}_6$ , phenanthrene, and dibenzphenanthrene gives the figures 6, 7, 8, 9, and 10. The reasons are discussed. H. W.

**Raman effect and problems of constitution. IX. Stability of the aromatic C-X linking.** K. W. F. KOHLRAUSCH (Ber., 1936, 69, [B], 527—532; cf. this vol., 136, 137).—It is shown mathematically that in compounds  $\text{PhX}$  ( $\text{X}=\text{I}, \text{Br}, \text{SH}, \text{Cl}, \text{Me}, \text{F}, \text{OH}, \text{NH}_2$ ),  $p\text{-C}_6\text{H}_4\text{X}_2$ , and  $1:3:5\text{-C}_6\text{H}_3\text{X}_3$  the individual substituents have no important constitutive influence on the ring and that all C-X linkings are similarly affected by the transition from the aliphatic to the aromatic C atom. The change in the strength of union on entrance of a new C-X linking is almost independent of the presence or absence of a second C-X linking in the *m*- or *p*-position. The aromatic C-X linking is about 20% stronger than the aliphatic linking. H. W.

**Oxidation of aromatic hydrocarbons at high pressures. I. Benzene. II. Toluene. III. Ethylbenzene.** D. M. NEWITT and J. H. BURGONNE (Proc. Roy. Soc., 1936, A, 153, 448—462).—At suitable temp. and pressures the slow combustion of  $\text{C}_6\text{H}_6$  proceeds smoothly without any induction period or sudden change in reaction velocity, whereas  $\text{PhMe}$  and  $\text{PhEt}$  exhibit well-marked induction periods, and in each case oxidation of the nucleus and side-chains occurs simultaneously. Combustion takes place by hydroxylation of either the ring or the side-chain, giving as primary products  $\text{PhOH}$  and alcohols respectively. For comparable rates of reaction,  $\text{C}_6\text{H}_6\text{-O}_2$  mixtures require a higher temp. than either  $\text{PhMe-O}_2$  or  $\text{PhEt-O}_2$  mixtures of similar composition. Increased surface retards the rate of oxidation of  $\text{C}_6\text{H}_6$  but has no effect on  $\text{PhMe}$  or  $\text{PhEt}$ ; the addition of  $\text{N}_2$  retards all three reactions equally. Probably a "chain" mechanism is involved in each case, but a difference exists in the chain-propagating reactions according to whether oxidation of the nucleus or side-chain is taking place. The course of combustion up to the point at which rupture of the ring occurs may be represented:  $\text{C}_6\text{H}_6 \rightarrow$

$\text{PhOH} \rightarrow 1:4\text{-C}_6\text{H}_4(\text{OH})_2 \rightarrow 1:2:4\text{-C}_6\text{H}_3(\text{OH})_3 \rightarrow \text{C}_6\text{H}_4\text{O}_2 \rightarrow \text{ring ruptures}$ . In suitable circumstances, as much as 53.5% of the C of the  $\text{C}_6\text{H}_6$  burnt appears as  $\text{PhOH}$ .  $\text{PhMe} \rightarrow \text{CH}_2\text{Ph}\cdot\text{OH} \rightarrow \text{CHPh}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + \text{PhCHO} \rightarrow \text{BzOH} \rightarrow \text{ring ruptures}$ . Oxidation of the nucleus gives mainly  $2:4\text{-C}_6\text{H}_3\text{Me}(\text{OH})_2$ . Under suitable conditions either one of the side-chain derivatives may be obtained in optimum amounts.  $\text{PhEt} \rightarrow \text{CHPhMe}\cdot\text{OH} \rightarrow \text{CPhMe}(\text{OH})_2 \rightarrow \text{COPhMe} \rightarrow \text{COPh}\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{COPh}\cdot\text{CH}(\text{OH})_2 \rightarrow \text{PhCHO} \rightarrow \text{BzOH} \rightarrow \text{ring ruptures}$ . Oxidation of the nucleus gives mainly  $2:4\text{-C}_6\text{H}_3\text{Et}(\text{OH})_2$ .

L. L. B.

**Chlorination of benzene.** F. F. KRIVONOS (Ukrain. Chem. J., 1935, 10, 417—427).—Stirring the  $\text{C}_6\text{H}_6$  during chlorination leads to diminution in the amount of polychlorides formed, and to a greater yield of  $\text{PhCl}$ . R. T.

**Halogenation. XIII. Bromination and iodination of some halogenated benzenes.** P. S. VARMA and S. SHANKARARAYANAN (J. Indian Chem. Soc., 1936, 13, 31—33).—Substitution of  $p\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $\text{PhBr}$ ,  $p\text{-C}_6\text{H}_4\text{Br}$ , and  $\text{PhI}$  by  $\text{Br}$  and  $\text{I}$  in presence of halogenating agents gives known derivatives of  $\text{C}_6\text{H}_6$ . F. R. G.

**Replacement of chlorine by fluorine in organic compounds.** H. B. GOTTLIEB (J. Amer. Chem. Soc., 1936, 58, 532—533).— $2:4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Cl}$  with successive amounts of anhyd.  $\text{KF}$  in  $\text{PhNO}_2$  at  $205^\circ$  gives 30% of  $2:4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{F}$ , m.p.  $24\text{--}25^\circ$ , which reacts slowly with  $\text{H}_2\text{O}$  at  $60^\circ$  forming  $\text{HF}$ . *Diphenoxyphosphoryl fluoride*, b.p.  $150\text{--}155^\circ/6\text{ mm.}$ , similarly prepared in 7% yield from  $(\text{OPh})_2\text{POCl}$  at  $90\text{--}100^\circ$ , is decomposed rapidly by  $\text{H}_2\text{O}$  and when distilled in a vac. undergoes partial decomp. to  $\text{Ph}_3\text{PO}_4$  and  $\text{POF}_3$ . H. B.

**Chlorination of toluene in presence of (a) activated charcoals, and (b) iron-impregnated silica gel. Production of side-chain substitution, nuclear substitution, and tolan derivatives.** J. B. FIRTH and T. A. SMITH (J.C.S., 1936, 337—339).—Addition of heat-activated sugar-C, better if iodised or Fe-impregnated, increases the rate of chlorination and amount of side-chain substitution of  $\text{PhMe}$  in the dark. Prolonged reaction gives  $2:2'\text{-dichlorotolan dichloride}$ , b.p. about  $220^\circ/30\text{ mm.}$ , m.p. of isomerides between  $139^\circ$  and  $170^\circ$ . Fe-impregnated  $\text{SiO}_2$  gel increases nuclear substitution, giving  $2:4:5\text{-C}_6\text{H}_2\text{Cl}_3\text{Me}$  and a substance,  $\text{C}_{14}\text{H}_{10}\text{Cl}_2$ , m.p.  $145^\circ$ , and much glue-like material.  $\text{CH}_2\text{PhCl}$  and  $\text{SiO}_2$  gel give a similar glue exothermally. R. S. C.

**Velocity of reaction between *o*-nitrobenzyl bromide and pyridine. Mechanism of side-chain reactions, etc.** IV. J. W. BAKER (J.C.S., 1936, 399—400; cf. this vol., 195).— $o\text{-NO}_2\text{C}_6\text{H}_4\text{-CH}_2\text{Br}$  reacts with  $\text{C}_5\text{H}_5\text{N}$  slightly faster than does  $\text{CH}_2\text{PhBr}$ , but not fast enough for the *o*- $\text{NO}_2$  to account for the much faster reaction of the  $2:4\text{-(NO}_2)_2$ -compound. R. S. C.

**Derivatives of *tert*-butylbenzene and transmitted polar effects.** (THE LATE) J. B. SHOE-SMITH and A. MACKIE (J.C.S., 1936, 300—303).—Boiling *m*- and *p*- $\text{C}_6\text{H}_4\text{MeBu}^t$  and  $\text{Br}$  give *m*-, b.p.



115.5°/8 mm., and *p*-tert.-butylbenzyl bromide (I), m.p. 12–13°, b.p. 132.5°/14 mm., oxidised to *m*-, m.p. 127°,  $k$   $5.2 \times 10^{-5}$ , and *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup>CO<sub>2</sub>H, m.p. 165° (lit. 164°),  $k$   $4.2 \times 10^{-5}$ , respectively. (I) and HI-AcOH give *p*-tert.-butylbenzyl iodide, m.p. 29.5–30.5°. The relative vals. of  $k$  of the acids and of the rates of hydrolysis of the bromides in aq. EtOH ( $p > m$ -Bu<sup>γ</sup> > unsubstituted) indicate both electro-merie and inductive effects due to Bu<sup>γ</sup>, but the relative ease of reduction of the bromides by HI ( $m > p$ -Bu<sup>γ</sup> > unsubstituted) requires an additional explanation not yet apparent. R. S. C.

***o*-Nitrophenylsulphur chloride (*o*-nitrobenzenesulphenyl chloride).** M. H. HUBACHER (Org. Syntheses, 1935, 15, 45–47).—NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SCl is obtained by the action of Cl<sub>2</sub> in CCl<sub>4</sub> on (o-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·S)<sub>2</sub>. CH. ABS. (r)

**Mechanism of additive reactions. Kinetic study of addition of methyl hypobromite to stilbene.** P. D. BARTLETT and D. S. TARBELL (J. Amer. Chem. Soc., 1936, 58, 466–474).—Reaction between (·CHPh)<sub>2</sub> and Br in MeOH at 0°, whereby OMe·CHPh·CHPhBr (I) is formed in 99% yield, is not inhibited by O<sub>2</sub>. The rate is steadily diminished by increased concn. of added Br<sup>-</sup> (using solutions of const. ionic strength 0.2, containing NaBr supplemented by PhSO<sub>3</sub>Li); the yield of (I) also decreases (83% in presence of 0.2M-NaBr) whilst that of (·CHPhBr)<sub>2</sub> increases. The rate is not, however, diminished by H<sup>+</sup>, indicating that MeOBr is not responsible for the production of (I). The kinetics are of the second order only when the initial concn. of Br<sup>-</sup> is much > that formed during the reaction; they indicate a two-stage mechanism with mol. Br as the active agent. The results are inconsistent with any mechanism attributing activity to Br<sup>+</sup> or to MeOBr catalysed by acid. The following changes are considered to occur: (·CHPh)<sub>2</sub> + Br<sub>2</sub> → CHPhBr·CHPh (II) + Br<sup>-</sup>; (II) + MeOH → (I) + H<sup>+</sup>; (II) + Br<sup>-</sup> → (·CHPhBr)<sub>2</sub>. H. B.

**Structure of naphthalene.** E. BERGMANN and J. HIRSBERG (J.C.S., 1936, 331–336).—The effect of 2-Cl on  $k$  of 1-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H and of 1- and 3-Cl on  $k$  of 2-C<sub>10</sub>H<sub>7</sub>·CO<sub>2</sub>H and on the rates of hydrolysis of the esters is not identical, indicating that the C1–C2 and C2–C3 linkings differ in nature and that the linkings in C<sub>10</sub>H<sub>8</sub> are static. Some close effect (possibly steric) is exerted by 1- and 8-substituents on one another, particularly noticeable in dipole moments. 3-Amino-2-naphthoic acid yields *Et* 3-chloro-2-naphthoate, b.p. 195–197°/18 mm., m.p. 57–59°. 9:1-C<sub>10</sub>H<sub>6</sub>Cl·CO<sub>2</sub>H, m.p. 169–170° (*Me* ester, b.p. 188–189°/16.2 mm.), *Me* 1-chloro-2-naphthoate, m.p. 48–49°, 2-, m.p. 76°, and 1-naphthoate, b.p. 165°/17 mm., and 2-chloro-1-naphthoate, b.p. 176–180°/18.5 mm., m.p. 50°, are described. 8:1-C<sub>10</sub>H<sub>6</sub>Cl·NH<sub>2</sub> gives the diazonium borofluoride, m.p. 106–107° (decomp.), and leads to 1-chloro-8-fluoro-, m.p. 44°, b.p. 130–132°/12.5 mm., -bromo-, m.p. 94–95° (lit. 87–88°, 119°), and -iodo-naphthalene, m.p. 79–80°, b.p. 197–198°/19 mm., 1:8-C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>, m.p. 84–85°, and 9-chloro-1-naphthonitrile, m.p. 145–146°, b.p. 242–244°/15.5 mm. R. S. C.

**Nitration of polycyclic aromatic hydrocarbons by means of nitrous fumes.** (SIGNA.) L. MONTI, V. MARTELLO, and F. VALENTE (Gazzetta, 1936, 66, 31–38).—Acenaphthene treated in Et<sub>2</sub>O or in light petroleum at 15–16° with nitrous fumes yields 3-nitroacenaphthene; in C<sub>6</sub>H<sub>6</sub> or AcOH at 8–10°, or with liquid N<sub>2</sub>O<sub>4</sub>, the 3:4-(NO<sub>2</sub>)<sub>2</sub>-compound is formed. Fluorene in any of these solvents at low temp. gives 2-nitrofluorene; in AcOH at 90–95°, a mixture of the 2:5- and 2:7-(NO<sub>2</sub>)<sub>2</sub>-compounds is obtained. Ph<sub>2</sub> is unchanged at 0–25°; in AcOH or petroleum at 90–95°, or with liquid N<sub>2</sub>O<sub>4</sub> at room temp., 4-nitrodiphenyl is formed, whilst prolonged action of nitrous fumes at 90–95° yields a mixture of the 4:4'- and 4:2'-(NO<sub>2</sub>)<sub>2</sub>-compounds. CHPh<sub>3</sub> is not nitrated, but gives CPh<sub>3</sub>·OH, or, at 0° in EtOH, its nitrite. CH<sub>2</sub>Ph<sub>2</sub> and (·CH<sub>2</sub>Ph)<sub>2</sub> are not appreciably nitrated. E. W. W.

**Thermolysis of cholesteryl chloride.** E. BERGMANN and F. BERGMANN (Chem. and Ind., 1936, 272–273).—When heated for 3 hr. at 300° in dry N<sub>2</sub>, cholesteryl chloride affords (by loss of 1 mol. of HCl) a distillate, b.p. 118–125°/758.5 mm., containing 75–67% of C<sub>8</sub>H<sub>18</sub> and 25–33% of C<sub>8</sub>H<sub>16</sub>, and a residue from which are isolated (1) a small amount of a hydrocarbon (C, 88.8; H, 11.2%), b.p. 156–157°/30 mm., [α]<sub>D</sub> +17.3° in C<sub>6</sub>H<sub>6</sub>; (2) a hydrocarbon C<sub>15</sub>H<sub>28</sub> or (?) C<sub>16</sub>H<sub>24</sub>, b.p. 150–155°/0.03 mm., [α]<sub>D</sub> +34.9° in C<sub>6</sub>H<sub>6</sub>, containing 2 double linkings, one of which is resistant to Br-titration (partial structure suggested); and (3), the main fraction, a tetracyclic hydrocarbon C<sub>19</sub>H<sub>30</sub> (lit. C<sub>19</sub>H<sub>28</sub>), b.p. 180–185°/0.02 mm., [α]<sub>D</sub> +31.4° in C<sub>6</sub>H<sub>6</sub>, containing only 1 double linking, showing that pyrolysis is accompanied by H transfer. J. W. B.

**[Reversible chemical absorption of free oxygen by organic compounds.]** A. SCHÖNBERG (Ber., 1936, 69, [B], 532–533).—A question of priority regarding rubenes. H. W.

**Reversible oxidisability of organic compounds. Reducible, but not dissociable, monoxide of diphenyldi-*p*-bromophenylrubene.** L. ENDERLIN (Compt. rend., 1936, 202, 669–671; cf. A., 1935, 650).—The oxide (I), C<sub>42</sub>H<sub>26</sub>OBr<sub>2</sub>, m.p. 284–285° (when free from solvent of crystallisation), most simply prepared by oxidation (15% HNO<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>) of diphenyldi-*p*-bromophenylrubene (II), is not dissociable by heat but is reduced (Fe, AcOH) to (II). (I), which is probably an *endo*-oxide, is also obtained by dehydration of dihydroxydiphenyldi-*p*-bromophenylrubene and by partial reduction (Zn, AcOH) of the dissociable dioxide of (II). H. B.

**Interaction of sulphur dichloride with substances containing the reactive methylene group.** II. K. G. NAIK and S. A. VAISHNAV (J. Indian Chem. Soc., 1936, 13, 25–27).—SCl<sub>2</sub> with acetoacetyl-amides (I) in pure, dry C<sub>6</sub>H<sub>6</sub> gives CSAc·CO·NHR, which with Na<sub>2</sub>S yields (I) and with KOH yields NH<sub>2</sub>R. The following were prepared: α-thion-acetoacet-anilide, m.p. 196°, -*o*-, m.p. 184°, and -*p*-toluidide, m.p. 130°, -*α*-, m.p. 184°, and -β-naphthylamide, m.p. 179°, -1:4:5-, m.p. 209°, and -1:3:4-xylylide, m.p. 201°. F. R. G.



**Interaction of thionyl chloride with substances containing the reactive methylene group.** V. K. G. NAIK and S. A. VAISHNAV (J. Indian Chem. Soc., 1936, 13, 28—30).— $\text{SOCl}_2$  reacts with malonarylamides in presence of Cu with presumed intermediate formation of  $\text{SCL}_2$ ,  $\text{SO}_2$ , and  $\text{CuCl}_2$  to give  $\text{CS}(\text{CO}\cdot\text{NHR})_2$  (cf. preceding abstract). The following were prepared: *thionmalondi-phenylamide*, m.p.  $105^\circ$  (shrinks at  $80^\circ$ ), -o-, m.p.  $138^\circ$  (shrinks at  $110^\circ$ ), -p-, m.p.  $108^\circ$  (shrinks at  $60^\circ$ ), and -*m-tolylamide*, m.p.  $114^\circ$  (shrinks at  $60^\circ$ ), - $\alpha$ -*naphthylamide*, m.p.  $168^\circ$ , -1:3:4-, m.p.  $126^\circ$  (shrinks at  $95^\circ$ ), and -1:4:5-*xylylidide*, m.p.  $146^\circ$  (shrinks at  $100^\circ$ ). F. R. G.

[o- and p-Derivatives of o-toluidine.] 2:6-Diacetamidotoluene. A. KORULEV and E. ROSTOV-TZEVA (Ber., 1936, 69, [B], 640).—The non-cryst. product of the technical prep. of 1:2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  from a mixture of o- and p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$  is reduced and acetylated. The product is treated with EtOH, which dissolves 2:4-diacetamidotoluene leaving 2:6-diacetamidotoluene (I), m.p.  $309\text{--}311^\circ$ . Since (I) is smoothly hydrolysed to 1:2:6- $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$ , m.p.  $103\text{--}104^\circ$ , and obtained from 1:2:6- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ , the m.p.  $202^\circ$  recorded for (I) by Green *et al.* (J.C.S., 1891, 59, 1017) requires correction. H. W.

**Secondary reactions in reduction of aromatic nitro-compounds. Rôle of ferrous salts in reduction process.** K. G. MISUTSCH (J. pr. Chem., 1936, [ii], 145, 60—64).— $\text{C}_6\text{H}_4\text{Hal}\cdot\text{NH}_2$  are not formed during reduction of  $\text{PhNO}_2$  by Sn (or  $\text{SnCl}_2$ ) and 6:86N-HCl, -HBr, or -HF in presence of AcOH and 1 mol. of  $\text{FeHal}_2$ . Since  $\text{NACPhCl}$  with  $\text{FeCl}_2$ -dil. HCl or HI gives  $\text{NHAcPh}$  and no  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHAc}$ , the function of the  $\text{FeHal}_2$  (above) is to reduce the intermediate  $\text{NHPhHal}$  to  $\text{NH}_2\text{Ph}$ . Reduction (Sn, HBr) of  $\text{PhNO}_2$  in absence of  $\text{FeBr}_2$  affords p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$  (44.85% of total amine) and small amounts of axoxybenzene and p- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  (formed by rearrangement of  $\text{NHPh}\cdot\text{OH}$ ; this occurs much more slowly than the changes  $\text{NHPh}\cdot\text{OH} \rightarrow \text{NHPhBr} \rightarrow \text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ ). H. B.

**Aromatic N-substituted cyanoamides.** J. BIECHLER (Compt. rend., 1936, 202, 666—667).—p-Anisyl-, m.p.  $33^\circ$ , p-phenetyl-, m.p.  $69^\circ$ , and 4-chloro-3-aminophenyl-, m.p.  $136^\circ$ , -dicyanoamides are prepared (cf. A., 1935, 482) from  $\text{KNAr}\cdot\text{CN}$  and  $\text{CNBr}$ ; o-tolyl-, m.p.  $36^\circ$ , p-chlorophenyl-, m.p.  $59^\circ$ , and  $\alpha$ -naphthyl-, m.p.  $126^\circ$ , -dicyanoamides are similarly obtained (cf. *loc. cit.*) using  $\text{CNCl}$ .  $\text{KNPh}\cdot\text{CN}$  (I) and  $\text{CPh}_2\text{Cl}$  give phenylcyanoamidotriphenylmethane, m.p.  $124^\circ$ ;  $\text{CPh}_2\text{Cl}_2$  (?) similarly affords di(phenylcyanoamido)diphenylmethane, m.p. about  $200^\circ$ , whilst  $\text{COPh}\cdot\text{CH}_2\text{Br}$  yields phenacylphenylcyanoamide, m.p.  $123^\circ$ . (I) and  $\text{S}_2\text{Cl}_2$  give di(phenylcyanoamido)-disulphide, m.p.  $83^\circ$ ;  $\text{AsCl}_3$  affords tri(phenylcyanoamido)arsine, m.p. about  $250^\circ$ . A bromophenylcyanoamide is obtained from (I) and Br. Me, m.p.  $63^\circ$ ,  $\text{CH}_2\text{Cl}$ , m.p.  $48^\circ$ , and  $\text{CCl}_3$ , m.p.  $84\text{--}85^\circ$  (with liberation of  $\text{COCl}_2$ ), phenylcyanoamidocarbonates are prepared. H. B.

**Substituted naphthalenesulphonic acids and their derivatives.** W. M. CUMMING and G. D. MUIR (J. Roy. Tech. Coll., 1936, 3, 562—568).—Diazotised

1:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$  (I) with KI and  $\text{C}_5\text{H}_5\text{N}$  (or  $\text{COMe}_2$ ) gives the 1:8-sultone, and after saturation with NaCl, the Na salt of 1:8- $\text{C}_{10}\text{H}_6\text{I}\cdot\text{SO}_3\text{H}$  (cf. A., 1934, 519). The *chloride*, m.p.  $115^\circ$ , of the latter yields, with dil. aq.  $\text{NH}_3$  in cold  $\text{COMe}_2$ , the *amide*, m.p.  $187^\circ$  (decomp.), or, in boiling  $\text{COMe}_2$ , the 1:8-naphthasultam. The *anilide*, m.p.  $140^\circ$ , is converted by Cu in boiling EtOH into the N-phenylsultam, new m.p.  $165^\circ$ . An improved prep. of 1:8- $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{SO}_3\text{H}$  from the solid diazo-compound of (I) and cold  $\text{Cu}_2\text{Cl}_2$  in conc. HCl is described. Neither this nor the  $\text{C}_5\text{H}_5\text{N}$  method is successful for 1:8- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{SO}_3\text{H}$ ; its *chloride*, m.p.  $110^\circ$ , is, however, obtained by adding the solid diazo-compound to the cold suspension obtained after boiling  $\text{Cu}_2\text{O}$  in aq.  $\text{NH}_4\text{Br}$ , by adding KCl, and treating the product with  $\text{PCl}_5$ . By adding the diazo-compound to  $\text{CuCN}$ , 1:8- $\text{CN}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$  is obtained (*chloride*, m.p.  $139^\circ$ ; *amide*, m.p.  $334\text{--}336^\circ$ ). The diazo-compound treated with Cu in conc. HCl, with Cu in  $\text{Cu}_2\text{Cl}_2\text{--HCl}$ , with  $\text{Sn}(\text{OH})_2$ , or with Zn in  $\text{H}_2\text{O}$  gives 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ . The diazo-compound from 2:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$  and KI, followed by KOH, gives the K salt (+ $\text{H}_2\text{O}$ ) of 2:1- $\text{C}_{10}\text{H}_6\text{I}\cdot\text{SO}_3\text{H}$  (*chloride*, m.p.  $109.5^\circ$ ; *amide*, m.p.  $154^\circ$ ); with the suspension from  $\text{Cu}_2\text{O}$  and  $\text{NH}_4\text{Br}$ , followed by KCl, the K salt of 2:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{SO}_3\text{H}$  (*chloride*, m.p.  $97^\circ$ ; *amide*, m.p.  $140^\circ$ ) is obtained. 1:4-, 1:5-, and 1:8- $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$  have been identified among the respective reaction products of the diazo-compounds from 1:4-, 1:5-, and 1:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$  and a solution of  $\text{CuSO}_4$  in aq.  $\text{NH}_3$ , treated with  $\text{SO}_2$ . E. W. W.

**Carbonitrosohydrazines. IV. Azohydroxamic acids [and hydrochloric acid]** A. QUILICO and R. JUSTONI (Gazzetta, 1936, 66, 19—22; cf. A., 1935, 855).—When p-chlorobenzene- and p-toluene-azoformhydroxamic acids are boiled with conc. HCl, they are chlorinated in the nucleus and reduced, yielding, respectively, 2:4-dichlorobenzene-, m.p.  $184\text{--}185^\circ$ , and 2-chloro-p-toluene-hydrazoformhydroxamic acid, m.p.  $169^\circ$ , which are reduced respectively to 2:4-dichloroaniline and 2-chloro-p-toluidine. E. W. W.

**Influence of cyclisation on "colour" of molecules. Absorption of diphenyleneazone and its mono- and di-oxides.** (MME.) P. RAMART-LUCAS and (MLE.) D. BIQUARD (Bull. Soc. chim., 1936, [v], 3, 430—435).—Comparison of the absorption spectra of  $(\text{NPh})_2$  and diphenyleneazone (I) (Tauber, A., 1892, 183) shows that, unlike the case of carbocyclic compounds, cyclisation is accompanied by a marked hypsochromic effect and a diminution in absorption intensity (ascribed to deformation of the valency angles). The curves for axoxybenzene (II) and the mono- and di-oxides of (I) show little difference. The absorption intensity of o-azoxytoluene is < that of (II). H. B.

**Velocity of diazotation.** E. ROSTOV-TZEVA (Anilinokras. Prom., 1935, 5, 199—201).—The velocity of diazotisation of aromatic amines is determined relatively to that of benzidine, giving a series of characteristic ratios  $k/k_1$ , where  $k$  and  $k_1$  are the respective velocity coeffs. The content of each con-



stituent in binary mixtures of isomeric amines can be derived from determination of  $k_1/k$  for the mixture.

R. T.

**Electronic theory of valency and the constitution of aromatic diazo-compounds.** P. B. SARKAR (J. Indian Chem. Soc., 1936, 13, 19—22).—Theoretical. The structure of diazonium compounds and of normal and *iso*-diazotates can be explained by electronic theory.

F. R. G.

**$\alpha$ - and  $\beta$ -Anthracenediazonium salts.** M. BATEGAY and P. BOEHLER (Compt. rend., 1936, 202, 769—771).— $\beta$ -Anthramine hydrochloride at 0° affords a sol. diazonium chloride (+ $ZnCl_2$ , decomp. about 105°; + $CdCl_2$ ), which is decomposed by light. The  $\alpha$ -isomeride (+ $ZnCl_2$ , decomp. about 100°) is similar.

J. L. D.

**Phosphoric acid as a condensing agent.** A. E. TSCHITSCHIBABIN (Bull. Acad. Sci. U.R.S.S., 1935, 951—969).—Alkylation of phenols is readily effected by heating mixtures of the alcohol, the phenol, and  $H_3PO_4$ . Thus, *o*-tert.-butyl-*m*-cresol, b.p. 121—122°/16 mm., m.p. 23°, is obtained from  $Bu^tOH$ , *o*-cresol, and  $H_3PO_4$  at 50°; *o*-sec.-butyl-, b.p. 111—116°/12 mm., *o*-tert.-amyl-, b.p. 119—122°/10 mm., and *o*-menthyl-*m*-cresol, b.p. 153—156°/2.5 mm., *o*-tert.-butyl-, b.p. 122.5°/14 mm., m.p. 27° (lit. 85—86°), and *o*- and *p*-benzyl-*o*-cresol, *o*-tert.-butyl-*p*-cresol, b.p. 118—119°/14 mm., m.p. 44°, *o*-tert.-butyl-, b.p. 125.5—126°/17 mm., and *o*-isopropyl-*m*-xyleneol, b.p. 127—130°/17 mm., tert.-butyl- $\beta$ -naphthol, b.p. 186—189°/13 mm., m.p. 113°, 4-tert.-butyl-, b.p. 134—136°/1.5 mm. ( $Me_2$  ether, b.p. 126—129°/13 mm., m.p. 4°), and 4:6-di-tert.-butyl-resorcinol, m.p. 121° ( $Me_2$  ether, b.p. 136—140°/13 mm., m.p. 76°), are obtained analogously. *m*-Cresol and octene yield *o*-octyl-*m*-cresol, b.p. 153—154°/11 mm., and  $PhOH$  and allyl alcohol afford *o*-propenylphenol, b.p. 200—205°.

R. T.

**Condensation of aliphatic alcohols with aromatic compounds in presence of aluminium chloride.** I. R. C. HUSTON and T. Y. HSIEH (J. Amer. Chem. Soc., 1936, 58, 439—441).— $CHAlk_2OH$  (1 equiv.) added to a well-stirred mixture of  $C_6H_6$  (2—5 equivs.) and  $AlCl_3$  (0.5 equiv.) at < 30° gives 25—28% of  $CHPhAlk_2$ ;  $PhPr^s$ ,  $CHPhMeEt$ ,  $CHPhMePr^s$ , and  $CHPhMePr^s$  are thus prepared.  $Bu^tOH$  similarly affords 67% of  $PhBu^t$  whilst  $CH_2AlkOH$  (I) do not react.  $Alk_3OH$  (0.25 mol.),  $PhOH$  (0.25 mol.), and  $AlCl_3$  (0.125 mol.) in light petroleum at 25—30° give 45—60% of  $p-OH-C_6H_4Alk_3$ ; (I) ( $Alk=Me-Pr$ ) and *sec*.- $BuOH$  do not react, whilst  $Pr^sOH$  affords a small amount of an unidentified product. The following are described:  $p-C_6H_4Bu^tOH$  (benzenesulphonate, m.p. 70—71°; *p*-toluenesulphonate, m.p. 109—110°); *p*-tert.-amylphenol (benzenesulphonate, b.p. 184—185°/3 mm.; *p*-toluenesulphonate, m.p. 54—55°);  $\beta$ -*p*-hydroxyphenyl- $\beta$ -methylpentane (II), b.p. 259—261°/740 mm., m.p. 37—38° (from  $CMe_2Pr^sOH$ ) (benzoate, b.p. 169—171°/3 mm.; benzenesulphonate, b.p. 174—175°/3 mm.; *p*-toluenesulphonate, b.p. 194—195°/3 mm.);  $\beta$ -*p*-hydroxyphenyl- $\beta$ -*γ*-dimethylbutane (III), b.p. 266—268°/740 mm., m.p. 105—106° (from  $CMe_2Pr^sOH$ ) (benzoate, m.p. 54—55°; benzenesulphonate, b.p. 178—179°/3

mm.; *p*-toluenesulphonate, b.p. 187—188°/3 mm.);  $\gamma$ -*p*-hydroxyphenyl- $\gamma$ -methylpentane (IV), b.p. 268—269°/740 mm., m.p. 59—60° (from  $CMeEt_2OH$ ) (benzoate, m.p. 77—78°; benzenesulphonate, b.p. 183—184°/3 mm.; *p*-toluenesulphonate, b.p. 188—189°/3 mm.).  $CPhMe_2Pr^s$ ,  $CPhMe_2Pr^s$ , and  $CPhMeEt_2$  with  $HNO_3$  (*d* 1.52) at room temp. give the *p*- $NO_2$ -derivatives, b.p. 124—126°/3 mm., 122—124°/3 mm., and 123—125°/3 mm., respectively [which are all oxidised by  $HNO_3$  (*d* 1.2) at 130° to  $p-NO_2-C_6H_4CO_2H$ ], reduced (Sn, conc.  $HCl$ ) to the *p*- $NH_2$ -derivatives, b.p. 107—109°/3 mm., 109—111°/3 mm., and 108—110°/3 mm., respectively, which are then converted (diazo-method) into (II), (III), and (IV), respectively.

H. B.

**Comparative acetylation of naphthols.** A. LEMAN (Compt. rend., 1936, 202, 579—581; see A., 1935, 856).—The order of the reactivity of the OH towards  $Ac_2O$  in  $C_5H_5N$  solution is  $\alpha$ - and  $\beta$ - $C_{10}H_7OH > 1:5 > 1:7$ - $C_{10}H_6(OH)_2$ . In  $AcOH$  solution the order is  $\beta$ - $C_{10}H_7OH > 1:7$ - $C_{10}H_6(OH)_2 > \alpha$ - $C_{10}H_7OH$  and  $1:5$ - $C_{10}H_6(OH)_2$ .

J. N. A.

**Interaction of groups in the same molecule.** J. BOESEKEN, P. C. HENRIQUEZ, and J. J. VAN DER SPEK (Rec. trav. chim., 1936, 55, 145—152).—Factors, especially abnormal dipole moments ( $\mu$ ), pointing to mutual influences of groups in the same mol. are reviewed.  $\mu$  of pyrocatechol cyclic ethers is determined, and is as follows: *o*-methylene-, 1.0; *o*-isopropylidene-, 1.02; *o*- $\alpha$ -phenylethylidene-, 1.05; and 4-bromo-, 2.70; 4-chloro-, 2.74; 4:5-dibromo-, 3.28; and 4:5-dichloro-*o*-methylene-dioxybenzene, 3.39. These vals. are much > those calc. by vectorial addition, on the assumption that the total moment is in the normal direction, and slightly > those calc. on the converse assumption. Thus there is a strong mutual interaction, either between the ether groups and the halogen atoms, or between the moments which constitute a part of the 5-ring.

E. W. W.

**Bromo-derivatives of pyrocatechol.** J. FREJKA and B. ŠEFRÁNAK (Coll. Czech. Chem. Comm., 1936, 8, 130—139).— $o-C_6H_4(OH)_2$  (I) with Br (4 mols.) in cold  $CHCl_3$  or, better, in conc.  $H_2SO_4$ , gives its  $Br_2$  derivative, m.p. 191—192°. Lit. methods fail to give the 3:4:5- $Br_3$ -derivative (II), m.p. 144° (corr.), which is obtained by the action of  $Br-CHCl_3$  or Br vapour on a 3%  $CHCl_3$  solution of (I) at < 20° (monohydrate could not be obtained;  $Ac_2$  derivative, m.p. 120°), characterised by conversion ( $MeI-MeOH-K_2CO_3$ ) into its known  $Me_2$  ether. With Br (2 mols.)- $AcOH$  a 22% solution of (I) in  $AcOH$  (Cousin, A., 1895, i, 456) or  $CO_2-Br$  vapour into (I)- $CHCl_3$ , gives the 4:5- $Br_2$ -derivative (III), but if  $SO_2-Br$  vapour is passed into (I)- $CHCl_3$  at room temp. an 80% yield of the 3:4- $Br_2$ -derivative, m.p. 73—74° ( $Ac_2$  derivative, m.p. 95—96°) [converted by  $Br-CHCl_3$  into (II)], is obtained. (III) is not obtained by the method of Kohn *et al.* (A., 1927, 966), which gives only a mixture, possibly containing the 3:6- $Br_2$ -derivative, m.p. 120° ( $Ac$  derivative, m.p. about 170°), which could not be isolated pure.

J. W. B.

**$\beta$ -Phenyl sulphide.** O. HINSBERG (Ber., 1936, 69, [B], 492—495; cf. A., 1929, 310).—The yield of  $\beta$ -Ph (isophenyl) sulphide (I) is greatly increased when



the action of  $\text{HClO}_4$  on  $\alpha$ -Ph sulphide (II) is effected in considerable amounts of  $\text{AcOH}$  or  $\text{EtCO}_2\text{H}$ . The product is treated with  $\text{MeOH-KOH}$  and light petroleum and (I), b.p.  $324-329^\circ/\text{atm. pressure}$ , is readily isolated by fractional distillation of the petroleum extract. (I) is not isomerised to (II) when repeatedly distilled or heated at  $290-300^\circ$  in a sealed tube, but transformation occurs when it is boiled with  $\text{P}_2\text{O}_5$ . (I) is transformed at  $16^\circ$  by  $\text{HClO}_4$  into its perchlorate, which is produced from diphenylsulphonium hydr-oxide (III) and  $\text{HClO}_4$  in  $\text{AcOH}$  at room temp., thus indicating a constitutive change during the transformation of (I) into (III). The residues from the distillation of (I) contain *diphenylphenylene disulphide*,  $\text{C}_6\text{H}_4(\text{SPh})_2$ , m.p.  $80^\circ$ , converted by  $\text{H}_2\text{O}_2$  in  $\text{AcOH}$  into the corresponding *disulphone*, m.p.  $229^\circ$ . (II) and  $\text{HClO}_4$  in boiling  $\text{MeOH}$  afford  $\alpha$ -*diphenylmethylsulphonium perchlorate*,  $\text{SPh}_2\text{Me}\cdot\text{ClO}_4$ , m.p.  $76^\circ$ , which breaks down in warm  $\text{EtOH}$  containing  $\text{KOAc}$  into (I),  $\text{KClO}_4$ , and  $\text{MeOH}$ .  $\beta$ -*Diphenylmethylsulphonium perchlorate*, which does not solidify at  $-10^\circ$ , and *phenyldimethylsulphonium perchlorate*, m.p.  $160^\circ$ , are obtained analogously. H. W.

**cycloHexene peroxide.** H. HOCK and O. SCHRADER (Naturwiss., 1936, 24, 159; cf. Stephens, A., 1928, 401).—Irradiation of *cyclohexene* in  $\text{O}_2$  yields 20% of the peroxide (I), isolated (96% purity) by distillation in high vac.; presence of eosin doubles the velocity of reaction. Treatment of (I) with  $1-2N\text{-H}_2\text{SO}_4$  affords 50% of *cis-cyclohexane-1:2-diol*, m.p.  $104^\circ$ , and 10–20% of *cyclopentenaldehyde (semicarbazide)*, m.p.  $208^\circ$  and with conc.  $\text{NaOH}$   $\Delta^1$ -*cyclohexen-3-ol (naphthylurethane)*, m.p.  $156^\circ$  [also afforded by reduction of (I) with aq.  $\text{Na}_2\text{SO}_3$ ]. F. O. H.

**Osmic acid esters as intermediate products in oxidations.** R. CRIGEE (Annalen, 1936, 522, 75–96).—Böeseken's view (cf. A., 1920, ii, 219) that the production of *cis*-diols from olefines and  $\text{NaClO}_3$  in presence of a little  $\text{OsO}_4$  (Hofmann, A., 1913, ii, 62, 609) occurs through the intermediate ester,

$\text{R}\begin{matrix} \text{CH}\cdot\text{O} \\ \diagup \\ \text{CH}\cdot\text{O} \end{matrix}\text{OsO}_2$ , is proved by the following results.

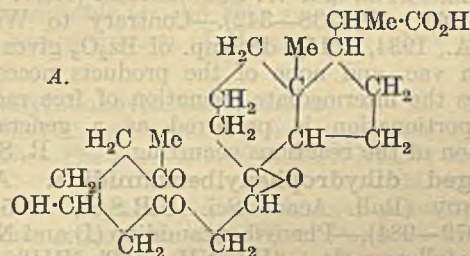
Such esters (decomp. temp. quoted after substance) are prepared from acenaphthylene (I),  $236^\circ$ , indene,  $204^\circ$ , 1:4-dihydronaphthalene,  $170^\circ$ , and  $\Delta^9$ -octahydronaphthalene,  $200^\circ$ , in 89–99% yield by treatment with an equiv. of  $\text{OsO}_4$  in abs.  $\text{Et}_2\text{O}$ . These are converted by oxidative hydrolysis ( $M/3\text{-NaClO}_3$  in dioxan- $\text{AcOH}$ ) or, better, by reductive hydrolysis (aq.  $\text{EtOH-Na}_2\text{SO}_3$ ) [whereby the insol. salt,  $\text{Na}_4\text{Os}(\text{SO}_3)_3\cdot 6\text{H}_2\text{O}$ , is also produced] into *cis*-7:8-dihydroxyacenaphthene (II), *cis*-1:2-dihydroxyindane (III), *cis*-2:3-dihydroxy-1:2:3:4-tetrahydronaphthalene, and *cis*-9:10-dihydroxydecahydronaphthalene, m.p.  $89.5^\circ$  [oxidised by  $\text{Pb}(\text{OAc})_4$  in  $\text{C}_6\text{H}_6$  to *cyclo-decane-1:6-dione* (Hückel *et al.*, A., 1930, 76)], respectively. The above ester from (I) forms a 1:2-additive compound with  $\text{C}_5\text{H}_5\text{N}$ ; this is converted by warm  $\text{AcOH}$  or  $0.2N\text{-NaOH}$  in  $\text{H}_2$  (and subsequent acidification) into the diester (IV), 1:8- $\text{C}_{10}\text{H}_6\begin{matrix} \text{CH}\cdot\text{O} \\ \diagup \\ \text{CH}\cdot\text{O} \end{matrix}\text{OsO}\begin{matrix} \text{O}\cdot\text{CH} \\ \diagdown \\ \text{O}\cdot\text{CH} \end{matrix}\text{C}_{10}\text{H}_6$ -1:8, decomp.  $292^\circ$  [ $\text{K}_2$  salt (+ $4\text{H}_2\text{O}$ )], also obtained (a) on attempted hydrolysis ( $\text{H}_2\text{O}$  or  $\text{EtOH-HCl}$  in dioxan; alkali

followed by  $\text{CO}_2$ ) of the original ester, (b) from the ester and (II), (III), or *cis-cyclohexanediol* (V) in dioxan, and (c) from (II) and  $\text{K}_2\text{OsO}_4$  in 1%  $\text{KOH}$  followed by dil.  $\text{AcOH}$ . Analogous diesters are also prepared [method (c)] from *cis*-7:8-dihydroxy-7:8-diphenylacenaphthene (VI), decomp.  $274^\circ$ , (III), decomp.  $204^\circ$ , (V), decomp.  $165^\circ$ , ( $\text{CMe}_2\cdot\text{OH}$ ) $_2$ , decomp.  $197^\circ$ , and  $\beta$ -anethole glycol, decomp.  $171^\circ$ ; esters could not be prepared from *trans*-diols. Similar diesters (as  $\text{K}_2$  salts) are obtained from hydrobenzoin and isohydrobenzoin. The monoester from (I) with (VI) (but not the *trans*-isomeride) gives a mixed diester of (II) and (VI) together with smaller amounts of (IV) and the above diester of (VI). Os in the above compounds is determined by oxidation with  $\text{CrO}_3$ +conc.  $\text{H}_2\text{SO}_4$ ; the  $\text{OsO}_4$  formed is distilled into a mixture of  $0.4N\text{-KI}$ ,  $2N\text{-H}_2\text{SO}_4$ , and  $\text{CHCl}_3$ , and then titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ .

*cycloHexene* (VII) in  $\text{O}_2$  and sunlight yields  $\Delta^2$ -*cyclohexenyl H peroxide* (VIII); in presence of, e.g.,  $\text{OsO}_2$ , which is oxidised by (VIII) to  $\text{OsO}_4$ , the following reactions occur:  $(\text{VII}) + \text{OsO}_4 \rightarrow \text{C}_6\text{H}_8\begin{matrix} \text{CH}\cdot\text{O} \\ \diagup \\ \text{CH}\cdot\text{O} \end{matrix}\text{OsO}_2$ , which is then oxidised by (VIII) to  $(\text{CH}_2)_4(\text{CHO})_2$ ; (VIII) is thus reduced to *cyclohexenol*. Willstätter and Sonnenfeld's results (A., 1913, i, 1200) on the autoxidation of (VII) in presence of Os and  $\text{OsO}_2$  are thus satisfactorily explained.

[With W. RICHTER.] The esters  $\begin{matrix} \text{CHR}\cdot\text{O} \\ \diagup \\ \text{CHR}\cdot\text{O} \end{matrix}\text{OsO}_2$ , when treated with  $\text{H}_2\text{O}_2$  in absence of  $\text{H}_2\text{O}$  undergo oxidative fission to  $\text{RCHO}$ ,  $\text{R'CHO}$ , and  $\text{OsO}_3$  (which then gives  $\text{OsO}_4$ ). Thus stilbene,  $\text{H}_2\text{O}_2$ , and a little  $\text{OsO}_4$  in  $\text{Et}_2\text{O}$ +anhyd.  $\text{Na}_2\text{SO}_4$  give 77% of  $\text{PhCHO}$  and a little  $\text{BzOH}$ . Anethole, *isoeugenol* Me ether, *isocugenol* acetate, and *isosafrole* similarly afford  $\text{MeCHO}$  (54–98%) and *p*- $\text{OME}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , veratraldehyde, acetylvanillin, and piperonal, respectively, in 47–75% yield; small amounts of the corresponding  $\text{ArCO}_2\text{H}$  are also produced. H. B.

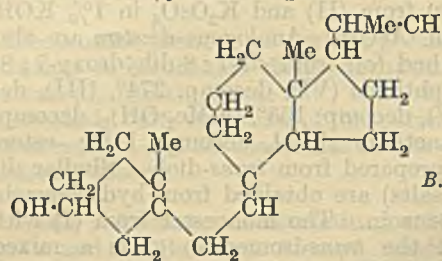
**Constitution of dihydrovitamin- $D_2$ .** S. VON REICHEL and M. DEPPE (Z. physiol. Chem., 1936, 239, 143–146; cf. this vol., 69).—The allophanate of dihydrovitamin- $D_2$  (I) in  $\text{CHCl}_3$  gives, with  $\text{BzO}_2\text{H}$ ,



the trioxide (II), m.p.  $190^\circ$ ,  $[\alpha]_D^{19} -3.4^\circ$  in  $\text{CHCl}_3$ , 3 O being taken up. (II) with  $\text{CrO}_3$  in  $\text{AcOH}$  gives a monocarboxylic acid (III), m.p.  $219^\circ$ ,  $[\alpha]_D^{20} -23.3^\circ$  in  $\text{AcOH}$ , which yields the *OH-acid*,  $\text{C}_{22}\text{H}_{34}\text{O}_6$ , m.p.  $244^\circ$  (Me ester, m.p.  $216^\circ$ , and its acetate, m.p.  $155-156^\circ$ ,  $[\alpha]_D^{19} -55^\circ$ ), when boiled with  $\text{KOH}$  in  $\text{EtOH}$  and gives the  $\text{CHI}_3$  reaction, but does not react with  $\text{NH}_2\text{OH}$  or semicarbazide or absorb ultra-violet light. The oxidation yields also a neutral substance,  $\text{C}_{30}\text{H}_{48}\text{O}_8\text{N}_2$ , m.p.  $239-240^\circ$ ,  $[\alpha]_D^{20} -68.2^\circ$  in  $\text{CHCl}_3$ , which does not



absorb ultra-violet light. When (II) in  $\text{CHCl}_3$  is treated with  $\text{O}_3$  and the product oxidised with  $\text{CrO}_3$



in AcOH (III) is produced. The structures A and B are therefore assigned to (III) and (I), respectively.

W. McC.

**Sterols. IV. Androsterone derivatives.** R. E. MARKER. **V. epiCholesterol.** R. E. MARKER, T. S. OAKWOOD, and H. M. CROOKS (J. Amer. Chem. Soc., 1936, 58, 480—481, 481—483).—IV. Reduction (Na, amyl alcohol) of androsterone-oxime gives 17-aminoandrosterone [hydrochloride, m.p. 340° (decomp.)], converted (diazotization) into 3:17-androstanediol, m.p. 218—220°, which, like isoandrosterone, is oxidised ( $\text{CrO}_3$ , AcOH) to 3:17-androstanedione, m.p. 128—129°. Similar reduction of the oxime of  $\alpha$ -3-chloroandrosterone (I) affords 17-aminoandrosterone [hydrochloride, m.p. 345° (decomp.)], converted into 17-androstanol, m.p. 166°, which is also prepared by reduction of (I).

V. Cholesteryl chloride and Mg give Mg dl-cholesteryl chloride (II), which with dry  $\text{O}_2$  at  $-7^\circ$  to  $0^\circ$  affords cholesterol and epicholesterol (III), m.p. 141°, not pptd. by digitonin. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{Et}_2\text{O}$ ) of (III) gives a quant. yield of epicholesterol, thus showing the presence of the  $\Delta^{5:6}$  double linking. (II) and  $\text{CO}_2$  at  $0^\circ$  afford dl- $\Delta^5$ -cholestene-3-carboxylic acid, m.p. 222—225° (Me, m.p. 101.5—102.5°, and Et, m.p. 82.5—83°, esters), reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{Et}_2\text{O}$ -AcOH) to dl-cholestane-3-carboxylic acid, m.p. 209—211° (Me, m.p. 70—71°, and Et, m.p. 66.5—67.5°, esters). Cholesteryl bromide similarly affords Mg dl-cholesteryl bromide.

H. B.

**Thermal decomposition of diacyl peroxides.** H. ERLÉNMEYER and W. SCHOENAUER (Helv. Chim. Acta, 1936, 19, 338—342).—Contrary to Wieland *et al.* (A., 1934, 1215), decomp. of  $\text{Bz}_2\text{O}_2$  gives  $\text{C}_6\text{H}_6$  even in vac. and none of the products necessarily involves the intermediate formation of free radicals. Disproportionation is preferred as a general explanation of the reactions occurring.

R. S. C.

**Alleged dihydrophenylbenzamidine.** A. V. KIRSANOV (Bull. Acad. Sci. U.R.S.S., 1935, No. 6—7, 979—984).—Phenylbenzamidine (I) and Na-Hg react as follows: (I) +  $2\text{H} \rightarrow \text{NH}_2\cdot\text{CHPh}\cdot\text{NHPh}$  (II)  $\rightarrow \text{NH}_3 + \text{CHPh}\cdot\text{NHPh}$  (III); (III) +  $\text{H}_2\text{O} \rightarrow \text{PhCHO} + \text{NH}_2\text{Ph}$ ; (III) +  $2\text{H} \rightarrow \text{CH}_2\text{Ph}\cdot\text{NHPh}$ ; (II)  $\rightarrow \text{NH}_2\text{Ph} + \text{CHPh}\cdot\text{NH}$  (IV); (IV) +  $2\text{H} \rightarrow \text{NH}_2\cdot\text{CH}_2\text{Ph}$ . (II) cannot be isolated from the reaction products, and probably decomposes immediately on formation; the product identified as (II) by Bernthsen *et al.* (A., 1880, 639) was probably unchanged (I).

R. T.

**Hexadeuterobenzene and a trideuterobenzoic acid.** H. ERLÉNMEYER, H. LOBECK, H. GÄRTNER, and A. EPPRECHT (Helv. Chim. Acta, 1936, 19,

336—337; cf. this vol., 61).—Hexadeuterobenzene of constitution  $\text{C}_6\text{D}_{5.59}\text{H}_{0.41}$  has b.p.  $79.4^\circ$ , m.p.  $6.8^\circ$ ,  $d_4^{20}$  0.9465,  $n_D^{20}$  1.4997. With  $\text{ClCO}\cdot\text{NH}_2$  and  $\text{AlCl}_3$  in  $\text{CS}_2$ , followed by decomp. of the complex with  $\text{H}_2\text{O}$ , this gives a benzamide, which, when hydrolysed, affords a nearly pure trideuterobenzoic acid,  $\text{C}_6\text{H}_{2.91}\text{H}_{2.08}\cdot\text{CO}_2\text{H}$ , m.p.  $121.3^\circ$ . The positions of the 3 D are unknown.

R. S. C.

**Asymmetric carbon atom, CHDRR'. II. Attempted resolution of a deuterio- $\beta$ -phenylpropionic acid.** H. ERLÉNMEYER and H. GÄRTNER (Helv. Chim. Acta, 1936, 19, 331—335; cf. this vol., 467).— $\text{C}_6\text{H}_2.18\text{D}_{2.82}\cdot\text{C}_2\text{H}_{1.62}\text{D}_{2.38}\cdot\text{CO}_2\text{H}$  could not be resolved by strychnine.

R. S. C.

**Mechanism of Perkin's reaction.** D. A. BRODSKI (Monatsh., 1936, 67, 137—140).—The study (A., 1933, 392) of the effect of NaOAc on the yield of  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (I) in Perkin's synthesis was overlooked by Böck *et al.* (A., 1934, 1348). The modes of formation and decomp. of  $\text{CHPh}(\text{OAc})_2$  are not considered to accord with their conclusion that it is involved in a side-reaction detrimental to the yield of (I).

H. G. M.

**Tafel rearrangement. II. Electrochemical reduction of ethyl cyclopentanecarboxylate.** H. STENZL, F. FICHTER, and H. ARNI (Helv. Chim. Acta, 1936, 19, 392—398; cf. A., 1934, 631).—Cathodic reduction of Et cyclopentanone-2-carboxylate gives cyclohexanol and some Et cyclopentane- and cyclopentan-2-carboxylate and Et, 1:1'-dihydroxy-1:1'-dicyclopentan-2:2'-dicarboxylate, m.p.  $108^\circ$  (corresponding acid, decomp.  $230^\circ$ ), which favours interpretation of the Tafel rearrangement by migration of acyl. Reduction of  $\text{CO}_2\text{Et}$  occurs only before the CO is reduced and is accompanied by migration of COR.

R. S. C.

**Synthetic substances resembling thyroxine from diphenyl ether.** K. H. SLOTTA and K. H. SOREMBÄ (Ber., 1936, 69, [B], 566—572).— $\text{p-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  and  $\text{MeNO}_2$  in EtOH are converted by KOH in  $\text{MeOH}\cdot\text{H}_2\text{O}$  at  $0^\circ$  into  $\omega$ -nitro-p-phenoxy-styrene, m.p.  $102^\circ$ , electrolytically reduced in EtOH-EtOAc-HCl to  $\beta$ -p-phenoxyphenylethylamine hydrochloride (I), m.p. 209—210°.  $\text{p-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  is transformed by KCN and  $(\text{NH}_4)_2\text{CO}_3$  in EtOH- $\text{H}_2\text{O}$  at  $80^\circ/10$ —12 atm. ( $\text{CO}_2$ ) into 5-p-phenoxyphenylhydantoin, m.p. 203—204°, hydrolysed by boiling 21% KOH to p-phenoxyphenylaminoacetic acid (II), m.p.  $242^\circ$  [hydrochloride, (III), m.p. 218—220° (decomp.)]. Hippuric acid, NaOAc,  $\text{p-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , and  $\text{Ac}_2\text{O}$  at  $100^\circ$  afford the azlactone,

$\text{CPh}\cdot\text{N} \begin{array}{c} \diagup \\ \text{O}-\text{CO} \end{array} \text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ , m.p.  $158^\circ$ , hydrolysed to  $\alpha$ -benzamido- $\beta$ -p-phenoxyphenylacrylic acid, m.p. 188—189°, which is converted by red P, HI ( $d$  1.7), and  $\text{Ac}_2\text{O}$  into  $\alpha$ -amino- $\beta$ -p-phenoxyphenylpropionic acid (IV) (deiododeoxythyroxine), m.p.  $247^\circ$  when rapidly heated [hydrochloride (V), m.p. 218—220° (decomp.)]. Similarly  $\text{p}'\cdot\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  gives successively the azlactone,  $\text{C}_{22}\text{H}_{14}\text{O}_3\text{NI}$ , m.p. 158—159°,  $\alpha$ -benzamido- $\beta$ -p-4'-iodophenoxyphenylacrylic acid, m.p. 222—223°, and  $\alpha$ -amino- $\beta$ -p-4'-iodophenoxyphenylpropionic acid (VI), m.p. 249—250°.



$p'$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·O·C<sub>6</sub>H<sub>4</sub>·CHO gives the *azlactone*, C<sub>22</sub>H<sub>14</sub>O<sub>5</sub>N<sub>2</sub>, m.p. 177°,  $\alpha$ -benzamido- $\beta$ -p-4'-nitrophenoxypheylacrylic acid, m.p. 210°, and  $\alpha$ -amino- $\beta$ -p-4'-aminophenoxyphenylpropionic acid (VII), m.p. 239—240° [hydrochloride, m.p. 270—275° (strong decomp.)]. Treatment of (III) with ICl in AcOH gives the *iodo-derivative*, m.p. 238—240°. Iodination of (IV) could not be effected by I and NaOH, I, KI, and conc. NH<sub>3</sub>, or by ICl in 2*N*-HCl whereas (V) with ICl in AcOH yields (VI) [hydrochloride, m.p. 235—240° (decomp.)]. No physiological activity is shown by (I), (II), (IV), (VI), or (VII). H. W.

**Condensation of piperonal with hippuric acid.** II. G. LABRUTO and L. IRRERA (Gazzetta, 1935, 65, 1201—1202).—The condensation product (I), the lactimide of  $\alpha$ -benzamido-3:4-methylenedioxy-cinnamic acid (II) [cf. A., 1934, 526, in which the formula (I) should read CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CH·CH<NBz  
CO

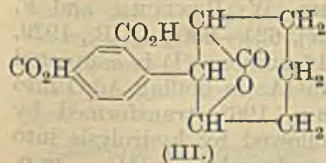
reacts with NPh·NH<sub>2</sub> to give a *compound*, C<sub>7</sub>H<sub>8</sub>ON, m.p. 220°, insol. in EtOH, and a *compound*, m.p. 130°, sol. in EtOH. When (II) is boiled with MeOH, the *Me ester*, C<sub>10</sub>H<sub>15</sub>O<sub>5</sub>N, m.p. 150°, is formed.

E. W. W.

**General method for synthesis of substituted phthalidecarboxylic acids.** S. K. CHAKRAVARTI and P. R. VENKATARAMAN (Current Sci., 1936, 4, 483—484).—*o*-Nitromandelic acid, and substituted acids, can be smoothly converted by FeSO<sub>4</sub> and Ba(OH)<sub>2</sub> into the corresponding NH<sub>2</sub>-acids, and then (Sandmeyer) into cyanomandelic acids, which are hydrolysed to phthalidecarboxylic acids. E. W. W.

**Bile acids. XLVIII. Method of production of the compound C<sub>24</sub>H<sub>36</sub>O<sub>10</sub>N<sub>2</sub> (bilianic acid series). Mode of action of nitric acid in oxidations.** M. SCHENCK (Z. physiol. Chem., 1936, 239, 135—142; cf. this vol., 74).—The compound is a lactamamide of which the precursor, in each of the 5 methods described, is the ketolactam. HNO<sub>2</sub> originally present or produced during the reaction is the active agent in the HNO<sub>3</sub> oxidation, which is restricted or prevented by addition of CO(NH<sub>2</sub>)<sub>2</sub>. W. McC.

**New diene syntheses. II.** E. LEHMANN (Ber., 1936, 69, [B], 631—635; cf. A., 1935, 978).—2-*m*-4'-Xylyl-2-methyl- $\Delta^3$ -tetrahydrobenzaldehyde (I) (*loc. cit.*) is reduced by Zn-Hg and 6*N*-HCl to 1:3:1':2'-tetramethyl- $\Delta^5$ -tetrahydrodiphenyl, b.p. 155—158°/12 mm. (very unstable *bromide*), which could not be satisfactorily dehydrogenated. (I) with CrO<sub>3</sub> in AcOH or with conc. aq. KOH affords 2-*m*-4'-xylyl-2-methyl- $\Delta^3$ -tetrahydrobenzoic acid (II), m.p. 102° (accompanied when NaOH is used by 2-*m*-4'-xylyl-2-methyl- $\Delta^3$ -tetrahydrobenzyl alcohol, b.p. 145—146°/0.8 mm.).



(III)

(II) is oxidised by KMnO<sub>4</sub> in alkaline solution to 1':2':3':4'-tetrahydrodiphenyl-1:3:2'-tricarboxylic acid or, more probably, the *lactone* (III), m.p. > 300°.

Phenylmethylallylcarbinol is transformed by PCl<sub>3</sub> in CHCl<sub>3</sub> or by HCl in EtOH into the corresponding unstable *chloride*, converted by KOH at 210—230° into  $\beta$ -phenyl- $\Delta^{8,9}$ -pentadiene (IV), which could not

be purified owing to its great ease of polymerisation. When heated with acraldehyde in C<sub>6</sub>H<sub>6</sub> at 100—105° it gives 2-phenyl-2-methyl- $\Delta^3$ -tetrahydrobenzaldehyde, b.p. 172—174°/12 mm., m.p. 48° (additive compound with NaHSO<sub>3</sub>). Similarly, *p*-tolylmethylallylcarbinol affords successively the corresponding *chloride*, impure  $\alpha$ -*p*-tolyl- $\Delta^{8,9}$ -pentadiene, and 2-*p*-tolyl-2-methyl- $\Delta^3$ -tetrahydrobenzaldehyde, b.p. 176—178°/12 mm., m.p. 51° (corresponding NaHSO<sub>3</sub> compound). H. W.

**Ethyl acetal of cyclohexanone, and its transformation into cyclohexenyl ethyl ether.** A. E. ARBUSOVA and B. M. MICHAILOVA (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 41—45).—cycloHexanone and CH(OEt)<sub>2</sub> in presence of H<sub>2</sub>SO<sub>4</sub>

afford CH<sub>2</sub><CH<sub>2</sub>·CH<sub>2</sub>>C(OEt)<sub>2</sub> (I), in 38% yield.

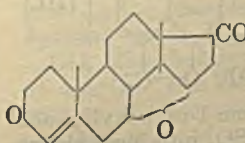
1:2:4 mixtures of (I), P<sub>2</sub>O<sub>5</sub>, and C<sub>5</sub>H<sub>5</sub>N (5 hr.; 100°) yield  $\Delta^1$ -cyclohexenyl Et ether. R. T.

**Pyrolysis of tetrahydronaphthyl naphthyl ketones.** L. F. FIESER and A. M. SELIGMAN (J. Amer. Chem. Soc., 1936, 58, 478—480; cf. A., 1935, 480).—The Grignard reagent from 1-bromo-5:6:7:8-tetrahydronaphthalene, b.p. 130°/2 mm. (from the 1-NH<sub>2</sub>-derivative), with  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>-COCl gives  $\alpha$ - $\alpha$ -tetrahydronaphthyl  $\alpha$ - (I), m.p. 107°, and  $\beta$ - (II), m.p. 98°, -C<sub>10</sub>H<sub>7</sub> ketone, respectively. (I) heated at 395—400°/45 min. in N<sub>2</sub> affords 1:12-trimethylene-chrysene, m.p. 116.5—117° (corr.) (*picrate*, m.p. 170—171°), oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH) to (probably) a *ketoguinone*, C<sub>21</sub>H<sub>12</sub>O<sub>3</sub>, m.p. 268—270° (decomp.). (II) heated at 400°/30 min. gives a *hydrocarbon* (III), C<sub>21</sub>H<sub>16</sub>, m.p. 113—115° (corr.) (*picrate*, m.p. 168—169°) (31%), a *hydrocarbon* (IV), C<sub>21</sub>H<sub>14</sub> (? dehydro-8:9-trimethylene-1:2-benzanthracene), m.p. 149—149.5° (corr.) (*picrate*, m.p. 146—147°) (10%), about 7% of (probably) 8:9-trimethylene-3:4-benzphenanthrene, m.p. 138—138.5° (corr.) (*picrate*, m.p. 125—126°), and a little of a *hydrocarbon*, C<sub>21</sub>H<sub>16</sub>, m.p. 96.5—97° (corr.). The hydrocarbon, m.p. 270°, previously obtained (*loc. cit.*) from crude (II), has not been encountered. (III) and (IV) are oxidised to *compounds*, C<sub>21</sub>H<sub>10</sub>O<sub>4</sub>, m.p. 220—223°, and C<sub>21</sub>H<sub>12</sub>O, m.p. 201°, respectively. Ketones containing the tetrahydrobenzo-group are thus unsuitable for the Elbs synthesis; dehydrogenation and migration of H may take place [as with (II)]. H. B.

**Phenylbenzoyldiazomethane.** C. D. NENITZ-ESCU and E. SOLOMONICA (Org. Syntheses, 1935, 15, 62—63).—The prep. from CPhBz·N·NH<sub>2</sub> is described. CH. ABS. (r)

**2':6'-Dihydroxy-4'-methoxy- $\beta$ -phenylpropio-phenone from essential oil of *Populus balsamifera*, L.**—See this vol., 533.

**Constituents of the adrenal gland. II. " $\beta$ -Adrenosterone."** T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 223—225).—The diketone, G (this



vol., 473), has no oestrogenic effect on mice, but one fifth of the activity of androsterone by the capon test; it is called *adrenosterone* and given the partial formula shown; it is probably a normal constituent of the adrenal gland.



The absorption spectrum of its disemicarbazone is given. R. S. C.

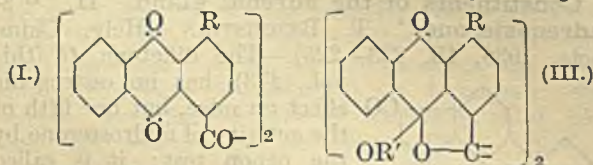
**Sex hormones. XIII. Preparation of 17-ethyltestosterone and the 3-trans-17-cis-diols of androstane and androstene.** Specificity of the sex hormones. L. RUZICKA and H. R. ROSENBERG (Helv. Chim. Acta, 1936, 19, 357—366; cf. this vol., 467).—Dehydro-trans-androsterone (I) and trans-androsterone (II) with MgMeI give mixtures. (I) affords 17-ethyl- $\Delta^5$ -androstene-3-trans-17- $\beta$ -diol (III), m.p. 199—200°, and 30—40% of  $\Delta^5$ -androstene-3-trans-17-cis-diols (IV), m.p. 173—173.5°, sublimes at 100°/0.01 mm. (diacetate, m.p. 149—151°). (I) affords 17-ethylandrostane-3-trans-17- $\beta$ -diol, m.p. 205°, and androstane-3-trans-17-cis-diols (V), m.p. 178—179°, sublimes at 150°/0.01 mm. (V) is also obtained by hydrogenation (PtO<sub>2</sub>) of (IV) in AcOH-EtOH and from (II) and MgPrI with a little 17-Pr derivative. (IV) and CrO<sub>3</sub> give androstane-3:17-dione. (III) and Br-AcOH, followed by CrO<sub>3</sub> (1.5 O), give 17-ethyltestosterone, m.p. 143°. New and revised data are given of the activity of 15 compounds by the capon and rat tests. 17-Methyltestosterone is the most active and also has considerable progesterone activity. The presence of a  $\Delta^4$ - or  $\Delta^5$ -ethylenic linking and the position of the 17-OH are without effect. 3-cis-are more effective than 3-trans-OH-compounds. Me in position 17 raises the efficiency, Et reduces it.

R. S. C.

**Behaviour of magnesium diphenyl bromide with benzoquinone.** D. E. WORRALL and S. COHEN (J. Amer. Chem. Soc., 1936, 58, 533).—*p*-C<sub>6</sub>H<sub>4</sub>Ph-MgBr (I) and *p*-C<sub>6</sub>H<sub>4</sub>O<sub>2</sub> give (*p*-C<sub>6</sub>H<sub>4</sub>Ph)<sub>2</sub> (44%) [also formed from (I) and (NPh)<sub>2</sub>], *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, and smaller amounts of Ph<sub>2</sub> and *p*-C<sub>6</sub>H<sub>4</sub>Ph-OH. Hydrocarbon formation does not occur with MgPhBr or MgBu<sup>n</sup>Br and *p*-C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>. H. B.

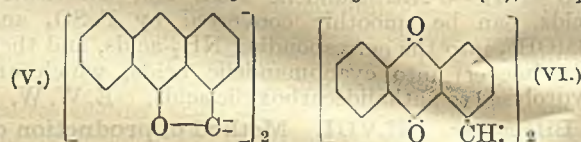
**Sugar-absorption by hydroxyanthraquinones.** I. S. MÜLLER (Magyar chem. Fol., 1934, 40, 135—146; Chem. Zentr., 1935, ii, 514—515).—Co-ordination between the 1-OH and the CO is assumed to occur; the effect of 2- and 8-OH groups in lowering the reactivity of the 1-OH is due to their action in stabilising the ring so formed. H. N. R.

**1:1'-Dianthraquinonyl glyoxal and the anthraflavone of the  $\alpha$ -series.** R. SCHOLL and H. D. WALLENSTEIN (Ber., 1936, 69, [B], 503—513).—Oxidation of 4-chloro-1-methylantraquinone with MnO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> and successive treatments of the product with boiling H<sub>2</sub>O and C<sub>5</sub>H<sub>5</sub>N (whereby autoxidation takes place) yields 4:4'-dichloro-1:1'-dianthraquinonyl glyoxal [(I) R=Cl], decomp. 280—300°, which readily gives an alkaline vat from which it cannot be regenerated, is oxidised by HNO<sub>3</sub> in



PhNO<sub>2</sub> to 4-chloroanthraquinone-1-carboxylic acid (II), and is transformed by Me<sub>2</sub>SO<sub>4</sub> into Me 4-chloroanthraquinone-1-carboxylate. Treatment of (I) with

conc. H<sub>2</sub>SO<sub>4</sub> under defined conditions leads to the violet hexasulphate of the lactol form of 4:4'-dichloro-1:1'-dianthraquinonyl ethylenediol [(III) R=Cl, R'=H], which passes when treated with H<sub>2</sub>O into a blue, then violet, powder and ultimately in presence of air affords (I). (III) and NaNO<sub>2</sub> in conc. H<sub>2</sub>SO<sub>4</sub> at 60—90° yield (II). Treatment of the sulphate of (III) with boiling EtOH gives the Et<sub>2</sub> ether [(III) R=Cl; R'=Et], m.p. 240—241°, which is not sensitive to light, does not give a vat, and is de-alkylated to (III) by conc. H<sub>2</sub>SO<sub>4</sub>. The corresponding Me<sub>2</sub> ether has m.p. 241—243°. 1:1'-Dianthraquinonyl glyoxal (IV) [(I) R=H], m.p. 320° (decomp.) when rapidly heated, is obtained by the oxidation of 1-methylantraquinone with MnO<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub> at 65—70°, from anthraquinone-1-carboxyl chloride and Na in xylene at 120—130°, or (best) from Bz-1-Bz'-1-dibenzanthronyl and CrO<sub>3</sub> in boiling AcOH. The corresponding cryst. dilactol sulphate is very sensitive towards H<sub>2</sub>O; with MeOH and EtOH it gives the corresponding ethers. (IV) is transformed by NaOMe in boiling MeOH into anthraquinone-1-carboxylic acid, is converted by NH<sub>2</sub>OH.HCl in boiling C<sub>5</sub>H<sub>5</sub>N into the (?) oxime, m.p. > 360°, and a substance C<sub>13</sub>H<sub>7</sub>O<sub>3</sub>N, m.p. 238—239°, and a bis-diazine, m.p. > 500°. Treatment of (IV) in conc. H<sub>2</sub>SO<sub>4</sub> with Cu powder at 50° gives the dianhydride of dianthramol-9:9'-yl-1:1'-ethylenediol (V), m.p.



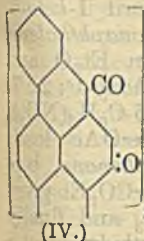
about 400°. A further argument in favour of the dilactol structure is found in the conversion of 1-methylantraquinone by KOH and a little anhyd. NaOAc in EtOH at 165° into s-1:1'-dianthraquinonyl ethylene [isoanthraflavone] (VI), m.p. > 360°, which dissolves in conc. H<sub>2</sub>SO<sub>4</sub> to a yellow solution which becomes bluish-red and then shows the absorption spectrum of the dilactol and yields (V) with Cu powder. The following compounds are incidentally described: 9:9'-dihydroxy-9:9'-dianthronyl-1:1'-dicarboxy-dilactone, m.p. 282° (decomp.), from anthraquinol-1-carboxylactone in boiling PhNO<sub>2</sub>, which behaves towards NaOH in the same manner as does (IV); acetic 4-chloroanthraquinone-1-carboxylic anhydride, which softens and evolves Ac<sub>2</sub>O at 141° and passes in C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> at 180° into 4-chloroanthraquinone-1-carboxylic anhydride, m.p. 260—262° (decomp.).

H. W.

**Perylene and its derivatives. LXVII. Vat dye of the isoviolanthrone series from perylene-1:12-quinone.** A. ZINKE, W. PENECKE, and F. HANUS (Ber., 1936, 69, [B], 624—630; cf. B., 1929, 891, 1008).—Perylene-1:12-quinone (I) is converted by Zn dust and anhyd. NaOAc in boiling Ac<sub>2</sub>O into 1:12-diacetoxyperylene, m.p. 196°, transformed by AlCl<sub>3</sub> and BzCl in CS<sub>2</sub> followed by hydrolysis into 1:12-dihydroxy-3:9-dibenzoylperylene (II), m.p. about 217° (decomp.). When heated with AlCl<sub>3</sub> (II) gives a blue vat dye also obtained from 1:12-dibenzoyldioxyperylene (III), which cannot be oxidised subsequently to the green dye (*loc. cit.*). The



latter compound is, however, obtained from (II) or (III) and  $\text{AlCl}_3$  in presence of  $\text{MnO}_2$  or from (I) and  $\text{BzCl}$  in absence of added oxidising agent. Oxidation of (II) with  $\text{PbO}_2$  gives a product insol. in  $\text{NaOH}$  which does not give the analytical data of 3:9-dibenzoylperylene-1:12-quinone. The production of the blue and green dyes from (II) indicates the occurrence of a Fries displacement during their formation from (III). Early interruption of the process or the use of milder conditions does not lead to the isolation of intermediate products but establishes the fission of (III). The dyes therefore arise from 1:12-dihydroxyperylene and  $\text{BzCl}$ . Since the green compound is converted by red P and HI ( $d$  1.7) at  $220^\circ$  into isoviolanthrene it has the constitution (IV). (I) is transformed by Br in  $\text{C}_6\text{H}_6$  into tetrabromotetrahydroperylene - 1:12-quinone, decomp.  $220\text{--}230^\circ$  after darkening at  $170^\circ$ , which passes in boiling  $\text{C}_5\text{H}_5\text{N}$  into dibromoperylene-1:12-quinone, m.p.  $272^\circ$  (decomp.). Dichlorodihydroperylene - 1:12-quinone,



from (I) and  $\text{Cl}_2$  in cold  $\text{C}_6\text{H}_6$ , is very unstable, readily yielding chloroperylene-1:12-quinone, m.p.  $271\text{--}272^\circ$  (decomp.). (I) with warm  $\text{HNO}_3$  ( $d$  1.34) affords dinitroperylene-1:12-quinone, decomp.  $> 300^\circ$ , transformed by Zn dust and  $\text{NaOAc}$  in boiling  $\text{Ac}_2\text{O}$  into tetra-acetyldiamino-1:12-diacetoxyperylene, m.p.  $246\text{--}247^\circ$ . 1:12-Di-*p*-bromobenzoyl-, m.p.  $247^\circ$ , and 1:12-dianisoyl-, m.p.  $188^\circ$ , dioxyperylene are described.

H. W.

Perylene and its derivatives. XLV. A tribenzoylperylene. A. ZINKE and E. GESELL. XLVI. A perylene-1:12-cycloperoxide. A. ZINKE and K. J. VON SCHIESZL [with F. HANUS] (Monatsh., 1936, 67, 187—192, 196—202).—XLV. 3:9-Dibenzoylperylene when heated (water-bath; 5 hr.) with anhyd.  $\text{AlCl}_3$  and  $\text{BzCl}$  affords a tribenzoylperylene (I), m.p.  $236\text{--}237^\circ$  [the  $(\text{NO}_2)_3$ -derivative, decomp. about  $300^\circ$ , is reduced by  $\text{NaOH}\text{--}\text{Na}_2\text{S}_2\text{O}_4$  (water-bath) to a dark blue compound], which on Clemmensen reduction yields a compound  $\text{C}_{41}\text{H}_{26}\text{O}_2$ , m.p.  $208^\circ$ , and when heated at  $160^\circ$  with  $\text{AlCl}_3$  gives a trace of an isoviolanthrone-like derivative. It is concluded that migration of Bz from position 3 or 9 during formation of (I) has not taken place, and that the third Bz is not in one of the remaining positions (cf. A., 1930, 1587).

XLVI. 1:12-Dihydroxyperylene (improved prep.) when heated at  $450\text{--}500^\circ$  with moist  $\text{ZnCl}_2$  and Zn yields perylene, but with anhyd.  $\text{ZnCl}_2$  at  $250\text{--}260^\circ$  yields also perylene-1:12-cycloperoxide, m.p. above  $340^\circ$  (cf. A., 1933, 552). This is very stable, being unaffected by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in boiling PhMe, or when heated with HI. Only a part dissolves in 20%  $\text{NaOH}\text{--}\text{MeOH}$  during 3 hr. at  $130^\circ$  (sealed vessel). In accord with the structure given, it cannot be used as a vat dye.

H. G. M.

Linalool in coriander oil. Oil from flowering *Coriandrum sativum*.—See B., 1936, 348.

Isomerisation of  $\alpha$ -pinene to an aliphatic terpene (alloocimene). VI. Isomerisation of nopinene,  $d$ - $\Delta^3$ -carene, camphene, and pinocam-

phone. B. A. ARBUSOV (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 4—5, 53—56; cf. A., 1935, 1246).—alloOcimine is obtained in 20% yield by passing nopinene over glass at  $345\text{--}350^\circ$ ; under these conditions  $\Delta^3$ -carene, camphene, and pinocamphone do not undergo conversion into (I).

R. T.

Terpenes and camphors. I. Isomerisation of  $\alpha$ -pinene by activated charcoal. T. MOCHIDA (J. Pharm. Soc. Japan, 1933, 53, 936—947).— $l$ - $\alpha$ -Pinene with active C at  $145\text{--}150^\circ$  affords 95—98% of monoterpenes (75—80% monocyclic, 20—25% camphene) and 2—3% of diterpenes;  $\text{B}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  catalyse the reaction. In the gaseous state camphene (12—30%), limonene, dipentene, diterpenes (6—7%), and *p*-cymene are produced.

CH. ABS. (r)

apoBornylene from camphenyl chloride. P. LIPP and J. DANIELS (Ber., 1936, 69, [B], 586—588).—The removal of HCl from camphenyl chloride (I) by  $\text{NaOEt}$  is effected with difficulty so that an exact repetition of Snitter's work (A., 1933, 1300) is impossible. Treatment of (I) with  $\text{KOPh}$  gives a semi-solid cryst. product from which apobornylene is readily isolated. Santene could not be detected. The composition of camphenylene appears to vary greatly and to depend on the mode of elimination of HCl from (I).

H. W.

Polyterpenes and polyterpenoids. CI. Constitution of cedrene and cedrol. L. RUZICKA and E. JUTASSY. CII. Constitution of components of the caryophyllene mixture. L. RUZICKA, W. ZIMMERMANN, and K. HUBER. CIII. Synthesis of the five isomeric methoxy-1:2:7-trimethylnaphthalenes (methoxysapotalins). L. RUZICKA, H. HÖSLI, and K. HOFMANN [with H. BLEULER, S. DEUTSCH, P. J. G. VAN HECK, L'ORANGE, O. NERACHER, E. VON ORELLI, G. PÜRNER, E. REICH, T. SCHINZEL, N. STERNBUCH, W. ZÜRCHER, G. ZUNANA, (FRLNS.) R. ALLEMANN and A. M. SIRKS]. CIV. Synthesis of 3:9:10-trimethyl- and 3:8-dimethyl-picene. L. RUZICKA and E. MÖRGELI. CV. Constitution of the trimethylnaphthols formed during dehydrogenation of triterpenes. Carbon skeleton of pentacyclic terpenes. L. RUZICKA, K. HOFMANN, and J. FREI (Helv. Chim. Acta, 1936, 19, 322—325, 343—353, 370—377, 377—386, 386—392; cf. this vol., 477).—CI. The formation of *p*-cymene at  $> 420^\circ$  does not necessarily indicate the presence of its C-skeleton in cedrene, which may have either of the formulæ shown. Cedrenedicarboxylic



acid with  $\text{HN}_3\text{--CHCl}_3$  and  $\text{H}_2\text{SO}_4$  at  $40\text{--}45^\circ$  gives a 40% yield of a diamine,  $\text{C}_{12}\text{H}_{24}\text{N}_2$  [picrate and hydrochloride, hygroscopic;  $\text{Ac}_2$  derivative, m.p.  $180\text{--}181^\circ$  (corr.)], the phosphate of which at about  $320^\circ$  gives a hydrocarbon,  $\text{C}_{12}\text{H}_{18}$ , b.p.  $85\text{--}87^\circ/10$  mm.

CII. The chemistry of caryophyllene (I) is discussed at length. Ruzicka's formula is preferred, mainly because the Me ester of the derived acid,  $\text{C}_{11}\text{H}_{18}\text{O}_2$ , and Me<sub>2</sub> ester of the acid,  $\text{C}_{13}\text{H}_{18}\text{O}_4$ , are completely hydrolysed by hot 0.1N-KOH-EtOH in 10 hr. *cis*-



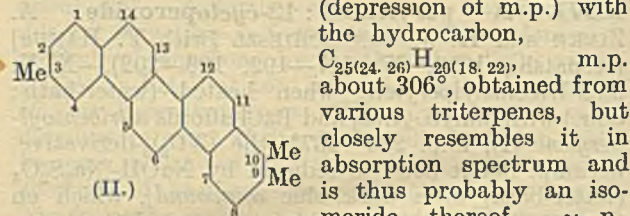
Norcaryophyllenic acid, m.p. 149—150°, is described. The neutral portion obtained on ozonisation of (I) in AcOH yields a ketone,  $C_{10}H_{18}O$ , b.p. 84—85°/12 mm. (*semicarbazone*, m.p. 181°; oxidised by  $KMnO_4$  to an acid,  $C_8H_{14}O_2$ , b.p. 108—110°/12 mm.), possibly  $CH_2<\overset{CMc_2}{\underset{CHMe}{C}}>CH\cdot CH_2Ac$ , and a diketone,  $C_{13}H_{22}O_2$  (lit.,  $C_{13}H_{20}O_2$ ), b.p. 136°/12 mm. (*disemicarbazone*, m.p. 219°, oxidised by  $KMnO_4$  to caryophyllenic acid and  $CO_2H\cdot CH_2\cdot CMe_2\cdot CO_2H$ ), possibly

$CH_2<\overset{CMc_2}{\underset{CHR}{C}}>CH\cdot CH_2Ac$  ( $R=CH_2\cdot CH_2Ac$ ). The dicarboxylic acid,  $C_{10}H_{16}O_4$  (A., 1931, 735), is obtained pure, b.p. about 175°/0.4 mm.; when heated with  $Ac_2O$  at 200° and then decarboxylated, it gives a ketone,  $C_{10}H_{14}O$  (*semicarbazone*, m.p. 186—188°).

CIH. The OH-compound, m.p. 153°, obtained from oleanolic acid by Se, with Ni-pumice in  $H_2$  at 300° gives 1 : 2 : 7- $C_{10}H_5Me_3$ , but its Me ether is not identical with any of the five possible methoxy-1 : 2 : 7-trimethylnaphthalenes, which are synthesised. 4-Methoxy-2 : 3-dimethylbenzaldehyde (prep. by a Gattermann reaction) with  $CHMeBr\cdot CO_2R$  and Mg (not Zn) in  $C_6H_6$  gives a 60—70% yield of a mixture of esters, (?) *Et*  $\beta$ -hydroxy- $\beta$ -4-methoxy-2 : 3-dimethylphenylisobutyrate and  $\beta$ -4-methoxy-2 : 3-dimethylphenyl- $\alpha$ -methylacrylate, from which the latter ester is obtained pure, b.p. 180—185°/12 mm., m.p. 49—50°, by dehydration with  $PBr_3$  in  $C_6H_6$ . Bouveault reduction then affords  $\beta$ -4-methoxy-2 : 3-dimethylphenylisobutyl alcohol, b.p. 170—175°/12 mm., converted by  $PBr_3$  at 100° into the bromide, b.p. 165—170°/12 mm. (decomp.), which leads by way of the nitrile to  $\gamma$ -4-methoxy-2 : 3-dimethylphenyl- $\beta$ -methyl-n-butyric acid, m.p. 107—108°, b.p. 165—170°/0.2 mm. The corresponding acid chloride (prep. by  $SOCl_2$ ) with  $AlCl_3$  in  $CS_2$  at 20° gives 1-keto-7-methoxy-3 : 5 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 158—160°/0.2 mm., reduced (Clemmensen) to a hydrocarbon, which with Pd-C at 300° gives 3-methoxy-1 : 2 : 7-trimethylnaphthalene, m.p. 69—70° [ $1 : 3 : 5-C_6H_3(NO_2)_3$  compound, m.p. 169—170°]. 2-Methoxy-4 : 5-dimethylacetophenone (prep. by Fries rearrangement of 1 : 2 : 4- $C_6H_3Me_2\cdot OAc$  and subsequent treatment with  $Me_2SO_4$ ), b.p. 150—152°/12 mm., with Br in  $Et_2O\cdot CHCl_3$  (3 : 1) gives the  $\omega$ -Bretone, which by condensation with  $CHMe(CO_2R)_2$  leads to  $\gamma$ -keto- $\gamma$ -2-methoxy-4 : 5-dimethylphenyl- $\alpha$ -methyl-n-butyric acid, b.p. 233—238°/15 mm., reduced (Clemmensen) to  $\gamma$ -2-methoxy-4 : 5-dimethylphenyl- $\alpha$ -methyl-n-butyric acid, b.p. 208—211°/15 mm. The corresponding acid chloride (prep. by  $SOCl_2$ ), b.p. 183—184°/15 mm., gives ( $AlCl_3$ ) 1-keto-5-methoxy-2 : 7 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 197—198°/15 mm., which affords (Clemmensen and then Pd-C) 4-methoxy-1 : 2 : 7-trimethylnaphthalene, m.p. 89—90°, b.p. 175—177°/15 mm. [ $1 : 3 : 5-C_6H_3(NO_2)_3$  compound, m.p. 193—194°].  $m-C_6H_4Me\cdot OAc$  leads (Fries;  $Me_2SO_4$ ) to 2-methoxy-4-methylacetophenone, b.p. 135—138°/15 mm., which yields the  $\omega$ -Br-ketone, b.p. 190°/15 mm. (decomp.), and thence  $[CHMe(CO_2R)_2]$   $\gamma$ -keto- $\gamma$ -3-methoxy-p-tolyl- $\alpha$ -methylbutyric, m.p. 121—122°, b.p. 225—230°/15 mm., and (Clemmensen)  $\gamma$ -3-methyl-p-tolyl- $\alpha$ -methylbutyric acid, b.p. 200—215°/15 mm. The chloride, b.p. 165—170°/13 mm., of the latter acid gives 1-keto-

5-methoxy-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 185—190°/15 mm., converted by  $MgMeI$  into the impure 1-hydroxy-1 : 2 : 7-trimethyltetrahydro compound, b.p. 165—170°/14 mm., which with Pd-C yields 5-methoxy-1 : 2 : 7-trimethylnaphthalene, m.p. 81—82° [ $1 : 3 : 5-C_6H_3(NO_2)_3$  compound, m.p. 212—213°]. 2-Methoxy-p-toluic acid (from the OH-acid by  $Me_2SO_4$  and subsequent hydrolysis), b.p. 168—170°/11 mm., m.p. 158°, gives the acid chloride, b.p. 127—129°/13 mm., and thence  $\omega$ -chloro-2-methoxy-4-methylacetophenone, b.p. 157—160°/10 mm. This with  $CHMe(CO_2R)_2$  leads to  $\gamma$ -keto- $\gamma$ -2-methoxy-p-tolyl- $\alpha$ -methyl-n-butyric acid, m.p. 106—107°. Clemmensen reduction and ring-closure afford 1-keto-6-methoxy-2 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 95—96°, converted by  $MgMeI$  in  $Et_2O$  and subsequent heating with Pd-C into 6-methoxy-1 : 2 : 7-trimethylnaphthalene, m.p. 83—84° [ $1 : 3 : 5-C_6H_3(NO_2)_2$  compound, m.p. 160—161°].  $o-C_6H_4Me\cdot OAc$  leads (Fries, etc.) to 2-methoxy-3-methylacetophenone, b.p. 125—128°/15 mm., which with  $CHMeBr\cdot CO_2Et$  gives a mixture of esters converted by  $PBr_3$  and finally  $NPhMe_2$  into *Et*  $\beta$ -2-methoxy-m-tolyl- $\alpha$ -methylcrotonate; Bouveault reduction affords  $\gamma$ -2-methoxy-m-tolyl- $\beta$ -methyl-n-butyl alcohol, b.p. about 165°/12 mm., converted by way of the bromide and nitrile into  $\gamma$ -2-methoxy-m-tolyl- $\beta$ -methyl-n-valeric acid, b.p. 146—147°/0.2 mm. The corresponding acid chloride with  $AlCl_3$  in  $CS_2$  gives 1-keto-5-methoxy-3 : 4 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 137—138°/15 mm., which yields 8-methoxy-1 : 2 : 7-trimethylnaphthalene, b.p. 151—153°/9 mm. [ $1 : 3 : 5-C_6H_3(NO_2)_3$  compound, m.p. 176—177°].

CIV. 3 : 9 : 10-Trimethylpicene (II) is not identical (depression of m.p.) with the hydrocarbon,

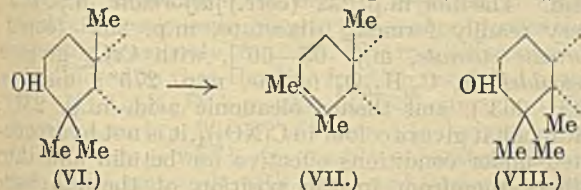


$C_{25(24, 26)}H_{20(18, 22)}$ , m.p. about 306°, obtained from various triterpenes, but closely resembles it in absorption spectrum and is thus probably an isomeride thereof.  $\gamma$ -p-Tolylbutyryl chloride, b.p. 132°/11 mm., with  $AlCl_3$  in  $CS_2$  gives a 90% yield of 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene (III), b.p. 131—132°/9 mm., converted by Pd-C at 300—320° in good yield into 7-methyl- $\alpha$ -naphthol, m.p. 110—111°, b.p. 155—156°/10 mm. With  $(NH_4)_2SO_3$  and aq.  $NH_3$  at 160—170° this gives 7-methyl- $\alpha$ -naphthylamine, m.p. 58—59°, b.p. 162°/10 mm. [Ac derivative, m.p. 178—179° (lit. 175—176°)], which [diazo-reaction;  $Hg(NO_3)_2\cdot KBr$ ] gives the salt,  $[C_{10}H_6Me\cdot N_2Br_2]\cdot HgBr_2$ , converted by heating with KBr into 1-bromo-7-methylnaphthalene, b.p. 144.5—146°/12 mm. (picrate, m.p. 101—102°). The Grignard reagent therefrom with  $(CH_2)_2O$  gives  $\beta$ -7-methylnaphthyl-1-ethyl alcohol, b.p. 154—157°/0.5 mm. (p-nitrobenzoate, m.p. 118—119°), and thence ( $SOCl_2\cdot NPhMe_2$ ) the chloride (IV), b.p. 124—125°/0.4 mm.  $\beta$ -3-o-Xylylethyl bromide and  $CH_2(CO_2R)_2$  lead to  $\gamma$ -3-xylyl-n-butyric acid; the corresponding chloride, b.p. 144—146°/10 mm., and  $AlCl_3$  in  $CS_2$  yield 1-keto-5 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 154—158°/8 mm., m.p. 61—62°, which with the Grignard reagent from (IV) gives  $\alpha$ -1-7-methylnaphthyl-



$\beta$ -1'-5' : 6'-dimethyl-3' : 4'-dihydronaphthylethane, b.p. 215—217°/0.3 mm., dehydrogenated by Pd-C to  $\alpha$ -1-7-methylnaphthyl- $\beta$ -1'-5' : 6'-dimethylnaphthylethane, b.p. 225—230°/0.2 mm., m.p. 108.5—109.5° (picrate, m.p. 167—168°). With  $\text{AlCl}_3$  in  $\text{CS}_2$  (3 days; room temp.) this gives (II), b.p. 270°/0.1 mm., m.p. 308—310° after sintering at 305°. The Grignard reagent from (IV) with (III) gives  $\alpha$ -1-7-methylnaphthyl- $\beta$ -1'-7'-methyl-3' : 4'-dihydronaphthylethane, b.p. 198—205°/0.2 mm., which yields (Pd-C)  $\alpha\beta$ -di-(1-7-methylnaphthyl)ethane, b.p. 220—225°/0.3 mm., m.p. 122.5—123.5°, and thence ( $\text{AlCl}_3$ ) 3 : 8-dimethylpicene, m.p. 293—294°. Temp. in this paper are corr.

CV. Hydrogenation ( $\text{PtO}_2$ ) of 7-methoxy-2 : 6-dimethylnaphthalene in AcOH at 60—70° gives the dimethyldecahydronaphthalene, converted by Pd-C at 300—320° into 2 : 6- $\text{C}_{10}\text{H}_8\text{Me}_2$ . The triterpene degradation product (V),  $\text{C}_{10}\text{H}_8\text{Me}_3\cdot\text{OH}$ , m.p. 153°, gives similarly 1 : 2 : 8-trimethyldecahydronaphthalene and thence 1 : 2 : 8- $\text{C}_{10}\text{H}_8\text{Me}_3$ . The conversion of (V) by Se or  $\text{H}_2$ -Ni at 300° into 1 : 2 : 7- $\text{C}_{10}\text{H}_8\text{Me}_3$  must thus be due to migration of Me; (V) is thus 7-hydroxy-1 : 2 : 8-trimethylnaphthalene. Formation of 1 : 2 : 7- $\text{C}_{10}\text{H}_8\text{Me}_3$  during treatment of pentacyclic terpenes



with Se or Ni is probably due either to a similar interchange of Me and OH or to a pinacolin change [(VI)  $\rightarrow$  (VII)]. Ring A of pentacyclic terpenes is probably as in either (VI) or (VIII). Other  $\text{C}_{10}\text{H}_8$  derivatives isolated may also (less probably) have been formed by such reactions and four structures are thus possible for ring E. Sixteen

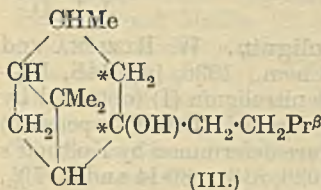
C-skeletons derived from picene are thus possible for triterpenes and all contain only isoprene units; (IX) is favoured.

R. S. C.

**Mono- and sesqui-terpene series. XI. [Caryophyllenes and related compounds.]** E. DEUSSEN (J. pr. Chem., 1936, [ii], 145, 31—59).—Caryophyllenic acid (I) (prep. essentially that of A., 1929, 931) (as chloride) and Br (1 mol.) give the  $\text{Br}_1$ -derivative, converted by aq.  $\text{Ba}(\text{OH})_2$  into impure hydroxycaryophyllenic acid (*Pb* and *Ba* salts), which is oxidised (2%  $\text{KMnO}_4$ , dil.  $\text{H}_2\text{SO}_4$ , room temp.) to  $\alpha$ -hydroxyisovaleric acid. KOH-fusion of pinic acid (prep.; von Beyer, A., 1896, i, 245) affords AcOH and isovaleric acid; more AcOH is obtained than with (I) (*loc. cit.*). Evidence (lit.) proving the homogeneity (cf. Ruzicka and Wind, A., 1931, 734) of  $\gamma$ -caryophyllene (II) is reviewed. The reactions of (II) are better explained by the Semmler-Deussen (cf. A., 1926, 1252) than the modified structure (Ruzicka, A., 1935, 866). The mechanism previously suggested (A., 1926, 1252) to explain the interconversion of the blue and colourless  $\beta$ -caryophyllene nitrosites is reaffirmed. Contrary to Chapman (A., 1928, 646;

1929, 450), humulene is considered to be identical with optically inactive  $\alpha$ -caryophyllene.

[With E. ROTTSCHIL.] Crude verbanol [obtained by reduction ( $\text{H}_2$ , Pt) of crude verbenol] is oxidised ( $\text{CrO}_3$ , 75% AcOH) to verbanone, b.p. 93—94°/8—9 mm.,  $\alpha$  +49.46° (10 cm.) [when purified through the semicarbazone, m.p. 225° (decomp.)], which with Mg isoamyl bromide gives the carbinol (III), b.p. 120—125°/8 mm., de-



hydrated ( $\text{KHSO}_4$  at 175°) to an impure hydrocarbon [as (III) with double linking at \*\*], b.p. 135°/17 mm.

isoCaryophyllene alcohol (IV) is oxidised ( $\text{MnO}_2$ , dil.  $\text{H}_2\text{SO}_4$ ) to  $\alpha$ - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ; definite products are not obtained by the prolonged action of fuming  $\text{HNO}_3$  at 60—100°. (IV) and Br (3 mols.) in AcOH-I (trace) give isocaryophyllene bromide (V), m.p. 61—62°; with 25—26 mols. of Br a product (A) (58.25—59.28% Br) results. Treatment of (A) with 20% EtOH-KOH and 50% NaOH (?) affords products containing less Br; KOH in boiling amyl alcohol removes almost all the Br. Little depression of m.p. is found with (V) and isocaryophyllene chloride or with  $\alpha$ -caryophyllene nitrosobromide and  $\alpha$ -bromocaryophyllene nitrosochloride. H. B.

**Lignin and related compounds. XX. Methanol lignin and its relation to the so-called "primary lignin" of Friedrich and Diwald.** E. G. KING and H. HIBBERT (Canad. J. Res., 1936, 14, B, 12—19; cf. A., 1935, 1373).—Treatment of spruce wood with 5% aq. NaOH at room temp. in  $\text{N}_2$  does not affect the properties or OMe content of the lignin extracted by MeOH. Treatment with 17% HCl leads to lignin of lower OMe content. Thus the "primary lignin" of Friedrich *et al.* (B., 1926, 151) is a degradation product. Hot alkali is without effect on methanol or "primary" lignin in absence of air, but in air gives an acid of lower OMe content. Lignin thus contains no ester groups (cf. *loc. cit.*). If dioxan solutions of lignins with 21% of OMe are treated with  $\text{Et}_2\text{O}$ , 80—85% is pptd., but the sol. portion has > 23% of OMe. R. S. C.

**Lignin and related compounds. XXI. Insoluble methanol lignin.** H. W. MACKINNEY and H. HIBBERT (Canad. J. Res., 1936, 14, B, 55—64).—Spruce wood meal when treated with MeOH dry HCl affords some sol. methanol lignin,  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_6(\text{OH})_4$  (A., 1934, 74), and the residue after complete methylation ( $\text{Me}_2\text{SO}_4$ ) followed by MeOH-dry HCl at 100° affords insol. methanol lignin (I),  $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OMe})_9$ , (OMe 31.1%), which cannot be further methylated or acetylated. (I) with a large excess of 40—59% HI at 100° is partly demethylated. The product (II) (OMe 4.6%) with  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  gains 4 OMe (III) [showing that 4 OH are acidic; the original lignin must contain three of these as OMe as only one is phenolic in character (A., 1934, 74)], and after acetylation ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ ) is converted by  $\text{Me}_2\text{SO}_4$  into a  $(\text{OMe})_5$ -derivative (OMe 18.5%), which indicates that demethylation of (I) is accompanied by secondary intramol. changes



involving loss of  $\text{H}_2\text{O}$  from 4 OH groups.  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  converts (III) into a *mono-p-toluene-sulphonate* (OMe 12.3%). (II) with  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  affords a  $\text{Ac}_4$  derivative. The basis of the lignin structure is probably a group of heterocyclic rings containing O. J. L. D.

**Acidity of pine nitrolignin.** W. RUZICKA and K. KURSCHNER (J. pr. Chem., 1936, [ii], 145, 18—22).—The acidities of the nitrolignin (I) (obtained by nitration of the technical lignin in EtOH-suspension) and its Ac derivative (II) are determined by Kolthoff's iodometric method (A., 1926, 813); 89.14 and 90.7%, respectively, of the H of the  $\text{CO}_2\text{H}$  are calc. to have reacted. The results afford a further proof that (I) contains  $\text{NO}_2$  and  $\text{CO}_2\text{H}$  in the ratio 1:1. The "iodometric acid vals." (cf. B., 1930, 1118) of (I) and (II) are determined under various conditions; hydrolysis is best accomplished with dil. aq. EtOH-NaOH at  $100^\circ$  (bath). H. B.

**Action of carbon disulphide and aqueous potassium hydroxide on alkali lignin.** R. L. GLOVER and J. W. BAIN (Canad. J. Res., 1936, 14, B, 65—75).—Alkali lignin (A., 1926, 209) shaken in dil. KOH with  $\text{CS}_2$  is converted into a lignin-like material containing chemically bound S. An interpretation of the results, involving the formation of a xanthate as the main reaction, is given. J. L. D.

**Constituents of natural phenolic resins. IV. Synthesis of dehydroanhydropicrodophyllin.** R. D. HAWORTH and J. RICHARDSON (J.C.S., 1936, 348—352).—Safrole oxide (I) and Et sodiomalonate give Et  $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone- $\alpha$ -carboxylate, b.p.  $210\text{--}215^\circ/0.5\text{ mm.}$ , which with Na and 3:4:5-trimethoxybenzoyl chloride affords Et  $\alpha$ -(3:4:5-trimethoxybenzoyl)- $\beta$ -(3:4-methylene-dioxybenzyl)butyrolactone- $\alpha$ -carboxylate, m.p.  $156\text{--}157^\circ$ . (I) and Et sodioacetate form  $\alpha$ -acetyl- $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone, m.p.  $91\text{--}92^\circ$ , which is hydrolysed with NaOH to Me  $\gamma$ -hydroxy- $\beta$ -(3:4-methylenedioxybenzyl)propyl ketone, m.p.  $79\text{--}80^\circ$ , or with MeOH-KOH to  $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone, b.p.  $183\text{--}186^\circ/0.5\text{ mm.}$ , and with Na and 3:4:5-trimethoxybenzoyl chloride gives  $\alpha$ -(3:4:5-trimethoxybenzoyl)- $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone, m.p.  $110\text{--}111^\circ$ . This lactone with MeOH-HCl yields the lactone of 1-hydroxy-6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)-3-hydroxymethyl-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid, m.p.  $138\text{--}139^\circ$ , dehydrated ( $\text{KHSO}_4$ ) to the lactone of 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)-3-hydroxymethyl-3:4-dihydronaphthalene-2-carboxylic acid, m.p.  $248\text{--}249^\circ$ , which with Pd or Pb( $\text{OAc}$ ) $_4$  in AcOH gives the lactone of 6:7-methylenedioxy-1-(3':4':5'-trimethoxyphenyl)-3-hydroxymethyl-naphthalene-2-carboxylic acid, identical with dehydroanhydropicrodophyllin. F. R. S.

**Identity of noroxylin and baicalein.** R. C. SHAH, C. R. MEHTA, and T. S. WHEELER (Current Sci., 1936, 4, 587).—A mixed m.p. indicates the identity. F. N. W.

**Distinction between strophanthins "g" and "k" on the basis of microchemical identification of the sugars obtained on fission.** R.

FISCHER and W. PAULUS (Sci. pharm., 1935, 6, 32—33; Chem. Zentr., 1935, ii, 722).—Strophanthin-g gives rhamnosephenylosazone and strophanthin-k gives glucosephenylosazone. H. N. R.

**Columbin. II. Bitter principles of Colombo root.** II. F. WESSELY, W. ISEMANN, G. SINGER, and K. SCHÖNOL (Annalen, 1936, 522, 41—47; cf. A., 1935, 1432).—A reply to Feist *et al.* (this vol., 89). The methods of isolation and determination of the purity of columbin are described. H. B.

**Constitution of aloins.** E. LÉGER (Bull. Soc. chim., 1936, [v], 3, 435—439; cf. A., 1931, 490).—Structures proposed by Rosenthaler (Pharm. Acta Helv., 1929, 4, 128), Hauser (A., 1932, 370), Cahn and Simonsen (*ibid.*, 1252), and MacDonnell and Gardner (A., 1934, 774) for barbaloin and aloemodin are criticised. H. B.

**Erythrodiol.** J. ZIMMERMANN (Helv. Chim. Acta, 1936, 19, 247—253).—Erythrodiol stearate, m.p.  $125^\circ$  (corr.) [isolation from *Erythroxylon novogranatense* (A., 1932, 1178) described], with  $\text{CrO}_3$  gives a compound (oxime,  $\text{C}_{45}\text{H}_{84}\text{O}_2\text{N}$ , m.p.  $132^\circ$ ) and thence oleanolic acid. The diol, m.p.  $232^\circ$  (corr.) [*diformate*, m.p.  $195^\circ$ , very readily formed; diacetate, m.p.  $232^\circ$  (corr.); formate stearate, m.p.  $65\text{--}66^\circ$ ], with  $\text{CrO}_3$  gives a ketoaldehyde,  $\text{C}_{30}\text{H}_{46}\text{O}_2$  (oxime, m.p.  $275^\circ$ ; dioxime, m.p.  $263^\circ$ ), and thence oleanonic acid, m.p.  $231^\circ$ ; although it gives a colour in  $\text{C}(\text{NO}_2)_4$ , it is not hydrogenated under conditions effective for betulin and thus differs therefrom in the position of the ethylenic linking and of the  $\cdot\text{CH}_2\cdot\text{OH}$ . R. S. C.

**Constituents of *Dicranopterus glauca*, Nakai.** I. New catechutannic substance, "dicranin." S. AKAI and K. NAKAZAWA (J. Pharm. Soc. Japan, 1933, 53, 891—903).—*Dicranin*,  $\text{C}_{44}\text{H}_{40}\text{O}_{18}$  (Ac, Bz, Me $_6$ , and Me $_{10}$  derivatives), containing 10 free OH, is extracted from the dried roots. KOH fusion affords  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and phloroglucinol. CH. ABS. (r)

**Fukugetin, the colouring matter of the bark of "Fukugi."** III. J. SHINODA and S. UEDA (J. Pharm. Soc. Japan, 1933, 53, 921—931).—Garcinol (I) (Ac $_3$  derivative, m.p.  $202^\circ$ ; Bz $_3$  derivative, m.p.  $224^\circ$ ; Et $_3$  ether, m.p.  $168.5^\circ$ ; dihydro-compound, m.p.  $242\text{--}243^\circ$ ; dihydrotrimethyl ether, m.p.  $95^\circ$ ) is now shown to be  $\text{C}_{16}\text{H}_{12}\text{O}_5$ . Alkali fusion of (I) yields phloroglucinol (III), while oxidation of its Me derivative (II) affords  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ; (I) contains 3 phenolic OH, one double linking, and a lactone ring. Possible formulæ are discussed. Alkali fusion of fukugetin (IV) affords (I), AcOH, 3:4-dihydroxyacetophenone, and (III); possible structures are discussed. Garcinin (Murakami, A., 1933, 398) is the Ac derivative, not an isomere of (IV). (II), with EtOH-NaOH, gives a substance,  $\text{C}_{19}\text{H}_{18}\text{O}_6\text{Na}_2$ , converted by MeI into a substance,  $\text{C}_{19}\text{H}_{18}\text{O}_6\text{Me}_2$ , m.p.  $146^\circ$ , which, on reduction, yields a substance,  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{Me}_2$ , m.p.  $117^\circ$ . CH. ABS. (r)

**Pigmentation of the ripening gourd blossom.** II.—See this vol., 651.

**Constituents of *Hydrangea paniculata*.** Hydrangin.—See this vol., 651.



**Condensation reactions of furfuraldehyde and its derivatives.** N. O. CALLOWAY (Iowa State Coll. J. Sci., 1934, 9, 141—143).—The halides of elements in groups III, IV, and V, and org. compounds containing active halogen, resinify furfuraldehyde. For introducing alkyl groups the order of efficiency of catalysts is  $\text{AlCl}_3 > \text{FeCl}_3 > \text{SnCl}_4$ ; for acylation the order is  $\text{SnCl}_4 > \text{FeCl}_3 > \text{AlCl}_3 > \text{TiCl}_4$ . The 5-alkyl-2-furoic acids have marked germicidal activity.

CH. ABS. (r)

**Synthesis of carlina oxide.** R. PAUL (Compt. rend., 1936, 202, 854—856; cf. A., 1933, 1055).—Furfuraldehyde and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$  give 2-hydroxy- $\alpha$ -phenyl- $\gamma$ -2-furylpropane, b.p. 165—167°/10 mm., which, distilled in  $\text{N}_2$ , gives  $\alpha$ -phenyl- $\gamma$ -2-furyl- $\Delta^2$ -propene, b.p. 138—140°/10 mm. The dibromide of this with  $\text{KOH}\cdot\text{EtOH}$  in  $\text{N}_2$  gives a little  $\alpha$ -benzyl- $\beta$ -2-furylacetylene, b.p. 164—166°/20 mm., which is probably identical with carlina oxide. J. N. A.

**Occurrence of furan derivatives in volatile oils.** III.  $\beta$ - and  $\gamma$ -Clausenan. B. S. RAO and K. S. SUBRAMANIAM (Proc. Indian Acad. Sci., 1936, 3, A, 31—37; cf. this vol., 429).—The leaves from *Clausena Willdenovii*, W. and A., collected in winter, yield oils closely resembling in physical properties those collected previously (A., 1935, 134) in a different place, but differed in that the first fraction consisted mainly of  $\gamma$ - (I),  $\text{C}_{10}\text{H}_{12}\text{O}$ , b.p. 103—104°/50 mm., and little  $\beta$ -clausenan, b.p. 96—97°/50 mm. (Ac derivative, b.p. 105°/32 mm.), which are readily separated since (I) does not form a salt with ferro- and ferri-cyanic acid. (I) is unchanged by  $\text{Ac}_2\text{O}$  etc., does not give a ketone with  $\text{KMnO}_4$ , and is reduced by  $\text{Na}\cdot\text{EtOH}$  to a  $\text{H}_4$ -derivative, b.p. 105°/100 mm. Physical data are given. R. S. C.

**Pyrone series.** III. Influence of the phenyl group in the Kostanecki reaction. I. M. HEILBRON, D. H. HEY, and B. LYTGOE (J.C.S., 1936, 295—300).— $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$  and  $\text{PhOAc}$  with 2-hydroxy-4-methoxyacetophenone give 7-methoxy-3-phenyl-4-methylcoumarin, hydrolysed ( $\text{NaOH}\cdot\text{MeOH}$ ) to 2:4-dimethoxy- $\alpha$ -phenyl- $\beta$ -methylcinnamic acid, m.p. 153·5°. 2:4-Dimethoxyacetophenone,  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$ , and Na yield 2:4-dimethoxy- $\omega$ -phenylacetylacetophenone, m.p. 91°, hydrolysed to 7-methoxy-2-benzylchromone, m.p. 192°.  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$  and  $\text{PhOAc}$  with 2-hydroxy-4-methoxypropionophenone afford 7-methoxy-2-phenyl-4-ethylcoumarin (I), m.p. 115° [hydrolysed ( $\text{NaOH}\cdot\text{MeOH}$ ) to 2:4-dimethoxy- $\alpha$ -phenyl- $\beta$ -ethylcinnamic acid, m.p. 137°], and 7-methoxy-2-benzyl-3-methylchromone, m.p. 102·5°. Resorcinol and  $\alpha$ -propionylphenylacetonitrile with  $\text{H}_2\text{SO}_4$  yield 7-hydroxy-3-phenyl-4-ethylcoumarin, methylated to (I). 2-Hydroxy-4-methoxyphenyl benzyl ketone,  $\text{NaOAc}$ , and  $\text{Ac}_2\text{O}$  afford 7-methoxy-3-phenyl-2-methylchromone (7-methoxy-3':4'-methyleneedioxy-3-phenyl-2-styrylchromone, m.p. 246°) and no coumarin, whilst the ketone and  $\text{NaOPr}$  and  $\text{Pr}_2\text{O}$  give 7-methoxy-3-phenyl-2-ethylchromone, m.p. 119·5°.  $\text{NaOPr}$ ,  $\text{Pr}_2\text{O}$ , and 2-hydroxy-4-methoxyacetophenone yield 7-methoxy-3:4-dimethylcoumarin and 7-methoxy-2-ethylchromone; with  $\text{EtOPr}$  and Na the ketone forms 5-methoxy-2-propionacetylphenol, m.p. 83·5° (cf. Heilbron *et al.*, A., 1934, 1361).

F. R. S.

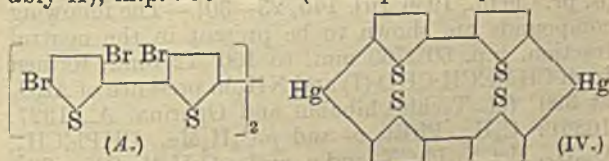
Dipole moments of two oxonium salts. See this vol., 550.

**Di-*p*-tolylene oxide of Sabatier.** I. Y. SUGII and T. SENGOKU (J. Pharm. Soc. Japan, 1933, 53, 951—952).—The “di-*p*-tolylene oxide,” m.p. 166°, of Sabatier and Mailhe (I) (A., 1910, i, 669) gives on oxidation a dicarboxylic acid,  $\text{C}_{11}\text{H}_8\text{O}_5$ , m.p. > 300° ( $\text{Me}_2$  ester, m.p. 257°), whereas the di-*p*-tolylene oxide, m.p. 64°, of Sugii gives dibenzfuran-3:6-dicarboxylic acid, m.p. > 300° ( $\text{Me}_2$  ester, m.p. 167°), independently synthesised from 3:6-diacetyldibenzfuran. (I), therefore, has not the supposed structure. CH. ABS. (r)

**Sabatier's products of catalytic oxidation of cresols with thorium oxide at high temperature.** T. SENGOKU (J. Pharm. Soc. Japan, 1933, 53, 962—978; cf. preceding abstract).—Oxidation of *o*-cresol with  $\text{PbO}$  gives a so-called “xanthone homologue” (I), m.p. 162—163°, which is oxidised ( $\text{CrO}_3\cdot\text{AcOH}$ ) to xanthone (II), and reduced ( $\text{Na}\cdot\text{EtOH}$ ) to xanthen (III); (I) is probably a mixture of (II) and (III). With  $\text{PbO}$ , *m*-cresol yields Sabatier's “di-*m*-tolylene oxide” (IV), m.p. 200° (A., 1910, i, 669), whilst *p*-cresol furnishes his “di-*p*-tolylene oxide” (V), m.p. 166°. Distillation of *o*-cresol with  $\text{ThO}_2$  yields (II) and (III); hence Sabatier's “di-*o*-tolylene oxide” is a mixture of (II) and (III). *p*-Cresol with  $\text{ThO}_2$  yields (V), which is oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7\cdot\text{AcOH}$ ) to a compound (VI), m.p. 143°, reduced ( $\text{Na}\cdot\text{EtOH}$ ) to (V). 2:5-Cresotic acid yields 2:7-dimethylxanthone, m.p. 143°, identical with (VI), reduced to 2:7-dimethylxanthen, m.p. 166°, identical with (V). Oxidation ( $\text{CrO}_3\cdot\text{AcOH}$ ) of (V) or (VI) yields xanthone-2:7-dicarboxylic acid, m.p. > 300° ( $\text{Me}_2$  ester, m.p. 257°). *m*-Cresol and  $\text{ThO}_2$  afford 3:6-dimethylxanthen, m.p. 200°. CH. ABS. (r)

**Steric configuration and the condition of some ring compounds.**—See this vol., 550.

**Thiophen series.** XXX. Derivatives of 2:2'-dithienyl and  $\alpha\alpha\alpha$ -tetrathienyl. W. STEINKOPF and W. KÖHLER (Annalen, 1936, 522, 17—27).—The Grignard reagent (prep.: A., 1934, 1108) from 2:3:4-tribromothiophen with anhyd.  $\text{CuCl}_2$  gives 3:4:3':4'-tetrabromo-2:2'-dithienyl, m.p. 110°. The tetrabromo-2:2'-dithienyl, m.p. 139—140°, of Auwers and Breddt (A., 1894, i, 444) is probably the 3:5:3':5'-derivative since it is converted by short treatment with  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  into a hexabromo- $\alpha\alpha\alpha$ -tetrathienyl (I) (probably A), m.p. 256—258° (accompanied by a trace of



$\text{Br}_2$ -derivative), and by 33% oleum into an octabromo- $\alpha\alpha\alpha$ -tetrathienyl (II), m.p. 297—299°. The formation of (II) probably involves a pentabromodithienyl, i.e., a Jacobsen rearrangement. (I) and (II) are brominated to decabromo- $\alpha\alpha\alpha$ -tetrathienyl, m.p. 324—326°, also formed from hexabromo-2:2'-dithienyl and oleum. 2:2'-Dithienyl (III),  $\text{HgCl}_2$ , and  $\text{NaOAc}$  in aq.  $\text{EtOH}$  give the 5:5'-( $\text{ClHg}$ ) $_2$ -derivative, which is converted by dil.  $\text{HCl}$  into (III),



by I-KI into 5:5'-di-iodo-2:2'-dithienyl, m.p. 164° [also obtained from (III), I, and yellow HgO in C<sub>6</sub>H<sub>6</sub>], and by NaI (4 mols.) in C<sub>5</sub>H<sub>5</sub>N into Hg<sub>2</sub> 5:5:5':5'-di-(2:2'-dithienylene) (IV). (III) and HgO in AcOH afford the (OAc·Hg)<sub>6</sub>-derivative, convertible into the (ClHg)<sub>6</sub>-derivative, decomp. when heated, and thence into hexaiodo-2:2'-dithienyl, m.p. 284—285°. (III) and fuming HNO<sub>3</sub> in Ac<sub>2</sub>O at 0—5° give 5-nitro-2:2'-dithienyl, m.p. 109°, which with Br affords hexabromo-2:2'-dithienyl, m.p. 257°. The hexabromodithienyl, m.p. 125°, of A., 1934, 1108 is wrongly described and should be deleted from the lit. Reaction between thiophen and pure CNBr does not always occur (cf. A., 1923, i, 124); a trace of Br is a catalyst. A Grignard reagent could not be prepared from 2:3-dibromothiophen. 2-Thienoyl chloride, 3:4-dibromothiophen, and AlCl<sub>3</sub> in light petroleum give 3:4-dibromo-2:2'-dithienyl ketone, m.p. 110—111°, brominated to the 3:4:5:4':5'-Br<sub>5</sub>-derivative, m.p. 143—144°. 5-Bromo-, b.p. 238—240°, m.p. 37—38°, 3:4-dibromo-, m.p. 84—85°, and 3:4:5-tribromo-, m.p. 83—85°, -2-thienoyl chlorides do not undergo the Friedel-Crafts reaction. Me 3:4:5-tribromo-2-thienoate has m.p. 113—116°.

H. B.

**Electrolytic reduction of N-methyl- and N-ethyl-succinimide.** B. SAKURAI (Bull. Chem. Soc. Japan, 1936, 11, 41—43).—The electrolytic reduction of N-methylsuccinimide can be carried beyond N-methylpyrrolidone (Lukes, A., 1930, 1296) by using a Zn-Hg cathode in 50% H<sub>2</sub>SO<sub>4</sub> at c.d. 100—125 amp. per sq. dm., at < 30°. N-Ethylsuccinimide under the same conditions gives N-ethylpyrrolidine, and when a Pb cathode in 10% H<sub>2</sub>SO<sub>4</sub> at 3 amp. per sq. dm. is used, gives N-ethylpyrrolidone.

E. W. W.

**Tetra-anisylpyrrole.** F. E. KING and G. D. PATERSON (J.C.S., 1936, 400).—Deoxyanisoin (phenylhydrazone, m.p. 79°), prepared by reducing (SnCl<sub>2</sub>-HCl) anisoin, with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub> and NaOAc gives anisyl p-methoxybenzyl ketazine, m.p. 155°, which is cyclised (HCl) to tetra-anisylpyrrole, m.p. 184°, demethylated to tetra-p-hydroxyphenylpyrrole (Ac derivative, m.p. 195°).

F. R. S.

**Fused "onium" salts as acids.** Reactions in fused pyridinium hydrochloride.—See this vol., 574.

**Neutral substances formed in Tschitschibabin's synthesis of β-collidine.** W. HUNTENBURG (J. pr. Chem., 1936, [ii], 145, 23—30).—The following compounds are shown to be present in the neutral fraction, b.p. 60°/760 mm. to 100°/12 mm., formed from CHMe·CH·CHO (I) and NH<sub>3</sub> in presence of Al<sub>2</sub>O<sub>3</sub> at 390° (cf. Tschitschibabin and Oparina, A., 1927, 1086): C<sub>6</sub>H<sub>6</sub>, PhEt, o- and p-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>, CHPh·CH<sub>2</sub>, C<sub>10</sub>H<sub>8</sub>, MeCN, PhCN, and o- and p-C<sub>6</sub>H<sub>4</sub>Me·CN. The probable modes of formation from (I) or its decomp. product MeCHO are discussed. Generally, the C<sub>6</sub>H<sub>6</sub> derivatives arise by aldol and similar condensations, whilst RCN result by dehydrogenation of CHR·NH. The main gaseous product is butadiene (probably formed by hydrogenation of cyclobutadiene).

H. B.

**s-Di-(α-picoly)thiocarbamide.** K. S. TOFT-SCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1,

77—78; cf. A., 1934, 1228).—Prolonged interaction of 6-amino-α-picoline with boiling CS<sub>2</sub> containing a little S affords s-di-(6-methyl-2-pyridyl)thiocarbamide, m.p. 158° (hydrochloride, m.p. 206°). J. L. D.

**Colour reaction of isatin with pyridine and acetic anhydride.** W. GRASSMANN and K. ARNM (Annalen, 1936, 522, 66—74).—Isatin (I), 1-acetyl-isatin, and oxindolylideneacetic acid,

NH< $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix}$ >C:CH·CO<sub>2</sub>H, with C<sub>5</sub>H<sub>5</sub>N and Ac<sub>2</sub>O give

a compound (II), C<sub>30</sub>H<sub>25</sub>O<sub>7</sub>N<sub>3</sub>, red-violet with metallic reflex, which contains 1 mol. of C<sub>5</sub>H<sub>5</sub>N (eliminated by distillation with conc. NaOH) and 3 Ac groups; 1-methylisatin similarly affords a compound, C<sub>28</sub>H<sub>25</sub>O<sub>5</sub>N<sub>3</sub>. Tetrahydroisoquinoline, (I), and Ac<sub>2</sub>O give an analogous compound (III), C<sub>34</sub>H<sub>31</sub>O<sub>7</sub>N<sub>3</sub>, converted by C<sub>5</sub>H<sub>5</sub>N-Ac<sub>2</sub>O into (II). Di-(1-acetyloxindolylidene)acetone (IV), (NAc< $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix}$ >C:CH·)<sub>2</sub>CO

[tetrabromide; p-nitrophenylhydrazone, obtained from (II), (III), or (IV) and p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> in AcOH], prepared from (I), Ac<sub>2</sub>O, and NaOAc, is spectroscopically identical with (II), which is, therefore, a compound of 1 mol. each of (IV), C<sub>5</sub>H<sub>5</sub>N, and AcOH. Reduction (Zn dust, AcOH; H<sub>2</sub>, PtO<sub>2</sub>, AcOH) of (II) or (IV) gives di-(1-acetyloxindolyl)acetone, m.p. 245°.

H. B.

**Polyhalogenated ketones. II. Indole.** G. SANNA (Rend. Seminar. Fac. Sci. R. Univ. Cagliari, 1934, 4, 28—33; Chem. Zentr., 1935, ii, 367; cf. A., 1931, 630).—CHCl<sub>2</sub>·COCl and Mg-indole (I) afford 1:3-bis(dichloroacetyl)indole and 3-dichloroacetylindole, m.p. 202°, yielding indole-3-carboxylic acid (II) on KOH fusion and 3-dibromoacetylindole with aq. KBr; treatment with dil. KOH affords indolyl-3-glycollic acid, m.p. 174°, whilst aq. NH<sub>3</sub> yields 3-carbamylindole, m.p. 201°. Similarly, CCl<sub>3</sub>·COCl and (I) yield 1:3-bis(trichloroacetyl)indole, m.p. 175°, and 3-trichloroacetylindole, m.p. 228°. The latter affords (II) with KOH, whilst, with K<sub>2</sub>CO<sub>3</sub>, it yields some indolyl-3-glyoxylic acid; it is unchanged by KBr or KI. H. N. R.

**Synthesis of δ-3-indolylvaleric acid.** Effects of indole acids on plants. R. H. F. MANSKE and L. C. LEITCH (Canad. J. Res., 1936, 14, B, 1—5).—The following are plant hormones: 3-indolylacetic > γ-3-indolylbutyric (I) > β-3-indolylpropionic > δ-3-indolylvaleric (II) > β-3-(4-methylindolyl)propionic (II) > indylene-1:3-diacetic acid. Root growth, particularly from stems, is increased most by (I). Et cycloheptanone-2-carboxylate (from suberone, Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and NaOEt), b.p. 135—138°/22 mm., and PhN<sub>2</sub>Cl in 20% KOH give a phenylhydrazone, which with hot EtOH-H<sub>2</sub>SO<sub>4</sub> yields a small amount of a substance, C<sub>29</sub>H<sub>34</sub>O<sub>7</sub>N<sub>2</sub>, m.p. 170° (with N<sub>2</sub>H<sub>4</sub>-MeOH gives a substance, C<sub>25</sub>H<sub>30</sub>N<sub>2</sub>, m.p. 146°), and a product, which with hot KOH-aq. EtOH affords a little pimelic acid and much δ-3-(2-carboxyindolyl)valeric acid, m.p. 204° (decomp.), decarboxylated at 210° to (II), m.p. 105° (Me ester, b.p. 210°/2 mm., m.p. 57°). In the prep. of the indolyl-butyric and -propionic acids adipic and glutaric acid, respectively, are also obtained. (II), m.p. 137°, is obtained similarly, but in poor yield, from Et cyclopentanonecarboxylate and p-C<sub>6</sub>H<sub>4</sub>Me·N<sub>2</sub>Cl. M.p. are corr. R. S. C.



$\alpha\beta$ -Diarylethylamines and their transformation into tetrahydroisoquinolines. II. B. REICHERT and W. HOFFMANN (Arch. Pharm., 1936, 274, 217—221; cf. this vol., 483).—3 : 4 : 5- $C_6H_2Me_3\cdot CHO$ ,  $CH_2Ph\cdot NO_2$ , and a little  $NH_2Me$  in EtOH give  $\alpha$ -nitro- $\alpha$ -phenyl- $\beta$ -3 : 4 : 5-trimethoxyphenylethylene ( $\alpha$ -nitro-3' : 4' : 5'-trimethoxystilbene) (I), m.p. 147°, and a little  $\alpha\gamma$ -dinitro- $\alpha\gamma$ -diphenyl- $\beta$ -3 : 4 : 5-trimethoxyphenylpropane, m.p. about 217° (decomp.). (I) is hydrogenated (Pd-C) in  $C_5H_5N$  to 3' : 4' : 5'-trimethoxydeoxybenzoixime, m.p. 83—84°, reduced (Na-Hg in EtOH) to  $\alpha$ -phenyl- $\beta$ -3 : 4 : 5-trimethoxyphenylethylamine, b.p. about 240°/14.5 mm. (hydrochloride, m.p. 224°), converted by  $CH_2O$  and HCl into 6 : 7 : 8-trimethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m.p. about 56—58° [hydrochloride, m.p. 258—261° (decomp.)]; NO-derivative, m.p. 127°]. R. S. C.

Ammonium salts containing the cetyl radical. E. MACOVSKI (Bull. Soc. chim., 1936, [v], 3, 498—500).—Trimethylcetylammmonium iodide, m.p. 247° (lit. 222°), and chloride, m.p. 240°, cetyl-pyridinium iodide, m.p. 101°, and chloride, m.p. 110°, -quinolinium iodide, m.p. 99°, and chloride, m.p. 114°, and -isoquinolinium iodide, m.p. 75°, and chloride, m.p. 95°, are described. H. B.

Bis-8-hydroxyquinoline inner complex salt of bivalent silver. Y. NAKATSUKA (Bull. Chem. Soc. Japan, 1936, 11, 45—48).—When 8-hydroxyquinoline in EtOH is added to  $AgOAc$  in hot instead of cold  $H_2O$ , the product is not the yellow complex,  $[(C_9H_6N\cdot O)Ag(C_9H_6N\cdot OH)]$  of  $Ag^+$ , but the green complex  $[(C_9H_6N\cdot O)_2Ag]$ , of  $Ag^+$ ; both crystallise +  $C_5H_5N$ . The complex,  $[(C_9H_6N\cdot O)_2Cu]$  is now obtained +  $2H_2O$ , +  $0.5H_2O$ , and +  $C_5H_5N$ . E. W. W.

Thalleioquinine reaction. II. (SIGNA.) L. MONTI and (SIGNA.) V. CIRELLI (Gazzetta, 1936, 66, 38—41).—The authors' views (A., 1935, 500) are confirmed. Aminoethyl condenses with  $CH_3Ac\cdot CO_2Et$  to form *Et*  $\beta$ -(4-hydroxy-2-methyl-5-isopropylanilino)-crotonate, m.p. 102—104°, which when heated in  $CO_2$  with paraffin oil at 320° gives 4 : 6-dihydroxy-2 : 8-dimethyl-5-isopropylquinoline, m.p. < 300° [picrate, m.p. 216—218°; platinichloride, m.p. 266—268° (both decomp.)]. This, in which position 5 is not free, does not give the thalleioquinine reaction. 8-Hydroxy-5-methylquinoline also fails to give the similar reaction, which is positive with 8-hydroxyquinoline (cf. loc. cit.). E. W. W.

Benzoylation of quinaldine oxide. M. HENZE (Ber., 1936, 69, [B], 534—536).—2-Methylquinoline 1-oxide appears to react in the hydrate form towards NaOH and BzCl, giving an ester which is isomerised to the  $\mu$ -base, which loses  $H_2O$  with formation of 1-benzoyloxy-2-methylene-1 : 2-dihydroquinoline (I), m.p. 52° (picrate, m.p. 164°; platinichloride, m.p. 120°). (I) is transformed by HCl into BzOH and 1-hydroxy-2-methylene-1 : 2-dihydroquinoline, m.p. 66° (picrate, m.p. 144°), which strongly reduces Fehling's and Ag solution, gives a red colour with  $FeCl_3$  in EtOH, and couples with  $p\text{-}SO_3H\cdot C_6H_4\cdot N_2Cl$ . H. W.

Acridine compounds and their antimalarial action. II. Compounds with cyano- and methylthiol groups. O. J. MAGIDSON and A. I.

TRAVIN (Ber., 1936, 69, [B], 537—544; cf. this vol., 484).—Replacement of the 7-Cl in 7-chloro-2-methoxyacridine derivatives by CN does not introduce sp. toxic properties, CN behaving biologically as a stable org. nitrile. Replacement of 2-OMe by 2-SMe has a negative influence on the antimalarial action and considerably increases the toxic effect. 3-Chloro-4-methylbenzonitrile suspended in 70%  $H_2SO_4$  at 55—70° is oxidised by  $K_2Cr_2O_7$  to 2-chloro-4-cyanobenzoic acid (I), m.p. 170—171°, the relatively poor yield being due to enclosure of the nitrile by the insol. acid so that the product contains unchanged nitrile and also 3-chloro-*p*-toluamide; on one occasion when agitation was inefficient, 2-chloro-*p*-carbamidobenzoic acid, m.p. 220° (K salt; hydrolysed to chloroterephthalic acid), was produced. (I),  $p\text{-}OMe\cdot C_6H_4\cdot NH_2$ ,  $K_2CO_3$ , and mol. Cu in boiling isoamyl alcohol afford 4-cyano-2-*p*-methoxyaminobenzoic acid, m.p. 195—196° (K salt), transformed by boiling  $POCl_3$  into 5-chloro-7-cyano-2-methoxyacridine (II), m.p. 228—230°. Condensation of (II) with 8-amino- $\alpha$ -diethylaminopentane in PhOH at 120—130° gives 7-cyano-5-8-diethylamino- $\alpha$ -methylbutylamino-2-methoxyacridine (dihydrochloride, m.p. 240—245°; oxalate, decomp. 180—185°). 7-Cyano-5- $\gamma$ -diethylamino-propylamino-2-methoxyacridine, m.p. 85—87° [dihydrochloride, m.p. 235—245° (decomp.)], and - $\beta$ -hydroxypropylamino-2-methoxyacridine [dihydrochloride (+  $2H_2O$ ), m.p. 220—225° (decomp.)] are obtained similarly. (II), PhOH, and  $NH_3$ —96% EtOH afford 7-cyano-2-methoxyacridone, decomp. 370—375°, whereas in abs. EtOH 7-cyano-5-amino-2-methoxyacridine (hydrochloride) is produced. (II) is hydrolysed by conc. HCl at 140° to 2-methoxyacridone-7-carboxylic acid, decomp. 380—400° (Na salt). 2 : 4- $C_6H_3Cl_2\cdot CO_2H$ , thio-*p*-anisidine,  $K_2CO_3$ , and mol. Cu in boiling isoamyl alcohol give 4-chloro-2-*p*-methylthiophenylaminobenzoic acid, m.p. 194—195°, converted by boiling  $POCl_3$  into 5 : 7-dichloro-2-methylthiolacridine (III), m.p. 182—183° (sulphate), from which 7-chloro-5-8-diethylamino- $\alpha$ -methylbutylamino-2-methylthiolacridine [dihydrochloride (+  $4H_2O$ ), m.p. 210°] and 7-chloro-5- $\gamma$ -diethylaminopropylamino-2-methylthiolacridine (dihydrochloride) are derived. (III) and boiling dil. HCl yield 7-chloro-2-methylthiolacridone, m.p. 335—337°. H. W.

[Acridine compounds and their antimalarial action.] H. MAUSS and F. MRETZSCH (Ber., 1936, 69, [B], 641).—A claim for priority against Magidson *et al.* (preceding abstract). H. W.

Synthesis of compounds with hypnotic properties. I. Alkoxymethylhydantoins. N. E. RIGLER [with H. R. HENZE] (J. Amer. Chem. Soc., 1936, 58, 474—477).— $OAlk\cdot CH_2\cdot CN$  [from  $OAlk\cdot CH_2Cl$  and  $Cu_2(CN)_2$  in  $C_6H_6$ ] and  $MgRBr$  give (cf. A., 1934, 871)  $OAlk\cdot CH_2\cdot COR$  (I), which with  $NH_4CN$  (Herbst and Johnson, A., 1932, 862) or  $(NH_4)_2SO_4$ , KCN, and aq.  $NH_3$  in MeOH (cf. Zelinsky and Stadnikoff, A., 1906, i, 425) afford  $OAlk\cdot CH_2\cdot CR(CN)\cdot NH_2$ . These with  $KNCO$  in 70% AcOH give  $OAlk\cdot CH_2\cdot CR(CN)\cdot NH\cdot CO\cdot NH_2$ , converted by 20% HCl into 5-alkyl- (or aryl)-5-alkoxymethylhydantoins (II). Some of the (II) are also prepared directly from (I) by the method of Bucherer *et al.* (A., 1934 1231). The following are described :



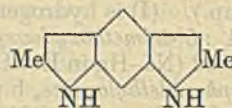
ethoxy-, b.p. 134—135°/755 mm., and isoamyloxy-, b.p. 186—187°/753 mm., acetonitriles; isoamyl methoxymethyl, b.p. 185—186°/752 mm., Et, b.p. 146—147°/752 mm., sec.-Bu, b.p. 172—173°/743 mm., isoamyl, b.p. 105—106°/35 mm., and Ph, b.p. 120—122°/15 mm., ethoxymethyl, and Et isoamyloxymethyl, b.p. 196—197°/752 mm., ketones;  $\alpha$ -amino- $\alpha$ -methoxy- and - $\alpha$ -ethoxy-methylisocyanonitrile (Bz derivatives, m.p. 103° and 66°, respectively; corresponding carbamides, m.p. 127—128° and 126.5°, respectively, and phenylcarbamides, m.p. 151—151.6° and 138°, respectively);  $\alpha$ -amino- $\beta$ -methyl- $\alpha$ -ethoxymethyl-valeronitrile (carbamide, m.p. 113.5—114.5°, and phenylcarbamide, m.p. 119—119.5°);  $\alpha$ -amino- $\alpha$ -ethoxy- and - $\alpha$ -isoamyloxy-methylbutyronitriles (carbamides, oils);  $\alpha$ -amino- $\beta$ -ethoxy- $\alpha$ -phenylpropionitrile (Ac, m.p. 164—165°, and Bz, m.p. 164°, derivatives; carbamide, m.p. 167°; phenylcarbamide, m.p. 167°); 5-isoamyl-5-methoxymethyl-, m.p. 195—196°, 5-ethyl-5-isoamyloxymethyl- (III), m.p. 107—108°, and 5-ethyl-, m.p. 147—148°, 5-sec.-butyl-, m.p. 164.5—165°, 5-isoamyl-, m.p. 179—180°, and 5-phenyl- (IV), m.p. 191.5°, 5-ethoxymethyl-hydantoins. All b.p. and m.p. are corr. (III) and (IV) (as Na salts) are not satisfactory soporifics. H. B.

**Oxidation of 1-phenyl-3-methyl-5-pyrazolone.** G. PERRONCITO (Gazzetta, 1935, 65, 1254—1258).—This is oxidised by  $\text{H}_3\text{AsO}_4$  in AcOH, or  $\text{KMnO}_4$  in HCl, to 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone (cf. A., 1935, 1380). With  $\text{H}_2\text{O}_2$  in NaOH,  $\text{AcCO}_2\text{H}$  phenylhydrazine is formed; with dry  $\text{H}_3\text{AsO}_4$  at 190°, a substance, m.p. 180°, is also formed, with a product, m.p. > 300°, and 4-anilo-1-phenyl-3-methyl-5-pyrazolone, m.p. 198° (obtainable from the pyrazolone and  $\text{PhNO}$  in  $\text{C}_6\text{H}_6$ ), by oxidation with  $\text{PhNO}_2$ . E. W. W.

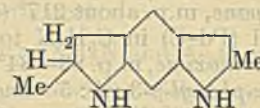
**Abnormal action of nitrous acid on hydrazides of organic acids.** (SIGNA.) M. FRERI (Atti R. Accad. Lincei, 1935, [vi], 22, 264—267; cf. A., 1934, 1372).—Citracondihydrazide (I) with  $\text{NaNO}_2$  and AcOH gives, with some azide, m.p. 114° (decomp.), 3:6-diketo-4-methyl-1:2:3:4-tetrahydropyrazine, m.p. 277° (synthesised from  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and  $\text{Et}_2$  citraconate); (I) in conc. aq. solution with  $\text{NaNO}_2$  and HCl yields 4-oximino-3-methyl-1:2:5-pyrazolone (II) (cf. A., 1904, i, 533). This with  $\text{O}_3$  yields 4-nitro-3-methyl-1:2:5-pyrazolone (III), m.p. 276° ( $\text{NH}_2\text{Ph}$  and  $\text{NHPh}\cdot\text{NH}_2$  salts), which with  $\text{CH}_2\text{N}_2$  yields 4-nitro-1:3:4-trimethylpyrazolone, m.p. 127°, also obtained by action of  $\text{HNO}_3\text{--H}_2\text{SO}_4$  on trimethylpyrazolone. (II) [or (III)] is reduced ( $\text{SnCl}_2$ ) to 4-amino-3-methylpyrazolone hydrochloride (IV), m.p. 225°, which condenses with aldehydes to form Schiff's bases: 4-(p-nitrobenzylidene-, m.p. 257° (decomp.), 4-(anisylidene-, m.p. 202°, and 4-(piperonylidene-, m.p. 245°, amino-3-methylpyrazolone. When (IV) is neutralised, it condenses to form the compound  $\text{Me}\cdot\text{C}_3\text{H}_2\text{ON}_2\cdot\text{N}\cdot\text{C}_3\text{HON}_2\cdot\text{Me}$ , which is reduced ( $\text{SnCl}_2$ ) to 4:4'-bis-(3-methylpyrazolyl)ammonium chloride, m.p. 247°. E. W. W.

**Indoles and isatogens.** XXII. Benzodipyrroles. III. 2:6-Dimethyl-lin-m-benzodipyrrole. P. RUGGLI and O. STRAUB [with O. SCHMID] (Helv. Chim. Acta, 1936, 19, 326—330; cf. A., 1935,

759).—Hydrogenation (Ni or Pd-black) of 4:6-dinitro-1:3-diacetylbenzene in  $\text{EtOAc--EtOH--H}_2\text{O}$  gives slowly poor yields of 2:6-dimethyl-lin-m-benzodipyrrole [2:2'-dimethylpyrrolo-4':5'-5:6-indole] (I), m.p. 232°, sublimes at 310—320°/vac., stable to short heating in  $\text{Ac}_2\text{O}$ , and 2:6-dimethyldihydro-lin-m-benzodipyrrole [2:2-dimethyl- $\Delta^4$ -pyrrolo-4':5'-5:6-indole] (II) (Ac derivative, m.p. 279°).



(I.)



(II.)

$\text{Et}_2$  4:6-dinitrophenylene-1:3-diacetoacetate affords at 50—60°  $\text{Et}_2$  2:6-dimethyl-lin-m-benzodipyrrole-3:5-dicarboxylate [2:2'-dimethylpyrrolo-4':5'-5:6-indole-3:3'-dicarboxylate], m.p. 342° (decomp.).

R. S. C.

**Determination of active hydrogen atoms in organic compounds by H-D isotope analysis.** H. ERLÉNMEYER, A. EPPRECHT, H. LOBECK, and H. GÄRTNER (Helv. Chim. Acta, 1936, 19, 354—357).—Recrystallisation of BzOH from  $\text{D}_2\text{O--H}_2\text{O}$  (H:D = 1:007) gives a mixture, m.p. 118.5°, of BzOH:BzOD = 1:117. Crystallisation of barbituric acid from  $\text{H}_2\text{O--D}_2\text{O}$  gives a mixture, but from 99.6%  $\text{D}_2\text{O}$  nearly pure tetradeuterobarbituric acid. Phenacetin is converted by crystallisation from  $\text{H}_2\text{O--D}_2\text{O}$  into nearly pure  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NDAc}$ . R. S. C.

**Derivatives of piperazine.** D. E. ADELSON and C. B. POLLARD (J. Amer. Chem. Soc., 1936, 58, 532).—Piperazinium di(dichloroacetate), m.p. 181° (corr.), and di-(o-acetoxybenzoate), m.p. 112—113° (corr.), 1:4-di-( $\beta$ -dihydroxypropyl)piperazine, m.p. 176—177° (corr.) [tetrabenzoate, m.p. 150—150.5° (corr.)], and 1:4-di- $\beta$ -carbethoxyethylpiperazine dihydrobromide (free base, decomp. < 100°), are described. H. B.

**Pyrimidines.** CXLIX. Reactions of 2-ethanesulphonylpyrimidines. J. M. SPRAGUE and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 423—426).—The 2-EtSO<sub>2</sub> group reacts like Hal and is (generally) readily replaced by OH, OAlk, and NH<sub>2</sub>. Thus, 4-chloro- (I) and 4-ethoxy- (II) 2-ethanesulphonyl-5-methylpyrimidines with EtOH-NaOEt at room temp. give 2:4-diethoxy-5-methylpyrimidine; 4-chloro-5-bromo- and 5-bromo-4-ethoxy- (III) 2-ethanesulphonylpyrimidines similarly afford 5-bromo-2:4-diethoxy-5-methylpyrimidine, whilst Et 4-amino-2-ethanesulphonylpyrimidine-5-carboxylate (IV) yields Et 4-amino-2-ethoxypyrimidine-5-carboxylate, m.p. 105—105.5°, hydrolysed (evaporation with conc. HCl) to the corresponding 2-OH-ester. Et 2:4-dichloro- (V) and 4-chloro-2-ethanesulphonylpyrimidine-5-carboxylates with EtOH-NaOEt give (probably) Et 4-hydroxy-2-ethoxypyrimidine-5-carboxylate, m.p. 186—186.5°; (V) also yields the 2:4-(OEt)<sub>2</sub>-ester, m.p. 33.5—34°. 2-Ethanesulphonyl-4-ethoxypyrimidine, (II), and (III) with 10% NaOH afford 2-hydroxy-4-ethoxy-, 2-hydroxy-4-ethoxy-5-methyl-, m.p. 212—213°, and 5-bromo-2-hydroxy-4-ethoxy-, m.p. 234°, -pyrimidine, respectively. (I) and (IV) with EtOH-NH<sub>3</sub> at 100—110° give 4-amino-2-ethanesulphonyl-5-



*methylpyrimidine*, m.p. 135.5–136.5° [hydrolysed (HCl) to 5-methylcytosine], and *Et* 2:4-diaminopyrimidine-5-carboxylate, m.p. 204–205°, respectively; (II) does not react at 100–130°. (II) and  $\text{NH}_2\text{Ph}$  at 100° (bath) or 130° in  $\text{CO}_2$  afford 2-anilino-4-ethoxy-5-methylpyrimidine, m.p. 120.5–121°, hydrolysed (conc. HCl) to the 4-OH-derivative, m.p. 254–255° (also obtained from 4-hydroxy-2-ethylthiol-5-methylpyrimidine and  $\text{NH}_2\text{Ph}$  at 100°). H. B.

**Indigotin.** *cis*-Indigotin. G. HELLER [with R. BARTHEL] (Ber., 1936, 69, [B], 563–565).—Indigotin (I), moistened with EtOH, is converted by  $\text{AgOAc}$  in  $\text{H}_2\text{O}$  at 100° into anhydroisatinantranilide; reaction is not purely catalytic and is never complete owing to the formation of anti-catalysts. Other acetates under similar conditions have no marked action whereas  $\text{Pb}(\text{OAc})_4$  in cold AcOH transforms (I) into dehydroindigotin diacetate with traces of isatin. References to the lit. prove that *cis*-indigotin is a stable material differing characteristically in properties from the *trans*-form. H. W.

**Mechanism of the reaction of pyridine and its derivatives with alkali amides.** M. KABATSOHN (Bull. Acad. Sci. U.R.S.S., 1935, No. 6–7, 971–978).—The formation of dipyridyl and diquinolyl derivatives in the reaction between  $\text{NaNH}_2$  and  $\text{C}_5\text{H}_5\text{N}$  derivatives in liquid  $\text{NH}_3$  is explained on the basis of entry of Na into the nucleus or side-chain of one mol., which then condenses with a second mol. R. T.

**Nitro- and amino-3-arylphthalaz-4-ones, and corresponding 1-methyl compounds.** F. M. ROWE, G. M. HEATH, and C. V. PATEL (J.C.S., 1936, 311–315).—Nitro-3-arylphthalaz-4-ones and corresponding 1-Me compounds have been prepared by condensing nitroarylhydrazines with *o*-phthalaldehydic acid and acetophenone-*o*-carboxylic acid, respectively, followed by ring-closure of the resulting hydrazones. Amino-3-aryl-1-methylphthalaz-4-ones are obtained by reducing the corresponding  $\text{NO}_2$ -compounds with  $\text{Na}_2\text{S}$ -EtOH- $\text{H}_2\text{O}$ , but usually compounds with  $\text{Na}_2\text{S}$ -EtOH- $\text{H}_2\text{O}$  are best prepared from the hydrazone and aq.  $\text{Na}_2\text{S}$ , which effects ring-closure and reduction. The following have been prepared: *o*-carboxybenzaldehyde-2'-nitro-, m.p. 229°, -4'-nitro-2'-methyl-, -2'-chloro-, m.p. 229°, -2':6'-dichloro-, m.p. 225–226°, -2'-bromo-, m.p. 204°, and -2':6'-dibromo-4'-nitro-phenylhydrazone, m.p. 220°; 2'-nitro-, m.p. 201°, 2'-amino-, m.p. 184° (Ac derivative, m.p. 237°), 3'-amino- (Ac derivative, m.p. 225°), 4'-amino-2'-methyl-, m.p. 187–188° (Ac derivative, m.p. 214°), 2'-chloro-4'-nitro-, m.p. 171°, and -4'-amino-, m.p. 186° (Ac derivative, m.p. 247°), 2':6'-dichloro-4'-nitro-, m.p. 225–226°, and -4'-amino-, m.p. 226° (Ac derivative, m.p. 281°), 2'-bromo-4'-nitro-, m.p. 154°, and -amino-, m.p. 203° (Ac derivative, m.p. 251°), and 2':6'-dibromo-4'-nitro-, m.p. 190°, and -amino-phenyl-3-phenylphthalaz-4-one, m.p. 255° (Ac derivative, m.p. 257°); *o*-carboxyacetophenone-2', -3', and -4'-nitro-, -4'-nitro-2'-methyl-, m.p. 145°, -2'-chloro-, m.p. 166°, -2':6'-dichloro-, m.p. 135°, -2'-bromo-, and -2':6'-dibromo-4'-nitro-phenylhydrazone, m.p. 237°, 2'-amino-, m.p. 239° (Ac derivative, m.p. 241°), 3'-amino-, m.p.

173° (Ac derivative, m.p. 220°), -4'-amino-, m.p. 206–207° (Ac derivative, m.p. 252°), 4'-nitro-, m.p. 178° and 4'-amino-2-methyl-, m.p. 191° (Ac derivative, m.p. 235°), 2'-chloro-4'-nitro-, m.p. 206° and -4'-amino-, m.p. 197° (Ac derivative, m.p. 247°), 2':6'-dichloro-4'-nitro-, m.p. 235°, and -4'-amino-, m.p. 279° (Ac derivative, m.p. 320°), 2'-bromo-4'-amino-, m.p. 130° (decomp.) (Ac derivative, m.p. 255°), and 2':6'-dibromo-4'-nitro-, m.p. 237°, and -amino-3-phenyl-1-methylphthalaz-4-one, m.p. 274° (Ac derivative, m.p. 315°). The stabilities of the hydrazones are compared. F. R. S.

**Phenacylhydrazine.** M. BUSCH and K. KÜSPERT (J. pr. Chem., 1936, [ii], 144, 273–290).—Phenacylhydrazine (A., 1928, 997) [phenylhydrazone diacetate, m.p. 103° (decomp.), readily hydrolysed by aq. mineral acid; semicarbazone hydrochloride (I)] and PhCHO in EtOH-AcOH give benzaldehydephenacylhydrazone, m.p. 94° [Ac derivative (II), m.p. 163°], which reacts with  $\text{NHPh}\cdot\text{NH}_2$  at its CO group to form its phenylhydrazone (III), m.p. 190° (decomp.) (sinters at 187°) [Ac derivative,  $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{N}\cdot\text{Ac}\cdot\text{N}\cdot\text{CHPh}$ , m.p. 191°, formed with (II) by the action of  $\text{Ac}_2\text{O}$ ]. (III) and EtOH-HCl at 50° give  $\text{NH}_3$ , PhCHO, and (probably) the unstable  $\text{NPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}\cdot\text{NH}_2$ . Short treatment of (I) with alkali affords the carbazinic acid,  $\text{NH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}_2\text{H}$ , sinters about 200° and then decomp.; prolonged treatment gives 4-amino-3-keto-6-phenyl-2:3:4:5-tetrahydro-1:2:4-triazine, m.p. 200° [(4-)CHPh derivative (+EtOH), m.p. 203°], converted by  $\text{HNO}_2$  into 3-keto-6-phenyl-tetrahydro-1:2:4-triazine, m.p. 228° (softens at 224°). (I) and PhCHO in EtOH at 40–50° give 4-benzylideneamino-3:6-diphenyltetrahydro-1:2:4-triazine-2-carboxylamide, m.p. 205–206°. (III) and PhCHO in  $\text{CHCl}_3$  + a little EtOH-HCl afford 4-benzylideneamino-2:3:6-triphenyltetrahydro-1:2:4-triazine, m.p. 159°, converted by  $\text{NHPh}\cdot\text{NH}_2$  (2 mols.) in EtOH-AcOH into (III) and  $\text{NHPh}\cdot\text{N}\cdot\text{CHPh}$ , and by 12% EtOH-HCl into 2:3:6-triphenyl-2:3-dihydro-1:2:4-triazine, m.p. 164°, yellow (forming a red hydrochloride). Similarly, (III) and aq.  $\text{CH}_2\text{O}$  in EtOH- $\text{CHCl}_3$  give the (4-)benzylidene derivative (IV), m.p. 159–160°, of 4-amino-2:6-diphenyltetrahydro-1:2:4-triazine (V), m.p. 130° [from (IV) and  $\text{NHPh}\cdot\text{NH}_2$ ], converted by  $\text{HNO}_2$  into the 4-NO-derivative (VI), m.p. 109–110° (decomp.), of 2:6-diphenyltetrahydro-1:2:4-triazine (VII), m.p. 160° [obtained by reduction (Zn dust, AcOH) of (VI)]. (IV) or (V) and aq. EtOH-HCl give 2:6-diphenyl-2:3-dihydro-1:2:4-triazine, m.p. 94°, yellow [red hydrochloride, m.p. 152° (darkens > 145°)], reduced (Zn dust, AcOH) to (VII). 4-Benzylideneamino-2:6-diphenyl-3-methyl-, m.p. 126°, and -3:3-dimethyl-, m.p. 176°, and -2:3:6-triphenyl-3-methyl-, m.p. 153–154°, -tetrahydro-1:2:4-triazine are similarly formed from (III) and  $\text{MeCHO}$ ,  $\text{COMe}_2$ , and  $\text{COPhMe}$ , respectively. (III) and  $\text{COCl}_2$  in  $\text{C}_6\text{H}_6$  give 4-benzylideneamino-3-keto-2:6-diphenyltetrahydro-1:2:4-triazine, m.p. 199°. All the above tetrahydro-derivatives are 2:3:4:5. The production (*loc. cit.*) of 3-keto-2:5-diphenyl-3:4-dihydropyrazine from  $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NH}_2$  is considered to involve loss of  $\text{NH}_3$  and subsequent reaction of 2 mols. of phenylglyoxalimide (as  $\text{OH}\cdot\text{CPh}\cdot\text{C}\cdot\text{NH}$ ). H. B.



**$\gamma$ -Triazines. XXXII. Catalytic hydrogenations in the  $\gamma$ -triazine group. I. Conversion of dihydroxymethyltriazine into the so-called trigenic acid of Liebig and Wöhler.** A. OSTROGOVICH and G. OSTROGOVICH (Gazzetta, 1936, 66, 48—57).—Dihydroxymethyltriazine is rapidly reduced catalytically (new type of vessel illustrated), or slowly by Al-Hg, Na-Hg, or Sn-HCl (but not by Zn), to dihydroxymethyltriazidine (cycloethylidenebiuret), m.p. 272—273° (decomp.) (acetate; semihydrochloride; semiaurichloride; semipicrate;  $Ac_2$  derivative, m.p. 171—172°), which is identical with the "trigenic acid" of Liebig and Wöhler (Annalen, 1846, 59, 296), but, apart from forming a Ag salt, has no acid properties.

E. W. W.

**1-Chloro-3:4-dinitrobenzene series. IV. A.** MANGINI (Gazzetta, 1935, 65, 1191—1200).—1:3:4- $C_6H_3Cl(NO_2)_2$  (I) reacts very slowly with *p*-nitrophenylhydrazine to give 5-chloro-2:4'-dinitrohydrazobenzene, m.p. 190.5—192° (decomp.), which is converted by  $Ac_2O$  into 5-chloro-2-*p*-nitrophenyl-1:2:3-benztriazole 1-oxide, m.p. 143—144°. (I) with allylamine forms 5-chloro-2-nitro-*N*-allylaniline, m.p. 52—53°; with *p*- $C_6H_4Br \cdot NH_2$  forms 5-chloro-4'-bromo-2-nitrodiphenylamine, m.p. 161—162°, which with Sn and HCl, followed by  $HNO_2$ , yields 6-chloro-1-*p*-bromophenyl-1:2:3-benztriazole, m.p. 209—210°; and with *p*- $C_6H_4Ph \cdot NH_2$  forms 5-chloro-2-nitro-*N*-*p*-diphenyl-aniline, m.p. 138—139°, reduced and converted by  $HNO_2$  into 6-chloro-1-*p*-diphenyl-1:2:3-benztriazole, m.p. 175—176°. (I) reacts more slowly with 2-aminopyridine than with  $NH_2Ph$  etc., and gives 2-(5'-chloro-2'-nitroanilino)pyridine, m.p. 152.5—153.5°. (I) with *p*-toluidine forms 5-chloro-2-nitro-4'-methyl-diphenylamine, m.p. 125—126° (cf. A., 1935, 1489), reduced to the hydrochloride, m.p. 187—189°, of the 2- $NH_2$ -compound, new m.p. 66.5—67.5° ( $Ac$  derivative, m.p. 126.5—127.5°), which is converted by  $AcOH$  and  $NaNO_2$  into 6-chloro-1-*p*-tolyl-1:2:3-benztriazole, m.p. 239—241°. Colour reactions of various diphenylamines with  $HNO_2$  and with  $HNO_3$  are tabulated; *NN'*-bis-(5''-chloro-2''-nitrophenyl)benzidine gives a reddish-violet colour with 1/64,000 of the former, or 1/130,000 of the latter.

E. W. W.

**Pyrimidines. CLI. Constitution of dibarbituric acid.** R. D. HOTCHKISS and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 525—528).—Dibarbituric acid (I), now shown to be

$CO \begin{array}{c} \text{NH} \cdot CO \\ \text{NH} \cdot CO \end{array} \text{C}^5 = \text{C}^4 \begin{array}{c} \text{CH}_2 \cdot CO \\ \text{NH} \cdot CO \end{array} NH$  (cf. Conrad and Guthzeit, A., 1883, 314), formed when barbituric acid is heated at 150—170° in dry glycerol, is methylated ( $Me_2SO_4$ , aq. KOH, 25°) to the 1:1':3'- $Me_3$  (+ $H_2O$ ) (II), m.p. (anhyd.) 286—287° (corr.), or 1:3:1':3'- $Me_4$  (III), m.p. 271.5—272.5° (corr.) (*K* salt), derivatives. Reduction [ $H_2$  (130—140 atm.), Raney Ni, dioxan, 150°] of (II) results in fission at the C:C; 1:3-dimethylbarbituric acid and 1-methyl-4:5-dihydrouracil (IV), m.p. 129.5—131° (corr.), are isolated. (III) and an excess of  $Br \cdot H_2O$  give 2 mols. of 5:5-dibromo-1:3-dimethylbarbituric acid. 4-Phenyl-1-methyl-4:5-dihydrouracil, m.p. 149—151° (corr.), and (IV) are synthesised (cf. Fischer and Leuchs, A., 1903, i, 12) from  $MeNCO$  and  $NH_2 \cdot CHPh \cdot CH_2 \cdot CO_2H$

and  $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , respectively. (I) is unaffected by boiling 6*N*-HCl or 2—20% KOH, or red P and  $AcOH$ -I. Contrary to von Baeyer (Annalen, 1864, 130, 145), the  $Br_2$ -derivative of (I) and  $AcOH$ -conc. HBr give Br and a reduction product.

H. B.

**Pyrazolone and indazole derivatives of diphenyl.** E. VOTTA (Gazzetta, 1936, 66, 16—19).—4:4'-Dihydrazinodiphenyl-3:3'-dicarboxylic acid (I) is converted by  $Ac_2O \cdot NaOAc$  into the 1:2:1':2'- $Ac_4$  derivative, m.p. < 300°, of 3:3'-diketotetrahydro-5:5'-di-indazolyl, m.p. < 300°, also obtained (impure) by heating (I).  $POCl_3$  and (I) at 120° yield 3:3'-dichloro-5:5'-di-indazolyl, m.p. < 330°, which is converted by  $EtI \cdot KOH$  in  $EtOH$  into its 2:2'- $Et_2$  derivative, m.p. 149°, and into decomp. products.

E. W. W.

**Mechanism of the lumichrome degradation of flavins.** P. KARRER, T. KÖBNER, and F. ZEHENDER (Helv. Chim. Acta, 1936, 19, 261—264).—That lumichrome degradation of flavins consists of oxidation of the side-chain is proved by synthesis of a typical reaction product. The  $\beta$ -position in the side-chain is particularly susceptible to this oxidation if it carries an OH. 9- $\gamma$ -Hydroxy-*n*-propylisoalloxazine, when kept in MeOH in daylight for 14 days, gives *Me*  $\gamma$ -9-isoalloxazinylpropionate, m.p. > 330°.  $\beta$ -o-Nitroanilinopropionic acid (prep. by condensation of  $NH_2 \cdot CHMe \cdot CO_2Et$  and *o*- $C_6H_4Cl \cdot NO_2$  in  $C_6H_5N$ , followed by hydrolysis), m.p. 152°, is hydrogenated (Ni; 90°/20—25 atm.) in  $EtOH$  to the  $(NH_2)_2$ -compound, which with alloxan in  $EtOH$  gives  $\gamma$ -9-isoalloxazinylpropionic acid.

R. S. C.

**Improved synthesis of lactoflavin and 6:7-dimethyl-9-1'-arabitylisoalloxazine.** P. KARRER and H. F. MEERWEIN (Helv. Chim. Acta, 1936, 19, 264—269).—The synthesis of lactoflavin (38% yield), m.p. 282°, and 6:7-dimethyl-9-1'-arabitylisoalloxazine, m.p. 294° (A., 1935, 1510), is improved by preparing the diazo-compounds with  $PhN_2Cl$  and using  $Na_2S_2O_4$  for the reduction. The good yields in the last stages prove the uniformity of the diazo-compounds.

[With A. SEEBACH.] *N*-*p*-Tolylglycamine, m.p. 139.5°, and  $PhN_2Cl$  give the benzenediazoamino-compound, decomp. about 146°, so that this method of synthesis of flavins is limited to those which start with 3:4-dialkylanilines.

R. S. C.

**Magnetic properties and structure of the haemochromogens and related substances.** L. PAULING and C. D. CORYELL (Proc. Nat. Acad. Sci., 1936, 22, 159—163).—The results indicate four unpaired electrons in  $Fe^{++}$  protoporphyrin, and five in the corresponding  $Fe^{+++}$  compound, showing that the Fe is linked to the four N by ionic linkings. Haemochromogens formed with globin,  $C_5H_5N$ , nicotine, cyanide, or Ni contain no unpaired electrons.

F. A. A.

**Optical absorption of porphyrins.**—See this vol., 545.

**Oximinoacetophenone.** F. ANGELICO and S. CUSMANO (Gazzetta, 1936, 66, 3—8).—This substance reacts with  $NH_2OH \cdot HCl$  to give not benzhydroxamic acid but aminophenylfurazan (I) (A., 1923, i, 857),

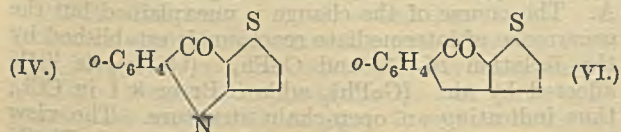


with phenylglyoxime and oximinophenylacetonitrile (II).  $\text{HNO}_2$  and (I) in AcOH yield 3:3'-diphenyl-4:4'-azoisminofurazan (cf. A., 1923, i, 854), m.p. 157—158° (explosive K salt), and (II). With  $\text{NH}_2\text{OH}$  in alkaline solution, (II) yields (I). E. W. W.

**Action of formaldehyde on hydroxyquinolines.** (SIGNA.) L. MONTI and (SIGNA.) V. CIRELLI (Gazzetta, 1936, 66, 42—48).—4-Hydroxyquinoline, its 8- and 6-Me derivatives, and 4-hydroxy-2-phenylquinoline are, respectively, converted by  $\text{CH}_2\text{O}$  in dil.  $\text{H}_2\text{SO}_4$  at 20—25° into 4-hydroxy-2-methyl-, m.p. 100—102° [picrate, m.p. 178—180° (decomp.)], -2:8-dimethyl-, m.p. 139—140° [picrate, m.p. 195—196° (decomp.)], -2:6-dimethyl-, m.p. 154—156° [picrate, m.p. 195—200° (decomp.)], and -2-phenyl-3-quinolylcarbinol cyclomethylene ether, m.p. 124—126° [picrate, m.p. 186—190° (decomp.)]. E. W. W.

**Action of nitric acid on unsaturated compounds. XII. Structure of products of the reaction of nitric acid with citraconic acid.** A. QUILICO (Gazzetta, 1935, 65, 1203—1213).—Eulite,  $\text{C}_6\text{H}_5\text{O}_7\text{N}_4$ , m.p. 102°, obtained by action of  $\text{HNO}_3$  on citraconic acid, is now prepared, with mesaconic acid and AcOH, from citraconic anhydride and  $\text{HNO}_3$ . With NaOEt it yields a Na salt (of an *aci*-form), which couples with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  to a substance, decomp. 70°, and similarly with  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\text{Cl}$ . With PhCHO, piperonal, anisaldehyde, and cinnamaldehyde it gives compounds,  $\text{C}_{13}\text{H}_{10}\text{O}_7\text{N}_4$ , m.p. 146°,  $\text{C}_{14}\text{H}_{10}\text{O}_9\text{N}_4$ , m.p. 187°,  $\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_4$ , m.p. 157°, and  $\text{C}_{15}\text{H}_{12}\text{O}_9\text{N}_4$ , m.p. 172°, respectively. The  $\cdot\text{CH}_2\cdot\text{NO}_2$  group is therefore present. Reduction ( $\text{SnCl}_2$ ) of eulite yields two bases,  $\text{C}_6\text{H}_5\text{O}_2\text{N}_3$  ( $\text{Bz}_2$  derivative, m.p. 157°) and  $\text{C}_6\text{H}_{11}\text{ON}_3$  ( $\text{Bz}_2$  derivative, m.p. 177°).  $\text{KMnO}_4$  oxidation of eulite gives AcOH. Eulite thus probably contains the units,  $\begin{smallmatrix} \text{C}\cdot\text{N} \\ \text{C}\cdot\text{C} \end{smallmatrix} > \text{O}$ , Me, H,  $\cdot\text{C}(\text{NO}_2)_2$ , and  $\cdot\text{CH}_2\cdot\text{NO}_2$ . E. W. W.

**Thiophen series. XXXI. Preparation of thiophen analogues of acridone and fluorenone.** W. STEINKOFF and E. GÜNTHER (Annalen, 1936, 522, 28—34).—Thiophen (I),  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  give 60% of *o*-nitrophenyl 2-thienyl ketone (II), m.p. 97—98°, reduced ( $\text{Sn}$ , conc. HCl) to C-2'-thienyl-anthranil [2:2'-thienyl-4-benzoxazole] (III), m.p. 77—78°, which resembles phenylanthranil (Bamberger and Lindberg, A., 1909, i, 511). Reduction (Zn dust, 20% NaOH, EtOH) of (II) and subsequent treatment with conc. HCl affords 3:5-dichloroanthranilic acid, probably formed thus: (II)  $\rightarrow o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO} \rightarrow o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \rightarrow 2:3:5\text{-NH}_2\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$  (cf. Bamberger *et al.*, A., 1899, i, 341). (III) heated in paraffin oil passes into 2:3-*o*-benzo-5:6:2':3'-thiopheno-4-pyridone (IV), m.p. about 320° (decomp.), which exhibits slight blue fluorescence in conc.



$\text{H}_2\text{SO}_4$  or EtOH-alkali only. 2-*p*-Toluenesulphonamidobenzoyl chloride, (I), and  $\text{AlCl}_3$  in  $\text{CS}_2$  give the

$p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  derivative, m.p. 125°, of *o*-aminophenyl 2-thienyl ketone (V), m.p. 53—54° (hydrochloride, m.p. 188—189°). When the diazo-solution from (V) is heated varying yields of *o*-phenylene 2:3-thienylene ketone (VI), m.p. 109—110°, and *o*-hydroxyphenyl 2-thienyl ketone, m.p. 21°, result. Attempted reduction (P-HI; Clemmensen) of (VI) causes decomp.

H. B.

**Isomerism of glycothiodiazolines.** H. WUYTS and R. VERSTRAETEN (Bull. Soc. chim. Belg., 1936, 45, 65—75).—*d*- or *l*-Arabinose with  $\beta$ -phenylthioacet- $\alpha$ -phenylhydrazine affords arabothiodiazolines, easily separable by fractional crystallisation. The more sol. have  $[\alpha]_{\text{D}}^{20} +650^\circ$  and  $+708^\circ$  for the *l*- and *d*-derivatives, respectively. The m.p. are: more sol. *l*-, 194.8—197.2°, *d*-, 194.8—197.2°; less sol. *l*-, 198°, *d*-, 197.6°. *d*-Galactothiodiazoline,  $[\alpha]_{\text{D}}^{20} +1109.6^\circ \rightarrow +106.6^\circ$  in several weeks, possibly as a result of mutarotation, is decomposed by light. Theoretical considerations are advanced to explain this isomerism.

J. L. D.

**Alkaloids of Senecio species. II.** R. H. F. MANSKE (Canad. J. Res., 1936, 14, B, 6—11; cf. A., 1932, 286).—12 *Senecio* species contain fumaric acid. *S. jacobaea* contains quercetin. *S. vulgaris*, L., contains 0.15—0.17% of senecionine, m.p. 222°, hydrolysed to retronecine and a cryst. acid. *S. mikanioides* (Walp.), Otto, yields a substance,  $(\text{C}_5\text{H}_8\text{O}_2)_n$  ( $n=12$ ), m.p. 64°, and 0.02% of amorphous mikanoidine,  $\text{C}_{21}\text{H}_{29}\text{O}_6\text{N}$ , hydrolysed to mikanecine (? dihydro-retronecine),  $\text{C}_8\text{H}_{15}\text{O}_2\text{N}$ , an oil (picrate, m.p. 186°), and mikanecic acid,  $\text{C}_{13}\text{H}_{16}\text{O}_5$ , m.p. 240°. *S. aureus*, L., yields 0.006% of aureine,  $\text{C}_{18}\text{H}_{25}\text{O}_5\text{N}$ , m.p. 238° (decomp.). An alkaloid was isolated from *Echium vulgare*, L.; none was obtained from *S. cineraria*, *clivorum*, *nemorensis*, *veitchianus*, *palmaris*, or *ledebouri*. Retrorsine methiodide and  $\text{Ag}_2\text{O}$  in hot  $\text{H}_2\text{O}$  give a methohydroxide, decomposed by cautious heating to give a substance,  $\text{C}_{13}\text{H}_{18}\text{O}_6$  (possibly lactaldehyde retronecate), m.p. 125° (with KOH gives retronecic acid), and a substance,  $\text{C}_9\text{H}_{13}\text{O}_3\text{N}$ , m.p. 256° (decomp.), probably a betaine. Benzoylretronecine behaves similarly. K retronecate,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{Me}$ , and a trace of KI in MeOH gives hydroxyacetone retronecate, m.p. 137°.

R. S. C.

**Alkaloids of Anabasis aphylla. XII. Attempted synthesis of anabesine; chemistry of 2:3'-dipyridyl.** G. MENSCHIKOV and A. GRIGOROVITSCH (Ber., 1936, 69, [B], 496—499).—Addition of MeI to 2:3'-dipyridyl (I) in abs. EtOH at room temp. affords exclusively 2-pyridyl-3'-pyridinium methiodide, m.p. 167—168°, converted by  $\text{Ag}_2\text{O}$  into the quaternary hydroxide (II) which is oxidised by  $\text{KMnO}_4$  to 2- $\text{C}_5\text{H}_4\text{N}\cdot\text{CO}_2\text{H}$  (III). Reduction of (II) with Sn and conc. HCl gives the base  $\text{C}_{11}\text{H}_{16}\text{N}_2$ , b.p. 120—122°/15 mm., oxidised to (III). 2-Pyridyl-3'-pyridinium hydriodide, m.p. 162—163°, and MeI in EtOH at 100° give a mixture of 2:3'-dipyridyl dimethiodide, m.p. 196—197°, and dihydriodide, m.p. 204—206°, also obtained directly from their components. Partial reduction of (I) in alkaline solution (Na-abs. EtOH) appears to affect both rings at approx. the same rate, the products being unchanged (I) and 2:3'-dipiperidyl (IV), m.p. 68—69°. Partial dehydrogenation of (IV)



by AgOAc in AcOH at 180° affects both rings simultaneously, giving a mixture of unchanged (IV) and (I). H. W.

**l-Ephedrine**, a degradation product of the alkaloids in *Aconitum napellus*. W. FREUDENBERG and E. F. ROGERS (J. Amer. Chem. Soc., 1936, 58, 533—534).—Destructive distillation of the total alkaloids (as hydrochloride) over cryst. Ba(OH)<sub>2</sub> gives hydrocarbons, NH<sub>2</sub>Me, and a basic oil containing l-ephedrine. H. B.

**Preparation of quinine aurothiosulphate**. Q. MINGOLA (Gazzetta, 1935, 65, 1258—1260).—A claim of prior prep. of this compound (cf. A., 1931, 1172), with different properties from the form described by Picon (A., 1935, 49, 366). E. W. W.

**Structural analogue of cinchene and its behaviour towards acid**. J. KENNER and B. K. NAND [with, in part, R. GRINDLEY] (Ber., 1936, 69, [B], 635—639; cf. A., 1935, 766).—Condensation of CH<sub>2</sub>Ph·CO<sub>2</sub>Et with the Et ester of *N*-benzoylmeroquinene (I) by NaOEt in C<sub>6</sub>H<sub>6</sub> at 100° affords the corresponding β-CO ester, the Cu compound, C<sub>26</sub>H<sub>28</sub>O<sub>4</sub>NCu, m.p. 226—227°, of which is converted by boiling 25% HCl into BzOH and 8-benzylidene-3-vinylquinuclidine (II), m.p. 158° (methiodide, m.p. 199°; tetrabromide, m.p. 117—119°). Hydrogenation of (II) in 5% HCl (PdCl<sub>2</sub>) gives 8-benzylidene-3-ethylquinuclidine, m.p. 182—183° [dibromide, m.p. 105—106° (decomp.)], the constitution of which follows from the similar hydrogenation of cinchene to dihydrocinchene, m.p. 144—145°. Hydrolytic fission of (II) with HBr (*d* 1.49) at 180—190° affords PhMe and meroquinene Et ester hydrochloride, m.p. 164—165°. With H<sub>2</sub>SO<sub>4</sub> of varied concns. PhMe is similarly obtained with a product which after basification and distillation gives an alkaline distillate with an odour of piperidine. The basic, salt-forming quinoline nucleus is therefore responsible for the production of apocinchene from cinchene and conc. acids and it must be assumed that this is due to prevention of the lepidine-meroquinene fission which occurs with more dil. acid. If the intermediate production of a ketone X·CO·CH<sub>2</sub>Ph be postulated the reaction is similar to the hydrolysis of substituted deoxybenzoins. Quinolyl-2-acetaldehyde (oxime, m.p. 201—202°, and the corresponding nitrile) is oxidised by KMnO<sub>4</sub> in alkaline solution to quinolyl-2-acetic acid (picrate, m.p. 236—237°), the Et ester, m.p. 68—69°, of which could not be condensed with Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or (I). Oxidation of 4-quinolyl Me ketone by SeO<sub>2</sub> in presence of PhMe affords cinchoninic acid, also obtained from 4-quinolyl CH<sub>2</sub>Br ketone. H. W.

[Synthesis of benzyltetrahydroisoquinoline bases under "physiological" conditions.] G. HAHN and O. SCHALES (Ber., 1936, 69, [B], 622—623; cf. A., 1935, 357).—A reply to Späth *et al.* (this vol., 489). H. W.

**Alkaloids of Chinese gelsemium**, Ta-ch'a-yeh. T. Q. CHOU (Chinese J. Physiol., 1936, 10, 79—84; cf. A., 1931, 871).—Koumine, kouminine, gelsemine, and kounidine (I), C<sub>21</sub>H<sub>24</sub>O<sub>5</sub>N<sub>2</sub>, m.p. 315° (hydrochloride, m.p. 318°), have been isolated from the leaves and stems of Ta-ch'a-yeh, which has been

identified as *G. elegans*. Tested on mice, (I) caused muscular weakness and had a marked inhibitory effect on the respiratory centre. J. N. A.

**Alkaloids of Ungernia Sewertzovii** (Rgl.), Fedsch. S. NORKINA and A. OREKHOV (Ber., 1936, 69, [B], 500—503).—Percolation of the dried bulbs with C<sub>2</sub>H<sub>5</sub>Cl<sub>2</sub> affords *ungernine* (I), C<sub>39</sub>H<sub>44</sub>O<sub>11</sub>N<sub>2</sub>, m.p. 210—211°, [α]<sub>D</sub><sup>25</sup> +148.9° in CHCl<sub>3</sub>, which is more freely present in the dark outer portions than in the white inner portions of the bulb. (I) contains 2 OH and 2 OMe and is a diacidic di-*tert.* base giving a *dimethiodide* (II), m.p. 220—223°, a *picrate*, m.p. 205—208° (decomp.), and a *perchlorate*, m.p. 105—108° (decomp.), [α]<sub>D</sub><sup>25</sup> +109.6° in MeOH. The function of the remaining O atoms is undecided. Hydrogenation (PtO<sub>2</sub>) of (I) affords *tetrahydroungernine*, m.p. 180—183°, [α]<sub>D</sub><sup>25</sup> +106.6° in CHCl<sub>3</sub> [*dihydriodide*, m.p. 223—224° (decomp.); *picrate*, m.p. 190—193° (decomp.); *methiodide*, m.p. 170—172°]. Successive treatment of (II) with Ag<sub>2</sub>O and boiling H<sub>2</sub>O yields the *substance* (III), C<sub>27</sub>H<sub>24</sub>O<sub>6</sub> (or C<sub>27</sub>H<sub>22</sub>O<sub>6</sub>), m.p. 113—115°, [α]<sub>D</sub><sup>25</sup> ±0°, which contains 2 OH but is free from OMe; basic compounds could not be isolated. (I) is stable towards boiling KOH-MeOH but is slowly transformed by boiling KOH-H<sub>2</sub>O into (III).

**Punarnava or Baerhaavia diffusa**, Linn. II. Isolation of punarnavine.—See this vol., 652.

**Organic compounds of gold. VI. Heterocyclic compounds**. A. BURAWOY and C. S. GIBSON (J.C.S., 1936, 324—327).—The Mg-CH<sub>2</sub>(CH<sub>2</sub>·CH<sub>2</sub>Br)<sub>2</sub> reaction product and HAuBr<sub>4</sub> give *ethylenediaminocyclopentamethylenegold bromide*, decomp. 150° (*n*-triacontane obtained in hydrocarbon by-products), which with HBr yields *cyclopentamethylenemonebromogold*, decomp. 80°. The Mg compound with pyridinetrichlorogold affords *ethylenediaminocyclo-decamethylenegold bromide*. Evidence of the formation of analogous compounds containing larger heterocyclic rings has also been obtained.

F. R. S.

**Germanium. XVI. Germanium phenyl**. R. SCHWARZ and M. SCHMEISSER (Ber., 1936, 69, [B], 579—585; cf. A., 1931, 1435).—GePhCl<sub>3</sub> is obtained in 75% yield by heating GePh<sub>4</sub> and GeCl<sub>4</sub> at 350° for 36 hr. Distillation of the product yields fractions, b.p. 105°/12 mm., 128°/12 mm., and 142°/12 mm., respectively; those of lower b.p. pass into those of higher b.p. when heated at appropriate temp. and polymeric forms appear to be indicated, but each fraction is unimol. in C<sub>6</sub>H<sub>6</sub> (GePh<sub>2</sub>Cl<sub>2</sub> and GePh<sub>3</sub>Cl have b.p. 223°/12 mm. and b.p. 285°/12 mm., respectively). GePhCl<sub>3</sub> reacts unsatisfactorily with Na in boiling xylene. Better results are obtained when Na is replaced by K. In presence of O<sub>2</sub> oxidation occurs but good yields are secured in CO<sub>2</sub> but not in N<sub>2</sub> or A. The course of the change is unexplained but the occurrence of intermediate reactions is established by the isolation of Ge and GePh<sub>4</sub>. (GePh)<sub>6</sub> is little affected by air. (GePh)<sub>6</sub> adds 8 Br or 8 I in CCl<sub>4</sub>, thus indicating an open-chain structure. The view is supported by the production of a *substance* Ge<sub>6</sub>Ph<sub>6</sub>O<sub>3</sub> from (GePh)<sub>6</sub> and O<sub>2</sub> in boiling xylene since the mol. wt. (about 2900) would require the formation of a



chain of about 18 Ge atoms from the ring, which is improbable. The reaction  $XPhCl_3 + 3K = XPh + 3KCl$  for the series C, Se, Ge, Sn occurs with increasing ease of removal of halogen. Under the chosen conditions it does not take place with  $CPhCl_3$ , is not quant. with  $SePhCl_3$ , occurs smoothly and relatively rapidly with  $GePhCl_3$ , and very easily with  $SnPhCl_3$ , but is then followed by disproportionation to  $SnPh_4$  and Sn.

H. W.

**Mercurated derivatives of thymol and carvacrol.** J. B. BURT (J. Amer. Pharm. Assoc., 1936, 25, 112—117).—Carvacrol with  $Hg(OAc)_2$  in EtOH yields mainly *mono-* and some *di-chloromercuricarvacrol*; in presence of AcOH, *acetoxymmercuricarvacrol*, decomp. 173—174°, is produced. The Me ethers of chloromercuri-thymol and -carvacrol are prepared similarly.

F. O. H.

**Thiophen series. XXXII. Mercuration of bromo- and iodo-thiophens.** W. STEINKOPF, R. RÖSLER, and L. SETZER (Annalen, 1936, 522, 35—40).—Mercuration is effected with  $HgO$  in AcOH (unless stated otherwise). The following are then prepared by the usual methods: 2-bromo-3:4:5-tri(chloromercuri)- and -3:4:5-tri-iodo-, m.p. 170°; 2:3-dibromo-4:5-di(chloromercuri)- (I), m.p. 300° (with darkening), and -4:5-di-iodo-, m.p. 142°; 2:5-dibromo-3:4-di(chloromercuri)-, m.p. 300—305° (darkens about 290°), and -3:4-di-iodo-, m.p. 147°; 3:4-dibromo-2:5-di(chloromercuri)- (II), m.p. 317° (previous sintering), and -2:5-di-iodo-, m.p. 145°; 2:3:4-tribromo-5-chloromercuri- (III), m.p. 236° (formed using  $HgCl_2$  in aq. EtOH-NaOAc); 2:3:5-tribromo-4-chloromercuri-, m.p. 270° (does not react with I-KI); 2-iodo-3:4:5-tri(chloromercuri)-, m.p. 290° (decomp.; darkens at 280°), and 2:5-di-iodo-3:4-di(chloromercuri)-thiophen. (I) and NaI in  $C_5H_5N$  give  $Hg_2$  4:5:4':5':4-tetrabromo-2:3:2':3'-dithienylene (cf. A., 1923, i, 125); (II) similarly affords  $Hg_2$  3:4:3':4'-tetrabromo-2:5:2':5'-dithienylene. (III) and NaI in  $COMe_2$  give  $Hg$  2:3:4:2':3':4'-hexabromo-5:5'-dithienyl, m.p. 291°.

H. B.

**Constitution of glutokyrin. III. Collagen.** W. GRASSMANN and K. RIEDERLE (Biochem. Z., 1936, 284, 177—188; cf. A., 1934, 271).—The basic  $NH_2$ -acid fraction (equiv. to 2/3 of the total N) from hydrolysates of glutokyrin is arginine and lysine (1:1); 1/3 of the  $(NH_2)_1$ -acid fraction is proline or hydroxyproline (which form peptides by linking of the  $:NH$  group), the remainder being acyclic  $NH_2$ -acids. The structures of the parent peptide chains and their bearing on those of gelatin and collagen are discussed.

F. O. H.

**Chemical groups of proteins which possess affinity for polysaccharides. VIII. Hydroxyproline, histidine, and lysine. IX. Rôle of  $\cdot CO \cdot NH \cdot$  linking.** S. J. VON PRZYŁĘCKI, J. CICHOCKA, and H. RAFAŁOWSKA (Biochem. Z., 1936, 284, 169—176; cf. this vol., 90).—Hydroxyproline, histidine, lysine, and creatinine do not form complexes with amylose (I) at  $p_H$  4, 7, or 8 as indicated by changes in  $\alpha$ ; arginine (II) + (I) at  $p_H > 7$ , however, show vals. of  $\alpha < \text{sum of the constituent vals.}$  The group  $\cdot CO \cdot NH \cdot$  does not appear to par-

ticipate in the phenomenon; glycyltyrosine, however, forms complexes. (II) and tyrosine appear to be the only constituent  $NH_2$ -acids concerned. F. O. H.

**Substituted proteins. II. Iodination of hæmoglobin and globin. III. Iodination of nitroglobin.** H. BAUER and E. STRAUSS (Biochem. Z., 1936, 284, 197—230, 231—237).—II. The coagulation of hæmoglobin (I) by heat,  $COMe_2$ ,  $CHCl_3$ , or  $CO(NH_2)_2$ , together with the properties of derived products, indicate that both (I) and globin are complexes of six units each of mol. wt. approx. 11,680. Iodination of (I), globin, paraglobins, etc. under various conditions shows that the linking of the units is by the glyoxaline groups of constituent histidine (II). Thus dissociation produces an increase in I val. from 4.17 to 9.56%. Hæmatin-free globin is more sensitive to lytic agents than is (I); hence the hæmatin complex has a stabilising influence on the coherence of the constituent units of the complex. Physical denaturation of (I) is not attended by dissociation. The orientation, affinity, and characteristics of the units are discussed.

III. Iodination of nitroglobin (III) in neutral, acid, and alkaline media give I vals. of 3.88—6.29%, indicating that (II) and not tyrosine is the I-carrier. The effective (II) in (I), globin, and (III) forms respectively 1/3, 1/2, and 2/3 of the total (II).

F. O. H.

**Pattern of proteins.** D. M. WRINCH (Nature, 1936, 137, 411—412).—Theoretical.

L. S. T.

**Method of introducing elementary arsenic, antimony, and bismuth into proteins.** P. MASCHERPA and L. CALLEGARI (Arch. ital. Biol., 1934, 91, 107—122; Chem. Zentr., 1935, ii, 401—402).—The powdered element is shaken with the protein solution in the absence of  $O_2$ .

H. N. R.

**Influence of  $p_H$  on the formation of salt-protein compounds between arsenic, antimony, bismuth, and albumin.** P. MASCHERPA and L. CALLEGARI (Arch. ital. Biol., 1934, 91, 115—122; Chem. Zentr., 1935, ii, 402; cf. preceding abstract).—With falling  $p_H$  the solubility of As and Sb in gelatin solutions diminishes, whilst that of Co increases.

H. N. R.

**Determination of organic nitrogen.** H. A. SCHUETTE and F. C. OPPEN (Trans. Wis. Acad. Sci., 1935, 29, 355—380).—A review.

**Identification of acids and esters.** D. V. N. HARDY (J.C.S., 1936, 398).—The acidic component of an ester is readily identified by conversion by  $NHR \cdot MgX$  into the anilide or substituted anilide.

R. S. C.

**Colour reaction of titanium with ascorbic acid and other molecules containing the group  $\cdot C(OH) : C(OH) \cdot$ .**—See this vol., 580.

**Application of copper salts of polyhydric alcohols to the detection and determination of reducing sugars.** V. M. PLATKOVSKAJA and T. I. VECHOTKO (J. Appl. Chem. Russ., 1936, 9, 177—181).—Glycerol and mannitol may be substituted for Na K tartrate in Fehling's solution.

R. T.



**Phospho- and silico-tungstates.** E. KAHANE and M. KAHANE (Bull. Soc. chim., 1936, [v], 3, 621—625).—Attention is directed to the suitability of the phospho- and silico-tungstates of org. bases for determination of the mol. wt. of the base. Such complexes have a const. composition and are free from  $H_2O$  of crystallisation. E. S. H.

**Quantitative investigations of amino-acids and peptides. I. Quantitative formaldehyde titration using a glass electrode.** M. S. DUNN and A. LOSIAKOV (J. Biol. Chem., 1936, 113, 359—369).—Details are given of a method for determination (error  $\pm 0.1\%$ ) of  $NH_2$ -acids and peptides by titration in 37.5% aq.  $CH_2O$  (freed from  $HCO_2H$  by basic Mg carbonate) with 0.3N-NaOH (mechanical stirring) using a glass electrode. Determination of  $NH_2$ -acids is unaffected by the presence of a foreign  $NH_2$ -acid if there is a  $10^4$ -fold difference between their apparent acid dissociation consts., but with peptides containing an  $NH_2$ -acid the no. of equivs. of NaOH is that required for the sum of the two constituents. Numerous examples are given, and other methods are briefly discussed. J. W. B.

**Some causes of error in the determination of  $\alpha$ -amino-acids by the ninhydrin reaction.** M. POLONOVSKI (Compt. rend. Soc. Biol., 1936, 121, 1103—1105).— $CO(NH_2)_2$  and creatine in large quantities interfere with the reaction. Proteins are removed by phosphotungstic acid for determination of  $(NH_2)_1$ -acids, and by saturation with  $(NH_4)_2SO_4$  for total  $NH_2$ -acids,  $(NH_2)_2$ -acids being calc. by difference.  $p_H$  must be made about 6.0 for the determination. R. N. C.

**Separation of amino-acids.**—See this vol., 561.

**Displacement of oxidation-reduction potential on illumination of methylene-blue solutions containing iron.**—See this vol., 566.

**Determination of pyridine according to the "Erganzungsbuch 5."** H. LEONHARDT and R. KLOCKMANN (Pharm. Ztg., 1936, 81, 345).—For the titration of  $C_5H_5N$  with HCl (the final concn. being approx. 0.5N), Me-violet 6B is a better indicator than Me-orange. With the latter, titration must be continued until a definite red colour is obtained. W. O. K.

**Phloroglucinol and diphenylbarbituric acid methods for determination of furfuraldehyde.** N. V. KOSCHKIN and V. P. TOKAREV (J. Appl. Chem. Russ., 1936, 9, 171—176).—*NN'*-Diphenylbarbituric acid (I) and furfuraldehyde (II) in aq. HCl afford practically insol. *furfurylidene-NN'-diphenylbarbituric acid*,  $+H_2O$ , decomp. at  $> 245^\circ$ . (II) is determined by steam-distilling the material under analysis in presence of 12% HCl, and adding a 4-fold excess of a 0.5% solution of the K salt of (I). The ppt. is collected after 12 hr., washed with boiling 2.5% NaOAc and with  $H_2O$ , dried at  $120^\circ$ , and weighed. The accuracy is of the same order as with the phloroglucinol method. R. T.

**Determination of alkaloids.** M. I. SMIRNOVA and G. N. SERBINA (Bull. Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 309—314).—A suitable modification of the nephelometric method is described. Ivanov's micro-method gave good results with fractions of a mg. CH. ABS (p)

**Colorimetric determination of morphine and its derivatives.**—See this vol., 536.

**Micro-determination of morphine.**—See this vol., 652.

## Biochemistry.

**Regulation of respiration with oxygen-poor air mixtures.** A. J. ANTHONY (Pflüger's Archiv, 1935, 236, 435—439). R. N. C.

**Gaseous exchange in growing ducks.** A. K. DANILOVA and A. N. POSTNIKOVA (Bied. Zentr. [Tierernähr.], 1935, 7, B, 158—183).—Variations in catabolic rates with advancing age of ducks are examined. Max. vals. occur at approx. 10 days. A. G. P.

**Effects of inhalation of carbon dioxide on the carbon dioxide capacity of arterial blood.** H. E. HIMWICH, E. F. GILDEA, N. RAKIETEN, and D. DuBOIS (J. Biol. Chem., 1936, 113, 383—389).—Exposure to  $CO_2$  (5—8%) for approx. 0.5 hr. caused a decrease of  $CO_2$  capacity in all human subjects and in 3 out of 4 dogs examined. After  $< 55$  min. there was a rise of  $CO_2$  capacity in all cases. The compensatory increase of  $CO_2$  capacity which diminishes the fall in  $p_H$  is not the first response to inhalation of  $CO_2$ . The acid-base equilibrium of the serum showed no accumulation of unknown acid, neither was there a shift of fluid in the serum, which might have explained such changes. J. N. A.

**Diffusion of carbonic acid through the skin.** K. KRAMER and H. SARRE (Arch. exp. Path. Pharm. 1936, 180, 545—556).—Changes in  $[CO_2]$  of  $CO_2$ -containing or -free  $H_2O$  in contact with skin indicate a purely physical diffusion of  $CO_2$  dissolved (as in  $H_2O$ ) in the cutaneous tissue. The exchange depends on the blood supply. Exposure to an atm. of  $CO_2$  (when the uptake of  $CO_2$  averages 26 c.c. per 33 sq. cm. of skin) produces no change in the rate of subsequent diffusion, indicating a removal of penetrated  $CO_2$  by blood. F. O. H.

**Voluntary hyperpnea and behaviour of alveolar carbon dioxide, alkaline reserve, and blood-proteins in man.** W. JAROSZEWICZ (Compt. rend. Soc. Biol., 1936, 121, 917—920).—Alveolar  $CO_2$  and the alkaline reserve are always decreased. Blood-proteins decrease in all cases of pronounced, and in most cases of less pronounced, tetanic reflex action; in its absence they generally rise. R. N. C.

**Measurement of red-cell volume: conductivity measurements.** E. PONDER (J. Physiol., 1935, 85, 439—449). R. N. C.



**Permeability of erythrocytes. III. Cation content of erythrocytes of rabbit's blood in hyper- and hypo-tonic sera.** H. DAVSON (Biochem. J., 1936, 30, 391—393).—The changes in vol. of rabbit's erythrocytes in hyper- and hypo-tonic solutions are < those to be expected on the basis of complete cationic impermeability, but the anomalies are < those described by Ponder and Saslow (J. Physiol., 1930, 70, 169; 1931, 73, 267) and are not to be correlated with the penetration of  $K^+$  and  $Na^+$  (cf. A., 1934, 673). P. W. C.

**Hæmoglobin regeneration as influenced by diet and other factors.** G. H. WHIPPLE (J. Amer. Med. Assoc., 1935, 104, 791—793).—A summary.

CH. ABS. (p)

**Rôle of inorganic substances and amino-acids in the regeneration of hæmoglobin in the rat.** H. L. KEIL (Iowa State Coll. J. Sci., 1934, 9, 169—170).—Attempted replacement of Cu by other elements and various  $NH_2$ -acids as hæmotinics was unsuccessful. Intraperitoneal injection of Fe citrate or chloride or of dil. HCl gave temporary relief. Injection or feeding of sol. or insol. Cu compounds, with or without Fe, causes regeneration.

CH. ABS. (p)

**Isoelectric point of adsorbed hæmoglobin.** H. L. WHITE and B. R. MONAGHAN (J. Biol. Chem., 1936, 113, 371—374).—As the purity of adsorbed hæmoglobin increases, the isoelectric point approaches 6.8, the val. obtained by the moving boundary method. Using the microscopical method, a protein must be pure to get correct vals. of mobilities and isoelectric point, but the electrical properties are not altered by adsorption on quartz or glass.

J. N. A.

**Localisation of hæmoglobin and its derivatives in some aphrodites.** C. RAPHAËL (Compt. rend., 1936, 202, 588—590).—Hæmoglobin is present in the circulatory system and in the pigment of the pharyngeal sheath. Oxyhæmoglobin and hæmatin (I) occur in the papillæ which cover the edge of the sheath, and large quantities of (I), together with small amounts of bile pigments, in the cæcum.

J. N. A.

**Hepatic function. III. Effect of cholecystectomy.** A. CANTEROW, E. GARTMAN, and G. RICHUTI (Arch. Surg., 1935, 30, 865—874).—Changes in serum-bilirubin are recorded and discussed.

CH. ABS. (p)

**Colloid osmotic pressure of the blood in normal and pathological conditions. XIV. Effect of blood transfusion on colloid osmotic pressure in normal and anæmic rabbits.** N. ONOZAKI. XV. Effect of infusions of gum arabic. N. ONOZAKI and Y. SANADA. XVI. Effect of vegetative nerve poisons. N. ONOZAKI (Tôhoku J. Exp. Med., 1935, 25, 1—13, 120—130, 131—147).—XIV. The colloid osmotic pressure ( $P$ ) of blood after injection of physiological saline parallels the decreased protein (I) and hæmoglobin (II) content, the  $P$  per unit (I) remaining const. The increased  $P$  after transfusion is > that corresponding with the increased (I) content.

XV. Intravenous injection of 6—12% solutions of gum into rabbits decreased serum-(I) and blood-(II). The  $P$  increased by an amount > that of the gum introduced.

XVI. Ergotamine, pilocarpine, and choline produced significant changes. Atropine had no action.

CH. ABS. (p)

**Precipitation of serum-proteins by ammonium sulphate: [serum of] normal man.** A. ROCHE, M. DORIER, and L. SAMUEL (Compt. rend. Soc. Biol., 1936, 121, 1019—1021).—Globulins (I) are pptd. between 30% and 60%, and albumins between 60% and 70% of saturation with  $(NH_4)_2SO_4$ . (I) are not pptd. fractionally, as in horse serum. The (II)/(I) ratio obtained by 50% saturation is 1; the true ratio at 60% saturation is 0.5.

R. N. C.

**Effect of fasting on the serum-protein concentration of the rat: existence of an immediately utilisable circulating protein fraction.** H. C. TORBERT (J. Exp. Med., 1935, 62, 1—10).—No evidence of a circulating, available plasma-protein was obtained. The decline in serum-protein after fasting involves principally the albumin fraction.

CH. ABS. (p)

**[Electrical] conductivity of serum after administration of calcium and ultra-violet irradiation.** A. DELL'AQUILA and F. JAIA (Arch. Farm. sperim., 1935, 60, 578—586).—Intravenous injection of aq.  $CaCl_2$  has no effect on  $\kappa$  of blood or serum, but subsequent ultra-violet irradiation lowers  $\kappa$ . The phenomenon occurs *in vitro*, but to a smaller extent than *in vivo*.

F. O. H.

**Dispersion by blood-serum of a partly-flocculated serum-globulin fraction.** C. MOREL (Compt. rend. Soc. Biol., 1936, 121, 836—837).—The globulins are partly flocculated by dilution of the serum within a certain range of  $p_H$ . The dispersive power of the serum falls with  $p_H$ . It is increased by heating the serum at the upper limit of this  $p_H$  range, the effect of heating falling rapidly with  $p_H$  to zero at approx. the middle of the range, below which flocculation is increased by heat, the effect augmenting as  $p_H$  falls to the lower limit.

R. N. C.

**Stability of blood-serum.** R. JONNARD (Compt. rend. Soc. Biol., 1936, 121, 841—843).—The ratio of the serum concn. to the [EtOH] necessary for flocculation is inversely  $\propto$  the hydration of the serum-colloids, and increases with the serum concn., the curve being linear at acid reactions. The ratio increases with acidity for any fixed serum concn.

R. N. C.

**Micro-determination of serum-albumins and -globulins.** A. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 1022—1023).—Globulins are pptd. from the serum by half saturation with  $(NH_4)_2SO_4$ ; albumins are determined in the filtrate and total proteins in the serum by the micro-Kjeldahl method after pptn. with tannin acetate or Hedin's reagent.

R. N. C.

**Determination of euglobulin.** R. GILLE (Compt. rend. Soc. Biol., 1936, 121, 906—908).—Dialysis of globulins previously separated from serum by pptn. with  $MgSO_4$  produces a euglobulin fraction > that from direct dialysis of the serum, and containing much pseudoglobulin. The  $(NH_4)_2SO_4$  technique of Porges and Spiro gives high vals., but pptn. with excess of 1/3-saturated  $(NH_4)_2SO_4$  solution or 14% of  $Na_2SO_4$  produces trustworthy results.

R. N. C.



**Volumetric micro-determination of phosphatides, free cholesterol, cholesteryl ester, neutral fat, and total lipins of blood, plasma, and corpuscles.** S. KATSURA, T. HATAKEYAMA, and K. TAJIMA (*Biochem. Z.*, 1936, 284, 312; cf. *A.*, 1934, 673).—Some improvements in the method are given.

F. O. H.

**Micro-determination of blood-sugar with hypiodite.** E. GUBAREV and M. RUTES (*Bull. Soc. Chim. biol.*, 1936, 18, 395—400).—The blood (0.2 c.c.) is freed from albumin with aq. AcOH and oxidised with NaOI.

A. L.

**Blood-sugar level after sectioning the pancreatic duct in rabbits.** T. DEGUCHI (*Tôhoku J. Exp. Med.*, 1934, 24, 368—373).—Bilateral ligation of the duct caused neither hyper- nor hypo-glycaemia in rabbits.

CH. ABS. (p)

**Determination of alcohol in blood by Widmark's method.** C. HEGLER (*Deut. med. Woch.*, 1935, 61, 288—291; *Chem. Zentr.*, 1935, ii, 729).—The Widmark test is usually, but not decisively, an evidence of alcoholic influence. In chronic alcoholism, low vals. are frequently found.

J. S. A.

**Technique of Widmark blood-alcohol determination for serial investigations.** H. R. KANITZ (*Deut. Z. ges. gerichtl. Med.*, 1935, 24, 273—274; *Chem. Zentr.*, 1935, ii, 729).—Improved procedure is described.

J. S. A.

**Chloropenic hyperazotæmia.** S. MARINO (*Arch. Farn. sperim.*, 1935, 60, 564—571).—The incidence of hyperazotæmia in chloropenia is discussed with reference to increased formation of urea and to changes in the re-absorption by the renal tubules.

F. O. H.

**Resection of the small intestine.** P. BARCO and S. L. PASTORINO (*Pathologica*, 1935, 27, 285—293).—Blood-Ca, -K, -P, -glucose, and -cholesterol increased immediately after resection and subsequently decreased to normal in 30—60 days.

CH. ABS. (p)

**[Blood-]bromine problem.** I. SCHMITT and H. KIRCHHOFF (*Deut. tierärztl. Woch.*, 1935, 43, 227—230; *Chem. Zentr.*, 1935, ii, 1053).—The blood-Br vals. for a no. of animals are given.

R. N. C.

**Velocity of intra-hepatic blood circulation.** I. ENESCO and C. ISAC (*Bull. Acad. Méd. Roumanie*, 1936, 1, 168—178).—Following intravenous and oral administration of KI, I appears in the saliva within 1—2.5 and 7—15 min., respectively. With oral and rectal administration, the difference in time of appearance, 2—5 min., represents the time of intra-hepatic circulation. The influence of disease is discussed.

F. O. H.

**Potassium and calcium in the blood of pigeons after resection and electrical excitation of the wing nerves.** R. CERNATESCU and A. MEYER (*Vol. Jubilaire C. I. Parhon*, Sep., 8 pp.).—Excitation disturbed the equilibrium of K<sup>+</sup> and Ca<sup>++</sup> in serum. The effect varied with the individual, the change in [K<sup>+</sup>] appearing first and being > that in [Ca<sup>++</sup>].

CH. ABS. (p)

**Extraction of lead by means of diphenylthiocarbazone.** L. ELLIS (*Analyst*, 1936, 61, 178—179).—For the determination of Pb in blood the "titri-

metric extraction" method of Wilkins *et al.* (*A.*, 1935, 531) is simpler and more convenient than that involving complete oxidation of the dithizone (I). The first Pb-(I) complex is extracted with 1% HNO<sub>3</sub> and, after removal of CHCl<sub>3</sub>, the combined extracts are used directly for the colorimetric comparison.

E. H. S.

**Soap hæmolysis as a fatty acid hæmolysis.** A. MEDVECZKY and L. VOTIN (*Biochem. Z.*, 1936, 284, 244—246).—Hæmolysis by Na oleate is due to liberated oleic acid, the reaction for both not occurring at  $p_H$  8.5—9.0, but increasing as  $p_H$  decreases from 8.0 to 4.5.

F. O. H.

**Venom of *Lachesis (Bothrops)* snakes. II. Preparation of bothropotoxin.** D. VON KLOBU-SITZKY (*Arch. exp. Path. Pharm.*, 1936, 180, 479—481).—The highly purified toxin (free from N, P, Fe, and halogens; min. lethal dose 0.055—0.060 mg.) (cf. *A.*, 1935, 1394) is prepared from aq. NaCl extracts of the dried venom by acid-heat-coagulation of proteins, removal of impurities by dil. alkali, pptn. with EtOH, and dialysis.

F. O. H.

**Chemical aspects of immunity.** A. SORDELLI (*Anal. Asoc. Quím. Argentina*, 1935, 23, 106—125).—A lecture.

**Antigenic character of proteins heated in sucrose media.** W. MUTSAARS and J. ALEXANDER (*Compt. rend. Soc. Biol.*, 1936, 121, 898—899).—Sucrose in high concns. prevents the destruction of the antigenic power of serum-proteins by heating to 75°.

R. N. C.

**Influence of nutrition on the natural immunity reactions of the blood and on skin reactions to bacterial toxins.** E. M. J. ANDERSON and A. H. H. FRASER (*J. Immunol.*, 1934, 27, 1—16; *Chem. Zentr.*, 1935, ii, 396).—Caloric dietary deficiency decreased the hæmolytic activity of sheep serum to rabbit red-cells but increased its agglutinating power with *Br. abortus*. Cod-liver oil and Ca had no effect on the natural immunity reactions.

G. H. F.

**Immunological study of the reduction of disulphide groups in proteins.** D. BLUMENTHAL (*J. Biol. Chem.*, 1936, 113, 433—437).—The influence of reduction of serum- (I) and ov-albumin (II) by thioglycolic acid and cysteine, respectively, and re-oxidation by H<sub>2</sub>O<sub>2</sub> on their antigenic properties is determined by injecting them into rabbits and measuring the N content of the ppts. formed with the antisera. Reduction and re-oxidation of (I) decreases the N pptd. in the cross reaction as compared with the homologous pptn., and prevents the usual inhibition of pptn. by excess of antigen. Similar treatment of (II) has no influence on its immunological behaviour.

H. D.

**Effect of concentration of ammonia and of the time factor on the antigenic properties of a deformalised anavaccine.** A. A. KLIMENTOVA and E. S. AVTONOMOVA (*Arch. Sci. biol. U.S.S.R.*, 1934, 35, B, 837—842).—Treatment of typhoid (formalised) vaccine with aq. NH<sub>3</sub> to remove excess of CH<sub>3</sub>O, followed by neutralisation to  $p_H$  7.1 with HCl, did not lower the antigenic potency. Prolonged treatment (24 hr.) with NH<sub>3</sub> lowered the titre.

CH. ABS. (p)



**Effect of phenol on the antigenic and immunising properties of formalinised vaccines.** L. A. TSCHERNAJA and N. P. IVANOV (Arch. Sci. biol. U.S.S.R., 1934, 35, B, 821—823).—Neither  $\text{CH}_2\text{O}$  treatment nor the further addition of 0.5% PhOH affected the potency of typhoid vaccines.

CH. ABS. (p)

**Dynamics of the transformation of diphtheria toxins of various types into anatoxins.** T. I. IVANOVA and V. N. KALNINA (Arch. Sci. biol. U.S.S.R., 1934, 35, B, 631—640).—The mechanism of the change is examined.

CH. ABS. (p)

**Purification of antidyenteric serum with sodium sulphate.** O. GARCIA, R. VILLAMIL, and C. PAÑGANIBAN (Philippine J. Sci., 1935, 58, 471—479).—To the dil. serum is added  $\text{Na}_2\text{SO}_4$  to produce a final concn. of 20 g. per 100 c.c. The ppt. is washed and dissolved in  $\text{H}_2\text{O}$ , and the solution is dialysed.

A. G. P.

**Rôle of the toxin in staphylococcal infection.** F. C. O. VALENTINE (Lancet, 1936, 230, 526—531; cf. *ibid.*, 1932, 222, 506).—Methods of preparing the toxin and of determining the leucocidin (I) in toxin and the anti-(I) in serum are described. Fresh evidence that  $\alpha$ -hemolysin and (I) are distinct substances is provided.

L. S. T.

**Chemioaccine producing in the rabbit immunity against tubercle infection.** M. MACHEBEUF and J. DIERYCK (Compt. rend., 1936, 202, 164—166).—Tubercle bacilli, treated with  $\text{H}_2\text{O}$  and then with  $\text{COMe}_2$  and  $\text{Et}_2\text{O}$  to remove toxic non-antigenic substances, possess high immunising activity.

W. O. K.

**Crystal orientation in tooth-enamel.** W. F. BALE and H. C. HODGE (Naturwiss., 1936, 24, 141—142).—The cryst. substance of tooth-enamel is identical with that of the dentine, but differences in the X-ray diffraction diagrams arise owing to preferential crystal orientation in the enamel, which is seldom found in the dentine.

A. J. M.

**Dissolution rate of apatite in an average mouth.** P. J. BREKHUS and W. D. ARMSTRONG (J. Dental Res., 1934, 14, 455—456).—Slow dissolution confirms that the inorg. matter of tooth enamel is apatite.

CH. ABS. (p)

**Histo-chemical localisation of chlorine in the gastric mucosa.** L. LISON (Compt. rend. Soc. Biol., 1936, 121, 900—902).—The lining cells of the mucosa of laboratory animals contain no Cl.

R. N. C.

**Changes in potassium and calcium content in the gravid uterus.** H. WINKLER (Monatsschr. Geburtsh. Gynäkol., 1935, 100, 211).—The K content of the non-pregnant human uterus (mean 1.61% of dried musculature in 9 cases) is very variable. It rises slowly during the earlier part of pregnancy and very rapidly during the last few months (to 2.5%). Ca is much more uniform (0.5%), but drops below the non-pregnant val. near term.

NUTR. ABS. (m)

**Determination of  $\alpha$ -amino-acids by the ninhydrin reaction.**—See this vol., 620.

**Biogenic amines in toxicological investigations.** A. VERDINO (Deut. Z. ges. gerichtl. Med.,

1935, 25, 74—78; Chem. Zentr., 1935, ii, 889).—Tyramine and a base, probably  $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_2$ , were isolated from a corpse 3 months after interment.

J. S. A.

**Total glutathione in tissue: determination and distribution in normal animals.** L. BINET and G. WELLER (Bull. Soc. Chim. biol., 1936, 18, 358—378).—The author's method for the determination of glutathione (I) (A., 1935, 1153) is applied to the tissue of *Carassius auratus* and to various animal organs. Large variations in the oxidised (I) content of the individual tissues are observed; in the intestine there is none, but the val. rises to 20—50% of the total (I) in lung and brain. The total (I) content shows less individual variation, and is characteristic of each tissue.

A. L.

**Amino-acids of the mixed proteins of ox muscle. Basic amino-acids.** H. G. REES (Analyst, 1936, 61, 160—164).—Arginine (6.18%), histidine (0.52%), and lysine (7.18%) have been determined in the mixed proteins [N 15.87% (amide, 7.2%; humin, 1.6%; basic, 24.3%;  $\text{NH}_2$ , 66.6%; non- $\text{NH}_2$ , 0.8%)] of ox muscle by Vickery's modification of Kessel's procedure.

E. H. S.

**Determination of the fatty acids in monoaminophosphatides.** M. FLATTER (Bull. Soc. Chim. biol., 1936, 18, 406—413).—Attempts are made to avoid low vals. in the determination of the fats resulting from hydrolysis of monoaminophosphatides. A modification of the method of Lemeland (A., 1922, ii, 666) and hydrolysis in AcOH solution with 3N-HCl were best, giving almost theoretical results with lecithin.

A. L.

**Seasonal differences in the fat and protein content of nerve tissue of the frog.** J. ROSENBERG (Arch. internat. Physiol., 1935, 41, 429—433).—In the cerebrospinal tracts the N content was 14.7—16.0 mg. (mean 15.3 mg.) and in the sciatic nerves 18.0—20.2 mg. (mean 19.1 mg.) per g. of fresh material, being highest in May and June and lowest in Feb. and July. The corresponding fatty acid contents were 46.9—67.6 mg. (mean 61.9 mg.) and 88.1—130.0 mg. (mean 119.2 mg.), being highest in summer and autumn and lowest during hibernation.

NUTR. ABS. (m)

**Bio-organic chemistry of the proteins.** V. SADIKOV (Arch. Sci. biol. U.S.S.R., 1934, 35, A, 297—331).—A theoretical discussion of the structure of constituent groups which are components of living protein systems.

CH. ABS. (p)

**Influence of method of preparation and of cations on the isoelectric point of ovalbumin.** E. R. B. SMITH (J. Biol. Chem., 1936, 113, 473—478).—The isoelectric point of ovalbumin is independent of the salt used for recrystallisation; it decreases linearly with the ionic strength of the buffers used, and the slope of the ionic strength against isoelectric point varies with the ions in the OAc' buffer mixtures.

H. D.

**Proteins of muscle in rigor.** A. E. MRSKY (J. Gen. Physiol., 1936, 19, 571—575).—No activation of -SH groups accompanies the formation of insol. protein in rigor, but occurs in subsequent denaturation.

H. G. R.



### Thiol and disulphide groups of proteins.

IV. Thiol groups of the proteins of muscle. A. E. MIRSKY (J. Gen. Physiol., 1936, 19, 559—570).—Denaturation or increased  $p_H$  causes a rise in the no. of active -SH groups in the proteins of minced muscle (halibut, *Rana catesbiana*, rabbit), except that of the crust. lens. Little denatured protein is present in minced muscle. H. G. R.

Formation of myelin studied in polarised light. G. LEBOUcq (Compt. rend. Soc. Biol., 1936, 121, 875—877).—Myelin appears very late in the embryonic life of the rat, but crystals of cholesterol or its esters are observed at earlier stages. R. N. C.

Proteins of hen egg-yolk. M. PIETTRE (Compt. rend., 1936, 202, 699—701).—An albumin and a myxoprotein are isolated and examined. The fatty matter contains cholesterol. Bilirubin is also present. A. G. P.

Gravimetric determination of total body- and organ-protein. T. ADDIS, L. J. POO, W. LEW, and D. W. YUEN (J. Biol. Chem., 1936, 113, 497—504).—The general method is to drop the fresh tissue into boiling OAc' buffer at  $p_H$  5 which prevents autolysis, ppts. the proteins, and removes  $H_2O$ -sol. compounds. Fats are removed by hot EtOH, and the residual protein is dried in a vac. and weighed. Detailed procedures for the different organs are given, together with data obtained on normal rats. F. A. A.

Iodination of hæmoglobin, globin, and nitroglobin.—See this vol., 619.

Visual cycle and protein denaturation. A. E. MIRSKY (Proc. Nat. Acad. Sci., 1936, 22, 147—149).—Visual purple is considered to consist of a protein conjugated with a carotenoid (retinene), and this complex is reversibly denatured by light. The denatured complex (visual yellow) is in equilibrium with its constituents. The energy requirements found approx. agree with those expected of such a reaction. F. A. A.

New forms of visual purple found in sea fishes: visual cells of origin. L. E. BAYLISS, R. J. LYTHGOE, and K. TANSLEY (Proc. Roy. Soc., 1936, B, 120, 95—113).—A no. of new forms of visual purple, found in sea fishes, with max. of absorption between 505 and 545  $m\mu$ , are described. Absorption curves, obtained by a null-point photo-electric spectrophotometer, are given. The instrument gave accurate results using only 0.5 c.c. of solution and with a light intensity not high enough to bleach the visual purple. E. A. H. R.

Anomalies in the absorption spectrum and bleaching kinetics of visual purple. A. M. CHASE (J. Gen. Physiol., 1936, 19, 577—599).—During bleaching of visual purple by light, winter extractions show an intermediate yellow colour not observed in summer extractions; these conditions can be simulated by variation in the  $p_H$ , since an indicator (yellow in acid, colourless in alkali) is formed as an intermediate in the decomp. Temp. has no effect on the bleaching of alkaline solutions, but acid solutions at low temp. approximate to winter conditions and at higher temp.

to summer. No variation of  $p_H$  is observed during bleaching or in summer or winter extractions. H. G. R.

Erythrocrucorin (hæmoglobin) of the nervous system of *Aphrodite*. J. ROCHE and C. RAPHAËL (Compt. rend. Soc. Biol., 1936, 121, 1024—1026).—The pigment (I) shows bands at 576.4 and 539.5  $m\mu$ , whilst the reduced form shows one band at 557  $m\mu$ . CO forms a compound with bands at 570.6 and 538  $m\mu$ .  $C_5H_5N$  and  $Na_2S_2O_4$  produce a hæmochromogen spectroscopically identical with protohæmatin. The isoelectric point of (I) is  $p_H$  5.8, showing that (I) is related to both muscular hæmoglobins and erythrocrucorins. R. N. C.

Muscular hæmoglobin and cytochrome. J. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 1026—1028).— $N_2H_4$  reduces muscular methæmoglobin to a hæmochromogen (bands at 525, 552—554, and 570—572  $m\mu$ ), and to hæmoglobin, which forms oxyhæmoglobin with atm.  $O_2$ . There is no evidence of a reversible transformation to cytochrome. R. N. C.

Nature and permeability of chitin. II. Permeability of the uncalcified chitin lining the foregut of *Homarus*. C. M. YONGE (Proc. Roy. Soc., 1936, B, 120, 15—41).—The bounding cuticle of the integument is removed by prolonged treatment with  $N$ -alkali. The permeabilities of fresh and treated membranes to fatty acids, mineral acids, alkalis, and  $Cl'$  are very different. Rigidity is conferred on chitin by impregnation with scleroproteins or Ca salts, and its high permeability is limited by the cuticle. E. A. H. R.

X-Ray investigations of chitin.—See this vol., 414.

"Adrenosterone."—See this vol., 605.

Separation of hæmatopoietic principles from liver. B. EISLER, E. HAMMARSTEN, and H. THEORELL (Naturwiss., 1936, 24, 142—143).—During cataphoresis of active liver extracts at  $p_H$  4.5—6.6, substances  $R$  and  $E$  migrate to the anode and cathode, respectively.  $R$  increases reticulocytes but not erythrocytes and is stable to heat or changes in  $p_H$ , whilst  $E$  does not change the blood picture;  $R+E$ , however, increase reticulocytes and subsequently erythrocytes.  $R$  can be replaced by substances such as  $Na_4$  thymonucleate. F. O. H.

Dietary requirements for lactation. IV. Nature of factor  $L$ , a specific dietary factor for lactation. W. NAKAHARA, F. INUKAI, and S. UGAMI (Bull. Agric. Chem. Soc. Japan, 1936, 12, 1—8).—The factor is separated from liver extracts by making use of the facts that it is not adsorbed by fuller's earth, that it is pptd. from the non-adsorbable fraction by  $Ba(OH)_2$  and MeOH, and from the decomposed Ba ppt. by phosphotungstic acid. The final ppt. was active in doses of < 50 mg. per rat. H. D.

Hæmocyanin in heavy water.—See this vol., 563.

Determination of diffusion constants of proteins by a refractometric method.—See this vol., 563.

Rôle of coacervation in the resorption of fats.—See this vol., 563.



**Blood-coagulation-accelerating properties of maternal milk.** W. KRASZEWSKI and L. LINDENFELD (Klin. Woch., 1935, 14, 863—864).—The acceleration is due to a cytozyme.  
R. N. C.

**Heating of human milk and its nutritional results: converging point for human milk.** W. CATEL (Deut. med. Woch., 1935, 61, 985—988).  
R. N. C.

**Inhibition of coffee diuresis by milk and milk products.** K. HITZENBERGER and D. ROLLER (Wien. Arch. inn. Med., 1935, 27, 133—141; Chem. Zentr., 1935, ii, 874).—The inhibition is probably due to lecithin.  
R. N. C.

**Tyndall light of milk.**—See this vol., 562.

**Permeability of the mammary gland.** M. PIETTRE (Compt. rend., 1936, 202, 166—169).—Low secretory activity of the mammary gland associated with low lactose content of the milk results in high [Cl] in consequence of a more complete equilibrium with serum-Cl being established. Thus the apparent compensation of osmotic pressure frequently observed is accidental and not essential.  
W. O. K.

**Colloid osmotic pressure of the hæmolymphs of some terrestrial invertebrates.** P. MEYER (Nature, 1936, 137, 401—402; cf. A., 1935, 1516, 1524).—The colloid osmotic pressure of the body fluids of marine and terrestrial gastropod molluscs is practically identical, but rises steadily from crustaceans to arachnids and insects.  
L. S. T.

**Composition of saliva from the separate glands in children.** A. I. MACHTINGER and A. J. FEDOROV (Arch. Sci. biol. U.S.S.R., 1934, 34, 587—590).—Parotid saliva in children of 12—14 years is richer in amylase and org. matter than that of the submaxillary. The parotid is the chief digestive gland in children.  
CH. ABS. (*p*)

**Human saliva. II. Procedure for calcium analysis.** W. W. WAINWRIGHT (J. Dental Res., 1934, 14, 425—434).—The centrifuged sample is treated with  $\text{CCl}_3 \cdot \text{CO}_2\text{H}$  and again centrifuged. Ca is determined by pptn. as  $\text{CaC}_2\text{O}_4$  and titration with  $\text{KMnO}_4$ .  
CH. ABS. (*p*)

**Bile pigments. I. Ehrlich's test for urobilinogen and Schlesinger's reaction for urobilin.** H. N. NAUMANN (Biochem. J., 1936, 30, 347—351).—The Ehrlich test for urobilinogen with  $p\text{-NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$  in HCl is most satisfactory when carried out at 20° with a final [HCl] of 2.5%; the more important interfering substances in urine are detailed. The Jaffé-Schlesinger test for urobilin is quite sp.  
H. D.

**Role of coacervation in the formation of biliary calculi.** A. DE KUTHY (J. Chim. phys., 1936, 33, 180—182; cf. A., 1935, 580, 1006).—The pptn. of cholesterol in the gall-bladder is attributed to coacervation by protein.  
R. S.

**Effect of jejunal feeding on gastric acidity.** A. A. APPELL (Arch. Surg., 1935, 30, 875—880).—Gastric contents had a lower  $p_{\text{H}}$  and more acid after a milk-syrup diet given by jejunum than when given by mouth. The jejunal content was slightly more alkaline after jejunal than after oral feeding. Gastric

secretion was increased by food constituents in the (ascending) order, sucrose, peptone, butter, glucose, cream, meat extract, glycine, cottonseed oil, casein.

CH. ABS. (*p*)

**Hydrochloric acid and gastric motility.** C. C. DIMITRIU and T. TANASOKA (Bull. Acad. Méd. Roumanie, 1936, 1, 212—218).—The motility and HCl secretion of the human stomach are independent.

F. O. H.

**Therapeutics of [gastric] hyperacidity.** G. WALLBACH (Arch. Farm. speriment., 1935, 60, 587—594).

F. O. H.

**Composition of the gastric mucosa.** M. BEREND and E. FARKAS (Magyar orvosi Arch., 1935, 36, 72—74; Chem. Zentr., 1935, ii, 65).—Neither esters of HCl nor enzymes which can hydrolyse them occur in the gastric juice. Commercial pepsin preps. contain bound sugar, whilst cryst. pepsin is sugar-free. A powerful reducing substance can be extracted by EtOH from the gastric mucosa of the horse, after previous extraction with  $\text{COMe}_2$  and  $\text{Et}_2\text{O}$ ; its purification and properties are described.  
R. N. C.

**Osmotic pressure of the contents of the stomach compartments of the sheep.** D. G. DAVEY (J. Agric. Sci., 1936, 26, 328—330).—Vals. for the abomasum were almost identical with those for blood.  
A. G. P.

**Oxygen and nitrogen content of the urine.** A. SIMON (Pflüger's Archiv, 1935, 236, 705—709).—Urinary  $\text{O}_2$  and  $\text{N}_2$  are dependent on the concn. and  $\alpha$  the  $d$  of the urine. The  $\text{O}_2$  tension is independent of the concn. and is of the order of those of arterial and pre-capillary blood.  $\text{O}_2$  and  $\text{N}_2$  are increased in urine excreted at high atm. pressure; the  $\text{O}_2$  tension is then  $>$  that of 100% saturated hæmoglobin, but  $<$  the alveolar  $\text{O}_2$  tension.  
R. N. C.

**Paths of excretion and mineral balance in animals drinking saline and alkaline waters.** V. G. HELLER and M. HADDAD (J. Biol. Chem., 1936, 113, 439—447; cf. A., 1934, 1020).—90% of injected Cl<sup>-</sup> was excreted in the urine of rats; increasing the S and P intake increased the retention and urinary excretion.  $\text{CaCl}_2$  is better absorbed than other Ca salts; 3% of ingested  $\text{CaCl}_2$  is eliminated in the urine as compared with 10% of  $\text{MgCl}_2$ .  
H. D.

**Urinary excretion of silica in non-silicotic humans.** L. J. GOLDWATER (J. Ind. Hyg., 1936, 18, 163—166).—In non-silicotic humans, even on a const. diet, the urinary  $[\text{SiO}_2]$  shows very wide fluctuations, correlated with the urinary  $d$ . Caution is therefore required in the interpretation of urinary  $\text{SiO}_2$  findings.  
W. O. K.

**Knoop's histidine reaction in urine.** P. E. SIMOLA and V. MÄNTYLÄ (Suomen Kem., 1936, B, 9, 4—5).—The test is modified by adjusting the acidity of the urine to  $p_{\text{H}}$  4.5—5.5, by heating the reaction mixture for a short time only, and by adding amyl alcohol which extracts the coloured product. A positive reaction was obtained with 62% of the pregnancy urines examined. The reaction is not due to histidine.  
A. G. P.



**Simplified detection of defence enzymes in urine.** E. ABDERHALDEN (*Fermentforsch.*, 1936, **15**, 93—120; cf. A., 1935, 1268).—Further simplification is attained by heating the sample (0.5 c.c.) at 100° in an oven instead of boiling. 7.5—25 c.c. (usually 10 c.c.) of urine are required. W. McC.

**Chemical detection of pregnancy.** W. HECKSTEDEN (*Deut. Z. ges. gerichtl. Med.*, 1935, **24**, 253—257; *Chem. Zentr.*, 1935, ii, 889).—The Kapeller-Adler detection of histidine in urine is untrustworthy. J. S. A.

**Liver injury by chloroform, nitrogen metabolism, and conservation. Liver function and hæmoglobin production in anæmia.** F. S. DAFT, F. S. ROBSCHT-ROBBINS, and G. H. WHIPPLE (*J. Biol. Chem.*, 1936, **113**, 391—404).—The fasting anæmic dog when given Fe by vein forms new hæmoglobin, whether the liver is normal or injured by  $\text{CHCl}_3$  anæsthesia, except in the final stages of liver injury. The liver still forms urea, and there is an increase in the amount of uric acid, urinary N, and creatine. The creatine is probably derived from muscle-tissue injured by toxic products from dead and autolysing liver cells. J. N. A.

**Blood-sugar content and blood pressure during anaphylactic shock in non-anæsthetised and non-fastened dogs.** M. OHGURI (*Tôhoku J. Exp. Med.*, 1935, **25**, 437—444).—A transitory decrease in blood-sugar was followed by hyperglycæmia with a return to normal in 1.0—1.5 hr. CH. ABS. (p)

**Adrenaline discharge, blood-sugar, and blood pressure during anaphylactic shock in non-anæsthetised and non-fastened dogs.** H. SATO, M. OHGURI, and M. WADA (*Tôhoku J. Exp. Med.*, 1935, **25**, 504—519).—Adrenaline output increased during shock and preceded hyperglycæmia by 2—10 min. CH. ABS. (p)

**Gas protection. I. Treatment of phosphorus burns.** O. MUNTSCHE (*Gasschutz u. Luftschutz*, 1935, **5**, 103—104; *Chem. Zentr.*, 1935, ii, 880).—Repeated immersion in 5% aq.  $\text{NaHCO}_3$  is recommended. H. N. R.

**Chemistry and cancer. Chemical carcinogenic agents.** R. LEROUX (*Chim. et Ind.*, 1936, **35**, 520—524).—A lecture.

**Effect of hormones on the development of tumours.** W. JEZERSKI (*Endokrinol.*, 1935, **15**, 250—253; *Chem. Zentr.*, 1935, ii, 65). R. N. C.

**Carcinogenic activity and substantivity.** W. BRADLEY (*Nature*, 1936, **137**, 404—405).—An analogy between the dyeing properties and the carcinogenic activity of certain anthracene derivatives is discussed. L. S. T.

**Rôle of ultra-violet rays in the development of cancer provoked by the sun.** A. H. ROFFO (*Lancet*, 1936, **230**, 472—474).—The sun's rays can produce malignant tumours in man and in rats without the intervention of other agents. Irradiation produces a local excess of cholesterol before histological changes are observed. L. S. T.

**Differentiation between the principle of the urine of cancer active on the adrenal cortex,**

**and the principle active on the ovary.** M. ARON (*Compt. rend. Soc. Biol.*, 1936, **121**, 973—975).—Theoretical. R. N. C.

**Absence of bile salts from blood-serum in cancer.** D. ABRAGAM (*Compt. rend. Soc. Biol.*, 1936, **121**, 950—951).—The vanillin- $\text{H}_3\text{PO}_4$  reaction is negative. R. N. C.

**Blood colouring matter of cancerous subjects.** E. SEHRT (*Münch. med. Woch.*, 1935, **82**, 624—625; *Chem. Zentr.*, 1935, ii, 866—867).—A confirmatory blood-test for cancer is described. H. N. R.

**Total sulphur and iodine in normal and malignant tissues.** H. TOYODA, S. KISHI, and W. NAKAHARA (*Gann*, 1935, **29**, 29—39).—The total S content of Fujinawa rat sarcoma, Bashford mouse carcinoma, or Rous chicken sarcoma was  $\approx$  that of normal kidney or spleen but  $>$  that of skeletal muscle, blood, heart, or liver. Tumour tissue contains more I than does normal liver or muscle. In sarcoma-bearing rats the total S of various tissues was  $>$  normal and generally paralleled by increased I contents. The I content of the thyroid was  $<$  normal. CH. ABS. (p)

**Metabolism of malignant tumour. I. Influence of amino-acids on the tissue respiration of tumour.** S. MIYAO (*Gann*, 1935, **29**, 10—28).—Effects of a no. of  $\text{NH}_2$ -acids on tumour tissue are compared with those on normal spleen and liver tissues. CH. ABS. (p)

**Production of carcinoma of the liver by feeding o-aminoazotoluene.** T. SASAKI and T. YOSHIDA (*Virchows Arch.*, 1935, **295**, 175—200). NUTR. ABS. (m)

**Formation of sarcoma by repeated injections of highly concentrated glucose solutions in rats fed with o-aminoazotoluene.** Y. NISHIYAMA (*Gann*, 1935, **29**, 1—9). CH. ABS. (p)

**Soluble organo-metallic complexes of dehydroascorbic acid. Increase of their effects on cancers by variation of the metal.** F. ARLOING, A. MOREL, and A. JOSSERAND (*Compt. rend.*, 1936, **202**, 598—600; cf. A., 1935, 1526).— $\text{Fe}^{\text{III}}$ -Pb-Na and  $\text{Fe}^{\text{III}}$ -Ba-Na complexes of dehydroascorbic acid can be used for the treatment of gastric cancer, but with buccopharyngeal cancers they are less active than the  $\text{Fe}^{\text{III}}$ -Na complex. Cu-Na, Cu-Pb-Na, and Cu-Ba-Na complexes have actions  $<$  those of the  $\text{Fe}^{\text{III}}$  complexes. The effect of a complex decreases after a time, but is renewed by using another complex containing the same fundamental metal. J. N. A.

**Aqueous extracts of enamel and dentine in relation to dental caries.** M. KARSHAN, R. WEINER, and N. STOFKY (*J. Dental Res.*, 1934, **14**, 445—454).—Aq. extracts contained Ca, Mg, P, and a substance reacting with lactic acid to give  $\text{CO}_2$ . First extractions contained Na and Cl. After 5 extractions only apatite dissolved. Extracts of enamel reacted positively to Folin's PhOH reagent and gave a negative biuret test. Dentine contains a sol. protein which was relatively smaller in amount in carious teeth. CH. ABS. (p)

**Effect of vitamin-C on the causative agent of diphtheria.** P. POLONYI (*Wien. med. Woch.*, 1935,



85, 685—686).—Vitamin-*C* has a favourable action in diphtheria, and reduces the virulence of the bacilli.

R. N. C.

Di-iodotyrosine and Lugol's solution in the treatment of hyperthyroidism. H. GOTTA (*Z. klin. Med.*, 1935, 128, 1—11; *Chem. Zentr.*, 1935, ii, 72—73).—The therapeutic effects are the same.

R. N. C.

Jaundice due to phenobarbital. C. A. BIRCH (*Lancet*, 1936, 230, 478—479).

L. S. T.

Reduced glutathione in leprosy. R. O. PRUDHOMME (*Compt. rend. Soc. Biol.*, 1936, 121, 1167—1169).—Reduced glutathione of the liver and spleen is normal if the organs themselves are not affected. The val. is reduced when there is considerable penetration of leprosy tissue.

H. G. R.

Six-day treatment with atebriane, atebriane+plasmoquine-simplex, plasmoquine-compositum, quinoplasmine, and quinine. A. KIRILOV-DRENOVSKI (*Arch. Schiffs- u. Tropen-Hyg.*, 1935, 39, 243—252; *Chem. Zentr.*, 1935, ii, 1058).—The atebriane-plasmoquine is most effective.

H. N. R.

Rôle of the liver in the mechanism of uranium glycosuria. R. WEEKERS (*Compt. rend. Soc. Biol.*, 1936, 121, 868—870).—Liver-glycogen is reduced in acute and sub-acute U nephritis in the rat. Glycogen storage of the liver is reduced only in sub-acute nephritis with intermittent glycosuria, which is hence not due to liver disorder.

R. N. C.

Composition of plasma and red blood-cells in nephropathy. A. FIESCHI and P. LARIZZA (*Minerva Med.*, 1935, 1, 629—630).—In renal sclerosis the Na, K, inorg. S, and P of red cells increases and protein-S decreases. Similar conditions occur in acute nephritis and there is an accompanying hypochloræmia.

CH. ABS. (*p*)

Calcium and phosphorus metabolism in osteomalacia. IV. Acute parathyroid hormone poisoning. H. I. CHU, S. K. CHOU, K. C. CHEN, S. H. WANG, S. H. LIU, and R. R. HANNON (*Chinese Med. J.*, 1936, 50, 1—16).—In a male showing marked skeletal deformities indicative of osteomalacia, serum-Ca and -inorg. P were normal and relatively insensitive to treatment with vitamin-D and ultra-violet irradiation. 80 units daily of parathyroid hormone for four days resulted in marked hypercalcaemia, vomiting, collapse, and death.

F. A. A.

Tyrosine index of polypeptidæmia in malaria therapy [of paralysis]. P. TOMESCO, N. G. IONESCO, and P. CONSTANTINESCO (*Compt. rend. Soc. Biol.*, 1936, 121, 1209—1211).—The val. decreases at first and then rises, generally to > the original.

H. G. R.

Pregnancy tests. S. ASCHHEIM (*J. Amer. Med. Assoc.*, 1935, 104, 1324—1329).—The mouse test and Friedman's method are described.

CH. ABS. (*p*)

Inorganic composition of blood serum in schizoprenics. E. T. MINKER-BOGDANOVA, S. A. POVORINSKAJA, and J. A. POVORINSKI (*Arch. Sci. biol. U.S.S.R.*, 1934, 36, B, 339—343).—Variations in serum-Na, -K, -Ca, -Mg, -inorg. P, and -Cl in schizoprenics were > in normal individuals. In general

vals. for Ca were > and for Na and Cl < normal. The K/Ca and Na/Ca ratios were markedly < normal.

CH. ABS. (*p*)

Impregnation of the organism by dust. IV. Laboratory animals. R. FABRE and E. KAHANE (*J. Pharm. Chim.*, 1936, [viii], 23, 217—232).—Examination of various organs of rabbits, guinea-pigs, and rats exposed to dust-laden (coal, sandstone) air indicates that the particles (even when 0.1—0.2 mm. diameter) are transported (at least partly by the blood) to various tissues, where they remain chemically unchanged.

F. O. H.

Mechanism of the protective action of bismuth in experimental syphilis. C. LEVADITI, G. HORNUS, A. VAISMAN, and Y. MANIN (*Bull. Acad. Méd.*, 1934, 112, 306—317; *Chem. Zentr.*, 1935, ii, 1059; cf. A., 1935, 1159).—Bivotol is more effective than trépol against experimental syphilis in rabbits.

H. N. R.

Nitrogen and mineral metabolism in *T. congolense* disease. M. H. FRENCH (*Ann. Rep. Dept. Vet. Sci. Tanganyika*, 1934, (1935), 59—64).—Infected oxen and sheep show an increased rate of excretion of N, Ca, K, and P. Mg balances appear not to be disturbed. The effect on Na and Cl metabolism appears to depend on the level of intake.

NUTR. ABS. (*m*)

Variations in the catalase content of human blood. D. DERIBAS and J. KORNMAN (Bull. Soc. Chim. biol., 1936, 18, 418—423).—The blood-catalase in tuberculosis varies with the nature of the therapeutic treatment, the temp., and the mental state of the individuals.

A. L.

Effect of prolonged muscular exercise on metabolism. F. C. COURTICE and C. G. DOUGLAS (*Proc. Roy. Soc.*, 1936, B, 119, 381—439).—Confirmatory evidence is obtained that a high-carbohydrate diet taken on the day preceding the exercise may have an effect on some aspects of metabolism > that of an ingestion of easily assimilable carbohydrate shortly before exercise. During rest after exercise, very little conversion of fat into carbohydrate occurs. The principal factor causing low R.Q. and ketosis is the low ratio of carbohydrate to fat oxidised. Blood-sugar level remains normal but evidence of a reduced sugar-tolerance is obtained.

A. G. P.

Metabolism of nerve-tissue of the frog during (A) rest and (B) stimulation. J. ROSENBERG (*Arch. internat. Physiol.*, 1935, 41, 434—445, 446—455).—(A) In resting isolated tissues in Ringer's solution the cerebrospinal (white) tracts consume more O<sub>2</sub> and lose more nitrogenous (I) and fatty substances (II) than do the sciatic nerves. The loss of (II) is > and about = that of (I) in the cerebrospinal tracts and sciatic nerves, respectively. Hibernation causes an increase in N and fat metabolism and a decrease in O<sub>2</sub> consumption. Possibly the disappearance of (I) and (II) from nerve-tissue occurs without the intervention of free O<sub>2</sub>.

(B) Electrical stimulation causes an increase, which  $\propto$  the strength and frequency of the current, in the metabolism of nerve-tissue.

NUTR. ABS. (*m*)

Changes in living substance involved in the reversible transition into the dead state. D.



NASONOV and V. ALEXANDROV (Arch. Sci. biol. U.S.S.R., 1934, **36**, A, 95—112).—The authors' work on adsorption phenomena at cell surfaces as influenced by chemical agents is reviewed. CH. ABS. (p)

**Adsorption and bioelectric potential in frog skin.** K. MOTOKAWA (Japan. J. Med. Sci., III, 1935, **3**, 177—201).—The e.m.f. across frog skin is measured by bathing one side in Ringer's and the other in test solutions. With low [NaCl] non-electrolytes in the test solution lowered the e.m.f. in the order glucose > sucrose > urea. The order is reversed when the [NaCl] is higher. The NaCl in the adsorption layer of the skin causes the e.m.f. and is displaced by added non-electrolytes. CH. ABS. (p)

**Influence of valency and concentration of ions on the potential difference of frog skin.** K. MOTOKAWA (Japan. J. Med. Sci., III, 1935, **3**, 203—209).—Frog skin has an inner asymmetry which is increased by anions and decreased by cations (cf. preceding abstract). CH. ABS. (p)

**Membranes as models of physiological objects. (Permeability and salt absorption.)** R. HOBER (Naturwiss., 1936, **24**, 196—202).—A lecture.

**Nutrition question.** R. HUTCHISON (Lancet, 1936, **230**, 583—585).—A discussion. L. S. T.

**Problems of animal nutrition and animal husbandry in Northern Nigeria.** A. W. ANDERSON and O. T. FAULKNER (Imp. Bur. Animal Nutrition Tech. Comm., 1933, No. 4, 52 pp.).—Nigerian pasture contains less N, Ca, P, and K than does European pasture. Supplements of steamed bone flour and NaCl had no beneficial action. Pica (controlled by  $\text{Na}_2\text{CO}_3$ ) was not associated with shortage of Ca or P in the diet. CH. ABS. (p)

**Diet and colour of birds.** H. L. RATCLIFFE (Nature, 1936, **137**, 402).—Inclusion in the diet of a greater variety of proteins, more fat-sol. vitamins, and more mineral salts, especially of Ca and P, restores much of the natural colouring lost in captivity. L. S. T.

**Effect of alkali and vegetable feeding on blood-uric acid and urate excretion.** W. MORACZEWSKI, S. GRZYCKI, T. SADOWSKI, and W. GUCWA (Klin. Woch., 1935, **14**, 557—562).—Feeding with purine-rich substances together with apples lowers blood- and urinary urates, whereas potatoes or alkali instead of apples increase them.  $\text{H}_2\text{O}$  lowers blood-urate by accelerating its renal excretion. R. N. C.

**Increase in weight due to [feeding of] wheat, oats, and barley to rats on a vitamin-A-free diet.** M. MALMBERG and H. VON EULER (Biochem. Z., 1936, **284**, 238—243).—The three cereals have a growth-promoting action possibly due to xanthophyll and other carotenoids present. F. O. H.

(A) Influence of acid- or base-forming diet on metabolism of rabbits at work and rest. J. M. HEFTER and E. L. GLINKA-TSCHERNORUTZKAJA. (B) Influence of myolysate on metabolism of rabbits kept on an acid- or base-forming diet. (C) Action of myolysate on blood-sugar content on an acid- or base-forming diet, at rest or at work. E. L. GLINKA-TSCHERNORUTZKAJA (J. Physiol.

U.S.S.R., 1935, **18**, 78—83, 84—88, 89—92).—(A) The alkali reserve decreased on acid-forming and increased on base-forming diets. Work had no effect on metabolism with either diet.

(B) Injection of myolysate (I) increased the total N excretion, urinary  $\text{NH}_3$ , and the total and reduced glutathione, and decreased the alkali reserve. Effects were more marked with a base-forming than with an acid-forming diet.

(C) Injection of 0.1 c.c. of standard (I) caused an increase in blood-sugar which was greater with a base-forming than with an acid-forming diet and greater at rest than at work. 0.01 c.c. of (I) produces the opposite effect. CH. ABS. (p)

**Comparative influence of hay and grass, ensiled without mineral acid, on the acid-base equilibrium of cattle.** E. BROUWER and N. D. DIJKSTRA (Bied. Zentr. [Tierernähr.], 1935, **7**, B, 361—371).—The  $p_{\text{H}}$  of urine and the total  $\text{CO}_2$  were somewhat lower when silage was fed, but the corresponding vals. for blood-plasma were the same as when hay was used. Org. acids in silage were utilised and showed no tendency to accumulate at any stage of metabolism. A. G. P.

**Effect of progressive ripening of fodders on the mineral nutrition of cattle.** I. Mineral composition and mineral balance. A. V. IYER. II. Urine characteristics. N. K. AYYAR. III. Blood characteristics. N. C. DAS GUPTA (Indian J. Vet. Sci., 1935, **5**, 129—139, 140—147, 148—157).—I. The mineral composition of various types of hay was determined. In bullocks the stage of maturity had a marked effect on mineral assimilation. The digestibility of the protein apparently bore no relationship to the  $\text{P}_2\text{O}_5$  content of the fodder.

II. Feeding early cut fodders resulted in the elimination of large vols. of urine because of the high alkali content. With more mature fodder, the vol. of the urine and the total fixed bases fell and the  $p_{\text{H}}$  tended to decrease. As the urine became more acid there was an increased deflexion of CaO and MgO to this path of excretion.

III. The serum-Ca level was unrelated to the Ca content or the Ca : P ratio of the fodder. It was most influenced by the stage of maturity. The serum-P level was affected by the nature of the fodder and the dietary P level. NUTR. ABS. (m)

**Effect of yeast on malnutrition of rats caused by a high sucrose diet.** H. ARIYAMA (J. Agric. Chem. Soc. Japan, 1936, **12**, 1—10).—The factor in yeast which enables rats to thrive on high-sucrose diets containing all the known vitamins is extracted by dil. aq. EtOH, adsorbed on acid clay, and is completely destroyed by autoclaving at  $p_{\text{H}}$  8; EtOH extracts of ox liver or green vegetables have a smaller potency than the yeast extracts. H. D.

**Effects of uncomplicated phosphorus deficiency on oestrus cycle, reproduction, and composition of tissues of mature dairy cows.** C. H. ECKLES, L. S. PALMER, T. W. GULLICKSON, C. P. FITCH, W. L. BOYD, L. BISHOP, and J. W. NELSON (Cornell Vegetarian, 1935, **25**, 22—43).—Over a period of 2—3 years. P deficiency did not cause abnormal



cestrus, but breeding efficiency declined somewhat. In muscle-tissue Ca increased, and P and Mg decreased. Ill effects observed in cattle in P-deficient areas cannot be attributed to P deficiency alone (cf. B., 1934, 859).

CH. ABS. (p)

**Carbohydrate feeding.** E. BAUER (Z. Kinderheilk., 1935, 57, 116—123; Chem. Zentr., 1935, ii, 1054).—The result of a sugar-charging test depends on the carbohydrate (I) uptake as well as the time. The depression of the blood-sugar curve increases to a limiting val. of (I) uptake; an increase of insulin secretion to the max. capacity of the pancreas is responsible.

R. N. C.

**Relation of rate of absorption of glucose to body-weight and surface, intestinal weight, and content of intestinal phosphatase in rats. Influence of diet on the phosphatase content of the intestine.** H. G. K. WESTENBRINK (Arch. Néerl. Physiol., 1936, 21, 18—37).—The rate of absorption of glucose is independent of the wt. and surface of the body and the phosphatase (I) content of the small intestine; its relation to the wt. of the small intestine (which is independent of the body-wt.) is indefinite. Starting from the stomach, after a slight increase the (I) content of the small intestine decreases to  $\frac{1}{3}$  of the max. Variations in protein, carbohydrate, and fat in the diet do not alter the (I) content of the small intestine.

E. P.

**Gaseous metabolism of small animals.** G. HÜNERFELD (Arch. exp. Path. Pharm., 1936, 180, 509—517).—The application of the apparatus of Hecht (*ibid.*, 1932, 166, 5) and its testing by combustion of EtOH are described.

F. O. H.

**Anoxia and experimental catatonia.** J. JONGBLOED (Arch. Néerl. Physiol., 1936, 21, 144—161).—Diminution of the atm. pressure, dilution of the atm. with indifferent gases, inhibition of the  $O_2$  transport in the blood by respiration of CO or injection of methylene-blue or  $Na_2S_2O_3$ , and poisoning of the respiratory enzymes by injection of KCN or  $HgCl_2$  produce catatonia, possibly due to anoxia of the central nervous system. The restriction of the  $O_2$  supply of the brain following obstruction of the capillaries by injection of lycopodium produces similar phenomena.

E. P.

**Metabolism of isolated fat-tissue. III. Respiratory quotient and the influence of nutrients *in vitro* and *in vivo*.** W. HENLE and G. SZPINGER (Arch. exp. Path. Pharm., 1936, 180, 672—689).—Isolated surviving fat from rat's testis has  $Q_{O_2}$  0.06—0.07 [measured by a modified Dickens and Simer technique (A., 1932, 644)] and R.Q. approx. 0.75, the latter being increased by addition of 0.2%, and decreased by that of 0.01%, of glucose; the increase due to  $AcCO_2H$  is  $>$  that due to glucose. The fat of carbohydrate-fed rats has a high initial R.Q. of approx. 1.25 which rapidly sinks to vals. found in starving animals. The bearing of the data on sugar-fat metabolism is discussed.

F. O. H.

**Metabolism of normal and tumour tissue.**

**XIV. Metabolism of medulla of kidney.** F. DICKENS and H. WEIL-MALHERBE. **XV. Respiratory quotient of brain cortex.** F. DICKENS (Biochem. J., 1936, 30, 659—660, 661—664).—XIV. The

general vals. for aerobic and anaerobic glycolysis of medulla of kidney of György (A., 1928, 1396) are confirmed, showing the tissue to be very strongly glycolysing. That aerobic glycolysis disappears in serum was not confirmed, the vals. in serum and Ringer's solution being the same. The R.Q. was approx. 1 and kidney, like retina, has an anaerobic type of metabolism due probably to disparity between blood ( $O_2$ ) supply and energy requirements of the tissue *in vivo*.

**XV. The R.Q. vals. of rat-brain cortex** were those expected on statistical grounds for a tissue of R.Q. 1. The lower vals. of Elliot and Baker (A., 1935, 1529) are probably due not to prolonged action of salt solution but to inadequate gas equilibrium resulting from the large amount of tissue used.

P. W. C.

**Co-operation of plant and animal proteins in active and general metabolism.** A. BICKEL (Biochem. Z., 1936, 284, 297—307).—Determinations of C : N and "vacate"  $O_2$  : N ratios in the urine of rats fed on various proteins indicate that, in addition to each protein having a more or less characteristic metabolic action, modifications occur on admixture. A balance of animal and plant proteins in diets is therefore of importance.

F. O. H.

**Growth and development. XXXVII. Interrelations between protein intake, endogenous nitrogen excretion, and biological value of protein.** U. S. ASHWORTH (Missouri Agric. Exp. Sta. Res. Bull., 1935, No. 228, 14 pp.).—Endogenous N excretion was not appreciably affected by the nature of the protein fed, unless the reserve body-protein was considerably depleted by a prolonged preliminary period on a N-free diet.

A. G. P.

**Parenteral administration of nitrogenous substances in artificial feeding.** K. TSUDA (Tōhoku J. Exp. Med., 1934, 24, 380—404).—Parenteral administration of mixed  $NH_2$ -acids or protein degradation products partly prevents autogenous protein catabolism in fasting dogs. Intraperitoneal injection of milk has the same effect. A positive N balance may be set up by such injections.

CH. ABS. (p)

**Constituents of mulberry leaves. IX.** K. KISHI (J. Agric. Chem. Soc. Japan, 1935, 11, 232—241).—The principal protein of the leaves is sol. in alkaline EtOH. The ratio of sol. to total protein increases with maturation. The quantities of silk-protein and of body-protein are influenced by the quality and quantity of protein and sol. carbohydrates in leaves (cf. A., 1935, 1146).

CH. ABS. (p)

**Physiology of sulphur in exogenous protein metabolism.** R. RAZAFIMAHERY (Ann. Physiol. Physicochim. biol., 1935, 11, 327—353).—In the pig sudden changes from a strict carbohydrate diet to a diet rich in protein or in the reverse direction are accompanied first by the anabolism or catabolism of reserve protein having S content  $<$  that of tissue-protein. During growth the N : S ratio of the material retained on a mixed diet is  $\approx 20$ . The coeff. of utilisation of protein, calc. on the basis of S, is  $<$  that of N. The corresponding changes in neutral and ethereal S are discussed.

NUTR. ABS. (m)

**Cystine deficiency of lucerne proteins. Effect of heat and incubation on their growth-pro-**



moting value. J. H. KELLERMANN (Onderstepoort J. Vet. Sci., 1935, 4, 437—452).—The deficiency from which young rats suffer when fed on a ration with lucerne meal as the sole source of protein is made good by the addition of 0.1% of *l*-cystine. A combination of yellow maize and lucerne or of maize and teff gave a protein adequate for growth. Incubation of lucerne meal with the "ruminal juice" of a sheep at 37° for 2 days or heating with H<sub>2</sub>O at 120° for 1 hr. did not improve the growth-promoting val. of lucerne meal proteins. NUTR. ABS. (m)

**Mechanism of the synthesis of thymonucleic acid during the development of the sea-urchin's egg.** J. BRACHET (Bull. Soc. Chim. biol., 1936, 18, 305—317).—The unfertilised eggs contain a pentose-nucleic acid similar to zymonucleic acid. This supports the view that there is a partial synthesis of thymonucleic acid, which appears as the eggs develop. A. L.

**Effect of food phosphatides on the chemical composition of the body.** A. K. PICKAT, O. I. KURTZINA, and N. S. SJENIN (Problems of Nutrition, Moscow, 1935, 4, 68—77).—In white rats receiving a mixed or a fat-free diet additions of 50 mg. of lecithin (I) per 100 g. of body-wt. to either diet led to a storage of lipin chiefly as neutral fat in the whole body and in the individual organs, and to increased glycogen in liver and muscle. The (I) and cholesterol were  $\times$  those of control animals. NUTR. ABS. (m)

**Fat metabolism.** P. E. VERKADE and J. VAN DER LEE (Chem. Weekblad, 1936, 33, 163—172).—A review. S. C.

**Fat metabolism in fishes. IX. Fats of some aquatic plants.** J. A. LOVERN (Biochem. J., 1936, 30, 387—390).—The compositions of the mixed fatty acids of several fresh-H<sub>2</sub>O and marine algæ, a pondweed, and a marine diatom are tabulated. The plant fats do not show the difference previously noted (A., 1935, 653) for fats of fish, plankton crustacea, etc. (viz., that the fat of fresh-H<sub>2</sub>O species contains more C<sub>16</sub>—C<sub>18</sub> and less C<sub>20</sub>—C<sub>22</sub> acids). Algal fats fall into groups agreeing with their botanical relationships and no difference between salt- and fresh-H<sub>2</sub>O forms was detected. The diatom and the pondweed had fats similar to those of green algæ. Whilst fresh-H<sub>2</sub>O plankton crustacea deposit ingested fat unchanged in type, the corresponding marine species appear to modify it considerably. P. W. C.

**Absorption of fat through the large intestine.** R. KITAGAWA (Tôhoku J. Exp. Med., 1934, 24, 329—349).—Finely dispersed fat is absorbed through the large, and the lower part of the small, intestine of dogs without preliminary lipolysis. CH. ABS. (p)

**Deuterium as an indicator in the study of intermediary metabolism. V. Desaturation of fatty acids in the organism.** R. SCHOENHEIMER and D. RITTENBERG (J. Biol. Chem., 1936, 113, 505—510).—Unsaturated D-containing fatty acids are found in the body-fatty acids of mice fed with a D-containing saturated acid; thus desaturation takes place in the organism. F. A. A.

**Rendering liver completely free from glycogen.** Y. OTOMO and S. NAGAO (Tôhoku J. Exp.

Med., 1935, 25, 63—79).—Intravenous injection of an emulsion of cod-liver oil and lecithin causes complete disappearance of hepatic glycogen. CH. ABS. (p)

**Conversion of glycogen into lactic acid by muscle extracts of normal and diabetic dogs.** T. CAHN and J. HOUGET (Compt. rend., 1936, 202, 354—356).—Muscle extracts of normal dogs when incubated with glycogen (I) at 37° and  $p_H$  8.14 show rapid glycogenesis at first; the rate then decreases rapidly. 60—65% of the (I) which disappears is converted into lactic acid; MeCHO, AcCHO, and AcCO<sub>2</sub>H are present only in traces. Extracts of the muscles of pancreatectomised dogs behave similarly, but have a feebler glycogenic power. J. L. D.

**Rôle of glucose in muscle biochemistry.** M. CAMIS (Arch. ital. Biol., 1934, 91, 35—59; Chem. Zentr., 1935, ii, 550).—CH<sub>2</sub>I·CO<sub>2</sub>H (I) inhibits lactic acid (II) formation from glycogen (III) in the isolated perfused rabbit's heart, but not from glucose (IV) in the perfusion liquid. The cat's heart untreated with (I) can form (II) from (III), but not from (IV). R. N. C.

**Initial transformations of glycogenolysis: function of hexosemonophosphoric ester.** P. OSTERN, J. A. GUTHKE, and J. TERSZAKOWEC (Compt. rend. Soc. Biol., 1936, 121, 1133—1136).—Previous conclusions (this vol., 370) are confirmed. H. G. R.

**Glycolysis in the retina.** G. POSSENTI (Riv. Patol. sper., 1935, 15, 183—194).—The lactic acid (I) production from glucose (II) by the retina is much > that from hexosediphosphoric acid (III). From  $\alpha$ -glycerophosphoric (IV) and phosphoglyceric acid (V), although they are actively attacked, the (I) production is very small and is not increased by mixing (IV) and (V) or by addition of AcCO<sub>2</sub>H to (IV). (III), (IV), and (V) show an induction period for (I) production, due probably to dephosphorylation. There is no liberation of H<sub>3</sub>PO<sub>4</sub> from the retina during (II) fermentation. NUTR. ABS. (m)

**Fructose metabolism in the intact animal.** J. N. DAVIDSON, W. O. KERMACK, D. M. MOWAT, and C. P. STEWART (Biochem. J., 1936, 30, 433—441).—After ingestion or injection of fructose (I) in rabbits, there is a disappearance of (I) and an increase in the secretion of insulin (II). (II) has no effect on the rate of removal of (I) from blood, and it is concluded that (I) is converted into glucose, which is then metabolised under the influence of (II). Two methods for the determination of (I) in blood are described. J. N. A.

**Metabolism of *d*-xylose.** N. R. BLATHERWICK, P. J. BRADSHAW, O. S. CULLIMORE, M. E. EWING, H. W. LARSON, and S. D. SAWYER (J. Biol. Chem., 1936, 113, 405—410; cf. Miller and Lewis, A., 1932, 1282).—Feeding of xylose to white rats increased the content of non-fermentable reducing substances in the liver, muscles, blood, and kidneys. There were no changes in the glycogen or lactic acid content of liver and muscles, nor in blood-lactic acid. Blood-glucose was increased. The availability of xylose to the animal is probably low. J. N. A.

**Destruction of 1:2:5:6-dibenzanthracene in the mouse.** I. BERENBLUM and L. P. KENDAL



(Biochem. J., 1936, 30, 429—432; cf. A., 1934, 1127).—A method for determination of 1:2:5:6-dibenzanthracene (I) in the mouse is described. 2 mg. of (I) given intraperitoneally in lard or in colloidal solution had nearly all disappeared after 3 weeks. (I) was not found in the excreta. Hence the mouse can metabolise (I). J. N. A.

Effect of inspiration of oxygen and of air rich in carbon dioxide or poor in oxygen on the energy level and intermediate carbohydrate metabolism. V. Changes in lactic acid resynthesis in nephrectomised animals. K. KODERA (Tōhoku J. Exp. Med., 1934, 24, 21—36; cf. A., 1935, 520).—Blood-lactic acid (I) in rabbits increases after nephrectomy without change in blood- $\text{CO}_2$  (II) but with slight decrease in  $\text{O}_2$  consumption. These effects are unchanged by inhalation of  $\text{O}_2$ : air containing 5—10% of  $\text{CO}_2$  intensifies the change in (II), whereas air containing < 10% of  $\text{O}_2$  increases and accelerates the change in (I). The return of (I), (II), and  $\text{O}_2$  consumption to normal is delayed by nephrectomy whatever the composition of the air inhaled.

CH. ABS. (p)

Metabolism of pyruvic acid in the retina. G. POSSENTI (Riv. Patol. sper., 1935, 15, 229—234).—Anaerobically the retina produces little or no  $\text{CO}_2$  from  $\text{AcCO}_2\text{H}$ , but aerobically the  $\text{O}_2$  consumption is markedly increased, the R.Q., normally 0.8—0.9, being > 1.

NUTR. ABS. (m)

Metal catalysts in biological oxidations. I. The simple system: thioglycollic acid, buffer, metal, dithioglycollic acid. II. Tissue inhibitors. M. S. KHARASCH, R. R. LEGAULT, A. B. WILDER, and R. W. GERARD (J. Biol. Chem., 1936, 113, 537—555, 557—569).—I. The results of varying the  $\text{O}_2$  tension, temp., and  $p_{\text{H}}$  on the rate of oxidation of  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  by  $\text{O}_2$  and of the catalytic influence of  $\text{Mn}^{++}$ ,  $\text{Cu}^{++}$ , and  $\text{Fe}^{++}$  on this reaction, are given. Catalysis by the metal ions depends on  $p_{\text{H}}$  and on the nature of the buffer ions present. In  $\text{CO}_3^{--}$  buffers the activity of  $\text{Fe}^{++}$  with  $\text{Cu}^{++}$  or  $\text{Mn}^{++}$  is additive, but  $\text{Cu}^{++}$  and  $\text{Mn}^{++}$  together show greatly increased activity. Phosphate ions inhibit catalysis by  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$  but accelerate that by  $\text{Cu}^{++}$ ; org. phosphates do not affect catalysis by  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ . Catalysis by  $\text{Cu}^{++}$  in phosphate buffers is decreased by  $\text{Mn}^{++}$  and increased by  $\text{Fe}^{++}$ . The reaction product, dithioglycollic acid, accelerates the reaction in all buffers and by all three metals.

II. A no. of substances, tested for their action on the catalytic activity of metals on the oxidation of  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , show inhibitory action approx.  $\propto$  the stability of complexes formed with the metals. No influence attributable to the colloidal state appears. Beef and chicken muscle extracts inhibit catalysis by  $\text{Fe}^{++}$  but slightly accelerate that by  $\text{Cu}^{++}$  and  $\text{Mn}^{++}$ . Sarcoma extracts behave similarly, but less powerfully. Chicken liver extracts are inactive to  $\text{Fe}^{++}$ , accelerate  $\text{Mn}^{++}$ , and inhibit  $\text{Cu}^{++}$ . This latter inhibition is approx. parallel to the efficacy of the extracts in pernicious anaemia. F. A. A.

Brain metabolism. I. Glutamic acid. H. WEIL-MALHERBE (Biochem. J., 1936, 30, 665—676).—l(+)-Glutamic acid (I) is the only  $\text{NH}_2$ -acid oxidised

by brain and yields  $\alpha$ -ketoglutaric acid (II) (2:4-dinitrophenylhydrazones, m.p. 224°) and  $\text{NH}_3$  and later gives  $\text{H}_2\text{O} + \text{CO}_2$ . d(-)-Glutamic acid (III) is not attacked so long as it is bound in the cell or to some constituent of the cell, but in solution only (III) is oxidised. The  $\text{NH}_3$  derived from (I) disappears in secondary reactions leading to and beyond glutamine (IV). The reaction  $(\text{I}) \rightleftharpoons (\text{II})$  is reversible. An increased amount of  $\text{NH}_2\text{-N}$  is found in presence of glucose,  $\text{AcCO}_2\text{H}$ , and (II). It appears that (II) is intermediate in the oxidation of  $\text{AcCO}_2\text{H}$ , and the same reactions which lead to the disappearance of  $\text{NH}_3$  and formation of (IV) in presence of (I) can be arrived at from (II),  $\text{AcCO}_2\text{H}$ , or glucose. *In vivo* the glutamic acid deaminase is probably concerned rather with synthesis than breakdown of (I). P. W. C.

Neo-formation of ethyl alcohol in the human corpse during putrefaction. M. NICLOUX (Compt. rend. Soc. Biol., 1936, 121, 975—978).—EtOH is present in all the tissues 17 days after death.

R. N. C.

Metabolism of organic sulphur in infants. J. SURANYI (Nourrisson, 1934, 22, 377—383).—Human or cow's milk does not contain enough free cysteine (I) to be determined colorimetrically. Very small quantities are detected in colostrum. Neutral S (0.02—0.03 mg. per 100 ml.) occurs in colostrum and increases later. Human milk contains 8—120 mg. per 100 ml. and cow's milk 60—80 mg. of (I) after acid hydrolysis. Faeces of normal infants do not contain significant amounts of (I). Diarrhoeal faeces contain  $\geq$  100 mg. per 100 g., so that the loss is not sufficient to cause a negative (I) balance. (I) is frequently found in urine, in amounts < 25 mg. per 100 ml. in breast-fed and < 10 mg. in artificially fed infants. The excretion is higher in marasmus, acute infections, and toxicosis.

NUTR. ABS. (m)

Sulphur metabolism in inanition. E. F. TERROINE and R. RAZAFIMAHERY (Ann. Physiol. Physicochim. biol., 1935, 11, 354—387).—When complete fasting replaced a period of protein starvation during which excretion of endogenous N had reached a min., a sharp rise in N excretion first occurred, followed by a rapid fall. The rise in S excretion was slight compared with that of N. Later, N and S excretions rose slightly with slow fall in N:S ratio. In the premortal period there was a sudden and marked rise in N and S excretion and further fall in the N:S ratio, due to preferential catabolism of muscle and/or to degradation of S-containing  $\text{NH}_2$ -acids. Changes in neutral and ethereal S are also described. NUTR. ABS. (m)

Iodine metabolism of the adult rat in relation to trauma, thyroid activity, and diet. V. V. COLE and G. M. CURTIS (J. Pharm. Exp. Ther., 1936, 56, 351—358).—The I balance, thyroid- and body-I of rats were uninfluenced by injected thyrotropic hormone or by the myxoedema following thyroidectomy; increasing the I intake from  $3 \times 10^{-6}$  to  $5 \times 10^{-5}$  g. per day left the thyroid-I unchanged but doubled the body-I. H. D.

Chlorine requirements of farm animals, with especial reference to the effect of chlorine on the metabolism of the pig. G. A. MORR (Diss. Aberdeen, 1934—1935).—In pigs an increased intake



of Cl tends to improve N retention, possibly because of better digestion. There was a tendency to better live-wt. increase and a better return per lb. of food consumed when NaCl was added to the diet than when Na citrate and CaCl<sub>2</sub> were added. The effect of these salts on blood constituents was negligible.

NUTR. ABS. (m)

**Assimilation of iron during the development of the chick embryo.** A. SZEJNMAN-ROZENBERG (*Acta Biol. exp.*, 1933—1934, 8, 3244).—Fe assimilation appeared to be retarded during the periods of max. wt. increase around the 12th and 18th days of development. The amount of Fe in the liver was relatively  $\frac{1}{2}$  in the entire embryo. The developing embryo assimilated 96% of the available Fe in the egg.

NUTR. ABS. (m)

**Sodium metabolism. Influence of sodium deficiency on blood-urea and -amino-acid in pigs.** P. SONHOORL (*Arch. Néerl. Physiol.*, 1936, 21, 130—143; cf. A., 1934, 803).—Blood-urea and -NH<sub>2</sub>-acid increase, the rise in NH<sub>2</sub>-acid being due to restricted synthesis of protein.

E. P.

**Sodium requirement of chicks: results of an almost sodium-free diet.** B. SJOLLEMA (*Bied. Zentr. [Tierernähr.]*, 1935, 7, B, 184—197).—Deficiency of Na in the ration (< 0.013%) retards the growth of chicks by restricting the formation of body-fluids. The Na requirement is met by approx. 0.4—0.5% of Na in the diet.

A. G. P.

**Total electrolyte content of animals and its probable relation to the distribution of body-water.** H. E. HARRISON, D. C. DARROW, and H. YANNET (*J. Biol. Chem.*, 1936, 113, 515—529).—Whole bodies, and various organs, of dogs, monkeys, and rabbits were analysed for H<sub>2</sub>O, Na, K, Cl, P, N, and fat. Assuming that the extra-cellular H<sub>2</sub>O contains all the Cl<sup>-</sup>, and that its electrolyte content is similar to that of the serum, the relative vols. of intra- and extra-cellular H<sub>2</sub>O in the body and tissues, and the concn. of solutes in them, are calc. Extra-cellular H<sub>2</sub>O comprises about 27% of the body-wt., intra-cellular H<sub>2</sub>O varying from 29 to 45%, being lower in the fat animals. The proportion varies in different tissues, but analogous tissues of different animals show similar vals. 25% of the Na in the body exists in bone and cartilage in an insol. or non-ionised form.

F. A. A.

**Aluminium. II. Storage of intravenously injected aluminium in the dog.** D. F. EVELETH and V. V. MYERS (*J. Biol. Chem.*, 1936, 113, 467—471; cf. this vol., 652).—Al is stored primarily in the liver, spleen, and kidney, and appears immediately in the bile and urine.

H. D.

**Dependence of the change in irradiated caseinogen on the intensity of irradiation.** W. OLBRICH (*Biochem. Z.*, 1936, 284, 308—311).—Data for urinary C, N, and "vacate"-O<sub>2</sub> of rats fed on caseinogen exposed to two different intensities of  $\gamma$ -irradiation from meso-Th indicate a parallel difference in the action on metabolism.

F. O. H.

**Physico-chemical action of X-rays on the organism.** V. G. D. LIEBER (*Strahlenther.*, 1935,

52, 497—511; *Chem. Zentr.*, 1935, ii, 387).—The influence of X-rays on bone growth is discussed.

H. N. R.

**Biological action of neutron rays.** J. H. LAWRENCE and E. O. LAWRENCE (*Proc. Nat. Acad. Sci.*, 1936, 22, 124—133).—Irradiation of rats by high-speed neutrons, obtained by deuteron bombardment of a Be target, lowers the lymphocyte count and finally produces death. The effectiveness, per Roentgen unit of ionisation produced in air, is 10 times that of X-irradiation; per ion produced in the rat, the ratio is probably about 5.

F. A. A.

**Relative effectiveness of X-rays and fast neutrons in retarding growth.** R. E. ZIRKLE and P. C. AEBERSOLD (*Proc. Nat. Acad. Sci.*, 1936, 22, 134—138; cf. preceding abstract).—The effectiveness of fast neutrons in retarding the growth of wheat seedlings is 20 times that of X-rays.

F. A. A.

**Excitation and accommodation in nerve.** A. V. HILL (*Proc. Roy. Soc.*, 1936, B, 119, 305—354).—A theory of the electrical stimulation of nerves is advanced, and equations and curves for currents of various forms, applied in different ways, are deduced. The time const. of accommodation,  $\lambda$ , decreases with rising temp., and is affected by [Ca<sup>++</sup>].

**Measurement of accommodation in nerve.** D. Y. SOLANDT (*Proc. Roy. Soc.*, 1936, B, 119, 355—379).—Increase of [Ca<sup>++</sup>] or [K<sup>+</sup>] lowers  $\lambda$  (cf. preceding abstract); Mg<sup>++</sup>, Sr<sup>++</sup>, and Ba<sup>++</sup> produce similar but smaller effects. Decrease of [Ca<sup>++</sup>] increases  $\lambda$ , its val. tending to  $\infty$  at [Ca<sup>++</sup>]=0. The effect of varying [Ca<sup>++</sup>] on the time const. of excitation,  $k$ , is much < that on  $\lambda$ , showing that these const. are independent of each other.

**Redistribution of calcium and potassium in blood and muscles.** I. R. BACHROMEYEV and L. N. PAVLOVA (*J. Physiol. U.S.S.R.*, 1935, 18, 69—77).—Irritation of the central end of the sciatic nerve increases the ionised and total Ca and P in blood, plasma, and erythrocytes, and decreases the vals. in muscle. Irritation after removal of the thyroid increases the total K in plasma and erythrocytes, but Ca vals. are unchanged. Irritation of the upper laryngeal nerve increases blood- and plasma-Ca and decreases that in muscles. Changes in K vary with time.

CH. ABS. (p)

**Action of heavy water on isolated organs.** F. VERZAR and C. HAFTER (*Pflüger's Archiv*, 1935, 236, 714—716).

R. N. C.

**Are free gases in thermal waters absorbed by the skin during bathing?** A. MOUGEOT and AUBERTOT (*Arch. med. Hydrol.*, 1934, 12, 292—293).—The CO<sub>2</sub> content of the exhaled air in man is increased during bathing in a carbonated thermal bath, and in the case of a radioactive bath the exhaled air becomes radioactive.

R. N. C.

**Action of Lurisia waters on uric acid and on uric urinary calculi.** L. FRANCESCONI and R. BRUNA (*Annali Chim. Appl.*, 1936, 26, 34—38).—Various mineral waters from the Lurisia district of Italy are analysed, and their solvent action on uric acid and on urinary calculi, both before and after



the removal of the radioactive emanation which they contain, is examined. E. W. W.

**Fluorine and mottled enamel.** M. C. SMITH, E. M. LANTZ, and H. V. SMITH (J. Amer. Dent. Assoc., 1935, 22, 817-829).—In Arizona, in communities with mottled enamel the  $H_2O$  supply contained 1-6 p.p.m. of F, whereas in non-endemic communities the val. was < 1. If F was present in toxic amounts in the food or  $H_2O$ , mottling could not be prevented by increased intakes of Ca, P, or vitamin-D. F intake interferes with the calcification of the teeth, causing a decrease in size, wt., and ash content, and an increase in the Ca:P ratio. In young rats F feeding impaired ability to metabolise Ca and P, interfered with body growth, and retarded the rate of eruption of incisors. Girls with mottled teeth (4 p.p.m. of F in the  $H_2O$ ) showed no significant variation from normal in the retention of Ca or P, but the amount excreted in the urine was greater. NUTR. ABS. (m)

**Clinical manifestations of high and low plasma-magnesium. Danger of Epsom salt purgation.** A. D. HIRSCHFELDER and V. G. HAURY (J. Amer. Med. Assoc., 1934, 102, 1138-1141).—Normally 40% of ingested Mg is excreted in the urine in 24 hr. A clinical syndrome of high plasma-Mg may be induced in patients with renal insufficiency by doses of  $MgSO_4$ . CH. ABS. (p)

**Possible lipotropic action of alkylammonium compounds.** E. H. MAWSON and A. DEM. WELCH (Biochem. J., 1936, 30, 417-418).— $NHMe_3Cl$  had no lipotropic action, and increased the amount of fat in rat liver, whilst  $NMe_3EtCl$ ,  $NMe_4Cl$ , and  $NMe_3PhCl$  were inactive, but exerted a powerful toxic effect of the curare type. J. N. A.

**Effect of sodium glutamate on digestion.** P. C. HSÜ and W. H. ADOLPH (J. Chinese Chem. Soc., 1936, 4, 42-44).—Na *d*-glutamate does not affect the rate of digestion of carbohydrates, fed as steamed rice to rats. R. S. C.

**Action of benzene in leucæmia.** I. KALAPOS (Klin. Woch., 1935, 14, 864-867; Chem. Zentr., 1935, ii, 1057).— $C_6H_6$  may be useful, alone or in conjunction with X-rays. H. N. R.

**Mode of action of picrotoxin.** H. SCHRIEVER and G. PERSCHMANN (Pflüger's Archiv, 1935, 236, 497-514). R. N. C.

**Experimental influencing of liver-lipase.** G. DELL'ACQUA (Z. klin. Med., 1935, 128, 95-97; Chem. Zentr., 1935, ii, 62-63).—Liver-lipase in mice is depressed by feeding with lard or sugar, by insulin, adrenaline, and particularly by P poisoning. R. N. C.

(A) Fraxin, a fraction of *Fraxinus borealis*, Nakai. (B) Effect of fraxin on uric acid excretion. (C) Mechanism of diuresis caused by fraxin. G. IIDA (Tôhoku J. Exp. Med., 1935, 25, 454-470, 471-475, 26, 1-8).—(A) The glucoside is obtained from the cortex of the tree. Physiological activities are described.

(B) Increased urinary excretion of uric acid caused by fraxin is > that effected by atophan. CH. ABS. (p)

**Methylene-blue therapy and its scientific foundation.** O. EICHLER (Fortschr. Ther., 1935, 11, 336-344; Chem. Zentr., 1935, ii, 880).—The use of methylene-blue is based on its capacity for reversible reduction, although certain conclusions based on this are not borne out in practice. H. N. R.

**Effect of creatine on muscle tonus.** F. M. CHIANCONE (Arch. ital. Biol., 1933, 90, 22-25; Chem. Zentr., 1935, ii, 550). R. N. C.

[Pharmacology of] choline and certain analogues. II. Cationic exchange as a means of reaction of choline, acetylcholine, and their analogues with cells. M. H. ROEPKE and A. D. WELCH (J. Pharm. Exp. Ther., 1936, 56, 319-326; cf. A., 1935, 1411).—The rate of esterase hydrolysis of acetylcholine (I) is identical with those of its P and As analogues. The exchange adsorption of choline with Na and Ca zeolites is > that of arsenocholine and equal to that of (I). H. D.

**Peripheral circulatory activity of histamine.** D. MATEFF and M. SCHNEIDER (Pflüger's Archiv, 1935, 236, 606-635). R. N. C.

**Mechanism of the action of di-iodotyrosine.** M. WACHSTEIN (Wien. klin. Woch., 1934, 47, 1579-1580).—Di-iodotyrosine in large quantities increases the resistance of the mouse to MeCN, and does not antagonise the similar action of thyroxine. R. N. C.

**Action of di-iodotyrosine in thyrotoxicosis.** M. YRIAT, A. DAGNINO, and A. E. BIANCHI (Rev. assoc. med. Argentina, 1935, 49, 309-318).—Basal metabolism was decreased. Effects observed were identical with those produced by an equiv. dosage of inorg. I. CH. ABS. (p)

**Pharmacodynamics of bile acids. Influence of active groups. I. Cardio-vascular and respiratory action.** I. MANTA and P. VANCEA (Arch. exp. Path. Pharm., 1936, 180, 631-638).—The action of cholic and deoxycholic acids and their Ac derivatives, and of dehydro- and dehydrodeoxy-cholic acids and their oximes and semicarbazones on the dog's carotid blood pressure was determined. Introduction of  $\cdot OH$  or, to a greater extent, of  $\cdot OAc$  produces vascular activity in cholanic acid. Oxidation of  $\cdot CH_2\cdot OH$  to  $\cdot CO\cdot$  diminishes the action, which is further modified (to different degrees) by formation of oxime or semicarbazone. F. O. H.

**Action of low-molecular autoclave hydrolysates.** I. N. KASAKOV (Arch. exp. Path. Pharm., 1936, 180, 482-497).—Injection of extensively hydrolysed liver, kidney, adrenal, etc. into normal and diseased rats produces increases in oxidation processes and absorptive power of the reticulo-endothelial system, and changes in the dispersivity of colloid systems, metabolism, and tonus of the nervous system. Therapeutic applications are indicated. F. O. H.

**Physiological and pathological actions of some fresh and autolysed organ extracts, especially pancreas extracts.** L. MICHELAZZI (Arch. ital. Biol., 1934, 90, 157-164; Chem. Zentr., 1935, ii, 393). G. H. F.



Action of the vagus on the frog's heart maintained in absence of potash. W. HERZ (Pflüger's Archiv, 1935, 236, 298—300). R. N. C.

Life-saving action of ovarian preparations in severe bleeding from hæmophilia. K. FRANKE and S. LITZNER (Med. Klinik, 1935, 31, 520—521; Chem. Zentr., 1935, ii, 872). R. N. C.

Effects of sodium ethyl-*n*-hexylbarbiturate (ortal sodium) and of sodium ethylisoamylbarbiturate (sodium amytal) on excised smooth muscle. C. M. GRUBER, R. SCHOLTEN, A. DENOTE, and J. F. WILSON (J. Pharm. Exp. Ther., 1936, 56, 341—350).—Na amytal and, to a greater extent, ortal decrease the tonus and the amplitude of the rhythmic contraction of excised intestine and uterus. Both lower the  $p_H$  of Locke's solution. H. D.

Alkoxymethylhydantoins.—See this vol., 613.

Influence of the combined acid on the anæsthetic power of various salts of novocaine. J. RÉGNIER, R. DELANGE, and R. DAVID (Compt. rend., 1936, 202, 591—592).—Phthalic, hippuric, and nicotinic acids completely annul the anæsthetic activity (rabbit's cornea), whilst phenylbutyric, undecic, and  $\alpha$ -phenylvaleric acids increase the activity 50, 55, and 63 times, respectively. In general the activity of the salt increases with the no. of C in the acid, and decreases if the latter is substituted with  $\cdot\text{CO}_2\text{H}$ ,  $\cdot\text{OH}$ ,  $\cdot\text{NH}_2$ , or  $\cdot\text{Br}$ . The phenylpropionate and isobutyrate are most suitable for clinical use. J. N. A.

Relation between constitution and anæsthetic activity of 2-alkoxyquinoline derivatives.—See this vol., 482.

Changes of blood-proteins in salyrgan diuresis. A. O. SCHALLY (Deuts. Arch. klin. Med., 1935, 177, 368—376; Chem. Zentr., 1935, ii, 79). H. J. E.

[Pharmacognosy of] *Lacinaria* species. B. V. CHRISTENSEN and G. M. HOCKING (J. Amer. Pharm. Assoc., 1936, 25, 15—18).—Constituents of *L. spicata* and *tenuifolia* include a sterol, m.p. 116°, and possibly coumarin. Extracts have a stimulant and cardiac action in man, but no distinct diuretic effect. F. O. H.

Mydriatics and myotics from the Brazilian flora. F. W. FREISE (Süddeut. Apoth.-Ztg., 1935, 75, 333—335; Chem. Zentr., 1935, ii, 719—720).—Various preps. are described. A substance,  $\text{C}_{15}\text{H}_{22}\text{ON}$ , m.p. 112—114°, b.p. 172°, is the active principle of "itua," a *Gnetum* species, whilst the active principle of *Moringa aptera*, Gaertn., is a substance,  $\text{C}_{15}\text{H}_{23}\text{O}_3\text{N}_2$ . H. N. R.

Pharmacological action of *Erythrina corallo-dendron*. I. SIMON (Arch. Farm. speriment., 1935, 59, 193—209). R. N. C.

Identity of the sympathomimetic action of broom and adrenaline: effects on the yohimbine-ised rabbit. H. BUSQUET and C. VISCHNIAC (Compt. rend. Soc. Biol., 1936, 121, 1151—1152). H. G. R.

Acridine compounds and their antimalarial action.—See this vol., 613.

Importance of the kidneys in standardisation of digitalis [in cats]. B. BOUCEK (J. Amer. Pharm. Assoc., 1936, 25, 97—99).— $\text{UO}_2(\text{NO}_3)_2$ -induced or naturally-occurring inflammation of the kidneys increases the resistance of cats to lethal doses of digitalis extracts. F. O. H.

Rate of elimination and accumulation of digitalis glucosides and strophanthin. L. LENDLE (Arch. exp. Path. Pharm., 1936, 180, 518—538).—Crit. infusion velocities in cats and rabbits indicate a rapid detoxication of digitoxin (I) in the body; thus 20% of the lethal dose of (I) or strophanthin (II) is destroyed by rabbits in  $\geq 1$  hr. With cats, the action is not so marked [6% of (II) and 2% of (I)]. The basic accumulative doses [shown by the response to *g*-(II)] are digitoxin 3, *k*-strophanthin 7.5—10, and digilanid 6.5% of the min. lethal dose. F. O. H.

Influence of ergotamine on thermal regulation in the organism. S. FORSTER (Med. Doswicz. Spol., 1935, 19, 152—175).—Ergotamine depresses gaseous exchange by inhibiting  $\text{O}_2$  consumption, and counteracts the increased exchange induced by thyroxine and 2:4-dinitronaphthol in rats, pigeons, and rabbits. Urinary and faecal N diminishes on the 1st and 2nd days after administration. Blood-sugar is decreased in rabbits and pigeons and increased in guinea-pigs. CH. ABS. (p)

Antagonism between curarine and prostigmine, and its relation to the myasthenia problem. G. BRISCOE (Lancet, 1936, 230, 469—472).—Either prostigmine or curarine can produce acute depressant effects (not identical). Their mutual antagonism is such that normal muscular action can be maintained when poisonous doses are administered together. A theory of chemical transmission of excitation explains the results. L. S. T.

Bulbocapnine. RAYMOND-HAMET (Compt. rend., 1936, 202, 357—359).—The hypotensive effect of small doses of  $\beta$ -3:4-dihydroxyphenylethyl- $\beta$ -hydroxyethylamine (I) is accentuated by true sympatholytic substances, but is diminished by bulbocapnine (II), which, however, paralyses the renal vasoconstrictors, a reaction used hitherto as a criterion of sympatholytic activity. (II) has only a slight effect in diminishing hypertension due to adrenaline. Hypotension due to (I), which stimulates the vasodilators  $>$  does adrenaline, is abolished by (II). J. L. D.

[Pharmacology of] morphine, codeine, and their derivatives. IX. Methyl ethers of the morphine and codeine series. N. B. EDDY (J. Pharm. Exp. Ther., 1935, 55, 127—135; cf. A., 1933, 965).—Methylation of the alcoholic OH in morphine, dihydromorphine, codeine, dihydro- and  $\mu$ -codeine increases the toxicity to mice; analgesic and stimulatory effects are increased in the cat and the depressant action in the rat. H. D.

Local irritant action of quinine preparations. G. JOACHIMOGLU and N. KLISSIUNIS (Praktika, 1934, 9, 127—130; Chem. Zentr., 1935, ii, 1057).—Injection of quinine causes disturbance of the gastro-intestinal tract. H. N. R.

Diabetogenic action of some derivatives of phloridzin. A. LAMBRECHTS (Compt. rend. Soc.



Biol., 1936, 121, 870—872).—Phloretin, phlorin, and phloridzin hepta-acetate all produce glycosuria in the dog, but the Me ethers of phloridzin are devoid of action. Free phenolic  $\cdot\text{OH}$ , but not a glucose residue, is apparently necessary for the activity. R. N. C.

**Antioxidant properties of medicaments used as antipyretics.** A. BOUTARIO and J. A. GAUTIER (Compt. rend., 1936, 202, 596—598).—The effect of phenols, arylamines, semicarbazide, pyrazolone, and some alkaloids on the oxidation of  $\text{PhCHO}$  and  $\text{FeSO}_4$  and the reduction of methylene-blue by hepatic tissue has been studied. Antipyretics behave generally as negative catalysts towards oxidation and oxidation-reduction, the intensity of their action varying with the conditions and amount used. J. N. A.

**Increase in the hæmolytic power of lecithin by saponin: detection of small quantities of saponin.** B. S. LEVIN (Compt. rend. Soc. Biol., 1936, 121, 1181—1183).—The reaction will detect saponin at a concn. of 1 in  $25 \times 10^6$ . H. G. R.

**Snake poisons.** F. MICHEEL and K. KRAFT (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., III, 1935, 1, 85—93; Chem. Zentr., 1935, ii, 545).—The venom of the cobra, *Naja flava*, ultra-filtration of which is compared with that of peptone and albumin, loses its activity in  $\frac{1}{2}$  hr. at  $95^\circ$  and  $p_H$  13, but is more stable in acid media. Acid hydrolysates are inactive, but activity is restored to the filterable portion by adding proteins of high mol. wt. (e.g., albumose or gelatin); peptones of low mol. wt., or non-protein colloids, e.g., starch or agar, are ineffective. The poison is apparently active only when adsorbed on a colloidal protein mol. H. J. E.

**Selenium in proteins from toxic foodstuffs.**—See B., 1936, 344.

**Toxicity of organ lipins. Poisoning by polypeptides.** P. ÉTIENNE-MARTIN (Presse méd., 1935, 43, 361—363; Chem. Zentr., 1935, ii, 880).—Both lipins and polypeptides may show some toxicity. H. N. R.

**Toxicity of perchlorates.** E. KAHANE (Bull. Soc. Chim. biol., 1936, 18, 352—357).—Intravenous injection of 0.5 g. and intramuscular injection of 1.0 g. of  $\text{NaClO}_4$  have little toxic effect on the rabbit. The min. toxic dose for *Carassius auratus* is 1% in the  $\text{H}_2\text{O}$ .  $\text{ClO}_4^-$  is therefore only feebly toxic. A. L.

**Chronic carbon monoxide poisoning.** H. GERBIS (Deut. med. Woch., 61, 991—994; Chem. Zentr., 1935, ii, 1059).—Polemical against Süpfle (A., 1935, 530); chronic CO poisoning can occur. H. N. R.

**Changes in carbohydrate metabolism due to carbon monoxide poisoning.** E. SCHULZE (Arch. exp. Path. Pharm., 1936, 180, 649—655).—The changes (normally diminutions) in blood-sugar and liver-glycogen (I) are abnormal [e.g., initial hyperglycæmia and, with small doses, subsequent (I) formation] in CO-poisoned mice: these changes and the parallelism between the increased resistance to MeCN poisoning and fall in (I) indicate a rapid initial adrenal, and a slow subsequent thyroid, action. F. O. H.

**Lead content of duodenal juice in cases of saturnism.** N. ALIAVDIN and E. PEREGOOD (J. Ind. Hyg., 1936, 18, 139).—In a considerable proportion of patients suffering from Pb poisoning, the duodenal juice contains Pb (up to 1.8 mg. per 100 c.c.). W. O. K.

**Normal absorption and excretion of lead.** A. A. KEHOE, F. THAMANN, and J. CHOLAK (J. Amer. Med. Assoc., 1935, 104, 90—92).—Spectrographic data for the Pb content of urine, fæces, and blood are given. Chemical methods give low vals. CH. ABS. (p)

**Comparison of histological and quantitative spectrographic investigations of mercury poisoning.** R. MÜLLER and K. SCHEINER (Arch. exp. Path. Pharm., 1936, 180, 718—730).—There was no parallelism between extent of tissue injury and Hg content in the large intestine and kidney of Hg-poisoned guinea-pigs. F. O. H.

**Urinary excretion of phosphorus during experimental poisoning by uranium nitrate.** R. WEEKERS (Compt. rend. Soc. Biol., 1936, 121, 866—868).— $\text{UO}_2(\text{NO}_3)_2$  increases urinary excretion of  $\text{PO}_4'''$  in the dog. The action does not affect blood-P, but is a direct one on the kidney. R. N. C.

**Effect of various therapeutic agents in animals with hepatic damage caused by phosphorus.** S. NAGAO (Tôhoku J. Exp. Med., 1934, 24, 529—554).—Rabbits poisoned by P can synthesise glycogen (I) from carbohydrates if large amounts are administered. Fructose (II) is more effective in this respect than glucose or sucrose. Synthesis of (I) is accompanied by a decrease in hepatic fat deposition. Insulin and lecithin are of no val. Adrenaline, in clinical doses, is ineffective and may inhibit the action of (II). CH. ABS. (p)

**Enzymes in yellow tobacco.** T. NITO and E. KITAMURA (J. Agric. Chem. Soc. Japan, 1936, 12, 87—95).—The distribution of enzymes in the fresh, fermented, flue-dried, and unfermented leaves of yellow tobacco was determined. H. D.

**Properties of glyoxalase. Effect of  $p_H$ , temperature, and amino-acids on dried glyoxalase.** J. GIRŠAVIČIUS, P. H. EFENDI, and A. P. RYZHOVA (Fermentforsch., 1936, 15, 32—43; cf. A., 1935, 1026).—The activity of dried glyoxalase (I) preps. is measured by titrating the acid produced from the substrate. The rate of the reaction, which is of zero order,  $\propto$  the amount of (I). Glutamic acid, tryptophan, and, to a smaller extent, histidine, arginine, tyrosine, aspartic acid, and indicators retard the reaction, whilst glycine, alanine, leucine, and  $\text{PO}_4'''$  have no effect. The temp. coeff. at  $10^\circ$  is 2—2.5 and decreases as temp. rises. At  $> 50^\circ$  the rate of reaction decreases with time whilst increasing inactivation of (I) with time occurs as the temp. is raised. W. McC.

**Effect of ascorbic acid on the action of tyrosinase on *l*-tyrosine, *l*-3:4-dihydroxyphenylalanine, and *l*-adrenaline.** E. ABDERHALDEN (Fermentforsch., 1936, 15, 24—31; cf. A., 1934, 1138).—The production of 3:4-dihydroxyphenylalanine (I) from tyrosine (II) by tyrosinase (III) and the action



of (III) on (I) and adrenaline (IV) are not inhibited by ascorbic acid (V), (V) with  $O_2$ , cysteine (VI) (but not cystine), and reduced glutathione. (V) produces (I) from (II), the action being accelerated by (III), but no (I) is produced by (VI) if (III) is absent.  $Fe^{+++}$  inhibits the action of (III). The spontaneous colouring of (I) and (IV) is inhibited by glycine (VII), (VI), and aspartic and glutamic acids and retarded by asparagine, histidine, and alanine. (VII) retards the colouring when (III) is present.

W. McC.

**Oxidising enzyme.** M. GHIRON (J. Trop. Med. Hyg., 1935, 38, 108—109).—Aq. extracts of dried liver contain an enzyme which oxidises fatty acids to  $CO_2$  and  $H_2O$ . Its activity is weakened at  $60^\circ$  and is destroyed at  $70^\circ$ .

CH. ABS. (p)

**Oxidation of neutral salicylates in alkaline medium, and particularly sodium salicylate in presence of sodium hydrogen carbonate.** U. B. MARTINS (Tribuna farm., 1934, 8, 8—10, 30—31).—Moulding and blackening of Na salicylate- $NaHCO_3$  solutions is prevented by addition of KI, KCN,  $CH_2O$ , or  $CuSO_4$ . An oxidase is probably responsible for the formation of the black substances.

CH. ABS. (p)

**Peroxidase reaction.** LIV. Prolongation of the rapid peroxidase reaction of blood-leucocytes as a sign of avitaminosis-B. LV. Prolongation of minimum peroxidase staining time as an early sign of avitaminosis-B: mechanism of the prolongation. T. SUZUKI. LVI. Constancy of the Arakawa reaction in milk of a lactating woman during a year. Y. UGA. LVII. Effect of urine of lactating women on leucocyte peroxidase: relationship with avitaminotic urine. T. SUZUKI. LVIII. Effect of urine extract on leucocyte peroxidase: early laboratory finding of avitaminosis-B. T. SUZUKI and A. TAKAMATSU (Tōhoku J. Exp. Med., 1935, 25, 186—200, 201—217, 564—574, 575—587, 588—595; cf. A., 1935, 1266).—LIV. The retardation of the reaction is due to an  $Et_2O$ -sol. substance in blood.

LVII. Urine of women secreting milk showing a negative Arakawa test retards the peroxidase staining time of normal blood neutrophils.

LVIII. The urinary constituent which retards peroxidase staining is removed by  $Et_2O$ -extraction and resembles  $AcCHO$ .

CH. ABS. (p)

**Mechanism of the action of peroxidase.** M. PADOA and D. GARILLI (G. Biol. appl. Ind. chim., 1935, 5, 1—16; Chem. Zentr., 1935, ii, 704).—Beet- and castor-peroxidase (I) are activated by  $Ca^{++}$  in the  $p_H$  range 6.5—7.2.  $Mg^{++}$  has a smaller effect on castor-(I). Activation by  $\alpha$ -alanine occurs in the same  $p_H$  range. An e.m.f. is set up by interposing a collodion membrane between a (I)- $CaSO_4$  solution and a  $CaSO_4$  solution of similar concn. Oxidase preps. are activated by  $Mn^{++}$ .

A. G. P.

**Determination of catalase.** D. DERIBAS and J. KORNMAN (Bull. Soc. Chim. biol., 1936, 18, 414—417).—The method, a modification of that of Bach and Zonkova (A., 1922, i, 392), gives the "potential activity" of the blood-catalase, and involves the

determination of the  $H_2O_2$  decomposed in 24 hr. at  $25^\circ$ .

A. L.

**Action of dyes and other substances on milk dehydrogenase. Identity of Schardinger enzyme with xanthine oxidase.** K. P. BASU and S. P. MUKHERJEE (J. Indian Chem. Soc., 1936, 13, 11—18).—Oxidation of xanthine,  $MeCHO$ , and  $o$ - $OH-C_6H_4-CHO$  by xanthine oxidase (cf. Dixon *et al.*, A., 1924, i, 1380) is inhibited to the same extent for each compound by 12 out of 14 basic dyes, pyrogallol, and gallic acid, and by 10 out of 12 acidic dyes.  $CO(NHEt)_2$  and  $CO(NHPh)_2$ , ethyl- and phenyl-urethane, and  $Na_2S_2O_4$  are without effect. Only one enzyme is involved.

F. R. G.

**Effect of enzymic dephosphorylation of cozymase on its action in the dehydrogenase system of peas.** N. LICHTENSTEIN (Fermentforsch., 1936, 15, 44—48; cf. A., 1935, 1277).—The action of cozymase is not inhibited by veronal- $NaOAc$ , borate, and  $NH_3-NH_4Cl$  buffers but is considerably diminished when  $H_3PO_4$  is liberated from cozymase by phosphatase.

W. McC.

**$\alpha$ -Glycerophosphate dehydrogenase.** D. E. GREEN (Biochem. J., 1936, 30, 629—644).—The enzyme (occurring in rabbit's tissues, especially brain) oxidises only (—) $\alpha$ -glycerophosphate (I) (cf. Meyerhof and Kiessling, A., 1933, 1080), the natural muscle isomeride, the products being mainly glycer-aldehyde phosphate and possibly some dihydroxy-acetone phosphate;  $AcCHO$  is a decomp. product. The enzyme, which is not involved in the reaction between (I) and  $AcCO_2H$ , is inhibited by octyl alcohol and ethylurethane but not by KCN,  $NaN_3$ ,  $NaF$ , or  $CH_3I \cdot CO_2Na$ . The reaction between the dehydrogenase system and mol.  $O_2$  is catalysed by cytochrome c (which is reduced and oxidised approx. 300 times per min.) but not by flavoprotein, flavin, ascorbic acid, or adrenaline.

F. O. H.

**Conditions of determination of the reducing activity of tissues.** A. CHEVALLIER and H. ROUX (Compt. rend. Soc. Biol., 1936, 121, 1017—1019).—The time of reduction of methylene-blue by sections of guinea-pig liver tissue is inversely  $\propto$  the surface area if thin sections are used; with thick sections the relation does not hold. The reducing power of the sections is decreased by prolonged washing in Ringer's solution.

R. N. C.

**Liver glycogenase.** T. H. HODGSON (Biochem. J., 1936, 30, 542—548).—The prep. of rabbit liver glycogenase (I) is described. (I) converts glycogen and maltose quantitatively into glucose, the action, unlike that of amylase, being unaffected by  $NaCl$ . The activity of (I) is optimal on the alkaline side of neutrality and is but little altered over a range of  $p_H$  encountered under physiological conditions. No significant decrease in the (I) content of liver results from administration of convulsive doses of insulin. (I) is destroyed by dialysis. The bearing of the results on the problem of glycogenolysis is discussed.

P. W. C.

**Mechanism of degradation of starch by amylases.** I. Nature of the early fission products. II. Kinetics of action of  $\alpha$ - and  $\beta$ -amylases on



starch, its components and partial degradation products. G. G. FREEMAN and R. H. HOPKINS (Biochem. J., 1936, 30, 442—445, 446—450).—I.  $\alpha$ -Malt- and -pancreatic amylase produce some maltose (I) in the early stages of hydrolysis of sol. starch (II), but most of the reducing material consists of dextrans.  $\beta$ -Malt-amylase and the amylase of ungerminated barley produce (I) in the early stages, the remaining material resembling (II). It is confirmed that  $\alpha$ -amylases hydrolyse (II) into dextrans whilst  $\beta$ -amylases remove successive mols. of (I).

II. The rates of hydrolysis of sol. (II), amylo-amylose (III), erythroamylose (IV),  $\alpha$ -amylodextrin (V), achroodextrin (VI), and glycogen (VII) by  $\alpha$ -malt-amylase and  $\beta$ -malt- or barley-amylase have been determined. A mixture of the  $\alpha$ - and  $\beta$ -enzymes in low concn. acts additively in the hydrolysis of sol. (II), whilst a high concn. of  $\beta$ - promotes hydrolysis at rates  $>$  the sum of the component rates. Mixtures of  $\alpha$ - and  $\beta$ - behave similarly towards (V) and (VII). (VI) is hydrolysed by  $\beta$ - more rapidly than by  $\alpha$ -amylase, (III) yields nearly 100% of (I) by the action of  $\beta$ -, whilst (IV) is hydrolysed with greater difficulty than sol. (II). Both amylases hydrolyse the same non-(V) portion of sol. (II), whilst only the  $\alpha$ - can attack (V).

J. N. A.

Degradation of starch by amylases. III. Mutarotation of fission products. G. G. FREEMAN and R. H. HOPKINS (Biochem. J., 1936, 30, 451—456).—The sense of the mutarotation is characteristic of the enzyme and independent of the substrate. In the early stages,  $\alpha$ -amylase produces reducing dextrans and a little  $\alpha$ -maltose, the latter increasing later, whereas  $\beta$ -amylase produces  $\beta$ -maltose only.

H. G. R.

Influence of alcohol on maltase. R. J. VUARAMBOY (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 209—214).—The inactivation of maltase by EtOH increases with the time of contact. Variations in the  $p_H$  of the EtOH from 5.2 to 8.4 have no effect on this inactivation. Invertase is but little affected by EtOH.

E. A. H. R.

$\beta$ -Glucosidase action.—See this vol., 593.

Specificity of galactosidases. R. WEIDENHAGEN and A. RENNER (Z. Wirts. Zuckerind., 1936, 86, 22—56).—The non-identity of the maltose- and melibiose-splitting enzymes of bottom-fermentation yeast is confirmed; each enzyme can be obtained free from the other. The ratio of the rates of hydrolysis of melibiose and  $\alpha$ -phenylgalactoside by the  $\alpha$ -galactosidase of bottom-fermentation yeast is practically unaffected by adsorption and elution of the enzyme, but different ratios apply to the  $\alpha$ -galactosidases of malt, taka-diastase, and sweet and bitter almonds. A study of the relative rates of hydrolysis of salicin and lactose by the emulsin of almonds at different stages of purification throws doubt on the identity of  $\beta$ -glucosidase with  $\beta$ -galactosidase.

J. H. L.

Action of esterase in presence of organic solvents. E. A. SYM (Biochem. J., 1936, 30, 609—617).—Esterification (determined in the solvent phase by decrease in acidity and alcohol concn.) by pig's pancreatic esterase of  $\text{Bu}^n\text{OH}-\text{PrCO}_2\text{H}$  (and other acids) in presence of  $\text{COMe}_2$ ,  $\text{C}_6\text{H}_6$ , and  $\text{CCl}_4$

was investigated. The velocity of reaction rises with increasing concn. of acid and, up to a max. val., following which it decreases, of alcohol; this phenomenon is partly explained by the partition coeffs. of substrates between  $\text{H}_2\text{O}$  and org. solvent.

F. O. H.

Lipolytic enzyme of *Galleria mellonella*. N. FRIESSINGER and A. GAJDOS (Compt. rend. Soc. Biol., 1936, 121, 1152—1154).—A glycerol extract of the larvæ contains an enzyme which hydrolyses tributyrin.

H. G. R.

Proteinase in the milky juice of *Calotropis gigantea*. Its purification and activation by ascorbic acid and glutathione. K. P. BASU and M. C. NATH (J. Indian Chem. Soc., 1936, 13, 34—39).—The juice contains glutathione 2.094 mg., ascorbic acid 0.211 mg., and cysteine 0.180 mg. per c.c., all of which activate the enzyme previously isolated (A., 1933, 876).

F. R. G.

Proteolytic enzymes of sprouted wheat. J. D. MOUNFIELD (Biochem. J., 1936, 30, 549—557).—Aq. extracts of sprouted wheat contain a protease (I) having an optimum  $p_H$  of 4.1 for decomp. of edestin. The substrate concn. for half the max. velocity (which occurs in  $> 2\%$  solution at  $40^\circ$ ) is 0.5%. The course of the early stages of the reaction appeared to follow the Schutz-Arrhenius rule but no const. val. for  $K_m$  was attained. (I) shows a crit. inactivation temp. of  $54^\circ$  at  $p_H$  6 and is spontaneously inactivated on keeping at  $18^\circ$  for 4—5 weeks with PhMe. The activity of (I) is considerably reduced by citrate or  $\text{Cl}'$ . The extract also contains a dipeptidase which attacks leucylglycine optimally at  $p_H$  7.3 and glycylglycine at  $p_H$  7.9 and is completely inactivated by keeping for 5 days at  $18^\circ$  in presence of PhMe.

P. W. C.

Specific defence proteases in the study of inheritance. I. Tests with pure breeds [of guinea-pigs]. E. ABDERHALDEN (Fermentforsch., 1936, 15, 49—92).—The high degree of breed specificity (usually also sex specificity) observed when the defence enzyme test is applied to pure breeds indicates that the blood and tissues of the separate breeds contain proteins which are distinguishable by means of the test.

W. McC.

Manganese salts as activators of arginase. G. KLEIN and W. ZIESE (Klin. Woch., 1935, 14, 205—206; Chem. Zentr., 1935, ii, 704).— $\text{MnSO}_4$  activates arginase (purified or otherwise) in cell suspensions, tissue sections, sarcoma cells, and tumours. This action occurs *in vitro* in the presence of CO or HCN and is unrelated to the redox potential.

A. G. P.

Occurrence of prolinase.—See this vol., 596.

Urease in the mucous membrane of the intestine of the foetus. A. CARDIN (Arch. ital. Biol., 1934, 91, 96—100; Chem. Zentr., 1933, ii, 869).—Urease occurs in the foetal intestine after 4 months and is probably concerned in the mechanism of HCl secretion. None occurs in cats and dogs.

A. G. P.

Activators of glycolysis. H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1936, 239, 83—88; cf. A., 1935, 1278).—Comparison of the activating effects of animal adenylic acid (I) and cozymase (II)



on the production of lactic acid from glycogen in presence of hexose diphosphate proves the greater efficiency of (II) in the natural state or after inactivation by heat. The rate of elimination of adenine is approx. the same with (I) and (II) whereas (II) loses  $\text{PO}_4'''$  more rapidly than does (I). This is attributed to loss of  $\text{PO}_4'''$  from (II) by two concurrent reactions. H. W.

**Lipochromes and glycolysis.** C. FRISCH, E. LEDERER, and R. WILLHEIM (Bull. Soc. Chim. biol., 1936, 18, 401—405).—Like carotene, lutein and zeaxanthin increase glycolysis by muscle extract.

A. L.

**Specificity of the adenylpyrophosphatase of liver extract.** A. HAASE (Z. physiol. Chem., 1936, 239, 1—14).—Extracts of rabbit and swine liver liberate  $\text{H}_3\text{PO}_4$  from adenylpyrophosphoric acid (I), adenylic acid (II), lactacidogen (III), and  $\text{Na}_4\text{P}_2\text{O}_7$ . The optimum condition for the dephosphorylation of (I) and (II) is  $p_{\text{H}}$  9 and for the fission of  $\text{Na}_4\text{P}_2\text{O}_7$  is  $p_{\text{H}}$  7.0. At  $p_{\text{H}}$  7.0 fission of (III) is scarcely appreciable, but attains about 20% after 4 hr. at 38° and  $p_{\text{H}}$  9. Dephosphorylation of (II) is more rapid than that of (I). Selective damage to adenylpyrophosphatase (IV) does not occur when the liver extract is warmed with  $\text{NH}_4\text{Cl}$ , the fission of (I) and (II) being decreased in the same proportion; the action of phosphatase on  $\text{Na}_4\text{P}_2\text{O}_7$  is, however, very much weakened. (IV) probably affects all three phosphoric groups of (I). By treatment of liver extracts with  $\text{NH}_4\text{Cl}$  (IV) loses so much activity that the process is unsuitable for the establishment of small displacements between free and combined pyrophosphate.

H. W.

**Fission of natural laevorotatory phosphoglyceric acid by muscle extract.** T. ROHLER (Z. physiol. Chem., 1936, 239, 15—29).—An enzyme can be extracted from muscle by physiological NaCl solution or by 2%  $\text{NaHCO}_3$  which hydrolyses phosphoglyceric acid (I) to  $\text{H}_3\text{PO}_4$  and  $\text{AcCO}_2\text{H}$  (usually in equiv. quantities). A large difference in the velocities of isomerisation of (I) to phosphopyruvic acid and of fission of the latter is unlikely. Fission of (I) proceeds most rapidly between  $p_{\text{H}}$  6.8 and 8.0. Isomerisation and fission of (I) is very slight in acid solution. H. W.

**Mechanism of lysozyme action.** K. MEYER, J. W. PALMER, R. THOMPSON, and D. KHORAZO (J. Biol. Chem., 1936, 113, 479—486).—Lysozyme, prepared from *Sarcina*, had no protease, kinase, amylase, lipase, or phosphatase activity; it liberated reducing sugars from the mucins or polysaccharides from *Sarcina*, and also one from a mucin from egg-white. No action was observed with a variety of naturally occurring mucins and polysaccharides.

H. D.

**Lacto-mannitic enzymes. II. Lactic acid in the mannitic fermentation of fructose.** V. BOLCATO (Annali Chim. Appl., 1936, 26, 24—30).—The proportion of lactic acid (I) to  $\text{AcOH}$  in the mannitic fermentation of fructose (cf. A., 1933, 1333) after different intervals shows no regularity, and on addition of (I) to the system the quantity produced is reduced

only slightly. Formation of (I) is regarded as an independent enzymic activity. E. W. W.

**Hydrogenlyases. IV. Synthesis of formic acid by bacteria.** D. D. WOODS (Biochem. J., 1936, 30, 515—527).—When washed suspensions of *B. coli* and other organisms are shaken in  $\text{H}_2 + \text{CO}_2$ ,  $\text{HCO}_2\text{H}$  is produced. The distribution of the enzyme effecting this reaction is identical with that of formic hydrogenlyase (I). The presence of the enzyme in the washed cells is conditioned, as with (I), by the presence of  $\text{HCO}_2'$  in the culture medium, and both systems are sensitive to the same poisons. The same enzyme therefore probably catalyses both synthesis and breakdown of  $\text{HCO}_2\text{H}$ , the action of (I) being reversible. This view is confirmed by the free energy and heat calc. for the reaction. P. W. C.

**Galactozymase as an adaptive enzyme.** M. STEPHENSON and J. YUDKIN (Biochem. J., 1936, 30, 506—514).—Galactozymase (I) of *S. cerevisiae* is an adaptive enzyme, adaptation occurring in aq. solutions of galactose (II) and without cell multiplication. A study of total and viable counts suggests that it is not only viable cells which are capable of adaptation. The activity of (I) and of glucozymase is independent of cell viability. Adapted cells lose their (I) completely after fermenting glucose and regain it in presence of (II). P. W. C.

**Preparation of intermediary enzyme from yeast.** E. NEGELEIN and W. GERISCHER (Biochem. Z., 1936, 284, 289—296).—The enzyme (this vol., 380) (isoelectric point,  $p_{\text{H}}$  4.82) in yeast press-juice is purified by successively removing protein at  $p_{\text{H}}$  4.6, adding NaOH to  $p_{\text{H}}$  9 (which ppts. inert matter and stabilises the solution), fractionally pptg. with  $(\text{NH}_4)_2\text{SO}_4$ , pptg. by EtOH, and finally isoelectrically pptg. from  $\text{H}_2\text{O}$ . The product (102 mg. from 5 litres of press-juice) contains 8.5% of the initial activity. F. O. H.

**Influence of monochromatic light on (A) proteolytic enzymes in yeast, (B) oxidation-reduction enzymes of yeast, (C) yeast amylase. I, II.** R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1936, 12, 19—20, 20, 21—22).—(A) Proteolysis is most marked in red light.

(B) The  $\lambda$  of illumination has but little effect on oxidation-reduction processes in yeasts; the reactions are possibly faster in red light.

(C) i. Amylase activity is most marked in red light.

(C) ii. The extent of reaction increases with increasing intensity of a monochromatic source of light.

E. A. H. R.

**Respiration-increasing action of potassium cyanide.** P. E. LINDAHL and Å. ÖRSTRÖM (Naturwiss., 1936, 24, 142).—The gaseous metabolism of top yeast in presence of dihydroxyacetone (I) is increased by 40% by 0.0015M-KCN; 0.002M- and 0.005M-KCN produce no effect and a decrease, respectively. Fermentation of (I) is accelerated by 0.001M-KCN; CO has a similar effect. The phenomenon is due to the dual action of KCN or CO, viz., acceleration of an anaerobic reaction common to respiration and fermentation and inhibition of the Fe-containing respiratory enzyme. F. O. H.



**Stimulation of yeast proliferation by pantothenic acid.** O. W. RICHARDS (J. Biol. Chem., 1936, 113, 531—536).—The stimulation of the growth of yeast by pantothenic acid (I) is more marked with old (7-day) than with fresh, rapidly growing cultures. The effect is most marked 18—24 hr. after seeding, and there is little effect on the final yield. The observations suggest that the effect of (I) is in stimulating the recovery of the budding rate of older, differentiated, yeast cells. F. A. A.

**Preservation and rate of respiration of yeasts in the presence of glucose.** F. CHODAT and A. MIRIMANOFF (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 189—194; cf. A., 1935, 1538).—The addition of glucose (I) to the culture medium inhibits the ageing effect shown by *Endomyces anomalus* at low temp. (6°), the respiration rate remaining almost unaltered for days. The normal decrease in rate of respiration cannot be attributed to toxic products formed in the medium. Addition of (I) to the medium by increasing the osmotic pressure decreases the ease of extraction of diffusible substances from the cells. Diffusion of cozymase would thus be inhibited, and the maintenance of the respiratory powers of the yeast be explained. E. A. H. R.

**Effect of aëration on alcoholic fermentation.** Y. TOMODA (J. Soc. Chem. Ind. Japan, 1936, 39, 56B).—Aëration depresses the formation of EtOH but increases considerably the amounts of MeCHO and glycerol (10% on sugar converted). S. C.

**Succinic acid and glycerol in alcoholic fermentation.** L. GENEVOIS (Bull. Soc. Chim. biol., 1936, 18, 295—300).—A study of the glycerol (I), succinic acid (II), and AcOH (III) content of various Italian, German, French, and Swiss wines shows that  $g = (5s + 2a)$ , where  $g$ ,  $s$ , and  $a$  are the no. of mols. of (I), (II), and (III), respectively, is always positive. A. L.

**Detection of adenosinetriphosphoric acid in bottom yeast.** N. DAS (Svensk Kem. Tidskr., 1936, 48, 22—24).—This acid was obtained as the Ba salt from a  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  extract of fresh, pressed brewers' yeast. Its identity with that obtained from top yeast and from muscle (cf. A., 1931, 418) was established. J. N. A.

**Squalene as a constituent of yeast fat.**—See B., 1936, 378.

**Hydrogenation of conjugated double linkings by fermenting yeast.**—See this vol., 588.

**Nickel nitroprusside reaction for reduced glutathione.**—See this vol., 597.

**Biochemistry of moulds.** P. W. CLUTTERBUCK (J.S.C.I., 1936, 55, 55—61T).—A summary of recent work.

**Sporulation of *Helminthosporium avenae* and *Alternaria solani* in artificial culture.** W. A. R. D. WESTON (Trans. Brit. Mycol. Soc., 1936, 20, 112—114).—Sporulation of these moulds occurs only after exposure to visible light of high intensity for 10—15 min. E. B. H.

**Some root fungi.** S. RENNER (Phytopath. Z., 1935, 8, 457—487).—Fungi developing on roots of

*Salix repens* and *Acer pseudoplatanus* do not provide a factor necessary for the germination of seeds. No evidence of N fixation by the organism was obtained. A. G. P.

**Thermogenesis in hay-inhabiting fungi.** J. W. HARRISON (Iowa State Coll. J. Sci., 1934, 9, 37—59).—Increased temp. produced by various species of fungi is most marked during active germination, and is not paralleled by the rate of evolution of  $\text{CO}_2$ . CH. ABS. (p)

**Mechanism of fermentation of arabinose by *Aspergillus oryzae*.** I. T. TADOKORO (J. Agric. Chem. Soc. Japan, 1935, 11, 167—173).—The products of fermentation included citric, formic, glycollic, and kojic acids, but not malic or lactic acid, EtOH, MeCHO, AcOH, or  $\text{COMe}_2$ . The mechanism of the changes is discussed. CH. ABS. (p)

**Degradation of fatty acids by mould fungi.**—See B., 1936, 284.

**Production of hydroxylamine from ammonia by *Aspergillus niger*.** M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Compt. rend., 1936, 202, 696—698).—Small amounts of  $\text{NH}_2\text{OH}$  occur when  $\text{NO}_3^-$  or  $\text{NH}_4^+$  provide the N source.  $\text{NH}_2\text{OH}$  probably represents a definite stage in the N metabolism of the mould. A. G. P.

**Structure of the chitin of fungi.** K. H. MEYER and W. LOTMAR (Arch. Sci. phys. nat., 1935, [v], 17, Suppl., 287—288).—Chitin from *Phycomyces blakesleeanus* possesses the same structure as that from animal sources. R. S.

**Incorporation of deuterium into living organisms. III.** K. H. GEIB and K. F. BONHOEFFER (Z. physikal. Chem., 1936, 175, 459—468; cf. this vol., 256).—In solutions of glucose in 95%  $\text{D}_2\text{O}$  *Aspergillus niger* and *Penicillium glaucum* grow only about half as rapidly as in solutions in  $\text{H}_2\text{O}$ . About 30% of the H content of the mould is rapidly exchangeable for D from  $\text{D}_2\text{O}$ , and the proportion of D in the hydrogen incorporated into the mould and not removable by washing with  $\text{H}_2\text{O}$  is about half that in the water of the solution. The proportion of D in the hydrogen of moulds grown in  $\text{AcCO}_2\text{H}$  solution is  $>$  this. There is no growth in solutions of deuteropyruvic acid in  $\text{D}_2\text{O}$ . R. C.

**Concentration of foodstuff as the quantitative factor in the growth of a population of infusoria.** J. MONOD and G. TESSIER (Compt. rend., 1936, 202, 162—164).—The rate of multiplication of *Glaucoma piriformis*  $\propto$  the concn. of the nutrient when this is small, but asymptotically approaches an upper limit when the concn. is large. W. O. K.

**Mechanism of chemotherapeutic action. XII.** Comparison of the binding of some chemotherapeutic agents by normal and resistant trypanosomes. J. T. PEDLOW and L. REINER (J. Pharm. Exp. Ther., 1935, 55, 179—199).—The binding of As by normal and As-resistant strains of *Trypanosoma equiperdum in vitro* from solutions of neosarsphenamine and Mapharsen solutions in concns. such that they would kill both strains in the same time was the same; factors influencing the killing time were without



effect on the binding. *In vivo* normal trypanosomes bind more As than As-resistant strains, whilst the latter bind less acriflavine (I) than do normal strains, the difference *in vivo* being  $>$  *in vitro*. Previous treatment of the rats with (I) was without influence on the binding of As by trypanosomes. Hence the theory that acquired resistance to As compounds is due to a loss of binding groups is incorrect. H. D.

**Changes in acidity during biological processes.** F. SANDER (Biochem. Z., 1936, 284, 189—196).—The resulting changes in  $[H^+]$  of the systems  $SiO_2$ , starch, C, humic acid,  $NH_4$  and Na zeolites, and  $AlCl_3$  with  $H_2O$  and various concns. of aq. KCl, NaOAc,  $(NH_4)_2SO_4$ , NaCl,  $Na_2SO_4$ , and NaOH were determined. The data and their correlation with natural or artificial culture media and with bacterial ( $NO_2^-$ ,  $NO_3^-$  and N-forming) systems are discussed. F. O. H.

**Biochemistry of bacteria.** T. K. WALKER (J.S.C.I., 1936, 55, 61—66r).—A review of recent developments.

**Deamination of alanine.** E. AUBEL and F. EGAMI (Compt. rend., 1936, 202, 675—676).—The action of various narcotics shows that the bacterial system effecting the deamination of *l*-alanine (I) differs from that acting on *d*-alanine but resembles that producing  $AcCO_2H$  from lactic acid (II) (in presence of  $NO_3^-$ ). The latter system is not identical with that effecting the same transformation in presence of methylene-blue as H-acceptor. Hence dehydrogenation of (I) cannot proceed by way of (II) (cf. A., 1935, 1282). A. G. P.

**Soil microbiology. VIII. Nodule bacteria of Leguminosae.** S. VINOGRADSKY [with H. VINOGRADSKY] (Ann. Inst. Pasteur., 1936, 56, 221—250: cf. A., 1933, 537, 989).—In N-free cultures growth of the nodule organisms is poor. Addition of N as  $NH_4^+$ , amides, or amines improves development, sugar consumption increasing with the amount of N supplied. Fixation of N is, however, very small. Org. sources of N (extracts of yeast, leaves, roots, etc.) further increase development and initiate N fixation. Elimination of  $NH_3$  by the organisms occurs only during N fixation. Evolution of  $NH_3$  by nodules is not prevented by  $CHCl_3$  or PhMe, or by drying ( $50^\circ$ ) and prolonged storage. The  $NH_3$  produced is derived from atm. sources. A. G. P.

**Root nodule bacteria of leguminous plants. XVIII. Breakdown of proteins by the root nodule bacteria.** A. I. VIRTANEN and T. LAINE (Biochem. J., 1936, 30, 377—381).—Incubation of strains of *Rhizobium* with milk-proteins (I), gelatin (II), and the cell-proteins of the bacteria produced a very slow hydrolysis. Small amounts of  $NH_3$  were produced from (I) and (II) in the absence of PhMe. H. D.

**Biology of Azotobacter. I. Filterability of Azotobacter. II. Nitrogen content of filtrates from Azotobacter cultures.** M. ROBERG (Jahrb. wiss. Bot., 1935, 82, 1—27, 65—98).—I. No form of the organism passed a bacterial filter.

II. Filtrates from cultures contained N compounds. No  $NH_3$  was formed until the energy source was exhausted. The amount of sol. N produced varied

with the species. *Aspergillus niger* and *B. mesentericus* utilised these N compounds. A. G. P.

**Origin and significance of ammonia formed by Azotobacter.** D. BURK and C. K. HORNER (Soil Sci., 1936, 41, 81—122).—Extracellular  $NH_3$  produced by *A. vinelandii* and *A. chroococcum* is derived from normal cell constituents and not by direct synthesis from atm.  $N_2$ . Under suitable conditions (optima,  $p_H$  7.8—8.0 and  $30$ — $40^\circ$ ) 50% of the cellular N may appear as  $NH_3$ . The influence of  $O_2$  on oxidation of cell material is independent of the pressure (0.01—1.0 atm.). Aerobic production of  $NH_3$  is closely related to the oxidation of cell-protein. Anaerobically,  $NH_3$  is formed by hydrolytic processes not involving production of  $CO_2$ . The mechanism of these changes is discussed. A. G. P.

**Oxidation of mannose to mannonic acid by B. gluconicum (Hermann).** S. HERMANN and P. NEUSCHUL (Bull. Soc. Chim. biol., 1936, 18, 390—394).—Yields of 60—70% are obtained, the mannonic acid being identified as the Ca salt  $(C_6H_{11}O_7)_2Ca \cdot H_2O$ . A. L.

**Mechanism of glucose dissimilation by propionic acid bacteria.** H. G. WOOD and C. H. WERKMAN (Biochem. J., 1936, 30, 618—623).—Quant. data of the products of  $EtCO_2H$  fermentation indicate the formation (possibly from 2 mols. of AcOH) of succinic acid, which is decarboxylated to  $EtCO_2H$ . The possibility of formation of  $EtCO_2H$  from a 3-C intermediate or by 4- and 2-C cleavage of glucose (cf. Virtanen, B., 1924, 687; 1925, 1007) is discussed. F. O. H.

**Activation of lower fatty acids by propionic acid bacteria.** R. W. STONE, H. G. WOOD, and C. H. WERKMAN (Biochem. J., 1936, 30, 624—628).—Determinations of  $E_h$  of systems of lower fatty acids and resting bacteria indicate that AcOH,  $EtCO_2H$ , and, to a smaller extent,  $HCO_2H$  are caused to donate  $H_2$  to methylene-blue (and, with AcOH, to nitrates and *o*-chlorophenol-indophenol) at  $p_H$  5—7;  $PrCO_2H$  and  $BuCO_2H$  are not thus activated. The bearing of the data on  $EtCO_2H$  fermentation is discussed. F. O. H.

**Optical properties of the fermentation lactic acids. II. Behaviour of lactic acid bacteria on addition of inactive and active lactic acids to the fermentation liquids.** H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 96—100).—*S. lactis bulgaricus* produces more *d*-lactic acid (I) than normally when *dl*-(I) is added to the incubation mixture (aq. glucose); *L. pentosaceticus* gives a final product of *dl*-(I) even when *d*- or *l*-(I) is added during fermentation. H. D.

**Fermentation of cellulose by thermophilic bacteria. V. Colloidal substances produced. VI. Formation of lactic acid.** Y. TOMODA (J. Soc. Chem. Ind. Japan, 1936, 39, 57b).—V. Colloidal substances reported by Scott *et al.* (A., 1930, 1218) are proteins, and not formed directly from the cellulose (I); only very small amounts of colloidal substances are real degradation products of (I).

VI. The yield of lactic acid (II) is  $> 10\%$  of the



(I). In analysing the products  $\text{AcOH}$  and  $\text{PrCO}_2\text{H}$  are removed by steam-distillation, and (II) and  $\text{H}_2\text{SO}_4$  in the residue are partly separated by extraction with amyl alcohol.  $\text{AcOH}$  and  $\text{PrCO}_2\text{H}$  are partly separated by extraction with  $\text{Et}_2\text{O}$ .

A. G.

Action of 2:4-dinitrophenol on respiration and oxidation of *Aerobacter cloacae*. F. H. JOHNSON (J. Tenn. Acad. Sci., 1934, 9, 288—291).—In concns. of 4—6 mg. per 100 c.c., 2:4-dinitrophenol is toxic and effects some oxidation of the cell. Smaller proportions are stimulative. CH. ABS. (p)

Nucleoproteins from *B. anthracis*. R. FERRA-MOLA (Anal. Assoc. Quím. Argentina, 1935, 23, 93—105).—*B. anthracis* gives at  $p_{\text{H}}$  3.8—4 an insol. nucleoprotein, separated by  $\text{AcOH}$  into an insol. protein (elementary analysis) and a sol. nucleic acid which with 15%  $\text{H}_2\text{SO}_4$  yields guanine and adenine. The biological activity (immunised horse serum) resides in the protein fraction. F. R. G.

Biochemical and serological differentiation of the *Brucella* group: its significance for epidemiology. P. A. VERSCHLOVA (Arch. Sci. biol. U.S.S.R., 35, B, 513—541).—Bovine and porcine but not *melitensis* forms produce  $\text{H}_2\text{S}$  under conditions in which  $\text{CO}_2$  accumulation is prevented, porcine types yielding the greater quantity. The bacteriostatic dye technique gives better differentiation. CH. ABS. (p)

Comparative value of the method of Koser, the Voges-Proskauer test, and the methyl-red reaction to differentiate *B. coli* of faecal and telluric origin. F. VAN DEN BRANDEN and J. GEENS (Compt. rend. Soc. Biol., 1936, 121, 893—895). R. N. C.

Nature of diphtheria toxin. Purified, powdered toxin. S. HOSOYA, A. MOMMA, T. TANAKA, and K. KAGABE (Compt. rend. Soc. Biol., 1936, 121, 1191—1192). H. G. R.

Meningococcus infection. VIII. Type I specific substance. H. W. SCHERP and G. RAKE (J. Exp. Med., 1935, 61, 753—769).—Isolation of the type-sp. substance is described. It is probably the Na salt of a polysaccharide acid, yields 45% of reducing sugars on hydrolysis, is unaffected by tryptic digestion, and does not give a biuret test. CH. ABS. (p)

Use of sodium deoxycholate for the identification of pneumococci. E. LEIFSON (J. Amer. Med. Assoc., 1935, 104, 213).—In media of  $p_{\text{H}}$   $\leq$  6.5 pneumococcus but not streptococcus cultures are cleared by the reagent. CH. ABS. (p)

Existence of a staphylococcal paratoxin. P. NÉLIS (Compt. rend. Soc. Biol., 1936, 121, 808—810). R. N. C.

Cellular reactions to acetone-soluble fat from mycobacteria and streptococci. Effect of neutralisation on the biological activity of the tuberculo-lipin and of the phthioic acid derived from it. K. C. SMITHBURN and F. R. SABIN (J. Exp. Med., 1935, 61, 771—782).—The reaction induced by  $\text{COMe}_2$ -sol. fat of the tubercle bacillus is simpler and

less extensive if the material is neutralised. Neutralisation of the fat or of phthioic acid does not lower the tuberculogenic potency. The fat from streptococci is similarly irritating but does not produce tuberculous tissue. CH. ABS. (p)

Diacetyl as tubercle-bactericidal constituent of Finnish wood-tar. Y. W. JALANDER (Arch. exp. Path. Pharm., 1936, 180, 628—630).— $\text{Ac}_2$  (synthetic or from wood-tar), especially as vapour, has a bactericidal action on tubercle bacilli.

F. O. H.

Effect of concentration of glycerol and asparagine on the weight-yields of *B. tuberculosis* and on the  $p_{\text{H}}$  of cultures in Sauton's medium. R. K. GOYAL (Compt. rend. Soc. Biol., 1936, 121, 1165—1167).—Optimum yields are obtained with 1.2% asparagine and 6% (vol.) glycerol.

H. G. R.

Sterilising action of acids. VI. Sterilising action of halogenated fatty acids on putrefactive bacteria, *B. typhosus*, and *V. cholerae*. S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1936, 12, 22—26). E. A. H. R.

Mechanism of bactericidal action of radioactive radiations. I. Theoretical. II. Experimental;  $\alpha$ - and  $\beta$ -particles. D. R. LEA, R. B. HAINES, and C. A. COULSON (Proc. Roy. Soc., 1936, B, 120, 47—63, 63—76).—I. Possible mechanisms of the bactericidal action of  $\alpha$ - and  $\beta$ -radiations are discussed. The "target" hypothesis seems best to fit the facts.

II. Bacteria in thin gelatin films are exposed to radiations of small penetrating power. The fraction surviving is an exponentially diminishing function of the time of irradiation. The rate of disinfection is independent of temp. and  $\propto$  the intensity of radiation. The results are expressed in terms of mean ionisation dosage required to produce death, and by "target areas." E. A. H. R.

Antiseptic action of certain 2-furyl mercurials. N. M. PHATAK and C. D. LEAKE (J. Pharm. Exp. Ther., 1936, 56, 265—268).—Furyl Hg salts have antiseptic powers  $<$  those of Ph Hg<sup>II</sup> salts, and substitution of halogens or alkyl in the Ph or furan nuclei lowers the toxicity of the compounds. H. D.

Bactericidal action of mercury. M. LISBONNE and R. SEIGNEURIN (Compt. rend., 1936, 202, 169—171).—The addition of Hg to  $\text{H}_2\text{O}$  renders the latter bactericidal. W. O. K.

Adsorption of foot and mouth disease virus on alumina. A. HANSEN and S. SCHMIDT (Compt. rend. Soc. Biol., 1936, 121, 1239—1242).—The virus is completely adsorbed and may be eluted to a small extent with dil.  $\text{PO}_4'''$  buffer at  $p_{\text{H}}$  7.6. H. G. R.

Complex of foot and mouth disease virus with alumina and its pathogenic and immunising properties. S. SCHMIDT and A. HANSEN (Compt. rend. Soc. Biol., 1936, 121, 1236—1239).—Guinea-pigs, which show no signs of fever, are rapidly immunised by intracutaneous introduction of the complex. H. G. R.



**Determination of the dimensions of ultra-viruses by ultrafiltration: virus of herpes.** C. LEVADITI, M. PAÏC, and D. KRASSNOFF (*Compt. rend. Soc. Biol.*, 1936, **121**, 805—808).—The virulence of the ultravirus is inversely  $\propto$  the size of the particles. R. N. C.

**Physicochemical characterisation of the filterable viruses of mosaic.** K. S. SUCHOV (*Virus Dis. Plants, Crimea and Ukraine*, 1934, 31—38).—The virus of tomato fern-leaf is not killed by  $\text{CO}_2$  or EtOH or destroyed by pepsin. Tomato "streak" tissues exerted a mitogenetic action on yeast.

CH. ABS. (p)

**Action of hormones on the plumage of birds.** G. MONTALENTI (*Rass. Clin. Terap.*, 1934, **33**, 6—21; *Chem. Zentr.*, 1935, ii, 711). R. N. C.

**Influence of different hormones on the hydrogen-ion concentration of blood-plasma.** II. Relation between thyroid and insulin. III. Influence of adrenals. IV. Relation between adrenaline and thyroid and between adrenaline and insulin. V. Influence of the gonads. N. NAKATSUGAWA (*Folia Endocrinol. Japon.*, 1933, **8**, 105—106; **9**, 24—25, 43—44, 45—46; cf. A., 1934, 1409).—II. Injection of insulin (I) in rabbits with slight hyperthyroidism causes an increased acidotic and a decreased alkalotic phase. In severe hyperthyroidism both phases decrease. Thyroidectomised animals show increased acidosis but no alkalosis after injection. When glucose is given with (I) acidosis was insignificant but alkalosis increased.

III. Injection of adrenaline (II) lowers the plasma- $p_H$ . Cortex extract causes slightly increased vals. Ingested thyroid and adrenals are antagonistic. Insulin is synergistic with adrenals.

IV. Acidosis following injection of (II) is decreased by feeding thyroid powder and by insulin, and augmented by thyroidectomy. Initial acidosis after (I) was diminished by injecting (II), but the following acidosis was unchanged.

V. Plasma- $p_H$  of female animals is lowered by feeding interstitial tissue from cow ovaries and raised by feeding corpus luteum and by oöphorectomy.

CH. ABS. (p)

**Lipæmia caused by absorption of the products of intestinal putrefaction of proteins and effects of the various hormones on this condition.** III. Effect of extirpation of adrenals. IV. Effect of insulin and of insulin plus glucose. M. MITANI (*Folia Endocrinol. Japon.*, 1933, **8**, 94; cf. A., 1934, 1398).—III. Extirpation of adrenals in rabbits results in an increase in blood-fat, -lipin, and (notably) -cholesterol. Lipæmia produced by assimilation of products of protein decomp. in the intestine is more marked in adrenalectomised than in normal animals.

IV. Lipæmia following the feeding of decomp. products of proteins is reduced by insulin (I) and further reduced by (I) + glucose. CH. ABS. (p)

**Passage of hormones (choline, adrenaline, posterior pituitary hormone) from the mother through the placenta to the foetus.** L. CATTANEO (*Arch. ital. Biol.*, **90**, 100—110; *Chem. Zentr.*, 1935, ii, 71). R. N. C.

**Action of adrenaline in the monkey.** C. J. STORM (*Acta Brev. neerl. Physiol.*, 1935, **5**, 57—60). R. N. C.

**Use of adrenaline in intravenous injections of atebirin.** C. J. STORM (*Acta Brev. neerl. Physiol.*, 1935, **5**, 60—63). R. N. C.

**Intra-vascular injection of adrenaline into dogs. Hyperglycæmia and dosage by different methods of administration.** A. BAUDOUIN, H. BÉNARD, J. LEWIN, and J. SALLET (*Compt. rend. Soc. Biol.*, 1936, **121**, 1157—1159).—Hyperglycæmia is more readily produced when adrenaline is administered through the portal system. H. G. R.

**Sensitisation by cocaine of the hypertonic effects of adrenaline.** H. HERRMANN, G. MORIN, and J. VIAL (*Compt. rend. Soc. Biol.*, 1936, **121**, 998—1000). R. N. C.

**Sparteine, an antagonist of yohimbine in adrenaline hyperglycæmia.** R. HAZARD (*Compt. rend.*, 1936, **202**, 345—347).—Sparteine (10—20 mg. per kg.) largely antagonises the effect of 7 mg. of yohimbine chloride in suppressing the hyperglycæmic effect of adrenaline (0.1 mg. per kg.) in young rabbits. J. L. D.

**Effect of endocrine gland secretions on the adrenaline formation and content of the adrenals.** O. RICHTER (*Endocrinol.*, 1935, **15**, 305—320; *Chem. Zentr.*, 1935, ii, 1052).—Adrenaline (I) discharge from the adrenals in the rat is increased by feeding with thyroid or thymus, or injection of insulin or posterior pituitary hormone, (I) formation showing a preliminary increase, which is soon negated by the discharge, the medulla exhausting itself. Thyroidectomy increases (I) formation without affecting discharge, splanchnicotomy prevents (I) discharge, whilst ovariectomy increases both formation and discharge of (I). R. N. C.

**Does administration of adrenaline alter the adrenaline content of the adrenals in rabbits?** J. KANOWOKA (*Tôhoku J. Exp. Med.*, 1934, **24**, 572—579).—No change results from intravenous injection. CH. ABS. (p)

**Adrenaline content of adrenal glands of dogs.** J. KANOWOKA (*Tôhoku J. Exp. Med.*, 1934, **24**, 463—467).—Various methods of assay are compared. CH. ABS. (p)

**Adrenaline content of the adrenal capsules after destruction of the dorso-lumbo-sacral marrow in the dog.** H. HERRMANN, J. DECHAUME, and G. MOREN (*Compt. rend. Soc. Biol.*, 1936, **121**, 1000—1002).—Adrenaline is depressed by destruction of the marrow, but tends to recover during the survival period. R. N. C.

**Anaphylactic shock and adrenaline content of adrenal glands.** J. KANOWOKA and S. KANOWOKA (*Tôhoku J. Exp. Med.*, 1935, **25**, 249—257).—In sensitised rabbits shock induced by injection of horse serum caused a decrease in adrenaline (I) content of the glands, unaffected by sectioning the splanchnic nerve, and probably due to destruction, rather than increased liberation, of (I).

CH. ABS. (p)



**Adrenaline content of adrenal glands of rabbits in peptone poisoning.** J. KANOWOKA (Tôhoku J. Exp. Med., 1935, 25, 244—248).—Vals. decreased slightly in animals showing signs of peptone poisoning except when death immediately followed the injection.

CH. ABS. (p)

**Identification of the muscle-active adrenal cortex hormone.** K. LANG and B. STUBER (Biochem. Z., 1936, 284, 256—269).—Adrenal cortex contains a hormone [not identical with that of Swingle *et al.* (A., 1933, 320)] characterised by its ability in suitable doses to delay fatigue in active muscle; large doses, however, accelerate fatigue. The isolated principle is mainly a fatty acid ester (Me stearate?) and its action is typical of esters of higher fatty acids which, like adrenal cortex extracts, enhance phosphagen synthesis in muscle.

F. O. H.

**Adrenal cortex. II. Factors diminishing blood-lipins.** K. LANG and B. STUBER (Biochem. Z., 1936, 284, 270—278).—The principles contained in adrenal cortex extracts responsible for the lowering of blood-phosphatides and -cholesterol in rabbits are esters of fatty acids with low and high no. of C atoms, respectively; thus the effects are produced by Me undecate and oleate, respectively. Injection of Me oleate increases sterol excretion. The factors of Schmitz and Kühnau (A., 1933, 642) are probably similar substances.

F. O. H.

**Adrenal cortex. IV. Effect of sodium salts in sustaining the adrenalectomised dog.** G. A. HARROP, L. J. SOFFER, W. M. NICHOLSON, and M. STRAUSS (J. Exp. Med., 1935, 61, 839—860).—Bilaterally adrenalectomised dogs are maintained in apparently normal condition by administration of NaCl and NaHCO<sub>3</sub>. Adrenal hormone is concerned in regulating renal excretion of Na. CH. ABS. (p)

**Action of cortical hormone on choline metabolism.** G. MARANON and S. A. COLLAZO (Rev. franç. Endocrinol., 1935, 13, 1—23; Chem. Zentr., 1935, ii, 71).—Blood-cholesterol (I)  $\propto$  the activity of the adrenal cortex. Cortical hormone in man increases (I) and also bile-cholesterol, and is probably associated with the increased excretion of cholesterol in the bile.

R. N. C.

**Action of cortical hormone on blood-cholesterol.** C. V. MEDVEI (Z. klin. Med., 1935, 128, 58—67; Chem. Zentr., 1935, ii, 71—72).—Blood-cholesterol in healthy men is depressed by the cortical extract of Swingle and Pfiffner, is high in Addison's disease, and low in cases of cortical hyperfunction.

R. N. C.

**Secretion of the pituitary.** E. KYLIN (Acta med. Scand., 1935, 85, 457—472).

R. N. C.

**Diabetogenic, thyrotropic, adrenotropic, and parathyrotropic factors of the pituitary.** J. B. COLLIP (J. Amer. Med. Assoc., 1935, 104, 827—832, 916—921).—A review.

CH. ABS. (p)

**Growth hormone of the anterior pituitary.** M. EVANS (J. Amer. Med. Assoc., 1935, 104, 1232—1237).—A review.

CH. ABS. (p)

**Anterior pituitary and carbohydrate metabolism.** F. HÖGLER and F. ZELL (Wien. Arch. inn.

Med., 1935, 27, 141—159; Chem. Zentr., 1935, ii, 872—873).—Tonephin (I) causes an increase of blood-sugar in rabbits which reaches a max. in 20—60 min.; temp. rises slightly. Pharmacological or operative exclusion of the cerebrum and brain-stem does not affect the action of (I), which is probably one of glycogen mobilisation.

R. N. C.

**Chromatophorotropic principle (intermedin) of the pars intermedia of the pituitary.** B. ZONDEK (J. Amer. Med. Assoc., 1935, 104, 637—638).—Intermedin is thermo- and psycho-stable but easily destroyed by proteolytic enzymes and ultra-violet rays. Distribution of the hormone in cattle pituitaries is examined.

CH. ABS. (p)

**Purification of the pressor and oxytocic hormones of the pituitary gland: chemistry of the products.** R. L. STEHLE and A. M. FRASER (J. Pharm. Exp. Ther., 1935, 55, 136—151).—The crude hormone prep. was purified by the method of Stehle (A., 1934, 117) and fractionated with MeOH and AcOEt. The activities of the pressor and oxytocic preps. were 100 and 125 times those of standard pituitary powders; both appeared to be polypeptides containing tyrosine, cystine, and arginine. Phenylalanine, glutamic and aspartic acids, and leucine appeared to be absent from the pressor prep.

H. D.

**Physiological variations in the internal secretion of the pancreas. XIV. Action of posterior pituitary extract and of its hypertensive and oxytocic fractions on secretion of adrenaline and insulin.** E. ZUNZ and J. LA BARRE (Arch. internat. Physiol., 1935, 41, 538—568).—Pitressin (but not pitocin) in doses of 3 units per kg. cause hyperglycaemia in chloralised dogs with and without ligation of the adrenal veins, by stimulating adrenaline secretion. Later, both substances increased insulin secretion shown by hypoglycaemia. These effects persisted after thyroidectomy. Pituitrin caused hyperglycaemia not so marked as that produced by the pressor factor alone. Chloretone produced slight hypoglycaemia.

NUTR. ABS. (m)

**Hormones and external sex organs.** O. O. FELLNER (Endocrinol., 1935, 15, 232—243; Chem. Zentr., 1935, ii, 67).

R. N. C.

**Gonadotropic hormones in the treatment of sterility in man.** V. E. LLOYD (Lancet, 1936, 230, 474—475).—Administration of antuitrin-S effected a cure.

L. S. T.

**Effect of progestin on the mammary gland of the rat.** J. FREUD and S. E. DE JONGH (Acta Brev. neerl. Physiol., 1935, 5, 47—48).

R. N. C.

**Effect of sex and adrenal cortex hormones on serum-lipase.** J. BAUER and F. FEIL (Z. klin. Med., 1935, 128, 90—94; Chem. Zentr., 1935, ii, 62).—Follicular hormone causes a fall of serum-lipase (I) in rabbits of both sexes, followed occasionally by a rise to > normal. The male hormone does not depress (I) in male animals and can even increase it. Cortical hormone depresses (I) in male animals after an interval of some weeks, but does not affect it in females.

R. N. C.



**Spectrographic detection of the oestrogenic hormone in human pregnancy urine.** H. BERRY and B. GOUZON (*Compt. rend.*, 1936, 202, 686—687).—The hormone, separated from acid-hydrolysed urine by adsorption and elution, is dissolved in  $\text{CHCl}_3$  and shaken with  $\text{H}_2\text{SO}_4$ . The brownish-green, fluorescent colour obtained shows on spectrographic examination the band characteristic of folliculin or dihydrofolliculin. Urine from males or non-pregnant females yields the fluorescence but not the characteristic band. A. G. P.

**Corpus luteum hormone and its purification.** E. FELS (*Arch. Gynäkol.*, 1934, 158, 364—391; *Chem. Zentr.*, 1935, ii, 67—68). R. N. C.

**Ovarian hormones and carbohydrate metabolism. I. Ovarian hormones and blood-sugar.** E. DE AMILIBIA, M. M. MENDIZÁBAL, and J. BOTELLA-LLUSIÁ. **II. Effect of ovarian hormones on liver-glycogen.** J. BOTELLA-LLUSIÁ, E. DE AMILIBIA, and M. M. MENDIZÁBAL (*Arch. Gynäkol.*, 1935, 159, 453—460, 461—464).—I. In fasting immature guinea-pigs folliculin (I) raised and corpus luteum hormone (II) lowered the blood-sugar level during the 6 hr. following injection. Thyroidectomy abolished these effects.

II. In male albino rats, daily injections of (I) and (II) produced, respectively, a 50% decrease and increase in the glycogen content of the liver.

Nutr. Abs. (m)

**Gonadotropic factors of climacteric urine.** A. LIPSCHÜTZ (*Klin. Woch.*, 1935, 14, 532—533; *Chem. Zentr.*, 1935, ii, 391).—The gonadotropic complex contains  $\approx 3$  factors: oestrogenic (I), luteinising (II), and a third (III) which sensitises the follicles to (II). Anterior pituitary of male rats contains (II) and (III), and causes luteinisation of ovaries of infantile rats but (III) is absent from pituitaries of female rats. Climacteric urine contains (III), and therefore, administered in combination with anterior pituitary from female rats, causes luteinisation.

G. H. F.

**Effectiveness of theelol by oral administration.** L. W. ROWE and A. E. SIMOND (*J. Amer. Pharm. Assoc.*, 1936, 25, 201—205).—When orally administered, theelol (from human urine) is 5 times as active as theelin (from mare's urine of pregnancy). Oral dosage to rats of oestrogenic substances in amounts sufficient to produce oestrus in spayed rats reduces by 75% the time necessary for attainment of sexual maturity. Discrepancies between international standard and experimental rat units are discussed.

F. O. H.

**Effect of follicular hormone on ossification in castrated dogs.** M. TAUSK and P. DE FREMERY (*Acta Brev. neerl. Physiol.*, 1935, 5, 19—22; *Chem. Zentr.*, 1935, ii, 390).—Administration of folliculin to castrated fox terriers caused precocious ossification of the epiphysis.

G. H. F.

**Relation between creatine metabolism and the function of the sex glands.** R. USUI, T. MIWA, and K. AOKI (*Klin. Woch.*, 1935, 14, 720—721).—Administration of male sex hormone to old men and patients with Addison's disease lowers urinary creatine.

Ch. Abs. (p)

**Male sex hormone. IV. Hormone from testis of swine. II.** A. OGATA and S. HIRANO (*J. Pharm. Soc. Japan*, 1933, 53, 869—890).—The hormone (I) is sparingly sol. in hexane, is not oxidised by cold  $\text{KMnO}_4$ , and is partly adsorbed by C. 70% EtOH separates a cholesterol-free fraction. Cock's comb tests are described. Ch. Abs. (p)

**Testis hormone.** C. R. MOORE (*J. Amer. Med. Assoc.*, 1935, 104, 1405—1411).—The hormone is probably a keto-alcohol. Only animal tests are serviceable for its detection. Ch. Abs. (p)

**Assay and effect of testosterone on rats compared with those of other sexual hormones.** V. KORENCHESKY, M. DENNISON, and I. BROVINS (*Biochem. J.*, 1936, 30, 558—575).—The biological properties of artificial testosterone (I) and the combined effect of (I) with oestrone (II) or oestradiol (III) are investigated. With castrated male rats, the relationship between dose of (I) and the effect on the genital organs is investigated statistically. The sexual glands, atrophied during 51 days after castration, were not completely restored by injections for 23 days (except in the case of the preputial glands). The wts. of somatic glands and organs were, however, generally restored to normal vals. Injection of (II) or (III) caused considerable increase in the seminal vesicles, small increases in the prostate and preputial glands, but no change in the penis. (II) or (III) injected with (I) showed only slight co-operative effect on the wts. of the atrophied seminal vesicles and prostate. With ovariectomised female rats, (I) produced enlargement of the atrophied sexual organs but not to normal wt. (except for the preputial glands) and decrease in wt. of the thymus. There was marked co-operative effect between (I) and (II) in restoring atrophied organs. Androsteronediol (IV) and (I), unlike androsterone, bring about normal development of the male organs; both (IV) and (I) produce changes similar to those after injection of progesterone, and if injected along with (II), produce changes resembling those in pregnancy. P. W. C.

**Action of testicular hormone on development of the hen's comb.** E. RAMIREZ and M. D. RIVERO (*J. Amer. Pharm. Assoc.*, 1936, 25, 99—102).—Enlargement of the comb following administration of testicular hormone occurs in normal hens, which could therefore be substituted for Leghorn capons for standardisation purposes. F. O. H.

**Sterols as precursors of hormones, vitamins, and other physiologically important compounds.** A. WINDAUS (*Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl.*, III, 1935, [ii], 1, 59—83; *Chem. Zentr.*, 1935, ii, 702).—A lecture. H. N. R.

**Preparation of 17-ethyltestosterone and 3-trans-17-cis-diols of androstane and androstene. Specificity of the sex hormones.**—See this vol., 606.

**Effect of zinc salts on the action of insulin.** D. A. SCOTT and A. M. FISHER (*J. Pharm. Exp. Ther.*, 1935, 55, 206—221; cf. A., 1934, 1267).—Addition of 0.01% of Zn to insulin (I) solutions decreases the activity by 60%. 0.1% of Zn delays the hypoglycaemic action of (I) in rabbits although



the quantity of glucose metabolised is unchanged.  $\text{CoCl}_2$  and K alum are without influence on the activity of (I), whilst Ni has a similar effect to that of Zn.

H. D.

Microscopic observation of the absorption of insulin and protamine insulinate. H. K. BEECHER and A. KROGH (*Nature*, 1936, 137, 458).—The rate of absorption and the distribution of particles of insulin and protamine insulinate dyed with methylene-blue in the lymphatics and tissue spaces of rabbits' ears are recorded.

L. S. T.

Has insulin thrombokinase-like properties or is it contaminated with the latter? G. SANT (*Pharm. Tijdschr. Nederl.-Indië*, 1934, 11, 335—337; *Chem. Zentr.*, 1935, ii, 545).—One of the above alternatives is probably the case.

R. N. C.

Has insulin an important effect on serum-albumins? G. SANT (*Pharm. Tijdschr. Nederl.-Indië*, 1934, 11, 274—276; *Chem. Zentr.*, 1935, ii, 545).—Insulin decreases  $\alpha$  and  $\eta$  of serum and increases the turbidity produced by  $\text{EtOH}$ . The  $\text{NaCl}$  present in commercial insulin is only slightly responsible.

R. N. C.

Individuality of vegetable insulinoids and vitamin-B. H. LABBÉ and E. DONARD (*Bull. Acad. Méd.*, 1935, 113, 625—626).—The insulin-like extract exhibits neither a preventive nor a curative effect on avitaminosis-B in rats. The insulin-like action is hence not due to -B.

R. N. C.

Physiology of the thyro-activator in amphibia. I. Acceleration of metamorphosis in the larvæ of salamanders. E. UHLENHUTH and S. S. SCHWARTZBACH (*Endokrinol.*, 1935, 15, 329—341; *Chem. Zentr.*, 1935, ii, 1050—1051).—Metamorphosis in normal and thyroidectomised salamanders is accelerated by thyrotropic hormone.

R. N. C.

Effect of hormones on the dynamics of cardiac stimulants. I. Action of thyroxine. R. AGNOLI and G. MARAGLIANO (*Arch. Sci. biol.*, 1934, 20, 498—514; *Chem. Zentr.*, 1935, ii, 711).

R. N. C.

Relationship between the iodine content of the diet and the thyroxine content of blood. U. G. BJLSMA, J. W. LE HEUX, and M. A. B. TOXOPEUS (*Nederland. Tijdschr. Geneesk.*, 1935, 79, 3159).—In dogs on a diet poor in I the thyroxine (I) content decreased; on giving 0.000025 mg. of I it returned to the normal level: 100 mg. did not produce any further rise. With diet rich in I the (I) content was slightly > normal and 0.025 mg. of I per day lowered it.

NUTR. ABS. (*m*)

Effect of thyroid and thyroxine on the chloride content of muscle. M. CAHANE (*Bull. Soc. Chim. biol.*, 1936, 18, 424—427).—The Cl' content of the muscle-tissue of rats receiving thyroid powder and thyroxine daily was > that of normal animals.

A. L.

Depression of serum-lipase by thyroxine and its inhibition. IV. J. BAUER and L. FEIL (*Z. klin. Med.*, 1935, 128, 77—89; *Chem. Zentr.*, 1935, ii, 62).—Repeated injection of lipid extract of the pancreas in rabbits inhibits the depression of serum-lipase (I) by thyroxine (II) and also its toxic action.

The extract alone causes an increase of (I) in rabbits, and a temporary fall, followed by a rise, in healthy and hyperthyroidian men of (I).

R. N. C.

Effect of the thyroid on body-weight and nitrogen excretion. A. FIORI (*Rass. Clin. Terap.*, 1934, 33, 40—46; *Chem. Zentr.*, 1935, ii, 711).—There is no correlation between the amount of thyroid fed to animals and the loss of body-wt. Thyroid preps. cannot be evaluated by determination of N excretion by guinea-pigs.

R. N. C.

Detoxicating hormone of the liver. LV. Anti-thyroid action of yakriton. I. HORIUCHI and F. OHSAKO. LVI. Effect of yakriton on blood-calcium. Y. UGA. LVII. Inhibiting effect of yakriton on the hypoglycæmic action of insulin. A. TAKAMATSU and Y. UGA. LVIII. Effect of yakriton in one-fifth R.A.U. on blood picture including nuclear shift. R. SHIBATA. LIX. Inhibiting effect of yakriton on the hyperglycæmic [?] action of insulin. A. TAKAMATSU. LX. Correlation between sedimentation rate of blood and detoxicating power of liver. M. YOSHIDA (*Tôhoku J. Exp. Med.*, 1934, 24, 505—515, 516—520, 521—528; 1935, 26, 31—45, 46—51, 52—59).—LV. Yakriton (I) antagonises the effect of dried thyroid and thyroxine on tadpoles.

LVI. (I) inhibits hypercalcaemia caused by injection of Ca gluconate in rabbits.

LX. Intraperitoneal injection of  $\text{NH}_4\text{Cl}$  has no effect on the sedimentation rate in rabbits having actively detoxicating livers (cf. A., 1935, 538).

CH. ABS. (*p*)

Stimulating action of pig's stomach powder on secretion of vagotonin by the pancreas. D. SANTENOISE, P. L. DROUET, C. FRANCK, and M. VIDACOVITCH (*Compt. rend. Soc. Biol.*, 1936, 121, 927—928).—The powder is effective when given orally to the dog.

R. N. C.

Stimulating action of secretin on the secretion of vagotonin by the pancreas. L. MERKLEN, C. FRANCK, and R. GRANDPIERRE (*Compt. rend. Soc. Biol.*, 1936, 121, 925—926).

R. N. C.

Absorption-spectral analysis especially as applied to vitamins and hormones. L. FUCHS (*Oesterr. Chem.-Ztg.*, 1936, 39, 43—47).—A lecture.

Vitamin content of different forms of diet. H. SCHROEDER and V. WITTMANN (*Münch. med. Woch.*, 1935, 82, 988—990).—The vitamin contents of a no. of diets are given; many are deficient in -B<sub>1</sub> and -B<sub>2</sub>, and to a lesser extent in -C, but -A and -D are seldom low.

R. N. C.

Storage of vitamin-A in the guinea-pig. A. CHEVALLIER and Y. CHORON (*Compt. rend. Soc. Biol.*, 1936, 121, 1015—1016).—Guinea-pigs cannot store vitamin-A (I) when fed with carotene (II) or with livers of (I)-deficient rats, but (I) is stored in the liver on feeding with the livers of rats fed with green vegetables. The factor transforming (II) into (I) either is not present in rat liver or cannot be utilised by the guinea-pig.

R. N. C.

Vitamin-A content of pasture plants.—See B., 1936, 346.



**Determination of vitamin-A.** J. F. WARD and R. T. M. HAINES (*Nature*, 1936, **137**, 402—403; cf. this vol., 390). L. S. T.

**Determination of vitamin-A.** ANON. (*Nature*, 1936, **137**, 383—384; cf. this vol., 390).—A summary of the Medical Research Council's report. L. S. T.

**Determination of vitamin-A in body-fluids.** M. VAN EEKELLEN (*Klin. Woch.*, 1934, **14**, 829—830; cf. Rosenthal, this vol., 253).—The  $\text{SbCl}_3$  colour reaction is sufficiently accurate to be used for vitamin-A determination. The Rosenthal reaction is only feebly sensitive and is also given by cholesterol, so that it cannot be used for determination of -A in blood. R. N. C.

**Nature of the sugar in diet and the onset of avitaminosis-A.** L. RANDOIN and S. QUEUILLE (*Compt. rend. Soc. Biol.*, 1936, **121**, 1172—1177).—No difference was noted when the sugar was varied. H. G. R.

**Relation of the vitamin-B complex to the metabolism of keto-acids.** P. E. SIMOLA (*Suomen Kem.*, 1936, **9**, B, 4).—Urine of vitamin-B-deficient rats contained an acid resembling  $\alpha$ -ketoglutaric acid. The blood also contained increased proportions of carbonyl compounds. A. G. P.

**Efficacy of fats in decreasing vitamin-B requirements.** W. D. SALMON and J. G. GOODMAN (44th Ann. Rept. Alabama Agric. Exp. Sta., 1933, 22).—The effect of various fats in delaying the onset of beri-beri is examined. CH. ABS. (p)

**Ability of vitamin-B-deficient rats to utilise d-glucose.** G. A. SCHRADER (44th Ann. Rept. Alabama Agric. Exp. Sta., 1933, 20—22).—Rats suffering from beri-beri utilise d-glucose for both heat production and glycogen formation. Comparison is made with animals receiving adequate and insufficient supplies of vitamin-B. CH. ABS. (p)

**Use of various rat assay methods in comparing crystalline vitamin-B<sub>1</sub> preparations.** F. F. HEYROTH (*Biochem. J.*, 1936, **30**, 645—650).—The potency of three cryst. vitamin-B<sub>1</sub> preps. assayed by the rat method are, in order of decreasing activity; Peters', Ohdake (rice), and Ohdake (yeast), the differences being only slightly > the limits of accuracy. The min. curative dose for the rat is 1.2 times the pigeon day dose and 6.6 times the day dose required for prevention of severe symptoms. Different vals. are obtained for curative dose adopting different criteria for marking the return of symptoms but the order of activity of the different preps. is the same with any particular criterion. P. W. C.

**Chemical nature of vitamin-B<sub>1</sub> deduced from ultra-violet absorption spectra.** F. F. HEYROTH and J. R. LOOFBOUROW (*Biochem. J.*, 1936, **30**, 651—658).—The diversity of the ultra-violet absorption spectra of vitamin-B<sub>1</sub> is attributed to reversible dissociation of -B<sub>1</sub> into an aminopyrimidine (I) derivative and a thiazole derivative and to deamination of the (I), the two processes occurring independently and to varied extents according to the conditions used. The curves of Peters and Philpot for acid EtOH solutions most nearly represent -B<sub>1</sub>, those of Holliday in neutral EtOH the result of the breaking

of the quaternary linkages of the thiazole, whilst other curves represent intermediate stages accompanied by some deamination of the pyrimidine (II). The (II) component of -B<sub>1</sub> has one  $\text{NH}_2$ , one OH, and two Me (or one Et) groups and spectroscopic evidence suggests that the OH group is probably not in the 2-position. P. W. C.

**Action of vitamin-B<sub>1</sub> on carbohydrate metabolism.** S. LAJOS (*Biochem. Z.*, 1936, **284**, 279—288).—Intraperitoneal injection of glucose + vitamin-B<sub>1</sub> into fasting rats increases liver- and muscle-glycogen, an action resembling, but more prolonged than, that of insulin. The concomitant hypoglycaemia is not so marked as that due to insulin. F. O. H.

**Vitamin-B<sub>1</sub> and -B<sub>2</sub> in growth and lactation of rats.** Effects of extracts of vitamin-B<sub>1</sub> and -B<sub>2</sub>. Distribution of vitamin-B<sub>2</sub>. J. F. FEASTER (*Iowa State Coll. J. Sci.*, 1934, **9**, 147—149).—The -B<sub>1</sub> and -B<sub>2</sub> requirements for lactation were 3—5 times those for the young growing animals. Extracts of grain, liver, and yeast were less effective than the materials themselves. CH. ABS. (p)

**Growth-promoting action of flavinphosphoric acids.** R. KUHN and H. RUDY (*Z. physiol. Chem.*, 1936, **239**, 47—48).—The growth-promoting action of synthetic vitamin-B<sub>2</sub>-phosphoric acid (I) (A., 1935, 545) is approx. equal to that of the natural material (II). Differences in the rates of hydrolysis of (I), (II), and flavinphosphoric acid from yeast could not be detected. H. W.

**Correlation between avitaminosis-B<sub>4</sub> and the composition of the diet.** C. Y. CHEN and H. ARIYAMA (*J. Agric. Chem. Soc. Japan*, 1935, **11**, 250—254).—The extraction of vitamin-B<sub>4</sub> from yeast is described. Lack of dietary fat is unrelated to avitaminosis-B<sub>4</sub>. CH. ABS. (p)

**Synthesis of vitamin-C in the organism of the suckling infant.** II. P. ROHMER, N. BEZSSONOFF, and E. STOERR (*Bull. Acad. Méd.*, 1935, **113**, 669—674).—Synthesis of vitamin-C in the infant is rendered insufficient by various pathogenic factors; the cessation of excretion of -C in the urine indicates the need for its oral administration. R. N. C.

**Synthesis of ascorbic acid in young organisms.** G. MOURIQUAND, A. COEUR, and P. VIENNOIS (*Compt. rend. Soc. Biol.*, 1936, **121**, 1005—1006).—Ascorbic acid is not synthesised in the guinea-pig foetus or the young animal. R. N. C.

**Incapacity of the animal to store reserves of vitamin-C.** P. ROHMER, N. BEZSSONOFF, and E. STOERR (*Compt. rend. Soc. Biol.*, 1936, **121**, 988—991).—Ascorbic acid (I) is fixed in an unstable condition in certain tissues in the young guinea-pig, and is rapidly eliminated in avitaminosis. (I) in the cerebrospinal fluid of suckling infants is raised by feeding with (I), but falls rapidly in avitaminosis to the level at which it is maintained by synthesis. R. N. C.

**Storage of ascorbic acid in the intestinal wall of the guinea-pig.** E. JACOBSEN (*Acta med. Scand.*, 1935, **85**, 419—424).—The intestinal vitamin-C in guinea-pigs on a diet deficient in -C falls rapidly and



parallel with -C of the liver and adrenals. Storage of -C is independent of the route of administration, and the deposition is almost  $\propto$  the dose given if this is not large. -C when given in large doses is deposited first in the intestinal wall, and is removed in about 3 hr. to the other -C depôts; intraperitoneal administration supplies the liver more rapidly than oral administration.

R. N. C.

Effect of ascorbic acid on the vegetative system and on acid-alkaline equilibrium. R. TISLOWITZ (Compt. rend. Soc. Biol., 1936, 121, 916—917).—The alkaline reserve in the dog is increased.

R. N. C.

Vitamins and water metabolism: effect of ascorbic acid on diuresis. R. TISLOWITZ (Compt. rend. Soc. Biol., 1936, 121, 914—916).—Diuresis in the dog is increased, possibly as a result of dehydration of the tissues and increased hydrophilia of the blood.

R. N. C.

Diphtheria anatoxin and vitamin-C. M. PHILIPPE and E. HARDE (Compt. rend. Soc. Biol., 1936, 121, 940—942).—The anatoxin does not affect liver- or adrenal-ascorbic acid in the guinea-pig.

R. N. C.

Vitamin-C and blood-sugar. W. STEPP, H. SCHROEDER, and E. ALTENBURGER (Klin. Woch., 1935, 14, 933—934).—Injection of ascorbic acid causes a fall of blood-sugar (I) and the action of simultaneously-injected insulin is strengthened. In many cases, particularly in diabetes, (I) is not depressed.

R. N. C.

Vitamin-C and blood. A. BÖGER and W. MARTIN (Münch. med. Woch., 1935, 82, 899—901).—Vitamin-C in large quantities increases the thrombocyte count in thrombopenia.

R. N. C.

Alleged presence of dehydroascorbic acid in blood. A. E. KELLIE and S. S. ZILVA (Biochem. J., 1936, 30, 361—368).—The view that blood converts ascorbic acid (I) into its dehydro-derivative is investigated. After treatment with  $H_2S$ , the plasma of normal, scorbutic, and (I)-injected guinea-pigs acquires the property of reducing indophenol to the same extent.  $CCl_3 \cdot CO_2H$  extracts of plasma, erythrocytes, and whole blood behave similarly but to a smaller degree. The ultra-violet absorption spectra of normal and  $H_2S$ -treated plasma are the same. It is concluded that the increased reduction of the plasma on treatment with  $H_2S$  is an artefact, and that blood with its erythrocytes intact is incapable of dehydrogenating (I) *in vivo*.

H. D.

Particularly high vitamin-C content of the cerebrospinal fluid in the prematurely and normally new-born. P. ROHMER, N. BEZSSONOFF, and E. STÖRR (Compt. rend. Soc. Biol., 1936, 121, 987—988).—The normal val. is doubled in normally, and quadrupled in prematurely, new-born children, indicating that the foetus has an ascorbic acid-synthesising power that is lost at birth.

R. N. C.

Vitamin-C in the urine of healthy and diseased men. E. GABBE (Klin. Woch., 1935, 14, 613; cf. von Drigalski, this vol., 120).—The -C val. of Drigalski is due largely to thioneine, -C being present in the non-reactive oxidised form.

R. N. C.

Vitamin-C content of the liver of new-born infants. K. U. TOVERUD (Arch. Dis. Childhood, 1935, 10, 313—318).—The average amounts were 7.01 mg. per 100 g. (full term infants) and 6.05 mg. (premature infants). The extreme variations were 2.7—10.4 mg.

NUTR. ABS. (m)

Histochemistry. VI. Quantitative distribution of vitamin-C in the small intestine. D. GLICK and G. R. BISKIND (J. Biol. Chem., 1936, 113, 427—432; cf. this vol., 530).—The amounts of vitamin-C expressed as mg. per g. of tissue in the duodenum of the cow are: mucosa 0.20, Brunner's glands 0.24, submucosa 0.10, muscle 0.06; and in the jejunum: mucosa 0.26, submucosa 0.10, and muscle 0.03.

J. N. A.

Effect of oxidases on determination of ascorbic acid. M. VAN EEKELLEN (Acta brev. neerl. Physiol., 1935, 5, 78—80).—McHenry and Graham's observation (A., 1935, 1287) that there was more titratable vitamin-C (I) in cooked than in raw vegetables is attributed to the conversion of (I) into dehydro-ascorbic acid in the fresh food by an oxidase which, however, is destroyed by cooking. This is avoided by preliminary pptn. of the sample with  $Hg(OAc)_2$  and treatment with  $H_2S$ . An analogous phenomenon occurs in blood extracts due to unavoidable oxidation of (I) by the erythrocytes.

NUTR. ABS. (m)

Determination of vitamin-C in foodstuffs.—See B., 1936, 391.

Avitaminosis-A in presence of variable amounts of vitamin-D. L. ÉMERIQUE (Bull. Soc. Chim. biol., 1936, 18, 384—389).—Whilst small quantities (> the necessary min.) of vitamin-D increase the growth and survival of rats under avitaminosis-A, larger quantities do not further improve the growth, and the period of survival is shorter.

A. L.

Total metabolism trials with rats. Influence of vitamin-D. W. SCHOCH (Bied. Zentr. [Tierernähr.], 1935, 7, B, 382—443).—Vitamin-D has no influence on energy metabolism or protein digestibility. A method of determining the net energy val. of foods is described.

A. G. P.

Dermal absorption of vitamin-D. P. S. ASTROWE and R. A. MORGEN (Amer. J. Dis. Children, 1935, 49, 912—922).—Viosterol is absorbed in effective amounts through the skin of rats.

CH. ABS. (p)

Antirachitic cow's milk. Antirachitic value of irradiated cow's milk and milk produced by cows fed with irradiated yeast. H. J. GERSTENBERGER, A. J. HORESH, A. L. VAN HORN, W. E. KRAUSE, and R. M. BETHKE (J. Amer. Med. Assoc., 1935, 104, 816—826).—No difference in efficiency was observed when fed to infants at the same vitamin-D level.

CH. ABS. (p)

Antirachitic value of hay. Vitamin-D sparing action of magnesium.—See B., 1936, 346.

Antirachitic action of irradiated cholesterol for chicks. B. SJOLLEMA and W. C. BARBAS (Bied. Zentr. [Tierernähr.], 1935, 7, B, 235—263).—Calcification in rachitic chicks (examined radiographically)



became normal within 10 days of administration of irradiated cholesterol (I) with a sufficiency of Ca. Little improvement resulted from use of (I) without Ca; with cod-liver oil (II) recovery was slower. Changes in serum-Ca and -inorg. P were similar after treatment with (I) and (II). Mineral metabolism remained disturbed until calcification of the pituitary was complete. A. G. P.

**Antirachitic action of phosphorus and of inorganic and organic phosphorus compounds.** R. LECOQ (Bull. Acad. Méd., 1935, 113, 760—767).—A review. R. N. C.

**Constitution of dihydrovitamin- $D_2$ .**—See this vol., 603.

**Vitamin-E unit.** A. J. PACINI and D. R. LINN (J. Amer. Pharm. Assoc., 1936, 25, 206—207).—A convenient expression of the val. of a vitamin-E prep. is given by dividing  $10^3$  by the no. of mg. of the prep. required daily by pregnant rats on an -E-free diet to produce a normal litter. F. O. H.

**Carbonic anhydrase and photosynthesis.** G. O. BURR (Proc. Roy. Soc., 1936, B, 120, 42—47).—The observed rate of photosynthesis by green plants is far > the rate of uncatalysed  $CO_2$  hydration. As, in addition, carbonic anhydrase cannot be detected in ground leaf tissues, it seems doubtful that  $CO_2$  must be hydrated before reacting with chlorophyll. E. A. H. R.

**Determination of rates of photosynthesis [in plants] under natural conditions.** E. BAZUIRINA and V. TSCHESNOKOV (Trav. Soc. natural. Leningrad, Sect. bot., 61, 221—247).—Investigations carried out in a current of air give the most satisfactory results. CH. ABS. (p)

**Carbon dioxide factor in photosynthesis.** V. TSCHESNOKOV and E. BAZUIRINA (Trav. Soc. natural. Leningrad, Sect. bot., 61, 323—376).—Reported increases in photosynthesis due to artificially increased  $[CO_2]$  are attributed to experimental error. CH. ABS. (p)

**Causes of liberation of large quantities of carbon dioxide in light by leaves of green plants.** V. TSCHESNOKOV, O. GRETSCHUTSCHINA, and I. JERMOLAJEVA (Trans. Soc. natural. Leningrad, Sect. bot., 61, 377—400).—Respiration intensity of leaves of *Fragaria vesca* varies from 1.0 to 20.0 mg. of  $CO_2$  per sq. dm. per hr. CH. ABS. (p)

**Factors determining winter hardiness in lucerne.** C. R. MEGEE (J. Amer. Soc. Agron., 1935, 27, 685—698).—No direct relationship was apparent between winter hardiness and the heat of wetting, swelling,  $H_2O$  equiv., f.p., composition, respiration, or rate of loss of  $H_2O$  from roots of lucerne. Inheritable factors are probably concerned. A. G. P.

**Photosynthesis of carbohydrates.** F. N. KRASHENINIKOV (Uspek. Chim., 1935, 4, 138—164).—The structure of chlorophyll and the mechanism of carbohydrate synthesis are discussed. CH. ABS. (p)

**Winter hardiness of clover. I. Effect of cutting on carbohydrate reserves in red clover roots.** A. I. VIRTANEN and M. NURMIA (J. Agric.

Sci., 1936, 26, 288—295).—Cutting causes a rapid decrease in the insol. sugar content of roots, min. vals. being reached in 12—15 days irrespective of the time of cutting. Recovery of the initial carbohydrate level is attained more quickly in autumn than in June-July. Sol. sugars are not greatly affected by cutting. A. G. P.

**Physico-chemical properties of plastid stroma and imbibition.** A. MAIGE (Compt. rend., 1936, 202, 677—679).—The mechanism of formation of starch grains in plant cells is examined. A. G. P.

**Changes in the osmotic value of the expressed sap of leaves and small twigs of *Larrea tridentata* as influenced by environmental conditions.** T. D. MALLERY (Ecol. Monog., 1935, 5, 1—35).—Changes in the osmotic pressure of leaf saps are regulated by external and not by internal factors. Seasonal, climatic, and soil factors are examined. CH. ABS. (p)

**Cell size and structure in plants as affected by various inorganic elements.** B. F. LUTMAN (Vermont Agric. Exp. Sta. Bull., 1934, No. 383, 54 pp.).—Tissue examination of various species of plants grown in mineral-deficient cultures is described. A. G. P.

**Pathological changes in plant cells caused by the action of potassium iodide: nature of the X-bodies.** K. S. SUCHOV and M. N. LANSHINA (Virus Dis. Plants, Crimea and Ukraine, 1934, 122—124).—Watering beet seedlings with 0.01% aq. KI caused necrosis and formation of intracellular inclusions resembling X-bodies found in cells of virus-infected plants. CH. ABS. (p)

**Physiological importance of mineral elements in plants. VII. Effects of potassium and chloride ions on diastase of broad bean leaves.** W. O. JAMES and M. CATTLE. **VIII. Variation in potassium content of potato leaves during the day.** N. L. PENSTON (New Phytol., 1935, 34, 283—295, 296—309; cf. A., 1934, 217).—VII. The presence of K in the nutrient effects an increase in the diastatic activity of broad bean leaves but is probably without action on the extracted enzyme.  $Cl^-$  has no action when supplied in the nutrient but markedly activates the enzyme extract. Within the plant  $K^+$  possesses greater mobility than other cations except  $H^+$  but has no appreciable influence on the distribution of  $Cl^-$ . Colloidal ppts. from extracts of plant materials usually contain diastase but frequently no  $K^+$ .

**VIII. The K content of potato leaves showed daily variations with a max. at 3—4 p.m., variations being smaller when transpiration was low. Max. K vals. correspond with max. dry wt.,  $H_2O$  content, and residual ash wt.** A. G. P.

**Plasmolysis. Influence of alkali salts on deplasmolysis of plant cells.** H. KAHN (Acta Comment. Univ. Tartu., 1934, A, 26, No. 4, 61 pp.).—The effect of ions on the rate of diffusion of  $H_2O$  through protoplasm was in the order,  $Rb > Cs > NH_4$ ;  $K > Na > Li$ , and  $SCN^- > AcO^- > Br^- > NO_3^- > Cl^-$ ; tartrate > citrate >  $SO_4^{--}$ . Salts penetrate as



ions and all plasmolytes effect reversible changes in the colloid condition of the protoplasm.

CH. ABS. (p)

**Sulphur in biology : action on cell evolution.** G. ZIRPOLO (Pontif. acad. Sci. Nov. Lyncei, Sci. Nunc. Radiophon., 1935, No. 36, 9—10).—Treatment of seed with 1% aq.  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{S}$  increased the growth of *Brassica oleracea*. Eggs of *Paracentrotus lividus* showed a negative effect. CH. ABS. (p)

**Action of glycerol on *Saprolegnia*.** F. MOREAU (Compt. rend., 1936, 202, 152—154).—*Achyla colorata* is unaffected by the presence of 3—4% of glycerol in the medium; higher concns. exert inhibitory and toxic effects, 10—20% preventing development though not causing death. W. O. K.

**Formation of nicotine in *Nicotiana* after feeding with proline.** A. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 87—90).—Klein and Linser's results (A., 1933, 1344) are incorrectly interpreted. Feeding with proline causes a decrease in the nicotine content of the plants. A. G. P.

**Effect of gonadotropic hormones on plants.** C. SERONO and A. CRUTO (Arch. ital. Biol., 1934, 91, 93—95; Chem. Zentr., 1935, ii, 391).—The growth and flowering of beans (*Vicia faba*) was not affected by manuring with gonadotropic hormone. Treated plants fruited but the controls did not. G. H. F.

**Action of sodium nitrate on infection of lucerne root-hairs by nodule bacteria.** H. G. THORNTON (Proc. Roy. Soc., 1936, 119, B, 474—492).—Secretions of nodule bacteria increase the no. of root hairs in lucerne, and stimulate and produce irregular growth of the hairs. Solutions of  $\text{NaNO}_3$  (0.1%) inhibit these effects and prevent infection of roots by bacteria. The action of  $\text{NaNO}_3$  is mitigated by addition of glucose to media. A. G. P.

**Root nodule bacteria of leguminous plants.** XVII. **Effect of air content of the medium on the development and function of the nodule (continued).** A. I. VIRTANEN and S. VON HAUSEN (J. Agric. Sci., 1936, 26, 281—287; cf. A., 1935, 787).—Growth and nodulation of peas in a N-free medium were improved by aëration. Nodulation is prevented by passing a stream of  $\text{N}_2$  through the medium. No excretion of N compounds into the medium was observed in aërated  $\text{H}_2\text{O}$ -cultures of peas. In aërated sand-cultures considerable amounts of N were excreted. A. G. P.

**Fixation of nitrogen in root nodules.** A. I. VIRTANEN and T. LAINE (Suomen Kem., 1936, 9, B, 5).—Extracts of (initially) N-free media after growth of inoculated pea seedlings contain, in addition to aspartic acid (I) and lysine, small amounts of  $\text{NO}_3^-$  probably derived from  $\text{NH}_4\text{OH}$  (II). (I) may be formed from (II) and oxalacetic acid. A. G. P.

**Excretion of nitrogenous compounds from the root nodules of leguminous plants inoculated with different strains of the nodule organism.** A. I. VIRTANEN, S. VON HAUSEN, and T. LAINE (Suomen Kem., 1936, 9, B, 5).—The amount of N excreted varies widely with the strain of the organism concerned. A. G. P.

**Carbohydrate-nitrogen relation in symbiotic nitrogen fixation.** P. W. WILSON (Wisconsin Agric. Exp. Sta. Res. Bull., 1935, No. 129, 40 pp.).—The carbohydrate-N balance in plants effects a more or less sp. response in the no., size, and distribution of nodules, the amount of N fixed, the onset and duration of the N-hunger stage, and the influence of light, fixed N, and environmental conditions. Plants are classified into five groups on the basis of differences in carbohydrate-N balance. A. G. P.

**Changes in composition of sprouting mungo seeds.** P. ROCHANAPURANANDA (Univ. Philippines Nat. Appl. Sci. Bull., 1934, 4, 127—147).—As germination proceeds the % of  $\text{H}_2\text{O}$ , ash, fat, and protein (I) increases and that of carbohydrates (II) declines. Reducing sugars appear at the second day and increase gradually accompanied by a decrease in the amount of starch. Absence of light lowers the (I) : (II) ratio. CH. ABS. (p)

**Transformation of higher fatty acids into carbohydrate during germination of pumpkin seed.** I. A. ZELLER. II. **Determination of carbohydrates.** K. ENSER (Jahrb. wiss. Bot., 1935, 82, 123—157, 158—169).—I. During the early stage of germination (4—6 days) the fatty acid content of seeds decreases and additional carbohydrates appear. Infiltration of K sorbate also increases starch formation in the seedlings. The normal decomp. of starch in seedling autolysates is retarded by  $\beta$ -hydroxybutyric, succinic, or lactic acid, and is reversed to a starch-forming process by  $\text{AcOH}$ ,  $\text{MeCHO}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , sorbic acid, or  $\text{AcCO}_2\text{H}$ . The bearing of these results on the fatty acid  $\rightarrow$  carbohydrate change is discussed.

II. Detailed carbohydrate data from the above experiments are recorded and discussed. A. G. P.

**Plant respiration.** VI. **Relation of respiration of potatoes to the concentration of sugars and to the accumulation of a depressant at low temperatures.** [iii]. **Relation of respiration to concentration of sucrose.** J. BARKER. [iv]. **Relation between respiration in air and in nitrogen of certain seeds in which carbohydrates constitute the chief food reserve.** W. LEACH (Proc. Roy. Soc., 1936, B, 119, 453—473, 507—521).—VI. [iii]. The forms of the respiration/glucose, respiration/fructose, and respiration/total sugar relations vary widely with the sucrose (I)/hexose (II) quotient during sweetening and desweetening. On the other hand the respiration/(I) relation in these stages and also while the (I)/(II) quotient was changing conformed closely with the enzymic rectangular hyperbola for the rate of reaction/substrate relation for an enzyme reaction *in vitro*. These results are interpreted as showing that (I) is closely related to the substrate supply for respiration and that neither glucose nor fructose is associated with this function. In samples of low sugar content the (I)/(II) quotient is markedly affected by changes of temp. (cf. A., 1933, 435).

VI. [iv]. During anaerobiosis carbohydrate-storing seeds (like oil seeds) accumulate an easily oxidisable substance, which is rapidly respired during subsequent exposure of the seeds to  $\text{O}_2$ . Transference of seeds from air to an atm. of  $\text{N}_2$  decreases  $\text{CO}_2$  production



to 33% as is to be anticipated if (II) is then only partially oxidised to  $\text{CO}_2$  and  $\text{EtOH}$ . The mechanism of respiration is discussed (cf. A., 1934, 1271).

A. G. P.

Influence of heteroauxin on growth of root hairs and roots of *Agrostemma githago*, L. A. MEESTERS (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 91—97).—Root hairs are less sensitive than roots to the growth-inhibiting action of heteroauxin (I). Solutions of  $\text{AcOH}$  having the same  $p_H$  as that of (I) show no inhibitory action. (I) does not produce chemotropic curvature in root hairs.

A. G. P.

Synthesis of  $\delta$ -3-indolylvaleric acid. Effects of indole acids on plants.—See this vol., 612.

Factors affecting the formation of local lesions by tobacco mosaic virus. J. CALDWELL (Proc. Roy. Soc., 1936, B, 119, 493—507).—The action of trypsin in preventing virus infection is due to its effect on the virus rather than on the plant. Horse serum and  $\text{AgNO}_3$  produce similar effects.

A. G. P.

Mineral matter of certain leguminous crops.

I. Inorganic constituents of underground parts.

II. Nodule formation and titanium supply. K.

KONISHI and T. TSUGE (Mem. Coll. Agric. Kyoto, 1936, No. 37, 1—24, 24—35).—I. Spectrographic detection of traces of Li, Sr, Cr, Zn, Ni, Cu, Co, V, Mo, Bb, and B is recorded. Ba, Mn, and Ti were present in somewhat larger amounts. The Ti content of nodules was  $>$  that of roots. In acid-tolerant species (lupins, serratella, and soya bean) the P content of nodules was  $>$  that of roots, but in lucerne, clover, and other acid-sensitive species the nodules contained more Na and Ca. No differences in the % of other secondary elements in roots and nodules were apparent.  $\text{K}_2\text{TiO}_3$  and  $\text{Ti}(\text{SO}_4)_2$  increased nodulation and crop yields, the effective range of concn. of the latter being  $<$  that of the former.

A. G. P.

Variations in the contents of some of the constituents of the ash of potatoes. H. STEUDEL (Deut. med. Woch., 1935, 61, 872).— $\text{P}_2\text{O}_5$  and  $\text{SO}_3$  show considerable oscillations.

R. N. C.

Comparative boron contents of plants grown in the same soil. G. BERTRAND and H. L. DE WAAL (Compt. rend., 1936, 202, 605—609).—The B contents of several plant species varied considerably. A general relationship is probable between the capacity of a species to accumulate B and its position in the botanical classification.

A. G. P.

Comparative sulphur and nitrogen contents of plants grown in the same soil. G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1936, 202, 261—264; cf. this vol., 395).—The N content of a wide variety of plants ranges from 2.04 to 5.32%. The S/N ratio is probably closely related to the quantities of  $\text{SO}_4^{--}$  used as fertiliser.

J. L. D.

Nitrogen distribution in tea. W. S. SHAW (United Planters Assoc. S. India, Bull. 7, 1934, 3 pp.).—No  $\text{H}_2\text{O}$ -sol. protein is present, 50—75% of the sol. N occurring as caffeine. The insol. N (40—47% of the total) occurs mainly as glutelin.

P. G. M.

Determination of sugars in the leaf of the mangold (*Beta vulgaris*). I. Fructose, glucose,

and sucrose. II. Use of basic lead acetate, charcoal, and yeast to avoid interference by substances other than sugars. III. Application of copper reagents to unclarified extracts. IV. Tests for raffinose, maltose, galactose, and pentose. J. E. VAN DER PLANK (Biochem. J., 1936, 30, 457—483).—I. The method of Harding and Downs (A., 1933, 964) has been modified to give reproducible results. Fructose (I) is determined, after oxidation of glucose (II) by alkaline I and removal of excess of I, by Cu or  $\text{Fe}(\text{CN})_6^{--}$  reagents. For determining sucrose (III), the sugar is inverted by invertase in conc. solution and the actual determination carried out after dilution, to minimise the reducing effect of the invertase.

II. In unclarified extracts, (III) is determined without interference; with the Cu reagent the error occurs in the determination of (II) and with the  $\text{Fe}(\text{CN})_6^{--}$  reagent in that of (I) and (II). Clarification is best carried out with dibasic Pb acetate after concn. and without neutralisation to avoid loss of (II), avoiding washing of the ppt.;  $\text{Na}_2\text{HPO}_4$  is used for removing excess of Pb. Yeast in conjunction with the Cu reagent may be used to allow for interfering matter in unclarified extracts and an empirical correction factor for this is given. The use of C for clarification is not recommended.

III. With a high concn. of impurities, the solution must be diluted before analysis.

IV. Raffinose, maltose, galactose, or pentoses could not be detected in extracts by selective fermentation.

H. G. R.

Determination of reducing sugars and sucrose in plant materials. W. Z. HASSID (Ind. Eng. Chem. [Anal.], 1936, 8, 138—140).—Small amounts of sugars are determined in plant extracts by treating the clarified and decolorised solution with excess of alkaline  $\text{K}_3\text{Fe}(\text{CN})_6$  solution and titrating the excess, after oxidation, with  $\text{Ce}(\text{SO}_4)_2$  (o-phenanthroline- $\text{FeSO}_4$  as indicator). The method is rapid and accurate over a wide range and gives slightly higher results than the Munson-Walker Cu method. Sucrose, if present, is hydrolysed by invertase before oxidation.

S. C.

Crystalline d-galacturonic acid from tobacco.—See this vol., 591.

Occurrence of amygdonitrileglucoside in the genus *Cotoneaster*, and in the leaves of *Cydonia vulgaris*, Pers. V. PLOUVIER (Compt. rend., 1936, 202, 352—354; cf. A., 1935, 1181).—Determinations of the glucose/HCN ratio in many species of *Cotoneaster* show that the HCN is usually, although not always, present as amygdonitrileglucoside (I). Amygdaloside probably occurs in some species. The prulaurasoside isolated by Hérissé (A., 1906, i, 31) is probably formed during its isolation. Leaves of *Cydonia vulgaris* also afford (I).

J. L. D.

Comparative velocities of hydrolysis of certain glucosides under the influence of ultra-violet rays, acids, and enzymes.—See this vol., 572.

Determination of starch in plant tissues. G. W. PUCHER and H. B. VICKERY (Ind. Eng. Chem. [Anal.], 1936, 8, 92—97).—The sample is dried rapidly



at 70–80°, extracted completely with 75% EtOH, redried, and finely milled. Starch (I) is then extracted with either 21% HCl at 20–22°, or with 46% aq.  $\text{CaCl}_2$  at 100°. After adjusting the acidity, (I) is pptd. with KI–I solution, the ppt. separated, decomposed with NaOH–EtOH, and (I) isolated by centrifuging. (I) is finally converted into starch–I and the colour measured in a Pulfrich spectrophotometer, calibrated with potato starch standards. The HCl method of extraction is preferred since aq.  $\text{CaCl}_2$  may destroy (I) especially at higher temp. in presence of traces of acid.  $\text{CaCl}_2$ -extracts will not keep but HCl-extracts are stable for long periods at 0°. Results are < those obtained by hydrolysis–sugar-reduction methods, but more trustworthy. The method is very sp. and results are accurate to 3% with 1–3 mg. of (I) and to < 10% with 0.1 mg. S. C.

**Fruit of *Lagenaria vulgaris*, Seringe (bitter variety).** I. Constituents of the oil from the seeds. R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934–1935, 5, 227–233).— $\text{C}_6\text{H}_6$  extracts an oil (19.1%) which when hydrolysed (EtOH–KOH) affords, in nearly equal proportions, saturated (palmitic, stearic, and arachidic) and unsaturated (oleic and linoleic) acids. The unsaponifiable material (2%) is sitosterol. J. L. D.

**Seeds of *Hygrophyla spinosa*.** N. L. PHALNIKAR, K. S. NARGUND, and D. D. KANGA (J. Univ. Bombay, 1935, 4, Part II, 146–152).—The seeds contain an oil giving, when hydrolysed, 25% of solid (myristic 5.5, palmitic 73, and stearic 21.4%) and 75% of liquid acids (di- and mono-unsaturated), and containing 7.5% of unsaponifiable matter, including a little of a substance, m.p. 114–115°. R. S. C.

**Crystalline constituent of essential oil of matsubasa (*Shizandra nigra*, Maxim.).** I. T. SENGOKU (J. Pharm. Soc. Japan, 1933, 53, 947–951).—The substance  $\text{C}_{13}\text{H}_{26}\text{O}$ , m.p. 28°, is *Me undecyl ketone*, which is also prepared by dry distillation of Ba laurate and  $\text{Ba}(\text{OAc})_2$ . CH. ABS. (p)

**Chemistry of slash-pine (*Pinus caribaea*, Morelet).** II. Fats, waxes, and resins of the growing tips. J. A. HALL and O. GISVOLD (J. Biol. Chem., 1936, 113, 487–496; cf. A., 1935, 864).—A light petroleum extract of the young growing tips yielded paraffins ( $\text{C}_8$ – $\text{C}_9$ ),  $\alpha$ -pinene, melissic, palmitic, behenic, oleic, linoleic, and abietic acids, melissyl alcohol, *n*-nonacosan- $\kappa$ -ol, a sitosterol, and a sitosterolin. H. D.

**Isolation of carotene and sterols from the unsaponifiable matter of cocksfoot.** A. POLLARD (Biochem. J., 1936, 30, 382–386).—The unsaponifiable fraction of the light petroleum extract of dried cocksfoot contains carotene (only the  $\beta$ -isomeride), xanthophyll, and sterols consisting chiefly of sitosterol; ergosterol was separated as ergopinacol (acetate, m.p. 204°). H. D.

**Pigmentation of the ripening gourd blossom.** II. L. ZECHMEISTER, T. BÉRES, and E. UJHELYI (Ber., 1936, 69, [B], 573–574; cf. A., 1935, 1180).—The isolation of *petaloxanthin* (I),  $\text{C}_{40}\text{H}_{58}(\text{O})_3$ , m.p. 211–212° (corr.) in oil-bath, m.p. 202° (Berl), from the portion of the crude carotenoids most

sparingly sol. in  $\text{CS}_2$  is described. In m.p., spectroscopic behaviour, solubility, colour, and cryst. form (I) is nearly identical with antheraxanthin (Karrer *et al.*, this vol., 239) but chromatographic analysis with  $\text{Ca}(\text{OH})_2$  in  $\text{C}_6\text{H}_6$  shows the pigments to be distinct from one another. H. W.

**Flower colouring by a membrane pigment in *Leonotis*.** L. GEITLER (Oesterr. bot. Z., 1934, 83, 284–287; Chem. Zentr., 1935, ii, 871).—The orange-red colour of the flower crown of *L. leonurus* is conditioned exclusively by a membrane pigment which is neither anthocyanin nor carotenoid. A. G. P.

**Extraction and separation of the chlorophyll pigments.** H. M. JENNISON and L. M. COOLEY (J. Tennessee Acad. Sci., 1934, 9, 273–277).—Details of the separation of carotene, xanthophyll, and  $\alpha$ - and  $\beta$ -chlorophyll are given. CH. ABS. (p)

**Distribution of pigments in the testa of some varieties of soya beans.** V. G. ALEXANDROV and O. G. ALEXANDROVA (Bull. appl. Bot. U.S.S.R., 1934, Ser. 3, No. 4, 3–47).—The basic type of pigmentation consists of an anthocyanin (I) blue pigment in the cell juice and chlorophyll in plastids. Yellow cell walls contain phlobaphen. Absence of colour in the cell may result from total absence of the chromogene or the presence of a colourless isomeride of the (I) pigment. CH. ABS. (p)

**Fukugetin, the colouring matter of the bark of "Fukugi."**—See this vol., 610.

**Constituents of *Hydrangea paniculata*.** Hydragin. A. HASHIMOTO and T. KAWANA (J. Pharm. Soc. Japan, 1935, 55, 183–186).—Extraction of the dried flowers with  $\text{C}_6\text{H}_6$  affords *hydragin* (I),  $\text{C}_9\text{H}_6\text{O}_3$ , m.p. 224° (*Me ether*, m.p. 114°). A compound apparently identical with (I) is obtained from malic acid, resorcinol, and conc. HCl. CH. ABS. (r)

**Occurrence of furan derivatives in volatile oils.** III.  $\beta$ - and  $\gamma$ -Clausenan.—See this vol., 611.

**Telfairic acid.**—See this vol., 590.

**Existence of *d*-catechin in the bark of the peach tree.** A. M. COLLOT and J. RABATÉ (Compt. rend., 1936, 202, 1208–1210).—EtOH or Et<sub>2</sub>O extracts about 2% of *d*-catechin [ $\text{Ac}_5$ , m.p. 131°, and  $\text{Bz}_5$  derivatives, m.p. 165° (cf. A., 1921, i, 576)]. J. L. D.

**Aroma of tea.** W. S. SHAW (United Planters Assoc. S. India, Bull. 8, 1934, 12 pp.).—Evidence is given in support of the theory that oxytheotannin is largely responsible for the aroma of tea. P. G. M.

**Pectic substances in tea.** W. S. SHAW (United Planters Assoc. S. India, Bull. 6, 1934, 20 pp.).—The green leaf contains a smaller amount of  $\text{H}_2\text{O}$ -sol. pectin (I) (1.65% as Ca pectate) than most other leaves, but the  $\text{H}_2\text{C}_2\text{O}_4$ -sol. (I) content (4.91%) is > that of any except the potato leaf. Black tea contains a greater % (31.0) of the total as  $\text{H}_2\text{O}$ -sol. (I) than does the green leaf (25.3). (I) protects the theotannin from pptn. by salts of heavy metals during infusion and allows the formation of the caffeine salt. P. G. M.

**Constituents of *Dicranopteris glauca*, Nakai.**—See this vol., 610.



**Umbauba** ("imbauba"), *Cecropia peltata*. E. T. DA FONSECA (Rev. flora med., 1935, 1, 289—296).—The active principle of the leaves is a toxic saponin resembling ambain. No alkaloid is present.

CH. ABS. (p)

**Artemisia rigida** (Nutt.), Gray. H. C. VINCENT and R. L. McMURRAY (Amer. J. Pharm., 1936, 108, 107—109).—The flowering plants and leaves of this shrub give with ligroin 5.02, Et<sub>2</sub>O 3.51, dry EtOH 17.78, and 1% HCl 3.63% of extract (calc. on dry wt.), and yield 14.4% of ash (sand 10.55, SiO<sub>2</sub> 11.59, P<sub>2</sub>O<sub>5</sub> 4.57, Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub> 3.95, CaO 17.55, MgO 6.38, Cl 2.09, and SO<sub>3</sub> 8.67%). The roots contain inulin. Santonin is absent.

R. S. C.

**Action of *Nuphar luteum* on the heart.** M. BULAJEWSKI (Wiadom. farm., 1935, 62, 15—18, 29—32, 43—47, 52—62; Chem. Zentr., 1935, ii, 552).—Nymphalin (I) is present in *N. luteum*, and is obtained pure by crystallisation of an EtOH extract at -10° to -15°, dissolving in org. media, and freezing out. It is pptd. by NaCl from the EtOH extract together with wax, which is removed by saponification. The cryst. (I), m.p. approx. 40°, gives a violet colour with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>OH and H<sub>2</sub>SO<sub>4</sub> and reduces Fehling's solution after hydrolysis. It occurs in the flowers and sap, but not roots, of *N. luteum*.

R. N. C.

**Mexican poppy, *Argemone mexicana*, L.** O. DE ALMEIDA (Rev. flora med., 1935, 1, 271—282).—The poppy contains protopine and berberine, but no morphine.

CH. ABS. (p)

**Punarnava or *Berhaavia diffusa*, Linn.** II. Isolation of punarnavine. R. R. AGARWAL and S. DUTT (Proc. Acad. Sci. Agra and Oudh, 1934—35, 5, 240—242; cf. this vol., 533).—Boiling EtOH extracts berhaavic acid and punarnavine (0.01%), m.p. 235° (decomp.) after sintering at 187° (hydrochloride, m.p. 135°), which exhibits many colour reactions of alkaloids.

J. L. D.

**Toxic principle of ragwort (*Senecio Jacobaea*, L.).** I. J. R. HOSKING and C. W. BRANDT (New Zealand J. Sci. Tech., 1936, 14, 638—644).—An alkaloid C<sub>18</sub>H<sub>25</sub>O<sub>6</sub>N is isolated. It is probably jacobine (A., 1932, 286) and is considered to be the cause of Winton disease. No saponins are present.

A. G. P.

**Alkaloids of Chinese gelsemium, Ta-Ch'a-Yeh.**—See this vol., 618.

**Alkaloids of *Senecio* species.**—See this vol., 617.

**Alkaloids of *Sinomenium* and *Cocculus*.**—See this vol., 491.

**Fractionation of barley and malt proteins.** R. C. ROSE and J. A. ANDERSON (Canad. J. Res., 1936, 14, C, 109—116).—The suitability of 5% aq. K<sub>2</sub>SO<sub>4</sub> for the separation of albumin and globulin from the less sol. proteins is confirmed. The insol. protein is probably a complex, only a portion of which is sol. in 70% EtOH. Use of the latter for fractionation of the complex is purely arbitrary. Malting produces no appreciable change in the proteins of hulls. In the kernel there is a general breakdown of protein. In the acrospire, non-protein-N, salt-sol. protein, and glutelin increase, the hordein

remaining practically unchanged. The glutelin of the acrospire and that of the kernel differ in amide- and arginine-N.

A. G. P.

**Micro-determination of morphine in urine, blood, and other biological fluids.** W. DECKERT (Arch. exp. Path. Pharm., 1936, 180, 656—671).—The method depends on determining the turbidity produced by aq. morphine (I) with (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>·(NH<sub>4</sub>)<sub>3</sub>VO<sub>4</sub> and is applicable to 1—10 c.c. of urine or blood. After addition of NaHCO<sub>3</sub>, (I) is extracted from tissue-fluids etc. by EtOAc or HCO<sub>2</sub>Et. The urine of men receiving daily 0.015 g. of (I) contains determinable (accuracy  $\pm 10\%$ ) amounts of (I).

F. O. H.

**Chemical composition of *Aconitum napellus* and physiological evaluation of standardised dry extracts.** R. FREUDWEILER (Pharm. Acta Helv., 1935, 10, 51—58; Chem. Zentr., 1935, ii, 883).—A physiological method, based on toxicity to guinea-pigs, is preferred to chemical methods.

H. N. R.

**Pharmacological evaluation of *Allium* preparations.** U. HINTZELMANN (Fortschr. Ther., 1935, 11, 359—361; Chem. Zentr., 1935, ii, 883).—The method is based on the observation that garlic preps. prolong the life of mice given a lethal dose of vigantol.

H. N. R.

**Self-sealing vessels for storage of solutions used in the Van Slyke gasometric methods.** F. E. HOLMES (J. Biol. Chem., 1936, 113, 411—415).—The two vessels described eliminate the glass stop-cock in the alkaline stream of the vessel used by Van Slyke, *et al.* (A., 1933, 1314) and the modified Hempel pipette, and also provide an automatic Hg seal for the tip of the delivery tube of the Guest-Holmes vessel (A., 1935, 1218).

J. N. A.

**Determination of ethyl alcohol in body-fluids.** H. NEWMAN (J. Pharm. Exp. Ther., 1936, 56, 278—283).—1 mg. of EtOH may be determined in body-fluids with an error of 1.5% by vac. distillation into K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> and titration of the unoxidised K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with KI and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

H. D.

**Aluminium. I. Colorimetric determination of aluminium in biological material.** D. F. EVELETH and V. V. MYERS (J. Biol. Chem., 1936, 113, 449—465).—Al is determined in tissues by dry ashing, pptn. of the Al and Fe as phosphates, separation of these by means of NaOH, NH<sub>4</sub>CNS, or cupferron, and then colorimetrically with alizarin or aurin. Alizarin gave higher vals. in tissue digests than aurin due to the presence of Ca and interfering substances.

H. D.

**Micro-determination of titanium in the organism by extraction and photometry.** L. MAILLARD and J. ETTORI (Compt. rend., 1936, 202, 594—596).—The ashed tissue, dissolved in 5% H<sub>2</sub>SO<sub>4</sub>, is treated in presence of Fe with nitrosophenylhydroxylamine (I). The ppt. is dissolved in H<sub>2</sub>SO<sub>4</sub>, Fe removed by H<sub>2</sub>S, and the solution re-pptd. by (I) in presence of Zr, Ti being determined in the ppt. by oxidation with H<sub>2</sub>O<sub>2</sub> and photometric examination of the TiO<sub>3</sub> formed. Muscle and blood contain approx. 8 and 3  $\times 10^{-6}$  g. per 100 g., respectively.

J. N. A.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JUNE, 1936.

### General, Physical, and Inorganic Chemistry.

Excitation of the hydrogen lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  by ultra-short electric waves. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1936, 12, 1—3).—Excitation of  $H_2$  in an electrodeless tube by means of 20-cm. waves, obtained from a magnetron, or for higher power a triode, is described. The method produces a steady excitation, without the presence of the Stark effect, and the fine structure of the lines can be readily photographed. A. J. M.

Limits of the continuous spectrum and line intensities for helium. H. O. JANKO (Z. Physik, 1936, 99, 169—188).—Spectral and probe electron energy measurements in the plasma of the He discharge indicate exchange interaction of highly excited neutral atoms with electrons in addition to ordinary recombination. A. B. D. C.

Paschen-Back effect. III.  $2S^2P$  multiplets in strong fields. IV. Mutual spin-orbit interaction in two-electron spectra. J. B. GREEN and R. A. LORING (Physical Rev., 1936, [ii], 49, 630—632, 632—634; cf. A., 1934, 137).—III. The theory is discussed and verified experimentally. The  $2S^2P$  multiplet of Li  $\lambda$  6708 was resolved in reversal and showed the fine structure predicted but not previously observed.

IV. Investigations for the Be triplet  $\lambda$  3321  $3P^3S$  gave patterns in good agreement with calculations which take account of the interaction between the spin of one electron and the orbit of the other. N. M. B.

Magnetic moment of  ${}^6\text{Li}$ . H. SOHÜLER and T. SCHMIDT (Z. Physik, 1936, 99, 285—287).—Assuming the mechanical moment to be 1, the magnetic moment is 0.6 nuclear magnetons. A. B. D. C.

Magnetic moment of the  ${}^7\text{Li}$  nucleus. J. H. BARTLETT, jun., and J. J. GIBBONS, jun. (Physical Rev., 1936, [ii], 49, 552).—The val. calc. from wave functions for Li is 4.58, disagreeing with 3.28 and 3.20 as calc. from experimental data (cf. Fox and Rabi, this vol., 1). N. M. B.

Absorption spectra of oxygen due to interaction forces. I. Absorption bands of the ( $\text{O}_2\text{-O}_2$ ) molecule. H. SALOW and W. STEINER (Z. Physik, 1936, 99, 137—158).—Bands observed between 6299 and 3150 Å. have been ascribed to ( $\text{O}_2\text{-O}_2$ ) mols. or collision pairs; they have been so allocated because of the variation of their shape and intensity with pressure between 40 and 160 atm., and foreign gas pressures up to 100 atm. A. B. D. C.

Stark effect in neon. W. STEUBING and H. KINDLER (Z. Physik, 1936, 99, 103—108).

A. B. D. C.

Mean lifetime of metastable neon atoms. E. W. PIKE (Physical Rev., 1936, [ii], 49, 513—515).—The concn. as a function of illumination intensity of excited atoms in the Townsend discharge in Ne, illuminated with red light from an auxiliary discharge in Ne, is computed from the electronic properties of Ne. The mean lifetimes of the metastable and resonance states are evaluated by comparison with direct measurements. N. M. B.

Penning's "new photo-effect" in pure neon. E. W. PIKE (Physical Rev., 1936, [ii], 49, 515—518; cf. preceding abstract).—The maintaining voltage of a Townsend discharge in pure Ne, measured as a function of the illumination of the discharge with light from a Ne arc, was, in contrast to the case for slightly impure Ne, almost insensitive to illumination over a wide range of pressure, current, tube form, and cathode material. With progressive cleaning of the gas the change in maintaining voltage passed from a small positive val. through zero to a small negative val. N. M. B.

Extinction of fluorescence of sodium. V. KONDRATEEV and M. SISKIN (Physikal. Z. Soviet-union, 1936, 8, 644—666).—The effect of various gases ( $\text{A}$ ,  $\text{N}_2$ ,  $\text{NO}$ , and  $\text{O}_2$ ) on the extinction of the  $D$  fluorescence of Na has been investigated. The effective cross-section, characteristic of the extinction capacity, of  $\text{A}$  was independent of the energy ( $e$ ) of the Na atoms within wide limits. In the case of  $\text{N}_2$  and  $\text{NO}$  there is dependence on  $e$  which is connected with the existence of two types of photochemical breakdown of the NaI vapour used for the fluorescence. The greatest extinction effect is given by  $\text{NO}$  and  $\text{O}_2$ ; this is not connected with the fact that with these mols. there is a resonance between the vibrational energy of the mols. and the energy of electron excitation of Na, but it is suggested that the principal factor determining the effectiveness of a gas in extinguishing the fluorescence is the chemical force of interaction between the mols. A. J. M.

A-Bands of sulphur. E. OLSSON (Z. Physik, 1936, 99, 114—118).—Predissociation limits were observed at 2825 Å. Odd rotation levels are absent from the ground state, indicating zero nuclear spin. A. B. D. C.

Polarisation of resonance radiation from calcium and the effect of weak magnetic fields.



A. STEINHÄUSER (Z. Physik, 1936, 99, 300).—Corrections (cf. A., 1935, 1183). A. B. D. C.

**Na I-like spectra of the elements titanium to copper (Ti XII—Cu XIX).** B. EDLÉN (Nature, 1936, 137, 531—532).—Using an improved vac. spark spectrograph, the outstanding lines of the K I- and A I-like spectra have been revealed in the spectra of the elements from Ti to Zn XII and XIII. Lines belonging to Na I-, Mg I-, and Al I-like spectra have also been identified, those of Na I being the most intense and complete. The two most persistent transitions  $3d^2D-4f^2F$  and  $3p^2P-4d^2D$  have been traced through Cu XIX. L. S. T.

**Iron arc spectrum in the infra-red.** N. R. TAWDE and V. S. PATANKAR (J. Univ. Bombay, 1935, 4, Part II, 65—69).—66 lines of the Fe arc in air have been measured in the region 7937—10,216 Å. and compared with previous data. J. W. S.

**Spectroscopic investigation of discharges at high gas pressure.** W. W. WATSON and G. F. HULL, jun. (Physical Rev., 1936, [ii], 49, 592—596).—Spectra of high-energy discharges between Cu, Al, C, Mg, In, and Be electrodes in  $N_2$ ,  $O_2$ ,  $H_2$ , and He at pressures up to 15 atm. were examined at high dispersion. With the continuous spectrum background, absorption bands due to AlH, MgH, BeO, and CN were observed. Data for broadening and shift, in each case to the red, and for the pressure-broadening of the Al resonance lines are given. The breadths and shifts of the emission lines are attributed mainly to interat. Stark effect and slight resonance broadening, and the contours and pressure shifts of the self-reversals correspond with those due to van der Waals forces between Al atoms and gas mols. N. M. B.

**Polarisation of the radiation  $\lambda = 2139$  Å. emitted by optical resonance of an atomic beam of zinc.** P. SOLEILLET and S. NIKITINE (Compt. rend., 1936, 202, 1046—1047).—In a magnetic field of 0.53 gauss in the direction of the exciting ray 2139 Å. the radiation emitted by an at. beam of Zn at right angles to the exciting ray is 74% polarised. R. S. B.

**New system of bands of  $Se_2$  in the red.** B. ROSEN and F. MONFORT (Bull. Acad. roy. Belg., 1936, [v], 22, 215—218).—The new system, ranging from 16,706—14,842  $cm^{-1}$ , has the same upper level as the principal system  $^1\Sigma-^2\Sigma$ . The lower level is at approx. 9250  $cm^{-1}$  above the normal of the  $Se_2$  mol. A. J. M.

**Spectrum of selenium in the red and photographic infra-red.** B. ROSEN and F. MONFORT (Physica, 1936, 3, 257—265).—The emission bands on the long- $\lambda$  side of the main  $^1\Sigma-^1\Sigma$  system of  $Se_2$  have been investigated. The results are discussed in relation to the heat of dissociation of  $Se_2$ . A new band system in the red is recorded. L. J. J.

**Origin of the broad bands in selenium and tellurium vapours.** B. ROSEN, M. DÉSIRANT, and L. NEVEN (Nature, 1936, 137, 498).—Broad bands observed in the absorption spectra of  $Se_2$  and  $Te_2$  for temp. up to 1000° confirm the interpretation previously given (A., 1935, 1291). L. S. T.

**Fluted bands of tellurium vapour.** M. DÉSIRANT and A. MINNE (Compt. rend., 1936, 202, 1272—1273).—The broad bands of  $Te_2$  at  $\lambda > 5250$  Å. consist of two series extending to 6100 Å. and 6500 Å., respectively. The bands are due to transitions between an electronic state with an ill-defined min., and the higher vibrational levels of the ground state. L. J. J.

**Magnetic moment of the nucleus and hyperfine structures in the spectrum of doubly ionised antimony; structure of the arc line 3723.** J. S. BADAMI (J. Univ. Bombay, 1935, 4, Part II, 86—93).—The hyperfine structures of two doublets of the Sb III spectrum have been measured. After reclassification of the terms of this spectrum by interchanging  $6s^2S$  and  $5s5p^2S$  terms, a val. of approx. 2.7 proton-magneton is obtained for the magnetic moment of the  $^{121}Sb$  nucleus. The structure of the 3723 Å. line is interpreted, taking the mechanical moment of the nucleus as  $(5/2)h/2\pi$  for both isotopes. J. W. S.

**Spectrum of doubly-ionised antimony.** S. G. KRISHNAMURTY (Indian J. Physics, 1936, 10, 83—90).—The analysis of the spectrum of Sb II due to Lang and Vestine (A., 1933, 2) has been modified and extended. A. J. M.

**Nuclear spin of iodine from the spectrum of  $I_2$ .** L. A. STRAIT and F. A. JENKINS (Physical Rev., 1936, [ii], 49, 635; cf. Tolansky, this vol., 262).—Measurements of the alternating intensities in the mol. spectrum confirm the val. 5/2 for the nuclear spin. N. M. B.

**F-Terms of Ce IV.** R. J. LANG (Physical Rev., 1936, [ii], 49, 552).—Preliminary data for the terms are given. N. M. B.

**Hyperfine structure of platinum isotopes. I. Isotopes of platinum and their centre of gravity.** (FRL.) B. JAECKEL and H. KOPFERMANN (Z. Physik, 1936, 99, 492—502).—Four isotopes, 194, 195, 196, and 198, are present in the intensity ratio 10 : 9 : 7 : 2.  $^{195}Pt$  has mechanical moment  $\frac{1}{2}$ . A. B. D. C.

**Effect of added inert gas on the high-pressure mercury discharge.** W. ELENBAAS (Physica, 1936, 3, 219—236).—The extra energy loss is due to an increase in heat conduction caused by the presence of inert gas atoms. L. J. J.

**Zeeman effect of the hyperfine structure components of the mercury resonance line 2537 Å.** A. ZVIRONAS (Nature, 1936, 137, 531). L. S. T.

**Application of the theory of the coherence of vibrations.** P. SOLEILLET (Compt. rend., 1936, 202, 1167—1168).—Theoretical. Polarisation of some excited Hg lines is considered. M. S. B.

**Theory of pressure-broadening of spectral lines.** E. GORA (Proc. Indian Acad. Sci., 1936, 3, A, 272—284).—Coupling between the energy levels of excited atoms and the virtual oscillators which determine the dispersion of the perturbing gas leads to a relation between the refractive index of the latter and the red shift of spectral lines. Other interactions affect width and violet shift. L. J. J.

**Pressure effects in band spectra.** H. MARGENAU (Physical Rev., 1936, [ii], 49, 596—597).—



A simple theory of pressure effects due to foreign perturbing mols. without permanent polarity shows that shift and broadening are similar to those in the case of at. lines as a result of van der Waals interactions. Calculations and formulæ for models of a rigid rotator and simple harmonic oscillator show that the effects are almost independent of vibrational and rotational quantum nos.

N. M. B.

**Mechanism in the positive column of a discharge.** L. S. ORNSTEIN, H. BRINKMAN, and T. HAMADA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 315—324).—Theoretical. The shapes of the intensity curves for the bands of  $N_2$  and  $N_2^+$  over the tube radius are discussed.

R. S. B.

**A-Type doubling in  $^3\Pi$  states of diatomic molecules intermediate between Hund's cases a and b.** M. H. HEBB (Physical Rev., 1936, [ii], 49, 610—618).—Mathematical.

N. M. B.

**Temperature of helium in the high-frequency discharge.** J. ROIG (Compt. rend., 1936, 202, 1044—1046).—The temp. of He at 0.57—0.93 mm. in a high-frequency discharge running at 1760—2160 volts with  $\lambda=14$  m. is 187—250° as measured by an air thermometer. Calc. and observed interferometric measurements agree approx.

R. S. B.

**Helium-tungsten arc.** O. STÜBING (Helv. phys. Acta, 1935, 8, 165—196; Chem. Zentr., 1935, ii, 980).—Relations between current, voltage, arc length, and pressure have been investigated between 11 and 500 mm. pressure.

J. S. A.

**Preliminary stages of spark formation in various gases by the use of the Wilson chamber.** U. NAKAYA and F. YAMASAKI (Proc. Roy. Soc., 1936, A, 153, 542—554).—Using a modification of the previous apparatus (A., 1935, 557), cloud photographs have been taken of sparks in  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $H_2$ , NO, and in air mixed with small amounts of org. vapours. The form and structure of the preliminary discharge are different for different gases, each gas showing a characteristic feature peculiar to itself.

L. L. B.

**Production of metallic spectra by shock waves.** H. MURAOUR and A. MICHEL-LEVY (Compt. rend., 1936, 202, 949—950).—Line spectra of various metals were excited by the passage of a shock wave from the detonation of a mixture of  $C(NO_2)_4$  and PhMe through A containing the metal or its oxide in suspension. They resembled the spark spectra.

H. J. E.

**Structure of the spark striking to the surface of a solution.** P. JOLIBOIS (Compt. rend., 1936, 202, 400—402; cf. A., 1935, 831).—When a spark is passed between a Pt electrode and aq.  $CuSO_4$  (10%) with the Pt positive, the latter becomes very hot, and the spectrum contains only the first and second negative bands of  $N_2$  and the 3064 Å.  $H_2O$  band. With the Pt negative, the latter is less heated and a spectrum of  $N_2$  is obtained throughout the length of the spark, the Cu spectrum from near the liquid, and a very intense H spectrum, containing the  $H_\alpha$  and  $H_\beta$  lines and the secondary H spectrum, from a luminous spot on the electrolyte. The observations suggest that the positively charged  $H_2$  at the surface of the

liquid forms the electrode and causes the pptn. of  $Cu(OH)_2$  on passage of the current.

J. W. S.

**Broadening of the lines in the radiation from hissing arcs.** T. PECZALSKI (Compt. rend., 1936, 202, 1040—1042; cf. this vol., 438).—With increased evaporation of fused salt in contact with the anode of a C arc the arc hisses and the spectral lines for NaCl and  $CaCl_2$  are wider than for a silent arc, the concn. of vapour being increased 20 times.

R. S. B.

**Rapid measurements of probe characteristics of a gas discharge by means of oscillograph tubes.** J. DÜRRWANG (Helv. phys. acta, 1935, 8, 333—369; Chem. Zentr., 1935, ii, 1138).—Dynamic characteristics of arc discharges have been investigated. The introduction of volatile salts (e.g., Na or Cu halides) into a C arc produces alterations in the discharge which may be correlated with the ionisation potential of the metal.

J. S. A.

**Electric arcs with liquid positive pole.** M. PIERUCCI (Nuovo Cim., 1935, [ii], 12, 1—3; Chem. Zentr., 1935, ii, 1138).—A short arc may be struck between a C electrode and the surface of an aq. electrolyte. With a.c., a rectifying action is observed, the electrolyte functioning as positive pole only. The arc spectrum comprises the continuum of the electrodes and the gas lines, with the Balmer H lines when  $H_2SO_4$  solutions are used. With shallow liquid layers the arc may strike through to the containing graphite crucible, then emitting strongly the spectra of the dissolved electrolytes.

J. S. A.

**Evaluation of ultra-violet solar radiation of short-wave lengths.** W. W. COBLENTZ and R. STAIR (Proc. Nat. Acad. Sci., 1936, 22, 229—233).—A summary of recent experimental investigations and results.

N. M. B.

**Bright line spectrum of Nova Herculis.** F. L. WHIPPLE and (Miss) C. P. GAPOSCHKIN (Proc. Nat. Acad. Sci., 1936, 22, 195—200).

**Spectra of early-type stars in the near ultra-violet region.** P. SWINGS and M. DESIRANT (Astrophys. J., 1936, 83, 31—46).—The spectra of three B and eleven A stars have been measured for  $\lambda\lambda$  between 3570 and 3930 Å. The behaviour of the elements is discussed.

L. S. T.

**K-Series for aluminium, manganese, and sodium.** V. KUNZL (Z. Physik, 1936, 99, 481—491).—New lines have been observed in  $\alpha$  and  $\beta$  groups (cf. A., 1935, 1292).

A. B. D. C.

**Excitation potential, relative intensities, and wave-lengths of the  $K\alpha''$  X-ray satellite line.** L. G. PARRATT (Physical Rev., 1936, [ii], 49, 502—507).—Data and ionisation curves of the line are given for S (16) to V (23). The excitation potential is 4070±250 volts, and the line is attributed to a  $KM \rightarrow LM$  transition. The relative intensity  $K\alpha''/K\alpha_1$  varies with at. no., reaching a max. of 2.3% at Ca (20).

N. M. B.

**Variation of the atomic structure factor of potassium with X-ray wave-length.** S. K. ALLISON and W. P. JESSE (Physical Rev., 1936, [ii], 49, 483—494).—Using a special vac. ionisation spectrometer the diffracted power in the Debye-Scherrer



rings from NaCl, NaF, LiF, and KF powders has been compared. For KF, with the range 1.538–4.146 Å., the expected decrease of the crystal structure factor on the short- $\lambda$  side was observed; beyond the  $K$  edge of  $K$  the factor rose again, but considerably more than predicted. It is concluded that HönI's computations based on the wave-mechanical theory of  $X$ -ray dispersion do not correctly give the observed structure factor differences for the (200) diffraction halo from powdered KF on the long and short  $\lambda$  sides of the  $K$  edge. The predicted invariance of the structure factor decrement due to  $K$  electrons with scattering angle for light elements is confirmed. N. M. B.

**Auger effect and relative intensity of  $L$ -emission lines.** D. COSTER and K. W. DE LANGEN (Physica, 1936, 3, 282–288).—The relative intensities of the  $L\beta_1$ ,  $\beta_2$ , and  $\beta_3$  lines of Ag, Sn, and Sb have been determined. With Ag, the Auger effect  $L_I \rightarrow L_{III}$  with ejection of an  $M$  electron can take place, and this leads to markedly smaller vals. of the intensity ratios  $\beta_3 : \beta_1$  and  $\beta_2 : \beta_1$ . L. J. J.

**Relativistic theory of the Auger effect.** H. S. W. MASSEY and E. H. S. BURHOP (Proc. Roy. Soc., 1936, A, 153, 661–682).—Calculations have been made of the probability of the internal conversion of the  $K$  series radiation for Au arising from the interaction of the  $L_I L_{II}$ ,  $L_I L_{III}$ , and  $L_{II} L_{III}$  shells, using Møller's method (A., 1932, 980). Less accurate calculations have also been made for Ag. Appreciable relativistic effects have been found for both metals, most marked in the case of Au. L. L. B.

**$K$  X-Ray absorption spectra of some compounds of bromine and rubidium.** S. T. STEPHENSON (Physical Rev., 1936, [ii], 49, 495–498).—Using powder absorbing screens with a double-crystal ionisation spectrometer and MeI in the ionisation chamber to eliminate the effect of Br in MeBr, the  $K$  X-ray absorption spectrum of Br in KBr, RbBr, CdBr<sub>2</sub>, and NaBrO<sub>3</sub> and of Rb in RbBr was obtained. The widths of the Br and Rb edges were about 9 and 11 volts, respectively. No discontinuity due to a possible simultaneous ejection of  $K$  and  $L$  electrons was observed. N. M. B.

**Ultra-soft X-ray absorption edges from the emulsion and sensitisers of photographic plates.** J. M. BAČKOVSKÝ and V. DOLEJŠEK (Z. Physik, 1936, 99, 42–51).—The intense absorption of ultra-soft X-rays gives inverted absorption edges of K, Cl, and Ca ( $L_{II-III}$  edges) as well as those of Ag and Br. A. B. D. C.

**Approximate method for the calculation of the work of emission of electrons from metals.** E. H. B. BARTELINK (Physica, 1936, 3, 193–204).—Mathematical. L. J. J.

**Relation between secondary emission and work function.** L. R. G. TRELOAR (Nature, 1936, 137, 579).—Secondary emission from a Mo filament with different degrees of Ba surface has been investigated. L. S. T.

**Electron emission of the cathode of an arc.** M. J. DRUYVESTEYN (Nature, 1936, 137, 580).—A new way in which electrons may escape from the cathode of an arc is suggested. L. S. T.

**Production of intense beams of slow electrons.** R. PLANTOL (Compt. rend., 1936, 202, 1267–1268).—A supplementary grid, at a high positive potential, is interposed between the emitting filament and the principal grid. L. J. J.

**Theoretical cross-section for  $K$ -electron ionisation by electron impact.** W. W. WETZEL (Physical Rev., 1936, [ii], 49, 531–534).—Mathematical. An expression is found for the cross-section as a function of the at. no., the ionisation potential of the  $K$  shell, and the energy of the colliding electron. N. M. B.

**Distribution of electron velocities in the magnetic field.** T. V. IONESCU and C. MIHUL (Compt. rend., 1936, 202, 1160–1162).—Electrons produced by a heated W filament were accelerated by different voltages (240–1920 volts) between two grids, under the action of a magnetic field (0–43.2 gauss). The resulting ionisation currents in the gas space between the second grid and a plate at different voltages were plotted against the plate voltage. M. S. B.

**Collision of slow electrons in pure oxygen. Electronic affinity.** L. GOLDSTEIN (Compt. rend., 1936, 202, 924–926).—Pure dry O<sub>2</sub> behaves towards electrons of energy 0.1–5.9 e.v. like rare gases. Electrons of greater energy dissociate O<sub>2</sub>, but they are not captured by mol. O<sub>2</sub>. H. J. E.

**Determination of the velocity distribution of electrons in a low-pressure discharge tube.** A. H. VAN GORCUM (Physica, 1936, 3, 207–218).—A method of applying Druyvesteyn's formula (A., 1930, 1490) is described. The velocity distribution in a Ne tube changes to a Maxwellian one as the positive column is approached from the cathode side. L. J. J.

**Motion of electrons in electric and magnetic fields taking into consideration the action of the space charge.** S. J. BRAUDE (Physikal. Z. Sovietunion, 1936, 8, 667–674; cf. A., 1935, 1294).—Theoretical. The motion of electrons in crossed electric and magnetic fields with space charge is investigated for a cylindrical condenser. A. J. M.

**Positron theory and proper energies.** R. SERBER (Physical Rev., 1936, [ii], 49, 545–550).—Mathematical. N. M. B.

**Production of positrons from bismuth.** H. P. DE (Indian J. Physics, 1936, 10, 103–108).—The production of positrons from Bi bombarded with neutrons and other radiations from a mixture of MsTh, Ra, and BeO was examined by the cloud-chamber method, using a stereo-camera. For 282 electron tracks there were 20 positron tracks. The energy of the positrons was  $10^5$ – $4.5 \times 10^6$  e.v. It is suggested that the positron emission is due to internal conversion of high-energy  $\gamma$ -radiation. A. J. M.

**Sign of the magnetic moment of the proton and of the deuteron.** J. M. B. KELLOGG, I. I. RABI, and J. R. ZACHARIAS (Nature, 1936, 137, 658).—Both moments are positive. L. S. T.

**Production of high-velocity ions for the disintegration of atomic nuclei.** R. J. MOON and W. D. HARKINS (Science, 1936, 83, 244). L. S. T.



**Kinetic energy of positive thermions of some halides.** (MLE.) C. TUDOR (Bull. Acad. Sci. Roumaine, 1935, 17, 111—115).—Positive ion emission has been studied with the chlorides of Sn, Zn, Sr, Cd, Cu<sup>I</sup>, and Li, Ba(NO<sub>3</sub>)<sub>2</sub>, SrBr<sub>2</sub>, KBr, CdI<sub>2</sub>, and ZnI<sub>2</sub>. The mean kinetic energy of the ions has been determined. R. S. B.

**Ionisation and luminescence of atomic beams in a high vacuum.** R. PLANIOL (Compt. rend., 1936, 202, 1032—1033; cf. A., 1935, 599).—An improved apparatus is described. The passage of electrons through an at. beam is marked by a luminescence which increases with the intensity of the beam and changes from violet to blue. The light is emitted in the visible and ultra-violet. R. S. B.

**Direct determination of the effective radius of strongly vibrating molecules by the molecular beam method.** N. SASAKI and E. NISHIBORI (Proc. Imp. Acad. Tokyo, 1936, 12, 10—12).—The mols. are strongly excited photochemically and their effective radius is found by the mol. beam method. For I<sub>2</sub> the ratio of the effective radius of the excited mol. to that of the unexcited mol. is 2.56. A. J. M.

**Ionisation of a molecular beam by electron collision and investigation of the ions produced by the mass spectrograph.** N. SASAKI and E. NISHIBORI (Proc. Imp. Acad. Tokyo, 1936, 12, 13—15).—The investigation of the primary products of a reaction by the mol. beam method is described. The beams of mols. are ionised and then examined by the mass spectrograph. The method can be used to study the ionisation of mols., or, by crossing beams, the products of reactions. A. J. M.

**Sixth Report of the Committee on Atomic Weights of the International Union of Chemistry.** G. P. BAXTER, O. HÖNIGSCHMID, and P. LEBEAU (J. Amer. Chem. Soc., 1936, 58, 541—548).—Changes have been made in the at. wt. of Ta (180.88) and Ra (226.05). Pa (at. wt. 231) has been added to the table. E. S. H.

**Relative at. wt. of oxygen in water and in air; atmospheric distribution of the oxygen isotopes and the chemical standard of at. wts.** M. DOLE (J. Chem. Physics, 1936, 4, 268—275).—Density measurements on H<sub>2</sub>O made from tank H<sub>2</sub> and O<sub>2</sub> from the air and from tank H<sub>2</sub> and O<sub>2</sub> from the H<sub>2</sub>O of Lake Michigan are recorded. The former is 6.0±0.6 p.p.m. heavier, corresponding with a difference of 0.000108±0.00001 at. wt. units between the at. wts. of O in air and H<sub>2</sub>O. The results are discussed in relation to existing data. The possibility of accounting for the observed difference by isotopic exchange and gravitational equilibria in the stratosphere, and its bearing on the basis of at. wt. standards, are considered. L. J. J.

**Eighth isotope of molybdenum.** J. DE GIER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 327—329).—Using Mo(CO)<sub>6</sub>+50% O<sub>2</sub> in the discharge a new isotope <sup>102</sup>Mo has been detected, in agreement with Sitte's prediction (cf. A., 1935, 1295). The provisional abundance is 2—3%. R. S. B.

**At. wt. of rubidium.** E. H. ARCHIBALD and J. G. HOOLEY (J. Amer. Chem. Soc., 1934, 58, 618—619).—From determinations of the ratios RbBr:Ag and RbBr:AgBr, the at. wt. of Rb is 85.481.

E. S. H.

**At. wt. of germanium. II. Analysis of germanium tetrachloride.** O. HÖNIGSCHMID and K. WINTERSBERGER (Z. anorg. Chem., 1936, 227, 17—24; cf. this vol., 5).—The mean of nine nephelometric titrations of GeCl<sub>4</sub>, the prep. of which is described, gives Ge 72.59±0.006, in agreement with the val. previously obtained. F. L. U.

**Existence of <sup>5</sup>Li.** A. K. BREWER (Physical Rev., 1936, [ii], 49, 635).—The mass spectra for Li ions emitted thermally from an impregnated Pt source show a peak in the mass no. 5 position and evidence favours <sup>5</sup>Li as its origin. The abundance ratio for the new peak was <sup>7</sup>Li/<sup>5</sup>Li=20,000±1000. N. M. B.

**New data on isotopes.** F. W. ASTON (Nature, 1936, 137, 613; cf. this vol., 400).—Isotopic wts. obtained by the doublet method are <sup>10</sup>B 10.0161±0.0003, <sup>14</sup>N 14.0073±0.0005, <sup>19</sup>F 19.0045±0.0006, <sup>20</sup>Ne 19.9986±0.0006, <sup>27</sup>Al 26.9909, <sup>28</sup>Si 27.9860, <sup>29</sup>Si 28.9864±0.0008, and <sup>40</sup>A 39.9754±0.0014. The corresponding packing fractions are 16.1, 5.28, 2.36, -0.70, -3.3, -5.0, -4.7, and -6.15, respectively. The present position with regard to some doubtful isotopes is reviewed. The existence of <sup>58</sup>Fe and <sup>64</sup>Ni is supported by the work of de Gier and Zeeman (this vol., 5, 130), but evidence as to <sup>61</sup>Ni is still conflicting. If the lines 148 and 150 obtained by Dempster are due to isotopes of Nd, as is probable, the discrepancy between the physical and chemical at. wts. of Nd may disappear. Revised vals. for the percentage abundances of the various isotopes of Cd, Sn, and Pb are given. L. S. T.

**Periodic system of the elements and element 93.** M. CARRANZA (Bol. Soc. Quim. Peru, 1935, 1, 41—45).—A review. L. A. O'N.

**Radioactivity of samarium.** R. HOSEMANN (Z. Physik, 1936, 99, 405—427).—The range of α-rays emitted at the rate of 89 per sec. per g. is 1.13 cm. in air at 15° and 760 mm. A. B. D. C.

**Existence of the α<sub>5</sub> radiation and the separation of the magnetic spectrum of thorium-C into two series.** S. ROSENBLUM (Compt. rend., 1936, 202, 943—946; cf. A., 1932, 442).—A discussion. The existence of α<sub>5</sub> radiation is reaffirmed. Its intensity is low. H. J. E.

**Tracks of the α-particles of thorium and its products.** H. J. TAYLOR and V. D. DABHOLKAR (Proc. Indian Acad. Sci., 1936, 3, A, 265—271).—The tracks of α-particles emitted from atoms of the Th series in a photographic emulsion have been recorded (cf. A., 1935, 910). Single tracks and stars, characteristic of the individual atoms of the various members of the series, are obtained. L. J. J.

**Intensity of fine-structure groups in the α-ray magnetic spectra of radioactinium and its products.** S. ROSENBLUM, M. GUILLOT, and (MLE.) M. PEREY (Compt. rend., 1936, 202, 1274—1276).—Data are recorded for the relative intensities of



11 known lines of RdAc and 4 of Ac-X. Four new lines are recorded for actinon, and two new lines for Ac-C.

L. J. J.

**Tracks of swift nuclei in photographic emulsions.** H. J. TAYLOR (J. Univ. Bombay, 1935, 4, Part II, 70—73; cf. A., 1935, 910).—The photographic method is not so widely applicable as the cloud chamber method, but has greater sensitivity in recording the tracks of  $\alpha$ -particles, recoil protons, and tracks resulting from nuclear disintegration under neutron bombardment. Investigations can cover all tracks over longer periods, and being recorded in small area enable rare events, e.g., the reaction  $^{10}\text{B} + ^1_0\text{n} \rightarrow ^4\text{He} + ^4\text{He} + ^3\text{He}$ , to be observed.

J. W. S.

**Calorimetric measurements of the energy of disintegration in the actinium family.** A. SANIELEVICI (Compt. rend., 1936, 202, 1055—1057).—Using an adiabatic micro-calorimeter the following energy ( $E$ ) changes have been measured: for Ac in equilibrium  $E$  ( $\alpha$ +recoil) =  $7.15 \times 10^{-3}$  g.-cal. per g. per hr.; for Ac  $\rightarrow$  Ac-C''  $E$  ( $\alpha$ +recoil) represents 90.9,  $E$  ( $\beta$  primary) 2.4, and  $E$  ( $\gamma$ + $\beta$  secondary) 6.7% of the whole. The mean  $E$  of the  $\beta$ -rays of Ac-B is  $3.7 \times 10^5 \pm 3\%$  e.v.

R. S. B.

**Continuous  $\beta$  spectrum of actinium-B.** M. LECOIN (Compt. rend., 1936, 202, 1057—1059; cf. A., 1935, 1048).—The  $\beta$  spectrum of initially pure Ac-B has been studied. The curve for disintegration no. against energy shows a max. at  $5 \times 10^5$  e.v. after allowing for the influence of Ac-C''. The mean energy for the  $\beta$ -radiation of Ac-B is  $3.6 \times 10^5$  e.v., in agreement with Sanielevici (see above). The higher limit of the spectrum occurs at  $9.5 \times 10^5$  e.v.

R. S. B.

**Radiation from the active deposit of actinium.** J. SURUGUE (Compt. rend., 1936, 202, 410—411; cf. A., 1933, 659).—The energies of the  $\beta$ -rays from the active deposit of Ac, as compared with the  $F$  ray of Th-B, are found to be 0.4% > previously recorded. A new ray of high energy (813 e.kv.) is found and attributed to the transformation Ac-B  $\rightarrow$  Ac-C. The change Ac  $\rightarrow$  Ac-C'' yields only the  $\beta$ -ray of 350 e.kv., in accord with the fine structure of the  $\alpha$ -radiation.

J. W. S.

**Continuous  $\beta$ -ray spectrum of radium-C''.** L. GOLDSTEIN and M. LECOIN (Compt. rend., 1936, 202, 1169—1170).—The  $\beta$ -ray spectrum of Ra-C'' has been photographed using a Wilson expansion chamber. Under the experimental conditions positrons were distinguished from electrons and thus possible interferences from the disintegration of the synthetic element  $\text{R}_9\text{F}$ , produced by the bombardment of N by the  $\alpha$ -rays of Ra-C', could be eliminated. It is shown that at least two energy quanta, equal to a total of  $3.4 \times 10^6$  e.v., are emitted in the disintegration of Ra-C''.

M. S. B.

**Slow neutrons.** E. FERMI and F. RASETTI (Nuovo Cim., 1935, [ii], 12, 201—210; Chem. Zentr., 1935, ii, 1127).—Data are given for the absorption coeffs. of B and Cd for neutrons slowed by elastic collision with H atoms. The absorption mechanism may differ as an unstable radioactive isotope or a stable isotope is formed by neutron capture.

J. S. A.

**Absorption of slow neutrons.** C. H. COLLIE (Nature, 1936, 137, 614).—The absorption of slow neutrons from a Rn-Be source by several elements has been measured using an improved arrangement. The absorption band of Cd occurs in the range 0—1.5 e.v. and a very narrow absorption band (0—0.1 e.v.) is indicated. The band for In occurs in the same range and partly overlaps that of Cd. No effect due to the sp. absorption of Au or Ag could be found.

L. S. T.

**Capture of slow neutrons.** G. BREIT and E. WIGNER (Physical Rev., 1936, [ii], 49, 519—531).—Mathematical. Considerations are given to account for the contradiction of current theories of the large cross-section of slow neutrons by frequent absence of strong scattering in good absorbers and existence of resonance bands.

N. M. B.

**Retardation of neutrons by collision with protons.** E. LAMLA (Naturwiss., 1936, 24, 251—252).—Theoretical. The energy distribution of neutrons after collision with protons is calc., both particles being treated as elastic spheres.

A. J. M.

**Diffraction of slow neutrons by crystalline substances.** W. M. ELSASSER (Compt. rend., 1936, 202, 1029—1030).—Theoretical. Crit. angles of  $26^\circ$  have been calc. for Ni and Fe, and  $25^\circ$  for Cu.

R. S. B.

**Disintegration of boron.** D. ROAF (Proc. Roy. Soc., 1936, A, 153, 568—576).—Using  $\text{BF}_3$  in a Wilson chamber, the recoils from the disintegration of  $^{10}\text{B}$  by neutrons have been photographed and their energy has been measured. Most of the disintegrations were caused by neutrons of  $< 2 \times 10^4$  e.v., but one was observed due to a neutron of energy  $> 10^5$  e.v. The energy released in the reaction  $^{10}\text{B} + ^1_0\text{n} = ^7\text{Li} + ^4\text{He}$  is  $1.50 \pm 0.05 \times 10^{-3}$  units of at. mass. The  $^{10}\text{B}$  mass has been corr. to  $10.0136 \pm 0.0014$ .

L. L. B.

**Radioactivity and atomic theory.** (LORD) RUTHERFORD (J.C.S., 1936, 508—516).—Faraday lecture.

**Deviation in passing through magnetised iron of (I) high-energy charged particles, (II) cosmic-ray charged particles.** (I) W. F. G. SWANN, (II) W. E. DANFORTH, and W. F. G. SWANN (Physical Rev., 1936, [ii], 49, 574—582, 582—591).—I. Mathematical.

II. Investigations by means of Geiger counters of the deflexions of cosmic-ray electrons in passing through the saturated Fe core of an electromagnet are described. Observed effects are compared with calc. results to determine limits of the effective magnetic vector within the Fe.

N. M. B.

**Geomagnetic effect on cosmic radiation in the stratosphere.** M. G. E. COSYNS (Nature, 1936, 137, 616).

L. S. T.

**Structure of cosmic rays.** R. HILGERT and W. BOTHE (Z. Physik, 1936, 99, 353—362).

A. B. D. C.

**Nature and range of radiation particles (collision radiation) involved in Hoffmann collisions.** H. NIE (Z. Physik, 1936, 99, 453—480).—The effect of various thicknesses of Pb, Fe, and Al shields is described.

A. B. D. C.



**Relationship between Hoffmann collisions and showers.** J. BØGGILD (Naturwiss., 1936, 24, 280—281). A. J. M.

**Rôle of chemistry in the study of atomic transmutation.** F. A. PANETH (Nature, 1936, 137, 560—562).—A review. L. S. T.

**Artificially radioactive materials.** E. SEGRÈ (Nuovo Cim., 1935, [ii], 12, 232—239; Chem. Zentr., 1935, ii, 1129).—The life periods of a no. of artificial radio-elements are correlated with the hardness of the emitted  $\beta$ -radiation, as measured by absorption in Al. The variation in intensity of different activities of the same element on activation with fast and slow neutrons (e.g., comparison of the behaviour of the 20-min. and 23-hr. periods of Ga) is discussed.

J. S. A.

**Nuclear processes with the mean corpuscular energy of star centres.** R. DÖPEL (Naturwiss., 1936, 24, 237).—The nuclear reactions  ${}^2_1\text{D} + {}^2_1\text{D} = {}^3_1\text{H} + {}^1_1\text{H}$  and  ${}^2_1\text{D} + {}^2_1\text{D} = {}^3_2\text{He} + {}^1_0\text{n}$  have been observed at potentials < previously. The efficiency of the first reaction was  $10^{-16}$  at 5 kv., and  $10^{-14}$  at 15 kv. The efficiency of the second reaction was somewhat greater. 5000 e.kv. corresponds with the mean energy of the atoms in the centre of a star at a temp. of  $4 \times 10^7$ . Hence transmutation occurring in stars can now be investigated in the laboratory under similar conditions.

A. J. M.

**Radioactive elements of low atomic number.** W. A. FOWLER, L. A. DELSASSO, and C. C. LAURITSEN (Physical Rev., 1936, [ii], 49, 561—574).—Radioactive elements of low at. no. were produced by bombarding Li, B, C,  $\text{NaNO}_2$ , and  $\text{CaF}$  with high-velocity deuterons. The energy distribution of the electrons and positrons emitted was determined by a Wilson cloud-chamber and magnetic field. The electron and positron spectra max. energy ranges are 5—13 and 1—2 m.e.v., respectively. The form of the spectra agrees with the Konopinski theory (cf. A., 1935, 1048). Data are tabulated for the radioactive elements  ${}^3_1\text{B}$ ,  ${}^{11}_5\text{C}$ ,  ${}^{13}_6\text{N}$ ,  ${}^{15}_7\text{O}$ ,  ${}^{17}_8\text{F}$ ,  ${}^{7}_3\text{Li}$ ,  ${}^{10}_5\text{B}$ ,  ${}^{10}_5\text{N}$ , and  ${}^{19}_9\text{F}$ .

N. M. B.

**Radioactive argon.** A. H. SNELL (Physical Rev., 1936, [ii], 49, 555—560).—When bombarded with high-speed deuterons, A yields a radioactive product with decay period  $110 \pm 1$  min., and emitting negative electrons. The activity is shown chemically to be due to an A isotope, and the reaction is probably  ${}^{40}_{18}\text{A} + {}^2_1\text{H} = {}^{41}_{18}\text{A} + {}^1_1\text{H}$ . Absorption measurements of the  $\beta$ -particles show a max. energy of about 1.1 mv. (cf. Kurie, this vol., 542). The excitation function of the radioactivity favours the Oppenheimer-Phillips (cf. A., 1935, 1296) rather than the Gamow theory for this type of reaction. The same radioactive substance was made by intense bombardment of A by neutrons.

N. M. B.

**Time decay of atomic nuclear processes.** R. DÖPEL (Z. Physik, 1936, 99, 161—168).—Time decay of  $\alpha$ -ray artificial radioactivity was detected for In, Cs, and Ce.

A. B. D. C.

**Artificial radioactivity of tin.** M. E. NAHMIAS (Compt. rend., 1936, 202, 1050—1052).—Sn shows a feeble induced radioactivity after irradiation by

neutrons from Rn-Be in air and paraffin. Chemically pure and commercial Sn give the same result, probably due to the reaction  ${}^{123}_{50}\text{Sn} + {}^1_0\text{n} \rightarrow {}^{123}_{50}\text{Sn} \rightarrow {}^{123}_{51}\text{Sb} + e^-$ , the small % of the isotope 122 (5%) accounting for the feebleness of the induced radioactivity. The period is 5.3—7.1 min.

R. S. B.

**Induced radioactivity of nickel and tin.** R. NAIDU (Nature, 1936, 137, 578—579).—When irradiated by slow neutrons from a Rn-Be source, Geiger-Müller counters with walls of Ni and Sn show induced radioactivity. With Ni the half-life period is  $180 \pm 10$  min. and with Sn,  $8 \pm 2$  and  $18 \pm 2$  min.

L. S. T.

**Artificial radioactivity produced by bombardment with neutrons. VII—IX.** E. AMALDI, O. D'AGOSTINO, E. FERMI, B. PONTECORVO, F. RASETTI, and E. SEGRÈ (Ric. sci. Prog. tec., 1934, 5, II, 467—470; 1935, 6, I, 123—125, 435—437; Chem. Zentr., 1935, ii, 969—970).—VII. New activities and their respective half-life periods are recorded for K, Ga, Cd, In, Sb, Pr, Mn, As, and Rh. Separation of the active material by Szilard and Chalmers' method (A., 1934, 1152) has been applied to Cl, As, and Mn in org. and inorg. compounds. Effective collision areas for Cl, Co, Ag, Cd, In, I, Pr, Au, and Hg are recorded. Increase in the efficiency of activation by surrounding the neutron source with Pb, graphite, and basalt in place of H compounds is discussed.

VIII. Half-val. periods are recorded for Mg, Si, Ba, Gd and W (new activities), and for Si, P, V, Ga, Br, Ag, I, Pr, Re, Ir, and Au (more accurate data).  $\gamma$ -Ray activity has been detected with Rh, Br, V, Mn, Cu, Ga, In, Sb, I, W. For B, the nuclear reaction  ${}^{10}_5\text{B} + {}^1_0\text{n} = {}^7_3\text{Li} + {}^4_2\text{He}$  is advanced. Chemical separation of the active species produced from Sb, W, and Re show them to be isotopes of these elements.

IX. Accurate life periods are recorded for Al, S, Cl, Cu, Zn, Ga, Rh, Sb, and Th. Chemical separation of the active material from P, Cl, Cu, Ga, and Si shows the activity to belong to an isotope of the same element; the activity of Zn is due to a Cu isotope. The 10-sec., 13-min., and 100-min. activities of neutron-activated U are attributed to successive transformations, probably of the elements 92, 93, and 94, all of at. wt. 239. Co, Cu, and Au emit  $\gamma$ -rays.

J. S. A.

**Artificial radioactivity induced by neutron bombardment.** I. V. KURTSCHATOV, G. D. LATISCHEV, L. M. NEMENOV, and I. P. SELINOV (Physikal. Z. Sovietunion, 1936, 8, 589—594; cf. A., 1935, 1050).—The radioactivity produced in Pd, Re, and Os when bombarded with slow neutrons was investigated. In the case of Pd, the existence of two active substances of half-life 15 min. and 12 hr., respectively (Fermi, A., 1934, 1284), has been confirmed, and two further substances of half-life 3 min. and approx. 60 hr., respectively, have been found. With Re, two radioactive substances of half-life 20 and 85 hr., respectively, have been obtained. Os gives only a very weak activity of half-life approx. 40 hr.

A. J. M.

**Intensity of scattered radiation from moving free electrons.** E. C. G. STUECKELBERG (Helv. phys. Acta, 1935, 8, 197—204; Chem. Zentr., 1935, ii, 986).—Theoretical.

J. S. A.



**Electronic nature of light.** J. L. DESTOUCHES (Compt. rend., 1936, 202, 921—923).—Theoretical.

H. J. E.

**Concept of [chemical] element.** (MLLE.) C. RAMNOUX and J. MARTINET (Bull. Soc. chim., 1935, [v], 2, 1474—1485).—The present meaning of the word "element" is not sufficiently precise. Considerable restriction in its use is suggested, to avoid confusion and ambiguities.

R. C. M.

**Properties of the spin of a system of corpuscles.** J. L. DESTOUCHES (Compt. rend., 1936, 202, 387—389).—Mathematical.

J. W. S.

**Deviations from the Maxwell equations resulting from the theory of the positron.** N. KEMMER and V. WEISSKOPF (Nature, 1936, 137, 659).

L. S. T.

**Structure of atomic nuclei.** H. A. WILSON (Proc. Roy. Soc., 1936, A, 153, 493—504; cf. this vol., 266).—The energies of formation of several atoms have been calc. from nuclear reaction energies. Assuming that the energy is due to the formation of linkings between the neutrons and protons forming the atom, arrangements of neutrons and protons and linking energies are found which give the correct vals. of energies of formation.

L. L. B.

**Origin of mass in neutrons and protons.** M. N. SAHA (Indian J. Physics, 1936, 10, 141—153).—Theoretical.

A. J. M.

**Neutron-proton exchange interaction.** M. S. PLESSET (Physical Rev., 1936, [ii], 49, 551; cf. Breit, this vol., 134).—Mathematical.

N. M. B.

**Conservation of energy and momentum in atomic processes.** E. J. WILLIAMS (Nature, 1936, 137, 614—615).—The uncertainty principle is discussed in connexion with Shankland's results (this vol., 265).

L. S. T.

**Exchange rules in the neutrino theory of light.** P. JORDAN (Z. Physik, 1936, 99, 109—113).

A. B. D. C.

**Heisenberg's oscillator model and nuclear moments.** P. PAVINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 169—171).—Using a simplified Hartree method with the "eigen"-functions of the spatial harmonic oscillator to describe the states of the individual particles, in conjunction with the Lande assumption that only the unpaired proton is responsible for the mechanical and magnetic moments of a nucleus, it is possible to calculate these moments, in agreement with experiment.

A. J. M.

**Theory of the relativistic degenerate corpuscular gases and their employment in the atomistic theory of Brownian molecular motion.** M. SATÔ (Sci. Rep. Tôhoku, 1936, 24, 565—586).—On the basis of Glaser's theory (A., 1935, 679) the dynamics of the pressure of light and the atomistic theory of Brownian movement have been studied. Earlier work (A., 1934, 252) is discussed.

M. S. B.

**Oil-drop method and the electronic charge.** E. BACKLIN and H. FLEMBERG (Nature, 1936, 137, 655—656).—Preliminary results with an improved apparatus give  $e = 4.800 \times 10^{-10}$  abs. e.s.u. in good agreement with spectroscopic vals.

L. S. T.

**Measurement of  $e/m$  with a triode valve.** S. RAM (Indian J. Physics, 1936, 10, 127—132).—The val. of  $e/m$  has been found by observing the effect of a magnetic field on the grid current of a triode. Two formulæ gave mean vals. for  $e/m$  of  $1.77 \times 10^7$  and  $1.79 \times 10^7$ , respectively.

A. J. M.

**Relation between the fundamental constants of physics.** A. HAAS (Physical Rev., 1936, [ii], 49, 636).—Mathematical.

N. M. B.

**New electrodynamics and the fine structure constant.** L. INFELD (Nature, 1936, 137, 658).

L. S. T.

**Determination of the constant  $\alpha$  of fine structure by the unitary theory of the electromagnetic field.** S. A. DE MAYOLO (Bol. Soc. Quim. Peru, 1935, 1, 26—40).—The unitary theory, by which the electromagnetic field in a vac. is due to central forces exerted between two equal non-corpuscular quantities of electricity, of opposite sign, in dynamic equilibrium, moving with the velocity of light, is further developed.

L. A. O'N.

**Absorption spectra of iodine solutions. I. Solutions in mineral acids.** A. V. PAMFILOV and R. V. TEIS (J. Gen. Chem. Russ., 1935, 5, 1833—1838).—The absorption spectra of I in aq. HCl or H<sub>2</sub>SO<sub>4</sub> are of the same type as in org. solvents.

R. T.

**Ultra-violet absorption of ice.** E. J. CASSEL (Proc. Roy. Soc., 1936, A, 153, 534—541).—The thin films of ice used showed a continuous absorption with a long- $\lambda$  limit at about 1670 Å., which varied only slowly with the thickness of the film, indicating an abrupt rise in the coeff. of absorption. The absorption band of ice is shifted towards short waves relatively to that of vapour by 0.6—0.7 e.v. The absorption of heavy ice begins at a shorter  $\lambda$  than that of light ice, and the amount of the shift is of the same order of magnitude as that found for H<sub>2</sub>O vapour by Franck and Wood (A., 1934, 828).

L. L. B.

**New bands of nitric oxide.** M. DUFFIEUX and L. GRILLET (Compt. rend., 1936, 202, 937—939; cf. A., 1935, 1051).—Measurements of rotational fine structure are recorded for the bands about 6000 Å. previously described, which are attributed to ionised NO.

H. J. E.

**Absorption spectra of (A) the hydrogen chloride molecule, (B) the hydrogen bromide molecule, and their upper unstable states.** H. TRIVEDI (Proc. Nat. Acad. Sci. India, 1936, 6, 18—28, 29—34).—(A) The absorption coeffs. at temp. in the range 20—980° were obtained photographically in an investigation of the continuous absorption spectrum of HCl, and the contributions of individual vibrational levels to the total absorption were found. The vals. of the mol. consts. for the unstable state calc. from observational data at different sets of  $\lambda\lambda$  are in good agreement. The energy of dissociation of the mol. in its unstable state corresponds with the heat of formation of the mol. determined thermochemically.

(B) Investigations and results for HBr are reported similarly to the case of HCl. Analogous agreements are obtained.

N. M. B.



**Absorption spectra of hydrochloric acid and various chlorides in the far ultra-violet.** R. TRÉHIN (Ann. Physique, 1936, [xi], 5, 445—607; cf. A., 1935, 9, 805; 1934, 581; 1933, 111, 1226; 1932, 107; 1931, 19).—Results are given for investigations of the effect of temp. and concn. on the absorption of HCl liquefied, aq., and in Et<sub>2</sub>O, in the range 2816—1990 Å., and of the alkali and alkaline-earth chlorides in aq. solution, of NaCl in glycerol, and of rock-salt, in the range 2500—2170 Å. For the aq. solutions the absorption increases as  $\lambda\lambda$  decrease, the effect being more marked with rise of temp. and concn. For each  $\lambda$  and temp. the extinction coeff. increases with concn.; the mol. extinction coeff. increases considerably for low concns. For a given  $\lambda$  and concn. the absorption increases with rise of temp., particularly at higher temp. and shorter  $\lambda\lambda$ , and more rapidly for the acid than for the salts, and as the cation is less hydrated. Results are discussed in relation to the theory of strong electrolytes.

N. M. B.

**Rotation-vibration spectrum of ammonia.** N. VERLEGER (Naturwiss., 1936, 24, 237).—A new region of strong absorption has been found, extending from 11,600 to 12,400 Å. It has the same origin as the 10,230 Å. band recently observed and both probably consist of two separate bands, the stronger being that lying farther in the infra-red. A weaker absorption band has been observed at 12,660 Å. and consists of a series of strong lines between which is a definite fine structure. A similar weak absorption follows the 10,230 Å. strong band, at 10,900 Å.

A. J. M.

**Band spectra of PH and NH.** C. GILBERT (Physical Rev., 1936, [ii], 49, 619—624).—Formulae for the effect of mol. rotation on spin multiplets are considered for triplet cases, and mol. consts. are calc. Results are compared with experimental data for the  $\lambda$  3400 band of PH and the  $\lambda$  3360 band of NH.

N. M. B.

**Spectrum of SiF.** R. K. ASUNDI and R. SAMUEL (Current Sci., 1936, 4, 649).—A preliminary announcement of a revised vibrational analysis of the  $\alpha$ - and  $\beta$ -bands, and an analysis of the  $\gamma$ -bands. The consts. of the mol. in its various electronic states are given.

N. M. B.

**Isotope displacements in the band spectrum of mercury deuteride.** S. MROZOWSKI (Z. Physik, 1936, 99, 236—251).

A. B. D. C.

**Ultra-violet bands of beryllium oxide.** A. CICCONE (Ric. sci. Prog. tec., 1935, 6, 123; Chem. Zentr., 1935, ii, 976).—The BeO bands from a vac. arc between Be electrodes in O<sub>2</sub> are recorded.

**Absorption spectrum of lead oxide (PbO).** H. G. HOWELL (Proc. Roy. Soc., 1936, A, 153, 683—698).—The spectrum stretches from 2600 to 6000 Å. and contains 5 systems, 3 of which are found in emission. The vibrational consts. of all the levels involved have been determined. The ground state probably dissociates into 2 excited atoms. The spectra of the related mols. PbS, PbO, SnS, SnO, GeS, and GeO are compared; among other similarities, it is found that the vibrational frequency varies from

state to state in a similar manner with oxide and sulphide mols.

L. L. B.

**Absorption spectra of nitrates in the vapour state.** M. I. HAQ and R. SAMUEL (Nature, 1936, 137, 496).—The absorption spectra of K, Ag, Mg, and Pb nitrates, obtained by heating the salt in a vac. to approx. 100° > m.p., show a flat and diffuse max. of selective absorption between 270 and 260 m $\mu$ , indicating that the nitrates are covalently bound in the vapour state. Some nitrites and sulphates show a similar phenomenon.

L. S. T.

**Carbon monoxide bands  $A^1\Pi \rightarrow X^1\Sigma$  (IV Pos.).** L. GERÖ (Z. Physik, 1936, 99, 52—64).—Rotation analysis is given between 1950 and 2700 Å.

A. B. D. C.

**Predissociation in the  $A^1\Pi$  level of CO; dissociation energy of carbon monoxide at 6.9 volts?** R. SCHMID and L. GERÖ (Z. Physik, 1936, 99, 281—284).—The predissociation limits at 9.57, 11.06, and 11.54 volts are best co-ordinated by the assumption of a ground level dissociation energy of 6.9 volts. The reaction  $C_{solid} \rightarrow C(^5S)$  is given as 177 kg.-cal.

A. B. D. C.

**Transmission of visible light through artificial homogeneous clouds.** G. R. PARANJPE and N. N. BHAGVAT (J. Univ. Bombay, 1935, 4, Part II, 28—64).—The transmission of light through clouds of H<sub>2</sub>O, CHCl<sub>3</sub>, and CCl<sub>4</sub> agrees fairly well with Stratton and Houghton's theory (Physical Rev., 1931, [ii], 38, 159). With kerosene only partial agreement is obtained, and with EtOH, PhMe, and NH<sub>2</sub>Ph no agreement. No conclusions can be reached relating the effect with the refractive index of the liquid. For all liquids except EtOH and NH<sub>2</sub>Ph red light is transmitted better than blue by large drops, contrary to theory.

J. W. S.

**Ultra-violet spectra of bromine derivatives of aniline.** (MME.) M. P. RUMPF and P. RUMPF (Compt. rend., 1936, 202, 1063—1065).—The absorption of NH<sub>2</sub>Ph and its Br<sub>1</sub>-, Br<sub>2</sub>-, Br<sub>3</sub>-, and Br<sub>5</sub>-derivatives, *p*-C<sub>6</sub>H<sub>4</sub>Cl-NH<sub>2</sub>, 4-chloro- and 4-nitro-2:6-dibromoaniline have been determined in EtOH and C<sub>6</sub>H<sub>14</sub>. There is only one band in EtOH in contrast to the many bands in C<sub>6</sub>H<sub>14</sub>. Replacement of H by Br displaces the absorption max. towards the higher  $\lambda$ , the displacement increasing in the order *m*, *o*, and *p*, with the exception of *o*- and *m*-C<sub>6</sub>H<sub>4</sub>Br-NH<sub>2</sub>, for which the max. occur in the same position. Cl has the same influence as Br, but NO<sub>2</sub> is more effective in displacing the bands. On acetylation of the *p*-Br<sub>1</sub>- and the 2:4:6-Br<sub>3</sub>-derivatives the bands disappear, but in alcoholic NaOH intense absorption occurs. The Br<sub>1</sub>- and Br<sub>3</sub>-derivatives in aq. EtOH containing HCl give no bands, except for 2:6-C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>-NH<sub>2</sub>, which is a very weak base.

R. S. B.

**Influence of cyclisation on the "colour" of molecules. Ultra-violet absorption of derivatives of diphenylurethane and fluorene.**—See this vol., 726.

**Absorption spectra. I. Application to intermediate products of dyes.** (MLLE.) C. L. HARBERTS, P. M. HEERTJES, L. J. N. VAN DER HULST, and



H. I. WATERMAN (Bull. Soc. chim., 1936, [v], 3, 643—655).—The absorption spectra of  $\text{NH}_2\text{Ph}$ ,  $\text{NH}_2\text{Ph}\cdot\text{HCl}$ ,  $\text{PhN}_2\text{Cl}$ , *p*-toluidine, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\text{Cl}$ , and  $(\text{NPh})_2$  in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , or hexane have been determined.

E. S. H.

**Spectrochemistry of organic nitrogen compounds.** (MME.) RAMART-LUCAS (Bull. Soc. chim., 1936, [v], 3, 723—738).—A preliminary discussion.

E. S. H.

**Absorption and deformation of valency angles.** (MME.) RAMART-LUCAS (Bull. Soc. chim., 1936, [v], 3, 738—745).—A preliminary discussion of work to be published on the absorption spectra of org. compounds.

E. S. H.

**State of the benzene molecule in solution.**—See this vol., 713.

**Absorption spectrum of dinaphthopyrone.** W. SATURNINA (Acta phys. polon., 1933, 2, 283—284; Chem. Zentr., 1935, ii, 1159).—Three max. (3540, 3375, and 3175 Å.) are shown. H. N. R.

**Optical absorption of porphyrins.** V. A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1936, 176, 81—124; cf. this vol., 545).—In normal porphyrins with an oximated CO group the  $\text{:N}\cdot\text{OH}$  group has little effect on the optical absorption, whereas with porphyrins having one CO group only, and that in the isocyclic ring, the effect of the  $\text{:N}\cdot\text{OH}$  is greater, the absorption curve being of the rhodo-type. In general, the effect of the  $\text{:N}\cdot\text{OH}$  is in the direction of a curve of the rhodo-type. Porphyrins with a  $\cdot\text{CN}$  directly attached to one of the nuclei of the porphin framework have a curve of a pronounced rhodo-type. Various substitutions in the dihydroporphyrin system have a particularly marked effect on the mol. extinction coeff.,  $\epsilon$ , of the red band I; the influence on the other bands is relatively slight. A  $\cdot\text{CHO}$  in position 3 or, to a much smaller extent, a  $\text{:N}\cdot\text{OH}$  depresses  $\epsilon$ . Introduction of Mg raises  $\epsilon$  considerably, and shifts the band max.  $\beta\delta$ -Diminocoproporphyrin II  $\text{Me}_4$  ester (this vol., 86) appears to be a coproporphyrin II  $\text{Me}_4$  ester in which only the  $\beta$ - and  $\delta$ -C atoms are replaced by *tert.* N. The  $\cdot\text{CO}_2\text{Me}$  in the position 6 in the chlorins has little effect on the optical absorption. A  $\text{C}\cdot\text{OH}$  or similar group with a free CO group at the  $\gamma$ -C of the porphin system changes the type of the spectrum. The "green anhydride" of Fischer *et al.* (A., 1931, 431) appears to be an anhydride of rhodoporphyrin-XV- $\gamma$ -carboxylic acid. The phyllochlorin obtained by heating phylloporphyrin with  $\text{NaOEt}$  (A., 1929, 941) differs from natural dihydrophyllochlorin only in being optically inactive.

R. C.

**Ultra-violet spectrum of hæmoglobin derivatives and bile pigment.** G. A. ADAMS (Nature, 1936, 137, 578).—Many derivatives of hæmoglobin (enumerated) show an absorption band in the region of 4100 Å., due to the porphyrin ring system in the hæm radical, and independent of the nature of the globin present. With bilirubin there is no characteristic band at 4100 Å., but a somewhat indefinite absorption from 5000 to approx. 4300 Å. L. S. T.

**Ultra-violet absorption of Cellophane and of tissues and vegetable organs.** E. GILLES (Compt.

rend., 1936, 202, 968—970).—The transmission of Cellophane is variable. Absorption becomes considerable at approx. 2200—2600 Å. Vegetable membrane transmits light down to 2397 Å. Absorption by leaves is intense. Data for various species are given.

H. J. E.

**Infra-red reflexion spectra of silicates.** II. F. MATOSSI and H. KRÜGER (Z. Physik, 1936, 99, 1—23).—Spectra are given between 8 and 26  $\mu$  for 26 silicates: willemite, zircon, fayalite, olivine, sillimanite, chondrodite, thortveitite, hemimorphite, benitoite, cordierite, ænigmatite, anthophyllite, serpentine, antigorite, agalmatholite, nepheline, cancrinite, scapolite, sodalite, natrolite, danburite, datolite, axinite, epidote, zoisite, and leucite. The spectra fit the scheme already proposed (cf. A., 1934, 829).  $\text{Be}_2\text{SiO}_4$  and  $\text{Li}_2\text{WO}_4$  spectra are compared.

A. B. D. C.

**Infra-red absorption of organic compounds containing hydroxyl and imino-groups.**—See this vol., 718.

**Near infra-red bands of methane.** I. General survey, and a new band at 11,050 Å. W. H. J. CHILDS (Proc. Roy. Soc., 1936, A, 153, 555—567).—The near infra-red bands of  $\text{CH}_4$  in the region 10,000—12,000 Å. have been photographed under high dispersion. Much new detail has been observed in the bands at 11,350, 11,620, and 11,870 Å., and two new bands have been discovered at 11,050 and 11,230 Å. The latter is interpreted as the second harmonic of the fundamental at 3.3  $\mu$ , and is described in detail. Several inaccuracies in the consts. of the  $\text{CH}_4$  mol. derived from Cooley's measurements (A., 1926, 659) are indicated.  $I$  in the ground state =  $5.267 \times 10^{-40}$  g.cm.<sup>2</sup>, and the vibration moments of momentum in the 7.7 and 3.3  $\mu$  bands are 0.45 and 0.050, respectively.

L. L. B.

**Rotation-vibration spectrum of acetylene in the photographic infra-red.** G. W. FUNKE (Z. Physik, 1936, 99, 341—352).—Nine new bands are recorded in this region.

A. B. D. C.

**Near infra-red absorption of hydrocarbons.** II. Gaseous paraffins, olefines, and acetylene. P. GÄNSWEIN and R. MECKE. III. Halogen derivatives of methane, ethane, and ethylene. O. VIERLING and R. MECKE. IV. Anharmonic valency vibrations of polyatomic molecules. R. MECKE (Z. Physik, 1936, 99, 189—203, 204—216, 217—255).—II. Absorption is given between 10,000 and 7000 Å. for  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_6\text{H}_{12}$ ,  $\text{C}_8\text{H}_{14}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_4\text{H}_6$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_4\text{H}_2$ ,  $\text{C}_4\text{H}_4$ , and  $\text{MeCHO}$ . Different degrees of saturation give different absorption regions for the third CH overtone: paraffins absorb between 8950 and 9150 Å., olefines between 8600 and 8750 Å., and acetylenes from 7850 to 7900 Å. (cf. A., 1935, 1444).

III. The third CH overtone was examined for the 6 Cl- and Br-derivatives of  $\text{CH}_4$ , for 5 Cl- and 3 Br-derivatives of  $\text{C}_2\text{H}_6$ , for 3 Cl-derivatives of  $\text{C}_2\text{H}_4$ , and for  $\text{C}_3\text{H}_7\text{Cl}$  and  $\text{C}_3\text{H}_5\text{Cl}$ . The change in CH bands with halogen substitution is small compared with saturation of the C-C valency, except for unsymmetrical compounds (as  $\text{C}_2\text{H}_3\text{Cl}_3$ ) where bands are ascribed to larger groups (as  $\text{CHCl}_2\cdot$ ).



IV. Anharmonic vibration levels are investigated with Schrödinger's vibration equation taking into account perturbations of the second order. Various degrees of coupling and resonance are discussed, particularly in relation to ascribing frequencies to at. groups. The CH group has loose coupling, and its overtones can be described in terms of the fundamental frequency in the ordinary manner.

A. B. D. C.

**Residual ray bands of LiF and MgO.** K. KORTH (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 187—194; Chem. Zentr., 1935, ii, 976).—The proper frequencies of mols. on the surface of LiF and MgO crystals differ from those of mols. in the interior. The reflexion max.  $\beta$  and transmission min.  $\delta$  are due to interior mols.; the reflexion max.  $\alpha$  and transmission min.  $\gamma$  are due to surface mols. J. S. A.

**Isolation of the 4358 Å. triplet of the mercury arc for use in Raman spectra.** C. SANNIÉ, L. AMY, and V. POREMSKI (Compt. rend., 1936, 202, 1042—1044).—The ratio between the densities of the lines 4358 and 4046 Å. transmitted by  $\text{PhNO}_2$  is 60; the ratios for 4358 and 4916 Å. transmitted by gentian-violet, rhodamine-S and -5G extra are 10.8, 15.2, and 19. A filter for removing lines of the Hg arc other than 4358 Å. in the neighbourhood of this line consists of 6%  $\text{PhNO}_2$  and 0.01% rhodamine-5G extra in EtOH, the transmission being 1/1000 for 4046 and 4916 Å., and 0.95 for 4358 Å. The filter changes slowly under the influence of light.

R. S. B.

**Polarisation of the Raman bands of water and deuterium oxide.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 201—205).—In the three principal Raman bands of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  the depolarisation increases with frequency shift. The bands 1235 and 175  $\text{cm}^{-1}$  of  $\text{D}_2\text{O}$  are 50—60% and 6/7 depolarised, respectively. The bands 175, 500, and 750  $\text{cm}^{-1}$  of  $\text{H}_2\text{O}$  are highly depolarised. The results are discussed.

L. J. J.

**Chlorotitanic acid. Raman spectrum.** (MME.) M. E. P. RUMPF (Compt. rend., 1936, 202, 950—952).—Mixtures of  $\text{TiCl}_4$  and HCl show new Raman lines at 251.7, 340, and 463  $\text{cm}^{-1}$  which, by analogy with corresponding lines for  $\text{H}_2\text{SnCl}_6$ , are attributed to  $\text{H}_2\text{TiCl}_6$ . The new lines are not observed in a dil. HCl solution of  $\text{TiCl}_4$ .

H. J. E.

**Raman spectrum of acetylene.** S. BHAGAVANTAM and A. V. RAO (J. Chem. Physics, 1936, 4, 293).—The frequencies given by  $\text{C}_2\text{H}_2$  gas are 589, 646, 1973, and 3371  $\text{cm}^{-1}$ . Glockler and Morrell's assumption of a bent mol. (this vol., 269) is unnecessary.

L. J. J.

**Raman spectra of deuteriochloroform and deuteromethyl alcohol. Vibration model of the type  $\text{XY}_3\text{Z}$ .** O. REDLICH and F. PORDES (Monatsh., 1936, 67, 203—212).—The prep. of  $\text{CDCl}_3$  (from  $\text{CCl}_3\text{CHO}$  and KOD) and  $\text{MeOD}$  [from  $\text{Mg}(\text{OMe})_2$  and  $\text{D}_2\text{O}$ ] is described. Their Raman spectra confirm previously found relations between the frequencies of isotopes. The relations between frequency and force consts. are deduced for the  $\text{XY}_3\text{Z}$ -type mol. and the consts. of a central and valency-energy model deduced. The data for  $\text{CDCl}_3$  can be inter-

preted either on a central energy model or on a central and valency energy model. J. W. S.

**Raman spectra and vibrations of mono-deuterobenzene and *p*-dideuterobenzene.** O. REDLICH and W. STRICKS (Monatsh., 1936, 67, 213—221; cf. this vol., 137).—Data recorded previously are expanded and discussed. J. W. S.

**Interpretation of the Raman spectra of formic acid and metallic formates.** J. GUPTA (Indian J. Physics, 1936, 10, 117—125).—The Raman spectra of  $\text{HCO}_2\text{H}$  (liquid and aq. solution), Na, Ba, and Cd formates (solid and aq. solution), and an aq. solution of  $\text{CCl}_3\cdot\text{CO}_2\text{Na}$  have been investigated. The line 2963  $\text{cm}^{-1}$  observed in the case of pure  $\text{HCO}_2\text{H}$  is also present in the aq. solution of the acid, but in the solid formates it is split into two lines, 2963 and 2574  $\text{cm}^{-1}$ ; the former is absent from the Raman spectra of solutions of the salts, its place being taken by a line at 2834  $\text{cm}^{-1}$ . The 1398  $\text{cm}^{-1}$  line in the spectrum of  $\text{HCO}_2\text{H}$  is also replaced by two (1353, 1375  $\text{cm}^{-1}$ ) in aq. solutions of the salts, and the two lines at 1675 and 1724  $\text{cm}^{-1}$  for the acid are replaced by one at 1650  $\text{cm}^{-1}$  in solutions of the salts. The shift of the 1398 line to 1353  $\text{cm}^{-1}$  cannot be explained as due to the deformation vibration of CH in the  $\cdot\text{CHO}$  (Venkateswaran, this vol., 268), which is responsible for the 1375 line. It is assumed to be due to the oscillation of the  $\text{O}\cdot\text{C}\cdot\text{O}$  group in the Hantzsch structure of formates. A. J. M.

**Constitution of formic acid and formates.** P. B. SARKAR and B. C. RAY (Nature, 1936, 137, 495—469; cf. A., 1934, 586).—Raman spectra of solutions of  $\text{HCO}_2\text{H}$  and formates, and the infra-red absorption curves of  $\text{HCO}_2\text{Na}$ , solid and in aq. solution, indicate that  $\text{HCO}_2\text{H}$  and solid formates are normal in structure for they show the  $\cdot\text{CH}\cdot$  linking. Prototropic change of the true formate ion,  $\text{H}\cdot\text{C}(\text{O})\cdot\text{H}$  into  $\text{C}(\text{O})\cdot\text{OH}$  is suggested to account for this. L. S. T.

**Constitution of formic acid and formates.** I. T. S. WHEELER. II. T. R. SESHADRI. III. R. M. HALASYAM (Current Sci., 1936, 4, 650—651).—I. The parachor vals. for  $\text{HCO}_2\text{H}$  are discussed (cf. Halasyam, this vol., 412).

II, III. Polemical.

N. M. B.

**Raman and infra-red spectra of stereoisomeric 1:3- and 1:4-dimethylcyclohexanes and of 1:1-dimethylcyclohexane.** J. LECOMTE, L. PIAUX, and O. MILLER (Bull. Soc. chim. Belg., 1936, 45, 123—129).—The Raman and infra-red spectra of the 1:3- and 1:4-stereoisomerides do not show any resemblance to those of 1:1-dimethylcyclohexane, nor yet to those of the 1:2-derivatives previously examined (A., 1934, 345, 716). As regards the relation between Raman and infra-red spectra for any one compound, in some cases the same bands appear in both types of spectra, but not with the same intensity. In other cases important bands in one spectrum never appear at all in the other. Investigation of one spectrum alone, therefore, is not sufficient to give all the modes of vibration of these mols. M. S. B.

**Raman effect of methylcyclopentano derivatives.** M. GODCHOT, (MLLE.) G. CAUQUIL, and R.



CALAS (Compt. rend., 1936, 202, 1129—1130).—Ketonic, alcoholic, and acetic ester derivatives possess the principal frequencies of the methylcyclopentane nucleus (cf. A., 1932, 559). Ketones and esters give the characteristic C:O frequency, 1744  $\text{cm}^{-1}$ . Corresponding optically active and racemic compounds have identical spectra. For the range 200—800  $\text{cm}^{-1}$  there is a strong resemblance between the spectra of *cis*- and *trans*-alcohols, but not of the corresponding esters. M. S. B.

**Raman spectrum and constitution of pyrazole and of some of its derivatives.** G. B. BONINO and R. MANZONI-ANSIDEI (Atti R. Accad. Lincei, 1935, [vi], 22, 438—443).—Raman lines for pyrazole (I) and its Me derivatives are recorded. The spectrum of (I) contains 11 lines, similar to those of thiophen and pyrrole, but there are no lines characteristic of the double linking. O. J. W.

**Raman spectrum of dimethylfurazan and of dimethyloxidiazole.** R. MANZONI-ANSIDEI (Atti R. Accad. Lincei, 1935, [vi], 22, 444—447).—The Raman spectra of dimethylfurazan and of dimethyloxidiazole contain 21 and 18 lines, respectively (cf. A., 1933, 886). O. J. W.

**Raman spectrum of some substituted pyrrole-aldehydes.** G. B. BONINO, R. MANZONI-ANSIDEI, and D. DINELLI (Atti R. Accad. Lincei, 1935, [vi], 22, 448—452).—The Raman spectra of the *C*-alkyl-pyrrolealdehydes investigated all show an intense diffuse line at 1620—1650  $\text{cm}^{-1}$ , which can be attributed to the strongly perturbed C:O group, and also a line at 1560—1570  $\text{cm}^{-1}$ , which does not occur in the spectrum of pyrrole-2-aldehyde and is probably due to a double linking. O. J. W.

**Light scattered by cloudy media and its polarisation.** H. VON DEM BORNE (Z. Physik, 1936, 99, 73—102).—Scattering was investigated for smokes and vapours by means of a  $\text{Cu}_2\text{O}$  cell at 0.55 and 1.0  $\mu$ . A scattering function was determined and applied to meteorological problems. A. B. D. C.

**Scattering of light in optical glasses.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 211—220).—The intensity and polarisation of the light scattered transversely by 17 optical glasses has been studied, with the incident light unpolarised, horizontally polarised, and vertically polarised. All the glasses gave a weak fluorescence. The depolarisation measurements indicate the presence of anisotropic mol. aggregates of size not small compared with the  $\lambda$  of light. L. J. J.

**Emission of ultra-violet radiation in the Reboul effect.** O. VIKTORIN (Compt. rend., 1936, 202, 941—943).—Very feeble radiation (2600—2000 Å.) was detected with a photo-counter. H. J. E.

**Radiation emitted in the dehydration and hydration of quinine sulphate.** R. AUDUBERT and M. PROST (Compt. rend., 1936, 202, 1047—1049; cf. A., 1935, 1055).—The ultra-violet radiation emitted on the dehydration on heating and hydration of quinine sulphate has been studied using a CuI photo-cell sensitive to 2000—2500 Å. The emission accompanying hydration is 6—8 times that given on dehydration. The radiation comes from the sur-

face layers, since it is independent of the thickness of the specimens used. A strong magnetic field has no effect. On dehydration of the salt the radiation is probably partly due to a modification in the crystal structure. The energy emitted on hydration is only 10<sup>-11</sup>—10<sup>-12</sup>% of the heat of hydration. R. S. B.

**Phosphorescent beryllium nitride.** S. SATOH (Sci. Papers Inst. Phys. Chem. Tokyo, 1936, 29, 41—46; cf. A., 1934, 741).— $\text{Be}_3\text{N}_2$  gives strong phosphorescence when mixed with  $\text{Al}_2\text{O}_3$  and excited by a Hg-vapour lamp. The phosphorescence increases with the % of  $\text{Al}_2\text{O}_3$  up to a max. at 30%, and does not occur without excitation. 2% of Ti and Zr confer no phosphorescence on  $\text{Be}_3\text{N}_2$ ; 2% of Mn gives a feeble effect. The cathode-ray spectrum of  $\text{Be}_3\text{N}_2 + 30\%$   $\text{Al}_2\text{O}_3$  is continuous at 4200—4900 Å., with a max. at approx. 4650 Å. The spectra of Be,  $\text{Be}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  are very faint. R. S. B.

**Relations between luminescent power and lattice structure. I. Layered-lattice crystals.** A. KUTZELNIGG (Angew. Chem., 1936, 49, 267—268).—A lecture. E. S. H.

**Fluorescence spectra of deuteroporphyrin and pyroporphyrin; fine structure, emission in the near infra-red.** C. DHÉRE and O. BIERMACHER (Compt. rend., 1936, 202, 442—444).—The fluorescence spectrum of deuteroporphyrin in  $\text{Et}_2\text{O}$  shows a principal band at 6230 Å. and six other bands in the orange and red region. Pyroporphyrin shows analogous bands. Copro-, deuter-, and pyro-porphyrin show supplementary bands in the near infra-red of shorter  $\lambda$  than those of protoporphyrin. The infra-red fluorescence is probably due to photo-porphyrins produced by the irradiation. J. W. S.

**Carcinogenic action and absorption and fluorescence spectra of 1:2-benzpyrene.** C. SANNIÉ (Biochem. J., 1936, 30, 704—706).—Ultra-violet absorption and fluorescence spectra of 1:2-benzpyrene, 4-keto-1':2':3':4'-tetrahydro-1:2-benzpyrene, and  $\beta$ -1-pyrenoylpropionic acid in different solvents and in different states of purity, and of various fractions of Schroeter mixture, are given. It is unlikely that the fluorescence spectra characteristic of purified hydrocarbons would be recognisable in complex mixtures. H. D.

**Fluorescence spectrum of 1:2-benzpyrene.** W. V. MAYNEORD (Biochem. J., 1936, 30, 707—708).—The fluorescence spectrum of 1:2-benzpyrene is determined and the influence of impurities alleged by Sannié (see above) is denied. H. D.

**Inhibiting action of alkaloids on the fluorescent power of uranine in relation to the antioxidant properties of these substances.** A. BOUTARIC and J. BOUCHARD (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 35—40).—A method for the comparison of the intensity of fluorescence of two different solutions is described. The diminution of the fluorescent power of uranine (I) by the action of different alkaloids at const.  $p_H$  in aq. solution as salts, or in EtOH solution as free bases, is much < by the action of the corresponding amine oxides, or genalkaloids (II), which are no longer antioxidants. The diminution in inhibiting action on the fluorescence of (I)



apparently runs parallel with the disappearance of antioxidant properties in (II) and with the reduction in toxicity also observed. M. S. B.

**Becquerel effect and photochemical sensitivity of some fluorescent dyes.** (MLLE.) C. STORA (Compt. rend., 1936, 202, 408—410).—It is concluded that the Becquerel effect and the photochemical sensitivity of a dye depend both on oxidation-reduction phenomena and on the presence of certain groups in the mol. The recovery of photosensitivity at the expense of the medium indicates the essential rôle played by the solvent. The same relation to fluorescence exists for the photo-voltaic effect as for photochemical sensitivity. J. W. S.

**Contact potential measurements on tungsten films.** D. B. LANGMUIR (Physical Rev., 1936, [ii], 49, 428—435).—Changes in contact potential, produced by varying the amount of Th on the surface and by varying the temp., were measured for a W filament by using a tube containing two filaments. Electron emission with very low accelerating fields is compared with the contact potential on the same surface and at the same temp.; the theoretical law is obeyed but not for higher fields or with differences of temp. An increasingly negative contact potential is shown with rising temp., the activated surface having the larger rate of change. Pure W shows a temp. coeff. of opposite sign, indicating a decreasing work function with rising temp. N. M. B.

**Photo-electric electron yield with counter tubes.** W. CHRISTOPH (Physikal. Z., 1936, 37, 265—269).—Counter tubes fail to register all the electrons emitted from the cathode. Increase in field strength gives an increase in photo-electric yield, and this increase is greater when the irradiating light is of longer  $\lambda$ . The difference between electrons counted and those emitted is the greater, the smaller is the difference between the limiting  $\lambda$  of the metal concerned and the  $\lambda$  of the incident light. A. J. M.

**Surface photo-electric effect in metals. II.** K. MITCHELL (Proc. Roy. Soc., 1936, A, 153, 513—533).—Theoretical. Spectral distribution curves for (a) polarised and (b) unpolarised light, and (c) energy distribution curves are calc. (b) show excellent agreement with experimental results for alkali metals, and (c) agree with Brady's results (A., 1935, 4).

L. L. B.

**Electrical evidence on calcite imperfection.** F. C. FRANK (Nature, 1936, 137, 656—657; cf. this vol., 404).—Joffé's work on electrical conduction in calcite (Ann. Physik, 1923, 72, 473) indicates the existence of lattice spaces unfilled by  $\text{Ca}^{++}$  ions, affecting the val. of  $e$ . L. S. T.

**Influence of the nature and position of groups on the photo-potential of substituted aromatic amines.** (MLLE.) H. T. NGA (Compt. rend., 1936, 202, 1049—1050; cf. A., 1935, 1463).—The photo-potential given by 0.05N solutions of *o*-, *m*-, and *p*-Me,  $-\text{NO}_2$ , and -halogen derivatives of  $\text{NH}_2\text{Ph}$  in 0.005N aq. KI, KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{HCO}_2\text{Na}$ , and  $\text{KClO}_3$  at 18° have been measured, using a Hg-vapour lamp for excitation. The quantities of energy absorbed by the various compounds are approx. the

same, and all, except  $\text{C}_6\text{H}_4\text{I}\cdot\text{NH}_2$ , are stable during the experiment. The photo-effect increases from *o* to *m*, but *m* and *p* are identical. A parallel is drawn between the photo-voltaic effect and chemical reactivity. R. S. B.

**Effects of heat and ultra-violet light on the rectifying action of some crystals.** B. K. SEN (Indian J. Physics, 1936, 10, 91—102).—The action of heat and ultra-violet light on the rectifying properties of pyrolusite, galena, Cu pyrites, zincite, "Master" crystal, and particularly Fe pyrites has been investigated. The rectifying power diminishes with rise of temp., but, contrary to Khastgir *et al.* (A., 1935, 12, 682), does not disappear entirely below 200°. Irradiation of the crystal with ultra-violet light causes an increase in conductivity of all crystals examined, but the effect on rectification was small. A. J. M.

**Photo-electric barrier layer effect.** R. DEAGLIO (Atti R. Accad. Sci. Torino, 1934, 70, I, 272—275; Chem. Zentr., 1935, ii, 1137).—A Ag-Cu<sub>2</sub>O single-crystal contact rectifier showed no photo-electric barrier-layer effect, indicating the independence of the photo-electric and the unidirectional conduction effects. J. S. A.

**Changes in absorption of weak high-frequency electric fields by liquids as a function of the voltage of the field.** E. K. SAVOJSKI and B. M. KOSIREV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 109—113).—The absorption curve for AcOH shows a series of step-like discontinuities with increasing field strength. They do not depend on temp. (18—25°) or on the [AcOH]. H. J. E.

**Changes of absorption of weak electric fields of high frequency in certain substances as a function of the strength of these fields. II.** E. K. SAVOJSKI and B. M. KOSIREV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 219—220).—The crit. strengths of the high-frequency field in the range 130—180 volts per cm. in liquid AcOH persist in the solid, indicating that their existence is due to some intramol. process. The no. and val. of crit. potentials in the range 375—480 volts per cm. are the same in solid AcOH and NaOAc. N. M. B.

**Electric spark discharge in insulating liquids.** F. KOPPELMANN (Z. tech. Physik, 1935, 16, 125—141; Chem. Zentr., 1935, ii, 979).—A comprehensive review of the phenomena and theory of the discharge. J. S. A.

**Spectral distribution of the depolarisation current for X-irradiated KCl crystals.** N. KALABUCHOV and J. KURSHEV (Z. Physik, 1936, 99, 254—258).—The spectral distribution curve has two max. at 570 and 630 m $\mu$ ; the first indicates a level 1.86 volts above the conducting zone, and the second is ascribed to a level associated with  $\text{K}^+$  ions. A. B. D. C.

**Electrical conductivity of thin films of rubidium on [Pyrex] glass surfaces.** A. C. B. LOVELL (Nature, 1936, 137, 493—494).—The resistivity of films a few atoms thick deposited at 64—90° abs. is somewhat > that of the metal in bulk, but different from that previously reported. L. S. T.



**Electret.** H. NUMAKURA (J. Electrochem. Assoc. Japan, 1935, 3, 89—92).—An electret is formed by solidifying a mixture of rosin with ceresin or beeswax, or of ceresin with mastic or dammar, etc., in an electric field of 2 kv. per cm. The charges on surfaces cut perpendicular to the electric field are due to orientation of the polar mols. during solidification. The property disappears on heating for 24 hr. at 55°.

H. J. E.

**Relation between electrical conductivity and the coefficient of internal friction in melted salts.** S. KARPATSCHEV and A. STROMBERG (J. Phys. Chem. U.S.S.R., 1934, 5, 1283—1291).—A theoretical relationship between the conductivity, internal friction, mol. wt., and  $d$  is derived. Experimental vals. for the alkali and Ag halides and nitrates are 1.4—2.2 times too large.

CH. ABS. (e)

**Theory of electrolytic conduction and diffusion in crystals. III. Calculation of energies of disarray and threshold energies. Effect of pressure on electrolytic conduction.** W. JOST and G. NEHLEP (Z. physikal. Chem., 1936, B, 32, 1—21; cf. A., 1934, 949).—The previous calculations of energy of polarisation and disarray (*ibid.*, 11) have, by taking account of the displacement of the ions in the vicinity of a point of disarray, been so far improved and rendered more precise that it is possible to decide in a particular case whether the disarray consists in the presence of ionic voids of one sign together with an equiv. no. of ions in the intra-lattice space or the presence of equiv. nos. of voids of both signs (cf. A., 1935, 1302, 1305). It appears certain that the disarray in lattices of salts with ions of similar size and polarisability and not too large dielectric consts. is of the second type. Owing to the considerable effect of repulsive forces on the threshold energy which must be exceeded for migration of a void to be possible, the conductivity must be measurably influenced by pressure, the magnitude of the effect depending on which type of disarray is involved.

R. C.

**Direct-voltage experiments with electrolytically produced aluminium oxide.** G. FRANCKENSTEIN (Ann. Physik, 1936, [v], 26, 17—54).—The dielectric properties of electrolytically produced films of  $Al_2O_3$  (thickness 10—100  $\mu$ ) were investigated using d.c. The surface conductivity does not depend on the structure or method of prep. of the film, but on the humidity of the atm. by an exponential law. The methods by which  $H_2O$  is taken up by the surface are discussed. The conductivity through the film depends on the method of prep. Conductivity increases exponentially with the voltage, and is diminished by drying. It is impossible to remove  $H_2O$  completely from thick films. The resistance varies linearly with thickness for thin layers, and exponentially for thick ones. For thin layers, electrical breakdown occurs across air in the pores of the film, but for thick films breakdown is thermal. The breakdown potential is not affected by humidity. Investigation of after-effects showed the existence of a considerable back-current and back-e.m.f., decaying exponentially with time.

A. J. M.

**Polarisation of liquids and their saturated vapours in the critical temperature region.**

J. MARSDEN and O. MAASS (Canad. J. Res., 1936, 14, B, 90—95; cf. this vol., 139).—The polarisations of the liquid and the saturated vapour of MeOEt and  $C_3H_8$  are identical at the crit. temp. The liquid polarisation is a const. below the crit. temp., whilst that of the saturated vapour decreases according to a characteristic curve.

R. S.

**Magnetic change of the dielectric constant of liquids.** A. PIÉKARA and M. SCHÉNER (Compt. rend., 1936, 202, 1159—1160; cf. A., 1935, 1192).—A correction. The apparatus previously employed has been altered to reduce condenser deformation and the vals. obtained for  $\Delta\epsilon \times 10^4$  are now all < the following:  $C_6H_6$  5,  $CCl_4$  3, PhMe 3,  $CS_2$  5.

M. S. B.

**Dielectric constant of a space containing electrons.** S. P. PRASAD and M. N. VERMA (Z. Physik, 1936, 99, 552—561).—The dielectric const. increases with electron concn. and with decreasing  $\lambda$ .

A. B. D. C.

**Molecular interactions and structure of liquids.** P. GIRARD and P. ABADIE (Compt. rend., 1936, 202, 398—400; cf. A., 1935, 1187).—The time of relaxation-concn. curves for solutions of  $H_2O$  in dioxan and of dichlorohydrin in  $C_6H_6$  show max. at low concns., suggesting that the semi-cryst. state appears when the ratio of electrostatic energy to thermal agitation attains a definite val. Applying Martin's equation (A., 1934, 1063) for the change in energy of a dipole in passing from one medium to another, to the max. of these curves, values of  $\Delta w$  are about  $3 \times 10^{-15}$  erg for most mols. The extrapolated val. for pure  $H_2O$  is  $4 \times 10^{-14}$  erg, equal to the energy of mol. agitation, whilst for other mols. it is less. Hence the semi-cryst. state of liquid  $H_2O$  is highly developed at room temp.

J. W. S.

**Anisotropy of the optical polarisation field in liquids. I, II.** B. S. R. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 240—243, 244—248).—I. Data are recorded for the variation of refractive index with temp. for  $CS_2$ ,  $C_6H_6$ ,  $C_6H_{14}$ , and  $CCl_4$ .  $R_L$  is independent of temp. in the case of  $CCl_4$ , but in the other cases increases with rise of temp., showing that the optical polarisation field is anisotropic.

II. The consts. of anisotropy are calc., and the temp. dependence of the depolarisation of the scattered light deduced, from the above data.

L. J. J.

**Birefringence by mechanical deformation of pure liquids.** C. SADRON (Compt. rend., 1936, 202, 404—406; cf. Vorländer and Walter, A., 1926, 110).—Repetition of measurements on  $C_7H_{15}OH$  and  $C_8H_{17}OH$ , using velocities of drum rotation well below the crit. velocity, yielded vals. of 4.5 and 6.5 ( $\times 10^{-12}$ ), respectively, for their dynamic birefringences. Raman and Krishnan's theory (A., 1928, 573) predicts  $7.4 \times 10^{-12}$  for  $C_7H_{15}OH$ . The vals. for oleic acid, cinnamaldehyde,  $C_{12}H_{25}OH$ , and  $CH_3PhOH$  are 360, 51.6, 29.6, and  $17.5 (\times 10^{-12})$ , respectively.

J. W. S.

**Electro-optical Kerr effect in methane, ethylene, and ethane.** W. M. BREAZEALE (Physical Rev., 1936, [ii], 49, 625—626; cf. A., 1935, 1192).—Measurements of the Kerr effect were made at 6500 Å., pressures 30—100 atm., and temp. 15—55°.



Results, with the aid of the Langevin-Born theory, give for the Kerr const. at n.t.p. and 6500 Å, the vals.  $\times 10^{12}$ :  $\text{CH}_4$  3.66,  $\text{C}_2\text{H}_2$  16.3, and  $\text{C}_2\text{H}_4$  10.4.

N. M. B.

**Curves of constant affinity in the phase changes of single substances.** J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1936, 22, [v], 252-264).—Theoretical.

D. R. D.

**Theory of homopolar valency. Significance of the fission rule for olefines and radicals.** O. SCHMIDT (Z. Elektrochem., 1936, 42, 175-184; cf. A., 1932, 716; 1935, 1286).—The wave-mechanical treatment of homopolar valency is inferior to the statistical method in which the direction of the electron spin is taken into account. The question is discussed with reference to the thermal decomp. of olefines and radicals.

F. L. U.

**Use of a Geiger-Müller counter for the study of the diffraction of X-rays by a gas.** W. VAN DER GRINTEN and H. BRASSEUR (Nature, 1936, 137, 657).—Replacement of the photographic plate by a Geiger-Müller counter gives good results for the Cl-Cl distance in  $\text{CCl}_4$ .

L. S. T.

**Peculiarities of water and aqueous solutions.** H. ULICH (Angew. Chem., 1936, 49, 279-282).—A discussion of the anomalies mainly linked with association.

E. S. H.

**Condensed helium at absolute zero.** F. LONDON (Proc. Roy. Soc., 1936, A, 153, 576-583).—The usual methods of lattice theory cannot be applied to the He lattice, owing to the fact that its zero point energy is of the same order of magnitude as the interaction energy, and has a decisive effect on the constitution of the lattice. The fact that closest packed structure is stable only under pressure explains why solid He can only exist, even at  $0^\circ$  abs., under pressure. If no external pressure is applied, a configuration with the co-ordination no. 4 is shown to have considerably lower energy, and gives a rough model of the liquid modification of He which is stable at  $0^\circ$  abs.

L. L. B.

**The liquid state and interatomic forces.** I, II. S. FRANCHETTI (Atti R. Accad. Lincei, 1935, [vi], 22, 433-438, 585-593).—Mathematical and theoretical.

O. J. W.

**Symmetry of a crystal lattice and its electron levels.** F. HUND (Z. Physik, 1936, 99, 119-136).—Qual. rules are deduced to determine whether or not a crystal is an insulator.

A. B. D. C.

**The three-centre problem.** II. G. S. GORDADSE (Z. Physik, 1936, 99, 287-299; cf. A., 1935, 1298).—Mathematical. The results are used to obtain energy formulæ for  $\text{H}_2^+$  and  $\text{H}_3^{++}$ .

A. B. D. C.

**Accommodation coefficient of deuterium.** W. B. MANN and W. C. NEWELL (Nature, 1936, 137, 662).—The accommodation coeffs. of  $\text{H}_2$ , 99.2%  $\text{D}_2$ , and He relative to a Pt wire at  $100.7^\circ$ , with the surrounding gas at approx.  $16^\circ$ , are 0.24(3), 0.30(8), and 0.29(4), respectively.

L. S. T.

**Hydrogen atoms.** V. BARGMANN (Z. Physik, 1936, 99, 576-582).—Pauli's matrix equation for H leads to Fock's results (cf. this vol., 266).

A. B. D. C.

**Concentration of deuterium in organic compounds.** II. General discussion with particular reference to benzene. M. DOLE (J. Amer. Chem. Soc., 1936, 58, 580-585; cf. A., 1934, 853).—A crit. review of published work. The at. wt. of H in org. compounds is considered to be more nearly normal than has been suspected hitherto.

E. S. H.

**Vibrations of tetrahedral pentatomic molecules.** V. General criteria for potential functions. (MISS) J. E. ROSENTHAL (Physical Rev., 1936, [ii], 49, 535-537; cf. A., 1934, 1293).—If the forces along the linkings of the  $\text{YX}_4$  mol. are fairly large compared with "interaction forces," the ambiguity in the vals. of the consts. in the potential energy function is removed. The ratio of the masses of the Y and X atoms determines the chemically correct set of force consts. Limiting vals. of the const. for the Y-X linking in  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{SnBr}_4$ ,  $\text{SO}_4^{--}$ , and  $\text{ClO}_4^-$  are given.

N. M. B.

**Vibration-rotation energy levels of polyatomic molecules.** I. Mathematical theory of semi-rigid asymmetrical top molecules. E. B. WILSON and J. B. HOWARD (J. Chem. Physics, 1936, 4, 260-268).—Mathematical.

L. J. J.

**Minimum potential for ozone formation by electron collision.** F. KRÜGER and C. ZICKERMANN (Z. Physik, 1936, 99, 428-452).—This min. potential is 6.3 volts, and indicates that  $\text{O}_2$  has to be dissociated into one excited and one non-excited O atom for formation of  $\text{O}_3$ .

A. B. D. C.

**Significance of electron collision experiments with CO and bond energy values of C-C and H-C from the assumption  $D(\text{CO})=6.9$  volts.** R. SCHMID (Z. Physik, 1936, 99, 274-280).—The crit. potential of CO gives the dissociation energy of 6.9 volts, and this gives 3.76 volts per C-C linking, and 4.4 volts per C-H linking.

A. B. D. C.

**Dissociation products of the CN molecule assuming a dissociation energy of 6.9 volts for CO.** R. SCHMID (Z. Physik, 1936, 99, 562-568).—A dissociation energy of 6.9 volts for CO gives CN dissociating into  $\text{C}(^5S)+\text{N}(^4S)$  atoms at 8.15 volts.

A. B. D. C.

**Calculation of rotation energy constants of molecules from a formula and its application to the calculation of dissociation energies.** E. A. HYLLERAAS (Naturwiss., 1936, 24, 279-280).—A formula is derived and applied to the calculation of the dissociation energy of the CdH mol.

A. J. M.

**Rotation of molecules in fields of octahedral symmetry.** A. F. DEVONSHIRE (Proc. Roy. Soc., 1936, A, 153, 601-621).—Mathematical. The solution of Schrödinger's equation for a diat. mol. rotating in a field of octahedral symmetry is discussed.

L. L. B.

**Absolute value of C-H linking moment, and sign of charge of the hydrogen atom in organic carbon compounds.** H. G. TRIESCHMANN (Z. physikal. Chem., 1936, B, 32, 22-26).—From calculation of the approx. moments of the aliphatic C-H and C-Cl linkings it seems probable that the H in the C-H linking is negative (cf. this vol., 268).

R. C.



**Nature of the chemical binding of certain oxides and sulphides.** P. K. SEN-GUPTA (J. Univ. Bombay, 1935, 4, Part II, 74—82).—From the infra-red absorptions of ZnS, ZnO, CdS, CdO, HgS, CaO, SrO, and BaO it is concluded that the linking is ionic in nature (cf. A., 1934, 237). J. W. S.

**Ferromagnetic saturation moment.** L. NÉEL (Compt. rend., 1936, 202, 1269—1272).—Theoretical. The discrepancy between observed saturation moment and that calc. from the Curie const. can be explained by incomplete orientation of magnetic moments at saturation, due to coupling between atoms being intermittent and subject to statistical laws.

L. J. J.

**Cavitation and surface tension. II.** F. K. T. VAN IJERSON (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 330—339).—The theory of the appearance and disappearance of small bubbles when H<sub>2</sub>O containing air passes a convergent-divergent constriction in a tube is discussed. In the divergent portion the bubbles disappear suddenly and the resultant shock erodes the walls, as in pumps. It is shown that oil increases the contact angle for air-steel from 22.5° to 90°, the air bubbles becoming hemispherical on a greasy surface. Oil increases cavitation owing to the decrease in  $\sigma$  for air-H<sub>2</sub>O and the increase in  $\sigma$  for air-wall, both effects increasing the adhesion of the bubble to the wall.

R. S. B.

**Quantitative determination of scattering of X-rays by microcrystalline layers.** J. BRENTANO (Z. Physik, 1936, 99, 65—72).—Experimental details are discussed.

A. B. D. C.

**Scattering of X-rays from amorphous substances and their molecular distribution.** M. OGURA (Sci. Rep. Tôhoku, 1936, 24, 587—594).—The Debye-Menke method (A., 1930, 1350; 1932, 986) of calculating mol. distribution in amorphous substances is applied to polyat. compounds.

M. S. B.

**External form of the crystal and its effect on the interference phenomena of the space lattice.** M. VON LAUE (Ann. Physik, 1936, [v], 26, 55—68).—Theoretical. Effects of the external form of a crystal on the sharpness of the interference pattern are observed with electron diffraction, but not with X-rays. The elementary theory of space-lattice interference is extended to take this into account, and the general laws governing the intensity in the neighbourhood of the interference spots are derived. The theory is applied to the observations of Kirchner *et al.* (A., 1935, 1451).

A. J. M.

**Energy levels of electrons in a one dimensional lattice with localised defects ("Lockerstellen"). Application to electric discharge.** A. SOKOLOV and N. MACHALOVA (Z. Physik, 1936, 99, 503—517).—Localised defects give levels in the normally "forbidden" zone. These are dependent on the potential energy associated with the defects and the electron energy; they explain discharge through dielectrics.

A. B. D. C.

**Growth and structure of electrolytically prepared aluminium oxide layers.** T. RUMMEL (Z. Physik, 1936, 99, 518—551).—Highly insulating

layers > 1  $\mu$  thick have been obtained free from corrosion. Their dielectric properties are largely dependent on the hydroxide content.

A. B. D. C.

**Surface layers of crystals.** (Sir) J. LARMOR (Nature, 1936, 137, 575—576).

L. S. T.

**The Beilby layer.** G. I. FINCH and A. G. QUARRELL (Nature, 1936, 137, 516—519).—A review.

L. S. T.

**Influence of temperature on asterism of crystals.** S. DEMBICKA (Acta phys. polon., 1933, 2, 285—290; Chem. Zentr., 1935, ii, 1132).—The asterism of slightly deformed Al, NaCl, and CaSO<sub>4</sub> crystals was unaffected by temp. In the case of Al, asterism disappeared on recrystallisation at higher temp.

J. S. A.

**Röntgenographic detection of lattice deformation in cold-deformed nickel.** W. E. SCHMID and E. A. W. MÜLLER (Z. tech. Physik, 1935, 16, 161—164; Chem. Zentr., 1935, ii, 972).—From measurements of the intensity, line breadth, and lattice spacing of the (024) reflexion from Ni, a relation is derived between deformation, applied stress, and compressibility. Inner stresses are calc.

J. S. A.

**X-Ray diffraction study of liquid sodium.** L. P. TARASOV and B. E. WARREN (J. Chem. Physics, 1936, 4, 236—238).—The radial distribution of atoms about any atom in liquid Na at 103° has been determined by Fourier analysis of the scattering curve for monochromatic Mo K $\alpha$  radiation. The distribution curve is essentially a smoothed-out distribution curve for the cryst. phase, showing concns. at 4.0 and 7 Å., and a dip at 5.0 Å.

L. J. J.

**Distribution of impurities on crystallisation.** D. D. SARATOVKIN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 323—326).—The conditions controlling the separation of impurities in the layers between crystallites are discussed and are applied to the slow melting of impure ice, the formation of Widmannstätten structures (system Fe-C), of etch figures, and of dendritic crystals. With the crystallisation of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in presence of CoCl<sub>2</sub> as added impurity the coloured intermediate layers of impurity could be observed.

R. S. B.

**Effect of naphthalene-2-sulphonic acid on the crystallisation of copper sulphate pentahydrate.** F. BARILLET (Compt. rend., 1936, 202, 1194—1195).—Crystallographic data are given for the CuSO<sub>4</sub>.5H<sub>2</sub>O crystals separated from solutions of const. Cu content containing varying proportions of 2-C<sub>10</sub>H<sub>7</sub>SO<sub>3</sub>Na.

M. S. B.

**Modifications of the crystal faces of uric acid by the addition of dyes to the mother-liquor.** P. GAUBERT (Compt. rend., 1936, 202, 1192—1194).—Considerable deviations from the original cryst. forms are produced and the character of the deviations varies with the dye. The polychroism of the crystals and the distribution of the dye between crystals and mother-liquor indicate that solid solutions are formed.

M. S. B.

**Structure of CuAl<sub>2</sub>.** A. K. TRAPEZNIKOV (J. Phys. Chem. U.S.S.R., 1934, 5, 1177—1185).—The structure proposed by Owen and Preston (A., 1924, ii, 111) is not supported by X-ray data. The lattice



consts. are  $a\ 6.054 \pm 0.003$ ,  $c\ 4.87_4$  A.; symmetry classes  $V^d$ ,  $C_4$ ,  $D_4$ . Bradley and Jones' data are confirmed (cf. A., 1933, 454). CH. ABS. (e)

**Crystal structure of  $\text{Fe}_3\text{Ti}$ .** W. JELLINGHAUS (Z. anorg. Chem., 1936, 227, 62—64).—X-Ray powder diagrams of Fe with 24% Ti gave  $a\ 5.19$  A.,  $c/a\ 1.57$ , and a tetragonal lattice. Since, assuming that the unit cell contains four mols. of  $\text{Fe}_3\text{Ti}$ , the calc.  $d$  agrees fairly with that of an alloy of the same composition, it is inferred that such alloys contain the compound  $\text{Fe}_3\text{Ti}$ . This conclusion is supported by the fact that the lattice of  $\text{Al}_3\text{Ti}$  is also tetragonal.

F. L. U.

**Crystal structure of chlorine.** W. H. KEESOM and K. W. TACONIS (Physica, 1936, 3, 237—242, and Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 314).—Data obtained at  $-185^\circ$  with the X-ray goniometer (A., 1935, 839) are recorded. They give a tetragonal lattice with  $a\ 8.56$  and  $c\ 6.12$  A.;  $d\ 2.09$ , 8 mols. per unit cell. Intensities of Debye-Scherrer lines agree with the space-group  $D_{2h}^{16}$ , and the Cl—Cl distance in  $\text{Cl}_2\ 1.99$  A.

L. J. J.

**Structure of ice III.** R. L. MCFARLAN (J. Chem. Physics, 1936, 4, 253—259).—X-Ray diffraction measurements at  $-155^\circ$  give a body-centred orthorhombic structure, with  $a\ 10.20$ ,  $b\ 5.87$ ,  $c\ 7.17$  A. The space-group is  $V_{2h}^{28}$ —*Ibam*, with 16 mols. in the unit cell, giving  $d\ 1.105$ . Each  $\text{O}''$  ion is surrounded by a distorted tetrahedron of  $\text{O}''$  ions;  $\text{H}^+$  ions are assumed to lie midway between pairs of neighbouring  $\text{O}''$  ions. The mechanism of the transition between the different forms of ice is discussed.

L. J. J.

**Nature of lattice disarray in silver bromide.** C. WAGNER and J. BEYER (Z. physikal. Chem., 1936, B, 32, 113—116).—Measurements of  $d$  and the lattice const. at  $410^\circ$  have indicated that the electrical conductivity is due to  $\text{Ag}^+$  ions moving into the spaces between the lattice points and leaving their normal positions vacant; there are no vacant positions in the anion lattice.

R. C.

**Basic salts. XIII. Constitution of solid basic salts of bivalent metals. I. Basic cobalt halides with single-layer lattice.** W. FEITKNECHT (Helv. Chim. Acta, 1936, 19, 467—474).—Lattice dimensions have been determined for  $\text{CoCl}_2 \cdot 3\text{Co}(\text{OH})_2$ ,  $\text{CoBr}_2 \cdot 3\text{Co}(\text{OH})_2$ , and the corresponding mixed basic halide. They all possess single-layer lattices, i.e., there is a statistical exchange of  $\text{OH}^+$  with halide ion. Replacement of  $\text{Cl}^+$  by  $\text{Br}^+$  causes a marked extension of the lattice. Replacement of  $\text{OH}^+$  by halide ion produces a small extension only in the single-layer lattice, but a large one in the double-layer type.

M. S. B.

**Structure of cupric ammonium bromide.** A. SILBERSTEIN (Compt. rend., 1936, 202, 1196—1197).—The vals. of the parameters  $u$ ,  $v$ , and  $w$  of the structure of  $\text{CuBr}_2 \cdot 2\text{NH}_4\text{Br} \cdot 2\text{H}_2\text{O}$  (cf. this vol., 143) have been calc. by comparison with the isomorphous  $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$  and interat. distances are given. The salt is complex and  $\text{H}_2\text{O}$  enters into the formation

Y Y

of the complex ion  $[\text{CuBr}_4(\text{H}_2\text{O})_2]''$ , but in solution it reacts as a mixture of its constituent salts.

M. S. B.

**Structure and alterations of structure of  $\text{NiS}$  and  $\text{NiSe}$ .** G. R. LEVI and A. BARONI (Z. Krist., 1936, 92, 210—215).—Various forms of  $\text{NiS}$  have been prepared and studied by X-rays and electron diffraction methods.  $\gamma$ - $\text{NiS}$  is identical with millerite (rhombohedral);  $\beta$ - $\text{NiS}$  is the usual synthetic compound (hexagonal). The crystallinity is ill-defined, and grows with time.  $\alpha$ - $\text{NiS}$  is amorphous and unstable in air. The transition  $\gamma$ - $\text{NiS}$  to  $\beta$ - $\text{NiS}$  is studied. Analogous properties are shown by the selenides.

B. W. R.

**Structure determinations of the complex sulphides. I. Structure of tin sulphide  $\text{SnS}$  and teallite  $\text{PbSnS}_2$ . II. Crystal chemistry of the sulpho-salts of arsenic, antimony, and bismuth.** W. HOFMANN (Z. Krist., 1935, 92, 161—1xx, 1xx—185).—I.  $\text{SnS}$  is rhombic, 4 mols. in cell,  $a_0\ 3.98$ ,  $b_0\ 4.33$ ,  $c_0\ 11.18$  A., space-group  $V_{2h}^{16}$ . Parameters are determined completely from intensity measurements; the structure is a deformed galena structure. Teallite is rhombic,  $a_0\ 4.04$ ,  $b_0\ 4.28$ ,  $c_0\ 11.33$  A., with similar structure.

II. The position of the S with reference to the metal atom is discussed and the chains of  $\text{SbS}_3$  pyramids are further described. The existence in needle-like crystals of further chains of  $\text{SbS}_3$  and  $\text{BiS}_3$  pyramids,  $\text{PbS}_6$  octahedra, and  $\text{CuS}_4$  and  $\text{FeS}_4$  tetrahedra is suggested.

B. W. R.

**Crystallographic structure of isomorphous compounds  $(\text{M}^{\text{IV}})^+\text{P}_2\text{O}_7$ .** G. R. LEVI and G. PEYRONEL (Z. Krist., 1936, 92, 190—209).—The structure of compounds  $\text{M}^{\text{IV}}\text{P}_2\text{O}_7$  ( $\text{M}=\text{Si}, \text{Ti}, \text{Sn}, \text{Zr}, \text{Hf}$ ) has been determined in order to find the shape of the radical  $(\text{P}_2\text{O}_7)^{\text{IV}-}$ . All these pyrophosphates are cubic, space-group  $T_h^6$ , 4 mols. in cell. Vals. of  $a_0$  and  $d$  are given. Exact at. distances for the P and O atoms are given, based on intensity measurements.  $\text{Hf}^{\text{IV}+}$  is found to have a slightly smaller at. radius than  $\text{Zr}^{\text{IV}+}$ .

B. W. R.

**Rotation of anionic polyhedra in cubic crystals.**

**I. Perchlorates.** C. FINBAK and O. HASSEL (Z. physikal. Chem., 1936, B, 32, 130—134).—Examination of the high-temp. structures of  $\text{NaClO}_4$ ,  $\text{KClO}_4$ , and  $\text{NH}_4\text{ClO}_4$  by means of powder diagrams has yielded results which are irreconcilable with those of Herrmann and Ilge (A., 1930, 528) or of Braekken and Harang (A., 1931, 549) and are explained more satisfactorily by assuming that the  $\text{ClO}_4^-$  in these lattices are capable of rotation, than by supposing the O to occupy fixed positions.

R. C.

**Crystal structure of magnesium and nickel antimonates.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 241—252).—X-Ray measurements indicate the structure  $[\text{M}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$ , where  $\text{M}=\text{Mg}$  or  $\text{Ni}$ . The following data are given for the Mg and Ni compounds, respectively:  $a\ 16.079$ ,  $16.019$ ,  $c\ 9.841$ ,  $9.768$  A.; vol. of unit cell (6 mols.)  $2203$ ,  $2171 \times 10^{-24}$  c.c.;  $d_{\text{calc.}}\ 2.633$ ,  $2.802$ ;  $d_{\text{obs.}}\ 2.598$ ,  $2.77$ ; space-group  $D_{2d}^{14}$ .

O. J. W.



**Structures and formulæ of the Prussian-blues and related compounds.** J. F. KEGGIN and F. D. MILES (Nature, 1936, 137, 577—578).—The at. arrangements in the cubic structures, obtained from X-ray analysis, are outlined. In Prussian-blues,  $\text{Fe}^{\text{III}}\text{RFe}^{\text{II}}(\text{CN})_6$  where R is Na, K, Rb, or  $\text{NH}_4$ ,  $a$  is 10.2 Å., and in "Ru-purple," in which Ru replaces  $\text{Fe}^{\text{II}}$ ,  $a$  is 10.4 Å. The white ferrocyanides  $\text{Fe}^{\text{II}}\text{R}_2\text{Fe}^{\text{II}}(\text{CN})_6$ , where R is Na, K, Rb, Cs, or  $\text{NH}_4$ , have  $a$  5.1 Å. and form a series closely related to the above. Berlin-green,  $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ , the oxidation product of Prussian-blue, has  $a$  5.1 Å., and *cupriferricyanides*,  $\text{Cu}^{\text{II}}\text{RFe}^{\text{III}}(\text{CN})_6$  have  $a$  slightly < 10.2 Å. All structures are similar, but between the members of each class the difference in size of the alkali ions produces a slight variation in the lattice spacings. Blues containing no alkalis have been prepared, and the cubic  $\text{Fe}-(\text{CN})$  skeleton has  $a$  10.2 Å. approx.

L. S. T.

**Influence of structure on the explosive properties of organic compounds.** V. V. VASILEVSKI, F. I. BLOSCHTEIN, and B. D. KUSTRJA (J. Gen. Chem. Russ., 1935, 5, 1652—1667).—The space model of the mol. of 2:4:6-trinitrobenzazide (I) shows that its existence is compatible only with a ring structure for the  $\cdot\text{N}_3$  group. The prep. of (I),  $\text{BzN}_3$ , and *o*- and *m*-nitrobenzazide is described, and m.p.,  $d$ ,  $n$ , and solubility data are recorded. The above azides undergo thermal decomp. to yield carbimides, the heat of decomp. of the  $\cdot\text{N}_3$  group being 70.2 kg.-cal.

R. T.

**X-Ray investigation of the crystals of benzoin.** M. PRASAD and J. SHANKER (J. Indian Chem. Soc., 1936, 13, 123—127).—The unit cell, which contains 4 mols., has  $a$  18.75,  $b$  5.72,  $c$  10.46 Å.,  $\beta$   $106^\circ 50\frac{1}{2}'$ , space-group  $C_{2h}^2$ ; the axial ratio agrees fairly well with the val. recorded in Groth's treatise.

C. R. H.

**X-Ray diffraction intensity of the two liquid phases of *p*-azoxyanisole.** G. W. STEWART (J. Chem. Physics, 1936, 4, 231—236).—The intensity distribution curve for the liquid crystal at  $125^\circ$  resembles that of the transparent liquid at  $150^\circ$ , but has a narrower peak, with greater max. intensity and steeper slope on the zero-angle side. The regularity of structure in the liquid-crystal swarms of  $10^5$ — $10^6$  mols. is > that in the cybotactic groups of 25—50 mols. in the liquid. The swarms tend to set their mol. axes perpendicular to the temp. gradient.

L. J. J.

**Crystallographic relationships between isomerides (ephedrine and  $\psi$ -ephedrine) and between *dl*-compounds and their components.** B. GOSSNER and H. NEFF (Neues Jahrb. Mineral., A, 1935, 69, Beil.-Bd., 347—363; Chem. Zentr., 1935, ii, 997—998; cf. A., 1935, 152).—Crystallographic data are given for  $\alpha$ - $\psi$ -, *dl*- $\psi$ -, *l*-, and *dl*-ephedrine, *l*-, *dl*- (not a racemate but a *dl*-mixture), and  $\alpha$ - $\psi$ -methylephedrine.

H. N. R.

**Diffraction of X-rays by Bence-Jones protein.** A. MAGNUS-LEVY, K. H. MEYER, and W. LOTMAR (Nature, 1936, 137, 616—617).—The spacings and intensities recorded for the cryst. protein are similar to those of oxyhæmoglobin (A., 1935, 687). The

unit cell is large and should contain at least one "chemical" mol. of protein.

L. S. T.

**X-Ray studies of crystallite orientation in cellulose fibres. II. Synthetic fibres from bacterial cellulose membranes.** W. A. SISSON (J. Physical Chem., 1936, 40, 343—359; cf. A., 1935, 286).—From an X-ray study of cellulose membranes synthesised from various sugars by *Acetobacter xylinus*, and subjected to different kinds of mechanical treatment, it is inferred that the crystallites are oriented with the chain-axes parallel to the direction in which the sample is elongated, and that the (101) planes are oriented normal to the direction in which it is constricted. Further, the crystallites possess a major orienting tendency with reference to the chain-axis, and a minor or selective one with reference to the (101) plane.

F. L. U.

**Structure and properties of "byssus" or silk of oysters.** G. CENTOLA (Gazzetta, 1936, 66, 71—80).—The chemical and X-ray investigation of byssus (in its natural state, and stretched) shows that it consists of a mixture of chains of complex (keratin type) and chains of simple (silk fibroin type)  $\text{NH}_2$ -acids. It is the only natural fibre in which the mols. have no orientation, and this accounts for its physical properties.

O. J. W.

**Crystal orientation in tooth-enamel.**—See this vol., 623.

**Diffraction of rapid electrons in crystallised rock-salt. II.** S. G. PINSKER and L. I. TATARINOVA (Physikal. Z. Sovietunion, 1936, 8, 602—625; cf. A., 1935, 1309).—In the investigation of the scattering of rapid electrons at NaCl crystals obtained from solutions of different concn. (1%, 0.5%, 0.2%) the type of diagram obtained varied with the concn. of the solution. The normal Debye pattern was obtained from crystals from the 1% solution, but those from the more dil. solutions gave mainly point diagrams, corresponding with single crystals. Intermediate types of pattern, consisting of Debye rings and irregularly placed spots, were also obtained. The theory is discussed, and the application of the results to the study of thin crystal sheets is described.

A. J. M.

**Determination of atomic distances in the thallium and tellurium halides by electron diffraction.** W. GREYER (Ann. Physik, 1936, [v], 26, 1—16).—The separation of the atoms in  $\text{TlCl}$ ,  $\text{TlBr}$ ,  $\text{TlI}$ ,  $\text{TeCl}_2$ , and  $\text{TeBr}_2$  has been determined by electron diffraction experiments with their vapours. For  $\text{TlCl}$ ,  $\text{TlBr}$ , and  $\text{TlI}$  the respective distances are 2.55, 2.68, and 2.87 Å. For the distances  $\text{Te-Cl}$  and  $\text{Te-Br}$  the vals. are 2.36 and 2.49 Å., respectively. It is not possible to decide whether the mols. of  $\text{TeCl}_2$  and  $\text{TeBr}_2$  are linear or bent, but if they are bent the angle is  $> 150^\circ$ . There is good agreement with results obtained from band spectra.

A. J. M.

(A) Effects accompanying the diffraction of low-speed electrons. (B) Penetration of low-speed diffracted electrons. H. E. FARNSWORTH (Physical Rev., 1936, [ii], 49, 598—605, 605—609; cf. A., 1932, 789; 1933, 761).—(A) Investigation of the effect of density and arrangement of atoms in the



surface plane on the fine structure of electron diffraction beams from a Ag single crystal, made by observing the structure of the diffraction beams corresponding with Bragg reflexions from two sets of planes for two different boundary planes of the crystal, show that the changes in fine-structure characteristics due to a change in the surface at. layer are small compared with the differences in those of the beams from different sets of at. planes. A new type of directional effect, showing a dependence of beam structure on the direction of the diffracted beam in the crystal, was observed.

(B) A known no. of at. layers of Ag was deposited on the surface of single crystals of Cu and Au by evaporation in vac. The no. of at. planes responsible for diffracting low-speed electrons was investigated by results for depth of penetration obtained from measurements on diffraction as a function of surface layer thickness for electron beams of different energies.  $\pm 50\%$  of the max. of each diffraction beam from a thick Ag crystal is due to the surface at. layer, and  $\pm 90\%$  to a surface layer two atoms thick.

N. M. B.

**Molecular structure of nitromethane from electron diffraction by the vapour.** C. DEGARD (Compt. rend., 1936, 202, 1278—1280).—Two diffraction maxima are obtained, from which two mol. models are calc. The O—O distance does not correspond with the sum of the at. or ionic radii.

L. J. J.

**Variation with temperature of the piezo-electric effect in quartz.** A. PITT and D. W. R. MCKINLEY (Canad. J. Res., 1936, 14, A, 57—65; cf. A., 1935, 1197).—The piezo-electric activity of quartz has been studied by static and dynamic methods between  $4^\circ$  and  $813^\circ$  abs. The activity, which decreases sharply by  $10\%$  below  $5.5^\circ$  abs., is const. up to  $470^\circ$ , above which it diminishes to zero at  $813^\circ$  abs.

R. S.

**Magnetic behaviour in the chromium-sulphur system.** H. HARALDSEN and A. NEUBER (Naturwiss., 1936, 24, 280).—Investigation of the susceptibility of Cr-S preps. over the concn. range  $\text{CrS}-\text{Cr}_2\text{S}_3$  shows that there is a considerable increase in magnetism at a concn. corresponding with  $\text{CrS}_{1.75}$ . This is analogous to the behaviour of Fe pyrites, which shows a max. in magnetisation at  $\text{FeS}_{1.12}$ . The effect of temp. on the prep. of max. magnetisation was studied. Above  $165^\circ$  abs. it behaves as a ferromagnetic substance with a Curie point approx.  $310^\circ$  abs. There is a sudden decrease in magnetisation below  $165^\circ$  abs., a behaviour similar to, but more marked than, that of magnetite.

A. J. M.

**New magnetostriction experiment.** J. L. SNOEK (Physica, 1936, 3, 205—206).—Perrier's experiment (Helv. phys. Acta, 1935, 8, 427) depends on the presence of a film of oxide, and is a variant of the Wiedemann effect.

L. J. J.

**Arkadiev's method applied to elimination of skin effect and to investigation of dynamic magnetisation curves.** O. VELETZKAIA (Z. Physik, 1936, 99, 569—575).—Magnetic permeability and loss curves, freed from skin effects, agree with the

theory of magnetic viscosity for low field intensities and for audio and radio frequencies. A. B. D. C.

**Atomic theory of the magneto-caloric effect.** K. HONDA and T. HIRONE (Nature, 1936, 137, 492).—The temp. changes of Fe, Ni, and Co with magnetisation, calc. by means of the Honda-Okubo theory of ferromagnetism, agree with experimental vals. obtained by Okamura. L. S. T.

**Change of thermal energy due to magnetisation in ferromagnetic substances.** T. OKAMURA (Sci. Rep. Tôhoku, 1936, 24, 745—807).—The absorption and evolution of heat during magnetisation has been determined for Fe, Ni, Co, steel, K.S. magnet steel, Ni-Fe alloy, and single Fe crystals. Reversible (magneto-caloric) and irreversible (magnetic hysteresis) changes occur. In the initial magnetisation, starting from the magnetically neutral state, the curves of irreversible effect for all the ferromagnetics studied have the same form as the curve of magnetisation. The reversible heat curves, plotted against field, are similar for all but Co. In weak fields the heat is absorbed and absorption at first increases, reaches a max., decreases, and finally changes to heat evolution. For Co, absorption only is observed. In cyclic magnetisation, starting from max. fields, the irreversible effect does not appear until zero field is approached. On passing to the negative side heat evolution becomes marked and then approaches a saturation val. The irreversible heat effect is in satisfactory agreement with the val. calc. on the basis of the Honda-Okubo theory of ferromagnetic substances, and the reversible effect is that to be expected on thermodynamic grounds. M. S. B.

**Antiferromagnetic exchange problem at low temperature.** L. HULTHÉN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 190—200).—Mathematical. O. J. W.

**Influence of the thermal variation of the molecular field on the Curie constant.** L. NÉEL (Compt. rend., 1936, 202, 1038—1040; cf. A., 1935, 1063).—Theoretical. The Curie const.  $C$  given by  $C/\chi = T - \theta$ , ( $\theta$  is at. magnetic susceptibility,  $T$  the abs. temp., and  $\chi$  the Curie point) is corr. for the influence of the mol. field. For Ni and Co the new const.  $C_0 = 0.379$  and  $0.99$ , respectively, corresponding with 1 and 2 uncompensated spins per atom and electron configurations  $3d^9 4s$  and  $3d^8 4s$ . By analogy Fe should have 3 uncompensated spins and an electron configuration  $3d^7 4s$ , and should have a val. of  $C_0 = 1.862$ ;  $C = 1.23$  and the val. of  $C_0 - C$  is considered reasonable when allowance is made for the mol. field.

R. S. B.

**Ferromagnetism of nickel.** J. C. SLATER (Physical Rev., 1936, [ii], 49, 537—545).—By using metallic energy levels extrapolated from Cu to Ni, the energy difference between a non-magnetic and a ferromagnetic state with permanent magnetic moment is calc. for Ni; the ferromagnetic state is the stable one. Saturation magnetic moment and Curie point are calc. in agreement with experiment. N. M. B.

**Adhesion of two metallic surfaces in a vacuum, and the diminution of the adhesion in certain**



gases. R. HOLM and B. KIRSCHSTEIN (Wiss. Veröff. Siemens-Werken, 1936, 15, 122—127).—The adhesion of metallic surfaces was investigated in connexion with the formation of a surface film on the metals. The inclination of a wire when the substance (in the form of a cylinder threaded on the wire) would just slide down was determined for the contacts Ni-Ni, Pt-Pt, Ni-Pt, and graphite-Ni. In vac. and in inert gases ( $N_2$  and A) the outgassed metals adhered so strongly that no sliding occurred even at an inclination of  $90^\circ$ , but for graphite-Ni, and in all cases in  $O_2$ ,  $H_2$ ,  $H_2O$  vapour, and some org. vapours, sliding occurred, pointing to the existence, under these conditions, of a surface film on the metals.

A. J. M.

Quantum mechanical calculation of the elastic constants of univalent metals. K. FUCHS (Proc. Roy. Soc., 1936, A, 153, 622—639).—The elastic consts. of Li, Na, K, and Cu have been calc. by means of an extension of the method used by Wigner and Seitz (A., 1933, 660) for calculating the lattice energy and compressibility of univalent metals. Good agreement with the observed vals. is obtained for Cu. As no experimental data exist for the alkalis, the Debye characteristic temp. are calc. for Li, Na, and K from the theoretical elastic consts., and compared with the vals. observed at low temp. The agreement is satisfactory. The Cauchy relations are not satisfied.

L. L. B.

New form of crystalline quartz at  $-183.5^\circ$ . H. OSTERBERG (Physical Rev., 1936, [ii], 49, 552—553).—Specially oriented Y cuts of quartz ceased abruptly to oscillate piezoelectrically near the b.p. of liquid air. The transformation to the new  $\delta$  form was at  $-183.5^\circ$ . The discontinuity in the optical rotatory power at the  $\alpha \leftrightarrow \delta$  transition was investigated; the changes were more abrupt at the  $\alpha \rightarrow \delta$  than at the  $\delta \rightarrow \alpha$  transition, but were much less rapid than the simultaneous piezoelectric changes. The  $\delta \rightarrow \alpha$  transition temp. must be above  $-182.4^\circ$ .

N. M. B.

Influence of mechanical deformation on the transformation velocity of polymorphic metals. II. The influence of metallic impurities. E. COHEN and A. K. W. A. VAN LIESHOUT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 352—358; cf. A., 1935, 688).—1% of Bi, Pb, Sb, Cd, and Ag decreases and 0.01—1% of Al and Zn greatly increases the speed of transformation of mechanically deformed Sn at  $-50^\circ$ . The influence of Zn is a max. with 0.05% (also at  $0^\circ$ ). The influence of 0.05% of Al and Zn has also been studied at  $0^\circ$ ,  $-11^\circ$ , and  $-22^\circ$ .

R. S. B.

Localisation of the transition points of allotropic metals by means of the method of Saladin and Le Chatelier. E. ROSENBOHM and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 366—374).—When Ni is heated in a high vac. a transition  $\alpha \rightleftharpoons \beta$  occurs sharply at  $369-370^\circ$ . On cooling, the transition temp. ( $T$ ) is  $6^\circ <$  before, and this difference increases with the speed of cooling. In presence of 50—60 mm. of  $H_2$   $T = 363-364^\circ$  on heating and cooling, and at 2—60 mm. the change in  $T$  from the val. in a vac. is independent

of pressure. Discrepancies in the literature in the vals. for  $T$  are probably due to adsorbed gases. With  $AuSb_2$  transitions occur at  $355^\circ$  and  $404^\circ$ . The second,  $\beta \rightleftharpoons \alpha$ , occurs much more slowly and, unlike the first,  $\beta \rightleftharpoons \gamma$ , shows hysteresis on cooling. With the  $\beta \rightleftharpoons \gamma$  the temp. coeff. of  $c_p$  is the same for both forms.

R. S. B.

Polar isomorphism. A. E. FERSMAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 119—122).—A discussion. Hahn's law is restated as follows: the ions of the elements are caught in another crystal lattice from dispersed solutions only if their size and type allow them to form with this lattice an isomorphous structure, and if this structure is more advantageous, as regards energy, than the pure crystal.

H. J. E.

Electrical conductivity of transition metals. N. F. MOTT (Proc. Roy. Soc., 1936, A, 153, 699—717; cf. A., 1935, 1063).—Mathematical. A formal theory of conductivity for metals, such as the transition metals, where the conduction electrons occupy two Brillouin zones, is developed. Certain anomalies in the resistance-temp. curves of the paramagnetic metals Pd, Pt, and Ta are explained. The resistance of ferromagnetic metals is discussed, and an expression obtained for the decrease of the resistance of Ni in a magnetic field. It is shown qualitatively why the alloy Cu-Ni has zero temp. coeff. at room temp.

L. L. B.

Measurement of the electrical resistance of metals as function of the temperature by means of a twin galvanometer with photographic recording. E. ROSENBOHM and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 374—383).—The increments in electrical resistance ( $R$ ) per  $10^\circ$  for Ni in a vac. increase regularly up to  $358^\circ$  and then rapidly decrease to a const. val. at  $380^\circ$ . At  $350-365^\circ$  an inflexion occurs in the  $R-T$  curve, perhaps associated with the change  $\alpha \rightarrow \alpha'$  (hexagonal). In presence of 60 mm. of  $H_2$   $R$  is  $>$  for the pure metal, but the temp. coeff. is unchanged up to  $345^\circ$ , when  $H_2$  begins to be released from the metal. At  $345-375^\circ$  there is indication of the formation of the  $\alpha'$  phase.

R. S. B.

Diamagnetic susceptibility of heavy water. F. E. HOARE (Nature, 1936, 137, 497—498).—The val. obtained by Gouy's method for 99.2%  $D_2O$  is  $0.648 \pm 0.001 \times 10^{-6}$  unit at  $20^\circ$ , corresponding with a mol. susceptibility of 12.96.

L. S. T.

Magnetic susceptibility of disubstituted benzene derivatives. K. KIDO (Sci. Rep. Tôhoku, 1936, 24, 701—706).—31 derivatives have been examined and most of the results are in satisfactory agreement with calc. vals. The mol. susceptibility of  $p$ -derivatives is generally  $<$  that of the corresponding  $o$ -derivatives.

M. S. B.

Magnetic properties and structure of the haemochromogens and related substances.—See this vol., 616.

Diffraction of light by ultrasonic waves. R. LUCAS (Compt. rend., 1936, 202, 1165—1166).—An apparatus for testing the validity of the different



theories relative to the diffraction of light by ultrasonic waves is described. M. S. B.

**Diffraction of light by progressive ultrasonic waves.** E. HIEDEMANN and E. SCHREUER (Z. Physik, 1936, 99, 363—368).—An extension of Raman and Nath's theory (cf. this vol., 148) to cover frequency changes and an ultrasonic field of finite width. A. B. D. C.

**Diffraction of light by ultrasonic waves.** S. M. RITOV (Physikal. Z. Sovietunion, 1936, 8, 626—643).—The theory of Debye and Brillouin is extended, the case of small angle of incidence being treated. To test the results, a goniometer was used to investigate the diffraction with ultrasonic waves in liquids ( $C_6H_6$  and PhMe) and in quartz. There is satisfactory agreement. A. J. M.

**Ultrasonic velocities in some organic liquids.** II. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 3, A, 285—289).—Data are recorded for ultrasonic velocities and adiabatic compressibilities of a no. of di-esters, *o*-, *m*-, and *p*-xylene, quinoline, and *o*-toluidine, for  $7.37 \times 10^6$  cycles per sec. and room temp. L. J. J.

**Heat capacities of quartz, cristobalite, and tridymite at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 568—570).—Data are recorded for the range 50—300° abs. The corresponding entropies are 10.06, 10.34, and 10.50, respectively. E. S. H.

**Heat capacities of vanadium, vanadium trioxide, vanadium tetroxide, and vanadium pentoxide at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 564—566).—Data are recorded for the range 55—300° abs. The corresponding entropies have been calc. E. S. H.

**Heat capacity of lead sulphate at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 567).—Data are recorded for 55—300° abs. The calc. entropy is 35.2. E. S. H.

**Limiting high-temperature rotational partition function of non-rigid molecules.** I. General theory. II.  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ ,  $CHMe_3$ ,  $CMe_4$ , and *n*-butane. III. Benzene and its eleven methyl derivatives. L. S. KASSEL (J. Chem. Physics, 1936, 4, 276—282).—The theory of Eidinoff and Aston (A., 1935, 1064) is developed and applied to the calculation of mol. entropies, giving results in agreement with third-law data. L. J. J.

**Heat of evaporation of heavy hydrogen.** K. CLUSIUS and J. BARTHOLOMÉ (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 49—58; Chem. Zentr., 1935, ii, 961—962).—The latent heat of evaporation  $L$  of  $D_2$  (cf. A., 1935, 155) at 19.6° abs. has been directly measured in a liquid- $H_2$  calorimeter.  $L$ , corr. to the ideal gas state by means of the equation of state for  $H_2$ , is 304.7 g.-cal. per mol.  $L_0$  at 0° abs. is calc. as 274.0 g.-cal., giving a measured difference of 90.6 g.-cal. in zero-point energy between  $H_2$  and  $D_2$ . The entropy  $S_{\text{therm}}$  of  $D_2$  at 298.1° abs. = 33.927; total entropy = 39.02 in agreement with the calc. val. The following Trouton's consts. at low temp. are recorded: He 4.8,  $H_2$  10.6,  $D_2$  12.9, Ne 14.9. J. S. A.

**Variations of the physical properties of some liquids in the neighbourhood of the m.p.** A. BANCHETTI (Gazzetta, 1936, 66, 65—71).—The rate of cooling of anethole does not show any sudden change at the m.p. when the liquid is cooled slowly and remains supercooled (cf. A., 1900, ii, 465).

O. J. W.  
**Melting curve of a compound partly dissociated into its components.** J. J. VAN LAAR (Physica, 1936, 3, 255—256).—A claim of priority (cf. Młodziejowski, A., 1935, 582). L. J. J.

**Preliminary experiments on temperature equilibria at very low temperatures.** N. KÜRTI, B. V. ROLLIN, and F. SIMON (Physica, 1936, 3, 266—274).—The rate of establishment of temp. equilibrium at temp. obtained by the magnetic method has been examined. Equilibrium between  $Fe^{III} NH_4$  alum (I) and liquid He at 0.2° abs. is attained in 30 sec., so that the time-const. for the equilibrium spin system-lattice is < this. The thermal conductivities of (I) and  $Cr^{III} K$  alum between 0.07° and 0.16° abs. are  $\sim 10^{-5}$  c.g.s.; hence attainment of equilibrium within the salt is slow. L. J. J.

**Universal expression for the limits of physico-chemical relations.** G. A. KORSHENOVSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 1321—1331).—Theoretical. CH. ABS. (e)

**Quantum statistics of melting.** L. TARSCHISCH (Z. Physik, 1936, 99, 259—273).—A theory of melting is deduced from Debye's theory of sp. heats and Born's dynamics of crystals, using the Fermi-Debye statistics. A. B. D. C.

**Liquid densities of propylene and methyl ethyl ether as determined by a modified dilatometer method.** D. B. PALL and O. MAASS (Canad. J. Res., 1936, 14, B, 96—104).—An improved dilatometric apparatus is described and with it the  $d$  of  $C_3H_6$  and MeOEt have been determined from 20° to 80° and 70° to 120°, respectively. The law of corresponding states is obeyed to within < 0.96° of the crit. temp. R. S.

**Vapour pressures of the xylenes and mesitylene.** L. S. KASSEL (J. Amer. Chem. Soc., 1936, 58, 670—671).—For *o*-xylene (0—80°)  $\log_{10} P = -2830.0/T - 5 \log_{10} T + 22.7480$ ; *m*-xylene (0—80°)  $-2876.3/T - 5 \log_{10} T + 22.9424$ ; *p*-xylene (0—80°)  $-2930.0/T - 5 \log_{10} T + 23.1000$ ; mesitylene (0—100°)  $-3104.5/T - 5 \log_{10} T + 23.1929$ . The calc. entropies of vaporisation to a perfect gas at 25° and 1 atm. are 24.35, 25.24, 25.96, and 26.39 e.u., respectively. E. S. H.

**Calculation of van der Waals  $a$  and  $b$ .** J. E. VERSCHAFFELT (Wis. nat. Tijdschr., 1935, 7, 149—154; Chem. Zentr., 1935, ii, 1143).—A crit. review. J. S. A.

**General constant of van der Waals.** R. LAUTÉ (Compt. rend., 1936, 202, 1059—1061).—Theoretical. The van der Waals const.  $a$ , defined by  $\log P_c/P = a_1 \{(T_c/T) - 1\}$ , where  $P_c$  and  $T_c$  are the crit. pressure and temp., is replaced by  $a_2 = \lambda/[4.571 T_c (1 - 1/P_c)]$ , where  $\lambda$  is the mol. latent heat of vaporisation at the b.p. ( $T_1$ ). The agreement between  $a_1$  and  $a_2$  is good even for "abnormal" liquids, for which  $a_1 < 2.8$



or  $> 3.2$ . With sufficient accuracy  $\lambda = 4.3a_2T_c$ . The empirical relation  $\lambda/T_c = 3.589 \log T_c + 1.13 + 0.00559T_c$  has also been derived, and using this and writing  $T_c/T_1 = 3/2$  a third const.  $a_3$ , agreeing sufficiently well with  $a_1$  and  $a_2$ , is deduced.  $a_3 = 0.7621 \times \log T_1 + 0.5822 + 0.001322T_1$ . R. S. B.

**Thermodynamic equilibrium in the gravitational field.** F. O. KOENIG (J. Physical Chem., 1936, 40, 373—378).—Mathematical. F. L. U.

**Variation in volume of heavy water on freezing.** J. TIMMERMANS, M. HENNAUT-ROLAND, and D. ROZENTAL (Compt. rend., 1936, 202, 1061—1063; cf. A., 1935, 815).—Vals. of  $d$  for pure  $D_2O$  have been determined.  $d^{4.3} = 1.10573$ ,  $d^{11.6} = 1.10621$ ,  $d^{20} = 1.10556$ , giving by extrapolation  $d^{3.82} = 1.1057$ , and sp. vol. at  $3.82^\circ = 0.9044$ . For the solid  $d^0 = 1.01475$ , and  $d^5$  for  $H_2O = 0.9159$ . The sp. vols. of solid and liquid  $D_2O$  at approx.  $0^\circ$  differ by 0.0811, which agrees sufficiently with published vals.;  $dT/dp$  as calc. using the Clausius-Clapeyron equation also agrees with published vals. and is approx. the same for  $D_2O$  and  $H_2O$ , viz., 0.00705° per kg. per sq. cm. R. S. B.

**Thermal expansion of water.** I. V. IPATOV (J. Phys. Chem. U.S.S.R., 1934, 5, 1230—1231).—Experimental vals. ( $0$ — $100^\circ$ ) are expressed by equations. CH. ABS. (c)

**Thermal expansion of solids at low temperatures** (Cu, Ni, Fe, zinc blende, LiF, calcite, aragonite,  $NH_4Cl$ ). H. ADENSTEDT (Ann. Physik, 1936, [v], 26, 69—96).—The thermal expansion was investigated over the range  $0^\circ$  to  $-195^\circ$  by an interference method. A metal thermostat operating between these temp. is described. The coeff. of expansion ( $\alpha$ ) of Cu, Ni, and Fe over this range agrees with vals. obtained from the formula of Grüneisen for regular monat. substances. The anomalies recorded by Simon *et al.* (A., 1930, 986) were not observed. Zn blende was investigated down to  $-253^\circ$ , and gives at the lower temp. a negative val. for  $\beta [(1/V_0)(\delta l/\beta T)]$ . For LiF,  $\alpha$  agrees with the Grüneisen formula except at the lower temp. With falling temp.  $\alpha$  for aragonite approaches the val. for a monat. solid, but calcite shows a negative vol. expansion at  $-172^\circ$ . In the case of  $NH_4Cl$  the transition point at  $-31^\circ$  was verified. The behaviour of  $\beta$  for  $NH_4Cl$  indicates that the transition is homogeneous. A. J. M.

**Negative expansion coefficient of silver iodide.** E. COHEN and H. L. BREDÉE (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 358—360).—The val. for the expansion coeff. of AgI determined by Jones and Jelen (cf. this vol., 279) is considered to be in error, since these authors used a mixture of  $\alpha$ - and  $\beta$ -AgI, and  $\beta \rightarrow \alpha$  during the experiment. Pure  $\alpha$ -AgI has the coeff. found by Fizeau, viz.,  $-4.1 \times 10^{-6}$  at  $40^\circ$ . R. S. B.

**Viscosity of gaseous oxygen at low temperatures; effect of pressure.** A. VAN ITTERBEEK and (MLLE.) A. CLAES (Physica, 1936, 3, 275—281).—Data obtained by the oscillating-disc method are recorded for  $293.8^\circ$ ,  $90.1^\circ$ ,  $79.8^\circ$ , and  $72.0^\circ$  abs., and  $10^{-5}$ — $760$  mm. pressure.  $\eta$  is independent of pressure

down to about 5 mm. The calc. ratios of the mean mol. velocities at the temp. studied agree with the Maxwell-Boltzmann distribution. L. J. J.

**New comparison of the viscosity of  $D_2O$  with that of  $H_2O$ .** W. N. BAKER (J. Chem. Physics, 1936, 4, 294—295).—Between  $5^\circ$  and  $35^\circ$ ,  $\eta$  for  $D_2O$  is approx. equal to  $\eta$  for  $H_2O$  at a temp.  $8.5^\circ$  lower. L. J. J.

**Viscosity of liquid metals.** D. V. COLGATE (J. Univ. Bombay, 1935, 4, Part II, 83—85).—Formulae are derived relating the viscosity of a monat. liquid with (a) the at. wt., m.p., and at. vol. at the m.p., and (b) with  $d$ , the at. wt., the Debye characteristic temp., and a const. dependent on the cryst. structure of the metal. The calc. vals. are in fair accord with experiment for Cd, Hg, Cu, Sn, and Pb. J. W. S.

**Diffusion isotherms for binary mixtures.** H. LEMONDE (Compt. rend., 1936, 202, 468—470).—Diffusion coeffs. ( $D$ ) have been determined for the following mixtures:  $H_2O$  with MeOH, EtOH, PrOH,  $Pr^2OH$ ;  $CHCl_3$  with  $Et_2O$ ,  $COMe$ , EtOH;  $C_6H_6$  with  $CHCl_3$ , MeOH, EtOH,  $C_6H_{14}$ ; PhMe with EtOH.  $D \times$  viscosity ( $\eta$ ) is const. only for very dil. solutions. In general the  $D\eta$  curves show a max. or min. or both, the deviations apparently depending on the tendency to association.  $D$ -composition curves for homologous compounds in the same solvent have the same form. In dil. solution  $D \propto$  vol. concn. F. L. U.

**Viscosities of aqueous solutions of nitric acid at low temperatures.** D. SCHOFIELD (Bol. Soc. Quim. Peru, 1935, 1, 7—25).—At  $-17^\circ$ , the fluidity-concn. curve shows max. deviation from the ideal mixture curve at  $HNO_3.H_2O$ . A thermostat suitable for temp. below  $0^\circ$  is described. L. A. O'N.

**Viscosity and conductivity in the system: fused  $KCl$ - $LiCl$ .** S. V. KARPATSHEV, A. G. STROMBERG, and V. N. PODTSCHAINOVA (J. Gen. Chem. Russ., 1935, 5, 1517—1526).—Conductivity and viscosity data for the range  $400$ — $900^\circ$  indicate that Stokes' law is not applicable to the system. R. T.

**Thermal conductivity of liquids. Binary mixtures of water and glycerol.** O. K. BATES (Ind. Eng. Chem., 1936, 28, 494—498).—In a modification of the apparatus previously employed (B., 1933, 415) thermal conductivity measurements have been made for a complete range of mixtures of  $H_2O$  and glycerol (I) at  $10$ — $80^\circ$ . The coeff. of thermal conductivity of pure (I) is independent of temp. over the range considered. M. S. B.

**Vaporisation equilibria in the binary salt mixture  $HgCl_2$ - $HgBr_2$ , and in the reciprocal salt-pair (Na, K) (Cl, Br).** H. HINTZ and K. JELLINEK (Z. Elektrochem., 1936, 42, 187—200; cf. A., 1933, 770).—Comparison of the total v.p. of liquid  $HgCl_2$ - $HgBr_2$  mixtures with the partial pressures of the components, measured at  $238^\circ$ , indicates that the liquid behaves as an ideal mixture, that no compound is formed, and that only single mols. are present. Similar measurements at  $1250^\circ$  for the mixtures  $NaCl$ - $KCl$ ,  $NaBr$ - $KBr$ ,  $NaCl$ - $NaBr$ , and  $KCl$ - $KBr$  lead to the same conclusions with regard



to these mixtures. A diagram of the vapour equilibria of the reciprocal salt-pair NaCl-KBr is given.

F. L. U.

**Vapour pressure of the binary system,  $\text{PbCl}_2$ -AgCl.** D. N. TARASENKOV and A. V. BOGOSLOVSKAJA (J. Gen. Chem. Russ., 1935, 5, 1687-1689).—V.-p. data are recorded for the interval 500-800°. It is concluded that  $\text{PbCl}_2$  may be separated from AgCl by distillation at 700-800°.

R. T.

**Heat of vaporisation in the system carbon disulphide-methyl alcohol.** S. I. TSCHERBOV (J. Gen. Chem. Russ., 1935, 5, 1645-1651).—Vrevski's equation connecting the latent heat of vaporisation of a liquid mixture with those of its components, the composition of the vapour phase, and the differential heat of dilution of the components (A., 1930, 404) is shown to hold for the system  $\text{CS}_2$ -MeOH at 20°.

R. T.

**Phase equilibria in hydrocarbon systems. XII. Specific heats of some mixtures of propane, *n*-butane, and *n*-pentane.** B. H. SAGE, H. S. BACKHUS, and T. VERMEULEN (Ind. Eng. Chem., 1936, 28, 489-493).—Sp. heats at const. pressure have been determined for binary mixtures of  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_5\text{H}_{12}$  at 21-104° in the condensed liquid phase. The mixtures follow closely the laws of ideal solutions as was indicated by determining pressure-vol.-temp. relations for  $\text{C}_3\text{H}_8$ - $\text{C}_5\text{H}_{12}$  mixtures and calculating heat content and entropy.

M. S. B.

**Diffusion and azeotropism in binary mixtures.** H. LEMONDE (Compt. rend., 1936, 202, 1069-1071; cf. this vol., 674).—The diffusion coeff. ( $D$ ) increases or decreases with concn. in a binary mixture according as the v.p. decreases or increases, provided that the v.p. departs sufficiently from the linear law. Mixtures may be classified in terms of the function  $D\eta$  which seems to be very sensitive to variations in the magnitude of the intermol. forces.

R. S. B.

**Orthobaric azeotropes. Esters-halides.** M. LECAT (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 41-54; cf. this vol., 280).—Data are given for 434 binary systems formed by 80 esters and 63 halogenated hydrocarbons. These include 148 cases of azeotropism (23 negative).

M. S. B.

**Solubility in liquids of gas mixtures under pressure. II. Thermodynamical calculation of solubility in water of a mixture of nitrogen and hydrogen under pressure.** I. R. KRITSCHESKI and J. S. KASARNOVSKI (Z. physikal. Chem., 1936, 176, 48-54; cf. this vol., 29, 30).—Assuming that a 1:3 mixture of  $\text{N}_2$  and  $\text{H}_2$  is equiv. to an infinitely dil. solution of  $\text{N}_2$  in  $\text{H}_2$ , the partial mol. vols. and fugacities of  $\text{N}_2$  in a mixture containing 76.42%  $\text{H}_2$  and the solubility in  $\text{H}_2\text{O}$  of  $\text{H}_2$  and  $\text{N}_2$  from this mixture have been calc. for pressures of 50-1000 atm. at 25°. The results agree with published experimental data.

R. C.

**Solubility of lanthanum in mercury from 0° to 50°.** W. G. PARKS and J. L. CAMPANELLA (J. Physical Chem., 1936, 40, 333-341).—The solubility of La in Hg between 0° and 50° is low, and is given by:  $\log N = -1020/T' - 0.4575$  ( $N$ =at. fraction of

La,  $T'$ =abs. temp.). La amalgam is considered unsuitable for precise c.m.f. measurements.

F. L. U.

**Solubility of lead bromate and its activity coefficients in solutions of electrolytes.** F. H. MACDOUGALL and E. J. HOFFMAN (J. Physical Chem., 1936, 40, 317-331; cf. A., 1930, 699).—The solubility of  $\text{Pb}(\text{BrO}_3)_2$  in  $\text{H}_2\text{O}$ , and in presence of nitrates of K, Na, Li, Ca, Sr, and Pb, has been determined at 25°. The theory of Debye and Hückel is not valid for these solutions if complete ionisation is assumed. Activity coeffs. are calc. assuming the stages: (1)  $\text{Pb}(\text{BrO}_3)_2 \rightleftharpoons \text{PbBrO}_3 + \text{BrO}_3^-$ ; (2)  $\text{PbBrO}_3 \rightleftharpoons \text{Pb}^{++} + \text{BrO}_3^-$ .

F. L. U.

**Solubility of lead sulphate in aqueous sulphuric acid at high concentrations.** H. D. CROCKFORD and J. A. ADDLESTONE (J. Physical Chem., 1936, 40, 303-305; cf. A., 1935, 159).—Solubilities of  $\text{PbSO}_4$  at 0°, 25°, 35°, and 50° are given for  $[\text{H}_2\text{SO}_4] > 80\%$ . At 0°  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  may exist as solids. At the higher temp. the only solid phase is  $\text{PbSO}_4$ . The  $\text{PbSO}_4$ - $\text{H}_2\text{SO}_4$  eutectic is at 5.4°.

F. L. U.

**Solubility in water and aqueous sodium chloride of  $\alpha$ -naphthylaminemonosulphonic acids and their sodium salts.** P. I. SOKOLOV (Anilinokras. Prom., 1935, 5, 149-153).—Solubility data are recorded for  $\alpha$ -naphthylamine-2-, -4-, -5-, -6-, -7-, and -8-sulphonic acids and their Na salts at 25°.

R. T.

**Influence of degree of dispersion on physico-chemical constants. VI.** E. COHEN and J. J. A. BLEKKINGH (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 154-163; cf. this vol., 20).—The solubility of salicylic acid at 25° has been studied under various conditions. The previously recorded high and discrepant vals. are attributed to the high degree of dispersion of the solid phase and to the presence of about 0.2% of  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ .

O. J. W.

**Solidification diagram of copper-zinc alloys.** W. BRONIEWSKI, J. T. JABLONSKI, and S. MAJ (Compt. rend., 1936, 202, 411-414).—The m.-p. diagram of Cu-Zn alloys indicates the presence of the compounds  $\text{CuZn}$ ,  $\text{CuZn}_2$ , and  $\text{CuZn}_6$ .  $\text{CuZn}$  and  $\text{CuZn}_6$  show allotropic changes at about 460° and 600°, respectively.

J. W. S.

**Study of copper-tin alloys by X-ray analysis.** E. A. OWEN and E. WILLIAMS (J. Inst. Metals, 1936, 58, Advance copy, 153-167).—The  $\delta$ -phase in Cu-Sn alloys is a solid solution with a range varying from zero at the eutectoid point (67.45% Cu, 330°) to 0.48% at 550°. The  $\eta$ -phase is also a solid solution extending from 61.68 to 62.10% at 250° and from 61.68 to 62.20% Cu at 530°. Below 330°  $\delta$  decomposes into  $\alpha + \eta$ .

A. R. P.

**Orientation in peritectic structures.** A. B. GRENINGER (Nature, 1936, 137, 657-658).—X-Ray investigation of the reaction  $\alpha + \text{liquid} \rightarrow \beta$  in the Cu-Zn system shows that the orientations assumed by the  $\beta$ -phase are definitely related to the orientation of the  $\alpha$ -phase. Seeding the crystallisation of a pure  $\beta$ -alloy (52% Cu) with a Cu single crystal gives the sequence Cu crystal seed, primary cryst.  $\alpha$ -phase



having the same orientation as the Cu seed, large  $\beta$ -grains having a narrow rim of segregated  $\alpha$ -phase and originating in the peritectic reaction  $\alpha + \text{liquid} \rightarrow \beta$ .  
L. S. T.

**Electrical conductivity and equilibrium diagram for binary alloys. XIX. System sodium-thallium.** G. GRUBE and A. SCHMIDT (Z. Elektrochem., 1936, 42, 201—209; cf. this vol., 151).—In addition to NaTl and NaTl<sub>2</sub>, the existence of compounds Na<sub>2</sub>Tl and Na<sub>6</sub>Tl is established by thermal analysis and conductivity measurements. Solid solutions occur over a wide range in systems rich in Tl. NaTl melts without decomp. at 305°, whilst the other compounds are formed as a result of solid reactions. Alloys with Na 17—24 at.-%, after quenching from 200°, undergo considerable hardening at room temp.  
F. L. U.

**Constitution of tin-rich antimony-tin alloys.** D. HANSON and W. T. PELL-WALPOLE (J. Inst. Metals, 1936, 58, Advance copy, 79—90).—The system up to 14% Sb has been examined by thermal analysis, micrographically, and by the electrical resistance method. The liquidus consists of two branches, the first corresponding with the separation of the  $\alpha$ -Sn solid solution and the second with the separation of cuboid- $\delta$ ; at 246° a peritectic reaction occurs between  $\delta$  and liquid (9% Sb) to form  $\alpha$  (10.5% Sb). The solubility of Sb in Sn decreases from 10.5% at 246° to 4% at 190° and to 3.5% at 100°. Characteristic microstructures are illustrated.  
A. R. P.

**Over-structure phenomena in nickel-arsenic alloys.** F. LAVES (Fortschr. Min., 1935, 19, 33—37; Chem. Zentr., 1935, ii, 972—973).—Rotation photographs obtained with tetragonal Ni<sub>3</sub>As<sub>2</sub> (maucherite) give  $a$  3.45,  $c$  21.7 Å., with a superposed two-dimensional overstructure having  $a$  6.9 Å.  
J. S. A.

**Mixed crystal problem.** H. O'DANIEL (Fortschr. Min., 1935, 19, 48—52; Chem. Zentr., 1935, ii, 1126).—The possible ratios of mixed crystal components which permit the development of a perfect overstructure are discussed.  
J. S. A.

**New method of separation of radium by rapid reduction in barium content.** (MME.) B. E. MARQUES (J. Chim. phys., 1936, 33, 306—316).—Previous experimental evidence (this vol., 421) indicates that, by slow evaporation at 20° of saturated aq. BaBr<sub>2</sub> containing Ra, until about 60% of the BaBr<sub>2</sub> has crystallised out, practically the whole of the RaBr<sub>2</sub> present may be conc. in the BaBr<sub>2</sub> crystals. By successive dissolution and partial recrystallisation a product rich in Ra may be obtained with comparatively little loss.  
M. S. B.

**Radon hydrate.** B. A. NIKITIN (Z. anorg. Chem., 1936, 227, 81—93).—Rn left in contact with snow at -3.5° remains entirely in the gas phase, but if SO<sub>2</sub> is introduced into the latter, the Rn is transferred to the solid phase SO<sub>2</sub>.6H<sub>2</sub>O. The distribution of Rn between the gaseous and solid phases has been measured, for different relative amounts of the phases, and when equilibrium is reached, both from SO<sub>2</sub>+Rn in contact with snow and from Rn in contact with preformed SO<sub>2</sub>.6H<sub>2</sub>O. Under these conditions the

partition factor  $D = [\text{Rn}]_{\text{cryst}}/[\text{Rn}]_{\text{gas}} - [\text{SO}_2]_{\text{gas}}/[\text{SO}_2]_{\text{cryst}}$  is const. = 0.57. Similar experiments with H<sub>2</sub>S.6H<sub>2</sub>O give  $D = 2.4$ . The results afford conclusive evidence of the existence of Rn.6H<sub>2</sub>O isomorphous with the hexahydrates of SO<sub>2</sub> and H<sub>2</sub>S, and occupying an intermediate position with regard to stability. All experiments were carried out at -3.5°, below the eutectic temp. of H<sub>2</sub>O and the respective hydrates  
F. L. U.

**Adsorption of nitrogen on tungsten.** J. K. ROBERTS (Nature, 1936, 137, 659—660).—Amounts of N<sub>2</sub> insufficient to cover a W wire are rapidly and completely adsorbed, leaving a negligible residual pressure. N<sub>2</sub> thus resembles H<sub>2</sub> (cf. this vol., 282).  
L. S. T.

**Diffusion of hydrogen through copper.** E. O. BRAATEN and G. F. CLARK (Proc. Roy. Soc., 1936, A, 153, 504—512).—The rate of diffusion of H<sub>2</sub> through Cu has been determined for several temp. and pressures. The rate varies with the pressure in a manner consistent with the equation of Smithells and Ransley (A., 1935, 692); the adsorption factor causes a slight departure from the equation at about 2 mm. The effect of temp. is given by the usual exponential relation.  
L. L. B.

**Adsorption of radon by glass.** S. C. LIND and R. LIVINGSTON (J. Physical Chem., 1936, 40, 419—420; cf. A., 1933, 564).—Rn in Pyrex glass bulbs undergoes slow irreversible adsorption on the walls, amounting to 16% in 68 hr. The need for taking account of this effect in quant. work is emphasised.  
F. L. U.

**Pre-Gibbs adsorption by surface rearrangement.** J. W. MCBAIN (Nature, 1936, 137, 659).—The possible existence of a preliminary factor contributing to the lowering of  $\eta$ , viz., an interchange of positions between mols. of solute and solvent within a few mol. diameters of the surface, is discussed in relation to the low vals. of  $\eta$  shown by soap solutions.  
L. S. T.

**Method of studying conditions within diffusion layers.** T. TEORELL (J. Biol. Chem., 1936, 113, 735—748).—An apparatus is described for measuring diffusion gradients by the use of a no. of membranes in series separated by well-stirred solutions so that the diffusion gradients occur exclusively in the membranes. Analysis of the solutions in the chambers bounded by these membranes permits the plotting of these gradients.  
H. D.

**Sorption of iodine by polyvinyl alcohol.** W. GALLAY (Canad. J. Res., 1936, 14, B, 105—113).—The adsorption isotherms of I on polyvinyl alcohol polymerides pptd. by NaCl and by MgSO<sub>4</sub> have been studied. When MeOH and EtOH are the pptg. agents, the adsorption follows the simple distribution law. Adsorption of NaHCO<sub>3</sub> on the NaCl-pptd. alcohol is also linear, but the I adsorption is not affected by pretreatment with electrolytes. It is suggested that a certain colloidal size and a certain type of linking are necessary for the formation of blue I compounds.  
R. S.

**Adsorption of proteins. Influence of hydrogen-ion concentration on the adsorption of hæmoglobin by kaolin.** M. PAÍĆ and (MLLE.) V.



DEUTSCH (Compt. rend., 1936, 202, 1283—1285).—The adsorption isotherms in presence of various buffer solutions show a discontinuity at low concns. With varying  $p_H$ , the adsorption passes through a max., the position of which depends on the buffer concn.

L. J. J.

**Inner adsorption in salt crystals. III. Nature of inclusion of ZnS in CuS.** D. BALAREV (Z. anal. Chem., 1935, 102, 408—411; cf. A., 1927, 925).—Polemical against Kolthoff (A., 1932, 481). The ease with which ZnS, copptd. with CuS, is extracted by HCl is held to point to its true inner adsorption in the CuS lattice.

J. S. A.

**Coprecipitation and after-precipitation. Ageing of precipitates. I.** M. KOLTHOFF (Z. anal. Chem., 1936, 104, 321—333).—Polemical against Balarev (preceding abstract). The author's views are summarised.

J. S. A.

**Gas-solid equilibria. VI. Adsorption from binary gas mixtures by silica gel.** B. LAMBERT and H. S. HEAVEN (Proc. Roy. Soc., 1936, A, 153, 584—600).—The pressure-concn. equilibria at 0° between SiO<sub>2</sub> gel and O<sub>2</sub>-A, O<sub>2</sub>-N<sub>2</sub>, and O<sub>2</sub>-He mixtures (containing equal proportions of the two gases in each case) have been investigated. A procedure is described by means of which it is possible to determine the vols. of the two gases X and Y adsorbed and the partial pressures of X and Y in the equilibrium gaseous phase: (a) when either X or Y is given priority of contact with the solid adsorbent; and (b) when X and Y in equal concns. reach the adsorbent simultaneously. With O<sub>2</sub>-A mixtures, when the O<sub>2</sub> is given priority of contact, the adsorbed phase at equilibrium contains 3 times as much O<sub>2</sub> as A; when A is given priority of contact, the adsorbed phase contains half as much O<sub>2</sub> as A; and when the two gases reach the gel simultaneously, equal amounts of O<sub>2</sub> and A are found in the adsorbed phase. A theory of adsorption is suggested, involving the assumption of an adsorbed phase consisting of two layers of gas mols. With O<sub>2</sub>-N<sub>2</sub> mixtures, O<sub>2</sub> is adsorbed more, and N<sub>2</sub> less, than each would be in the absence of the other. With O<sub>2</sub>-He mixtures, O<sub>2</sub> is adsorbed as it would be in the absence of He, provided that the gel has previously been thoroughly "washed out" with O<sub>2</sub>. The adsorptive power for He at 0° is negligible.

L. L. B.

**Active oxides. XCIV. Sorptive capacity of goethite during dehydration.** J. HAMPEL (Z. Elektrochem., 1936, 42, 185—187).—From expts. with Congo-red, acid fuchsin, and eosin in MeOH solution the relation between the sorptive capacity of artificially prepared goethite in various stages of dehydration and the ratio H<sub>2</sub>O/Fe<sub>2</sub>O<sub>3</sub> has been determined and is interpreted in accordance with conclusions previously reached (A., 1935, 1204; this vol., 441).

F. L. U.

**Solution state of film-forming substances.** J. SCHREIBER and O. BAUER (Kolloid-Beih., 1936, 43, 363—416).—The viscosity of solutions of many resins, highly-polymerised substances, such as rubber and its derivatives, and cellulose nitrate in a large no. of org. solvents has been determined. The effects

of changing and mixing the solvents are discussed for the several systems, but wider generalisations have not been deduced.

E. S. H.

**Wettability of quartz, calcite, and gypsum by molten sulphur.** K. N. SAMOCHVALOV and N. A. HELD (Kolloid-Z., 1936, 75, 89—74).—Wetting by S at 120° and 140° in H<sub>2</sub>O, air, and H<sub>2</sub>O vapour has been investigated by autoclave procedure. Addition of Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, or oak-bark extract reduces the wettability of CaSO<sub>4</sub>·0.5H<sub>2</sub>O or CaCO<sub>3</sub> by S, and of SiO<sub>2</sub> by bituminous S.

E. S. H.

**Laminar systems. III. Formation of thin layers of bismuth and lead sulphides on the surface of bismuth and lead salt solutions.** S. G. MOKRUSCHIN, R. B. GINSBURG, and N. M. DEM-JANOVA (Kolloid-Z., 1936, 75, 10—14; cf. A., 1935, 1317).—The prep. of films of Bi<sub>2</sub>S<sub>3</sub> or PbS, with a max. thickness of 1500—2000 Å., on the surface of aq. Bi(NO<sub>3</sub>)<sub>3</sub> or Pb(OAc)<sub>2</sub> by the action of H<sub>2</sub>S is described.

E. S. H.

**Mechanical resistance of the skin of alumina and its influence on the surface tension of the fused metal.** A. PORTEVIN and P. BASTIEN (Compt. rend., 1936, 202, 1072—1074).—The mechanical resistance of the skin of Al<sub>2</sub>O<sub>3</sub> formed on Al by heating for approx. 1 min. at 700° is 1960 dynes per cm. The thickness of the film is 10<sup>-5</sup> cm., giving a tensile strength of 2 kg. per sq. mm., which is much > that for cryst. Al<sub>2</sub>O<sub>3</sub>. The surface tension of Al fused in air is 840 dynes per cm., but for Al fused in A it is 300 dynes per cm.

R. S. R.

**Surface activity and absorption of amino-acids. V. Diamino-acids. VI. Position isomerides of monoamino-acids.** T. ITO (J. Agric. Chem. Soc. Japan, 1936, 12, 204—207, 208—215).—V. Histidine (I), lysine (II), and arginine (III), over the range  $p_H$  1—13, have very little influence on the  $\gamma$  of H<sub>2</sub>O; both neutral mols. and ions are surface inactive. The max. adsorption of (I) on charcoal occurs at  $p_H$  7.5, whilst for (II) and (III) the max. are at  $p_H$  9.5. The order of adsorption for (II) and (III) is neutral mol. < anion > cation, and for (I) neutral mol. > anion = cation.

VI. The reduction of  $\gamma$  by various NH<sub>2</sub>-acids follows the order  $\alpha$ -aminohexoxic >  $\alpha$ -aminovaleric >  $\epsilon$ -aminohexoxic >  $\gamma$ -aminovaleric >  $\delta$ -aminovaleric acid (IV). On charcoal the cations are adsorbed as strongly as the neutral mols. but the anions are less readily adsorbed. In the case of (IV) the adsorption of the cation is > that of the neutral mol.

J. N. A.

**Surface tension of systems containing a tautomeric substance.** R. V. MERTZLIN (J. Phys. Chem. U.S.S.R., 1934, 5, 1210—1214).—Surface tension measurements for the system PhNO<sub>2</sub>-o-OH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub> at 20—130° show the existence of two tautomeric forms of the latter. The surface tension isotherms are convex. to the concn. axis at temp. above, and concave below, the region of tautomeric change.

CH. ABS. (e)

**Influence of denaturation on spreading of proteins on a water surface.** H. NEURATH (J. Physical Chem., 1936, 40, 361—368).—Pressure-area



relations for films of ovalbumin (I) and serum-albumin (II) on  $H_2O$  have been determined. Spreading is greater at the isoelectric point ( $p_H$  4.8) than at  $p_H$  4.4. (II) spreads to an area (1.05 sq. m. per mg.) 15% > for (I). Previous denaturation by heat completely prevents, and irradiation with ultra-violet light partly inhibits, spreading. Fully spread films can be caused to collapse by irradiation. An explanation of the observations is given. F. L. U.

**Formation of Liesegang rings in presence of precipitates.** B. N. SEN (J. Physical Chem., 1936, 40, 369—372).—The formation of Liesegang rings of Prussian-blue by diffusion of aq.  $K_3Fe(CN)_6$  into magmas of  $CaSO_4$  or  $BaSO_4$  and aq.  $FeCl_3$  has been studied. F. L. U.

**Dependence on temperature of the apparent molecular volume of dissolved electrolytes.** I. B. PESCE (Gazzetta, 1936, 66, 99—104).—Measurements of  $d$  for KCl and NaCl solutions of varying concn. at 0.06°, 25°, 45°, 65°, and 85° are recorded. The apparent mol. vol. of both salts is a max. at 65°. O. J. W.

**Measurement of coefficient of diffusion of electrolytes.** L. J. KURTZ and A. G. SAMARTZEV (J. Phys. Chem. U.S.S.R., 1934, 5, 1424—1428).—Changes of concn. of the layers near the electrodes during electrolysis were measured with a polarising microscope and Lebedev interferometer. Vals. for the diffusion coeff. of  $ZnSO_4$  are given.

CH. ABS. (e)

**Viscosity of aqueous solutions of electrolytes as a function of concentration. III. Caesium iodide and potassium permanganate.** G. JONES and H. J. FORNWALT (J. Amer. Chem. Soc., 1936, 58, 619—625; cf. this vol., 22).—Determinations have been made at 0° and 25° over a wide range of concn. The variation of  $d$  with concn. can be expressed by Root's equation. CsI is more effective than any other known salt in lowering the  $\eta$  of  $H_2O$ ; the effect is an additive property of the ions.  $KMnO_4$  reduces the  $\eta$  of  $H_2O$ . The influence of interionic attraction on  $\eta$  is discussed. E. S. H.

**Abnormal vapour pressures in potassium chloride solutions.** A. R. WEIR (Coll. Czech. Chem. Comm., 1936, 8, 149—169).—The v.p. of aq. KCl solutions has been studied by (a) determination of the rate of distillation or condensation of  $H_2O$  in the capillary limb of an inverted U-tube, the wide limb of which contains the solution at a different temp.; (b) passing air through the solution, then over  $P_2O_5$ , and weighing; (c) direct determination of the v.p. of solutions prepared in vac. Solutions containing 58 g. of KCl per 1000 g. of  $H_2O$  exhibit variable and abnormally high v.p., indicating the presence of a metastable condition. Data relating to other physical properties at this concn. show similar variations. R. S.

**Positive platinum sols.** N. BACH and N. BALASCHOWA (Nature, 1936, 137, 617).—These have been prepared by the regulated oxidation of negative  $H_2$ -Pt sols. The particles behave like small Pt gas electrodes. Cataphoretic velocities of the sols corresponding with different degrees of oxidation are recorded. L. S. T.

### Colloidal solutions in concentrated electrolytes.

A. VORT (J. Physical Chem., 1936, 40, 307—315).—Sols of Pd, Pt, Au, and their sulphides, AgCl, AgBr, AgI, C, and S in 96%  $H_2SO_4$  or 87%  $H_3PO_4$  may remain stable for several weeks. In some cases slow pptn. occurs, but the ppt. can be redispersed by shaking. Stable sols of some of the above have also been prepared in saturated solutions of  $CaCl_2$  and KOAc. Dilution with  $H_2O$  invariably results in irreversible coagulation. The stability is not due to high viscosity, nor can cataphoresis of the particles be observed. The solutions all show a high electrical conductivity compared with ordinary sols. It is suggested that stability is due to solvation.

F. L. U.

**Relation between electro-chemical constitution and colloid structure of pure dyes sols.** W. PAULI and F. LANG (Monatsh., 1936, 67, 159—186).—By electro-dialysis and electro-decantation, very pure blue acidoid dye sols have been prepared from Congo-red (I), Congo-rubin (II), Congo-cornith G (III), benzopurpurin 4B (IV), and Chicago-blue 6B (V), the variation of their mol. conductivity with temp. and dilution being studied and compared with that of the basic dye sol of night-blue. The energy of association increases with increased internal salt formation and with the increase in polar acid groups arising from ammonolysis of the internal salt. Association hysteresis occurs and equilibrium vals. of the conductivity are obtained only after keeping at any prescribed temp. (II) and (III) have a greater conductivity than (I); this is attributed to the presence of OH in place of  $NH_2$ . The behaviour of (IV) and (V) is also in accord with their respective constitutions. The structure of dye sols and their relation to soap and protein sols are discussed. J. W. S.

**Production of oxide cathodes of colloidal structure.** E. PATAI and Z. TOMASCHEK (Kolloid-Z., 1936, 75, 80—88; cf. this vol., 566).—Hydrosols of alkaline-earth carbonates are prepared by leading  $CO_2$  into  $Ba(OH)_2$  dissolved in aq. glycerol or  $(CH_2OH)_2$ . The sols are suitable for electrophoretic deposition on metals to give oxide cathodes. E. S. H.

**Highly-polymerised compounds. CXXXIV. Distribution of mol. wts. in highly-polymerised mixtures and determination of mean mol. wt.** G. V. SCHULZ (Z. physikal. Chem., 1936, B, 32, 27—45; cf. this vol., 314).—The relations between the frequency and mass distribution functions and the mean mol. wt.,  $M$ , are deduced mathematically. By means of the distribution function the difference between the average mol. wt. of a mixture of polymeride homologues determined viscosimetrically and  $M$  can be calc. The distribution functions of a polystyrene fraction, a polymerised isobutylene (I), and a cellulose nitrate (II) of high mol. wt. have been determined. Calculation of the difference between the viscosimetric mol. wt. and  $M$  has shown that in the determination of the mol. wt. by the viscosimetric method the presence of moderate amounts of other polymerides does not cause notable error. The difference in the distribution functions of (I) and (II) indicates that the processes by which cellulose is



elaborated in the plant and the synthetic polymeride formed are fundamentally different. Staudinger's viscosity law is valid to within a few % for cellulose and substances of similar structure for degrees of polymerisation of 10–1000. R. C.

**Structures of precipitates. II. Effect of  $Mg^{++}$ ,  $Zn^{++}$ ,  $Ni^{++}$ ,  $Cu^{++}$ ,  $Mn^{++}$ , and  $Cd^{++}$  ions on peptisability of secondary particles of barium sulphate precipitates. III. Occlusion phenomena with barium sulphate precipitates.** B. TEŽAK (Z. physikal. Chem., 1936, B, 32, 46–51, 52–64; cf. this vol., 427).—II. The peptisability of  $BaSO_4$  pptd. from a mixture of aq.  $BaCl_2$  and  $XSO_4$  of concns. 0.02–0.05*N* decreases as *X* is varied in the order  $Mg^{++} > Zn^{++} > Ni^{++} > Cu^{++} > Mn^{++} > Cd^{++}$ . It is related to the sorption of these ions on the  $BaSO_4$  and to their hydration.

III. The effect of variation of the conditions of pptn. on the amount of Cl occluded by the ppt. formed from  $BaCl_2$  and  $Na_2SO_4$  has been studied. It appears that the occlusion is due to adsorption on the primary particles. The ions present as complementary ions in the adsorption layer may considerably influence the composition of the primary adsorption layers of the lattice ions; e.g., in pptn. with  $Ba(NO_3)_2$  the  $NO_3^-$  ions may cause preferential adsorption of  $Ba^{++}$ , the ppt. being charged positively, whereas with  $BaCl_2$  as precipitant under similar conditions the ppt. is negatively charged owing to preferential adsorption of  $SO_4^{--}$  ions. R. C.

**Viscosity and lyotropic numbers** E. M. BRUNS (Rec. trav. chim., 1936, 55, 297–300).—A reply to Merkel (this vol., 426). E. S. H.

**Directed coagulation in aerosols.** D. BEISCHER and A. WINKEL (Z. physikal. Chem., 1936, 176, 1–10).—An aerosol of dimethylaminoazobenzene coagulates at a rate essentially in accordance with Smoluchowski's theory. With an aerosol of aminoazobenzene (I) the coagulation coeff. is exceptionally large, and the relation between  $1/n$  and  $t$  becomes linear only after coagulation has proceeded for some time. This anomaly is due to the pyro-electric properties of (I). Condensation of the vapour yields crystals of colloidal dimensions in which on cooling a pyro-electric moment appears, and the particles attract and orient each other, giving long strings consisting of up to 50 particles joined end to end. Certain foreign substances inhibit the pyro-electric effect, and coagulation is then normal. A method of determining pyro-electric moments is described which consists in observing the deflexion produced when a homogeneous electric field is applied to a crystal suspended by a quartz fibre. R. C.

**Influence of alkalinity of glass on the viscosity of dilute solutions of cellulose nitrate in ether-alcohol.** J. GRÉVY (Compt. rend., 1936, 202, 480–482; cf. A., 1935, 581).—The viscosity ( $\eta$ ) of 0.3% solutions of cellulose nitrate in  $Et_2O$ – $EtOH$  ( $EtOH$  60 wt.-%) kept in glass vessels decreases at a rate depending on the nature of the glass and the extent of the surface of contact. It is greatest with ordinary glass cleaned with  $H_2O$ , and least for Pyrex

glass cleaned with  $CrO_3$  and  $H_2SO_4$ . Experiments in which small amounts of  $K_2CO_3$  or  $Na_2CO_3$  were added indicate that the alkalinity of the glass is responsible. F. L. U.

**Viscosity measurements during the coagulation of titanium dioxide sol by mixtures of electrolytes and non-electrolytes.** (Miss) O. JOSEPH and S. M. MERTA (J. Univ. Bombay, 1935, 4, Part II, 123–131).—The influence of  $MeOH$ ,  $EtOH$ , and  $PrOH$  on the changes with time of the viscosity of  $TiO_2$  sol, dialysed to different extents, on addition of  $KCl$ ,  $MgCl_2$ , and  $AlCl_3$  has been investigated. In each case the viscosity increases on addition of alcohol, in accord with the view that the dielectric const. of the medium is reduced and hence the density of charge on the particle, with consequent increased hydration. The addition also increases the rate of coagulation, indicating that either the rate of aggregation or the rate of hydration of the particles is increased. The periodic nature of the viscosity-time curve decreases with increasing purity of the sol. J. W. S.

**Coagulation of dilute oil emulsions by mercuric chloride: evidence for the discontinuity of the change in the slow region.** S. S. JOSHI and S. P. SARKAR (J. Univ. Bombay, 1935, 4, Part II, 140–145).—The coagulation of oil emulsions has been studied from variations in viscosity ( $\eta$ ), transparency, and refractive index. The discontinuities in the  $\eta$ -time curve are the more pronounced the lower is the electrolyte concn. The coagulation is always accompanied by a small initial decrease in  $\eta$  during the first 20–30 min., resulting in some cases in a nett decrease in  $\eta$  during coagulation. The change in transparency is rapid initially, but becomes almost zero in later stages. The refractive index decreases during coagulation, and this tendency is the greater the higher is the electrolyte concn. The results are only partly in accord with the view that the refractivity approximates to that of the continuous medium, modified by the presence of electrolyte. In some cases the change in refractive index is also discontinuous. J. W. S.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity. II. Influence of sol concentration on flocculation value.** W. OSTWALD (Kolloid-Z., 1936, 75, 39–59; cf. this vol., 157).—A crit. discussion of published data. Increase of sol concn. may (a) sensitise the sol to univalent ions and stabilise it to multivalent ions (typical of hydrophobic sols), (b) stabilise the sol to all types of electrolytes (metal hydroxide sols, Prussian-blue, etc.), or (c) sensitise the sol to all electrolytes ( $NH_4Ph-H_2O$  emulsions). Flocculation vals. are considered in terms of the activity coeffs. of the dominating ions. E. S. H.

**Viscosity of suspensions and solutions. V. Influence of Brownian movement on the viscosity of ellipsoid suspensions.** E. GUTH. VI. Viscosity of rod-like suspensions. F. EIRICH, H. MARGARETHA, and M. BENZL (Kolloid-Z., 1936, 75, 15–20, 20–37; cf. this vol., 562).—V. Mathematical. VI. Investigation of suspensions containing rod-like particles of glass, or natural or artificial silk shows that the measured viscosity depends on the orientation



of the particles, and thus varies with the streaming velocity and with the design of the viscosimeter.

E. S. H.

**Quantitative relations in the lyotropic series.** E. H. BÜCHNER (Kolloid-Z., 1936, 75, 1—9).—A critical discussion of published work.

E. S. H.

**Influence of the addition of small quantities of electrolytes on a copper ferrocyanide sol in reference to the flocculation produced by the same electrolytes.** A. BOUTARIC and (Mlle.) P. BERTHIER (Bull. Soc. chim., 1936, [v], 3, 696—701).—Addition of small amounts of LiCl, KCl, or  $\text{NH}_4\text{Cl}$  stabilises the sol towards coagulation by larger amounts of the same electrolytes. The effect depends on the time interval which elapses before the more conc. electrolyte solution is added; protection increases at first as the time interval increases, passes through a max., and finally disappears. The effect is not observed with  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ , or  $\text{AlCl}_3$ .

E. S. H.

**Problems of the theory of diffusion.** T. KATSURAI and K. KAWASHIMO (Kolloid-Z., 1936, 75, 37—39).—Mathematical.

E. S. H.

**Swelling power of caoutchouc in solvent mixtures in relation to their dielectric polarisation.** N. JERMOLENKO and S. LEVINA (Kolloid-Z., 1936, 75, 59—65).—The swelling of caoutchouc in binary mixtures of  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , PhMe,  $\text{PhNO}_2$ ,  $\text{COMe}_2$ , EtOH, and  $\text{CHCl}_3$  has been examined. In mixtures of two polar or non-polar solvents the swelling is parallel to the change in mol. polarisation of the mixture. The effects are irregular in mixtures of polar with non-polar solvents, but in some cases the degree of swelling is in the opposite sense to the change in mol. polarisation. The swelling of caoutchouc in  $\text{C}_6\text{H}_6\text{--CHCl}_3$  is increased by addition of EtOH.

E. S. H.

**Gelatin dichromate.** II. E. ELÖD and H. BERCELI (Kolloid-Z., 1936, 75, 66—73; cf. B., 1936, 465).—Degradation of gelatin by hydrolysis at  $100^\circ$ , or the addition of gelatin degradation products or albumin, increases the rate of dissolution of gelatin- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , and decreases the light-sensitivity.

E. S. H.

**Dilatometric study of various ternary glasses.** E. RENCKER (Bull. Soc. chim., 1935, [v], 2, 1389—1407; cf. A., 1935, 36).—Cubical expansion coeffs. and temp. of transformation have been determined for  $\text{SiO}_2\text{--Na}_2\text{O--X}$  glasses, where  $\text{X}=\text{Al}_2\text{O}_3$ , BeO, MgO, ZnO, CaO. The law of additivity of expansion coeffs. of Winkelmann and Schott (Ann. Physik, 1894, 51, 735) was found applicable within 3%, in all melts except those containing  $>15\%$   $\text{Al}_2\text{O}_3$ , but the coeffs. for the individual oxides given by these authors, and by English and Turner (B., 1928, 262), do not accord either with one another or with the present measurements, and a new set of vals. are calc. Partial replacement of the  $\text{SiO}_2$  in a  $\text{SiO}_2\text{--Na}_2\text{O}$  glass by X raises the transformation temp. in the order: ZnO, CaO, MgO,  $\text{Al}_2\text{O}_3$ , BeO; glasses containing more than 15% BeO devitrify on cooling, due to their high basicity.

R. C. M.

**Inertia and chemical activity of the rare gases.** VI. Elimination of helium from the

compound platinum-helium and from radium salts at different temperatures. H. DAMIANOVICH (Anal. soc. cient. Argentina, 1934, 118, 227—241; cf. A., 1934, 1296).—It is suggested that He which can be eliminated from Ra salts by heating is held by certain impurities, in a combination of the type found in the Pt-He compound.

CH. ABS. (e)

**Influence of foreign substances on fluorescent power. Colourless inhibitors.** J. BOUCHARD (J. Chim. phys., 1936, 33, 325—344).—Increase of mol. association by the addition of electrolytes (I) to a conc. solution of fluorescent substance (II) decreases the fluorescent power. Variation of fluorescent power with the concn. of (II) follows an exponential law the more closely the greater is the concn. of (I).  $k$  (cf. this vol., 408) increases with concn. of (I), but in very conc. solutions only of (II) in conditions where a modification of the absorption spectrum of dissolved (II) appears. Expressions relating the action of a large no. of colourless org. and inorg. inhibitors (III) on uranine solutions (IV) to the concn. of (III) and (IV) are given. The  $h$  of (III) diminishes with decreasing dielectric const. and with increasing  $n$ . In general  $h$  varies parallel with  $k$ . The most active (III) are typical antioxidants. Relative vals. of  $h$  for different (III) vary with (II).

M. S. B.

**Dissociation of strong electrolytes in concentrated solutions.** I. R. RAO and C. S. RAO (Nature, 1936, 137, 580).—Raman spectra indicate that (i) all oxy-acids dissociate progressively with increasing dilution, (ii) the halogen acids are completely dissociated even in conc. solutions, (iii) the acid salts of the alkalis are completely dissociated into alkali ion and the acid radical, the further dissociation of which is progressive, and (iv) all other salts of the alkalis and alkaline earths are completely dissociated even in saturated solutions. An explanation of these results based on the electronic theory of valency is discussed.

L. S. T.

**Effect of ionic charge on acidity of an acid.** G. SCHWARZENBACH (Z. physikal. Chem., 1936, 176, 133—153).—Experimental evidence is adduced to show that the difference in acidity between two acids which differ only by an ionic charge, i.e., the nuclear charge of some atom in the mol., is solely a function of the distance between the seat of this charge and the seat of the proton which is released from the acid; there is no evidence of any influence exerted by an electrostatic difference between the acid groups of the two acids. This is also generally true when the ionic charge by which the acids differ is a proton. It thus becomes possible to calculate from the difference in acidity the work done in separating the acid proton from the ionic charge, and in this way an experimental potential curve for the vicinity of an ionic charge in a polar medium may be derived. This curve differs from  $e^2/rD$ . The above considerations have been utilised to calculate the acidities of certain acids which cannot be examined experimentally.

R. C.

**Influence of a substituent on the acidity of an organic acid.** II. G. SCHWARZENBACH and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 493—504).—Normal acidity potentials have been determined at



20° for  $\text{EtCO}_2\text{H}$ ,  $\text{CH}_2\text{Et}\cdot\text{CO}_2\text{H}$ ,  $\text{CHPr}_2\cdot\text{CO}_2\text{H}$  and for the  $\text{Et}_1$  esters of malonic, diethyl- and dipropyl-malonic acids in 18.1–95.0 vol.-%  $\text{EtOH}$ . It is concluded that electrostatic effects are mainly absent and that the influence of the substituents considered is electronic (cf. A., 1934, 1310). The mechanism of the electronic effect is discussed. M. S. B.

**First dissociation constant of carbonic acid at various temperatures.** Y. KAUKO and J. CARLBERG (Z. physikal. Chem., 1936, 176, 11–19).—The first dissociation const. at 0–25° has been determined by  $p_{\text{H}}$  measurements on aq.  $\text{NaHCO}_3$  through which  $\text{CO}_2$  is passing. The results agree with those of Kendall (A., 1916, ii, 512), but not with those of MacInnes *et al.* (A., 1935, 1321). R. C.

**Anomalies in the dissociation constant of some halogenated organic acids.** III. M. BETTI and E. LUCCHI (Atti R. Accad. Lincei, 1935, [vi], 22, 367–370; cf. this vol., 564).—For the two acids  $\text{trans-C}_6\text{H}_4\text{X}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ )  $K$  at 25° =  $0.39 \times 10^{-4}$ , which is nearly the same as the val. for cinnamic acid ( $K=0.365 \times 10^{-4}$ ). O. J. W.

**Quantitative investigations of amino-acids and peptides.** II. Apparent dissociation constants in aqueous formaldehyde solution. M. S. DUNN and A. LOSHAKOFF (J. Biol. Chem., 1936, 113, 691–694; cf. this vol., 620).—Vals. of  $pK'_a$  in aq.  $\text{CH}_2\text{O}$  of a no. of  $\text{NH}_2$ -acids have been determined. H. D.

**Differential dissolution of sodium bromide in its aqueous solutions and the activity coefficients of sodium bromide in concentrated aqueous solutions.** F. MURATA (J. Chem. Soc. Japan, 1935, 56, 588–595).—The e.m.f. of the cell  $\text{Na}$  (amalgam, 0.2203%) |  $\text{NaBr}$ , aq. ( $m$ ),  $\text{HgBr}$  |  $\text{Hg}$  has been determined for various vals. of  $m$  and of temp. The free-energy change in the differential dissolution of  $\text{NaBr}$  in aq. solution and the activity coeff. are calc. The heat of dissolution of  $\text{NaBr}\cdot 2\text{H}_2\text{O}$  at 25° is  $-2933$  g.-cal. CH. ABS. (e)

**Thermodynamic properties of cadmium sulphate in aqueous alcohol.** V. K. LAMER and E. L. CARPENTER (J. Physical Chem., 1936, 40, 287–302; cf. A., 1934, 31).—The influence of increasing  $\text{EtOH}$  content on the partial free energy, heat content, and heat capacity of  $\text{CdSO}_4$  in aq.- $\text{EtOH}$  solution has been determined. The val. of the mean ionic radius of the ions, calc. from the Born equation, agrees fairly with that of the distance of closest approach calc. by the extended theory of Debye and Hückel. F. L. U.

**Selenites of sodium, potassium, and ammonium in aqueous solution.** J. JANICKIS and H. GUTMANAITIS (Z. anorg. Chem., 1936, 227, 1–16; cf. A., 1932, 584).—Solubilities of  $\text{Na}$ ,  $\text{K}$ , and  $\text{NH}_4$  selenites in  $\text{H}_2\text{O}$ , and f.p. of the solutions, have been determined down to their respective cryohydric points. Conductivities have been measured between 0.0002  $M$  and 2  $M$ . The normal salts behave as ternary, and  $\text{NaHSeO}_3$  and  $\text{KHSeO}_3$ , except at great dilution, as binary, electrolytes. The  $\text{NH}_4$  salt behaves according to:  $(\text{NH}_4)_2\text{SeO}_5 + \text{H}_2\text{O} \rightleftharpoons 2\text{NH}_4\text{HSeO}_3$ . The behaviour of the tetraselenites is expressed by:  $\text{MH}_3(\text{SeO}_3)_2 \rightleftharpoons \text{M}' + [\text{H}_3(\text{SeO}_3)_2]' \rightleftharpoons \text{HSeO}_3' + \text{H}_2\text{SeO}_3$ . F. L. U.

**Hydrolysis of inorganic salts and chemistry of high-molecular hydrolysis products, including iso- and heteropoly-compounds.** III. G. JANDER and K. F. JAHR (Kolloid-Beih., 1936, 43, 295–362; cf. A., 1934, 489).—Mainly a crit. summary of published work, with additional experimental data relative to the diffusion, conductivity, and light absorption of aq. salts of  $\text{Mg}$ ,  $\text{Zn}$ ,  $\text{VO}_2^{\text{II}}$ ,  $\text{Be}$ ,  $\text{Al}$ ,  $\text{ZrO}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Cr}^{\text{III}}$ . E. S. H.

**Polarimetric study of nickel malate.** J. L. DELSAL (Compt. rend., 1936, 202, 1280–1282).—When  $\text{NaOH}$  is added to solutions containing  $\text{Ni}(\text{NO}_3)_2$  and excess of malic acid, the rotatory power passes through min. and max. vals., corresponding with the formation of  $\text{Ni}$  malate and  $\text{Na}$  nickelomalate, respectively. The formation of a sol. complex nickelomalic acid is indicated. L. J. J.

**Application of thermodynamics to chemical equilibria in homogeneous systems.** M. W. MUND (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 15–34).—Theoretical. M. S. B.

**Diagrams representing physico-chemical analyses of irrational systems.** M. USANOVITSCH (J. Gen. Chem. Russ., 1935, 5, 1757–1761).—Polemical, in reply to Ust-Katschkintzev (this vol., 22). R. T.

**Heterogeneous gaseous equilibria  $\text{NaCl} + \text{HBr} \rightleftharpoons \text{NaBr} + \text{HCl}$  and  $\text{KCl} + \text{HBr} \rightleftharpoons \text{KBr} + \text{HCl}$ .** K. JELLINEK, W. WLODARSKI, and T. ARCZYNSKI (Z. anorg. Chem., 1936, 227, 43–51; cf. this vol., 674).—Equilibria in the system  $\text{NaCl} + \text{HBr}$  have been determined at 850–950°, and in  $\text{KCl} + \text{HBr}$  at 765–850°. In both the condensed phase is homogeneous liquid  $[(\text{Na}, \text{K})\text{Cl} + (\text{Na}, \text{K})\text{Br}]$  which behaves as an ideal mixture. Heats of reaction are calc. F. L. U.

**Equilibria  $\text{Cl}_2 + 2\text{KBr} \rightleftharpoons 2\text{KCl} + \text{Br}_2$  and  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$ .** K. JELLINEK and H. SCHÜTZ (Z. anorg. Chem., 1936, 227, 52–61; cf. A., 1933, 783).—Determination of the equilibrium const. in the above reactions at 800° gives  $N_{\text{KCl}}^2 p_{\text{Br}_2} / N_{\text{KBr}}^2 p_{\text{Cl}_2} = 303$ , and  $p_{\text{Cl}_2} p_{\text{Br}_2} / p_{\text{BrCl}}^2 = 0.12$  ( $N$ =mol. fraction,  $p$ =partial pressure). The dissociation const. for  $\text{BrCl}$  is nearly independent of temp. F. L. U.

**Equilibrium diagram of the system barium fluoride-magnesium fluoride.** U. NISIOKA and M. OKAMOTO (Kinz.-no-Kenk., 1935, 12, 220–225).—Data are recorded. The compound  $\text{BaF}_2 \cdot 2\text{MgF}_2$  is formed. It forms a eutectic with  $\text{BaF}_2$  at 912° (17%  $\text{MgF}_2$ ). A glassy mass could not be obtained by quenching the melt. CH. ABS. (e)

**Dissociation pressure of cupric sulphate pentahydrate.** K. SANO (Sci. Rep. Tôhoku, 1936, 24, 719–723).—Measurements have been made by a statical method using Jackson's glass-spring manometer at 48–82° and the results are in fair agreement with earlier ones obtained in the tensimeter. The relation  $\log P_{\text{H}_2\text{O}} = -2,894.47/T + 10.611$  holds. Thermodynamical data for the reaction  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$  are  $\Delta F_{298}^\circ$  5146 g.-cal.,  $\Delta H_{298}^\circ$  26,578 g.-cal., and  $\Delta S_{298}^\circ$  71.01 e.s.u. M. S. B.

**Dissociation of smithsonite.** R. MEHMET and G. VALENSI (Bull. Soc. chim., 1935, [v], 2, 1295–



1300).—Decomp. pressures obtained by the static method at 250° and 290°, are > those given by Centnerszwer's dynamic method (A., 1924, ii, 655), but much < the equilibrium vals. calc. from published heats of dissociation, due to the low rate of decomp. below 300°. The formation of a solid solution of ZnO in ZnCO<sub>3</sub> is improbable. R. C. M.

**Mutual relation between silicates and sulphides.** A. S. GINSBERG (Trav. Inst. pét. Acad. Sci. U.R.S.S., 1933, 4, 21—45).—The systems Fe<sub>2</sub>SiO<sub>4</sub>—FeS, MnSiO<sub>3</sub>—FeS, and Mn<sub>2</sub>SiO<sub>4</sub>—FeS have been studied. The components are characterised by limited miscibility in the liquid state. CH. ABS. (e)

**Equilibria of metal fluorides with water vapour.** L. DOMANGE (Compt. rend., 1936, 202, 1276—1277; cf. A., 1935, 448, 1088).—Data are recorded for equilibrium HF—H<sub>2</sub>O concns. with a no. of fluorides at high temp. Heats of reaction at const. pressure are calc. from the data. L. J. J.

**Equilibrium diagrams of the systems** (A) CaO, Al<sub>2</sub>O<sub>3</sub>, 2SiO<sub>2</sub>—CaO, TiO<sub>2</sub>, and (B) CaO, MgO, 2SiO<sub>2</sub>—CaO, TiO<sub>2</sub>. U. NISIOKA (Sci. Rep. Tôhoku, 1936, 24, 707—713, 714—718).—(A) The quenched mixtures were examined microscopically under reflected light. There is an eutectic at 1350° and 35% CaO, TiO<sub>2</sub> by wt.

(B) There is a simple eutectic at 1270° and 32% by wt. of CaO, TiO<sub>2</sub>. M. S. B.

**Equilibria in the system cobalt sulphate-sulphuric acid-water.** L. L. KLJATSOHKO-GURVITSCH and H. OGANDSHANOVA (J. Gen. Chem. Russ., 1935, 5, 1781—1785).—Solubility data are recorded for CoSO<sub>4</sub> in H<sub>2</sub>O and aq. H<sub>2</sub>SO<sub>4</sub> at 0° and 20°. Crystallisation of CoSO<sub>4</sub>·7H<sub>2</sub>O is at a max. in presence of 35% H<sub>2</sub>SO<sub>4</sub> at 0°, and of 26.8% at 20°. R. T.

**Thermodynamic study of systems of the type PbCl<sub>2</sub>—RCl—H<sub>2</sub>O at 25°.** A. R. WEIR (Coll. Czech. Chem. Comm., 1936, 8, 93—113).—H<sub>2</sub>O activities have been derived from measurements of the v.p. of solutions of widely varying concns. Abnormal changes of v.p. are found in the vicinity of the system with PbCl<sub>2</sub> and KCl, 2PbCl<sub>2</sub> as solid phases. J. G. A. G.

**Systems antimony (or bismuth) iodide-alkali iodide-water.** F. FRANÇOIS and M. L. DELVAULLE (Bull. Soc. chim., 1936, [v], 3, 687—696).—Equilibrium data at 12—16° have been obtained. The systems contain many double salts, which are isomorphous when Sb is replaced by Bi. Interchange of alkali metal (Na, K, Li, NH<sub>4</sub>) may produce double salts of different type. E. S. H.

**Thermochemistry of titanium oxides. I. The equilibrium, 2TiO<sub>2</sub> + H<sub>2</sub> ⇌ Ti<sub>2</sub>O<sub>3</sub> + H<sub>2</sub>O.** N. NASU (J. Chem. Soc. Japan, 1935, 56, 542—551).—The heterogeneous equilibrium was studied at 1022—1282° abs. CH. ABS. (e)

**Heats of combustion and sublimation.** H. C. BLANCK and K. L. WOLF (Z. physikal. Chem., 1936, B, 32, 139—144).—These quantities have been determined for succinic acid and several derivatives. The results show that of the esters of the isomeric

tartaric acids the meso-compounds have the greatest internal energy contents, which is ascribed to difference in the extent of intramol. association of the OH groups. R. C.

**Dissociation energies of carbon monoxide and CN, and heat of sublimation of carbon.** G. HERZBERG (Nature, 1936, 137, 620).—Brons' val. of 193.9 kg.-cal. for D<sub>CO</sub> (this vol., 8) is not necessarily correct; a val. of 209.7 kg.-cal. is also compatible with available pre-dissociation data, and gives a val. for the heat of sublimation of C, viz., 125.1 kg.-cal., more in keeping with the val. of 143 kg.-cal. obtained from thermal data. L. S. T.

**Electric conductivity of the system acetic anhydride-water.** N. A. TRIFONOV and V. F. UST-KATSHKINTZEV (J. Phys. Chem. U.S.S.R., 1934, 5, 1215—1221).—Measurements at 0°, 50°, and 72.5° show max. at 3.5—4.5 and 90, and a min. at 50, mol.-% of Ac<sub>2</sub>O. The temp. coeff. of conductivity has a max. at 50 mol.-%. Formation of AcOH is indicated. CH. ABS. (e)

**Nature of the glass electrode potential. I.** H. YOSHIMURA (J. Biochem. Japan, 1936, 23, 91—100).—The deviation of the slope of the calibration line of *E* against *p*<sub>H</sub>, (*E*<sub>1</sub>—*E*<sub>2</sub>)/(*p*<sub>H1</sub>—*p*<sub>H2</sub>), from the theoretical is shown (by coating with paraffin wax) to be due, not to the "deviation film" of liquid on the non-immersed part of the electrode, but to the nature of the glass membrane, every part of which has its own val. of *E*, the observed *E* being the average of all parts in proportion to their respective *κ*. F. O. H.

**Electrolytic polarisation capacity and the atomic mechanism of hydrogen electrodes.** T. NOGUCHI (J. Electrochem. Assoc. Japan, 1935, 3, 141—149).—Data for the polarisation capacity of Pt electrodes dipped in H<sub>2</sub>SO<sub>4</sub> are given. A discharged atom should be deposited on a Pt atom in the surface at. grating of the electrode. The H absorbed by Pt should, at the higher c.d., increase the active surface of the electrode. CH. ABS. (e)

**Influence of light on electrode potential and corrosion phenomena of certain non-ferrous metals.** C. O. BANNISTER and R. RIGBY (J. Inst. Metals, 1936, 56, Advance copy, 91—108).—Apparatus for continuously recording changes of e.m.f. when an electrode is illuminated under the influence of a regulated supply of O<sub>2</sub> is described. The effect of light is considerable in the case of Al, Pb, and Zn in the presence of O<sub>2</sub>, the aerated and illuminated electrode becoming more cathodic. The max. light effect is shown by violet and near ultra-violet light; the observed effects are attributed to the catalytically accelerated formation of protective oxide films. A. R. P.

**Diffusion potentials and ionic activities.** J. J. HERMANS (Z. physikal. Chem., 1936, 176, 55—64).—Correction of Nernst's diffusion potential formula to allow for interionic forces gives as the limiting law for infinite dilution  $\epsilon = [(l_1 - l_2)(l_1 + l_2)](RT/F)(\log c + A\sqrt{c})$ , where *A* is a const. which can be calc. from known magnitudes. This expression is compatible with the assumption that at high dilutions the ionic



activity coeffs. of HCl are equal. The deductions of Szabó (A., 1935, 1323) are criticised. R. C.

**Ionic activities of sodium and potassium chlorides.** Z. SZABÓ (Z. physikal. Chem., 1936, 176, 125—130).—The equation for diffusion potential deduced theoretically by Hermans, taking account of interionic forces (preceding abstract), gives for the experimentally accessible concn. range of 0.0005—0.02*M* the same results for HCl as the author's empirical equation (A., 1935, 1323, 1325). For KCl/KCl up to *M* the diffusion potential may be represented by the empirical equation  $\epsilon = 1.04 \log (m_1/m_2)$  indicating that the ionic activities are equal even in conc. solutions. For NaCl/NaCl the equation is  $\epsilon = 12.31 \log (m_1/m_2)$  up to 0.5*M*, also indicating equality of the ionic activities. R. C.

**Diffusion potentials and ionic activities.** J. J. HERMANS (Z. physikal. Chem., 1936, 176, 131—132).—Polemical against Szabó (preceding abstract). A method of determining diffusion potentials at high concns. without using ionic activities is suggested. R. C.

**Polarographic studies with the dropping mercury electrode. IV. Measurement of the polarisation capacity.** D. ILKOVIČ (Coll. Czech. Chem. Comm., 1936, 8, 170—177; cf. this vol., 430).—The polarisation capacity *k* of the dropping Hg electrode has been determined polarographically using the relation  $Q = qk\pi$ , where *Q* is the quantity of electricity, *q* the surface of the drop, and  $\pi$  the potential. With cathodic polarisation in 0.1*N*-KCl,  $k = 22.3 \times 10^{-6}$  and with anodic polarisation  $k = 42.2 \times 10^{-6}$  farad per sq. cm. In very pure solutions the Hg sometimes acquires the potential of a reversible H electrode. R. S.

**Polarographic studies with the dropping mercury cathode. LVIII. Electro-reduction of dicyanogen and oxamic acid.** J. BREZINA and J. HEYROVSKÝ (Coll. Czech. Chem. Comm., 1936, 8, 114—124).—In aq. solutions of NaOAc, C<sub>2</sub>N<sub>2</sub> causes an increase of current when the potential of the dropping Hg cathode is -1.15 volt with respect to the *N*-Hg<sub>2</sub>Cl<sub>2</sub> electrode; this is attributed to direct electro-reduction of C<sub>2</sub>N<sub>2</sub>. The second increase of current at -1.55 volt is probably due to electro-reduction of oxamic acid or its salt. As the age of the solution increases, the first polarographic "wave" diminishes and the second increases. C<sub>2</sub>N<sub>2</sub> has no effect on current-voltage curves of alkaline solutions, and in neutral or slightly acid solutions the second "wave" develops slowly but does not appear in more acid solutions. The results are interpreted in terms of the hydrolysis of C<sub>2</sub>N<sub>2</sub>. 10<sup>-5</sup>—10<sup>-6</sup> g.-mol. per litre of C<sub>2</sub>N<sub>2</sub> and oxamic acid can be detected polarographically. J. G. A. G.

**Theory of passivity. XXIX. Theory of the barrier layer in aluminium.** W. J. MÜLLER [with E. LÖW] (Z. Elektrochem., 1936, 42, 166—175; cf. A., 1935, 1326).—The formation of an oxide layer on specially pure (99.998%) Al immersed in saturated aq. NaHCO<sub>3</sub> is much more rapid than when ordinary "pure" Al is used, and smaller residual currents are observed. With an applied p.d. < 2 volts conduction

is not unidirectional, whilst above this the cathodic current is several hundred times > the anodic. The effect is not due to formation of gaseous O<sub>2</sub>, but is fully explained by the electro-osmotic theory.

F. L. U.

**Electrochemical investigation of [mixed solutions of] aluminium and potassium bromides in solvent mixtures.** V. A. PLOTNIKOV, O. K. KUDRA, and J. F. MEJENNY (Z. physikal. Chem., 1936, 176, 154—159).—The decomp. voltages of solutions in EtBr and PhMe increase considerably on addition of small amounts of PhNO<sub>2</sub>; further additions have a smaller effect. For an equimol. ratio of AlBr<sub>3</sub> to PhNO<sub>2</sub> the conductivity in dil. solutions is a max. and in conc. solutions a min. It is inferred that a complex containing AlBr<sub>3</sub>, KBr, and PhNO<sub>2</sub> is present in solution. On electrolysis a coherent deposit of K separates on the cathode; with certain solvents the current yield may rise to 40%. R. C.

**Dissociation constants of reductone and of its product of oxidation by iodine.** G. CARPÉNI (Compt. rend., 1936, 202, 1065—1067).—The dissociation const. of reductone [OH·CH·C(OH)·CHO] at 20±0.5° is  $1.17 \times 10^{-5}$ , as calc. from titrimetric data. The NaOH titrimetric curves for the solution obtained by oxidising reductone with aq. I give a dissociation const.  $2 \times 10^{-4}$  (*K*<sub>1</sub>), in agreement with oxidation-reduction potentials (cf. this vol., 292). With *p*<sub>H</sub> > 4.6 the p.d. after each addition of NaOH falls exponentially; the decrease is at first small, but becomes large at *p*<sub>H</sub> 6—9.5. After 24—48 hr. the equilibrium mixture gives a second dissociation const.  $2.5 \times 10^{-6}$  (*K*<sub>2</sub>). A return titration by HCl gives a new curve which is not modified by a new titration with NaOH; this curve shows an exaltation of acidity, *K*<sub>1</sub> and *K*<sub>2</sub> becoming  $5 \times 10^{-4}$  and  $6.8 \times 10^{-5}$ , respectively. A parallel is drawn with the behaviour of oxyascorbic acid. R. S. B.

**Nature of complexes of phenols with amines.** L. P. KULEV (J. Gen. Chem. Russ., 1935, 5, 1566—1575).—The e.m.f. developed when Na and Pt electrodes are immersed in PhOH in C<sub>6</sub>H<sub>6</sub> in presence of C<sub>5</sub>H<sub>5</sub>N is at a max. for 25—30% of PhOH. At this concn. in absence of C<sub>6</sub>H<sub>6</sub> the e.m.f. is at a min., but rises on progressive addition of C<sub>6</sub>H<sub>6</sub> to the C<sub>5</sub>H<sub>5</sub>N solution. H<sub>2</sub>O, PhNO<sub>2</sub>, and *m*-nitrotoluene have a similar effect, Pr<sup>o</sup>OH, Bu<sup>o</sup>OH, and Bu<sup>o</sup>OH have the opposite effect, and Pr<sup>s</sup>OH and *o*-nitrotoluene are without action when added to 25% PhOH in C<sub>5</sub>H<sub>5</sub>N, but at other concns. of PhOH the effects of adding these compounds may be entirely different. Of a no. of phenols examined, PhOH is the most active; the activity of the cresols diminishes in the order *m*- > *p*- > *o*-. The above effects are ascribed to formation of mol. complexes, the possible structure of which is discussed. The complexes are more readily formed with C<sub>5</sub>H<sub>5</sub>N than with NH<sub>2</sub>Ph or NPhMe<sub>2</sub>. The high e.m.f. obtained in presence of NEt<sub>3</sub> is considered to be a consequence of formation of the salt NH<sub>2</sub>Et<sub>3</sub>·OPh. R. T.

**Chemical reaction and atomic theory.** J. M. BRJVOET (Chem. Weekblad, 1936, 33, 222—231, 270—277).—Theoretical. The factors determining



the occurrence and velocity of reactions and the magnitude of equilibrium consts. are discussed in the light of modern developments of wave mechanics.

D. R. D.

**Calculation of intermediate reactions in homogeneous systems.** A. SKRABAL (Z. Elektrochem., 1936, 42, 228—246).—Mathematical. Complete reaction schemes are developed on the basis of the kinetic theory for various types of intermediate reaction (cf. A., 1935, 39, 707, 1328). C. R. H.

**Homogeneous unimolecular decomposition reactions of gases. II.** F. PATAT (Z. Elektrochem., 1936, 42, 265—276).—A further review (cf. this vol., 293).

**Recent developments in reaction kinetics, especially gas explosions.** J. A. HVEDING (Tids. Kjemi, 1936, 16, 50—55).—A review. M. H. M. A.

**Equilibrium constants and velocity constants.** M. G. EVANS and M. POLANYI (Nature, 1936, 137, 530—531).—A generalised expression, from which the known relationship between  $k$  and  $K$  of certain related chemical reactions can be deduced as specialised cases, is derived from thermodynamic considerations. L. S. T.

**Viscosity, plasticity, and diffusion as examples of absolute reaction rates.** H. EYRING (J. Chem. Physics, 1936, 4, 283—291).—Theoretical. L. J. J.

**Absolute rate of reactions in condensed phases.** E. A. MOELWYN-HUGHES (J. Chem. Physics, 1936, 4, 292). H. EYRING and W. F. K. WYNNE-JONES (*ibid.*, 293; cf. A., 1935, 1205).—Criticism and a reply. L. J. J.

**Influence of pressure, concentration, and temperature on the speed of the slow oxidation and the ease of spontaneous inflammation of mixtures of oxygen and *n*-pentane below 300°.** M. PRETTE (Compt. rend., 1936, 202, 954—956).—Increase in the initial pressure in a 36% C<sub>5</sub>H<sub>12</sub>-O<sub>2</sub> mixture shortens the lag before ignition. The min. lag was observed in an equimol. mixture. H. J. E.

**Slow combustion of benzene and other hydrocarbons.** J. AMIEL (Compt. rend., 1936, 202, 946—948).—The fraction of C<sub>6</sub>H<sub>6</sub> oxidised at a time  $t$  and temp.  $T$  is given empirically by  $\gamma = 10^{(A/T) + Bt} - 10^{CT + D}$ . Similar expressions are valid for the oxidation of C<sub>2</sub>H<sub>2</sub> or C<sub>3</sub>H<sub>8</sub>. H. J. E.

**Decomposition of azomethane. I. Apparatus.** D. V. SICKMAN and O. K. RICE. **II. Pure azomethane and azomethane in presence of helium.** O. K. RICE and D. V. SICKMAN (J. Chem. Physics, 1936, 4, 239—241, 242—251).—I. A manometer adapted to the measurement of small changes in a large total pressure is described.

**II.** Kinetic data at 290° and 310° are recorded for  $p_{\text{Me}_3\text{N}}$ , 0.35—25 mm. and  $p_{\text{He}}/p_{\text{Me}_3\text{N}}$ , 5 and 10. The pressure dependence of  $k$  is in better agreement with the theory of Rice, Ramsperger, and Kassel than are Ramsperger's results (A., 1927, 737). He has an activating efficiency 0.120 of that of Me<sub>3</sub>N<sub>2</sub>. The evidence is against a chain mechanism. L. J. J.

**Mechanism of thermal reaction between gaseous iodine monochloride and hydrogen. A.**

SHERMAN and N. LI (J. Amer. Chem. Soc., 1936, 58, 690—691).—Theoretical. E. S. H.

**Flame speeds in moist carbon monoxide-oxygen mixtures.** V. VORONKOV and A. SOKOLIK (Nature, 1936, 137, 533—534).—Curves obtained for the speeds of propagation of flame in various CO+O<sub>2</sub> mixtures at different pressures are reproduced. Their form is not connected with hygroscopic conditions (cf. this vol., 163), but with a change in the temp. of spontaneous combustion for const. time lag. L. S. T.

**Kinetics of the reaction between hydrogen and sulphur. III.** (i) Reaction at 350—412° and 50—150 mm. (ii) Behaviour of sulphur on a hot glass surface. R. P. COOK and P. L. ROBINSON (J.C.S., 1936, 454—456).—(i) The kinetics of the reaction are the same as at the lower temp. previously investigated (A., 1935, 307), and the rise of temp. does not increase the heterogeneous reaction (cf. *ibid.*, 586).

(ii) At the reaction temp. employed (*loc. cit.*), liquid S does not "wet" glass in vac. or in an atm. of H<sub>2</sub>, and does not form a visible film on the internal surface of the reaction vessel (cf. J.C.S., 1923, 123, 696). J. G. A. G.

**Mechanism of decomposition of ethylene iodide.** R. A. OGG, jun. (J. Amer. Chem. Soc., 1936, 58, 607—609).—Theoretical. The kinetic results are explained by a chain mechanism. A similar conclusion is reached for the decomp. of di-iodopropyl alcohol and the photo-bromination of cinnamic acid. E. S. H.

**Kinetics of formation and decomposition of dicyclopentadiene.** B. S. KHAMBATA and A. WASSERMANN (Nature, 1936, 137, 496—497).—The reaction cyclopentadiene + cyclopentadiene  $\rightleftharpoons$  dicyclopentadiene is bimol. in the direct and unimol. in the reverse directions. No chain mechanism appears to be involved. Measurements of the direct reaction in C<sub>6</sub>H<sub>6</sub> between 15° and 55° and of the decomp. in paraffin between 135° and 175° show the Arrhenius equation to be valid. L. S. T.

**Relationships between reaction velocities and ionisation constants.** J. F. J. DIPPY and H. B. WATSON (J.C.S., 1936, 436—440; cf. A., 1935, 1465; this vol., 296).—It follows from accurate vals. of the dissociation consts.,  $K$ , of the acids of the reference series that the supposed linear relationships (*loc. cit.*) are approx. only. Electromeric effects cause divergences, and the connexion does not follow from known relationships of velocity coeffs. and  $K$  with dipole moment. The effects of variations in the non-exponential term of the Arrhenius equation are considered. J. G. A. G.

**Kinetic salt effect in fourth-order reaction BrO<sub>3</sub>' + Br' + 2H'  $\rightarrow$ .** M. SCLAR and L. C. RIESCH (J. Amer. Chem. Soc., 1936, 58, 667—670).—The rates of reaction in presence of allyl alcohol have been determined at different temp. and ionic strengths and compared with published data. The energy of activation has been calc. The results show that the fourth-order rate-determining reaction is reversible, so that the max. rate of reaction can be obtained



only when a primary reaction product is removed with sufficient rapidity to prevent a reversal of the reaction. Allyl alcohol and  $\text{H}_2\text{O}_2$  are equally efficient in removing a primary reaction product. E. S. H.

**Collision frequency in solution: kinetics of diene synthesis in solution and in the gaseous state.** A. WASSERMANN (Nature, 1936, 137, 497).—Comparison of the kinetics of various bimol. diene syntheses shows that with slow reactions in solution the collision frequency of mols. is  $\ll$  in the gas phase. L. S. T.

**Kinetics of a thermal polycondensation.** H. DOSTAL and R. RAFF (Z. physikal. Chem., 1936, B, 32, 117—129).—The rate of condensation of *p*-cresol with  $\text{CH}_2\text{O}$  in aq. solution at 100—130° has been determined. The energy of activation is about 20 kg.-cal. per mol. Equations for the kinetics of such reactions are deduced theoretically. R. C.

**Reactions between oxalic acid, iodine, and the iodate and iodide ions. III. Kinetics of oxalic acid-iodine reaction.** E. ABEL, K. HILFERDING, and O. SMETANA (Z. physikal. Chem., 1936, B, 32, 85—107; cf. A., 1935, 587).—Determination of the rate,  $v$ , of  $5\text{H}_2\text{C}_2\text{O}_4 + 2\text{HIO}_3 = \text{I}_2 + 10\text{CO}_2 + 6\text{H}_2\text{O}$  at 25—60° has given results agreeing with the mechanism previously suggested (A., 1931, 690). Depending on the concns.,  $v$  varies between two limits, given by  $v \propto \sqrt{[\text{IO}_3^-][\text{I}_2][\text{H}^+]^2}$  and  $v \propto \sqrt{([\text{IO}_3^-][\text{I}_2]^2\Sigma^2)}$  (where  $\Sigma = [\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-]$ ), which is in accordance with the above mechanism if it is assumed that for the intermediate products  $\text{I}'$  and  $\text{HIO}$  the stationary and equilibrium concns. are practically equal. The inhibiting action of  $\text{HCN}$  is due solely to its reaction with the inductor,  $\text{I}_2$ . The velocities of  $\text{IO}_3' + 2\text{H}' + \text{I}' = \text{HIO}_2 + \text{HIO}$  and  $\text{IO}_3' + 2\text{H}' + 2\text{I}' = 2\text{HIO} + \text{IO}'$  at 50° have been determined. R. C.

**Kinetics of a bimolecular association in benzene solution and in the gaseous state.** A. WASSERMANN (Nature, 1936, 137, 707—708).—The reaction between acetaldehyde and cyclopentadiene in  $\text{C}_6\text{H}_6$ , as in the gaseous state (this vol., 297), is a homogeneous bimol. association. The collision frequency in the gaseous phase is of the same order as the "apparent" collision frequency in solution. L. S. T.

**Progressive elimination of bromine in the aqueous hydrolysis of sodium bromoacetate.** H. BROOKE and H. M. DAWSON (J.C.S., 1936, 497—504; cf. A., 1933, 1125).—From measurements of the initial velocity of formation of  $\text{Br}'$  in mixtures of  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$  (I) and  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (II), it is inferred that the hydrolysis  $(\text{I}) + \text{H}_2\text{O} \rightarrow (\text{II}) + \text{NaBr}$  is due to six independent bimol. processes in which  $\text{CH}_2\text{Br}\cdot\text{CO}_2'$  (III) or  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$  reacts with  $\text{H}_2\text{O}$  or (III) or glycollate ion. Intermediate complexes also affect the rate of the hydrolysis, but the data from the above experiments, which, apart from the absence of complexes, correspond with successive stages of the reaction, are quantitatively explained in terms of the six simple reactions. The complexity of the hydrolytic process is emphasised and the approx. conformity to a unimol. formula is accidental. J. G. A. G.

**Sucrose inversion in  $\text{D}_2\text{O}$ - $\text{H}_2\text{O}$ .** W. H. HAMILL and V. K. LAMER (J. Chem. Physics, 1936, 4, 294).—

$k$  in  $\text{D}_2\text{O}$ - $\text{H}_2\text{O}$  mixtures is a linear function of  $F_{\text{H}^+} = [\text{D}^+]/([\text{D}^+] + [\text{H}^+])$ . L. J. J.

**Rate of dissolution of copper in dilute aqueous reagents.** C. V. KING and L. WEIDENHAMMER (J. Amer. Chem. Soc., 1936, 58, 602—607).—Determinations of temp. coeff., influence of rate of rotation of Cu, and variation with viscosity (by adding sucrose) show that the rate of dissolution in  $\text{Fe}^{III}$  solutions is controlled mainly by diffusion, but that in  $\text{AcOH}$  solutions mainly by chemical reaction. E. S. H.

**Causes of anomaly in the kinetics of the oxidation of metallic powders.** G. VALENSI (Compt. rend., 1936, 202, 414—416; cf. this vol., 434).—Irregularities in the surfaces of the particles, porosity of the particles, and unevenness of grain size all lead to anomalies in the velocity of oxidation of metallic powders, points of low radius of curvature being most easily attacked, whilst depressions and porous regions become filled with the more voluminous oxide and protected against further attack. J. W. S.

**Atmospheric rusting of iron.**—See B., 1936, 411.

**Catalysis by fusions.** E. W. R. STREACIE and E. M. ELKIN (J. Amer. Chem. Soc., 1936, 58, 691—692).—A reply to criticism (cf. this vol., 167).

E. S. H.

**Action of esterase in presence of organic solvents.**—See this vol., 637.

**Catalysts for the autoxidation of saturated cyclic hydrocarbons.** R. DUPONT (Bull. Soc. chim. Belg., 1936, 45, 113—122).—The catalytic action of the acetylacetonates of  $\text{Fe}^{III}$ ,  $\text{Cu}^{II}$ ,  $\text{Ce}^{III}$ ,  $\text{Mn}^{III}$ ,  $\text{Co}^{II}$ , and  $\text{Co}^{III}$  on the absorption of  $\text{O}_2$  by 1:4-dimethylcyclohexane (I) and phenylcyclopentane (II) has been examined. Two types of reaction curves have been observed, one autocatalytic, always found for (II) and also for (I) when the catalyst concn. is  $< 1\%$ , and the other catalytic and characteristic of (I) for a catalyst concn.  $> 1\%$ . M. S. B.

**Delayed oxidation of cysteine and ascorbic acid.** E. BAUR and H. PREIS (Z. physikal. Chem., 1936, B, 32, 65—83).—The oxidation by gaseous  $\text{O}_2$  of cysteine (I) in aq. solution of  $p_{\text{H}}$  7.6 with Cu as catalyst is retarded by low concns. of  $\text{Fe}^{III}$  and  $\text{Mn}^{II}$  and accelerated by higher concns., whilst salts of some other metals cause retardation only. In most cases the retardation is related to the inhibitor concn.,  $c$ , by the Baur-Ouellet law, whilst in the others it  $\propto c$ . Some cations have only an accelerating effect. Anions, org. substances, and some cations have no effect. In the oxidation of ascorbic acid in aq. solution at  $p_{\text{H}}$  5.3 with Cu as catalyst, (I), cystine, and phenylalanine at high dilution cause retardation, whilst other oxidation-reduction systems have no effect. Heavy-metal salts have an indefinite or no effect, and  $\text{CN}'$  and  $\text{I}'$  bind the catalyst. There is no connexion between the oxidation-reduction potential of the foreign substance and its inhibiting action. The results generally support Baur's mol. electrolysis theory. R. C.

**Preparation of platinum oxide for catalytic hydrogenations.** W. F. BRUCE (J. Amer. Chem. Soc., 1936, 58, 687—688).—The catalyst is prepared



by heating gradually a mixture of  $(\text{NH}_4)_2\text{PtCl}_6$  and  $\text{NaNO}_3$ , and keeping at  $500^\circ$  for 25–30 min.

E. S. H.

**Reactions in thin films.** A. I. ZOLIN (J. Phys. Chem. U.S.S.R., 1934, 5, 1299–1309).—The hydrogenation of  $\text{C}_2\text{H}_4$  with a colloidal Pd catalyst in presence of saponin occurs in the liquid phase in the walls of the colloidal foam bubbles. The presence of foam, due to the saponin, increases the rate 10 times at room temp.  $\text{H}_2$  tends to collect in the upper layers of the foam, due to more rapid diffusion.

CH. ABS. (e)

**Effect of promoters on molybdenum catalysts in hydrogenation.** F. E. T. KINGMAN and E. K. RIDEAL (Nature, 1936, 137, 529).—P, Ni, Cr, and Si markedly enhance, whilst Sn and Th depress, the catalytic activity of Mo oxide for the hydrogenation of PhOH at 1 atm.

L. S. T.

**Oxidation of alkali halides by molecular oxygen in presence of mercury and active charcoal.** V. A. PIANKOV (J. Gen. Chem. Russ., 1935, 5, 1543–1550).—The process  $4\text{MX} + \text{O}_2 + 2\text{H}_2\text{O} + 2\text{Hg} \rightarrow 2\text{HgX}_2 + 4\text{MOH}$  takes place when air is bubbled through a solution of alkali halide in presence of Hg; the velocity of the reaction rises in the series  $\text{Cl} < \text{Br} < \text{I}$ . The reaction is catalysed by active C, in presence of which max. velocity is attained at  $50^\circ$ . R. T.

**Promoter concentration and catalysis.** R. H. GRIFFITH (Nature, 1936, 137, 538).—For the decomp. of  $\text{C}_6\text{H}_{14}$  at  $500^\circ$  by Mo oxide catalysts the ratio of the no. of atoms of Na, Cr, Ce, Al, Ba, B, and Th (as oxides) to the no. of atoms of Mo necessary for max. promoter action is the same as that observed with Si (B., 1935, 292). With easily reducible oxides, e.g., those of Pb, Fe, or Cu, the promoter concn. required is one half. For the conversion of PhOH into  $\text{C}_6\text{H}_6$  by hydrogenation at  $450^\circ/1$  atm. with Mo oxide as catalyst the optimum concn. is  $>$  in the above reaction, but is practically the same for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

L. S. T.

**[Catalytic] synthesis of higher alcohols under pressure.**—See B., 1936, 404.

**Carbon oxysulphide.** J. MILBAUER (Z. Elektrochem., 1936, 42, 226–227).—The effect of 32 metallic catalysts on the decomp. of COS by  $\text{H}_2\text{SO}_4$  at temp. up to  $250^\circ$  has been studied by measurement of the rate of formation of  $\text{SO}_2$ . Spongy Pd, Se, and Pt have the greatest effect, whilst the alkali metals and alkaline earths show a slight anticatalytic effect.

C. R. H.

**Active oxides. LXXXXV. Influence of various gases on the reaction between zinc oxide and chromium trioxide.** G. F. HÜTTIG, S. CASSIRER, and E. STROTZER (Z. Elektrochem., 1936, 42, 215–222).—The hygroscopicity and magnetic susceptibility of equimol. mixtures of  $\text{ZnO}$  and  $\text{Cr}_2\text{O}_3$ , which have been heated at various temp. up to  $500^\circ$  in vac., have been measured. With rise of temp., surface activity, as indicated by hygroscopic data, gives place to a period of inactivity which in turn is followed by activity due to internal diffusion. Finally, at about  $400^\circ$ , the activity is again reduced, which, with a rapid increase in the magnetic property, indicates the form-

ation of cryst.  $\text{ZnCr}_2\text{O}_4$ . The influence of A,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , MeOH,  $\text{N}_2\text{O}$ , and air on the reaction has likewise been investigated.

C. R. H.

**Tin vanadate as a catalyst in the oxidation of toluene to benzoic acid.** R. HUITEMA and G. W. BROWN (J. Physical Chem., 1936, 40, 531–542).—The catalytic effect of Sn vanadate in the oxidation of PhMe to BzOH is affected by the extent to which it may have been previously heated. In the oxidation reaction, temp. and  $[\text{O}_2]$  affect the ratio  $\text{CO}_2 : \text{BzOH}$ , but diluents, e.g.,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , appear to have no effect. Anthraquinone and PhCHO are by-products.

M. S. B.

**Hydrogenation of carbonyl compounds by Raney nickel covered by metals of the platinum family. Influence of alkalis.** M. DELÉPINE and A. HOREAU (Compt. rend., 1936, 202, 995–998; cf. this vol., 457).—The speed of hydrogenation ( $v$ ) of COMeEt at room temp. and atm. pressure in presence of Ni is increased by depositing Pt group metals on the Ni. The efficiency of the added metals increases in the order Pd; Ru and Rh; Os, Ir, and Pt. Cu is without action, and Au has a small influence only. The addition of  $\text{Na}_2\text{CO}_3$  solution increases  $v$ . Similar detailed results have been obtained with  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ , and the following hydrogenations have been effected on Pt+Ni:  $\beta$ -cholestanone  $\rightarrow$  mainly dihydroepicholesterol, furfuraldehyde  $\rightarrow$  furyl alcohol,  $d$ - and  $r$ -pinonic acids  $\rightarrow$  the corresponding alcoholic acids,  $d$ -,  $l$ -, and  $r$ -hydroxyketopinanes  $\rightarrow$  dihydroxypinanes, and  $d$ -camphor  $\rightarrow$  mainly  $l$ -isoborneol. With Ni and Ir  $v$  for COMeEt is approx. const. above a small % of Ir, Pt, Ir, and Rh alloy with a small quantity of Ni, which remains with the Pt etc. after dissolving the catalyst in dil. HCl.

R. S. B.

**Amorphous and crystalline oxide hydrate and oxides. XXV. Formation of ozone and hydrogen peroxide from metallic peroxide compounds formed by the oxidation of metallic salts and metallic oxides with potassium persulphate.** A. KRAUSE and G. SZMIDT (Ber., 1936, 69, [B], 805–811).—Co,  $\text{Ti}^{\text{IV}}$ , and  $\text{Zr}^{\text{IV}}$  resemble  $\text{Fe}^{\text{III}}$  in their ability to form  $\text{O}_3$  and perheteropolyacids in the system  $\text{K}_2\text{S}_2\text{O}_8\text{--H}_2\text{SO}_4$ . The apparent inability of other elements (e.g., Ce, Cr, and U) to form similar acids may be due to their very marked catalytic ability to decompose  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ . An unexpectedly great " $\text{O}_3$  effect" is observed during the oxidation of Ag ferrite with  $\text{K}_2\text{S}_2\text{O}_8$  in  $0.3N\text{--H}_2\text{SO}_4$ . Simple Ag compounds ( $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{SO}_4$ ) also yield much  $\text{H}_2\text{O}_2$ , probably due to catalytic action associated with the formation of  $\text{Ag}_2\text{O}_2$ , its decomp., and re-formation. Under otherwise similar conditions metallic Ag gives solely  $\text{O}_3$ . Catalytic influences which accelerate the decomp. of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are also observed in the systems.

H. W.

**Preparation of manganese catalysts for recovery of sulphur from hydrogen sulphide.**—See B., 1936, 452.

**Determination of the activity of contact catalysts for the sulphuric acid industry.**—See B., 1936, 406.



**Electrolytic oxidation and reduction of calcium cyanamide.** G. CALCAGNI and G. LAZZARI (*Annali Chim. Appl.*, 1936, 26, 43—49).— $\text{CaCN}_2$ , digested for approx. 12 days in 20%  $\text{H}_2\text{SO}_4$  and then electrolysed (3 hr. at 5 amp. and 14 volts), yields  $\text{NH}_3$  (up to 6.7% of the total N) at the cathode and  $\text{HNO}_2$  (with some  $\text{HNO}_3$ ) at the anode. F. O. H.

**Electrolysis of sodium nitrate in liquid ammonia.** E. I. ACHUMOV, N. A. GÖNTSCHAROV, and E. A. EZEROVA (*J. Gen. Chem. Russ.*, 1935, 5, 1744—1753).—V.p. data are recorded for saturated solutions of  $\text{NaNO}_3$  in liquid  $\text{NH}_3$  at 0—30°, and conductivity data at -16° to 30°. During electrolysis the anode process is:  $6\text{NH}_3' \rightarrow 4\text{NH}_3 + \text{N}_2$ ;  $\text{NH}_4' + \text{NO}_3' \rightleftharpoons \text{NH}_4\text{NO}_3$ ;  $\text{NH}_4\text{NO}_3 + \text{NaNH}_2 \rightarrow \text{NaNO}_3 + 2\text{NH}_3$ , and the cathode process  $\text{Na} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{H}$ ;  $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}$ ;  $\text{NaNH}_2 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{NH}_3$ . The process as a whole is represented by  $6\text{NaNO}_3 + 14\text{NH}_3 \rightarrow 6\text{NH}_4\text{NO}_3 + 6\text{NaNH}_2 + 3\text{H}_2 + \text{N}_2$ . R. T.

**Electrolytic reductions of organic compounds at alloy cathodes. I. Reduction of aliphatic ketones to hydrocarbons at cadmium amalgams.** S. SWANN, jun., H. J. READ, and F. C. HOWARD (*Trans. Electrochem. Soc.*, 1936, 69, Preprint 24).—The electrolytic reduction of  $\text{COMePr}^a$  to  $n\text{-C}_5\text{H}_{12}$  has been studied at Cd-Hg cathodes containing 0—100% of Cd. When the yield is plotted against the composition of the amalgam, inflexions are obtained at points that correspond with phase changes in the amalgam. E. S. H.

**Transformation of a thin layer of copper sulphide under the influence of metallic copper is of an electrolytic nature.** H. DEVAUX (*Compt. rend.*, 1926, 202, 368—370; cf. this vol., 435).—When two strips of Cu foil are floated on aq.  $\text{CuSO}_4$  and a film of  $\text{CuS}$  is formed between them, the development of a blue colour on the  $\text{CuS}$  begins at each foil and spreads from them with equal velocity. However, if a p.d. is applied between the foils it accelerates on the side of the negative electrode and becomes slower on the positive side. The colour change is attributed to deposition of Cu on the conducting  $\text{CuS}$  film. J. W. S.

**Mechanism of the electrolytic polishing of copper.** P. JACQUET (*Compt. rend.*, 1936, 202, 402—404; cf. this vol., 305, 571).—Factors favouring the diffusion of the products of attack (agitation, decreased acid concn., rise of temp.) raise the min. c.d. necessary for electrolytic polishing. During electrolysis a liquid zone is produced in contact with the anode of a thickness which is diminished by these factors and is of high resistance. This layer, being deeper in contact with grooves than opposite ridges, causes the latter to be first attacked. When  $\text{HPO}_3$  is used as electrolyte this layer is first formed, but, contrary to the behaviour with  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{P}_2\text{O}_7$ , it later forms a solid crust. J. W. S.

**Anodic behaviour of organic salts of copper.** G. KRAVTSOV (*Compt. rend.*, 1936, 202, 1036—1038).—In the electrolysis of  $\text{CuSO}_4$ ,  $\text{Cu}(\text{HCO}_2)_2$ ,  $\text{Cu}(\text{OAc})_2$ , and  $\text{Cu}(\text{EtCO}_2)_2$  with Cu anodes the ratio  $R$  of the apparent loss of wt. of anode to the wt. of Cu deposited in a voltameter = 1 or < 1 corresponding

with apparent valencies of 2 or 1—2. In the latter case  $\text{Cu}_2\text{O}$  is deposited on the anode by hydrolysis of  $\text{Cu}^+$  salts. Increase in c.d., and increase in dilution (except with salts of  $\text{HCO}_2\text{H}$  and  $\text{EtCO}_2\text{H}$ ) reduces the formation of  $\text{Cu}^+$  salts. The time of electrolysis influences  $R$  considerably with many solutions, owing partly to the influence of  $\text{Cu}^{++}$  dissolved from the anode. The reactions  $\text{Cu} \rightarrow \text{Cu}^{++}$ ,  $\text{Cu} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}_2\text{O}$  occur, and are confirmed by a study of p.d.—time curves. R. S. B.

**Simultaneous electrodeposition of thallium and zinc.** W. G. PARKS and I. M. LE BARON (*Trans. Electrochem. Soc.*, 1936, 69, Preprint 14, 171—182).—The electrolyte contains  $\text{TlClO}_4$  and  $\text{Zn}(\text{NO}_3)_2$  and is operated at c.d. 0.2—0.9 amp. per sq. dm. Unless the Tl content of the deposit is low oxidation is rapid. No serviceable plates were obtained. Only the eutectic cast and deposited alloys have similar structures. From cathodic potential measurements the composition of the deposit obtained at a given c.d. can be predicted. J. W. C.

**Electrolytic production of boron and its alloys.**—See B., 1936, 414.

**Alkaline plating baths containing ethanolamines. II. Nickel. III. Cobalt.**—See B., 1936, 458.

**Influence of composition of electrolyte in the electrolysis of carnallite.**—See B., 1936, 458.

**Electroplated gold.**—See B., 1936, 458.

**Synthesis of ammonia by cathodic sputtering of lead.** P. JOLIBOIS and F. OLMER (*Compt. rend.*, 1936, 202, 1268—1269; cf. A., 1935, 1087).—The yield of  $\text{NH}_3$  per watt dissipated increases with the pressure of the  $\text{N}_2\text{-H}_2$  mixture. Prolonged cathodic action produces an equilibrium concn. of  $\text{NH}_3$  corresponding closely with the thermodynamic val. at room temp. L. J. J.

**Formation of hydrogen peroxide in the electrodeless discharge in water vapour.** R. W. CAMPBELL and W. H. RODEBUSH (*J. Chem. Physics*, 1936, 4, 293).—When the dissociated  $\text{H}_2\text{O}$  vapour is passed through a liquid-air trap, formation of  $\text{H}_2\text{O}_2$  takes place exclusively in the latter. L. J. J.

**Constitution of mixed organo-magnesium compounds.**—See this vol., 743.

**Photochemical sensitivity of mercuric nitrate.** S. SCHLIVITCH and D. NIKOLITCH (*Bull. Soc. Chim. Yougoslav.*, 1935, 6, 159—163).—The e.m.f. set up in a photogalvanic cell by illumination ( $\lambda > 4600 \text{ \AA}$ ) of aq.  $\text{Hg}(\text{NO}_3)_2$  is increased in presence of  $\text{EtOH}$  or glycerol. R. T.

**Photolysis of nitrates (spectrophotometric determination of potassium nitrate; catalytic action of manganous salts).** H. VOGELS (*Bull. Acad. roy. Belg.*, 1936, [v], 22, 320—333; cf. A., 1912, ii, 862).—The photochemical reduction of  $\text{KNO}_3$  to  $\text{KNO}_2$  in aq. solutions of varying  $p_H$  has been studied, using the absorption at 3650  $\text{\AA}$ . as a measure of  $[\text{KNO}_2]$ . The  $p_H$  falls during the reaction, which does not lead to the establishment of the simple equilibrium  $2\text{KNO}_3 \rightleftharpoons 2\text{KNO}_2 + \text{O}_2$ . The mechanism is discussed. The velocity increases considerably



with change of  $p_H$  from 7 to 10, but is little affected by further rise in  $p_H$ . The reaction is accelerated by  $Mn^{II}$  salts and by tartrates. The effect with the former is not immediate, suggesting that the true catalyst is Mn in a higher state of oxidation.

D. R. D.

**Photographic photometry in the extreme ultra-violet.** (MME.) R. MONTAGNE and R. RICARD (Compt. rend., 1936, 202, 477—479).—The factors of contrast for const. times of exposure and const. illumination respectively are const. within 10% over the range  $\lambda$  2000—1250 Å. for plates sensitised with Na salicylate.

F. L. U.

**New process of development. Photo-electrochemical process.** K. M. KOSONOGOVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 167—168).—A polished Cu electrode, covered with  $Cu_2I_2$  by dipping in I in EtOH, is placed in  $Pb(NO_3)_2$  solution and polarised at a potential about 0.3 volt < the normal electrode potential. At the illuminated parts, the electrode is covered with a greenish deposit. This can be strengthened by colouring with dyes, e.g., rhodamine-B.

A. J. M.

**Photochemical formation of ethylene iodide in solutions of carbon tetrachloride.** R. E. DE-RIGHT and E. O. WIGG (J. Amer. Chem. Soc., 1936, 58, 693).— $C_2H_4I_2$  is formed when solutions of  $C_2H_4$  and I in  $CCl_4$  are exposed to red light. The rate of reaction depends on the pressure of  $C_2H_4$  and decreases with decreasing [I]. No measurable dark reaction occurs. The mechanism is discussed.

E. S. H.

**Photolysis of acetic acid.** M. BURTON (J. Amer. Chem. Soc., 1936, 58, 692).—Evidence for the formation of Me and at. H is given.

E. S. H.

**Photobromination of acetylene dichloride in the gaseous state and in carbon tetrachloride solution.** J. C. GHOSH, S. K. BHATTACHARYA, and S. C. BHATTACHARYA (Z. physikal. Chem., 1936, B, 32, 145—157).—The rate of reaction at 30° and 40° in light of  $\lambda$  546, 436, and 406 m $\mu$  has been determined. In both reactions the unimol. velocity coeff. in respect of  $[Br_2]$ ,  $k$ ,  $\propto$  the square root of the energy absorbed, the temp. coeff. is 1.4, and the graph of  $1/k$  against  $1/\text{mean } [C_2H_2Cl_2]$  is rectilinear. Reaction in the gaseous state is about 30 times as rapid as in solution. These results agree with the mechanism previously suggested (A., 1930, 1260). The concn. of Br atoms in the stationary state and the velocity coeff. and activation energy of  $Br + Br_2 \rightarrow Br_3$  have been calc.; apparently there is a steric factor of  $\sim 10^{-2}$ . Quantum yields have been determined.

R. C.

**Addition of bromine and iodine to compounds with an ethylene linking. Photobromination of ethyl *m*-nitrobenzylidenemalonate, bromination of fumaric and maleic acids, addition of iodine to allyl alcohol.** A. BERTHOUD and M. MOSSET (J. Chim. phys., 1936, 33, 272—305).—The photobromination of Et *m*-nitrobenzylidenemalonate in  $CCl_4$  is similar to that of cinnamic acid or stilbene (A., 1927, 528). The bromination of maleic (I) and fumaric (II) acids is not influenced by light and is more rapid for the ions than for the undissociated

mols.  $Br_2$  reacts more rapidly than  $Br_3$  on (I), but the opposite is the case for (II). The addition of I to allyl alcohol in  $H_2O$  is also uninfluenced by light, but the action is reversible. In  $CCl_4$  solution, however, there is a light reaction similar to photobromination. In the dark a reaction appears to take place mainly through the agency of  $HI_2$ . HI acts as an accelerator.

M. S. B.

**Photo-oxidation of succinic acid by methylene-blue sensitised by uranyl salts.** J. C. GHOSH, T. BANERJEE, and B. BHATTA (Z. physikal. Chem., 1936, B, 32, 163—167).—In light of  $\lambda$  366 m $\mu$  the reaction is, after an initial period of induction, of zero order in respect of methylene-blue. The velocity coeff.,  $k$ ,  $\propto$  the intensity of incident radiation but is independent of the  $p_H$ , and the graph of  $1/k$  against  $1/\text{succinic acid (I) concn.}$  is rectilinear. Only half the collisions between the excited  $UO_2^{++}$  ion and the (I) mol. are effective.

R. C.

**Photochemical oxidation of mandelic acid by bromine with uranyl salts as ultra-violet sensitisers.** J. C. GHOSH and B. B. ROY (Z. physikal. Chem., 1936, B, 32, 158—162).—Below 313 m $\mu$  this is purely a sensitised reaction and unimol. in respect of  $Br_2$ . The velocity coeff.,  $k$ ,  $\propto$  the square root of the incident energy and  $\propto$  the square root of the energy absorbed by the  $UO_2SO_4$  and a graph of  $1/k$  against  $1/\text{mandelic acid concn.}$  is rectilinear. The quantum yield is large. These results are accounted for by assuming that each quantum absorbed by the  $UO_2^{++}$  ion resolves a  $Br_2$  mol. into atoms which then set up chains of the type previously suggested (A., 1930, 1260).

R. C.

**Radiochemical synthesis and decomposition of hydrogen bromide.** S. C. LIND and R. LIVINGSTON (J. Amer. Chem. Soc., 1936, 58, 612—617).—The reaction rate under the influence of Rn has been determined at 25° by measuring the pressure of  $H_2$  when the reaction vessel was immersed in liquid  $O_2$ . A theory of reaction, which is consistent with the data, has been developed, and a relation between the ion pair yield and the initial pressures deduced.

E. S. H.

**Action of  $\alpha$ -particles on mixtures of nitrogen and oxygen.** R. CLOETENS (Bull. Soc. chim. Belg., 1936, 45, 97—112).—Measurements of the changes with time of the pressure  $p$  of  $Rn-O_2-N_2$  mixtures indicate that an initial diminution of  $p$  takes place at a rate which is a function of the concn. of the constituents of the mixture. A rapid increase in  $p$  follows and then a final slow decrease. The results are discussed on the basis of ionic yields calc. on the assumption of gaseous reactions of the type  $A+B \rightarrow AB$ .

M. S. B.

**Preparation of distilled water in a vacuum.** J. THOMANN and A. KÄLIN (Pharm. Acta Helv., 1935, 10, 96—101; Chem. Zentr., 1935, ii, 1212).— $H_2O$  distilled in vac. is not necessarily sterile, whereas  $H_2O$  distilled at 100° is sterile.

H. N. R.

**Reaction of formaldehyde with hydrogen peroxide in heavy water. Non-exchangeability of hydrogen atoms of formaldehyde.** K. WIRTZ and K. F. BONHOEFFER (Z. physikal. Chem., 1936,



**B, 32, 108—112).**—In the reaction of  $\text{CH}_2\text{O}$  with  $\text{H}_2\text{O}_2$  in  $\text{D}_2\text{O}$  solution there is evolved no D but only H, which therefore originates entirely in the  $\text{CH}_2\text{O}$ . This result supports Wieland and Winger's mechanism of the reaction (A., 1923, i, 850). None of the H atoms of  $\text{CH}_2\text{O}$  is exchangeable for D in  $\text{D}_2\text{O}$ .

R. C.

**Effect of heavy water on the colour of hydrated salts.** J. BELL (Nature, 1936, 137, 534).—Solutions of  $\text{CuSO}_4$  in 99.5%  $\text{D}_2\text{O}$  are less intensely coloured than solutions of equal concn. in  $\text{H}_2\text{O}$ . Solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$  are readily distinguishable by the difference in tint.

L. S. T.

**Bis-8-hydroxyquinoline inner complex salt of bivalent silver.**—See this vol., 613.

**Fluoberyllates and their analogy with sulphates. IV. Double salts of rubidium and caesium fluoberyllates. V. Double salts of thallous fluoberyllate.** N. RÂY (Z. anorg. Chem., 1936, 227, 32—36, 103—106; cf. A., 1932, 706).—IV. The following salts are described:  $\text{M}^I\text{BeF}_4 \cdot \text{M}^{II}\text{BeF}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{M}^I = \text{Rb}$ ,  $\text{M}^{II} = \text{Co}$ ,  $\text{Zn}$ ,  $\text{Cu}$ ,  $\text{Cd}$ ,  $\text{Fe}^{II}$ );  $\text{Cs}_2\text{BeF}_4 \cdot \text{NiBeF}_4 \cdot 6\text{H}_2\text{O}$ .

V. The salts  $\text{Tl}_2\text{BeF}_4 \cdot \text{M}^{II}\text{BeF}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{M}^{II} = \text{Ni}$ ,  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ) are described. The properties of all of the above are similar to those of the corresponding sulphates, and the mol. vols. are of the same order of magnitude.

F. L. U.

**Basic magnesium sulphatocarbonate.** (MME.) L. WALTER-LÉVY (Compt. rend., 1936, 202, 1074—1076).—Aq.  $\text{KHCO}_3$  was added to aq.  $\text{MgSO}_4$  at  $70^\circ$  and boiled, and the ppt. obtained up to 2 hr. examined by X-rays and chemical analysis.  $4\text{MgO} \cdot 2\text{CO}_2 \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$  is deposited with  $\text{MgSO}_4$  2—5 mols. per litre.

R. S. B.

**Magnesium cyanamide.** A. PERRET and R. PERROT (Compt. rend., 1936, 202, 420—422).— $\text{Mg}(\text{CN})_2$  changes slowly at  $300^\circ$  and rapidly above  $600^\circ$ , yielding  $\text{MgCN}_2$ , which is also obtained on heating  $\text{Mg}_2\text{Fe}(\text{CN})_6$ .  $\text{Mg}[\text{N}(\text{CN})_2]_2$ , when heated above  $500^\circ$ , also yields  $\text{MgCN}_2$ , which decomposes into its elements at about  $750^\circ$ .  $\text{MgCl}_2$  reacts with  $\text{NaCN}$  at  $400^\circ$  in presence of reduced Fe, and at  $500^\circ$  is absence of catalyst, yielding  $\text{MgCN}_2$ . The relative instability of  $\text{MgCN}_2$  compared with alkaline-earth cyanamides is attributed to the weakness of the  $\text{Mg-N}$  linking and the volatility of Mg.

J. W. S.

**Marginal effect in the dissolution of magnesium in aqueous organic acids.** J. V. DURDIN and A. M. MARKEVITSCH (J. Gen. Chem. Russ., 1935, 5, 1690—1695).—When a Mg plate with part of its surface protected with paraffin wax is immersed in aq. org. acids, the most intense corrosion is observed around the margin of the protected area; this effect is not observed in presence of  $\text{EtOH}$ , or using mineral acids. The effect is ascribed initially to adsorption of acid at the paraffin wax-metal-solution boundary, and in the latter stages to more intense stirring of the solution by  $\text{H}_2$  bubbles in the cavity formed below the margin of the wax.

R. T.

**Decrease of a calcite crystal in an active isotropic medium; corrosion figures in dolomite.** L. ROYER (Compt. rend., 1936, 202, 429—431).

—The action of *d*- and *l*-tartaric, *l*-malic, and *l*-aspartic acids on the  $a^1$  (111) face of calcite or dolomite yields equilateral triangular planes, as with inactive acids, but on the  $b^1$  (110) and  $c^2$  (211) faces of calcite the active acids yield asymetric corrosion planes, whilst with inactive acids they are symmetrical.

J. W. S.

**Conversion of strontium sulphate into carbonate.** G. GALLO (Annali Chim. Appl., 1936, 26, 109—115).—The most favourable conditions for the conversion of pptd.  $\text{SrSO}_4$  (I) and celestine (II) into  $\text{SrCO}_3$ , by means of  $(\text{NH}_4)_2\text{CO}_3$  solution, are: (1) < 5 parts  $\text{H}_2\text{O}$  to 1 part (I) or (II); (2) temp.  $40$ — $50^\circ$ ; (3) > 25%  $(\text{NH}_4)_2\text{SO}_4$  in solution for (I) and > 15% for (II); (4) slightly increased pressure; (5) amount of  $(\text{NH}_4)_2\text{CO}_3$ , just above theoretical. (I) is more easily convertible than (II). Yields were 98.5% and 96.39%, respectively.

L. A. O'N.

**Barium osmichloride.** F. PUCHE (Compt. rend., 1936, 202, 1285—1286).— $\text{BaOsCl}_6$ , prepared by the action of  $\text{Cl}_2$  on Os and  $\text{BaCl}_2$  at  $350^\circ$ , forms orange crystals sol. in  $\text{H}_2\text{O}$  and  $\text{EtOH}$ , dissociating reversibly above  $430^\circ$ . Data are recorded for equilibrium dissociation pressures of  $\text{Cl}_2$  at  $719$ — $947^\circ$  abs.

L. J. J.

**Method of dissolving pitchblende for the preparation of radium standards.** V. H. MATULA (Coll. Czech. Chem. Comm., 1936, 8, 178—184).—The pitchblende (I) is fused with  $\text{Na}_2\text{CO}_3$  in a Pt crucible, the melt dissolved in  $\text{HCl}$ , and the  $\text{SiO}_2$  separated. This is decomposed by  $\text{HF}$  and any residue dissolved in  $\text{HNO}_3$ . The method is applicable to all (I) and is superior to the acid decomp. The Boltwood coeff. applies in the case of old, unweathered, (I).

R. S.

**Exothermic transformations of aluminium oxide.** D. AYDALIAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 173—175).—When  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  is dehydrated there is a distortion of the lattice, but no exothermic effect could be observed with the  $\text{Al}_2\text{O}_3$  produced. Hence the effect is probably not concerned with distortion of the lattice, contrary to Parravano (A., 1928, 1190).  $\text{Al}_2\text{O}_3$  obtained by pptg. an aq. solution of  $\text{Al}(\text{NO}_3)_3$  with aq.  $\text{NH}_3$ , and by dehydrating  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  are identical, and give an exothermic arrest at  $850^\circ$ , as does  $\text{Al}_2\text{O}_3$  obtained by heating  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .

A. J. M.

**Separation of rare earths by chromatographic adsorption.** E. LANGE and K. NAGEL (Z. Elektrochem., 1936, 42, 210).—Theoretical.

F. L. U.

**Graphite formation. II. Chemical nature of graphite and amorphous carbon.** A. E. BALFOUR, H. L. RILEY, and R. M. ROBINSON (J.C.S., 1936, 456—461).—Evidence for the chemical resemblance of graphite and the triarylmethyls is supported by the facts that the capacity of sugar charcoal to absorb  $\text{H}_2$  decreases with temp. above  $900^\circ$  whilst the wet-oxidation rate (this vol., 178) increases and the sp. electrical resistance decreases. The wet oxidation of C free from H is very rapid. The graphitisation of coke is increased with the rapidity of carbonisation.

F. R. G.

**Reaction of carbonyl chloride with hexamethylenetetramine.** N. A. PUSHIN and R. D. ZIVADI-



NOVIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 165—168).— $(\text{CH}_2)_6\text{N}_4$  and  $\text{COCl}_2$  in  $\text{CHCl}_3$  yield a 1:1 compound, m.p. 187—190°, decomposed by  $\text{H}_2\text{O}$  to yield  $\text{CH}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{CO}_2$ . R. T.

**Silica fluff.** C. A. JACOBSON (J. Physical Chem., 1936, 40, 413—418).—The product formed by drying slowly at room temp. hydrated  $\text{SiO}_2$  obtained by the action of  $\text{SiF}_4$  on  $\text{H}_2\text{O}$  has  $d$  1.018 and composition  $12\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . The material in its usual state of packing has an apparent  $d$  0.025 and can flow like a liquid through narrow tubes. Its chemical nature is discussed. F. L. U.

**Titanium. II. Decomposition of titanomagnetite concentrate with dilute sulphuric acid.** E. G. SCHTANDEL (J. Gen. Chem. Russ., 1935, 5, 1629—1633).—The rate of dissolution in aq.  $\text{H}_2\text{SO}_4$  of  $\text{Fe}_2\text{O}_3$  in titanomagnetite is  $>$  that of  $\text{TiO}_2$ . In both cases it rises rapidly with increasing  $[\text{H}_2\text{SO}_4]$  to 30%, and then continues to rise more slowly; it is greater at higher than at lower temp. R. T.

**Composition of titanium nitride.** E. A. OSTROUMOV (Z. anorg. Chem., 1936, 227, 37—42).—Ti nitrides, when heated in a stream of  $\text{Cl}_2$ , are completely converted into  $\text{TiCl}_4$  below 300°, at which temp. neither  $\text{TiO}_2$  nor lower oxides are perceptibly attacked. Examination of technical and laboratory Ti nitride preps. by this method showed a varying content of  $\text{TiO}_2$ . In two specimens the nitride fraction corresponded with  $\text{Ti}_5\text{N}_6$ , whilst the remainder appeared to contain a mixture of nitrides. F. L. U.

**Lead complexes of hydroxy-acids.**—See this vol., 706.

**Preparation of pure  $\text{N}_2\text{O}_4$ .** A. V. TOPTSCHIEV (J. Gen. Chem. Russ., 1935, 5, 1718—1722).— $\text{H}_2\text{SO}_4$  is added to saturated aq.  $\text{NaNO}_2$ , and sufficient  $\text{O}_2$  is mixed with the gases to convert  $\text{NO}$  into  $\text{NO}_2$ . No advantage is gained by using  $\text{V}_2\text{O}_5$  catalyst at 20—200°, and higher yields of  $\text{N}_2\text{O}_4$  are obtained at low than at high temp. R. T.

**Preparation and b.p. of phosphorus trichloride.** I. TEODOREANU (Bull. Acad. Sci. Roumaine, 1935, 17, 38—40).—An apparatus for the prep. of pure  $\text{PCl}_3$  is described. The b.p. is 75.5—76°/749—755.9 mm. R. S. B.

**Hydrolysis of phosphorus dichloronitrides and their amines.** A. M. DE FICQUELMONT (Compt. rend., 1936, 202, 423—425; cf. this vol., 566).—Treatment of an  $\text{Et}_2\text{O}$  solution of  $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$  (I) with  $\text{NaOAc}$  solution yields  $\text{P}_3\text{N}_2\text{O}_3\text{H}_4\text{Na}_3$  (II). The slowness of hydrolysis of (I) suggests a difference in its mechanism from the hydrolysis of the trimeric and tetrameric chlorohydrins, probably owing to the solidity of the linking of the  $\text{NH}_2$ -groups. This makes it improbable that  $\text{P}_4\text{N}_4\text{O}_8\text{H}_8$  is an intermediate product in the formation of (II).  $\text{P}_4\text{N}_4\text{O}_8\text{H}_8$  yields very little  $\text{P}_3\text{N}_2\text{O}_3\text{H}_7$  on hydrolysis. J. W. S.

**Double decomposition in solution of sodium niobates with metal salts.** P. SUE (Compt. rend., 1936, 202, 486—488; cf. A., 1935, 825).—Conductometric titration of various metal salts with  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$  (I) and  $7\text{Na}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5 \cdot 32\text{H}_2\text{O}$  (II) indicates the formation of corresponding niobates as

follows: with (I), Ca, Sr, Ba, Ag, Cu,  $\text{Hg}^{\text{I}}$ , Tl, Zn, Cd, Co, Ni, Mn, Pb; with (II), Ag, Tl, Mg, Ca, Sr, Ba. F. L. U.

**Etherates of iodobismuthous and iodoantimonious acids.** V. AUGER and (MLLE.) N. IVANOV (Compt. rend., 1936, 202, 484—486).—The following compounds are described:  $\text{HBI}_4 \cdot 16\text{H}_2\text{O} \cdot 10\text{Et}_2\text{O}$ ;  $\text{HSbI}_4 \cdot 5\text{H}_2\text{O}$  (yellow prisms);  $\text{HSbI}_4 \cdot 11\text{H}_2\text{O} \cdot 13\text{Et}_2\text{O}$ . F. L. U.

**Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their high-molecular compounds. XXXI. Hydrolysis and properties of bismuth perchlorate.** M. PRYTZ and P. NAGEL (Z. anorg. Chem., 1936, 227, 65—80; cf. A., 1935, 181, 703).—Conductometric, potentiometric, and thermometric titrations, and measurements of diffusion and of optical absorption, indicate that  $\text{Bi}(\text{ClO}_4)_3$  is stable only in presence of very conc.  $\text{HClO}_4$  when the solution is 0.1M with respect to Bi. With  $\text{HClO}_4$ :  $\text{BiO} \cdot \text{OH} = 6.5$  hydrolysis to  $\text{BiOH}(\text{ClO}_4)_2$  is complete. With decreasing  $[\text{HClO}_4]$  further hydrolysis to  $(\text{BiOH})_2\text{O}(\text{ClO}_4)_2$  occurs, accompanied by condensation which, at  $\text{HClO}_4$ :  $\text{BiO} \cdot \text{OH} < 2.5$ , yields  $(\text{BiOH})_4\text{O}_3(\text{ClO}_4)_2$ . The compounds  $\text{Bi}_2\text{O}_3(\text{OH})_3(\text{ClO}_4)_2$  and  $\text{Bi}_2\text{O}_3(\text{OH})\text{ClO}_4$  (bimol. in solution) have been prepared and analysed. Their solubility in  $\text{H}_2\text{O}$  is about 0.025 mol. per litre, in contrast to the readily sol.  $\text{BiOClO}_4$ . F. L. U.

**Hydrolysis of protoactinium and its reaction with sodium thiosulphate in acid solutions.** CHENG DA-CHANG and H. LI (J. Chinese Chem. Soc., 1936, 4, 93—97).—When acid solutions of active  $\text{TiO}_2$  are treated with  $\text{Na}_2\text{S}_2\text{O}_3$  in the presence of  $(\text{NH}_4)_2\text{MoO}_4$  or a Cu salt, some Pa is pptd. with the  $\text{MoS}_3$  or  $\text{CuS}$ . In slightly acid solutions hydrolysis occurs and Pa is pptd. with the Ti, little Pa being pptd. with the sulphide. C. R. H.

**Entrainment of protoactinium by titanium and a method of purification.** (MME.) EMMANUEL ZAVIZZIANO (Compt. rend., 1936, 202, 1052—1054).—In the chemical purification of ppt. of active Ti, Sn is only partly eliminated from a mixture of Ti, Sn, Bi, Pb, and Pa hydroxides by  $\text{NaOH}$ , but on treating the mixed hydroxides with yellow  $(\text{NH}_4)_2\text{S}$ , Ti and Pa remain as hydroxides, Sn forms a sol. polysulphide, and Bi and Pb form insol. sulphides. Treatment of the residue with dil.  $\text{HF}$  dissolves the hydroxides of Ti and Pa (with radioactive impurities). For radioactive purification, 1 c.c. of conc.  $\text{H}_2\text{SO}_4$  is added to the  $\text{HF}$  solution,  $\text{HF}$  is evaporated off, and  $\text{H}_2\text{O}$  and aq.  $\text{NH}_3$  are added. The hydroxides are then dissolved in  $\text{HCl}$  and a few drops of 1% nitrates of La, Bi, Th, Pb, and Ba are added. The whole is pptd. hot by aq.  $\text{NH}_3$ , and the ppt. is washed with 2%  $(\text{NH}_4)_2\text{SO}_4$  to remove all  $\text{NH}_3$ , since this gives with  $\text{HF}$  double fluorides of Pa and  $\text{NH}_4$  and of Ti and  $\text{NH}_4$  which are incompletely pptd. by  $\text{NH}_3$ . The hydroxides of Pa and Ta alone dissolve in  $\text{HF}$ . The whole is repeated 3 or 4 times. For the concn. of Pa, a few drops of  $\text{H}_2\text{O}_2$  are added to the dil. solution in  $\text{H}_2\text{SO}_4$ , which is then heated just to boiling. A part of the Ti is pptd. as  $\text{TiO}_2$ , and entrains a proportion of Pa which varies with the concn. of acid, the % of  $\text{H}_2\text{O}_2$ , and the temp. R. S. B.



**Thiosulphato-compounds.** I. H. BRINTZINGER and W. ECKARDT (Z. anorg. Chem., 1936, 227, 107—111).—Dialysis coeffs. of complex ions formed from salts of various heavy metals and  $\text{Na}_2\text{S}_2\text{O}_3$  have been measured at 18°. The calc. ionic wts. indicate the existence of the following ( $\text{S}_2\text{O}_3=\text{X}$ ):  $[\text{Ag}_2\text{X}_2]''$ ;  $[\text{Cu}_2\text{X}_2]''$ ;  $[\text{Ti}_2\text{X}_2]''$ ;  $[\text{M}^{\text{II}}\text{X}_3]'''$  ( $\text{M}^{\text{II}}=\text{Mn, Fe, Co, Ni, Zn, Cd}$ ). F. L. U.

**Molybdenum blues.** V. AUGER (Compt. rend., 1936, 202, 1180—1182).—The unstable Mo blue obtained by dissolution of  $\text{MoO}_3$  in conc.  $\text{H}_2\text{SO}_4$  can form stable blue complexes with alcohols,  $\text{C}_2\text{Me}_2$ , and  $\text{AcOH}$ . The stable complex with  $\text{AcOH}$  has been isolated and analysed. Its composition appears to be  $\text{Mo}_2\text{O}_5 \cdot 4\text{MoO}_3 \cdot \text{SO}_3 \cdot 4\text{AcOH} \cdot 4\text{H}_2\text{O}$ .  $\text{SO}_3$  is not in a form precipitable by  $\text{BaCl}_2$ . M. S. B.

**Polarimetric study of the formation of complex molybdosaccharates.** H. PARISELLE and F. CHIRVANI (Compt. rend., 1936, 202, 482—484; cf. A., 1934, 252, 992).—Polarimetric observations of K or  $\text{NH}_4$  molybdates with saccharic acid ( $\text{SaH}_2$ ) or  $\text{SaK}_2$  in aq. solution indicate the existence of the compounds  $3\text{SaH}_2 \cdot 7\text{MoO}_3 \cdot 3(\text{K}, \text{NH}_4)_2\text{O}$ ,  $M[\alpha] -70^\circ$ ; and  $3\text{SaH}(\text{K}, \text{NH}_4) \cdot 7\text{MoO}_3 \cdot 3(\text{K}, \text{NH}_4)_2\text{O}$ ,  $M[\alpha] +1050^\circ$ . F. L. U.

**Preparation of hydrofluoric acid.** A. BOOKHEM (J. Chem. Educ., 1936, 13, 93). L. S. T.

**Chrétien's iodine sulphate.** F. FICHTER and A. DINGER (Helv. Chim. Acta, 1936, 19, 607—608).—Chrétien's formula,  $\text{I}_2\text{O}_3 \cdot \text{SO}_3 \cdot 0.5\text{H}_2\text{O}$  (A., 1897, ii, 138), is confirmed, but not that of Bahl *et al.*,  $\text{I}_2\text{O}_3 \cdot \text{H}_2\text{SO}_4$  (A., 1935, 1335). Further, the compound  $\text{I}_2\text{O}_4 \cdot \text{H}_2\text{SO}_4$ , described by the latter, was probably simply  $\text{I}_2\text{O}_3 \cdot \text{SO}_3 \cdot 0.5\text{H}_2\text{O}$  partly decomposed by  $\text{H}_2\text{O}$ . M. S. B.

**Anionic iron.** R. SCHOLDER [with H. WEBER, CHRISTOPH, and DOLGE] (Angew. Chem., 1936, 49, 255—259).—By the action of boiling aq.  $\text{NaOH}$  on reduced Fe in the absence of  $\text{O}_2$ , Fe is dissolved as  $\text{Fe}^{\text{II}}$ , with the simultaneous evolution of 2 atoms of H per atom of Fe dissolved, up to a limiting concn. which is a max. with 55%  $\text{NaOH}$ . With massive Fe, action is similar but proceeds less far. The limiting concn. of Fe is conditioned by electrochemical considerations, and in glass vessels is  $>$  in Fe or Ag, due to formation of silicato-ferroates from dissolved  $\text{SiO}_2$ . From the blue alkaline solution the ferroate  $\text{FeO} \cdot \text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$  (I) or  $\text{Na}_2[\text{Fe}(\text{OH})_4]$  is deposited on cooling, and with  $\text{Ba}(\text{OH})_2$  or  $\text{Sr}(\text{OH})_2$  gives  $\text{FeO} \cdot 2(\text{Ba}, \text{Sr})\text{O} \cdot 3\text{H}_2\text{O}$  or  $(\text{Ba}, \text{Sr})_2[\text{Fe}(\text{OH})_6]$ , in conformity with the hydroxo-salts of Zn, Co, and Cu. Addition of  $\text{H}_2\text{O}$  ppts.  $\text{Fe}(\text{OH})_2$ . Atm. oxidation of the solution of (I) at 20—25° gives the ferrite  $\text{Na}_3[\text{Fe}(\text{OH})_8] \cdot 5-6\text{H}_2\text{O}$ , and at 30—70° gives  $\text{Na}_4[\text{Fe}(\text{OH})_7 \cdot \text{H}_2\text{O}] \cdot 1-2\text{H}_2\text{O}$ . The 50%  $\text{NaOH}$  solution of (I) at 100—125° yields an olive-green meta-ferrite,  $\text{NaFeO}_2$  (II), isomeric or polymeric with the red  $\text{NaFeO}_2$  (III) prepared by the action of  $\text{Fe}_2\text{O}_3$  on fused  $\text{NaOH}$ . (III) is formed also by the oxidation of boiling 55—60%  $\text{NaOH}$  solutions of (I), and differs from (II) in being stable to dil.  $\text{NaOH}$ .  $\text{Na}_2\text{S}$  gives with solutions of (I) green solutions depositing the thiohydroferroate  $\text{Na}_3[\text{S} \cdot \text{Fe}(\text{OH})_3] \cdot 2\text{H}_2\text{O}$ . Ferrite solutions similarly give

$\text{Na}_8[(\text{H}_2\text{O})(\text{HO})_6\text{Fe} \cdot \text{S} \cdot \text{Fe}(\text{OH})_6(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ . Under no conditions was  $\text{K}_2\text{FeO}_5$  formed (cf. A., 1927, 433), and its existence is improbable. J. S. A.

**Autoxidation of iron, manganese, and cobalt hydroxides.** J. HERMAN (Compt. rend., 1936, 202, 419—420; cf. A., 1935, 834).—The amount of  $\text{O}_2$  absorbed by  $\text{Fe}(\text{OH})_2$  pptd. by  $\text{KOH}$  from excess of  $\text{FeSO}_4$  in an atm. of  $\text{O}_2$  increases with time to attain a limiting val. in 2 min. This amount is  $>$  that corresponding with transformation into  $\text{Fe}^{\text{III}}$ . With  $\text{MnSO}_4$  there is a rapid initial absorption, followed by slow reaction  $\propto$  time, attaining a limit corresponding, approx., with the conversion into  $\text{Mn}^{\text{III}}$ . If excess of  $\text{KOH}$  is present, however, this state is passed. With excess of  $\text{CoSO}_4$  a green ppt. is obtained which is almost non-oxidisable under the conditions investigated. The same results are obtained with the respective chlorides. J. W. S.

**Action of anhydrous ferric chloride on anhydrous acetic and formic acids.** H. FUNK and M. DEMMEL (Z. anorg. Chem., 1936, 227, 94—102; cf. A., 1931, 1020).—Interaction of anhyd.  $\text{FeCl}_3$  and anhyd.  $\text{AcOH}$  yields the compound  $[\text{Fe}_3(\text{OAc})_6]\text{Cl}_3 \cdot \text{AcOH}$  (I), in which the  $\text{AcOH}$  is directly replaceable by  $\text{Et}_2\text{O}$ . (I) reacts with  $\text{EtOH}$ ,  $\text{MeOH}$ ,  $\text{C}_2\text{Me}_2$ , and dioxan to give the following compounds ( $[\text{Fe}_3(\text{OAc})_5\text{OH}]\text{Cl}_3=\text{Z}$ ):  $\text{Z} \cdot 4\text{EtOH}$ ;  $\text{Z} \cdot 4\text{MeOH}$ ;  $\text{Z} \cdot 1.5\text{C}_2\text{Me}_2$ ;  $\text{Z} \cdot 4\text{C}_4\text{H}_8\text{O}_2$ ;  $\text{Z} \cdot 2\text{C}_4\text{H}_8\text{O}_2$ .  $\text{FeCl}_3$  with  $\text{HCO}_2\text{H}$  (95%) gives  $\text{Fe}(\text{HCO}_2)_3\text{Cl} \cdot \text{H}_2\text{O}$ , which is also obtained with anhyd.  $\text{HCO}_2\text{H}$ ,  $\text{CO}$  being evolved in the latter case. The product could not be dehydrated. F. L. U.

**Reaction of ferric salts with organic acids.** A. ZAIDES (J. Gen. Chem. Russ., 1935, 5, 1530—1536).— $\text{Fe}(\text{OH})_3$  does not react chemically with  $\text{AcOH}$  or  $\text{HCO}_2\text{H}$ , the only effect being that of peptisation of the gel. With  $\text{H}_2\text{C}_2\text{O}_4$  a complex, probably  $\text{Fe}[\text{Fe}(\text{C}_2\text{O}_4)_3]$ , is formed. R. T.

**Amorphous and crystalline oxide hydrates and oxides.** XXIV. Autoxidation and induction actions of ferrous hydroxide in presence of  $\gamma\text{-FeO} \cdot \text{OH}$ . A. KRAUSE and Z. ERNST (Ber., 1936, 69, [B], 656—664; cf. A., 1935, 1335).—The action of air on an undisturbed ammoniacal mixture of  $\text{Fe}(\text{OH})_2$  and  $\gamma\text{-FeO} \cdot \text{OH}$  causes oxidation of  $\text{Fe}(\text{OH})_2$  and ferro-ferrite reaction which may interfere with one another. The relative rates of the two reactions govern the processes occurring in the system,  $\text{Fe}(\text{OH})_2$ — $\gamma\text{-FeO} \cdot \text{OH}$ . During autoxidation  $\text{Fe}(\text{OH})_2$  behaves as inductor and acceptor, the activating no. being about 2. Higher vals. are explained by the hypothesis that the double  $\text{O}_2$  excess absorbed by 2 mols. of  $\text{Fe}(\text{OH})_2$  cannot oxidise the 2 additional  $\text{Fe}(\text{OH})_2$  mols. which have previously combined with  $\gamma\text{-FeO} \cdot \text{OH}$  to produce the black ferro-ferrite; the latter is stable towards atm. oxidation. The chemistry of the process is complex and may be considered as a chain reaction.  $\text{H}_2\text{O}_2$  is produced. In presence of  $\text{EtOH}$  as acceptor the activation no. is about 3. If ferro-ferrite reaction does not occur in the system  $\text{Fe}(\text{OH})_2$ — $\gamma\text{-FeO} \cdot \text{OH}$  [as when  $\text{Fe}(\text{OH})_2$  is rapidly oxidised], the activation no. is about 1 or 1.4 or 2 with  $\text{EtOH}$  and  $\text{NaAsO}_3$ , respectively, as acceptor. In such cases  $\gamma\text{-FeO} \cdot \text{OH}$  is without influence. H. W.



**Basic salts. XII Chemistry and morphology of basic salts of bivalent metals. IV. Basic cobalt bromides.** W. FEITKNECHT and G. FISCHER (Helv. Chim. Acta, 1936, 19, 448—466; cf. A., 1935, 716).—Four basic  $\text{Co}^{\text{II}}$  bromides exist. The green basic bromide I is pptd. at room temp., as a disperse gel, from aq.  $\text{CoBr}_2$  of concn. 1.5—approx.  $3.5 \times 10^{-2} M$  by < the equiv. quantity of  $\text{NaOH}$ . At  $100^\circ$  the upper limit falls to  $0.5 M$ . The ppt. becomes microcryst. by slow hydrolysis at higher temp. It is probably metastable only under all conditions. After long ageing or slow hydrolysis the compound contains more  $\text{Co(OH)}_2$  than corresponds with the formula  $\text{CoBr}_2 \cdot 9\text{Co(OH)}_2$ . The initial ppt. contains 7—11  $\text{Co(OH)}_2$  to each  $\text{CoBr}_2$ , according to the end concn. of the solution. From data relating to this compound the solubility product of  $\text{Co(OH)}_2$  is  $3.3 \times 10^{-15}$ . Basic bromide II,  $\text{CoBr}_2 \cdot 3\text{Co(OH)}_2$ , is reddish-violet and coarsely cryst., the form changing with the temp. of separation, which must be above room temp. It is stable towards  $\text{H}_2\text{O}$ . Basic bromide III is formed, not very readily, as dark bluish-violet crystals of unknown composition, by warming I in  $3.5 \times 10^{-2}$ — $0.1 M$ - $\text{CoBr}_2$ . I, II, and III give characteristic X-ray diagrams. A rose-coloured basic bromide IV is obtained as a partly amorphous product by heating bromide I in a sealed tube above  $150^\circ$  in dil. aq.  $\text{CoBr}_2$ . A mixed basic chloride-bromide, isomorphous with basic chloride II, and of composition  $\text{CoCl}_{1.34}\text{Br}_{0.66} \cdot 3\text{Co(OH)}_2$ , has also been obtained. M. S. B.

**Complex salts of dipyriddy with bivalent tervalent cobalt.** F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 164—175; cf. A., 1935, 714).—Analyses and crystallographic data for the following complex salts are given:  $[\text{Co(dipy)}_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2\text{CO}_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_3]\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2\text{CO}_3]_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_3](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2\text{CO}_3]\text{NO}_3 \cdot 5\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_3]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ;  $[\text{Co(dipy)}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ . O. J. W.

**Hydrolysis of basic nickel sulphate.** G. GIRE (Compt. rend., 1936, 202, 1182—1184).— $\text{H}_2\text{O}$  gradually reacts with the compound  $5\text{NiO} \cdot \text{SO}_3 \cdot n\text{H}_2\text{O}$  (I) previously obtained (A., 1935, 716), dissolving  $\text{NiSO}_4$  and forming insol.  $\text{Ni(OH)}_2$ . There are no indications of the existence of any salt more basic than (I). M. S. B.

**Oxyhalides of nickel obtained by Sénarmont's synthesis.** A. FERRARI and R. CURTI (Gazzetta, 1936, 66, 104—114).—When  $\text{CaCO}_3$  is heated with aq.  $\text{CoCl}_2$  in a sealed tube  $\text{CoCO}_3$  is formed. With  $\text{NiCl}_2$  no  $\text{NiCO}_3$ , but the compound  $3\text{Ni(OH)}_2 \cdot \text{NiCl}_2$  (I), is formed. This substance is hexagonal, and on further heating with  $\text{NiCl}_2$  gives the compound  $\text{Ni(OH)}_2 \cdot \text{NiCl}_2$ . A compound analogous to (I) can be obtained by using  $\text{NiBr}_2$ . These substances are probably solid solutions. O. J. W.

**Complex compounds of semicarbazides.** K. A. JENSEN and E. RANCKE-MADSEN (Z. anorg. Chem., 1936, 227, 25—31; cf. A., 1934, 1188).—The following compounds of semicarbazide (=sem) and its deriv-

atives are described:  $[\text{Ni sem}_2]\text{Cl}_2$ ;  $[\text{Ni sem}_2]\text{SO}_4$ ;  $[\text{Ni sem}_3]\text{Cl}_2$ ;  $[\text{Co sem}_3](\text{NO}_3)_2$ ;  $[\text{Ni}(\text{CON}_3\text{H}_4)_2]$ ;  $[\text{Cu}(\text{NHAc} \cdot \text{NH}_2)_2]\text{SO}_4$ ;  $[\text{Ni}(\text{NHAc} \cdot \text{NH}_2)_3]\text{SO}_4$ ;  $[\text{Ni}(\text{EtO} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2)_3]\text{SO}_4$ ;  $[\text{Ni}(\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2)_3](\text{NO}_3)_2$ ;  $[\text{Cu}(\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2)_2](\text{NO}_3)_2$ ;  $[\text{Ni}(\text{NH} \cdot \text{C}(\text{O}) \cdot \text{NMe} \cdot \text{NH}_2)_2]$ ;  $[\text{Ni}(\text{NH} \cdot \text{C}(\text{O}) \cdot \text{NMe} \cdot \text{NHMe})_2, \text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{NHMe}]$ ;  $[\text{Cu}(\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{NHMe})_2]\text{SO}_4$ ;  $[\text{Ni}(\text{NHPh} \cdot \text{CS} \cdot \text{NMe} \cdot \text{NHMe})_2]\text{Cl}_2$ .

F. L. U.

**Osmic acid esters as intermediate products in oxidations.**—See this vol., 603.

**Quantitative spectral analysis.** W. VAN TONGEREN (Chem. Weekblad, 1936, 33, 249).—A correction (cf. this vol., 441). S. C.

**Spark and arc spectrum of pure iron as accessory for qualitative emission spectrum analysis. Iron alloys.** H. HAMMERSCHMID, C. F. LINSTRÖM, and G. SCHEIBE (Mitt. Forsch. Anst. Konz. Gutehoffnungshütte, 1935, 3, 223—229; Chem. Zentr., 1935, ii, 1221—1222).—Procedure and sensitive lines for the detection of the elements commonly alloyed with or present in Fe are recorded. J. S. A.

**Theory of titration error.** S. KUPPI (Z. anal. Chem., 1936, 104, 390—400).—Expressions are developed for the calculation of titration errors in those acidimetric and pptn. analyses in which the end-point does not coincide with the true equivalence point. J. S. A.

**Application of polarographic method in analytical chemistry. I. Theoretical introduction.** H. J. ANTWEILER (Z. anal. Chem., 1935, 102, 385—393).—The principles of the method are reviewed, and modified apparatus is described. J. S. A.

**Titrimetric colorimetry.** P. KARSTEN (Pharm. Weekblad, 1935, 72, 1327—1339).—The method of varying the thickness of a standard solution is untrustworthy, since Beer's law is rarely applicable, and that of preparing a series of standards is tedious and less accurate than the method recommended, viz.: equal quantities of the reagent are placed in two similar Nessler glasses; to one is added a known vol. of the solution to be analysed, whilst to the other a standard solution of the substance to be determined is added from a burette until the colours match. For determining  $\text{Fe}^{\text{III}}$ , 50 c.c. of the reagent (I) should contain 2.5 c.c. of  $4N\text{-HNO}_3$  and 5 c.c. of  $N\text{-KCNS}$ , the suitable concn. (II) of Fe being 0.04—0.10 mg. in 50 c.c. of solution, the thickness of which is 10 cm.; substances which interfere (III) are Bi, Co,  $\text{Hg}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ , Ag, Ni, oxalate, phosphate, and alkali and alkaline-earth sulphates, chlorides, and nitrates. Corresponding data for other determinations are: CNS' determination: (I) 2 c.c.  $4N\text{-HNO}_3$  and 0.5 c.c.  $N\text{-FeCl}_3$ ; (II) 0.15—0.40 mg. Bi determination: (I) 2.5 c.c.  $4N\text{-HNO}_3$  or  $\text{-H}_2\text{SO}_4$ , 5 c.c. 20% KI, 6 drops 1%  $\text{NaHSO}_3$ ; (II) 0.05—0.15 mg.; (III) Cu, Pb, Sb, Ag, Fe, Cl'. Cu determination:  $\text{NH}_3$  method—(I) 5 c.c. 10%  $\text{NH}_3$ ; (II) 0.5—3.0 mg.; (III) Bi, Co, Ni, Cr, Fe;  $\text{Fe}(\text{CN})_6$  method—(I) 1 c.c. 10%  $\text{AcOH}$ , 1 c.c.  $N\text{-NaHCO}_3$ , 2—3 drops 1%  $\text{K}_4\text{Fe}(\text{CN})_6$ , 1 c.c. 10%  $\text{NH}_4\text{Cl}$ ; (II) 0.15—0.30 mg.; (III) Zn, Hg.



Co, Cr, Fe; Na diethyldithiocarbamate (IV) method—0.5 c.c. 10%  $\text{NH}_3$ , 1 c.c. 1% gum arabic, 5 c.c. 0.1% (IV); (II) 0.01—0.05 mg.; (III) Pb, Zn, Al, Bi, Hg, Cr, Ag, Sb, Sn, Mn, Ni, Co, Fe;  $\text{Na}_2\text{S}$  method—(I) 1 c.c. 10%  $\text{AcOH}$ , 1 drop 10%  $\text{Na}_2\text{S}$  in glycerol, 1 g.  $\text{NH}_4\text{Cl}$ ; (II) 0.03—0.10 mg.; (III) Pb, Zn, Hg, Bi, Cd, Ni, Co, Sn, Sb, As, Fe; in presence of Pb, 2 c.c. 4*N*- $\text{H}_2\text{SO}_4$  may be used in place of the  $\text{AcOH}$ . Pb determination with  $\text{Na}_2\text{S}$  as in the case of Cu (with  $\text{AcOH}$ )—(II) 0.8—0.20 mg. (*sic*); (III) Cu, Zn, Hg, Bi, Cd, Ni, Co, Sn, Sb, As, Fe—or in alkaline solution: (I) 2.5 c.c. 10%  $\text{NH}_3$ , 1 drop 10%  $\text{Na}_2\text{S}$  in glycerol, 1 g.  $\text{NH}_4\text{Cl}$ ; (II) 0.05—0.10 mg.; (III) Fe, Hg, Bi, Cd, Co, Mn, Cr, Sb, Sn; if Ni, Ag, Cu, or Zn is present, KCN must be added. Cr determination: diphenylcarbazide (V) method—to the solution containing Cr 4*N*- $\text{HNO}_3$  is added until the acidity reaches 1.0—1.5*N*, followed by 1 c.c. 0.1*N*- $\text{AgNO}_3$  and 1 g.  $\text{NH}_4\text{SO}_4$ . The solution is boiled for 3 min., cooled, and poured into the Nessler glass. 0.5 c.c. of (V) solution, containing 2 g. of (V) dissolved in 10 c.c. of glacial  $\text{AcOH}$  and diluted to 100 c.c. with 96%  $\text{EtOH}$ , are finally added; (II) 0.003—0.010 mg.; (III) Mn [reduce  $\text{MnO}_4^-$  with  $\text{H}_2\text{C}_2\text{O}_4$  before adding (V)], Fe,  $\text{Cl}^-$ . If the  $\text{CrO}_4^{2-}$  is determined directly, without adding (V), (II) is 1.4 mg. Mn determination: boil for 5 min. with either 5 c.c. 50%  $\text{H}_2\text{SO}_4$ , 1 c.c. 0.1*N*- $\text{AgNO}_3$ , and 0.5 g.  $\text{NH}_4\text{SO}_4$ , or 2—3 c.c. 85%  $\text{H}_3\text{PO}_4$  and 0.25% periodate; (II) 0.06—0.16 mg.; (III) Cr,  $\text{Cl}^-$  (in first case). Phenolphthalein determination: (I) 1 c.c. 0.1*N*- $\text{NaOH}$ ; (II) 0.02—0.07 mg. Salicylic acid determination: (I) 2 c.c.  $\text{FeCl}_3$  solution containing 54 mg.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 10 c.c. glacial  $\text{AcOH}$  diluted to 100 c.c. with  $\text{H}_2\text{O}$ ; (II) 0.15—0.25 mg.; (III) benzoic, cinnamic, tartaric, oxalic, and phosphoric acids and their salts,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{Na}_2\text{CO}_3$ . Adrenaline determination: (I) 1 c.c. 10%  $(\text{NH}_4)_2\text{MoO}_4$ ; (II) 0.5—2.0 mg.; (III) other pyrocatechol derivatives. Fe may be removed with  $\text{Na}_4\text{P}_2\text{O}_7$ . D. R. D.

**Ebulliometric determination of small amounts of water.** M. WOJCIECHOWSKI (Nature, 1936, 137, 707).—The sensitivity of the method is markedly increased by using the azeotropic mixture  $\text{Pr}^\circ\text{OH}$ - $\text{PhMe}$  instead of  $\text{EtOH}$ - $\text{C}_6\text{H}_6$ . L. S. T.

**Hydrogen peroxide reaction with diphenylcarbazide.** L. N. LAPIN (Z. anal. Chem., 1935, 102, 418—420).— $\text{K}_2\text{Cr}_2\text{O}_7$  is added to the acidified solution, forming perchromic acid (I) which is extracted with  $\text{Et}_2\text{O}$  (peroxide-free). The (I) in the  $\text{Et}_2\text{O}$  layer formed from 0.005 mg. of  $\text{H}_2\text{O}_2$  gives a violet coloration with an  $\text{EtOH}$ - $\text{Et}_2\text{O}$  solution of diphenylcarbazide (II). Alternatively, Br may be added to the acidified test solution to oxidise  $\text{Fe}^{II}$ ,  $\text{S}^{II}$ , etc., followed by 2 c.c. of 0.00002*N*- $\text{K}_2\text{CrO}_4$ . Free Br is removed by adding  $\text{PhOH}$ . On adding (II), no violet coloration or a weakened colour is obtained in presence of  $\text{H}_2\text{O}_2$ , due to the formation of (I), and its rapid decomposition. The method may be used to determine minute amounts of  $\text{H}_2\text{O}_2$ . J. S. A.

**Micro-determination of chlorine.** I. M. KOBENMAN (Mikrochem., 1936, 19, 144—146).—Free Cl in  $\text{H}_2\text{O}$  is titrated with aq. Me-red or, better, with 0.001*M*-Me-orange. J. S. A.

**Nephelometric micro-determination of chlorine and its application to determination of chlorine in [ash of] organic substances.** F. ALTEN and E. HILLE (Mikrochem., 1936, 19, 118—128).—Stable  $\text{AgCl}$  sols are formed by the addition of  $\text{Cl}^-$  to a solution of 0.01*N*- $\text{AgNO}_3$ +0.05*N*- $\text{Al}(\text{NO}_3)_3$ +0.05*N*- $\text{Ca}(\text{NO}_3)_2$ +0.1*N*- $\text{NaNO}_3$ . The turbidity formed may be measured photometrically, and is  $\propto \text{Cl}^-$ . The method is applicable to 0—0.25 mg. of Cl. Org. materials (plant tissue etc.) are ashed, with the addition of lactose+ $\text{Na}_2\text{O}_2$ . The residue is dissolved in  $\text{H}_2\text{O}$ , and treated with 10%  $\text{H}_2\text{SO}_4$  at 70—80° to destroy  $\text{CN}^-$ . Cl in the filtered solution is then determined as above. J. S. A.

**Determination of hydrobromic acid in presence of hydrochloric acid.** G. G. LONGINESCU and E. I. PRUNDEANU (Bull. Acad. Sci. Roumaine, 1935, 17, 47—51).—The solution containing  $\text{Cl}^-$  and  $\text{Br}^-$  is shaken with  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , and petrol, when the Br liberated by the  $\text{H}_2\text{O}_2$  is absorbed by the petrol.  $\text{HCl}$  remains in the aq. layer and can be determined as  $\text{AgCl}$ . The petrol layer is reduced by Na and  $\text{C}_2\text{H}_{11}\text{OH}$  and the Br determined as  $\text{AgBr}$ , volatilisation on heating being avoided. Results are accurate to 0.06%. R. S. B.

**Separation of bromides from chlorides by means of iodic acid.** L. MARTINI (Annali Chim. Appl., 1936, 26, 102—105).—Kolthoff's modification of Bugarszky's method (Z. anal. Chem., 1921, 60, 405) gives satisfactory results in the presence of a limited amount of  $\text{Cl}^-$  if the Br content is  $\leq 7$ —8 mg. L. A. O'N.

**Reactions occurring during the absorption of nitrous vapours by potassium iodide solutions.** M. DODÉ (Compt. rend., 1936, 202, 1076—1078; cf. this vol., 439).—The action of  $\text{NO}_2$  on aq. KI is expressed by:  $\text{N}_2\text{O}_4 + 2\text{KI} = 2\text{KNO}_2 + 2\text{I}$  (1);  $\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$  (2);  $\text{HNO}_2 + \text{KI} = \text{NO} + \text{KOH} + \text{I}$  (3);  $\text{HNO}_3 + \text{KOH} = \text{KNO}_3 + \text{H}_2\text{O}$  (4);  $2\text{N}_2\text{O}_3 + 2\text{H}_2\text{O} = 4\text{HNO}_2$ ,  $4\text{HNO}_2 + 2\text{KI} = 2\text{KNO}_2 + 2\text{NO} + 2\text{I} + 2\text{H}_2\text{O}$  (5). In presence of  $\text{O}_2$  the NO liberated in (3) is oxidised in the gas phase when the vol. of solution is small, or otherwise directly to  $\text{HNO}_2$  in solution. The indirect production of nitrite by (5) increases with the dilution. The difference in hydrolysis of  $\text{NO}_2$  and  $\text{NOCl}$  may be explained.  $\text{N}_2\text{O}_4$  is equiv. to 2I, as may be proved: (a) in the titration of I by  $\text{Na}_2\text{S}_2\text{O}_3$  in presence of nitrites; I consumed by oxidation of  $\text{NaNO}_2$  is entirely regenerated by  $\text{NaNO}_2 + 2\text{HI} = \text{NaI} + \text{H}_2\text{O} + \text{I} + \text{NO}$ ,  $\text{NO} + \frac{1}{2}\text{O}_2 + \text{KI} = \text{KNO}_2 + \text{I}$  or  $\text{NO} + \text{O}_2 + \text{KI} = \text{KNO}_3 + \text{I}$ ; (b) iodometric titration of acids by the action of the acid on a mixture of  $\text{KNO}_2$  and KI in presence of  $\text{O}_2$ ; (c) determination of  $\text{NO}_2$  and  $\text{Cl}_2$  in a mixture. Analytical application for the determination of nitrous vapours is discussed. R. S. B.

**Determination and detection of fluoride ion with lanthanum.** J. FISCHER [with E. MÜLLER and H. KNOTHE] (Z. anal. Chem., 1936, 104, 344—346).—The determination of F by pptn. as  $\text{LaF}_3$  (cf. A., 1925, ii, 598) is not practicable owing to the strong adsorptive properties of  $\text{LaF}_3$ . As a qual. test, by pptg. from  $\text{AcOH}$  solution in presence of dyes (*e.g.*, eosin)



the dye is taken up, giving a red ppt. Limiting concn., 1 in 50,000. J. S. A.

**Determination of ozone and nitrogen peroxide in air.** G. A. GORODETZKI (J. Appl. Chem. Russ., 1936, 9, 353—361).—Trustworthy results are not obtained in the iodometric determination of  $O_3$  in air, since  $NO_2$ , which is invariably produced at the same time as  $O_3$ , gives the same reactions.  $O_3$  is determined by shaking a sample of air (10 litres) with 50 ml. of standard aq.  $NaNO_2$  (1 ml. equiv. to 0.0005 mg. of  $O_3$ ) and 2 ml. of 0.01M- $MnSO_4$ . 3 ml. of Griess-Ilosvay reagent are added to 20 ml. of the solution, which is warmed at 70—80° for 3—5 min., and  $H_2O$  is added to 25 ml. The coloration is compared with that given by the standard. R. T.

**Quantitative analysis by the Raman effect of sulphato-nitric mixtures.** J. CHÉDIN (Compt. rend., 1936, 202, 1067—1069).—The % of  $N_2O_5$  in mixtures of  $HNO_3$  and  $H_2SO_4$  has been determined by observing the Raman spectrum,  $N_2O_5$  giving, among other lines, an intense line  $\Delta\nu=1398\text{ cm}^{-1}$ . The  $HNO_3$  is entirely dehydrated up to approx. 15%, and the % of  $N_2O_5$  in the mixture is a max. at approx. 20% of  $HNO_3$ . It follows that in mixtures of oleum and  $HNO_3$  the dehydration of  $HNO_3$  is complete at a much higher % of  $HNO_3$ . R. S. B.

**Determination of nitrogen by Kjeldahl's method. Ammonia distillation.** J. SPEIRS and W. J. MITCHELL (J. Inst. Brew., 1936, 42, 247—250).—Loss of  $NH_3$  could not be demonstrated during Kjeldahl distillations carried out by the method of Ford *et al.* (see B., 1933, 842), either in modifications wherein the  $NaOH$  was added before or after the commencement of boiling, or with various described modifications of the apparatus (cf. Miller, this vol., 302). Further, the use of air-saturated  $H_2O$  or the passage of air through the boiling mixture caused no loss, whilst slow boiling held no advantage. I. A. P.

**Copper selenite as a catalyst in the Kjeldahl nitrogen determination.** E. J. SCHWÖGLER, B. J. BABLER, and L. C. HURD (J. Biol. Chem., 1936, 113, 749—751).— $CuSeO_3 \cdot 2H_2O$  is a better catalyst for Kjeldahl digestion than are those at present in use. H. D.

**Kjeldahl decomposition using selenium.** K. TAUFEL, H. THALER, and K. STARKE (Angew. Chem., 1936, 49, 265—266).—Se is adequate as a catalyst; addition of  $CuSO_4$  gives satisfactory results, but  $K_2SO_4$  leads to some loss of N. J. S. A.

**Modified technique for Kjeldahl procedure.** A. HENWOOD and R. M. GAREY (J. Franklin Inst., 1936, 221, 531—538).—Procedure is outlined for a rapid modification of the macro-Kjeldahl process, using one tenth of the usual quantity of material. J. S. A.

**Determination of nitrate by means of Devarda's alloy.** M. B. DONALD (Analyst, 1936, 60, 249—250).—Reduction is optimal when 1 g. of  $NaNO_3$  is treated with 3 g. of alloy and 2 g. of  $NaOH$  in 250 c.c. of  $H_2O$ . E. C. S.

**Drop method of detection of ammonium.** N. A. TANANAEV and A. A. BUDKEVITSCH (J. Appl.

Chem. Russ., 1936, 9, 362—363, 369—371).—A drop of conc. aq.  $NaOH$  is added to a drop of the solution, which, if turbid, is then filtered through a capillary. A drop of Nessler's reagent is then placed on a drop of the filtrate on filter-paper, when a yellow stain is obtained in presence of  $< 3 \times 10^{-7}$  g. of  $NH_4^+$ . If the solution contains Ag, Hg, or Pb, a drop is placed on a drop of 2N- $NaOH$  on filter-paper, 2 drops of 2N- $NaOH$  are added, and a capillary containing Nessler's reagent is drawn across the spot; a peripheral coloration is obtained in presence of  $< 2 \times 10^{-6}$  g. of  $NH_4^+$ . R. T.

**Azorubin, a new reagent for detection of nitrates and nitrites.** F. SKOUTIL (Chem. Listy, 1936, 30, 74—77).—1—3 drops of aq. 0.01% azorubin are added to 1—2 c.c. of solution, and 1—2 c.c. of conc.  $H_2SO_4$  are added, when a blue ring appears at the  $H_2SO_4$ - $H_2O$  interface; this will be separated from the aq. layer by a yellow ring if the solution contains  $< 1.25 \times 10^{-6}$  g. of  $NaNO_3$  or  $NaNO_2$ . The reaction is also given by  $ClO_3^+$ ,  $BrO_3^+$ ,  $IO_3^+$ ,  $IO^+$ ,  $SeO_4^{++}$ ,  $SeO_4^{--}$ ,  $TeO_4^{++}$ ,  $Fe(CN)_6^{--}$ ,  $H_2O_2$ ,  $CrO_4$ ,  $MnO_4$ , and  $VO_3^+$ , but not by  $Fe^{++}$ ,  $Fe(CN)_6^{--}$ , or oleum. R. T.

**Effect of fluorine on precipitation of phosphoric acid with ammonium molybdate.** F. W. NEUHAUS (Z. anal. Chem., 1936, 104, 416—417; cf. this vol., 303).—The effect is already well known. J. S. A.

**Colorimetric determination of orthophosphate in presence of meta- and pyro-phosphate.** K. BORATYŃSKI (Z. anal. Chem., 1935, 102, 421—428).— $P_2O_7^{--}$  and  $PO_3^+$  do not give the Mo-blue reaction.  $PO_4^{--}$  may be determined colorimetrically in presence of  $P_2O_7^{--}$  and  $PO_3^+$  by addition of  $(NH_4)_2MoO_4$  and reduction with 1 : 2 : 4- $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H$  or  $p\text{-OH} \cdot C_6H_4 \cdot NHMe \cdot H_2SO_4$  at 25°. In presence of a large excess of  $P_2O_7^{--}$  the  $(NH_4)_2MoO_4$  must be increased, owing to the formation of a stable pyrophosphate-molybdic compound. J. S. A.

**Colorimetric determination of phosphoric and arsenic acid with ascorbic acid.** R. AMMON and K. HINSBERG (Z. physiol. Chem., 1936, 239, 207—216).—Ascorbic acid (I) may usefully be used as reducing agent in the method of Lohmann *et al.* (A., 1927, 69).  $AsO_4^{--}$  and (I) can also be determined under certain conditions but determination of  $AsO_4^{--}$  and  $PO_4^{--}$  in presence of each other is possible only with the help of other methods. W. McC.

**Determination of phosphate in presence of arsenate.** J. COURTOIS (J. Pharm. Chim., 1936, [viii], 13, 404—418).— $PO_4^{--}$  is determined by Copaux' approx. method, being pptd. selectively by  $Na_2MoO_4$  in presence of  $Et_2O$  from  $H_2SO_4$  solutions. Alternatively,  $AsO_4^{--}$  may be reduced to  $AsO_3^{--}$  by  $SO_2$  in  $H_2SO_4$  solution, or in biological fluids by  $Hl$ . In the latter case  $PO_4^{--}$  is pptd. as  $MgNH_4PO_4$ , which is redissolved and determined as before. J. S. A.

**Assay of hypophosphites.**—See B., 1936, 475.

**Sources of error in arsenic determination by Gutzeit's reaction on paper strips.** W. MÜHLSTEDT (Z. anal. Chem., 1936, 104, 333—344).—A crit. review of published methods. Constancy in the humidity of the gas is essential. J. S. A.



**Detection of small amounts of arsenic by electrolytic reduction.** M. T. KOSLOVSKY and A. J. PENNER (Mikrochem., 1936, 19, 89—97).—As, present in 12% aq.  $\text{H}_2\text{SO}_4$  solution, is reduced electrolytically in an undivided cell at a Hg cathode to  $\text{AsH}_3$ . By separating the gases liberated at the anode and cathode, respectively,  $10^{-6}$  g. of As may be detected. In alkaline solution  $\text{AsO}_3^{3-}$ , but not  $\text{AsO}_4^{3-}$ , is reduced to  $\text{AsH}_3$ . J. S. A.

**Direct determination of small amounts of arsenic in presence of mercury.** J. GANGL and H. DIETERICH (Mikrochem., 1936, 19, 253—261).—By effecting reduction with Zn in hot solution, As is reduced quantitatively to  $\text{AsH}_3$  in presence of a large excess of Hg, and is determined titrimetrically from the mirror formed by thermal decomp. of the  $\text{AsH}_3$  produced. J. S. A.

**Determination of carbon dioxide in carbonates.**—See B., 1936, 406.

**Rapid determinations of carbon dioxide in gaseous atmospheres.**—See B., 1936, 478.

**Sensitive reaction for potassium.** H. FREDHOLM (Z. anal. Chem., 1936, 104, 400—405).—Diluturic (5-nitrobarbituric) acid, prepared by direct nitration of barbituric acid at  $100^\circ$ , gives a characteristically cryst. ppt. with K at concns.  $> 0.09$  mg. of K per c.c. The Rb,  $\text{NH}_4$ , Mg, and Ba salts are also sparingly sol. and characteristic in crystal habit. J. S. A.

**Phthalic acid as reagent for optical identification of some metals and alkaloids.** K. P. YORKS and M. L. WILLARD (Mikrochem., 1936, 19, 227—229).—Optical properties of K, Co, Cu, Hg, Sr, Zn, Ni, quinine, brucine, and strychnine phthalates are recorded. J. S. A.

**Volumetric determination of sodium.** A. B. LEWIN (Z. anal. Chem., 1936, 104, 406—413).—The conc. neutral or slightly alkaline solution, containing  $> 0.1$  g. of Na, is treated at  $> 12^\circ$  with saturated aq.  $\text{K}_2\text{HSbO}_4$  (obtained by fusing  $\text{Sb}_2\text{O}_5$  with 6 mol. proportions of  $\text{KNO}_3$ ).  $\text{Na}_2\text{HSbO}_4$  is pptd. completely on addition of EtOH. The ppt. is redissolved in  $\text{H}_2\text{O}$ , and reduced with  $\text{HCl} + \text{Na}_2\text{SO}_3$ .  $\text{SO}_2$  is boiled off, and Sb is finally titrated with  $0.02N\text{-KBrO}_3$ . J. S. A.

**Spectrographic determination of certain elements by the arc process.** K. KONISHI and T. TSUGE (J. Agric. Chem. Soc. Japan, 1936, 12, 216—248).—Minute amounts of elements in soils and plants are determined by examination of their emission spectra. The min. amount of element varies from  $1\text{--}5 \times 10^{-4}$  mg. for Na and Ca to  $> 0.1$  mg. for Cs. The advantages of the method are simplicity, speed, and sensitivity. J. N. A.

**Analysis and separation of the more important anions.** F. POZNA and E. MIGRAY (Annali Chim. Appl., 1936, 26, 81—83).—The detection of inorg. anions and  $\text{OAc}'$  is described. F. O. H.

**Analysis of solutions of salts of heavy metals.** F. POZNA and E. MIGRAY (Annali Chim. Appl., 1936, 26, 78—80).—A method for the detection of

all the common metals in solutions free from Ca, Ba, and Sr is described. F. O. H.

**Simplified method of separating and identifying cations of second group.** E. CHIRNOAGA (Z. anal. Chem., 1936, 104, 356—358).—The sulphide ppt. is divided into two portions: (a) As is dissolved on boiling with  $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{NH}_3$ , and may be repptd. with  $\text{H}_2\text{S}$ ; (b) Cd, Bi, Sb, and Sn are dissolved by  $2N\text{-HCl} + \text{H}_2\text{O}_2$ . Cd is pptd. as CdS from the solution obtained by adding an excess of aq.  $\text{NH}_3$ ; Bi, Sb, and Sn as ordinarily. (c) The residue ( $\text{CuS} + \text{HgS}$ ) is dissolved in conc.  $\text{HCl} + \text{H}_2\text{O}_2$ . J. S. A.

**Microchemical determination of silver.** J. DONAU (Mikrochem., 1936, 19, 108—117).—Ag is determined in the  $\text{HNO}_3$  solution from the inquantation of Au alloys, or in the  $\text{HNO}_3$  solution of Ag alloys. Ag is displaced from solution by Cu (in the form of wire) at  $100^\circ$ . Supernatant liquid is sucked off, and the Ag is washed and dried *in situ*. J. S. A.

**Qualitative micro-separations.** A. A. BENEDETTI-PICHLER and W. F. SPIKES (Mikrochem., 1936, 19, 239—244).—Ag, Pb, and Tl, are pptd. with HBr. Pb and Tl are extracted with  $\text{H}_2\text{O} + \text{Br}$ . Pb is pptd. as  $\text{PbSO}_4$ , which is converted into  $\text{K}_2\text{PbCu}(\text{NO}_2)_6$ , and  $\text{Tl}^{III}$  is reduced with  $\text{SO}_2$  and repptd. as TlI. J. S. A.

**Determination of lead in drinking water.**—See B., 1936, 430.

**Volumetric analysis of lead chromate.**—See B., 1936, 419.

**Detection of thallium.** L. KUHLEBERG (Mikrochem., 1936, 19, 183—186).— $\text{Tl}^{III}$  oxidises  $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}(\text{C}_6\text{H}_4\text{-NEt}_2\text{-}p)_2$  (I) (prep. described) to an intense green dye.  $\text{Tl}^I$  is oxidised by  $\text{K}_3\text{Fe}(\text{CN})_6$  to the very insol.  $\text{Tl}(\text{OH})_3$ , which is filtered through a micro-filter. The paper is spotted with (I), dissolved in AcOH; limiting concn.  $10^{-7}M$ . In presence of other cations, Pb is pptd. with  $\text{Na}_2\text{SO}_4$ , and other metals with NaOH before pptg.  $\text{Tl}(\text{OH})_3$ . J. S. A.

**Drop colorimetric determination of copper.** N. A. TANANAEV and A. I. IVANOVA (J. Appl. Chem. Russ., 1936, 9, 364—366).—The intensity of coloration obtained when a drop of aq.  $\text{K}_3\text{Fe}(\text{CN})_6$  is placed on a drop of solution is compared with those given by a series of standard Cu solutions. The procedure for determination of Cu in ores is described. R. T.

**Qualitative micro-analysis.** F. FEIGL and R. UZEL (Mikrochem., 1936, 19, 132—143).—(a) For the detection of Cu, a drop of the solution under test is treated with 0.1% aq.  $\text{K}_2\text{TeO}_4$  or  $\text{KIO}_4$  and made alkaline with NaOH.  $\text{K}_2\text{S}_2\text{O}_8$  is added, and the solution is heated to  $100^\circ$ . In presence of  $< 0.02 \times 10^{-6}$  g. of Cu a yellow to red coloration is produced, due to the formation of tervalent Cu compounds.  $\text{NH}_4^+$ , or an excess of Cr or Mn, should be absent. Conversely, by adding  $0.00002M\text{-CuSO}_4$ ,  $0.5 \times 10^{-6}$  g. of Te (as  $\text{H}_6\text{TeO}_6$ ) or  $2 \times 10^{-6}$  g. of  $\text{H}_6\text{IO}_6$  may be detected in presence of other strongly oxidising anions. Te, in presence of 20,000 parts of Se, and  $\text{H}_6\text{IO}_6$  may also be detected by their inhibiting action on the catalytic effect of Cu on the oxidation



of  $Mn^{++}$  to  $MnO_4^-$  by  $NaOBr$ . (b)  $NH_2OH$  is detected by adding  $FeSO_4$ , and then making alkaline with  $NaOH$ .  $NH_2OH$  forms  $Fe(OH)_3 + NH_3$ , which is detected by its action on  $AgNO_3 + MnSO_4$  (A., 1933, 798). (c)  $Na_2[Fe(CN)_5NO]$  gives with piperidine in  $AcOH$  solution the salt  $Na_3[Fe(CN)_5C_5H_{11}N] \cdot 6H_2O$ , which gives, on filter-paper, a green fleck with  $< 0.05 \times 10^{-6}$  g. of Co. Hg, Cu, Ag, Pb, Bi, and Ni which interfere are first removed as insol. salts; Fe is converted into  $FePO_4$ . J. S. A.

**Determination of aluminium by means of aniline.** T. KOZU (J. Chem. Soc. Japan, 1935, 56, 562—569).—Al can be pptd. from a K alum solution by adding saturated aq.  $NH_2Ph$ . The  $p_H$  of the solution when pptn. is complete is 4.45—4.50. The ppt. is collected, washed, and weighed as  $Al_2O_3$ .

CH. ABS. (e)

**Aluminium alizarinate. Colorimetric determination of aluminium.** A. K. BABKO (J. Appl. Chem. Russ., 1936, 9, 375—378).—The compound  $Al(C_{14}H_7O_4)_3$  is formed in presence of considerable excess of alizarin (I), whilst when excess of  $Al^{+++}$  is present a maximally saturated adsorption compound approximating to  $Al_2(C_{14}H_7O_4)_3$  is obtained. The rate of increase of the concn. of the lake is  $<$  that of  $Al^{+++}$ , at const. concn. of (I); at const. concn. of (I) and Al the ratio of (I) to Al in the compound rises with increasing dilution. R. T.

**Detection of gallium using colour reactions.** N. S. POLUEKTOV (Mikrochem., 1936, 19, 248—252).—Ga gives with alizarin in presence of  $NH_3 + NH_4Cl$  a bright red lake. The sensitivity is enhanced by concentrating the ppt. at an  $Et_2O-H_2O$  interface. Ga, but not Al or In, gives with  $K_4Fe(CN)_6 + MnCl_2$  in presence of oxidising agents (e.g.,  $KBrO_3$ ) a sensitive reddish-brown coloration or ppt. Ga is best separated from other metals by extraction of  $GaCl_3$  with  $Et_2O$ , followed by extraction from the  $Et_2O$  layer by means of  $NaOH$ . Ga is then pptd. by means of 8-hydroxyquinoline before applying drop tests.

J. S. A.

**Determination of manganese in cobalt alloys.**—See B., 1936, 412.

**Colorimetric determination of iron with thiocyanates.** K. STEINHAUSER and H. GINSBERG (Z. anal. Chem., 1936, 104, 385—390).—The red  $Fe(CNS)_3$  coloration is stabilised by extracting it with  $Et_2O$  saturated with  $SO_2$  (I). The solution is acidified with conc.  $HCl$ , and treated with  $KCNS$ .  $EtOH$  is added, and the solution is extracted with (I). The coloured  $Et_2O$  solution is photometered by filtered blue or green light. J. S. A.

**Determination of traces of ferric iron in blood serum.**—See this vol., 747.

**Determination of tungsten in wolframite by chlorination.**—See B., 1936, 413.

**Determination of tungsten and silicon in steels by means of perchloric acid.**—See B., 1936, 457.

**Detection and colorimetric determination of tin by means of substituted 1:2-dimercaptobenzenes.** A specific reagent for tin. R. E. D. CLARK (Analyst, 1936, 60, 242—245).—A few drops

of 0.2% 4:1:2- $C_6H_3Cl(SH)_2$  or 4:1:2- $C_6H_3Me(SH)_2$  in aq.  $NaOH$  are added to the solution of Sn in  $> 15\%$  aq.  $HCl$ ; on warming in presence of  $< 1$  p.p.m. of  $Sn^{II}$ , a pink or red colour is formed within a few sec. With  $Sn^{IV}$  the colour takes longer to develop and the test is less sensitive. Bi gives a brick-red ppt. which cannot be mistaken for the magenta-red of Sn. The reaction is applied to the colorimetric determination of Sn, by means of which 1.5—6 p.p.m. may be determined to within 10%. E. C. S.

**Drop method of detection of antimony.** N. A. TANANAEV and L. M. RABINOVITSCH (J. Appl. Chem. Russ., 1936, 9, 369—371).—The solution is heated with  $HCl$  and Fe for 3—4 min., allowed to settle, the supernatant liquid is poured off, and the sediment (Pb, Hg, Bi, Cu, Sb, and excess of Fe) is washed by decantation and transferred as a suspension to a second tube. It is then treated with hot conc.  $HNO_3$ , when a white ppt. is obtained in presence of  $< 0.1$  mg. of Sb. R. T.

**Analytical chemistry of tantalum, niobium, and their mineral associates.** XXX. Beryllium. W. R. SCHÖELLER and H. W. WEBB (Analyst, 1936, 60, 235—242; cf. A., 1935, 838, 1217).—For its determination, the ppt. of  $BeO$  obtained by treatment with aq.  $NH_3$  or tannin (I) in presence of alkali sulphate is fused with  $Na_2CO_3$  and extracted with  $H_2O$ , as for the separation of Be from Al (cf. A., 1912, ii, 687);  $BeO$  is quantitatively pptd. from aq.  $NH_3$ -tartrate by (I). The earth-acid ppt. obtained by tartaric hydrolysis (cf. A., 1930, 184) does not occlude  $BeO$ . Ti, Nb, and Ta are separated from Be as well as from Zr etc. by pptn. with (I) from  $C_2O_4^{--}$  solution half-saturated with  $NH_4Cl$  (cf. A., 1932, 1012). U is separated from Be by pptn. as ferrocyanide.

E. C. S.

**Detection and determination of gold by means of filter-paper impregnated with reducing substances.** R. N. COSTEANU (Z. anal. Chem., 1936, 104, 351—355).—The alloy is treated with  $HNO_3$  to remove Ag and Cu, and the residue is dissolved in  $HCl + HNO_3$ , and diluted to a known vol. A standard drop of the solution is applied to paper impregnated with  $SnCl_2$ , benzidine, quinol,  $NH_2OH \cdot HCl$ , or other suitable reducing agent, and the intensity of the fleck obtained is matched against that given by solutions of known  $[Au]$ . J. S. A.

**Liquid-operated thermostat.** A. R. PEARSON and R. E. NORRIS (J.S.C.I., 1936, 55, 127—128t).—Part of the wall of the regulator vessel is made in re-entrant form, of material having high thermal conductivity and expansion.

**Apparatus for heating inflammable solvents.** B. MELKON (Amer. J. Pharm., 1936, 108, 95—98).—An asbestos-lined paint can enclosing an electric lamp is used as heating bath. R. S. C.

**Measurement of the thermal conductivity of gases.** T. H. LABY (Nature, 1936, 137, 741).—Advantages of the use of a thick in preference to a thin wire are discussed. L. S. T.

**Fluorescencethermoscope.** H. EICHLER (Chem.-Ztg., 1936, 60, 357).—Solutions of Magdala-red in solvents containing OH- or  $CO_2H$ -groups change from



violet to yellowish-red with sudden appearance of fluorescence when the m.p. of the solvent is exceeded. This property is utilised in a thermoscope, comprising a thin-walled glass tube containing such a solution, loaded with Pb at one end so as to float in liquids, which permits ready observation when a certain temp. is exceeded. Solvents suitable for the specified temp. are:  $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (213°),  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (159°), BzOH (121°),  $m\text{-C}_6\text{H}_4(\text{OH})_2$  (118°), thymol (51°), PhOH (42°),  $p\text{-cresol}$  (36°),  $o\text{-cresol}$  (31°), AcOH (17°),  $\text{HCO}_2\text{H}$  (9°), and  $m\text{-cresol}$  (3°). For intermediate temp. mixed solvents are used, whilst below 0° the solvent can be  $\text{CH}_2\text{O}$ , MeOH, EtOH, glycerol, or  $\text{COMe}_2$ . J. W. S.

**Spectropolarimetry with metallic mirrors in the far ultra-violet.** R. SERVANT (Compt. rend., 1936, 202, 476—477).—An arrangement suitable for polarimetry with light sources between  $\lambda$  2500 and 1850 Å. is described. F. L. U.

**Technique for obtaining X-ray powder patterns.** R. A. STEPHEN and R. J. BARNES (Nature, 1936, 137, 532—533; cf. this vol., 45). L. S. T.

**Demonstrating and measuring approximately the index of refraction of crystalline substances for X-rays.** H. C. HOYT and G. A. LINDSAY (Physical Rev., 1936, [ii], 49, 498—501).—By reflecting the same spectral line simultaneously from two faces of a crystal by turning the crystal so that for the proper reflecting angle the rays fall at the intersection of the two faces,  $n$  can be obtained by a simple calculation from the width included between the reflected and refracted portions of the line. The method has been confirmed for a cerussite crystal. N. M. B.

**Drop-plate for the observation of turbidity in the dark field.** S. WEHRLI (Helv. Chim. Acta, 1936, 19, 505—506).—A method of illuminating small drops of liquid in the investigation of pptn. reactions is described. M. S. B.

**Measurement of dielectric constant for very short waves with a registering apparatus.** R. FREYMAN (Compt. rend., 1936, 202, 952—954).—Drude's method is applied, the resonance curve being recorded photographically with a galvanometer. Measurements are recorded for certain aromatic N compounds ( $\lambda$  3.72—2.41 m.). H. J. E.

**Counter for  $\alpha$ -particles.** S. S. VASSILIEV (Nature, 1936, 137, 533). L. S. T.

**Characterisation and designation of new counters for elementary rays and photo-electrons.** Spark counter. H. GREINACHER (Helv. phys. Acta, 1935, 8, 265—266; Chem. Zentr., 1935, ii, 1219).—Counters based on a spark discharge between metal and liquid, or dissimilar metal electrodes, are described. J. S. A.

**New counting methods for elementary rays and photo-electrons.** H. GREINACHER (Z. tech. Physik., 1935, 16, 165—170; Chem. Zentr., 1935, ii, 1219; cf. preceding abstract). J. S. A.

**Comparison of photo-emissive and photo-voltaic devices [for measuring radiant energy].** E. D. WILSON (Trans. Electrochem. Soc., 1936, 69,

Preprint 19, 221—228).—Useful characteristics of each type of photo-cell are discussed. By suitable construction and the use of various filters, photo-electric devices can be suited to any particular range of the spectrum, from the ultra-violet to the near infra-red ( $\lambda$  1.4  $\mu$ ). By using fluorescent screens and suitable filters the intensity of X-ray radiations can be measured. J. W. C.

**Barrier layers and photoelectricity.** J. ROULEAU (Compt. rend., 1936, 202, 470—472; cf. A., 1935, 585).—In cells of the metal- $\text{Cu}_2\text{O}$  type the photo-electric effect and contact rectification are both independent of the sp. resistance of the  $\text{Cu}_2\text{O}$  in bulk, whilst both increase with the contact resistance and are therefore related to it. F. L. U.

**Electrophoresis cell for microscopic observations.** M. E. SMITH and M. W. LASSIE (J. Physical Chem., 1936, 40, 399—412).—A cell of new design is described. Observations are made at the axis, where the electro-osmotic flow is zero, and the velocity gradient a min. Mobilities of quartz particles in  $\text{H}_2\text{O}$  so measured agree with vals. determined by the usual methods. The respective electrophoretic and electro-osmotic velocities of quartz in  $\text{H}_2\text{O}$  and of  $\text{H}_2\text{O}$  in a quartz tube are 3.0 and  $-3.1 \mu$  per sec. per volt per cm. F. L. U.

**$p_H$  conversion chart.** W. H. GOSS (J. Washington Acad. Sci., 1936, 26, 150—156).—The chart facilitates conversion of e.m.f. into  $p_H$  vals. with reference to various electrodes. A. G. P.

**Automatic precision burettes.** F. KÖHLER (Chem. Fabr., 1936, 9, 115—116).—The two types of burette described are filled automatically from the supply bottle to which they are attached, by the use of compressed air or suction, respectively. A. B. M.

**Precision apparatus for mixing gases in various proportions.** B. N. SINGH and P. B. MATHUR (Science, 1936, 83, 309—310). L. S. T.

**Washing tube for gas analyses.** O. HACKL (Z. anal. Chem., 1936, 104, 359).—Priority is claimed over Cauer (this vol., 577). J. S. A.

**Drainage errors and U-tube viscosimeters.**—See B., 1936, 436.

**Suspended-level viscosimeter.**—See B., 1936, 436.

**Specific gravity balance.** P. F. KERR (Amer. Min., 1936, 21, 121—124).—The apparatus described is particularly suitable for crystals, small masses of minerals, or gem stones. L. S. T.

**Arsenic combustion tubes.** G. LOCKEMANN (Angew. Chem., 1936, 49, 252).—Tubes with 2 and 3 compartments separated by constrictions, for use in the Marsh-Liebig method of As detection, are described. M. S. B.

**Sucrose as a standard for obtaining absolute viscosities.** T. H. MESSENGER (J. Res. Assoc. Brit. Rubber Manuf., 1936, 5, 25—35).—Viscosities and  $d$  of aq. sucrose solutions are tabulated and the use of such solutions as standards in viscosimetry is demonstrated. R. S.



**Micro-Kjeldahl flask.** A. SOLTYS (Mikrochem., 1936, 19, 304—305).—By setting the neck at an angle, loss by bumping or splashing is avoided. J. S. A.

**Simplified form of Schöbel heating mortar.** SCHOTT UND GEN. (Mikrochem., 1936, 19, 164; cf. A., 1934, 425). J. S. A.

**Apparatus for recrystallisation of small amounts.** B. K. BLOUNT (Mikrochem., 1936, 19, 162—163).—The substance, in a sintered glass funnel, is suspended below the condenser from which the solvent is refluxed. J. S. A.

**Demountable centrifuge tubes for gravimetric determinations.** S. D. ELEK (Mikrochem., 1936, 19, 129—131). J. S. A.

**Shaker with lengthwise and cross motions.** G. LOCKEMANN and P. LOCH (Chem. Fabr., 1935, 9, 200). D. R. H.

**Mirrors obtained by evaporation in a vacuum.** L. DUNOYER (Compt. rend., 1936, 202, 474—476).—In depositing a metallic mirror (e.g., Al) by evaporation it is essential for good adherence that the residual gas pressure should correspond with a mean free path of the same order as the max. distance of the vapour source from the surface to be covered. Deposits of uniform thickness can be obtained by suitable relative movement of source and surface. Flaws in the receiving surface, or defects in polishing, are reproduced in the deposited metal. In the absence of any defects the metallic surface, unlike chemical deposits, shows no diffuse reflexion. F. L. U.

**Comparative method for measuring aqueous vapour and dissociation pressures, with some applications.** E. M. COLLINS and A. W. C. MENZIES (J. Physical Chem., 1936, 40, 379—397; cf. A., 1934, 248).—The method described depends on measurement (by weighing) of the change in concn. of a small amount of aq.  $\text{H}_2\text{SO}_4$  during the attainment of equilibrium,

through the vapour phase, with a large amount of the material, the aq. v.p. of which is required. The substances are placed in an exhausted sealed tube, and equilibrium is approached from both directions. The method is suitable for temp. up to  $130^\circ$ . Data for six salt hydrate systems are recorded. F. L. U.

**Rapid and exact transference of a precipitate to a filter.** G. G. LONGINESCU and I. I. PRUNDEANU (Bull. Acad. Sci. Roumaine, 1936, 17, 151—154).—Pptn. and washing are carried out in a funnel, and the ppt. is transferred directly to the crucible. H. G. R.

**Sliding ground-glass joint.** J. FINE (Rev. Sci. Instr., 1936, [ii], 7, 192).—A short connecting piece has joints at each end ground on the inside, both tapers pointing in the same direction. It can therefore be telescoped over the tube which enters it at its narrower end. C. W. G.

**Simplified apparatus for high hydrostatic pressures.** L. H. ADAMS (Rev. Sci. Instr., 1936, [ii], 7, 174—177).—A simple piston is forced into a 19-mm. hole in a steel block. Leakage is prevented by a rubber plug and a layer of oil moving ahead of the piston. Pressure is measured by a Hg-in-glass piezometer tube inside the piston. 10,000 atm. can be reached. C. W. G.

**Average pore size of diaphragms.** H. B. BULL and L. S. MOYER (Science, 1936, 83, 242—243).—The radius of powdered quartz diaphragms ranged from 1.4 to  $30\ \mu$  according to the degree of grinding, whilst that of cellulose membranes varied from 0.88 to  $0.98\ \mu$ . L. S. T.

**Cullen chemical manuscript of 1753.** L. DOBBIN (Ann. Sci., 1936, 1, 138—156).

**Thomas Cochrane's MS. notes of Black's chemical lectures, 1767—1768.** D. MCKIE (Ann. Sci., 1936, 1, 101—110).

## Geochemistry.

**Explanation of the relatively large concentration of  $\text{O}^{18}$  in the atmosphere.** C. H. GREENE and R. J. VOSKUYL (J. Amer. Chem. Soc., 1936, 58, 693—694).—Attention is directed to the rôle played by the respiration of plants. E. S. H.

**Carbon dioxide content of atmospheric air.** J. B. S. HALDANE (Nature, 1936, 137, 575).—An improved form of the Haldane gas analysis apparatus adapted for the determination of  $\text{CO}_2$  only permits rapid analyses with an accuracy of 1 or 2 parts in  $10^5$  using 20 c.c. of air. The  $\text{CO}_2$  in country air at 4 to 70 ft. above ground level varied between 21 and 44 parts in  $10^5$ . Diurnal variation due to photosynthesis is marked between July and October, but not in December. Exhalation of  $\text{CO}_2$  from the soil is definite, the mean excess being 5.4 parts in  $10^5$  at ground-level compared with a height of 4 ft. above. The effect of combustion is marked, the average val. for London being 65 parts in  $10^5$ . Other variations due to causes at present uncertain are recorded. L. S. T.

**Alkali metals in natural waters.** R. BOSSUET (Compt. rend., 1936, 202, 1162—1164).—A large no. of samples of natural  $\text{H}_2\text{O}$  have been examined in the  $\text{O}_2\text{—C}_2\text{H}_2$  flame for alkali metals. The presence of Na and K increases the sensitivity of the test for Rb and Cs. All five alkali metals have been found in most cases, but Cs is absent (i.e.,  $< 10^{-3}$  mg. per litre) in certain cases where  $\text{Ca}(\text{HCO}_3)_2$  or  $\text{CaSO}_4$  predominate, and in some other samples. M. S. B.

**Chemical and physico-chemical analysis of the mineral water of Fontecchio.** L. BELLUCCI, M. SGARZI, and A. BARILLARO (Annali Chim. Appl. 1936, 26, 130—138).—The  $\text{H}_2\text{O}$  has an odour of  $\text{H}_2\text{S}$ . Analytical data, physico-chemical properties, and radioactivity are recorded. L. A. O'N.

**Activity of non-pathogenic bacteria in the thermal water of Aix-les-Bains and Aix-Burtscheid.** II. A. SCHLOEMER (Z. Unters. Lebensm., 1936, 71, 268—273; cf. A., 1933, 691; 1934, 53).—The  $\text{NO}_2^-$  in the thermal  $\text{H}_2\text{O}$  is due entirely to the



growth of nitrifying bacteria. The deposit is largely due to the action of  $\text{CaCO}_3$ - and  $\text{SiO}_2$ -bacteria, but deposition of  $\text{CaCO}_3$  is facilitated by the low  $\text{CO}_2$  content of the  $\text{H}_2\text{O}$ . E. C. S.

**Chemical and biological characteristics of the Lake of Massaciuccoli.** G. BRUNELLI and G. CANNICCI (Atti R. Accad. Lincei, 1935, [vi], 22, 598—604).—A preliminary description. O. J. W.

**Carbon dioxide and hydrogen ion content of the lake waters of N.E. Wisconsin.** C. JUDAY, E. A. BIRGE and V. W. MELOCHE (Trans. Wis. Acad. Sci., 1936, 29, 1—82).—Data for 518 lakes are recorded, showing annual variation and variation with depth. C. W. G.

**Analysis of thermal spring at Lipik.** S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1935, 6, 169—177).—The I content has diminished exponentially since 1870. R. T.

**Mineral water of Rogaska Slatina.** A. REŽEK (Bull. Soc. Chim. Yougoslav., 1935, 6, 179—187).—The  $\text{H}_2\text{O}$  activates salivary and pancreatic amylases (optimum  $p_{\text{H}}$  6.0—6.4 and 6.0—6.8, respectively). The mechanism of activation is discussed. R. T.

**Boron content of oil-field waters.** S. G. ZEITLIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 123—126).—Data are recorded for samples from the Baku, Dagestanskiye Ogni, Novogroznenskoie, and Turkestan regions. The borax content of the dry residue was 0.5—0.6%. H. J. E.

**Waters, magmatic and meteoric.** F. E. KEEP (Econ. Geol., 1936, 31, 118—121).—A discussion (cf. A., 1935, 1343) relating mainly to Witwatersrand water. L. S. T.

**Concentration of  $\text{D}_2\text{O}$  in natural ice. III.** E. BARONI and A. FINK (Monatsh., 1936, 67, 193—195; cf. A., 1935, 953).—Snow, independent of age, has the same  $\text{D}_2\text{O}$  content as normal  $\text{H}_2\text{O}$ , but hoar frost samples have 15—50% greater concn. than normal. It is concluded that concn. of  $\text{D}_2\text{O}$  is possible under natural conditions such as hoar frost formation and slow evaporation of glaciers. J. W. S.

**Theoretical consideration of ideal liquid inclusions.** S. T. YUSTER (Amer. J. Sci., 1936, [v], 31, 363—372).—Calculations are made of the temp. and pressures which existed at the time when liquids and gases were enclosed in crystals. L. J. S.

**Crystallisation process of basalt.** T. F. W. BARTH (Amer. J. Sci., 1936, [v], 31, 321—351; cf. A., 1931, 708, 816; 1932, 494).—Further discussion on the crystallisation of feldspar and pyroxene in basaltic magma with progressive alteration in the composition of the magma. L. J. S.

**Occurrence of claudetite in Imperial County, California.** V. C. KELLEY (Amer. Min., 1936, 21, 137—138).—An occurrence in a vein composed mainly of kaolin, gypsum, halloysite, and S is described. L. S. T.

**Accessory minerals of the Wolf Mountain granite, Llano County, Texas.** R. E. MCADAMS (Amer. Min., 1936, 21, 128—135).—The percentages of the accessory minerals biotite, hornblende, mag-

netite (I), muscovite, apatite (II), zircon (III), titanite (IV), monazite, rutile, chlorite, fluorite (V), garnet, tourmaline, brookite, ilmenite, and pyrite are tabulated. A yellow, isotropic mineral, as yet unidentified, is also present. The Wolf Mountain granite, the Bear Mountain granite, and the quartz porphyry have different accessory mineral assemblages. The former and the Lone Grove granites apparently had a common parent magma. The Bear Mountain granite, with its more abundant (V), is probably younger than these granites, and of the same age as the quartz porphyry. The ratio of (III) to (II) appears to increase toward the bottom of the Wolf Mountain mass, where (I) is also conc. The % of (IV) increases as the border of Wolf Mountain is approached. L. S. T.

**Chemical composition of the eruptive rock of Cupaello (Rieti).** F. RODOLICO (Atti R. Accad. Lincei, 1935, [vi], 22, 469—472).—The following composition is given:  $\text{SiO}_2$  42.64,  $\text{TiO}_2$  0.87,  $\text{P}_2\text{O}_5$  1.26,  $\text{SO}_2$  0.62,  $\text{Al}_2\text{O}_3$  7.01,  $\text{Fe}_2\text{O}_3$  5.78,  $\text{FeO}$  1.66,  $\text{MnO}$  0.16,  $\text{MgO}$  10.86,  $\text{CaO}$  14.53,  $\text{Na}_2\text{O}$  0.71,  $\text{K}_2\text{O}$  5.61,  $\text{H}_2\text{O} +$  6.22,  $\text{H}_2\text{O} -$  2.28, total 100.21%; d 2.61. O. J. W.

**New crystal-bearing glass from Macusani (Peru).** F. HEIDE (Naturwiss., 1936, 24, 281—282).—A description of a glass containing crystals, and identical with that discovered by Linck (Chem. Erde, 1926, 2, 157) at Paucartambo (Peru), is given. A. J. M.

**Ore-bearing zones of the metal deposits of Karakstan.** N. KASSIN (Problem. Sovet. Geol., 1933, 4, 58—63).—The deposits are described. CH. ABS. (e)

**Radium discoveries in N.W. Canada.** H. S. SPENCE (Sands, Clays and Min., 1935, 2, No. 3, 8—23).—A review. H. J. E.

**Zermattite and schweizerite from Dshemarakly-tjube Mt. in the Karatschai region, Caucasus.** D. SERDIUTSCHENKO (Mém. Soc. russe Min., 1932, 61, 94—100).—These minerals were deposited from  $\text{H}_2\text{O}$  solutions genetically connected with the intrusion of a quartz-keratophyre, and are exceptionally rich in  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ . CH. ABS. (e)

**Petrology of the Hartley district. III. Contact metamorphism of the upper Devonian (Lambian) series.** G. A. JOPLIN (Proc. Linnean Soc. N.S. Wales, 1935, 60, 16—50). CH. ABS. (e)

**Bolivian tin belt.** F. AHLFELD (Econ. Geol., 1936, 31, 48—72).—The Bolivian metallogenetic province contains chiefly Sn, W, Mo, As, Bi, Cu, Zn, Pb, Sb, commonly Ag, and rarely Au, Ni, Co, and Hg. B is very common, whilst Be and U are absent. The minerals and their paragenesis, the rock alteration, and the ore deposits are described, and the genesis of the deposits is discussed. L. S. T.

**Hydrothermal oxidation of manganese minerals.** S. A. TRENGOVE (Econ. Geol., 1936, 31, 29—47).—Rhodochrosite (I) is readily decomposed and oxidised by steam in 24 hr. at temp.  $> 170^\circ$ . Pyrolusite is probably present in the alteration product. Oxidation increases with temp. up to approx.  $300^\circ$ , above which temp. complex alteration products



are formed. High pressure or the addition of  $\text{CO}_2$  to the steam retards decomp. Oxidation occurs slowly at high pressures when small amounts of  $\text{HCl}$  are present and more rapidly at pressures nearer 1 atm. (I) is stable at room temp. in air, and at  $250^\circ$  when steam or other sources of  $\text{O}_2$  is absent. Decomp. commences at approx.  $275^\circ$  and oxidation due to the decomp. of the contained  $\text{CO}_2$  occurs. Fowlerite shows no hydrothermal oxidation at temp.  $> 400^\circ$ . The bearing of these results on the genesis of Mn oxide ore deposits in various parts of the world is discussed. L. S. T.

**Battle Branch gold mine, Auraria, Georgia.** C. F. PARK, jun., and R. A. WILSON (Econ. Geol., 1936, 31, 73—92).—The mineralogy of the deposit is unusual and three stages are recognised. An early high-temp. stage produced coarsely cryst. silicates, such as garnet (almandite common), cummingtonite, kyanite, and micas, probably formed by recrystallisation of minerals in the country rock. During an intermediate stage ankerite, quartz, and pyrrhotite were deposited, and the last stage produced chlorite, galena (I), and Au. The Au in the rich shoots is contemporaneous with (I) and is of hypogene origin. The soil and saprolite extend to a max. depth of 80 ft., and mechanical enrichment of Au has occurred in the latter. L. S. T.

**Geology and ore deposits of the Central Patricia gold mine, Ontario.** J. M. CORMIE (Econ. Geol., 1936, 31, 93—103).—These ore bodies are sulphide-rich masses formed by fracture filling and by replacement of the Fe formation in which they occur. Pyrrhotite (I) and arsenopyrite (II) are predominant, whilst chalcopyrite (III) and pyrite (IV) are less abundant. The non-metallic minerals are quartz (black and white), chlorite, and carbonate. Au is the only economically valuable mineral in the ores and is associated with all the sulphides except (IV); Ag is present in minor amounts. The mineral succession is (IV), quartz veins; fracturing; (I), (III), and gangue; fracturing; (II); fracturing. The hypothermal genesis of the deposit is discussed. L. S. T.

**Cinnabar deposits in S.W. Arkansas.** N. H. STEARN (Econ. Geol., 1936, 31, 1—28).—The deposits occurring in the Athens Plateau are described. The ores are mainly fracture fillings in the sandstone with dickite, cinnabar, and quartz as the principal minerals, and small amounts of pyrite, stibnite, and siderite. They are hydrothermal in origin. The tenor of the ore in place is approx. 10 lb. of Hg per ton of rock. Secondary minerals are meta-cinnabar, Hg, eglestonite, livingstonite, calomel, chaledony or opal, hydrated Fe oxide, and stibiconite. L. S. T.

**High-temperature mineral associations at moderate to shallow depth.** B. S. BUTLER (Econ. Geol., 1936, 31, 115—118).—A discussion (cf. A., 1935, 955). L. S. T.

**Gabbros and associated xenolithic complexes of the Haddo House district, Aberdeenshire.** H. H. READ (Quart. J. Geol. Soc., 1935, 91, 591—638).—The country rocks into which the Haddo

House igneous masses intrude consist of andalusite-cordierite-schists, pebbly grits, and cordierite-biotite-gneisses. The gabbro mass consists of olivine- and quartz-gabbro, both considered to be of primary igneous origin, and norite and cordierite-norite which contain abundant xenoliths. The mechanism of the production of the noritic rocks, by assimilation of argillaceous material, is discussed. The gabbros and their xenolithic complexes are intruded by a later granite and by innumerable granitic and pegmatitic dykes. The conditions of formation of monomineralic calc-silicate rocks, such as those of diopside and wollastonite, are discussed. L. S. T.

**Base of the Gault in Sussex.** J. F. KIRKALDY (Quart. J. Geol. Soc., 1935, 91, 519—537).—The glauconitic sandy clays and layers of hard phosphatic nodules composing the base of the Gault and a bed of limonitic grit are described. Conditions of deposition of the beds are discussed. L. S. T.

**Basic intrusive rocks associated with the Cambrian inlier near Malvern.** F. G. H. BLYTH (Quart. J. Geol. Soc., 1935, 91, 463—478).—A petrological and chemical examination of minor intrusions in the Cambrian strata near Eastnor, Herefordshire. L. S. T.

**Age relations of the Ward ores, Boulder County, Colorado.** E. E. WAHLSTROM (Econ. Geol., 1936, 31, 104—114).—Structure, paragenesis, and age relations of the ore deposits of the Ward district are discussed. The predominant mineralisation is auriferous quartz-pyrite-chalcopyrite ores occasionally with small amounts of molybdenite, wolframite, sphalerite, and specularite. At White Raven mine important amounts of galena-Ag carbonate ore occur. The Au-Cu ore was probably deposited under conditions of medium to high temp. and high pressure from solutions originating from the same magma chamber which gave rise to the Tertiary (?) intrusives. The Pb-Ag ore was probably deposited under conditions of low to medium temp. L. S. T.

**Occurrence and properties of herzenbergite.** P. RAMDOHR (Z. Krist., 1935, 92, 186—189).—A description of naturally occurring  $\text{SnS}$ . B. W. R.

**Dielectric constant of mineral powders.** J. L. ROSENHOLTZ and D. T. SMITH (Amer. Min., 1936, 21, No. 2, 11 pp.).—Data for 160 minerals are recorded. C. W. G.

**Scheelite from the mines of Gerrei in Sardinia.** A. PELLOUX (Atti R. Accad. Lincei, 1935, [vi], 22, 554—556).—Crystallographic data are recorded. O. J. W.

**Geochemical frequency of barium.** C. J. VAN NIEUWENBURG and R. H. DEWALD (Rec. trav. chim., 1936, 55, 263—266).—The Ba content of igneous rocks is  $<$  the Sr content. E. S. H.

**Enrichment of heavy spar by alkaline weathering solutions in a Frankish keuper-arkose, and its regional and geochemical significance.** S. KLEIN (Z. deut. geol. Ges., 1935, 87, 320—332; Chem. Zentr., 1935, ii, 1152).—The origin of  $\text{BaSO}_4$  deposits by the solvent action of alkali carbonates on feldspar is discussed. J. S. A.



**Granitic injection processes in the Columbia quadrangle, South Carolina.** T. L. KESLER (J. Geol., 1936, 44, 32—44).—The effects of intrusion of granite are described. L. S. T.

**Clay colloids as a cause of bedding in sedimentary rocks.** W. D. KELLER (J. Geol., 1936, 44, 52—59).—Colloidal clay of the montmorillonite-beidellite group extracted from the Putnam soil of Missouri flocculates to relatively coarse aggregates oriented so as to resemble crystals. Their platy shape resembles that of the mineral in a bedded clay shale. The possibility that the lamination of shale develops from deposition of colloidal clay is discussed. L. S. T.

**Probable non-existence of arsenoferrite.** M. J. BUEGER (Amer. Min., 1936, 21, 70—71).—X-Ray examination of the apparently isotropic mineral of composition corresponding with  $\text{FeAs}_2$  described by Poshag and Short (A., 1931, 817) shows that the mineral is not cubic and that it is identical with lollingite. L. S. T.

**X-Ray powder diffraction data for antlerite and brochantite.** A. W. WALDO (Amer. Min., 1936, 21, 71—73).—The data previously given for antlerite (1) (A., 1935, 1474) apply to brochantite and not to (1). L. S. T.

**Andalusite in pegmatite.** J. MURDOCH (Amer. Min., 1936, 21, 68—69).—Pegmatite dykes cutting the magnesite deposits at Winchester, California, contain reddish-brown andalusite (I). Sillimanite replaces some of the (I). L. S. T.

**Bustamite from [Saline Valley,] Inyo County, California.** J. MURDOCH and R. W. WEBB (Amer. Min., 1936, 21, 69—70).—Bustamite occurs in numerous boulders of a silicate rock. L. S. T.

**Analyses of thulite.** S. A. NORTHROP (Amer. Min., 1936, 21, 73).—An additional analysis is recorded (this vol., 308). L. S. T.

**Distribution of the chief mineral deposits of Morocco.** F. BLONDEL and J. BONDON (Compt. rend., 1936, 202, 1197—1198).—Recent data on the age, distribution, and origin of the different mineral deposits of Morocco are summarised. M. S. B.

**Ligneous substances in lacustrine materials.** J. F. STEINER and V. W. MELOCHE (Trans. Wis. Acad. Sci., 1935, 29, 389—402).—Analyses for C, N, protein, and lignin are given. C. W. G.

**Vanadium in the petroleum and bitumens of the U.S.S.R.** A. P. VINOGRADOV and G. G. BERGMAN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 349—352; cf. A., 1934, 1380).—The distribution of V in the petroleum and bitumens of the U.S.S.R. has been determined. Deposits of the Devonian period contain the highest and those of the Jurassic period the lowest % of V. From much of the data it appears that V occurs  $\propto$  the % of org. matter in the rock, in Ishma asphaltite. The view that V passes into the petroleum from aq. solution in presence of  $\text{H}_2\text{S}$ , the V being held as  $\text{V}_2\text{S}_5$ , is considered disproved. It is probable that the V comes from the mud of continental sea basins in which V has been conc. by marine organisms. R. S. B.

**Extra-terrestrial hydrocarbons and petroleum genesis.** F. M. VAN TUYL and B. H. PARKER (Bull. Amer. Assoc. Petroleum Geol., 1935, 19, 900—902).—A discussion. CH. ABS. (e)

**Age and conditions of formation of brown coals in the Upper Zeya plain.** G. E. BRIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 355—359).—Brown coals of *d* 1.44 found in the Sektakhan mountains are described. R. S. B.

## Organic Chemistry.

**Structural chemistry.** N. V. SIDGWICK (J.C.S., 1936, 533—538).—Presidential address.

**Action of aluminium chloride on paraffins. Autodestructive alkylation.** V. N. IPATIEV and A. V. GROSSE (Ind. Eng. Chem., 1936, 28, 461—464).— $n\text{-C}_4\text{H}_{10}$ ,  $\text{-C}_6\text{H}_{14}$ ,  $\text{-C}_7\text{H}_{16}$ , or  $\beta\beta\delta$ -trimethylpentane with  $\text{AlCl}_3$  and  $\text{HCl}$  gives complex mixtures of paraffins of lower and higher mol. wt. together with unsaturated hydrocarbons according to four types of reaction: (a) formation of paraffin and olefine of lower mol. wt.; (b) addition of olefine to paraffin; (c) isomerisation regarded as (a) followed by (b); (d) polymerisation of olefines followed by (b). The products were separated by Podbielniak distillation, b.p. and  $n_D^{20}$  being recorded for the fractions obtained. F. R. G.

**Isomerisation of hydrocarbons. II. Isomerisation of *n*-hexane and *n*-octane in presence of aluminium chloride.** B. L. MOLDAVSKI, M. V. KOBILSKAJA, and S. E. LIFSCHITZ (J. Gen. Chem. Russ., 1935, 5, 1791—1797).—Up to 30% of  $n\text{-C}_6\text{H}_{14}$  or  $\text{-C}_8\text{H}_{18}$  is converted into *iso*- $\text{C}_6\text{H}_{14}$  or  $\text{-C}_8\text{H}_{18}$  by

the action of  $\text{AlCl}_3$  at 20—90°. The velocity of the reaction is greatly increased by  $\text{HCl}$ . R. T.

**Preparation of isooctane.** G. S. PARKS and S. S. TODD (Ind. Eng. Chem., 1936, 28, 418—419).—The temp. conditions for the conversion of *isobutene* into  $\beta\beta\delta$ -trimethylpentane are deduced from thermochemical data. F. R. G.

**Methylnonanes.** G. CALINGAERT and H. SOROOS (J. Amer. Chem. Soc., 1936, 58, 635—636).—The following are obtained by simultaneous dehydration and hydrogenation of the alcohols quoted with  $\text{H}_2$  (200 atm.) and Raney Ni at 250° (after the preliminary absorption of  $\text{H}_2$  ceases, the  $\text{H}_2\text{O}$  formed is removed and the product reduced further):  $\beta$ -methylnonane (I), b.p. 166.8°/760 mm., m.p.  $-74.69 \pm 0.05^\circ$  ( $\beta$ -methylnonan- $\gamma$ -ol, from  $\text{MgPr}^2\text{Br}$  and  $n\text{-C}_6\text{H}_{13}\text{CHO}$ );  $\gamma$ -methylnonane (II), b.p. 167.8°/760 mm., m.p.  $-84.86 \pm 0.03^\circ$  ( $\gamma$ -methylnonan- $\gamma$ -ol, from  $\text{MgEtBr}$  and *Me n*-hexyl ketone);  $\delta$ -methylnonane, b.p. 165.7°/760 mm., m.p.  $-101.62 \pm 0.05^\circ$  (f.p. and m.-p. curves indicate a second form of m.p.  $-99 \pm 0.1^\circ$ ) ( $\delta$ -methylnonan- $\delta$ -ol, from  $\text{MgPr}^2\text{Br}$  and *Me*



*n*-amyl ketone);  $\epsilon$ -methylnonane, b.p. 165.1°/760 mm., m.p.  $-86.8 \pm 0.03^\circ$  ( $\epsilon$ -methylnonan- $\epsilon$ -ol, from  $\text{MgBu}^\circ\text{Br}$  and  $\text{EtOAc}$ ). Vals. of  $d_4^{20}$ ,  $n_D^{20}$ , and crit. solution temp. in  $\text{NH}_2\text{Ph}$  are given. The influence of structure on the physical properties is discussed. The data for (I) and (II), compared with *n*-decane, are in agreement with those predicted (this vol., 309).

H. B.

**Olefine elimination.** E. D. HUGHES and C. K. INGOLD (Chem. and Ind., 1936, 312—313, 422).—Polemical with Taylor (this vol., 587).

**Olefine formation.** W. TAYLOR (Chem. and Ind., 1936, 383—384).—Polemical (see above).

**Polymerisation.** XV. Polymerisation of *n*-butylene. S. V. LEBEDEV and S. M. ORLOV. XVI. Polymerisation of isobutylene by the action of floridin at low temperatures. S. V. LEBEDEV and J. A. BORGMAN (J. Gen. Chem. Russ., 1935, 5, 1589—1594, 1595—1606).—XV.  $\text{CHMe}:\text{CHMe}$  (I) yields 80—85% of polymerides when left with floridin at room temp. for 6 months; the product contains 43% of the dimeride (II), b.p. 115—116°/756 mm., and 15—18% of the trimeride (III) of (I), b.p. 78—79°/18 mm. (II) is oxidised by  $\text{KMnO}_4$  in aq.  $\text{COMe}_2$  at room temp. to yield  $\text{COMe}:\text{CHMeEt}$  (IV),  $\gamma\delta$ -dimethylhexane- $\beta\gamma$ -diol (V), b.p. 110—112°/14 mm., m.p. 55°, *Me*  $\alpha$ -hydroxy- $\alpha\beta$ -dimethylbutyl ketone (VI), b.p. 110—118°/14 mm. (semicarbazone, m.p. 170°),  $\text{COMeEt}$ ,  $\text{AcOH}$ , and  $\text{EtCO}_2\text{H}$ ; it is hence concluded that (II) is  $\text{CHMeEt}:\text{CHMe}$ . The oxidation of (II) proceeds as follows: (II)  $\rightarrow$  (V)  $\rightarrow$  (VI)  $\rightarrow$  (IV)  $\rightarrow$   $\text{COMeEt} + \text{EtCO}_2\text{H} + \text{AcOH}$ .

XVI. The % polymerisation of  $\text{CMe}_2:\text{CH}_2$  in presence of floridin increases to a max. as the temp. falls to  $-65^\circ$ , and is greatest when the activation temp. of the catalyst is  $300^\circ$ . The mol. wt. of the polymerides rises uninterruptedly with falling temp.; formation of products of high mol. wt. is most actively catalysed by floridin activated at  $200^\circ$ . The mol. wt. of the polymerides varies from 112 to 12,000. The polymerides obtained at  $-70^\circ$  with floridin activated at  $300^\circ$  consist of  $\text{C}_8\text{H}_{16}$  3.4,  $\text{C}_{12}\text{H}_{24}$  20.7,  $\text{C}_{16}\text{H}_{32}$  15.3,  $\text{C}_{24}\text{H}_{48}$  10.8,  $\text{C}_{28}\text{H}_{56}$  5.4, and higher polymerides 44.4%.

R. T.

**Action of certain silicates on hydrocarbons possessing the *tert.*-butyl radical.** S. V. LEBEDEV and N. A. KUDRJAFTZEV (J. Gen. Chem. Russ., 1935, 5, 1859—1865).—In presence of floridin  $\text{CHBu}^\circ:\text{CH}_2$  is converted into  $\text{CMe}_2:\text{CMe}_2$  (I) ( $160-170^\circ$ ), and  $\text{CHBu}^\circ:\text{CHMe}$  into  $\text{CMe}_2:\text{CMeEt}$  (II) ( $150-270^\circ$ ), whilst (I), (II), and  $\text{CBu}^\circ:\text{CH}$  ( $145-360^\circ$ ) are unaffected.

R. T.

**Determination of piperylene by means of maleic anhydride.** V. P. KRAUSE, A. M. KOGAN, and M. A. POLIEVKTOVA (Sintet. Kautschuk, 1934, No. 3, 30—33).—Piperylene with maleic anhydride (I) forms 3-methyl- $\Delta^4$ -tetrahydrophthalic anhydride and rubber-like polymerides. The reaction is carried out in a weighed sealed flask for 30 min. at  $70-75^\circ$ , the product which is non-volatile in vac. at room temp. being weighed. Excess of (I) decreases the formation of polymeride.

CH. ABS. (e)

**Determination of diallyl and dipropenyl in their mixtures by the hydrogenation method.** J. M. SLOBODIN (J. Gen. Chem. Russ., 1935, 5, 1830—1832).—Dipropenyl (I) undergoes hydrogenation only after complete saturation of diallyl (II); the composition of (I)-(II) mixtures can be determined from velocity of hydrogenation data.

R. T.

**Dimerisation of  $\Delta^{\alpha\gamma}$ -butadiene.** S. V. LEBEDEV and S. R. SERGIENKO (J. Gen. Chem. Russ., 1935, 5, 1839—1858).—Divinyl is converted into  $\Delta^3$ -cyclohexenylethylene (I) by heating at  $150^\circ$  for 120 hr.; (I) yields *cis*-, m.p.  $74-75^\circ$ , and *trans*-3:4-dibromo-1- $\alpha\beta$ -dibromoethylcyclohexane, m.p.  $101.5^\circ$ , and  $\alpha$ -bromoethyl-, b.p.  $102-104^\circ/20$  mm., and  $\alpha\beta$ -dibromoethyl- $\Delta^3$ -cyclohexene, b.p.  $105-118^\circ/3$  mm., with Br in  $\text{Et}_2\text{O}$  at  $0^\circ$ . (I) is very gradually converted at  $150^\circ$  into  $\Delta^1$ -cyclohexenylethylene.

R. T.

**Raman effect and organic chemistry.** Allyl isomerism in the case of the bromohexenes. (MLLES.) H. VAN RISSEGHEM and B. GREY (Compt. rend., 1936, 202, 489—491).— $\text{PBr}_3$  and propylvinylcarbinol give  $\text{CHPrBr}:\text{CH}:\text{CH}_2$  (I) and  $\text{CHPr}:\text{CH}:\text{CH}_2\text{Br}$  (II), separated by distillation under reduced pressure. Isomerisation of (I) and (II) into an equilibrium mixture [90—95% (II)] occurs on repeated distillation at  $100^\circ$  in a sealed tube, and was followed by means of the Raman lines near  $1650\text{ cm}^{-1}$  characteristic of the double linking. The isomerisation of (I) and (II) explains the formation of the same mixture from either of the corresponding alcohols.

H. G. M.

**Bromides obtained by action of phosphorus tribromide on propylvinylcarbinol, and the corresponding acetates.** (MLLES.) B. GREY and H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1930, 45, 177—185).—Propylvinylcarbinol with  $\text{PBr}_3$  in  $\text{C}_5\text{H}_5\text{N}$  below  $0^\circ$  affords *trans*- $\Delta^3$ -hexene (I), b.p.  $57.5-58^\circ/25$  mm., and  $\gamma$ -bromo- $\Delta^3$ -hexene (II), b.p.  $51-52^\circ/36$  mm. On keeping (I) passes partly into (II) (cf. A., 1935, 1480; also preceding abstract). (I) with  $\text{NaOAc}$  affords *trans*- $\Delta^3$ -hexenyl acetate (III) (cf. A., 1928, 1112), whilst (II) gives a mixture of  $\gamma$ -acetoxy- $\Delta^3$ -hexene, b.p.  $49-50^\circ/16$  mm., and (III). Either Ac derivative is stable at  $100^\circ$ .

J. L. D.

**Alkylacetylenes and their additive compounds.** IX. Reaction of allyl bromide with acetylenic Grignard reagents. J. P. DANEHY, D. B. KILLIAN, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 611—612).— $\text{CH}_2:\text{CH}:\text{CH}_2:\text{C}:\text{CR}$  (I) could not be prepared from  $\text{CH}_2:\text{CH}:\text{CH}_2\text{Br}$  (II) and  $\text{CR}:\text{C}:\text{MgX}$  in  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , or di-*n*-amyl ether; reaction occurs, however, in presence of anhyd.  $\text{Cu}_2\text{Cl}_2$  or  $\text{Cu}_2\text{Br}_2$ , and to a smaller extent with  $\text{Cu}_2(\text{CN})_2$  or  $\text{CuHal}_2$ . Cu-bronze,  $\text{Cu}_2\text{S}$ , and  $\text{CuS}$  are not catalysts. Vinyl-[(I)  $\text{R}=\text{CH}_2:\text{CH}:$ ], b.p.  $109-110^\circ/750$  mm. (explodes violently on attempted combustion), butyl-, b.p.  $58^\circ/22$  mm., amyl-, b.p.  $73-74^\circ/22$  mm., and phenyl-, b.p.  $107-108^\circ/22$  mm., -alkylacetylenes are described.  $\beta$ -Methyl- $\Delta^7$ -octinen- $\beta$ -ol, b.p.  $92-93^\circ/33$  mm., is formed from  $\text{COMe}_2$  and  $\text{CBu}^\circ:\text{C}:\text{MgBr}$  even in presence of (II).

H. B.

**Trifluoronitrosomethane,  $\text{CF}_3\text{NO}$ .** III. O. RUFF and M. GIESE (Ber., 1936, 69, [B], 684—689).—



The production of trifluoronitrosomethane by the action of F on technical AgCN is due to the presence of  $\text{AgNO}_3$  or, possibly,  $\text{Ag}_2\text{O}$ ; the best yields are obtained from  $\text{AgCN}-\text{CaF}_2-\text{KNO}_3-\text{Ag}_2\text{O}$  (1:2:0.3:0.3). The blue fraction, formerly regarded as homogeneous  $\text{CF}_3\cdot\text{NO}$ , corresponds in all portions according to mol. wt. and analyses with the at. ratio  $\text{CF}_3\cdot\text{NO}$ . It has b.p.  $-84^\circ$ , m.p.  $-196.6^\circ$ . The gas is unchanged in contact with glass, 96%  $\text{H}_2\text{SO}_4$ , 60%  $\text{HNO}_3$ , 35%  $\text{HCl}$ ,  $\text{Hg}$ ,  $\text{AcOH}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CrO}_3-\text{AcOH}$ ,  $\text{HSO}_4$ ,  $\text{KMnO}_4$  with 10%  $\text{H}_2\text{SO}_4$  or  $\text{AcOH}$ ,  $\text{H}_2\text{O}_2$ , or  $\text{H}_2\text{S}$ , but becomes decolorised in presence of 8%  $\text{NaOH}$ , active C,  $\text{Mn}_2\text{O}_7$  in  $\text{AcOH}$ , Zn dust and  $\text{AcOH}$ , Pd-sponge and dil.  $\text{HCl}$ . It therefore contains about 50–48% of the colourless isomeride  $\text{COF}\cdot\text{NF}_2$  which is so stable that the chemical properties of the blue fraction are almost identical with those of homogeneous  $\text{CF}_3\cdot\text{NO}$ . H. W.

**Chlorofluoroethanes and chlorofluoroethyl-  
enes.** II. A. L. HENNE and E. C. LADD. III. A. L. HENNE and D. M. HUBBARD (J. Amer. Chem. Soc., 1936, 58, 402–403, 404–406; cf. A., 1934, 1089).—II. The prep. of the following compounds is described:  $\text{CHCl}_2\cdot\text{CCl}_2\text{F}$ , m.p.  $-82.6^\circ$ , b.p.  $116.6^\circ$ ;  $\text{CHClF}\cdot\text{CCl}_3$ , m.p.  $-95.35^\circ$ , b.p.  $117.0^\circ$ ;  $\text{CHCl}_2\cdot\text{CClF}_2$ , b.p.  $71.9^\circ$ ;  $\text{CHClF}\cdot\text{CCl}_2\text{F}$ , b.p.  $72.5^\circ$ ;  $\text{CHF}_2\cdot\text{CCl}_3$ , b.p.  $73.0^\circ$ ;  $\text{CHClF}\cdot\text{CF}_2\text{Cl}$ , b.p.  $28.0^\circ$ ;  $\text{CHF}_2\cdot\text{CF}_2\text{Cl}$ , b.p.  $-12^\circ$ ;  $\text{CHF}\cdot\text{CCl}_2$ , m.p.  $-108.8^\circ$ , b.p.  $37.3^\circ$ ;  $\text{CHCl}\cdot\text{CClF}$ , b.p.  $35.1^\circ$ ;  $\text{CHCl}\cdot\text{CF}_2$ , b.p.  $2.4^\circ$ ;  $\text{CHClBr}\cdot\text{CClFBr}$ , b.p.  $163.5^\circ$ ;  $\text{CHClBr}\cdot\text{CF}_2\text{Br}$ , b.p.  $118.7^\circ$ . The preferential course of fluorination during synthesis is discussed.

III. Fluorination of  $\text{CH}_2\text{Cl}\cdot\text{CCl}_3$  with  $\text{SbF}_3$  gives  $\alpha\beta\beta$ -trichloro- $\beta$ -fluoroethane, m.p.  $-104.7^\circ$ , b.p.  $88.0^\circ$ , and  $\alpha\beta$ -dichloro- $\beta\beta$ -difluoroethane, m.p.  $-101.2^\circ$ , b.p.  $46.8^\circ$ . E. S. H.

**Preparation of *n*-heptyl bromide.** C. L. TSENG, T. S. HO, and (Miss) P. T. CHIA (Sci. Rep. Nat. Univ. Peking, 1936, 1, 17–18).— $\text{HBr}-\text{H}_2\text{SO}_4$ ,  $\text{NaBr}-\text{H}_2\text{SO}_4$ , and  $\text{PBr}_3$  give 66–69, 60.4, and 64.5%, respectively, of  $n\text{-C}_7\text{H}_{15}\text{Br}$ . R. S. C.

**Hydroxyl linking in *n*-aliphatic alcohols.** D. A. WILSON (Nature, 1936, 137, 617–618).—A discussion. L. S. T.

**Hydrogen linking between oxygen atoms in organic compounds.** G. E. HILBERT, O. R. WULF, S. B. HENDRICKS, and U. LIDDEL (J. Amer. Chem. Soc., 1936, 58, 548–555; cf. A., 1935, 563).—The following compounds give no infra-red absorption characteristic of mols. containing the OH group:  $\text{CH}_3\text{Ac}$ ,  $\text{CH}_3\text{BzAc}$ ,  $\text{CH}_3\text{Bz}$ ,  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , *p*-homosalicylaldehyde, Me and Ph salicylates, Me 3:5-dibromosalicylate,  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , 2:1- $\text{C}_{10}\text{H}_6\text{Ac}\cdot\text{OH}$ , 1:2- $\text{C}_{10}\text{H}_6\text{Bz}\cdot\text{OH}$ , 2-hydroxy-5-methylbenzophenone, dihydrorotenol, 1-hydroxyanthraquinone,  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ ,  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , 2:6-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\cdot\text{OH}$ , 1:2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , 1:4:1:5, and 1:8-dihydroxyanthraquinones, 5:8-dihydroxy-1:4-naphthaquinone, naphthazarin, 2:4- and 4:6-diacetyl- and -dinitro-resorcinols, 2-nitro-resorcinol, 2:2'-dihydroxy-1:1'-dinaphthyl sulphone, 2:2'-dihydroxybenzophenone, derritol, and Et 2:5-dihydroxyterephthalate. The above compounds are

chelated (singly or doubly) through H. The following show OH absorption (which often differs from that of simple alcohols) and are not, therefore, chelated: aldol,  $\alpha$ - and  $\beta$ -benzilmonoximes, benzoin,  $\alpha$ - and  $\beta$ -benzoinoxime acetates, Et and Bu<sup>a</sup> *d*-tartrates, Et mesotartrate,  $o\text{-C}_6\text{H}_4(\text{OH})_2$ , and  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ . 9-Keto-10-nitromethyl-9:10-dihydro-10-phenanthrol is considered not to contain a H linking. 3-Nitropyrocatechol appears to contain a single chelate linking (cf. Baker, A., 1935, 85). Et 3:6-dibromo-2:5-dihydroxyterephthalate (I) is probably not chelated; the  $\text{CO}_2\text{Et}$  groups are probably displaced owing to the proximity of the Br. A structure is suggested for (I); it indicates the possibility of *cis*- and *trans*-forms of (I) and resolution of, e.g., alkyl 3-bromo-4- or -5-aminosalicylates. H. B.

**Reaction products of ethyl alcohol and sodium hydroxide.** D. WILLIAMS and R. W. BOST (J. Chem. Physics, 1936, 4, 251–253).— $\text{NaOH}$  and  $\text{EtOH}$  when heated in the absence of  $\text{H}_2\text{O}$  form  $\text{NaOEt}$  and  $\text{H}_2\text{O}$ , which latter can be detected by means of its absorption band at  $4.7\ \mu$ , by the Cu acetylide method, and by its reaction with  $\text{CaC}_2$ . The reaction goes to 75–100% completion. L. J. J.

**Mechanism of contact conversion of alcohols into diethylenic hydrocarbons by the method of S. V. Lebedev.** J. A. GORIN and O. M. NEIMARK (J. Gen. Chem. Russ., 1935, 5, 1772–1780).—The chief product obtained when  $\text{PrOH}$  is passed over a mixed dehydrating-dehydrogenating catalyst (not specified) at  $400^\circ$  is  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CHMe}$ ;  $\text{CHMe}\cdot\text{CH}_2$ ,  $\text{EtCHO}$ ,  $\text{CMe}_2\cdot\text{CHEt}$ , isohexane, and  $\text{H}_2$  are obtained as by-products. R. T.

**Highly unsaturated alcohols in sperm blubber oil.** Y. TOYAMA and G. AKIYAMA (Bull. Chem. Soc. Japan, 1936, 11, 29–34).—The high-boiling fraction of the unsaponifiable matter of the oil contains clupanodonyl (docosapentenol; A., 1926, 1226) and catadonyl (eicosatetraenol; Br<sub>8</sub>, blackens at about  $240^\circ$ , and *Ac* derivatives) alcohols. The latter is hydrogenated to *n*-eicosanol. H. G. M.

**Hydrogenation of acetylene derivatives.** XXIII. Dihexylbutinenediol. J. S. SALKIND [with V. I. TZERESCHKO] (J. Gen. Chem. Russ., 1935, 5, 1768–1771).—Two isomerides of  $(\text{Me}\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{OH})\cdot\text{C})_2$  are described, (I), m.p.  $47-49^\circ$ , and (II), m.p.  $68-70^\circ$ . (I), when hydrogenated (Pd), yields two isomerides of  $(\text{Me}\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{OH})\cdot\text{CH})_2$ , one (III), m.p.  $44-45^\circ$ , and the other (IV) an oil, b.p.  $195-200^\circ/14\ \text{mm}$ . (dibromide, m.p.  $140^\circ$ ); (III) gives hexadecane- $\eta\kappa$ -diol (V), m.p.  $85-86^\circ$ , and (IV) an isomeride (VI) of (V), m.p.  $105-106^\circ$ , when further hydrogenated. The dibromide, m.p.  $97-98^\circ$ , obtained from the mixture of (I) and (II) eliminates Br when treated with Zn in  $\text{EtOH}$ , to yield a product (VII), m.p.  $53-54^\circ$ , isomeric with (II). It is concluded that (I) is a mixture of optical (?) isomerides, and that hydrogenation proceeds as follows: (VII)  $\rightarrow$  (III)  $\rightarrow$  (V); (II)  $\rightarrow$  (IV)  $\rightarrow$  (VI). R. T.

**Catalytic action of monoses on the condensation of aldehydes.** II. Synthesis of pentarythritol. A. KUZIN (J. Gen. Chem. Russ. 1935



5, 1527—1529).—Glucose or fructose catalyses the condensation of  $\text{CH}_2\text{O}$  and  $\text{MeCHO}$  to pentaerythritol.

R. T.

**Isomeric monoalkyl ethers of  $\beta$ -methylpropane- $\alpha\beta$ -diol from  $\alpha\beta$ -epoxy- $\beta$ -methylpropane.** C. E. SPARKS and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 671—672).— $\alpha\beta$ -Epoxy- $\beta$ -methylpropane (I) (1 mol.) with 3 mols. of  $\text{MeOH}$ ,  $\text{EtOH}$ , and  $\text{Pr}^\text{OH}$  (rate of reaction and yield diminish in this order) at 230—270° under pressure give  $\text{OAlk}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$  [ $\text{Alk}=\text{Pr}^\text{a}$  (II), b.p. 162—163°/739.2 mm.] and  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OAlk}$  [ $\text{Alk}=\text{Pr}^\text{a}$ , b.p. 147—147.5°/748.6 mm. (lit. 150—151°/763 mm.)]. (I) heated with  $\text{Pr}^\text{OH}$  and 10%  $\text{H}_2\text{SO}_4$  affords (II).

H. B.

**Radiate ethers of pentaerythritol.** H. J. BACKER and G. DIJKIN (Rec. trav. chim., 1935, 55, 22—32).—The prep. of the following *pentaerythritol ethers* is described:  $\text{Me}_4$  (I), m.p. 30—30.5°, b.p. 196—198°;  $\text{Et}_4$ , b.p. 230—231°/763 mm. (cf. lit.);  $\text{Pr}^\text{a}_4$ , b.p. 124—127°/3 mm.;  $\text{Bu}^\text{y}_2$ , m.p. 102—104°; *tetractetyl*, m.p. 57.5—59°;  $\text{Ph}_4$  (II), m.p. 113—113.5° [ $(\text{NO}_2)_8$ -derivative, decomp. about 114°]; *tetra-p-bromophenyl* (III), m.p. 153—157° (crystallises from  $\text{C}_6\text{H}_6\text{--CHCl}_3$  with 2 mols. of  $\text{C}_6\text{H}_6$ ), also obtained by bromination of (II); *tetra-p-chlorophenyl* (IV), m.p. 141—142°; *tetra-p-tolyl* (V), m.p. 96°;  $(\text{CH}_2\text{Ph})_4$ , b.p. 246—250°; *tetra-p-tert.-butylphenyl*, m.p. 168—169° ( $\text{Br}_4$ -derivative, m.p. 231—232°); *tetra-p-tert.-amylphenyl*, m.p. 193—194.5°;  $(\alpha\text{-C}_{10}\text{H}_7)_4$ , m.p. 170—171.5° (*monopicate*, m.p. 200—201.5°);  $(\beta\text{-C}_{10}\text{H}_7)_4$ , m.p. 119—120° (*dipicate*, m.p. 189.5—190.5°). (II) when boiled with  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  is converted into an *isomeride*, m.p. 97—98°, also obtained when  $\text{C}(\text{CH}_2\text{Br})_4$  is heated with  $\text{PhOH}$  and  $\text{Na}$ . This does not react with  $\text{AcCl}$  or dissolve in alkali; its  $(\text{NO}_2)_8$ -derivative, decomp. about 115°, however, is readily sol. in  $\text{COMe}_2$  and in  $\text{KOEt}\text{--EtOH}$ . (IV) when heated with  $\text{AlCl}_3$  in light petroleum gives a *compound*, m.p. 218—220°, considered to be  $\text{C}(\text{CH}_2\text{O})_4\text{C}_6\text{H}_3\text{Cl}$ . A similar *compound*, m.p. 169—170°, is obtained from (V) with  $\text{AlCl}_3$ , and is also formed from  $\text{C}(\text{CH}_2\text{Br})_4$ ,  $\text{Na}$ , and *p*-cresol together with an *isomeride*, m.p. 100.5—101.5°, of (V). The crystallographic properties of (I)—(V) have been determined (by P. TERPSTRA).

H. G. M.

**Syntheses of glycerides by means of triphenylmethyl compounds. II. Diglycerides.** P. E. VERKADE and J. VAN DER LEE (Rec. trav. chim., 1936, 55, 267—277).— $\alpha$ -Monostearin (I) and  $\text{CPh}_3\text{Cl}$  in quinoline afford  $\gamma$ -triphenylmethylglyceryl  $\alpha$ -stearate (II), m.p. 66.5—67°, and  $\beta\gamma$ -ditriphenylmethylglyceryl  $\alpha$ -stearate. Similarly,  $\alpha$ -monopalmitin affords  $\gamma$ -triphenylmethylglyceryl  $\alpha$ -palmitate (III), m.p. 61.5—62°. (II) and  $\gamma$ -triphenylmethylglyceryl  $\alpha\beta$ -distearate are also obtained from triphenylmethylglycerol and stearyl chloride (IV). Palmityl chloride and (II) give  $\gamma$ -triphenylmethylglyceryl  $\beta$ -palmitate  $\alpha$ -stearate (V), m.p. 37—37.5°, and (III) and (IV) give  $\gamma$ -triphenylmethylglyceryl  $\alpha$ -palmitate  $\beta$ -stearate (VI), m.p. 57—57.5°. Removal of  $\text{CPh}_3$  from (V) and from (VI) affords glyceryl  $\alpha$ -stearate  $\gamma$ -palmitate.

P. G. C.

**Constituents of the adrenal gland. III. Sulphur-containing substance.** T. REICHSTEIN

and A. GOLDSCHMIDT (Helv. Chim. Acta, 1936, 19, 401—402; cf. this vol., 605).— $\text{S}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$  with 27%  $\text{H}_2\text{O}_2$  (1 mol.) in a little  $\text{AcOH}$  gives *di- $\beta$ -hydroxyethyl sulphoxide* (I), m.p. 112—113° (corr.) (reduces  $\text{KMnO}_4$  at 0° instantaneously), identical with the substance isolated from the adrenal gland. Solubility relations show that (I) occurs naturally as ester of a fatty acid. Possibly, however, the SO is produced during isolation.

R. S. C.

**Thio-derivatives of glycerol. I. Preparation of  $\alpha$ -monothioglycerol.** L. SMITH and B. SJÖBERG (Ber., 1936, 69, [B], 678—680).— $\beta\gamma$ -isoPropylidenedioxypropyl chloride is converted by  $\text{K}_2\text{S}_2$  at 100° into *di- $\beta\gamma$ -isopropylidenedioxypropyl disulphide*, b.p. 165°/3 mm., which is hydrolysed by 2.5N- $\text{H}_2\text{SO}_4$  and then electrolytically reduced at a Pb electrode to  $\alpha$ -thiolpropene- $\beta\gamma$ -diol [ $\alpha$ -monothioglycerol], b.p. 112°/3 mm. Essentially the same substance appears to result from  $\beta\gamma$ -oxidopropyl alcohol and  $\text{H}_2\text{S}$  in presence of  $\text{Ba}(\text{OH})_2$  at room temp.

H. W.

**$\beta$ -Oxidation and  $\omega$ -oxidation.** B. FLASCHEN-TRÄGER and K. BERNHARD (Rec. trav. chim., 1936, 55, 278—281).—A reply to Verkade *et al.* (this vol., 234).

P. G. C.

**$\psi$ -Halogens. XXXII. Reaction of the silver salts of monobasic organic acids with iodine in the presence of benzene.** L. BIRCKENBACH and K. MEISENHEIMER (Ber., 1936, 69, [B], 723—729).—The possible actions between I and the Ag salts of monobasic org. acids in presence of  $\text{C}_6\text{H}_6$  are represented:  $\text{R}\cdot\text{CO}_2\text{Ag} + \text{I}_2 \rightleftharpoons \text{R}\cdot\text{CO}_2\text{I} + \text{AgI}$ ;  $\text{R}\cdot\text{CO}_2\text{I} + \text{C}_6\text{H}_6 \rightarrow$  (a)  $\text{PhI} + \text{R}\cdot\text{CO}_2\text{H}$  or (b)  $\text{ROBz} + \text{HI}$ ;  $\text{HI} + \text{R}\cdot\text{CO}_2\text{Ag} = \text{R}\cdot\text{CO}_2\text{H} + \text{AgI}$ ;  $\text{R}\cdot\text{CO}_2\text{I} + \text{R}\cdot\text{CO}_2\text{Ag} \rightleftharpoons [\text{R}\cdot\text{CO}_2\text{I}, \text{AgO}_2\text{C}\cdot\text{R}] \rightarrow$  (c)  $\text{R}\cdot\text{CO}_2\text{R} + \text{CO}_2 + \text{AgI}$ . With aliphatic acids reaction (c) is so much more rapid than (a) or (b) that substitution occurs to only a slight extent, if at all. With  $\text{BzOH}$  the reactions are about equally rapid, whereas with substituted benzoic acids substitution is so much the faster process that only a slight evolution of  $\text{CO}_2$  is observed. With aliphatic acids change (b) does not occur appreciably except in the case of  $\text{AcOH}$ . With  $\text{AgOBz}$  approx. equal amounts of  $\text{PhI}$  and  $\text{PhOBz}$  are formed, but the latter may arise according to (c). Among the isomeric nitro-, chloro-, and methylbenzoic acids the *p*-derivatives followed by the *m*-compounds react most markedly according to (b), the *o*-derivatives exclusively in accordance with (a). The results appear related to the electrolytic dissociation consts. of the acid. The action of  $\text{Cl}_2$  or  $\text{Br}$  on  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{Ag}$  in  $\text{C}_6\text{H}_6$  is examined in cold solution in the dark; it takes place without evolution of  $\text{CO}_2$ , giving mainly  $\text{PhCl}$  and  $\text{PhBr}$ , respectively, with 0% and 6% of  $\text{Ph}$  ester. Substitution of  $\text{PhCl}$  for  $\text{C}_6\text{H}_6$  in the reaction of  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{Ag}$  and I considerably diminishes the rate of substitution (recognisable by increased evolution of  $\text{CO}_2$ ) without influencing the ratio of changes (a) and (b), whereas  $\text{PhOMe}$  enhances substitution and a complete displacement towards direction (a).

H. W.

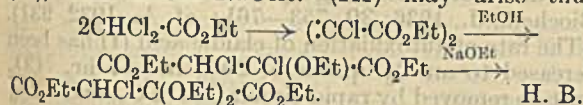
**Preparation of cellulose acetate. I. Preparation of acetyl chloride.** Y. KATO and S. FUJINO



(J. Electrochem. Assoc. Japan, 1935, 3, 42—46).—Cl<sub>2</sub> is passed into a mixture of PCl<sub>3</sub> and AcOH.

CH. ABS. (r)

**Products of reaction of ethyl dichloroacetate with alcoholic sodium ethoxide.** A. C. COPE (J. Amer. Chem. Soc., 1936, 58, 570—572).—Contrary to Wohl and Lange (A., 1908, i, 943), CHCl<sub>2</sub>·CO<sub>2</sub>Et (I) (1 mol.) and EtOH·NaOEt (1.5 mols.) give 22% of CH(OEt)<sub>2</sub>·CO<sub>2</sub>Et (II), b.p. 84—85°/14 mm., and 42% of Et α-chloro-β-diethoxysuccinate (III), b.p. 122—125° (slight decomp.)/2 mm. (III) heated at 170—250° affords CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, small amounts of HCO<sub>2</sub>Et, Et<sub>2</sub>CO<sub>3</sub>, and EtOH, 23% of CHCl(CO<sub>2</sub>Et)<sub>2</sub>, and 58% of Et α-chloro-β-ethoxymaleate, b.p. 150—152°/17 mm. [free acid (+H<sub>2</sub>O), m.p. 77—77.5°, m.p. (anhyd.) 88—88.5° (anhydride, m.p. 37—37.5°)]. (III) is hydrolysed by aq. EtOH·HCl (trace) to Et<sub>2</sub> oxalochloroacetate. (III) is not obtained from OEt·CHCl·CO<sub>2</sub>Et and EtOH·NaOEt or from (I), (II), and EtOH·NaOEt. (III) may arise thus:



**Grignard reactions with ethyl β-chloropropionate.** I. C. WEIZMANN and E. BERGMANN (J.C.S., 1936, 401—402).—MgRBr and MgRCl with CH<sub>2</sub>Cl·CH<sub>2</sub>·CO<sub>2</sub>Et give, respectively, CH<sub>2</sub>Cl·CH·CR<sub>2</sub> and CH<sub>2</sub>Cl·CH<sub>2</sub>·CR<sub>2</sub>·OH which with KOH yields CH<sub>2</sub>·CH·CR<sub>2</sub>·OH. The following new carbinols were prepared: *dibenzyl-β-chloroethyl*-, b.p. 214°/22 mm., 206°/8 mm., 192°/3 mm.; *dibenzylvinyl*-, b.p. 145—146°/1 mm., reduced (Pd—BaSO<sub>4</sub>) to *dibenzylethyl*-, b.p. 190—192°/12 mm. [also prep. from CO(CH<sub>2</sub>Ph)<sub>2</sub> and MgEtBr], *dibenzyl-β-piperidinoethyl*-, b.p. 224—225°/5 mm., m.p. 45—46° (p-nitrobenzoate, m.p. 138—139°); p-aminobenzoate, b.p. 245—250°/25 mm., m.p. 147—148°, β-chlorotriethyl-, b.p. 118—119°/54 mm., β-piperidinotriethyl-, b.p. 105—106°/3 mm. [p-nitrobenzoate, m.p. 148° (alcoholate, m.p. 100°; hydrochloride, cryst.)], β-chloroethyldibutyl-, b.p. 128—133°/4 mm., dibutylvinyl-, b.p. 125°/34 mm., β-piperidinoethyldibutyl-, b.p. 140—143°/5 mm. MgPhBr with CH<sub>2</sub>Cl·CH<sub>2</sub>·CO<sub>2</sub>Et gives γγ-diphenylallyl chloride, b.p. 159—161°/4 mm. (converted by MgPhBr into CPh<sub>2</sub>·CH·CH<sub>2</sub>Ph), and CH<sub>2</sub>Cl·CH<sub>2</sub>·COPh, identified as CH<sub>2</sub>Ph·CH<sub>2</sub>·COPh. F. R. G.

**Comparison of a group of isomeric ethylenic chlorides (allyl-crotonic isomerism) amongst themselves and with the corresponding bromides, on the basis of reactions and mobility of hydrogen.** R. RAMBAUD (Bull. Soc. chim., 1936, [v], 3, 134—141).—Et γ-chlorocrotonate (I) (improved prep.) reacts with hot and cold solutions of alkalis, alkali acetates, NH<sub>3</sub>·H<sub>2</sub>O [product isolated was the *picrate*, m.p. 130—150° (decomp.)], of γ-aminocrotonic acid, and alkaline-earth iodides, giving the same products as are obtained from the γ-Br-compound (cf. A., 1935, 63, 64). The reaction with NaOEt is an exception (*ibid.*, 1105). (I) reacts about twice as rapidly as Et α-chloro-Δ<sup>8</sup>-butenoic acid (II) with NaI in CMe<sub>2</sub>, whereas Et α-chlorocrotonate does not react. (II) is oxidised by AgOH probably to Et<sub>2</sub> αα'-dichloro-αα'-divinylsuccinate. H. G. M.

**Geometrical isomerism of halogen-substituted ethylenic acids. Synthesis of β-bromo-Δ<sup>8</sup>-pentenoic acids.** A. E. FAVORSKI and V. O. MOCHNATSCHE (J. Gen. Chem. Russ., 1935, 5, 1668—1678).—CEt·C·CO<sub>2</sub>H (I) (K, +2H<sub>2</sub>O, Na, +2H<sub>2</sub>O, Ca, +0.5H<sub>2</sub>O, Sr, +1.5H<sub>2</sub>O, Mg, +3H<sub>2</sub>O, Ba, +0.5H<sub>2</sub>O, salts), obtained by boiling a paraffin solution of αβ-dibromobutane with NaNH<sub>2</sub> and saturating the product with CO<sub>2</sub>, reacts with aq. HBr at 0° to yield two stereoisomerides of CEtBr·CH·CO<sub>2</sub>H (II), one, m.p. 24—26° (K, +2H<sub>2</sub>O, and Ca salts), and the other, m.p. 53.5—54° (K, +H<sub>2</sub>O, Ba, +0.5H<sub>2</sub>O, and Ca, +4H<sub>2</sub>O, salts). α-Bromovaleric acid, b.p. 109.5—110.5°/6.5 mm. (lit. 67°/10 mm.) (Na, +0.5H<sub>2</sub>O, Ca, +7H<sub>2</sub>O, Mg, +H<sub>2</sub>O, and Sr, +H<sub>2</sub>O, salts), and Br (145—160°; 6 hr.) yield αα-dibromovaleric acid, b.p. 118—128°/10 mm., converted by steam-distillation into α-bromo-Δ<sup>8</sup>-pentenoic acid, b.p. 113—115°/5 mm. (Ca, Ba, and K salts). Both forms of (II) regenerate (I) when heated with aq. Ba(OH)<sub>2</sub>. R. T.

**Decenoic acid C<sub>10</sub>H<sub>18</sub>O<sub>2</sub> in sperm head oil.** Y. TOYAMA and T. TSUCHIYA (Bull. Chem. Soc. Japan, 1936, 11, 26—29).—The isolation of Δ<sup>8</sup>-decenoic acid from sperm head oil is described. Its constitution is established by hydrogenation to decanoic acid and by oxidation of the Me ester in CMe<sub>2</sub> by KMnO<sub>4</sub> to azelaic and formic acids. H. G. M.

**Transposition of the double linking in Δ<sup>4</sup>- and Δ<sup>8</sup>-oleic acids.** I. I. VANIN and A. A. TSCHERNJAROVA (J. Gen. Chem. Russ., 1935, 5, 1537—1542).—Δ<sup>4</sup>-Oleic acid in AcOH and HCl at 0° yield 1-chlorostearic acid, which with NiCO<sub>3</sub> (190—210°; 3 hr.) affords isooleic acid, Me·[CH<sub>2</sub>]<sub>6</sub>·CH·CH·[CH<sub>2</sub>]<sub>8</sub>·CO<sub>2</sub>H, m.p. 43—44°. Δ<sup>4</sup>-Oleic acid and HCl yield 7-chlorostearic acid, converted similarly into Me·[CH<sub>2</sub>]<sub>9</sub>·CH·CH·[CH<sub>2</sub>]<sub>5</sub>·CO<sub>2</sub>H, m.p. 51—52°. R. T.

**Halogenation of the thiocyanates of polyethylenic acids. Synthesis of halogenothiocyanates of ethyl linoleate.** W. KIMURA (Ber., 1936, 69, [B], 786—789).—Et linoleate is obtained by the successive action of Zn dust and conc. H<sub>2</sub>SO<sub>4</sub> on tetrabromostearic acid in abs. EtOH. It is converted by (CNS)<sub>2</sub> in CCl<sub>4</sub> into Et 9*α*-dithiocyano-Δ<sup>8</sup>-octadecenoate, which with Cl<sub>2</sub> or Br respectively in cold Et<sub>2</sub>O affords Et λμ-dichloro- and λμ-dibromo-9*α*-dithiocyanostearate. With Wijs' and Hanns' solutions Et λμ-chloroiodo- and λμ-bromoiodo-9*α*-dithiocyanostearate result. H. W.

**Polymerisation of the methyl esters of higher unsaturated fatty acids. XVII. Increase in the iodine value of the polymerisation product.** K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 31—36; cf. A., 1934, 755).—The Me esters of the fatty acids of linseed and sesame oil, and Me oleate show no increase in I val. even after being in contact with I during 24 hr., but after heating at 280—290° for several hr. the increase may amount to 16.7 units, and is the higher the greater is the unsaturation of the starting material. Intermol. polymerides, unhydrolysable substances derived from them, and substances of high b.p. are responsible for the increase. Some substitution occurs in the poly-



merisation product, but the reaction is mainly additive. J. L. D.

**Interaction between the methyl esters of unsaturated aliphatic acids of the  $C_{20}$  and  $C_{22}$  class, containing four and five ethenoid linkings respectively, and maleic anhydride.** R. S. MORRELL and W. R. DAVIS (J.S.C.I., 1936, 55, 101—103r).—The Diels-Alder synthesis between conjugated diene systems and maleic anhydride has been extended to the Me esters of unsaturated  $C_{20}$  and  $C_{22}$  acids occurring in fish oils. No reaction of the type was found with either of these esters, although the former contained four and the latter five ethenoid linkings, respectively. The absence of conjugation indicated by these results is in accordance with existing work on the structure of the acids. An impurity in the  $C_{20}$  ester produced a small amount of amorphous heteropolymeride, probably composed of an oxidised pentaethylenic mol. in combination with three mols. of anhydride.

**Lead complexes of hydroxy-acids.** H. PARSSELLE (Compt. rend., 1936, 202, 1173—1176).—Pb tartrate exists in two forms; the hydrated salt first pptd. has an acid reaction, but changes subsequently into an anhyd. neutral form. The action of aq. NaOH on an equimol. mixture of tartaric acid and  $Pb(NO_3)_2$  has been followed polarimetrically. The ppt. first obtained redissolves in excess of NaOH, giving a *l*-complex in solution. The rotatory power is a function of  $[NaOH]$ , becoming positive and then negative again as this increases. With aq.  $NH_3$  the solution always remains *l*. A comparison with the behaviour of Pb saccharate in aq. KOH is made. The *l*-complex first produced becomes *d* as  $[KOH]$  increases, but there is no return to *l* with further increase of  $[KOH]$ . M. S. B.

**Determination of keto-enolic mixtures.** F. SEIDEL, W. THIER, A. UBER, and J. DITTMER (Ber., 1936, 69, [B], 650—653).—In presence of  $OAc \cdot CMe \cdot CH \cdot CO_2Et$  the enolic fraction of  $CHAc \cdot CO_2Et$  can be determined by titration with 0.2N-NaOH or  $-Ba(OH)_2$  in presence of phenolphthalein, since  $OAc \cdot OMe \cdot CH \cdot CO_2Et$  does not react appreciably with alkali. The results agree with those of Meyer's Br titration. The % enol in  $CHAc_2$  can be similarly determined, but the procedure fails with  $CH_2Ac \cdot CO_2Et$ . H. W.

**Acetolic condensations of ethyl acetoacetate with acetaldehyde.** H. GAULT and T. WENDLING (Bull. Soc. chim., 1936, [v], 3, 53—70; cf. A., 1935, 65).— $CH_2Ac \cdot CO_2Et$ ,  $MeCHO$ ,  $K_2CO_3$ , and  $H_2O$  give Et di- $\alpha'$ -hydroxyethylacetoacetate (I) and an oil consisting of  $Et_2$  ethylidenebisacetoacetate and some  $Et_2$  dimethylcyclohexenedicarboxylate, or of Et  $\alpha'$ -hydroxyethylacetoacetate, according to the temp. at which it was separated.  $NHEt_2$  or KOH may be used instead of  $K_2CO_3$  in the prep. of (I), but the  $H_2O$  cannot be replaced by EtOH. The stability of (I) at various temp. in the pure state and in  $H_2O$ , EtOH, and  $Et_2O$  is recorded. H. G. M.

**Preparation of macrocyclic lactones by depolymerisation.** E. W. SPANAGEL and W. H. CAROTHERS (J. Amer. Chem. Soc., 1936, 58, 654—656).—The

polyesters from  $OH \cdot [CH_2]_n \cdot CO_2H$  ( $n=9, 12, 13$ ) and  $OH \cdot [CH_2]_n \cdot O \cdot [CH_2]_{10} \cdot CO_2H$  ( $n=2-4$ ) are depolymerised at  $270^\circ/1$  mm. in presence of (usually) a little  $MgCl_2 \cdot 6H_2O$  to the mono- (main product with higher members) and/or di-meric lactones; this method (cf. A., 1935, 844) is simpler and quicker than that of Stoll and Rouvé (A., 1934, 1201; 1935, 1351). The following are new:  $\kappa\beta'$ -hydroxyethoxyundecomono- (I), b.p.  $108-111^\circ/1$  mm., m.p.  $8^\circ$ , and -di-, m.p.  $106-107^\circ$ , -lactones;  $\kappa\delta'$ -hydroxybutoxyundecomono-lactone (II), b.p.  $129-131^\circ/1$  mm., m.p.  $-19^\circ$ . (I) and (II) have musk-like odours.  $\kappa\beta'$ -Hydroxyethoxy-, m.p.  $48-50^\circ$ ,  $\kappa\gamma'$ -hydroxypropoxy-, m.p.  $51^\circ$ , and  $\kappa\delta'$ -hydroxybutoxy-, m.p.  $53^\circ$ , -undecolic acids are prepared from  $\kappa$ -bromoundecolic acid and  $OH \cdot [CH_2]_n \cdot ONa$  in  $(CH_2)_n(OH)_2$ . The effects of temp. and catalyst on the depolymerisation are studied.

H. B.

**Autoxidation of fatty acids. II. Oxidoelaidic acid and some cleavage products.** G. W. ELLIS (Biochem. J., 1936, 30, 753—761; cf. A., 1932, 931).—The rate of autoxidation of elaidic acid (I) has been increased to an  $O_2$  uptake of 20% in  $<7$  hr.  $CO_2$  must be removed by rapid circulation of  $O_2$ , and 0.2% of Co, as elaidate, be added. Oxidoelaidic acid, m.p.  $55.5^\circ$ , is formed to the extent of 16-20% of (I) oxidised. A similar oxidation of oleic acid yielded 20% of the same acid with a small amount of oxido-oleic acid. Autoxidation of (I) also yields azelaic, suberic, nonoic, and octoic acids, and a trace of  $H_2C_2O_4$ . J. N. A.

**Micrometric oxalic acid titration.** J. RENAUDIN (J. Pharm. Chim., 1936, [viii], 23, 447—454).—Micrometric titration of  $H_2C_2O_4$  with  $KMnO_4$  by the usual procedure using hot solutions is not trustworthy. Cold titration with 0.01N- $Na_2S_2O_3$  after addition of excess of 0.01N- $KMnO_4$  and KI is more accurate. Addition of  $MnSO_4$  accelerates the liberation of I and is desirable in the presence of mineral salts.

E. H. S.

**$\alpha$ -Deoxy-*l*-ascorbic acid.** F. MICHEEL and K. HASSE (Ber., 1936, 69, [B], 879—881).—*iso*Propylideneascorbic acid (improved prep.) is transformed into K  $\alpha$ -acetyl- $\beta\gamma$ -isopropylidenethreonate, which with  $SOCl_2$  at room temp. affords  $\alpha$ -acetyl- $\beta\gamma$ -isopropylidenethreonyl chloride, b.p.  $124-126^\circ/14$  mm. This is condensed with  $CHNa(CO_2Et)_2$  in anhyd.  $Et_2O$ , and the product is boiled with EtOH and then hydrolysed with dil. HCl, thus giving Et  $\alpha$ -deoxy-*l*-ascorbic- $\alpha$ -carboxylate,  $OH \cdot CH_2 \cdot CH(OH) \cdot CH \begin{smallmatrix} \diagup CO \cdot CH \cdot CO_2Et \\ \diagdown O \cdot CO \end{smallmatrix}$ , m.p.  $116-117^\circ$ ,  $[\alpha]_D^{20} +94.9^\circ$  in EtOH, transformed by NaOH-MeOH into  $\alpha$ -deoxy-*l*-ascorbic acid,  $OH \cdot CH_2 \cdot CH(OH) \cdot CH \begin{smallmatrix} \diagup C(OH) \cdot CH \\ \diagdown O \cdot CO \end{smallmatrix}$ , m.p.  $170^\circ$  after softening.

H. W.

**[Isolation of crystalline *d*-galacturonic acid from tobacco.]** F. EHRLICH (Ber., 1936, 69, [B], 920).—A question of priority (cf. Collatz, this vol., 591).

H. W.

**Walden inversion reactions of *d*-(+)-*p*-toluenesulphonoxypionic acid and amide and their derivatives.** C. M. BEAN, J. KENYON, and H. PHILLIPS (J.C.S., 1936, 303—311).—*p*-Toluenesulphonoxypionic acid is partly resolved through



the quinine salt, but the optically pure acid is obtained from *d*-lactic acid. The *d*-(+)-acid and  $\text{SOCl}_2$  give *d*-(+)- $\alpha$ -*p*-toluenesulphonylpropionyl chloride, b.p.  $140\text{--}145^\circ < 0.1$  mm., m.p.  $53^\circ$ ,  $[\alpha]_{5461}^{20} +3.69^\circ$  in  $\text{C}_6\text{H}_6$ ; the *l*-(-)-chloride with  $\text{LiCl}$  in  $\text{COMe}_2$  yields (+)- $\alpha$ -chloropropionyl chloride, converted into Et (+)- $\alpha$ -chloropropionate. *l*-(-)- $\alpha$ -*p*-Toluenesulphonylpropionamide and  $\text{KOAc}$  in EtOH give *d*-(+)- $\alpha$ -acetoxypropionamide, b.p.  $128\text{--}131^\circ < 0.1$  mm., m.p.  $59\text{--}60^\circ$ ,  $\alpha_{5461}^{20} +4.26^\circ$ . Et *l*-(-)-lactate, converted into the acid and treated successively with  $\text{AcCl}$ ,  $\text{SOCl}_2$ , and  $\text{CH}_2\text{Cl}_2$  and  $\text{NH}_3$ , yields *l*-(-)- $\alpha$ -acetoxypropionamide, b.p.  $104\text{--}105^\circ < 0.1$  mm., m.p.  $59\text{--}60^\circ$ ,  $\alpha_{5461}^{20} -17.7^\circ$ . *d*-(+)- $\alpha$ -Toluenesulphonylpropionamide with  $\text{KOBz}$  affords *d*-(+)- $\alpha$ -benzoyloxypropionamide, m.p.  $127\text{--}128^\circ$ ,  $[\alpha]_{5461}^{20} +66.6^\circ$  in EtOH, also obtained from Et *l*-(-)-lactate. *l*-(-)- $\alpha$ -*p*-Toluenesulphonylpropionanilide (I) with  $\text{KOAc}$  leads to *d*-(+)- $\alpha$ -acetoxypropionanilide,  $[\alpha]_{5461}^{20} +12.7^\circ$  in EtOH; the *l*-(-)-compound, obtained from  $\text{NH}_2\text{Ph}$  and (-)-acetoxypropionyl chloride, has m.p.  $121^\circ$  and  $[\alpha]_{5461}^{20} -12.2^\circ$  in EtOH. *d*-(-)- $\alpha$ -Benzoyloxypropionanilide, obtained from (I) and  $\text{KOBz}$ , has m.p.  $160^\circ$ ,  $[\alpha]_{5461}^{20} -12.0^\circ$  in EtOH, and the *l*-(+)-compound, m.p.  $160^\circ$ ,  $[\alpha]_{5461}^{20} +15.0^\circ$  in EtOH, is prepared from Et *l*-(-)-lactate, through *l*-(+)- $\alpha$ -benzoyloxypropionyl chloride, b.p.  $98^\circ < 0.1$  mm.,  $[\alpha]_{5461}^{20} +51.3^\circ$ .  $\beta$ -Naphthylamine and *l*-(-)- $\alpha$ -*p*-toluenesulphonylpropionyl chloride give *l*-(-)- $\alpha$ -*p*-toluenesulphonylpropiono- $\beta$ -naphthalide, m.p.  $128^\circ$ ,  $[\alpha]_{5461}^{20} -123.8^\circ$  in EtOH.

*dl*- $\alpha$ -*p*-Toluenesulphonylpropionyl chloride and Na *p*-toluenesulphonamide lead to *dl*- $\alpha$ -*p*-toluenesulphonyl-N-*p*-toluenesulphonylpropionamide, m.p.  $137^\circ$ , and similarly *K* *l*- $\alpha$ -*p*-toluenesulphonyl-N-*p*-toluenesulphonylpropionamide, m.p.  $160^\circ$  (decomp.),  $[\alpha]_{5461}^{20} -79.4^\circ$  in  $\text{COMe}_2$ , is derived. The *K* salt and EtOH yield *l*-(-)- $\alpha$ -ethoxy-N-*p*-toluenesulphonylpropionamide, m.p.  $80\text{--}81^\circ$ ,  $[\alpha]_{5893}^{20} -10.0^\circ$  in EtOH, which can also be obtained from Et *l*-(-)-lactate.

*d*-(+)- $\alpha$ -Chloro-N-*p*-toluenesulphonylpropionamide, m.p.  $118^\circ$ ,  $[\alpha]_{5467}^{20} +29.7^\circ$  in EtOH, may be obtained from the *l*-(-)- $\alpha$ -*p*-toluenesulphonyl compound and  $\text{LiCl}$ , or from Et *d*-(+)- $\alpha$ -chloropropionate. *l*-(-)- $\alpha$ -*p*-Toluenesulphonyl-N-*o*-carboxyphenylpropionamide, m.p.  $131^\circ$ ,  $[\alpha]_{5893}^{20} -102.4^\circ$  in EtOH, with  $\text{LiCl}$  affords *d*-(+)- $\alpha$ -chloro-N-*o*-carboxyphenylpropionamide, m.p.  $148^\circ$ ,  $[\alpha]_{5893}^{20} +3.34^\circ$  in  $\text{CHCl}_3$  [also derived from *d*-(+)- $\alpha$ -chloropropionyl chloride], and its Na salt with  $\text{NaOEt}$  and  $\text{LiCl}$  yields the lactone of  $\alpha$ -hydroxy-N-*o*-carboxyphenylpropionamide, m.p.  $236\text{--}238^\circ$ ,  $[\alpha]_{5893}^{20} -449^\circ$  in EtOH. Na *l*-(-)- $\alpha$ -*p*-toluenesulphonyl-N-*p*-carboxyphenylpropionamide on heating forms the "lactone" of  $\alpha$ -hydroxy-N-*p*-carboxyphenylpropionamide, decomp.  $270\text{--}290^\circ$ ,  $[\alpha]_{5893}^{20} -161^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , whilst the free amide with  $\text{NH}_2\text{Ph}$  and  $\text{LiCl}$  gives *d*-(+)- $\alpha$ -chloro-N-*p*-carboxyphenylpropionamide, m.p.  $230\text{--}233^\circ$ ,  $[\alpha]_{5893}^{20} +18.0^\circ$  in EtOH. The replacement of the  $\alpha$ -*p*-toluenesulphonyl groups in the neutral compounds by either  $\text{OAc}$  or  $\text{OBz}$  occurs with inversion.

F. R. S.

Fission of disulphides by alkali. II. Hydrolytic fission of the disulphide linking. A. SCHÖBERL and H. ECK (Annalen, 1936, 522, 97--115).—

Partly a more detailed account of work previously reviewed (A., 1935, 1106). Alkaline hydrolysis of  $(\text{S}\cdot\text{CHR}\cdot\text{CO}_2\text{H})_2$  gives  $\text{SH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  (A) and  $\text{OH}\cdot\text{S}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  (B); (B) then decompose to  $\text{H}_2\text{S}$  and  $\text{COR}\cdot\text{CO}_2\text{H}$  (C) [R may be H; when R is  $\text{CO}_2\text{H}$  or  $\text{CH}_2\cdot\text{CO}_2\text{H}$ , the intermediate  $\text{CO}(\text{CO}_2\text{H})_2$  or  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$  loses  $\text{CO}_2$  to give  $\text{CHO}\cdot\text{CO}_2\text{H}$  or  $\text{AcCO}_2\text{H}$ , respectively]. It is probable that (B) also undergo slight disproportionation to (A) and  $\text{SO}_2\text{H}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ . The formation of (C) is demonstrated by carrying out the hydrolysis with aq.  $\text{NaOH}$  in presence of  $\text{Pb}(\text{OAc})_2$  (to remove  $\text{H}_2\text{S}$ ) and  $p\text{-NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (I); acidification of the filtrate affords  $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CR}\cdot\text{CO}_2\text{H}$ . Under these conditions  $\alpha\alpha'$ -disulphidobisphenylacetic acid (A., 1934, 1348) yields 25.6% of phenylglyoxylic acid *p*-carboxyphenylhydrazone, m.p.  $217\text{--}219^\circ$ ;  $[\text{S}\cdot\text{CH}(\text{CO}_2\text{H})_2]_2$  and  $(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  afford 49.3 and 50%, respectively, of glyoxylic acid *p*-carboxyphenylhydrazone, decomp.  $> 265^\circ$  [also obtained from  $\text{CHCl}_2\cdot\text{CO}_2\text{H}$  and (I) in conc. aq.  $\text{KOH}$ ], whilst  $(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$  and  $\alpha\alpha'$ -disulphidodisuccinic acid (II) give 67.5 and 32%, respectively, of pyruvic acid *p*-carboxyphenylhydrazone (III), decomp.  $236^\circ$  ( $\text{Me}_2$  ester, m.p.  $166^\circ$ , prepared with  $\text{MeOH}\cdot\text{HCl}$ ). A neutral solution of the Na salt of (II) is hydrolysed when boiled; in presence of (I), 1-phenyl-5-pyrazolone-3:4'-dicarboxylic acid (IV) [ $\text{Me}_2$  ester, m.p.  $242^\circ$  (decomp.)] and some (III) are produced. (III) is also obtained from  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and (I) in aq.  $\text{NaOH}$ ; in neutral solution (III) and (IV) result, whilst in acid (IV) is the sole product. The  $\text{Me}_2$  ester of 1-phenyl-5-pyrazolone-3:3'-dicarboxylic acid has m.p.  $198^\circ$  (decomp.).

Hydrolysis (aq.  $\text{NaOH}$ ) of  $\alpha\alpha'$ -disulphidobis- $\beta$ -phenylpropionic acid [formed by oxidation (5%  $\text{H}_2\text{O}_2$ , trace of  $\text{FeSO}_4$ ) of  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{SH})\cdot\text{CO}_2\text{H}$  (Gränacher, A., 1922, i, 849) in neutral solution] gives  $\alpha$ -thiolcinnamic acid, m.p.  $129^\circ$  (sinters at  $125^\circ$ ) (lit.  $119^\circ$ ) [oxidised (0.1*N*-I in EtOH or  $\text{AcOH}$ ) to  $\alpha\alpha'$ -disulphidobiscinnamic acid, m.p.  $179^\circ$ ], which may arise (partly) by loss of  $\text{H}_2\text{O}$  from the intermediate  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{S}\cdot\text{OH})\cdot\text{CO}_2\text{H}$ . H. B.

Formation of hydrogen cyanide and formaldehyde by oxidation of organic substances. R. FOSSE (Compt. rend., 1936, 202, 445--448).— $\text{CH}_2\text{O}$  has been detected in the ammoniacal oxidation (electrolytic or  $\text{KMnO}_4$ ) of glucose (I), sucrose,  $(\text{CH}_2\cdot\text{OH})_2$ , glycerol (II), mannitol,  $\text{COMe}_2$ ,  $\text{AcOH}$ , and glycine, which also form  $\text{CO}(\text{NH}_2)_2$ ,  $\text{HCNO}$ , and  $\text{HCN}$ . In the cases of (I) and (II),  $\text{CH}_2\text{O}$  is shown to be an intermediate in the formation of  $\text{HCNO}$  and  $\text{CO}(\text{NH}_2)_2$ . It is suggested that respiratory oxidation *in vivo* produces, in addition to energy, highly active intermediates for the synthesis of org. matter. Oxidation of  $\text{CH}_2\text{O}$  by Parrod's method (A., 1935, 1109) yields no  $\text{HCN}$ . H. G. M.

Colorimetric determination of acetaldehyde. III. S. HÄHNEL (Svensk Kem. Tidskr., 1936, 48, 61--64).—Modifications of the author's method (B., 1933, 328; this vol., 191) are described.

M. H. M. A.

Effect of the reaction products on the thermal decomposition of gaseous acetaldehyde. M.



LETORT (Compt. rend., 1936, 202, 491—494; cf. A., 1934, 1073).—The decomp. of MeCHO is retarded by the products of reaction ( $\text{CO} + \text{CH}_4$ ) (cf. A., 1926, 804; 1936, 191). An expression is developed which shows how, for the decomp. of pure MeCHO, the retardation due to the products changes the order of the reaction from 1.5 at the beginning to 1.8 during the course of the reaction. The mean observed val. for the latter is 1.87. H. G. M.

**Condensation of chloral and bromal with polyhydric alcohols.** A. N. MELDRUM and G. M. VAD (J. Indian Chem. Soc., 1936, 13, 118—122).—s-Di-( $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethoxy)ethane (I) (de Forcrand, A., 1889, 689) (diacetate, b.p. 132—134°/15 mm., formed using  $\text{Ac}_2\text{O}$  at room temp.) with  $\text{Ac}_2\text{O}$ -conc.  $\text{H}_2\text{SO}_4$  or boiling  $\text{AcCl}$  gives the anhydro-derivative,  $\text{CH}_2\text{O} \cdot \text{CH}(\text{CCl}_3) > \text{O}$ , m.p. 144°, which is stable

to hot conc.  $\text{HNO}_3$ , boiling alkali, and conc. aq.  $\text{NH}_3$  at 110°. Distillation of (I) under atm. pressure affords glycol  $\beta\beta\beta$ -trichloroethylidene ether [2-trichloromethyl-1:3-dioxolan], b.p. 200°, m.p. 42°, reduced (Zn dust,  $\text{AcOH}$ ) to the  $\beta\beta$ -dichloroethylidene ether, b.p. 118°/25 mm. Glycerol, chloral, and  $\text{H}_2\text{SO}_4$  give  $\gamma$ -hydroxy- $\alpha\beta$ -di-( $\beta'\beta'\beta'$ -trichloro- $\alpha'$ -hydroxyethoxy)propane (II), b.p. 145—150°/15 mm., oxidised (conc.  $\text{HNO}_3$  at 0°) to the acid,  $\text{O} < \text{CH}(\text{CCl}_3) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{CCl}_3) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m.p. 192—193° ( $\text{Na} + 2.5\text{H}_2\text{O}$ , and  $\text{Ba} + 2\text{H}_2\text{O}$ , salts). Distillation of (II) under 70 mm. pressure affords glycerol  $\alpha\beta$ - $\beta'\beta'\beta'$ -trichloroethylidene ether [4-hydroxymethyl-2-trichloromethyl-1:3-dioxolan], b.p. 162—164°/25 mm. (cf. Yoder, A., 1923, i, 309) (acetate, b.p. 205°/120 mm.; nitrate, m.p. 64°; Me ether, b.p. 140—142°/15 mm.; corresponding chloride, b.p. 130°/15 mm.), which is reduced to glycerol  $\alpha\beta$ - $\beta'\beta'\beta'$ -dichloroethylidene ether, b.p. 160°/20 mm. (acetate, b.p. 188°/30 mm.). Erythritol  $\alpha\beta$ -di-( $\beta'\beta'\beta'$ -trichloro- $\alpha'$ -hydroxyethyl) ether, m.p. 167—171° (tetra-acetate, m.p. 164°), is formed from erythritol and chloral at 100°.  $(\text{CH}_2\text{OH})_2$  and  $\text{CBr}_3 \cdot \text{CH}(\text{OH})_2$  (III) at 130—140° give s-di-( $\beta\beta\beta$ -tribromo- $\alpha$ -hydroxyethoxy)ethane, b.p. 145—147°/25 mm. (diacetate, b.p. 196°/135 mm.), which when distilled passes into glycol  $\beta\beta\beta$ -tribromoethylidene ether, m.p. 103—104°, also formed from  $(\text{CH}_2\text{OH})_2$ , (III), and conc.  $\text{H}_2\text{SO}_4$ . Glycerol and (III) similarly yield  $\gamma$ -hydroxy- $\alpha\beta$ -di-( $\beta'\beta'\beta'$ -tribromo- $\alpha'$ -hydroxyethoxy)propane (IV), b.p. 205°/25 mm. (triacetate, b.p. 190°/155 mm.); in presence of conc.  $\text{H}_2\text{SO}_4$ , glycerol  $\alpha\beta\gamma$ -tri-( $\beta'\beta'\beta'$ -tribromo- $\alpha'$ -hydroxyethyl) ether (V) results. Distillation of (IV) and (V) under reduced pressure affords glycerol  $\alpha\beta$ - $\beta'\beta'\beta'$ -tribromoethylidene ether, b.p. 210°/60 mm., and its  $\gamma$ - $\beta'\beta'\beta'$ -tribromo- $\alpha'$ -hydroxyethyl ether, b.p. 145°/20 mm., respectively. H. B.

**isoPropylideneglyceraldehyde. III. Synthesis of d-fructose and d-sorbose from d-glyceraldehyde or d-glyceraldehyde and dihydroxyacetone.** H. O. L. FISCHER and E. BAER (Helv. Chim. Acta, 1936, 19, 519—532; cf. A., 1934, 635).—d-OH- $\text{CH}_2\text{CH}(\text{OH})\text{CHO}$  (I) (prep. from diisopropylidenemannitol improved to give a 86.2% yield) and 0.01N-Ba(OH) $_2$  give 95% of a 1:1-mixture of d-fructose (II) and d-sorbose (III), determined as phenylosazones; (II) is isolated free as Ca salt in

good yield, the mother-liquor giving (III) after removal of the residual (II) by fermentation. The reaction is shown polarimetrically to be complete in 2 hr. (I),  $\text{CO}(\text{CH}_2\text{OH})_2$  (IV), and  $\text{Ba}(\text{OH})_2$ , however, give a similar mixture in 40 min. Reaction thus proceeds by slow change of (I) to (IV), followed by a faster condensation of the enolic form of (I) with (IV). The above reaction and the fact that iso-propylideneglyceraldehyde gives a branched-chain product show that condensation occurs only with  $\text{OH} \cdot \text{CH}_2 \cdot \text{COR}$ . Absence of d-psicose and d-tagatose from the products shows preferential formation of products with opposite configurations at C3 and C4.

[With H. POLLOK.] A similar reaction occurs with  $\text{CH}_2\text{O}$  and  $\text{CH}_2\text{AcOH}$ , giving a 25% yield of  $\text{COMe} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , m.p. 37—38° (also obtained from  $\text{COMe} \cdot \text{CH} \cdot \text{CH}_3$  and  $\text{KMnO}_4$  or  $\text{KClO}_3$ - $\text{OsO}_4$ ), which in turn with  $\text{CH}_2\text{O}$  gives a  $\text{C}_5$ -sugar.

R. S. C.

**Electrolytic reduction of organic compounds at the dropping mercury electrode.** I. A. WINKEL and G. PROSKE (Ber., 1936, 69, [B], 693—706).—Under the experimental conditions introduction of Me into  $\text{CH}_2\text{O}$  diminishes the reducibility, the effect being enhanced when a second Me becomes attached to CO, but not when Me is replaced by Et. Introduction of further Me groups into  $\text{COMe}_2$  does not alter its behaviour; cyclo-hexanone and -pentanone resemble aliphatic ketones. Ph behaves oppositely to Me. With aromatic ketones the polarographic stages are very distinct, so that the method is peculiarly adapted to the aromatic series. When in the  $\alpha$ -position to CO the effect of Ph is lost; it therefore depends on the presence of a conjugated system. Condensed ring residues are more effective than is Ph. The reduction potential is markedly affected by halogen, notably by I, and a second halogen enhances the effect of the first. OH attached to CO inhibits its reduction. The reduction potential is displaced towards the positive in sequence of decreasing effect by  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ ,  $1\text{-C}_{10}\text{H}_7$ , Ph, and towards the negative by OH and Me. The influence of the several groups can be qualitatively evaluated by addition or subtraction of the vals. for the individual groups, but a quant. measurement is not yet possible, since the displacement of the potential depends on its abs. val. H. W.

**Conditions of condensation of acetone molecules with each other.** P. P. SURMIN (J. Gen. Chem. Russ., 1935, 5, 1639—1641).—Condensation of  $\text{COMe}_2$  proceeds most energetically in alkaline media, alcoholic alkalis being more efficacious than aq. The greatest yields of condensation products are obtained in presence of  $\text{CaC}_2$  at the b.p.; the relative yields of products of higher b.p. rise with increasing amount of  $\text{CaC}_2$ . R. T.

**Semicarbazones of [dialkyl] ketones.** H. S. RHINESMITH (J. Amer. Chem. Soc., 1936, 58, 596—597).— $\text{CHEt}(\text{CO}_2\text{Et})_2$ ,  $\text{COMe} \cdot \text{CH} \cdot \text{CH}_3$ , and  $\text{EtOH} \cdot \text{NaOEt}$  (trace) give Et heptan- $\beta$ -one- $\varepsilon\epsilon$ -dicarboxylate, b.p. 136—138°/2 mm. (semicarbazone, m.p. 116.5—117.5°), hydrolysed (cold dil.  $\text{EtOH} \cdot \text{KOH}$ ) to the Et H ester, b.p. 71—73°/2 mm. (semicarbazone, m.p. 114—115°), and thence (conc.  $\text{EtOH} \cdot \text{KOH}$ ) to the



free acid, decarboxylated at  $130^\circ$  to *heptan- $\beta$ -one- $\epsilon$ -carboxylic acid*, b.p.  $135\text{--}137^\circ/2$  mm. [*semicarbazone*, m.p.  $127\text{--}129^\circ$ ; *Me ester*, b.p.  $75^\circ/2$  mm. (*semicarbazone*, m.p.  $108^\circ$ )].  $\text{CHEt}_2\cdot\text{CH}_2\text{Br}$ , b.p.  $144\text{--}145^\circ$  (from the alcohol and  $\text{PBr}_3$ ), with  $\text{NaCN}$  in 50%  $\text{EtOH}$  affords  $\text{CHEt}_2\cdot\text{CH}_2\cdot\text{CN}$ , b.p.  $164\text{--}166^\circ$ , which with  $\text{MgEtBr}$  yields  *$\epsilon$ -ethylheptan- $\gamma$ -one*, b.p.  $171\text{--}173^\circ/760$  mm. (*semicarbazone*, m.p.  $133\text{--}134^\circ$ ). Oxidation ( $\text{CrO}_3$ ) of the carbinol from  $\text{Bu}^\delta\text{CHO}$  and  $\text{MgEtBr}$  gives  *$\epsilon$ -methylhexan- $\gamma$ -one*, b.p.  $135\text{--}137^\circ/760$  mm. (*semicarbazone*, m.p.  $149\text{--}150^\circ$ ). The *semicarbazones* of  $\gamma$ -, b.p.  $136\text{--}139^\circ/760$  mm., and  $\delta$ -, b.p.  $137\text{--}139^\circ/760$  mm., -methylhexan- $\beta$ -one have m.p.  $69\text{--}70^\circ$  and  $127\text{--}128^\circ$ , respectively; that of  *$\epsilon$ -methylhexan- $\beta$ -one*, b.p.  $143\text{--}144^\circ/760$  mm., has m.p.  $146\text{--}147^\circ$  (lit.  $141^\circ$ ). The Grignard reagent from  $\text{CHMeEt}\cdot\text{CH}_2\text{I}$ , b.p.  $137\text{--}140^\circ$  (alcohol from *sec.*- $\text{BuMgI}$  and  $\text{CH}_2\text{O}$ ) and  $\text{PrCHO}$  give a carbinol, b.p.  $157\text{--}163^\circ$ , oxidised ( $\text{CrO}_3$ ) to  *$\zeta$ -methyloctan- $\delta$ -one* (*semicarbazone*, m.p.  $75^\circ$ ).

H. B.

**Colour reaction of hexoses and their polymericides, and its application to colorimetric determination of glucose in blood.** J. A. SANCHEZ [with R. C. D'ALESSIO] (*J. Pharm. Chim.*, 1936, [viii], 13, 377—387).—Hexoses and polysaccharides derived from them, but not pentoses, give a rose-red coloration, the intensity of which is  $\propto$  hexose concn., when their dil. (e.g., 1 : 5,000) aq. solution is treated with warm conc.  $\text{H}_2\text{SO}_4$ . The absorption spectrum contains three bands (except in the case of galactose) with max. at 5300, 4920, and 5520 Å. For the detection or determination of glucose (I), total blood or blood-serum is deproteinised with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ , and the colour produced by the above reaction is matched against that given by similarly treated blood-serum, freed from (I) by allowing glycolysis to proceed to completion at  $37^\circ$ , to which known amounts of (I) are added. The method is suitable for solutions with  $< 0.1\%$  of (I).

J. S. A.

**Cupro-alkali metal carbonate solution in the determination of reducing sugars. II. Modification of Pellet's solution.** C. Y. CHANG and H. A. SCHUETTE (*Trans. Wis. Acad. Sci.*, 1935, 29, 381—388; cf. A., 1931, 199).—Pellet's  $\text{CuSO}_4\text{--NH}_4\text{Cl}\text{--Na K tartrate--Na}_2\text{CO}_3$  solution (A., 1875, 666; 1878, 612) slowly and irreversibly deposits a ppt. and loses in reducing power (17.3% in 515 hr.). Mixture of  $\text{CuSO}_4\text{--NH}_4\text{Cl}$  and tartrate- $\text{Na}_2\text{CO}_3$  solutions in the proportions of Pellet's solution immediately prior to the test leads to erratic results. More reproducible results and stable solutions are obtained by increasing the alkalinity, max. reducing power being found with 4.5*N*- $\text{Na}_2\text{CO}_3$ ; reaction is then complete in 40 min. at  $90^\circ$ . The reagents recommended are: (A)  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  343.5 and  $\text{NH}_4\text{Cl}$  34.35 g. per litre; (B) Na K tartrate 216.52 and  $\text{Na}_2\text{CO}_3$  283.5 g. per litre. Solutions (A) and (B) are mixed in the proportions 1 : 4 just before use; 20 ml. of the mixed reagent and  $\approx 0.1$  g. of glucose or fructose or 0.22 g. of lactose or maltose in a total vol. of 80 ml. are heated in a stoppered flask at  $90^\circ$  for 45 min. Cu equivs. of the above-mentioned sugars are given; they are higher than for Pellet's solution, thus giving increased accuracy. This technique requires no blank

determination, gives zero results for sucrose, and is accurate for mixtures of all the sugars named except for that of lactose with much sucrose. The reason for this exception is unknown.

R. S. C.

**Benedict's qualitative [sugar] test.** J. FINE (*Brit. Med. J.*, 1935, I, 1169—1170).—The test is adapted to the quant. examination of glucose.

CH. ABS. (p)

**Synthesis of 5 : 6-benzhydrylidene-1 : 2-*iso*-propylidene- $\alpha$ -*D*-glucofuranose.** Catalytic

hydrogenation of acetals of aromatic ketones and sugars. P. E. PAPADAKIS (*J. Amer. Chem. Soc.*, 1936, 58, 665—666).—1 : 2-*iso*Propylideneglucose (I) and  $\text{CPh}_2\text{Cl}_2$  in  $\text{C}_5\text{H}_5\text{N}$  at  $0^\circ$  give 5 : 6-benzhydrylidene-1 : 2-*isopropylideneglucose*, m.p.  $147\text{--}148^\circ$ ,  $[\alpha]_D^{25} + 21.7^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , which does not react with  $\text{CPh}_3\text{Cl}$  and is reduced ( $\text{H}_2$ , Pd,  $\text{MeOH--AcOH}$ ) to (I) and  $\text{CH}_2\text{Ph}_2$ .  $\text{CPh}_2(\text{OMe})_2$  (from  $\text{CPh}_2\text{Cl}_2$  and  $\text{MeOH}$  in  $\text{C}_5\text{H}_5\text{N}$ ) is similarly reduced to  $\text{CH}_2\text{Ph}_2$ .

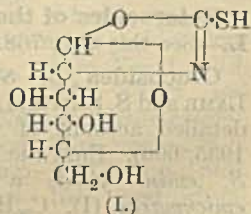
H. B.

**Behaviour of glucose towards thiocyanic acid.**

G. ZEMPLÉN, Á. GERECs, and M. RADOS (*Ber.*, 1936, 69, [B], 748—754).—Treatment of glucose and KCNS in  $\text{H}_2\text{O}$  with 12*N*-HCl at room temp. slowly affords  $\mu$ -thiol-glucosazoline (I), m.p.  $172^\circ$ ,  $[\alpha]_D^{20} + 34.12^\circ$  in  $\text{H}_2\text{O}$ . It does not reduce Fehling's solution. It does not behave towards alkali as a lactone, but its optical behaviour when treated with increasing quantities of NaOH indicates salt formation (I) with or without enolisation. N is partly evolved as  $\text{NH}_3$  when it is boiled with alkalis.  $\text{Hg}(\text{OAc})_2$  gives cryst. additive compounds with varying Hg content. S is removed with difficulty by metallic salts, readily by oxidising agents. Reducing agents cause production of COS or  $\text{H}_2\text{S}$ , but do not give homogeneous products. With  $\text{NHPh}\cdot\text{NH}_2$  (I) affords glucosephenylosazone in good yield. It is very sensitive towards hot 10% HCl; reducing substances are formed, but the reducing power remains  $<$  that calc. for glucose. (I) with anhyd. NaOAc and  $\text{Ac}_2\text{O}$  at  $100^\circ$  gives the corresponding *tetra-acetate* (II), m.p.  $120^\circ$ ,  $[\alpha]_D^{25} + 123.9^\circ$  in  $\text{CHCl}_3$ , hydrolysed by NaOMe in  $\text{CHCl}_3$  to (I) and unchanged by boiling EtOH or  $\text{NH}_3\text{--MeOH}$  at  $0^\circ$ . Partial hydrolysis of (II) by NaOMe- $\text{CHCl}_3$  yields the *triacetate*, m.p.  $131.9^\circ$ ,  $[\alpha]_D^{20} + 107^\circ$  in  $\text{CHCl}_3$ , re-acetylated to (II). (I), NaOH, and  $\text{H}_2\text{O}_2$  give  $\mu$ -hydroxy-glucosazoline,  $[\alpha]_D^{20} + 6.79^\circ$  in  $\text{H}_2\text{O}$ , which reduces Fehling's solution to an extent depending on the duration of heating, is sensitive to boiling acids, loses part of its N as  $\text{NH}_3$  when boiled with alkalis, and affords a yellow oil when treated with  $\text{NHPh}\cdot\text{NH}_2$ . Its *triacetate*, m.p.  $139^\circ$ ,  $[\alpha]_D^{17} + 58.86^\circ$  in  $\text{CHCl}_3$ , is obtained by the action of  $\text{H}_2\text{S}$  in EtOH- $\text{AcOH}$  on the Hg derivative  $\text{C}_{26}\text{H}_{32}\text{O}_{18}\text{N}_2\text{Hg}$ , m.p.  $245^\circ$  (decomp.), prepared from (II) and HgO in BuOH, and is converted by NaOAc and  $\text{Ac}_2\text{O}$  at  $100^\circ$  into the *tetra-acetate*, m.p.  $95^\circ$ ,  $[\alpha]_D^{17} + 104.8^\circ$  in  $\text{CHCl}_3$ .

H. W.

**Nature of sucrose caramel.** G. VON ELBE (*J. Amer. Chem. Soc.*, 1936, 58, 600—601; cf. Cunningham and Dorée, *J.C.S.*, 1917, 111, 589).—





Caramel (I), prepared by heating sucrose (loss  $\pm 12\%$ ) at atm. pressure or in a vac., is a colloidal dispersion of a lyophobic, humic substance (II) in a mixture of two protective substances (III), decomp.  $> 95^\circ$ ,  $[\alpha]_D^{25} +24.5^\circ$ , and (IV), decomp.  $> 140^\circ$ ,  $[\alpha]_D^{25} +63^\circ$ . Extraction of (I) with successive quantities of MeOH followed by  $H_2O$  removes most of (III) and (IV); the residual (II) coagulates irreversibly to a dark brown, insol., and infusible mass showing a diffuse X-ray pattern. (III) and (IV) are separated by repeated pptn. of (IV) from MeOH with PrOH; they are thermally unstable, hygroscopic, amorphous powders which yield acetates. (III) and  $NHPh \cdot NH_2$  give glucosazone and an oily product; (IV) affords similar products only after hydrolysis. (III) and (IV) show marked thermal stability and resistance to dissolution in presence of (II). H. B.

**Action of pyridine on maltose.** R. SUTRA (Bull. Soc. chim., 1936, [v], 3, 145).—Maltose (I) when crystallised from  $C_5H_5N$  gives the compound,  $C_{12}H_{22}O_{11} \cdot 2C_5H_5N$ , m.p.  $106^\circ$ , stable at room temp., but decomposed by EtOH, regenerating (I).

H. G. M.

**Heterosides of the fruits of *Sophora japonica*, L.**—See this vol., 768.

**Glucosides of *Strophanthus emini*.** I. D. LAMB and S. SMITH (J.C.S., 1936, 442—447).—A more detailed account of work previously reported (B., 1935, 606). Enzymic hydrolysis of strophanthin from *S. emini* yields a new cardio-tonic monoside, *emicymarin* (I),  $C_{30}H_{46}O_9$ , sinters  $160^\circ$ , m.p.  $207^\circ$  (indefinite),  $[\alpha]_{5461}^{20} +15.8^\circ$ ,  $[\alpha]_{5461}^{20} +12.8^\circ$  in EtOH {tetrahydrate;  $Ac_3$  derivative, m.p. about  $278^\circ$ ,  $[\alpha]_{5461}^{20} +27.8^\circ$ ,  $[\alpha]_{5461}^{20} +22.8^\circ$  in MeOH;  $H_2$ -derivative, m.p.  $151^\circ$  (indefinite after sintering),  $[\alpha]_{5461}^{25} +11.2^\circ$ ,  $[\alpha]_{5461}^{19} +8.6^\circ$  in EtOH, iso-compound, m.p. about  $270^\circ$  (previous sintering),  $[\alpha]_{5461}^{25} +30.9^\circ$ ,  $[\alpha]_{5461}^{20} +26.2^\circ$  in  $C_5H_5N$ , identical with trianhydroperiplogenin (Jacobs *et al.*, A., 1933, 1038)}, *anhydroemicymarigenin*,  $C_{28}H_{32}O_4$ , m.p.  $269$ — $277^\circ$ ,  $[\alpha]_{5461}^{24} +67^\circ$ ,  $[\alpha]_{5461}^{24} +59^\circ$  in  $C_5H_5N$ , and digitalose, m.p.  $106^\circ$  (after sintering; m.p. rises on keeping), converted by Br into digitalonolactone, m.p.  $137$ — $138^\circ$ . (I) is an unsaturated  $\Delta^8$ -lactone; by enzymic hydrolysis it gives a monoside, *allo-emicymarin*, m.p.  $248^\circ$  (sinters  $240^\circ$ ),  $[\alpha]_{5461}^{20} +29.7^\circ$ ,  $[\alpha]_{5461}^{23} +24.6^\circ$  in 95% EtOH, identical with the monoside obtained by Jacobs *et al.* (A., 1933, 278) direct from the seeds.

F. R. G.

**Constituents of *Epimedium macranthum*, Morr and Decne.** I. **Chemical constitution of a new flavone glucoside of *E. macranthum*.** 1. S. AKAI (J. Pharm. Soc. Japan, 1935, 55, 537—599).—Extraction of the dry leaves and roots with MeOH affords *icariin* (I),  $C_{33}H_{39}O_{15} \cdot OMe$ , m.p.  $231$ — $235^\circ$ ,  $[\alpha]_D^{15} -87.09^\circ$  in  $C_5H_5N$  ( $Ac_3$  derivative, m.p.  $120^\circ$ ), which is hydrolysed (dil.  $H_2SO_4$ ) to *icariside* I (II),  $C_{26}H_{29}O_{11} \cdot OMe$ , m.p.  $256^\circ$ ,  $[\alpha]_D^{15} -28.39^\circ$  in  $C_5H_5N$  ( $Ac_7$  derivative, m.p.  $143^\circ$ ;  $Bz_7$  derivative, m.p.  $151.5^\circ$ ), and rhamnose. Under other conditions (I) is hydrolysed to (II) and *anhydroicaritin* (III),  $C_{21}H_{17}O_3(OH)_3$ , m.p.  $242$ — $243^\circ$  ( $Ac_3$  derivative, m.p.  $185^\circ$ ;  $Bz_3$  derivative, m.p.  $190.5^\circ$ ; *dimethylate*, m.p.  $176^\circ$ ; *trimethylate*, m.p.  $146$ — $147^\circ$ ; *dihydro-trimethyl ether*, m.p.  $134^\circ$ ; *dibromotrimethyl ether*,

m.p.  $189^\circ$ ;  $Me_3$  ether hydrochloride, m.p.  $162^\circ$ ). Hydrolysis of (II) with 50%  $H_2SO_4$  yields  $\beta$ -*anhydroicaritin* (IV),  $C_{20}H_{17}O_5 \cdot OMe$ , m.p.  $222$ — $223^\circ$  ( $Ac_3$  derivative, m.p.  $228^\circ$ ;  $Bz_2$  derivative, m.p.  $299^\circ$ ;  $Me_1$  ether, m.p.  $191^\circ$ ;  $Me_2$  ether, m.p.  $221$ — $222^\circ$ ), and glucose (V). Demethylation of (IV) gives 4'-*demethyl- $\beta$ -anhydroicaritin*,  $C_{20}H_{18}O_6$ , m.p.  $308$ — $309^\circ$  ( $Ac_3$  derivative, m.p.  $208^\circ$ ). (II) and (IV), with alkali at  $250$ — $260^\circ$ , yield phloroglucinol (VI) and *p-OH-C\_6H\_4 \cdot CO\_2H*. With 35% KOH in the presence of  $H_2$ , (II) yields (III) and *icaritin* (VII),  $C_{21}H_{22}O_7$ , m.p.  $239$ — $239.5^\circ$  ( $Ac_3$  derivative, m.p.  $212^\circ$ ;  $Ac_4$  derivative, m.p.  $146.5^\circ$ ;  $Bz_4$  derivative, m.p.  $184^\circ$ ;  $Me_2$  ether, m.p.  $168.5^\circ$ ;  $Me_3$  ether, m.p.  $174^\circ$ , and its *phenylurethane*, m.p.  $213$ — $214^\circ$ , which with dil.  $H_2SO_4$  affords (IV). The  $Me_2$  ether of (III) with 10% EtOH-KOH yields anisic acid (VIII) and *icaritol* II,  $C_{13}H_{13}O_3(OMe)_2$ , m.p.  $106^\circ$  (*oxime*, m.p.  $162$ — $163^\circ$ ; *Me ether*, m.p.  $99^\circ$ ), which, with KOH at  $250$ — $260^\circ$ , yields (VI) and  $Bu^iCO_2H$ . The  $Me_3$  ether of (III) similarly affords (VIII) and *icaritol* I (IX),  $C_{13}H_{13}O_2(OMe)_3$ , m.p.  $128^\circ$  (*oxime*, m.p.  $115^\circ$ ; *oxime* of *Me* derivative, m.p.  $139^\circ$ ;  $Br_2$ -derivative, m.p.  $154^\circ$ ; *hydrochloride*, m.p.  $106^\circ$ ), hydrogenated to *dihydroicaritol* I, m.p.  $118$ — $118.5^\circ$ . Oxidation ( $CrO_3$ ) of the *Me* ether of (VII) gives  $COMe_2$  (?) and an aldehyde. With  $H_2SO_4$ , (IX) is cyclised to  $\beta$ -*icaritol* I,  $C_{13}H_{13}O_2 \cdot OMe$ , m.p.  $82^\circ$  (*oxime*, m.p.  $165^\circ$ ). On hydrolysis with emulsin, (I) yields *icariside* II (X),  $C_{27}H_{30}O_{10}$ , m.p.  $204$ — $205^\circ$ ,  $[\alpha]_D^{15} -128.03^\circ$  in EtOH ( $Ac_5$  derivative, m.p.  $88^\circ$ ;  $Bz_5$  derivative, m.p.  $225^\circ$ ), and  $\beta$ -glucose. (X), with dil.  $H_2SO_4$ , yields (III) and rhamnose, and, with 35% KOH, (III) and (VIII). (II) is hydrolysed by emulsin to (III) and (V). The *Me* derivative of (X) is hydrolysed (dil.  $H_2SO_4$ ) to *anhydroicaritin* 7-*Me ether*, m.p.  $204^\circ$ , further methylated to *anhydroicaritin* 3 : 7-*Me\_2 ether*, m.p.  $174^\circ$ . CH. ABS. (r)

**Highly polymerised compounds. CXXXVI. Structure of starch. CXXXVII. Macromolecular structure of lichenin.** H. STAUDINGER and H. EILERS (Ber., 1936, 69, [B], 819—848, 848—851).—CXXXVI. Enzymic degradation of potato starch gives products of mol. wt. 10,000—20,000, which are very difficult to purify and free from ash. Controlled degradation with 2N-HCl or  $HCO_2H$  gives more amenable materials of mol. wt. 10,000—100,000, which can be fractionated by pptn. from  $H_2O$  by MeOH. The viscosity of these products has been measured in  $H_2O$ ,  $HCO \cdot NH_2$ , N-NaOH, and  $HCO_2H$  under varied conditions of temp. and concn. It is thus shown that the particles consist of macromols., and not micelles; the conclusion is strengthened by the conversion of degraded starches into their acetates, from which they are regenerated unchanged by cautious hydrolysis in absence of air. Nitrating acid causes degradation of the starch mol. which precedes esterification, since the nitrates are relatively stable in the mixture of acids. The form of the extended starch mol. differs greatly from that of the cellulose mol.  $K_m$  of starch is 8—10 times  $<$  that of cellulose, so that a starch mol. equal in length to a cellulose mol. has about 8—10 times its wt. and contains 8—10 times as many glucose residues. A zigzag or meander



form of the starch mol. is suggested which harmonises with its greater solubility. According to physical properties, starches of mol. wt. 10,000–100,000 are hemicolloidal in character, whereas according to particle wt. they belong to the mesocolloids. For this reason they have been frequently regarded as relatively simple, whereas they are of high mol. wt.

CXXXVII. The vals.  $\eta_{sp}/C_{gm}$  are const. for solutions of lichenin (I) in Schweitzer's reagent and *N*-NaOH provided the viscosity is low and  $n_{sp}$  is the same for solutions of equal concn. in either solvent within the experimental limits. A macromol. structure of the colloidal particles of (I) is thus indicated; probably this is branched or bent. Treatment of (I) with nitrating acid caused degradation which precedes esterification.

H. W.

**$\alpha$ -Amino- $\beta$ - $\gamma$ -dihydroxy-*n*-butyric acid. III.** H. O. L. FISCHER and L. FELDMANN (Helv. Chim. Acta, 1936, 19, 532–537; cf. A., 1932, 930).—*d*-iso-Propyrideneglyceraldehyde (prep. without isolation from diisopropylidenemannitol) in MeOH with  $NH_3$ , followed by HCl, gives a 30% yield of  $\alpha$ -amino- $\beta$ - $\gamma$ -dihydroxy-*n*-butyric acid, decomp. 215° (discoloration from about 190°),  $[\alpha]_D^{20} -13.73^\circ$  in  $H_2O$  [Cu salt; phenylcarbamide, +  $H_2O$ , m.p. 165° (decomp.),  $[\alpha]_D^{17} +29.8^\circ$  as Na salt in  $H_2O$ , and 2- $C_{10}H_7 \cdot SO_2$  derivative, m.p. 180–181° (decomp. from 178–179°),  $[\alpha]_D^{25-27} +12.5-13.45^\circ$  as Na salt in  $H_2O$ ], in which the configuration of the  $>CH \cdot OH$  is fixed. The Strecker synthesis proceeds better with the isopropylidene than with the OH-compound.

R. S. C.

**Synthesis of a  $\alpha\alpha'$ -diamino- $\beta\beta'$ -dihydroxyadipic acid.** H. O. L. FISCHER and L. FELDMANN (Helv. Chim. Acta, 1936, 19, 538–543).—*iso*Propylidene-*d*-tartaraldehyde gives, by the Strecker synthesis,  $\alpha\alpha'$ -diamino- $\beta\beta'$ -dihydroxyadipic acid, m.p. 255–256° (decomp. from about 235°),  $[\alpha]_D^{22-25} -24.1^\circ$  to  $-25.09^\circ$  in HCl [Cu salt, +  $H_2O$ ; diphenylcarbamide derivative, m.p. 181–183° (decomp. from about 170°),  $[\alpha]_D^{17} +26.9 \pm 2^\circ$  in dry EtOH], in which the configuration of both  $>CH \cdot OH$  is known. The acid gives a deep blue colour with ninhydrin, but other reactions are negative; it is not deaminated by rat's liver or kidney.

R. S. C.

**Form of polypeptide chains. I. *dl*-Alanine-hexapeptide.** G. BOEHM (Biochem. Z., 1936, 284, 322–328).—Aq. sols of hexa-(*dl*-alanyl)-*dl*-alanine (Abderhalden, A., 1932, 503) exhibit strongly positive streaming double refraction, both in "streaky" solutions containing needle-shaped particles and in solutions containing only amierons; this shows the presence of long anisotropic micelles, and indicates a long chain formation, and not a spherical structure for the free peptide in solution.

F. O. H.

**Isolation of *dl*-arginine from kidney autolysate.**—See this vol., 749.

**Constitution of reduction product of chloral-acetamide.** A. N. MELDRUM and G. M. VAD (J. Indian Chem. Soc., 1936, 13, 117–118).—In agreement with Yelburgi and Wheeler (A., 1934, 770),  $CCl_3 \cdot CH(OH) \cdot NHAc$  (I) is reduced to  $CCl_2 \cdot CH \cdot NHAc$ , since the latter with  $Cl_2$  in  $CHCl_3$  at  $<60^\circ$  gives *acet- $\alpha\beta\beta\beta$ -tetrachloroethylamide*, m.p. 128° [also obtained

from (I) and  $PCl_5$ ], which with  $NH_2Ph$  in  $C_6H_6$  affords *acet- $\beta\beta\beta$ -trichloro- $\alpha$ -anilinoethylamide*, m.p. 146°.

H. B.

**Carbon suboxide and its reactions with amines.** E. A. PAUW (Rec. trav. chim., 1936, 55, 216–226).— $C_3O_2$  [determined by adding a measured vol. of its solution in  $Et_2O$  to excess of  $CO_2$ -free  $H_2O$ , and titrating  $CH_2(CO_2H)_2$  by  $CO_3^{2-}$ -free alkali (phenolphthalein)] reacts in  $Et_2O$  with amines  $NHRR'$  to form malondiamides  $CH_2(CO \cdot NRR')_2$ , diamines yielding heterocyclic compounds.  $NH_3$  and aliphatic primary amines have been used to give the diamides  $CH_2(CO \cdot NHR)_2$ , where  $R = H, Me, Et, Pr^a, Bu^a, Bu^b, [CH_2]_4 \cdot Me, [CH_2]_2 \cdot Pr^b$ , and  $[CH_2]_6 \cdot Me$ , and to give *malon-diallylamide*, m.p. 149°, and *-dibenzylamide*, m.p. 141° [both also obtained from  $CH_2(CO_2Et)_2$ ].  $NHMe_2, NHEt_2, NHPr^a_2, NHBu^a_2$ , piperidine, and piperazine, do not give isolable products with  $C_3O_2$ .  $NHBu^b_2$  and  $NH([CH_2]_2 \cdot Pr^b)_2$  give, however, *malon-bis(diisobutylamide)*, m.p. 276°, and *-bis(diisoamylamide)*, m.p. 289°. The appropriate diamines yield *malonpentamethylenediamide*,  $CH_2[CO \cdot NH \cdot CH_2 \cdot CH_2]_2CH_2$ , m.p. 221–222°, and its *NN'*-*dibenzyl*, m.p. 123–124°, and *N-benzhydryl*, m.p. 112–114°, analogues. Aromatic amines yield malondiamides,  $CH_2(CO \cdot NH \cdot C_6H_4 \cdot X)_2$ , where  $X = H, p\text{-}Cl, p\text{-}Br, p\text{-}I, o\text{-}, m\text{-},$  and  $p\text{-}Me, p\text{-}OMe, p\text{-}OEt$ , and  $m\text{-}NO_2$ , and *malon-di-o-*, m.p. 176°, and *-di-m-chloro-*, m.p. 164°, *-di-o-*, m.p. 175°, and *-di-m-bromo-*, m.p. 175°, and *-di-m-iodo-anilide*, m.p. 182°, *-di-o-*, m.p. 164°, and *-di-m-anisidide*, m.p. 151°, and *-di-o-*, m.p. 165°, and *-di-m-phenetidide*, m.p. 157°; all these are also prepared from  $CH_2(CO_2Et)_2$ . *Malon-di-o-iodo-anilide*, m.p. 177°, and *-di-N-methylanilide* are further prepared from  $C_3O_2$ , which does not, however, yield *malondi-p-nitroanilide* [prepared from  $CH_2(CO_2Et)_2$ ].  $o\text{-}NO_2 \cdot C_6H_4 \cdot NH_2$  does not combine with  $C_3O_2$  or with  $CH_2(CO_2Et)_2$ , nor does  $NHPhEt$  combine with  $C_3O_2$ . *Malondi-p-phenetidide* is nitrated to *malondi-2-nitro-p-phenetidide*, m.p. 165–166°, hydrolysed to 2-nitro-*p*-phenetidino. *l*-Bornylamine yields *l-malondibornylamide*, m.p. 187° (from  $C_3O_2$ ), or 192° [from  $CH_2(CO_2Et)_2$ ],  $[\alpha]_D^{20} -46^\circ$ . *l*-Menthylamine does not react with  $CH_2(CO_2Et)_2$ , but with  $C_3O_2$  gives *l-malondimenthylamide*, m.p. 177°,  $[\alpha]_D^{20} -87.3^\circ$ .  $\alpha$ - and  $\beta$ - $C_{10}H_7 \cdot NH_2$  with  $C_3O_2$  give the corresponding diamides. 2-Aminopyridine combines with 1 mol. only of  $C_3O_2$  (to give a ketenium base?). 5- and 8-Aminoquinoline react with  $C_3O_2$  to form *malon-di-5-*, m.p. 265–271°, and *-di-8-quinolylamide*, m.p. 200–204°. The following are obtained from the appropriate amino-esters and  $C_3O_2$ : *Et\_2 malondiamidoacetate*, m.p. 107°, *Et\_2 malondi- $\alpha$ -amidoisobutyrate*, and the *Et\_2* esters of *dl*-malondialanide, and *malondisarcoside*.  $NH_2 \cdot CH_2 \cdot CO_2H$  and  $NH_2 \cdot CO_2Et$  do not react with  $C_3O_2$ . The relative ease of formation, qual. solubility, and taste of the above diamides are recorded.

E. W. W.

**Reaction between organic sulphur compounds and hydrogen peroxide. III. Reaction mechanism.** 1. R. KITAMURA (J. Pharm. Soc. Japan, 1935, 55, 300–349).—In alkaline solution  $H_2O_2$  oxidises  $R \cdot CS \cdot NHR'$  to  $R \cdot CO \cdot NHR'$ ; the reaction mechanism and factors influencing the course



of the reaction are discussed. In neutral or acid solution sulphinic acids, disulphides, etc. are formed.

CH. ABS. (r)

**Structure and formulæ of Prussian-blues and related compounds.**—See this vol., 670.

**Boron hydrides. V. Ethyl- and *n*-propyl-diboranes. VI. Action of ammonia on methyl-diboranes.** H. I. SCHLESINGER, L. HORVITZ, and A. B. BURG (J. Amer. Chem. Soc., 1936, 58, 407—409, 409—414; cf. A., 1935, 738).—V. The prep. of *mono*-, *di*-, b.p. 67.1°, *tri*-, and *tetra-ethyl*-, m.p. —56.3°, *mono*- and *di-propyl-diborane* is described. The compounds are analogous to the corresponding Me derivatives of  $B_2H_6$ .

VI. The prep. of  $B_3MeN_3H_5$ , m.p. —59°, b.p. 87°;  $B_3Me_2N_3H_4$ , m.p. —48°, b.p. 107°; and  $B_3Me_3N_3H_3$ , m.p. 31.5°, b.p. 129°, is described. V.p. and heats of vaporisation have been determined and Trouton's const. has been evaluated.  $BM_2 \cdot NH_2$  appears to exist in several forms between —60° and room temp.

E. S. H.

**Alkaline-earth cacodylates. I.** R. TIOLLAIS (Bull. Soc. chim., 1936, [v], 3, 70—87).—Pure Ca (+9, and 1  $H_2O$ , and anhyd.), Ba (+9, 3, and 1  $H_2O$ ), and Sr (+13, 3, and 1  $H_2O$ ) cacodylates are prepared from cacodylic acid and the appropriate hydroxide. The solubility curves show breaks corresponding with changes in the no. of mols. of  $H_2O$  of crystallisation. The solubilities of the anhyd. and the fully hydrated salts in MeOH and 95% and 100% EtOH have been determined. Aq. solutions of the salts are decomposed by atm.  $CO_2$ , and with  $H_2S$  give compounds, probably thiocacodylates.

H. G. M.

**Synthesis of dihalogeno-thallium organic compounds.** N. N. MELNIKOV and G. P. GRATSCHEVA (J. Gen. Chem. Russ., 1935, 5, 1786—1790).—Compounds of the type  $TlRX_2$  are readily prepared by the general reactions:  $TlR_2X (I) + TlX_3 (II) \rightarrow 2TlRX_2 (III)$ ;  $2TlR_3 + (II) \rightarrow 3(III)$ . Different by-products, in amounts increasing with the at. wt. of X, are formed by the reactions:  $(I) + (II) \rightarrow Tl_2X_4 + 2RX$ ;  $(III) \rightarrow RX + TlX$ ;  $2(III) \rightarrow (I) + (II)$ ;  $TlR_3 + (II) \rightarrow (I) + RX + TlX$ ;  $2TlR_3 + (II) \rightarrow 2(I) + TlX + R_2$ . The following compounds are described:  $TlMeBr_2$ , decomp. at 140—160°,  $TlEtCl_2$ , decomp. at 180°,  $TlEtBr_2$ , decomp. at 140—160° (1:1 compound with  $C_5H_5N$ ), *iso*- $C_5H_{11} \cdot TlCl_2$ , decomp. at 210°, *iso*- $C_5H_{11} \cdot TlBr_2$ , decomp. at 95—110°, *p*- $C_6H_4Cl \cdot TlCl_2$ ,  $TlPhCl_2$ , decomp. at 240°. R. T.

**Magnetochemical investigations of organic substances. VII. Pentaphenylcyclopentadienyl.** E. MÜLLER and I. MÜLLER-RODLOFF (Ber., 1936, 69, [B], 665—668; cf. A., 1935, 1453).—At room temp. the observed data for the solid material are in harmony with a completely monomeric radical and the  $\Sigma$  condition. Curie's law is not quite exactly obeyed, but the small divergencies do not indicate an appreciable course moment. At lower temp. the divergencies are less than those observed with tridiphenylmethyl, and are possibly due to changes in the cryst. condition or incipient association. All C and N radicals examined appear to exist almost exclusively in the  $\Sigma$  condition.

H. W.

**Catalytic dehydrogenation of cyclohexane.** V. I. KARSHEV, M. G. SEVERJANOVA, and A. N. SIVOVA (J. Appl. Chem. Russ., 1936, 9, 269—278).—The activity of a no. of catalysts in promoting dehydrogenation of cyclohexane at 500—550°, with production of aromatic compounds, rises in the series  $Al_2O_3 < Cr-Cu-H_3PO_4-Al_2O_3 < CrO_3-H_3PO_4 < Cr-Cu$ . R. T.

**Thermal decomposition of dimethylcyclohexanes.** J. A. ARBUSOV and B. M. MICHAILOV (Compt. rend. Acad. Sci., U.R.S.S., 1935, 4, 337—340; cf. A., 1935, 73).—The yields of butadiene (mol. % calc. on the hydrocarbon decomposed) obtained by heating 1:2- (I), 1:3- (II), and 1:4-dimethylcyclohexane (III) with  $H_2O$  at 700—750° are, respectively, 20.7, 18.4, and 23.9. The other gaseous products [vol. % in parentheses for (I), (II), and (III), respectively] obtained (at 700°) are  $H_2$  (18.4, 16.8, 17.0), saturated hydrocarbons (31.1, 32.0, 29.7), unsaturated hydrocarbons (50.0, 50.8, 52.6), acetylenic hydrocarbons (1.5, 1.3, 0.9),  $C_3H_6 + C_4H_8$  (14.4, 22.3, 24.1), and  $C_2H_4$  (26.8, 19.1, 16.8). J. W. B.

**Fluorocyclohexane.** F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 105—121).—When cyclohexyl bromide (I) is distilled (Pt vessels) at 130° (5—6 days) with  $Hg_2F_2$ , and finally at 140°/100 mm., a 30% yield of cyclohexyl fluoride (II), b.p. 43.2°/100 mm., f.p. 13°, is obtained with unchanged (I), 31% of cyclohexene (III) (removed by Br-addition at 0°), HF, HBr, and, by extraction of the residue with boiling  $C_6H_6$ , a polymeride ( $C_6H_{10}$ )<sub>n</sub> of (III). When heated, especially in glass, (II) readily loses HF to give (III); conc.  $H_2SO_4$ ,  $Mg(ClO_4)_2$ ,  $P_2O_5$ ,  $CaCl_2$ , and HF, but not Pt-black, catalyse this elimination. (II) is stable towards dil. NaOH and fused  $K_2CO_3$ , and is attacked only slowly by Na to give (III), cyclohexane, and a trace of a liquid, b.p. 232—235°, probably a mixture of cyclohexylcyclohexene and dicyclohexyl. No appreciable formation of a Grignard compound occurs with (II)-Mg-Et<sub>2</sub>O. With  $MgPhBr$  and  $MgEtBr$  the main reaction is removal of HF to form (III). With Br-AcOH (II) gives mainly 1:2-dibromocyclohexane [from the initial product, (III)] and only a trace of bromofluorocyclohexane, b.p. 80°/30 mm.; reaction is rapid in light and is catalysed by the liberated HBr. With fuming  $HNO_3$  at —10° (II) gives adipic and a trace of picric acid.

J. W. B.

**Catalytic reduction of organic fluorine compounds. III. Reduction of cyclohexyl fluoride.** F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 122—124).—Contrary to the rapid hydrogenation of PhF with  $H_2$ -Pt-black, with elimination of HF, absorption of  $H_2$  by cyclohexyl fluoride is negligible under the same conditions. An electronic explanation, based on the symmetrical group  $\cdot CH_2F$  in the latter and the unsymmetrical group  $>CHF$  in the former, is outlined.

J. W. B.

**Autoxidation of cyclic ethylenic hydrocarbons. I.** R. DUPONT (Bull. Soc. chim. Belg., 1936, 45, 57—64).—Autoxidation of 1-methyl- $\Delta^1$ -cyclohexene yields 1-methyl- $\Delta^1$ -cyclohexen-6-one, methylcyclohexenol, and 1-methyl-*trans*-1:2-cyclohexanediol, whilst 1-methyl- $\Delta^3$ -cyclohexene gives an unidentified



peroxide, b.p. 67—70°, and 1-methyl-*trans*-3:4-cyclohexanediol. The gaseous products contain approx. 50% of H<sub>2</sub> in each case. R. S.

**Processes of dehydration. IV. Dehydrogenation of cycloheptane, cyclooctane, and methylated cycloheptanes to aromatic hydrocarbons.** L. RUZICKA and C. F. SEIDEL (Helv. Chim. Acta, 1936, 19, 424—433).—*cyclo*-Heptane (I) and -octane (II) derivatives with Se give C<sub>8</sub>H<sub>6</sub> derivatives under the conditions normally used for obtaining C<sub>10</sub>H<sub>8</sub> derivatives from their H<sub>10</sub>-derivatives. (I) is unchanged at 350—360°, but at 440° gives PhMe. Methylcycloheptane, unchanged at 410°, gives at 440° PhEt, *o*- and *p*-xylene. (II) at 390—410° gives *p*-xylene. 1:2:2-Trimethylcycloheptane (from the semicarbazone of the 3-ketone and Na-EtOH at 200—210°), b.p. 104—105°/100 mm., with Se at 420° (only slowly at 400°) gives *m*-C<sub>6</sub>H<sub>4</sub>MePr and 1:2:3-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> (III); with Pd at 420° it affords (III) and other products. 1:1:4-Trimethyl-Δ<sup>1</sup>-cycloheptene (*eucarvene*) (IV) (from tetrahydrocarveol and KHSO<sub>4</sub> at 210°), b.p. 161—165°/720 mm., is almost unaffected by Se at 340°, but at 370° gives a hydrocarbon, oxidised to *m*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, but 1:1:4-trimethylcycloheptane (*eucarvene*) (from tetrahydroeucarvone-semicarbazone and Na-EtOH at 200—210°), b.p. 162—163°/720 mm., with Se at 390—400° gives *m*-C<sub>6</sub>H<sub>4</sub>MeEt and (III). *cyclo*Pentadecane and Se at 390—410° give a mixture, which does not contain aromatic hydrocarbons. 1:1:3-Trimethyl-2-butylcyclohexane (from tetrahydroionone semicarbazone), b.p. 94—95°/10 mm., is unaffected by Se at 350°, but at 390—400° affords *m*-xylene and 1:3:2-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>Bu. *trans*-Decalin and Se at 370—390° (not at 340—360°) or, better, Pd-C at 320—340° give C<sub>10</sub>H<sub>8</sub>. The structures of the products are proved by oxidation to acids and by-products may have been undetected. It is uncertain whether fission precedes dehydrogenation or vice versa and whether (IV) yields *m*-C<sub>6</sub>H<sub>4</sub>MeEt or *m*-xylene [by way of (III)].

R. S. C.

**Fused carbon rings. VII. Preparation of cyclic hydrocarbons from unsaturated tertiary alcohols. Synthesis of *cis*-9-methyl-octalin and -decalin, and a proof of the presence of the angular methyl group.** D. C. HIBBIT and R. P. LINSTEAD (J.C.S., 1936, 470—476).—CHR:CH[CH<sub>2</sub>]<sub>n</sub>·CO<sub>2</sub>Et (cf. A., 1931, 935; 1935, 195) with MgMeI gives CHR:CH[CH<sub>2</sub>]<sub>n</sub>·CMe<sub>2</sub>·OH (I) which with H<sub>3</sub>PO<sub>4</sub> yields CHR:CH[CH<sub>2</sub>]<sub>n-1</sub>·CH:CMe<sub>2</sub> when *n*=1, R=Et and when *n*=2, R=H or Me, but when *n*=3, R=H, yields 1:1-dimethyl-Δ<sup>3</sup>-cyclohexene. The following new *pentenylcarbinols* (I) were prepared: *dimethyl*-Δ<sup>4</sup>, b.p. 65—66°/15 mm. (*phenylurethane*, m.p. 67—68°), *dimethyl*-Δ<sup>3</sup>, b.p. 70°/17 mm. (*phenylurethane*, m.p. 89°), *dimethyl*-Δ<sup>2</sup>, b.p. 63—64°/20 mm., m.p. -27° to -28° (corr.). A method for the synthesis of 9-methyloctalin is deduced. The Na compound from Et cyclohexanone-2-carboxylate in PhMe with CH<sub>2</sub>:CH·CH<sub>2</sub>·CH<sub>2</sub>Br yields Et 2-Δ<sup>7</sup>-butenylcyclohexanone-2-carboxylate, b.p. 156—158°/25 mm., hydrolysed [Ba(OH)<sub>2</sub>] to 2-Δ<sup>7</sup>-butenylcyclohexanone (II), b.p. 112—114°/28 mm. (*semicarbazone*, m.p. 127°) and the acid (not

purified) corresponding with Et 1-Δ<sup>7</sup>-butenylpimelate, b.p. 161—162°/11 mm., converted (Dieckmann) into Et 2-Δ<sup>7</sup>-butenylcyclohexanone-6-carboxylate, b.p. 146—148°/11 mm., hydrolysed [Ba(OH)<sub>2</sub>] to 1-Δ<sup>7</sup>-butenylpimelic acid, m.p. 39°, and (II), converted (Grignard) into 1-methyl-2-Δ<sup>7</sup>-butenylcyclohexanol, b.p. 102—104°/13 mm., dehydrated (H<sub>3</sub>PO<sub>4</sub>) to *cis*-9-methyl-Δ<sup>2</sup>-octalin (III), b.p. 82°/14 mm., reduced (H<sub>2</sub>-Pt) to *cis*-9-methyldecalin, b.p. 82°/11 mm., converted by AlCl<sub>3</sub> into *trans*-9-methyldecalin. The structure of (III) is proved by oxidation (KMnO<sub>4</sub>) to *trans*-, m.p. 194—196°, and *cis*-1-methylcyclohexane-1:2-diacetic acid, m.p. 160—163°, both of which are converted [Ba(OH)<sub>2</sub>] with loss of CO<sub>2</sub> into 9-methyl-2-hydrindanone, b.p. 109°/20 mm., 219°/760 mm., m.p. indefinite (glass) (*trans*- and *cis*-semicarbazones, m.p. 238° and 220°), oxidised (HNO<sub>3</sub>) to *trans*-, m.p. 162—164°, and *cis*-1-methylcyclohexane-1:2-dicarboxylic acid, m.p. 175°. *n*<sub>D</sub>, *d*, and [R]<sub>D</sub> are recorded for many of these compounds. F. R. G.

**Metallic titanium in organic synthesis.** V. N. SHARMA and S. DUTT (J. Indian Chem. Soc., 1935, 12, 774—780).—Ti may be successfully used as the metallic reactant in Zincke's and Friedel and Crafts' reactions, but is unsatisfactory for Ullmann's reaction, reaction occurring only when the halogen is loosely bound in the org. mol. It is unsatisfactory as a neutral reducing agent. Several examples of each reaction are given. H. G. M.

**Influence of solvent on the course of chemical reactions. V. State of the benzene molecule in solution.** K. LAUER and R. ODA (Ber., 1936, 69, [B], 851—861; cf. this vol., 300).—Examination of the absorption spectrum of C<sub>6</sub>H<sub>6</sub> in AcOH, cyclohexane (I), cyclohexene (II), and C<sub>2</sub>Me<sub>4</sub> combined with Henri's earlier measurements shows that all bands of it are displaced towards longer λ in all the media used, that the permanent dipole of the solvent does not appear to be related to the displacement, and that the most marked total displacement occurs in CCl<sub>4</sub>. The solvent appears to exercise three actions which result in band displacements of the solute; (a) impediment of the association of the dissolved mols. by formation of its proper, voluminous associates, (b) hindrance of association by its own mol. form, and (c) association of the solvent mols. with the solute mols. Saturated dipolar mols. such as H<sub>2</sub>O, EtOH, and Et<sub>2</sub>O belong to the first group, saturated non-polar mols. such as hexane and (I) to the second group. All three actions are present simultaneously in AcOH. C<sub>2</sub>Me<sub>4</sub>, (II), and liquid C<sub>6</sub>H<sub>6</sub> belong to group (b), whilst CCl<sub>4</sub> is the sole exclusive representative of group c. Determination of the rates of reaction of Br on C<sub>6</sub>H<sub>6</sub>, PhMe, and tetrahydronaphthalene in hexane shows that bromination occurs at associated and non-associated C<sub>6</sub>H<sub>6</sub> mols. The apparent constancy of the heat of activation in very dil. solution is caused by the small heat of association. The rapid reaction after further dilution is due to increase in the no. of non-associated mols. recognised by the increasing action const. The reason of the increase of the action const. in conc. solution is increase in the mol. size by association and the consequent increase of the



sensitive region. The results of measurements in  $\text{H}_2\text{O}$ ,  $\text{AcOH}$ , and  $\text{CCl}_4$  are discussed. It is concluded that the displacements observed in the spectrum of non-polar mols. in various solvents is caused by the formation of organised mol. aggregates in which the individual mols. have an altered affinity field and changed region of susceptibility. All reactions hitherto investigated occur with associated and non-associated mols. Heats of dissolution, solvation, and association of the partners in the reaction are expressed in the criteria of the changes, so that addition occurs previously to substitution. H. W.

**Preparation of deuterobenzene.** A. KLIT and A. LANGSETH (Z. physikal. Chem., 1936, 176, 65—80).— $\text{C}_6\text{D}_6$  containing up to 98% D has been prepared by exchange reaction between  $\text{DCl}$  and  $\text{C}_6\text{H}_6$  catalysed by anhyd.  $\text{AlCl}_3$ . For pure  $\text{C}_6\text{D}_6$  the vals.  $d_4^{20}$  0.9483 and m.p.  $6.64^\circ$  have been calc. The equilibrium const. of the simplified exchange reaction  $\text{CH} + \text{DCl} \rightleftharpoons \text{CD} + \text{HCl}$  is  $\sim 1.6$ . In a mixture of various deuterobenzenes not containing a catalyst there is no exchange of H atoms between the mols. When exchange occurs, the D atoms are distributed between the benzene nuclei in such a way that the product is a mixture of the possible isomeric deuterobenzenes in such proportions as correspond with the laws of probability. R. C.

**Reactions of hexadeuterobenzene.** H. ERLMEYER, H. LOBECK, and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 546—547).—When  $\text{C}_6\text{D}_6$ ,  $\text{ClCO}\cdot\text{NH}_2$ , and  $\text{AlCl}_3$  react in  $\text{CS}_2$  and the complex is decomposed with 99.6%  $\text{D}_2\text{O}$ , the amide (I) gives on hydrolysis  $\text{C}_6\text{D}_5\text{CO}_2\text{H}$ , as when the complex is decomposed with  $\text{H}_2\text{O}$  (this vol., 604), showing that exchange of D with the H of  $\text{ClCO}\cdot\text{NH}_2$  occurs during condensation. (I) gives by the Hofmann reaction  $\text{C}_6\text{D}_5\text{CH}_2\text{NHAc}$ , m.p.  $114.3^\circ$ , i.e., without exchange of H and D. Reaction of  $\text{C}_6\text{D}_6$  with  $\text{PhNCO}$  and  $\text{AlCl}_3$  in  $\text{CS}_2$ , followed by decomp. with  $\text{D}_2\text{O}$ , gives nearly pure  $\text{C}_6\text{D}_5\text{CONDPh}$ , which with molten  $\text{KOH}$  loses D to give  $\text{C}_6\text{D}_5\text{CO}_2\text{H}$ . R. S. C.

**Additive products of halogens and benzene derivatives.** IV. Addition of chlorine and bromine to monohalogenobenzenes. T. VAN DER LINDEN (Rec. trav. chim., 1936, 55, 282—292).— $\text{Cl}_2$  and  $\text{PhF}$ , exposed to light in a sealed tube, afford *chlorofluorobenzene hexachloride*, m.p.  $213\text{--}215^\circ$ , *fluorobenzene hexachloride*, b.p.  $112\text{--}117.5^\circ/0.5\text{--}0.6\text{ mm.}$ , and a more highly chlorinated product. Similarly,  $\text{Cl}_2$  and  $\text{PhBr}$  afford a *chlorobromobenzene hexachloride*, m.p.  $254\text{--}256^\circ$ , and unidentified products.  $\text{Cl}_2$  and  $\text{PhI}$  give  $\text{C}_6\text{Cl}_5\text{I}$ ,  $p\text{-C}_6\text{H}_4\text{ClI}$ , and probably  $2:4:5\text{-C}_6\text{H}_2\text{Cl}_3\text{I}$ ; no additive products were found.  $\text{Br}$  (6 atoms) and  $\text{PhF}$  react with evolution of  $\text{HBr}$ ; after 7 months in sunlight in a sealed tube  $\text{Br}$  was still present. The crystals formed are probably *bromofluorobenzene hexabromide* (I), m.p.  $161^\circ$ ; an *isomeric*, m.p.  $252^\circ$ , a *bromofluorobenzene*, and a *dibromofluorobenzene* are also obtained.  $\text{Br}$  (1 atom) and  $\text{PhF}$  in 20 days afford a mixture of  $\text{C}_6\text{H}_4\text{BrF}$  isomerides, b.p.  $154\text{--}158^\circ$ , two *fluorobenzene hexabromides*, m.p.  $127\text{--}129^\circ$  and  $154\text{--}156^\circ$ , and (I).  $\text{Br}$  (1 atom) and  $\text{PhCl}$  afford  $p\text{-C}_6\text{H}_4\text{ClBr}$  and *chlorobenzene hexabromide*, m.p.  $126^\circ$ .  $\text{Br}$  and  $\text{PhBr}$  give  $p\text{-C}_6\text{H}_4\text{Br}_2$  and a

*bromobenzene hexabromide*, m.p.  $146^\circ$ .  $\text{Br}$  and  $\text{PhI}$  afford I and  $p\text{-C}_6\text{H}_4\text{BrI}$ . P. G. C.

**Action of aromatic nitro-compounds on magnesium aryl halides.** D. N. KIRSANOV and P. A. SOLODKOV (J. Gen. Chem. Russ., 1935, 5, 1487—1493).—The reaction consists of  $\text{RNO}_2 + \text{MgXR}' \rightarrow \text{ONRR}'\cdot\text{OMgX}$  (II); (I) + (II)  $\rightarrow \text{NRR}'\cdot\text{OMgX}$  (III) +  $\text{R}'\text{O}\cdot\text{MgX}$ ; (III) + 2(I)  $\rightarrow \text{RR}' + \text{NRR}'\cdot\text{MgX} + (\text{MgX})_2\text{O}$ . The final products have been isolated and identified in the cases  $\text{R}=\text{R}'=\text{Ph}$ ,  $\text{X}=\text{Br}$ ;  $\text{R}=\alpha\text{-C}_{10}\text{H}_7$ ,  $\text{R}'=\text{Ph}$ ,  $\text{X}=\text{Br}$ ;  $\text{R}=\text{Ph}$ ,  $\text{R}'=\alpha\text{-C}_{10}\text{H}_7$ ,  $\text{X}=\text{Br}$ ;  $\text{R}=\text{Ph}$ ,  $\text{R}'=p\text{-C}_6\text{H}_4\text{Me}$ ,  $\text{X}=\text{Br}$ . R. T.

**Attempted preparation of benzyl fluoride from phenyldiazomethane.** C. L. TSENG, (Miss) P. T. CHIA, and T. S. Ho (Sci. Rep. Nat. Univ. Peking, 1936, 1, 9—16).— $\text{CHPhN}_2$  and 40% aq.  $\text{H}_2\text{F}_2$  give  $(\text{CHPh})_2$  and a trace of  $\text{PhCHO}$ . R. S. C.

**Cracking process. Pyrolytic transformation of *p*-xylene and *m*-xylene.** G. BADDELEY and J. KENNER (Ber., 1936, 69, [B], 902—904).—Analogy is traced between the actions of heat and  $\text{AlCl}_3$  on hydrocarbons. Passage of *p*-xylene (I) vapour through a  $\text{SiO}_2$  tube at  $800^\circ$  gives  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , 2:6-dimethylantracene (II), and a little *m*-xylene (III). Under similar conditions (III) is much more extensively carbonised; it gives  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ ,  $\text{C}_{10}\text{H}_8$ , and anthracene, but apparently not (I) or (II). H. W.

**Chlorination and nitration by nitrosyl chloride.** R. PERROT (Compt. rend., 1936, 202, 494—495).—Addition of  $\text{NOCl}$  to phenylethylene derivatives in  $\text{CCl}_4$  at room temp. is always accompanied by oxidation, which accounts for the small yields of the expected nitrosochloride.  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$ , and sometimes  $\text{NH}_2\text{OH}\cdot\text{HCl}$  are also formed, together with an oil which loses  $\text{HCl}$  on distillation giving a mixture of nitrated and chlorinated products. Thus styrene yields  $\text{CHPhCl}\cdot\text{CH}_2\text{Cl}$ ,  $\text{CHPh}\cdot\text{CH}\cdot\text{NO}_2$ , and a compound, m.p.  $118^\circ$  (decomp.), which contains two N to one of Cl and behaves like a nitrosochloride, giving with  $\text{C}_6\text{H}_{11}\text{N}$  a nitro-amine, m.p.  $136^\circ$ .  $\alpha$ -Chlorostyrene is converted into its  $\alpha\beta$ -trichloro- and  $\alpha\beta$ -dichloro- $\beta$ -nitro, b.p.  $148\text{--}150^\circ/20\text{ mm.}$ , derivatives.  $\text{CPh}_2\cdot\text{CH}_2$  gives a mixture of  $\text{Cl}_2$ - and  $(\text{NO}_2)_2$ -derivatives, and some  $\text{CPh}_2\cdot\text{CH}\cdot\text{NO}_2$ .  $\text{CPh}_2\cdot\text{CHMe}$  gives its  $\beta$ -Cl-derivative, m.p.  $39^\circ$ , and a compound, m.p.  $103^\circ$ , considered to be  $\text{CPh}_2\text{Cl}\cdot\text{CHMe}\cdot\text{NO}_2$ .  $\text{CPh}_2\cdot\text{CMe}_2$  reacts slightly with  $\text{NOCl}$  and  $\text{CPh}_2\cdot\text{CPh}_2$  not at all, except at about  $150^\circ$  with the formation of  $\text{CPh}_2\text{Cl}_2$  and products containing nuclear Cl. Other styrene derivatives yield mixtures difficult to separate. *cycloHexene* gives a mixture of 1:2-dichloro- and chloronitroso-*cyclohexane*. H. G. M.

***o*-Divinylbenzene and naphthalene.** K. FRIES and H. BESTIAN [with, in part, W. KLAUDITZ] (Ber., 1936, 69, [B], 715—722).—Spectrochemical evidence shows that in the formation of  $\text{C}_{10}\text{H}_8$  from *o*-divinylbenzene (I) ring closure is not accompanied by "optical neutralisation of valencies," and does not therefore involve appreciable change in the state of union and the internal compensation of the conjugated system. The transition of  $\Delta^{7,8}$ -hexatriene into  $\text{C}_6\text{H}_6$  and of phenylbutadiene into  $\text{C}_{10}\text{H}_8$  is accom-



panied by marked change in optical properties and chemical behaviour.  $\beta\beta'$ -*o*-Phenylenediacrylic acid (II) (*Me*<sub>2</sub> ester, m.p. 68°, and its tetrabromide, m.p. 141°; *Et*<sub>2</sub> ester, m.p. 81°, and its tetrabromide, m.p. 138°; dichloride, m.p. 84°; dianilide, m.p. 231°) evolves CO<sub>2</sub> when heated with production of a (?) polymeride of (I); its Na salt is transformed by distillation with soda-lime mainly into C<sub>10</sub>H<sub>8</sub>. Short treatment of (II) with boiling Ac<sub>2</sub>O leads to the mixed anhydride, C<sub>6</sub>H<sub>4</sub>(CH:CH:CO·OAc)<sub>2</sub>, m.p. 94° (decomp.), which passes when heated at 120°/vac. into Ac<sub>2</sub>O and  $\beta\beta'$ -*o*-phenylenediacrylic anhydride, m.p. 254–256° (decomp.), unusually stable towards alkali hydroxide.  $\beta\beta'$ -*o*-Phenylenedipropionic acid, m.p. 171°, readily prepared by hydrogenating (II) under pressure at room temp. in presence of Ni, Co, or mixed Cu catalyst, is converted by the successive action of SOCl<sub>2</sub> and NH<sub>3</sub>·H<sub>2</sub>O into  $\beta\beta'$ -*o*-phenylenedipropionamide, m.p. 195°, transformed by KOH and Br into *o*- $\beta\beta'$ -diaminoethylbenzene, b.p. 130–131°/1 mm. [hydrochloride, m.p. 255–265° (decomp.); Ac<sub>2</sub>, m.p. 111°, and Bz<sub>2</sub>, m.p. 154°, derivatives], not identical with the product described by von Braun *et al.* (A., 1917, i, 130). The corresponding diquaternary iodide, C<sub>16</sub>H<sub>30</sub>N<sub>2</sub>I<sub>2</sub>, m.p. 310° (decomp.), is converted by treatment with Ag<sub>2</sub>O and distillation into (I), b.p. 73–74°/12 mm., which is stable in the dark, but rapidly polymerises in direct sunlight. Hydrogenation (PtO<sub>2</sub>) of (I) affords *o*-diethylbenzene, b.p. 66–67°/12 mm., 176–177°/760 mm. Partial hydrogenation of (I) and treatment of the product with Br in CHCl<sub>3</sub> leads to unchanged (I), its tetrabromide, and, mainly, *o*-ethyl- $\alpha\beta$ -dibromoethylbenzene, b.p. 141–142°/12 mm., which is debrominated by Mg in Et<sub>2</sub>O to *o*-ethylvinylbenzene, b.p. 68–68.5°/12 mm.

H. W.

**Plano-radiate compounds. III. Hexasulphones of hexamethylbenzene.** H. J. BACKER (Rec. trav. chim., 1936, 55, 17–21).—The following compounds, C<sub>6</sub>(CH<sub>2</sub>·SO<sub>2</sub>·R)<sub>6</sub>, are obtained by oxidation of the appropriate thio-ether with H<sub>2</sub>O<sub>2</sub>–AcOH: R=Me, m.p. > 360°; Et (+2AcOH), m.p. 340°; Pr<sup>n</sup>, m.p. 305°; Pr<sup>s</sup> (+2AcOH), m.p. 340°; Bu<sup>n</sup>, m.p. 315–316°; Bu<sup>s</sup>, m.p. 289–290°; *sec*-Bu (+AcOH), m.p. 260–261°; Bu<sup>r</sup>, m.p. > 360°; *n*-amyl, m.p. 279–281°; *tert*-amyl (+2AcOH), m.p. > 360°; *n*-hexyl, m.p. 266–267°; Ph (+AcOH), m.p. 320–325°; *p*-C<sub>6</sub>H<sub>4</sub>Me, m.p. 282°; *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>r</sup>, m.p. 295–300°; and CH<sub>2</sub>Ph, m.p. 334°. These compounds crystallise readily and are not very sol. C<sub>6</sub>(CH<sub>2</sub>·S·C<sub>6</sub>H<sub>4</sub>Bu<sup>r</sup>)<sub>6</sub> crystallises with 1 mol. of heptane, 2 mols. of C<sub>6</sub>H<sub>6</sub>, and 2 mols. of *m*-xylene, respectively, from these solvents.

H. G. M.

**Dipole moment and molecular structure.**  
**XVI. Configuration of ethylenic compounds.**  
 E. BERGMANN (J.C.S., 1936, 402–411).—A vanishing dipole moment ( $\mu$ ) for *isostilbene* (Wildschut, Diss., Delft, 1932), *stilbene* (Smyth *et al.*, A., 1931, 669), (NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CH)<sub>2</sub>, m.p. 225°, (CClPh)<sub>2</sub>, m.p. 144°, and (C[NO<sub>2</sub>]Ph)<sub>2</sub>, m.p. 186°, indicates a *trans* structure. The following finite vals. indicate a *cis* structure: (CClPh)<sub>2</sub>, m.p. 60°,  $\mu$  2.69, [compound with (CPh)<sub>2</sub>], m.p. 67–69°, (CBrPh)<sub>2</sub>, m.p. 68°,  $\mu$  2.53 [compound with (CPh)<sub>2</sub>], *p*-C<sub>6</sub>H<sub>4</sub>Cl·CPh:CCBrPh, m.p. 160°,  $\mu$  2.61, or m.p. 113°,  $\mu$  1.57, CPh:CClPh,  $\mu$  1.53. The following vals. of  $\mu$  were also obtained:  $\alpha$ -bromostilbene, m.p. 31°, 1.38 (liquid), 1.30, Et, 1.84, Et *allo*-, 1.77, Et  $\beta$ -phenyl-, 1.98, Me  $\alpha$ -phenyl-cinnamate, 1.92; *o*-C<sub>6</sub>H<sub>4</sub>Ph·CN, 3.81; Et *p*-nitro-, 3.50, and Me *p*-nitro- $\alpha$ -phenyl-cinnamate, 3.78, indicating *trans* structures; *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Et, 3.84; of Me, 1.89 Et, 1.98 (from acid m.p. 134°), and Me  $\alpha\beta$ -dibromocinnamate 2.68 (from acid, m.p. 100°) (the last is Ph > C:C < CO<sub>2</sub>H / Br > C:C < Br); of Et, 2.63 (from acid, m.p. 159°) and Me  $\beta$ -bromocinnamate, 1.81 (from acid, m.p. 134°) (the latter is Ph > C:C < CO<sub>2</sub>H / Br > C:C < H contrary to Auwers *et al.*; A., 1932, 271); benzylidene-, 2.92, benzylidene-*p*-bromo-, 2.93,  $\alpha\beta$ -dibromobenzylidene- (m.p. 113–114°), 3.17 (hence Ph > C:C < Br / Br > C:C < CPh),  $\beta$ -bromobenzylidene-, 3.59 (hence Ph > C:C < H / Br > C:C < CPh),  $\alpha$ -bromobenzylidene-, 3.87, *p*-bromobenzylidene-, 2.47 (hence *trans*), *pp'*-dibromobenzylidene-acetophenone, 2.03 (hence *trans*); CHPh:CCBr·CO<sub>2</sub>Et (from acid, m.p. 131°), 2.25 (from acid, m.p. 126°), 2.80; Et-, 1.75, Et *p*-nitro-, 4.58, Me *p*-bromo- $\beta$ -phenylpropionate, 2.39; NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·C:C·CO<sub>2</sub>Et, 3.54 (hence straight structure);  $\omega$ -nitro-, 4.48,  $\omega$ -chloro-, 1.40,  $\omega$ -bromo-, 1.51,  $\omega$ -ethoxy-styrene, 1.63.

F. R. G.

**Use of paramagnetism as a test for free radicals.** F. L. ALLEN and S. SUGDEN (J.C.S., 1936, 440–441).—Solid NPh<sub>2</sub>·N·C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>3</sub>, (p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C, and CPh<sub>2</sub>·OK are strongly paramagnetic and hence consist largely of free radicals. Solid 10:10'-bis-5:10-dihydrophenarsazine and CSpH<sub>2</sub> are diamagnetic, hence the former probably contains no free radical and the latter may be a free diradical.

F. R. G.

**Autoxidation of substituted difluoryls and dixanthyls.** H. W. SCHERF (J. Amer. Chem. Soc., 1936, 58, 576–580).—Autoxidation of 9:9'-diphenyl- (I), 9:9'-*di-p-tolyl*- (II), m.p. 216° (from 9-chloro-9-*p*-tolylfluorene, m.p. 96.5°, and Cu-bronze in N<sub>2</sub>), 9:9'-didiphenyl- (III), and 9:9'-dianisyl- (IV) -9:9'-difluoryls in *s*-C<sub>2</sub>H<sub>5</sub>Cl<sub>4</sub> (usually 0.01M solution) at 0° and 25° occurs principally by oxidation of the undissociated mol. and to a small extent by oxidation of the free radical. The rate for (I) is not affected by quinol (0.1 or 1%) or change in concn. With one exception, the ratio  $k_{O_2}/k_{air}$  is lower at 0° than at 25°. There is no parallelism between the rate of autoxidation [viz., (III) < (IV) < (II) < (I)] and degree of dissociation into free radicals [viz., (II) < (I) < (III) < (IV); determined in EtOBz and N<sub>2</sub> at 70°]. Autoxidation of dimethyl-, *disoamyl*-, and dibenzyl-dixanthyls at –11.2° to 50° is dependent (in the early stages of the reaction) on slow dissociation into free radicals and subsequent rapid oxidation (cf. Conant and Evans, A., 1929, 934).

H. B.

**Rubenes. Isomerisation of diphenylbis-*p*-bromophenylrubene into the corresponding pseudo-derivatives.** L. ENDERLIN (Compt. rend., 1936, 202, 495–497; cf. A., 1929, 549; this vol.,



462).—Diphenylbis-*p*-bromophenylrubene when treated in  $C_6H_6$  with  $H_2SO_4$  yields irreversibly two isomerides, m.p.  $340^\circ$  and m.p.  $240$ – $245^\circ$  and m.p.  $295^\circ$  after resolidification, separable by means of  $CS_2$ .

H. G. M.

**Reversible oxidisability of organic compounds: dihydroxide of diphenylbis-(*p*-bromophenyl)-rubene.** L. ENDERLIN (Compt. rend., 1936, 202, 1188–1190; cf. this vol., 600).—Prolonged oxidation of diphenylbis-*p*-bromophenylrubene in  $C_6H_6$  with 0.1%  $KMnO_4$  at room temp. affords dihydroxydihydrodiphenylbis-(*p*-bromophenyl)rubene,  $C_{42}H_{26}Br_2(OH)_2$ , decomp. at  $230^\circ$  (block), which is reduced ( $Fe-AcOH$ ) quantitatively to the rubene, and at  $220^\circ$  loses  $1H_2O$  to give a monoxide,  $C_{42}H_{26}Br_2O$ . Boiling  $AcOH$  or cold  $H_2SO_4$  removes  $2H_2O$  to give  $C_{42}H_{24}Br_2$ , which exhibits a violet fluorescence.

J. L. D.

**Mechanism of isomerisation of cyclic amines.**

**Action of potassium hydroxide on nitrosocyclopropylcarbamide.** V. P. GOLMOV (J. Gen. Chem. Russ., 1935, 5, 1562–1565).—cycloPropylamine and  $KCNO$  are dissolved in  $H_2O$ , the solution is evaporated to dryness at  $100^\circ$ , and the residue is extracted with  $EtOH$ , when cyclopropylcarbamide (I), m.p.  $123$ – $124^\circ$ , is obtained. (I) in aq.  $H_2SO_4$  and  $NaNO_2$  at  $0^\circ$  afford nitrosocyclopropylcarbamide, m.p.  $86^\circ$  (decomp.), which is converted, probably by way of diazocyclopropane, into  $CH_2:CH-CH_2-OH$  by aq.  $KOH$  at  $0^\circ$ .

R. T.

**Transposition of *N*-arylformimino-ethers,  $OEt-CH:NR$ .** M. GRUNFELD (Bull. Soc. chim., 1936, [v], 3, 668–674).—When passed over infusorial earth at  $200^\circ/17$  mm.,  $NPh:CH-OEt$  is largely unchanged; at  $300^\circ/15$  mm., it gives  $EtOH$ ,  $PhNC$ , and  $PhCN$ , whereas at  $400^\circ/65$  mm.  $EtOH$  and  $PhCN$  are formed exclusively.  $o-C_6H_4Me:N:CH-OEt$  is unchanged at  $180^\circ/13$  mm., gives  $EtOH$ ,  $o-C_6H_4Me:NC$ , and  $o-C_6H_4Me-CN$  at  $300^\circ/16$  mm., and  $EtOH$  and  $o-C_6H_4Me-CN$  at  $400^\circ/40$ – $50$  mm.  $p-C_6H_4Me:N:CH-OEt$  at  $300^\circ/18$ – $25$  mm. affords unchanged material,  $EtOH$ ,  $p-C_6H_4Me:NC$ , and  $p-C_6H_4Me-CN$ . Contrary to Wislicenus, diphenylformamidine is not produced when  $NPh:CH-OMe$  or  $NPh:CH-OEt$  is heated in a sealed tube at  $230$ – $240^\circ$ . Ethoxymethylene-*m*-toluidine, from  $m-C_6H_4Me:NH_2$  and  $CH(OEt)_3$  at  $125^\circ$  and subsequently at  $190$ – $210^\circ$ , has b.p.  $84^\circ/2$  mm.

H. W.

**Mechanism of amination by means of sodamide. I. Preparation of substituted amidines.**

A. V. KIRSANOV and J. N. IVASCHTSCHENKO (J. Gen. Chem. Russ., 1935, 5, 1494–1505).— $NPh:CHPh$  (I) in  $PhMe$  and  $NaNH_2$  (II) at  $120^\circ$  react as follows: (I) + (II)  $\rightarrow NH_2-CHPh-NPhNa \rightarrow NH_2-CPh:NPh$  (III) +  $NaH \rightarrow NHNa-CPh:NPh$  (IV) +  $2H$ ; (I) +  $2H \rightarrow NHPh-CH_2Ph$  (V); (III) + (II)  $\rightarrow$  (IV) +  $NH_3$ ;  $3(I) + 2NH_3 \rightarrow \begin{matrix} CHPh-NH \\ | \\ CHPh-N \end{matrix} \gg CPh$  (VI) +  $3NH_2Ph$ ; (VI) undergoes further conversion into lophine (VII). The yields of final products isolated were  $NH_2Ph$  12.0, (III) 19.6, (V) 14.9, and (VIII) 12.8%; the corresponding products and yields obtained when benzyldine-*p*-toluidine is substituted for (I) are *p*-toluidine 22.6, *p*-tolylbenzamidine 22.6, benzyl-*p*-toluidine 20.6, and (VII) 12.3%, whilst piperonylideneaniline yields the

*N*-phenylamidine of piperonylic acid, m.p.  $138$ – $139^\circ$ , and piperonylaniline. It is considered that the above mechanism also applies to the reaction of amination of  $C_6H_5N$  by (II).

R. T.

**Regulated hydrolysis of acetyl derivatives of reducing sugars.** M. FRÈREJACQUE (Compt. rend., 1936, 202, 1190–1192).—Glucose  $\beta$ -penta-acetate (I) in 95%  $EtOH$  containing some  $AcOH$  with  $p-C_6H_4Me-NH_2$  at room temp. affords  $\beta$ -tetra-acetylglucosidyl-*p*-toluidide (cf. A., 1928, 870). With  $NH_2Ph$ , (I) similarly affords a mixture of the anilides of the  $\alpha$ - and  $\beta$ -tetra-acetates. The following are prepared:  $\alpha$ -tetra-acetylglucosidylanilide, m.p.  $143^\circ$ ;  $\beta$ -tetra-acetylglucosidylacetyl-anilide, m.p.  $100^\circ$ , *p*-toluidide, m.p.  $142^\circ$ , *p*-bromoanilide, m.p.  $134^\circ$ ;  $\alpha$ -, m.p.  $197^\circ$ , and  $\beta$ -hepta-acetyl-lactosidyl-anilide (I), m.p.  $152^\circ$ , and *p*-toluidide, m.p.  $202^\circ$ ;  $\beta$ -hepta-acetyl-maltosidyl-anilide (II), m.p.  $205^\circ$ , and *p*-toluidide, m.p.  $182^\circ$ ;  $\beta$ -hepta-acetylcellobiosidyl-anilide (III), m.p.  $218^\circ$ , and *p*-toluidide, m.p.  $215^\circ$ . (I), (II), and (III) show mutarotation and are easily hydrolysed, but after acetylation, they neither mutarotate nor are they easily hydrolysed.

J. L. D.

**Attempted cyclisation of *N*- $\beta$ -hydroxyethyl-aniline, and its benzoyl derivatives.** P. P. SCHORIGIN and V. N. BELOV (J. Gen. Chem. Russ., 1935, 5, 1707–1717).—Attempts to obtain dihydroindole by the dehydration of  $NHPh-CH_2-CH_2-OH$  (I) (picrate, m.p.  $124$ – $125^\circ$ ), under different conditions (passing the vapour in a stream of  $CO_2$  over kaolin at  $450$ – $520^\circ$ , heating with  $H_2C_2O_4$ ,  $AlCl_3$ , or  $Na$ ), were unsuccessful. A small amount of *N*-vinylaniline, m.p.  $66$ – $67.5^\circ$  (*Bz* derivative, m.p.  $191$ – $192^\circ$ ), was obtained by heating with  $Na$  for 2 hr. at  $260$ – $280^\circ$ . The *Bz* derivative of (I) yields the *O*-monobenzoate (II) [picrate, m.p.  $150^\circ$ ; *N*-*Me* derivative, m.p.  $46$ – $48^\circ$  (picrate, m.p.  $163$ – $164^\circ$ )] of (I) when hydrolysed with  $EtOH-KOH$ ; under very mild conditions of hydrolysis an intermediate product, m.p.  $74$ – $75^\circ$ , probably  $NPh-\begin{matrix} CH_2 \\ | \\ CPh(OH)-O \end{matrix}-CH_2$ , is obtained. The *N*-*Bz* derivative of (I) readily undergoes conversion into (II).

R. T.

**Rhodanisation of organic compounds.** S. A. ZABOEV (J. Gen. Chem. Russ., 1935, 5, 1607–1610).—*p*- $SCN-C_6H_4-NMe_2$  (I) is obtained in good yield from  $NPhMe_2$  (II),  $NH_4CNS$ , and  $CaOCl_2$  in aq.  $AcOH$ , at room temp., or by passing  $Cl_2$  at  $-10^\circ$  into an aq.  $AcOH$  solution of (II) and  $KCNS$ . (I) is converted into  $(NMe_2-C_6H_4-S)_2$  by boiling with aq.  $KOH$ .  $5:1:2-CNS-C_6H_3Me-NH_2$  and *p*- $CNS-C_6H_4-OH$  have been prepared similarly from *o*-toluidine and  $PhOH$ , respectively.

R. T.

**Rearrangement of carbamyl-sulphones and -sulphides.** W. J. EVANS and S. SMILES (J.C.S., 1936, 329–331).—2-Nitrophenyl-thioacetanilide, m.p.  $159$ – $160^\circ$ , is oxidised to -sulphonylacetanilide, m.p.  $151$ – $152^\circ$ , which undergoes rearrangement ( $NaOH$ ) to 2-nitro-*N*-acetyldiphenylamine. Similarly, 2-nitrophenyl-sulphonylacetate, m.p.  $207^\circ$ , obtained from -thioaceto-*m*-nitroanilide, m.p.  $216$ – $217^\circ$ , is rearranged to 2:3'-dinitrodiphenylamine. 2-Nitrophenylsulphonyl-, m.p.  $155$ – $156^\circ$ , obtained from -thioacetamide, m.p.  $178$ – $179^\circ$ , does not undergo rearrangement.



$\beta$ -2-Nitrophenyl-thiopropionanilide, m.p. 166°, obtained from the corresponding acid, m.p. 147°, is oxidised to the -sulphonyl compound, m.p. 186—187°, neither sulphide nor sulphone undergoing rearrangement, possibly owing to the steric relationships. 2-o-Nitrophenylthiobenzamide, m.p. 164°, and -anilide, m.p. 127—128°, obtained from the acid chloride, are oxidised, respectively, to 2-o-nitrobenzenesulphonylbenzamide, m.p. 193—194°, and -anilide, m.p. 184°. Rearrangement, followed by methylation, of these compounds gives, respectively, 2-methylthiolbenzo-o-nitroanilide, m.p. 111°, and -2'-nitrodiphenylamide, m.p. 146—147°, and 2-methylsulphonylbenzo-o-nitroanilide, m.p. 221°, and -2'-nitrodiphenylamide, m.p. 206°.

F. R. S.

**3-Nitro-4-aminodiphenylmethane and its derivatives.** W. A. WATERS (J.C.S., 1935, 1875).—4-Acetamidodiphenylmethane when treated at 25° during 1 hr. with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in  $\text{Ac}_2\text{O}$  (Menke's method) affords 3-nitro-4-acetamidodiphenylmethane (I), m.p. 99°, also obtained when a warm solution of 4-aminodiphenylmethane in  $\text{Ac}_2\text{O}$  is similarly treated with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ — $\text{Ac}_2\text{O}$ , and hydrolysed by  $\text{H}_2\text{SO}_4$ — $\text{EtOH}$  to 3-nitro-4-aminodiphenylmethane, m.p. 78° (5-Br-derivative, m.p. 71°). (I) with  $\text{H}_2\text{SO}_4$ — $\text{AcOH}$ — $\text{HNO}_3$  yields 3:4'-dinitroacetamidodiphenylmethane (A., 1933, 1044), also obtained together with some 3:5-dinitro-4-acetamidodiphenylmethane, m.p. 81—82°, when (I) is treated by Menke's method.

H. G. M.

**Optical activity in relation to tautomeric change.** V. Kinetic status of ionic intermediates in prototropy. S. K. HSÜ, C. K. INGOLD, and C. L. WILSON (J.C.S., 1935, 1778—1785).—The velocity coeffs. and equilibrium consts. of isomerisation of *dl*-benzhydrylidene- $\alpha$ -phenylethylamine (I) and of *dl*-benzylidene-*p*-phenylbenzhydrylamine (II) have been determined and compared, respectively, with the rate of racemisation of optically active (I) and the rate of mutarotation of the system optically active (II)+its isomeride. The results accord with the view that loss of optical activity does not occur in any reversibly formed intermediate state in the isomerisation process (cf. A., 1934, 260), and that the ionisation products of these systems do not become kinetically free during isomerisation. Prototropy in the methyleneazomethine system therefore occurs by a termol. mechanism of the type proposed by Lowry (A., 1927, 1150), the bimol. mechanism (cf. A., 1926, 939) being restricted to more acid systems such as carboxyl ( $[\text{H}]\cdot\text{O}\cdot\text{C}\cdot\text{O}$ ) and acetone ( $[\text{H}]\cdot\text{O}\cdot\text{C}\cdot\text{C}$ ). *p*-Phenylbenzophenone-2:4-dinitrophenylhydrazone has m.p. 217—217.5°. H. G. M.

**Preparation of Freund's acid from  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid.** G. I. OSTROSHINSKAJA (Anilinokras. Prom., 1935, 5, 138—143).—1:3:6- $\text{NH}_2\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$  (I) is obtained in 93% yield by boiling a mixture of 1:3:6:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_3$ , aq. NaOH, and Zn dust for 7 hr. The dichloride of (I) has m.p. 149° (lit. 157°).

R. T.

**Determination and purification of  $\beta$ -naphthylamine in the presence of  $\alpha$ -naphthylamine, and**

3 B

**properties of some sulphonyl derivatives.** H. H. HODGSON and E. W. SMITH (J.C.S., 1935, 1854—1856).—The solubilities of *p*-toluenesulphon- $\alpha$ - (I) and  $\beta$ -naphthalide (II) in 20% aq. NaOH at 16° are 125 g. and 3 g. per litre, but in 2% aq. KOH are 85 g. and 66 g. per litre, respectively. (II) is completely pptd. by  $\leq 10\%$  aq. NaOH from a solution of (I) and (II) in 2% NaOH, provided [(I)] is  $\geq 20\%$ , thus permitting the determination of  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  (III) in presence of  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  (IV). (III) may be purified from (IV) by pptn. from  $\text{C}_6\text{H}_6$  by HCl, or by neutralising an acid solution of the mixture, the hydrochloride of (III) or (III) itself being pptd. first, respectively. Na<sup>+</sup> can easily be detected when  $[\text{Na}^+]$  is  $> 2\%$  by addition of (II)— $\text{KOH}$ — $\text{H}_2\text{O}$ . 2:4:1- $(\text{NO}_2)_2\text{C}_{10}\text{H}_5\cdot\text{NH}_2$  (improved prep.) has m.p. 242° (lit. 239°). The following are described: Na salt, m.p. 370°, of (II); Na, m.p. 256°, Na ( $+\text{H}_2\text{O}$ ), Na ( $+\text{H}_2\text{O}$ ), m.p. 85°, K, m.p. 232°, and K ( $+\text{H}_2\text{O}$ ) salts of *m*-nitrobenzenesulphon- $\alpha$ -naphthalide; *m*-nitrobenzenesulphon- $\beta$ -naphthalide, m.p. 166.5° [Na, m.p. 290°, Na ( $+\text{H}_2\text{O}$ ), and Na ( $+\text{H}_2\text{O}$ ), m.p. about 77°; K, m.p. 240°, K ( $+\text{H}_2\text{O}$ ), K ( $+\text{H}_2\text{O}$ ), m.p. about 70°; Ba, m.p. about 280° (with charring), and Ba ( $+\text{H}_2\text{O}$ ) salts].

H. G. M.

**Preparation and properties of some 1:2-diaminocyclohexanes.** F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 384—393).—2-Methylcyclohexanone with  $\text{Et}_2\text{C}_2\text{O}_4$  and NaOEt— $\text{EtOH}$  at  $-15^\circ$  affords its 6-glyoxylic acid and the corresponding *Et* ester, converted by heating at 210—220° into *Et* 2-methylcyclohexanone-6-carboxylate, b.p. 115—116.5°/12—13 mm., converted by 6% aq. KOH—NaNO<sub>2</sub> and 30%  $\text{H}_2\text{SO}_4$  at room temp. into 6-oximino-2-methylcyclohexanone (I), m.p. 167° (decomp.), a (?) stereoisomeric oxime (II), m.p. 65°, and an oily mixture of oximes. (I) with  $\text{NH}_2\text{OH}\cdot\text{HCl}$ —NaOMe— $\text{MeOH}$  affords 2:3-dioximino-1-methylcyclohexane (III), m.p. 167° [differs in its reactions from that obtained by Wallach *et al.* (A., 1924, i, 862), which was probably a mixture of (III) and (IV)]; (II) similarly gives a dioxime (IV), m.p. 140°. Reduction of (III) with Na-boiling  $\text{EtOH}$  affords 2:3-diamino-1-methylcyclohexane, b.p. 84°/12 mm. (isolated as its hydrochloride  $+\text{H}_2\text{O}$ ), also obtained, together with 3-amino-1-methylcyclohexane, b.p. 41°/12 mm. (Bz derivative, m.p. 106°), by similar reduction of the dioxime obtained from the oily mixed oximes. By similar series of reactions are obtained 2-oximinocyclohexanone (from *Et* cyclohexanone-2-carboxylate), the dioxime, m.p. 187—189°, and trans-1:2-diaminocyclohexane, b.p. 79—81°/15 mm. (resolvable); *Et* 3-methylcyclohexanone-6-carboxylate, b.p. 118—120°/13 mm., 6-oximino-3-methylcyclohexanone, m.p. 159°, the dioxime, m.p. 180—181° (also obtained from *Et* 4-methylcyclohexanone-6-carboxylate, b.p. 113—115°/13 mm.), and 3:4-diamino-1-methylcyclohexane, b.p. 81.5°/13 mm. 3:4-Diamino-1-methyl-4-isopropylcyclohexane (diaminomenthane), b.p. 110—113°/12 mm., is obtained by a modification of the method of Kononov *et al.* (A., 1898, i, 530). Crystallographic data and reactions with metallic salts are given for many of the above compounds.

J. W. B.



**Derivatives of 4:4'-diaminodiphenylmethane.** G. D. PARKES and R. H. H. MORLEY (J.C.S., 1936, 315—317).—Bromination of 4:4'-diacetamidodiphenylmethane gives the 3:3'-Br<sub>2</sub>-derivative, m.p. 198°, hydrolysed to 3:3'-dibromo-4:4'-diaminodiphenylmethane dihydrochloride, m.p. 285° (decomp.), from which is prepared through the tetrazo-compound the corresponding 4:4'-dihydrazinodiphenylmethane dihydrochloride, m.p. 279° (decomp.). 3:3'-Dibromo-4:4'-dibenzamidodiphenylmethane has m.p. 217°. The following have been prepared from the appropriate dihydrazine and the carbonyl compound: 4:4'-bis-o-, m.p. 189°, m-, m.p. 192°, and p-nitrobenzylidenehydrazino-, m.p. 218°; 4:4'-bis-salicylidenehydrazino-, m.p. 252°, -β-phenylethylidenehydrazino-, m.p. 174°, and -γ-phenyl-α-methylallylidenehydrazino-, m.p. 222°; 3:3'-dibromo-4:4'-bis-benzylidenehydrazino-, m.p. 165°, -o-nitrobenzylidenehydrazino-, m.p. 234°, m-, m.p. 278°, and p-, m.p. 255° (decomp.), -salicylidenehydrazino- m.p. 236° (decomp.), and -p-hydroxybenzylidenehydrazino-diphenylmethane, m.p. 238° (decomp.). F. R. S.

**Salt formation of homonuclear naphthalene derivatives.** H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1935, 1850—1854).—2-Nitroaceto-1-naphthalide (I) when treated with AcOH-Cl<sub>2</sub> at 100° (30 min.) yields its 4-Cl-derivative (II), m.p. 219°, hydrolysed to 4-chloro-2-nitro-α-naphthylamine (III), m.p. 202°. This when treated with H<sub>2</sub>SO<sub>4</sub>-NaNO<sub>2</sub> below 20° and then heated with EtOH (water-bath, 90 min.) affords 1-chloro-3-nitronaphthalene, m.p. 127°, which when heated with SnCl<sub>2</sub>-HCl-EtOH gives 4-chloro-β-naphthylamine stannichloride, which with 2% aq. NaOH gives 4-chloro-β-naphthylamine, m.p. 68°. The corresponding 4-Br-derivative (stannichloride; Ac derivative, m.p. 186.5°) was similarly prepared. 2:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> and Hg(OAc)<sub>2</sub>-boiling AcOH yield 2-nitro-α-naphthylamine 4-mercuriacetate, m.p. 242° [the corresponding mercurichloride, m.p. 289°, mercuribromide, m.p. 248°, mercuri-iodide, m.p. 237°, and mercurihydroxide, m.p. above 360° (decomp.)], which with Cl<sub>2</sub> or Br in AcOH gave the corresponding 4-Cl- or 4-Br-derivative, respectively, and when boiled with KI-H<sub>2</sub>O yields the 4-I-derivative, m.p. 195.5° (lit. 192—193°). This when deaminated and subsequently reduced (SnCl<sub>2</sub>-EtOH) affords 4-iodo-2-naphthylamine, m.p. 76° (Ac, m.p. 201°, and Bz derivative, m.p. 145°), as the stannichloride. 4:2:1-NO<sub>2</sub>·C<sub>10</sub>H<sub>5</sub>Cl·NH<sub>2</sub> when boiled with hydrated SnCl<sub>2</sub>, EtOH, and HCl gives 2-chloro-1:4-naphthylenediamine monohydrochloride (IV), diazotisation of which proceeded normally at first but subsequently the diazo-solution deposited a deep purple powder, m.p. above 360° (decomp.). The diamine, m.p. 114° (NN'-Ac<sub>2</sub>, m.p. 314°, and NN'-Bz<sub>2</sub> derivative, m.p. 255°), obtained from (IV), is readily oxidised by 2% alkaline KMnO<sub>4</sub> to 2-chloro-1:4-naphthaquinone. Similarly 2-chloro-4-nitroaceto-1-naphthalide when reduced (hydrated SnCl<sub>2</sub>-HCl-EtOH) affords 2-chloro-1-N-acetyl-1:4-naphthylenediamine, m.p. 215°, as the stannichloride, from which the base was obtained with NaOH. The following were prepared by similar methods: 2-bromo-1:4-naphthylenediamine, m.p. 110° (stannichloride; monohydrochloride; Ac<sub>2</sub>, m.p.

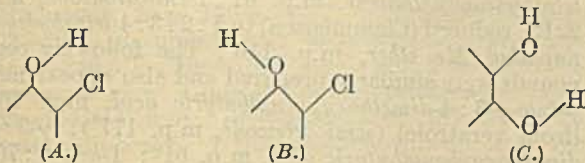
318°, and Bz<sub>2</sub> derivative, m.p. 259°), oxidised to 2-bromo-1:4-naphthaquinone; 2-bromo-4-nitroaceto-1-naphthalide, m.p. 239° (obtained from the amine), with boiling 20% aq. NaOH affords 2-bromo-4-nitro-α-naphthol, m.p. 236°, and is reduced to 2-bromo-1-N-acetyl-1:4-naphthylenediamine, m.p. 217° (stannichloride); 2-iodo-1:4-naphthylenediamine, m.p. 119° (monohydrochloride; NN'-Ac<sub>2</sub>, m.p. 322°, and NN'-Bz<sub>2</sub> derivative, m.p. 262°), oxidised by alkaline 2% KMnO<sub>4</sub> to 2-iodo-1:4-naphthaquinone, m.p. 120°; 2-iodo-4-nitroaceto-1-naphthalide, m.p. 222° (prepared by heating 4-nitro-α-naphthylamine 2-mercuriacetate with Ac<sub>2</sub>O and boiling the resulting 4-nitroaceto-1-naphthalide 2-mercuriacetate, m.p. 270°, with aq. KI-I), with boiling 20% aq. NaOH affords 2-iodo-4-nitro-α-naphthol, m.p. 229°, and is reduced to 2-iodo-1-N-acetyl-1:4-naphthylenediamine, m.p. 235° (stannichloride); 4-chloro-1:2-naphthylenediamine (V), m.p. 95° (monohydrochloride; with Ac<sub>2</sub>O at 35—40° gives the 2-N-Ac derivative (VI), m.p. 235°), obtained from (III); 4-chloro-1-N-acetyl-1:2-naphthylenediamine (VII), m.p. 243° (stannichloride), obtained from (II), yields (with Ac<sub>2</sub>O) the Ac<sub>2</sub> derivative, m.p. 174°, of (V), not obtained from (VI) and boiling Ac<sub>2</sub>O; 4-chloro-1:2-naphthaquinone, m.p. 188° [readily obtained by air-oxidation of (VII)]; 4-bromo-1:2-naphthylenediamine (VIII), m.p. 97° (monohydrochloride; 2-N-Ac derivative, m.p. 225°, obtained from the base and boiling Ac<sub>2</sub>O). (I) with Br-AcOH above 45° yields 4-bromo-2-nitroaceto-1-naphthalide, m.p. 239°, reduced to 4-bromo-1-N-acetyl-1:2-naphthylenediamine, m.p. 248° (stannichloride), converted by boiling Ac<sub>2</sub>O into the NN'-Ac<sub>2</sub> derivative, m.p. 225°, of (VIII), not obtained from the 2-N-Ac isomeride and Ac<sub>2</sub>O. The following were similarly prepared: 4-iodo-1:2-naphthylenediamine, m.p. 98° [monohydrochloride; 2-N-Ac, m.p. 238°, and NN'-Ac<sub>2</sub> derivative, m.p. 167°; 1-N-Ac derivative, m.p. 271° (stannichloride)]. The stability of the salts of the foregoing bases is discussed. H. G. M.

**Decomposition of azo-compounds by mineral acids.**—See B., 1936, 311.

**Interpretation of infra-red absorption of organic compounds containing hydroxyl and imino-groups.** L. PAULING (J. Amer. Chem. Soc., 1936, 58, 94—98).—The single sharp absorption peak (in the region 6200—7200 cm.<sup>-1</sup>) exhibited by 21 of the 32 substances investigated by Wulf and Liddel (A., 1933, 1102; 1935, 1189) indicates that the OH or NH groups in the dissolved mols. have nearly the same characteristic frequencies; in the mols. containing 2 or more OH or NH, there is little interaction between such groups. The C=O in phenols has some C=O character (resulting from resonance with a structure such as  $\cdot\bar{C}_2\cdot\bar{C}_1\cdot\bar{O}-H$ ), thus tending to cause the H atom to lie in the plane of the rest of the mol. PhOH and s-C<sub>6</sub>H<sub>4</sub>Cl<sub>3</sub>·OH can thus assume either of two equiv. configurations (cf. below); the OH frequency for s-C<sub>6</sub>H<sub>4</sub>Cl<sub>3</sub>·OH (6390 cm.<sup>-1</sup>) will, however, owing to the attraction of the (+)-H by the (-)-Cl, be < that for PhOH (7050 cm.<sup>-1</sup>) (cf. Badger, A., 1934, 477). o-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>·OH can exist in *cis*- (A) and *trans*- (B) forms; owing to the stabilising effect of the



tendency for interaction of H and Cl, the former should be the more stable and predominate. The



curve for  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$  contains two peaks (large at 6910, small at 7050  $\text{cm}^{-1}$ ) and indicates the presence of about 91% of (A) and 9% of (B). The free energy difference of (A) and (B) is about 1400 g.-cal. per mol.  $o\text{-C}_6\text{H}_4(\text{OH})_2$  has structure (C); the two (equal) peaks at 6970 and 7060  $\text{cm}^{-1}$  represent *cis*- and *trans*-OH, respectively. Weak chelation is considered to occur in Et lactate and tartrate and benzoic, but not in  $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$ . The splitting of the  $\text{NH}$ -absorption for pyrrole (and  $\text{NHAcPh}$ ) is probably due to the existence (in solution) of mols. of (mainly) coplanar (H of NH in plane of ring) and non-coplanar forms. Carbazole and tetraphenylpyrrole have coplanar configurations. The tendency for  $\text{CO}\leftarrow\text{HN}$  chelation (as in phenanthraquinoneimine) is much  $<$   $\text{CO}\leftarrow\text{HO}$ . H. B.

**Chloro-alkylation of anisole; synthesis of vinylanisole.** R. QUELET (Compt. rend., 1936, 202, 956—958).—Chloro-ethylation is effected by saturating at  $0^\circ$  with HCl a mixture of 1 mol. of anisole, 1 mol. of paraldehyde, and 100 g. of conc. HCl. The product is washed with  $\text{H}_2\text{O}$  and extracted with light petroleum. Warming with  $\text{C}_5\text{H}_5\text{N}$  gives a mixture of *o*- and *p*-vinylanisole, b.p.  $91\text{--}94^\circ/16\text{ mm.}$ , in 40% yield.  $\alpha\alpha$ -Di-*p*-anisylethane is also formed.  $\alpha$ -Chloropropylanisole is similarly obtained in 20% yield with  $\text{H}_3\text{PO}_4$  as catalyst, and  $\alpha$ -chlorobutylanisole in 50% yield with HCl as catalyst; these yield respectively a mixture of anethole and *o*-methoxy- $\Delta^2$ -propenylbenzene, and of *o*- and *p*-methoxy- $\Delta^2$ -butenylbenzene. P. G. M.

#### Halogenation of phenolic ethers and anilides.

**V. Alkyl and  $\omega$ -substituted-alkyl ethers. VI. Benzyl and substituted-benzyl ethers.** B. JONES (J.C.S., 1935, 1831—1835, 1835—1840).—V. The velocity coeffs. of chlorination at  $20^\circ$  of a no. of ethers of the type  $\text{C}_6\text{H}_4\text{X}\cdot\text{OR}$  ( $\text{X}=\text{o-}$  and  $\text{p-CO}_2\text{H}$ , hal.;  $\text{R}=\text{alk.}$ ,  $[\text{CH}_2]_n\cdot\text{Br}$ ,  $[\text{CH}_2]_n\cdot\text{Ph}$ ) in AcOH containing 1%  $\text{H}_2\text{O}$  have been determined. The reactivity of *n*-alkyl ethers is const. from  $\text{R}=\text{Pr}$  to  $\text{R}=\text{heptyl}$ , but is slightly lower when  $\text{R}=\text{octyl}$  and *cetyl*.  $\omega\text{-Br-}$  and  $\omega\text{-Ph}$  substituents depress the reactivity, the effect decreasing with increasing chain-length. The following ethers have been prepared: *p*-chlorophenyl *n*-amyl, b.p.  $132\text{--}133^\circ/12\text{ mm.}$ , *n*-hexyl, b.p.  $172^\circ/34\text{ mm.}$ , *n*-heptyl, b.p.  $162^\circ/14\text{ mm.}$ , and *cetyl*, m.p.  $48^\circ$ ; *p*-bromophenyl *cetyl*, m.p.  $49^\circ$ ; *o*-chlorophenyl *Pr*, b.p.  $119^\circ/26\text{ mm.}$ , *Pr*<sup>2</sup> (I), b.p.  $93^\circ/12\text{ mm.}$ , *Bu*<sup>2</sup>, b.p.  $117^\circ/13\text{ mm.}$ , *n*-amyl, b.p.  $117^\circ/13\text{ mm.}$ ; *p*-bromophenyl  $\gamma$ -bromopropyl, m.p.  $49.5^\circ$ , b.p.  $169^\circ/12\text{ mm.}$  (by-product trimethylene glycol bis-*p*-bromophenyl ether, m.p.  $143^\circ$ ). *p*- $\beta$ -Phenylethoxybenzoic acid has m.p.  $160^\circ$ , and *p*- $\gamma$ -phenylpropoxybenzoic acid has m.p.  $166^\circ$ .

VI. The velocity coeffs. of chlorination at  $20^\circ$  of a no. of ethers of the type  $\text{C}_6\text{H}_4\text{X}\cdot\text{OR}$  ( $\text{X}=\text{o-}$  and  $\text{p-CO}_2\text{H}$ , Cl, Br;  $\text{R}=\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Y}$  where  $\text{Y}=\text{o-}$ , *m*-, and *p*-Me, -F, -Cl, -NO<sub>2</sub>, and *m*- and *p*-Br) in AcOH containing 1%  $\text{H}_2\text{O}$  have been determined (cf. A., 1932, 26). The majority (including those of the preceding paper) accord with the view that each of the groups X and R contributes a characteristic additive quota to the activation energy of chlorination. (I) and ethers of salicylic acid give anomalous results. The order of reactivity for *p*-substituents in the  $\text{CH}_2\text{Ph}$  radical is  $\text{Me} > \text{H} > \text{F} > \text{Cl} > \text{Br} > \text{NO}_2$ ; in the *m*-position the halogens show almost identical effects. The reactivity of the *o*- and *m*-halogenobenzyl ethers is  $<$  that of the *p*-compounds. The results indicate a mesomeric effect in the order  $\text{F} > \text{Cl} > \text{Br}$ . The following have been prepared:—*p*-chlorophenyl ethers: *m*-, b.p.  $223\text{--}225^\circ/12\text{ mm.}$ , and *p*-, m.p.  $60^\circ$ , -fluoro-; *o*-, b.p.  $191^\circ/12\text{ mm.}$ , *m*-, b.p.  $222\text{--}224^\circ/12\text{ mm.}$ , and *p*-, m.p.  $60^\circ$ , -chloro-; *m*-, m.p.  $43^\circ$ , and *p*-, m.p.  $93^\circ$ , -bromo-; *p*-methyl-, m.p.  $97^\circ$ , and *o*-nitro-benzyl, m.p.  $73^\circ$ ; *o*-chlorophenyl ethers: *p*-fluoro-, m.p.  $35^\circ$ , b.p.  $170^\circ/12\text{ mm.}$ , *p*-chloro-, m.p.  $69^\circ$ , *p*-methyl-, m.p.  $76^\circ$ , and *o*-nitro-benzyl, m.p.  $84.5^\circ$ ; *p*-bromophenyl ethers: *p*-chloro-, m.p.  $98^\circ$ , and *p*-methyl-benzyl, m.p.  $105^\circ$ ; *o*-bromophenyl ethers: *p*-chloro-, m.p.  $69^\circ$ , and *o*-, m.p.  $107^\circ$ , and *m*-, m.p.  $100^\circ$ , -nitro-benzyl. *p*-(*p*-Fluorobenzoyloxy)benzoic acid has m.p.  $213^\circ$ , the corresponding *p*'-chloro-acid, m.p.  $218^\circ$ , and *p*'-bromo-acid, m.p.  $231^\circ$ . *p*-(*p*-Methylbenzoyloxy)benzoic acid has m.p.  $212^\circ$ , and the corresponding *m*'-methyl-acid, m.p.  $157^\circ$ . *p*-(*m*'-Fluorobenzoyloxy)benzoic acid has m.p.  $194^\circ$ , the corresponding *m*'-chloro-acid, m.p.  $194^\circ$ , and *m*'-bromo-acid, m.p.  $202^\circ$ . *p*-(*o*'-Fluorobenzoyloxy)benzoic acid has m.p.  $181^\circ$ , the corresponding *o*'-chloro-acid, m.p.  $189^\circ$ , and the *o*'-methyl-acid, m.p.  $169^\circ$ . *o*-Benzoyloxybenzoic acid has m.p.  $77^\circ$  and *o*-(*p*'-fluorobenzoyloxy)benzoic acid, m.p.  $87^\circ$ , the corresponding *p*'-chloro-acid, m.p.  $115^\circ$ , and the *p*'-methyl-acid, m.p.  $111^\circ$ .

H. G. M.

***o*-Nitrophenylsulphenates of phenols.** E. K. LEARMONTH and S. SMILES (J.C.S., 1936, 327—328).—The 2-nitrophenylsulphenates of the phenols are obtained from  $2:1\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SCl}$  and the Na phenoxide and converted into the OH-sulphides with HCl. 2-Nitrophenylsulphenates of *m*-4- (I), m.p.  $85^\circ$ , and *m*-5-xylene (II), m.p.  $74^\circ$ , 2-chloro-, m.p.  $118\text{--}120^\circ$ , and 2:6-dichloro-*m*-5-xylene, m.p.  $125\text{--}127^\circ$ , 5-chloro-*p*-2-xylene, m.p.  $120^\circ$  and  $\psi$ -cumenol, m.p.  $103^\circ$ , have been prepared. (I) gives 2-nitro-2'-hydroxy-3:5'-dimethyldiphenyl sulphide (*Me* ether, m.p.  $79^\circ$ ). 2-Nitro-4'-hydroxy-2':6'-dimethyldiphenyl sulphide, m.p.  $154^\circ$  [from (II)] (*Ac* derivative, m.p.  $121^\circ$ ; *Me* ether, m.p.  $130^\circ$ ), is oxidised to the sulphone, m.p.  $218^\circ$  (decomp.). 3'-Chloro-2-nitro-6'-hydroxy-2':4'-dimethyldiphenyl sulphide forms an *Ac* derivative, m.p.  $145^\circ$ , and a *Me* ether, m.p.  $156^\circ$ , and 2-nitro-2'-hydroxy-3':5':6'-trimethyldiphenyl sulphide gives an *Ac* derivative, m.p.  $135^\circ$ . F. R. S.

**Benzylation of phenol.** L. McMASTER and W. M. BRUNER (Ind. Eng. Chem., 1936, 28, 505—506).— $\text{CH}_2\text{PhCl}$  dropped slowly into  $\text{PhOH}$  (10 mols.) at  $150^\circ$ , yields *o*- (52.7%) and *p*- (39.9%)  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$



together with 2:4- and 2:6-(CH<sub>2</sub>Ph)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·OH which are separated in a 40-in. Vigreux column. The effect of varying the temp. and mol. ratio is recorded.

F. R. G.

**Hydrolysis and thermal decomposition of mixed diacyl derivatives of 4-chloro-2-aminothiophenol.** H. P. LANKELMA and E. VOPIČKA (J. Amer. Chem. Soc., 1936, 58, 609—611; cf. A., 1931, 348).—4-Chloro-2-cinnamamidothiophenyl cinnamate, m.p. 172—173°, and 4-chloro-2-phenylacetamidothiophenyl phenylacetate, m.p. 149°, are hydrolysed (method: *loc. cit.*) to 4-chloro-2-cinnamamidothiophenol, m.p. 153—155° (acetate, m.p. 138°; benzoate, m.p. 164—165°), and 4-chloro-2-phenylacetamidothiophenol (I), m.p. 126° [acetate (II), m.p. 122—123°; benzoate, m.p. 161°], respectively. 4-Chloro-2-acetamidothiophenyl phenylacetate (III), m.p. 149°, and cinnamate, m.p. 142°, and 4-chloro-2-benzamidothiophenyl phenylacetate, m.p. 154°, and cinnamate, m.p. 122°, are described. Hydrolysis (EtOH-KOH at room temp.) of each pair of isomeric NS-diacyl derivatives gives the same N-acyl derivative (migration of acyl between S and N thus occurring), which when crystallised from EtOH passes into the corresponding benzthiazole (also formed by thermal decomp. of each pair of isomerides); for the following pairs the first-named group is eliminated on hydrolysis: Ac-CH<sub>2</sub>Ph·CO·; Ac-cinnamyl; CH<sub>2</sub>Ph·CO·-Bz; Bz-cinnamyl; Ac-Bz. Thus, (II) and (III) give (I) and then 5-chloro-2-benzylbenzthiazole, m.p. 81—82°.

H. B.

**Alkylated phenolic hydroxy-indenes and -indanes. Synthesis involving condensation of diacetone alcohol or pinacol with phenols.** J. B. NIEDERL, V. NIEDERL, and S. REZNEK (J. Amer. Chem. Soc., 1936, 58, 657—659).—Diacetone alcohol (I) (1 mol.), PhOH (1 mol.), and ZnCl<sub>2</sub> (2 mols.) at 180—210° give polymeric 5-hydroxy-1:1:3-trimethylindene, b.p. 250—255°/3 mm., m.p. 80—90°, pyrolysis of which affords 10—15% of 5-hydroxy-1:1:3-trimethylindane (II), b.p. 263—267°, m.p. 119° [(NO<sub>2</sub>)<sub>2</sub>·, m.p. 112°, and Br<sub>2</sub>·, m.p. 190°, derivatives; Me ether, an oil (*Br*-derivative, m.p. 69°)], oxidised (conc. HNO<sub>3</sub>) to 4-hydroxyphthalic acid and anhydride and *m*-OH·C<sub>6</sub>H<sub>4</sub>·COMe. Non-cryst. hydroxytetramethylindanes (not investigated) are similarly formed from the cresols and (I); guaiacol leads to 5-hydroxy-(?)methoxy-1:1:3-trimethylindane, b.p. 258—265°. Pinacol and PhOH similarly lead to 5-hydroxy-1:1:2-trimethylindane, m.p. 121°. Cryst. products could not be obtained from diacetone glycol (β-methylpentane-βδ-diol). Numerous by-products (e.g., COMe<sub>2</sub>, mesityl oxide, phenolic and non-phenolic chromans, *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>γ</sup>·OH, resins) are also formed in the condensations. (II) appears to possess slight oestrogenic activity.

H. B.

**Condensation of succinic anhydride with phenols and phenolic ethers. Synthesis of derivatives of tetrahydronaphthalene.** P. C. MITTER and S. DE (J. Indian Chem. Soc., 1935, 12, 747).—PhOMe, succinic anhydride, and AlCl<sub>3</sub> in (·CHCl<sub>2</sub>)<sub>2</sub> give γ-keto-γ-*p*-methoxyphenylbutyric acid [semicarbazone, m.p. 185—186° (decomp.)] in good yield (cf. A., 1934, 652). This on Clemmensen reduction

gives γ-*p*-methoxyphenylbutyric acid, m.p. 60°, dehydrated by P<sub>2</sub>O<sub>5</sub> in C<sub>6</sub>H<sub>6</sub> to 1-keto-7-methoxy-1:2:3:4-tetrahydronaphthalene, m.p. 61° (semicarbazone, m.p. 221°), reduced (Clemmensen) to 1:2:3:4-tetrahydro-7-naphthyl Me ether, m.p. 146°. The following compounds were similarly prepared and also appear new: γ-keto-γ-3:4-dimethoxyphenylbutyric acid, m.p. 163° (from veratrole) (semicarbazone, m.p. 177°); γ-3:4-dimethoxyphenylbutyric acid, m.p. 61°; 1-keto-6:7(=7:8)-dimethoxy-1:2:3:4-tetrahydronaphthalene, m.p. 99—100° (semicarbazone, m.p. 242—243°); and γ-o-hydroxyphenylbutyric acid, m.p. 65—66°. H. G. M.

**Naphthalene series. IV. Hydrolysis of α-naphthylamine by dilute sulphuric acid.** N. N. VOROSHCHEV and A. V. GUTORKO (J. Gen. Chem. Russ., 1935, 5, 1581—1585).—Max. yields of α-C<sub>10</sub>H<sub>7</sub>·OH are obtained at 200°, taking 1 mol. of H<sub>2</sub>SO<sub>4</sub> per mol. of α-C<sub>10</sub>H<sub>7</sub>NH<sub>2</sub>; the concn. of the acid is immaterial.

R. T.

**Diaryls and their derivatives. VIII. Influence of acidity of the medium on interaction of β-naphthol with ferric chloride.** J. S. JOFFE, S. G. KUZNETZOV, and S. LITOVSKI (J. Gen. Chem. Russ., 1935, 5, 1685—1686).—In the reaction between β-C<sub>10</sub>H<sub>7</sub>·OH and aq. FeCl<sub>3</sub> the yield of 2:2'-dihydroxy-1:1'-dinaphthyl falls, and that of 1:2-C<sub>10</sub>H<sub>6</sub>Cl·OH rises, with increasing [HCl].

R. T.

**Phenanthrene series. I. 2-Methoxy-1-methylphenanthrene.** P. HILL, W. F. SHORT, and (in part) (MISS) A. HIGGINBOTTOM. **II. 7-Methoxy-1-methylphenanthrene and a new route to phenanthrene.** W. F. SHORT, H. STROMBERG, and A. E. WILES. **III. 9-Hydroxyphenanthrene.** I. R. SHERWOOD, W. F. SHORT, and J. WOODCOCK (J.C.S., 1936, 317—319, 319—322, 322—324).—I. 1:2-C<sub>10</sub>H<sub>6</sub>Me·OMe, succinic anhydride, and AlCl<sub>3</sub> give β-(2-methoxy-1-methyl-6-naphthoyl)propionic acid, m.p. 161—162°, reduced (Hg-Zn) to γ-(2-methoxy-1-methyl-6-naphthyl)butyric acid, m.p. 123—123·5°, which with SnCl<sub>4</sub>-HCl forms 1-keto-7-methoxy-8-methyl-1:2:3:4-phenanthrene, m.p. 107° (2,4-dinitrophenylhydrazine, m.p. 281°). Reduction (Zn-Hg) of the keto-compound affords 7-methoxy-8-methyl-1:2:3:4-tetrahydrophenanthrene, m.p. 111—112°, dehydrogenated (Se) to 2-methoxy-1-methylphenanthrene, m.p. 161°, which is demethylated to the 2-OH-compound, m.p. 196—197°. 4-Methylphenanthrene (cf. Radcliffe *et al.*, A., 1931, 1282) has m.p. 49—50°.

II. β-C<sub>10</sub>H<sub>7</sub>·OMe, succinic anhydride, and AlCl<sub>3</sub> in CS<sub>2</sub> give β-(2-methoxy-1-naphthoyl)propionic acid, m.p. 136·5—137·5° (*Et* ester, m.p. 41—42°), whilst in PhNO<sub>2</sub>, a mixture of 1 part of this acid with 4 parts of β-(2-methoxy-6-naphthoyl)propionic acid (I), m.p. 148·5—149° (*Me* ester, m.p. 98°), is formed (cf. Fieser and Peters, A., 1933, 67). The *Et* ester of (I) and MgMeI, followed by acidification, yield γ-(2-methoxy-6-naphthyl)-Δ<sup>β</sup>-pentenoic acid, m.p. 171—171·5°, reduced (PtO<sub>2</sub>-H<sub>2</sub>) to γ-(2-methoxy-6-naphthyl)-*n*-valeric acid, m.p. 121·5°, which is dehydrated (P<sub>2</sub>O<sub>5</sub>) to 4-keto-7-methoxy-1-methyl-1:2:3:4-tetrahydrophenanthrene, b.p. 195°/0·8 mm. [2:4-dinitrophenylhydrazine, m.p. 241° (decomp.)]. Reduction (Zn-Hg)



and dehydrogenation (Se) of the cyclic ketone gives 7-methoxy-1-methylphenanthrene, m.p. 133.5–134.5°, demethylated to the 7-OH-compound, m.p. 190–191° [acetate, m.p. 135.5–136°, *acetoxiquinone*, m.p. 202–207° (decomp.), and *acetoxiquinoxaline*, m.p. 244.5–246.5°]. Mg *o*-tolyl iodide and 2-methylcyclohexanone give 1-*o*-tolyl-2-methylcyclohexanol, b.p. 153–154°/14 mm., dehydrogenated (S) to 2:2'-dimethyldiphenyl. 2-Methylcyclohexanone and the Grignard compound of 6-bromo-*m*-tolyl Me ether afford 1-(5'-methoxy-*o*-tolyl)-2-methyl- $\Delta^1$ -cyclohexene, b.p. 154–155°/13 mm., dehydrogenated (HI) to 4-hydroxy-2:2'-dimethyldiphenyl, m.p. 105°.

III. *Et diphenyl-2-acetate*, b.p. 154–155°/4 mm. (from 2-phenylcyclohexanone,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ , and Zn), with  $\text{H}_2\text{SO}_4$  forms 9-hydroxyphenanthrene. The Grignard compound of 3-bromo-*p*-tolyl Me ether and cyclohexanone afford 1-(4'-methoxy-*m*-tolyl)- $\Delta^1$ -cyclohexene, dehydrated ( $\text{KHSO}_4$ ) to 1-(4'-methoxy-*m*-tolyl)- $\Delta^1$ -cyclohexene, b.p. 163°/20 mm., which is oxidised ( $\text{BzO}_2\text{H}$ ) to the oxide, isomerised to 2-(4'-methoxy-*m*-tolyl)cyclohexanone (*semicarbazone*, m.p. 199–200°).

F. R. S.

Manufacture of pyrene compounds [hydroxy-pyrenes and their sulphonic acids].—See B., 1936, 361.

Preparation of *sec*.-alkyl- and chloro-*sec*.-alkyl-resorcinols.—See B., 1936, 443.

Colour reactions of quinol in solid state. S. J. FRENCH and D. J. SAUNDERS (J. Amer. Chem. Soc., 1936, 58, 689–690).—The colours produced (cf. Mالدینی, A., 1914, ii, 681) when solid quinol (I) is mixed with various solid salts depend on the presence of traces of  $\text{H}_2\text{O}$  (cf. *loc. cit.*); anhyd. salts give no colour, whilst an excess of  $\text{H}_2\text{O}$  leads to yellow solutions. The colour varies from grey through blue and green to black, is roughly  $\propto$  the increasing alkalinity of the salt [also shown by using solid buffers of  $p_{\text{H}}$  (in solution)  $> 10.4$ ], and is given only by salts of acids having ionisation consts.  $<$  that of (I) (primary stage). The reaction can be used to distinguish between, e.g.,  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  (no colour),  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  (no colour), (I) and *o*- or *m*- $\text{C}_6\text{H}_4(\text{OH})_2$  (which do not show similar colour reactions), hydrated and anhyd. salts. H. B.

Oxidation of quinol and of chloroquinol in presence of ammonium sulphite. Oxidation of a quinoldisulphonic acid in presence of ammonia. (Mlle.) Y. GARREAU (Compt. rend., 1936, 202, 1186–1188).—Quinol or chloroquinol in dil. aq.  $\text{NH}_3$  containing  $(\text{NH}_4)_2\text{S}$ , and  $\text{Cu}(\text{OH})_2$  afford  $\alpha$ -(I) (cf. A., 1935, 338) and  $\beta$ -diaminobenzoquinonedisulphonic acid [ $+2\text{H}_2\text{O}$ ;  $(\text{NH}_4)_2$  salt  $+3\text{H}_2\text{O}$ , decomp. at 240°, which loses  $1\text{H}_2\text{O}$  at 120°;  $\text{NH}_4$  salt  $+1\text{H}_2\text{O}$  (II)] either of which with warm KOH gives a K quinoldisulphonate. (II) affords ppts. with some bases of biological interest (cf. this vol., 337). J. L. D.

New method of condensation. C. MARSCHALK (Bull. Soc. chim., 1936, [v], 3, 121–124).—Condensation of two mols. of a  $\text{C}_6\text{H}_6$  or  $\text{C}_{10}\text{H}_8$  derivative takes place in presence of  $\text{H}_3\text{BO}_3$ – $\text{H}_2\text{SO}_4$ –anthraquinone-1:5- or -1:8-disulphonic acid, the H eliminated converting the latter into a leuco-derivative from

which the sulphonic acid may be regenerated. In this way  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{OEt}$  gives 4:4'-diethoxy- $\alpha$ -dinaphthyl (A., 1922, i, 1336), and 1:5- $\text{C}_{10}\text{H}_6(\text{OH})_2$  yields a compound, readily oxidised by the air, insol. in boiling  $\text{H}_2\text{O}$ , sol. in alkalis, but which does not couple with diazotised  $p$ - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ . The method is suitable for compounds sensitive to oxidising agents.

H. G. M.

Metabolism of polycyclic compounds. II. Production of dihydroxydihydroanthraceneglycuronic acid from anthracene. E. BOYLAND and A. A. LEVI (Biochem. J., 1936, 30, 728–731).—The glycuronic acid compound (I) excreted when rabbits are fed a diet containing anthracene (A., 1936, 234), when warmed with dil. HCl gave anthrylglycuronic acid (II),  $\alpha_{\text{D}}^{20}$   $-52^\circ$  in dioxan, Na salt,  $-79^\circ$  (in water), which with boiling 0.2N- $\text{H}_2\text{SO}_4$  yielded a compound, probably  $\alpha$ -anthrol (*Ac* derivative, m.p. 127°). Oxidation of (I) with  $\text{CrO}_3$ – $\text{AcOH}$  and of (II) with alkaline  $\text{KMnO}_4$  gave compounds, m.p. 185–186° and 193°, respectively, probably both 1-hydroxyanthraquinone. (I) with alkaline  $\text{KMnO}_4$  gave 2:3- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ . (I) is reduced with  $\text{H}_2$  (Pd) to a compound,  $\text{C}_{20}\text{H}_{22}\text{O}_8\cdot 2\text{H}_2\text{O}$ , m.p. 188°, probably 1:2-dihydroxy-1:2:3:4-tetrahydroanthraceneglycuronic acid, which with 2N-HCl yielded a compound, m.p. 149°, probably 2-keto-1:2:3:4-tetrahydroanthracene. Rats fed the same diet excrete much less glycuronic acid, but it is probable that they excrete an analogous levorotatory compound which is readily hydrolysed to (II). It is concluded that (I) is 1:2-dihydroxy-1:2-dihydroanthracene-1-glycuronic acid.

P. W. C.

Action of thionyl chloride on cyclohexanol. P. CARRÉ and D. LIBERMANN (Bull. Soc. chim., 1936, [v], 3, 144).—The dehydration of cyclohexanol to cyclohexene by  $\text{SOCl}_2$ , and the decomp. of cyclohexyl sulphite when distilled under reduced pressure, are confirmed (cf. A., 1935, 480, 1492).

H. G. M.

cycloHexylvinylcarbinol. S. N. DANILOV and S. M. RIZOV (J. Gen. Chem. Russ., 1935, 5, 1696–1698).—Mg cyclohexyl bromide and acetaldehyde in  $\text{Et}_2\text{O}$  yield cyclohexylvinylcarbinol, b.p. 89–91°/12 mm., the acetate, b.p. 94–103°/14 mm., of which was brominated, and the product treated with  $\text{AgOAc}$  in  $\text{AcOH}$  at 120°, to yield probably  $\text{C}_6\text{H}_{11}\cdot\text{CH}(\text{OAc})\cdot\text{CBr}\cdot\text{CH}_2$ , b.p. 143–145°/2 mm.

R. T.

Mutual influence of radicals on their migration. Dehydration of phenyltert.-amylcarbinol. A. E. FAVORSKI and P. A. TICHOMOLOV (J. Gen. Chem. Russ., 1935, 5, 1679–1684).— $\text{COPhPr}$ ,  $\text{NaNH}_2$ , and MeI afford *Ph* tert.-amyl ketone, b.p. 106–107°/8 mm., reduced by Na in  $\text{EtOH}$  to the corresponding carbinol (I), b.p. 124.5–125.5°/12–13 mm. (I) is converted by distillation from  $\text{KHSO}_4$  into  $\alpha$ 3-dimethyl- $\beta$ -ethylstyrene, b.p. 99.5–100°/22.5 mm., 206.5–207°/764 mm., which yields  $\text{COPhMe}$  and  $\text{COMeEt}$  when ozonised.

R. T.

Manufacture of [triarylmethane] dyes.—See B., 1936, 361.

dl-Tolylalanine and its bacterial decomposition. T. SASAKI and I. OTSUKA (J. Biochem. Japan,



1936, 23, 139—146).—Glycine anhydride condensed with *o*-tolualdehyde (Sasaki, A., 1921, i, 196) yields 3:6-di-(*o*-methylbenzylidene)-2:5-diketopiperazine, m.p. 273—274° [corresponding *m*-, m.p. 246—247° (decomp.), and *p*-compounds], reduced and hydrolysed to β-(*o*-tolyl)-α-alanine, m.p. 259—260° (decomp.) (anhydride, m.p. 228—230°) [corresponding *m*- (Böhm, A., 1914, i, 358) and *p*-compound (Dakin, A., 1911, ii, 416), and their anhydrides, m.p. 187—188° and 257—258°, respectively]. With *B. proteus*, only *p*-tolyl-alanine of the three isomerides yields β-(*p*-tolyl)-α-lactic acid, m.p. 79—80° (uncorr.),  $[\alpha]_{D}^{20} +27.82^\circ$  (Na salt in H<sub>2</sub>O). F. O. H.

**Complex formation between polynitro-compounds and aromatic hydrocarbons. II. The system 2:4-dinitro-2'-methylthiophenyl-6-carboxylic acid-benzene.** D. L. HAMMICK and R. B. WILLIAMS (J.C.S., 1935, 1856—1860).—*r*-2:4-Dinitro-2'-methylthiophenyl-6-carboxylic acid (I) [improved prep.; monohydrate, m.p. 120° (decomp.) on rapid heating; mono-MeOH complex, m.p. 130—135° (decomp.) on rapid heating] forms complexes with C<sub>6</sub>H<sub>6</sub> in the molar ratios 2:1 and 1:1, m.p. about 138° and 128°, respectively (cf. A., 1930, 1287). (I) when resolved with brucine gives an active acid,  $[\alpha]_{5791} -19.4^\circ$  (cf. *loc. cit.*), but with *d*-α-phenylethylamine an acid (II), m.p. 135°,  $[\alpha]_{5791} +89.1^\circ$  in EtOH [d-α-phenylethylamine salt, m.p. 218°,  $[\alpha]_{5791} +57.1^\circ$  in CMe<sub>2</sub>; monohydrate, m.p. 80—85° (decomp.),  $[\alpha]_{5791} +84.6^\circ$ ; mono-MeOH complex, m.p. 90—100° (decomp.) on rapid heating], was obtained. The activity in EtOH of (II) is unchanged by complex formation with H<sub>2</sub>O, MeOH, or C<sub>6</sub>H<sub>6</sub> (cf. *loc. cit.*). Crystallisation of a mixture of (I) and (II) from C<sub>6</sub>H<sub>6</sub> gives mother-liquors richer in (II), the C<sub>6</sub>H<sub>6</sub> complex of (I) being sparingly sol. Only partial separation, however, can thus be obtained. Similarly 4:6:4'-trinitrodiphenic acid can be further resolved by crystallisation from C<sub>6</sub>H<sub>6</sub>. When resolved by quinine, the acid has  $[\alpha]_{5461} -24.6^\circ$  in Et<sub>2</sub>O, but after recrystallisation from C<sub>6</sub>H<sub>6</sub> the mother-liquors gave an acid of  $[\alpha]_{5461} -42.2^\circ$  in Et<sub>2</sub>O. H. G. M.

**Apparent cases of liquid-crystal formation in *p*-alkoxybenzoic acids.** B. JONES (J.C.S., 1935, 1874).—The following *p*-alkoxybenzoic acids, prepared by refluxing *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H with KOH-H<sub>2</sub>O and the appropriate alkyl iodide, melt sharply to milky liquids which at a higher temp. suddenly become clear. When the temp. is lowered 0.5—1.0° the clear liquid appears to become a mass of fine crystals (cf. A., 1930, 87). The transition point is given in parentheses. *p*-*n*-Amyloxy- (122°), m.p. 148°, *p*-*n*-hexyloxy- (105°), m.p. 150°, *p*-*n*-heptyloxy- (91°), m.p. 145°, *p*-*n*-octyloxy- (100°), m.p. 145°, *p*-cetyloxy-benzoic acid (99°), m.p. 131°. H. G. M.

**Action of sulphuric acid on diarylphthalins. II. Mechanism of reaction.** F. F. BLICKE and R. A. PATELSKI (J. Amer. Chem. Soc., 1936, 58, 559—562).—The production of a 2:5-diaryl-3:4-benzofuran (I) from a diarylphthalin (II) and conc. H<sub>2</sub>SO<sub>4</sub> is considered to occur thus: (II) is converted into ArH and an α-arylphthalide (by way of the benzhydrol-2-carboxylic acid), which then recombine to give either the 2-arylbzhydrol (III) or 2-hydroxy-

2:5-diaryl-2:5-dihydro-3:4-benzofuran (IV); (III) or (IV) is then dehydrated to (I). This view is supported by the prep. of 2:5-dianisyl-3:4-benzofuran (V) from α-anisylphthalide (VI), PhOMe, and conc. H<sub>2</sub>SO<sub>4</sub>; (V) is oxidised (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AcOH-H<sub>2</sub>SO<sub>4</sub>) to 4'-methoxy-2-anisoylbzphenone (VII). Similarly, (VI) and PhOH or α-*p*-hydroxyphenylphthalide (VIII) and PhOMe give 2-*p*-hydroxyphenyl-5-anisyl-3:4-benzofuran, converted by successive oxidation and methylation (Me<sub>2</sub>SO<sub>4</sub>, 10% NaOH) into (VII); (VIII) and PhOH afford 2:5-di-*p*-hydroxyphenyl-3:4-benzofuran, oxidised to 4'-hydroxy-2-*p*-hydroxybenzoylbzphenone. Attempted prep. of compounds of type (III) results in the production of (I). Thus, *o*-CN·C<sub>6</sub>H<sub>4</sub>·CHO (IX) (*p*-bromophenylhydrazine, m.p. 194—195°), from *o*-CN·C<sub>6</sub>H<sub>4</sub>·CHBr<sub>2</sub> and AgNO<sub>3</sub> in 95% EtOH, with MgPhBr gives the imine, m.p. 126—127°, of 2-benzoylbzhydrol; this is hydrolysed (HCl-COMe<sub>2</sub>) to 2:5-diphenyl-3:4-benzofuran, oxidised to 2-benzoylbzphenone. Similarly, the crude imine from (IX) and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·MgI is hydrolysed to (V). 2-Benzoylbzphenone and MgPhBr afford 2-benzyltriphenylcarbinol (X), m.p. 133—134°, which is converted by cold conc. H<sub>2</sub>SO<sub>4</sub> or hot AcOH into 9:9-diphenyl-9:10-dihydroanthracene. (X) is oxidised by dil. HNO<sub>3</sub> to 9:9-diphenyl-10-anthrone. H. B.

**Ester condensation and ketal acetals. Existence of carbon monoxide acetals.** F. ADICKES (Ber., 1936, 69, [B], 654—656).—A reply to Scheibler (cf. this vol., 66), whose "phenylketen methyl benzoyl acetal" is probably *Me* β-benzoyloxy-α-β-diphenylacrylate. H. W.

**Action of nitrogen dioxide on tetraphenylsuccinonitrile.** G. WITTIG and U. PÖCKELS (Ber., 1936, 69, [B], 790—792).—(CPh<sub>2</sub>·CN)<sub>2</sub> does not react with NO in boiling xylene alone or in presence of Cu powder or I. It is very readily converted by NO<sub>2</sub> in CHCl<sub>3</sub> into nitrodiphenylacetone (I), m.p. 44—46°, the change affecting both radical and undissociated mol. Boiling, somewhat dil AcOH transforms (I) into benzilonitrile (II), m.p. 127—130° (decomp.), converted by alkali or boiling H<sub>2</sub>O into CPh<sub>2</sub> and HCN. (II) could not be obtained from CPh<sub>2</sub> and HCN in acid medium. LiPh and BzCN react very readily, but even at -60° the adduct passes into LiCN and CPh<sub>2</sub>, transformed further into CPh<sub>2</sub>·OH. H. W.

**Electrosynthesis of aromatic carboxylic acids. I. Electrolysis of opianic acid.** V. M. RODIONOV, V. N. BELOV, and V. V. LEVTSCHENKO (J. Gen. Chem. Russ., 1935, 5, 1817—1829).—When K opianate is electrolysed with a constantly renewed Hg cathode, α-, m.p. 244—245°, and β-dimeconyl, m.p. 215°, are obtained; the compounds represent the racemic and meso-forms of dimeconyl. The α-isomeride is synthesised from opianyl chloride and Na-Hg in C<sub>6</sub>H<sub>6</sub> at room temp. R. T.

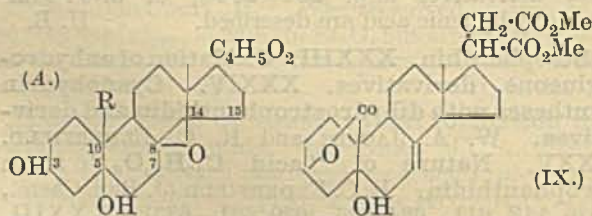
**Carbon syntheses with malonic acid and related compounds. II. Aromatic aldehydes.** A. MICHAEL and N. WEINER (J. Amer. Chem. Soc., 1936, 58, 680—684; cf. A., 1933, 1142).—ArCHO cannot be condensed (using Ac<sub>2</sub>O-conc. H<sub>2</sub>SO<sub>4</sub>; Meldrum, J.C.S., 1908, 93, 605) with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>,







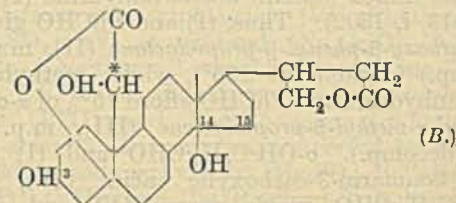
hydration of the  $\cdot O \cdot$  ring and subsequent loss of  $2H_2O$  by 50% AcOH at  $100^\circ$  into an *anhydrolactone* (VI),  $C_{23}H_{30}O_6$ , m.p.  $260-284^\circ$ ,  $[\alpha]_D^{25} +98^\circ$  in  $C_5H_5N$  [(3-*benzoate*, m.p.  $265^\circ$ ; (5-*sulphite*, m.p.  $242-243^\circ$ , obtained using  $SOCl_2$  at  $0^\circ$ ). (VI) is also obtained from (II) and 0.1*N*-NaOH followed by 5%  $KMnO_4$  in  $C_5H_5N$ . Oxidation (Kiliani's  $CrO_3$  solution; 90% AcOH) of (VI) gives a *ketoanhydrolactone*,  $C_{23}H_{28}O_6$ , m.p.  $251^\circ$ , thus showing the presence of  $C_{(3)}H \cdot OH$ ; catalytic reduction results in the uptake of 1 mol. of  $H_2$ . (VI) thus appears to contain the  $\Delta^{14:15}$  (or  $\Delta^{7:8}$ ) double linking and the  $C_{(10)} \cdot CO \cdot O \cdot C_{(8)}$  (or  $C_{(10)} \cdot CO \cdot O \cdot C_{(14)}$ ) group. (V) and 50% AcOH at  $100^\circ$  followed by a little 5%  $H_2SO_4$ , give (by fission of  $\cdot O \cdot$  ring and then loss of  $2H_2O$ ) a *dianhydrolactone Me ester*,  $C_{24}H_{32}O_6$ , m.p.  $199^\circ$  (softens about  $190^\circ$ ), which probably contains  $C_{(10)} \cdot CO_2Me$  and the  $\Delta^{7:8}$  and  $\Delta^{14:15}$  double linkings. Reduction ( $H_2$ ,  $PtO_2$ , EtOH) of (II) furnishes the *trihydroxylactone oxide* (A,  $R=CH_2 \cdot OH$ ), m.p.  $265^\circ$ ,  $[\alpha]_D^{25} +47^\circ$  in  $C_5H_5N$  [*dibenzoate* (VII), softens about  $145-150^\circ$  and then melts slowly], converted by hot 50% AcOH into an isomeric *trihydroxylactone oxide* (VIII), m.p.  $282^\circ$  (decomp.),  $[\alpha]_D^{25} +83^\circ$  in  $C_5H_5N$  (*benzoate*, m.p.  $274-275^\circ$ ), which is oxidised ( $CrO_3$ , 90% AcOH) to a *ketodihydroxylactone oxide*,  $C_{23}H_{32}O_6$ , m.p.  $272^\circ$  (decomp.) (softens about  $260^\circ$ ). (VIII) thus appears to contain OH groups at  $C_{(3)}$ ,  $C_{(5)}$ , and  $C_{(14)}$  (or  $C_{(8)}$ ) and the  $C_{(10)} \cdot CH_2 \cdot O \cdot C_{(8)}$  (or  $C_{(10)} \cdot CH_2 \cdot O \cdot C_{(14)}$ ) group. (VII) and 75% AcOH-10%  $H_2SO_4$  give, however, the *dibenzoate*, m.p.  $210-211^\circ$ , of a pentahydroxylactone, i.e.,  $C_{(3)} \cdot OBz$ ,  $C_{(10)} \cdot CH_2 \cdot OBz$ , and OH at  $C_{(5)}$ ,  $C_{(8)}$ , and  $C_{(14)}$ . Oxidation ( $BzO_2H$  or  $KMnO_4$ -AcOH) of  $Me_2$  anhydro- $\beta$ -isostrophanthic lactone acid ester (A., 1929, 1456) also affords an *oxide*, m.p.  $244-245^\circ$  (softens at  $240^\circ$ ),  $[\alpha]_D^{25} -26^\circ$  in  $C_5H_5N$ , converted by 50% AcOH-10%  $H_2SO_4$  into the *dianhydrolactone Me ester* (IX), m.p.  $178-180^\circ$ .



It is concluded that (I), (III), and (IV) contain either the  $\Delta^{14:15}$  or  $\Delta^{8:14}$  double linking; the former may predominate in alkaline, the latter in neutral and acid, solution; alternatively, both forms may occur simultaneously but oxidation proceed at different rates. The  $\beta$ -anhydrodigitoxigenin (X) of Smith (A., 1935, 1226) can be converted into the  $\alpha$ -isomeride (XI) by conc. acid. Dehydration of digitoxigenin may thus give (X) and then (by isomerisation) (XI). The change (X)  $\rightarrow$  (XI) may, however, involve merely a shift of the double linking.

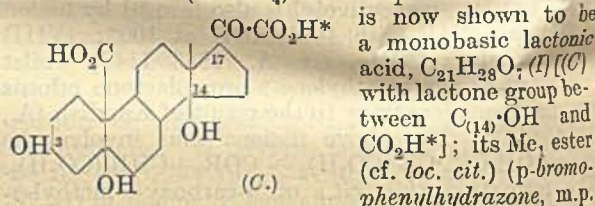
XXXIV. Dihydrostrophanthidin with KCN and  $NH_4Cl$  in aq. EtOH gives a cyanohydrin (not isolated), hydrolysed (hot aq. AcOH) to  $\alpha$ -, m.p.  $254^\circ$  (decomp.),  $[\alpha]_D^{25} -36^\circ$  in  $C_5H_5N$  [*benzoate* (I), m.p.  $320^\circ$ ], and  $\beta$ -, m.p.  $235^\circ$  (decomp.) (softens about  $175^\circ$ ),  $[\alpha]_D^{25} +30^\circ$  in  $C_5H_5N$ , *homodilactones* [as (B)], the isomerism being due to the creation of a new centre of asym-

metry at  $C^*$ . These are both oxidised (Kiliani's  $CrO_3$  solution; 90% AcOH) to the *diketohomodilactone*



[(B) with  $C_{(3)}H \cdot OH$  and  $C^*H \cdot OH$  both  $=CO$ ], m.p.  $189-190^\circ$  (decomp.),  $[\alpha]_D^{25} +75^\circ$  in  $C_5H_5N$ , and are dehydrated (loss of  $H_2O$  between  $C_{(14)}$  and  $C_{(15)}$ ) to  $\alpha$ -, m.p.  $302-303^\circ$ ,  $[\alpha]_D^{25} -72^\circ$  in  $C_5H_5N$ , and  $\beta$ -, m.p.  $305^\circ$  (decomp.) (previous softening), -*anhydrohomodilactones*, respectively, by aq. EtOH-HCl. (II) is similarly oxidised to the *anhydroidiketohomolactone*, m.p.  $196^\circ$  (decomp.) (softens about  $191^\circ$ ). Dihydrostrophanthidin benzoate with KCN and  $NH_4Cl$  in aq.  $C_5H_5N$  affords a *cyanohydrin*, m.p.  $258^\circ$  (decomp.), hydrolysed (repeated evaporation with 50% AcOH) to a *homodilactone benzoate*, m.p.  $305-306^\circ$  (decomp.) [isomeric with (I)], dehydrated to the *anhydrohomodilactone benzoate*, m.p.  $265-268^\circ$  (slight previous softening),  $[\alpha]_D^{25} -38^\circ$  in  $C_5H_5N$ .

XXXV. The acid,  $C_{23}H_{30}O_8$ , previously obtained (A., 1924, i, 65) by successive alkaline hydrolysis and oxidation ( $KMnO_4$ ) of strophanthidin acid,



is now shown to be a monobasic *lactonic acid*,  $C_{21}H_{28}O_7$  [(I) (C) with lactone group between  $C_{(14)} \cdot OH$  and  $CO_2H^*$ ]; its Me ester (cf. *loc. cit.*) (*p*-bromophenylhydrazone, m.p.  $273^\circ$ ) is oxidised ( $C_{(3)}H \cdot OH \rightarrow CO$ ) to the corresponding *diketolactonic ester*, m.p.  $228^\circ$  [*dioxime*, m.p.  $233^\circ$  (decomp.) (sinters about  $210^\circ$ )]. Alkaline hydrolysis of (I) thus gives the dibasic keto-acid (C) (in which  $C_{(14)} \cdot OH$  and  $C_{(17)} \cdot CO \cdot CO_2H$  are *trans*, thus preventing relactonisation), which affords a compound with *o*-phenylenediamine, m.p.  $222-224^\circ$  (decomp.), and is oxidised (dil.  $H_2O_2$ ) to the *dicarboxylic acid* [(C) with  $\cdot CO \cdot CO_2H = CO_2H$ ], m.p.  $295^\circ$  (decomp.) ( $Me_2$  ester, m.p.  $200^\circ$ ). The formulæ for other derivatives (*loc. cit.*) of (I) are revised.

H. B.

Synthesis of conjugated bile acids. II. Glycodeoxycholic acid. F. CORTESE and L. BATT-  
MAN (J. Biol. Chem., 1936, 113, 779-785).—The unstable *chloride*, m.p.  $104^\circ$  (corr.; slight decomp.), of diformyldeoxycholic acid (I) with conc. aq.  $NH_3$  and a little conc. aq. NaOH gives deoxycholamide, m.p.  $188-189^\circ$  (corr.) (softens about  $162^\circ$ ). Glycodeoxycholic acid ( $+H_2O$ ) (II) [prep. essentially by procedure described (A., 1935, 1237) for glycodeoxycholic acid] appears to exist in normal, m.p.  $107^\circ$ , and para, m.p.  $186-187^\circ$  (corr.), forms. (II) forms mixed crystals with small amounts of stearic (III) and the choleic acids from (III) and oleic acid. The "glycodeoxycholic acids" of Wahlgren (A., 1903, i, 302) and Sekitoo (A., 1931, 1179) are mixtures of (II) and a small amount of fatty acid; xylene-glycodeoxycholic acid



(Sekitoo, *loc. cit.*) is probably impure (II). Et deoxycholate, (I), and (II) do not form co-ordination compounds with (III); free OH and CO<sub>2</sub>H groups thus appear necessary (as in deoxycholic acid) for such reaction. The so-called "choleic acid principle" (Wieland and Sorge, A., 1916, i, 710) appears to be of no practical importance either in digestion or in the transport of cholesterol in bile. H. B.

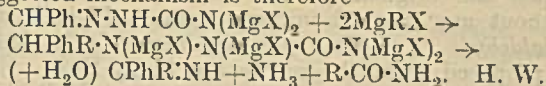
**Synthesis of cyclohexane-1:1:4:4-tetracarboxylic and -1:4-dicarboxylic acids.** V. V. FEOLAKTIKOV and A. A. IVANOV (J. Gen. Chem. Russ., 1935, 5, 1558—1561).—Mg[CH(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> in EtOH yield Et<sub>4</sub> cyclohexane-1:1:4:4-tetracarboxylate, m.p. 75.5—76.5°, converted by alkaline hydrolysis into the free acid, which decomposes at 240° to yield *cis-trans-cyclohexane-1:4-dicarboxylic acid*. R. T.

**Hydrogen cyanide. VII. Aldehydes from aromatic hydrocarbons.** L. E. HINKEL, E. E. AYLING, and J. H. BEYNON (J.C.S., 1936, 339—346).—The application of the HCN synthesis of aromatic aldehydes has been extended to substituted benzenes and to polynuclear hydrocarbons. By the introduction of suitable liquid reaction media, such as C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, PhCl, and *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>, it has been possible to extend the synthesis to solid hydrocarbons and to facilitate the complete conversion of hydrocarbon into aldehyde. The influence of the solvent on the reaction, with reference to the secondary action of the AlCl<sub>3</sub> on the hydrocarbon and the temp. and reaction period, is discussed. C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> appears to enhance the aldehyde synthesis with most hydrocarbons, but with certain hydrocarbons it increases the tendency to polymerisation.

The following have been prepared: 1:6-dimethyl-4-naphthaldehyde, b.p. 191.5°/16 mm. (oxime, m.p. 123°; semicarbazone, m.p. 202°; phenylhydrazone, m.p. 110°); 2:6-dimethyl-1-naphthaldehyde, m.p. 57° (oxime, m.p. 122—123°; semicarbazone, m.p. 214°; phenylhydrazone, m.p. 122°; NH<sub>2</sub>Ph derivative, m.p. 78°); anthracene-9-aldehyde, m.p. 104—105° (NH<sub>2</sub>Ph derivative, m.p. 175°; phenylhydrazone, m.p. 207°; oxime, m.p. 186—187°; semicarbazone, m.p. 291°); acenaphthene-3-aldehyde, m.p. 87° (phenylhydrazone, m.p. 140°; 2:4-dinitrophenylhydrazone, m.p. 273°; oxime, m.p. 126.5°; semicarbazone, m.p. 234°; NH<sub>2</sub>Ph derivative, m.p. 97°); fluorene-2-aldehyde, m.p. 90° (NH<sub>2</sub>Ph derivative, m.p. 158°; phenylhydrazone, m.p. 202—203°; oxime, m.p. 156—157°; semicarbazone, m.p. 278°). The prep. of the aldehydes by the substitution of chloromethyleneformamide for HCN and HCl has been extended to acenaphthene, anthracene, hydrindene, and C<sub>10</sub>H<sub>8</sub>; but with Ph<sub>2</sub> in PhCl, diphenyl-4-aldehyde, and in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, diphenyl-4:4'-dialdehyde are obtained. F. R. S.

**Action of mixed organo-magnesium derivatives on benzaldehydesemicarbazone.** (MLLE.) D. BIQUARD (Bull. Soc. chim., 1936, 3, [v], 666—668).—The action of MgEtBr on CHPh·N·NH·CO·NH<sub>2</sub> (I) establishes the presence of 3 active H and leads to CPhEt and EtCO·NH<sub>2</sub>. Similarly (I) and MgBuCl afford CPhBu and BuCO·NH<sub>2</sub>. The possible intermediate formation of CO(NH<sub>2</sub>)<sub>2</sub> is negatived by the non-formation of the amides from

this source, whilst the products from NH<sub>2</sub>·CO·NHPh are quite different from those from (I). The suggested mechanism is therefore



**Formation of half-acetals of aldehydes, CH<sub>2</sub>R·CHO.** Nature of their solution in benzyl alcohol. II. Constitution of phenyl- and *p*-tolyl-acetaldehyde and hydratropaldehyde on the basis of their electron distribution. A. MÜLLER (Helv. Chim. Acta, 1936, 19, 225—234; cf. A., 1934, 1301).—When CH<sub>2</sub>Ph·OH (I) is mixed with *p*-C<sub>6</sub>H<sub>4</sub>Me·CH<sub>2</sub>·CHO (II), CH<sub>2</sub>Ph·CHO (III), or CHPhMe·CHO (IV), gradual evolution of heat and change in  $\eta$ , capillariscopic behaviour, and  $n$  occur. Enolisation is involved in the change, since the mixture of (I) and (III) does not immediately absorb acid-free Br in CCl<sub>4</sub>; after some time rapid absorption occurs. The relative amounts of the changes in physical consts. show that the order of reactivity is (III) > (II) > (IV). Compound formation is proved by isolation of an unstable 1:1-additive compound of (I) and (II), m.p. 61–62° after sintering at 58°, formulated as *p*-C<sub>6</sub>H<sub>4</sub>Me·CH·CH·OH ···· CH<sub>2</sub>Ph·OH, but no such product could be obtained from (III) or (IV). The above phenomena, allied to electronic considerations which are in line with the relative reactivities, confirm the previously (*loc. cit.*) propounded mechanism: CH<sub>2</sub>R·CHO + R'·OH → CH<sub>2</sub>R·CHO ···· R'·OH → CHR·CH·OH ···· R'·OH → CH<sub>2</sub>R·CH(OH)·OR'. R. S. C.

**Cannizzaro reaction. IV. Halogeno-derivatives of *m*-hydroxybenzaldehyde.** G. LOCK [with G. NOTTES] (Monatsh., 1936, 67, 320—327; cf. A., 1935, 1238).—Treatment of *m*-OH·C<sub>6</sub>H<sub>4</sub>·CHO with Cl<sub>2</sub> in AcOH at 100° and of the crude product with SnCl<sub>2</sub> in conc. HCl gives 3:2:4:5:6-OH·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 197—198°, in 88.5% yield; it is converted by 50% KOH at 100° into 2:3:4:6-C<sub>6</sub>H<sub>4</sub>Cl·OH and HCO<sub>2</sub>K. 3:2:4:5:6-OEt·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 68.5°, similarly gives 2:3:4:6-C<sub>6</sub>H<sub>4</sub>Cl·OEt and HCO<sub>2</sub>K. 3:6-OH·C<sub>6</sub>H<sub>4</sub>Br·CHO (I) and Cl<sub>2</sub> in AcOH at 40—50° give 2-chloro-6-bromo-3-hydroxybenzaldehyde, m.p. 137° (corr.) (Et ether, m.p. 87°; phenylhydrazone, m.p. 107°), transformed by 50% KOH at 100° into 2:4-C<sub>6</sub>H<sub>3</sub>ClBr·OH and HCO<sub>2</sub>K. Further chlorination of (I) affords 2:4-dichloro-6-bromo-3-hydroxybenzaldehyde, m.p. 111° [Et ether, m.p. 73°; oxime, m.p. 181° (corr.)], which yields 2:6:4-C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>Br·OH and HCO<sub>2</sub>K. 3:2-OH·C<sub>6</sub>H<sub>3</sub>I·CHO and 50% KOH at 100° give 2-iodo-3-hydroxybenzyl alcohol, m.p. 154° (corr.), and 3:2-OH·C<sub>6</sub>H<sub>3</sub>I·CO<sub>2</sub>H. 4:6-Dibromo-2-iodo-3-hydroxybenzaldehyde, m.p. 133.5° (corr.) (oxime, m.p. 168°), gives 4:6:2-C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>I·OH. H. W.

**Preparation of aldehydes from nitriles (Stephen's method).**  $\gamma$ -Phthalimidobutaldehyde. F. E. KING, P. L'ECUYER, and (in part) H. T. OPENSHAW (J.C.S., 1936, 352—354).—The modification recently introduced into Stephen's method for the prep. of aldehydes from nitriles (A., 1934, 89) has been applied to the prep. of  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·CHO



(2:4-dinitrophenylhydrazones) and  $o$ -C<sub>6</sub>H<sub>4</sub>Me·CHO (2:4-dinitrophenylhydrazone, m.p. 193—194°), for which the original process is unsatisfactory, but without any marked improvement.  $\gamma$ -Phthalimido-butanaldehyde (2:4-dinitrophenylhydrazone, m.p. 184°) is prepared from the nitrile and SnCl<sub>2</sub>·HCl.

F. R. S.

**Preparation of acenaphthylene glycol and some condensation reactions of naphthalene-1:8-dialdehyde.** B. K. BLOUNT and A. WEISSBERGER (J.C.S., 1936, 336—337).—Reduction of acenaphthenequinone with Na-Hg and EtOH in N<sub>2</sub> gives *cis*-acenaphthylene glycol, oxidised to 1:8-C<sub>10</sub>H<sub>6</sub>(CHO)<sub>2</sub>, which condenses with acetonedicarboxylic acid and MeNH<sub>2</sub> to 1-methyl-2:6(1':8')-naphthapiperid-4-one, isolated as the *picrate*, m.p. 197°, and the *picrate*, m.p. 165—166°, of a base, C<sub>13</sub>H<sub>13</sub>N.

F. R. S.

**Beckmann rearrangement of 2-alkyl-cyclopentanone- and -cyclohexanone-oximes.** J. G. HILDEBRAND, jun., and M. T. BOBERT (J. Amer. Chem. Soc., 1936, 58, 650—652).—Et 2-propylcyclopentanone-2-carboxylate, b.p. 136.5—138°/28 mm. (*semicarbazone*, m.p. 160—161°), prepared by propylation of Et cyclopentanone-2-carboxylate (improved prep.), is hydrolysed (conc. HCl) to 2-propylcyclopentanone [oxime (I), b.p. 120—121.5°/13 mm.]. 2-Methyl- and 2-ethyl-cyclopentanoneoximes and (I) are converted by hot 75—80% H<sub>2</sub>SO<sub>4</sub> into 6-methyl-, 6-ethyl-, m.p. 88.5—89.6° (corr.), and 6-propyl- (II), m.p. 91.5—92.4°, -2-piperidone, respectively (59—76% yield); none of the 3-alkyl-2-piperidone is produced. 2-Methylcyclohexanoneoxime and 96.4% H<sub>2</sub>SO<sub>4</sub> give 97% of the *lactam*, m.p. 90.5—91.5° (cf. Wallach, A., 1906, i, 514), of  $\epsilon$ -aminoheptonic acid, m.p. 196—197.5° (corr.), which is deaminated (98% HI) to  $n$ -C<sub>6</sub>H<sub>13</sub>·CO<sub>2</sub>H. (II) is also obtained when homoconic (8-amino-octic) acid (Baum, A., 1886, 562) is heated at 165°.

H. B.

**Behaviour of keten in the Friedel-Crafts reaction.** F. S. SPRING and T. VICKERSTAFF (J.C.S., 1935, 1873—1874).—Keten (cf. A., 1934, 1091) when passed at 0° into C<sub>6</sub>H<sub>6</sub>-AlCl<sub>3</sub> gives C<sub>6</sub>H<sub>5</sub>Me and some  $p$ -C<sub>6</sub>H<sub>4</sub>Et·COMe (*semicarbazone*, m.p. 196°); the latter is considered to be due to the presence of C<sub>2</sub>H<sub>4</sub> in keten. PhOH when treated with keten at 80° gives its Ac derivative (cf. *loc. cit.*).

H. G. M.

**Influence of cyclisation on the "colour" of molecules.** Ultra-violet absorption of derivatives of diphenylmethane and fluorene. (MME.) RAMART-LUCAS and M. J. HOCH (Bull. Soc. chim., 1935, [v], 2, 1376—1380).—Comparison of the ultra-violet absorption spectra of CH<sub>2</sub>Ph<sub>2</sub>, CHPh<sub>2</sub>, CMePh<sub>2</sub>·OH, CPh<sub>2</sub>·CHMe, C<sub>6</sub>Ph<sub>2</sub>, and CPh<sub>2</sub>·N·OH in EtOH or C<sub>6</sub>H<sub>12</sub> with the spectra of, respectively, fluorene (I), 9-phenylfluorene, 9-hydroxy-9-ethylfluorene, 9-ethylidenefluorene, fluorenone (*semicarbazone*, m.p. 245°), and its oxime, shows that an *o*-linking between the two Ph in CH<sub>2</sub>Ph<sub>2</sub> causes a large displacement of absorption towards the visible and an alteration in the form of the absorption curves. The absorption spectra of (I) in the lit. show fine bands which are due to an impurity.

J. W. B.

**Walden inversion. XIII. Configurative relationship between optically active desylamine and benzoin.** A. MCKENZIE and D. J. C. PRIE (Ber., 1936, 69, [B], 876—879).—(–)-Benzoin and (+)-desylamine have the same configuration. Reduction of desylamine hydrochloride by Na-Hg in EtOH-AcOH affords  $\beta$ -hydroxy- $\alpha\beta$ -diphenylethylamine (I), m.p. 164° (identical with the product from  $\beta$ -benzilmonoxime), and a trace of the *iso*-compound, m.p. 130°; reduction in presence of Pt gives (I) exclusively. (–)-Desylamine hydrochloride gives (+)- $\beta$ -hydroxy- $\alpha\beta$ -diphenylethylamine, m.p. 141—143°, [ $\alpha$ ]<sub>D</sub> +10.4° in EtOH. (–)-Benzoin- $\alpha$ -oxime affords (–)- $\beta$ -hydroxy- $\alpha\beta$ -diphenylethylamine, m.p. 141—142°, [ $\alpha$ ]<sub>D</sub> –10° in EtOH, also obtained from the corresponding  $\beta$ -oxime.

H. W.

**Retene. V. Structure of 6-acetylretene.** D. E. ADELSON and M. T. BOBERT (J. Amer. Chem. Soc., 1936, 58, 653—654).—The acetylretene (I), m.p. 99.5—100° (corr.), obtained by a slight modification of the method previously used (A., 1931, 1297) is the 6-derivative, since its oxime is converted by PCl<sub>5</sub> in Et<sub>2</sub>O into the *Ac* derivative, m.p. 240—240.5° (corr.) (decomp.), of 6-aminoretene (II), m.p. 139.5—140° (corr.). (II) is converted (diazo-method) into 6-retenol. Retene-6-carboxylic acid is conveniently prepared from (I) and I-KI in dioxan-10% NaOH.

H. B.

**Uneven halides. II. Uneven halides of the benzanthrone series.** K. BRASS and E. CLAR (Ber., 1936, 69, [B], 690—692).—Benzanthrone unites with Br and I in the ratio 1:1 giving dark, moderately stable compounds. With excess of I compounds of indefinite stoicheiometric composition are obtained which lose the excess of halogen when warmed in vac. and give the compound with ratio 1:1. 1-Bromobenzanthrone combines with Br and I in the ratios 2:1 and 3:2, respectively. All the substances yield the halogen quantitatively to mild reducing agents and pass into the initial materials. The observations confirm the conclusion that the trihalides of perylene (A., 1933, 57) have the composition C<sub>20</sub>H<sub>12</sub>Br+Br<sub>2</sub> and C<sub>20</sub>H<sub>12</sub>I+I<sub>2</sub>, respectively.

H. W.

**Novel ring systems. II. 1:8-Naphthaloylnaphthalene.** W. KNAPP (Monatsh., 1936, 67, 332—343).—1:8-C<sub>10</sub>H<sub>6</sub>(CO)<sub>2</sub>O is converted by MgPhBr in Et<sub>2</sub>O into 8-benzoyl-1-naphthoic acid, m.p. 129—130°, which is scarcely affected by warm, conc. H<sub>2</sub>SO<sub>4</sub>, P<sub>2</sub>O<sub>5</sub> in PhMe, or AlCl<sub>3</sub>-NaCl at 130°. 8-1'-Naphthoyl-1-naphthoic acid and P<sub>2</sub>O<sub>5</sub> in boiling PhMe afford 1:8-naphthaloylnaphthalene (I), m.p. about 350° (incipient decomp.), in about 10% yield, also obtained by use of AlCl<sub>3</sub>-NaCl at 140° or of conc. H<sub>2</sub>SO<sub>4</sub> at 150°. (I) dissolves in conc. NaOH with production of a Na salt. The Mg derivative of 1:2-C<sub>10</sub>H<sub>6</sub>Br·OMe, m.p. 83—84° (prep. from  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OMe and Br in AcOH described), and 1:8-C<sub>10</sub>H<sub>6</sub>(CO)<sub>2</sub>O give 8-2-methoxynaphthaloylnaphthoic acid, m.p. 215—217°, converted by P<sub>2</sub>O<sub>5</sub> in boiling PhMe into 2-methoxy-1:8-naphthaloylnaphthalene (II), m.p. about 370° (Na salt). 1:8-C<sub>10</sub>H<sub>6</sub>(CO)<sub>2</sub>O,  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH, and AlCl<sub>3</sub> at 200—210° yield 2-hydroxy-1:8-naphthaloylnaphthalene, m.p. about 360° (decomp.) (Na salt), transformed with difficulty by



Me<sub>2</sub>SO<sub>4</sub> into (II). 1 : 8-C<sub>10</sub>H<sub>6</sub>(COCl)<sub>2</sub>, β-C<sub>10</sub>H<sub>7</sub>OMe, and AlCl<sub>3</sub> in boiling C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> give a product C<sub>22</sub>H<sub>12</sub>O<sub>3</sub>, m.p. about 340°, which yields very small amounts of a hydrocarbon, m.p. 155–158°, when distilled with Zn dust.

H. W.

**Formation of s-dibenzocyclodocosanedione.** M. UENAKA and B. KUBOTA (Bull. Chem. Soc. Japan, 1936, 11, 19–26).—o-Phenylenediacrylic acid is obtained together with some phthalyl alcohol Et<sub>2</sub> ether and o-ethoxymethylcinnamic acid, m.p. 130–130.5° (corr.) [Et ester, b.p. 140–141°/2 mm.; dibromide, m.p. 168–169° (corr.); dihydro-derivative, m.p. 85°], from o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub>, CClna(CO<sub>2</sub>Et)<sub>2</sub> (containing some Cl<sub>2</sub>-ester), and KOH-EtOH, and is reduced (Na-Hg) to o-phenylenedipropionic acid (I). The formation of some β-(o-ethylphenyl)propionic acid was also observed. The Et<sub>2</sub> ester of (I) is reduced (Na-EtOH) to o-phenylenedipropyl alcohol, m.p. 56–57° (p-xenylcarbamate, m.p. 187°), converted by HBr into the dibromide, b.p. 187–189°/7.5 mm., which on malonation and subsequent hydrolysis and heating gives o-phenylenedivaleric acid, m.p. 148–149° (corr.). The Th salt of this acid, when heated at 0.008–0.009 mm. pressure, gives s-dibenzocyclodocosanedione, m.p. 133.5° (corr.) [semicarbazone, decomp. 205–208° (corr.); p-nitrophenylhydrazone, m.p. 168–172°]. An 11-membered ring-monoketone was not formed.

H. G. M.

**Preparation of βγ-Δ<sup>5</sup>-unsaturated ketones of the sterol series.** 17-Ethyltestosterone. A. BUTENANDT and J. SCHMIDT-THOMÉ (Ber., 1936, 69, [B], 882–888).—βγ-Δ<sup>5</sup>-Unsaturated ketones of the sterol group are readily obtained when 5 : 6-dibromoketones are debrominated by short treatment with Zn dust in warm MeOH or EtOH; under these conditions displacement of the double linking is not observed. Thus, cholesterol dibromide is transformed into Δ<sup>5</sup>-cholestenone (I), m.p. 127° after softening (? partial isomerisation to the Δ<sup>4</sup>-compound), [α]<sub>D</sub><sup>20</sup> –4.2° in CHCl<sub>3</sub> [oxime, m.p. 188° (decomp.)]. Analogously, dehydroandrosterone is brominated at the double linking and debrominated by Zn dust in MeOH after oxidation of OH to Δ<sup>5</sup>-androstene-3 : 17-dione, m.p. 158° after softening at 140° (dioxime, m.p. about 205° after incipient decomp. at 180°). The constitution of the ketones is established by the observations that (I) yields a dibromide identical with that obtained by the oxidation of cholesterol dibromide and that debromination of the latter with Zn dust and MeOH affords cholesterol. The βγ-Δ<sup>5</sup>-unsaturated ketones are readily isomerised to the Δ<sup>4</sup>-compounds when heated in dil. (mineral) acidic or alkaline solution. In neutral solvents they can be crystallised unchanged. 29-Unsaturated ketones can be obtained from the 5 : 6-dibromides by feebly acidic MeOH or EtOH in place of the usual AcOH. 17-Ethyl-Δ<sup>5</sup>-androstene-17-ol-3-one (previously regarded as the Δ<sup>4</sup>-compound) is converted by short warming with EtOH containing a little H<sub>2</sub>SO<sub>4</sub> into the isomeric 17-ethyltestosterone, m.p. 139° [semicarbazone, m.p. 230° (decomp.)], also obtained directly from 17-ethylandrostenediol by successive bromination, oxidation, and debromination by Zn dust in MeOH-H<sub>2</sub>SO<sub>4</sub>. When distilled in a

high vac. it gives the doubly unsaturated ketone, C<sub>21</sub>H<sub>30</sub>O, m.p. 135° [semicarbazone, m.p. about 225° (decomp.)].

H. W.

**Δ<sup>5</sup>-Pregnene-3 : 20-dione, an isomeride of progesterone.** U. WESTPHAL and J. SCHMIDT-THOMÉ (Ber., 1936, 69, [B], 889–892).—Δ<sup>5</sup>-Pregnene-3-ol-2-one is brominated (=2Br) in AcOH and then oxidised with CrO<sub>3</sub>; the product is debrominated by Zn dust in MeOH to Δ<sup>5</sup>-pregnene-3 : 20-dione (I), m.p. 158–160°, [α]<sub>D</sub><sup>20</sup> +65.5° in CHCl<sub>3</sub> [dioxime, m.p. 203–205° (darkening), complete decomp. 207°]. (I) is so readily transformed by H<sub>2</sub>SO<sub>4</sub>-EtOH into α- and β-progesterone that the process can be followed polarimetrically. After being heated above its m.p. in a glass tube (I) shows an increase in [α], probably due to partial wandering of the double linking.

H. W.

**Chelation. IV. Some properties of 2 : 3-dihydroxyphenyl ketones.** W. BAKER and A. R. SMITH (J.C.S., 1936, 346–348).—The volatility and solubility of 2 : 3-dihydroxyacetophenone indicate a greater degree of chelation than the normal for a pyrocatechol derivative. 2 : 3-Dimethoxybenzaldehyde (I) and MgPhBr give 2 : 3-dimethoxy-benzhydrol, m.p. 79°, oxidised (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>) to the benzophenone (2 : 4-dinitrophenylhydrazone, m.p. 152°), which is demethylated to 2 : 3-dihydroxybenzophenone, m.p. 65°. (I) and Mg anisyl bromide form 2 : 3 : 4'-trimethoxy-benzhydrol, b.p. 250°/17 mm., which is oxidised to the benzophenone, m.p. 86°, demethylated to 2 : 3 : 4'-trihydroxybenzophenone, m.p. 169°. The OH-ketones give strong yellow dyeings with Al<sub>2</sub>O<sub>3</sub> mordant.

F. R. S.

**Stereochemical investigations in the anisoin group.** A. MCKENZIE and D. J. C. PIRIE (Ber., 1936, 69, [B], 861–875).—Me r-p-methoxymandelate, m.p. 37–38°, obtained from MeI and p-OMe-C<sub>6</sub>H<sub>4</sub>·CH(OH)·CO<sub>2</sub>Ag [treatment of the acid with MeOH (EtOH) and H<sub>2</sub>SO<sub>4</sub> gives impure products], is transformed by NH<sub>3</sub>-EtOH at 0° into p-methoxymandelamide, m.p. 163–164°, which with Mg anisyl bromide affords r-anisoin (I), m.p. 112–113°. r-p-Methoxymandelic acid is resolved into its optical antipodes by cinchonine in H<sub>2</sub>O. d-p-Methoxymandelic acid has m.p. 104–105°, [α]<sub>D</sub><sup>20</sup> +176.2° in H<sub>2</sub>O, [α]<sub>D</sub><sup>20.3</sup> +213.7° in CHCl<sub>3</sub> (other vals. recorded), whilst the l-acid has m.p. 104–105°, [α]<sub>D</sub> –146.5° in H<sub>2</sub>O. Me (+)-p-methoxymandelate has m.p. 63–64°, [α]<sub>D</sub><sup>20</sup> +245°, [α]<sub>D</sub><sup>20.5</sup> +295.8° in CS<sub>2</sub>, [α]<sub>D</sub><sup>20</sup> +119.7°, [α]<sub>D</sub><sup>20.3</sup> +144.1° in COMe, [α]<sub>D</sub><sup>20.6</sup> +140.3°, [α]<sub>D</sub><sup>20.6</sup> +168.9° in EtOH, whereas m.p. 63–64°, [α]<sub>D</sub><sup>20</sup> –245.8° in CS<sub>2</sub> are recorded for the corresponding (–)-ester. (+)-p-Methoxymandelamide, m.p. 143–144°, [α]<sub>D</sub><sup>21</sup> +79.2°, [α]<sub>D</sub><sup>21.1</sup> +93.4° in COMe<sub>2</sub>, [α]<sub>D</sub><sup>21</sup> +90.6°, [α]<sub>D</sub><sup>21.1</sup> +107.6° in H<sub>2</sub>O, is slowly racemised by EtOH-KOH, the steady fall in [α] being preceded by a slight rise. (–)-p-Methoxymandelamide has m.p. 143–144°, [α]<sub>D</sub><sup>20</sup> –78.3° in COMe<sub>2</sub>, (+)-Anisoin (II) has m.p. 132–133°, [α]<sub>D</sub><sup>20.5</sup> +60.9°, [α]<sub>D</sub><sup>20.5</sup> +72.8° in COMe<sub>2</sub>, [α]<sub>D</sub><sup>20.5</sup> +78°, [α]<sub>D</sub><sup>20.5</sup> +93.3° in EtOH, [α]<sub>D</sub><sup>20.3</sup> +102.4°, [α]<sub>D</sub><sup>20.3</sup> +122.4° in CHCl<sub>3</sub>, [α]<sub>D</sub><sup>20.5</sup> +292°, [α]<sub>D</sub><sup>20.5</sup> +357.2° in CS<sub>2</sub>, whilst for (–)-anisoin (III), m.p. 132–133°, [α]<sub>D</sub><sup>19.5</sup> –60.2°, [α]<sub>D</sub><sup>19.5</sup> –72.5° are recorded. (I) is transformed by



warm 0.1N-KOH-EtOH into anisil (IV) and anisic acid. Under somewhat similar conditions (II) is slowly inactivated with production of (I) and (IV). (II) when heated at 140° for 10 min. in glass appears unchanged but gives (I) when heated for 2.5 hr. at 150°. (III) is fairly rapidly inactivated in piperidine or by a little  $\text{SOCl}_2$  in  $\text{CHCl}_3$ . (—)-Anisoil Me ether, m.p. 60–61°,  $[\alpha]_D^{20} -58.2^\circ$ ,  $[\alpha]_{5461}^{20} -67.1^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{20} -63.9^\circ$ ,  $[\alpha]_{5461}^{20} -74.6^\circ$  in EtOH,  $[\alpha]_D^{18} +66^\circ$  in heptane, is rapidly racemised by KOH-EtOH. r-Anisoil acetate, obtained by use of  $\text{AcCl}$ , has m.p. 94–95°. The corresponding (—)-compound, m.p. 77.5–78.5°,  $[\alpha]_D^{16} -152^\circ$ ,  $[\alpha]_{5461}^{16} -187^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{16} -139^\circ$ ,  $[\alpha]_{5461}^{16} -171^\circ$  in EtOH, is rapidly hydrolysed by KOH-EtOH to (I). (II) is transformed by  $\text{MgMeI}$  into  $\beta$ -(—)-methylhydroanisoil, m.p. 102–103.5°,  $[\alpha]_D^{20} -18.2^\circ$ ,  $[\alpha]_{5461}^{20} -22.7^\circ$  in  $\text{COMe}_2$ . r- $\beta$ -Methylhydroanisoil, m.p. 82–83°, is amorphous. Catalytic reduction ( $\text{Pt-PtO}_2$  in EtOH at 50–60°) of (III) leads to hydroanisoil, m.p. 172°, and, possibly, (+)-isohydroanisoil. Reduction of non-cryst. r-anisoiloxime by Na-Hg in EtOH-AcOH affords dianisylhydroxyethylamine (IV),  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m.p. 143–144° [hydrochloride, m.p. 212–213°; platinichloride, m.p. 177° (decomp.)], and the iso-base, m.p. 135–136°. Deamination of (IV) by  $\text{NaNO}_2$  in dil.  $\text{H}_2\text{SO}_4$  gives a substance, m.p. 100–101.5°, and *cis*- $\alpha$ - $\beta$ -di-*p*-methoxyphenylethylene oxide, m.p. 142–143°.

H. W.

Catalytic oxidations in aqueous solution. III. Oxidation of anthracene, quinol, and substituted quinols. H. W. UNDERWOOD, jun., and W. L. WALSH (J. Amer. Chem. Soc., 1936, 58, 646–647).—*p*-Benzoquinone and its Me, Cl-, and Br-derivatives are obtained in 90–94% yield by oxidation of the quinols with  $\text{NaClO}_3$  and a little  $\text{V}_2\text{O}_5$  in cooled 2%  $\text{H}_2\text{SO}_4$ ; 1:4- $\text{C}_{10}\text{H}_6(\text{OH})_2$  gives 93% of 1:4-naphthaquinone. Anthracene (in hot AcOH+2%  $\text{H}_2\text{SO}_4$ ; caution necessary) similarly affords 90% of anthraquinone. Poor yields of oxidation products are obtained from  $\text{NH}_2\text{Ph}$ , *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , and 1:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . PhMe, phenanthrene, cyclohexanol, borneol, and camphor were unaffected even on prolonged heating.

H. B.

Synthesis of plumbagin. L. F. FIESER and J. T. DUNN (J. Amer. Chem. Soc., 1936, 58, 572–575).—The product from *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$  and Et sodio- $\alpha$ -acetylsuccinate in  $\text{Et}_2\text{O}$  is hydrolysed (aq. KOH) to  $\beta$ -*m*-toluoylpropionic acid, m.p. 115–117° (purified through the semicarbazone, m.p. 191–193°), reduced (modified Clemmensen) to  $\gamma$ -*m*-tolylbutyric acid, m.p. 35–36°, the chloride of which is converted (method: Org. Synth., 1935, 15, 77) into 1-keto-6-methyl-1:2:3:4-tetrahydronaphthalene, b.p. 129–132°/5 mm. This and Br in  $\text{CS}_2$  at 5° give the 2-Br-derivative, m.p. 75–76°, converted by  $\text{NPhEt}_3$  into 6-methyl- $\alpha$ -naphthol, m.p. 83–84°. Oxidation ( $\text{CrO}_3$ , AcOH at 0°–room temp.) of 6:1- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{OAc}$ , b.p. about 124°/2 mm., affords 5-acetoxy-2-methyl-1:4-naphthaquinone, m.p. 117–118°, which with Zn dust and  $\text{Ac}_2\text{O}$ -NaOAc gives 1:4:5-triacetoxy-2-methylnaphthalene, m.p. 125–126°. Successive hydrolysis (5% NaOH and trace of  $\text{Na}_2\text{S}_2\text{O}_4$  in  $\text{N}_2$ )

and oxidation ( $\text{K}_2\text{Cr}_2\text{O}_7$ , dil.  $\text{H}_2\text{SO}_4$ ) of this affords 5-hydroxy-2-methyl-1:4-naphthaquinone (I), m.p. 78–79°, which is identical with plumbagin [Ac derivative, m.p. 117–118° (lit. 115° and 138°)].  $\beta$ -*p*-Toluoylpropionic acid, m.p. 124–126° [from  $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$  and PhMe by the Friedel-Crafts reaction], is similarly converted into  $\gamma$ -*p*-tolylbutyric acid, m.p. 60–61°, and thence into 1-keto-7-methyl-1:2:3:4-tetrahydronaphthalene, an oil, 7-methyl- $\alpha$ -naphthol, m.p. 108–109° (acetate, m.p. 38–39°), and 8-hydroxy-2-methyl-1:4-naphthaquinone, m.p. 157–158° (acetate, m.p. 115–116°) [which, like (I), forms a coloured boroacetate complex].

H. B.

Anthracene. X. Preparation and hydrolysis of polyhydroxyanthraquinoneglucosides. H. FOSTER [with J. H. GARDNER] (J. Amer. Chem. Soc., 1936, 58, 597–599).—1:5-Dihydroxyanthraquinone and acetobromo-*d*-glucose give (method: Takahashi, J. Pharm. Soc. Japan, 1925, 585, 969) the tetraacetate, m.p. 214.4°, of 1:5-dihydroxyanthraquinone- $\beta$ -*d*-glucoside (I), m.p. 255.2°. Hydrolysis (method: A., 1935, 983) of (I) and 1:8-dihydroxy-, m.p. 240°, and 1:8-dihydroxy-3-methyl-, m.p. 255.2°, -anthraquinone- $\beta$ -*d*-glucosides occurs in decreasing ease with 0.05N-KOH, dil. borax, and 0.05N-HCl, and gives the original dihydroxyanthraquinones; no reduction takes place. These results indicate that barbaloin is not an aloemodinarabinoside (Léger, A., 1917, i, 276). All m.p. are corr.

H. B.

Synthesis of 1:2-phthaloylanthraquinone-6-carboxylic acid. R. SCHOLL, G. VON HORNDORF, and H. K. MEYER (Ber., 1936, 69, [B], 706–712).—1-Benzoylanthraquinone-2':4'-dicarboxylic acid, m.p. 306–307° (decomp.), is obtained by chlorination of *m*-xylyl anthraquinonyl ketone (I) to  $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{CCl}_2)_2$  in  $\text{C}_6\text{H}_5\text{Cl}_3$  at 150° and treatment of the product with boiling 75% AcOH or by oxidising (I) with dil.  $\text{HNO}_3$  at 180°; it is reduced by Zn dust and 30% NaOH at 170° to 1-benzylanthracene-2':4'-dicarboxylic acid (II), m.p. 243–245° (decomp.), converted by boiling  $\text{POCl}_3$  into naphth-2':3'-1:2-anthr-10-one-6-carboxylic acid (III), which does not dissolve in  $\text{NH}_3\cdot\text{H}_2\text{O}$ , but is slowly sol. in boiling KOH- $\text{H}_2\text{O}$  or KOH-EtOH with production of naphth-2':3'-1:2-anthr-10-ol-6-carboxylic acid (III), more readily obtained from (II) and  $\text{ZnCl}_2$  at 175°. Still more readily (II) is transformed by boiling  $\text{Ac}_2\text{O}$  containing a trace of HI (*d* 1.7) into acetic naphth-2':3'-1:2-acetanthr-10-ol-6-carboxylic anhydride, decomp. about 305° after softening at 190°, converted by boiling  $\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}$  into naphth-2':3'-1:2-acetanthr-10-ol-6-carboxylic acid, decomp. 315°, which is hydrolysed by boiling NaOH to (IV). (III) is converted by red P and HI (*d* 1.7) at 190° into 9:10:1':4'-tetrahydronaphth-2':3'-1:2-anthr-6-carboxylic acid, m.p. 290–300° after softening, which is oxidised by  $\text{CrO}_3$  in AcOH to 1:2-phthaloylanthraquinone-6-carboxylic acid, incipient decomp. 340° ( $\text{NH}_4$  salt; corresponding diazine,  $\text{C}_{23}\text{H}_{10}\text{O}_4\text{N}_2$ ); attempts to decarboxylate it to ang-phthaloylanthraquinone were unsuccessful. 4-Benzyl-1-methylnaphthalene-2'-carboxylic acid is converted by boiling  $\text{Ac}_2\text{O}$  containing HI or HCl into 3-methyl-1:2-benz-anthr-10-yl acetate, m.p. 195°.

H. W.



**Catalytic hydrogenation under high pressure. Essential oils and esters.** L. PALFRAY and S. SABETAY (Bull. Soc. chim., 1936, [v], 3, 682—687).—Catalytic hydrogenation (Ni) of certain essential oils under high pressure at about 240° causes partial reduction of esters to primary alcohols. Under similar conditions Et laurate affords dodecanol in 62% yield and some hydrocarbon, whilst  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$  gives  $\beta$ -cyclohexylethyl alcohol, also obtained from  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$ . H. W.

**Formation of nitrosites.** T. K. GAPONENKOV (J. Gen. Chem. Russ., 1935, 5, 1485—1486).—Max. yields of nitrosite are obtained from  $\beta$ -phellandrene,  $\text{NaNO}_2$ , and AcOH when the solvent is 1:1 light petroleum-Et<sub>2</sub>O, at low temp., and in absence of excess of AcOH. R. T.

**Polymerisation of pinene.** H. I. WATERMAN, J. J. LEENDERTSE, and W. A. A. B. KOELENMID (Rec. trav. chim., 1936, 55, 7—12).—Polymerisation of pinene in  $\text{C}_5\text{H}_{12}$  occurs at  $-15^\circ$  with  $\text{AlCl}_3$ . No gases are evolved, and some light-coloured resin, almost free from O, is formed. The fractions of the product have been studied before and after hydrogenation. Vals. for  $r_L$  after hydrogenation suggest that polymerisation takes place without the opening or closing of rings. Pinene when hydrogenated (Nickelsguhr) at 200—250° (pressure about 100 kg. per sq. cm.) gives a product agreeing fairly well in properties with pinane in the lit. H. G. M.

**endo-exo-Isomerism in alicyclic alcohols of borneol type.** I. G. KOMPPA and S. BECKMANN (Annalen, 1936, 522, 137—150; cf. Biltz, A., 1899, i, 297, ii, 634; Hückel *et al.*, A., 1935, 745).—The mol. wts. of the 14 sec.-alcohols containing the 1:2:2-dicycloheptane ring are determined (f.p. method in  $\text{C}_6\text{H}_6$ ) for different concns. and the % association (*A*) calc. for a concn. of 0.06 mol. per 100 g.  $\text{C}_6\text{H}_6$ . The alcohols form 3 groups: (i) *A* = 54—58, those with no substituent near the OH; (ii) *A* = 33—44, those with the OH "screened" by 1 substituent; (iii) *A* = 19—24, those with the OH "hindered" by substituents from 2 sides. The effect of, e.g.,  $\text{C}_7\text{Me}$  is of decisive importance;  $\text{C}_8$  has little or no effect. Borneol, 4-methylborneol, and  $\alpha$ -fenchocamphorol (*apoborneol*) are considered to have *endo*-OH, whilst *isoborneol*, 4-methylisoborneol, and *isofenchol* have *exo*-OH.  $\alpha$ -Santenone alcohol and  $\alpha$ -santenol have *endo*- and *exo*-OH, respectively; both contain  $\text{C}_7\text{Me}$  in the *trans* position. Definite conclusions are not yet possible for  $\alpha$ - and  $\beta$ -norborneols, camphenilols I and II,  $\beta$ -fenchocamphorol, and  $\alpha$ -fenchol. H. B.

**Racemisation and camphene transformation.** J. HOUBEN and E. PFANKUCH (Ber., 1936, 63, [B], 899—901).—A reply to Nametkin *et al.* (A., 1935, 89). H. W.

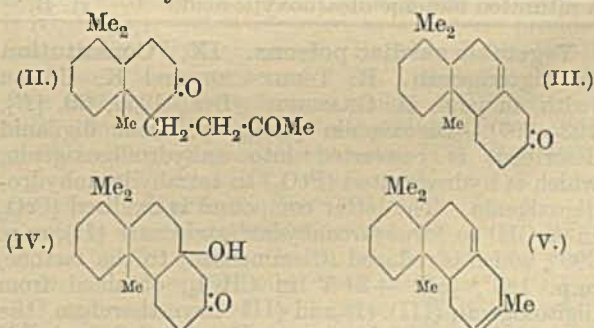
**Hydrogenation of carbonyl compounds.**—See this vol., 686.

**Preparation of *d-trans*- $\pi$ -oxocamphor from isoketopinic acid.**—See B., 1936, 444.

**4-Methylisantenol and 4-methylsantenylamine.** G. KOMPPA and G. A. NYMAN (Ber., 1936, 69, [B], 712—716; cf. A., 1935, 865).—4-Methylsantenol, m.p. 33—34.5° (*loc. cit.*), is transformed by

$o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at 100° into 4-methylsantenyl *H phthalate*, m.p. 135—136°, hydrolysed to the alcohol, m.p. 36—37°. Reduction of 4-methylsantenone with Na and EtOH affords 4-methylisantenol, b.p. 200—200.5°, m.p. 40—42° (*H phthalate*, m.p. 143—144°; phenylurethane, m.p. 93—94.5°). 4-Methylsantenoneoxime, m.p. 110.5—111.5° (*Bz derivative*, m.p. 83—84°), is reduced by Na and boiling abs. EtOH to 4-methylsantenylamine, b.p. 62°/8 mm. [*hydrochloride* (I); *aurichloride*, m.p. about 163° after softening; *platinichloride*, m.p. 266—269°; *picrate*, m.p. 242—244° (decomp.); *Bz derivative*, m.p. 153.5—154.5°]. Treatment of (I) with  $\text{HNO}_2$  does not give a homogeneous alcohol. H. W.

**Diterpene alcohol from the wood of *Dacrydium biforme*.** II. Ozonisation of manool. J. R. HOSKING (Ber., 1936, 69, [B], 780—785; cf. A., 1935, 1127).—Ozonisation of manool (I) in  $\text{CCl}_4$  at 0° and decomp. of the ozonide by  $\text{H}_2\text{O}$  at 100° gives the non-cryst. diketone (II), b.p. 159—160°/0.1 mm. (non-cryst. compounds with  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  and  $\text{NH}_2\text{OH}$  and ill-defined derivatives with aminoguanidine or picric acid), which does not reduce dil.  $\text{KMnO}_4$  at 20°. If (II) is warmed with NaOEt or heated with HCl at 0° followed by NaOH-EtOH it is transformed into



the cryst. ketone (III), m.p. 71° (*semicarbazone*, m.p. 188°). Treatment of (II) with 2% NaOH-EtOH at 20° or with piperidine in  $\text{C}_6\text{H}_6$  affords the compound (IV), m.p. 199°, which is saturated and contains 1 active OH (Zerevitinov). Excess of  $\text{MgMeI}$  converts (IV) with loss of  $2\text{H}_2\text{O}$  into the liquid hydrocarbon (V), b.p. 127—130°/0.1 mm. (hydrogenated to the substance  $\text{C}_{18}\text{H}_{32}$ , b.p. 120°/0.1 mm.), which is dehydrogenated by Se at 340° to 1:7-dimethylphenanthrene. Oxidation of (I) by  $\text{KMnO}_4$  (=80) in  $\text{COMe}_2$  gives an unsaturated ketone,  $\text{C}_{17}\text{H}_{28}\text{O}$ , b.p. 137—138°/0.1 mm. (*semicarbazone*, m.p. 185—186°), hydrogenated ( $\text{PtO}_2$  in EtOAc) to a saturated ketone (*semicarbazone*, m.p. 199—200°). H. W.

**Biochemistry of micro-organisms. XLIX. Palitantin, a metabolic product of *Penicillium palitans*.** Westling. J. H. BIRKINSHAW and H. RAISTRICK (Biochem. J., 1936, 30, 801—808).—Three strains of the mould, grown in Raulin-Thom glucose medium, yielded palitantin (I),  $\text{C}_{14}\text{H}_{22}\text{O}_4$ , m.p. 163—165° [*semicarbazone*, m.p. 212—213° (decomp.); *phenylhydrazone*, m.p. 175—176°; *oxime*, m.p. 104—106°; 2:4-dinitrophenylhydrazones, m.p. 209°; *di-p-bromobenzoate*, m.p. 153—154°]. (I), which contains  $\cdot\text{CHO}$ , 2 OH, and  $\times$  two double linkings, is hydrogenated ( $\text{Pd-C}$ ) to tetrahydropalitantin (II), m.p. 116°



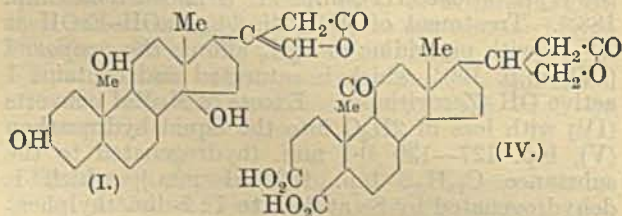
(semicarbazone, m.p. 188—189°), further reduced (Na-Hg) to  $\alpha$ -, m.p. 142—143°, and  $\beta$ -hexahydro-palitanin, m.p. 98—99°, and oxidised (NaOI) to tetrahydropalitanic acid, m.p. 110° (to an opaque liquid clearing at 135°). Oxidation of (I) by  $\text{HgI}_2$ -KI affords palitanic acid,  $\text{C}_{14}\text{H}_{22}\text{O}_5$ , m.p. 145—148°, whilst that by  $\text{Ag}_2\text{O}$  followed by esterification with  $\text{CH}_2\text{N}_2$  and treatment with aq.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  yields the dihydrazide, m.p. 201—202°, of a dicarboxylic acid,  $\text{C}_{13}\text{H}_{20}\text{O}_5$  (or of its lactone); similar treatment of (II) gives the dihydrazide, m.p. 188—190°, of a dicarboxylic acid,  $\text{C}_{13}\text{H}_{24}\text{O}_5$  (or of its lactone).

F. O. H.

**Bitter principles of Colombo root.** IV. K. FEIST and R. BRACHVOGEL (Annalen, 1936, 522, 185—190).—KOH-fusion of columbin (I) gives some 2-methylterephthalic acid in addition to 2:4- $\text{C}_6\text{H}_3\text{Me}_2\text{CO}_2\text{H}$  (A., 1935, 1245). (I) is reduced by Pd-black and boiling tetrahydronaphthalene to hydrochasanthnic acid (*ibid.*, 864), and thus contains a lactone ring. Chasmanthin is not oxidised by  $\text{SeO}_2$ , but its Me ether with 5%  $\text{KMnO}_4$  in a slightly alkaline medium affords merochasmanthnic acid Me ether,  $\text{C}_{16}\text{H}_{20}\text{O}_8$ , m.p. 248° (decomp.) ( $\text{Me}_2$  ester, m.p. 254—255°, hydrolysed with difficulty, which appears to be a saturated lactonic dicarboxylic acid.

H. B.

**Vegetable cardiac poisons.** IX. Constitution of digoxigenin. R. TSCHESCHE and K. BOHLE [with, in part, H. GRASSHOFF] (Ber., 1936, 69, [B], 793—797).—Digoxigenin (I) (prep. from digilanid described) is converted into anhydrodigoxigenin, which is hydrogenated ( $\text{PtO}_2$ ) to tetrahydroanhydrodigoxigenin. The latter compound is oxidised ( $\text{CrO}_3$  in  $\text{AcOH}$ ) to tetrahydroanhydrodigoxigenone (II), m.p. 290°, which is reduced (Clemmensen) to the lactone, m.p. 185°,  $[\alpha]_{\text{D}}^{25} +34.5^\circ$  in  $\text{CHCl}_3$ , obtained from digitoxigenin (III). (I) and (III) have therefore the same skeleton. Oxidation of (II) with  $\text{CrO}_3$  in  $\text{AcOH}$

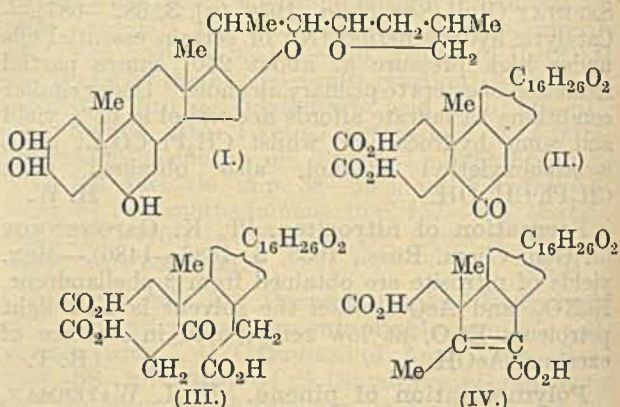


gives the acid (IV), m.p. 306° ( $\text{Me}$  ester, m.p. 160—161°), which passes when heated into the ketone,  $\text{C}_{22}\text{H}_{30}\text{O}_4$ , m.p. 228—229°, and is hydrogenated to the substance,  $\text{C}_{23}\text{H}_{34}\text{O}_7$ , m.p. 266—267°. (I) has probably the structure shown.

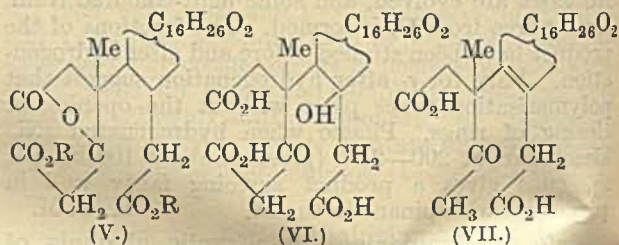
H. W.

**Saponins of the cyclopentanohydrophenanthrene group.** IV. Constitution of digitogenin and digitogin. R. TSCHESCHE and A. HAGEDORN (Ber., 1936, 69, [B], 797—805).—Mainly theoretical. Reasons are advanced for assigning the structure (I) to digitogenin. Digitogenic acid, obtained by cautious oxidation of (I) with  $\text{CrO}_3$ , is shown to be a  $\gamma$ -CO-acid (II), which accounts for its inability to lose  $\text{CO}_2$  (cf. Windaus *et al.*, A., 1925, i, 1082). Oxydigitogenic acid, obtained from (II) and  $\text{KMnO}_4$ , its decarboxylation product, and the enol-lactone

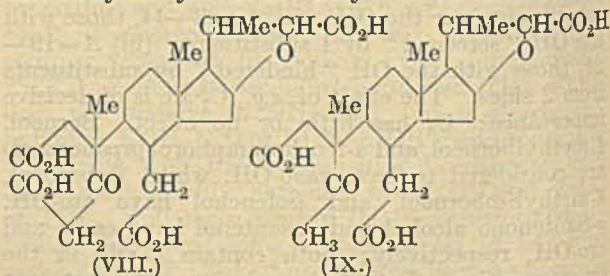
obtained by heating its esters are formulated according to (III), (IV), and (V).



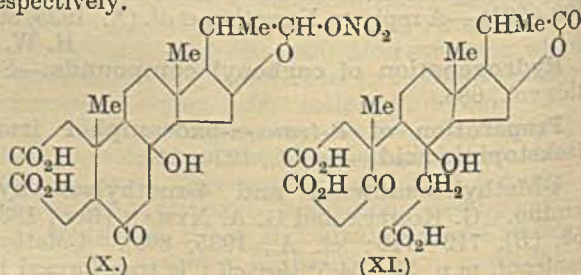
Digitic acid (VI) obtained by drastic oxidation of (III) contains a new *tert*-OH (Zerevitinov) probably at 8-C or 9-C. The constitutions (VI) and (VII) are



assigned to it and anhydrodigitic acid obtained from it by loss of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when treated with  $\text{AcOH}$  and  $\text{HCl}$ . The pentacarboxylic acid,  $\text{C}_{26}\text{H}_{38}\text{O}_{12}$ , of Windaus *et al.* (*loc. cit.*) is shown to be a tetracarboxylic acid (VIII)+ $\text{H}_2\text{O}$  very firmly attached. It loses  $\text{CO}_2$  when heated and gives the tricarboxylic acid (IX)+ $\text{H}_2\text{O}$ , the composition of which is confirmed by analyses of the anhydrous  $\text{Me}$  ester.



The lactol nitrate obtained by oxidation of digitonic acid with  $\text{HNO}_3$  (Windaus and Shah, A., 1926, 404) and the ketocarboxylic acid obtained by treating it with  $\text{KMnO}_4$  are formulated according to (X) and (XI), respectively.



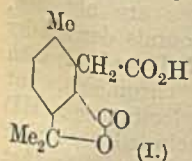


The production of  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  from gigtogenin and (I) is readily understood but  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$  appears to be derived by complete rupture of the whole ring system. H. W.

**Phenol- and methylglycol- [ $\beta$ -methoxyethyl alcohol]-lignin from spruce wood.** W. FUCHS (J. Amer. Chem. Soc. 1936, 58, 673—680).—PhOH-lignin (I) [large-scale prep. from spruce wood flour (A), PhOH, and conc. HCl at 85—90°] is partly adsorbed by activated C from an EtOH-solution. The unadsorbed material is then fractionated by  $\text{Et}_2\text{O}$ , EtOAc, and aq.  $\text{Na}_2\text{CO}_3$ ; successive extraction of the C with EtOH gives further fractions. Similarly, methylglycol-lignin (II) [prep. from (A),  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , and conc. HCl at 121° under pressure] is partly adsorbed by C from a  $\text{COMe}_2$  solution; fractionation of the unadsorbed part is effected with  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , and aq.  $\text{Na}_2\text{CO}_3$ . Several of the fractions are analysed for C, H, and OMe (using AcOH—HI; elimination of  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  does not occur to any appreciable extent); acetylation ( $\text{Ac}_2\text{O} + 0.2\%$  conc.  $\text{H}_2\text{SO}_4$  at 100°) gives products which are insol. in dil. alkali (showing absence of  $\text{CO}_2\text{H}$ ) but sol. in  $\text{C}_6\text{H}_6$  (cf. Wedekind and Katz, A., 1929, 799). Potentiometric titration indicates, however, that the fractions are mixtures of several compounds. Contrary to Hägglund, the combined PhOH (2.4—26.5%) in fractions of (I) is eliminated by treatment with red P and AcOH—HI (or AcOH—HBr, whereby a sugar-like substance is also produced), thus proving the presence of  $>\text{C}(\text{OPh})_2$  (cf. A., 1929, 1282) or  $:\text{C}(\text{OPh})$  (cf. Brauns and Hibbert, A., 1935, 1373). KOH-fusion of fractions from (I) and (II) gives  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  (0.8—11% of lignin), 3:4-(OH) $_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$  (4.3—16.1% of lignin),  $o\text{-C}_6\text{H}_4(\text{OH})_2$ , and (probably) phenol-2:4-dicarboxylic acid; oxidation (AcOH— $\text{HNO}_3$ ) affords picric and benzenecarboxylic acids. A possible structure for spruce lignin is given. The original must be consulted for details.

H. B.

**Picrotoxin. II. Picrotone and picrotonol.** D. MERCER and A. ROBERTSON (J.C.S., 1936, 288—294).—Oxidation ( $\text{KMnO}_4$ ) of picrotonol yields  $\alpha\alpha$ -4-trimethylphthalide-3-acetic acid (I), decarboxylated to tetramethylphthalide, in agreement with Horrmann and Hagendorn (A., 1921, i, 347) and contrary to Angelico (A., 1910, i, 404).  $\beta$ -o-Tolylpropionyl chloride, obtained from *o*-toluoyl chloride and Et sodiomalonate, with  $\text{AlCl}_3\text{-C}_6\text{H}_6$  followed by amyl nitrite-HCl, gives 2-oximino-4-methyl-1-hydrindone, m.p. 215° (decomp.). The oximino-compound with *p*-toluenesulphonyl chloride yields *o*-tolylacetone-trile-3-carboxylic acid, m.p. 142—143°, hydrolysed to 6-methylbromophthalic acid, m.p. 195—196° (anhydride, m.p. 150°), also obtained with  $\text{COMe}_2$  from (I) and KOH. Hydrolysis of picrotoxinin ozonide gives  $\text{CH}_2\text{O}$ ,  $\text{HCO}_2\text{H}$ , and picrotoxinone, indicating the presence of  $:\text{C}(\text{CH}_2\text{CO}_2\text{H})$  in picrotoxinin (II). Hydrogenation (Pt) of (II) affords  $\alpha$ -dihydropicrotoxinin, m.p. 252°, which with  $\text{H}_2\text{SO}_4$  forms dihydropicrotoxic acid (III), whilst with a Pd catalyst in EtOAc,  $\beta$ -dihydropicrotoxinin, m.p. 256—



257°,  $[\alpha]_D^{20} - 24.69^\circ$  in  $\text{COMe}_2$ , is obtained, unaffected by  $\text{H}_2\text{SO}_4$ . Hydrogenation with Pd in EtOH—HCl gives a substance, which is a mixture of at least three compounds, and with  $\text{H}_2\text{SO}_4$  yields (III) and picrotonol (*p*-nitrobenzoate, m.p. 155°). (III) and MeI— $\text{Ag}_2\text{O}$  form *Me O-dimethyldihydropicrotozoate*, m.p. 146—147°,  $[\alpha]_D^{20} + 95.93^\circ$  in  $\text{CHCl}_3$ , hydrolysed to the acid, m.p. 206—207°. The possible structure of picrotoxinin is discussed on the basis of the C-skeleton for picrotonol.

F. R. S.

**Gentiopiecin. I.** Y. ASAHINA, J. ASANO, Y. TANASE, and Y. UENO (Ber., 1936, 69, [B], 771—779).—Gentiopiecin (I), obtained from the root of *Gentiana scabra*, Bunge, var. *Buergeri*, Maxim, has m.p. (anhyd.) 191°, m.p. (+0.5 $\text{H}_2\text{O}$ ) 121°. It gives a dark red condensation product with  $\text{NHPh}\cdot\text{NH}_2$ , a *p*-nitrophenylhydrazide,  $\text{C}_{22}\text{H}_{27}\text{O}_{11}\text{N}_2$ , m.p. 199° (decomp.), and an isopropylidene derivative, m.p. 228°. When hydrolysed by emulsin at room temp. it affords insol. gentiogenin (II) (cf. Tanret, A., 1905, i, 655) and sol. *eugentiogenin* (III),  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , m.p. 123°,  $[\alpha]_D^{20} \pm 0^\circ$  in  $\text{CHCl}_3$  (*p*-nitrophenylhydrazone, decomp. 180°), which does not give Tanret's reaction or a blue colour after dissolution in alkali and acidification with conc.  $\text{H}_2\text{SO}_4$ . (II), m.p. 184° (decomp.), is  $(\text{C}_{10}\text{H}_{10}\text{O}_4)_2$  and is regarded as a dimeric product from (III). Hydrolysis of (I) with KOH—EtOH establishes the presence of 1 Ac. Oxidation of (I) with  $\text{KMnO}_4$  after hydrolysis yields AcOH, whereas  $\text{H}_2\text{O}_2$  affords  $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ . (I) and  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  at 100° give *gentiopiecin tetra-acetate* (IV), m.p. 139°,  $[\alpha]_D^{17} - 164.7^\circ$  in  $\text{CHCl}_3$ , which yields  $\text{CH}_2\text{O}$  after ozonolysis. Hydrogenation (Pd—C in EtOAc) of (I) leads to *tetrahydropiecin* (V), m.p. 190°,  $[\alpha]_D^{20} - 75.13^\circ$  in abs. EtOH, which does not yield a volatile acid when boiled with excess of  $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$ , and is converted by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into *tetrahydropiecin tetra-acetate*, m.p. 208°, also obtained by hydrogenation of (IV). Oxidation of (V) with  $\text{KMnO}_4$  affords  $\text{EtCO}_2\text{H}$ , whilst dry distillation of it gives  $\text{Pr}^n\text{CHO}$ . (V) is hydrolysed by emulsin to *tetrahydroprotopiecin* (VI)  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , m.p. 98°,  $[\alpha]_D^{20} + 214.9^\circ$  [*p*-nitrophenylhydrazone, m.p. 184° (decomp.)], which immediately reduces  $\text{MnO}_4^-$  but does not give a colour with  $\text{FeCl}_3$ . Hydrogenation (Pd—C in  $\text{H}_2\text{O}$ ) of (I) affords *hexahydroprotopiecin* (VII),  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , m.p. 140°,  $[\alpha]_D^{19} + 161.0^\circ$  in abs. EtOH, which does not reduce  $\text{NH}_3\text{-Ag}_2\text{O}$  or  $\text{KMnO}_4$  in  $\text{COMe}_2$  [also obtained from (VI)], hexahydropiecin and glucose. Oxidation of (VII) by  $\text{CrO}_3$  in AcOH gives a compound,  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , m.p. 93°,  $[\alpha]_D^{20} - 30.53^\circ$  in abs. EtOH.

H. W.

**Saponins. XI. Sapogenin of the roots of *Momordica cochinchinensis* (Laur), Spreng. S.** KUWADA and Y. FUWA (J. Pharm. Soc. Japan, 1935, 55, 467—473).—Momordin (saponin from *M. cochinchinensis*) is hydrolysed to *momorgenin* (I),  $\text{C}_{30}\text{H}_{48}\text{O}_3$ , decomp. 309.8° (corr.),  $[\alpha]_D^{20} + 78.3^\circ$  in  $\text{COMe}_2$  [K salt; monoacetate, m.p. 266° (corr.); Me ester (II), m.p. 203° (Ac derivative, m.p. 220°); benzoate, m.p. 261° (Me ester, m.p. 269°)]. (II) does not depress the m.p. of Me oleanolate and (I) resembles oleanolic acid in many respects.

CH. ABS. (r)



**Saponin of the seeds of *Eschulus turbinata*, Blume.** I. T. MATSUKAWA (J. Pharm. Soc. Japan, 1935, 55, 350—357).—*Japoescinin*,  $C_{65}H_{101}O_{30}$ , m.p. about  $200^{\circ}$  (decomp.), is obtained from Japanese *E. turbinata* by an improved method; it is hydrolysed to a *prosapogenin*,  $C_{59}H_{94}O_{25}$ , m.p.  $210^{\circ}$  (corr.) (*di-bromide*, m.p.  $175^{\circ}$ ), further hydrolysed to *japoescigenin* (I),  $C_{35\text{ or }36}H_{58\text{ or }60}O_7$ , m.p.  $258^{\circ}$  (corr.), possibly isomeric with Winterstein's escigenin (A., 1931, 1159). (I) contains 4 active H (Zerevitinov) and on hydrolysis yields *japoescigenol* (II),  $C_{30\text{ or }31}H_{52\text{ or }51}O_6$ , m.p.  $307^{\circ}$  [*monobromide*, m.p.  $196^{\circ}$  (decomp.)]; *tetra-acetate*, m.p.  $198^{\circ}$  (corr.), and *tiglic acid*. (II) contains 5 active H (probably 5 OH, the remaining O being in a bridge) and one double linking. CH. ABS. (r)

**Hydrogenation of acetylene derivatives.** XXII. **Dihydroxycyclohexylacetylene.** J. S. SALKIND [with T. E. ZALESSKAJA, D. I. ROZANOV, and G. V. TSHELINCEV] (J. Gen. Chem. Russ., 1935, 5, 1723—1727).—1:1'-Dihydroxy-1:1'-dicyclohexylacetylene (I) ( $Ac_2$  derivative, b.p.  $164$ — $170^{\circ}$ , m.p.  $45.5$ — $46.5^{\circ}$ ) and Br in  $CHCl_3$  afford  $\alpha\beta$ - *dibromo- $\alpha\beta$ -dicyclohexylethylene 1:1'-oxide*, m.p.  $106.5$ — $107.5^{\circ}$ . (I) is readily hydrogenated (Pd) to 1:1'-*dihydroxy-1:1'-dicyclohexylethylene*, m.p.  $152^{\circ}$ , which yields adipic acid when oxidised with  $KMnO_4$ . R. T.

**Conversion of furfuraldehyde into hydrocarbons.** N. A. ORLOV and O. A. RJABTSCHENKO (J. Appl. Chem. Russ., 1936, 9, 249—253).—Furfuraldehyde reacts with  $H_2$  in presence of  $MoS_3$  ( $270^{\circ}$ /150 atm.; 3—4 hr.) to yield sylvan, tetrahydrosylvan, EtOH, and  $CHMePr\cdot OH$ ; at  $330$ — $350^{\circ}$  (1.5—2 hr.) the product consists chiefly of *n*-pentane, together with unsaturated condensation products. R. T.

**True effect of cyclisation on the "colour" of molecules.** Ultra-violet absorption of *o*-methoxyacetophenone,  $\beta$ -coumaranone, and  $\gamma$ -chromanone. (MME.) RAMART-LUCAS and M. VAN COWENBERGH (Bull. Soc. chim., 1935, [v], 2, 1381—1383).—The ultra-violet absorption spectra of *o*-OMe- $C_6H_4\cdot COMe$ ,  $\gamma$ -chromanone, and  $\beta$ -coumaranone in EtOH are closely similar, displacement towards the visible increasing in the order given, i.e., being the greater the smaller is the no. of atoms in closed chain. J. W. B.

**Synthesis of 1:2-diphenylcoumarones.** B. I. ARVENTI (Bull. Soc. chim., 1936, [v], 3, 598—603).—When heated at  $250$ — $290^{\circ}$  *o*-benzoyloxydiphenylacetic acids lose  $CO_2$  and  $H_2O$  with production of 1:2-diphenylcoumarones. Thus, *o*-benzoyloxydiphenylacetic acid at  $290^{\circ}$  gives  $CO_2$ ,  $H_2O$ , BzOH, 1:2-diphenylcoumarone, m.p.  $123^{\circ}$  (identified by oxidation with  $CrO_3$  to *o*- $C_6H_4\cdot Bz\cdot OH$ ), and *o*-hydroxydiphenylacetolactone. *p*- $C_6H_4\cdot Cl\cdot OH$  and  $OH\cdot CHPh\cdot CO_2H$  yield 4-chloro-2-hydroxydiphenylacetic acid, the Bz derivative of which at  $260$ — $280^{\circ}$  gives 4-chloro-1:2-diphenylcoumarone, m.p.  $118^{\circ}$ , oxidised to 5-chloro-2-benzoyloxybenzophenone, m.p.  $112^{\circ}$ , whence 5-chloro-2-hydroxybenzophenone, m.p.  $94$ — $95^{\circ}$ . 1:2-Diphenyl-4-methylcoumarone, m.p.  $114^{\circ}$ , and 1:2-diphenyl-5-methylcoumarone, m.p.  $93^{\circ}$ , are described. H. W.

**Reaction between quinones and sodium enolates.** IV.  $\psi$ -Cumoquinone and sodio-acetoacetic and -malonic esters. L. I. SMITH and C. W. MACMULLEN (J. Amer. Chem. Soc., 1936, 58, 629—635).—Trimethyl-*p*-benzoquinone ( $\psi$ -cumoquinone) (I) and  $CHNa\cdot Ac\cdot CO_2Et$  in EtOH give 4-hydroxy-1:3:5:6-tetramethylcoumarone (II), m.p.  $138$ — $139^{\circ}$  (*benzoate*, m.p.  $145$ — $145.5^{\circ}$ ; *Me ether*, m.p.  $60$ — $61^{\circ}$ ), some 4-hydroxy-3:5:6-trimethylisocoumaranone (III), m.p.  $197$ — $198^{\circ}$ , and a resin [which when treated with Zn dust and aq. AcOH affords a considerable amount of (III)]. When the reaction is carried out in  $C_6H_6$ , (II) is the main product. (II) and (III) arise by ring-closure (in two ways) of the intermediate 2:5:3:4:6-(OH) $_2C_6Me_3\cdot CHAc\cdot CO_2Et$  and subsequent ketone or acid fission; a coumarin is not produced (cf. this vol., 480). (III) is the sole product from (I) and  $CHNa(CO_2Et)_2$ . Methylation ( $Me_2SO_4$ ,  $MeOH\cdot KOH$ ) of (III) gives 3:6-dimethoxy-2:4:5-trimethylphenylacetic acid (IV), m.p.  $158$ — $159^{\circ}$ . 2:4:5- $C_6H_2Me_3\cdot CHO$  (V) [from  $\psi$ -cumene (VI),  $Zn(CN)_2$ , and  $HCl$  in  $C_6H_6$ ] is reduced (Zn, aq. AcOH) to the impure acetate, b.p.  $141$ — $150^{\circ}/9$  mm., of 2:4:5-trimethylbenzyl alcohol, m.p.  $83$ — $83.5^{\circ}$  (cf. Krömer, A., 1891, 1351); the chloride, b.p.  $110^{\circ}/5$  mm. [prepared using conc.  $HCl$  or by chloromethylation (method: von Braun and Nelles, A., 1934, 879) of (VI)], with aq. EtOH-NaCN gives the nitrile, b.p.  $133$ — $137^{\circ}/4$  mm., m.p.  $9$ — $10^{\circ}$ , of 2:4:5-trimethylphenylacetic acid (VII), m.p.  $128$ — $129^{\circ}$  (lit.  $118^{\circ}$ ). (VII) is also obtained by reduction (red P, 45%  $HI$ , AcOH) of 2:4:5-trimethylmandelic acid, m.p.  $133$ — $135^{\circ}$  [from (V); method: Corson *et al.*, Org. Synth., 1932, 1, 329], and from 2:4:5- $C_6H_2Me_3\cdot COMe$  by Willgerdt and Scholtz' method (A., 1910, i, 392). 3:6-Dinitro-2:4:5-trimethylphenylacetic acid, m.p.  $203$ — $203.5^{\circ}$ , from (VII) and fuming  $HNO_3$  in  $CHCl_3$  + conc.  $H_2SO_4$  at  $0^{\circ}$ —room temp., is reduced by  $H_2$  (40 lb.),  $PtO_2$ , EtOH to 5-nitro-, and by  $H_2$  (1300 lb.), Raney Ni, EtOH at  $80^{\circ}$  to 5-amino-, m.p.  $260$ — $261^{\circ}$ , -4:6:7-trimethyl-oxindole. The latter is hydrolysed by aq.  $Ba(OH)_2$  at  $160^{\circ}$  to 3:6-diamino-2:4:5-trimethylphenylacetic acid; diazotisation of this and heating the resulting solution gives a product, m.p.  $176$ — $183^{\circ}$ , which with Zn and AcOH affords (III).  $HCl$  passed into 3:6-dimethoxy- $\psi$ -cumene, aq.  $CH_2O$ , and conc.  $HCl$  at  $70^{\circ}$  gives 3:6-dimethoxy-2:4:5-trimethylbenzyl chloride, b.p.  $134$ — $135^{\circ}/3.5$  mm., m.p.  $63$ — $63.5^{\circ}$ , converted by aq. EtOH-NaCN into the nitrile, m.p.  $90$ — $91^{\circ}$ , of (IV). H. B.

**Hydroxy-carbonyl compounds.** XI. Phosphoryl chloride as a condensing agent. (Miss) I. GOODALL and A. ROBERTSON (J.C.S., 1936, 426—428).—*p*-Xylenol does not condense with  $CH_2Ac\cdot CO_2Et$  in presence of  $POCl_3$  but with Et  $\alpha$ -methyl- (I), Et  $\alpha$ -ethyl- (II), and Et  $\alpha$ -benzyl-acetoacetate (III), and Et benzoylacetate (IV), chromones are obtained, identical with the respective compounds derived by the  $P_2O_5$  method. Condensation of (I) and (II) with *m*-4-xylenol ( $POCl_3$ ) also yields chromones, but  $CH_2Ac\cdot CO_2Et$  gives 4:6:8-trimethylcoumarin: (III) and (IV) do not react. It is concluded that with  $POCl_3$  the course of the reaction tends to follow that obtaining with  $P_2O_5$ . The following have been pre-



pared: 2:5:8-trimethyl-, m.p. 81°, 2:3:5:8-tetramethyl-, m.p. 96.5—97.5°, 2:5:8-trimethyl-3-ethyl-, m.p. 86.5°, 3-benzyl-2:5:8-trimethyl-chromone, m.p. 101°, and 2-(3':4'-methylenedioxy)styryl-5:8-dimethyl-, m.p. 183°, -3:5:8-trimethyl-, m.p. 226°, -5:8-dimethyl-3-ethyl-, m.p. 153°, and -3-benzyl-5:8-dimethyl-chromone, m.p. 222°, and 5:8-dimethylflavone, m.p. 171°.

F. R. S.

**Synthesis of a natural colouring matter.** R. ROBINSON (Proc. Roy. Inst., 1936, 29, 41—56).—An account of the synthesis of pelargonin chloride.

**Amino-alcohols derived from 1:2:3:4-tetrahydrodibenzfuran.** R. A. ROBINSON and E. MOSSETTIG (J. Amer. Chem. Soc., 1936, 58, 688—689; cf. this vol., 209).—7-Bromoacetyl-1:2:3:4-tetrahydrodibenzfuran, m.p. 81—82° (all m.p. are corr.), and the appropriate base give 7-dimethylamino- (hydrochloride, m.p. 244—247°), 7-diethylamino- (hydrochloride, m.p. 202—210°), 7-piperidino- (hydrochloride, m.p. 235—239°), and 7-1':2':3':4'-tetrahydroisoquinolino- (hydrochloride, m.p. 260—264°), -acetyl-1:2:3:4-tetrahydrodibenzfurans. 7-β-Dimethylamino- (hydrochloride, m.p. 220—222°), 7-β-piperidino- (hydrochloride, m.p. 230—232°), and 7-β-1':2':3':4'-tetrahydroisoquinolino- (hydrochloride, m.p. 197—200°), -α-hydroxyethyl-1:2:3:4-tetrahydrodibenzfurans are prepared (with difficulty) by catalytic reduction of the  $\text{NR}_2\cdot\text{CH}_2\cdot\text{CO}$  derivatives. H. B.

**Constitution of oroxylin.** R. C. SHAH, C. R. MEHTA, and T. S. WHEELER (Current Sci., 1935, 4, 406).—Oroxylin, m.p. 231—232° (lit. 225°), from the root bark of *Oroxylum indicum*, Vent., has 1 OMe (cf. J.C.S., 1901, 79, 954) and is shown by demethylation and by methylation to be 5:7-dihydroxy-6-methoxyflavone. The colour reaction obtained by previous workers from (I) with dil. alkali is due to baicalein (5:6:7-trihydroxyflavone) present as an impurity.

H. G. M.

**Natural coumarins.** XVII. **Synthesis of xanthotoxin.** E. SPÄTH and M. PAILER (Ber., 1936, 69, [B], 767—770).—Hydrogenation (Pd-C in AcOH at 40—45°) of 6:7-dihydroxycoumaranone affords 6:7-dihydroxycoumaran (I), m.p. 112°, and a substance, m.p. 132° (I), lactic acid, and conc.  $\text{H}_2\text{SO}_4$  at 120° afford 4':5'-dihydroxanthotoxinol (II), m.p. 202°, converted by  $\text{CH}_3\text{N}_2$  in MeOH into 4':5'-dihydroxanthotoxin, m.p. 163°, which is dehydrogenated (Pd-sponge at 170°) to xanthotoxin, m.p. 146°.

H. W.

**Analogues of rotenone and related compounds.** I. Chromeno-(3':4':4:3)-coumarins. W. HILTON, R. W. H. O'DONNELL, F. P. REED, A. ROBERTSON, and G. L. RUSBY (J.C.S., 1936, 423—426).—Resorcinol and Et 3-hydroxy-6:7-dimethoxy-Δ<sup>3</sup>-chromene-4-carboxylate (I) with  $\text{H}_2\text{SO}_4$  give 7-hydroxy-6':7'-dimethoxychromeno-(3':4':4:3)-coumarin (+ $\text{H}_2\text{O}$ ), m.p. 245° (acetate, m.p. 220—221°). Similar condensation of (I) with the appropriate phenol and either  $\text{H}_2\text{SO}_4$  or HCl-EtOH leads to the following chromeno-(3':4':4:3)-coumarins: 7:8-dihydroxy- (+ $\text{H}_2\text{O}$ ), m.p. 274° (decomp.) (diacetate, m.p. 232—

233°), and 5:7-diacetoxy-6':7'-dimethoxy-, m.p. > 300°; 7-hydroxy-6':7'-dimethoxy-, m.p. 230—231° (acetate, m.p. 137°), 7-hydroxy-7'-methoxy-, m.p. 228° (acetate, m.p. 219°), and 7-hydroxy-8'-methoxy-8-isomethyl-, m.p. 245° (acetate, m.p. 188°); 7-hydroxy-, m.p. 266° (acetate, m.p. 222°), 7:8-dihydroxy-, m.p. 254° (diacetate, m.p. 231.5°), and 5:7-dihydroxy-7'-methoxy-, m.p. 309° (diacetate, m.p. 253°); 7-hydroxy-, m.p. 269° (acetate, m.p. 232°), 7:8-dihydroxy-, m.p. 277° [diacetate, m.p. 264° (decomp.)], and 5:7-dihydroxy-8'-methoxy- (diacetate, m.p. 224°). Et phenoxycetic-2-acetate, m.p. 48—49°, and Na in PhMe afford Et chroman-3-one-4-carboxylate, which with resorcinol in HCl-EtOH yields 7-hydroxychromeno-(3':4':4:3)-coumarin, m.p. 276—278° (acetate, m.p. 214—215°).

F. R. S.

**Synthesis of rotenone and its derivatives.** IX. R. W. H. O'DONNELL, F. P. REED, and A. ROBERTSON (J.C.S., 1936, 419—422).—The Et ester of 6-methoxyphenoxyacetic-2-acetic acid, m.p. 166°, prepared from the azlactone of Et 2-aldehyde-6-methoxyphenoxyacetate, NaOH, and  $\text{H}_2\text{O}_2$ , is cyclised (Na) to Et 3-hydroxy-8-methoxy-Δ<sup>3</sup>-chromene-4-carboxylate (I), m.p. 87°, the Ac derivative, m.p. 72°, of which is reduced ( $\text{H}_2$ -Pt) and hydrolysed to 8-methoxychroman-4-carboxylic acid, m.p. 110°. (I) is reduced ( $\text{H}_2$ -Pt) to Et 3-hydroxy-8-methoxychroman-4-carboxylate, m.p. 85° (Ac derivative, m.p. 94°), hydrolysed to the acid, m.p. 197° (decomp.), which with  $\text{Ac}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}$  gives 8-methoxy-Δ<sup>3</sup>-chromene-4-carboxylic acid, m.p. 170°. 5-Methoxyphenoxyacetic-2-acetic acid, m.p. 163°, obtained by oxidation of the pyruvic acid, gives an Et ester, b.p. 178—180°/1 mm., m.p. 37°, which is cyclised to Et 3-hydroxy-7-methoxy-Δ<sup>3</sup>-chromene-4-carboxylate (II), m.p. 62—63° (Ac derivative, m.p. 51°). This acetate is reduced to 7-methoxychroman-4-carboxylic acid, m.p. 78°, whilst (II) is hydrogenated to Et 3-hydroxy-7-methoxychroman-4-carboxylate, m.p. 97°, hydrolysed to 7-methoxy-Δ<sup>3</sup>-chromene-4-carboxylic acid, m.p. 131°. The course of the reduction of enol acetates is discussed.

F. R. S.

**Reduction experiments with 2:3:4:5-tetraphenylthiophen.** E. BERGMANN (J.C.S., 1936, 505).—Reduction (Na-amyl alcohol) of tetraphenylthiophen gives αβγδ-tetraphenylbutane, m.p. 86°, and 1:2-diphenyl-3-benzylhydrindene, m.p. 182°, but no reduction occurs with Zn-HCl (cf. Fromm and Achert, A., 1903, i, 340).

F. R. S.

**Hydroxypyrrole nitrones.** II. A. H. BLATT (J. Amer. Chem. Soc., 1936, 58, 590—594).—When 2-hydroxy-2:3:5-triphenylpyrrolene nitrone (I), m.p. about 180° (decomp.) (prep. A., 1935, 355, whereby a little of a N-free substance, m.p. 204°, is also formed), is dissolved in aq. 5% NaOH and the solution acidified with AcOH, the oxime (II), m.p. about 180° (decomp.), of αβ-dibenzoyl-α-phenylethylene (loc. cit.) is pptd.; acidification with HCl or HBr gives (I). (II) is best converted into (I) by a little HCl in  $\text{COMe}_2$ . Methylation ( $\text{MeI}$ ,  $\text{MeOH-NaOMe}$ ) of (II) affords the Me ether (III) (loc. cit.) of (I); with  $\text{Me}_2\text{SO}_4$  and aq. NaOH, (III) (formation favoured by low alkali concn. and rise of temp.) and the Me ether, m.p. 121°, of (II) result. (I) and  $\text{Ac}_2\text{O}$  at 80° give 1:4-diacetoxy-2:3:5-triphenylpyrrole (IV), m.p.



151°, reduced (Zn dust, AcOH, little CuSO<sub>4</sub>) to 4-acetoxy-2:3:5-triphenylpyrrole, m.p. 188°, and thence (red P, I, AcOH) to 2:3:5-triphenylpyrrole (V). (II) and Ac<sub>2</sub>O afford the normal acetate (VI) (*loc. cit.*). The production of (IV) from (I) is explained by the following reactions: (a) acetylation of 2-OH, (b) addition of Ac<sub>2</sub>O to the nitron system, (c) migration of OAc from C2 to C4, (d) loss of AcOH between C4 and C5. (I), (II), or (VI) and AcCl give diacetylhydroxamic acid, 4-chloro-2:3:5-triphenylfuran, and (mainly) 4-chloro-1-acetoxy-2:3:5-triphenylpyrrole, m.p. 152°, which is reduced (Zn dust, AcOH, traces of CuSO<sub>4</sub>, and HCl) to 4-chloro-2:3:5-triphenylpyrrole, m.p. 140–141°, and thence (P, HI) to (V).

H. B.

**Extension of Michael's reaction.** V. T. N. GHOSH (J. Indian Chem. Soc., 1935, 12, 692–698; cf. A., 1934, 1010).— $\alpha\alpha'$ -Et<sub>2</sub> acetonetetracarboxylic dianilide (I) with boiling AcOH-Ac<sub>2</sub>O gives Et<sub>2</sub> 2:4-diphenylcarbamidocyclobutanone-2:4-carboxylate, m.p. 248° (decomp.) (semicarbazone, m.p. > 270°). Similarly, (I) with MeCHO, *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, and CHPh·CH·CHO, respectively, instead of CH<sub>2</sub>O, gives Et<sub>2</sub> 2:4-diphenylcarbamido-3-methyl-, m.p. 200–202° (decomp.), -3-*o*-anisyl-, m.p. 205–206°, and -3- $\beta$ -phenylvinyl-, m.p. 249–250° (decomp.), -cyclobutanone-2:4-dicarboxylate. (I) with COMePh-Ac<sub>2</sub>O (reflux; 2 hr.) gives traces of two compounds, m.p. 224–225° (decomp.) and 303–304° (decomp.), the former being sol. and the latter insol. in alkali. CO(CH<sub>2</sub>-CO<sub>2</sub>Et)<sub>2</sub> (II) when treated in Et<sub>2</sub>O successively with Na and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NCO (III) gives 3-carbethoxy-2:4:6-triketo-1- $\alpha$ -naphthylpiperidine (IV), m.p. 191–192° (decomp.) (Na salt), also obtained directly from (II) and (III), and hydrolysed to 2:4:6-triketo-1- $\alpha$ -naphthylpiperidine (V), m.p. 249–250° (decomp.). (IV) when refluxed with CHPh·CH·CHO or with *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO yields, respectively, 3-carbethoxy-2:4:6-triketo-1- $\alpha$ -naphthyl-3:5-cinnamylidene-, m.p. 236–237° (decomp.), and -3:5-*o*-nitrobenzylidene-, m.p. > 300°, -piperidine. Similarly, 2:4:6-triketo- $\alpha$ -naphthyl-3:5-cinnamylidene-, m.p. 263–264°, and -3:5-*o*-nitrobenzylidene-, m.p. 233–235°, -piperidine, both insol. in alkali, were prepared from (V). (II) when treated in abs. Et<sub>2</sub>O successively with Na and carbethoxythiocarbimide in PhMe yields Et<sub>2</sub> 2:6-dicarbethoxyiminothiopyran-4-one-3:5-dicarboxylate, m.p. 122–123°. The ring structure is proved by the absence of mercaptan properties and stability to HgO. The Na<sub>2</sub>-derivative of Et 2:6-diketo-4:4-dimethylcyclohexane-3:5-dicarboxylate does not react with PhNCO.

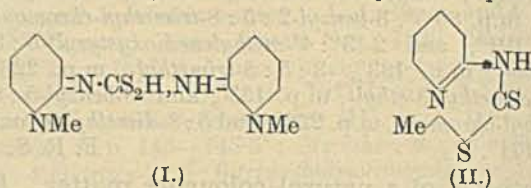
H. G. M.

**Production of piperidine derivatives.**—See B., 1936, 476.

**Syntheses in the pyridine series.** A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1936, [v], 3, 762–779).—A lecture.

**Action of carbon disulphide on methylpyridonimine.** K. S. TOPSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 23–26).—Methylpyridonimine (prepared from 2-C<sub>5</sub>H<sub>4</sub>N·NH<sub>2</sub> and MeI) with CS<sub>2</sub>-EtOH gives the methylpyridonimine salt (I), m.p. 160°, of N-methylpyridinedithiocarbamic acid, but with CS<sub>2</sub> alone gives N-methylpyridodithiadiazole (II),

m.p. 135°, b.p. 173°/3 mm. without decomp., sparingly sol. in H<sub>2</sub>O and unaffected by conc. aq. NaOH.



H. G. M.

**$\beta$ -(2-Pyridyl)alanine.** J. OVERHOFF, J. BOEKE, and A. GORTER (Rec. trav. chim., 1936, 55, 293–296).— $\omega$ -(2-Pyridyl)methylamine [from 2-cyanopyridine and Cr(OAc)<sub>3</sub>] is converted by NaNO<sub>2</sub>-HCl into chloro-(2-pyridyl)methane, b.p. 73–76°/10 mm. (picrate, m.p. 152–153°); interaction with C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>N·CNa(CO<sub>2</sub>Et)<sub>2</sub> then affords Et<sub>2</sub>  $\alpha$ -(2-pyridyl)- $\beta$ -phthalimidoethane- $\beta\beta$ -dicarboxylate, m.p. 120°, hydrolysed by HCl to  $\beta$ -(2-pyridyl)alanine dihydrochloride (I), m.p. 209–210°; (I) with 2 equivs. of Ag<sub>2</sub>O affords  $\beta$ -(2-pyridyl)alanine, m.p. 216–217° (decomp.). {Picrate [from (I) and OH·C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>3</sub>], m.p. 164–165°; monohydrochloride [from (I) and 1 equiv. of Ag<sub>2</sub>O], m.p. 190–191°} P. G. C.

**Nitration method of 8-nitro-6-methoxyquinoline.** K. S. TOPSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 263–264).—Addition of HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> to 8-nitro-6-methoxyquinoline in H<sub>2</sub>SO<sub>4</sub> below 40° gives 5:8-dinitro-6-methoxyquinoline, m.p. 234°, in good yield.

H. G. M.

**Cases of mobility of the nitro-group.**  
**Mobility of the nitro-group in 5:8-dinitro-6-methoxyquinoline.** K. S. TOPSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 264–266; cf. preceding abstract).—5:8-Dinitro-6-methoxyquinoline when heated with  $\delta$ -amino- $\alpha$ -diethylaminopentane gives 5-nitro-8-(8-diethylamino- $\alpha$ -methylbutyl)amino-6-methoxyquinoline, reduced by SnCl<sub>2</sub>-HCl to the corresponding 5-NH<sub>2</sub>-derivative, b.p. 250°/3 mm., which gives a salt, m.p. 165°, with 1 mol. of di-(2-hydroxy-3-carboxynaphthyl)methane. This salt is also obtained by similar methods from the nitration product of 8-(8-diethylamino- $\alpha$ -methylbutyl)amino-6-methoxyquinoline.

H. G. M.

**Changes of "colour" which accompany the conversion of amino-acids and amides into lactams in the benzene series.** (MME.) RAMART-LUCAS and (MLEE.) BIQUARD (Bull. Soc. chim., 1935, [v], 2, 1383–1388).—The ultra-violet absorption spectra of Na *o*-aminophenylacetate and -propionate closely resemble that of *o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>. Cyclisation of the side-chain affects the spectra (1) by altering the nature of the chromophores, and (2) by the true effect of cyclisation. The absorption spectra of the corresponding cyclic compounds oxindole and its *N*-Me and 1:3:3-Me<sub>3</sub> (I) derivatives are closely similar, as are also the spectra of 2-keto-1:2:3:4-tetrahydroquinoline and its 1-Me and 1:4-Me<sub>2</sub> (II) derivatives. All these, therefore, have a lactam structure, and conversion of an NH<sub>2</sub>-acid into the lactam is accompanied by a hypsochromic effect. Comparison of the spectra of *o*-C<sub>6</sub>H<sub>4</sub>Me·NMe·CO·CMe<sub>2</sub>Bu<sup>a</sup> with those of (I) and (II) shows that the true effect of cyclisation is a bathochromic one.

J. W. B.



**Synthesis of Plasmocide** [8-( $\gamma$ -*N*-diethylaminopropyl)amino-6-methoxyquinoline methylene bis-salicylate]. O. J. MAGIDSON, I. T. STRUKOV, M. D. BOBISCHEV, and S. F. TORF (J. Appl. Chem. Russ., 1936, 9, 304—321).—8-Amino-6-methoxyquinoline (I) is prepared on the industrial scale by the steps:  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2 \rightarrow p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \rightarrow p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \rightarrow p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \rightarrow m\text{-nitro-}p\text{-anisidine} \rightarrow 8\text{-nitro-6-methoxyquinoline} \rightarrow$  (I).  $\text{NEt}_2\cdot[\text{CH}_2]_3\text{Cl}$  (II) was obtained as follows: glycerol  $\rightarrow$  diformin  $\rightarrow$  allyl formate  $\rightarrow \text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br} \rightarrow$  (II). (I) and (II) are condensed to yield 8-( $\gamma$ -*N*-diethylaminopropyl)amino-6-methoxyquinoline, the methylene bis-salicylate of which has marked plasmocidal properties. R. T.

**Syntheses in the 2-phenylquinoline series.** I. **Synthesis of bromine-substituted 2-phenylquinoline-4-carboxylic acids.** Reactivity of the bromine therein. Curtius degradation of 6- and 4'-bromoatophan. K. FEIST and M. KUKLINSKI (Arch. Pharm., 1936, 274, 244—255).—5-Bromoisatin,  $\text{COPhMe}$ , and 33%  $\text{KOH}$  at  $100^\circ$  give 6-bromo-2-phenylquinoline-4-carboxylic acid (I), m.p.  $239.5^\circ$ , which affords successively the *Et* ester, m.p.  $97.5^\circ$ , hydrazide, +  $\text{EtOH}$ , m.p.  $226^\circ$  [benzylidene, m.p.  $271^\circ$ , and salicylidene derivative, +  $2\text{EtOH}$  (lost only slowly at  $130^\circ$ ), double m.p.  $153^\circ$  and  $237^\circ$ ], azide, m.p.  $113^\circ$ , and urethane, m.p.  $192^\circ$ , and 6-bromo-4-amino-2-phenylquinoline, m.p.  $209^\circ$  (hydrochloride, m.p.  $328^\circ$ ;  $\text{Ac}_2$  derivative, m.p.  $166^\circ$ ). Isatin and  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COMe}$ , m.p.  $53.5^\circ$ , afford similarly 2-p-bromophenylquinoline-4-carboxylic acid (II), m.p.  $241^\circ$ , the *Et* ester, m.p.  $95^\circ$ , hydrazide, m.p.  $247.5^\circ$  (benzylidene, +  $\text{EtOH}$ , m.p.  $245^\circ$ , and salicylidene derivative, m.p.  $274^\circ$ ), azide, m.p.  $96^\circ$ , and urethane, m.p.  $154^\circ$ , and 4-amino-2-p-bromophenylquinoline, m.p.  $164^\circ$  (hydrochloride, m.p.  $326^\circ$ ;  $\text{Ac}_2$  derivative, m.p.  $231.5^\circ$ ). The Br in (I) is unreactive, since with  $\text{NH}_2\text{Me}$  in  $\text{EtOH}$  at  $200^\circ$  it affords only the methylamide, m.p.  $244^\circ$ , hydrolysed to (I) by alkali. Further, activated Mg does not react with (I), (II), 4-bromo-2-phenylquinoline, or *Et* 3-bromo-2-phenylquinoline-4-carboxylate, m.p.  $88.5^\circ$ . The prep. of 3-bromo-2-phenylquinoline-4-carboxylic acid, m.p.  $236^\circ$  (lit.  $231^\circ$ ), is improved. R. S. C.

**Acridones.** VII. **Acridol**, a tautomeric form of acridone. I. TANASESCU and E. RAMONTIANU (Bull. Soc. chim., 1935, [v], 2, 1485—1488).—The red substance, m.p.  $350^\circ$ , obtained from 5-chloroacridine in boiling  $\text{PhNO}_2$  (Marzin, A., 1933, 1059, where the m.p.  $250^\circ$  is an error) is really acridone, m.p.  $354^\circ$ , and not 5-hydroxyacridine, the colouring matter being an impurity. J. W. B.

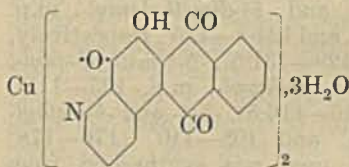
**Meso-derivatives of acridine.** IV. **9-Phenoxyacridines.** V. **Derivatives of 9-aminoacridine.** N. S. DROZDOV and O. M. TSCHERNITZOV (J. Gen. Chem. Russ., 1935, 5, 1576—1580, 1736—1743).—IV. 5-Chloroacridine and  $\text{PhOH}$  at  $100^\circ$  yield the hydrochloride of 5:5-diphenoxy-5:10-dihydroacridine, converted by aq.  $\text{NH}_3$  into 5-phenoxyacridine (I), m.p.  $125\text{—}126^\circ$  (lit.  $112^\circ$ ). The following derivatives of (I) have been prepared analogously: 5-phenoxy-3-methoxy- (II), m.p.  $151\text{—}152^\circ$  (hydrochloride, m.p.  $222\text{—}225^\circ$ ), 2-chloro-, m.p.  $169\text{—}170^\circ$ , and 3-nitro-5-phenoxy-7-methoxy-acridine (III), m.p.  $173^\circ$ , 2-

chloro-, m.p.  $191\text{—}194^\circ$ , and 3-nitro-5:5-diphenoxy-7-methoxy-5:10-dihydroacridine hydrochloride, m.p.  $173^\circ$ . The above substances are converted into the corresponding acridones by boiling with dil. acids.

V. 5-Aminoacridine (IV) is obtained in theoretical yield by adding  $\text{NH}_4\text{Cl}$  to (I) in fused  $\text{PhOH}$  at  $100^\circ$ , and treating the hydrochloride of (IV) so obtained with aq.  $\text{NH}_3$ . The following derivatives of (IV) are obtained analogously: from (II) and  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_2\text{Me}\cdot\text{HCl}$ , or  $\text{NH}_2\text{Ph}\cdot\text{HCl}$ , 5-amino-, m.p.  $231^\circ$ , 5-methylamino-, m.p.  $176^\circ$  (hydrochloride, +  $2\text{H}_2\text{O}$ , m.p.  $272\text{—}275^\circ$ ), and 5-anilino-3-methoxyacridine, m.p.  $202\text{—}203^\circ$  (hydrochloride, m.p.  $262\text{—}266^\circ$ ); from 3:5-dichloro-7-methoxyacridine,  $\text{PhOH}$ , and  $\gamma$ -piperidino- $\beta$ -hydroxypropylamine, 1-phenyl-2:3-dimethyl-5-pyrazolone, or *p*-anisidine, 3-chloro-5-( $\gamma$ -piperidino- $\beta$ -hydroxypropyl)amino- (hydrochloride, m.p.  $105\text{—}110^\circ$ ), 3-chloro-5-(1'-phenyl-2':3'-dimethyl-5'-pyrazolonyl)- (hydrochloride, m.p.  $250^\circ$ ), or 3-chloro-*p*-anisidino-7-methoxyacridine, m.p.  $203\text{—}204^\circ$  [hydrochloride, m.p.  $277\text{—}278^\circ$  (decomp.)]; from (III) and  $\text{NHPh}_2$  or *p*-anisidine hydrochloride, 3-nitro-5-anilino-, m.p.  $224^\circ$  (+  $\text{EtOH}$ , decomp.  $105\text{—}110^\circ$ ), and 3-nitro-5-*p*-anisidino-7-methoxyacridine, m.p.  $212\text{—}213^\circ$ . 5-Piperidino-3-methoxyacridine, m.p.  $102\text{—}103^\circ$ , is prepared by heating (II) with  $\text{PhOH}$  and piperidine at  $100^\circ$ . R. T.

**Copper lake of alizarin-blue base** (1:2-dihydroxyanthraquinone-3-quinoline). I. CHEMLITZKAJA, M. KOROVIN, and E. GOLDMAN (Anilinokras. Prom., 1935, 5, 135—137).

—The salt of annexed constitution is pptd. when a solution of the base in conc.  $\text{H}_2\text{SO}_4$  is added to aq.  $\text{CuSO}_4$ . R. T.



**Isomerisation of saturated and unsaturated hydantoins.** D. A. HAHN and M. K. SEIKEL (J. Amer. Chem. Soc., 1936, 58, 647—649).—Successive treatment of 5-benzylidene-3-methylhydantoin with  $\text{EtOH}\text{--}\text{NaOEt}$  and  $\text{CHPhBr}\cdot\text{CO}_2\text{Et}$  gives *Et* 5-benzylidene-3-methylhydantoin-1-phenylacetate (I), m.p.  $134\text{—}135^\circ$ ; an isomeride (II), m.p.  $106.5\text{—}107.5^\circ$ , is obtained from (VI) or (VIII), below, and  $\text{EtOH}\text{--}\text{HCl}$ . Hydrolysis (aq.  $\text{EtOH}\text{--}\text{NaOH}$ ) of (I) affords the *Na* salts, m.p.  $288^\circ$  (decomp.) (III) and  $217^\circ$  (decomp.) (IV) [corresponding *Ba* salts, m.p.  $213\text{—}215^\circ$  (decomp.) (V) and  $312\text{—}320^\circ$  (decomp.) (VI)], of two forms of 5-benzylidene-3-methylhydantoin-1-phenylacetic acid, m.p.  $186\text{—}187^\circ$  (VII) and  $170^\circ$  (VIII). The various pairs in the series (I)—(VIII) are geometrical isomerides. Reduction [red P and  $\text{HI}$  (d 1.7) at  $105\text{—}110^\circ$ ] of (I), (VII), or (VIII) gives 5-benzyl-3-methylhydantoin-1-phenylacetic acid (+  $\text{H}_2\text{O}$ ) (IX), m.p. (anhyd.)  $147\text{—}147.5^\circ$ ; an isomeride (X), m.p.  $129\text{—}131^\circ$ , is obtained by acidification of (XIV) and (XVI) (below). Crude (IX) and  $\text{EtOH}\text{--}\text{HCl}$  afford isomeric *Et* esters, m.p.  $123.5\text{—}124.5^\circ$  (XI) and  $60\text{—}61.5^\circ$  (XII), which are hydrolysed (aq.  $\text{EtOH}\text{--}\text{NaOH}$ ) to the corresponding *Na* salts, m.p.  $156\text{—}157^\circ$  (XIII) and  $293\text{—}295^\circ$  (XIV) [corresponding *Ba* salts, m.p.  $284^\circ$  (decomp.) (XV) and  $300\text{—}307^\circ$  (decomp.) (XVI)], of (IX) and (X), respectively.



The various pairs of (IX)—(XVI) are stereoisomeric forms. (IX) is hydrolysed by aq. Ba(OH)<sub>2</sub> to  $\beta$ -phenylalanine-*N*-phenylacetic acid. H. B.

**Relation of structure of dialkylbarbituric acids to length of their [anæsthetic] action.** H. A. SHONLE, J. H. WALDO, A. K. KELTCH, and H. W. COLES (J. Amer. Chem. Soc., 1936, 58, 585—587).—The appropriate bromide and CNaEt(CO<sub>2</sub>Et)<sub>2</sub> in EtOH give *Et ethyl- $\alpha\delta$* -, *- $\alpha\gamma$* -, and *- $\beta\delta$ -dimethylamyl*-, b.p. 133—134°/7.5 mm., 126—127°/4 mm., and 140—141°/10 mm., respectively, *- $\alpha$ -propylbutyl*-, b.p. 110—111°/3 mm., *- $\delta$ -methylheptyl*-, b.p. 115—116°/1 mm., *- $\beta\delta$ -dimethylhexyl*-, b.p. 107—109°/1 mm., *- $\beta$ -ethylhexyl*-, b.p. 127—130°/4 mm., *- $\beta$ - and  $\delta$ -methylamyl*-, b.p. 103—105°/2 mm. and 108°/2 mm., respectively, *- $\gamma$ - and  $\epsilon$ -methyl- $\beta$ -ethylhexyl*-, b.p. 120—123°/2.5 mm. and 125—128°/1 mm., respectively, *- $\alpha\gamma$ -dimethylbutyl*-, b.p. 97.5—99°/3 mm., and *- $\beta$ -ethylbutyl*-, b.p. 167°/30 mm., *-malonates*. The following bromides (primary prepared with PBr<sub>3</sub> or HBr-conc. H<sub>2</sub>SO<sub>4</sub>; *sec.* usually obtained with dry HBr) are new:  *$\alpha\delta$* -,  *$\alpha\gamma$* -, and  *$\beta\delta$ -dimethylamyl*-, b.p. 67—72°/40 mm., 67—71°/40 mm., 65—66°/27 mm., respectively,  *$\delta$ -methylheptyl*-, b.p. 73—74°/16 mm.,  *$\beta\delta$ -dimethylhexyl*-, b.p. 76—81°/22 mm.,  *$\beta$ -ethylhexyl*-, b.p. 93—98°/40 mm., and  *$\gamma$ - and  $\epsilon$ -methyl- $\beta$ -ethylhexyl*-, b.p. 88—92°/20 mm. and 84—92°/20 mm., respectively. The above malonates and CO(NH<sub>2</sub>)<sub>2</sub> in EtOH—NaOEt give *5-ethyl-5- $\alpha\delta$* -, *- $\alpha\gamma$* -, and *- $\beta\delta$ -dimethylamyl*-, m.p. 136—136.6°, 126—127°, and 124.8—125°, respectively, *-5- $\alpha$ -propylbutyl*-, m.p. 129—131.5°, *-5- $\delta$ -methylheptyl*-, m.p. 77—79°, *-5- $\beta\delta$ -dimethylhexyl*-, m.p. 105—115°, *-5- $\beta$ -ethylhexyl*-, m.p. 116—116.5°, *-5- $\beta$ - and  $\delta$ -methylamyl*-, m.p. 151—154° and 108—110° [176—178° when original alcohol used was synthesised from MgBu<sup>8</sup>Br and (CH<sub>2</sub>)<sub>2</sub>O or from Mg isoamyl bromide and CH<sub>2</sub>O], respectively, *-5- $\gamma$ - and  $\epsilon$ -methyl- $\beta$ -hexyl*-, m.p. 150—152° and 134.8—135.6°, respectively, *-5- $\alpha\gamma$ -dimethylbutyl*-, m.p. 173.5—174.5°, and *-5- $\beta$ -ethylbutyl*-, m.p. 134—134.5° (lit. 125°), *-barbituric acids*. Some of these acids are also prepared from CN·C<sub>2</sub>H<sub>5</sub>·CO<sub>2</sub>Et; the esters with R= $\beta\delta$ -dimethylamyl, b.p. 128°/3—4 mm.,  $\alpha$ -propylbutyl, b.p. 131°/2—3 mm., and  $\beta$ -ethylhexyl, b.p. 152—153°/4 mm., are described. Et  $\alpha$ -propylbutylcyanoacetate has b.p. 123—125°/3 mm. Pharmacological data for the acids are given; the duration of anæsthetic action bears no direct relationship to the amount of acid required to produce anæsthesia or to the mol. wt. of the complex alkyl group. H. B.

**Preparation of a barbituric acid and salts thereof.**—See B., 1936, 395.

**Ferric complexes of antipyrine.** J. V. DUBSKÝ, E. KRAMETZ, and J. TRTÍLEK (Coll. Czech. Chem. Comm., 1936, 8, 141—148; cf. A., 1935, 1252).—Dark brown [Fe(CN)<sub>5</sub>NO<sub>2</sub>]Fe<sub>4</sub>B<sub>4</sub>H<sub>2</sub>O (B=antipyrine), decomp. 110°, is pptd. by addition of cold aq. FeCl<sub>3</sub> to [Fe(CN)<sub>5</sub>NO<sub>2</sub>]Na<sub>3</sub> and antipyrine, whilst greyish-brown [Fe(CN)<sub>5</sub>NO<sub>2</sub>]Fe<sub>2</sub>·3B may be similarly obtained from [Fe(CN)<sub>5</sub>NO<sub>2</sub>]K<sub>3</sub>. [Fe(CN)<sub>5</sub>NO<sub>2</sub>]Na<sub>4</sub> gives a compound of the Prussian-blue type with FeCl<sub>3</sub> whilst [Fe(CN)<sub>5</sub>NH<sub>3</sub>]Na<sub>3</sub> yields greenish-blue [Fe(CN)<sub>5</sub>NH<sub>3</sub>]Fe<sub>2</sub>·8H<sub>2</sub>O. The compounds

[Fe(CN)<sub>5</sub>NH<sub>3</sub>]Fe<sub>2</sub>·3B, [Fe(CN)<sub>6</sub>]Fe<sub>2</sub>·3B·8H<sub>2</sub>O, and [Cr(SCN)<sub>6</sub>]Fe<sub>2</sub>·3B·8H<sub>2</sub>O have also been prepared.

R. S.

**Glucosides of the glyoxaline series.** E. BERGMANN and H. HEIMHOLD (J.C.S., 1936, 505—506).—Ag glyoxaline with tetra-acetobromoglucose gives *tetra-acetoglucosidoglyoxaline*, m.p. 205—208°, deacetylated to *glucosidoglyoxaline*, m.p. 217°; similarly *triacetorhamnosidoglyoxaline*, m.p. 177—179°, is deacetylated to *rhamnosidoglyoxaline*, m.p. 153—156°.

F. R. S.

**Action of isatin on  $\alpha$ -naphthyl ethyl ether.** C. MARSHALK (Bull. Soc. chim., 1936, [v], 3, [A], 124—129, [B], 129—134).—[A] 4:4'-Diethoxy-1:1'-dinaphthyl (I) is formed from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OEt (II) and isatin with cold 83% H<sub>2</sub>SO<sub>4</sub>, but not with conc. H<sub>2</sub>SO<sub>4</sub> when other products, one (III) of which is insol. in cold H<sub>2</sub>O, alkalis, and boiling PhMe, are formed (cf. A., 1927, 673). The formation of (I) is probably due to the interaction of excess of (II) with (III), and not to oxidation by H<sub>2</sub>SO<sub>4</sub>. The reaction is analogous to that previously described (this vol., 721). Isatin (III) itself, however, does not act as the H-acceptor. (I) is also obtained when (II) is treated with phenanthraquinone and H<sub>2</sub>SO<sub>4</sub> in the cold.

[B] (II), (III), and 93.5% H<sub>2</sub>SO<sub>4</sub> give a compound, m.p. 255—256° when carefully purified, identical with 3-(4'-ethoxy-1'-naphthyl)dioxindole, obtained from OEt·C<sub>10</sub>H<sub>6</sub>·MgBr and (III). This with (II) and 84% H<sub>2</sub>SO<sub>4</sub> gives (I) and a compound, m.p. 214—215°, also obtained in the reaction between (II), (III), and 84% H<sub>2</sub>SO<sub>4</sub>. The formation of (I) requires 3 mols. of (II) for one of (III). H. G. M.

**Complex salts of dipyriddy with bivalent and trivalent cobalt.**—See this vol., 692.

**Quinazolines. XLI. Synthesis of some new 4-quinazoline derivatives from *p*-bromoaniline, formaldehyde, and hydrochloric acid.** S. E. CAIRNCROSS and M. T. BOGERT (Coll. Czech. Chem. Comm., 1935, 7, 548—554).—6-Bromo-3-*p*-bromophenyl-4-quinazoline (I), m.p. 257°, but not the expected quinazoline, is formed together with two other bases, m.p. 204° and 193—196°, when *p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub> is heated (70°, 1 hr.) with HCl—H<sub>2</sub>SO<sub>4</sub>—H<sub>2</sub>O and CH<sub>2</sub>O, methylal, or CH<sub>2</sub>Cl<sub>2</sub>, and is also obtained when 5-bromoanthranilic acid and *p*-C<sub>6</sub>H<sub>4</sub>Br·NH·CHO are heated in an evacuated flask (2 hr.). It is unaffected when heated with H<sub>2</sub>SO<sub>4</sub> at 60°, HCO<sub>2</sub>H—H<sub>2</sub>SO<sub>4</sub>, Ac<sub>2</sub>O, AcCl—NaOAc, KMnO<sub>4</sub> at 70°, or by HNO<sub>3</sub>, but is reduced (Pd—CaCO<sub>3</sub>, H<sub>2</sub> 19 lb. per sq. in.) to 3-phenyl-4-quinazoline, also obtained by heating anthranilic acid with NHPh·CHO. (I) when heated (sealed vessel, 6 hr., 85—90°) with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in EtOH yields 6-bromo-3-amino-4-quinazoline, m.p. 227—228.2°, reduced (Pd—CaCO<sub>3</sub>—H<sub>2</sub>) to 3-amino-4-quinazoline, m.p. 210—211°, which when diazotised and coupled with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH gives a reddish-brown dye, and is also obtained on heating 3-phenyl-4-quinazoline with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (cf. Paal *et al.*, who considered the product to be a hydrazone; A., 1890, 71). H. G. M.

**Imidochlorides. III. Reaction of anilide imidochlorides and ethyl sodiomalonate.** R. C.



SHAH and V. R. HEERAMANECK. IV. Condensation of anilide imidochlorides with urethanes. New synthesis of 4-hydroxy-2-phenylquinazolines. R. C. SHAH and M. B. ICHAPORIA (J.C.S., 1936, 428—430, 431—432).—III. Condensation of anilide imidochlorides with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and its Na derivative in PhMe gives chiefly mono- and little di-condensation products; the mono-condensation products are cyclised to the corresponding quinolines. *p*- $\text{C}_6\text{H}_4\text{MeNH}_2$  and Et (anilobenzyl)malonate (I) afford (anilobenzyl)malonodi-*p*-toluidide, m.p. 208—210°, or on further heating the *p*-toluidide of 4-hydroxy-2-phenylquinoline-3-carboxylic acid, m.p. 255—257°. (I) with BzCl and Na yields Et benzoyl(anilobenzyl)malonate, m.p. 156—158°. The following have been similarly prepared: Et (anilo-*p*-nitrobenzyl)malonate, m.p. 101°, Et 4-hydroxy-2-(*p*-nitrophenyl)quinoline-3-carboxylate, m.p. 239—241°, and the carboxylic acid, m.p. 197—199° (efferv.); Et (anilo-*o*-chlorobenzyl)malonate, m.p. 77°, Et 4-hydroxy-2-*o*-chlorophenylquinoline-3-carboxylate, m.p. 239—242°, and the carboxylic acid, m.p. 242—244°; Et (*p*-nitroanilobenzyl)malonate, m.p. 103°, Et 6-nitro-4-hydroxy-2-phenylquinoline-3-carboxylate, m.p. >300°, and the carboxylic acid, m.p. 295—297°; 4-hydroxy-2-phenyl-8-methylquinoline-3-carboxylic acid, m.p. 201—203° (decomp.); Et (m-, m.p. 67—68°, and Et (*p*-tolyliminobenzyl)malonate, m.p. 62—63°, Et 4-hydroxy-2-phenyl-(5 or 7-), m.p. 237—240°, and -(7 or 5)-methylquinoline-3-carboxylate, m.p. 225—228°, 4-hydroxy-2-phenyl-6-methylquinoline-3-carboxylic acid, m.p. 209—211° (decomp.); benzo-*o*-chloroanilide imidochloride, b.p. 214—215°/40 mm., *o*-chlorophenylbenzamidide, m.p. 113—114° (hydrochloride, m.p. 219—220°); Et (*o*-chloroanilobenzyl)malonate, m.p. 104—105°, Et 8-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate, m.p. 155—156°, and the carboxylic acid, m.p. 184—186°; benzo-*m*-chloroanilide imidochloride, b.p. 229—231°/50 mm., *m*-chlorophenylbenzamidide, m.p. 123—124° (hydrochloride, m.p. 233—235°); Et (5 or 7)-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate, m.p. 234—237°; Et (*p*-chloroanilobenzyl)malonate, m.p. 75°, Et 6-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate, m.p. 251—252°, and the carboxylic acid, m.p. 300°.

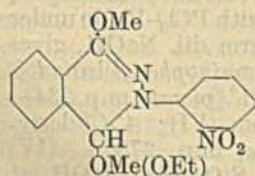
IV. Benzanilide imidochloride and the Na derivative of urethane condense to (anilobenzyl)urethane (hydrochloride, m.p. 215—217°), which with  $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$  forms *s*-(anilobenzyl)- $\alpha$ -naphthylcarbamide, m.p. 258—260°. (I) similarly condenses with Me carbamate to Me (anilobenzyl)carbamate, and with acetylurethane to acetyl(anilobenzyl)urethane, m.p. 85—88°, cyclised to 3-acetyl-2-phenyl-4-quinazoline, m.p. 233°. Benzo- $\alpha$ -naphthalide imidochloride and urethane afford  $\alpha$ -naphthyliminobenzylurethane, cyclised to 4-hydroxy-2-phenyl-1:3-naphthaisodiazine, m.p. 300°; ( $\beta$ -naphthyliminobenzyl)urethane, cyclised to 4-hydroxy-2-phenyl-2:4-naphthaisodiazine, m.p. 295—298°, is similarly obtained. F. R. S.

A reaction of certain diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid. XIII. Fission of the naphthalene nucleus and subsequent closure in two directions. F. M. ROWE, W. C. DOVEY, B. GARFORTH, E. LEVIN, J. D. PASK, and A. T. PETERS. XIV. Preparation of 1:4-diketo-

3-(nitroaryl)tetrahydrophthalazines or 4-keto-1-hydroxy-3-(nitroaryl)-3:4-dihydrophthalazines and related compounds. F. M. ROWE, J. G. GILLAN, and A. T. PETERS (J.C.S., 1935, 1796—1808, 1808—1815; cf. A., 1935, 1253).—XIII. 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$  and diazotised *o*-nitroaniline give 2'-nitrobenzene- $\beta$ -naphthol-1-diazosulphonate, which dissolves in aq.  $\text{Na}_2\text{CO}_3$  giving Na 1-(2'-nitrobenzeneazo)- $\beta$ -naphthaquinone-1-sulphonate (I). This when treated with cold conc. NaOH and then HCl gives Na benzaldehyde-2'-nitrophenylhydrazono- $\omega$ -sulphonate-2- $\beta$ -acrylic acid (II) (the corresponding 4'- and 5'-chloro-2'-nitro-compounds were similarly prepared), which when boiled with HCl (8 hr.) yields benzo-2'-nitrophenylhydrazide-2- $\beta$ -acrylic acid (III), m.p. 220—225° (4'-Cl-derivative, m.p. 272—278°), and 2-(2'-nitrophenylamino)isoindolinone-3-acetic acid (IV), m.p. 224—225° [Me, m.p. 164°, and Et ester, m.p. 153°; anilide, m.p. 272°; 4'-Cl-derivative, m.p. 278° (Me ester, m.p. 152°; anilide, m.p. 268°); 5'-Cl-derivative, m.p. 248° (Me, m.p. 182°, and Et ester, m.p. 184°)], obtained when (III) melts, or is boiled with  $\text{PhNO}_2$  or aq.  $\text{Na}_2\text{CO}_3$  (a similar interconversion occurs also with the 4'-Cl-derivatives). (IV) [or (III)] when refluxed with  $\text{Ac}_2\text{O}$ , or better with  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  (3 hr.), or with  $\text{PCl}_5\cdot\text{PhMe}$  (2 hr.) yields 2:5-diketo-3-(2'-nitrophenyl)isoindolinopyrazolidocoline (V), m.p. 209° (4'-, m.p. 248—249°, and 5'-Cl-derivatives, m.p. 209°), hydrolysed to (IV) and reduced by  $\text{Fe}\cdot\text{AcOH}\cdot\text{H}_2\text{O}$  to 2:5-diketo-3-(2'-aminophenyl)isoindolinopyrazolidocoline (VI), m.p. 234—236° [Ac derivative (VII), m.p. 175—176°; 4'-Cl-derivative, m.p. 253—254° (Ac derivative, m.p. 242—243°)]. This when treated (a) with  $\text{H}_2\text{SO}_4$  at 70° and then with NaOH, (b) with  $\text{PCl}_5\cdot\text{PhMe}$  under reflux (2 hr.) and then with warm dil. NaOH, gives 2:2'-anhydro-2:5-diketo-3-(2'-aminophenyl)isoindolinopyrazolidocoline, m.p. 219—221° [picrate, m.p. 234—236°, also obtained directly from (VI); 4'-Cl-derivative, m.p. 238—239° (sulphate, m.p. 278°)]. (IV) when treated with NaOH- $\text{Na}_2\text{S}_2\text{O}_5\cdot\text{H}_2\text{O}\cdot\text{EtOH}$  at 70°, or with  $\text{SnCl}_2$ , is reduced to 2-(2'-aminophenylamino)isoindolinone-3-acetic acid, m.p. 182—183° (decomp.) [4'-Cl-derivative, m.p. 195° (decomp.)], converted by  $\text{Ac}_2\text{O}$  or  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$  into (VII), and when refluxed with  $\text{H}_2\text{SO}_4$  into 2-(2'-aminophenylamino)isoindolinone-3-acetic acid lactam, m.p. 227° (hydrobromide, m.p. 264—265°; picrate, m.p. 229—230°; 4'-Cl-derivative, m.p. 237°). (I) and (II) when kept with NaOH each yield Na H 3-(2'-nitrophenyl)-3:4-dihydrophthalazine-1-sulphonate-4-acetate [4'- and 5'- (impure) -Cl-derivatives], converted by boiling  $\text{H}_2\text{O}\cdot\text{HCl}$  into 1-hydroxy-3-(2'-nitrophenyl)-3:4-dihydrophthalazine-4-acetic acid (VIII), m.p. 248° [Me, m.p. 146°, and Et ester, m.p. 163°; anilide, m.p. 128°; 4'-Cl-derivative, m.p. 229—230° (Me, m.p. 163—164°, and Et ester, m.p. 145°; anilide, m.p. 130°); 5'-Cl-derivative, m.p. 241—242° (Me, m.p. 163°, and Et ester, m.p. 153°; anilide, m.p. 223°)]. The N-Me ether [1-keto-3-(2'-nitrophenyl)-2-methyltetrahydrophthalazine-4-acetic acid] has m.p. 207° [Me ester, m.p. 133—134°; 4'-Cl-derivative, m.p. 207° (Me ester, m.p. 129—130°); 5'-Cl-derivative, m.p. 225° (Me ester, m.p. 143°)]. (VIII) is reduced by boiling  $\text{AcOH}\cdot\text{H}_2\text{O}\cdot\text{Fe}$  (5 min.) to 1-keto-3-(2'-aminophenyl)-2-methyltetrahydrophthalazine-4-acetic acid [lactam,



m.p. 315–317°; 4'-Cl-derivative, m.p. 225°, resolidifying and melting again at 300° (decomp.) (lactam, m.p. 321°), and by boiling AcOH–H<sub>2</sub>O–Fe (10 min.), or by SnCl<sub>2</sub>, to 1-hydroxy-3-(2'-aminophenyl)-3:4-dihydrophthalazine-4-acetic acid (IX), m.p. 160°, resolidifying at 170° and melting again at 293–294° [lactam, m.p. 293°; 4'-Cl-derivative (X), m.p. 214°, resolidifying at 220°, and remelting at 304° (lactam, m.p. 304°); lactam of 5'-Cl-derivative has m.p. 303–304°]. (VIII) when refluxed with Ac<sub>2</sub>O–C<sub>5</sub>H<sub>5</sub>N yields (V); the 4'- and 5'-Cl derivatives of (VIII) undergo a similar conversion. (X) or its lactam when refluxed with dil. H<sub>2</sub>SO<sub>4</sub> yields 4'-chloro-2'-amino-3-phenylphthalaz-1-one, sublimes at 300–350° (Ac derivative, m.p. 130–131°). Similar treatment of (IX) gives a compound, m.p. 165°, with the expected properties of 2'-amino-3-phenylphthalaz-1-one despite the poor analyses. It is converted by boiling solvents into a colourless substance, m.p. >360°, and is reduced by hot H<sub>2</sub>SO<sub>4</sub>–Zn to o-benzylenebenzimidazole, also obtained from (IX) with SnCl<sub>2</sub>–conc. HCl and then Sn–HCl. 5-Chloro-o-benzylenebenzimidazole (XI), m.p. 242°, similarly prepared from (X) and also obtained from o-C<sub>6</sub>H<sub>4</sub>(CHO)<sub>2</sub>, 4:1:2-C<sub>6</sub>H<sub>3</sub>Cl(NH<sub>2</sub>)<sub>2</sub>, H<sub>2</sub>O, and Na<sub>2</sub>CO<sub>3</sub>, is oxidised by KMnO<sub>4</sub>–AcOH to 5-chloro-o-benzylenebenzimidazole, m.p. 156°, converted by boiling aq. Na<sub>2</sub>CO<sub>3</sub> into 5-chloro-2-phenylbenzimidazole-o-carboxylic acid, m.p. 285°. (VIII) when refluxed with H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O (2 hr.) gives, on neutralisation with NaOH, 2'-nitro-3-phenylphthalaz-1-one, m.p. 266° (picrate, m.p. 214–215°), reduced by Na<sub>2</sub>S–H<sub>2</sub>O to an intractable resin, and converted by Me<sub>2</sub>SO<sub>4</sub>–PhNO<sub>2</sub> at



(XII.)

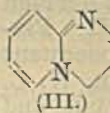
110–120° into the compounds (XII), m.p. 135° from MeOH, and 150° from EtOH, decomposed by heat but without formation of 4-keto-1-methoxy-3-(2'-nitrophenyl)-3:4-dihydrophthalazine. Similarly 4'-chloro-2'-nitro-3-phenylphthalaz-1-one, m.p. 233° (similarly prepared), gives methylation products, m.p. 138° from MeOH, and 110° from EtOH, decomposed by heat but not to the corresponding 4-keto-compound, and is reduced by Na<sub>2</sub>S–H<sub>2</sub>O to a resin and by Zn–H<sub>2</sub>SO<sub>4</sub> to (XI). (VIII) when treated with H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O–Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives 2'-nitro-3-phenyl-4-methylphthalaz-1-one (XIII), m.p. 226° (decomp.) (picrate, m.p. 217°). This and the corresponding 4'-chloro-2'-nitro-compound (XIV), m.p. 237° (picrate, m.p. 233°), are methylated by Me<sub>2</sub>SO<sub>4</sub>, but the products do not have the expected properties. (IX) and (X) or their lactams, when treated with H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O–Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> give, respectively, 2'-amino-, m.p. 302°, and 4'-chloro-2'-amino-3-phenylphthalaz-1-one-4-acetic acid lactam, m.p. 314°, converted by Na<sub>2</sub>S–H<sub>2</sub>O into the NH<sub>2</sub>-acid, m.p. 287°, resolidifying and then melting at 314°. The foregoing lactams when treated with boiling Na<sub>2</sub>S–H<sub>2</sub>O or NaOH–H<sub>2</sub>O yield 2'-amino-, m.p. 218° (Ac derivative, m.p. 274°), and 4'-chloro-2'-amino-3-phenyl-4-methylphthalaz-1-one, m.p. 257° (Ac derivative, m.p. 296°), respectively, also obtained from (XIII) and (XIV) with boiling Na<sub>2</sub>S–H<sub>2</sub>O, and reduced by H<sub>2</sub>SO<sub>4</sub>–Zn–H<sub>2</sub>O to 1-keto-3-(2'-aminophenyl)-4-methyltetrahydrophthalazine, m.p. 221°, and its 4'-Cl-derivative, m.p.

200°, respectively, also obtained by a similar reduction of (XIII) and (XIV).

XIV. p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH·NH<sub>2</sub> (XV) and o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O (XVI) in CHCl<sub>3</sub> give o-carboxybenzo-4'-nitrophenylhydrazide, m.p. 241–245°, converted by boiling PhNO<sub>2</sub> into phthalyl-4'-nitrophenylhydrazide (A., 1906, i, 588), also obtained when (XV) and (XVI) are heated at 150° (10 min.). This when refluxed (18 hr.) with NaOEt–EtOH gives 1:4-diketo-3-(4'-nitrophenyl)tetrahydrophthalazine (XVII) [Ag salt (XVIII)], also obtained by KMnO<sub>4</sub> oxidation of 1-hydroxy-3-(4'-nitrophenyl)-3:4-dihydrophthalazine-4-acetic acid, and converted by boiling Ac<sub>2</sub>O into 4-keto-1-acetoxy-3-(4'-nitrophenyl)-3:4-dihydrophthalazine, m.p. 222°, also obtained from (XVIII) and Ac<sub>2</sub>O, and hydrolysed by boiling EtOH–H<sub>2</sub>O–HCl to (XVII). (XVIII) when refluxed with MeI–MeOH gives 4-keto-1-methoxy-3-(4'-nitrophenyl)-3:4-dihydrophthalazine. The following compounds are described: o-carboxybenzo-3'-nitro-, m.p. 193–194° with ring closure, resolidifying, and remelting at 217–219°, -2'-nitro-, m.p. 290–294°, -4'-nitro-2'-methyl-, m.p. 219°, -2'-chloro-4'-nitro-, m.p. 270–275°, -2'-bromo-4'-nitro-, m.p. 232° with ring closure, resolidifying and melting again at 280–282°, -2':6'-dichloro-4'-nitro-, m.p. 192°, -2':6'-dibromo-4'-nitro-, m.p. 200°, with ring closure, resolidifying and melting again at 227°, -phenylhydrazide; phthalyl-3'-nitro-, m.p. 227–228°, -2'-nitro-, m.p. 293–294°, -4'-nitro-2'-methyl-, m.p. 228°, -2'-chloro-4'-nitro-, m.p. 267°, -2'-bromo-4'-nitro-, m.p. 282–283°, -2':6'-dichloro-4'-nitro-, m.p. 202°, -2':6'-dibromo-4'-nitro-, m.p. 230°, -phenylhydrazide; Ag salts of 1:4-diketo-3-(3'-nitrophenyl)- and -(4'-nitro-2'-methylphenyl)-tetrahydrophthalazine, also obtained from the appropriate substituted 3-phenylphthalaz-1-one; 1:4-diketo-3-(2'-nitrophenyl)-, m.p. 293–294° (Ag salt), -2'-chloro-4'-nitrophenyl-, m.p. 271–272° (Ag salt), -(2'-bromo-4'-nitrophenyl)-, m.p. 273–274°, -(2':6'-dichloro-4'-nitrophenyl)-, m.p. 309–310°, -(2':6'-dibromo-4'-nitrophenyl)-, m.p. 235–260°, -tetrahydrophthalazine; 4-keto-1-methoxy-3-(2'-nitrophenyl)-, m.p. 176–177°, -(2'-chloro-4'-nitrophenyl)-, m.p. 193–194°, -(2'-bromo-4'-nitrophenyl)-, m.p. 167–168°, -(2':6'-dichloro-4'-nitrophenyl)-, m.p. 178–179°, -phenyl-, m.p. 109–111°, -3:4-dihydrophthalazine; 2:6-dichloro-, m.p. 133° (PhCHO derivative, m.p. 153°), and 2:6-dibromo-, m.p. 135–136° (two modifications; PhCHO derivative, m.p. 168–169°), -4-nitrophenylhydrazine. The Ag salt of 1:4-diketo-3-phenyltetrahydrophthalazine when refluxed with EtI and EtOH yields 4-keto-1-ethoxy-3-phenyl-3:4-dihydrophthalazine, an O-Et ether described previously as a N-Et ether (cf. A., 1887, 668; J.C.S., 1920, 117, 719).

H. G. M.

Action of αγ-chlorobromopropane on 2-amino-pyridine. S. M. SCHERLIN and V. S. VELITSCHKIN (J. Gen. Chem. Russ., 1935, 5, 1586–1588).—2-Aminopyridine (I) and CH<sub>2</sub>Cl·CH<sub>2</sub>·CH<sub>2</sub>Br (II) are allowed to interact at room temp., the reaction mixture is boiled for 20 hr., cooled, and the upper layer of unchanged (II) is removed. The lower layer is dissolved in aq. NaOH, and unchanged (I) is removed by steam-distillation. The base (III), b.p. 144–





145°/10 mm., m.p. 55—56° (*picrate*, m.p. 172—173°; *hydrochloride*, m.p. 82—83°), is isolated from the residue. (III) is converted by Na in boiling EtOH into the corresponding  $H_6$ -derivative, b.p. 85—90°/10 mm. R. T.

**Cyanine dye series. V. Dyes derived from 9-methylphenanthridine.** L. G. S. BROOKER and G. H. KEYES (J. Amer. Chem. Soc., 1936, 58, 659—662; cf. this vol., 348).—The etho-*p*-toluenesulphonate (I) of 9-methylphenanthridine [*ethiodide* (II), m.p. 237—239° (decomp.), from (I) and aq. MeOH-KI] with 2-iodopyridine ethiodide in  $Pr^oOH-NEt_3$  gives 27% of 1:1'-*diethyl*-3':4'-*benzo*-2'-*pyrido*-2'-*cyanine iodide* (III), m.p. 221—224° (decomp.). 1:1'-*Diethyl*-3:4'-*benzo*-, m.p. 259—262° (decomp.), and 1:1'-*diethyl*-3:4:5':6'-*dibenzo*-, m.p. 250—251° (decomp.), 2:2'-*cyanine iodides* are similarly prepared from 2-iodoquinoline ethiodide (IV) [with (II)] and 2-iodo- $\beta$ -naphthquinoline ethiodide (V) [with (I)], respectively. (I) and  $CH(OEt)_3$  in  $C_5H_5N$ , followed by KI, give 1:1'-*diethyl*-3:4:3':4'-*benzo*-2:2'-*carbocyanine iodide*, m.p. 234—235° (decomp.). 1:1'-*Diethyl*-5':6'-*benzo*-2'-*pyrido*-2'-*cyanine iodide*, m.p. 268—270° (decomp.), is formed from 2-methylpyridine ethiodide, (V), and 1-methylpiperidine in EtOH. Improved preps. of 1:1'-*diethyl*-5:6'-*benzo*- [from (IV) and  $\beta$ -naphthquinoline etho-*p*-toluenesulphonate] (cf. Hamer, A., 1928, 307) and 1:1'-*diethyl*-5:6:5':6'-*dibenzo*-2:2'-*cyanine iodides* (cf. Hamer and Kelly, A., 1931, 741) are given. The dyes containing the phenanthridine nucleus have no sensitising action; the absorption max. lie nearer the blue than those of the isomerides containing the  $\beta$ -naphthquinoline nucleus. H. B.

**Orthochromatic sensitisation of photographic silver halide emulsions.**—See B., 1936, 477.

**Action of mixed organomagnesium derivatives on acetophenone semicarbazone.** (MELE.) D. BIQUARD (Bull. Soc. chim., 1935, [v], 3, 656—665).—Addition of acetophenonesemicarbazone (I) to  $MgEtBr$  or  $MgBuCl$  in anhyd.  $Et_2O$  establishes the presence of 3 and 4 active H in cold and hot solution, respectively, and affords small amounts of unchanged (I), a little  $COPhMe$ , and 60—70% yields of a substance (II),  $NH<\begin{smallmatrix} CH:CPh \\ CH=N \end{smallmatrix}>NH$ , m.p. 126° (*dibromide*, m.p. 145—148°; very hygroscopic *hydrochloride*; *platinichloride*, decomp. 252°). (II) is transformed by hot  $Ac_2O$  into the  $Ac_2$  derivative, m.p. 156° (*dibromide*, m.p. 170°), hydrolysed by HCl to (II) and by KOH to the  $Ac_1$  compound, m.p. 235°. Treatment of the product from (I) and  $MgEtBr$  with  $AcCl$  or  $Ac_2O$  ( $=MgEtBr$ ) in  $C_6H_6$  gives two compounds,  $N<\begin{smallmatrix} CH=CPh \\ CAc-NAc \end{smallmatrix}>NH$ , m.p. 273°, and  $N<\begin{smallmatrix} CH_2:CPh \\ CAc-NAc \end{smallmatrix}>N$ , m.p. 203°, readily separable from one another owing to their differing solubility in HCl. The constitutions assigned are supported by the spectroscopic evidence. H. W.

**Manufacture of isoalloxazine compounds.**—See B., 1936, 363.

**3:4:3':4''-Dipyrazolo-1':2':5':6'-naphthalene.** V. VESELY and A. MEDVEDEVA (Coll. Czech. Chem. Comm., 1936, 8, 125—129).—2:6- $C_{10}H_6Me_2$  is converted by  $HNO_3$  (*d* 1.51)- $AcOH$  at 100° into

its 1:5-( $NO_2$ )<sub>2</sub>-derivative, m.p. 179° [Mayer *et al.*, A., 1922, i, 999; the ( $NO_2$ )<sub>2</sub>-derivative, m.p. 186°, is probably the 1:8-compound], reduced by  $Fe-aq. AcOH-COMe_2$  to the ( $NH_2$ )<sub>2</sub>-derivative, the  $Ac_2$  derivative of which is converted by  $N_2O_3-AcOH$  at 40—50° into crude 1:5-*di*(nitrosoacetamido)-2:6-*dimethylnaphthalene*, m.p. 116—126° (decomp.) by boiling  $C_6H_6$  into 3:4:3':4''-*dipyrazolo*-1':2':5':6'-*naphthalene* (I) (1:1'- $Ac_2$  derivative, m.p. >330°). J. W. B.

**Leaf xanthophylls.** H. H. STRAIN (Science, 1936, 83, 241—242).—When leaf xanthophyll, freed from leaf constituents, is adsorbed on Tswett columns, three or four pigments resembling cryptoxanthin rapidly pass through the column. They are followed on the column by lutein (I) and isolutein (II), which is optically inactive and gives in  $Et_2O$  a deep blue colour with conc. HCl. Zeaxanthin (III), present in small amount, is found on the column above (II); it occurs in the leaves of barley, carrots, flaxseed, lettuce, sunflower, squash, and spinach. (III) is followed on the column by a pigment ( $[\alpha]_{D^{25}}^{20} +75^\circ$ , in  $CHCl_3$ ) having absorption curves similar to those of flavoxanthin. Another similar pigment having the same absorption curve, but with  $[\alpha]_{D^{25}}^{20} -56^\circ$  in  $CHCl_3$ , is adsorbed next on the column, and is followed by considerable amounts of a xanthophyll the absorption curves of which are intermediate in shape between those of (I) and the flavoxanthin-like pigments. Several xanthophylls occurring in small amounts are adsorbed finally. L. S. T.

**Chlorophyll. LXVI. Comparative oxidation of chlorophyllide and derivatives.** H. FISCHER and S. BREITNER. **LXVII. Active hydrogens in chlorophyll derivatives.** V. H. FISCHER and S. GOEBEL (Annalen, 1936, 522, 151—167, 168—185).—LXVI. Methylthylmaleimide (I) (accompanied, in some cases, by haematic acid) is formed in varying yield by oxidation ( $CrO_3$ , cold aq.  $H_2SO_4$ ) of methylchlorophyllide *a*, phaeophorbide *a*\*, dihydrophaeophorbide *a*, chlorins  $e_4^*$ ,  $e_6^*$ , and  $p_6^*$ , dihydrochlorins  $e_4$ ,  $e_6$ , and  $p_6$ , rhodochlorin, phaeopurpurins 7\* and 18\*, dihydrophaeopurpurins 7 and 18,  $\psi$ -chlorin  $p_6$ , rhodoverdo-, and  $\psi$ -verdo-porphyrins, and mesoporphyrin and its Cu salt. The yield is < that from derivatives from blood pigment. Certain irregularities are noted. Compounds marked \*, which contain the  $C_2-CH:CH_2$  group, generally give about 50% of the amount of (I) obtained from their dihydro-derivatives. In accordance with expectation, (I) is not formed from unreduced derivatives of chlorophyll *b*, i.e., compounds containing  $C_2-CH:CH_2$  and  $C_3-CHO$ ; rhodin *g*, and neorhodinporphyrin *g*<sub>3</sub> (II) give citraconimide (arising from ring III of the chlorophyll mol.). Dihydrorhodin *g*<sub>7</sub>, dihydrophaeophorbide *b*, and rhodinporphyrin *g*<sub>8</sub> (III) afford (I), since they contain the  $C_2-Et$  group.

The Cu salt, m.p. 237°, of rhodin *g*  $Me_3$  ester is



reduced catalytically in  $\text{COMe}_2$  or  $\text{AcOH}$  to the Cu salt,  $[\alpha] -366^\circ$ , of dihydrorhodin *g*  $\text{Me}_3$  ester. The Cu salt of rhodinporphyrin *g* has m.p.  $264^\circ$ . The oxime of (II) (as ester) is dehydrated ( $\text{Ac}_2\text{O}$ - $\text{KOAc}$ ) to the corresponding nitrile,  $\text{C}_{33}\text{H}_{23}\text{O}_2\text{N}_5$ , m.p.  $244^\circ$ . (III) is converted by 20%  $\text{HCl}$  at  $190$ – $200^\circ$  into 3-demethylphyllporphyrin (*Me* ester, m.p.  $242^\circ$ ). Phæophorbides *a* and *b*, obtained (usual method) from chlorophyll extracted by 90%  $\text{COMe}_2$  from nettles, lose  $\text{CO}_2\text{Me}$  when heated in  $\text{C}_5\text{H}_5\text{N}$ ; pyrophæophorbin *a* and *b*, which are OMe-free, are produced (cf. Conant and Hyde, A., 1930, 225). Methylphæophorbide *a* and *b* similarly lose  $\text{CO}_2\text{Me}$  and give pyrophæophorbide *a* and *b*, respectively. These results are considered to support the view (cf. Stoll, this vol., 392) that the original phytol group is attached to  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . Chlorophyll *a* (but no *b*) is present in the algæ *Asacusa nori*, *Bangia fuscopurpurea*, and *Polysiphonia nigrescans*.

[With K. HERRLE.] Phyllochlorin *Me* ester is reduced ( $\text{H}_2$ , Pd,  $\text{COMe}_2$ ) to dihydrophyllochlorin *Me* ester, m.p.  $148^\circ$ ,  $[\alpha]_{\text{D}}^{20} -619^\circ$  in  $\text{COMe}_2$ , which is identical (spectrum; Cu salt; alkaline degradation to phylloporphyrin) with the synthetic phyllochlorin of Treibs and Wiedemann (A., 1928, 1383).

LXVII. The no. of active H present in about 70 compounds (derivatives of phæophorbides *a* and *b*; phæoporphyrins *a* and *b*; phylloerythrins; chlorins; chloroporphyrins; rhodins; rhodinporphyrins; purpurins; phylloporphyrins) are determined by Schmitz-Dumont's method (A., 1934, 313). In most cases the results are in agreement with structures previously proposed. The vals. for verdo- and  $\psi$ -verdo-porphyrin esters are, however, inexplicable. The following conclusions are reached. The phæophorbides contain 2NH and an enolic OH (formation of which is suppressed by oximation); the  $\text{C}_{10}\cdot\text{CO}_2\text{Me}$  exerts a strong labilising action on the  $\text{C}_{10}\cdot\text{H}$ . Chlorins and rhodins are analogously constituted, the latter having  $\text{C}_3\cdot\text{CHO}$  for  $\text{C}_3\cdot\text{Me}$ ; these results are not in agreement with those deduced by Conant *et al.* (A., 1934, 1371) from potentiometric titrations. The relationship between green and red compounds in the porphyrin and purpurin series is discussed. Absorption spectra of many of the phyllins (prepared during the above determinations) and some of the original compounds are given.

H. B.

**Porphyrin synthesis.** Synthesis of porphin. P. ROTHMUND (J. Amer. Chem. Soc., 1936, 58, 625–627; cf. A., 1935, 1510).—Pyrrole (I) and  $\text{CH}_2\text{O}$  in  $\text{MeOH}-\text{C}_6\text{H}_5\text{N}$  at  $90$ – $95^\circ$  (sealed tube) give porphin (II) (phyllin; hæmin; complex Cu salt); at  $145$ – $155^\circ$ , a porphyrin of lower HCl val., which differs spectroscopically from (II), is formed. Absorption spectra for (II) and its salts are given.  $\alpha\beta\gamma\delta$ -Tetra-methyl-, -ethyl-, -propyl-, -phenyl-, and -furyl-porphins (not described) are similarly obtained from (I) and  $\text{MeCHO}$ ,  $\text{EtCHO}$ ,  $\text{PrCHO}$ ,  $\text{PhCHO}$ , and furfuraldehyde, respectively. Porphyrin formation also occurs (shown spectroscopically) with  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ ,  $\text{CHO}\cdot\text{CO}_2\text{H}$ , *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , vanillin, *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , and pyrrole-2-aldehyde. H. B.

**Optical absorption of porphyrins.**—See this vol., 662.

**Preparation of 1-methyl- $\alpha$ -naphthoxazole.** J. FRASER and F. M. HAMER (J.S.C.I., 1936, 55, 119–120T).—The original method (A., 1934, 115) has been improved to give a 39% yield.

**Dioximes.** CIX, CX. G. PONZIO (Gazzetta, 1936, 66, 114–119, 119–126).—CIX. The action of bases on  $\alpha$ -phenylglyoxime peroxide (I) (3-phenyl-1:2:5-oxadiazole 5-oxide) gives a product which was regarded by Wieland and Semper (A., 1908, i, 108) as a hydroxyphenylfurazan (4-hydroxy-3-phenyl-1:2:5-oxadiazole), but is now shown to be  $\alpha$ -oximino-phenylacetone nitrile oxide (II). (I) resembles (II) in behaviour towards  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{NH}_3$ ,  $\text{NH}_2\text{Ph}$ , etc.,  $\text{MgMeI}$ ,  $\text{Ac}_2\text{O}$ ,  $\text{Bz}_2\text{O}$ , aq.  $\text{EtOH}$ , and boiling 20%  $\text{HCl}$ , but differs from it in not combining with  $\text{NH}_2\text{Ph}$  in non-hydroxylic solvents, in not reacting with  $\text{POCl}_3$ , in not polymerising, and in being reduced by  $\text{Zn}-\text{AcOH}$  to  $\alpha$ -phenylglyoxime.

CX.  $\alpha$ -Phenylglyoxime treated with  $\text{N}_2\text{O}_4$ , with hot  $\text{MeOH}$ , and with  $\text{HCl}$ , gives (I). This, new m.p.  $111$ – $112^\circ$ , was regarded by Wieland (A., 1921, i, 606) as an unstable form from which crystallisation from  $\text{C}_6\text{H}_6$ ,  $\text{EtOH}$ , etc. gave a stable product. (I) exists, however, in one form only, and the recryst. product, m.p.  $85$ – $95^\circ$ , is a mixture of (I) and (II), as is shown by its giving chlorophenylglyoxime when treated with  $\text{HCl}$ , and by the formation of oximino-phenylacetone nitrile on reduction. Pure (I) suspended in  $\text{EtOH}$  and treated with  $\text{NH}_2\text{Ph}$  yields  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{NPh})\cdot\text{NH}\cdot\text{OH}$ . In 50%  $\text{EtOH}$ , (I) gives a product which with  $\text{Cu}(\text{OAc})_2$  gives a ppt. from which  $\text{H}_2\text{SO}_4$  liberates 4-benzamido-3-phenyl-1:2:5-oxadiazole, with phenylmetazonic acid. With xylene at  $137$ – $138^\circ$  (I) gives  $\beta$ -phenylglyoxime peroxide; with  $\text{AcOH}$ , 5-hydroxy-3-phenyl-1:2:4-oxadiazole (the sole product when  $\text{EtCO}_2\text{H}$  is used) and hydroxy-phenylglyoxime. (I) is reduced by  $\text{SnCl}_2$  to 3-phenyl-1:2:5-oxadiazole. With  $\text{MgMeI}$ , the compound,  $\text{OMgI}\cdot\text{N}:\text{CPh}\cdot\text{CMe}:\text{N}\cdot\text{OMgI}$  is formed, hydrolysed by  $\text{HCl}$  to  $\text{PhCN}$  and  $\alpha$ -phenylglyoxime;  $\alpha$ -diphenylglyoxime is obtained by using  $\text{MgPhBr}$ . With  $\text{Bz}_2\text{O}$  (I) gives the  $\text{Bz}_2$  derivative, m.p.  $165$ – $166^\circ$  (decomp.), of hydroxyphenylglyoxime, hydrolysed by  $\text{EtOH}$  to the  $\text{Bz}_2$  derivative, and by  $\text{NaOH}$  to 5-hydroxy-3-phenyl-1:2:5-oxadiazole.

E. W. W.

**Action of acetic anhydride on dibenzylidenehydrazine.** J. B. EKELEY and J. W. LEFFORGE (J. Amer. Chem. Soc., 1936, 58, 562–563).—( $\text{N}:\text{CHPh}$ )<sub>2</sub> (1 mol.) and  $\text{Ac}_2\text{O}$  (about 3 mols.) at  $127^\circ/624$  mm. give ( $\text{NHAc}$ )<sub>2</sub> (19%), 2:5-dimethyl-1:3:4-oxadiazole (14%), b.p.  $165$ – $169/624$  mm. [formed by dehydration of ( $\text{NHAc}$ )<sub>2</sub>], and  $\text{NHAc}\cdot\text{N}:\text{CHPh}$  (40%). Addition of  $\text{Ac}_2\text{O}$  to  $\text{N}:\text{CHAr}$  thus gives  $\text{NAc}\cdot\text{CHAr}\cdot\text{OAc}$  (cf. A., 1932, 384).

H. B.

**1-Methylbenzthiazole.** J. FRASER and F. M. HAMER (J.C.S., 1936, 507).—1-Methylbenzthiazole has m.p.  $14^\circ$ .

F. R. S.

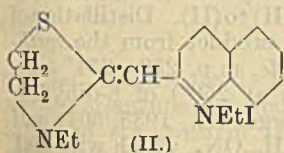
**Reactivity of the imino-group in 1-imino-2-methylbenzthiazoline.** L. M. CLARK (J.C.S., 1936, 507).—1-Imino-2-methylbenzthiazoline with  $\text{NH}_2\text{Ph}$  gives 1-anilo-, m.p.  $95.5^\circ$ , and with phenylthiocarbamide forms 1-phenylthiocarbamylimino-2-methylbenzthiazoline, m.p.  $184^\circ$ , and a substance, m.p.  $261^\circ$ ;



with quinaldine, it yields 2-methylthio-*p*-cyanine, m.p. 165° *platinichloride*. F. R. S.

**Chemical nature of vitamin-B<sub>1</sub>.**—See this vol., 646.

**Cyanine dye series. VI. Dyes derived from 2-methylthiazoline.** L. G. S. BROOKER (J. Amer. Chem. Soc., 1936, 58, 662—665; cf. this vol., 349).—2-Methylthiazoline ethiodide (I), m.p. 190—193° [the methiodide has m.p. 241—242° (decomp.)], and 2-iodoquinoline ethiodide in EtOH-NEt<sub>3</sub> give 3:1'-diethylthiazolino-2'-cyanine iodide (II), m.p. 226—227°. 2-Iodopyridine (Pr<sup>o</sup>OH-NEt<sub>3</sub>), 2-iodo-β-naphthquinoline (EtOH-NEt<sub>3</sub>), and quinoline (EtOH-



KOH) ethiodides with (I) afford 3:1'-diethylthiazolino-2'-pyridocyanine, m.p. 203—206°, 3:1'-diethyl-5':6'-benzthiazolino-2'-cyanine, m.p. 263—266°, and 3:1'-diethylthiazolino-4'-cyanine, m.p. 223—224°, iodides, respectively. 2-Methylthiazoline metho-*p*-toluenesulphonate and CH(OEt)<sub>3</sub> in C<sub>6</sub>H<sub>5</sub>N, followed by KI, give 3:3'-dimethylthiazolinocarbocyanine iodide, m.p. 250—252° [7-Et derivative, m.p. 248—250°, obtained using CEt(OMe)<sub>3</sub>], whilst (I) and CH(OEt)<sub>3</sub> similarly afford 3:3'-diethylthiazolinocarbocyanine iodide, m.p. 256—258° [7-Et derivative, m.p. 182—184°, formed from 2-methylthiazoline etho-*p*-toluenesulphonate and CEt(OMe)<sub>3</sub> followed by KI]. 2-*p*-Dimethylaminostyrylthiazoline ethiodide, m.p. 219—220°, is obtained from (I) and *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO in MeOH-piperidine. The new dyes are sensitizers; they absorb at shorter λ than analogous compounds prepared from other heterocyclic bases. H. B.

***d*-Nicotinic acid.** C. S. HICKS (Austral. J. Exp. Biol., 1936, 14, 39—43).—*d*-Nicotinic acid when methylated gives nicotine methiodide and when dehydrogenated (Pt-asbestos 320—330°) yields 2-(3-pyridyl)pyrrole. W. McC.

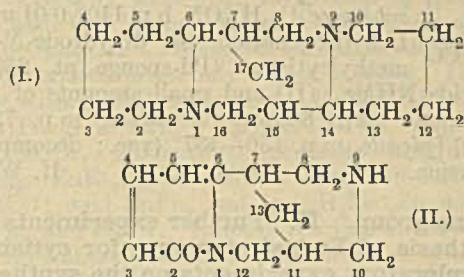
**Tobacco bases. VI. Synthesis of myosmine.** E. SPÄTH and L. MAMOLI (Ber., 1936, 69, [B], 757—760; cf. this vol., 489).—Pyrrolidone and Bz<sub>2</sub>O at 180° give 1-benzoylpyrrolidone, m.p. 92—93°, which, condensed with Et nicotinate (NaOEt), gives 1-benzoyl-3-nicotinoylpyrrolid-2-one. This (without isolation) is treated with fuming HCl whereby decarboxylation, decarboxylation, ring fission and subsequent closure lead in one operation to myosmine (2:3'-pyridyl-4:5-dihydropyrrole).

Reply is made to Reynolds and Robinson (this vol., 486). H. W.

**Lupin. IX. Monolupine, a new alkaloid from *Lupinus caudatus*.** Kellogg. J. F. COUCH (J. Amer. Chem. Soc., 1936, 58, 686—687).—*Monolupine* (I), C<sub>16</sub>H<sub>22</sub>ON<sub>2</sub> (+0.5H<sub>2</sub>O), b.p. 257—258°/4 mm., [α]<sub>D</sub><sup>20</sup> = -40.81° in EtOH [*dihydrochloride* (+2H<sub>2</sub>O), m.p. 115—116° (rapid heating), which when dried at 110° gives the *hydrochloride*, m.p. 280°; *aurichloride* (+3H<sub>2</sub>O), m.p. 167—168° (decomp.); *methiodide* (+H<sub>2</sub>O), m.p. 257°], is isolated (method: A., 1935, 97) in 0.44—0.5% yield from the dry plant. (I) resembles anagrine, is unsaturated (KMnO<sub>4</sub>), but

could not be reduced (Adams; electrolytic). *L. caudatus* thus differs from *L. palmeri* (*loc. cit.*). H. B.

**Numbering of sparteine molecule and its derivatives.** J. F. COUCH (J. Amer. Chem. Soc., 1936, 58, 688).—Structure (I) for sparteine shows its symmetrical character and relationship to other lupin alkaloids and to cytisine (II). Lupanine, hydroxylupanine, and anagrine become 2-keto-, 10-hydroxy-2-keto-, and 2-keto-3:4:5:6-tetra-dehydro-sparteine, respectively. Possible modes of biosynthesis of (I) and (II) are indicated.



H. B.

**Gramine.** H. VON EULER, H. ERDTMAN, and H. HELLSTRÖM (Ber., 1936, 69, [B], 743—747).—Although spectroscopically similar, gramine (I) is not identical with 2-dimethylaminomethyl- or 3-dimethylamino-2-methyl-indole. Distillation of (I) with Zn dust affords skatole in too small amount to indicate its constitution. (I) gives a red pine-shaving reaction but not the Ehrlich reaction. It gives a faint red colour with *p*-SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl in alkaline solution. It appears to be hydrolysed by acids to a substance not identical with atroxindole. It does not afford AcOH when oxidised by CrO<sub>3</sub>. A completely satisfactory structure cannot at present be assigned to (I), which is regarded provisionally as 2-methylethylaminoinole. H. W.

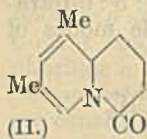
**Cactus alkaloids. XVII. Optical activity of pellotine.** E. SPÄTH and F. KESZTLER (Ber., 1936, 69, [B], 755—757).—Attempts to resolve *dl*-pellotine into its optical antipodes by *d*-tartaric acid in MeOH under unusually cautious conditions lead to the isolation of 1-pellotine (I), [α]<sub>D</sub><sup>20</sup> = -15.2° in CHCl<sub>3</sub>, for which optical homogeneity is not claimed. (I) is slowly racemised in H<sub>2</sub>O at 15—20°, very rapidly in alkaline solution, less readily in the presence of acid. Distillation in high vac. causes complete inactivation. Since the alkaloid is very readily racemised and the accompanying alkaloids are optically active it is concluded that the plants form the active modification which becomes racemised probably within the living cell, at any rate during storage and extraction. H. W.

**Action of perbenzoic acid on cinchona-bark alkaloids.** J. BECKER and J. SUSZKO (Arch. Chem. Farm., 1934, 1, 199—205).—Oxidation takes place at the quinuclidine N, the same amino-oxides being formed as with H<sub>2</sub>O<sub>2</sub>. Advantages of the use of BzO<sub>2</sub>H are discussed. CH. ABS. (r)

**Dehydrogenation of cytisine and product of the degradation of this base.** E. SPÄTH and F. GALINOVSKY (Ber., 1936, 69, [B], 761—766).—Dehydro-



genation of cytisine with Pd-sponge at 270—280° gives 2-hydroxy-6-methylquinoline with much resinous material. Similar treatment of tetrahydro- and octahydro-hemicitysilene affords 3:5-dimethyl-2-propylpyridine (I), b.p. (bath) 100—110°/10 mm. (picrate, m.p. 150—151°; methiodide, m.p. 127—128°), oxidised by acid  $\text{KMnO}_4$  to 3:5-dimethylpyridine-2-carboxylic acid and 5-methylnicotinic acid, and 8-keto-2:4-dimethyl- $\psi$ -quinolizine (II), m.p. 83° [hemihydrate, m.p. 64—65°; picrate, m.p. 149—150° (vac.; decomp.)], which absorbs  $4\text{H}_2$  (Pd-C in AcOH) giving the substance,  $\text{C}_{11}\text{H}_{19}\text{ON}$ , b.p. 110°/0.01 mm. Dehydrogenation of dihydrode-N-dimethylecytisine (Pd-sponge at 230—270°) yields  $\text{NHMe}_2$ , (II) and small amounts of (I).  $\alpha$ -Norlupinone gives 8-keto- $\psi$ -quinolizine, m.p. 72—73° (vac.) [picrate, m.p. 136—137° (vac.; decomp.)], and conyrene. H. W.



**Cytisine group. II. Further experiments on the synthesis of Ewins' structure for cytisine. III. Exploratory experiments on the synthesis of cytisine, sparteine, lupinine, and allied alkaloids.** S. N. CHAKRAVARTI and P. L. N. RAO (J. Annamalai Univ., 1936, 5, 254—258, 259—268).—II. Further unsuccessful attempts (cf. A., 1934, 195) are described. 6-Nitro-3-methylcinnamic acid (*loc. cit.*) has been reduced ( $\text{FeSO}_4\text{-NH}_3$ ) to the 6- $\text{NH}_2$ -compound, m.p. 195°, and the hydrochloride of this diazotised and reduced ( $\text{Na}_2\text{SO}_3\text{-HCl-Zn}$ ) to 1-amino-6-methyldihydrocarbostyril, m.p. 117° (with some 6-methyldihydrocarbostyril, m.p. 132—133°), in amount insufficient for cyclisation through 8- $\text{CH}_2$ . Attempted oxidation of 6:8-dimethylquinoline to 6-methylquinoline-8-carboxylic acid by  $\text{CrO}_3$ ,  $\text{SeO}_2$ , or dil.  $\text{HNO}_3$  gives unsatisfactory results; with a large excess of  $\text{CrO}_3$ , quinoline-6:8-dicarboxylic acid, m.p. > 300° is formed. The 6:8- $\text{Me}_2$  compound is converted by  $\text{Br-HBr}$  in  $\text{CHCl}_3$  into the hydrobromide, m.p. 125—140° (decomp.), of the  $\text{Br}_2$ -compound, which loses  $\text{HBr}$  at 160°, and when heated in  $\text{CHCl}_3$  gave, in an experiment which could not be repeated, a bromodimethylquinoline, m.p. 58°.

III. The successful prep. of 2-chloropyridine (I) from 1-methylpyridone (J.C.S., 1915, 107, 690) is confirmed (cf. A., 1932, 66). Attempts to condense (I) with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  or with  $\text{CH}_2[\text{CH}(\text{CO}_2\text{Et})_2]_2$  were unsuccessful. The last is converted into  $\text{CH}_2[\text{CH}(\text{CO}\cdot\text{NH}_2)_2]_2$ , which at 250° gives a poor yield of  $\text{CH}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ , reduced to a basic substance. Theoretical schemes for synthesising lupinine, sparteine, and cytisine are outlined.

E. W. W.

**Ergot alkaloids. VIII. Synthesis of 4-carbolinecarboxylic acids. IX. Structure of lysergic acid.** W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1936, 113, 759—765, 767—778).—VIII. Largely a more detailed account of work previously reviewed (this vol., 216). 3:4-Dimethyl-3:4:5:6-tetrahydro-4-carboline-5-carboxylic acid, m.p. 248° (decomp.) (previous darkening and softening), and the non-cryst. product formed from *N*-methyltryptophan, 10%  $\text{MeCHO}$ , and  $\text{N-H}_2\text{SO}_4$ , are both oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7$ , dil. AcOH) with loss of  $\text{CO}_2$  to 4-methyl-4-

carboline (*N*-methylharman), m.p. 180° (previous darkening) [sulphate, m.p. 273° (decomp.); dichromate]. 3-Methyltetrahydro-4-carboline-5-carboxylic acid (*loc. cit.*) similarly gives harman, whilst lysergic (I) and dihydrolysergic (II) acids afford amorphous acidic material.

IX. The structure previously suggested (this vol., 488) for (I) is revised to (A). Reduction ( $\text{H}_2$ , PtO<sub>2</sub>, AcOH) of the alkaloid,  $\text{C}_{19}\text{H}_{23}\text{O}_2\text{N}_3$  (ergometrine, etc.; cf. Kharasch *et al.*, this vol., 489), gives a  $\text{H}_2$ -derivative, m.p. 225—230° (decomp.) (sinters at 110°), hydrolysed (14%  $\text{MeOH-KOH}$ ) to (II). Distillation of the product from the methiodide, m.p. 253—254° (sinters at 250°) of  $\beta$ -dihydro lysergol (A., 1935, 504) and  $\text{Ag}_2\text{O}$  affords an oily base,  $\text{C}_{17}\text{H}_{22}\text{ON}_2$ , which with  $\text{MeI}$  followed by  $\text{Ag}_2\text{O}$  gives  $\text{NMe}_3$  [in accordance with structure (A)] and resin. The remainder of the paper has been abstracted previously (*loc. cit.*). H. B.

**Optical properties of ergometrine. I. BENNEKOU and S. A. SCHOU (Dansk Tidsskr. Farm., 1936, 10, 105—108).**—The blue fluorescence of ergometrine (I) solutions under ultra-violet radiation persists after its removal. The absorption max. of the spectrum of (I) solutions changes from 3160 to 2890 Å, whilst the other ergot alkaloids show a gradual decrease of absorption, owing to decomp.

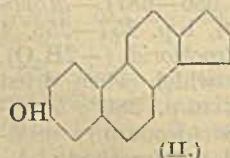
M. H. M. A.

**Veratrine alkaloids. III. Preparation of cevanthrol, and X-ray crystallographic examination of cevanthrol and cevanthridine.** B. K. BLOUNT and (MISS) D. CROWFOOT (J.C.S., 1936, 414—415).—Se dehydrogenation of cevine gives a base, cevanthridine (I) (cf. A., 1935, 505), and a phenolic compound, cevanthrol (II),  $\text{C}_{17}\text{H}_{16}\text{O}$ , m.p. 197—198° (Ac derivative, m.p. 138—139°). The results of X-ray crystallographic examination of (I) and (II) support a phenanthrene ring structure for (II) and a ring system of type (a) or (b) for (I).



F. R. S.

**Solanine and solanidine. A. SOLTYS and K. WALLENFELS (Ber., 1936, 69, [B], 811—818).**—Repeated extraction of solanine (I) with  $\text{COMe}_2$  and  $\text{Et}_2\text{O}$  causes its complete separation into solanidine (II) and solanine (III). (I) should therefore be deleted from the lit. Hydrolysis of (III) gives about

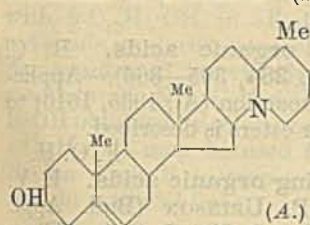


37.5% of (II) and 12.5% of solanthrene ( $\text{C}_7\text{H}_{15}\text{N}$ ) (IV). It is therefore very improbable that (IV) is formed from its proper glucoside. (II) does not yield

(IV) when hydrolysed. The presence of one and two double linkings in (II) and (IV), respectively, is con-



firmed, the double linkings in (IV) being hydrogenated with equal facility. To avoid confusion it is recommended that the completely saturated tetrahydrosolanthrene be designated solanidane. (II) is therefore solanidenol and its derivatives are termed in accordance with the Geneva nomenclature except that the name solanidine is retained. (II) affords a *mono-ozonide*



which does not permit degradation of the mol., since (II) is regenerated under varied conditions of fission. With digitonin (II) gives a ppt. suggesting a constitutional relationship with the sterols; this is confirmed

by the dehydrogenation of solanidiene by Se to methylcyclopentenophenanthrene. The present established structure of (II) is as shown. Attempts to degrade the  $C_7H_{15}N$  residue were unsuccessful. *Solanine methiodide*, m.p.  $230^\circ$ , when treated with moist  $Ag_2O$  and then distilled yields (II). Since N is *tert.* and the group  $C_7H_{15}N$  is unusually stable the structure (A) is suggested for (II).

H. W.

**Deltaline**, a new alkaloid from *Delphinium occidentale*, S. Wats. J. F. COUCH (J. Amer. Chem. Soc., 1936, 58, 684—685).—Details are given for the isolation of *deltaline* (I),  $C_{19}H_{24}ON(OH)_3(OMe)_2$ , m.p.  $180-181^\circ$ ,  $[\alpha]_D^{25} -27.86^\circ$  in EtOH [*Ac*<sub>3</sub> derivative, amorphous, m.p.  $270-272^\circ$ ; *aurichloride* ( $+3H_2O$ ), m.p.  $120-125^\circ$ ], from the dry plant, which contains 0.98% of total alkaloids [mainly (I)]. (I) is isomeric but not identical with *delcosine* (Markwood, A., 1925, i, 762).

H. B.

**Chemistry and pharmacological action of *Toddalea aculeata***. B. B. DEY, P. P. PILLAY, J. C. DAVID, and N. RAJAMANIKAM (Indian J. Med. Res., 1935, 22, 765—770).—Two alkaloids, *toddaline* (I),  $C_{20}H_{21}O_2N$ , m.p.  $269-270^\circ$  (*hydrochloride*, m.p.  $205-206^\circ$ ; several other salts described), and *toddalinine*, a N-free lactone, and a glucoside have been isolated from *Toddalea* root-bark. Both alkaloids give marked colour reactions. Crude (I) is converted by rubbing with EtOH-NH<sub>3</sub> into an insol. cryst. powder, m.p.  $204-206^\circ$ , which gives the same *hydrochloride*, and is probably another form of (I). The pharmacological action of (I) is described.

R. N. C.

**Toxic principle of ragwort (*Senecio Jacobaea*, L.)**.—See this vol., 652.

**Bark of *Moringa pteryosperma***.—See this vol., 768.

**2-Chloro-6-nitrobenzaldimercurioxide**.—See B., 1936, 361.

**Constitution of mixed organo-magnesium compounds**. C. DUVAL (Compt. rend., 1936, 202, 1184—1186).—When  $MgPhBr$  (I) in Et<sub>2</sub>O in an atm. of N<sub>2</sub> at  $0^\circ$  is electrolysed (cf. A., 1935, 1088), only Mg goes to the cathode. The anodic fluid contains Mg, Br ( $Mg/Br=1/2$ ),  $C_6H_6$ , and Et<sub>2</sub>O. If 8-hydroxyquinoline is introduced into the cell, the yellow colour due to  $Mg^{II}$  is seen at the cathode, and at the anode only after hydrolysis, which indicates that part of the

Mg in (I) is non-ionisable. The formula of (I) is probably  $[MgPh_2Br_2(Et_2O)_2]Mg$  (cf. A., 1912, i, 753).

J. L. D.

**Relative reactivities of organometallic compounds. VIII. Aluminium and zinc**. H. GILMAN and K. E. MARPLE (Rec. trav. chim., 1936, 55, 133—144).— $AlPh_3$  (I) and  $(p-C_6H_4Me)_3Al$  (II), best prepared from  $HgR_2$  and Al in xylene, under N<sub>2</sub>, and *Al tri-n-propyl*, b.p.  $137-138^\circ/22$  mm., obtained from  $MgPr^aBr$  and  $AlCl_3$  in Et<sub>2</sub>O, combine with  $PhNCO$  to form  $NHPhBz$ ,  $p-C_6H_4Me\cdot CO\cdot NHPh$ , and  $COPr^a\cdot NHPh$ ; with  $CO_2$ , (II) gives  $p-C_6H_4Me\cdot CO_2H$ , and with  $COPh_2$ ,  $p-C_6H_4Me\cdot CPh_2\cdot OH$ ; (I) similarly yields  $CPh_3\cdot OH$ . Passage of O<sub>2</sub> into a solution of (II) in cold xylene gives only 8% of *p*-cresol. (II) combines with  $PhCHO$  to form  $p-C_6H_4Me\cdot CHPh\cdot OH$ , and with  $PhCN$  to form  $p-C_6H_4Me\cdot CPh$ . With EtOBz or  $PhOBz$ , unidentified products are obtained.  $ZnPh_2$ ,  $ZnEt_2$ , and  $ZnPr^a_2$  react similarly with  $PhNCO$ ; and  $ZnPh_2$  and  $(p-C_6H_4Me)_2Zn$  with  $CO_2$ ,  $COPh_2$ , and  $PhCN$ . Rates of reaction of the above Al and Zn compounds are slower than those of Grignard compounds. Relative rates of combination of  $AlPh_3$ ,  $BPh_3$ ,  $ZnPh_2$ ,  $AlPr^a_3$ ,  $BPr^a_3$ ,  $ZnPr^a_2$ ,  $(p-C_6H_4Me)_3Al$ , and  $(p-C_6H_4Me)_2Zn$  with Michler's ketone are tabulated, and the colour reaction with the latter is examined and used as a means of studying rates of reaction with  $PhCHO$ ,  $COPh_2$ , and  $PhCN$ . The decreasing orders of reactivity  $\cdot CHO > \cdot CPh > \cdot CN$ , and  $AlR_3 > BR_3 > ZnR_2$ , are observed. Al displaces Hg more rapidly from  $HgR_2$  compounds ( $R=aryl$ ) than does Zn. The low reactivity of  $AlR_3$  compounds makes it improbable that these are intermediates in the Friedel-Crafts reaction.

E. W. W.

**Acridine salts of adenosinepolyphosphoric acids**. T. WAGNER-JAUREGG (Z. physiol. Chem., 1936, 239, 188—194).—The acids yield cryst.  $H_2O$ -sol. (hot) salts with acridine (I) as follows: adenosine-tri- (II) + 2(I), m.p.  $209^\circ$ , di- (III) + (I), m.p.  $215^\circ$ , -mono-phosphoric acid + (I), m.p.  $208^\circ$ , and also  $2H_4P_2O_7 + 3(I)$ , m.p.  $258-260^\circ$ . The salt of (III) is least sol. in hot  $H_2O$ . (II) also yields a salt with 3(I).  $NaNO_2$  in 55% AcOH converts (II) into inosinetriphosphoric acid (cf. Lohmann, A., 1931, 1184) and not into an isomeride of (II) (cf. Barrenscheen *et al.*, A., 1933, 1202).

W. McC.

**Structure of yeast nucleic acid**. K. HAGEN-GUTH (Z. physiol. Chem., 1936, 239, 127—134).—Small yields of cytosylic ( $Hg^{II}$ ,  $UO_2$ ,  $Pb$ , and *brucine*, m.p.  $189-190^\circ$ , salts) and uracylic acid (*Pb* salt) are obtained from yeast nucleic acid by hot acid hydrolysis followed by pptn. with  $Ag_2SO_4$ , etc. W. McC.

**Isolation of a fourth crystallisable jack bean globulin by digestion of canavalin with trypsin**.—See this vol., 768.

**Determination of nitrogen in compounds containing halogens by the hydrogenation method**. H. TER MEULEN and H. J. RAVENSWAAY (Chem. Weekblad, 1936, 33, 248—249).—Satisfactory results are obtained with compounds of high halogen contents when a few g. of soda-lime are placed in front of the catalyst as well as behind it.

S. C.



**Determination of nitrogen by Kjeldahl's method. Ammonia distillation.**—See this vol., 694.

**Determination of organic sulphur. I. Parr bomb method.** H. C. CHIANG and C. L. TSENG (Sci. Rep. Nat. Univ. Peking, 1936, 1, 19—41).—S in  $\text{CS}(\text{NH}_2)_2$ ,  $\text{SHBu}^a$ , and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  is determined by explosion with  $\text{Na}_2\text{O}_2$  and lactose with or without  $\text{KClO}_3$  or  $\text{KClO}_4$  and subsequent gravimetric or volumetric determination of  $\text{SO}_4^{2-}$ . R. S. C.

**Principles and methods of a chemical morphology of carbon compounds.** C. WEYGAND (Angew. Chem., 1936, 49, 243—251).—The morphological study of cryst. org. compounds is suggested as an aid to identification, and suitable microscopic methods are described. M. S. B.

**Analysis of S-methyl compounds by demethylation with hydrogen iodide.** (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1935, 44, 665—673).—Details are given for the semi-micro-determination of SMe by heating the compound with HI ( $d\ 1.7$ ); the resulting MeI vapours are freed from HI and  $\text{H}_2\text{S}$  by means of  $\text{Na}_2\text{CO}_3\text{--Na}_2\text{S}_2\text{O}_3$  and  $\text{CdSO}_4\text{--Na}_2\text{S}_2\text{O}_3$  solutions and are determined in the usual way. SMe compounds are demethylated at a lower temp. than NMe compounds, permitting the separate determination of these groups in compounds containing them both. H. G. M.

**Oxidimetric analysis of binary mixtures of organic compounds.** H. C. S. SNETHLAGE (Rec. trav. chim., 1936, 55, 58—60).—The method described for pure substances (A., 1935, 1390) may be used for binary mixtures by using  $\text{K}_2\text{Cr}_2\text{O}_7$  in 40% and 80%  $\text{H}_2\text{SO}_4$ , provided one of the components is not attacked and the other completely oxidises under the milder conditions. H. G. M.

**Titrimetric colorimetry.**—See this vol., 692.

**Diazometric method for the determination of diene hydrocarbons.** A. P. TERENTIEV, E. V. VINOGRADOVA, and G. D. GALPERN (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 267—272).—Diazotised  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (I) reacts quantitatively with  $\Delta^{1:3}$  dienes, but not at all with aromatic hydrocarbons or compounds with conjugated hetero-atoms (cf. lit.); one mol. of (I) reacts with one mol. of diene. Excess of (I) is used and the excess determined with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ . The method is suitable for the determination of dienes in mixtures of hydrocarbons of various types. H. G. M.

**Systematic detection of acetate.** L. J. CURTMAN and A. A. POLACHEK (Rec. trav. chim., 1936, 55, 153—156).—The green ppt. of  $\text{Cu}_4\text{O}_3\text{Cl}_2$  obtained when a solution containing  $\text{OAc}^+$  is boiled with  $\text{CuCl}_2$  (Reynoso, Compt. rend., 1855, 41, 278), when used as a qual. test (Field, J.C.S., 1873, 26, 575) will detect 1 mg.  $\text{NaOAc}$  (in a pure solution) and is thus more sensitive than the  $\text{FeCl}_3$  or odour tests. A solution of  $2M\text{-CuCl}_2\text{--}2M\text{-NaCl}$  is employed. If other acids are present, those with insol. Ag salts are first removed by adding  $0.5M\text{-AgNO}_3$ , and  $M\text{-CaCl}_2$  is added to ppt.  $\text{Ag}^+$  and  $\text{F}^-$ ; the solution is then made alkaline, evaporated, and neutralised.  $\text{ClO}_3^-$  if present is first reduced by  $\text{KNO}_2$ ;  $\text{NO}_2^-$  is oxidised by  $\text{HNO}_3$ . If

tartrate is present,  $\text{H}_2\text{SO}_4$  is added and  $\text{AcOH}$  distilled off and collected; if borate is present,  $\text{Na K tartrate}$  is added to give a non-volatile complex before distilling the  $\text{AcOH}$ . The solution is finally boiled with the  $\text{CuCl}_2$  solution. Procedure in each case is described in detail. E. W. W.

**Micro-determination of lactic and carbonic acids.**—See this vol., 768.

**Colour reactions of organic acids.** R. C. LOPEZ (Biochem. Z., 1936, 284, 365—366).—Application of the  $\text{C}_5\text{H}_5\text{N--Ac}_2\text{O}$  reaction (A., 1935, 1516) to various org. acids and their esters is described. F. O. H.

**Methods of determining organic acids.** E. V. SAPOSHNIKOVA and R. P. URINSON (Bull. Appl. Botany U.S.S.R., 1934, Ser. 3, No. 5, 255—272).—Modifications of the Hartmann and Hillig method of determining oxalic, citric, and tartaric acids are given. CH. ABS. (e)

**Precipitation of cystine by phosphotungstic acid.** M. DAMODARAN and T. G. SIVASWAMY (Biochem. J., 1936, 30, 750—752).—The extent of pptn. of cystine (I) by 24-phosphotungstic acid at any particular temp. is dependent on the concn. of (I). It is not complete at any concn., and below a certain min. val. no pptn. takes place. At the concn. of (I) usually present in protein hydrolysates only a small fraction is pptd. J. N. A.

**Colour reaction of histamine and complex salts of heavy metals with methylglyoxaline.** F. AXMACHER (Biochem. Z., 1936, 284, 339—342).—Aq. histamine and  $\text{CuSO}_4$  give a dark blue colour, modifications of which by treatment with oxidising and reducing agents, acids, and alkalis are described. Co salts give a brown colour (cf. Zimmermann, A., 1930, 648). Methylglyoxaline gives cryst. complex salts with Cu, Co, and Ni [e.g.,  $\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_6\text{SO}_4\cdot\text{Co}(\text{C}_4\text{H}_6\text{N}_2)_6(\text{NO}_3)_2$ ]. F. O. H.

**Test for thymine: keto-enolic type of diazo-test.** G. HUNTER (Biochem. J., 1936, 30, 745—749).—Thymine (I) coupled with diazotised sulph. anilic acid in  $\text{Na}_2\text{CO}_3$  solution gives an intense red colour when treated with  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$ .  $<0.01$  mg. of (I) can be detected; the test is not given by uracil or cytosine. The conditions for the "keto-enolic type" of diazo-test given by glucose,  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ ,  $\text{MeCHO}$ ,  $\text{COMe}_2$ , tyrosine, and (I) are (a) capacity for keto-enol tautomerism and (b) the presence of a reducing agent for the development of colour. J. N. A.

**Colour reaction of certain nitro-compounds.** P. K. BOSE and S. RAM (J. Indian Chem. Soc., 1936, 12, 687—689).—The colours (varying from cherry-red to indigo-blue) given by a no. of aromatic  $o\text{-NO}_2$  compounds in  $\text{EtOH}$  with uric acid- $\text{H}_2\text{O--KOH}$  at  $25^\circ$  and  $100^\circ$  are recorded. H. G. M.

**Detection of benzidine and tolidine present together.** L. KULBERG (J. Gen. Chem. Russ., 1935, 5, 1754—1756).—A drop of 10% aq.  $\text{CuSO}_4$  and a drop of 10% aq.  $\text{KNO}_3$  are placed on filter-paper, and a drop of the solution is added, when the spot turns blue in presence of  $o\text{-tolidine}$  (I), whilst benzidine (II) gives a brown ring with a blue centre. If the (II)



contains  $\pm 1\%$  of (I), the ring is green, and if the (I) contains  $\pm 1\%$  of (II) the spot has a colourless centre, and a blue ring with a rose-red margin. R. T.

**Determination of small quantities of benzoic acid.** E. B. JOHNSON (J.S.C.I., 1936, 55, 109—110T).—The BzOH is first nitrated, then reduced by Zn to  $m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , diazotised, and coupled with  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  in alkaline solution. The bright red shade produced is matched with an aq. solution of Azogermanine B previously standardised for known amounts of  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , and the amount of BzOH obtained by reference to curves. Alternatively,  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$  may be used for coupling; in this case Neolan Pink B is employed. The method can be used in artificial light.

**Analytical uses of Nessler's reagent. Detection of aldehydes. Determination of glucose.** I. M. GOSWAMI, H. N. DAS-GUPTA, and K. L. RAY (J. Indian Chem. Soc., 1935, 12, 714—718).—Alkaline Nessler's solution is reduced by aldehydes (except OH-aldehydes in which OH is unprotected) but not, contrary to Bougault *et al.* (A., 1922, ii, 666, 709), by ketones (OH-ketones excepted). The extent of the reduction by glucose (I) and fructose depends on the strength and nature of the alkali (NaOH, KOH, or  $\text{Na}_2\text{CO}_3$ ) and on the temp. Details for the determination of (I) are given. H. G. M.

**Bromide-resorcinol reaction. Reactions characteristic of phenols, opium alkaloids, and oxalic acid.** M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 676—681; cf. A., 1935, 961; B., 1935, 828).—The colour reactions of tartaric acid and  $\text{CCl}_3\cdot\text{CHO}$  in presence of KBr,  $\text{H}_2\text{SO}_4$ , and  $m\text{-C}_6\text{H}_4(\text{OH})_2$  are traced to the intermediate formation of  $\text{CHO}\cdot\text{CO}_2\text{H}$ . A reagent containing this substance is obtained by reducing 5%  $\text{H}_2\text{C}_2\text{O}_4$  solution with Al-Hg, filtering, and adding a few drops of conc.  $\text{H}_2\text{SO}_4$  to the filtrate. Its use in the characterisation of phenols and phenolic

acids is described. It can be employed in the differentiation of the chief opium alkaloids;  $\text{CCl}_3\cdot\text{CHO}$  in  $\text{H}_2\text{O}$  (2 : 10) can also be used but gives less intense colours.  $\text{H}_2\text{C}_2\text{O}_4$  is detected by reduction with Hg-Al and treatment of the reduced solution with conc.  $\text{H}_2\text{SO}_4$  and  $m\text{-C}_6\text{H}_4(\text{OH})_2$  whereby a blue colour is developed, whereas  $\text{HCO}_2\text{H}$ , AcOH, BzOH, lactic, citric, tartaric, salicylic, and uric acids,  $\text{COMe}_2$ , glycerol and the products of its oxidation give yellow-orange to red-brown colours. H. W.

**Colour reaction for rotenone.** R. S. CAHN and J. J. BOAM (Chem. and Ind., 1936, 384).—The  $\text{HCl}\text{-HNO}_3\text{-CHCl}_3$ -thymol test for rotenone (B., 1936, 467) is untrustworthy, since it depends more on the presence or production of  $\text{HNO}_2$  than on that of  $\text{HNO}_3$ . Pure  $\text{HNO}_3$  gives the colour only very slowly. R. S. C.

**New reaction of opium alkaloids and its application to the detection of certain oxidising agents.** M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 675—676).—A small quantity of the alkaloid or its salt is dissolved in 0.5 c.c. of 90—95% EtOH and treated with 1.5 c.c. of conc.  $\text{H}_2\text{SO}_4$ . After agitation the mixture is heated for 2—3 min. on the water-bath, cooled, and cautiously diluted with 5 c.c. of  $\text{H}_2\text{O}$ . The solution gives an orange-red colour with NaOCl which is not discharged by  $\text{SnCl}_2$ ; Br- $\text{H}_2\text{O}$  and  $\text{NaNO}_2$  give red colours. The reaction is positive with morphine, apomorphine, codeine, and their derivatives, negative with narceine and papaverine. Brucine and adrenaline give brown colours. Conversely, a stable reagent is obtained with codeine which affords a very sensitive test for NaOCl, Br- $\text{H}_2\text{O}$ , and  $\text{NaNO}_2$  but gives negative results with  $\text{NO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}_2$ , and metallic peroxides. H. W.

**Phthalic acid as reagent for optical identification of some metals and alkaloids.**—See this vol., 695.

## Biochemistry.

**Variations of the respiratory quotient of the frog and the turtle as a result of sharp changes of the temperature of the environment.** L. DONT-CHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 1456—1458).—The R.Q. rises or falls with the temp.; the variations have no metabolic significance, but represent the variations of retention of  $\text{CO}_2$  with temp. R. N. C.

**Respiratory quotient of the fasting frog and turtle maintained at 20°, 10°, and 5°.** L. DONT-CHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 1453—1455).—The R.Q. is unaffected by temp. within the above limits. R. N. C.

**Reticulocyte response in guinea-pigs following oral administration of certain antianæmic substances.** D. K. MILLER and C. P. RHOADS (New England J. Med., 1935, 213, 99—101).—Effects of a concentrate of rice polishings and autolysed yeast extract are examined. CH. ABS. (p)

**Action of sub-hæmolysing doses of mercuric chloride on the permeability of the erythrocyte.** M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1936, 121, 1125—1128).—The permeability is unaffected. R. N. C.

**Forensic detection of blood.** O. SCHMIDT (Deut. Z. ges. gerichtl. Med., 1935, 24, 419—424; Chem. Zentr., 1935, ii, 1223).—Fusion of hæmin with resorcinol (cf. Schumm, A., 1928, 1263) and PhOH yields compounds with characteristic absorption spectra. H. N. R.

**Determination of bilirubin in blood.** A. VÁZQUEZ, V. G. ALVAREZ, and E. MATHET (Arch. med. cir. esp., 1933 [July 26]).—To 1 c.c. of serum is added a solution (1 : 1000) of methylene-blue (I) until the green colour first appearing turns blue. 0.01 c.c. of (I) is equiv. to  $5.6 \times 10^{-8}$  g. of bilirubin. CH. ABS. (p)

**Buffering power of hæmoglobin denatured by heat.** H. NAGAOKA (J. Biochem. Japan, 1936, 23,



101—123).—Hæmoglobin (I), when heated at its isoelectric point in isotonic aq. KCl, denatures first in a sol. condition before mol. aggregation occurs, a certain parallelism existing between increase in buffering power and denaturation. At higher temp., the buffering power and  $O_2$  capacity decrease, the latter being a more exact criterion of the extent of denaturation. The change in  $p_H$  of (I) on heating at  $52^\circ$  for several hr. is only  $+0.02$ . Diminution of buffering power, due to denaturation, occurs during the prep. of (I). F. O. H.

**Hæmatological studies in Indians. I. Hæmoglobin determination methods.** L. E. NAPIER and C. R. DAS GUPTA (Indian J. Med. Res., 1935, 22, 809—825).—Hellige's method can be adapted for clinical purposes if the colour standard, tubes, and pipettes are first checked by an abs. method of hæmoglobin determination. R. N. C.

**Solubility of hæmocyanins in saline solutions and specificity.** A. ROCHE and J. ROCHE (Compt. rend. Soc. Biol., 1936, 121, 1512—1514).—The solubilities are similar to those of globulins, but the limiting concns. of  $(NH_4)_2SO_4$  for pptn. vary with the species. R. N. C.

**Fractional ultrafiltration of the hæmocyanin of the snail.** P. GRABAR (Compt. rend. Soc. Biol., 1936, 121, 1472—1474).—The end-point of ultrafiltration occurs with membranes of mean pore diameter  $86\text{ m}\mu$ . R. N. C.

**Specificity of the characters of the serum-proteins in different animals.** L. SAMUEL (Compt. rend. Soc. Biol., 1936, 121, 1514—1516).—The specificity shows itself in the no. of different globulin fractions and their zones of pptn. Slight variations are often found even in members of the same species. The albumin-globulin ratio can be considered only as an "index." R. N. C.

**Function of serum-proteins.** R. BIERICH, A. LANG, and A. ROSENBOHM (Biochem. Z., 1936, 284, 329—338).—Serum-albumin-I and -II [separated by fractional pptn. with  $(NH_4)_2SO_4$ ] are respectively increased and decreased by addition to the serum of isamine-blue, pyronine, bile acids, or porphyrin; that of azelaic or sebatic acid and, in some cases, extracts of -II from pathological serum, has the reverse effect. The significance of the phenomenon in disease is discussed. F. O. H.

**Changes in serum-proteins in cancer.** R. BIERICH and A. LANG (Biochem. Z., 1936, 248, 443—447).—Neither the Cu-electrode potential method of Ettisch *et al.* (A., 1931, 503) nor the determination of acid groups indicates any differentiation between the globulin, albumin-I and -II (cf. preceding abstract) of normal and of cancerous blood. The tryptophan content of albumin-II, however, is diminished. F. O. H.

**Amino-groups of the proteins of human serum. Action of formaldehyde and ninhydrin.** W. L. DULIÈRE (Biochem. J., 1936, 30, 770—772).—Serum contains an average of  $0.635\text{ mg.}$  of  $NH_2\text{-N}$  (determined by  $CH_2O$  titration) per  $100\text{ mg.}$  of dry protein, the albumin containing  $>$  the globulins. The purification and properties of the reaction products of the

proteins with  $CH_2O$  and ninhydrin are described. The ninhydrin-protein products do not react with  $CH_2O$ . J. N. A.

**Presence of serum-vitellin in vertebrate blood.** M. LASKOWSKI (Biochem. Z., 1936, 284, 318—321).—Data are given for the lipin-, phosphoprotein-, and acid-sol. P in the blood of various species of birds, reptiles, amphibia, and fishes during resting and spawning periods. F. O. H.

**Zinc-ferrocyanide deproteinisation and the nitrogen compounds of the plasma.** M. PAGET and G. GUYADER (Compt. rend. Soc. Biol., 1936, 121, 1105—1106).—The reagent (I) does not adsorb urea or  $NH_2$ -acids, but retains a variable fraction of the uric acid (II). The difference between total N of the  $CCl_3\cdot CO_2H$  and (I) filtrates is slightly  $>$  the polypeptide-N (difference between N of  $CCl_3\cdot CO_2H$  and phosphotungstic ppts.), but if allowance is made for retention of (II), the N of the filtrate is of the order of that of the phosphotungstic acid filtrate. The (I) filtrate can be used for determination of the tyrosine index. R. N. C.

**Xanthoproteic reaction: its application to the determination of the tyrosine index of serum-polypeptides and of blood-phenols.** R. LEFAUX (J. Pharm. Chim., 1936, [viii], 23, 437—445; cf. A., 1936, 356).—The colour of the phosphotungstic acid filtrate  $\propto$  the phenol content and is expressed as the "phenol index." E. H. S.

**Methyl derivatives of guanidine in blood: solitary and renal hypertension.** M. ZAPPA-COSTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 705—708).—Methylguanidines are determined in blood colorimetrically with  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$  after adsorption on C in alkaline solution. They are increased in hypertension, but the increase is not  $\propto$  the degree of hypertension or renal retention. R. N. C.

**Fatty acids of ox blood.** T. W. PARRY and J. A. B. SMITH (Biochem. J., 1936, 30, 592—598).—The fatty acids (70% yield) consisted of 26% of saturated acids (10% of  $C_{16}$ , 13% of  $C_{18}$ , and 3% of higher acids) and 69% of unsaturated acids (including 26% of  $C_{18}$ , of which approx. 20% was oleic and 6% linoleic, 33% of  $C_{20}$ , and 10% of  $C_{22}$ ). Neither linolenic nor any liquid saturated acid could be detected. W. O. K.

**Micro-determination of blood-fat.** L. POLLAK (Mikrochem., 1936, 19, 190—193).— $0.1\text{ c.c.}$  of blood is treated with  $\text{EtOH} + \text{Et}_2\text{O}$ , and the fat is saponified with  $\text{NaOH}$ . Fatty acids are liberated by acidifying with  $\text{H}_2\text{SO}_4$ , and are extracted with light petroleum. The latter is removed and the acids are oxidised at  $124^\circ$  by  $0.1N\text{-K}_2\text{Cr}_2\text{O}_7$  in 90%  $\text{H}_2\text{SO}_4$ , excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  being determined iodometrically. J. S. A.

**Colour reaction of hexoses and their polymerides and its application to colorimetric determination of glucose in blood.**—See this vol., 709.

**Blood-sugar of anodonts.** M. FLORKIN and G. BOSSON (Compt. rend. Soc. Biol., 1936, 121, 1348—1350).—The "true" blood-sugar of anodonts is about  $0.20\text{--}0.80\text{ mg.}$  per c.c., vals. being the same



whether the blood is drawn from the heart or the palmar sac. Non-fermentable reducing substances are increased by fasting for a year. R. N. C.

**Determination of copper in plasma and blood-cells by Warburg's cysteine oxidation method.** J. BJERRUM and V. HENRIQUES (Skand. Arch. Physiol., 1935, 72, 271—282).—The method gives results comparable with those obtained by Macfarlane's colorimetric method. In a normal rabbit the blood-Cu was about equally divided between plasma and cells. After intravenous injection of Cu salts there was a marked rise in plasma-Cu followed by a slow fall during which the cell-Cu rose until both plasma- and cell-Cu reached the same level, after which both fell to normal. NUTR. ABS. (m)

**Helium solubility in blood at increased pressures.** J. A. HAWKINS and C. W. SHILLING (J. Biol. Chem., 1936, 113, 649—653).—Solubility coeffs. of He in dog's blood equilibrated at atm. pressure varied from 0.083 to 0.089, and in ox blood from 0.080 to 0.091. The amount of He dissolved by whole blood under pressures of He of 1—6 atm.  $\propto$  pressure.

J. N. A.

**Determination of traces of ferric iron, as in blood-serum.** J. DUBNOFF and P. L. KIRK (Mikrochem., 1936, 19, 194—207).— $\text{Fe}^{III}$  in the  $\text{CCl}_3\text{CO}_2\text{H}$  filtrate of serum is titrated by a differential potentiometric method with  $\text{TiCl}_3$  in presence of KCNS. The use of standardised additions of KCNS and conditions of working is essential owing to slow reduction of  $\text{Fe}^{III}$  by KCNS.

J. S. A.

**Iron. X. Acid-soluble iron of plasma.** G. BARKAN (Z. physiol. Chem., 1936, 239, 97—108; cf. this vol., 109).—In human and horse blood the spontaneous transfer of Fe from corpuscles to plasma is not a diffusion; it is independent of hæmolysis and is unaffected by quinine and KCN but is generally restricted by CO. Transferred Fe is not adsorbed by  $\text{Al}_2\text{O}_3$ , whilst its ionisation by acids is not inhibited by CO. Plasma-Fe is usually reduced in experimental anæmias.

W. MCC.

**Determination of sodium in serum.** E. G. BALL and J. F. SADUSK, jun. (J. Biol. Chem., 1936, 113, 661—674).—The method, based on the pptn. of Na as  $\text{U Zn Na}$  acetate, reduction of  $\text{U}^{VI}$  to  $\text{U}^{IV}$ , and subsequent oxidation to  $\text{U}^{VI}$  by  $\text{K}_2\text{Cr}_2\text{O}_7$ , is applicable to 0.2 c.c. of serum (error < 1%).

J. N. A.

**Determination of diastase in blood. I. Causes of error in Ottenstein's method.** F. BALTZER and J. BRINCK (Klin. Woch., 1935, 14, 929—930; Chem. Zentr., 1935, ii, 1223).

H. N. R.

**Reduction of methylene-blue by the blood of young infants.** C. H. SMITH (Amer. J. Dis. Children, 1935, 49, 1189—1203).—The rate of decolorisation of methylene-blue by blood varies with age, and in presence of 3% aq. Na citrate is highest at  $p_H$  7.4—8.1 and does not occur at  $p_H$  6.3. The action is associated with erythrocyte constituents.

CH. ABS. (p)

**Heart-lung preparation with coagulable blood.** L. BRULL (Compt. rend. Soc. Biol., 1936, 121, 1351—1353).

R. N. C.

**Hæmolytic action of photofluorescein.** J. F. MENKE (Biol. Bull., 1935, 68, 360—362).—Prep. of photofluorescein (I) by irradiation of Na fluorescein is described. (I) hæmolyses rats' blood in the dark, to the same extent as does fluorescein (II) in light. (II) has no action in the dark.

CH. ABS. (p)

**Existence of an optimum concentration of eosin for photodynamic hæmolysis.** M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1936, 121, 1122—1125).—The optimum concn. is 0.02—0.03%.

R. N. C.

**Mechanism of anti-hæmolytic and-coagulatory action of blood-stabilising agents.** V. S. ILJIN (Biochem. Z., 1936, 284, 383—391).—Hæmolysis is inhibited by substances (e.g., Na citrate,  $\text{Ca}_2\text{C}_2\text{O}_4$ , NaF, hirudin) which inhibit coagulation; the action of those pptd. by  $\text{Ca}^{++}$  is suppressed by Ca, Mg, Sr, and Ba chlorides, which, however, enhance hirudin etc. The phenomenon is not related to combination with blood-Ca. Addition of fresh serum re-initiates hæmolysis, indicating the participation of complement, whilst the inhibition of coagulation by citrate etc. is due to reaction with prothrombin, which is therefore related to complement (cf. A., 1927, 787).

F. O. H.

**Anticoagulants. (A) Hypotensive action. (B) Effects of repeated injections. (C) Reciprocal action. (D) Effect of hypertensive and hypotensive substances on action of anticoagulants *in vivo*.** L. ROBUSCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 849—852, 852—856, 856—859, 860—864).

R. N. C.

**Anticoagulant action of arsenobenzenes.** H. GOLDIE (Compt. rend. Soc. Biol., 1936, 121, 1286—1290).—The anticoagulant power *in vitro* of sulph-arsenobenzene (I) is > that of novarsenobenzene (II) but the same *in vivo*. The min. anticoagulant dose of (I) *in vitro* is the same as the min. anti-alexie dose, suggesting that it inhibits a coagulant resembling alexin (possibly serozyme); the anticoagulant power of (II) is > its anti-alexie power, and its action is inhibited by excess of cytozyme. (I) and (II), like other anti-coagulants, change the isoelectric point and pptn. characters of serum and plasma, but only in a narrow range of  $p_H$ . Arsenobenzene 606 exhibits only a feeble anticoagulant action, and is insol. at neutrality and toxic.

R. N. C.

**Alexin and anti-alexin substances of horse serum.** H. GOLDIE (Compt. rend. Soc. Biol., 1936, 121, 1282—1286).—The activity of alexin (I) in a hæmolytic system is increased by adding pseudoglobulins (II) to the hæmolytic serum before adding (I); (II) probably fix anti-alexins in the serum.

R. N. C.

**Action of sucrose on alexin at high and low temperatures.** W. MUTSAARS and J. ROBERT (Compt. rend. Soc. Biol., 1936, 121, 1400—1402).—Sucrose protects alexin from inactivation at high but not at low temp.; this supports Madsen's view that the inactivation factors are different.

R. N. C.

**Effect of sucrose on the thermo-resistance of alexin.** W. MUTSAARS (Compt. rend. Soc. Biol., 1936, 121, 895—897).—The thermo-resistance is increased.

R. N. C.



**Minor hæmagglutinins.** Blood containing autoagglutinin, heteroagglutinins, hæmolysins, and a rouleau-forming substance. W. P. BELK (J. Lab. Clin. Med., 1935, 20, 1035—1042).—Data are obtained from the blood of a single patient recovering from mononucleosis. CH. ABS. (p)

**High agglutinin content of the serum of an injurious universal donor.** M. MULLER and E. BALGAIRIES (Compt. rend. Soc. Biol., 1936, 121, 1447—1449). R. N. C.

**Isohæmoagglutination and serum-albumins.** P. MICHON, M. VÉRAIN, and A. ZIEGLER (Compt. rend. Soc. Biol., 1936, 121, 1419—1420).—Isohæmoagglutinins are contained in the serum-globulins, serum being inactive. R. N. C.

**Isohæmoagglutination and viscosity.** P. MICHON, M. VÉRAIN, and A. ZIEGLER (Compt. rend. Soc. Biol., 1936, 121, 1417—1419).—Isohæmoagglutination is accompanied by a fall followed by a rise of  $\eta$ ; the variations are detectable at dilutions > those where agglutination is detected, and do not occur in non-agglutinating systems. R. N. C.

**Isolation of antibodies by fixation on an adsorbent-antigen system with subsequent regeneration.** K. MEYER and A. PIC (Ann. Inst. Pasteur, 1936, 56, 401—412).—After adsorption of an antigen, the adsorbent-antigen complex will adsorb the corresponding antibody, the latter being eluted with 0.9% aq. NaCl at 60°. H. G. R.

**Titration of therapeutic sera by neutralisation of antibody *in vitro*.** L. COTONI and J. POCHON (Compt. rend., 1936, 202, 1121—1123).—The method is rapid and trustworthy and reveals differences not observed in the *in-vivo* method. W. McC.

**Antigenic power of glycogen and starch.** A. GIOVANARDI (Boll. Soc. ital. Biol. sperim., 1935, 10, 777—780). R. N. C.

**Determination and calculation of the sensitisation of the complement-fixation reaction by titration with a fixed quantity of hæmolytic serum (anti-sheep hæmolytic system).** R. CROSNIER (Compt. rend. Soc. Biol., 1936, 121, 1306—1308). R. N. C.

**Viscosity of diphtheria toxin-antitoxin mixtures.** P. L. DU NOÛY and V. HAMON (Ann. Inst. Pasteur, 1936, 56, 359—375).—The increase in  $\eta$  of a toxin solution on adding a small quantity of antitoxin may be used to standardise the latter. H. G. R.

**Mechanism of the variations of the Nicloux coefficient *k* in normal, hydrated, and dehydrated *Gobio fluviatilis*.** G. FONTÈS, J. BRUNER, and A. LINDENBERG (Compt. rend. Soc. Biol., 1936, 121, 1458—1461).—Theoretical. R. N. C.

**Water impermeable to alcohol.** (A) G. FONTÈS. (B) M. NICLOUX (Compt. rend. Soc. Biol., 1936, 121, 1465—1470, 1470—1471).—Theoretical. R. N. C.

**Biochemistry of the vermiform appendix.** S. SUMIDA (J. Biochem. Japan, 1936, 23, 147—159).—Data are given for the physico-chemical properties, inorg. and org. constituents, and enzymes of the

appendix juice (rabbit, dog) and for the  $\text{NH}_2$ -acid distribution in the proteins of the mucosa and muscle layers. F. O. H.

**Behaviour of thyroid follicles in the Harvey-Loomis centrifuge microscope.** J. F. McCLENDON (Science, 1936, 83, 283—284).—At a centrifugal force of  $10^5$  to  $2 \times 10^5 g$  the colloid from the thyroid follicles is extruded, and pptn. of thyroglobulin then occurs. The mechanism of this extrusion is detailed. L. S. T.

**Chemistry of helminths. III. *Taenia solium*. IV. *Diphyllobothrium latum*. V. *Ascaris lumbricoides*.** I. A. SMORODINCEV and K. V. BEBESCHIS (J. Biochem. Japan, 1936, 23, 19—20, 21—22, 23—25).—Data are given for the dry wt., and contents of org. matter, ash, total N, and lipins of the worms, comparison being made between nematodes and cestodes. F. O. H.

**Chlorine content of feathers.** F. R. DODD (Analyst, 1936, 60, 252—253).—Untreated feathers (mixed) contained 0.609% of Cl. After treatment (washing with boiling  $\text{H}_2\text{O}$ ) the smaller grades (1—4) contained 0.051—0.085, and the larger (5 and 6) approx. 0.4%. The Cl, NaCl, and KCl contents of untreated feathers of several species are recorded. E. C. S.

**Iodine content of American fishery products.** E. J. COULSON (U.S. Bur. Fisheries, Invest. Rept., 1935, 1, No. 25, 7 pp.).—Of the fish tested (12 species fresh and canned) the highest vals. (parts per  $10^9$ ) were found in the haddock (average 26,100) and the mullet (average 20,490). The average for codfish was 5350, and for canned Chinook salmon 2010. Of 8 fish meals shrimp had 23,080, crab 19,440, whitefish 12,080, and menhaden 4500. All the other vals. were between 1000 and 2000. The average vals. for fish oils were cod-liver oil 7670, salmon oil 1980, and sardine oil from Maine 470 and from California 260. NUTR. ABS. (m)

**Presence of acetone in beef.** A. HOUDINIÈRE (Bull. Acad. vét. France, 1935, 8, 233—238).—Normal beef (muscle) contained 12 mg. of  $\text{COME}_2$  per 100 g. of tissue whilst in a heifer with milk fever 23 mg. were found. The  $\text{COME}_2$  was not removed by grilling but disappeared on prolonged boiling. NUTR. ABS. (m)

**Errors in the determination of ethyl alcohol in *Carassius auratus*.** G. FONTÈS, A. LINDENBERG, and R. GROSS (Compt. rend. Soc. Biol., 1936, 121, 1461—1465).—The presence of other substances volatile in steam makes the method of Nicloux untrustworthy. R. N. C.

**Highly unsaturated alcohols in sperm-blubber oil.**—See this vol., 703.

**Decenoic acid,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , in sperm-head oil.**—See this vol., 705.

**Evolution of natural fats: a general survey.** T. P. HILDITCH and J. A. LOVERN (Nature, 1936, 137, 478—481). L. S. T.

**Formation of adipocere.** MATZDORFF (Deut. Z. ges. gerichtl. Med., 1935, 24, 246—249; Chem. Zentr., 1935, ii, 1197).—Adipocere appears in the fat cells of the hypodermis of the body of a new-born



child kept for 7 days in flowing  $H_2O$  at  $11^\circ$  temp. and  $29^\circ$  of hardness. R. N. C.

**Physico-chemical studies on lecithin.** H. B. BULL and V. L. FRAMPTON (J. Amer. Chem. Soc., 1936, 58, 594—596).—Lecithin (I) prepared from egg-yolk by a modification of Sueyoshi's method (A., 1931, 975) contains a considerable amount of kephalin (II). Determinations of the isoelectric point ( $P$ ) of various specimens of (I) by the electrophoretic method (A., 1935, 933) and extrapolation to zero concn. of (II), gives a val. of  $p_H$  6.4 for (I) (cf. Chain and Kemp, *ibid.*, 194). The  $P$  of (I) is lowered considerably by admixed (II); divergent results (lit.) are thus explained. When an aq. suspension of (I)+(II) is kept the  $P$  falls. Titration curves for such suspensions are reported. H. B.

**Presence and distribution of some reducing substances in brain tissue.** M. MITOLO (Atti R. Accad. Lincei, 1935, [vi], 22, 359—365).—Vals. are given of the reducing power (with respect to 2:6-dichlorophenol-indophenol) of different parts of the brain tissue of toads, rats, pigeons, guinea-pigs, rabbits, cats, sheep, horses, and oxen. O. J. W.

**Carbohydrates of muscle extracts of normal and diabetic dogs.** T. CAHN and J. HOUGET (Compt. rend., 1936, 202, 985—986; cf. this vol., 630).—Both normal and diabetic muscle extracts can polymerise glucose to glycogen, although the reaction is 30—40% slower in the latter case. P. G. M.

**Isolation of *dl*-arginine from kidney autolysate.** H. A. HEINSEN (Z. physiol. Chem., 1936, 239, 162—164; cf. Ackermann, A., 1934, 874).—The lysine fraction (phosphotungstic acid ppt.) of the autolysate of ox-kidney yields *dl*-arginine (*disoziodolate*, m.p.  $201^\circ$ ). W. McC.

**Heat-denaturation of proteins as a chain reaction.** A. FISCHER (Nature, 1936, 137, 576—577).—The denaturation of highly-purified serum-globulin by heat ( $70^\circ$ ) is a chain reaction, and the denaturation process may be due to the appearance of  $\cdot NH_2$  or  $\cdot SH$  on the surface of the spherical protein mols. L. S. T.

**Storage of proteins in the liver.** H. LI (Chinese J. Physiol., 1936, 10, 7—26).—Loss of blood, hunger, muscular activity, or phloridzin poisoning produces disappearance of protein from rat-liver cells. Feeding with vegetable or animal protein leads to storage of protein in the liver. J. N. A.

**Chemistry of rigor mortis.** I. A. SMORODINCEV and N. V. NIKOLAEVA (J. Biochem. Japan, 1936, 23, 27—39).—Cow's flesh, cooled to approx.  $0^\circ$  immediately after slaughter, contains equal amounts of myosin (I), myogen (II), and stroma, 70% of the total N being extractable by 0.65*M*-saline solution at  $p_H$  9.1. The extractability of (I) and (II) decreases to varying extents over a period of 24—48 hr. at  $0^\circ$  and then remains approx. const. Data for changes at  $36^\circ$  are also given and the bearing of the results on muscle-enzyme action and rigor is discussed. F. O. H.

**Structure and properties of "byssus" or silk of oysters.**—See this vol., 670.

3 D

**Porphyrins in the incubated bird's egg.** A. A. H. VAN DEN BERGH and W. GROTEPASS (Compt. rend. Soc. Biol., 1936, 121, 1253—1258).—The shell of the hen's egg contains protoporphyrin (I), which is secreted simultaneously with Ca albuminate by the uterine mucosa. (I) is synthesised from the white of the germinating egg, simultaneously with hæmoglobin (II). (I) is not a degradation product of (II), but probably an intermediate product in its synthesis. R. N. C.

**Uroporphyrin-III.** J. WALDENSTRÖM (Z. physiol. Chem., 1936, 239, III—IV; cf. this vol., 503).—Isolation of uroporphyrin-III (from urine of acute porphyrinuria) prior to that by Mertens is claimed. The faces in some cases contained coproporphyrin-I which, together with uroporphyrin-I, occurred in the urine. W. McC.

**Lipochrome of pig's liver.** L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1936, 239, 147—148; cf. this vol., 499).—Fresh pig's liver contains about  $3 \times 10^{-5}\%$  of lipochrome of which  $\frac{2}{3} \times 10^{-6}\%$  is carotene. W. McC.

**Surface tension of cow's milk.** G. BELLE (Le Lait, 1936, 16, 13—30).—The  $\gamma$  of milk produced in the Casablanca district averaged 50.4 dynes per cm. During the 3 hr. after milking,  $\gamma$  decreased uniformly until it reached this const. val. The cooling of milk lowered  $\gamma$  considerably, an average val. of 47.7 dynes per cm. being reached at  $0^\circ$ . W. L. D.

**Surface tension of milk.** W. KOPACZEWSKI (Le Lait, 1936, 16, 356—359).—The  $\gamma$  of various milk samples was very uniform, averaging 53 dynes per cm. Dilution with  $H_2O$  does not change  $\gamma$  appreciably. The  $\gamma$  of separated milk differs only slightly from that of the corresponding whole milk; ageing of milk increases the val. by 2 dynes per cm. in 36 hr. Shaking milk for 5 min. increases  $\gamma$  by 2 dynes per cm. W. L. D.

**Ammonia content of cow's milk.** M. POLONOVSKI (Le Lait, 1936, 16, 232—234).—The average  $NH_3$ -N content of milk is 0.08%. The amount increases greatly on keeping or boiling. The increase on boiling is greater with old than with fresh milk. A low  $NH_3$  content in condensed milk is an indication of efficient preservation. W. L. D.

**Effect of certain ingested fatty oils on the composition of cow milk fat.** T. P. HILDITCH and H. M. THOMPSON (Biochem. J., 1936, 30, 677—691).—The milk fats from cows on winter diets supplemented with linseed or rape oils had higher oleic acid (I) contents; there was no evidence of the passage of the highly unsaturated linseed oil or the rape oil erucic ( $C_{22}$ ) acids into the fat. With rape oil a decrease in the palmitic acid content occurred. Supplementing the diet with cod-liver oil caused a large reduction in the content of lower saturated acids, a large increase in that of (I), and a smaller increase in the  $C_{20-22}$  unsaturated acids; palmitoleic acid was absent. By plotting the % of fully saturated glycerides against the % of saturated acids in the total acids in the control and test milk fats a straight line was obtained coincident with that obtained for animal depot fats (A., 1935, 645). The  $C_{20-22}$  unsaturated acids are probably



responsible for the sp. effect of cod-liver oil on lactating cows. H. D.

**Chemistry of cheese-ripening. III. Caseoglutin.** W. GRIMMER and W. LANGE (Milch. Forsch., 1936, 17, 352—375).—The mixture of two caseoglutins in Tilsiter cheese, ripened for 10 weeks, was separated and each fraction sub-divided into 3 fractions with  $\text{COMe}_2$ : (1) insol. in  $\text{COMe}_2$ ; (2) sol. in  $\text{COMe}_2$ , isoelectric point,  $p_H$  5.3; (3) sol. in  $\text{COMe}_2$ , isoelectric point,  $p_H$  7.0. The  $\text{NH}_2$ -acids of (1) showed a high content of leucine and proline. (3) contained only 0.05% of P, (1) and (2), 0.24—0.28%. W. L. D.

**Properties of milk-amylase and their modification by other milk constituents.** A. SCHLOEMER (Milch. Forsch., 1936, 17, 326—361).— $\text{Pb}(\text{OAc})_2$ ,  $\text{AcOH}$ , and citric acid sera of milk are suitable for studying milk-amylase but the enzyme is adsorbed on caseinogen pptd. from milk by  $\text{HCl}$ . Amylolytic activity of milk is inhibited by dialysis. The enzyme can be reactivated by  $\text{CaCl}_2$  and to a less degree by  $\text{NaCl}$ . The adsorption of amylase on the fat-caseinogen ppt. from milk and cream is greatest with high fat contents. A method of preparing the enzyme by dialysis of the  $\text{Pb}$  serum is described. W. L. D.

**Detection of narcotics, particularly barbituric acid derivatives, in various materials, especially cerebrospinal fluid and blood.** R. FISCHER and O. REISCH (Z. ges. exp. Med., 1935, 95, 739—753; Chem. Zentr., 1935, ii, 1223).—The drug (veronal, luminal, pernocton, medinal, dial, or evipan) is extracted with  $\text{Et}_2\text{O}$  and sublimed. H. N. R.

**Humoral distribution of sodium chloride in blood and exudates.** G. DELL'ACQUA (Boll. Soc. ital. Biol. speriment., 1935, 10, 765—768).— $[\text{NaCl}]$  in normal pleural and abdominal exudates and articular or cutaneous blister liquids is  $>$  that in serum, but  $<$  that in purulent liquids. In cirrhotics, serum- $\text{NaCl}$  is  $<$  abdominal exudate- $\text{NaCl}$  which is  $<$  cerebrospinal fluid- $\text{NaCl}$ . R. N. C.

**Lipase content of chyle. Absorption of digestive enzymes.** A. KÁLLÓ (Frankfurter Z. Path., 1935, 48, 305—309).—Chyle collected before passage through any lymph gland in dogs and chyle from a human cyst contained lipase (I) probably absorbed from the intestine and contributing in part to the (I) content of lymph and blood. NUTR. ABS. (m)

**Chemical and physical constants of the body-fluid of sacculine crabs.** A. DRILHON (Compt. rend., 1936, 202, 981—982).—In parasitised crabs the Ca, Mg, and protein contents of the lymph are  $>$  normal. There are two isoelectric points,  $p_H$  6 and 8; the lymph of normal crabs has only one at  $p_H$  6. P. G. M.

**Biliary sugar.** G. BALTACEANO and C. VASILIU (Compt. rend. Soc. Biol., 1938, 121, 1114—1116).—Biliary sugar is partly free and partly combined with proteins, and is related to blood-sugar. The content of sugar (especially that combined with protein) in bile from the gall-bladder is  $>$  that in bile from the duct. R. N. C.

**Ultra-violet spectrum of hæmoglobin derivatives and bile pigment.**—See this vol., 662.

**Relation between blood-sugar and exocrine pancreatic function.** C. O. HEBB (Arch. internat. Pharmacodyn., 1935, 52, 33—47).—In rabbits close parallelism exists between the lipase (I) content of the pancreatic juice and blood-glucose. Injection of glucose (II), but not of isotonic aq.  $\text{NaCl}$ ,  $\text{NaHCO}_3$ , or sucrose, caused an increase in (I) concn. This effect was not altered by adrenalectomy, but was abolished by atropine. During hyperglycæmia (II) was excreted in the juice, but atropine did not affect this excretion. NUTR. ABS. (m)

**Blood-sugar concentration and the external secretion of the pancreatic gland.** B. P. BABKIN (J. Amer. Med. Assoc., 1935, 105, 1659—1662).—A close relationship exists between blood-sugar and secretion by the pancreas. Hyperglycæmia always increased the output of enzymes from the acinous cells. Insulin hypoglycæmia lowered the concn. of enzymes in the pancreatic juice, this effect disappearing after vagotomy. NUTR. ABS. (m)

**Indoluria.** J. C. FORBES and R. C. NEALE (J. Lab. Clin. Med., 1935, 20, 1017—1024).—Indole is not found in normal urine, but occurs in various diseases. CH. ABS. (p)

**Simple, sensitive reaction for bilirubin in urine.** A. W. J. H. HOITINK (Nederl. Tijds. Geneesk., 1935, 79, 2928—2930; Chem. Zentr., 1935, ii, 1224).—A modification of Fouchet's method (A., 1918, ii, 415). H. N. R.

**Unsaponifiable fraction of rat's fæces.** E. AMMUNDSEN (Biochem. Z., 1936, 284, 313—317).—With fæces of rats on either dried milk or meat diets, the sterols are approx. 40% unsaturated (Br method), whilst the solubility of the digitonide in  $\text{MeOH}$  is the same and slightly  $>$  that of pure coprosterol (I). The unsaponifiable fraction on chromatographic analysis or distillation in a high vac. yields cetyl alcohol and a cryst. substance. The accuracy of determinations of (I) and dihydrocholesterol in their mixtures by the method of solubility of digitonides in  $\text{MeOH}$  is influenced by presence of  $\text{H}_2\text{O}$ , but not of  $\text{COMe}_2$ , or digitonin impurities. F. O. H.

**Effect of adrenalectomy on the colloidal state of [frog] muscle-proteins.** G. BENETATO and R. OPREAN (Compt. rend. Soc. Biol., 1936, 121, 1551—1552).—The "solubility" of the proteins is reduced. R. N. C.

**Effect of adrenalectomy on the  $p_H$  and buffering power of muscle.** G. BENETATO (Compt. rend. Soc. Biol., 1936, 121, 1547—1550).— $p_H$  and the buffering power in dogs are reduced. R. N. C.

**Anæmia of premature infants. II. Blood-iron and -hæmoglobin.** A. F. ABT (Amer. J. Dis. Children, 1935, 49, 1204—1218).—The blood-Fe of premature and full-term infants is similar at birth and tends to decrease at similar rates to a min. at the 12th week. The types of curves for Fe and hæmoglobin (I) are similar, but vals. for premature infants reach the lower levels at corresponding age periods. The ratio % (I)/% Fe is the same as for full-term infants. CH. ABS. (p)

**Iron content of teeth of normal and anæmic rats.** S. RATNER (J. Dent. Res., 1935, 15, 89—92).—



The Fe content of the upper incisors of anæmic rats was 0.0082–0.0251% (average 0.0144). After removal of hæmoglobin-Fe the average content was 0.0126%. The corresponding vals. for healthy rats were 0.0280–0.0308% (average 0.0298; after removal of hæmoglobin-Fe 0.0262). A rough correlation seemed to exist between colour depth of the teeth and Fe content. NUTR. ABS. (m)

**Agranulocytic angina.** Effects of toxic products of certain bacteria recovered from human stools and blood on the leucocytes of animals. W. M. HARRIS and H. J. SCHATTENBERG (J. Lab. Clin. Med., 1935, 20, 1053–1062).—Effects of toxic filtrates of cultures of *Clostridium welchii*, *Staphylococcus aureus*, *Salmonella enteritidis*, and *Streptococcus hemolyticus* from an affected patient are examined. CH. ABS. (p)

**Serum-calcium in arthritis.** E. F. HARTUNG and C. H. GREENE (J. Lab. Clin. Med., 1935, 20, 929–934).—Vals. were normal in rheumatoid arthritis but low in osteoarthritis. CH. ABS. (p)

**Calcium and phosphorus metabolism in generalised diseases of bones.** D. HUNTER (Proc. Roy. Soc. Med., 1935, 28, 1619–1638).—In hyperparathyroidism blood-Ca is high (12.6–23.6 mg. per 100 ml.), plasma-inorg. P is low (1.0–2.7 mg.), and urinary Ca is greatly increased. Results are somewhat similar in some cases of generalised osteoporosis with renal glycosuria, but here there is a much smaller increase in serum-Ca in relation to the increased urinary Ca. In focal osteitis fibrosa, exophthalmic goitre, and Paget's disease the blood-Ca and -P levels are normal. In exophthalmic goitre Ca excretion may be greatly increased. Urinary Ca is generally raised in Paget's disease and is normal in focal osteitis fibrosa. In multiple myelomatosis high serum-Ca vals. associated with increased Ca excretion are usually found. If renal insufficiency is also present the plasma-P is high. Secondary carcinomatous deposits in bones may result in a negative or positive Ca balance. In osteomalacia there is nearly always a decreased level of serum-Ca accompanied by a high faecal and low urinary output of Ca. NUTR. ABS. (m)

**Physico-chemical characteristics of body fluids in cancer patients.** G. J. GONZALEZ (Arch. med. cir. espec., 1933, No. 654).—Surface tension, sp. refraction,  $\eta$ , and cholesterol content of the blood are increased: electrical conductivity, glycaemia, and Ca content are lowered. Basal metabolism may increase initially but diminishes with the progress of the disease. Blood- $p_H$  decreases. CH. ABS. (p)

**Cancer. II. Determination of hydrogen-ion concentration of tissues in living animals by means of the capillary glass electrode.** C. VOEGTLIN, H. KAHLER, and R. H. FITCH (Nat. Inst. Health Bull., 1935, No. 164, 15–27).—Apparatus and technique are described. CH. ABS. (p)

**Gelation of serum-proteins in cancer.** W. KOPACZEWSKI (Compt. rend., 1936, 202, 990–992).—The acceleration of gelation of serum-proteins in cancer cannot be correlated with the indices of neoformation of the globulins and myxoproteins. P. G. M.

**Carcinogenic action and absorption and fluorescence spectra of 1:2-benzpyrene.**—See this vol., 664.

**Iron metabolism in cancer.** J. ROMHÁNYI and M. SCHMIDT (Frankfurter Z. Path., 1935, 48, 380–385).—In rats on which "Putnoky-Ehrlich" carcinoma has been grafted, growth of the tumour was accompanied by an initial fall of 33% in the Fe content of the liver, followed by an increase to 14% < normal. Tumour-Fe was const. throughout its growth. The Fe content of the spleen decreased about 14%, whilst there was a 31% increase in that of the kidneys. The excretion of Fe by kidney and bowel decreased 10% and 14%, respectively. NUTR. ABS. (m)

**Composition of normal and diseased organs. I. Normal, carcinomatous and sarcomatous lung.** B. LUSTIG (Biochem. Z., 1936, 284, 367–375).—Data for the contents of N, P, lipins, sterols, carbohydrate, and protein- and residual N are given. Increased contents of albumose and peptone in sarcomatous and of non-reducing and nucleal carbohydrate in carcinomatous lung occur. F. O. H.

**Effect of various goitre-producing diets on growth of carcinoma, sarcoma, and melanoma in animals.** K. SUGIURA and S. R. BENEDICT (Amer. J. Cancer, 1935, 23, 541–549).—Effects of goitrogenic diets with and without added I are compared. CH. ABS. (p)

**Complement fixation reactions in carcinoma.** H. W. LUNDY (J. Lab. Clin. Med., 1935, 20, 923–929).—Fractionation of the phosphatide of cancer tissue by various solvents is described. The antigen involved in fixation with cancer sera was stable at 125°, but was destroyed by treatment with  $C_5H_5N$  or  $(CH_2NH_2)_2$ . CH. ABS. (p)

**Effect of metabolic inhibitors on therapeutic irradiation of mouse tumours.** G. HARKER and W. MOPPETT (Austral. J. Exp. Biol., 1936, 14, 15–25).—Injection of KCN,  $KAg(CN)_2$ , and  $CH_3I \cdot CO_2Na$  increases the sensitivity of tumours to X-rays. The rate of destruction of  $KAg(CN)_2$  in the tissues is much < that of destruction of KCN. The capability of organs to destroy KCN varies greatly, brain being most destructive by far. W. McC.

**Chemistry of crystalline humour, normally and in cataract.** M. PAGET and G. LEVIN (J. Pharm. Chim., 1936, [viii], 23, 388–392).—In mammalian cataract the total ash, Ca, and cholesterol content of the cryst. humour are considerably, and that of S slightly, increased, whereas the K content is much decreased. J. S. A.

**Phosphorus compounds and bound sugars in the blood of diabetics.** M. MORIMUNE (Mitt. med. Akad. Kioto, 1935, 15, 853–860).—In diabetes without complications the bound sugar and the acid-insol. P were increased, the vals. appearing to run parallel. The vals. for P in other forms were normal. In diabetes with complications the bound sugar, total P, glycerophosphate, and acid-insol P were increased whilst the ester-P was decreased. NUTR. ABS. (m)

**Immunity in diabetes. II. Relative importance of nutritional state and of blood-sugar level**



in influencing development of the agglutinin after typhoid vaccine. R. RICHARDSON (J. Clin. Invest., 1935, 14, 389—392).—Rabbits with depleted liver-glycogen developed lower agglutinative titre after typhoid vaccine than did normal controls. No correlation was observed in diabetics between the fasting blood-sugar concn. and either the agglutinative titre developed after typhoid vaccine or the bactericidal power of the blood. CH. ABS. (p)

"Donaggio reaction" in diabetes. P. BIOCCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 737).

R. N. C.

Electrolyte balance in acute gout. J. H. TALBOT, B. M. JACOBSON, and S. A. OBERG (J. Clin. Invest., 1935, 14, 411—421).—Changes in  $H_2O$  and salt metabolism occur during acute gout attacks. Before clinical or subject evidence appeared, there was diuresis accompanied by negative Na and Cl balances, and increased excretion of K, Ca,  $NH_4$ , titratable acid,  $PO_4'''$ , and urate. Metabolism of acute gout is not defined by uric acid alone. CH. ABS. (p)

Leprosy: effect of vitamin- $B_1$ -deficient diet on the incubation period of rat leprosy. L. F. BADGER and W. H. SEBRELL (U.S. Publ. Health Repts., 1935, No. 50, 855—863).—The incubation period was shortened. CH. ABS. (p)

Composition of lipomas. E. STOLFI and G. STOLFI (Boll. Soc. ital. Biol. sperim., 1935, 10, 742—744).—The fat of lipomas and that of the subcutaneous connective tissue are chemically essentially the same. R. N. C.

Indole. IV. Indican-indole index of the blood in various experimental conditions. V. Indican-indole index of the blood in patients with normal liver and hepatic disease. VI. Microdetermination of free indole in blood. E. MACCHIA (Boll. Soc. ital. Biol. sperim., 1935, 10, 717—720, 720—722, 723—725).—IV. The index in the dog is scarcely changed by ligature of the renal peduncle, but is lowered by ligature of the hepatic peduncle and raised by removal of the intestine.

V. The index in normal patients is 10—16; it is reduced in hepatic disease, but increased in renal and intestinal affections.

VI. The serum is extracted with light petroleum + MeOH, and the extract washed with  $H_2O$  (and with conc. NaOH if icteric). The solution is treated with a modified Ehrlich reagent, and, after evaporation of solvent, indole is determined colorimetrically in AcOH solution. R. N. C.

Test for hippuric acid in diseases of the liver. A. J. QUICK (Arch. Int. Med., 1936, 57, 544—556).—Within 4 hr. of ingestion of 6 g. of NaOBz, approx. 3 g. of hippuric acid should be excreted. This val. is generally decreased in cases of hepatic disease.

H. G. R.

[Biological] synthesis of hippuric acid. P. F. VACCARO (Surg. Gynecol. Obstet., 1935, 61, 36—42).—Ingestion of NaOBz (5.9 g.) was followed by excretion of hippuric acid (3.5 g.) within 4 hr. Excretion was reduced in liver disease. CH. ABS. (p)

Liver-lipase in pathology and therapeutics. N. FIESSINGER and A. GAJDOS (Ann. Méd., 1935, 38,

405—426).—The lipase (I) of serum is believed to be similar to and derived from hepatic (I) and to differ from pancreatic (I). Serum-(I) was diminished in cirrhosis and tumour of the liver. Persistent elevation of the serum-(I) in dogs followed injection of hepatic (I); in liver perfusion experiments the (I) content of the perfusate was increased. NUTR. ABS. (m)

Thiocyanate treatment of mange in guinea-pigs. E. B. CARMICHAEL (Science, 1936, 83, 304).—A 2% solution of lauryl thiocyanate in cottonseed oil or a 5% aq. solution of "Loro" is effective.

L. S. T.

Virus aetiology of one form of lymphocytic meningitis. G. M. FINDLAY, N. S. ALCOCK, and R. O. STERN (Lancet, 1936, 230, 650—654).—The properties of a virus isolated from the cerebrospinal fluid of adults suffering from obscure symptoms associated with an increase of lymphocytes and its effect on various animals are described. L. S. T.

Glycine treatment of progressive myopathic muscular atrophy and creatine balance. L. PERRIA (Boll. Soc. ital. Biol. sperim., 1935, 10, 751—752).—The action of glycine on creatine (I) balance is variable, and the (I) elimination curve shows no tendency to revert to normal. R. N. C.

Creatine-creatinine excretion and the creatine content of muscle in nutritional muscular dystrophy. T. G. NI (Chinese J. Physiol., 1936, 10, 199—206; cf. Goettsch and Brown, A., 1932, 1057).—In muscular dystrophy caused by a special diet, the muscle-creatine (I) fell to a low level. In young guinea-pigs which had been fed the diet for some time, the urinary (I) increased, whilst creatinine (II) decreased. The early clinical symptoms of paralysis occurred some time after a significant rise in (I) and fall in (II). J. N. A.

Phosphatase of biopsy tissue in progressive myositis ossificans. W. E. WILKINS, E. M. REGEN and G. K. CARPENTER (Amer. J. Dis. Children, 1935, 49, 1219—1221).—Fibrous tissue and muscle from the region of lesions in the preossification stage showed high phosphatase activity. Heterotrophic bone and cartilage from an older lesion showed activity > that of a normal rib. Vals for normal tissue were low. CH. ABS. (p)

Indole and skatole content of the blood in kidney disease. M. ZAPPACOSTA (Boll. Soc. ital. Biol. sperim., 1935, 10, 708—710).—Blood-indole and -skatole are not increased in acute glomerular nephritis or nephrosis, but are moderately increased in renal sclerosis and uraemia, the increase being independent of the degree of injury. R. N. C.

Effect of renal denervation on patients suffering from nephritis. I. H. PAGE and G. J. HEUER (J. Clin. Invest., 1935, 14, 443—458).—Renal denervation in acute nephritis diminished protein excretion in most cases. Urea clearance was unaffected. CH. ABS. (p)

Neuritis in pregnancy successfully treated with vitamin- $B_1$ . G. W. THEOBALD (Lancet, 1936, 230, 834—837). L. S. T.



**Polypeptidæmia in pellagra.** I. ORNSTEIN and E. VASCAUTANU (Compt. rend. Soc. Biol., 1936, 121, 1440—1442).—Polypeptides generally show an increase which is not  $\propto$  the fall of blood-cholesterol or to blood-urea. R. N. C.

**Diet of sunflower seeds for the study of experimental polyneuritis.** A. ALLEGRI (Boll. Soc. ital. Biol. sperim., 1935, 10, 839—943). R. N. C.

**Follicular hormone and pregnancy diagnosis in women and in the mare.** S. L. SALA (Rev. sudamer. endocrinol., 1935, 18, 325—329).—Filtered urine (5 c.c.) is heated with 1 c.c. of HCl at 100° for 5 min., and after cooling is extracted with  $C_6H_6$ . After removal of  $C_6H_6$  the residue of the extract is dissolved in  $H_2SO_4$  (0.8 c.c.) and heated at 70—80° for a few min. Fluorescence, greenish by transmitted light, constitutes a positive test, which is trustworthy for mare's but not for human pregnancy. CH. ABS. (*p*)

**Determinations of prolactin and oestrin in pregnancy with special reference to late toxæmia and eclampsia.** G. VAN S. SMITH and O. W. SMITH (Surg. Gynecol. Obstet., 1935, 61, 27—35; cf. this vol., 229).—A peak level of prolactin (I) occurs in the 2nd—4th months of pregnancy. Oestrin (II) increases as pregnancy advances to term. In late toxæmia excess of (I) has probably been present for some time. Nausea in early pregnancy is associated with low (II). Neither (I) nor (II) is concerned in miscarriage. CH. ABS. (*p*)

**Unsalted diet and pregnancy. Chlorine contents of erythrocytes and plasma and their relationship to alkali reserve.** G. LAMBERT (Zentr. Gynäkol., 1935, 59, 2598—2601).—In pregnant women on ordinary diet there appeared to be no correlation between Cl index (cell-Cl: plasma-Cl) and alkali reserve. When the diet was poor in NaCl there was a slight decrease in cell- and plasma-Cl, but no change in the index or the alkali reserve. NUTR. ABS. (*m*)

**Mineral content of the silicotic lungs of an earthenware worker.** N. SUNDIUS, A. BYGÉN, and T. BRUCE (Trans. Ceram. Soc., 1936, 35, 167—181).—A method of extraction with  $H_2O_2$  by which lung dust (I) may be isolated almost unchanged is described. In the (I) of the worker, which was fairly uniformly distributed in the lung, all the components of the raw materials were found, although some increase in the kaolinite and mica, and decrease in the flint-quartz and feldspar contents, had resulted from separation by the air and the respiratory organs. The average diameter of most of the particles of the (I) was  $< 2-4 \times 10^{-3}$  mm. Chemical and X-ray examination showed that the mineralogical composition of the (I) was essentially the same as that of factory dust of similar grain-size, and that the dust had undergone little or no decomp. in the lung. A. L. R.

**X-Ray appearances of the lungs of electric arc welders.** A. T. DOIG and A. I. G. McLAUGHLIN (Lancet, 1936, 230, 771—775).—Alterations in the tissues due to inhalation of the fumes produced are described. The probable composition of the fumes is discussed. L. S. T.

**Blood chemistry of about five hundred patients with common skin diseases.** H. GOODWIN (J. Lab. Clin. Med., 1935, 20, 1048—1052).—Blood-sugar and -NaCl were generally within normal range, but relatively high -NaCl was associated with relatively low -sugar and *vice versa*. Urea-N and uric acid were not appreciably changed. CH. ABS. (*p*)

**Technique of the Bordet-Wassermann reaction in serum freed from the fraction precipitable by hydrochloric acid.** O. AUGUSTE (Compt. rend. Soc. Biol., 1936, 121, 1449—1450). R. N. C.

**Clinical value of prolactin determinations in tetroma testis.** M. CUTLER and S. E. OWEN (Amer. J. Cancer, 1935, 24, 318—325).—Affected patients excrete increased amounts of prolactin. CH. ABS. (*p*)

**Thyroid diseases and blood-chloride.** J. DECOURT and C. O. GUILLAUMIN (Compt. rend. Soc. Biol., 1936, 121, 1332—1335).—Corpuscular and plasma-Cl, both absolutely and relatively, are slightly reduced in myxœdema and increased in Basedow's disease and experimental hyperthyroidism in the rabbit. R. N. C.

**Mandelic acid and ammonium mandelate in the treatment of urinary infections.** H. E. HOLLING and R. PLATT (Lancet, 1936, 230, 769—771).—Treatment with Na mandelate +  $NH_4Cl$  or  $NH_4$  mandelate rendered the urine sterile in 2—21 days. L. S. T.

**Cholesterol in xanthomatosis.** L. NEKÁM, jun., and B. OTTENSTEIN (Klin. Woch., 1935, 14, 641—643).—Cholesteryl esters and lecithin are increased, and free cholesterol (I) is decreased, in xanthomatosis. Addition of liver- or pancreas-pulp to a (I) emulsion does not cause (I) decomp. under sterile conditions. Xanthomatosis is not associated with a functional disturbance of (I) breakdown. R. N. C.

**Old age and basal metabolism.** F. G. BENEDICT (New England J. Med., 1935, 212, 1111—1122).—Total metabolism per unit surface area and heat production per unit wt. have been determined in women of varying ages. CH. ABS. (*p*)

**Growth and basal metabolism. IV. Changes in the basal metabolism of children during the year.** I. NAKAGAWA (Amer. J. Dis. Children, 1935, 49, 1232—1239).—The total heat production of children aged 3—11 years increases by approx. 30 g.-cal. per day, and is expressed more satisfactorily by changes in wt. than by those in height or surface area. CH. ABS. (*p*)

**Basal metabolism of male Chinese in Manchuria.** F. G. BENEDICT and H. S. D. GARVEN (Chinese J. Physiol., 1936, 10, 141—146).—With 20 men, the average respiration rate was 15 and the  $O_2$  consumption 208 c.c. per min. The average metabolism was 3.5% below the Harris-Benedict standard. J. N. A.

**Variations in the processes of ossification in relation to normal and experimentally-modified rates of growth.** G. SCOZ and P. L. MARANGONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 678—680).—Phosphatase (I) in the bones of the rat falls in winter,



whilst blood-(I) is unchanged; the ossification processes are retarded but not modified. Thyroxine (II) in low concns. lowers body-wt., bone-(I) and -Ca, and increases blood-(I), in dogs and guinea-pigs, whilst in rats it retards the rate of growth and reduces blood-(I) and bone-Ca. Following the effects of (II), the rate of growth and bone-Ca and -P increase whilst blood-(I) falls, the vals. returning to normal after 27 days. Repeated doses of (II) in the rat cause a rise in bone-(I) and a fall in -Ca and -P.

R. N. C.

**Adrenal capsules and gaseous metabolism. I. II. Effect of pilocarpine on gaseous exchange in decapsulated rats.** G. MICHELE (Boll. Soc. ital. Biol. sperim., 1935, 10, 628—631, 631—633).—I. Gaseous exchange falls for the first few hr. after decapsulation, but rises again in animals surviving the following day; this does not support the hypothesis that the adrenal capsules control gaseous exchange by discharge of adrenaline.

II. Pilocarpine does not increase  $O_2$  consumption, and hastens death.

R. N. C.

**Oxidative metabolism in sea-urchins' eggs.** P. E. LINDAHL and L. O. ÖHMAN (Naturwiss., 1936, 24, 157—158).—The action of KCN on the respiration of the fertilised eggs at various stages indicates that part of the respiration is not inhibited and is therefore not related to the Fe-containing respiratory enzyme. An increase in the velocity of  $O_2$  transport in substrate activation is due to changes in the enzyme system. Other aspects (e.g., the rôle of "carriers") of respiration are discussed.

F. O. H.

**Formation of hydrogen cyanide and form-aldehyde by oxidation of organic substances.**—See this vol., 707.

**Reduction intensity of living cells.** A. J. KLUYVER and J. C. HOOGHEIDE (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 298—305; cf. A., 1934, 1138).—The reduction intensity of the living cell is only in a restricted sense a sp. property of the cell, and is determined at any moment by the nature of the metabolic processes in the cell. The oxidation-reduction potentials under well-defined metabolic conditions are characteristic for the reduction intensity of the cells if the medium contains a partly reduced redox system, capable of penetrating the cells. Vals. for  $r_H$  of 8.4—9.0 are characteristic for the reduction intensity of all cells under the conditions of alcoholic fermentation, whilst for lactic acid formation the vals. are 5.0—6.0.

J. N. A.

**Bile secretion and a diet rich in liver.** G. BALTACEANO and C. VASILIU (Compt. rend. Soc. Biol., 1936, 121, 1535—1537).—The diet increases bile secretion in the dog, but lowers cholesterol, acids, pigments, and inorg. substances, and  $\eta$  and  $n$  of the bile.

R. N. C.

**Pancreas diet and the biliary function of the liver.** G. BALTACEANO and C. VASILIU (Compt. rend. Soc. Biol., 1936, 121, 1537—1541).—During administration of pancreas diet to dogs, bile secretion is increased; elimination of bile salts (I), org. and inorg. substances is increased, pigment (II) elimination

is reduced, cholesterol (III) shows slight variations that tend to increase, and  $\eta$  and  $n$  of the bile are unaffected. After cessation of the diet, bile secretion and the constituents oscillate for a period, after which (I), (III), and the dry residue of the bile fall, whilst (II) and  $H_2O$  rise.

R. N. C.

**Nitrogenous metabolism in Manchuria. C. WANG** (Chinese J. Physiol., 1936, 10, 135—139).—Data are given for total, urea-,  $NH_3$ -, uric acid-, and creatinine-N in the urine of 32 men.

J. N. A.

**Nitrogen metabolism in infants.** M. V. MILLER-SHABANOVA (Acta paediat., 1935, 18, 192—210).—The blood of fasting children aged 1 month to 2 years contained 1—5.3 g. of total N per 100 ml., increasing with age. The vals. in well-nourished were > in dyspeptic infants. The val. rose to a max. 3—4 hr. after a meal, the height of the max. depending on the amount of protein in the diet. The max. with breast milk was 1.4—4.7 g. per 100 ml., with mixed feeding 2.1—7.7, and with cow's milk 2.04—8.54. The fasting val. for non-protein-N was 6—16 mg. per 100 ml. After feeding, vals. of 17—20 mg. were obtained, the relationship to the protein of ingested food being insignificant.

NUTR. ABS. (m)

**Rate of absorption of iodine and glycine from the gastro-intestinal tract in health and disease.** C. W. HEATH and H. W. FULLERTON (J. Clin. Invest., 1935, 14, 475—481).

CH. ABS. (p)

**Perfusion of the stomach. XII. Perfusion with ornithine and citrulline.** K. KITSUGAWA (J. Biochem. Japan, 1936, 23, 131—138).—Citrulline (A, 1933, 172), perfused through the dog's stomach, produces both arginine and ornithine, the latter (as when directly perfused) being decomposed into arginine,  $NH_3$ , and urea.

F. O. H.

**Renal excretion of creatinine in man.** J. A. SHANNON (J. Clin. Invest., 1935, 14, 403—410).—Increase in creatinine (I) in the plasma is associated with depression of (I) clearance, both abs. and relative to inulin clearance. Secretion of (I) by renal tubules is probable. Phloridzin brings the two clearances together by depressing tubular secretion of (I).

CH. ABS. (p)

**Transformations of adenosinetriphosphoric acid in muscle. III. Isolated muscle.** D. FERDMANN, O. FEINSCHMIDT, and M. DMITRENKO (Biochem. Z., 1936, 284, 392—400; cf. A., 1935, 778).—Activity of isolated frog's muscle results in decomp. of adenosinetriphosphoric acid and concomitant formation of  $P_2O_7^{4-}$  in amounts  $\propto$  the work done and the adenylic acid produced. Inosinetriphosphoric acid is not formed.

F. O. H.

**Presence of strychnine-barbituric complex in the urine of animals that have received separate injections of strychnine and barbituric acid.** V. DE LAVERGNE, P. KISSEL, WEILLER, and H. CHAHIDI (Compt. rend. Soc. Biol., 1936, 121, 1412—1413).—Both strychnine and barbiturate are found in alkaline  $Et_2O$  extracts of the (guinea-pig's) urine after hydrolysis with  $H_2SO_4$ .

**Production of dihydroxydihydroanthracene-glycuronic acid from anthracene.**—See this vol., 721.



Flavins and metabolism. III. Action of lactoflavin and methyl alcohol extract of liver on blood-glycolysis. A. J. CHARIT, S. A. NEUFACH, and K. N. MOROZOVA. IV. Seasonal changes in the flavin content of the liver in cattle. V. Effect of alloxan and thymonucleic acid in the diet on the flavin content of rats' liver. A. J. CHARIT and N. V. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 127—131, 177—180, 235—236).—III. Aërobic glycolysis in dog's blood is unaffected by addition of lactoflavin, which, however, greatly increases anaërobic disappearance of glucose without increasing lactic acid production. MeOH extract of ox liver does not affect anaërobic but intensifies aërobic glycolysis.

IV. Seasonal changes in the diet of cattle produce corresponding (sometimes very great) changes in the flavin (I) content of their livers (max. in summer, min. in spring). In men on meat diets liability to pellagra increases with decrease in (I) content of dietary liver.

V. Addition of 1 mg. daily of thymonucleic acid [possibly containing traces of (I)] to the diet of rats slightly increases the (I) content of their livers but that of alloxan does not affect the content.

W. MCC.

Carbohydrate metabolism of the liver. V. Sugar intake in the normal intact cat during glucose absorption. VI. Sugar output and intake in the daily digestive cycle. C. TSAI and C. YI (Chinese J. Physiol., 1936, 10, 87—102, 105—117; cf. A., 1934, 1251).—V. The glucose (I) content of the inflowing and outflowing hepatic blood in cats with permanent angiotomy cannulae was studied before and at various intervals during (I) absorption. During the first 3 hr. of absorption, inflow (I) was always > outflow (I). The (I) intake by the liver reached a max. between 1.5 and 2.5 hr. and ceased at 4 hr. after administration of (I). The liver- and muscle-glycogen increased in animals fed with (I), probably due to glycogen formation during absorption of (I). The liver of the decapitated cat showed an output > the inflow.

VI. With alimentary hyperglycæmia, intake of (I) was often > output. A high portal (I) level was necessary for intake to be > output, but there was no relation between arterial (I) levels and the relative amount of intake. Ingestion of a pure meat diet had no effect on the relative concns. of (I) between inflowing and outflowing blood. With cessation of absorption the hepatic outflowing (I) was always > the portal and arterial (I). The liver appeared to discharge (I) into the circulation at a relatively const. rate during the entire interval between meals.

J. N. A.

Carbohydrate metabolism. III. Relation of salt and water to the oxidation of glucose. J. A. JOHNSTON and J. W. MARONEY (Amer. J. Dis. Children, 1935, 49, 1240—1255; cf. A., 1935, 888).—Oxidation of glucose is accelerated by oral administration of acid salts ( $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ) and retarded by alkaline salts ( $\text{NaHCO}_3$ ). It is depressed by  $\text{NaCl}$  and  $\text{H}_2\text{O}$  while these are retained in the body, but increases subsequently. Following thyroxine administration glycogen stores are depleted, and acid

salts then inhibit oxidation completely, whereas alkaline salts have the reverse effect. CH. ABS. (p)

Activators of carbohydrate fission as water-soluble constituents of food. H. VON EULER and M. MALMBERG (Biochem. Z., 1936, 284, 455—460).—Addition of cryst. cozymase will not induce growth in rats fed on a vitamin- $\text{B}_4$ -free diet; that of a yeast-juice prep. (inactive alone) together with nicotinamide induces significant growth. Fractions from extracts of nerve and brain-tissue have a similar action. The rôle of cozymase and other factors of carbohydrate metabolism in nutrition is discussed.

F. O. H.

Nature of sugars in a theoretically complete and balanced diet; can they have any effect on the development and maintenance of the rat? L. RANDOIN and S. QUEUILLE (Compt. rend. Soc. Biol., 1936, 121, 1318—1323).—Growth and maintenance are normal with dextrin (I), sucrose, or maltose. Galactose and lactose exhibit toxic action. Glucose and fructose (II) produce normal growth, but maintenance is poor, particularly with (II), where loss of wt. occurs at maturity unless (I) is added.

R. N. C.

Excretion of inulin, xylose, and urea by normal and phloridzinised man. J. A. SHANNON and H. W. SMITH (J. Clin. Invest., 1935, 14, 393—401).—Inulin (I) clearance in man after intravenous infusion is independent of plasma concn. (I) is not secreted by human renal tubules. Xylose and sucrose are normally reabsorbed by the tubules from glomerular filtrate. Evidence against reabsorption of (I) should be obtained before (I) clearance is accepted as a measure of glomerular filtration. CH. ABS. (p)

Metabolism of fructose. VI. Influence of the level of ovarian function. A. W. ROWE, M. A. McMANUS and A. J. PLUMMER (J. Amer. Med. Assoc., 1935, 104, 451—455).—Ovarian function has little influence (cf. A., 1934, 1393). CH. ABS. (p)

Medical problems in mineral metabolism. I. Legacies of evolution. II. Sodium deficiencies in clinical medicine. III. Experimental human salt deficiency. R. A. McCANCE (Lancet, 1936, 230, 643—650, 704—710, 765—768, 823—830).—Lectures. L. S. T.

Absorption of mineral substances by the embryo of *Sepia officinalis*. S. RANZI (Atti R. Accad. Lincei, 1935, [vi], 22, 605—608).—The embryo can absorb the following elements from sea- $\text{H}_2\text{O}$ : Na, K, Ca, Mg, P, Cu, Fe, Mn, V, B, Li, Sr.

O. J. W.

General application of Loeb's ionic quotient. D. L. RUBINSTEIN, H. BURLAKOVA, and W. LYOVA (Biochem. Z., 1936, 284, 437—442).—With changes in the nutrient media of *Drosophila*, the Na : Ca ratio of the organism can be varied between 300 and 1.6; the movements of the flies appear to be unchanged (cf. A., 1934, 1035; 1935, 1017).

F. O. H.

Ionic equilibrium between the aqueous humour and blood plasma of cats. H. DAVSON, W. S. DUKE-ELDER, and G. H. BENHAM (Biochem. J., 1936, 30, 773—775; cf. Walker, A., 1933, 849).—Determinations of Na, K, and Cl indicate the existence



of a Donnan equilibrium between aq. humour and blood-plasma as far as these ions are concerned. The bearing of these results on the problem of glaucoma is discussed.  
J. N. A.

**Mechanism of the action of sodium chloride and bicarbonate in the maintenance of acid-base equilibrium.** A. SLATINEANU, I. BALTEANU, M. SIBI, M. FRANÇHE, and L. CANTACUZÈNE (Compt. rend. Soc. Biol., 1936, 121, 1423—1427).— $\text{NaHCO}_3$  rectifies acidosis in patients with increased corpuscle-plasma-Cl ratio, which is reduced to normal. Chloropenia with normal alkaline reserve is due to NaCl deficiency, whilst with reduced alkaline reserve it is due to Na deficiency and can be treated with  $\text{NaHCO}_3$ .  
R. N. C.

**Numerical analysis of Lars Spildo's investigations into the calcium metabolism of growing swine. Faecal calcium elimination and calcium absorption.** A. WESTERLUND (Lantbruksögsk. Ann., 1935, 2, 71—105).—The analysis (A., 1935, 1274) leads to the following conclusions. Ca:P ratio, vitamin-D intake, or acid-base balance had no effect on Ca excretion in faeces or Ca absorption. Both excretion and absorption of Ca were determined by Ca intake. With intakes of 2—5 g. per head per day there was no correlation between intake and faecal excretion. Absorption increased with intake up to a max. at about 8 g. total intake, or about 0.5 g. per kg. body-wt. At this level % absorption was 60.  
NUTR. ABS. (m)

**Bromine metabolism in man.** P. CHATAGNON and C. CHATAGNON (Compt. rend., 1936, 202, 1119—1120).—In manic-depressive insanity and similar diseases variations in blood-Br appear to depend on the intake of Br and on the Br:Cl ratio. There is no characteristic decrease in blood-Br and the Br content of the pituitary is not abnormally high (cf. Zondek *et al.*, A., 1933, 739).  
W. McC.

**Effects of low-phosphorus rations on growing pigs.** C. E. AUBEL, J. S. HUGHES, and H. F. LIENHARDT (J. Agric. Res., 1936, 52, 149—159).—Low-P rations induce lessened appetite, poor utilisation of food and storage of energy, inability to develop bone and muscle normally, decrease in blood-inorg. P, increased thirst, and corresponding urination.  
A. G. P.

**Comparative studies in the sulphur metabolism of the dog and pig.** J. A. STEKOL (J. Biol. Chem., 1936, 113, 675—682).—With dogs (but not pigs) on a protein-free diet, ingested isobarbituric acid readily yields ethereal sulphates in the urine, and the yield is increased by feeding in addition *l*-cystine, *dl*-methionine, cysteine, or  $\text{Na}_2\text{SO}_4$ . Like the dog, rabbit, and rat, the pig synthesises *p*-bromophenyl- and 1- $\alpha$ -naphthyl-mercapturic acids from PhBr and  $\text{C}_{10}\text{H}_8$ , respectively.  
J. N. A.

**Light and reproduction in game birds.** L. B. CLARK, S. L. LEONARD, and G. BUMP (Science, 1936, 83, 268).—Irradiation by a Mazda lamp stimulates growth in the reproductive organs of grouse, quail, and pheasants.  
L. S. T.

**Measures of radioactivity in zones of endemic goitre.** G. PIGHINI and O. RÜLKE (Boll. Soc. ital.

Biol. sperim., 1935, 10, 663—666).—Vals. of the ionising power of the air and  $\text{H}_2\text{O}$  of a no. of Italian districts are given.  
R. N. C.

**Radioactivity, iodine, and the thyroid.** G. PIGHINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 661—663).—I protects the thyroid of the rat against changes due to consumption of  $\text{H}_2\text{O}$  containing Rn.  
R. N. C.

**Physico-chemical properties and local anaesthetic action.** (A) Surface tension, adsorption, and prevention of adsorption. (B) Flocculation of colloids and relative lipin-solubility. C. ROHMANN and B. SCHEURLE (Arch. Pharm., 1936, 274, 225—235, 236—244).—(A) The anaesthetic efficiency of 12 compounds,  $p\text{-OR}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2[\text{CH}_2]_r\cdot\text{NEt}_2$  ( $\text{R}=\text{H}$  or alkyl), is approx. parallel to the lowering of  $\gamma$  of their 0.05M solutions at  $p_{\text{H}}$  5.9 (less so at that  $p_{\text{H}}$  which just prevents pptn. of free base) and to their efficiencies in preventing adsorption of glucose by C ("Verdrängungsadsorption"), but not to the amounts adsorbed on C. The parallelisms do not hold if  $\text{R}=\text{NEt}_2\cdot[\text{CH}_2]_2$  nor for four other local anaesthetics.

(B) Better parallelism than that described in (A) exists between efficiency, ability to ppt. colloidal albumose, and lipin-solubility (measured by partition between  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$  at  $p_{\text{H}}$  7.3). Exceptions exist amongst substances of different classes.  
R. S. C.

**Limits of action of hydrogen-ion concentration on vasal tonus: lung preparation of the dog.** G. RUSSO (Boll. Soc. ital. Biol. sperim., 1935, 10, 801—803).—The vessels dilate if  $p_{\text{H}}$  is lowered 0.2 unit from 7.2, and contract if  $p_{\text{H}}$  is raised by this val.  
R. N. C.

**Action of positive chemical stimuli on cultures in vitro.** I. Benzene. F. GUERCIO and R. ARNONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 621—622).  
R. N. C.

**Embryonic "induction" by chemical substances.** M. W. WOERDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 306—314).  
J. N. A.

**Cytological modifications of the hepatic cell through variation of the oxygen and carbon dioxide contents of the respired air.** M. MILLETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 755—757).  
R. N. C.

**Effect of compressed air on animals.** XVII. Combustion of ethyl alcohol injected into rats. XVIII. Combustion of ethyl alcohol injected in increasing doses. A. AGGAZZOTTI. XV. Oxygen and carbon dioxide in the expired air of the rabbit subjected to the action of compressed air. G. BUCCIARDI, M. LEONARDI, and E. FERRARINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 782—784, 784—786, 787—788).—XVII. EtOH oxidation is depressed by exposure to compressed air.

XVIII. EtOH oxidation increases progressively with the quantity injected until a limit is reached at which it tends to remain const.; it is always < that at atm. pressure.

XV.  $\text{CO}_2$  production and  $\text{O}_2$  consumption both increase with the pressure, the R.Q. remaining const.  
R. N. C.



**Action of calcium ions on the hypertension and hyperglycæmia due to potassium ions.** R. HAZARD (Compt. rend. Soc. Biol., 1936, 121, 1036—1039).—Ca<sup>++</sup> does not antagonise the action of K<sup>+</sup> in increasing the secretion of adrenaline (I), but reduces the hyperglycæmic action of (I). R. N. C.

**Influence on carbohydrate metabolism of experimentally induced hepatic changes.** IV. **Blocking of the reticulo-endothelial system with special reference to the Kupffer cell.** T. L. ALTHAUSEN, B. E. BLUMQUIST, and E. F. WHEDON (Amer. J. Digest. Dis. Nutrit., 1935, 2, 532—540).—Blocking of the reticulo-endothelial cells in rabbits by intravenous injection of C lowered the blood-sugar level, increased the tolerance to ingestion of glucose, decreased mobilisation of glycogen (I) from the liver when adrenaline was injected, and reduced the (I) content of liver and muscle. NUTR. ABS. (m)

**Convulsive action of glycerol.** A. LEVI (Boll. Soc. ital. Biol. sperim., 1935, 10, 780—781). R. N. C.

**Physiological properties of trichloroethylene.** H. TAYLOR (J. Ind. Hyg., 1936, 18, 175—193).—Continued inhalation of 0.05—0.2% C<sub>2</sub>HCl<sub>3</sub> by rats and dogs over a period of 6 months caused no pathological condition. H. D.

**Mechanism of the action of citrate ion on the heart and smooth muscle of amphibia.** G. RUSSO (Boll. Soc. ital. Biol. sperim., 1935, 10, 798—801).—The action is partly a sp. stimulation of the sympathetic nervous system, and partly a non-sp. fixation of Ca<sup>++</sup> ions. R. N. C.

**Behaviour of ascorbic acid and glutathione in the organs of guinea-pigs treated with various bacterial poisons.** I. Diphtheria toxin. II. Tetanus toxin. III. Koch's tuberculin. P. Nuzzi (Boll. Soc. ital. Biol. sperim., 1935, 10, 710—714, 714—715, 715—717).—I. Ascorbic acid (I) and glutathione (II) exhibit negligible changes in all the organs.

II. (I) shows no appreciable variation, but (II) is reduced to different extents.

III. (I) falls in the lungs and adrenals. (II) falls very slightly in the same organs and increases in the spleen. R. N. C.

**Action of 2:4-dinitrophenol on the isolated heart of the guinea-pig.** M. ALOISI (Boll. Soc. ital. Biol. sperim., 1935, 10, 746—748). R. N. C.

**Modifications of the physiological action of 3:4-dihydroxyphenyl-β-aminobutanol by substitution of methylamino- for the amino-group.** RAYMOND-HAMET (Compt. rend., 1936, 202, 690—692).—Replacement of the primary by a sec.-NH<sub>2</sub> increased the hypertensive action of the substance. This effect becomes less marked in lower homologues. A. G. P.

**Pathogenesis of tolylenediamine icterus.** T. OKA (Klin. Woch., 1935, 14, 861; Chem. Zentr., 1935, ii, 1211).—Effects following injection into dogs are described. H. N. R.

**Diabetogenic activity of substances related to phloridzin.** A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, 121, 1364—1366).—Dibromophloridzin

and arbutin, but not the azo-dyes azophloridzin, azophloretin, and azophloroglucinol, cause glycosuria when injected into the dog. R. N. C.

**Influence of certain lipins on the growth of a rabbit neoplasm.** A. R. HARNES (J. Lab. Clin. Med., 1935, 20, 1077—1079).—Subcutaneous injection of maize oil or EtOH-extract of ox brain retards the growth. CH. ABS. (p)

**Action of amino-acids on the contractions and the production of lactic acid by the isolated heart.** R. CRISMER (Compt. rend. Soc. Biol., 1936, 121, 1345—1347).—Lactic acid (I) production is increased by perfusion with neutral solutions containing glycine or phenylalanine; with a solution at  $p_H$  8.5 the increase balances the fall produced by the alkaline medium. The amplitude of contraction  $\propto$  (I) production. R. N. C.

**Action of acetylcholine on the formation of lactic acid and decomposition of phosphagen in the isolated muscle of the frog.** D. NACHMAN-SOHN and A. MARNAY (Compt. rend. Soc. Biol., 1936, 121, 1311—1314).—The processes are accelerated. The effect of acetylcholine on metabolism persists after the contraction it produces has disappeared, and it is not destroyed by contact for several hr. with the muscle in anaërobiosis. R. N. C.

**Sympathetic regulation of normal blood-sugar and metabolism of tissue-chlorides.** W. LIP-SCHITZ (Compt. rend. Soc. Biol., 1936, 121, 1295—1298).—The increase of blood-sugar and -Cl provoked by adrenaline (I) in rabbits is abolished by ergotamine (II), which causes a fall. Cl is also increased by ligation of an artery, this increase also being abolished by (II). Injection of CaCl<sub>2</sub> increases blood-Cl; the increase disappears with that of Ca, but while it persists tissue-NaCl migrates to the blood, probably through sympathetic excitation by Ca in a manner analogous to that of (I) and arterial ligation. R. N. C.

**Action of injectable liver extracts.** H. E. BÜTTNER (Fortschr. Ther., 1935, 11, 257—264; Chem. Zentr., 1935, ii, 1208). H. N. R.

**Effect of tissue extracts on esterification of cholesterol in serum.** W. M. SPERRY (J. Biol. Chem., 1936, 113, 599—606; cf. A., 1935, 1536).—When saline extracts of various tissues from different species of animals were incubated with ox, sheep, and human serum, esterification of the free cholesterol occurred, just as when the serum was incubated alone, but in most cases the extracts appeared to inhibit the reaction slightly. The results are not in agreement with those of Shope (A., 1929, 88) and a probable explanation is discussed. Thymol inhibits the esterification in ox serum. J. N. A.

**Reflex and direct respiratory action of some sympathomimetic substances.** E. BECCARI and A. BORIANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 774—777). R. N. C.

**Pantocaine L.** A. A. NABI (Lancet, 1936, 230, 779—780).—*p*-Butylaminobenzoyldimethylaminoethanol hydrochloride is a satisfactory spinal anæsthetic which produces no marked retention of urine or fall in blood pressure. L. S. T.



**Percaïne.** I. Action on the isolated frog's heart. II. Action on the isolated rabbit's heart. Comparison with the action of cocaine: antagonism with adrenaline. R. SANTI and B. ZWEIFEL (Boll. Soc. ital. Biol. sperim., 1935, 10, 648—652, 652—566). R. N. C.

**Anæsthetic action of dialkylbarbituric acids.**—See this vol., 736.

**Action of emetine on the activity of the adrenal and thyroid glands.** R. N. CHOPRA, J. C. GUPTA, and A. C. ROY (Indian J. Med. Res., 1935, 22, 771—776).—Parallel decreases in thyroid-I and adrenal adrenaline in the rabbit are recorded. R. N. C.

**Amphotropic action of ergotamine (ginergen) on the isolated toad's heart.** G. RUSSO (Boll. Soc. ital. Biol. sperim., 1935, 10, 803—805). R. N. C.

**Neutralising action *in vitro* of some chemical substances on the toxicity of curare.** H. VINCENT and F. MOREL (Compt. rend., 1936, 202, 803—805).—Very small amounts of the Na salts of oleic, linoleic, ricinoleic, salicylic, di-iodosalicylic,  $\alpha$ - and  $\beta$ -hydroxynaphthoic, and methylenebis- $\beta$ -hydroxynaphthoic acids when added to solutions of curare entirely neutralised the toxicity of the latter as determined by injection in a guinea-pig. J. N. A.

**Invasion of the body by animal poisons.** F. DURAN-REYNALS (Science, 1936, 83, 286—287). I. S. T.

**Toxicity and potential dangers of crude "Duprene."** W. F. VON OETTINGEN and W. DEICHMANN-GRUEBLER (J. Ind. Hyg., 1936, 18, 271—272).—The vapour from heated Duprene has no permanent toxic effect. H. D.

**$\beta$ -Chlorobutadiene (Chloroprene): its toxicity and pathology and the mechanism of its action.** W. F. VON OETTINGEN, W. C. HUEPER, W. DEICHMANN-GRUEBLER, and F. H. WILEY (J. Ind. Hyg., 1936, 18, 240—270).— $\beta$ -Chlorobutadiene is toxic, however administered. H. D.

**Selective adsorption of enzymes by cellulose.** H. TAUBER (J. Biol. Chem., 1936, 113, 753—757).—Cotton adsorbs pepsin (I) and catalase (rabbit's liver) strongly and peroxidase (horseradish) weakly; (I) is eluted by 0.9% aq. NaCl. H. D.

**Formation of respiration enzymes during germination of barley.** H. FINK, H. HAEHN, and E. ZENGER (Woch. Brau., 1936, 53, 65—69, 73—77, 83—87, 93—95, 101—103).—The mechanism of respiration is discussed. In a study of the anaerobic phase, the decolorisation of methylene-blue (I) by barley meal (source of dehydrase) is followed (modified Thunberg-Ahlgren technique) in presence of hexose diphosphate (II) ( $H_2$  donator), hot aq. extract of yeast (source of co-enzyme), and  $PO_4^{3-}$  buffer ( $p_H$  9.0). The dehydrase activity of resting barley is small, but increases markedly during malting (pale); with dark malt, a max. is attained after approx. one half the germination period. The enzyme resists heat-treatment and is not destroyed on kilning, but it is very sensitive to antiseptics and is destroyed by hot EtOH. For given amounts of (I) and (II) there is an optimal concn. of meal; increase in amount

of yeast extract causes an acceleration of dehydrogenation up to a definite max. val. A certain min. concn. of (II) is necessary; increases above this cause increased dehydrogenation, but there is no direct proportionality. The time of decolorisation  $\propto$  the concn. of (I) so long as this remains relatively small. Dehydrogenation is optimal at a faintly alkaline  $p_H$ ; with increasing acidity it is inhibited, but the acceleration of decolorisation in strongly alkaline media is due to chemical, and not to enzymic, action. Of numerous substances investigated as donator, (II) gave the greatest acceleration; other hexose phosphates have a smaller effect. Dehydrogenase may be extracted from malt readily by aq.  $K_2HPO_4$ , but with difficulty by  $H_2O$ . Malt contains some substance capable of acting as  $H_2$  donator, but no co-enzyme. The malt embryo contains the bulk of the dehydrogenase; the endosperm contains relatively little, whilst the rootlets and husk are almost inactive. It has not been possible to identify the products of decomp. of (II) produced by dehydrogenase activity. I. A. P.

**Peroxidase.** M. TAMAI (J. Biochem. Japan, 1936, 23, 1—17).—Purified peroxidase is free from ionic Fe. Addition of  $Cu^{++}$  (but not of  $Fe^{+++}$  or  $Mn^{++}$ ) activates, whilst that of KCN inhibits to an extent dependent on the purity of the prep. The activity of potato-peroxidase is greatly accelerated by storage of the potato tissue in  $H_2O$  and  $O_2$ . The nature of accompanying impurities, which partly inhibit the enzyme but also protect it from the action of KCN, is discussed. F. O. H.

**Cadmium and oxidation enzymes.** A. ZLATAROV (Biochem. Z., 1936, 284, 448—454).—Cd salts have a pronounced peroxidase- and catalase-like action on  $H_2O_2$ . Low concns. of  $CdCl_2$  or  $Cd(OAc)_2$  inhibit and high concns. enhance the activity of blood- and liver-catalase whilst all concns. of  $Cd(NO_3)_2$  inhibit the former; other Cd salts have a similar action. F. O. H.

**Spectroscopy of purified enzymes. II. Amylase and peroxidase.** R. ITOH (J. Biochem. Japan, 1936, 23, 125—130).—Spectroscopic and chemical examination of pancreatic amylase at various stages of purification confirms that it is not protein but carbohydrate in nature. Peroxidase appears to be a compound of protein and porphyrin-Fe complex, the activity being due to the latter (cf. A., 1935, 1535). F. O. H.

**Sisto- and eleuto-amylase.** R. DEPLANQUE (Woch. Brau., 1936, 53, 137—141).—A lecture.

**Action of  $\alpha$ -glucosidase on  $\alpha$ -methylglucoside and certain di- and tri-saccharides.** K. MYRBÄCK and S. MYRBÄCK (Svensk Kem. Tidskr., 1936, 48, 64—68).—Differences of action of maltases and invertases from different sources on  $\alpha$ -glucosidically-linked sugars show that Weidenhagen's theory of carbohydrase specificity is not generally valid. M. H. M. A.

**Liver-asparaginase.** Y. SUZUKI (J. Biochem. Japan, 1936, 23, 57—69).—Enzyme preps. from calf's and rabbit's liver hydrolyse (determined by  $NH_3$  liberation) asparagine, glycyl- and anhydroglycyl-



asparagine, pyrrolidonecarboxylamide (cf. Ishiyama, A., 1933, 723), and glucosamine. The data indicate two types of asparaginase with  $p_H$  optima of approx. 8.1. F. O. H.

**Cell membrane as a hindrance to the digestion of plant foods.** E. MANGOLD and H. JÄNSCH (Sitzungsber. Ges. naturf. Fr. Berl., 1935, Feb., 40—44).—Heupke's claim that enzymes can penetrate cells and digest their contents is questioned.

NUTR. ABS. (m)

**New type of enzyme in the intestinal tract.** M. BERGMANN and J. S. FRUTON (Science, 1936, 83, 306).—The action of erepsin on substances like glycyl-L-proline is due to a special enzyme which, unlike dipeptidase and aminopeptidase, is not appreciably inhibited by  $CN'$ . As  $>$  one quarter of the peptide linkings in proteins such as collagen and gelatin require the action of the new enzyme, its presence in the intestinal mucosa is significant.

L. S. T.

**Enzymic histochemistry. XVI. Digestion of keratin by larvæ of the clothes moth (*Tineola biselliella*, Humm.).** K. LINDERSTRÖM-LANG and F. DUSPIVA (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 4, 53—83).—Both the intestinal fluid and a glycerol extract of the intestines of *Tineola* have high proteolytic activity; with casein as substrate the optimum  $p_H$  is 9.3. This proteinase has no action on keratin (I) at this  $p_H$ , nor at the  $p_H$  of the intestinal fluid (9.6—10.2). Dissolution of wool, with cleavage of peptide linkings, takes place if a reducing agent (thioglycollic acid) is present to reduce the autoxidised cystine (II). There exists, in the middle intestine, a reducing system, possibly enzymic, able to reduce (II) to cysteine. (I) can thus be digested by the simultaneous action of this reducing system and the proteinase.

E. A. H. R.

**Proteolytic action of pancreatic juice, and of trypsin followed by erepsin.** C. LAURESCO (Arch. internat. Physiol., 1935, 42, 169—182).—Successive action of pancreatic juice and erepsin (I) produced a degradation of protein only slightly  $<$  that produced by pepsin, trypsin, and (I). This explains why N absorption remains very near to normal even in the absence of the stomach. The resistance offered by gelatin and gliadin may be due to the fact that peptides containing proline or glutamic acid tend to resist splitting by pancreatic juice.

NUTR. ABS. (m)

**Liberation of ammonia during enzymic proteolysis.** E. F. TERROINE and C. LAURESCO (Arch. internat. Physiol., 1935, 42, 205—222).—Proteolysis by pancreatic juice, activated by enterokinase or Ca, is always accompanied by production of  $NH_3$ . This is least in the first 24 hr. and cannot be explained by processes other than bacterial, although it appears to be modified somewhat by the nature of the proteolytic enzyme used.

NUTR. ABS. (m)

**Hydrolysis of crystalline pepsin by trypsin.** P. S. YANG (Chinese J. Physiol., 1936, 10, 1—5).—Trypsin hydrolysed pepsin (I) at  $p_H$  5.6 and 37—39°. The decrease of activity of (I) is accompanied by an increase of  $NH_2-N$ .

J. N. A.

**Proteases and ontogenesis. I. Cathepsin in the chick embryo.** E. MYSTKOWSKI (Biochem. J., 1936, 30, 765—769).—With gelatin, ovalbumin, and lecithovitellin (I) as substrates, the activity of cathepsin in connexion with the embryonic synthesis of protein is very small, with or without cysteine as activator. The optimum  $p_H$  is 4.7, whilst with (I) as substrate it is 5.8. The activity is not significantly changed during the whole developmental period of the embryo. The yolk-sac is 15—20 times more active than the embryo. No positive results on synthesis *in vitro* were obtained. J. N. A.

**Phosphatase of the prostate gland. II.** W. KUTSCHER and A. WÖRNER (Z. physiol. Chem., 1936, 239, 109—126; cf. this vol., 111).—The phosphatase is stable at  $p_H$  3.7—6.0, the inactivation at other reactions being independent of the concn. of substrate. Hydrolysis of  $\beta$ -glycerophosphate (I) is optimal at  $p_H$  5.2—6.2 and of phenylphosphoric acid at 4.0—5.4, the optimal concn. of (I) being about 0.153M. When the amount of P liberated is about 9%; the extent of hydrolysis  $\propto$  enzyme concn. The rate of reaction decreases with time. The enzyme is not activated by  $Mg^{++}$  and is inactivated by NaF (0.002—0.01M), org. solvents, and Et urethane but not by cysteine. Purification by electro-dialysis affords a product (N 7%) liberating 75% of its wt. of  $H_3PO_4$  per sec. W. McC.

**Variations in phosphatase activity of bone, kidney, and blood in experimental rickets.** G. SCOZ (Boll. Soc. ital. Biol. speriment., 1935, 10, 823—826).—The bone-Ca and rate of growth of the bones in rachitic rats are  $<$  those in normal animals; during curative treatment the rate of growth begins to increase before Ca. Phosphatase (I) in the blood of rachitic animals is increased, whilst kidney- and bone-(I) are increased in winter but diminished in summer. During curative treatment blood-(I) falls whilst kidney- and bone-(I) rise; when the cure is almost complete, bone-(I) is still slightly high whilst blood-(I) is low, as occurs when the ossification process is increased by thyroxine.

R. N. C.

**Influence of certain dyes on fermentation and respiration of yeast extract.** L. MICHAELIS and C. V. SMYTHE (J. Biol. Chem., 1936, 113, 717—734).—The effect of a no. of reversibly oxidisable and reducible dyes on the alcoholic fermentation by yeast extract is studied. The dyes fall into 3 groups, viz., (a) those that increase the  $O_2$  consumption but do not inhibit fermentation, (b) those that inhibit aerobic fermentation [the inhibition being suppressed by addition of hexose diphosphate (I)] and are sp. poisons for the enzymes responsible for the synthesis of (I), and (c) those that produce an irreversible inhibition of aerobic fermentation due to enzyme (e.g., carboxylase) destruction. No correlation between inhibition and oxidation-reduction potential was obtained. H. D.

**Trehalose in pressed yeast.** K. MYRBACK (Svensk Kem. Tidskr., 1936, 48, 55—61).—Pressed yeast contains as fermentable carbohydrate 13.3% of glycogen, the remainder being trehalose (I), which is absent from ordinary live yeast and brewer's



bottom yeast. It is isolated by extraction of the yeast with aq. EtOH, pptn. of protein, and evaporation (90% yield). The (I) content of pressed yeast falls slowly at 5°, rapidly in air at room temp., but may be preserved by vac. drying. (I) is fermented directly without preliminary conversion into glucose.

M. H. M. A.

**Application of micro-Kjeldahl-Pregl method to determination of total nitrogen in yeast.** M. SOBOTKA (Mikrochem., 1936, 19, 81—88).—N is completely converted into  $\text{NH}_3$  by a short heating with  $\text{H}_2\text{SO}_4$ , the oxidation being completed with 30%  $\text{H}_2\text{O}_2$ .  $\text{Hg}(\text{OAc})_2$  is the most suitable catalyst.

J. S. A.

**Occurrence of growth-promoting factor B in animal organs.** V. HARTELUS and S. HJORTH-HANSEN (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 11, 221—229).—Calf liver contains large amounts of the growth-promoting factor B (I) which acts on *Aspergillus niger* and yeast. The (I) content of calf liver is about 5 times that of cod liver, veal, or salted herring; that of cod meat is still lower. Calf- and cod-bile have a weak effect on the growth of yeast and none on that of *A. niger*. The high (I) content of calf liver may be due to the glycogen it contains.

E. A. H. R.

**Effect of acetate on the consumption of succinic acid by moulds.** V. S. BUTKEVITSCH and L. K. OSNICKAJA (Compt. rend. Acad. Sci., U.R.S.S., 1935, 4, 345—348).—The consumption of Na succinate (I) by *Aspergillus niger* is greatly restricted by addition of NaOAc, which is itself consumed. Added sugar does not affect the process. Citric acid is produced only if sugar is added.  $\text{H}_2\text{C}_2\text{O}_4$  is produced in amounts equiv. to the base liberated by consumption of (I) and NaOAc. The source of succinic acid which sometimes accumulates in moulds may be substances other than sugar and AcOH.

W. McC.

**Palitantin, a metabolic product of *Penicillium palitans*.**—See this vol., 729.

**Staining technique for protozoa.** D. L. SARGENT (Stain Tech., 1936, 11, 49—52).—A modification of Donaldson's I-eosin stain for intestinal protozoa contains colloidal I and aniline-red in dil. solution.

W. O. K.

**Chemistry and physiology of the sulphur bacteria.** H. J. BUNKER (Dept. Sci. Ind. Res., Chem. Res., Spec. Rept. No. 3, 1936, 48 pp.).—A review.

**Production of free sulphur from L-cystine by a soil bacterium.** H. H. BARBER and R. B. BURROWS (Biochem. J., 1936, 30, 599—603).—*Achromobacter cystinovorum*, a new Gram-negative bacillus isolated from soil, decomposes cystine in a medium containing no other source of C, N, or S with formation of  $\text{NH}_3$ , free S, and  $\text{CO}_2$  in equiv. proportions.

W. O. K.

**Bacterial reduction of sulphates.** J. W. YOUNG (Canad. J. Res., 1936, 14, B, 49—54).—Anaerobic sulphate-reducing strains of Gram-negative vibrios are isolated from deep well  $\text{H}_2\text{O}$ , from soil,

and from sewage. They grow best at  $p_{\text{H}}$  5—9 and utilise lactates but not formates as a source of C.

J. L. D.

**Microchemistry of sulphur bacteria.** A. MONTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 690—691).—The endocellular S droplets in colonies of S bacteria are converted into  $\text{Ag}_2\text{S}$  by  $\text{AgNO}_3$ .  $\text{Pb}(\text{OAc})_2$  removes the droplets in neutral solution, but in conc. KOH the S is partly converted into PbS.  $\text{HgCl}_2$  and  $\text{H}_2\text{PtCl}_6$  have relatively little action, whilst  $\text{OsO}_4$  fixes the protoplasm and droplets but does not penetrate the colony.

R. N. C.

**Activity of non-pathogenic bacteria in the thermal waters of Aix-les-Bains and Aix-Burtscheid.**—See this vol., 698.

**Biochemical activities of the acetic acid bacteria.** K. R. BUTLIN (Dept. Sci. Ind. Res., Chem. Res., Spec. Rept. No. 2, 47 pp.).—A survey.

**Fermentation of mannitol provoked by *B. coli* and *B. lactis aerogenes*.** V. CIANCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 730—732).—R. N. C.

**Action of photo-catalysts on the fermentation of lactose determined by *B. coli*.** G. GUERRINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 847—849).—The action of photo-catalysts is stimulant or inhibitory according to the quantity and quality of the catalyst.

R. N. C.

**Catalase activity of lactic acid bacteria.** D. TALCE-NIEDIA (Le Lait, 1936, 16, 225—232).—Certain strains of *Streptococcus lactis* produce catalase (I), but on culturing they show a low (I) activity (index by the volumetric method of 0.5—1.0). This activity, however, cannot be used as a basis for assessing the qualities of cultures of lactic acid bacteria.

W. L. D.

**Biochemistry of micro-organisms. VII. *Bacterium linens*.** W. GRIMMER and J. SCHMID (Milch. Forsch., 1936, 17, 286—302).—*B. linens* liberates leucine, isoleucine, and tyrosine from casein and deaminates other  $\text{NH}_2$ -acids. No indole or skatole is formed. The organism is closely related to *B. mesentericus*.

W. L. D.

**Effect of sulphur compounds on fermentation by propionic bacteria.** P. CHAIX and C. FROMAGEOT (Compt. rend., 1936, 202, 983—984).—0.1 mg. of cystine per 5 c.c. is sufficient to stimulate the max. activity of the bacteria. Methionine, glutathione (oxidised or reduced), thiolactic and thioglycolic acid have a similar action.

P. G. M.

**Fixation of nitrogen in leguminous root nodules.** A. I. VIRTANEN and T. LAINE (Suomen Kem., 1936, 9, B, 12; cf. A., 1935, 1551).—Nitrites detected in aq. extracts of sand cultures of peas arise from oximes originally present in the cultures. Aspartic acid, formed from  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , may be the primary product of N fixation.

R. S.

**DL-Tolylalanine and its bacterial decomposition.**—See this vol., 721.

**Biological oxidations. VI. Oxidation of pyruvic acid by gonococci.** E. S. G. BARRON (J. Biol. Chem., 1936, 113, 695—715; cf. A., 1935, 121).—The oxidation of  $\text{AcCO}_2\text{H}$  by the ketonoxidase from



gonococci has a temp. coeff. of 2.87 and is inhibited by  $\text{Na}_4\text{P}_2\text{O}_7$ , KCN, NaF, and a no. of org. compounds, but not by  $\text{H}_2\text{S}$  and CO. The existence of an activating enzyme for  $\text{AcCO}_2\text{H}$  oxidation is demonstrated.

H. D.

**Antigenic structure of *Vibrio cholerae*.** VIII. Specific carbohydrate content and serology of the acid-soluble fractions. R. W. LINTON, B. N. MITRA, and S. C. SEAL. IX. Dissociation and changes in chemical structure. R. W. LINTON, D. L. SRIVASTAVA, and B. N. MITRA (Indian J. Med. Res., 1935, 22, 617—632, 633—657).—VIII. Reducing substances (I) are high in the A and B acid-sol. fractions of *V. cholerae* but low in the residue. The two fractions probably represent the outer part of the organism. A contains most of the serological activity. The distribution of (I) between A and B shows a parallelism with the smoothness of the organisms, (I) in A being > in B in smooth organisms. The same parallelism is not shown with agglutinability. (I) are probably derived from the sp. polysaccharide (II) by hydrolysis.

IX. Dissociation in the vibrios is caused by change of (II) content, the appearance of new types of protein and carbohydrates in the organism, or by the presence of two types of (II) in unstable equilibrium in the strain. A third type of (II), containing glucose without aldobionic acid, is present in dissociants of the "medusa-head" type; dissociation to this stage is accompanied by transformation of (II) into a different type without loss. The El Tor vibrios form a chemically distinct group, which is related to the cholera vibrios through (II) and to the  $\text{H}_2\text{O}$  vibrios through (I).

R. N. C.

**Vibrio filtrates.** R. W. LINTON, H. SINGH, and S. C. SEAL (Indian J. Med. Res., 1935, 22, 659—674).—The factors producing the Schwartzmann phenomenon in filtrates from 20-hr. cultures of the four vibrios concerned are not sp., and are conc. by pptn. with EtOH or saturation with  $(\text{NH}_4)_2\text{SO}_4$ . Inorg. substances are removed from broth filtrates by fractional pptn. with EtOH, the active material appearing in the second fraction, but the differentiation does not occur with peptone- $\text{H}_2\text{O}$  filtrates.

R. N. C.

**Action of the sulphonamide radical on experimental streptococcal infection in the mouse.** P. GOISSEDET, R. DESPOIS, P. GAILLOT, and R. MAYER (Compt. rend. Soc. Biol., 1936, 121, 1082—1084).—Aromatic sulphonamides exhibit antistreptococcal activity.

R. N. C.

**Immunological specificity of staphylococci.** I. Occurrence of serological types. L. A. JULIANELLE and C. W. WIEGHARD. II. Chemical nature of the soluble specific substances. C. W. WIEGHARD and L. A. JULIANELLE. III. Interrelationships of cell constituents. L. A. JULIANELLE and C. W. WIEGHARD (J. Exp. Med., 1935, 62, 11—21).—I. At least two types of sol. sp. substances are derived from staphylococci.

II. Characteristics of two carbohydrates are given. Type A is unidentified. Type B yields glucose on hydrolysis. Immunological specificity of both types is lost on hydrolysis.

III. The two carbohydrates are type-sp. The protein of staphylococcus is species-sp.

CH. ABS. (p)

**Bactericidal action of some euflavine preparations on *Staphylococcus aureus* and *Bacillus pyocyaneus*.** K. A. KJÆR (Dansk Tidsskr. Farm., 1936, 10, 102—104).—Potency of the preps. is only slightly affected by variations in diaminoacridine hydrochloride content of 0.6—85.6%.

M. H. M. A.

**Lipins of tubercle bacilli.** XLIII. Composition of leprosin. R. J. ANDERSON, J. A. CROWDER, M. S. NEWMAN, and F. H. STODOLA (J. Biol. Chem., 1936, 113, 637—647).—The neutral wax-like substance [now termed leprosin (I)] previously isolated (A., 1932, 307) from *B. lepra* is purified by repeated pptn. from  $\text{Et}_2\text{O}$  with  $\text{COMe}_2$ ; it has m.p. 50—51°,  $[\alpha]_D + 4^\circ$  in  $\text{CHCl}_3$ , 1 val. (Hanus) 5, and is sterol-free. Hydrolysis ( $\text{EtOH-KOH}$ ) gives glycerol, *d*- $\beta$ -eicosanol (cf. this vol., 311), (probably) *d*- $\beta$ -octadecanol, myristic, palmitic, stearic, tetracosanoic, and a OH-acid (leprosinic acid) [20% of (I)], m.p. 62—63°,  $[\alpha]_D + 4^\circ$  in  $\text{CHCl}_3$  (Me ester, m.p. 51—52°; Ac, m.p. 42—43°, and Br-, m.p. 54—55°, derivatives).

H. B.

**"Acid wax" of human tubercle bacilli.** F. ULZER and H. GRUBER (Wiss. Mitt. österreich. Heilmittelstelle, 1935, 13, 1—3; Chem. Zentr., 1935, ii, 1196).—The unsaponifiability of the "acid wax" (I) and the non-existence of mycol are confirmed. (I) is the only constituent of the  $\text{Et}_2\text{O}$ -sol. fraction of the unsaponifiable lipins of tubercle bacilli.

R. N. C.

**Effect of fatty acids on tubercle and other acid-fast bacilli.** S. IJIMA (Tôhoku J. Exp. Med., 1935, 25, 424—436).—The inhibitory effect of acids decreases in the order  $\text{HCO}_2\text{H}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{AcOH}$ ,  $\text{PrCO}_2\text{H}$ , and progressively to decanoic acid, which completely inhibits growth at concn. of 1 in 10,000. Myristic, palmitic, and stearic acids have no action. Na salts are 0.1—0.02 as active as the free acids.

CH. ABS. (p)

**X-Ray studies of crystallite orientation in cellulose fibres.** II.—See this vol., 670.

**Physico-chemical properties of hog cholera virus.** I. Filterability as affected by hydrogen-ion concentration. II. Migration when subjected to electrophoresis. III. Attenuation of virus and production of immunity to hog cholera. L. H. SCHWARTZ (Iowa State Coll. J. Sci., 1934, 9, 187—193).—I. The virus over a  $p_H$  range of 5.0—9.0 passed all filters.

II. The virus migrated to the positive electrode.

III. Attenuation by ageing or by treatment with  $\text{CH}_2\text{O}$  or  $\text{PhOH}$ , or prep. in dil. blood and saturation with  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$ , or  $\text{CO}_2$  did not confer immunity. The latter was attained by saturating dil. blood with  $\text{H}_2$  or  $\text{O}_2$ .

CH. ABS. (p)

**Isoelectric precipitation of the tobacco mosaic virus complex.** R. J. BEST (Austral. J. Exp. Biol., 1936, 14, 1—13).—The virus is reversibly pptd. from the juice at  $p_H$  3—4 (max. > 99% at 3.4). The ppt., which contains 14% of N, consists entirely of virus or of virus united to material from which it cannot be



separated by elution, although relatively stable colloidal solutions are obtained by washing with buffer solutions at  $p_H$  2.8—2.3 and 4.5—7.5. W. McC.

**Hormonal properties of the pineal gland.** P. ENGEL (Wien. klin. Woch., 1935, 48, 481—486).—A review. R. N. C.

**Effect of adrenal preparations and vitamin-C on the sex cycle in castrated mice.** I. KAWAKAMI (J. Pharm. Soc. Japan, 1935, 55, 599—612).—Neither material produced any effect. CH. ABS. (p)

**Action of various hormones *in vitro* on the normal bone-marrow and in presence of germs.** I. Adrenal hormones. S. FIORENTINI (Boll. Soc. ital. Biol. sperim., 1935, 10, 740—742). R. N. C.

**Effects of stimulation of the adrenal gland on its content of ascorbic acid, adrenaline, and glutathione.** C. C. KUCHEL and M. L. MITCHELL (Austral. J. Exp. Biol., 1936, 14, 51—55).—Stimulation results in decrease in the ascorbic acid (I) content, the decrease having no const. relation to the accompanying decrease in adrenaline content. The ratio glutathione : (I) in the whole gland is only slightly affected by stimulation. W. McC.

**Adrenal gland extract causing luteinisation of the ovaries and endometrial hyperplasia.** R. ALLEN and G. BOURNE (Austral. J. Exp. Biol., 1936, 14, 45—50).—The extract is made with 8% aq.  $CCl_3 \cdot CO_2H$ . The active principle, which is very stable and insol. in  $Et_2O$ , is not identical with cortin. W. McC.

**Effect of the adrenal glands on calcium metabolism.** I. SCHOUR and J. M. ROGOFF (Science, 1936, 83, 267—268).—Characteristic disturbances in calcification of dentine occurring in the incisors of bilaterally adrenalectomised rats are described. A functional interrelationship between the adrenal and parathyroid glands is again (cf. A., 1934, 1409) indicated. L. S. T.

**Different reactions of the bulbar centre to adrenaline and pituitrin.** U. SACCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 671—675). R. N. C.

**Interrelationships among urinary, pituitary, and placental gonadotropic factors.** J. B. COLLIP (J. Amer. Med. Assoc., 1935, 104, 556—558).—A review. CH. ABS. (p)

**Pituitary gonadotropic hormones.** P. E. SMITH (J. Amer. Med. Assoc., 1935, 104, 553—556).—A review. CH. ABS. (p)

**General physiology of the anterior pituitary.** P. E. SMITH (J. Amer. Med. Assoc., 1935, 104, 548—553).—A review. CH. ABS. (p)

**Purified growth-hormone from ox anterior pituitary.** E. DINGEMANSE and J. FREUD (Acta Brev. neerl. Physiol., 1935, 5, 39—40).—The pituitary is dried with excess of  $COMe_2$  at low temp. and extracted with alkali. The hormone is purified by repeated adsorption on norite, elution with  $PhOH$ , and pptn. with  $EtOH-Et_2O$  (1 : 2). It is free from thyrotropic and lactogenic hormones, and is stable for 3 weeks over  $P_2O_5$ . R. N. C.

**Effect of anterior pituitary hormones on the male eel.** B. SCHREIBER (Boll. Soc. ital. Biol. sperim., 1935, 10, 818—821). R. N. C.

**Malignant tumours of the female genital organs as sources of hormones.** H. SIEBKE (Z. ges. Naturwiss., 1935, 1, 70—71; Chem. Zentr., 1935, ii, 1197).—Anterior pituitary hormones are found in the urine of women at the climacteric and menopause, or after irradiation of the genital organs or castration. Sex hormones appear in the urine of women with carcinoma of the genital organs or columnar cell carcinoma but disappear with the appearance of cachexia. R. N. C.

**Tumour of the pituitary induced with follicular hormone.** B. ZONDEK (Lancet, 1936, 230, 776—778; cf. this vol., 389). L. S. T.

**Physiology of oestrogenic principles.** E. ALLEN (J. Amer. Med. Assoc., 1935, 104, 1498—1502).—A review. CH. ABS. (p)

**Effects of prolonged administration of oestrin in rats.** C. S. MCEUEN, H. SELYE, and J. B. COLLIP (Lancet, 1936, 230, 775—776). L. S. T.

**Isolation of oestrone and equilin from pregnant mare's urine.** D. BEALL [with M. EDSON] (Biochem. J., 1936, 30, 577—581).—The acid-hydrolysed urine is extracted with  $PhMe$ , the "weak phenols" are separated by extraction with solvents, and after vac. distillation divided into  $C_6H_6$ -sol. and -insol. fractions. The ketonic compounds in the former are pptd. by  $Hg(OH)_2-NH_3$ , the equilin (I) and oestrone (II) in this ppt. being separated by  $EtOH$ . Acid hydrolysis of the equilin complex dissolved in the  $EtOH$ , followed by removal of the  $EtOH$  and vac. distillation, yielded a crude distillate from which pure (I) was recrystallised from 80%  $EtOH$ . Similarly, the  $Hg$ -ketone complex yielded a residue from which crude (II) is obtained by sublimation, purification by the quinoline reaction, and crystallisation from  $EtOH$ . (II) is directly isolated from the  $C_6H_6$ -insol. fraction by the quinoline reaction and recrystallisation. W. O. K.

**17-Ethyltestosterone.**  $\Delta^5$ -Pregnene-3 : 20-dione.—See this vol., 727.

**Culture *in vitro* of the female genital apparatus with folliculin.** F. GUERCIO and R. ARNONE (Boll. Soc. ital. Biol. sperim., 1935, 10, 622—624). R. N. C.

**Isolated amoeboid cells observed in cultures *in vitro* of uterine tissue (mucosa and muscular fibres) of the adult rabbit treated with gonadotropic hormone and folliculin.** F. GUERCIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 624—626). R. N. C.

**Action of folliculin and testicular extract on the residual chromic index.** M. POLONOVSKI, H. WAREMBOURG, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 121, 1451—1452).—Folliculin raises the index whilst testicular extract depresses it; the rise or fall in cancerous blood is > in normal blood. R. N. C.

**Oestrogenic action of androsterone.** E. WOLFF and A. GINGLINGER (Compt. rend. Soc. Biol., 1936, 121, 1476—1478). R. N. C.



Double (masculinising and feminising) action of androsterone on the genital tract of the chick embryo. E. WOLFF (Compt. rend. Soc. Biol., 1936, 121, 1474—1476). R. N. C.

Male hormones and accessory substances. R. DEANESLY and A. S. PARKES (Lancet, 1936, 230, 837—839).—In rats, the activity of androsterone or testosterone is markedly increased by an increase in the amount of various media, *e.g.*, olive, arachis, or castor oil, and  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , and by the addition of palmitic acid to the oil solution of testosterone. L. S. T.

Biological properties of testosterone. V. KORENCHESKY (Nature, 1936, 137, 494).—The effects of testosterone (I) on castrated male rats and on ovariectomised rats are described. Like androsterone and androsteronediol, (I) has some of the important properties of female hormones. L. S. T.

Preparation of vagotonin free from insulin. D. SANTENOISE, T. BRIEU, and E. STANKOFF (Compt. rend. Soc. Biol., 1936, 121, 1420—1422).—Depressor-free pancreatic extract is dissolved in  $\text{H}_2\text{O}$  and the vagotonin (I) is repeatedly pptd. with  $\text{LiCl}$  at  $p_{\text{H}}$  2.75 to remove impurities, dissolved in  $\text{EtOH}$ , and pptd. with  $\text{Et}_2\text{O}$  at  $-10^\circ$ . Insulin is removed by pptn. with 0.2%  $\text{K}_4\text{Fe}(\text{CN})_6$  at  $p_{\text{H}}$  3.2, and (I) is then repeatedly pptd. at  $p_{\text{H}}$  2.5 with  $\text{LiCl}$  and dissolved in  $\text{H}_2\text{O}$ , the  $p_{\text{H}}$  is adjusted to 6.0 with  $\text{LiOH}$ , and  $\text{LiCl}$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  are removed by dialysis; (I) is then repeatedly pptd. with  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ , washed, and dried over  $\text{P}_2\text{O}_5$ . R. N. C.

Effect of previous diet and insulin administration on adrenaline hyperglycaemia. R. BOLLER and K. MAKRYCOSTAS (Klin. Woch., 1935, 14, 646—647).—Hyperglycaemia due to adrenaline (I) is not affected by regulated diet for 6 days before injection. Administration of daily increasing doses of insulin up to the tolerance limit increases the response to (I); (I) secretion is also increased. R. N. C.

Action of insulin on the ovarian cycle. A. CRAINCEANU and L. COPELMAN (Compt. rend. Soc. Biol., 1936, 121, 1303—1304). R. N. C.

Blood-sugar, -chlorine, and -protein curves after injection of insulin. G. DELL'ACQUA (Boll. Soc. ital. Biol. sperim., 1935, 10, 761—765).—Following injection of insulin into normal and diabetic subjects, the hyperchloraemia  $\propto$  the hypoglycaemia, both levels showing small fluctuations; blood-proteins vary irregularly. R. N. C.

Insulin and body-weight. I. Variations in body-weight, glycogen content, and iodine value of adipose tissue. E. BOERI, G. SCOZ, and P. BAER. II. Variations of the composition of adipose tissue in insulinised animals. P. BAER, G. SCOZ, and E. BOERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 680—682, 682—685).—I. Glycogen and the I val. of the adipose tissue of rats and dogs are increased if > 6 daily injections of insulin (I) are given.

II. The  $\text{H}_2\text{O}$  content of the adipose tissue increases during the first 5—10 days of treatment, whilst fat decreases. Later,  $\text{H}_2\text{O}$  falls, and fat, glycogen, the I val., and body-wt. increase for 10 days, the body-wt. subsequently remaining const. whilst the other vals.

tend to return to normal. With carbohydrate (II) nutrition, (I) tends to induce synthesis of fats from (II).

R. N. C.

Effect of thyroxine on the protein-sulphur of the liver in the guinea-pig. G. SCOZ, P. L. MICHELI, and T. GUALTIEROTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 829—830).—S falls sharply in the first few days, afterwards rising steadily. R. N. C.

Effect of thyroxine on the extractable sulphur and vitamin-C content of the liver of the guinea-pig. G. SCOZ and T. GUALTIEROTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 830—832).—Extractable S of liver varies inversely and vitamin-C directly with body-wt. R. N. C.

Effect of thyroxine on the phosphatase power of the liver in the guinea-pig. G. SCOZ and G. CANTONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 833—834).—The phosphatase power falls and rises again with the wt. of the liver. R. N. C.

Effect of thyroxine on the catheptic and amylolytic activities of the liver in the guinea-pig. G. SCOZ and L. DE CARO (Boll. Soc. ital. Biol. sperim., 1935, 10, 826—828).—The activities are increased proportionately during the first few days when body-wt. falls; in the succeeding period the amylase activity falls below normal. R. N. C.

Action of thyroxine on body-weight and the weight and nitrogen content of some internal organs of the rat. G. SCOZ and P. L. MICHELI (Boll. Soc. ital. Biol. sperim., 1935, 10, 687—689).—Thyroxine increases the wt. of the liver and kidney of the rat, but the N contents of the dry organs are unaffected. R. N. C.

Thyrotropic hormone in non-pituitary tissues. L. BALLIF and I. GHERSOVICI (Compt. rend. Soc. Biol., 1936, 121, 1437—1438).—The hormone is not present in the ovary. R. N. C.

Induction of mammary ducts. A. DEAKIN (Nature, 1936, 137, 619—620).—Evidence for the presence of an inducing substance, sp. for a particular group of animals, which is responsible for the development of mammary ducts, is discussed. L. S. T.

Lactation and pregnancy. P. DE FREMERY and P. J. DENEKAMP (Acta Brev. neerl. Physiol., 1935, 5, 44—46).—Prolactin causes lactation and abortion in pregnant animals. R. N. C.

Incidence of rickets. "Gallosterol" as a source of vitamin-A with normal dietary phosphorus and calcium. S. MURAO (J. Biochem. Japan, 1936, 23, 71—90).—Deoxycholic acid (I) has a growth-inhibitory action on normal rats and, to a greater extent, on rats on vitamin-A- and -D-free diet; the effect does not occur in rats with excessive feeding of irradiated ergosterol (II). Administration of (II) irradiated for varying periods to rats on -A- and -D-free diets produces corresponding differences in the period necessary for onset of A-avitaminosis. The effect of (I)-vitamin-A ("gallosterol") on the incidence and degree of avitaminosis is described. F. O. H.

Effect of solvents on the spectral curve of vitamin-A and on its photochemical degradation. A. CHEVALIER, P. DUBOULOZ, and S. MANUEL



(Compt. rend. Soc. Biol., 1936, 121, 1495—1498).—The absorption curve shows slight modifications in different solvents, the max. in  $C_6H_{14}$  being shifted somewhat to the right of that in EtOH. Vitamin-A in  $C_6H_{14}$  solution is degraded photochemically to a series of products, the absorption max. of which lie progressively further to the right of that of -A.

R. N. C.

**Values of the motor chronaxia of the normal guinea-pig and the hepatic vitamin-A content.** A. CHEVALLIER and L. ESPY (Compt. rend. Soc. Biol., 1936, 121, 820—822).—Chronaxia and hepatic vitamin-A are related.

R. N. C.

**Localisation of vitamin-A in red blood corpuscles during their evolution in vertebrates.** P. JOYET-LAVERGNE (Compt. rend., 1936, 202, 1101—1102; cf. this vol., 257).—The content and localisation of the vitamin (I) in the corpuscles depends on their stage of evolution. The (I) content of young corpuscles is > that of old. When the corpuscles have a nucleolus (I) is localised there. In young corpuscles (I) is sometimes diffused throughout the nucleus.

W. McC.

**Content of vitamin-A in the liver of foetus and new-born.** W. NEUWEILER (Z. Vitaminforsch., 1936, 5, 104—110).—The % content of vitamin-A in the liver of foetal and new-born man is approx. equal to that in the liver of adults.

F. O. H.

**Vitamin-A value of halibut-liver oil.** B. AHMAD (Indian Med. Gaz., 1935, 70, 70—71).—Samples of oil failing to produce improvement in general health of children contained 25 times as much vitamin-A as did standard cod-liver oil, and cured xerophthalmia in -A-deficient rats.

CH. ABS. (p)

**Standardisation and determination of vitamin-A.** E. M. HUME and H. CHICK (Med. Res. Coun. Spec. Rep. Ser. No. 202, 1935, 61 pp.).—The specimen of carotene first used as a provisional international standard in 1931 was only 60% pure. It is recommended that 0.0006 mg. of pure  $\beta$ -carotene (I) should now be adopted as the international unit. The maintenance of the yellow colour of (I) is a trustworthy indication of the preservation of biological activity. Coconut oil with addition of quinol as a stabiliser is recommended as solvent. The potency of oil X, of the U.S.P., now adopted as a subsidiary international standard is 3000 international units per g. For the spectrophotometric determination of vitamin-A the factor 1600 is provisionally recommended for converting the extinction coeff. ( $E_{1\%}^{1\text{cm}}$  at 328  $m\mu$ ) into international units of -A per g.

NUTR. ABS. (m)

**Content of (a) vitamin-A, (b) vitamin-C in Hunan lachiao, *Capsicum annuum*, L., var. *longum*.** H. C. HO (Chinese J. Physiol., 1936, 10, 171—178, 179—185; cf. Szent-Györgyi, A., 1933, 433).—(a) Dried lachiao pods are fairly rich in vitamin-A, 0.3 g. of the powder giving a growth response in rats similar to that obtained with 0.006 mg. of carotene. Approx. one half is extracted by boiling EtOH.

(b) The fresh pods contain -C, 0.5—1.0 g. per day protecting guinea-pigs from scurvy. The -C content is entirely lost on drying.

J. N. A.

**Vitamin-A and -D content of the liver of new-born infants.** K. U. TOVERUD and F. ENDER (Acta paediat., 1935, 18, 174—191). **Vitamin-A and -D- in the liver of the newborn.** K. U. TOVERUD and F. ENDER (Norsk. Mag. Laegevidenskapen, 1935, 96, 947—960).—In 97 cases the vitamin-A val. was 0.2—517 blue units per g. of liver (mean 47.6 for premature, 28.8 for full term infants). These variations corresponded with variations in the -A content of the maternal diet in pregnancy. As regards -D content of livers from 44 of the above cases, 24 showed completely negative results, 15 slight healing of rickets in the test rats, and 5 fair healing, the -D content depending on the richness of the maternal diet.

NUTR. ABS. (m)

**Vitamin-A and -B requirements of young rats at a particular period of growth and when given a high-carbohydrate diet.** L. RANDOIN and R. NETTER (Compt. rend., 1936, 202, 1105—1107).—Newly weaned rats, on a diet rich in carbohydrate, but deprived of vitamin-A, continue to grow normally for about 6 weeks without symptoms of avitaminosis-A if they receive sufficient -B. Deprivation of -B with or without that of -A prevents growth and results in early death.

W. McC.

**Vitamin-B groups.** A. G. VAN VEEN (Geneesk. Tijds. Nederl.-Indië, 1934, 74, 1495—1603; Chem. Zentr., 1935, ii, 1203).

R. N. C.

**Vitamins and cultures *in vitro*. I. Action of vitamin-B on embryonal tissue cultures.** F. ROSSI (Boll. Soc. ital. Biol. sperim., 1935, 10, 843—847).—The vitamin exerts a toxic action, but in small concns. produces an initially increased rate of growth.

R. N. C.

**Pharmacological action of vitamin-B preparations and their constituents, particularly adenylothiomethylpentose.** C. HASEGAWA (Fukuoka Acta med., 1935, 28, 122—123).—A yeast extract containing B-vitamins caused stoppage of the frog's heart and of intestinal movements, with lowering of the blood-pressure, in rabbits. These effects were not produced by cryst. oryzanin, possessing a known -B<sub>1</sub> activity, but were produced by autoclaved yeast extract or by a mixture of adenylothiomethylpentose (I), adenine, nicotinic acid, hypoxanthine, and choline in the proportions in which they were present in the extract. The effects were similar to those produced by (I) and were considered to be due to (I).

NUTR. ABS. (m)

**Dynamics of the symptoms of polyavitaminosis in dogs.** M. S. LEVINSON (Z. Vitaminforsch., 1936, 5, 81—104).—Dogs fed on autoclaved diets develop polyavitaminosis within 2½—3 months. During the latent period (2 months), there are no outward symptoms but abnormalities in H<sub>2</sub>O-NaCl balance, diuresis, excretion of NH<sub>3</sub> and urea, and blood elements occur. The onset of ataxia, polyneuritis, skin lesions, etc. during the following period is mainly characteristic of B-avitaminosis.

F. O. H.

**Control and revision of the international standard for vitamin-B.** A. ALLEGRI (Boll. Soc. ital. Biol. sperim., 1935, 10, 836—839).

R. N. C.



**Isoelectric point of vitamin- $B_1$ .** G. NARASIMHAMURTHY (Current Sci., 1936, 4, 586—587).—The isoelectric point of pure vitamin- $B_1$  determined by electrophoresis and micro-cataphoresis methods is  $p_{\text{H}}$  9.2. F. N. W.

**Isoelectric point of vitamin- $B_1$ .** B. C. GUHA (Current Sci., 1936, 4, 653).—Comments (cf. preceding abstract). F. A. A.

**Potentiometric titrations of vitamin- $B_1$  and thiochrome.** A. G. OGSTON and R. A. PETERS (Biochem. J., 1936, 30, 736—741).—The titration curve of vitamin- $B_1$  on the acid side is completely described by one basic group of  $p_K$  4.8. Thiochrome shows a basic  $p_K$  of 5.6 and, like  $-B_1$ , a tendency for a drifting val. to the alkaline side. It has no  $-B_1$  activity by catatorulin test. P. W. C.

**Value of increased supply of vitamin- $B_1$  and iron in the diet of children. II.** J. R. ROSS and P. SUMMERFELDT (Amer. J. Dis. Children, 1935, 49, 1185—1188).—Increases in wt. resulting from substitution of special mixed cereals for ordinary cereals in the diet were  $>$  those attributable to their vitamin- $B$  content. CH. ABS. (p)

**Lactoflavin, a possible contaminant of vitamin-free diets.** G. C. SUPPLEE, G. E. FLANIGAN, Z. M. HANFORD, and S. ANSBACHER (J. Biol. Chem., 1936, 113, 787—792).—Lactoflavin (I), determined by the fluorescence method, is present in crude and certain "vitamin-free" caseinogen (II) preps. Repeated extraction of crude (II) with dil. aq. NaCl at the isoelectric point gives a prep. free from (I). H. D.

**Nature and partial isolation of the substance curative of the pellagra-like condition [in rats and chicks] due to dietary egg-white.** J. G. LEASE (Z. Vitaminforsch., 1936, 5, 110—118).—The principle (I) (not identical with vitamin- $B_2$ ) is not extracted from liver or kidney (in which it occurs) by org. solvents or  $H_2O$ . Acid- or protease-hydrolysates, however, yield aq. extracts containing (I), which is pptd. (from MeOH) by  $Et_2O$  and  $EtOAc$  but not by  $COMe_2$  or (from  $H_2O$ ) by protein-precipitants (excepting phosphotungstic acid). (I) is dialysable, gives a positive biuret reaction, and is stable to heat, acids, and alkalis but not to oxidation, autoclaving, or ultra-violet irradiation. (I) is active when administered orally or parenterally. F. O. H.

**Further evidence for the existence of vitamin- $B_1$ .** O. L. KLINE, C. A. ELVEHJEM, and E. B. HART (Biochem. J., 1936, 30, 780—784; cf. this vol., 390).—The existence of vitamin- $B_1$  and its necessity for the normal nutrition of rats are confirmed (cf. Reader, A., 1930, 380). J. N. A.

**Treatment of infantile scurvy with ascorbic acid.** E. GOETTSCH (Amer. J. Dis. Children, 1935, 49, 1441—1448).—Intravenous injection of 400 mg. of ascorbic acid caused rapid healing. Calcification was more rapid than when orange juice was given. CH. ABS. (p)

**Effect of administration of vitamin- $C$  on the reticulocytes in certain infectious diseases.** J. M. FAULKNER (New England J. Med., 1935, 213, 19—20). CH. ABS. (p)

**Effect of ascorbic acid on coagulation of blood in normal and pathological conditions.** L. COTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 697—700).—Ascorbic acid injected intravenously frequently reduces the time of coagulation, particularly in hæmophilia. R. N. C.

**Action of ascorbic acid on blood coagulation *in vitro* and *in vivo* in the rabbit.** C. J. HANUT (Compt. rend. Soc. Biol., 1936, 121, 1338—1340).—Ascorbic acid accelerates coagulation of recalcified oxalated blood *in vitro* at a concn. of 0.005—0.02% and retards it at higher concns. through its effect on the reaction of the mixture; when neutralised it does not affect coagulation. It accelerates coagulation of recalcified oxalated or citrated plasma from rabbits when injected intravenously. R. N. C.

**Action of ascorbic acid on blood coagulation in normal or vitamin- $C$ -deficient guinea-pigs.** C. J. HANUT (Compt. rend. Soc. Biol., 1936, 121, 1341—1342).—Ascorbic acid accelerates coagulation in normal animals, but does not affect it in the deficient animal that is showing signs of scurvy. R. N. C.

**Anticoagulant action *in vitro* of complex salts derived from vitamin- $C$  and copper, titanium, or zinc, associated with other metals.** F. ARLOING, A. MOREL, and A. JOSSEAND (Compt. rend. Soc. Biol., 1936, 121, 1479—1480).—The anticoagulant actions of Cu and Ti complexes are  $<$  those of Fe complexes. Zn in an Fe complex increases its anticoagulant action, unless Pb is also present, whilst complexes containing Zn without any other multivalent metal show the greatest anticoagulant action. R. N. C.

**Modifications of the antirachitic activity of orthophosphoric acid by fixation of alcoholic, phenolic, and glucosidic chains.** R. LECOQ and M. L. BARBAN (Bull. Soc. sci. Hyg. aliment., 1935, 23, 121—132; cf. A., 1935, 109, 238, 657).—The activity of  $H_3PO_4$  is not seriously affected by esterification with alcohols; it is slightly retarded in Na alkyl phosphates and accelerated in the Ca salts. Phenolic esterification inhibits the activity. The activity is scarcely affected by esterification with open-chain sugars, whether or not basic groups are present, but is largely inhibited by esterification with inositol. R. N. C.

**Ascorbic acid as a precursor of serum complement.** F. MARSH (Nature, 1936, 137, 618—619).—The complement complex diminishes or even disappears when ascorbic acid (I) is withdrawn from the food of the guinea-pig, and is restored to normal level by a diet rich in (I). L. S. T.

**Action of vitamin- $C$  on diphtheria toxin and the sensitivity of the whooping-cough bacillus to quinol and vitamin- $C$ .** O. GROOTTEN and N. BEZSSONOFF (Ann. Inst. Pasteur, 1936, 56, 413—426; cf. A., 1935, 1542).—Massive doses of neutralised ascorbic acid increase the resistance of guinea-pigs to diphtheria toxin. The activity is distinctly  $<$  that reported by Harde (A., 1934, 1271). H. G. R.

**Capacity of synthesis of ascorbic acid in the fetus.** A. GIROUD, A. S. RUIZ, R. RATSIMAMANGA, M. RABINOWICZ, and E. HARTMANN (Compt. rend. Soc.



Biol., 1936, 121, 1062—1063).—Fœtal ascorbic acid (I) is > maternal (I) in the organs of the rabbit, rat, and guinea-pig, but less in cattle and sheep; synthesis is probable in the first three species. R. N. C.

**Diminution of the iodine value of the liver- and adrenal fats of the guinea-pig in avitaminosis-C.** L. DE CARO and M. GIANI (Boll. Soc. ital. Biol. sperim., 1935, 10, 835). R. N. C.

**Variations of the ascorbic acid content in the puerperal state.** I. F. GUERCIO, G. PICINELLI, and H. HAMBURGER (Boll. Soc. ital. Biol. sperim., 1935, 10, 640—643).—Introductory. R. N. C.

**Vitamin-C content of the aqueous humour and its antiscorbutic action.** C. CELLA and I. D. GEORGESCU (Compt. rend. Soc. Biol., 1936, 121, 1116—1119). R. N. C.

**Vitamin-C content of different parts of the nervous system.** F. PLAUT and M. BÜLOW (Z. ges. Neurol. Psychiat., 1935, 153, 182—192).—The ascorbic acid content of all parts of the human brain declined with advancing age but at relatively different rates; the cerebral content was greatest in the fœtus, the cerebellar content in infancy, and that of the spinal cord in old age. The content of the cerebral and cerebellar cortex was > that of the medulla at all ages except in senility. Observations on the rabbit, dog, cat, and calf gave comparable results.

NUTR. ABS. (*m*)

**Distribution of vitamin-C in different parts of common Indian foodstuffs.** M. N. RUDRA (Biochem. J., 1936, 30, 701—703).—The vitamin-C (I) distribution in the skin, flesh, leaves, and seeds of 21 different fruits and vegetables was studied. (I) is more conc. in the skin than in the flesh; with root vegetables the greatest concn. is in the leaves. With animal foods the concns. were in the order: liver > kidney > bone-marrow > milk > heart > muscle.

H. D.

**Determination of ascorbic acid.** K. WACHHOLDER and H. H. PODESTÀ (Z. physiol. Chem., 1936, 239, 149—161).—The methods of Bezssonoff *et al.* (A., 1934, 1146), Fujita *et al.* (A., 1935, 793), and Tillmans are not sp. and should be rejected. Those of Folin (A., 1930, 630) and Martini *et al.* (A., 1934, 1271) are trustworthy but for each animal, organ, and fluid tests must be made to show which of the two methods gives the lower and hence more sp. val.

W. McC.

**Chemical and biological assay of vitamin-C.** H. C. HOU (Chinese J. Physiol., 1936, 10, 191—196).—In guinea-pigs the curve of response to different amounts of ascorbic acid (I) was a straight line. Satien pumelo juice gave nearly the same chemical and biological assay vals. for (I). Green amaranth grown with exclusion of short ultra-violet rays showed a difference between the two vals., but this was < that for amaranth grown in the open. Mixtures containing (I) and small amounts of lucerne were more active than when larger amounts of the latter were used.

J. N. A.

**Antirachitic factor in human milk.** I. A. SABRI and M. M. FIKRI (Arch. Dis. Childhood, 1935, 10, 377—380).—Irradiated (ultra-violet) fat from

the milk of healthy mothers with normal children afforded nearly complete protection from rickets when incorporated in the rachitogenic ration of rats to the extent of 4%, whilst that from mothers whose children were rachitic gave similar protection only when it constituted 8% of the diet.

NUTR. ABS. (*m*)

**Comparison of the vitamin-D contents of Guernsey and Shorthorn butter (milk).** S. K. KON and K. M. HENRY (Biochem. J., 1936, 30, 776—779).—Under similar conditions of feeding and management, butter fat from Guernsey and Shorthorn cows contained 0.35 and 0.28 international units of vitamin-D per g., respectively; the difference is not statistically significant. If the relationship is generally valid, the relative contents of the two milks could be expressed by the ratio of the % fat.

J. N. A.

**Dietary requirements for lactation.** V. Presence of a second lactation factor in yeast. W. NAKAHARA, F. INUKAI, S. KATO, and S. UGAMI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 47—52; cf. this vol., 227).—Yeast contains a second dietary factor,  $L_2$ , necessary for lactation. It is different from  $L_1$  (originally called  $L$  and obtained from liver and yeast) and is non-adsorbable on acid earth.

J. N. A.

**Nutritional deficiency causing gizzard erosions in chicks.** H. J. ALMQUIST and E. L. R. STOKSTAD (Nature, 1936, 137, 581—582).—Gizzard erosion is a separate deficiency disease which can be corr. by a new fat-sol. factor, probably vitamin in nature, present in kale and lucerne. The new factor, which is localised in the saponifiable fraction of the extracts, is distinct from the anti-hæmorrhagic vitamin.

L. S. T.

**Biological effectiveness of  $\alpha$ -particles as a function of ion concentration produced in their paths.** R. E. ZIRKLE (Amer. J. Cancer, 1935, 23, 558—567).—The effectiveness of irradiation ( $B$ ) of fern spores depends on the no. of ions produced in the nucleus and on the ionisation per unit path ( $I$ ) which varies in a characteristic manner along the path. The relationship,  $B = kI^{2.5}$ , is established ( $k$  is a proportionality const.).

CH. ABS. (*p*)

**Inheritance of sugar content in cucurbits.** V. V. ARASIMOVITSCH (Bull. Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 5—30).—Inheritable characteristics in respect of total sugars, sucrose (I), fructose (II), and glucose (III) are frequently observed in hybrids. (I), (II), and (III) are polymer characters, are dominant for some hybrids and absent from others. Dominance of (III) is more frequent than that of (II). (I) is often polymer-recessive.

CH. ABS. (*p*)

**Distribution and translocation of sugars in sugar-beet.** I. Sugars in the tissue elements of sugar-beet in relation to its sugar content. II. Connection between vascular bundles of separate rings in the root and vascular bundles of separate leaves. E. F. VOTCHAL (Nauch. Zap. Sach. Prom., 1934, 11, Book 40, No. 2, 34—36, 36—38).

CH. ABS. (*p*)

**Breeding of coumarin-free clover.** R. B. GELTSCHINSKAJA and M. A. BORDUNOVA (Bull.



Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 315—323).—The coumarin content of clover varies with individual plants and increases up to the flowering period. Vals. for red clover were 1.0—0.056 and for yellow clover 0.86—0.062%.

CH. ABS. (p)

**Chemotropic irritation of roots.** B. NIKLEWSKI, M. KAHLÓWNA, and M. DYDÓWNA (Polish Agric. Forest. Ann., 1935, 34, 457—489).— $K_2HPO_4$ ,  $KH_2PO_4$ ,  $K_2SO_4$ , and  $KNO_3$ , even in 0.0001M solutions, caused irritation of *Sinapis* roots.  $NH_4Cl$ ,  $KCl$ ,  $NaCl$ , and  $CaCl_2$  had little or no action. Non-electrolytes from stall manure, humus, etc. were irritant at dilutions of 1 in  $10^8$ . The action is associated with substances of certain mol. size.

CH. ABS. (p)

**Ionic antagonism in the phenomenon of imbibition.** D. KOHLER (Compt. rend. Soc. Biol., 1936, 121, 1308—1311).— $Na^+$ ,  $K^+$ ,  $Mg^{++}$ , and  $Ca^{++}$  act antagonistically to one another in their effects on imbibition by *Laminaria*, the coeff. of imbibition of mixtures of two of the ions being always < the calc. val. assuming that the effects are additive.  $Ca^{++}$  exhibits the greatest antagonism to the other ions.

R. N. C.

**Kinetics of penetration. XIII. Effect of  $p_H$  on the entrance of potassium into *Nitella* at low concentrations.** A. G. JACQUES (Proc. Nat. Acad. Sci., 1936, 22, 191—193).—Between  $p_H$  6 and 8, the tendency of K to enter the sap of *Nitella* cells from external solutions in which  $[K^+]=10^{-5}M$  decreases with rise of  $p_H$ , the  $[Cl^-]$  remaining const. F. A. A.

**Moisture relations of pecan leaves.** A. H. FINCH and C. W. VAN HORN (Science, 1936, 83, 260).—The % of  $H_2O$  in mature leaves is practically const. and independent of differences in soil- $H_2O$  when conditions for max. transpiration obtain. A considerable degree of drought may occur before transpiration ceases or before  $CO_2$  entrance into the leaf and the interruption of photosynthesis takes place. With a reduced N content and practically unimpaired photosynthesis conditions favouring carbohydrate storage are produced by moderate drying of the soil. Soil-moisture control may be an important means of regulating the formation and utilisation of carbohydrate reserves in the tree.

L. S. T.

**Cell sap of Characeae.** R. COLLANDER (Protoplasma, 1936, 25, 201—210).—Comparison of plants grown in fresh and in brackish  $H_2O$  shows differences in sap concn. which are  $\ll$  those in the two media. The difference between the total salt concn. in the sap and that of the corresponding medium is approx. the same in both cases. The case of absorption of cations is in the order  $K > Na > Ca, Mg$ . The ratio  $K/Na$  in the sap varies with the species. A. G. P.

**Relationship of the phosphate concentration of solution cultures to the type and size of root systems and the time of maturity of certain plants.** A. L. SOMMER (J. Agric. Res., 1936, 52, 133—148).—Increasing  $[PO_4^{---}]$  in the nutrient is associated with a decreasing root/top ratio and later maturation.

A. G. P.

**Rôle of potassium in the sugar synthesis of *Sorghum saccharatum* (sugar sorghum).**

I. N. G. CHOKKANNA (Z. Pflanz. Düng., 1936, 43, 43—69).—In flowing-nutrient cultures K protects the plant to some extent against the ill-effects of low temp. The height of the plants and the stem/leaf (wt.) ratio decrease with increasing K content. With conc. (stationary) media the major portion of the K intake occurs in the early growth stages. Evidence of "luxury" consumption is obtained. With increasing K dosage the ratio N/K and the amounts of Ca and P taken up by the plant decline. The ratio protein-/total N in leaves is > in stems and is unaffected by the K supply. The total sugar and the % sucrose (I) in the total increase with the K given. Within the plant K tends to maintain a neutral sap and suppress the inversion of (I) by acids or enzymes.

A. G. P.

**Effect of glycerol and mannose on metabolism of the nucleus in [embryonic cells of] the lupin.** G. DELOFFRE (Compt. rend. Soc. Biol., 1936, 121, 1100—1103).—Glycerol (I) and mannose (II) are both assimilable, producing regeneration and preventing diminution of the nucleus. (I) is more assimilable than (II), but < glucose. (II) acts partly as an assimilable substance, and partly as a toxic substance, causing withering and decay of the embryo.

R. N. C.

**Metabolism of the phosphorus compounds of the acorn during germination in light.** E. MICHEL-DURAND (Compt. rend., 1936, 202, 866—867).—Analysis of various parts of oak plants about 80 days old showed that P compounds were present mainly in the roots and leaves. The physiological activity of the organs is roots > leaves > cotyledons.

J. N. A.

**Effect of insulin on plant respiration.** N. L. PAL and U. N. CHATTERJI (Nature, 1936, 137, 535—536).—The leaves of *Hiptage madablota* and *Allium tuberosum* respire at a higher rate when injected with insulin (40 units per 100 c.c.) than when injected with  $H_2O$ . Phylloclades of *Opuntia Dillenii* show a lower rate of  $CO_2$  evolution.

L. S. T.

**Chlorophyll fluorescence and carbonic acid assimilation. V. Relation between leaf fluorescence and oxygen assimilation.** H. KAUTSKY and W. FLESCH (Biochem. Z., 1936, 284, 412—436).—The fluorescence of leaves of *Parietaria officinalis* on ultra-violet irradiation varies with the proportion of  $O_2$  in the surrounding atm. With < 0.5% of  $O_2$ , fluorescence does not increase with increased time of irradiation.  $CO_2$  apparently plays no part in the phenomenon. The effect with leaves differs from that of chlorophyll (I) adsorbed on  $Al(OH)_3$ , the curves indicating dissociation of  $O_2$  in the leaf. The rôle of (I),  $O_2$ , and  $CO_2$  in plant respiration is discussed.

F. O. H.

**Explanation of the relatively large concentration of  $O^{18}$  in the atmosphere.**—See this vol., 698.

**Plant growth in relation to partial pressures of oxygen.** B. N. SINGH and G. P. KAPOOR (Proc. Indian Acad. Sci., 1936, 3, B, 238—245).—With increasing  $[O_2]$  dry-matter production by wheat plants increases, at first roughly proportionally, subsequently reaching a stationary and finally a



declining phase. The initial increase is attributed to a stimulation of assimilation and respiratory processes. The age of the plants is an influential factor.

A. G. P.

**Different action of auxin-*a* and of heteroauxin.** J. VAN OVERBEEK (Proc. Nat. Acad. Sci., 1936, 22, 187—190).—The growth-substance curvatures of twice-decapitated *Avena* coleoptiles exposed to visible radiation are < those of non-irradiated controls, when pure auxin-*a* (I) or an extract containing auxin-*a* and -*b* is used; no difference is found when pure heteroauxin (II) (cf. Kögl *et al.*, A., 1934, 1418) is used. Sections of coleoptiles applied to agar blocks containing (I) or (II) cause destruction of these substances, (I) more rapidly than (II).

F. A. A.

**Cell sap acidity and the incidence of white-fly (*Bemesia gossypiperda*) on cottons.** M. A. HUSAIN, A. N. PURI, and K. N. TREHAN (Current Sci., 1936, 4, 486—487).—The gradient in  $p_H$  of cell sap from top to bottom of cotton plants varies with type and age of the plant. Incidence of white-fly attack is greater at higher  $p_H$  (after a time lag); immunity of some varieties to attack may be due to  $p_H$  of sap, and might thus be artificially induced.

E. W. W.

**Effect of lead on plant growth.** K. SCHARER and W. SCHROPP (Z. Pflanz. Düng., 1936, 43, 34—43).—In sand cultures barley, oats, and, notably, wheat were very sensitive to injury by Pb. Rye and maize were more resistant. Maize was affected by [Pb] > 10 mg. per litre of nutrient. Small concns. had a stimulatory action in some cases.

A. G. P.

**Action of sugars on *Saprolegnia*.** F. MOREAU (Compt. rend., 1936, 202, 1086—1087).—Dil. solutions of sugars are toxic to *Achlya colorata* (glucose and fructose > maltose and sucrose). Starch is non-toxic.

W. McC.

**Hydrocyanic acid production by leaves of *Photinia*, Lindl.** R. SALGUES (Compt. rend., 1936, 202, 971—973).—The loss of HCN during the period of rapid development attains a max. in September, following which the content rises until midwinter, and again declines until the leaves fall. The life cycle is 20 months.

P. G. M.

**Occurrence of cyanogenetic glucosides in *S. African species of Acacia*.** I. D. G. STEYN and C. RIMINGTON (Onderstepoort J. Vet. Sci., 1935, 4, 51—63).—The glucosides occurred in *A. giraffe*, *A. litakunensis*, *A. stolonifera*, *A. robusta* (without an enzyme effecting its decomp.), and *A. lasiopetala*. That from the last named (*acacipetalin*),  $C_{11}H_{17}O_6N$ , had m.p. 176—177,  $[\alpha]_D^{25}$  -35.96° and was rapidly decomposed by emulsin. *A. karroo* contained no glucoside. Means of feeding cyanogenetic pods to cattle with safety are described.

CH. ABS. (p)

**Composition of pure-bred and hybrid peas.** C. SOSA-BOURDOUIL (Compt. rend., 1936, 202, 1091—1093).—The C and H contents of *Pisum sativum*, L., *P. arvense*, L., and *P. Jomardii*, Schrank., of a cross between two varieties of the first, and of crosses between the first and each of the other two exhibit no appreciable differences but the N contents

of the crosses (1st—4th generation) are < those of the parent plants. In the crosses there is no direct relation between N content and colour or shape.

W. McC.

**Constituents of *Epimedium macranthum*.**—See this vol., 710.

**Heterosides of the fruits of *Sophora japonica*.** L. J. RABATÉ and J. DUSSY (Compt. rend., 1936, 202, 1117—1119; cf. Charaux *et al.*, A., 1935, 985, 1041).—In addition to sophoricoside, the pods of *S. japonica* contain rutoside and *sophoraflavanololide* (I) (yield 0.5%, m.p. 207—208°,  $[\alpha]_D$  -61° in EtOH. (I) is readily attacked by emulsin and, on hydrolysis with acid, yields a disaccharide (further hydrolysed to 2 mols. of glucose) and 3:5:7:4'-tetrahydroxy-flavone.

W. McC.

**Chemistry and pharmacological action of *Toddalea aculeata*.**—See this vol., 743.

**Saponin of the seeds of *Esculus turbinata*, Blume.**—See this vol., 732.

**Sapogenin of the roots of *Momordica cochinchinensis*.**—See this vol., 731.

**Chemical examination of the bark of *Moringa pterygosperma*.** S. GHOSH, R. N. CHOPRA, and A. DUTT (Indian J. Med. Res., 1935, 22, 785—788).—The bark contains a liquid base,  $C_7H_9N$  (*hydrochloride*, m.p. 254.4°,  $[\alpha]_D^{30}$  +1.8° in  $H_2O$ ), probably a  $C_5H_5N$  derivative or an ephedrine base, and an alkaloid, *moringinine*; it also contains org. acids, resins, a phytosterol, fixed and essential oils, and a waxy substance.

R. N. C.

**Deltaline, a new alkaloid from *Delphinium occidentale*.**—See this vol., 743.

**Monolupine, a new alkaloid from *Lupinus caudatus*.**—See this vol., 741.

**Isolation of a fourth crystallisable jack bean globulin by digestion of canavalin with trypsin.** J. B. SUMNER and S. F. HOWELL (J. Biol. Chem., 1936, 113, 607—610).—The *globulin*, obtained by tryptic digestion of canavalin (I), is sol. in  $H_2O$  and in 5% NaCl, but insol. in 0.2—1.0% NaCl at  $p_H$  6.5. The isoelectric point, determined by cataphoresis in 0.1N-OAc' buffer, is  $p_H$  4.8. It contains unoxidised S and tyrosine, but not tryptophan. A method for the prep. of (I) from jack bean meal is described.

J. N. A.

**Micro-determination of lactic and carbonic acids.** K. HINSBERG and R. AMMON (Biochem. Z., 1936, 284, 343—346).—Lactic acid is determined in blood (5 c.c.), pre-treated with  $CuSO_4$ - $Ca(OH)_2$ , by heating in a vac. in presence of  $MnSO_4$ - $KMnO_4$ , the  $MeCHO$  formed being absorbed in  $NaHSO_3$  and titrated iodometrically. Similar apparatus is used for  $CO_2$  (liberated by tartaric acid), which is absorbed in 0.2N-NaOH, excess of which is titrated by 0.1N-HCl in presence of phenolphthalein.

F. O. H.

**Spectrographic determination of certain elements by the arc process.**—See this vol., 695.

**Nephelometric micro-determination of chlorine in ash of organic materials.**—See this vol., 693.





# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JULY, 1936.

### General, Physical, and Inorganic Chemistry.

Intensity anomalies in the Lyman series of hydrogen. T. TAKAMINE and T. SUGA (Nature, 1936, 137, 827—828). L. S. T.

Oxygen in solar prominences. A. L. NARAYAN and T. ROYDS (Current Sci., 1936, 4, 734).—The  $O_2$  triplet at  $\lambda$  7770 Å. has been observed in a prominence at a height of 9000 miles above the chromosphere. L. J. J.

Zeeman and Paschen-Back effects in the case of extreme  $j$ - $j$  coupling.  $2p^5ns$  configurations of neon. P. JACQUINOT (Compt. rend., 1936, 202, 1578—1580). H. J. E.

Induced predissociation in the absorption spectrum of sulphur. V. KONDRATEEV and E. OLSSON (Z. Physik, 1936, 99, 671—676).—The energy of dissociation of the normal state of  $S_2$  is  $> 4.1$  volts. A. B. D. C.

Intensity distribution in the diffuse series of potassium. P. A. COENEN and H. A. KRAMERS (Physica, 1936, 3, 341—345).—Quantum-mechanical calculation of the intensities of the diffuse series of K is in accord with experiment (this vol., 261) and explains the anomaly of the exceptional weakness of the second line. J. W. S.

Colour phenomenon in "colloidal" potassium vapour. J. KUNZ (Physikal. Z., 1936, 37, 415).— $H_2$  is passed over molten K in an evacuated tube. On placing the tube in connexion with another exhausted tube an intense but short-lived colour appears in the second tube. The colour varies along the tube. The pptd. K is strongly photo-electric. A. J. M.

Lines in the arc spectrum of cobalt not emitted by Co I. M. T. ANTUNES and M. A. CATALAN (Anal. Fis. Quím., 1935, 33, 391—432).—A crit. examination is made of the lines between 2449 and 19,778 Å. attributed to Co, and a list of the respective levels, but omitting lines emitted by Co I, is given. F. R. G.

Structure of the spectrum of unexcited cobalt. M. A. CATALAN and M. T. ANTUNES (Anal. Fis. Quím., 1936, 34, 207—297).—For Co I,  $\lambda$  and  $\nu$  with emission and absorption intensities and levels are tabulated for the range 2012—18,273 Å. A supplement to the list of lines not emitted by Co I (see above) is also given. F. R. G.

Electrical quadrupole moment and magnetic moment of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . H. SCHÜLER and T. SCHMIDT (Z. Physik, 1936, 100, 113—116).—The quadrupole moment of the two isotopes is  $\sim 0.1 \times$

$10^{-24}$ , and the magnetic moments are 2.5 and 2.6 for 63 and 65, respectively. A. B. D. C.

Absorption spectrum of rubidium. N. T. ZÉ and W. W. PO (Compt. rend., 1936, 202, 1428—1430).—A no. of new lines, observed at 350—550°, are recorded. L. J. J.

Transmission and reflexion of thin silver layers in the infra-red and ultra-violet. F. GOOS (Z. Physik, 1936, 100, 95—112).—Transmission and reflexion data are given for Ag layers 0.8—142 m $\mu$  thick on quartz from 1050 to 265 m $\mu$ . A. B. D. C.

Spectra of xenon in the extreme ultra-violet. J. C. BOYCE (Physical Rev., 1936, [ii], 49, 730—732).—Using increased dispersion and resolving power, revised and extended data and classifications are tabulated for Xe I, II, III in the range  $\lambda\lambda$  2000—600. N. M. B.

Absorption spectrum of hydrogen. III. Auto-ionisation in the term  $3p-^1\Pi_u$  of  $H_2$  and its selection rules. Ionisation energy of  $H_2$ . H. BEUTLER and H. O. JÜNGER (Z. Physik, 1936, 100, 80—94; cf. this vol., 261).—The ionisation energy of  $H_2$  is  $124,429 + 13 \text{ cm.}^{-1}$ . A. B. D. C.

Reversal temperature and population of excited states in the caesium discharge. F. L. MOHLER (J. Res. Nat. Bur. Stand., 1936, 16, 227—231).—Data are recorded for the lines  $6S-nP$  ( $n=6-11$ ) at a no. of pressure and current vals. L. J. J.

Analytical and quantitative lines of hafnium in the arc spectrum. S. PINA DE RUBIES and J. G. AGUADO (Anal. Fis. Quím., 1935, 33, 549—565).—The method previously described (A., 1934, 48) is applied to Hf. A list of Hf lines and of those lines of other elements which might be mistaken for the principal Hf lines, is given. F. R. G.

Quartz mercury arc. A. J. ALLEN (Science, 1936, 83, 336). L. S. T.

Fluorescent emission of the mercury line 2537 Å. at pressures between  $10^3$  and  $10^1$  mm. P. PRINGSHEIM and O. D. SALTMARSH (Proc. Roy. Soc., 1936, A, 154, 90—95).—The degree of polarisation of the fluorescence radiation of Hg has been measured. The phenomena are analogous to those observed with Na vapour. It is considered that the observed fluorescence is due, not to Hg atoms, but to van der Waals mols. L. L. B.

Electrical quadrupole moment of the  $^{209}\text{Bi}$  nucleus. H. SCHÜLER and T. SCHMIDT (Z. Physik, 1936, 99, 717—728).—This quadrupole moment is  $-0.4 \times 10^{-24}$ . A. B. D. C.



Scale of wave-lengths in the infra-red solar spectrum. H. D. BABCOCK, C. E. MOORE, and W. P. HOGE (*Astrophys. J.*, 1936, **83**, 103—120).

L. S. T.

Ultra-violet spectrum of the night sky. A. ARNULF (*Compt. rend.*, 1936, **202**, 1412—1414).—Data are recorded for  $\lambda\lambda$  3556—2979 Å. L. J. J.

Enhancement of red lines and bands in the auroral spectrum from a sunlit atmosphere. L. VEGARD and E. TØNSBERG (*Nature*, 1936, **137**, 778—779).—Sunlight produces a pronounced enhancement of certain bands of the first positive group of  $N_2$ , and of the red line 6300 Å., which is due probably to production of  $O_3$  by the sun's radiation.

L. S. T.

Colour temperatures and continuous absorption of hydrogen for stars of the first spectral types. A. ARNULF, D. BARBIER, D. CHALONGE, and (ILLE.) R. CANAVAGGIA (*Compt. rend.*, 1936, **202**, 1571—1573).

H. J. E.

Search for the bands of boron compounds in stellar spectra. P. SWINGS (*Astrophys. J.*, 1936, **83**, 177—178).—BH bands in late-type stars could not be detected.

L. S. T.

Spectrum of Arcturus. S. G. HACKER (*Astrophys. J.*, 1936, **83**, 140—161).—At. and mol. spectra identified in the region 4119—6743 Å. are summarised.

L. S. T.

Resonance phenomena in ionised gases. W. SIGRIST (*Helv. phys. Acta*, 1935, **8**, 317—320; *Chem. Zentr.*, 1935, ii, 1316—1317).

H. J. E.

Sparks between flame electrodes. M. PIERUCCI (*Nuovo Cim.*, 1935, [ii], **12**, 240—242; *Chem. Zentr.*, 1935, ii, 1317).—A spark discharge between two Bunsen coal-gas flames, inclined towards one another so as to serve as electrodes, has been investigated, using plain gas flames and flames charged with salt solutions from an atomiser. In general at. but not ionic spectra are emitted.

J. S. A.

Investigation of electrical discharges in gases with the cloud chamber. E. FLEGLER and H. RÄTHER (*Z. Physik*, 1936, **99**, 635—642).—Study of initiation of self-maintained discharges shows that photo-ionisation, rather than space charge, gives the necessary initial conditions.

A. B. D. C.

Increase of sparking potential by irradiation with ultra-violet light. W. SEITZ and W. FÜCKS (*Naturwiss.*, 1936, **24**, 346).—Contrary to expectation, for certain cathodes (e.g., Ag) and gases (e.g., A) at moderate pressures, an increase in the sparking potential was observed when the cathode was irradiated with ultra-violet light. For a Zn cathode and A, however, the potential decreased.

A. J. M.

Spectral investigation of the thread ray discharge. W. HANLE and W. NOLLER (*Physikal. Z.*, 1936, **37**, 412—414).—The spectrum of the thread ray and its surrounding radiation has been investigated, and the electron velocity distribution in both radiations is obtained from a study of intensities in the line spectra. The methods of excitation are discussed, and the effect of an electric field on the radiation is examined.

A. J. M.

Fine structure of the  $L_{23}$  absorption edge of magnesium metal. H. W. B. SKINNER and J. E. JOHNSTON (*Nature*, 1936, **137**, 826—827).

L. S. T.

Absorption of soft X-rays in aluminium. G. B. BANDOPADHYAYA and A. T. MAITRA (*Phil. Mag.*, 1936, [vii], **21**, 869—880).—The mass absorption coeff. of Al was measured for  $\lambda\lambda$  7—24 Å.

H. J. E.

Atomic scattering factor of cadmium for Cu  $K\alpha$  radiation. G. W. BRINDLEY (*Proc. Leeds Phil. Soc.*, 1936, **3**, 200—207).—The intensities of reflexion of Cu  $K\alpha$  radiation from finely divided Cd have been measured and compared with those of Al, the at. scattering factor of the Cd atom at room temp. being deduced. The irregularities when plotted against  $\sin \theta/\lambda$ , similar to those found with Zn, indicate that in Cd the atoms have a greater mean amplitude of vibration parallel to the  $c$  axis than in the basal plane.

J. W. S.

Atomic scattering factor of zinc. C. M. KOTIN and J. LOSADA (*Anal. Fis. Quim.*, 1935, **33**, 597—601).—The scattering curve for Zn has been obtained by the Debye-Scherrer method, and is comparable with the theoretical curve of James *et al.* (cf. A., 1931, 889).

F. R. G.

Screening doublets of X-ray spectra. A. E. SANDSTROM (*Z. Physik*, 1936, **99**, 622—625).

A. B. D. C.

Constant  $A$  in Richardson's equation. E. WIGNER (*Physical Rev.*, 1936, [ii], **49**, 696—700).—The chemical const. of the electron gas in the high-temp. region, where all measurements are made, is different from its val. at very low temp. (cf. Herzfeld, A., 1930, 391). The high-temp. val. of the Richardson const.  $A$ , which thus differs from the low-temp. val., is calc. in terms of thermodynamic quantities.

N. M. B.

Theory of the work function. II. Surface double layer. J. BARDEEN (*Physical Rev.*, 1936, [ii], **49**, 653—663; cf. A., 1935, 1050).—In order to determine the moment of the electrostatic surface double layer, the electronic surface charge density is calc. For Na, the vals. for the work function and moment of the double layer are 2.35 and 0.4 e.v. (including the effect of polarisation forces), and 2.0 and 1.0 e.v. (omitting these forces), respectively.

N. M. B.

Photo-electric properties of sodium films on aluminium. J. J. BRADY and V. P. JACOBSMEYER (*Physical Rev.*, 1936, [ii], **49**, 670—675; cf. A., 1932, 1184).—The max. sensitivity of Na films on Al was not attained for a film thickness of < 80 mol. layers; it then remained const. for greater thicknesses. No detectable photo-current was observed for < 5 mol. layers. Spectral distribution curves, analysed according to Fowler's theory, indicate a const. val. of 5150 Å. for the threshold of the Na film for all film thicknesses. Current-voltage curves for different thicknesses, analysed according to Du Bridge's theory, indicate that the work function of the various films is the same, the val. for the freshly distilled Al on which the deposits were made being 4.08 volts, which gives the val. 3020 Å. for the threshold of Al. The photo-electric current showed a decrease, probably due to



surface migration of the Na atoms in forming aggregates, immediately after forming a film, but the decrease was much less for films  $> 50$  mol. layers.

N. M. B.

**Temperature of electrons ( $T_e$ ) in the positive column of a discharge in a mixture (Ne-Na).** W. UYTERHOEVEN and C. VERBURG (Compt. rend., 1936, 202, 1498—1500; cf. A., 1935, 1438).—The positive ionic current collected near the walls is a max. when the wall temp. is  $260^\circ$ .  $T_e$  ( $1T_e = 13,200^\circ$  abs.) is a max. at  $240^\circ$ , i.e., when there is 0.01 Na ion for 100 Ne, but decreases towards the centre of the tube. The increase in potential gradient is attributed to the presence of easily ionisable Na.

R. S.

**Influence of metastable atoms on the electron temperature in the positive column.** G. SPIWAK and E. REICHRUDEL (Physica, 1936, 3, 301—306).—At high c.d. and with large concns. of impurity, ionisation of the gases and impurities by collision with electrons plays the principal part in controlling electron temp., but with low c.d. and with small concns. of impurity metastable atoms have a considerable influence.

J. W. S.

**Cesium-oxygen films on tungsten.** J. H. LEES (Phil. Mag., 1936, [vii], 21, 1131—1139; cf. A., 1925, ii, 254).—Max. emission from Cs-coated W filaments at  $780^\circ$  abs. is observed after treatment with  $O_2$  at relatively high pressure, followed by momentary heating to  $1800^\circ$  abs. The emission is decreased by activation above  $2000^\circ$  abs., owing to evaporation of the activated O. The adsorption of  $O_2$  reaches equilibrium rapidly. Some evidence is obtained that  $O_2$  penetrates the W lattice.

J. W. S.

**Method of measuring secondary-electron emission from filaments.** L. R. G. TRELOAR (Proc. Physical Soc., 1936, 48, 488—497).—An indirect method is described, and gives results for W and Ta filaments in agreement with available data.

N. M. B.

**Electron energies and excitation in the helium positive column.** F. L. JONES (Proc. Physical Soc., 1936, 48, 513—526).—A distribution function is suggested to account for available data on the intensities of lines emitted from He discharges, the variation of the intensities with gas pressure is calc., and curves are drawn for the relative intensities of the various lines at different pressures, and compared with experimental curves. From the general agreement an expression for the distribution is given. Results indicate that the energy distribution of the majority of the electrons is determined by diffusion, but a small fraction form a group with Maxwell energy distribution, and of predominating influence in the He discharge at high pressure as regards excitation and ionisation.

N. M. B.

**Energy losses of electrons striking the nitrogen nucleus.** J. E. ROBERTS, R. WHIDDINGTON, and E. G. WOODROOFE (Proc. Leeds Phil. Soc., 1936, 3, 189—190).—When electrons of medium energy are passed through N, at low pressure, the scattered electrons, on analysis, show not only a strong line corresponding to elastic collisions without energy loss, but also bands corresponding to mol. excitations.

Singlet transition bands are observed at higher impact energy (120 e.v.) and triplet bands at 16—25 e.v. The max. of these bands correspond approx. in some cases with known spectroscopic vals.

J. W. S.

**Concentration of electron beams by gases.** I. SOKOLSKAJA (Tech. Phys. U.S.S.R., 1936, 3, 28—38).—The relations between the focal length and gas pressure, beam current, velocity, and wall potential in A were investigated.

H. J. E.

**Determination of electron velocity by means of probe measurements.** W. DENECKE and E. LUBCKE (Physikal. Z., 1936, 37, 347—350).—It is shown that by the use of several test wires arranged in a certain part of the positive column of a glow discharge it is possible to obtain the velocity distribution of electrons, the space potential, the electron c.d., and electron concn.

A. J. M.

**Change in secondary-electron emission of insulators and semi-conductors on irradiation with electrons.** M. KNOLL (Naturwiss., 1936, 24, 345).—If an insulator is irradiated with electrons (500—5000 volts) there is a considerable change in the secondary-electron emission when tested with another electron beam. The secondary emission factor was lowered for  $Al_2O_3$ , glass,  $Cu_2O$ , and certain phosphors.

A. J. M.

**Scattering of positrons by electrons with exchange on Dirac's theory of the positron.** H. J. BHABHA (Proc. Roy. Soc., 1936, A, 154, 195—206).—Exchange may take place between the electron initially observed and one of the virtual electrons in states of negative energy. The process may be considered as one in which the initial electron and positron have been annihilated, giving rise simultaneously to a new pair.

L. L. B.

**Theory of the positron.** A. PROCA (Compt. rend., 1936, 202, 1366—1368).

R. S.

**Production of electron pairs.** J. C. JAEGER (Nature, 1936, 137, 781—782).—The absorption cross-sections per atom for the production of positive-negative electron pairs by  $\gamma$ -rays have been determined for Sn, Tb, and Pb. The Born approximation gives vals. which are too low, but the error decreases rapidly with decreasing at. no. and increasing energy of the  $\gamma$ -rays.

L. S. T.

**Law of impulse maintenance with the annihilation of positrons.** A. I. ALICHANIAN, A. I. ALICHANOV, and L. A. ARZIMOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 287—288, and Nature, 1936, 137, 703—704).—A system of counter tubes was used to measure quanta set free on annihilation of positrons from radio-P (obtained by bombardment of Al with  $\alpha$ -particles from Ra-C'). It was shown that two quanta are emitted in opposite directions as required by the impulse maintenance law.

A. J. M.

**At. wts. by calculation.** A. C. WOODMANSEY (Phil. Mag., 1936, [vii], 21, 1079—1081).—The at. wts. of simple elements are represented satisfactorily by the expression at. wt. =  $0.9935x + 0.0140y$ , where  $x$  = mass no.,  $y$  = at. no.

J. W. S.



**At. wt. of cadmium.** O. HÖNIGSCHMID and R. SCHLEE (Z. anorg. Chem., 1936, 227, 184—192).—The mean of eight argentometric titrations of  $\text{CdCl}_2$  gives Cd 112.41+0.002 (Ag 107.880, Cl 35.457), and of five titrations of  $\text{CdBr}_2$ , 112.41+0.004. This val. is identical with the international at. wt., and differs from Aston's by 0.2 unit. F. L. U.

**Revision of at. wt. of chromium. II. Study of the relations  $\text{CrO}_2\text{Cl}_2 : 2\text{Ag}$  and  $\text{CrO}_2\text{Cl}_2 : 2\text{AgCl}$ .** F. GONZALEZ NÚÑEZ (Anal. Fís. Quím., 1935, 33, 533—548; cf. A, 1930, 1337).—The at. wt. of Cr has been redetermined as 52.013+0.001.

F. R. G.

**Enrichment of nitrogen in the isotope  $^{15}\text{N}$ .** D. E. WOOLDRIDGE and F. A. JENKINS (Physical Rev., 1936, [ii], 49, 704).—Further enrichment of  $^{13}\text{C}$  by diffusion of  $\text{CH}_4$  in a Hertz apparatus has been obtained (cf. this vol., 574). This method has been extended to  $\text{N}_2$ . Isotope band heads due to  $^{14}\text{N}^{15}\text{N}$  had an intensity corresponding with an abundance of 3 at.-%  $^{15}\text{N}$ , an enrichment factor of approx. 10. N. M. B.

**Isotopic constitution of strontium, barium, and indium.** J. P. BLEWETT and M. B. SAMPSON (Physical Rev., 1936, [ii], 49, 778).—Mass spectrograph analyses of the ions of Sr, Ba, and In emitted when oxides of these elements are heated on W filaments give evidence of isotopes  $^{84}\text{Sr}$  and  $^{134}\text{Ba}$ , with abundance 0.5 and 1.8%, respectively. Other isotopes of Sr of masses 82, 83, 85, 89, and 90 were present to <1 in 2000, 1000, 2000, 500, and 2000, respectively, Ba isotopes of masses 132, 133, 139, and 140 to <1 in 2000, 1000, 400, and 1000, respectively, and In isotopes of masses 110, 111, 112, 114, 116, 117, 118, and 119 to <1 in 5000, 10,000, 5000, 200, 5000, 10,000, 8000, and 30,000, respectively (cf. Szilard, A., 1935, 276). N. M. B.

**Proof of the existence of the odd cadmium isotopes by band spectroscopy.** A. HEIMER and E. HULTHEN (Naturwiss., 1936, 24, 377).—Examination of the  $\text{CdH}/\text{CdD}$  spectrum over the range 3300—3400 Å. shows the presence (in order of intensity) of the following isotopes of Cd: 114, 112, 110, 111, 113, 116. A. J. M.

**Isotope displacement in the arc spectrum of platinum.** S. TOLANSKY and E. LEE (Nature, 1936, 137, 908).—Even isotope displacements in the Pt I spectrum (tabulated) are in good agreement with the results of Jaeckel and Kopfermann (this vol., 654).  $^{195}\text{Pt}$  has a nuclear spin of  $\frac{1}{2}$ , and approx. abundances of the isotopes 198, 196, 195, and 194 are 1 : 4 : 4 : 5. L. S. T.

**Spontaneous and artificial transmutations of atom nuclei.** K. C. KAR (Phil. Mag., 1936, [vii], 21, 1067—1078; cf. A., 1934, 5).—Mathematical. The wave-statistical theory developed previously is extended to explain the emission of long range  $\alpha$ -particles by radioactive elements and to explain artificial disintegration. J. W. S.

**Collision forces between light nuclei.** C. B. O. MOHR and G. E. PRINGLE (Nature, 1936, 137, 865—866).—Calculations made from measurements of the angular distribution of scattering of the slower  $\alpha$ -particles

in  $\text{H}_2$ ,  $\text{D}_2$ , and He indicate that the forces which come into play act at distances  $>10^{-12}$  cm. If the current method of explanation is to be retained forces of range  $>e^2/mc^2$  must be included. L. S. T.

**Structure of neutrons and  $\beta$ -disintegration.** D. MEKSYN (Nature, 1936, 137, 906).—It is assumed that when a neutron is formed from a proton and an electron the excess of energy of the particles is transformed into rest mass, energy and momentum being conserved. L. S. T.

**Possible effect of screening in the theory of  $\beta$ -disintegration.** M. E. ROSE (Physical Rev., 1936, [ii], 49, 727—729; cf. Konopinski, A., 1935, 1048).—Various considerations and calculations individually lead to the conclusion that the effect of screening is negligible. N. M. B.

**End-points of the  $\beta$ -ray spectra of radium-E and thorium-C''.** F. C. CHAMPION and N. S. ALEXANDER (Nature, 1936, 137, 744).—The end-points occur at  $1.35 \times 10^6$  and  $2.25 \times 10^6$  e.v., respectively. L. S. T.

**Excitation of  $\gamma$ -rays in boron.** S. KIKUCHI, H. AOKI, and K. HUSIMI (Nature, 1936, 137, 745).—The emission of  $\gamma$ -rays from B in presence of slow neutrons is confirmed. L. S. T.

**Scattering of neutrons by protons.** M. GOLDBABER (Nature, 1936, 137, 824—825).—The mean free path of the neutrons obtained from  $\text{D}_2\text{O}$  bombarded by radio-Th is  $4.5 \pm 1.5$  cm. of paraffin. Disagreement with the theoretical val. of 1.3 shows that there is no evidence of the existence of an excited state of the deuteron and that another model of the proton-neutron interaction is required. L. S. T.

**Experiments with neutrons produced by the bombardment of deuterons with deuterons.** S. KIKUCHI, S. NAKAGAWA, H. AOKI, and K. FUSHIMI (Proc. Phys.-Math. Soc. Japan, 1935, 17, 189—193).—The Fermi photon effect has been studied with deuteron-deuteron neutrons. The production of slow neutrons and their absorption by various elements and salts have been studied. Fermi's results are confirmed. CH. ABS. (e)

**Properties of slow neutrons.** B. PONTECORVO (Nuovo Cim., 1935, [ii], 12, 211—222; Chem. Zentr., 1935, ii, 1312).—The activity effect of neutrons slowed down by passage through material containing H is much  $>$  that of neutrons slowed down by other materials (Pb,  $\text{SiO}_2$ , C). J. S. A.

**Cross-section measurements with slow neutrons of different velocities.** H. VON HALBAN, jun., and P. PREISWERK (Nature, 1936, 137, 905—906).—The cross-section for neutron capture by B decreases with increasing energy of the neutrons (cf. this vol., 402). Results for neutrons captured by Li, Dy, Ag, and Rh are also given. In general, cross-sections for resonance neutron capture and for capture of thermal neutrons are greatest for nuclei the resonance levels of which have the lowest energy. L. S. T.

**Disintegration of boron by neutrons.** R. J. WALEN (Compt. rend., 1936, 202, 1500—1502).—The results are in agreement with the equation  $^{10}\text{B} + \frac{1}{2}\text{n} \rightarrow \frac{3}{2}\text{Li} + \text{He} + \text{Q}$ . R. S.



**Transformation of boron by slow neutrons.** M. J. DEISENROTH-MISSOVSKI, G. D. LATISCHEV, L. I. RUSSINOV, and R. A. EICHELBERGER (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 351—353).—The effect on the no. of transmuted particles in the nuclear reaction  ${}^7\text{Li} + {}^4\text{He}$ , of layers of  $\text{H}_2\text{O}$  of various thicknesses interposed between the source of neutrons and the B compound ( $\text{Me}_3\text{BO}_3$ ) was investigated. The curve between no. of transmuted particles and thickness of  $\text{H}_2\text{O}$  layer may be explained by supposing either that the neutrons are absorbed in the  $\text{H}_2\text{O}$ , or that the absorption of slow neutrons by B shows a resonance effect. A. J. M.

**Absorption of slow neutrons in boron.** F. RASETTI, D. P. MITCHELL, G. A. FINK, and G. B. PEGRAM (Physical Rev., 1936, [ii], 49, 777).—Using a method similar to that employed for Ag and Cd (cf. this vol., 264), the dependence of the capture cross-section on neutron velocity was determined. Results indicate that the absorption of thermal energy neutrons follows the  $1/v$  law. N. M. B.

**Disintegration of nitrogen by slow neutrons.** T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1936, [ii], 49, 778).—The reaction is found to be giving the val.  $0.58 \pm 0.03$  m.e.v. for the energy of disintegration  $Q_\alpha$ , calc. from range measurements, and eliminating a previous discrepancy (cf. this vol., 403; Chadwick, *ibid.*, 5). N. M. B.

**Artificial radioactivity.** K. DIEBNER and E. GRASSMANN (Physikal. Z., 1936, 37, 359—383).—A review.

**Induced radioactivity of short period.** T. BJERGE (Nature, 1936, 137, 865).—An arrangement for detecting induced radioactivity  $> 0.3$  sec. is described. When bombarded by a neutron source ( $\text{Be} + \text{Rn}$ ) of 350 millicuries, Be gives a strong activity of  $0.9 \pm 0.2$  sec. half-val. period and max. energy of  $6$  to  $8 \times 10^6$  e.v. The effect is not increased by surrounding the source with paraffin wax. The process leading to the active nucleus is discussed. No new activities were detected with Li, B, C, N, O, F, Na, Al, Cl, Fe, Ni, Cu, Zn, Se, Ag, Cd, Sn, or Pb. L. S. T.

**Disintegration of boron into three  $\alpha$ -particles.** P. I. DEE and C. W. GILBERT (Proc. Roy. Soc., 1936, A, 154, 279—296).—The disintegration of B by artificially accelerated protons takes place as follows:  ${}^{10}\text{B} + {}^1\text{H} \rightarrow {}^4\text{He} + {}^4\text{He} + {}^4\text{He}$ . The total energy released in the reaction is  $8.7 \pm 0.2 \times 10^5$  e.v. A theoretical picture of the process, involving the existence of an unstable  ${}^8\text{Be}$  nucleus, is given. L. L. B.

**High-velocity positive ions.** V. Disintegration of boron. VI. Disintegration of carbon, nitrogen, and oxygen by deuterons. J. D. COCKCROFT and W. B. LEWIS (Proc. Roy. Soc., 1936, A, 154, 246—261, 261—279; cf. A., 1934, 826).—V. Experiments on the disintegration of B by deuterons of energy 300—600 kv. have established the existence of two homogeneous  $\alpha$ -particle groups of range 4.5 and 14.7 cm. for deuteron energies of 560 kv. These groups are assumed to result from transmmutations in which  ${}^8\text{Be}$  and  ${}^9\text{Be}$  are produced. Two continuous distributions of doubly charged

ionising particles are also observed, probably due to the break up of the  ${}^{10}\text{B}$ -deuteron system into 3  $\alpha$ -particles.

VI. The disintegration of C, N, and O<sub>2</sub> by deuterons has been reinvestigated by an improved method. Several new groups of particles have been discovered, and all the reaction energies determined to within about 0.1 mv. The new results are used to correct Bethe's mass scale, and to check the energy balance in the process of positron emission from radio-N<sub>2</sub>.

L. L. B.

**Separation of radioactive atoms from the stable isotopic atoms.** O. ERBACHER and K. PHILIPP (Z. physikal. Chem., 1936, 176, 169—181).—The radioactive species of halogens produced by the action of neutrons on a liquid non-ionised org. halogen compound (I) are formed as ions and can be removed by shaking with  $\text{H}_2\text{O}$ . The (I) which dissolves in the  $\text{H}_2\text{O}$  at the same time is subsequently removed by extraction with  $\text{C}_6\text{H}_6$ , giving a practically pure aq. solution of the radioactive ions. In this way  $10^{-16}$  g. of radioactive Br has been separated from 21 g. of inactive Br atoms. R. C.

**Preparation of artificially radioactive halogens in unweighable amount from the stable isotopes.** O. ERBACHER and K. PHILIPP (Ber., 1936, 69, [B], 893—898).— $\text{EtI}$ ,  $\text{EtBr}$ , or  $\text{C}_2\text{H}_5\text{Cl}_2$  is bombarded (method to be described) and shaken with blood charcoal which is then introduced into  $\text{H}_2\text{O}$  through which  $\text{H}_2$  bubbles in presence of Pt powder. When the mixture is boiled and filtered, the bulk of the radioactive halogen is contained in the  $\text{H}_2\text{O}$ , which remains clear after addition of  $\text{AgNO}_3$  and dil.  $\text{HNO}_3$ . H. W.

**Radioactive isotope of sulphur.** E. B. ANDERSEN (Z. physikal. Chem., 1936, B, 32, 237—242).—A radioactive isotope of half-life period  $\sim 80$  days and probably  ${}^{33}\text{S}$  is formed by the action of neutrons on the Cl in  $\text{CCl}_4$ . It has been used to study the reactions of thiosulphates. R. C.

**New transformation processes in the bombardment of uranium with neutrons. Elements beyond uranium.** O. HAHN, L. MEITNER, and F. STRASSMANN (Ber., 1936, 69, [B], 905—919; cf. A., 1935, 1050).—The production of the following at. types is observed by the bombardment of U with neutrons; the half-life periods and type of bombardment are given in parentheses:  ${}^{235}\text{Th}$  (4 min., slow);  ${}^{235}\text{Pa}$  (very short, slow);  ${}^{235}\text{U}$  ( $24 \pm 2$  min., slow);  ${}^{237}\text{U}$  (40 sec., rapid);  ${}^{239}\text{U}$  (10 sec., preferably slow);  ${}^{237}\text{eka-Re}$  ( $16 \pm 1$  min., rapid);  ${}^{239}\text{eka-Re}$  ( $2.2 \pm 0.2$  min., preferably slow);  ${}^{237}\text{eka-Os}$  (12 hr., rapid);  ${}^{239}\text{eka-Os}$  ( $59 \pm 2$  min., preferably slow);  ${}^{239}\text{eka-Ir}$  (3 days, preferably slow); (?)  $\text{eka-Pt}$  ( $\sim 3$  hr., preferably slow). H. W.

**Decrease of the primary cosmic radiation in different materials.** J. CLAY (Physica, 1936, 3, 332—340).—Measurement of the decrease of ionisation by cosmic radiation under thick layers of Fe and Pb proves that equilibrium between primary radiation and secondary effects is reached under layers  $> 400$  g. per sq. cm. Under such layers the decrease in Pb, Fe, and  $\text{H}_2\text{O} \propto$  density, in accord with a corpuscular



nature of the radiation. The coeff., however, is 0.00044 per g. per sq. cm., about one tenth of that in air. It is suggested that there are two independent types of primary radiation, both shower-producing, and to account for the decrease in intensity in H<sub>2</sub>O layers at different magnetic latitudes it is assumed that the hard and soft components consist of protons and electrons, respectively, the energy required to penetrate the atm. being  $4 \times 10^9$  e.v. for protons and about  $10^{10}$  e.v. for electrons. J. W. S.

**Range of a single shower particle produced by cosmic rays in lead, iron, and aluminium.** J. CLAY (Physica, 1936, 3, 352—358).—By arranging three counters under a shower-producing sheet, one being enclosed within an absorbing layer of variable thickness, and measuring the threefold coincidences of the counters, it has been shown that the particles have a definite range, which for Pb showers is 4.4 cm. in Pb, 5.6 cm. in Fe, and about 10 cm. in Al. Shower particles from Fe have a range of 5.2 cm. in Pb, whilst those from Al have still longer ranges. The calc. energies are 87, 104, and 168 ( $\times 10^6$ ) e.v. for Pb, Fe, and Al showers, respectively. J. W. S.

**Absorption of cosmic-ray showers in lead.** C. G. MONTGOMERY and D. D. MONTGOMERY. **Coincidence counter studies of cosmic-ray showers.** R. H. WOODWARD. **Geomagnetic analysis of cosmic radiation.** G. LEMAITRE and M. S. VALLARTA (Physical Rev., 1936, [ii], 49, 705—711, 711—718, 719—726; cf. A., 1935, 560). N. M. B.

**Interpretation of Shankland's experiment.** R. PEIERLS (Nature, 1936, 137, 904). L. S. T.

**Wave theory of the neutrino.** G. RUMER (Compt. rend., 1936, 202, 1484—1486; cf. A., 1935, 143). R. S.

**Neutrino theory of light.** M. BORN and N. S. N. NATH (Proc. Indian Acad. Sci., 1936, 3, A, 318—337).—Mathematical. A general survey. N. M. B.

**Constitution of atomic nuclei and their magnetic moments.** S. SHIMASAKI (Proc. Phys.-Math. Soc. Japan, 1935, 17, 177—188).—It is assumed that protons or neutrons do not exist free in the nucleus, but only in the form of deuterons or <sup>3</sup>H nuclei. Two deuterons, two <sup>3</sup>H nuclei, or one deuteron and one <sup>3</sup>H nucleus have a tendency to unite. The nuclei of elements with  $Z < 28$  are built principally by the addition of successive  $\alpha$ -particles. In heavier elements additions of two <sup>3</sup>H nuclei play the chief role. Vals. for nuclear magnetic moments are calc. which are in agreement with experimental vals. CH. ABS. (e)

**Scattering and absorption of particles by nuclei.** I. T. SEXL (Z. Physik, 1936, 99, 751—775).—Theoretical. A. B. D. C.

**Statistical distribution of absorbed light quanta in the nuclei of a photographic layer.** G. UNGAR (Z. Physik, 1936, 99, 688—694).—Theoretical. A. B. D. C.

**Fundamental equations of elementary particles.** A. PROCA (Compt. rend., 1936, 202, 1490—1492). R. S.

**Interaction of two particles.** H. R. HULME (Proc. Roy. Soc., 1936, A, 154, 487—500).—The interaction of a nuclear particle in an excited state with an electron in the *K*-shell is considered according to the methods of quantum electrodynamics.

L. L. B.

**Inertia of electrons in metals.** C. G. DARWIN (Proc. Roy. Soc., 1936, A, 154, 61—66).—According to the theory of metals, the effective mass of the free electrons is increased owing to the displacement of their energy levels by the cryst. field. This effect is, however, not shown in experiments on electron inertia. L. L. B.

**Wave functions for 1s2s<sup>1</sup>S helium.** A. S. COOLIDGE and H. M. JAMES (Physical Rev., 1936, [ii], 49, 676—687).—Mathematical. N. M. B.

**Ground state of lithium.** H. M. JAMES and A. S. COOLIDGE (Physical Rev., 1936, [ii], 49, 688—695).—Mathematical. Wave functions are examined. The calc. ionisation energy is  $5.363 \pm 0.007$  against  $5.364$  e.v. observed. N. M. B.

**Rational nomenclature for elementary corpuscles.** P. GRUNER (Physikal. Z., 1936, 37, 350—351).—The following names are proposed for corpuscles of mass approx.  $10^{-27}$  g. (present names in parentheses): nulliton (neutrino), positon (positron), negaton (electron); and for particles of mass about  $10^{-24}$  g. (general name, materion), proton (proton), neproton (negatively charged particle with the mass of the proton), neutron (neutron). A. J. M.

**Validity of the Franck-Condon principle for evaluation of intensity distribution in molecular spectra.** W. FINKELNBURG (Z. Physik, 1936, 99, 798—800).—This principle cannot be applied to transitions involving loosely linked bonds or states of repulsion. A. B. D. C.

**Intensity and form of the absorption bands of liquid oxygen.** R. GUILLIEN (Compt. rend., 1936, 202, 1373—1375; cf. A., 1934, 581).—The liquid O<sub>2</sub> bands 7635, 6290, 5769, 5325, 4773, and 4472 Å. have been studied and compared with data for compressed O<sub>2</sub>. R. S.

**The A band of liquid oxygen.** R. GUILLIEN (Compt. rend., 1936, 202, 1423—1425).—The band extends from <7595 to 7735 Å. Extinction coeffs. ( $\kappa$ ) have been measured in liquid N<sub>2</sub>-O<sub>2</sub> mixtures. The  $\kappa/\kappa_{\max} - 1/\lambda$  curve becomes narrower with increasing dilution. Data are recorded and discussed. L. J. J.

**Influence of temperature on the absorption spectrum of ozone.** E. VASSY (Compt. rend., 1936, 202, 1426—1428).—The spectrum is independent of pressure. The ratio of the extinction coeffs. at 20° and -80° for  $\lambda$  3372—3151 Å. are recorded. There is no temp. effect at the absorption max. 85% of the atm. O<sub>3</sub> is at <11 km. altitude. L. J. J.

**Band spectrum of the sulphur molecule.** E. OLSSON (Nature, 1936, 137, 745).—The internuclear distance of the S mol. obtained from the rotational analysis of six main absorption bands is 1.88 Å.; this should replace the accepted val. of 1.60 Å. L. S. T.



**Absorption spectrum of water, aqueous solutions, and alcohols between 0.70 and 0.95  $\mu$ .** E. GANZ (Ann. Physik, 1936, [v], 26, 331—348).—The effect of temp. on the absorption bands of  $H_2O$  at 0.77 and 0.845  $\mu$  has been investigated. The displacement of the absorption max. at 0.77  $\mu$  with temp. shows a discontinuity at 40—45°, in common with many other properties of  $H_2O$ . The absorption const. at the max.  $\propto$  thickness of  $H_2O$ . The absorption is considerably affected by ions (cf. following abstract). The quasicryst. structure of  $H_2O$  is established by small ions, but distorted by large ones. The absorption spectra of MeOH, EtOH,  $Pr^oOH$ , and  $Bu^oOH$  have also been investigated. A. J. M.

**Effect of temperature on the absorption bands of water in salt solutions.** E. GANZ and W. GERLACH (Physikal. Z., 1936, 37, 358—359).—The displacement and sharpening of the  $H_2O$  absorption band at 0.762  $\mu$  by raising the temp. from 10° to 90° have been investigated both for pure  $H_2O$  and for aq. solutions. The band is strengthened but not displaced in chloride solutions, whilst it is sharpened and displaced towards shorter  $\lambda$  in nitrate, chlorate, and particularly perchlorate solutions. The effect of temp. on the position of the absorption max. is directly connected with the displacement of the max. caused by addition of salt at lower temp. There is equivalence between the effect of temp. and of ions on the structure of  $H_2O$ . A. J. M.

**Collision potentials of  $C^+$  and  $C^{++}$  ions in  $CO$ , deduced from  $D(CO)=6.9$  volts.** R. SCHMID (Z. Physik, 1936, 99, 626—632).—A dissociation energy of 6.9 volts for  $CO$  gives the potential of  $C^+$  and  $C^{++}$  over the  $CO_2$  ground level as 29 and 54 volts, respectively.  $CO_2$  dissociates thus:  $CO_2+5.47$  volts  $\rightarrow CO(X^1\Sigma)+O(^3P)$ ,  $CO(X^1\Sigma)+6$  volts  $CO(a^3\Pi)$ , and  $CO(a^3\Pi)+5.22$  volts  $C(^5S)+O(^3P)$ . A. B. D. C.

**'Stark effect on absorption bands of nitric oxide.** G. BLET (Rev. Opt. theor. inst., 1935, 14, 62—67; Chem. Zentr., 1935, ii, 1315).—No broadening of the rotational lines in the band of  $NO$  at 2260  $\mu$  was observed. J. S. A.

**Band spectra of the hydrides of lithium. III. Potential curves and isotope relations.** F. H. CRAWFORD and T. JORGENSEN, jun. (Physical Rev., 1936, [ii], 49, 745—752; cf. A., 1935, 1051).—Theoretical. N. M. B.

**Band spectra of alkaline-earth hydrides.** B. GRUNDSTROM (Z. Physik, 1936, 99, 595—606).—Rotation analysis and heats of dissociation are given for  $CaH$ ,  $SrH$ ,  $BaH$ , and  $MgH$ ; the latter are 15,000, 14,000, 13,000, and 23,000  $cm^{-1}$ , respectively. A. B. D. C.

**Absorption spectrum of aqueous chlorine and hydrogen peroxide vapour.** W. C. FERGUSON, L. SLOTIN, and D. W. G. STYLE (Trans. Faraday Soc., 1936, 32, 956—962).—Data are recorded for the extinction coeffs. of aq.  $Cl_2$  and  $HOCl$  solutions, and of  $HOCl$  and  $H_2O_2$  vapours, for a no. of  $\lambda > 210$   $\mu$ . L. J. J.

**Continuous absorption spectrum of hydrogen iodide.** C. F. GOODEVE and A. W. C. TAYLOR (Proc. Roy. Soc., 1936, A, 154, 181—187).—The ex-

tinction coeffs. of  $HI$  have been measured, and the approx. course of the upper potential energy curve is calc. from the eigenfunction of the ground state and the observed extinction. The results favour the dissociation into normal atoms. L. L. B.

**Band spectrum of boron fluoride.** H. M. STRONG and H. P. KNAUSS (Physical Rev., 1936, [ii], 49, 740—744; cf. Dull, A., 1935, 562).—The spectrum of  $BF$  excited by the electrodeless discharge in  $BF_3$  has been photographed at high and low dispersion. 16 bands, degraded to the violet, were observed in the range  $\lambda$  3712—2580, resembling the  $CO$  bands corresponding with similar electronic configurations. Data and a vibrational analysis are given. N. M. B.

**Band systems and structure of  $SiF$ .** R. K. ASUNDI and R. SAMUEL (Proc. Indian Acad. Sci., 1936, 3, A, 346—359).—A detailed analysis, using the experimental data of Johnson (cf. A., 1927, 1005), is given. N. M. B.

**Absorption spectra of halides and oxyhalides of sulphur, selenium, and tellurium.** S. L. HUSSAIN and R. SAMUEL (Current Sci., 1936, 4, 734—736).—Data are recorded for absorption max. and long- $\lambda$  limits, agreeing with linking energies calc. from thermochemical data. Different absorption regions in the di- and tetra-halides correspond with splitting off of one and two halogen atoms, whilst in the oxychlorides two halogen atoms are split off simultaneously. The linking energies are approx. additive. L. J. J.

**Absorption spectra of sodium and potassium in melts of their halogen salts.** E. MOLIWO (Nachr. Ges. Wiss. Gottingen, 1935, [ii], 1, 203—207; Chem. Zentr., 1935, ii, 1510—1511).—The melts show broad absorption bands the position of which depends on the metal alone, being at 790  $m\mu$  for Na halides and 980  $m\mu$  for K halides. No simple relation exists between these bands and the absorption spectrum of the colour centres in the solid crystals. J. S. A.

**Absorption spectra and linkage of inorganic salts in the vapour state.** M. I. HAQ and R. SAMUEL (Nature, 1936, 137, 907—908; cf. this vol., 661).—The absorption spectra of  $H_2SO_4$ ,  $K_2SO_4$ ,  $Ag_2SO_4$ , and  $ZnSO_4$  in the vapour state indicate covalent linking in this state. The suggested structural formula for  $NH_4NO_3$  is  $(O:)_2N^+O^-N(H)_4$  with 5 covalent linkings in the vapour state. L. S. T.

**Spectral study of phenylhydrazine and derivatives.** (MLLE.) D. BIQUARD (Bull. Soc. chim., 1936, [v], 3, 909—916).—Ultra-violet absorption spectra of derivatives of  $NHPh \cdot NH_2$  and some aromatic diamines have been determined. Complex chromophores are indicated. E. S. H.

**Effect of X-rays on methylene-blue and on trimethylthionine.** W. STENSTROM and H. R. STREET (Proc. Soc. Exp. Biol. Med., 1935, 32, 1498—1500).—Absorption by both dyes is reduced, reduction in methylene-blue being  $>$  in trimethylthionine. R. N. C.

**Ultra-violet absorption spectra of certain proteins and amino-acids.** C. B. COULTER, F. M.



STONE, and E. A. KABAT (J. Gen. Physiol., 1936, 19, 739—752).—The absorption spectra (2500—3000 Å.) of a no. of proteins consist of 6—9 bands similar to those of tryptophan, tryosine, and phenylalanine shifted 10 to 35 Å. towards longer  $\lambda$ . That of pneumococcus type I antibody is similar to that of  $\psi$ -globulin.

H. G. R.

Effect of solvents on the spectral curve of vitamin-A.—See this vol., 763.

Absorption spectra of oestrone and related compounds in alkaline solution. R. K. CALLOW (Biochem. J., 1936, 30, 906—908).—Addition of NaOH to solutions of oestrone (I), oestradiol, and oestriol causes a shift of the ultra-violet absorption band towards the visible region but on the Me ether of (I) has no effect. The change is due to salt formation of the phenolic group in the 3 position and with (I) is not due to enolisation of the 17-keto-group.

P. W. C.

Absorption spectra of diphenyls.—See this vol., 723.

Christiansen filter effect in the infra-red. R. B. BARNES and L. G. BONNER (Physical Rev., 1936, [ii], 49, 732—740).—Prep., characteristics, and factors affecting data from the use of the filters are discussed. Results and curves are given for MgO, quartz, calcite, marble, CaSO<sub>4</sub>, the halides of Na, K, and Rb, LiF, CsCl, CsBr, TiCl, TiBr, and TlI dispersed in air, and for quartz, MgO, and NaCl dispersed in org. liquids. Transmission between 3  $\mu$  and 90  $\mu$  was measured.

N. M. B.

Infra-red spectra of H<sub>2</sub>S, HDS, and D<sub>2</sub>S. C. R. BAILEY, J. W. THOMPSON, and J. B. HALE (Physical Rev., 1936, [ii], 49, 777).—Data are contrasted and compared with those found by Nielsen (cf. this vol., 545).

N. M. B.

Spectra [of substituted methanes] in the near infra-red. C. CORIN (J. Chim. phys., 1936, 33, 427—428).—Data are recorded for CH<sub>4</sub>, MeCl, CH<sub>3</sub>Cl, CHCl<sub>3</sub>, and C<sub>6</sub>H<sub>14</sub> from 0.88 to 2.7  $\mu$ . The bands can be derived as harmonics or combinations of the four fundamental frequencies of the Raman spectra.

R. C. M.

Extreme infra-red dispersion of polar and non-polar liquids. C. H. CARTWRIGHT and J. ERRERA (Proc. Roy. Soc., 1936, A, 154, 138—157).—The absorption and reflexion of several polar and non-polar liquids have been measured between  $\lambda\lambda$  of 50 and 150  $\mu$ . Vals. calc. for the at. polarisation were in good agreement with those determined for mols. in the gaseous state. The relaxation times and apparent radii of the polar mols. were calc. from measurements on the abs. intensity of absorption. On diluting the liquids in non-polar solvents, a characteristic absorption band in H<sub>2</sub>O disappeared; this is therefore attributed to a quasi-cryst. structure. In all the other substances, however, the characteristic absorption bands remained in dil. solution, and are therefore due to intramol. vibrations.

L. L. B.

Raman spectra of "heavy" arsine, silicochloroform, and silicobromoform. J. M. DELROSSE (Nature, 1936, 137, 868).—Frequencies are recorded.

L. S. T.

Raman spectra of carbon and silicon tetrafluorides. D. M. YOST, E. N. LASSETTRE, and S. T. GROSS (J. Chem. Physics, 1936, 4, 325).—Data are recorded for liquid and gaseous states.

L. J. J.

Influence of temperature on Raman bands of water at  $\Delta\nu=510$ —780 cm.<sup>-1</sup> G. BOLLA (Nuovo Cim., 1935, [ii], 12, 243—246; Chem. Zentr., 1935, ii, 1316).—The bands do not disappear with rise of temp. (cf. Magat, A., 1934, 1056).

J. S. A.

Raman spectrum and electrolytic dissociation of selenic acid. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1936, 3, A, 307—317; cf. this vol., 547; Ganesan, A., 1935, 11).—Raman data are given for the state of solid, liquid, and aq. solution of concn. range 92.5—7.5 wt.-%. Marked changes in the position, intensity, and character of the lines are attributed to dissociation steps H<sub>2</sub>SeO<sub>4</sub>  $\rightarrow$  HSeO<sub>4</sub>' + H' and HSeO<sub>4</sub>'  $\rightarrow$  SeO<sub>4</sub>'' + H', the first stage starting from the solid and the second stage from about 50% concn. Results are compared with those for H<sub>2</sub>SO<sub>4</sub> (cf. Bell, A., 1935, 807) and conclusions on structure and apparent band shifts are drawn. Changes in the lines during solid-liquid transition are characteristic of heteropolar linkings in the acid mols.

N. M. B.

Raman effect in liquid ammonia and solutions of nitrates in liquid ammonia. G. COSTEANU (Compt. rend., 1936, 202, 1432—1434).—A new line, 3460 cm.<sup>-1</sup>, in liquid NH<sub>3</sub> is recorded. Dissolution of NH<sub>3</sub> in H<sub>2</sub>O produces a shift of +10—15 cm.<sup>-1</sup> for the lines 3210, 3300, 3380 cm.<sup>-1</sup>. The line 1048 cm.<sup>-1</sup> of NO<sub>3</sub>' in H<sub>2</sub>O solution is displaced towards shorter  $\lambda$  in NH<sub>3</sub> solution.

L. J. J.

Raman effect and its applications in organic chemistry. II. A. DADIEU (Angew. Chem., 1936, 49, 344—349).—A review.

H. J. E.

Raman spectrum of deuterobromoform. O. REDLICH and W. STRICKS (Monatsh., 1936, 67, 328—331; cf. A., 1935, 685).—The Raman spectrum of CDBr<sub>3</sub> has been measured and compared with that of CHBr<sub>3</sub>, the relationship being in accord with the authors' theory. Comparison of data for PH<sub>3</sub> and PD<sub>3</sub> indicates that there are missing frequencies for PH<sub>3</sub> between 550 and 780 cm.<sup>-1</sup> and for PD<sub>3</sub> between 790 and 1115 cm.<sup>-1</sup>

J. W. S.

Raman effect and dipole moment in relation to free rotation. III. Raman spectra of solid ethylene halides. S. MIZUSHIMA, Y. MORINO, and S. NOZIRI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 63—70; cf. A., 1935, 428).—The Raman spectra and dipole moments of solid and liquid C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> have been determined. It is concluded that the *trans*-configuration is adopted in the solid state, whilst in solutions the deviation from the *trans*-position varies with the solvent.

R. S.

Raman spectra of metallic formates and constitution of formic acid. C. S. VENKATESWARAN (Current Sci., 1936, 4, 736—737; cf. this vol., 268).—A reply to Halasyam (*ibid.*, 663). Raman spectral evidence for the presence of the -CHO group in HCO<sub>2</sub>H is summarised.

L. J. J.

Deuterium compounds. II. Raman spectra of deuterioacetic acid and deuterioacetone. W.



ENGLER (Z. physikal. Chem., 1936, B, 32, 471—474).—The spectra of  $\text{AcOD}$ ,  $\text{CD}_3\cdot\text{CO}_2\text{D}$ , and  $\text{CO}(\text{CD}_3)_2$  have been determined. R. C.

Raman spectrum of oxalic acid. J. H. HIBBEN (J. Chem. Physics, 1936, 4, 323—324).—Polemical against Angus and Leckie (this vol., 269). L. J. J.

[Raman spectrum of oxalic acid.] W. R. ANGUS and A. H. LECKIE (J. Chem. Physics, 1936, 4, 324).—A reply to the above. L. J. J.

Raman spectra of  $\beta$ -methyl- $\Delta^a$ - and  $\Delta^b$ -butene. —See this vol., 819.

Raman effect. LV. *cyclo*Pentyl derivatives. K. W. F. KOHLRAUSCH, A. W. REITZ, and W. STOCKMAIR (Z. physikal. Chem., 1936, B, 32, 229—236).—The Raman spectra of *cyclopentanone* and  $\text{C}_5\text{H}_n\text{X}$  ( $\text{X}=\text{OH}$ ,  $\text{NH}_2$ , Me, SH, Cl, Br, I) have been determined. The effect of substitution differs characteristically from that in *cyclohexyl* derivatives (this vol., 547), which is ascribed to the two C-H linkings of each  $\text{CH}_2$  group being equiv. in direction in a flat C- ring, but not in a non-planar  $\text{C}_6$  ring. The no. of lines suggests that the *cyclohexyl* halogen derivatives exist in two forms different in configuration. R. C.

Raman spectra of compounds belonging to the anethole, safrole, and eugenol groups. B. STSZ, E. PERROTTET, and E. BRINER (Helv. Chim. Acta, 1936, 19, 548—558).—Raman spectra are given for estragol, natural anethole (I) (=isomerised estragol), safrole, isosafrole, heliotropin, eugenol and its Me and Et ethers, isoeugenol (II) and its Me ether, vanillin and its Me ether (cf. A., 1935, 1446). They show the frequencies characteristic of the Ph nucleus, aliphatic and aromatic C-H, C=O, and C=C (in  $\text{CH}_2\text{R}\cdot\text{CH}:\text{CH}_2$  1638, in  $\text{CHR}:\text{CHMe}$  1654  $\text{cm}^{-1}$ ) linkings. (I) probably contains 100% *trans*-, (II) 80% *trans*- and 20% *cis*-compounds. R. S. C.

Raman effect. LVI. Raman effect and free rotation. IV. K. W. F. KOHLRAUSCH and (GROSS PRINZ) YPSILANTI (Z. physikal. Chem., 1936, B, 32, 407—416).—The Raman spectra of various straight-chain compounds, principally of the type  $\text{X}\cdot[\text{CH}_2]_3\cdot\text{Y}$ , have been determined. The results show that if the mol. of a dihalogenated paraffin with a four- or five-membered chain is of such character that by free rotation various spatial forms may be realised the no. of lines in the vibrational spectrum is increased. ( $\text{CHBrMe}$ )<sub>n</sub> apparently exists only in a *trans* form; the Me groups appear to give this form the preponderating stability. R. C.

*cyclo*Propane. Raman spectrum and polymerisation by ultra-violet light. L. HARRIS, A. A. ASHDOWN, and R. T. ARMSTRONG (J. Amer. Chem. Soc., 1936, 58, 852—853).—The Raman spectrum of *cyclopropane* (I) consists of 14 frequencies (cf. Lespiau *et al.*, A., 1932, 675; Kohlrausch and Koppl, A., 1934, 942); the strongest is at 1191  $\text{cm}^{-1}$ . A Hg-sensitised polymerisation of (I) to a viscous oil, b.p. about 300°/760 mm., occurs with Hg-radiation of  $\lambda$  2536 Å. H. B.

Raman spectrum of some substituted *cyclohexenes*. E. CANALS, M. MOUSSERON, L. SOUCHE, and P. PEYROT (Compt. rend., 1936, 202, 1519—

1521).—The Raman spectra of 1-methyl-, -ethyl-, -propyl-, -isopropyl-, -butyl-, -phenyl-, -benzyl-, and -*cyclohexyl*- $\Delta^1$ -*cyclohexene* (I) are similar to those of other *cyclohexenes* (cf. A., 1934, 10). The line 825  $\text{cm}^{-1}$  of *cyclohexene* is replaced by two in the regions 747—772 and 825—850, and in the Me, Et, and Pr derivatives the frequency of the line 758 varies inversely as the no. of C. The line 1440, characteristic of  $\text{CH}_2$ , is accompanied by a satellite 1453 in all cases except (I) which gives one line at 1443. R. S.

Raman effect and problems of constitution. X. Strain theory. K. W. F. KOHLRAUSCH and R. SEKA (Ber., 1936, 69, [B], 729—743).—Measurements are recorded for *cyclohexene*, *cyclopentane* (I), *cyclopentene*, *cyclopentadiene*,  $\alpha$ -*dicyclopentadiene* (II) and its  $\text{H}_2$ - and  $\text{H}_4$ -derivatives,  $\text{Me}_2$   $\alpha$ -*cis*-3 : 6-*endomethylene*- $\Delta^4$ -tetra- and -hexa-hydrophthalate,  $\text{Me}$  2 : 5-*endomethylene*- $\Delta^3$ -tetra- and -hexa-hydrobenzoate. The transition of (I) to *cyclopropane*, which according to model is accompanied by an increase in strain and according to thermochemistry by an increase in energy, involves a decrease in strength of the C-C linking when the spectra are evaluated by an approx. theoretical treatment of the vibration forms; the corresponding increment of the energy content is of the same order of magnitude as that determined thermochemically. In the unsaturated plane, five-membered ring for which the approx. strain in the ring according to model and, in particular, the deformation of the angle at the double linking cannot account for the increased energy content, the C:C frequency suffers a depression, probably mainly due to a diminution in the strength of the double linking. Different frequencies are shown by the two double linkings in (II) one of which is situated (Alder-Stein) in the slightly strained *cyclopentene* ring, whereas the other belongs to the greatly strained *dicycloheptene* ring. In this case the deformation of the angle at the double linking in the strained ring is not calculable, but the increase of its energy content is thermochemically established. The lower C:C frequency is due to the more slightly strained ring. The calc. increase of the energy content from the depression of the frequency agrees in order of magnitude with the results obtained thermochemically. H. W.

Nature of intermolecular oscillations in some organic crystals. S. C. SIRKAR (Indian J. Physics, 1936, 10, 109—116).—The Raman spectra of  $\text{C}_7\text{H}_8$  and  $\text{Ph}_2\text{O}$  have been investigated in the solids and in solution in MeOH and  $\text{C}_6\text{H}_{12}$ , at different temp. Certain of the Raman lines of these substances seem to be due to intermol. vibrations in groups of mols. which persist in the case of  $\text{Ph}_2\text{O}$ , but disappear almost completely in the case of  $\text{C}_{10}\text{H}_8$  when the substance is melted or dissolved. The directions of the displacements of the  $\text{C}_{10}\text{H}_8$  lines with temp. are in agreement with the lattice oscillation theory of Gross and Vuks (A., 1935, 564, 914), but the extent of the displacement is different for different lines, and is too great to be explained by this theory. The absorption spectra of  $\text{Ph}_2\text{O}$  and  $\text{C}_{10}\text{H}_8$  in the solids and in solution in MeOH and  $\text{C}_6\text{H}_{12}$  have also been investigated.



The positions of the bands for solid  $C_{10}H_8$  are different from those for solutions or vapour, but in the case of  $Ph_2O$  there is no appreciable difference in the absorption spectra of the solid, liquid, or solution. This may be due to the polar character of  $Ph_2O$ , which would allow the formation of stable polymerised groups, not completely broken down even in solution.

A. J. M.

Raman spectra and decomposition reactions of ozonides.—See this vol., 839.

Variation of intensity of scattered light with temperature. C. V. JOGARAO (Proc. Indian Acad. Sci., 1936, 3, A, 377—383).—The intensity of scattering increases in  $C_6H_6$  and  $AcOH$ , and decreases in  $PhNO_2$  and  $HCO_2H$ , with rise of temp. The differences are due to the aggregate effect of density scattering and orientation scattering; on separation, the former always increases with temp., and the latter sometimes increases ( $C_6H_6$ ) and sometimes decreases ( $PhNO_2$ ,  $AcOH$ , and  $HCO_2H$ ).

N. M. B.

Mechanism of the emission of light by chemical reactions. R. AUDUBERT (Compt. rend., 1936, 202, 406—407; cf. this vol., 407).—It is suggested that mols., after reaction, may retain both their energy of activation and the energy of reaction, and that their subsequent collisions of the fourth kind may give rise to the emission of quanta of high energy. Calculations for certain reactions are in accord with experiment.

J. W. S.

Emission of ultra-violet light during the anodic oxidation of aluminium. R. AUDUBERT and O. VIKTORIN (Compt. rend., 1936, 202, 1504—1507; cf. A., 1935, 1055).—The intensity of the ultra-violet light emitted decreases with time. There is no emission from an Al cathode.

R. S.

Thermoluminescence and chemiluminescence. H. STEINMETZ and M. ALT (Z. Krist., 1936, 92, 363—371).—These effects are discussed for several cases, especially the influence of impurities and the separation of chemical from thermal effects.

B. W. R.

Fluorescence of terbium salts in solutions. A. FILIPPOV, J. LARIONOV, and A. SEIDEL (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 253—256).—The fluorescence spectrum of aq. solutions of salts of the Y series of earths is ascribed entirely to  $Tb^{+++}$ . The intensity of the fluorescence depends largely on the method of prep. of the solution, being increased by heating the salt before dissolution, and destroyed by the presence of traces of  $HNO_3$ . The method may be used in the detection of traces of Tb.

A. J. M.

Inhibition of the fluorescence of methylene-blue by ferrous salts. K. WEBER (Naturwiss., 1936, 24, 318).—The observation of Hellstrom (this vol., 270) that the fluorescence of methylene-blue is inhibited by  $Fe^{++}$  ions is related to the fading of vat dyes when illuminated in presence of  $Fe^{++}$  ions (cf. this vol., 300), both being dependent on the more positive redox potential of the activated dye mol. (or ion) and its consequent reaction with  $Fe^{++}$ . The variation of the effect with  $p_H$  is attributed to the influence of the latter on the redox potential of the dye and of the ferro-ferrous system.

W. O. K.

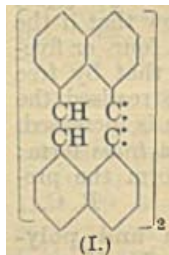
Phosphorescence and long-period fluorescence of organic dyes. P. PRINGSHEIM and H. VOGELS (J. Chim. phys., 1936, 33, 345—355).—Measurements of the decrease of intensity of light emitted by tryptaflavine adsorbed on  $SiO_2$  gel, when activation ceases, in high vac. at  $39^\circ$ ,  $18.5^\circ$ ,  $-37^\circ$ , and  $-190^\circ$  show that at  $-190^\circ$  the emission is a long-period fluorescence, whilst at the higher temp. it is a true phosphorescence in agreement with Jablonski (A., 1935, 682).

R. C. M.

Fluorescence of porphyrins. II. A. STERN and H. MOLVIG (Z. physikal. Chem., 1936, 176, 209—225; cf. this vol., 270).—Fluorescence spectra in dioxan have been determined. The displacement of the fluorescence band max. caused by partial alkyl substitution of the porphin system (I) is not always in the same direction as the displacement of the absorption max. The effect on the fluorescence of hydrogenation of the vinyl groups of (I) and the dihydro-porphin system has been examined. Me chlorophyllide *a* has a fluorescence spectrum of four bands, showing that Mg has a considerable effect on the fluorescence. The considerable similarity in the fluorescence spectra of  $\beta\delta$ -di-iminocoproporphyrin II Me<sub>4</sub> ester (II) (this vol., 86) and coproporphyrin II Me<sub>4</sub> ester shows that (II) must have a porphyrin structure and therefore contain *tert.* N. In aq. HCl solution (II) does not fluoresce, presumably due to salt formation at the  $\beta\delta$ -N atoms. Pyrromethenes do not fluoresce in HCl. It appears that fluorescence in the visible is caused by the presence of the pyrromethene structure in (I). When fluorescence is absent in HCl solution it may be inferred that N is present instead of the methene groups of (I). In porphyrins substituted only with alkyl there is present the same (I) as in all other normal porphyrins, and not a special form of (I). The fluorescence of the porphyrins is caused by the conjugated pyrrole nuclei, and the fluorescence spectrum is affected by the smallest changes in this structure.

R. C.

Fluorescence and duration of emission of fluorocyclene. M. MAKOWIECKA (Acta. phys. polon., 1934, 2, 357—359; Chem. Zentr., 1935, ii, 1336).—The fluorescence of fluorocyclene (I) in various solvents varies little with the solvent, and the spectral distribution of intensity is independent of the exciting  $\lambda$ . All four fluorescence bands exhibit the same degree of polarisation; at low temp. they become narrower and displaced towards longer  $\lambda$ . The mean duration of emission is  $2.9 \times 10^{-7}$  sec.



J. S. A.

Methods of determining the Volta effect. H. GERICKE (Physikal. Z., 1936, 37, 327—338).—A critical examination of the ionisation, condenser, photo-electric, and thermionic methods is given.

A. J. M.

Determination of the Volta effect for pure metals. F. KRÜGER and G. SCHULZ (Ann. Physik, 1936, [v], 26, 308—330).—The Volta effect was measured for a series of metals by a photo-electric method. For W, Ta, Fe, Ni, Ag, Cu, and Mo the



effect disappeared when the metals were completely outgassed by long heating in vac., and reappeared when the treated metals were allowed to remain in damp air. This supports the chemical theory of the effect. The photo-electric effect was also determined for these metals. The effect of heating in vac. was similar to that on the Volta effect, except at the beginning of the heating, where the photo-effect increases on removal of  $H_2O$  and gases from the metal whilst the Volta effect at once diminishes, being dependent only on the  $H_2O$  film. A. J. M.

**Photo-electric investigations of semi-conductors.** G. BERGMANN and J. HANSLER (Z. Physik, 1936, 100, 50—79).—Electrons in many semi-conductors move under the influence of light alone. Spectral sensitivities of these substances show max. that move to increased  $\lambda$  with increased mol. wt., provided the ions in question come from one column of the periodic table. A. B. D. C.

**Photo-effect for thin layers of aluminium and tantalum oxide.** G. ROSENTHAL (Z. Physik, 1936, 99, 607—621).—Ta oxide cells give greater photo-effects than the Al cells. A. B. D. C.

**Photo-electric sensitivity of palladium-silver alloys saturated with hydrogen.** F. KRUGER and W. KALLENBACH (Z. Physik, 1936, 99, 743—750).—Max. sensitivity occurs at 20% Ag with a subsidiary max. at 60 to 65% Ag, and these coincide with alloys of max.  $H_2$  absorption (cf. Schniedermann, A., 1932, 789). A. B. D. C.

**Internal photo-effect in potassium chloride under illumination with ultra-violet light.** N. KALABUCHOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 251—252).—On the basis of an energy scheme due to Tartakovski (A., 1935, 1306) it is to be expected that the internal photo-effect will occur with the allochromatic crystals NaCl and KCl without preliminary treatment, when they are irradiated by  $\lambda$  1602 and 1841 Å., respectively. This effect has been observed with KCl crystals using a  $H_2$  discharge tube with  $CaF_2$  window as light source. A. J. M.

**Crystal photo-effect for coloured Rochelle salt.** F. SEIDL (Z. Physik, 1936, 99, 633—634).—Rochelle salt coloured by radioactive radiation shows a secondary photo-effect. A. B. D. C.

**Nature of the surface conduction of cuprous oxide.** L. DUBAR (Compt. rend., 1936, 202, 1330—1332; cf. A., 1935, 1055).—The surface conduction is negligible after removing gas or forming a fresh surface in vac. H. J. E.

**Normal conductivity and reversion effects of solid paraffin subject to  $\gamma$ -rays.** F. SEIDL (Z. Physik, 1936, 99, 695—709).— $\gamma$ -Radiation increases normal conductivity and influences reversion phenomena. The greatest resistance of paraffin of m.p. 52—53° is  $3.3 \times 10^{18}$  ohm cm. A. B. D. C.

**Electrical conductivity of oxides of cobalt and iron. Recrystallisation of zinc oxide.** C. WAGNER and E. KOCH (Z. physikal. Chem., 1936, B, 32, 439—446).—The sp. conductivity,  $\kappa$ , of CoO and FeO at 800—1000° increases with the  $O_2$  pressure,  $p$ ; conduction is of the electron deficiency type

(cf. A., 1933, 888). For  $Co_3O_4$ ,  $Fe_3O_4$ , and  $Fe_2O_3$  at 900—1000°  $\kappa$  is practically independent of  $p$ . For  $Co_3O_4$  at room temp.  $\kappa$  varies with the previous treatment, i.e., depends on the presence of an excess of O, which varies with the temp. at which equilibration with the gas phase was last effected previously. The conductivity at high temp. is ascribed to the distribution of  $Co^{++}$  and  $Co^{+++}$  ions being partly irregular. When heated in  $H_2$  at 450° ZnO undergoes recrystallisation to a greater extent than if heated in  $O_2$  owing to both its elements being transportable through the gas phase as at. Zn and  $H_2O$ . R. C.

**Liquid ammonia as a solvent. VI. Dielectric constant of liquid ammonia.** H. M. GRUBB, J. F. CHITTRUM, and H. HUNT (J. Amer. Chem. Soc., 1936, 58, 776).—Vals. at 5°, 15°, 25°, and 35° are 18.94, 17.82, 16.90, and 16.26, respectively.

E. S. H.

**Determination of the dielectric constants of organic liquids at radio frequencies. II. Chlorobenzene and ethylene dichloride.** R. M. DAVIES (Phil. Mag., 1936, [vii], 21, 1008—1029; cf. this vol., 271).—The dielectric consts. of PhCl and  $C_2H_4Cl_2$  at 20°, 25° were 5.713<sub>5</sub>, 5.626<sub>3</sub> and 10.64<sub>7</sub>, 10.35<sub>8</sub>, respectively. H. J. E.

**Dispersion and absorption by viscous liquids at high frequencies.** W. DAHMS (Ann. Physik, 1936, [v], 26, 177—192).—Dielectric consts. and conductivities of fructose (I) and sucrose (II) solutions and  $PhNO_2$  for  $\lambda$  1.47—8.30 m. have been measured by Wenk's method (A., 1933, 925). The results with  $PhNO_2$  agree with Debye's theory. With the sugars, the dipole conductivity increases more slowly than  $\propto 1/\lambda^2$ , whilst at short  $\lambda$ ,  $\epsilon$  is < the statistical val. in the case of (I), but not of (II). L. J. J.

**Apparent dipole moments of benzene, *p*-dichlorobenzene, diphenyl, 4 : 4'-dichlorodiphenyl, and carbon disulphide in polar solvents.** C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1936, 487—491; cf. this vol., 140).—The dielectric consts. and  $d$  of solutions of the above substances in  $C_6H_6$ ,  $CHCl_3$ ,  $CCl_4$ ,  $PhCl$ ,  $PhNO_2$ ,  $NPhMe_2$ ,  $EtOBz$ , and  $PhCN$  have been determined. Assuming that the usual evaluation of dipole moments is valid for these cases, the data indicate that the induced moments of the solute  $\propto$  the dipole moment of the solvent, approx. The results suggest that the dipolar solvent units cluster around the solute with their dipoles in parallel rather than antiparallel alignment. The model leads to polarisabilities of the solute mols. in general accord with other vals. Alternative interpretations are discussed. J. G. A. G.

**Solvent effect in dipole-moment measurements. Polarisations of chloro- and nitrobenzene, chloroform, and bromoform in polar solvents.** R. J. W. LE FEVRE and P. RUSSELL (J.C.S., 1936, 491—495; cf. this vol., 140).—Dielectric consts. and  $d$  of binary mixtures of the above substances and of binary mixtures with  $C_6H_6$  and  $PhMe$  have been determined, and polarisations,  $P$ , and apparent dipole moments,  $\mu$ , calc. The tendency towards organised structure in liquids leads to models whereby the effects on  $P$  and  $\mu$  of the mutual



interaction of the mols. may be inferred. In conformity with the theory, the  $\mu$  of  $\text{PhNO}_2$  and  $\text{PhCl}$ , separate and mixed, in the liquid state are  $<$  in the gas state. The  $\mu$  of  $\text{PhNO}_2$  and  $\text{PhCl}$  are slightly depressed by dissolution in  $\text{CHCl}_3$ , but the  $\mu$  of  $\text{CHCl}_3$  and  $\text{CHBr}_3$  are raised by dissolution in  $\text{PhNO}_2$  and  $\text{PhCl}$ . J. G. A. G.

**Apparent dipole moment of paraldehyde in various solvents.** R. J. W. LE FEVRE and P. RUSSELL (J.C.S., 1936, 496—497).—The dielectric consts. and  $d$  of paraldehyde (I) and solutions of (I) in nine polar and non-polar solvents have been determined. Polarisation have been calc. The apparent dipole moment in the solvents is 1.68—2.26 D, that of (I) alone being 1.89 D. J. G. A. G.

**Refraction and dispersion of gases and vapours. VIII. Variation with temperature of molecular refraction of carbon dioxide and acetic acid vapour.** H. GOLDSCHMIDT and P. HOLEMANN (Z. physikal. Chem., 1936, B, 32, 341—352; cf. A., 1934, 348).—The refractivity,  $R_L$ , for 546.1 m $\mu$  of  $\text{CO}_2$  is const. to within 0.1% at 15—400°, but between 400° and 800° there is a rise of  $\sim 0.6\%$ , which is ascribed to the thermal excitation of higher vibrational states in the mol. With  $\text{AcOH}$  at 120—300°  $R_L$  falls with rising temp., and the effect on it of  $d$  and temp. indicates that the fall is due to dissociation of the double mols. Association to double mols. increases  $R_L$  by  $\sim 1.5\%$ . This increase may be due to increase in the probabilities of electron transition owing to mutual perturbation of the mols. in the complexes, and to the electron frequency determining  $R_L$  depending on the ionisation energy of the mol., which has been shown to fall on association. R. C.

**Change in refractivity and dispersion on transition from the vapour to the liquid state.** P. HOLEMANN (Z. physikal. Chem., 1936, B, 32, 353—368).—The mol. refractivity,  $R_L$ , of liquid  $\text{SiCl}_4$ ,  $\text{SnCl}_4$ , and  $\text{SnBr}_4$  at  $\lambda$  486.1, 587.6, and 656.3 m $\mu$  are represented by the dispersion formula  $R_L - R_\infty \lambda^2 / (\lambda^2 - \lambda_0^2)$ .  $R_L$  is smaller for the liquid than for the vapour state by an amount  $\Delta R$  which shows no clear parallelism with the dipole moment but increases in the order  $\text{CCl}_4 < \text{SiCl}_4 < \text{SnCl}_4 < \text{SnBr}_4$ . A similar effect for other compounds is shown by existing data. This change in  $R_L$  is best explained by supposing it to result from the superimposition of two effects: association in the liquid state, causing a rise in  $R_L$  and deviation of the internal field in the liquid from the Lorentz-Lorenz internal field, causing a fall in  $R_L$ . With  $\text{H}_2\text{O}$  a third at most of  $\Delta R$  can be explained by increase on condensation of the effect of the infra-red absorption bands on the refraction in the visible. On condensation  $R_\infty$  and  $\lambda_0$  also fall. R. C.

**Decrease in refraction of electrolyte solutions.** T. NEUGEBAUER (Z. Physik, 1936, 99, 677—687).—Theoretical. Changes in refraction of an electrolyte solution are not due to Debye effects, but to true association. A. B. D. C.

**Anisotropy of the optical polarisation field in liquids. III.** B. S. R. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 369—376).—The mol. refractivity of  $\text{PhNO}_2$  increases with temp., and for  $\text{H}_2\text{O}$  diminishes

slightly; for  $\text{AcOH}$  and  $\text{HCO}_2\text{H}$  it increases to a certain temp. and then diminishes. The coeffs. of anisotropy of the optical polarisation field are calc. for  $\text{AcOH}$  and  $\text{PhNO}_2$ . In the former, the polarisation field becomes more anisotropic, and in the latter, more isotropic, with rising temp. N. M. B.

**Variation of double refraction in celluloid with the amount of permanent stretch at constant temperature and at different temperatures.** F. C. HARRIS and B. R. SETH (Proc. Physical Soc., 1936, 48, 477—487).—Residual double refraction was measured at const. temp. at a no. of  $\lambda\lambda$  in the visible spectrum for specimens of celluloid subject to different amounts of permanent stretch by stretching beyond the elastic limit. Dispersion followed the law  $n/\lambda^2 = A - B\lambda$ , where  $n$  is the permanent double refraction at  $\lambda$  and  $A$  and  $B$  are consts.  $n$  had a max. for some val.  $\lambda_m$ , the vals. of  $\lambda_m$  increasing with permanent stretch. Temp. effects on dispersion and on  $\lambda_m$  were investigated. N. M. B.

**Dispersion of magnetic rotation of liquid mixtures.** H. POLTZ (Z. physikal. Chem., 1936, B, 32, 243—273; cf. A., 1932, 678).—It is deduced theoretically that  $\varphi = M[\omega]n\lambda^2/(n^2 + 2)^2$ , where  $M[\omega]$  is the mol. magnetic rotation, should have properties similar to those of the mol. refractive power,  $R_L$ , e.g., should obey the mixture rule.  $[\omega]$  in the visible and ultra-violet,  $n$  in the visible, and  $d$  have been measured for eight binary mixture over the whole concn. range.  $M[\omega]$  is additive primarily in mixtures with large association complexes or without sp. intermol. effects, whilst  $\varphi$  approximates to additivity most closely in non-associated mixtures. In general,  $R_L$  runs parallel with  $\varphi$ , and  $R_G$  with in mixtures. R. C.

**Kerr effect in polar molecules.** O. SPECCHIA and N. DALLAPORTA (Nuovo Cim., 1935, [ii], 12, 15—25; Chem. Zentr., 1935, ii, 1316).—The Kerr const. for castor oil has been determined at 21°, and an expression derived for its variation with temp. J. S. A.

**Maxwell effect in liquids.** G. G. PALDHIAKAR (Phil. Mag., 1936, [vii], 21, 1125—1130).—An expression is derived for the Maxwell const. which is in accord with experimental data on the birefringence in state of viscous flow for 4 paraffins and 9 aromatic compounds. J. W. S.

**Uses of the polar molecule concept in elementary chemistry.** S. J. FRENCH (J. Chem. Educ., 1936, 13, 122—130). L. S. T.

**Structure of the formate ion.** P. A. SMALL and J. H. WOLFENDEN (Nature, 1936, 137, 781).—A criticism (cf. this vol., 663). The slowness of the exchange process between the formate ion and  $\text{D}_2\text{O}$  does not support the views of Ray and Sarkar (*loc. cit.*). With  $\text{HCO}_2\text{K}$  in neutral solution 8% exchange occurs in 8 days at 100°; the exchange is accelerated in presence of alkali. L. S. T.

**Electronic theory of organic chemistry. V. Relations between the structure, reaction capacity, and polymerisation of organic compounds.** V. RASUMOVSKI (Bull. Soc. chim., 1936, [v], 3, 798—817).—A discussion. E. S. H.



**Orbital valency and directed properties in the theory of the chemical linking.** I, II. G. NORDHEIM-POSCHL (Ann. Physik, 1936, [v], 26, 258—280, 281—307).—An extension of the Heitler-London theory. Ground states of diat. mols., models of polyat. mols., theory of energy of combination, and double linkings are considered. A. J. M.

**Metallic binding.** I. P. GOMBAS (Z. Physik, 1936, 99, 729—742).—Statistical methods, applied to a lattice of positive ions surrounded by an electron gas, explain absence of conductivity from solid  $H_2$ , and give good vals. for the lattice const., lattice energy, heat of sublimation, and compressibility of K.

A. B. D. C.

**Metallic binding according to the combined approximation procedure.** H. HELLMANN and W. KASSATOTSCHKIN (J. Chem. Physics, 1936, 4, 324—325; cf. A., 1935, 278, 1058).—Calc. vals. for heats of sublimation and  $d_0$  are in satisfactory agreement with experimental data for Na, K, Rb, and Cs.

L. J. J.

**Wave-mechanical treatment of the LiH molecule.** J. K. KNIPP (J. Chem. Physics, 1936, 4, 300—307). Theoretical.

L. J. J.

**Rotation-vibration wave equation for a polyatomic molecule.** M. ELIASHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 295—298).—Mathematical.

A. J. M.

**Mechanism of addition to double linkings.** III. **Molecular forces between benzoquinone and cyclopentadiene.** A. WASSERMANN (J.C.S., 1936, 432—436).—London's approximation formula,  $= 3/2 \times P_k P_l / R^6 \times \Delta E_k \times \Delta E_l / (\Delta E_k + \Delta E_l)$  ( $R$  = distance between mols.  $k$  and  $l$ ) for the attraction energy for simple mols. due to the "dispersion effect" (A., 1930, 1239; 1931, 149) is extended to calculate energies between large org. mols. From  $\mu$  of C:O and C:C linkings, vals. of polarisability  $P$  are calc., and  $\Delta E$  for the conjugated double linking from an absorption band at 2400 Å. in benzoquinone (I) vapour. The lattice energy between mols. of the (I) lattice is 14.6 kg.-cal. per mol. Neglecting kinetic energy of the crystal and repulsive forces between mols., this should approximate to heat of sublimation (published val., 15 kg.-cal. per mol.). Lattice energy calc. on dipole and dipole-induction energy alone is only 7 kg.-cal. per mol. Similarly, attraction energies (due to dispersion effect) between (I) and cyclopentadiene in configurations suitable for (a) 1:2-, (b) *exo*-1:4-, and (c) *endo*-1:4-addition are calc. The val. is 9—10 kg.-cal. greater for (c) than for (a). Vals. are compared with the dipole-induction energies (cf. *loc. cit.*). E. W. W.

**Binding energies of molecular compounds of mono- and di-phenyl-polyene- and-polyinehydrocarbons with *s*-trinitrobenzene, and physical nature of secondary valency forces.** G. BRIEGLER and J. KAMBEITZ (Z. physikal. Chem., 1936, B, 32, 305—333; cf. this vol., 410).—In dil. solutions in indifferent solvents compound formation occurs in the ratio 1:1. The binding energies,  $E$ , have been determined by an optical method. The results are in harmony with Hückel's theory of the polar structure

of unsaturated aromatic systems (A., 1932, 901). The  $NO_2$ -compound (I) adds itself to one Ph nucleus of the hydrocarbon so that the nuclear plane of the latter is parallel to the plane of the ring of (I) and polarises the localised single  $\sigma$ -linkings and the  $p$ -electron cloud of the Ph nucleus. If in a monophenyl hydrocarbon the Ph nucleus or in a  $Ph_2$  hydrocarbon both Ph nuclei are conjugated with a continuously conjugated chain of double or triple linkings the perturbation caused by addition of the polar component in the  $p$ -electron cloud of one Ph nucleus and at first localised is transmitted over the whole mol., and  $E$  is comparatively high. Such transmission is prevented by interrupting the conjugation of the Ph nucleus with the conjugated aliphatic chain by interposition of a  $CH_2$  group; an abrupt fall in  $E$  results. There is a parallelism between the effects of constitution on the optical properties of certain mono- and di-phenyl hydrocarbons and on the  $E$  of their compounds with (I). R. C.

**Direct transmission of vibrational energy from one gas molecule to another on collision.** F. PATAT and E. BARTHOLOME (Z. physikal. Chem., 1936, B, 32, 396—406).—Comparison of existing data derived from measurements of sound dispersion and absorption for the frequency with which a mol. loses a vibrational quantum on collision with data for the stabilising action of gases on  $Br+Br$   $Br_2$  suggests that the direct transmission of vibrational energy from one mol. to another on collision plays an important part in reaction kinetics. In unimol. decomp. this appears to be the decisive type of energy exchange and occurs at practically every collision. R. C.

**Polarisation of hydrogen halides.** C. H. D. CLARK (Proc. Leeds Phil. Soc., 1936, 3, 208—217; cf. A., 1935, 569).—Polarisation data for H halides confirm that polarisability ( $\alpha$ )  $\propto$  (internuclear distance).<sup>3</sup> The depression of  $\alpha$  by a proton entering a halogen ion varies linearly with the Debye "apparent polarisability" of the halide. The vals. of the dielectric consts.,  $n_\infty$ , dipole moments, dipole distances,  $\alpha$ , deviation from additivity of inter-nuclear distance and mol. refraction, and the total, electron, and orientation polarisations of  $HF$ ,  $HCl$ ,  $HBr$ , and  $HI$  are calc. and related to the structures of the mols. The nature of the polarisation of element no. 85 is predicted.

J. W. S.

**Relation between polarisability and inter-nuclear distance for simple di-atoms.** F. R. GOSS (Proc. Leeds Phil. Soc., 1936, 3, 231—234).—The polarisability of simple di-atoms is  $kr^2/2$  for  $H_2$ ,  $(k-n/4)r^2$  for the  $KK$  period, and  $(k+0.20-n/4)r^2$  for higher periods, where  $k=3.85$  and  $n$  is the mol. group no. (cf. Clark, A., 1934, 476). J. W. S.

**Molecular constants and potential energy curves for diatomic molecules.** II. M. L. HUGGINS (J. Chem. Physics, 1936, 4, 308—312; cf. A., 1935, 1193).—Theoretical. The potential energy expression already employed is applied to diat. mols. containing heavier atoms. Calc. vals. of the equilibrium distance ( $r_e$ ) generally agree with experimental vals.

L. J. J.

**Spectroscopy and valency.** IV. **Periodic groups of hydride di-atoms.** C. H. D. CLARK.



**V. Periodic functions of hydride di-atoms.** C. H. D. CLARK and J. L. STOVES (Proc. Leeds Phil. Soc., 1936, 3, 218—220, 221—230; cf. A., 1935, 432).—IV. Hydride di-atoms are classified into periodic groups according to electron configurations. It is improbable that the normal ground state spin of a diat. hydride is  $> 1$  quantum unit.

V. The spectroscopic and bond consts. of hydride di-atoms plotted against the periodic group no. of the elements show no max. as found with non-hydride di-atoms. Hydrides of elements with 18 electrons within the valency group give characteristic curves distinct from those of inert gas structure in that min. are found at group III. J. W. S.

**Vibration-rotation energy levels of polyatomic molecules. II. Perturbations due to neighbouring vibrational states.** E. B. WILSON, jun. (J. Chem. Physics, 1936, 4, 313—316; cf. this vol., 667).—Mathematical. L. J. J.

**Rotation of polyatomic molecules.** E. BARTHOLOMÉ (Z. Elektrochem., 1936, 42, 341—359).—A review.

**Characteristic vibrations of mechanical molecular models. III. Plane six-membered ring and its derivatives.** F. TRENKLER (Physikal. Z., 1936, 37, 338—345; cf. A., 1935, 432, 918).—The characteristic frequencies and vibrational forms of mechanical models representing unsaturated six-membered rings (*cyclohexene*, 1:3- and 1:4-*cyclohexadiene*, 1:3:5-*cyclohexatriene*, and  $C_6H_6$ ) and mono- and di-derivatives of  $C_6H_6$  agree with those expected from theory. The type of vibration is almost independent of the no. and position of the double linkings. It was not possible to observe all the theoretical vibrations of tri-derivatives of  $C_6H_6$  and some of these deviate from theory. A. J. M.

**Parachor and chemical constitution. V. Structure of liquid crystals.** S. K. RAY (J. Indian Chem. Soc., 1936, 13, 194—197).—The parachors of liquid crystals of *p*-azoxy-anisole and -phenetole and *p*-methoxybenzylideneazine at first diminish with rise of temp., then rise suddenly by 12—14 units to the val. corresponding with the true m.p., after which the increases are gradual. This irregularity is explained on the assumption that 7 or 8 mols. are associated to form a complex mol., and rise of temp. breaks down the lateral cohesion between them. C. R. H.

**Parachors of methyl and ethyl nitrites and of nitromethane and nitroethane.** W. A. NOYES and B. SINGH (J. Amer. Chem. Soc., 1936, 58, 802—803).—The parachors of  $MeONO$  and  $EtONO$  agree closely with those of  $MeNO_2$  and  $EtNO_2$ . A hypothesis to explain the increase in parachor caused by a double covalency is advanced. E. S. H.

**Production of clear crystal diagrams in Quenstedt linear projection by means of  $\gamma$ -ray interference.** H. SEEMAN (Physikal. Z., 1936, 37, 345—347).—The production of  $\gamma$ -ray interference diagrams from rock-salt is described. The result is a Quenstedt projection of the lattice. A. J. M.

**Theory of the reflexion of X-rays by crystals.** C. MAUGUIN (Compt. rend., 1936, 202, 1375—1377).—Mathematical. R. S.

**Numerical method for two-dimensional Fourier synthesis.** C. A. BEEVERS and H. LIPSON (Nature, 1936, 137, 825—826). L. S. T.

**Lattice constants for 1936.** M. C. NEUBURGER (Z. Krist., 1936, 93, 1—36).—Tables give the best accepted figures for the lattice consts. of the elements, with their lattice types,  $d$ , at. wt., vol. occupied by the atom, distance of nearest neighbours, etc. References to the literature are given, and data as to the purity of the specimens measured. B. W. R.

**Complete fibre diagrams.** E. SAUTER (Z. Krist., 1936, 93, 93—106).—For obtaining the fullest information about fibre structure from X-rays there are advantages in using a conical film with axis parallel to the fibre axis. A camera suitable for such photographs is described, and examples of its use are given. The interpretation of the photographs is as simple as for the usual type. B. W. R.

**Relation between faults and growth-cessations in crystals.** E. HERLINGER (Z. Krist., 1936, 92, 372—379).—The occurrence of a fault in a crystal growth causes a disturbance of the lattice field which may eventually introduce further faults. The process is traced in detail; alterations of habit and of growth rate may be due to this cause. B. W. R.

**Structure of the real macro-crystal.** E. HERLINGER (Z. Krist., 1936, 92, 380—386).—Further consequences of the effects of faults, resulting in diminished energy of the surface of an irregular crystal as compared with that of the ideal crystal (cf. preceding abstract), are considered. B. W. R.

**Technique for the construction of models illustrating the arrangement and packing of atoms in crystals.** M. J. BUEGER and R. D. BUTLER (Amer. Min., 1936, 21, 150—172). L. S. T.

**Statistical theory of superlattices with unequal concentrations of the components.** R. PEIERLS (Proc. Roy. Soc., 1936, A, 154, 207—222).—Bethe's method (A., 1935, 1193) is generalised to include a cubic face-centred lattice of composition  $AB_3$  (e.g.,  $AuCu_3$ ). L. L. B.

**Influence of the symmetry of the medium on the symmetry of corrosion figures in crystals.** L. ROYER (Compt. rend., 1936, 202, 1346—1348; A., 1930, 21).—Definite corrosion figures were obtained from cryst. apatite and wulfenite with org. acids. Active and inactive acids (e.g., the tartaric acids) gave different and characteristic figures. The effect depends on the symmetry of the crystal and on that of the solution. H. J. E.

**Photometric measurement of the number of oriented crystallites in metallic wires.** J. G. DE LA CUEVA (Anal. Fis. Quim., 1935, 33, 433—437).—The Debye-Scherrer method can be adapted to the determination of the proportion of oriented crystallites in drawn Al wire. There is an increase from 51.72% for 1.78 mm. to 80% for 0.58 mm. diameter wire. The permanent residue of unoriented crystal-



lites is considered to occur in the surface layer and to be produced by friction during the drawing of the wire.

F. R. G.

**X-Ray study of the electrolytic deposition of cadmium.** A. RUBIO and J. G. DE LA CUEVA (Anal. Fis. Quím., 1935, 33, 521—532).—Cd deposited from a solution (1 litre) of CdO 39.4 g., KCN 128.2 g., Na<sub>2</sub>SO<sub>4</sub> 50.0 g., and NiSO<sub>4</sub> 1.0 g. with or without addition of colloid has a grain  $>10^{-6}$  cm. The lattice consts. are identical with those of ordinary Cd and the plane (1122) is oriented parallel to the plane of the sample. The influence of c.d., the nature of the cathode, and the presence of colloid on the orientation of the crystals is discussed.

F. R. G.

**To what class of symmetry does ordinary ice belong?** N. SELJAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 293—294).—X-Ray analysis of ice by the Laue method shows the existence of  $\alpha$ - and  $\beta$ -ice. The former belongs to one of the classes  $D_{6h}$ ,  $D_6$ ,  $C_{6v}$ , and  $D_{3h}$  (hexagonal ice), and the latter to one of the classes  $C_{3v}$  and  $C_3$  (rhombohedral ice). Both modifications are stable.  $\alpha$ -Ice is formed when the temp. of the surrounding air is a little  $<0^\circ$ , and  $\beta$ -ice at lower temp.

A. J. M.

**Morphological and structural relations in cuprite.** W. KLEBER and R. SCHROEDER (Neues Jahrb. Min., 1935, A, 69, 364—387; Chem. Zentr., 1935, ii, 1326).—From a review of the relevant crystallographic, optical, and X-ray data, cuprite is allocated to the space-group  $O^2$  of the trioctahedral crystal class.

J. S. A.

**Structure of  $\alpha$ -quartz.** P. H. WEI (Z. Krist., 1936, 92, 355—362).—Parameters for the already known structure are determined from intensity measurements. Primary extinction in the crystal is measured by abs. methods, and is considerable.

B. W. R.

**Structure of strontium and barium peroxides, SrO<sub>2</sub> and BaO<sub>2</sub>.** J. D. BERNAL, E. DJATLOVA, I. KARSANOVSKI, S. REICHSTEIN, and A. G. WARD (Z. Krist., 1936, 92, 344—354).—The structures are of the CaC<sub>2</sub> type,  $a_0$  5.02  $c_0$  6.55 and  $a_0$  5.34  $c_0$  6.77 Å., respectively. Space-group  $F4/mmm$ . The parameters are determined. The distance O—O is found to be 1.31 Å.

B. W. R.

**Lattice constant of galena with new Röntgen spectrometer.** E. VON ZEIPPEL (Ark. Mat. Astron. Fysik, 1935, 25, A, No. 8; Chem. Zentr., 1935, ii, 1326).—From precision measurements by a substitution method on a new type of instrument (described), using Ag  $K\alpha_1$  radiation in the first 4 orders,  $2d=5923.34$  Å. The half-val. width of the Ag  $K\alpha_1$  line = 5.6".

J. S. A.

**Rotation of anionic polyhedra in cubic crystal lattices. II. Borofluorides.** C. FINBAK and O. HASSEL (Z. physikal. Chem., 1936, B, 32, 433—438).—The X-ray diagrams of the cubic high-temp. forms of NH<sub>4</sub>BF<sub>4</sub> and KBF<sub>4</sub> point to a rotation of the anion as in perchlorates (cf. this vol., 669). In the transformation of KClO<sub>4</sub> and NH<sub>4</sub>BF<sub>4</sub> from the rhombic into the cubic form the occurrence of the displacement of anions and cations postulated by Herrmann and Ilge (A., 1931, 414) has been demonstrated.

In the rotation of anions there will be resonance between this rotation and the directed oscillation of the cations. In cubic KPF<sub>6</sub>, NH<sub>4</sub>PF<sub>6</sub>, and TlPF<sub>6</sub> there is rotation of the PF<sub>6</sub><sup>-</sup> ions.

R. C.

**Crystal structure of radium fluoride.** G. E. R. SCHULZE (Z. physikal. Chem., 1936, B, 32, 430—432).—RaF<sub>2</sub> crystallises in the fluorspar lattice with  $a$  6.368 Å. and  $d$  6.75. The radius of Ra<sup>++</sup> for co-ordination no. 6 is 1.52 Å.

R. C.

**Configuration of the azide ion.** L. K. FREVEL (J. Amer. Chem. Soc., 1936, 58, 779—782).—The N—N distances in crystals of NaN<sub>3</sub> and KN<sub>3</sub> have been determined by the X-ray method as  $1.150 \pm 0.016$  and  $1.145 \pm 0.017$  Å., respectively. In NH<sub>4</sub>N<sub>3</sub> it is  $1.165 \pm 0.021$  Å.

E. S. H.

**Space-group of calcium sulphate dihydrate.** J. PALACIOS and L. RIVOIR (Anal. Fis. Quím., 1935, 33, 518—520).—A re-examination of the crystal structure of gypsum (cf. A., 1930, 139) shows that, contrary to Onorato (A., 1930, 672), the space-group is  $C_{2h}$ .

F. R. G.

**Structure of some hydrates of sodium borate.** W. MINDER (Z. Krist., 1936, 92, 301—309).—Cell consts. and space-groups of the following compounds are determined: kernite Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O, tinkalconite Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·5H<sub>2</sub>O, borax Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O. The results are discussed in relation to the effective vol. occupied by the additional H<sub>2</sub>O.

B. W. R.

**Crystal structure of silver phosphate.** L. HELMHOLZ (J. Chem. Physics, 1936, 4, 316—322).—Laue and oscillation diagrams of Ag<sub>3</sub>PO<sub>4</sub> give 5.995 Å. for the edge of the cubic unit containing two mols. The space-group is  $T^4$ . A new val. for the O parameter has been obtained, giving P—O in :PO<sub>3</sub>  $1.61 \pm 0.03$  Å. The discrepancy with KH<sub>2</sub>PO<sub>4</sub> is due to covalent bond formation of O with Ag atoms, which must be treated as oscillators with tetragonal symmetry. The ratio of the amplitudes of vibration along and perpendicular to the tetragonal axis is calc.

L. J. J.

**Crystal structure of barium antimonate.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 652—661).—Ba(SbO<sub>3</sub>)<sub>2</sub>·8H<sub>2</sub>O forms monoclinic prismatic (pseudo-orthorhombic) crystals ( $a_0$  9.961,  $b_0$  12.506,  $c_0$  10.129 Å.;  $\beta$  87° 17'; 1 mol. in unit cell; space-group  $C_{2h}^2$ ). The Sb atoms are arranged in layers perpendicular to the  $b$  axis. The distance between such layers is 6.253 Å. The distance between Sb atoms in a layer is approx. 5 Å. Each Sb is surrounded by 6 O atoms, forming {Sb(OH)<sub>6</sub>}'. The composition is Ba{Sb(OH)<sub>6</sub>}<sub>2</sub>·2H<sub>2</sub>O.

H. J. E.

**Crystallography of lithium molybdatellurate.** J. D. H. DONNAY and J. MÉLON (Amer. Min., 1936, 21, 125—127).—3Li<sub>2</sub>O·TeO<sub>3</sub>·6MoO<sub>3</sub>·13H<sub>2</sub>O,  $d$   $2.2 \pm 0.1$ , hardness  $2\frac{1}{2}$ , rhombohedral-hexagonal, uniaxial negative,  $n_e$  1.612,  $n_w$  1.703 (both  $\pm 0.001$ ) for Na light.

L. S. T.

**Crystal structure of hexaethylbenzene.** H. K. PAL and A. C. GUHA (Z. Krist., 1936, 92, 392—394).—Goniometric measurements are given; the cell is triclinic with  $a_0$  9.90,  $b_0$  9.84,  $c_0$  6.10 Å.,  $\alpha$  58° 5',  $\beta$  103° 54',  $\gamma$  123° 43'.

B. W. R.



**Magnetic isotropy and crystal structure of hexaethylbenzene.** N. GANGULI (Z. Krist., 1936, 93, 42—46).—Magnetic measurements on single crystals are used to locate an approx. plane of magnetic symmetry, parallel to which the  $C_6$  rings of the mols. should lie. B. W. R.

**Molecular structure of quinhydrone.** J. PALACIOS and O. R. FOZ (Anal. Fis. Quím., 1935, 33, 627—642).—Contrary to the authors' earlier work (A., 1932, 904) quinhydrone (I) crystals are triclinic, pseudomonoclinic, pseudorhombic, and pseudohexagonal; space-group  $C_2$ ;  $a$  21.8,  $b$  6.04,  $c$  7.70 Å.; they exhibit a subperiodicity due to alternation of mols. of benzoquinone (II) and quinol (III). Vals. of  $\chi_m \times 10^6$  are (I) —84.2, (II) —33.3, (III) —64.5. (I) does not exist as a free radical. F. R. G.

**X-Ray analysis of the dibenzyl series. III. Structure of stilbene, tolane, and azobenzene.** J. M. ROBERTSON, M. PRASAD, and (MISS) I. WOODWARD (Proc. Roy. Soc., 1936, A, 154, 187—195; cf. A., 1933, 1107).—Detailed measurements have been made on stilbene, and sufficient preliminary data obtained for tolane and azobenzene to show that the three structures are closely similar. The space-group is  $C_{2h}^2$  ( $P2_1/a$ ), with 4 mols. per unit cell. In stilbene, the 4 mols. have centres of symmetry which coincide with 4 crystal centres; 2 of the mols. have orientations similar to that of dibenzyl, whilst the other 2 can be derived from them by a rotation of  $180^\circ$  about the  $a$  axis and a translation of  $\frac{1}{2}c$ . The proposed structure is compatible with the other physical properties of the crystal, including the magnetic data. L. L. B.

**Crystal structure of condensed ring compounds. I. 1:2-cycloPentenophenanthrene. II. 7-Methoxy-3':3'-dimethyl-1:2-cyclopentenophenanthrene and 7-methoxy-1:2-cyclopentenophenanthrene.** J. IBALL (Z. Krist., 1936, 92, 293—300; 93, 47—56).—I. The cell is monoclinic,  $a_0$  18.38,  $b_0$  5.83,  $c_0$  23.61 Å.,  $\beta$   $114.3^\circ$ ;  $d$  1.23; 8 mols. in cell; space-group  $B$   $2_{1/c}$ . The reflexion intensities show marked similarities with the analogous ones from chrysene, which enables the orientation of the mols. to be determined approx.

II. Both compounds are monoclinic, space-group  $C_{2h}^2$ ; cell data and optical data are given, and the probable position of the mols. in the cell is located on the basis of these data and the reflexion intensities.

B. W. R.

**Crystal studies on certain *p*-toluenesulphonamides. I. Nitrogen-substituted sulphonanilides. II. Nitrogen-substituted sulphon-*o*-toluidides. III. Nitrogen-substituted sulphon-*p*-toluidides.** G. H. YOUNG, W. J. KETH, and A. P. HONESS (Z. Krist., 1936, 92, 216—220, 395—401; 93, 107—112).—I. Crystallographic data are given for *p*-toluenesulphon-*N*-isopropylanilide, and for the corresponding *N*-*n*- and *N*-*sec*-Bu compounds.

II. A goniometric description of *p*-toluenesulphon-*N*-methyl-*o*-toluidide and the corresponding *N*-Et, -Pr $^\beta$ , -Pr $^\alpha$ , -Bu $^\alpha$ , -Bu $^\beta$ , and -isoamyl compounds.

III. Crystallographic descriptions of *p*-toluenesulphon-*N*-methyl-*p*-toluidide and the corresponding Et, Pr $^\beta$ , Bu $^\beta$ , *n*- and iso-amyl compounds are given.

**X-Ray studies on choleic acids.** Y. GO and O. KRATKY (Z. Krist., 1936, 92, 310—312).—Compounds of deoxycholic acid with the saturated fatty acids give sensibly the same X-ray photographs with from 3 to 22 C atoms. A typical set of photographs is analysed; the rhombic cell has  $a_0$  25.8,  $b_0$  13.5,  $c_0$  7.22 Å.; space-group probably  $V^3$ . B. W. R.

**X-Ray study of myosin.** W. T. ASTBURY and (MRS.) S. DICKINSON (Nature, 1936, 137, 909—910; cf. this vol., 623). L. S. T.

**Experiments with models on the theory of the Kikuchi lines.** A. LICHTENFELD and K. SCHWARZ (Naturwiss., 1936, 24, 377).—A reply to von Laue (cf. this vol., 554). A. J. M.

**Electron analysis: influence of the prolonged passage of a beam of electrons through thin films.** J. J. TRILLAT and S. OKETANI (Compt. rend., 1936, 202, 1332—1334).—The diffraction pattern from a thin crystal. Au film disappears gradually on exposing a single spot on the film continuously to the electron beam for  $1\frac{1}{2}$  hr. The effect is attributed to local heating (cf. Andrade and Martindale, A., 1935, 1449). H. J. E.

**Structure of thin metallic films deposited on rock-salt by vaporisation.** L. BRÜCK (Ann. Physik, 1936, [v], 26, 233—257).—The structure of films of Ag, Au, Al, Cu, Ni, Pd, Co, Fe, and Cr deposited on NaCl by vaporisation in vac. was investigated by electron diffraction. Above a temp. characteristic of each metal, films of Au, Ag, Al, Ni, Cu, and Pd possessed a mosaic structure, the crystallites being oriented in the same direction. Fe and Cr showed three directions of orientation. The previously discovered orientation rule for substances deposited on a crystal base holds only for deposition from solution.

A. J. M.

**Electron diffraction by single crystals.** O. SPECCHIA and N. DALLAPORTA (Nuovo Cim., 1935, [ii], 12, 4—14; Chem. Zentr., 1935, ii, 1311).—The formation of supplementary lines and bands in the diffraction pattern is discussed. J. S. A.

**Electron-diffraction study of the structure of electro-deposited metals.** G. I. FINCH and C. H. SUN (Trans. Faraday Soc., 1936, 32, 852—863).—The structure of electro- and chemically deposited metal films on metallic substrates has been studied. Orientation of the substrate crystals nearly always determines that of the electro-deposit, whilst films deposited on amorphous surfaces show normal orientation. Adhesion increases with orienting effect. An anomalous double diffraction observed with composite films is discussed. Chemical displacement leads to alloy formation. L. J. J.

**Diffraction of electrons by amalgam films.** A. E. AYLMEYER, G. I. FINCH, and S. FORDHAM (Trans. Faraday Soc., 1936, 32, 864—871).—Extra rings due to amalgam formation on Au, Ag, Cu, and Pd leaf have been investigated. Au and Ag form simple cubic amalgams with  $a$  17.81 and 17.94 Å., respectively, and Ag also forms two face-centred tetragonal amalgams. Pd is partly attacked. L. J. J.

**Structure of the paraffin chain studied by means of electron rays.** R. RIGAMONTI (Gazzetta,



1936, 66, 174—182).—Electron diffraction measurements with long-chain paraffin hydrocarbons confirm the results of X-ray investigations. The angle between the plane of symmetry of the paraffin chain and the (010) crystal plane is calc. to be  $35-50^\circ$  and the C-H distance 1.25 Å. These vals. are confirmed by steric considerations. O. J. W.

**δ-Quartz.** L. BALAMUTH, F. ROSE, and S. L. QUIMBY (Physical Rev., 1936, [ii], 49, 703).—Quartz can be piezoelectrically excited at a temp. as low as  $78^\circ$  abs., contrary to Osterberg's result (cf. this vol., 672). N. M. B.

**Changes in magnetisation of nickel and permalloy and of nickel-iron crystals in high fields.** G. GERLOFF (Z. Physik, 1936, 99, 585—594).—The susceptibility of Ni and permalloy attains a const. end val. at 4000 gauss, changing by  $< 6\%$  up to 5500 gauss. A. B. D. C.

**Conditions of demagnetisation of rhombohedral iron sesquioxide.** A. MICHEL (Compt. rend., 1936, 202, 1769—1771; cf. A., 1935, 1063).—Pptd.  $\text{Fe}_2\text{O}_3$ , annealed at  $700^\circ$ , shows a rapid increase in magnetisation above  $600^\circ$  (anomaly  $A$ ). On cooling again the magnetisation rises normally with decrease of temp. to below the Curie point, then attains a max., decreases slightly (anomaly  $a$ ) and thereafter remains approx. const. to room temp. On annealing at  $800-900^\circ$ ,  $A$  occurs at  $560^\circ$ , whilst  $a$  disappears, but after annealing above  $1000^\circ$ ,  $A$  is still lower. After annealing for several hr. at  $1300^\circ$ , normal reversible magnetisation curves are obtained. The min. temp. of demagnetisation of annealed  $\text{Fe}_2\text{O}_3$  can occur below the Curie point, but it is always above the temp. of anomaly  $a$ . J. W. S.

**Temperature variation of electron spin paramagnetism.** E. C. STONER (Proc. Leeds Phil. Soc., 1936, 3, 191—199).—Expressions are derived for the temp. variation of paramagnetic susceptibility due to electron spin. The bearing of the results on the magnetic properties of metals is discussed. J. W. S.

**Total reflecting power as a function of temperature in the neighbourhood of the Curie point.** L. S. ORNSTEIN and J. H. VAN DER VEEN (Physica, 1936, 3, 289—300).—The total reflecting power of Fe for  $\lambda$  6500 Å. and angle of incidence about  $15^\circ$  rises rapidly and continuously from about 62% to 66% when the temp. rises from  $1000^\circ$  to  $1100^\circ$  abs. It is concluded that the internal magnetic field does not disappear abruptly at the Curie point, but some remains up to  $1100^\circ$ . It is suggested that the Curie point for some regions of spontaneous magnetisation is a function of the orientation of the internal field towards the crystal lattice of this region. No large change in reflecting power occurs at the  $\beta$ - $\gamma$  transition point ( $1180^\circ$  abs.). J.

**Variation of Young's modulus with magnetisation and temperature in nickel.** S. SIEGEL and S. L. QUIMBY (Physical Rev., 1936, [ii], 49, 663—670).—For annealed polycryst. Ni, 99.7% pure, the % increase in Young's modulus,  $E$ ,  $\propto J^2$  ( $J$ —intensity of magnetisation) over 0—0.4 saturation at all temp. below  $311^\circ$ . The total increase in  $E$  from

the demagnetised to the saturated state is 6.7% at  $23^\circ$ , reaching a max. of 18.7% at  $185^\circ$ , and decreasing to zero at the Curie point. Results are in general agreement with Akulov's theory (cf. A., 1933, 1237). N. M. B.

**Plasticity of bismuth crystals.** H. J. GOUGH and H. L. COX (Nature, 1936, 137, 701).—Photomicrographs of Bi crystals showing deformation by "slip" following compression are reproduced. Deformation by twinning is more common. L. S. T.

**Dependence of plasticity on temperature.** H. EKSTEIN (Z. Krist., 1936, 92, 253—274).—The elastic properties of W single crystals at  $-185^\circ$  and  $16^\circ$ , of rock-salt over the range  $300^\circ$  to  $-250^\circ$ , and of bakelite over the range  $16^\circ$  to  $60^\circ$  have been measured. Agreeing with previous results on cryst. substances, the temp. variation is not sufficient to suggest that plasticity is thermal in origin; for the amorphous bakelite the very large variation of elastic consts. agrees with the temp. theory of plasticity. B. W. R.

**Photo-electric method for determining the elastic limit of an X-rayed rock-salt crystal.** M. N. PODASCHEVSKI (Physikal. Z. Sovietunion, 1935, 7, 399—409). CH. ABS. (e)

**Statistical molecular configuration and elastic properties of substances of high mol. wt.** W. KUHN (Naturwiss., 1936, 24, 346—347).—Theoretical. A. J. M.

**Elastic constants, electrical resistance, and thermal expansion of magnesium crystals.** E. GOENS and E. SCHMID (Physikal. Z., 1936, 37, 385—391).—The principal elastic consts., sp. resistance at room temp., relative electrical resistance over the temp. range  $-269^\circ$  to  $100^\circ$ , and the principal vals. of the thermal expansion over the range  $-253^\circ$  to  $200^\circ$  have been determined for single hexagonal Mg crystals for different crystallographic orientations. The anisotropy of these physical properties, though  $<$  that for Zn and Cd, is  $>$  would be expected considering the close resemblance of the Mg lattice to the hexagonal close-packed lattice. A. J. M.

**Principal elastic constants of single crystals of copper, gold, and lead.** E. GOENS (Physikal. Z., 1936, 37, 321—326).—The vals. of the principal elastic consts.,  $S_{11}$ ,  $S_{12}$ ,  $S_{44}$ , of single crystals of Cu, Au, and Pb, obtained by a dynamic method, were Cu, 14.91, —6.25, 13.28, respectively, Au, 23.30, —10.65, 23.80, respectively, and Pb, 93.0, —42.6, 69.4, respectively (all  $\times 10^{-13}$  sq. cm. per dyne). The corresponding principal elastic moduli,  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  were also calc. The Cauchy relation ( $C_{12} = C_{44}$ ) is not satisfied. The results for Cu do not agree with those of Kimura (A., 1933, 1237). A. J. M.

**State of electrolytically separated metals.** G. TAMMANN and H. JAACKS (Z. anorg. Chem., 1936, 227, 249—260).—Electrolytically separated metals, e.g., Cu, Fe, Zn, and Ni, have a hardness similar to that of cold-worked metal, and, in both cases, the structure is fibrous. The fibres are formed perpendicular to the cathode. The reflected Co  $K_\alpha$  line shows an increased sharpness of the interference lines on heating in all cases except Cu. The metals may contain considerable quantities of  $\text{H}_2$ , which is



removed by heat, but this appears to bear no relation to the hardness. The  $H_2$  content varies in the different layers of the electrolytic metal, causing scaling. The rate of dissolution of electrolytic Fe in acids varies with the treatment, the untreated Fe being less readily attacked than the fused or milled metal. The rate for electrolytic Zn is not much affected by treatment. The temp. of separation of a metal greatly affects polarisation. M. S. B.

**Orientation of oxide films on iron.** R. F. MEHL and E. L. McCANDLESS (Nature, 1936, 137, 702; A., 1935, 161).—X-Ray photographs of FeO films on single crystals of Fe show reflexions from  $Fe_3O_4$  resulting from partial decomp. of the wüstite phase. The  $Fe_3O_4$  is identically oriented with the FeO with all planes of the same indices in the two cubic lattices parallel. The same orientation relationship holds when an FeO film is grown by reduction on a natural crystal of magnetite. The Fe atoms determine the orientation relationship in the case of FeO on Fe and the oxygen atoms that of  $Fe_3O_4$  on  $Fe_3O_4$ . L. S. T.

**Isomorphism of organic compounds.** H. LETTRÉ, H. BARNBECK, and W. LEGER (Ber., 1936, 69, [B], 1151—1154).—Investigation of the systems from the hydroxy-, chloro-, and methyl-benzoic acids taken in corresponding pairs, of  $r\text{-OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  and  $r\text{-CHClPh}\cdot\text{CO}_2\text{H}$ , and of cholesterol and cholesteryl chloride combined with the results of Grimm (A., 1931, 1363) shows isomorphous replaceability between OH and Me in one of five cases, of OH and Cl in four of 12 cases, and of Cl and Me in six of nine instances examined. Formation of mixed crystals is not observed in the systems: stilbene-phenanthrene (I),  $(\text{CH}_2\text{Ph})_2$ -(I),  $\text{CHPh}\cdot\text{CPh}_2$ -benzylidene-fluorene,  $\text{C}_6\text{Ph}_3$ -9:10-diphenylphenanthrene. H. W.

**Application of the theory of thermal oscillations to the field of mesophases (liquid crystals).** H. ZOCHER (Kolloid-Z., 1936, 75, 161—163).—Theoretical. E. S. H.

**Mol.-wt. changes of sulphur monochloride.** W. A. PATRICK and N. HACKERMAN (J. Physical Chem., 1936, 40, 679—688).—Determinations in a modified Cottrell b.-p. apparatus, using  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , cyclohexane, and PhMe as solvents, show that the mol. wt. of  $\text{S}_2\text{Cl}_2$  is affected by its age, temp., solvent, and concn. The abnormal vals. are assumed to be due to the presence of a polymeride  $(\text{S}_2\text{Cl}_2)_2$ , which breaks up into  $\text{S}_8$  and  $\text{S}_2\text{Cl}_4$ . The change with concn. is also due to equilibrium between large and small mols. of S. E. S. H.

**Mol. wt. of fused yellow phosphorus.** N. D. LITVINOV (J. Appl. Chem. Russ., 1936, 9, 589—590).—The mol. wt. corresponds with  $\text{P}_4$  at 50—95°. R. T.

**Phenomenological theory of superconductivity.** E. SCHRÖDINGER (Nature, 1936, 137, 824).—London's theory (A., 1935, 689) is simplified. L. S. T.

**Conductance of salt crystals.** W. JOST (J. Chem. Physics, 1936, 4, 323).—A reply to Rodebush and Cooke (this vol., 138). L. J. J.

**Magnetic anisotropy of resorcinol.** K. LONSDALE (Nature, 1936, 137, 826).—Measurements of the diamagnetic anisotropy of a single crystal of resorcinol are recorded. The derived orientation of the mol. plane relative to the crystal axes agrees with the results of a Fourier analysis. L. S. T.

**Appearance of ferromagnetism in some paramagnetic salts at very low temperatures.** M. KURTI, P. LAINE, B. V. ROLLIN, and F. SIMON (Compt. rend., 1936, 202, 1576—1578).— $\text{NH}_4$  Fe alum behaves as a ferromagnetic substance at approx.  $0.01^\circ$  abs. H. J. E.

**Diamagnetic susceptibility of heavy water.** V. C. G. TREW and J. F. SPENCER (Nature, 1936, 137, 706).—Using a modified Gouy balance, the mass susceptibility obtained for 99.2%  $\text{D}_2\text{O}$ ,  $d$  1.1049, is  $0.637 \pm 0.001 \times 10^{-6}$  unit at  $20^\circ$  (cf. this vol., 672),  $\text{H}_2\text{O}$  being  $0.720 \times 10^{-6}$ . L. S. T.

**Magnetic susceptibility of chlorine hexoxide.** J. FARQUHARSON, C. F. GOODEVE, and F. D. RICHARDSON (Trans. Faraday Soc., 1936, 32, 790—795).—The magnetic susceptibility of solid and liquid  $\text{Cl}_2\text{O}_6$  has been measured between  $-40^\circ$  and  $10^\circ$ . The % of  $\text{ClO}_3$  present at various temp., and the corresponding equilibrium consts., have been calc. by using theoretical vals. for  $\text{Cl}_2\text{O}_6$  and  $\text{ClO}_3$ . The heat of dissociation is calc. to be  $1730 \pm 500$  g.-cal. per mol.  $\beta^{3.5} = 2.023 \pm 0.003$ ; coeff. of cubical expansion =  $12 \pm 3 \times 10^{-4}$ . F. L. U.

**Magnetochemical studies. XXI. Molybdenum and tungsten halides. Magnetic behaviour of compounds of the higher transitional elements.** W. KLEMM and H. STEINBERG (Z. anorg. Chem., 1936, 227, 193—213; cf. this vol., 556).—Susceptibilities of  $\text{MoCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{MoBr}_3$ ,  $\text{MoBr}_4$ ,  $\text{WCl}_3$ ,  $\text{WCl}_5$ ,  $\text{WCl}_6$ , and  $\text{WBr}_5$  have been determined at  $20^\circ$ ,  $-78^\circ$ , and  $-183^\circ$ . F. L. U.

**Magnetic study of mixed crystals of bivalent copper and silver.** L. CAPATOS and N. PERAKIS (Compt. rend., 1936, 202, 1773—1775).— $[\text{Ag}^{11}, 4\text{C}_5\text{H}_5\text{N}]\text{S}_2\text{O}_8$  and  $[\text{Cu}^{11}, 4\text{C}_5\text{H}_5\text{N}]\text{S}_2\text{O}_8$  have magnetic moments of 9.11 and 9.78 Weiss magnetons, respectively. Study of mixed crystals of these compounds shows that addition of small amounts of either compound to the other lowers the Curie const., but that a max. is attained at about equimol. concns. The Curie points change in parallel manner. J. W. S.

**Magnetochemical investigations. XXII. Magnetic behaviour of chromium-phenyl compounds.** W. KLEMM and (FRL.) A. NEUBER (Z. anorg. Chem., 1936, 227, 261—271).—The magnetic moment of Hein's Cr-Ph compounds (A., 1931, 1435) is approx. 1.73 Bohr magnetons, whether the compound contains 5, 4, or 3 Ph per Cr. It is concluded that  $\text{Cr}^{\text{V}}$  is present in all cases. Formulæ are discussed. M. S. B.

[Magnetic behaviour of chromium-phenyl compounds.] F. HEIN (Z. anorg. Chem., 1936, 227, 272; cf. preceding abstract).—A reference to the formulæ for Cr-Ph compounds. M. S. B.

**Polymerisation and diamagnetic susceptibility.** S. S. BHATNAGAR, M. B. NEVGI, and R. N.



MATHUR (Z. Physik, 1936, **100**, 141—144).—Polymerisation of anthracene,  $\text{COMe}_2$ ,  $\text{PhCHO}$ , furfuraldehyde, and  $\text{AcCN}$  leads to a decrease in sp. diamagnetic susceptibility. A. B. D. C.

Magnetic susceptibilities of organic substances in different physical states. A. BOSE (Phil. Mag., 1936, [vii], **21**, 1119—1125).—Within limits of experimental error the diamagnetic susceptibilities of 27 org. compounds investigated are independent of their physical state (single crystal, molten liquid, or solution). J. W. S.

Magnetic properties of superconductors. T. C. KEELEY and K. MENDELSSOHN (Proc. Roy. Soc., 1936, **A**, 154, 378—385; cf. A., 1935, 1309).—Previous experiments have been extended to a greater no. of superconducting substances, the specimens used being in the form of long rods in a longitudinal field. The change from superconductivity to the normal state takes place in a small temp. interval, which increases as the temp. falls. The steepness of the transition in Sn single crystals is much  $>$  in polycryst. Sn, and the transition region can be reduced further by using highly purified substances. L. L. B.

Ultrasonic velocities in liquid mixtures. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, **3**, A, 297—303; cf. this vol., 277).—Data and graphs of ultrasonic velocities and adiabatic compressibilities are given for binary liquid mixtures of  $\text{CCl}_4$  with  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ ,  $\text{EtOAc}$ , and tetralin. The types of curve found for adiabatic compressibility-concn. are similar to those previously found for intensity of scattered light-concn. (cf. A., 1934, 1056). N. M. B.

Absorption of ultrasonic waves in liquids. J. CLAEYS, J. ERRERA, and H. SACK (Compt. rend., 1936, **202**, 1493—1494).—The absorption coeffs. of ultrasonic waves in  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ , and  $\text{MeOAc}$  are  $>$  the theoretical. Addition of a small amount of  $\text{CCl}_4$  greatly diminishes the absorption in  $\text{CS}_2$ . The deviation from the classical theory is attributed to hysteresis of the adiabatic compressibility of liquids. R. S.

Measurements of absorption, velocity, and out-gassing [of liquids] in the ultrasonic region. C. SORENSEN (Ann. Physik, 1936, [v], **26**, 121—137).—Data are recorded for a no. of liquids at frequencies of 194—950 kHz. Except with  $\text{H}_2\text{O}$ , the absorption increases with frequency, and with  $\text{EtOH}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{PhMe}$  depends on the intensity of the radiation. The energy required to expel 1 c.c. of gas from  $\text{H}_2\text{O}$  and oil at a no. of frequencies has been measured. The velocity in  $\text{C}_6\text{H}_6$  decreases with increasing frequency. L. J. J.

Specific heats of the mineral oxides: vitreous silica, lime, alumina, as a function of temperature. A. THURET (Compt. rend., 1936, **202**, 1368—1370).—Equations in good agreement with experimental data have been deduced for the mean and the true sp. heats. R.

Hydrogen sulphide. Heat capacity and vapour pressure of solid and liquid. Heat of vaporisation. Comparison of thermodynamic and spectroscopic values of the entropy. W. F.

GIAUQUE and R. W. BLUE (J. Amer. Chem. Soc., 1936, **58**, 831—837).—Heat capacities have been determined from  $16^\circ$  abs. to the b.p. A transition was observed at  $103.52^\circ$  abs. and a large energy absorption, possibly ending in a transition, near  $126^\circ$  abs.  $\text{H}_2\text{S}$  has m.p.  $187.61^\circ$  abs., b.p.  $212.77^\circ$  abs., heat of fusion 568.1 and heat of vaporisation at the b.p. 4463 g.-cal. per mol. The v.p. has been determined over the range  $164.90$ — $213.17^\circ$  abs. The calc. mol. entropy of the gas at the b.p. is  $46.38 \pm 0.1$  e.u., neglecting the nuclear spin entropy. E. S. H.

Simplified method of calculating entropy of organic compounds. I. I. STRELKOV (Ukrain. Chem. J., 1936, **11**, 32—40).—The entropy of org. compounds at  $25^\circ$  is given by  $kC$ , where  $C$  is the mol. sp. heat, and  $k=1.1$  for solids, and 1.4 for liquids. R. T.

Changes in thermal and calorimetric values along the two fusion curves of helium. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 612—622).—The triple point is at  $1.774^\circ$  abs./28.91 atm. Data for the v.p. and latent heat are recorded. H. J. E.

Latent heat of tin in passing from the superconductive to the non-superconductive state. W. H. KEESOM and P. H. VAN LAER (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 573—574, and Physica, 1936, **3**, 371—384).—The val. obtained with fields of 50—140 gauss agrees with that calc. thermodynamically. The magnetic field within the Sn was zero so long as the whole body was superconductive. In the transition range it increased gradually. H. J. E.

F.p. and b.p. of propane. M. M. HICKS-BRUUN and J. H. BRUUN (J. Amer. Chem. Soc., 1936, **58**, 810—811).—After treatment with  $\text{ClSO}_3\text{H}$  and subsequent fractional distillation, propane has f.p.  $-187 \pm 0.1^\circ$  and b.p.  $-42.17 \pm 0.05^\circ$ . E. S. H.

Boiling under constant pressure. G. DUCH (J. Chim. phys., 1936, **33**, 414—426).—Approx. formulae are derived connecting the reduced mol. attraction force  $\varphi\gamma$ , the surface tension  $A$ , and the mol. radius  $r$  of a liquid. For a related group of org. liquids,  $\Delta\varphi\gamma/\Delta(1/r)$  and  $\Delta A/\Delta(1/r)$  should be const.; this is in general supported by published or experimental vals. of the physical quantities involved. R. C. M.

Thermal properties of halides. X. Vapour pressures and vapour densities of gallium trihalides. W. FISCHER and O. JUBERMANN (Z. anorg. Chem., 1936, **227**, 227—236).—M.p. determinations in quartz tubes in vac. give  $\text{GaCl}_3$   $77.9 \pm 0.2^\circ$ ,  $\text{GaBr}_3$   $121.5 \pm 0.6^\circ$ , and  $\text{GaI}_3$   $212 \pm 1^\circ$ . The v.p. of the unsaturated and saturated vapours has been determined with a quartz spiral manometer and the following vals. for the b.p. have been deduced:  $\text{GaCl}_3$   $201.3^\circ$ ,  $\text{GaBr}_3$   $279^\circ$  (at 750 mm.),  $\text{GaI}_3$   $346^\circ$ . The degree of dissociation of  $\text{Ga}_2\text{X}_6$  into  $2\text{GaX}_3$  has been calc. at m.p. and b.p. This increases from chloride to iodide whilst the heat of dissociation diminishes and the heat of volatilisation increases. M. S. B.



**Hydrocarbon vapour pressures.** E. R. COX (Ind. Eng. Chem., 1936, 28, 613—616).—V.-p. data for all hydrocarbons having mol. wt.  $> 30$  can be correlated by three equations, if b.p., crit. temp. and pressure are known, and the latter can be calc. for the normal paraffin series. H. C. M.

**Phase equilibria in hydrocarbon systems.**  
**XIII. Joule-Thomson coefficients of propane.** B. H. SAGE, E. R. KENNEDY, and W. N. LACEY (Ind. Eng. Chem., 1936, 28, 601—604).—Joule-Thomson coeffs. of pure  $C_3H_8$  gas were determined at six temp. between  $21^\circ$  and  $105^\circ$  and at pressures up to 550 lb. per sq. in. using a small automatically maintained const.-pressure drop across a radial-flow porous plug at a given temp. and pressure, the fall in temp. of the gas in passing through the plug being measured. H. C. M.

**Isotherms of ethylene between  $0^\circ$  and  $150^\circ$  and at pressures from 20 to 270 atmospheres.** A. MICHELS, J. DE GRUYTER, and F. NIESEN (Physica, 1936, 3, 346—351).—The isotherms have been measured at  $0^\circ$ ,  $25^\circ$ ,  $50^\circ$ ,  $75^\circ$ ,  $100^\circ$ ,  $125^\circ$ , and  $150^\circ$ , and empirical equations for  $pv$ , correct to 0.01%, are calc. for the respective temp. From the  $(pv_{t+12.5} - pv_{t-12.5})/25 - t$  curves for different densities it is concluded that  $c_v$  increases with increasing density to pass through a max. at the crit. density. J. W. S.

**Vapour pressure of mercury dimethyl.** F. RATMAN (J. Appl. Chem. Russ., 1936, 9, 591—593).—The v.p. is given by  $\log P = 6.53 - 1050/T - 11,000/T^2$ , at  $-60^\circ$  to  $100^\circ$ . R. T.

**Internal changes in the system  $SO_3$ .** I. A. SMITS and N. F. MOERMAN (Z. physikal. Chem., 1936, B, 32, 369—382).—The v.p.,  $p$ , of a specimen of  $\alpha$ - $SO_3$  prepared by partial evaporation of equilibrated  $\alpha$ - $SO_3$  and not in internal equilibrium increases with time according to a hyperbolic curve. Such  $SO_3$  begins to melt only at a temp. considerably above the triple point, showing that the mass is disequilibrated throughout. On irradiation with Cu K $\alpha$  radiation  $p$  rises at a const. rate to a val. corresponding with the v.p. of the  $\alpha$ -form in internal equilibrium, then remains const. It follows that X-rays accelerate equilibration. From measurements of the heat of mixing of molten  $SO_3$  with 83%  $H_2SO_4$  and the heats of dissolution in this solvent of disequilibrated and equilibrated  $\alpha$ - $SO_3$  the mol. heat of fusion of a disequilibrated specimen was found to  $-1.8$  kg.-cal., changing to  $-5.0$  kg.-cal. after irradiation with X-rays. This latter val. agrees with that calc. from v.-p. data for  $\alpha$ - $SO_3$  in internal equilibrium, showing that X-rays effect internal equilibration throughout the solid. R. C.

**Thermal conductivity of deuterium.** G. W. KANNULUIK (Nature, 1936, 137, 741).—The val. obtained at  $1.6^\circ$  for  $D_2$  is  $32.94 \pm 0.04 \times 10^{-5}$  g.-cal. per cm. per sec. per degree. L. S. T.

**Heat conductivity of liquid helium.** W. H. KEESOM and (MISS) A. P. KEESOM (Physica, 1936, 3, 359—360).—The thermal conductivity of liquid He II at  $1.4^\circ$  and  $1.75^\circ$  abs. is about 190 g.-cal. per degree cm. sec., or 200 times that of Cu at room temp.

and  $3 \times 10^6$  that of liquid He I. The term "supra-heat conductivity" is suggested for this phenomenon. J. W. S.

**Theory of viscosity of liquids.** D. B. MACLEOD (Trans. Faraday Soc., 1936, 32, 872—876).—An equation of the type of Andrade (A., 1934, 356) can be deduced from the author's equation for  $\eta$  (A., 1925, ii, 498) by taking into account associative van der Waals forces. L. J. J.

**Significance of viscosity.** H. R. SCHULZ (Z. Physik, 1936, 99, 666—668).—Greases are colloidal solutions, and may be used to determine the dependence of the coeff. of viscosity on time, temp., and shearing forces. A. B. D. C.

**Viscosities of some liquid refrigerants.** J. H. AWBERRY and E. GRIFFITHS (Proc. Physical Soc., 1936, 48, 372—380).—Using the method of timing the rate of fall of a closely fitting plug in a vertical tube filled with the liquid, and a special arrangement to prevent evaporation and bubble formation, data were obtained for  $\eta$  for  $SO_2$ ,  $MeCl$ ,  $EtCl$ ,  $CCl_2F_2$ , *cis*- and *trans*- $C_2H_2Cl_2$ , and  $CHCl_3$ , over the range  $-15^\circ$  to  $30^\circ$ . Results follow the law  $\eta = Ae^{a/T}$ , where  $T$  is the abs. temp. and  $A$  and  $a$  are consts. N. M. B.

**Structure viscosity.** W. PHILIPPOFF (Z. Spiritusind., 1936, 59, 157—158).—A survey of apparatus and technique, and discussion of published data for starch. E. S. H.

**Theory of structure viscosity. II. Streaming of structure-viscous substances.** W. PHILIPPOFF (Kolloid-Z., 1936, 75, 142—154; cf. A., 1935, 692).—Published work is discussed. E. S. H.

**Heterogeneous recombination and diffusion coefficients of halogen atoms.** E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 917—922).—The mechanism of heterogeneous recombination is discussed. Diffusion coeffs. of Br and I atoms through a no. of gases are calc. from measurements of the stationary dissociation of illuminated halogen vapours. L. J. J.

**Origin of the term "solute."** (STR) W. J. POPE (Nature, 1936, 137, 782). L. S. T.

**Thermal diffusion in deuterium mixtures.** K. E. GREW and B. E. ATKINS (Proc. Physical Soc., 1936, 48, 415—420).—Measurements of thermal diffusion effects in  $H_2$ - $N_2$  and  $D_2$ - $N_2$  mixtures over the temp. range  $-190^\circ$  to  $100^\circ$  indicate that  $H_2$  and  $D_2$  have the same type of mol. field. He- $N_2$  mixtures were also examined. N. M. B.

**Compressibility of aqueous solutions.** E. BRANDER (Soc. Scient. Fenn. Comm. Phys.-Math., 1936, 9, 1—8).—A theoretical expression for the compressibility of aq. solutions is developed which gives vals. in close agreement with recorded experimental data and with those calc. from Tammann's formula (A., 1896, ii, 13). R. C. M.

**Apparent volumes and apparent compressibilities of solutes in solution. III. Unsaturated and supersaturated solutions of calcium nitrate.** A. F. SCOTT and G. L. BRIDGER (J. Physical Chem., 1936, 40, 461—470).— $d$  and compressibility coeffs. have been determined for both unsaturated and super-



saturated solutions of  $\text{Ca}(\text{NO}_3)_2$  at  $35^\circ$ . There is no definite evidence of the existence of separate hydrates in solution. The influence of concn. on the apparent mol. vol. and compressibility is discussed.  $d^{25}$  for cryst.  $\text{Ca}(\text{NO}_3)_2$  is 1.896, in good agreement with previous vals. M. S. B.

**Viscosity and density of carbamide solutions.** N. D. LITVINOV and A. I. MELNIKOVA (J. Appl. Chem. Russ., 1936, 9, 583—588).—The  $\eta$  of 15–75% solutions at 15–90° is given by  $1/\eta = (2.4 - 0.2c)t + 0.067c - 0.01209c^2 + 50.463$ ; over the same range  $d = 1.0074 - 0.00048t + 0.0028c$ . R. T.

**Optical properties of liquid mixtures of ketones and alcohols.** T. TOMONARI (Z. physikal. Chem., 1936, B, 32, 202—221; cf. A., 1933, 669, 1114).—The sp. refractivity,  $r_L$ , of ketone-alcohol mixtures falls below the mixture rule val. by an amount which diminishes with increasing chain length of either component. The changes in  $n$ ,  $d$ , and  $r_L$  of the mixtures caused by small amounts of acid decrease in the same order, owing to increasing shielding of the OH and CO groups by alkyl groups; the changes increase with fall of temp. Acid has no effect on the state of  $\text{COMe}_2\text{-H}_2\text{O}$  mixtures, for here there is extensive complex formation in absence of acid. R. C.

**Specific heats and related properties of the binary system methyl alcohol-toluene.** L. S. MASON and E. R. WASHBURN (J. Physical Chem., 1936, 40, 481—491).—Sp. heats, heats of mixing, vol. contraction on mixing, and  $n$  have been determined for  $\text{MeOH-PhMe}$  mixtures at  $25^\circ$  and  $35^\circ$ . Heat capacities are  $>$  and  $n <$  required by the additivity rule. Mixing is always accompanied by heat absorption. The thermal effects are most pronounced in mixtures containing only a small proportion of  $\text{MeOH}$ , and it is suggested that they are due to dissociation of associated  $\text{MeOH}$  into simpler mol. aggregates. Changes of vol. and of  $n$  are attributed to combination of  $\text{MeOH}$  with  $\text{PhMe}$ . M. S. B.

**Thermal conductivity of water-glycerol mixtures.** S. ERK and A. KELLER (Physikal. Z., 1936, 37, 353—358).—Results for 18 to 88% glycerol at 6–72° are recorded and expressed in terms of an empirical equation. A. J. M.

**Properties of illuminated iodine solutions. II. Negative absorption effect in benzene and other solvents.** E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 816—823).—I solutions in  $\text{C}_6\text{H}_6$ ,  $\text{MeOH}$ , and  $\text{H}_2\text{O}$  show during strong illumination a reversible increase in their extinction coeff. which is  $\propto \sqrt{\text{light intensity}}$  and independent of  $[\text{I}]$  (cf. this vol., 437). For solutions in  $\text{CCl}_4\text{-C}_6\text{H}_6$  mixtures the effect is  $\propto [\text{C}_6\text{H}_6]$ . Explanations are suggested. F. L. U.

**Mutually surface-active liquids. Mixtures of sulphuric acid with nitrobenzene and with ether.**

C. BAILEY (J.C.S., 1936, 684—686).—Surface  $n$  n-composition curves for  $\text{H}_2\text{SO}_4\text{-PhNO}_2$  and  $\text{H}_2\text{SO}_4\text{-Et}_2\text{O}$  mixtures both show a min. at a small % of  $\text{H}_2\text{SO}_4$ . F. L. U.

**B.p. and composition of the vapour phase in the ternary system sulphuric acid-nitric acid-**

**water.** V. A. KIREEV, I. J. KLINOV, and A. N. GRIGOROVITSCH (J. Chem. Ind. Russ., 1936, 13, 346—348). R. T.

**Physical properties of the system ethyl alcohol-glycerol-water.** R. C. ERNST, C. H. WATKINS, and H. H. RUWE (J. Physical. Chem., 1936, 40, 627—635).—Surface tensions, viscosities,  $d$ ,  $n$ , and sp. heats have been determined at  $25^\circ$ . E. S. H.

**Commercially important systems of organic solvents. Vapour-liquid equilibrium data for the ternary system *n*-butanol-*n*-butyl acetate-water.** A. S. BRUNJES and C. C. FURNAS (Ind. Eng. Chem., 1936, 28, 573—580).—Equilibrium data at  $25^\circ$  are presented together with the  $d$  of ternary mixtures both saturated and unsaturated. It is shown that the composition of an unknown mixture of the alcohol and ester may be derived from a measurement of the amount of  $\text{H}_2\text{O}$  dissolved by the mixture. A saturated three-phase system when distilled leaves residues with a smaller  $\text{H}_2\text{O}$  content than the distillate, i.e., there is no true ternary azeotropic mixture. The azeotrope of  $\text{Bu}^n\text{OAc-H}_2\text{O}$  has b.p.  $95.5^\circ/760$  mm. and contains 29.44 mol.-% of  $\text{Bu}^n\text{OAc}$ . J. L. D.

**Vapour pressure of hydrogen fluoride, silicon fluoride, and water over solutions of the system  $\text{HF-H}_2\text{SiF}_6\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ .** N. CHAJDUKOV, Z. LINETZKAJA, and A. BOGNOVAROV (J. Appl. Chem. Russ., 1936, 9, 439—445).—V.-p. data are recorded for the systems  $\text{HF-H}_2\text{O}$  and  $\text{HF-H}_2\text{SiF}_6\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  at  $25\text{--}75^\circ$ . R. T.

**Application of the quantum theory of metals to the phase equilibrium in alloys.** S. T. KONOBEJEVSKI (Ann. Physik, 1936, [v], 26, 97—115).—Theoretical. The Hume-Rothery phase types (A., 1928, 111) represent energy minima corresponding with definite electron-gas concns. The thermodynamics of equilibria involving solid solutions are discussed from this viewpoint. L. J. J.

**Intermetallic compounds and mixed crystals.** U. DEHLINGER (Naturwiss., 1936, 24, 391—395).—A summary.

**X-Ray investigation of the equilibrium diagrams of aluminium-lithium alloys and the structure of  $\text{AlLi}$ .** G. KOMOVSKI and A. MAXIMOV (Z. Krist., 1936, 92, 275—283).—The equilibrium diagram up to 20.5% Li confirms the existence of two phases,  $\alpha$  and  $\beta$ . The  $\beta$ -phase is a compound  $\text{AlLi}$  which is cubic,  $a_0$  6.37 Å., with 16 atoms in the unit cell. The character of the  $\alpha$ -phase is not determined. B. W. R.

**Thermal and electrical conductivities of metals and alloys. II. Heat-resistant alloys from  $0^\circ$  to  $800^\circ$ .** R. W. POWELL (Proc. Physical Soc., 1936, 48, 381—392; cf. A., 1934, 1282).—Thermal conductivities, obtained by a comparative longitudinal-flow method, and electrical resistivities and Lorenz functions have been determined for various special steels, monel metal, and a Ni (80%)-Cr (20%) alloy, for temp. up to  $800^\circ$ . The Lorenz functions are abnormally high at room temp., but decrease with rise of temp. to a common val. at  $800^\circ$  of about  $0.62 \times 10^{-8}$ — $0.68 \times 10^{-8}$ . Results indicate that the thermal



conductivity of a metal can be approx. predicted from the electrical resistivity with an accuracy which increases with rise of temp. N. M. B.

**Electrical conductivity and phase diagram of binary alloys. The system sodium-lead.** H. KLAIBER (Z. Elektrochem., 1936, 42, 258—264).—Conductivities have been obtained for alloys containing up to 40 at.-% Na at temp. from 50° to 300°. The decrease in  $\kappa$  with increase in [Na] is discontinuous. There is no evidence for the formation of  $\text{Na}_2\text{Pb}_5$  as is suggested by the existence of a max. in the m.-p. curve. A phase diagram has been constructed. C. R. H.

**Cobalt-molybdenum system.** W. P. SYKES and H. F. GRAFF (Trans. Amer. Soc. Met., 1935, 23, 249—283).—The solid solubility of Mo in Co decreases from 26% at the eutectic temp. (1300°) to < 2% at 700°. The eutectic contains the hexagonal Co-rich solid solution ( $\gamma$ ), and  $\epsilon$ , a phase of formula  $\text{CoMo}$ .  $\epsilon$  is formed from the melt, on cooling, by a peritectic reaction at 1550° between the Co-rich liquid and the  $\eta$ -phase ( $\text{Co}_2\text{Mo}_3$ ). The  $\eta$ -phase forms at 1020° on cooling from the melt by a second peritectic reaction between the Co-rich liquid and the Mo-rich  $\delta$ -phase.  $\eta$  decomposes at 1250° on cooling into  $\epsilon$  and  $\delta$ . The  $\delta$ -phase is the Mo-rich solid solution (3% Co at 1600°). The face-centered cubic form of Co extends to 25% of Mo at 1310°, at which temp. it forms as the  $\beta$ -phase on cooling the hexagonal solid solution ( $\gamma + \epsilon \rightleftharpoons \beta$ ). At 1200° a hexagonal phase ( $\theta$ ) forms by the reaction  $\theta$  is stable at 1200—1050°. The transformation point of Co at 1020° is raised to approx. 1310° by 25% of Mo. The lower point (420°) is depressed to 240° by 1—2% of Mo. The Co-rich solid solution,  $\beta$ , undergoes age-hardening at > 450°. Max. hardness is observed in an alloy of Co with 15% Mo when aged for 100 hr. at 550°. CH. ABS. (e)

**Properties of Heusler's alloy, and the true specific heat of manganese and its discontinuity.** J. R. ASHWORTH (Proc. Physical Soc., 1936, 48, 456—468).—Measurements of density, intensity of magnetisation, crit. temp., Curie const., electrical resistivity and its temp. coeff., thermoelectric power, and sp. heat are recorded. The true sp. heat of Mn shows a very marked discontinuity at about 350°, near the crit. temp. of Heusler's alloy. The heat capacity of the alloy is additive, both above and below the crit. temp.; this is also true for magnetite. N. M. B.

**Problem of mixed crystals; Na-AgCl and Tl-CsCl mixed crystals with Al and Cr X-rays.** H. O'DANIEL (Z. Krist., 1936, 92, 221—252; cf. this vol., 676).—The energy relations of superlattices in mixed crystals are discussed, and an attempt is made to locate these lattices in Na-AgCl and Tl-CsCl mixed crystals, using X-radiation both of normal and of rather long  $\lambda$ . B. W. R.

**Permeability of palladium to hydrogen. Loss of diffusion power of pure palladium when heated. Regeneration of poisoned palladium.** V. LOMBARD, C. EICHNER, and M. ALBERT (Compt. rend., 1936, 202, 1777—1779).—A disc of pure Pd suffers a progressive and irreversible loss of diffusive

power on prolonged heating above 500—520° in presence of  $\text{H}_2$ , this loss being the more rapid the higher is the temp. This poisoning is arrested by lowering the temp. to < 450—500°. It thus appears that the state of max. permeability only is characteristic of the metal. The diffusive power can be restored considerably by heating to 500° in a current of air, cooling in air, and reducing the oxide film produced in  $\text{H}_2$  at < 140°. The loss of diffusive power is probably due to agglomeration of the fine surface granules. J. W. S.

**Temperature coefficient of solubility of hydrogen in organic solvents.** E. B. MAXTED and C. H. MOON (Trans. Faraday Soc., 1936, 32, 769—775).—The solubility of  $\text{H}_2$  in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ ,  $\text{EtOH}$ ,  $\text{AcOH}$ , and  $\text{EtOAc}$  has been determined over a wide range of temp. between 0° and 75°. In each case the temp. coeff. is positive. F. L. U.

**Solubility of carbon dioxide in aqueous solutions containing alcohol and sugars [at 15°].** H. A. SHOWALTER and J. B. FERGUSON (Canad. J. Res., 1936, 14, 120—126).—The absorption coeff.,  $\alpha$ , decreases approx. linearly with increasing concn. of sucrose, glucose, and fructose. J. G. A. G.

**Desorption of gases from aqueous solutions into air.** I. G. NAGATKIN (J. Appl. Chem. Russ., 1936, 9, 434—438).—The rate of desaturation of aq. solutions of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$ , and  $\text{O}_2$  when air is passed at const. velocity over the surface of the solution is  $\propto$  the depth of the column of solution, to the mol. wt. and dipole moment of the solute, and to its degree of association. The experimental data are in agreement with Guyer's equation (A., 1934, 483). R. T.

**Active oxides. XCIX. Solubilities of a mixture of magnesium and ferric oxides during the course of ageing.** G. F. HÜTTIG and E. ZEIDLER (Kolloid-Z., 1936, 75, 170—184; cf. this vol., 441).—The solubility in dil.  $\text{HCl}$  of ignited  $\text{MgO}$  or  $\text{Fe}_2\text{O}_3$  is a more const. quantity the higher is the temp. of ignition. With equimol. mixtures the solubility and variation with age pass through max. and min. as the temp. of ignition is raised. E. S. H.

**Solubility and activity coefficient of silver acetate in mixed solvents.** F. H. MACDOUGALL and C. E. BARTSCH (J. Physical Chem., 1936, 40, 649—659).—Solubilities of  $\text{AgOAc}$  at 25° in 10, 20, and 30%  $\text{EtOH-H}_2\text{O}$  in presence of K, Na, Li, Ca, Sr, and Ba nitrates have been determined. The solubility of  $\text{AgOAc}$  in  $\text{H}_2\text{O}$  at 25° is 0.06634 g.-mol. per litre. The Debye-Hückel equation is valid for the solutions investigated. Vals. of the mean ionic diameter are calc. for solutions containing  $\text{KNO}_3$  or  $\text{NaNO}_3$ . The activity coeff. of  $\text{AgOAc}$  in saturated solutions in  $\text{EtOH-H}_2\text{O}$  mixtures without added nitrates has been calc. E. S. H.

**Solubility of  $\alpha$ -valine in water.** J. B. DALTON and C. L. A. SCHMIDT (J. Gen. Physiol., 1936, 19, 767—771).—The solubility between 0° and 60° varies with the cryst. form. H. G. R.

**Solubilities of the dihalogenated  $l$ -tyrosines in ethyl alcohol-water mixtures.** P. S. WINNEK and



C. L. A. SCHMIDT (J. Gen. Physiol., 1935, **19**, 773—780).—The solubilities of dihalogenated *l*-tyrosines are first increased by the addition of EtOH and then decreased, whereas that of *l*-tyrosine is decreased. The apparent heat of dissolution of di-iodotyrosine in EtOH-H<sub>2</sub>O and the solubility of *dl*-thyroxine at 30° in org. solvents have been determined.

H. G. R.

**Distribution of picric acid between benzene and mixtures of light and heavy water.** P. GROSS and A. WISCHIN (Trans. Faraday Soc., 1936, **32**, 879—883).—The distribution const. with pure D<sub>2</sub>O at 18° is 4 times that with pure H<sub>2</sub>O; it is not a linear function of the D<sub>2</sub>O content. The effect is due to the different zero-point energies in the D and H linkings.

L. J. J.

**Structural changes taking place during the ageing of precipitates. X. Distribution coefficient of lead between the surface of barium sulphate and solution. Determination of specific surface of barium sulphate.** I. M. KOLTHOFF and W. M. MACNEVIN (J. Amer. Chem. Soc., 1936, **58**, 725—728; cf. this vol., 561).—The distribution coeff., *K*, of PbSO<sub>4</sub> between BaSO<sub>4</sub> and H<sub>2</sub>O is 0.12, and 0.067 between BaSO<sub>4</sub> and 50% EtOH at 25°. *K* decreases with increasing mol.-% of PbSO<sub>4</sub> in the surface of BaSO<sub>4</sub>. The determination of the sp. surface of aged BaSO<sub>4</sub> ppts. by the radioactive method is described.

E. S. H.

**Anomalous distribution of thorium-C'' between uni- and ter-valent thallium ions.** J. ZIRKLER (Z. Physik, 1936, **99**, 669—670).—Further evidence is given for the distribution previously recorded (cf. this vol., 282).

A. B. D. C.

**Sorption of sulphur dioxide by active charcoal. VII. Sorption equilibrium at low temperatures.** K. ARII (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 254—265; cf. this vol., 153).—Sorption of SO<sub>2</sub> between -40° and -10° on charcoal activated at 800° may be represented by the isotherms of Patrick or Gregg.

R. S.

**Reversibility of adsorption of dissolved substances on ash-free charcoal.** L. LEPIN and G. STRACHOVA (Z. physikal. Chem., 1936, **176**, 303—312).—For AcOH, the adsorption of which is essentially of the van der Waals type, the adsorption and desorption isotherms practically coincide. For HCO<sub>2</sub>H, the adsorption of which is partly mol. and partly due to surface reaction of the CO<sub>2</sub>H groups, the curves deviate somewhat, whilst with HCl and H<sub>2</sub>SO<sub>4</sub>, which are adsorbed mainly by surface reaction, the curves deviate widely. On readsorption after desorption the system moves back to the adsorption isotherm and vice versa. These observations are satisfactorily explained on the basis of Schilov's theory of surface compounds.

R. C.

**Mechanism of desorption of solvent vapours from active charcoal. I.** A. P. OKATOV and Z. I. LEVINA (J. Appl. Chem. Russ., 1936, **9**, 287—297).—Adsorbed EtOH is removed more easily than Et<sub>2</sub>O from C by a current of steam. In general, the energy required for desorption  $\propto$  the activity of the C, and the use of highly active C for solvent recovery is not therefore always advantageous.

R. T.

**Adsorption of the heavier rare gases by mercury.** H. M. CASSEL and K. NEUGEBAUER (J. Physical Chem., 1936, **40**, 523—530).—The surface tension of Hg in contact with Kr at 235° and 253° abs. and with Xe at temp. between 237° and 293° abs. has been measured at various pressures. The adsorbed quantities have been calc. by Gibbs' equation. The heats of adsorption are also derived and compared with the theoretical vals. on the basis of the dispersion theory of the van der Waals forces.

M. S. B.

**Adsorption of gases by glass walls. XIV. Kinetics of the adsorption of carbon dioxide by Jena glass.** V. ALEXANDRE (Anal. Fis. Quím., 1936, **34**, 315—319).—Using the technique employed previously (A., 1926, 1002), the adsorption of CO<sub>2</sub> by Jena glass between 760 and 190 mm. at 16° is found to be 0.25 of the adsorption by ordinary glass. The velocity of adsorption cannot be determined owing to the small quantities involved.

F. R. G.

**Sorption of gases by titania gel. II. Relation between the pressure and the sorbed amount of sulphur dioxide. I.** HIGUTI (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 266—285; cf. A., 1935, 1315).—Sorption and desorption between -40° and 40° have been studied and the results are considered in relation to current theories. The hysteresis phenomena can be explained by the capillary adsorption theory.

R. S.

**Chemisorption of carbon dioxide by reduced iron. Influence of the chemisorption on van der Waals adsorption of carbon dioxide at 0°.** K. KAWAKITA (Proc. Imp. Acad. Tokyo, 1936, **12**, 61—63).—The van der Waals adsorption (*a*) of CO<sub>2</sub>, which occurs rapidly at 0°, has been studied with Fe on which CO<sub>2</sub> has been chemisorbed at 300—400° [when Fe+CO<sub>2</sub> (ads.)=Fe<sub>3</sub>O<sub>4</sub>+CO (ads.) and 2CO (ads.)=C+CO<sub>2</sub> (ads.), the first reaction occurring only on active Fe centres and the second even on weak centres]. *a* is independent of the amount of chemisorption and time of evacuation after chemisorption, but is less if the desorption is performed at 0° than at 300—400°. With no evacuation after chemisorption *a* is small. The no. of adsorption centres for *a* on a fresh surface at 0° is approx. half that for a surface on which CO<sub>2</sub> has been chemisorbed at 300—400° and evacuated at the same temp., but the fraction of surface covered is approx. the same.

R. S. B.

**Activated adsorption of hydrogen on chromic oxide gel. Effect of gas pressure.** R. L. BURWELL, jun., and H. S. TAYLOR (J. Amer. Chem. Soc., 1936, **58**, 697—705).—Rates of adsorption have been measured at 195—491° abs. and 0.125—1 atm. The data show that the surface of Cr<sub>2</sub>O<sub>3</sub> gel is composite, with areas of characteristic activation energies ranging from low vals. to 21.7 kg.-cal. per mol. for a large and relatively uniform area. The influence of temp., pressure, and occupied surface on the velocity of adsorption on such an area has been examined. The slow process of adsorption appears to be an interaction between mols. adsorbed by van der Waals forces and surface atoms which receive the necessary surface energy.

E. S. H.



**Sorption of water vapour from air by means of silica gel.** E. L. KOPELOVITSCH and N. I. TROITZKAJA (*J. Appl. Chem. Russ.*, 1936, 9, 673—680).—Max. sorption is shown by acid-treated  $\text{SiO}_2$  gel which is characterised by its high percentage of small pores, and by the high apparent  $d$  (0.65) of the dry powder. Sorption of  $\text{H}_2\text{O}$  is favoured by low temp. and high partial  $\text{H}_2\text{O}$  pressure.  $\text{H}_2\text{O}$  is removed from saturated gel at  $200^\circ$  (75—90 min.). R. T.

**Ionic exchange and sorption of gases by chabasite.** E. RABINOWITCH and W. C. WOOD (*Trans. Faraday Soc.*, 1936, 32, 947—956; cf. *A.*, 1932, 458).—The sorption of  $\text{H}_2$  (at  $-190^\circ$ ),  $\text{N}_2$  ( $-190^\circ$  and  $-80^\circ$ ),  $\text{CO}_2$  ( $20^\circ$ ), and  $\text{C}_3\text{H}_8$  ( $20^\circ$ ) by a no. of chabasites (I) in which the Ca was replaced by a series of different cations, have been measured. Ca-, Sr-, and Ba-(I) have approx. identical sorption properties. With Cd-(I), sorption is less at low pressure, but the saturation val. is the same. The sorption capacity is abnormally low for  $\text{N}_2$  and  $\text{C}_3\text{H}_8$  on Na-(I), and for  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{C}_3\text{H}_8$  on K-(I). The results are discussed. L. J. J.

**Adsorption of electrolytes on crystal surfaces.** I. M. KOLTHOFF (*Chem. Weekblad*, 1936, 33, 321—324).—Polemical against de Brouckere (*this vol.*, 422). D. R. D.

**Effect of irradiation on adsorptive power of solids.** I. J. A. HEDVALL [with E. FRIDEN, T. LINDSTRAND, and E. SVENANDER] (*Z. physikal. Chem.*, 1936, B, 32, 383—395).—The previously reported increase in adsorptive power,  $A$ , of phosphors during illumination (*A.*, 1935, 1055) has been confirmed by further experiments. Ultra-violet light causes a greater increase than does white light. When irradiation ceases,  $A$  declines progressively, but tends to constancy at a val. is observed when there has been no irradiation. Substances other than phosphors exhibit similar effects on appropriate irradiation. Attempts to detect differences in the rate of dissolution of fluorophors in the light and in the dark have yielded negative results. R. C.

**Determination of heats of sorption from solutions at crystal surfaces.** N. A. HELD and I. A. KHAINSKY (*Kolloid-Z.*, 1936, 75, 287—288).—Preliminary results for the adsorption of Na oleate in aq. solution by  $\text{BaSO}_4$  are reported. E. S. H.

**Adsorption of proteins. Influence of salts on the adsorption of hæmoglobin by kaolin.** M. PAIĆ and (Mlle.) V. DEUTSCH (*Compt. rend.*, 1936, 202, 1514—1516; cf. *this vol.*, 676).—The adsorption is diminished by 0.1—1N-Na<sup>+</sup>, -K<sup>+</sup>, and -Ba<sup>++</sup> and by  $\text{N-SO}_4^{--}$ . The diminution produced by NaCNS and  $\text{Na}_3\text{PO}_4$  is mainly due to the increase in  $p_H$ . R. S.

**Adsorption of nitrogenous substances from aqueous solutions.**—See *this vol.*, 914.

**Binding of glacial phosphoric acid by the proteins of wheat flour.** L. W. SAMUEL and R. K. SCHOFIELD (*Trans. Faraday Soc.*, 1936, 32, 760—769; cf. *A.*, 1935, 300).—The capacity of 37 wheat flours to bind glacial phosphoric acid has been found by electrometric titration to vary from 6.7 to 10.1 milliequiv. per 100 g. of flour. Flours of higher N

content tend to bind more acid per g. of flour but less per g. of protein. The uptake per g. of gluten varies only slightly with acid concn. between 0.02 and 1.0N. Flour proteins do not bind the various  $(\text{HPO}_3)$  units in the proportion in which they exist in the original acid solution. F. L. U.

**Reduction of some adsorbed oxidation-reduction indicators.** H. A. ABRAMSON and I. R. TAYLOR (*J. Physiol. Chem.*, 1936, 40, 519—521).—Experiments on the reduction and re-oxidation of methylene-blue, litmus, and phenosafranine adsorbed on filter-paper indicate that the bonds responsible for adsorption do not affect appreciably those groups which are involved in the oxidation-reduction process. The ionisation of adsorbed protein is a similar example of this type of behaviour. A surface which adsorbs selectively one of the constituents of a reversible oxidation-reduction system may thus alter the oxidation-reduction potential. Data for  $p_H$  indicators are discussed in this connexion.

M. S. B.  
**Polarisation of the luminescence of dyes adsorbed on colloidal gels.** P. PRINGSHEIM and H. VOGELS (*J. Chim. phys.*, 1936, 33, 261—271).—The rate and character of the fixation of dyes on  $\text{SiO}_2$  gel have been studied by measuring the degree of polarisation ( $p$ ) of the fluorescence. The  $p$ -time curves have the general form of adsorption curves. The amount of adsorption varies considerably with the solvent. The fluorescence appears to be due to adsorbed ions and not to mols. M. S. B.

**Absorption and accumulation of solutes by living plant cells.**—See *this vol.*, 907.

**Simple kinetic theory of ionic exchange. I. Ions of equal valency.** H. JENNY (*J. Physical Chem.*, 1936, 40, 501—517).—A model for the mechanism of ionic exchange is described and an exchange adsorption isotherm derived which is verified by ionic exchange data for Putnam clay. The structure of the colloidal particles is apparently important. The equation is satisfactory for soil colloids and bentonite clays, all of which have plate-like structures and seem to exchange on the outer surface only; it is less satisfactory for permutites and certain zeolites which have ultra-microscopic pores and channels. If there are large differences in the nature of the exchanging ions discrepancies may also occur. There is a relationship between the base-exchange const. and the ratio of the electric potentials of the double layers, which suggests that ionic exchange is connected with the question of colloid stability. M. S. B.

**Theory of formation of surface films on metals. II.** C. WAGNER (*Z. physikal. Chem.*, 1936, B, 32, 447—462).—The theory previously advanced (*A.*, 1933, 564) has been combined with the results of the misplacement theory of electrical conductivity (*ibid.*, 588) to obtain relations between the rate of formation of surface films,  $k$ , and the pressure of the reacting gas,  $p$ . The diffusion coeffs. for the equalisation of concns. in ionic lattices deviating in composition from the integral stoicheiometric ratio have been calc. for various types of misplacement. For film formation on Ag by  $\text{Cl}_2$  and  $\text{Br}_2$  the parabolic



law (A., 1922, ii, 831) is valid and, as the above theory requires,  $k \propto \sqrt{p}$ . From the observed vals. of  $k$  it is calc. that for AgBr at 200° and  $p=0.23$  atm. the electrons are responsible for 17% of the conductivity; the observed val. is 12%. It is inferred that diffusion during film formation consists in the migration of equiv. amounts of Ag<sup>+</sup> ions and electrons from the metal through the film to the outer surface, where the real chemical reaction occurs. The conductivity is thus of the electron deficiency type.

R. C.

**Composition and structure of surface films on iron.** E. A. NIKIFOROV and N. A. GODINA (J. Appl. Chem. Russ., 1936, 9, 225—228).

R. T.

**Mobility of potassium on tungsten.** R. C. L. BOSWORTH (Proc. Roy. Soc., 1936, A, 154, 112—123).—The diffusion coeff. for the surface migration of films of K on W rises with increasing concn., whilst the associated activation energy falls. The activation energy of diffusion for an infinitely dil. film = 0.72 volt, and for a unimol. film = 0.29 volt. This fall in the val. is due to the existence of a spreading force caused by the mutual repulsion of the adions. The effective dipole moment of the adions has been calc. from vals. of the spreading force at different surface concns.

L. L. B.

**Diffusion of gases from capillary tubes.** G. COSTEANU and P. RENAUD (Compt. rend., 1936, 202, 1511—1514).—When a stream of H<sub>2</sub>O vapour at low pressure from a capillary tube impinges on Na, or a current of air containing H<sub>2</sub>S strikes a gelatin surface containing Pb(OAc)<sub>2</sub>, concentric annular stains are produced.

R. S.

**Mechanism of the rise of hydrosols and coloured solutions through porous materials.** A. BOUTARIC and (Mlle.) P. BERTHER (Compt. rend., 1936, 202, 1781—1783; cf. A., 1934, 840).—The fact that rise of sol particles or coloured ions through porous material (e.g., filter-paper) does not cease when the solute reaches the top of the porous material is explained by solute continuing to rise, owing to evaporation and to progressive swelling of the porous material.

J. W. S.

**Determination of Zsigmondy's gold number, foam number, and surface tension of sodium and potassium salts of saturated and unsaturated fatty acids.** N. N. GODBOLE and M. SAGGAPAL (Kolloid-Z., 1936, 75, 193—201).—Data for K and Na salts of saturated fatty acids (C<sub>4</sub>—C<sub>18</sub>) and for unsaturated and hydroxy-C<sub>18</sub> acids are recorded and discussed from the viewpoint of detergent requirements.

E. S. H.

**Energy transformations at interfaces.** H. KAUSKY (Kolloid-Z., 1936, 75, 164—169).—The adsorption of the three tautomeric aminophthalic acid hydrazides by basic and acid gels has been studied. The absorbates show different colours of fluorescence, corresponding with the several tautomerides which are obtained under different conditions of prep.

E. S. H.

**Creeping of saturated salt solutions.** T. H. HAZLEHURST, jun., H. C. MARTIN, and L. BREWER (J. Physical Chem., 1936, 40, 439—452; cf. Wash-

burn, A., 1927, 931).—Creeping of a solution over a surface is attributed to the preferential wetting of the surface by the solid solute. Previous views of the mechanism are considered and the influence of the nature of the supporting surface, the crystal habit of the solute, and the free surface energies involved are discussed.

M. S. B.

**Osmotic complexes in which the pressure can differ on the two sides of the membrane.** F. A. H. SCHREINEMAKERS and J. P. WERRE (Rec. trav. chim., 1936, 55, 301—314).—Pressure and vol. changes which take place during osmosis in complex systems characterised by various combinations of liquids are considered.

C. R. H.

**Action of allylamine and Novalgin on prepared animal membranes (goldbeater's skins).** R. RAFF and E. ABRAHAMCZIK (Z. ges. exp. Med., 1935, 95, 691—702; Chem. Zentr., 1935, ii, 1562).—Allylamine (I) and allyl formate increase the permeability to H<sub>2</sub>O; treatment with Novalgin checks the deterioration caused by (I).

H. N. R.

**Preparation of isotonic solutions.** H. BOHME (Arch. Pharm., 1936, 274, 255—267).

R. S. C.

**F.p. of aqueous solutions. X. Dioxan and its mixtures with lithium, sodium, and potassium chlorides.** G. SCATCHARD and M. A. BENEDICT (J. Amer. Chem. Soc., 1936, 58, 837—842; cf. A., 1935, 30).—The f.p. of aq. dioxan containing KCl, NaCl, or LiCl up to a total concn. of dioxan + ions of 2M have been determined. At low concns. the osmotic coeffs. of the mixtures are < the Debye-McAulay theory requires, but agree well with the second theory of Debye. The salting-out effects of M-salt solutions calc. from these results have nearly the same relative vals. as those measured directly for Et<sub>2</sub>O.

E. S. H.

**Dielectric constants of solutions of organic acids in ethyl alcohol and benzene.** R. C. GORE and H. T. BRISCOE (J. Physical Chem., 1936, 40, 619—625).—Solutions of 24 org. acids at concns. up to 100 mg.-mol. per litre have been examined. The curves are compared with those relating  $n$  and resistance functions of the same solutions with concn. The results show that the electrical saturation theory holds qualitatively in some cases, but not quantitatively. EtOH has dielectric const. 24.33 at 25° and  $n_D$  1.35921.

E. S. H.

**Mechanism of quenching of fluorescence in solutions.** J. WEISS and H. FISCHGOLD (Z. physikal. Chem., 1936, B, 32, 135—138).—The quenching may be regarded as a simple electron transfer from the quenching ion to the excited mol.,  $Fl^*$ , e.g.,  $Fl^* + Fe^{++} \rightarrow Fl + Fe^{+++}$ , or, in a heterogeneous system on a metal surface,  $Fl^* + Pt \rightarrow Fl + Pt^*$ . The energy of excitation of Fl has the effect of increased electro-affinity. In the homogeneous reaction with Fe at higher light intensities in absence of O<sub>2</sub> practically irreversible reduction may occur or a reversible photostationary state be set up, depending on the conditions.

R. C.

**Significance of van der Waals forces for properties of salt solutions.** G. KORTUM (Z. Elektrochem., 1936, 42, 287—292; cf. this vol., 425).—The



importance of van der Waals forces between ions and solvent mols. is discussed. F. L. U.

**Velocity of fall of "super-Stokes" particles.** N. FUCHS (Tech. Phys. U.S.S.R., 1936, 3, 254—257).—Theoretical. The validity of Stokes' law for small spheres has been studied. Calculations for solid particles of  $d$  4—12 falling in air show that Stokes' law ceases to apply at radius  $10\ \mu$ . Fluid particles, which flatten on falling, will have a smaller velocity than the calc. val. R. S. B.

**Preparation of gold sol.** A. C. HONIG (Pharm. Weekblad, 1936, 73, 614—617).—Au sols made from  $H_2O$  twice distilled in glass are not transparent. Transparency depends on the presence of traces of Sn in the solution and consistently good sols are obtained by using such  $H_2O$  collected in glass vessels containing a Sn rod. In the method recommended, 2.5 c.c. of 1%  $AuCl_3$ , 2.63 c.c. of 0.2N- $K_2CO_3$ , and 0.125 c.c. of 1%  $H_2C_2O_4$  solutions are added to 250 c.c. of the boiling  $H_2O$ ; the flask is removed from the flame, and 3 c.c. of 1%  $CH_2O$  solution are added with shaking. S. C.

**Negative ferric hydroxide sol. Preparation.** A. DAS and R. DE (J. Indian Chem. Soc., 1936, 13, 197—203).—Neutral  $Fe(OH)_3$  sol can be prepared by mixing equimol. quantities of  $FeCl_3$  and  $NaOH$  solutions in the presence of a stabiliser, e.g., alkaline citrate, tartrate, phosphate, silicate, sulphide, or carbonate, the stabilising effect decreasing in this order. C. R. H.

**Organosol of sulphur.** K. INABA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 298—300).—Amorphous S is pptd. from  $Na_2S_2O_3$  by  $HCl$ , dissolved in  $C_6H_6$  or  $EtOH$ , and the organosol obtained by irradiation with ultra-violet light. A no. of sols have been prepared for clinical use by distillation of  $C_6H_6$  from a mixture of "benzosol" and fat or oil. R. S.

**Synthesis of hydrosols of sparingly-soluble salts by electrolysis. II. Ferric phosphate hydrosols.** B. G. SAPROMETOV and E. I. SMOLIGINA (Kolloid-Z., 1936, 75, 291—297; cf. A., 1934, 1305).—The optimal conditions (c.d., temp., and concn. of  $Na_2HPO_4$ ) for the prep. of  $FePO_4$  sols have been determined. For the more stable sols the dispersity,  $\zeta$  potential, and resistance to flocculation by  $KCl$  have been determined. E. S. H.

**Liquid ammonia as a solvent. V. Metallic solutions.** J. F. CHITTUM and H. HUNT (J. Physical Chem., 1936, 40, 581—589).—Solutions of  $NH_4$  in liquid  $NH_3$  have been prepared by electrolysis of  $NH_4Cl$  at  $-60^\circ$  to  $-80^\circ$ . Solutions of alkali metals in liquid  $NH_3$  show the Tyndall effect; on electro-dialysis the alkali metal does not pass through the membrane. Such systems are discussed as colloid solutions. E. S. H.

**Physical chemistry of the autoclave process of sulphur melts. Formation and destruction of the three-phase sulphur emulsion.** K. N. SAMOCHVALOV and O. S. KOSHUCHOVA (Kolloid-Z., 1936, 75, 217—222).—The degree of emulsification in the system molten S—conc. aq.  $MgCl_2$  and the type of emulsion

(S as the inner or outer phase) have been studied under different conditions, using  $CaSO_4$  or  $SiO_2$  as emulsifiers. E. S. H.

**Brownian movement of a linear lattice. I.** BESSENOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 323—327).—Mathematical. A. J. M.

**Photographic observation of aerosol particles as an objective method of measurement.** A. WINKEL and W. WITT (Z. Elektrochem., 1936, 42, 281—285).—An optically defined vol. of aerosol, illuminated from opposite directions by two high-power lamp systems on the same optical axis, is photomicrographed with an exposure of 0.1 sec. Very fine particles can be thus recorded, and photophoresis is prevented. In studying coagulation the photographic method is preferred to visual counting, owing to the elimination of personal errors, and to the possibility of photographing an aerosol within a few sec. of its formation, and thus obtaining points at an early stage in the coagulation process. Examples are given of the photographic study of Brownian movement, sedimentation under gravity, and electric mobility. F. L. U.

**Behaviour of aerosols in the acoustic field. I.** O. BRANDT and E. HIEDEMANN (Kolloid-Z., 1936, 75, 129—135).—Kinemato-micrographic investigation has shown that aerosols (smoke,  $NH_4Cl$ , etc.) are coagulated when subjected to sound or ultrasonic waves. The increase in particle size has been determined by measurements of light absorption and rate of fall. E. S. H.

**Determination of size of micelles from the swelling of films.** S. PAFKOV (J. Appl. Chem. Russ., 1936, 9, 518—519).—Polemical, against Voskresenski (B., 1935, 719). R. T.

**Colour and opacity of emulsions.** J. F. MORSE (Trans. Faraday Soc., 1936, 32, 941—947).—A photo-electric photo-colorimeter is described. In a coloured emulsion the tone increases with degree of dispersion. Data are recorded for opacities of paraffin-aq. gum solution emulsions at different concns. and degrees of dispersion. For emulsions of grain size  $1\ \mu$ , the opacity is independent of concn. for concns.  $> 5\%$ . L. J. J.

**Dielectric constant of colloidal systems.** J. T. G. OVERBEEK (Natuurwetensch. Tijds., 1936, 18, 55—72).—The  $\epsilon$  of colloidal systems with  $H_2O$  as the disperse medium is affected by (1) differences in  $\epsilon$  of the disperse phase and disperse medium, which may increase or decrease  $\epsilon$ ; (2) the electric double layer effect, as yet unconfirmed experimentally, which will increase  $\epsilon$ ; (3) the permanent dipole moment of the particles increasing  $\epsilon$  at low  $\nu$ , confirmed with lyophilic colloids; (4) hydration decreasing  $\epsilon$  at high  $\nu$  but increasing  $\epsilon$  at low  $\nu$ . This last has been confirmed experimentally but an adequate explanation of the phenomenon is wanting. S. C.

**Diffusion potentials in colloidal systems.** H. B. STEINBACH (J. Cell. Comp. Physiol., 1935, 7, 291—300).—The potential between alkaline gelatin gels and applied electrolytes is considerable, and may be considered to be a diffusion potential between two electrolyte phases, the gel functioning as a slow-moving anion. R. N. C.



**Double layer in colloids.** H. R. KRUYT (*Natuurwetensch. Tijds.*, 1936, 18, 29—37).—A lecture on the theory of the electric double layer in colloids. S. C.

**Character of hydrophilic colloids. Hydration.** H. R. KRUYT (*Natuurwetensch. Tijds.*, 1936, 18, 38—43).—A lecture, discussing mainly dipole orientation in the hydration of colloids. S. C.

**Colloid behaviour of polymeric carbohydrates: starch, cellulose, and glycogen.** P. KOETS (*Natuurwetensch. Tijds.*, 1936, 18, 44—54).—A lecture dealing principally with the internal hydration and the electrical states of these systems. S. C.

**Mixtures of colloidal electrolytes with uni-univalent salts.** J. W. MCBAIN and (Miss) J. SEARLES (*J. Physical Chem.*, 1936, 40, 463—499).—The electrical conductivity and f.p. lowering of mixtures of ordinary electrolytes with alkali or H soaps are in good agreement with the additive mixture rule. The charges on the micelle are so widely spaced as to be practically independent. Thus the ionic strength of colloidal electrolytes is similar to that of uni-univalent electrolytes. M. S. B.

**Validity of the Lambert-Beer law in hydrophobic colloids.** F. B. GRIBNAU, H. R. KRUYT, and L. S. ORNSTEIN (*Kolloid-Z.*, 1936, 75, 262—268).—Experiments with Au and Se hydrosols confirm the validity of the law. E. S. H.

**Osmotic pressure of glycogen solutions.**—See this vol., 878.

**Viscosity and adsorption of starch sols.** J. H. C. MERCKEL (*Kolloid-Z.*, 1936, 75, 318—322).—The influence of Na salts of monobasic acids on the  $\eta$  of starch sols and the adsorption of the same salts by starch are in accordance with the lyotropic series. E. S. H.

**Structure mechanics of viscous-elastic continua. I. Hydrodynamic theory of anomalous turbulence.** H. UMSTATTER (*Kolloid-Z.*, 1936, 75, 135—142).—Mathematical. E. S. H.

**Coagulation of colloids. XI. Variation of optical refractivity during the coagulation of colloidal manganese dioxide and new evidence for the discontinuity of the change.** S. S. JOSHI and S. J. RAO (*J. Indian Chem. Soc.*, 1936, 13, 141—149).—Coagulation of colloidal  $MnO_2$  by conc. solutions of inorg. salts has been followed by the measurement of  $n$ . Further evidence is obtained that coagulation proceeds through discontinuous stages termed "zones of coagulation." (Cf. this vol., 426.) C. R. H.

**Flocculation of stannic oxide sols.** H. S. VAN KLOOSTER and A. PETROVICH (*J. Physical Chem.*, 1936, 40, 591—597).—The ease of peptisation of  $SnO_2$  sols by alkalis is in the order  $KOH > NaOH > NH_4OH > LiOH$ . When the sols are treated with alkali-metal salts, the flocculation vals. of the cations are in the order  $K > Na > NH_4 > Li$ , which indicates that colloidal  $SnO_2$  has hydrophilic properties. Addition of alcohol lowers the amount of electrolyte required for coagulation. The significance of hydration of the flocculating ions is discussed. E. S. H.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity. III. Flocculation by reversing electrolytes.** W. OSTWALD (*Kolloid-Z.*, 1936, 75, 297—317; cf. this vol., 157).—A crit. discussion of published work. E. S. H.

**Liesegang rings of manganese sulphide. II.** O. F. TOWER (*J. Physical Chem.*, 1936, 40, 599—602; cf. A., 1931, 924).—Periodic structures of  $MnS$  in  $SiO_2$  gel were found to be spaced in geometrical progression. The influence of diffusion, supersaturation, and adsorption is discussed. E. S. H.

**Quantitative analyses of Liesegang rings.** A. T. LINCOLN and J. C. HILLYER (*J. Physical Chem.*, 1936, 40, 645—647).—Quant. analyses of periodic structures of  $CuCrO_4$  in  $SiO_2$  gel have been made. Comparison with the conditions of pptn. in absence of the gel shows that the  $SiO_2$  gel inhibits the pptn. of  $CuCrO_4$  until higher concns. are reached. E. S. H.

**Mixed crystal formation of zinc sulphide post-precipitated with mercuric sulphide. Ageing of mercuric sulphide and of zinc sulphide.** R. MOLTZAU and I. M. KOLTHOFF (*J. Physical Chem.*, 1936, 40, 637—643).—X-Ray evidence shows that the ppts. form mixed crystals containing  $\approx 12$  mol.-% of  $ZnS$ . Ageing of the ppts. in the supernatant liquid at room temp. tends to perfect the cryst. state. Some of the variables affecting the transformation of black  $HgS$  to the red form have been noted. E. S. H.

**Effect of surface tension and electrical potential on the stability of mercury emulsions.** V. SIVERTZ, W. H. NAYLOR, and H. V. TARTAR (*J. Amer. Chem. Soc.*, 1936, 58, 782—786).—The  $Hg-H_2O$  interfacial tension is raised by adding K citrate, tartrate, or chloride. There is no relation between change of interfacial tension or  $p_H$  of solution and ease of emulsification in this system. Electrocapillary curves show that emulsifying and non-emulsifying agents give similar results. E. S. H.

**Dynamical principle of thixotropic solidification and its application.** W. HELLER (*Compt. rend.*, 1936, 202, 1507—1509).—Thixotropy is defined and the conditions for its appearance in hydrophilic colloids are indicated. R. S.

**Alumina gel, its preparation and properties.** H. BRÜCKNER and L. HIRTH (*Angew. Chem.*, 1936, 49, 360—362).—When Al salt solutions, containing about 2% of  $Al^{+++}$ , are pptd. by adding 25% excess of aq.  $NH_3$  and the product is washed repeatedly by decantation, an amorphous  $Al_2O_3$  gel is obtained, which resembles  $SiO_2$  gel. The relative rates of adsorption of  $H_2O$  vapour by amorphous and cryst.  $Al_2O_3$  gel and  $SiO_2$  gel have been compared. The amorphous  $Al_2O_3$  gel takes up a max. of 40%  $H_2O$  and can be regenerated by heating in air at 400—500°. E. S. H.

**Hydroxide and oxyhydrate gels, and their amphoteric properties.** A. KRAUSE (*Kolloid-Z.*, 1936, 75, 288—291).—Polemical (cf. this vol., 158). E. S. H.

**Gel system: cellulose nitrate-copper bronze.** W. E. GLOOR and H. M. SPURLIN (*J. Amer. Chem. Soc.*,



1936, 58, 854—855).—Gelation in this system appears to be caused by a reaction between Cu in some form and  $\text{NO}_3^-$  in the cellulose ester. The greater is the length of the chain mols. or the greater their concn., the less is the amount of bronzing powder required to form a stiff gel. E. S. H.

**Determination of temperature of maximum density of gels.** H. E. VON GRONOW (Z. anorg. Chem., 1936, 227, 221—224).—The temp. of max.  $d$  of gelatin gels, calc. from the contraction occurring when gelatin is dissolved in  $\text{H}_2\text{O}$ , and from the respective coeffs. of expansion, agree with those observed by Taffel (J.C.S., 1922, 121, 1971). The gels behave, on thermal expansion, precisely as if the gelatin were present in the form of anhyd. solid. F. L. U.

**Bound water in gelatin gel.** E. HATSCHKE (Trans. Faraday Soc., 1936, 32, 787—789).—A direct demonstration of "bound"  $\text{H}_2\text{O}$  in gelatin gel is based on the colour change accompanying the dehydration of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  contained in the gel. The change is complete when the  $\text{H}_2\text{O}$  content of the gel falls to 30.4—34.0%. F. L. U.

**Gelation of different kinds of gelatin.** R. REIGER and S. BACH (Kolloid-Z., 1936, 75, 322—325).—Investigation of the change of optical rotation of gelatin during the initial stages of gelation shows that for 4 different kinds of gelatin the abs. change is different, but the relative change is the same. E. S. H.

**Influence of ultrasonic waves on gels.** H. FREUNDLICH and K. SOLLNER (Trans. Faraday Soc., 1936, 32, 966—970).—The liquefaction of thixotropic gels by ultrasonic waves is due to cavitation, and does not occur if this is prevented. L. J. J.

**Physico-chemical properties of electrodialysed gels of silica, alumina, ferric hydroxide, and their mixture. I. Ion exchange.** P. B. BHATTACHARYA and K. GANGULI (J. Indian Chem. Soc., 1936, 13, 204—213).—Dried electrodialysed gels of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and mixtures of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  were treated with aq. solutions of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  and the amount of ion adsorption was measured.  $\text{SiO}_2$  did not adsorb  $\text{Cl}^-$  ions. Cation adsorption in the case of the mixed gels was always  $>$  that calc. from the adsorption of the components. C. R. H.

**Viscosity of thorium phosphate gel-forming mixtures during gelation.** S. M. MEHTA, M. U. PARMAR, and M. PRASAD (J. Indian Chem. Soc., 1936, 13, 128—135).—The  $\eta$  of  $\text{Th}_3(\text{PO}_4)_4$  during gelation, alone and in presence of  $\text{Th}(\text{NO}_3)_3$  and  $\text{H}_3\text{PO}_4$ , has been investigated. The  $\eta$  increases with time, at first slowly and then more rapidly, but there is no evidence of discontinuity in the  $\eta$ -time curves during gelation. Additions of  $\text{H}_3\text{PO}_4$  and  $\text{Th}(\text{NO}_3)_3$  respectively increase and decrease the rate of increase of  $\eta$  with time, the former being due to an increase in the no. of micelles in unit vol., and the latter to  $\text{Th}$  ions peptising  $\text{Th}_3(\text{PO}_4)_4$ , and so increasing the degree of dispersion of the micelles. Non-electrolytes decrease and electrolytes increase the rate of increase of  $\eta$  with time. C. R. H.

**Viscosity of fibrinogen.**—See this vol., 874.

**Isoelectric point of glycinin.** R. J. HARTMAN and L. T. CHENG (J. Physical Chem., 1936, 40, 453—459).—The electrophoresis of glycinin indicates that the isoelectric point is at 5.02. Min.  $\eta$ , min. solubility, and min. variation of electrical conductivity with change of  $p_H$  are at the same point within the limits of experimental error. This result confirms Loeb's view that the physical properties of a protein are related to the isoelectric point. M. S. B.

**Influence of mono- and poly-hydric alcohols and mono- and poly-saccharides on the absorption of fluid by gels.** L. I. WEBER and F. LEDERER (Biochem. Z., 1936, 285, 115—122).—A layer of  $\text{H}_2\text{O}$  or aq. solution of various non-electrolytes is placed above a gelatin gel and the effect on swelling noted. The power to remove  $\text{H}_2\text{O}$  from the gel increases with increasing no. of OH groups and with increasing mol. wt. Thus the effect increases in the series  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{PrOH}$ ,  $(\text{CH}_2\text{OH})_2$ , trimethylene glycol,  $\beta$ -butylene glycol and similarly in the series glycol, glycerol, erythritol, mannitol, glucose, maltose, sucrose, and lactose. Dextrin and starch have about the same action. The solubility of the solute has some effect but does not solely determine the degree of swelling. P. W. C.

**Cataphoretic migration velocity of inorganic colloids.** J. N. MUKHERJEE, S. G. CHAUDHURY, and B. N. GHOSH (Kolloid-Beih., 1936, 43, 417—466).—A summary of published work. The influence of dilution, electrolytes, non-electrolytes, and their mixtures, and the relation of electrophoresis to dielectric const. and crit. coagulation potential are discussed. E. S. H.

**Experimental test of the identity of electrokinetic potentials.** Electrosmosis and streaming potential measurements with a glass slit. R. DuBOIS and A. H. ROBERTS (J. Physical Chem., 1936, 40, 543—560).— $\zeta$ -potentials for very dil. aq. electrolytes ( $10^{-3}$ — $10^{-6}N$ ) obtained from electrosmosis experiments are nearly identical with those afforded by streaming potential measurements over most of the concn. range. Large discrepancies, however, occur at very low ionic concn. With  $10^{-5}N$ - $\text{AlCl}_3$  results of opposite sign are obtained by the two methods. M. S. B.

**Exchange reactions between heavy water and hydrogen compounds.**—See this vol., 819.

**Effect of isotopy on the position of chemical equilibrium.** J. M. BLIVOET (Chem. Weekblad, 1936, 33, 287—288).—Isotopy has no effect on chemical equilibrium as far as statistical wt. is concerned. The explanation given by Giauque and Overstreet (A., 1932, 695) is criticised and a more rational one offered. S. C.

**Equilibrium between ethyl alcohol, water, and ethyl ether in the gaseous phase.** G. SEMERANO (Gazzetta, 1936, 66, 162—169).—The equilibrium has been studied at  $249^\circ$  and  $266^\circ$  and 10—70 atm., using a mixture of Al oxide and phosphate as catalyst. From the linear relation between  $\log K$  and  $p$ , the



calc. vals. of  $K$  at 1 atm. are 7.25 and 7.69 at 249° and 266°, respectively. O. J. W.

**Equilibrium between *n*-propyl alcohol, water, and *n*-propyl ether in the gaseous phase.** G. SEMERANO (Gazzetta, 1936, 66, 170—172; cf. preceding abstract).—From measurements up to 32 atm. between 235° and 260° the val. of  $K$  at 1 atm. and 250° is calc. to be 11.0. O. J. W.

**Equilibrium between *n*-butyl alcohol, water, and *n*-butyl ether in the vapour state.** G. SEMERANO (Gazzetta, 1936, 66, 172—174; cf. preceding abstracts).—From measurements up to 20 atm. between 250° and 260° the calc. val. of  $K$  at 1 atm. and 250° is 14.0. O. J. W.

**Cryoscopic determination of the total hydration of potassium iodide ions.** (Mlle.) O. HUN (Compt. rend., 1936, 202, 1779—1781).—The apparent cryoscopic const. ( $A$ ), 1933, 460) for 0.5*N*-KI is 19.99, suggesting hydration represented by  $KI \cdot 8.6H_2O$  (cf. *ibid.*, 566;  $A$ , 1934, 728). J. W. S.

**Dissociation constant of hydrochloric acid.** R. A. ROBINSON (Trans. Faraday Soc., 1936, 32, 743—744).—The const.  $K = a_{H^+}a_{Cl^-}/[mol. fraction HCl]$  ( $a$ =activity) has been derived for 0.56—15.4*N*-HCl from v.-p. data, assuming the validity of Raoult's law.  $K$  varies from  $20 \times 10^{-6}$  at 0° to  $0.12 \times 10^{-6}$  at 50°. Log  $K$  gives a linear plot with  $1/T$ , from which the heat of dissociation is calc. to be 17.9 kg.-cal. F. L. U.

**Thermodynamics of hydrochloric acid in methyl alcohol-water mixtures from electromotive force measurements.** H. S. HARNED and H. C. THOMAS (J. Amer. Chem. Soc., 1936, 58, 761—766).—E.m.f. of the cells  $H_2|HCl(m)|$  in  $x\%$  MeOH,  $y\%$   $H_2O|AgCl-Ag$  have been determined at 5° intervals from 0° to 40° in 10—20 wt.-% MeOH, with acid concns. of 0.003—2*M*. The activity coeff. of the acid in MeOH- $H_2O$  mixtures of high dielectric const. can be calc. on the basis of the extended Debye-Hückel theory from the data for aq. solution. Methods of extrapolation of the e.m.f. data for the above cell have been studied and the standard potential of the cell in MeOH has been recalcd. The e.m.f. of transfer of the acid at unit activity from one solvent to another is discussed in relation to the Born theory, and vals. for the sum of the reciprocals of the ionic radii have been obtained. Equations and parameters for calculating the relative partial mol. heat content and sp. heat of the acid in 10 and 20% MeOH solutions are given. E. S. H.

**Second dissociation constant of carbonic acid.** Y. KAUKO and V. MANTERE (Z. physikal. Chem., 1936, 176, 187—201; cf. this vol., 29).—From the e.m.f. of the cell  $H_2|Na_2CO_3|saturated KCl|0.01*N*-HCl|0.09*N*-KCl|H_2$ , the  $H$  ion activity of  $10^{-4}$ — $10^{-3}$ *M*- $Na_2CO_3$  has been determined, leading to vals. of the above dissociation const. at 0—37°, having a possible error of  $\pm 7\%$ . The heat effect for the second dissociation is -2700 and -7500 kg.-cal. at 12.5—37 and 0—12.5°, respectively. R. C.

**Chemical constitution and dissociation constants of monocarboxylic acids. V. Further substituted benzoic and phenylacetic acids.**

J. F. J. DIPPEY and R. H. LEWIS (J.C.S., 1936, 644—649; cf.  $A$ , 1935, 581).—Vals. of  $K \times 10^5$ , both classical and thermodynamic, have been obtained by the conductivity method for *m*- and *p*-methyl-, *m*-methoxy-, *o*- and *m*-fluoro-, *m*-bromo-, *o*- and *m*-iodo-, *m*- and *p*-nitro-benzoic acids, and *o*- and *m*-iodophenylacetic acids. The results are discussed. F. L. U.

**Dissociation constants of polybasic acids. II.** W. R. MAXWELL and J. R. PARTINGTON (Trans. Faraday Soc., 1936, 32, 775—782; cf.  $A$ , 1935, 934).—The dissociation consts. of trimellitic, trimesic, mellophanic, prehnitic, and pyromellitic acids have been determined. The results support the hypothesis that the negative charge or charges on a dissociating ion produce an inhibiting effect which is a simple function of their no. and distance from the dissociating  $\cdot CO_2H$ . F. L. U.

**Proton affinities of sparingly soluble bases: benzdine.** E. B. R. PRIDEAUX and J. R. PARKINSON (Trans. Faraday Soc., 1936, 32, 963—966).—The dissociation const.  $k_b$ ,  $p_{k_1}$ , and  $p_{k_2}$  have been determined by colorimetric methods, by the electro-metric method in aq. alcoholic solution and extrapolation to zero  $[EtOH]$ , and colorimetrically in presence of solid base, giving, respectively,  $k_b \times 10^9$  1.25, —, 1.74;  $p_{k_1}$  5.097, 5.09, 5.23;  $p_{k_2}$  3.61, 3.79, —. L. J. J.

**Calorimetric study of the action of ammonia on cobalt chloride in water in presence of ammonium chloride.** M. CHATELET (J. Chim. phys., 1936, 33, 313—324).—Equilibria have been determined at 18° for the ions  $Co(NH_3)^{2+}$  and  $Co(NH_3)_3^{2+}$  previously detected (cf. this vol., 290).  $Co^{2+} + NH_3 \rightleftharpoons Co(NH_3)^{2+}$  gives  $K_1 = [Co^{2+}][NH_3]/[Co(NH_3)^{2+}] = 0.3$  and  $Co(NH_3)^{2+} + 2NH_3 \rightleftharpoons Co(NH_3)_3^{2+}$  gives  $K_2 = [Co(NH_3)^{2+}][NH_3]^2/[Co(NH_3)_3^{2+}] = 95$ . Thus the equilibrium const.  $K_3$ , corresponding with the formation of  $Co(NH_3)_3^{2+}$  from  $Co^{2+}$ , is  $K_1K_2 = 28$ . Heats of reaction have also been calc. M. S. B.

**Ferric sulphate in aqueous solutions of other sulphates.** F. K. CAMERON (J. Physical Chem., 1936, 40, 689—696).—In general, addition of  $Fe_2(SO_4)_3$  lowers the solubility of other sulphates. With  $FeSO_4$  no double salt is formed between 25° and 50°. With  $(NH_4)_2SO_4$  an alum is formed below 36°; the range of concn. in which it exists at 25° has been determined. With  $K_2SO_4$  an alum is formed below 16° over a wide concn. range; above 16°  $2K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 14H_2O$  is stable at all but very high or very low concns. of  $Fe_2(SO_4)_3$ . E. S. H.

**Lower cobalt sulphides. Equilibrium diagram of system Co-CoS.** H. HULSMANN and F. WEIBKE [with K. MEISEL] (Z. anorg. Chem., 1936, 227, 113—123; cf.  $A$ , 1935, 1335).—Thermal, microscopic, and X-ray analysis of the system Co-CoS confirms the results obtained by Friedrich ( $A$ , 1908, ii, 500). CoS melts at  $1135 \pm 10^\circ$ , and forms a homogeneous phase only in presence of a slight excess of S. The face-centred cubic lattice with  $a$  9.924 Å. characterises the  $\gamma$ -phase ( $Co_5S_5$ ). L. U.

**M.-p. diagram of boron trioxide-sodium metaborate melts.** E. JENCKEL (Z. anorg. Chem., 1936,



227, 214—220; cf. A., 1935, 704).—The m.-p. diagram of the system  $B_2O_3$ - $NaBO_2$  affords evidence of the compounds  $Na_2O, 4B_2O_3$ ,  $Na_2O, 3B_2O_3$ , and  $Na_2O, 2B_2O_3$ . The two former exist in stable and unstable modifications. F. L. U.

**System  $SO_3$ - $H_2O$  and absolute sulphuric acid.** E. MOLES and C. R. DE ROBLES (Anal. Fis. Quím., 1936, 34, 331—362).—The anomalous cryoscopic const. of  $H_2SO_4$  (cf. Oddo *et al.* A., 1918, ii, 352) is supposed to be connected with the equilibrium  $3H_2SO_4 \rightleftharpoons H_2SO_4 \cdot H_2O + H_2S_2O_7$ . F. R. G.

**Thermal dissociation of calcium carbonate.** J. C. SOUTHARD and P. H. ROYSTER (J. Physical Chem., 1936, 40, 435—438).—Measurements made with the use of a furnace in which a temp. of  $900^\circ$  could be maintained const. within  $0.04^\circ$  for over 30 hr. lead to pressures given by  $\log_{10} p_{\text{cm.}} = -9140/T + 0.382 \log_{10} T - 0.668 \times 10^{-3}T + 9.3171$ . The temp. corresponding with 1 atm. is  $894.4^\circ$ . M. S. B.

**Saturation pressure of ammonia in the thermal decomposition of zinc chloride diammine.** E. STAROKADOMSKAJA (J. Appl. Chem. Russ., 1936, 9, 599—602).—The pressure of  $NH_3$  over  $ZnCl_2 \cdot 2NH_3$  at  $220$ — $540^\circ$  ( $1$ — $40$  atm.) agrees with that calc. from Krasnov's formula (Bull. All-Soviet Union Thermotech. Inst., 1935, No. 11). R. T.

**Vapour pressure of nitric acid and ammonia over aqueous ammonium nitrate.** V. A. KLEVKE and J. D. CHASKINA (J. Chem. Ind. Russ., 1936, 13, 408—411).—The  $[HNO_3]$  of the vapour from boiling aq.  $NH_4NO_3$  is negligible for concns.  $< 65\%$ . The loss of  $NH_3$  involved in concentrating a  $60\%$  solution (containing  $0.5$  g. of excess  $NH_3$  per litre) to  $93\%$  amounts to  $4.5$ — $5$  kg. per ton of solution. R. T.

**Chemical transformations in ternary system copper-sulphur-oxygen.** G. SILLE (Metall u. Erz, 1935, 32, 270—283, 297—312; Chem. Zentr., 1935, ii, 1600).—The reactions undergone by the various binary systems involving Cu, CuO,  $Cu_2O$ ,  $CuSO_4$ , and  $Cu_2S$  are considered. Reactions tending to the irreversible formation of  $Cu_2S$  and  $Cu_2O$  preponderate. J. S. A.

**Three-component system  $CaO$ - $Al_2O_3$ - $H_2O$ .** II. **System rich in  $CaO$ .** R. NACKEN and R. MOSEBACH (Z. anorg. Chem., 1936, 227, 328—336).—The solubility of  $3CaO, Al_2O_3, 6H_2O$  (I) is  $0.6820$  g. per litre at  $30^\circ$ . The solid which first separates is  $2CaO, Al_2O_3, 7H_2O$ , but, as the proportion of  $CaO$  increases, (I) is more readily formed and ultimately free  $Ca(OH)_2$  is also present. It has not, so far, been possible to obtain the compound  $4CaO, Al_2O_3, 13H_2O$  under the conditions of these experiments. M. S. B.

**Solubility equilibria of sodium sulphate at temperatures from  $150^\circ$  to  $350^\circ$ .** II. **Effect of sodium hydroxide and sodium carbonate.** W. C. SCHROEDER, A. A. BERK, and A. GABRIEL (J. Amer. Chem. Soc., 1936, 58, 843—849; cf. A., 1935, 1314).—Equilibrium data for the system  $Na_2SO_4$ - $Na_2CO_3$ - $H_2O$  at intervals of  $50^\circ$  from  $150^\circ$  to  $350^\circ$  have been determined. The existence of  $Na_2CO_3 \cdot 2Na_2SO_4$  has been established. The effect of adding  $NaOH$  to the ternary system has been examined. E. S. H.

**Solubility in the system  $ZnCl_2$ - $HCl$ - $H_2O$  at  $25^\circ$ .** D. I. KUZNETZOV and A. A. KOSHUCHOVSKI (J. Appl. Chem. Russ., 1936, 9, 185—188).—Solubility data at  $25^\circ$  are recorded.  $60\%$  of the Zn content of saturated aq.  $ZnCl_2$  is pptd. as  $2ZnCl_2 \cdot HCl \cdot 2H_2O$  on saturation with  $HCl$ . R. T.

**Equilibria between water and the simple and double halides of cadmium and potassium.** H. HERING (Ann. Chim., 1936, [xi], 5, 483—586).—Data for the systems  $KCl$ - $CdCl_2$ - $H_2O$ ,  $KBr$ - $CdBr_2$ - $H_2O$ , and  $KI$ - $CdI_2$ - $H_2O$  (A., 1932, 469, 574; 1933, 906) are recorded.  $KBr, CdBr_2, H_2O$  (I),  $KBr, CdBr_2$ , and  $KBr$  coexist with solution at  $20.9^\circ$  and (I)+ $KBr$  at  $-18.1^\circ$ . Contrary to A., 1933, 906,  $CdI_2 \cdot 2KI \cdot 2H_2O$  (II) crystallises above  $-15.3^\circ$  and  $CdI_2 \cdot 2KI \cdot 3H_2O$  below  $-15.3^\circ$ . (II) and  $CdI_2 \cdot 2KI \cdot 0.5H_2O$  (III) coexist at  $81.4^\circ$ . (III) exists above  $76.3^\circ$  but is decomposed by  $H_2O$  forming  $KI$ . J. G. A. G.

**Ternary system manganese arsenate-arsenic acid-water.** G. GRUBE, A. HELLER, and W. HERRMANN (Z. Elektrochem., 1936, 42, 223—226).—Four solid phases are indicated:  $Mn_3(AsO_4)_n \cdot H_2O$ ,  $MnHASO_4 \cdot 4H_2O$ ,  $H_4[Mn(AsO_4)_2] \cdot 3H_2O$ , and  $H_4[Mn(AsO_4)_2]$ . When  $H_3AsO_4$  solutions containing  $Mn^{++}$  salts are electrolysed, it is found that  $Mn^{++}$  is gradually replaced by the complex Mn ions as the acid concn. is increased. C. R. H.

**Behaviour of silver fluoride in complex formation.** E. HAYEK (Monatsh., 1936, 68, 29—32; cf. A., 1935, 1203).— $AgI$  is sol. in conc. aq.  $AgF$  and yields a cryst. compound  $AgI, AgF \cdot 2H_2O$ . Migration experiments show the presence of a complex cation.  $AgBr$  behaves similarly, but the solubility of  $AgCl$  is only slightly increased. No reaction occurs with  $Ag_2O$ . F. L. U.

**System dodecoic acid-sodium hydroxide-water.** C. R. BURY and R. D. J. OWENS (Trans. Faraday Soc., 1936, 32, 782—787; cf. A., 1935, 303).—Phase equilibria at  $25^\circ$  are shown in a triangular diagram. Solid phases in equilibrium with solutions on the alkaline side are  $NaOH \cdot H_2O$ , anhyd. Na dodecoate ( $NaL$ ), and curd (degree of hydration undetermined). In equilibrium with solutions on the acid side are  $HL$ ,  $xNaL, yHL$ , and a liquid cryst. phase. The solubility of  $NaL$  is strongly depressed by  $NaOH$  and increased by  $HL$ . F. L. U.

**Thermal potential of a mixture.** J. E. VERSCHAFFELT (Wis- en nat. Tijds., 1935, 7, 121—132; Chem. Zentr., 1935, ii, 1318—1319).—Theoretical. J. S. A.

**Specific heat of gases as an aid in calculating equilibria.** C. SCHWARZ (Arch. Eisenhüttenw., 1935—1936, 9, 389—396).—Mathematical. Expressions have been derived for the sp. heat and heat content at any temp. of  $H_2$ ,  $O_2$ ,  $CO$ ,  $N_2$ ,  $NO$ ,  $OH$ ,  $H_2O$ ,  $CO_2$ ,  $N_2O$ ,  $CH_4$ , and  $C$ . A. R. P.

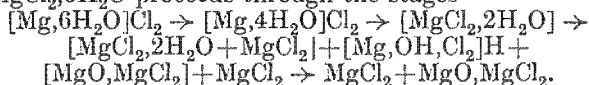
**Heat capacity of saturated sodium sulphate solution.** K. A. KOBE and C. H. ANDERSON (J. Physical Chem., 1936, 40, 429—433).—Over the range  $32.4$ — $102.8^\circ$  the heat capacity is given by  $C = 0.803 - 1.14 \times 10^{-4}t - 3.2 \times 10^{-6}t^2$ . The mean val. is  $0.780$  g.-cal. per g. of solution. The measured heat of



transition of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is 18,700, which agrees closely with the val. of 19,000 calc. from v.-p. data.

M. S. B.

**Specific heat of hydrates of magnesium chloride.** A. E. AUSHBEKOVITSCH (J. Appl. Chem. Russ., 1936, 9, 594—598).—On the basis of sp. heat measurements it is inferred that dehydration of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  proceeds through the stages



R. T.

**Calculation of activity coefficients. Electrolytic dissociation of nitric acid.** O. REDLICH and P. ROSENFELD (Monatsh., 1936, 67, 223—230).—Probable errors in the calculation of activity coeffs. from f.p. and e.m.f. data are discussed. Comparison of data for  $\text{HNO}_3$  indicates that relatively large divergencies may be found for the vals. of the dissociation consts. and related quantities for strong electrolytes.

J. W. S.

**Heat of formation and free energy of formation of boron nitride.** S. SATOH (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 53—62).—The heat of formation of BN calc. from its v.p. and from the sp. heats of B, BN, and  $\text{N}_2$  is 28,470 g.-cal., whilst  $\Delta F_{298^\circ} = 54,760$  g.-cal.

R. S.

**Thermochemistry of chloro-substituted benzoquinones and quinols.** G. SJÖSTRÖM (Svensk Kem. Tidskr., 1936, 48, 121—123).—Heats of combustion (kg.-cal.) at  $20^\circ$  (const. vol.) are: chloro- 619.4, 2:6-, 2:5-, and 2:3-dichloro- 584.8, 584.6, 583.9, trichloro- 549.6, and tetrachloro-benzoquinone 516.5, and for the corresponding -quinols 648.7, 610.0, 609.1, 611.8, 576.8, 545.0. The heats of reaction (reduction) of the above chlorobenzoquinones at  $20^\circ$  are respectively 38.8, 42.9, 43.6, 40.2, 40.9 (at  $18^\circ$ ), 39.5.

E. P.

**Activation energies of the addition of hydrogen halides to ethylene.** C. E. SUN and C. LIU (J. Chinese Chem. Soc., 1936, 4, 98—101).—An attempt to calculate the affinity of  $\text{C}_2\text{H}_4$  for HCl, HBr, and HI on the basis of activation energies. The calc. energies for the formation of EtCl, EtBr, and EtI are respectively 48.4, 39.0, and 31.5 kg.-cal.

C. R. H.

**Measurement of conductivity of very dilute electrolytes.** W. GRALLERT (Z. Elektrochem., 1936, 42, 330—336).—Errors are discussed, and portable apparatus suitable for laboratory use is described.

F. L. U.

**Electrical conductivity, viscosity, and diffusion of certain lanthanum salts.** L. W. ÖHOLM (Soc. Scient. Fenn. Comm. Phys.-Math., 1936, 9, No. 2, 14).—Viscosities, determined by Ostwald's method, are in the order  $\text{La}_2(\text{SO}_4)_3 > \text{LaCl}_3 > \text{La}(\text{NO}_3)_3$  at corresponding normalities. Redetermination of conductivities confirms substantially former results,  $\text{LaCl}_3$  having slightly greater vals. than  $\text{La}(\text{NO}_3)_3$ .  $\text{La}_2(\text{SO}_4)_3$  much smaller vals. The diffusibilities increase with dilution in a similar way to that of the conductivities. The diffusion consts. are in the order  $\text{LaCl}_3 > \text{La}(\text{NO}_3)_3 > \text{La}_2(\text{SO}_4)_3$ .

D. C. J.

**Cathodic current distribution in electrolytes.**

I. Zinc baths. E. MANTZELL (Z. Elektrochem., 1936, 42, 303—315; cf. A., 1935, 306).—Current distribution ( $D$ ) at the cathode has been studied under varying conditions in six different types of Zn-plating bath. In all types the effect of increasing c.d. is unfavourable. Some improvement results by decreasing  $[\text{Zn}^{++}]$  whilst the conductivity ( $\kappa$ ) is const., and in acid baths by increasing  $\kappa$  by the addition of  $\text{NH}_4$  salts. Under given conditions, cyanide baths show the best  $D$ , that in alkali zincate baths being relatively poor despite their high  $\kappa$ . The distribution of metal at the cathode follows  $D$  closely in acid baths, in which the current yield approaches 100%, but is more uniform than  $D$  in zincate and cyanide baths.

F. L. U.

**Transport numbers of paraffin-chain salts in aqueous solution.** I. Measurement of transport numbers of cetylpyridinium and cetyltrimethylammonium bromides and their interpretation in terms of micelle formation, with data for cetanesulphonic acid. G. S. HARTLEY, B. COLLIE, and C. S. SAMIS (Trans. Faraday Soc., 1936, 32, 795—815; cf. A., 1935, 299).—The transport nos. ( $T$ ) of the two paraffin-chain cations increase rapidly with increase of concn. in the range where the total equiv. conductivity ( $\lambda$ ) falls, finally becoming  $\gg 1$ . In the first part of this range the increase of  $T$  is so great that the  $\lambda$  of the cation is  $>$  its val. at infinite dilution, thus demonstrating the formation in this range of mobile micelles. The accompanying decrease of total  $\lambda$  is due to a braking effect caused by adherence to the micelles of  $\text{Br}^-$  ions, the mean mobility of which is negative over a considerable range of concn. The increase of total  $\lambda$  observed at moderate concns. is due, not directly to formation of more mobile micelles from less mobile simple ions, but to the liberation of compensating ions previously attached to the micelles. An approx. estimate of the size of the micelles is given.

F. L. U.

**Faraday's law and electrolysis by spark.** P. JOLIBOIS and P. DE BECO (Compt. rend., 1936, 202, 1496—1498; cf. A., 1935, 837).—If diffusion of the acid which is formed at the positive pole is prevented the quantity of oxide formed agrees with Faraday's law.

R. S.

**Bismuth electrode.** A. HOLMQVIST (Svensk Kem. Tidskr., 1936, 48, 106—120).—On varying  $[\text{Bi}^{+++}]$  in aq. HCl,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  free from air, the potential changes in accordance with Nernst's formula. The p.d. between a normal  $\text{H}_2$  electrode and a Bi electrode in 1M- $\text{Bi}^{+++}$  is 0.289 volt.

E. P.

**Behaviour of the cadmium electrode in alkaline nickel-cadmium accumulators.** G. GRUNE and E. DOETSCH (Z. Elektrochem., 1936, 42, 247—258).—Changes in terminal voltage, in the single electrode potential, and in the electrolyte during the charge and discharge of Ni-Cd accumulators have been studied. The behaviour of Cd electrodes which contain 14.6% of  $\text{Fe}_3\text{O}_4$  has been compared with that of pure Cd electrodes prepared in various ways.

C. R. H.

**Calculation of normal potential of metals and Henry constant of ions.** I. UHARA (Phil. Mag., 1936,



[vii], 21, 958—976).—Normal potentials of metals in  $H_2O$  and non-aq. solvents are deduced thermodynamically. Calc. and experimental vals. are compared. There is a parallelism between the Henry const. and the heat of hydration of ions. H. J. E.

**Electrometric potential and concentration of electrolytes.** (MLLE.) S. VEIL (Compt. rend., 1936, 202, 1665—1666).—If  $\pi_\sigma$  is the e.m.f. of saturated aq.  $CuCl_2$  of concn.  $\sigma$  and  $\pi$  at concn.  $c$ , then  $\pi = \pi_\sigma (c/\sigma)^k$  where  $k$  is approx.  $\frac{1}{2}$  for the concn. range  $\sigma = c/10,000$  at room temp. M. S. B.

**Thermodynamical exposition of the operation of reversible gas electrodes.** J. W. H. LUGG (J. Proc. Austral. Chem. Inst., 1936, 3, 126—130).—Theoretical. The significance of the metal holding the gas is discussed, and a theory of single electrode potential, in which the characteristics of the electrode metal are considered, is formulated. E. S. H.

**Physical significance of activity coefficients in reversible electrode equilibria.** J. W. BELTON (Phil. Mag., 1936, [vii], 21, 1140—1144).—A relationship is derived between the activity coeff. of an electrolyte and the p.d. between this electrolyte and the region where ion-neutralisation occurs (adsorption potential). J. W. S.

**Influence of  $p_H$  on the Becquerel effect of coloured electrodes.** (MLLE.) C. STORA (Compt. rend., 1936, 202, 1666—1668).—Dark potentials and photopotentials of oxidation-reduction indicators, such as Nile-blue and methylene-blue, and of derivatives of xanthane,  $CH_2Ph_2$ , and  $CHPh_3$ , have been determined. The rules which govern the influence of  $p_H$  on the Becquerel effect for electrodes in metallic salts do not, in general, appear to apply to coloured electrodes. Apart from catalysis of the photochemical reaction at the electrode by  $OH^\cdot$ , it is necessary to consider the variation with  $p_H$  of the absorption of the photosensitive compound and also to use monochromatic light in the experiments. M. S. B.

**Capillary-electric phenomena in molten salts.** S. KARPATSOV and A. STROMBERG (Z. physikal. Chem., 1936, 176, 182—186).—The electrocapillary curves of Sn, Pb, Cd, and Tl in contact with molten  $KCl-LiCl$  and  $KI-LiI$  mixtures and with molten Pb as auxiliary electrode have been determined. The p.d. of the max. on the curve for a given electrolyte varies considerably according to the metal with which it is in contact. From the curves for Sn the capacity,  $C$ , of the double layer as a function of the polarising voltage has been determined. The val. of  $C$  corresponding with the equilibrium potential of Sn in both electrolytes is 90—100  $\mu F$  per sq. cm. R. C.

**Electromotive force of movement of metals in water and their electrokinetic potential.** S. PROCORIU (Compt. rend., 1936, 202, 1371—1373; cf. A., 1930, 546).—For various metals the e.m.f. decreases with time in pure  $H_2O$ , but is const. in sucrose solution, and is of the same magnitude and sign as the electrokinetic potential. The influence of velocity and of the dielectric const. of the liquid has been studied. R. S.

**Hydroelectric and contact cells.** (MLLE.) S. VEIL (Bull. Soc. chim., 1936, [v], 3, 860—865).—When Pt is placed in contact with other metals in gelatin the e.m.f. vals. obtained are: Zn 1.01, Cd 0.72, Fe 0.59, Pb 0.54, Ni 0.28, Cu 0.22 volt. The relative importance of Volta effect and chemical action in electrolytic cells is discussed. E. S. H.

**Study of the cryolite-aluminium oxide cell with particular reference to decomposition voltage.** J. W. CUTHBERTSON and J. WADDINGTON (Trans. Faraday Soc., 1936, 32, 745—760).—At 1025° the decomp. voltages of cryolite and of cryolite with  $Al_2O_3$  (16%) are respectively 2.23 and 2.20 volts with Pt, and 1.7 and 1.5 volts with graphite, anodes. The decomp. voltage of cryolite falls nearly linearly with rising temp. In the Al cell the current is carried by the cryolite. The  $Al_2O_3$  is only slightly, if at all, ionised, and functions as both a cathodic and anodic depolariser, supplying Al at the cathode and regenerating  $AlF_3$  at the anode. F. L. U.

**Mechanism of the decomposition of aluminium-magnesium solid solutions.** P. LACOMBE and G. CHAUDRON (Compt. rend., 1936, 202, 1790—1792; cf. B., 1935, 678).—The dissolution potential of a quenched Mg-Al solid solution (9% Mg), after annealing below 280°, increases at first with time of annealing but later decreases almost to its initial val. The velocity of attack by acid of fixed concn. shows a corresponding max. This is interpreted as indicating that the constituent initially pptd. is unstable and richer in Mg than the compound  $Al_3Mg_2$ . J. W. S.

**Passivity of chromium. IV. Electromotive behaviour of chromium amalgam.** E. MULLER (Z. physikal. Chem., 1936, 176, 273—288; cf. A., 1932, 473).—In  $M-HCl$  at 20°, Cr amalgam oscillates periodically between the active and passive states, a phenomenon which is ascribed to the simultaneous occurrence of the processes  $Cr \rightarrow Cr^{++} + 2e$ ,  $2e + 2H^+ = H_2$ , the second of which tends to reduce the electrode potential below the val. required for the first. In  $M-H_2SO_4$  massive Cr is passive but can be permanently rendered active by weak cathodic polarisation. Cr amalgam is rendered active temporarily by polarisation, but becomes active on shaking. In  $M-HClO_4$  the behaviour is similar, except that shaking does not cause activation. In all three acids the amalgam is rendered passive by strong cathodic polarisation. The activation potentials in the various acids are < for massive Cr, but form the same sequence. The experimental results are incompatible with Muller's coating theory of passivity. R. C.

**Measure of acidity obtained from the electromotive force of a cell without liquid junction.** D. I. HITCHCOCK (J. Amer. Chem. Soc., 1936, 58, 855—856).—The product  $m_B \gamma_{H^+} \gamma_{Cl^-}$  is regarded as a promising measure of acidity in preference to  $p_H$ . E. S. H.

**Reduction potentials of organic systems. I. Bimolecular reduction of thioindigotindisulphonate.** A. E. REMICK (J. Amer. Chem. Soc., 1936, 58, 733—736).—The reduction potential ( $E'_0$ ) of the system thioindigotindisulphonate-leuco-compound at  $p_H$  2.02—7.61 and 25° varies linearly with



the concn. of the oxidant  $[K_3Fe(CN)_6]$  at const. % oxidation. The results conform to the thermodynamic equations for a one-step bimol. reduction involving 1e per mol. of dye. H. B.

**Oxidation-reduction potential of  $\alpha$ -amino-ketobutyric ester and of reductone.**—See this vol., 888.

**Bronsted's kinetic equation and the Debye theory.** II. A. MUSIL (Monatsh., 1936, 67, 269—319; cf. A., 1932, 1209).—Anomalies in the Debye theory are eliminated by application of the Bronsted equation, enabling the theory to be applied to reaction kinetic problems. The author's theory is supported by experimental data for the hydrolysis of esters of AcOH by alkali carbonates and hydroxides in presence of KCl,  $K_3Fe(CN)_6$ ,  $K_4Fe(CN)_6$ , and K silicotungstate. J. W. S.

**Reactions produced by adiabatic expansion in systems in chemical equilibrium.** P. MONTAGNE (Compt. rend., 1936, 202, 1430—1432).—Theoretical. L. J. J.

**Kinetics of recombination of bromine atoms.** II. E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 907—917; cf. A., 1935, 586).—The authors' optical method has been used to measure the stationary  $[Br]$  in illuminated  $Br_2$  vapour, and velocity coeffs. for three-body recombination in presence of He, A,  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CH_4$ , and  $CO_2$  have been determined. The recombination rate of Br is 2—3 times < that of I with the same third body. The results in mixtures and in pure  $Br_2$  agree with theory. L. J. J.

**Oxidation of silicon hydrides.** II. H. J. EMELÉUS and K. STEWART (J.C.S., 1936, 677—684; cf. A., 1935, 1207).—The lower crit. explosion pressures ( $P_l$ ) of mixtures of  $O_2$  with  $SiH_4$ ,  $Si_2H_6$ , and  $Si_3H_8$  and the upper crit. explosion pressures ( $P_u$ ) for mixtures of  $O_2$  with  $Si_2H_6$  and  $Si_3H_8$  have been studied as a function of the composition of the gas mixture and diameter of the glass explosion vessel.  $P_l$  is lowered and  $P_u$  raised by rise of temp. The inflammability of these compounds increases with increasing at. wt. The results are in accord with chain mechanisms analogous to that previously suggested for  $SiH_4$ . J. W. S.

**Influence of pressure on the spontaneous ignition of inflammable gas-air mixtures.** IV. **Methane-, ethane-, and propane-air mixtures.** D. T. A. TOWNEND and E. A. C. CHAMBERLAIN (Proc. Roy. Soc., 1936, A, 154, 95—112; cf. A., 1934, 151, 1179).—The influence of pressure up to 30 atm. on the ignition temp. of  $CH_4$ -,  $C_2H_6$ - and  $C_3H_8$ -air mixtures has been determined. With  $CH_4$ -air mixtures the ignition points are confined to an upper range even at pressures up to 30 atm. With  $C_3H_8$ -air mixtures, a lower-temp. ignition system develops at pressures > 13 atm.; 1% of MeCHO, however, produces a reduction of this to < 5 atm.  $C_3H_8$ -air mixtures show all the ignition features of the higher paraffins, ignition in the lower system being facilitated by the presence of MeCHO or EtCHO. The influence of pressure on pre-ignition time-lags has been investigated. L. L. B.

3 G

**Initial formation of alcohols during the slow combustion of methane and ethane at atmospheric pressure.** D. M. NEWITT and J. B. GARDNER (Proc. Roy. Soc., 1936, A, 154, 329—335).—During the slow combustion of  $CH_4$  and  $C_2H_6$  at atm. pressure MeOH and EtOH, respectively, are formed in quantities comparable with those of the corresponding aldehydes. Both alcohols and aldehydes are found during the induction period, but the ratio alcohol:aldehyde diminishes as the induction nears completion. The results prove that the formation of alcohol precedes that of the corresponding aldehyde. L. L. B.

**Slow combustion of methane, methyl alcohol, formaldehyde, and formic acid.** W. A. BONE and J. B. GARDNER (Proc. Roy. Soc., 1936, A, 154, 297—328).—The induction period in the slow combustion of  $CH_4$  at 390—420° is (a) uninfluenced by separately pre-heating the reactants or exposing the reacting medium to ultra-violet light; (b) lengthened by increasing the surface/vol. ratio of a  $SiO_2$  reaction vessel; (c) shortest with a  $2CH_4 + O_2$  medium; (d) characterised by the successive formation of small equilibrium amounts of MeOH and  $CH_2O$ ; (e) shortened by previous small additions of  $NO_2$ , but lengthened by addition of I. No peroxide was detected during the induction period. Under similar conditions, the slow oxidation of MeOH is much faster and less influenced by  $SiO_2$  surface than is that of  $CH_4$  at 390°. There is no appreciable induction period, although the reaction is accelerated by small additions of  $CH_2O$  or  $NO_2$ . The most reactive medium is  $2MeOH + O_2$ . The oxidation is marked by the intermediate successive formations of  $CH_2O$  and  $HCO_2H$ , and the end products are chiefly oxides of C and steam, with a high CO/ $CO_2$  ratio. In the slow combustion of  $CH_2O$ , no induction period is observed even at 275°, and the speed of the reaction is much > that of either MeOH or  $CH_4$ .  $HCO_2H$  is formed intermediately, together with performic acid (I) and "formaldehyde peroxide" (II), the latter being dependent on the prior formation of (I). The end products are again chiefly oxides of C and steam, with a high CO/ $CO_2$  ratio. Fair amounts of  $H_2$  are formed, probably from the decomp. of (II). Experiments made on the reactions of both 2:1 and 1:1  $HCO_2H/O_2$  mixtures between 340° and 470° showed a slower disappearance of  $O_2$  than thermal decomp. of  $HCO_2H$ . The gaseous products are chiefly CO,  $CO_2$ ,  $H_2O$ , and  $H_2$ , and there is no intermediate formation of a peracid or peroxide. The results all fit the hydroxylation theory. L. L. B.

**Slow combustion of formaldehyde.** R. SPENCE (J.C.S., 1936, 649—657).— $CH_2O$  reacts rapidly with  $O_2$  in Pyrex vessels at 317°. In unpacked vessels of < 1 mm. diameter the chief products are CO and  $H_2O$  but in vessels packed with powdered glass combination to form  $CO_2$  is complete. From the kinetics of the reaction a chain mechanism is proposed. J. W. S.

**Primary process in the thermal decomposition of formaldehyde and formic acid.** F. PATAT and H. SACHSSE (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., III, 1935, [ii], 1, 41—48; Chem.



Zentr., 1935, ii, 1526; cf. A., 1935, 708).—The decomp. in the presence of para- $H_2$  is studied. Since exchange is not observed it is concluded that the primary process involves saturated mols., contrary to the radical chain theory of Rice and Herzfeld (A., 1934, 369). H. N. R.

**Mechanism for the decomposition of ethylene oxide.** D. V. SICKMAN (J. Chem. Physics, 1936, 4, 297—299).—Theoretical. The kinetic data of Heckert and Mack (A., 1929, 1243) are in qual. agreement with an initial isomerisation to  $MeCHO$ , accompanied by a reaction producing free radicals which induce a chain decomp. of the  $MeCHO$ . L. J. J.

**Thermal decomposition of acetaldehyde and ethylene oxide.**—See this vol., 825.

**High-temperature pyrolysis of gaseous olefines.**—See this vol., 818.

**Thermal decomposition of ethylene oxide.**—See this vol., 820.

**Mechanism of flame extinction by carbon tetrachloride.**—See B., 1936, 482.

**Theory of detonation.**—See B., 1936, 525.

**Kinetics of thermal *cis-trans*-isomerisations.** V. G. B. KISTIAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1936, 58, 766—768).—With  $\Delta^2$ -butene the reaction is of approx. first order, but of second order with respect to initial pressure. A chain mechanism is suggested. The equilibrium composition at 633° and 620° abs. is 52.8% of *trans*-isomeride. E. S. H.

**Magnitude of radical concentration in homogeneous thermal decomposition of organic molecules.** I. Calculation of radical concentrations found by the para-hydrogen method, and the reaction  $CH_3 + H_2$ . II. Radical concentration in decomposition of dimethyl ether and propane. F. PATAT (Z. physikal. Chem., 1936, B, 32, 274—293, 294—304).—I. Partly a more detailed account of work previously described (this vol., 293). From observations of the photochemical decomp. of  $MeCHO$  the ratio  $k_1/k_2$  is found to be  $0.001e^{-(1870 \pm 900)/RT}$ . For  $Me + H \rightarrow CH_3 + H$  (I) there is a steric factor of  $\sim 10^{-4}$  and the energy of activation is  $\geq 9$  kg.-cal. The *p*- $H_2$  transformation in the photochemical decomp. of  $MeI$  and  $COMe_2$  observed by West (A., 1935, 1468) is not of paramagnetic nature, but is ascribed to H atoms formed by (I). The heat of formation of  $CH_4$  from  $Me + H$  is  $< 103$  kg.-cal.

II. The stationary  $[H]$  and  $[Me]$  in the thermal decomp. of  $Me_2O$  and  $C_3H_8$  have been determined. A review of all the available experimental data shows that in all the thermal decomp. in which the Rice-Herzfeld theory requires a chain mechanism radicals are actually formed, but in concns. so small as to be quite inadequate for the total decomp. by chains. In the homogeneous thermal decomp. of the org. mols. studied the first step is decomp. into saturated fragments, and the requisite energy of activation is  $<$  the linking energy of the weakest linking. R. C.

**Kinetic correlation of two reactions involving hydrogen peroxide.** Its oxidation by chlor-

amine-*T* and by chlorine. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1936, 58, 705—707).—Theoretical. A mechanism for the oxidation of  $H_2O_2$  by chloramine-*T*, based on published results, is advanced.

E. S. H.

**Velocity of diazotisation.** K. ROSTOVCEVA (Z. anal. Chem., 1936, 105, 32—35).—The velocity of diazotisation of aromatic amines, relative to that of benzidine (I), is determined by mixing a solution of the amine with an equal vol. of 0.1*N*-(I), both in conc.  $HCl$ . 0.1*N*- $NaNO_2$  is added at 5°, and after 15—20 min., (I) sulphate is pptd. by adding  $Na_2SO_4$ , and is determined volumetrically. It is proposed to employ the method for analysis of mixtures of isomeric amines. J. S. A.

**Glycoside fission in non-aqueous media.** I, II.—See this vol., 827.

**Reactivity of halogen compounds.** II. Rates of reaction and energies of activation of 1 : 2 : 4-chlorodinitrobenzene with aromatic primary amines. A. SINGH and D. H. PEACOCK (J. Physical Chem., 1936, 40, 669—678; cf. A., 1935, 1465).—The velocities of reaction of 1 : 2 : 4- $C_6H_3Cl(NO_2)_2$  with  $NH_2Ph$ , *o*-, *m*-, and *p*- $C_6H_4Me \cdot NH_2$ , *m*- and *p*- $C_6H_4Cl \cdot NH_2$  and  $-C_6H_4Br \cdot NH_2$ , *o*-, *m*-, and *p*-anisidine, and  $\alpha$ - and  $\beta$ - $C_{10}H_7 \cdot NH_2$  (0.4 and 0.8*M*) have been determined at 35° and 45°, and the energies of activation calc. The effect on the energy of activation of transferring a substituent from the *m*- to the *p*-position is as predicted by the Lapworth-Robinson hypothesis. The changes in energy of activation have been compared with the dipole moments.

E. S. H.

**Mode of action of solvents on chemical reaction velocity.** C. N. HINSHELWOOD (Trans. Faraday Soc., 1936, 32, 970—972).—Theoretical. The rate of an association reaction in solution may be determined by deactivation of the product by solvent mols. The kinetic phenomena resulting from such a mechanism are discussed. L. J. J.

**Inversion of sucrose in mixtures of light and heavy water.** P. GROSS, H. STEINER, and H. SUSS (Trans. Faraday Soc., 1936, 32, 883—889).—The rate of inversion of sucrose in  $H_2O$ - $D_2O$  mixtures containing  $H_2SO_4$  at 25° increases with the  $D_2O$  content, but not linearly. The effect is due to an increase in concn. of reacting complexes, the theory of which is discussed and shown to account for the effect with Et diazoacetate. L. J. J.

**Depolymerisation of water by capillarity and the inversion of sucrose.** E. TOPORESCU (Compt. rend., 1936, 202, 1672—1674).—The e.m.f. of a Pt-Ni couple in  $H_2O$  is changed if one of the electrodes is placed in capillary  $H_2O$ . This is attributed to depolymerisation of the  $H_2O$  in the capillary. By dialysis of aq. sucrose (I) through parchment-paper the rate of inversion of (I) is increased. On the assumption that depolymerisation of  $H_2O$  takes place in the capillaries of a porous body, this result is in agreement with an earlier observation that depolymerisation of  $H_2O$  by  $NaCl$  also increases the rate of inversion of (I) (cf. A., 1932, 346). M. S. B.



**Substitution and inversion of configuration.** E. BERGMANN, M. POLANYI, and A. L. SZABO (Trans. Faraday Soc., 1936, 32, 843—852; cf. A., 1933, 574).—The rate of racemisation of  $\text{CHMePr}^*\text{I}$  and  $\text{CHMeBu}^*\text{I}$  by  $\text{I}^-$  ions has been compared with the rates of exchange between halogens in related compounds. For the racemisation,  $k$  follows the Arrhenius equation with a temp.-independent factor of approx.  $10^{10}$ , and the  $k$  vals. for any set of analogous substitution or racemisation reactions form a continuous series. L. J. J.

**"Activated complex" theory and the influence of solvents on reaction velocity.** S. GLASSTONE (J.C.S., 1936, 723—724).—From the activated complex theory of reaction velocities (A., 1935, 827, 1205) it is deduced that association of reactant mols., but not of the activated complex, should increase reaction velocity ( $v$ ), whereas association of the activated complex and not of the reactants should decrease  $v$ . Compound formation between one or both reactants and the solvent should also decrease  $v$ .

J. W. S.

**Thermal decomposition of sodium and potassium azides.** W. E. GARNER and D. J. B. MARKE (J.C.S., 1936, 657—664).—The thermal decomp. of  $\text{KN}_3$  in K vapour is very much more rapid than in a vac., but that of  $\text{NaN}_3$  is only slightly catalysed by Na vapour. Microscopical examination of partly decomposed crystals shows that reaction begins on the surface and along lines, probably cracks in the crystal, but that with  $\text{KN}_3$  in a vac. reaction later penetrates to the interior. The energies of activation of  $\text{KN}_3$  and  $\text{NaN}_3$  are 36.1 and 34.4 kg.-cal., respectively. Comparison with other azides indicates that there is no relationship between sensitivity and activation energy.

J. W. S.

**Kinetic investigations by means of the photo-electric cell of the decomposition of sodium mercury sulphide by water and of sodium tungstate by excess of strong acids.** A. LOTTERMOSER and G. VON HESSLING (Kolloid-Z., 1936, 75, 184—192).—Technique for determining the rate of formation of a sol by turbidity measurements is described. The influence of concn. of reagents has been investigated.

E. S. H.

**Decomposition of ferrous oxide.** J. BÉNARD and G. CHAUDRON (Compt. rend., 1936, 202, 1336—1338; cf. A., 1924, ii, 617).—The rate at 350—480°, measured by the change in magnetic properties,  $\propto [\text{FeO}]^3$ . The reaction is  $8\text{FeO} = \text{Fe}_3\text{O}_4 + \text{a solid solution (Fe}_4\text{FeO)}$ . Formation of the solid solution is shown by an increase in the parameter of  $\text{FeO}$ , measured by X-rays, as the reaction progresses. Above 480° the order of the reaction decreases regularly.

H. J. E.

**Pyrolysis of chlorates and perchlorates.** I. M. CRESPI and J. L. G. CAAMANO (Anal. Fis. Quím., 1936, 34, 320—326).—Apparatus for measuring the initial decomp. temp. and velocity of evolution of gas during the pyrolysis is described. Data are given for the pyrolysis of  $\text{KClO}_3$  and  $\text{KClO}_4$  with or without addition of  $\text{SiO}_2$  and  $\text{KCl}$ . The pyrolysis is autocatalytic.

F R G

**Investigation of [thermal] decomposition of [solid] barium oxalate by emanation method.** B. SAGORTSCHEV (Z. physikal. Chem., 1936, 176, 295—302).—The progress with rise of temp. of the decomp. to give  $\text{BaCO}_3$  of various preps. with admixed Th-X has been followed by observing the emanating power,  $E$ . With loss of  $\text{CO}$   $E$  increases owing to increase in the surface of the crystal. A rise in  $E$  above 500° is apparently due to a loosening of the crystal resulting in increased mobility of its component units. R. C.

**Reaction chain in thermal denaturation of proteins.** A. FISCHER (Z. physikal. Chem., 1936, 176, 260—272).—A study of the denaturation of serum-globulin and ovalbumin at 70° has shown that the mechanism is identical with that of the coagulation of blood (cf. A., 1935, 1143). There is first produced a reactive form of protein, which then promotes denaturation, apparently by a chain mechanism. If a portion of a solution of a protein in which denaturation has set in is added to a fresh solution at 70° denaturation starts there at once. Denaturation probably comes about by groups anchored at lower temp. within the globular protein mol. coming up to the surface in some of the mols. due to the shift of equilibrium with temp., whereupon all the protein mols. orient themselves by a reorganisation of their surface groupings. This view is supported by the observations that denaturation can be suppressed by causing all the  $\text{NH}_2$  groups to react with  $\text{CH}_2\text{O}$ , and that heparin reacts with denatured proteins (cf. *ibid.*, 1002). R. C.

**Water-line corrosion.**—See B., 1936, 501.

**Reactions involving proton transfers.** R. P. BELL (Proc. Roy. Soc., 1936, A, 154, 414—429).—The step determining the rate of a reaction involving general catalysis by acids or bases is the transfer of a proton from catalyst to substrate, or vice versa. Bronsted's equation relating acid-base dissociation consts. to catalytic power is generalised to include the case in which the catalyst remains the same and the substrate varies. Equations are given for the rate at which a stream of particles in temp. equilibrium pass an unsymmetrical parabolic potential barrier, taking into account the "tunnel effect." Application of these to the present problem shows that the deviations from classical behaviour will be considerable, and that a linear relation between dissociation energy and activation energy will still lead to the Bronsted equation, but not to a simple relation between the apparent activation energy and the reaction velocity. L. L. B.

**Catalysis and inhibition of a homogeneous gas reaction. Influence of nitric oxide on the decomposition of diethyl ether.** L. A. K. STAVELEY and C. N. HINSHELWOOD (Proc. Roy. Soc., 1936, A, 154, 335—348).—Small quantities of  $\text{NO}$  inhibit the normal decomp. of  $\text{Et}_2\text{O}$ , a min. in the rate being observed with about 1—2 mm. of  $\text{NO}$ . Larger amounts, however, catalyse the decomp., the catalysis resembling that caused by  $\text{I}$  in that the activation energy is  $<$  that of the normal reaction and is distributed in two square terms only. The residual



reaction occurring in presence of NO has an activation energy of 67,000 g.-cal. These must be distributed in 18 square terms (9 degrees of freedom) to explain the observed rate. There is no difference between the dependence of rate on  $[\text{Et}_2\text{O}]$  in the inhibited and uninhibited reactions. A theory involving the existence of short chains is advanced to explain the results. L. L. B.

**Homogeneous catalytic oxidation of benzene.** R. H. GRIFFITH and S. G. HILL (Trans. Faraday Soc., 1936, 32, 829—836).—The homogeneous oxidation of  $\text{C}_6\text{H}_6$  vapour has been studied at about  $430^\circ$  using  $\text{EtNO}_3$  as a catalyst. A linear relationship is found between (1) time of half change ( $T$ ) and  $[\text{EtNO}_3]$ , (2)  $1/T$  and the ratio  $\text{O}_2/\text{C}_6\text{H}_6$ , (3)  $1/T$  and total pressure, (4)  $T$  and  $1/\text{abs. temp.}$ . The relationship is direct for (2), (3), and (4), and inverse for (1). With  $> 0.35\%$  of  $\text{EtNO}_3$  the reaction is explosive. Increase of surface (Pyrex glass) causes retardation, as does the introduction of  $\text{PbEt}_4$ . The results are discussed. F. L. U.

**Decomposition of diazoacetic ester catalysed by protons and deuterons.** P. GROSS, H. STEINER, and F. KRAUSS (Trans. Faraday Soc., 1936, 32, 877—879).—At  $0^\circ$  the hydrolysis is  $\sim 3$  times as rapid in pure  $\text{D}_2\text{O}$  as in pure  $\text{H}_2\text{O}$ . In mixtures the increase in rate is not a linear function of the D content. L. J. J.

**Effect of propyl alcohol on the hydrolysis of sulphuric acid esters.** K. H. BAUER and W. POETHKE (Fettchem. Umschau, 1936, 43, 69—71; cf. A., 1930, 1019).—Octadecylsulphuric acid (I) is readily hydrolysed by aq.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , but more slowly than is ricinoleosulphuric acid (II); the addition of  $\text{PrOH}$  to the reaction mixture reduces the speed of hydrolysis to a very marked degree in the case of (I) (but does not completely check it) and to a smaller extent in the case of (II). The difference in the hydrolytic behaviour of the two esters is quant. and not qual. as supposed by Seck (A., 1934, 604). E. L.

**Optical activity in relation to tautomeric change. VI. Comparison of the rates of racemisation and of bromination of a ketone. Further study under conditions of basic catalysis.** S. K. HSÜ and C. L. WILSON (J.C.S., 1936, 623—625; cf. A., 1934, 849).—The rates of bromination and racemisation of *d*-2-*o*-carboxybenzylindan-1-one in  $\text{AcOH}$  solution with  $\text{NaOAc}$  as catalyst are both unimol. and have comparable velocity coeffs. J. W. S.

**Santene inversion of fenchyl alcohol and its conditions.**—See this vol., 856.

**Induced oxidation in which ascorbic acid among others is the inductor.** W. P. JORISSEN and A. H. BELINFANTE (Rec. trav. chim., 1936, 55, 374—378).—Data for the induced oxidation of lactic acid (I) and arsenite solutions (II) by glycuronic and ascorbic acids show that (I) and (II) absorb approx. the same amount of  $\text{O}_2$  as the inductor. C. R. H.

**Catalysed reaction of magnesium ethyl bromide with ethyl bromide.**—See this vol., 830.

**Action of bromine on acetone in presence of various solvents.**—See this vol., 825.

**Oxidase-like action of certain complex metal salts.** Y. SHIBATA and K. SHIBATA (Iwata Inst. Plant Biochem., Publ. 2, 1936, 1—9).—About 60 complex amines of Co, Ni, Fe, Zn, Cd, Cu, Cr, and Ag have been classified according to their catalytic activity towards oxidation reactions. Myricetin (I) was used as an oxidation indicator. The oxidising activity of a catalyst appears to be in inverse ratio to its stability in aq. solution. All the Cr, Fe, and Ag compounds examined, with one Cd and some Co compounds, are inactive. Certain factors inhibiting the action of oxidase have a similar influence on active complex metal salts. These are the increased acidity of the medium, the action of certain enzyme poisons such as KCN,  $\text{HgCl}_2$ ,  $\text{NH}_2\text{OH}$ , etc., preliminary heating of the catalyst, and preliminary treatment of (I) with an inactive complex salt. It is suggested that the oxidation takes place through the medium of  $\text{H}_2\text{O}$  and that the action of the catalyst, whether oxidase or metal complex, is to increase the reactivity of the  $\text{H}_2\text{O}$  towards the substrate through combination with both mols. by co-ordinate linkings. It is also suggested that the active nucleus of an oxidase is a metal complex. M. S. B.

**Kinetics of the oxidising action of certain complex metal salts.** Y. SHIBATA and H. KANEKO (Iwata Inst. Plant Biochem., Publ. 2, 1936, 10—31).—The catalytic action of complex Co salts on the oxidation of pyrogallol (I) has been studied. The activity diminishes in the order purpureo-  $>$  roseo-  $>$  xantho-salts, the activity of the last being very small or zero. This is also the order in which reactivity with  $\text{H}_2\text{O}$  diminishes (cf. preceding abstract). After an induction period of varying length the reaction is unimol. For  $0.004M$ -(I) the optimum concn. of complex salt is approx.  $0.002M$ . At concn.  $c$  of catalyst  $< 0.002M$   $k_1/k_2 = (c_1/c_2)^{0.1}$ . The temp. coeff. of  $k$  increases with increasing inactivity of the catalyst so that, at high temp., it approaches the same val. for the three groups of salts. Inhibitors act as previously described for other catalysed oxidations (*loc. cit.*). M. S. B.

**Decomposition of hydrogen peroxide by complex metal salts.** Y. SHIBATA and H. KANEKO (Iwata Inst. Plant Biochem., Publ. 2, 1936, 32—39).—The catalytic decomp. of  $\text{H}_2\text{O}_2$  by  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  and  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  is unimol. and similar to that brought about by catalase or Pt sol.  $k$  depends on  $[\text{H}^+]$  and is a max. in feebly alkaline solution.  $k$  also depends on the concn.  $c$  of the complex salt and  $k_1/k_2 = (c_1/c_2)^{1.3}$ . The mean val. of the temp. coeff. for  $10^\circ$  is 1.77.  $\text{HgCl}_2$ , KCN,  $\text{KClO}_3$ , and  $\text{K}_4\text{Fe}(\text{CN})_6$  act as catalyst poisons. M. S. B.

**Oxidising action of colloids. I. Oxidation with colloidal metals.** Y. SHIBATA and H. KANEKO. II. Oxidation with colloidal metal hydroxides and silicates. H. KANEKO (Iwata Inst. Plant Biochem., Publ. 2, 1936, 40—54, 55—73).—I. The catalytic oxidation of pyrogallol in presence of Ag, Au, Cu, Hg, Bi, Sb, and Pt sols has been followed by measurements of the extinction coeff. with the spectrophotometer. The reaction is unimol. For dil. Pt sols the connexion between  $k$  and concn.  $c$  of the sol. is  $k_1/k_2 = (c_1/c_2)^{0.35}$  and the temp. coeff. is 1.21 per  $10^\circ$ . At  $40$ — $45^\circ$  the reaction begins to show irregularities.



II. The oxidation of pyrogallol is catalysed by colloidal hydroxides of Ti, Cr, Fe<sup>III</sup>, Mn<sup>II</sup>, Ni, Co, Cu, Zn, and Al, and by Mg (I), Al, and various natural colloidal silicates. The reaction is of the first order. (I) gives  $k_1/k_2 = (c_1/c_2)^{0.45}$  and a temp. coeff. of 1.24 per 10° below 40°. Addition of a complex metal salt with no catalytic power alone, [Co(NH<sub>3</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>] or [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> increases, to a remarkable extent, the catalytic action of colloidal metal hydroxides and especially of colloidal silicates. M. S. B.

**Catalytic oxidising action of colloids.** Y. SHIBATA and K. TAMASAKI (Iwata Inst. Plant Biochem., Publ. 2, 1936, 201—206).—The influence on O<sub>2</sub> absorption by pyrogallol (I) of certain metal sols, previously shown by a spectro-photometric method to catalyse the oxidation of (I), has been examined. Pt sol causes a marked absorption of O<sub>2</sub> which varies with the method of prep. of the sol, but Ag and Au sols produce no appreciable absorption. M. S. B.

**Iodide oxidation by complex metal salts.** A. WATANABE (Iwata Inst. Plant Biochem., Publ. 2, 1936, 74—87).—The catalytic oxidation of KI by Co amines is parallel with the influence of the latter on pyrogallol oxidation. The rate of the solution rises during the reaction, but this rise may be prevented by the use of buffers, and the buffered reaction is unimol. The optimum  $p_H$  for the reaction is approx. 6. The behaviour of the amines is similar to that of iodide-oxidases. The dependence of  $k$  on ammine concn. is expressed by  $k_1/k_2 = (c_1/c_2)^{0.36}$ . For const. ammine concn.  $k$  falls with diminution of initial [KI]. Determination of  $k$  for temp. 0—30° showed that a rapid increase takes place between 10° and 20°. M. S. B.

**Catalytic action of complex metal compounds.** K. SHIBATA and A. WATANABE (Iwata Inst. Plant Biochem., Publ. 2, 1936, 97—128).—The formation of indophenol from Nadi reagent ( $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  and  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$ ) has been employed in further investigations on the oxidising action of complex metal salts (cf. preceding abstracts). *m*-Phenols, which are not oxidisable, inhibit the oxidation of *o*- and *p*-phenols, probably by attaching themselves to the metal complex in place of the latter. Certain complexes can oxidise only in presence of H<sub>2</sub>O<sub>2</sub> and so behave like peroxidase. The accelerating action of these compounds on the catalytic oxidation by active amines is due to the presence of H<sub>2</sub>O<sub>2</sub> liberated in this process. The velocity of oxidation depends on the partial pressure of O<sub>2</sub>, but oxidation can take place in a vac. or a N<sub>2</sub> atm. if a H-acceptor, such as benzoquinone or phloroglucinol, capable of forming a co-ordination compound with the ammine, is added. This constitutes another resemblance between complex metal amines and dehydrases or oxidation-reduction enzymes. M. S. B.

**Asymmetric oxidation.** I. Y. SHIBATA and R. TSUCHIDA. II. Y. SHIBATA, Y. TANAKA, and S. GODA. III. **Inhibiting action of some asymmetric organic acids on asymmetric oxidation.** Y. SHIBATA and K. SAKAI (Iwata Inst. Plant Biochem., Publ. 2, 159—166, 167—174, 190—200).—I. By observing the changes in optical rotation during the catalytic oxidation of *r*:3:4-dihydroxyphenylalanine

(I) by  $l\text{-[Co en}_2\text{NH}_3\text{Cl]Br}_2$  (II) (en=ethylenediamine) it is found that selective oxidation of *l*-(I) takes place.

(II). The catalytic oxidation of *d*-catechin (III) by *d*- and *l*-(Co en<sub>2</sub>NH<sub>3</sub>Cl)Br<sub>2</sub> has been studied both by changes in rotation and also by the amount of O<sub>2</sub> absorbed. Oxidation is more rapid by the *d*- than by the *l*-complex. Oxidation of (III) by *r*-complex follows a similar course to that by *l*-complex instead of lying between *d*- and *l*-. There is thus an analogy with the action of certain natural enzymes.

III. The action of optically active inhibiting agents on the oxidation of *d*-catechin by *d*- and *l*-(II) in buffered solutions depends on the sign of the rotation of the inhibitor. Inhibition by the combinations *d*-(II) tartaric acid and *l*-(II)+*l*-tartaric acid is > by *d*+*l*- or *l*+*d*-combinations. *l*-Cysteine has a strong retarding influence on oxidation by both *d*-(II) and *l*-(II), but on *d*-(II) it is somewhat > on *l*-(II). The inhibiting action of *d*-bromocamphor-sulphonic acid on catalysis by *l*-(II) is > on that by *d*-(II). M. S. B.

**Oxidase-like action of certain complex metal salts.** Metol. Y. SHIBATA and K. YAMASAKI (Iwata Inst. Plant Biochem., Publ. 2, 1936, 180—189).—The autoxidation of  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}\cdot\text{H}_2\text{SO}_4$  (I) is inhibited by complex Co salts, the inhibiting action being parallel with the oxidising action of these salts on polyphenols (cf. preceding abstracts). The Co salt forms an insol. ppt. with (I). On the other hand complex Cr salts, which are not oxidation catalysts, have no inhibiting action on the autoxidation of (I) and form no ppt. This supports the assumption (cf. first abstract of this group) that combination between complex and polyphenol is necessary before oxidation is accelerated. KCN and Cr complexes, which are poisons for the accelerating action, have a similarly inhibiting effect on the retarding action. NH<sub>2</sub>OH, however, is an exception since, although a poison for catalytic oxidation, it accelerates the autoxidation of (I), but has practically no effect on the inhibiting action of Co complexes, the two effects being algebraically additive. M. S. B.

**Catalytic reduction of complex metal salts.** Y. SHIBATA and T. YAMABE (Iwata Inst. Plant Biochem., Publ. 2, 1936, 207—213).—The reduction of benzoquinone by H<sub>2</sub> is catalysed by complex Ni amines. The reaction is also accompanied by evolution of O<sub>2</sub>, probably due to the formation of H<sub>2</sub>O<sub>2</sub> during the course of the reaction and subsequent splitting up by the Ni complex (cf. a previous abstract). In order to follow the rate of H<sub>2</sub> absorption O<sub>2</sub> must be absorbed by pyrogallol. For the same Ni ammine the rate of reaction varies with the  $p_H$  of the solution. M. S. B.

**Mechanism of the catalytic exchange reaction between deuterium and water.** A. FARKAS (Trans. Faraday Soc., 1936, 32 922—932).—The velocity of the reaction between HD and H<sub>2</sub>O vapour on a Pt wire at 250—410° and 10—70 mm. is about 0.1 that of the ortho-para-H<sub>2</sub> conversion. The rate of the exchange reaction is independent of the H<sub>2</sub>O pressure and increases nearly linearly with D<sub>2</sub> pressure, indicating that H<sub>2</sub>O is strongly and H<sub>2</sub> weakly adsorbed.



*E* for the exchange reaction is 13.5 kg.-cal. The mechanism is discussed. L. J. J.

**Kinetics of para-ortho-hydrogen conversion on charcoal.** R. BURSTEIN and P. KASHTANOV (Trans. Faraday Soc., 1936, 32, 823—828; cf. A., 1935, 940).—The rate of the *o-p*-hydrogen conversion on C has a positive temp. coeff. between 20° and 573° abs., whilst when the C is poisoned it is negative in the range 90—300°, and positive between 300° and 573° abs. The results indicate the existence of two kinds of active centres, one of which becomes inactive at 20° abs. F. L. U.

**Catalytic preparation of sulphuryl chloride.**—See B., 1936, 493.

**Energetics of catalysis. VI. Kinetics of hydrogenation processes in liquid systems.** E. B. MAXTED and C. H. MOON (J.C.S., 1936, 635—637; cf. A., 1935, 1210).—The change in sign above 80—90° of the temp. coeff. of the reaction between crotonic acid and O<sub>2</sub> on a Pt surface is accompanied by a corresponding change in the kinetics of the reaction. This changes from zero order to approx. first order, in accord with the view that the change is due to a decrease in the concn. of acid adsorbed till it is insufficient to render the reaction independent of this concn. J. W. S.

**Catalytic esterification of alcohols without the use of acids.** P. J. IVANNIKOV and E. J. GAVRILOVA (J. Appl. Chem. Russ., 1936, 9, 490—491).—EtOAc or EtCO<sub>2</sub>Pr is obtained in 50—60% yield by passing EtOH or PrOH over a Cu-U catalyst at 240°.

R. T.

**Influence of the carrier on poisoning of platinum catalysts by arsenic.** I. E. ADADUROV, A. N. TZEITLIN, and L. M. ORLOVA (J. Appl. Chem. Russ., 1936, 9, 399—411).—The sensitivity to As<sub>2</sub>O<sub>3</sub> poisoning of Pt catalysts is at a min. when the radius of the cation of the carrier is 0.78 Å. (Mg, Sn, Zr), and the poisoned catalyst is most readily activated by heating in air or with CO-H<sub>2</sub>. A study of the catalytic action of Pt on Be, Mg, Ca, Sr, Ba, Ti, Sn, Si, Zr, Th, Al, Fe, and Cr sulphates or oxides shows that the action of the carrier depends on the radius, but not on the chemical nature, of the cation.

R. T.

**Effects of various fluorides on thermal synthesis of calcium silicates.** I. S. NAGAI and M. TAKAHARA (J. Soc. Chem. Ind. Japan, 1936, 39, 130—132B; cf. A., 1935, 1085).—The efficiency of fluorides as catalysts in the synthesis of Ca silicates decreases in the order Na<sub>3</sub>AlF<sub>6</sub>, NaF, Na<sub>2</sub>SiF<sub>6</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, and MgSiF<sub>6</sub>. Glass powder is slightly more efficient than feldspar. R. S.

**Catalytic oxidation by copper salts in presence of manganese salts.** P. THOMAS and (Mlle.) C. KALMAN (Compt. rend., 1936, 202, 1436—1437).—The oxidation of phenolphthalein or pyramidone by dil. H<sub>2</sub>O<sub>2</sub> solution in presence of Cu<sup>++</sup> is inhibited by Mn<sup>++</sup>. L. J. J.

**Accelerators and retarders in the reduction of silver salts.** G. OLLENDORFF and H. ANDRESEN (Z. wiss. Phot., 1936, 35, 119—123).—The speed of reduction of AgBr sols has been measured in the pre-

sence of various retarding agents, *e.g.*, gelatin, Tl salts, and accelerating agents, *e.g.*, Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, thiosinamine. Small amounts of KI accelerate reduction; with increasing amounts a min. speed is reached, and the rate then increases steadily with larger amounts. Lowering of *p<sub>H</sub>* (omission of alkali from normal developer) also retards development.

J. L.

**Oxidation catalysis. II. Chromium oxide as catalyst.** A. KUTZELNIGG and W. WAGNER. **III. General view.** A. KUTZELNIGG (Monatsh., 1936, 67, 231—240, 241—247; cf. A., 1930, 1133).—II. The activity of pure Cr<sub>2</sub>O<sub>3</sub> [prepared by heating Cr(OH)<sub>3</sub> in H<sub>2</sub>] in catalysing the oxidation of K<sub>4</sub>Fe(CN)<sub>6</sub> by atm. O<sub>2</sub> rises with increase of drying temp. up to 450°, beyond which it decreases rapidly to zero. There is a secondary max. in the activity curve at 200°. The active Cr<sub>2</sub>O<sub>3</sub> is olive-brown and amorphous, whilst the strongly heated inactive material is green and cryst. The particle size remains approx. const. When prepared in presence of O<sub>2</sub>, the black oxide shows max. activity after heating at 300°. Finely divided Cr<sub>2</sub>O<sub>3</sub> prepared by decomp. of Hg<sub>2</sub>CrO<sub>4</sub> has the greatest activity and "glossy Cr<sub>2</sub>O<sub>3</sub>" the least of a no. of preps. tested, the products of decomp. of (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub>, Cr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>, and Cr(NO<sub>3</sub>)<sub>3</sub> being intermediate.

III. Besides Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CuO show max. activity in catalysing the atm. oxidation of K<sub>4</sub>Fe(CN)<sub>6</sub> when prepared at certain temp. This is associated with the elimination of adsorbed H<sub>2</sub>O layers or salts from the powders. Whereas animal charcoal promotes the reduction of K<sub>3</sub>Fe(CN)<sub>6</sub> in alkaline solution, only slight catalytic effect is found with MnO<sub>2</sub> and fuller's earth and none with NiO, Fe<sub>2</sub>O<sub>3</sub>, CuO, SiO<sub>2</sub> gel, PbO<sub>2</sub>, ZnO, or Ag<sub>2</sub>O. Oxides which catalyse the decomp. of K<sub>4</sub>Fe(CN)<sub>6</sub> also promote the evolution of O<sub>2</sub> from KClO<sub>3</sub>, KMnO<sub>4</sub>, HgO, Ag<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub>, the most active oxides being those of elements at the min. of the at. vol. curve. J. W. S.

**Kinetics of hydrogenation of ethylene on skeletal contact catalysts.** G. M. SCHWAB and H. ZORN (Z. physikal. Chem., 1936, B, 32, 169—201).—Catalysts have been prepared by making alloys with the compositions NiSi, NiSi<sub>2</sub>, and NiAl<sub>3</sub> and removing the Al with NaOH. The hydrogenation has been studied at 0—180° under total pressures, *p*, of 50—250 mm. During reaction the activity, *a*, of the catalyst falls, and may even decline at room temp., due to ageing. For a given catalyst *a* ∝ (*m*/*d*)<sup>2/3</sup> (*m*=wt.), indicating that *a* is a linear function of the grain surface of the vol. near the surface. On fresh catalysts there are numerous active centres chiefly within the grains and accessible to the reactants only by diffusion, and the rate of the process as a whole is determined by the rate of diffusion. With fewer and less active centres the rate of hydrogenation is determined by the rate of a normal chemical reaction, requiring activation. The kinetics of the reaction on NiSi after ageing are of this type. Here reaction is of the first order in respect of *p*, but of fractional orders in respect of the partial pressures of H<sub>2</sub>, *p*<sub>1</sub>, and C<sub>2</sub>H<sub>4</sub>, *p*<sub>2</sub>. The Langmuir-Hinshelwood theory is valid and the rate is given



by  $-dp/dt = kp_1p_2/(1+bp_1+cp_2)$ , where  $b$  and  $c$  are adsorption coeffs. The true heat of activation is  $18.7 \pm 1$  kg.-cal., a val. which excludes the possibility of any "tunnel" reaction, and the calc. optimum temp. is  $450-470^\circ$  abs. On the more active  $\text{NiSi}_2$  and  $\text{NiAl}_2$  the kinetics are formally similar, but  $b$  and  $c$  are not adsorption coeffs. and the rate of diffusion is the governing factor;  $\text{C}_2\text{H}_4$  now retards the reaction. X-Ray diagrams show that the active centres are probably located in the amorphous part of the catalysts. R. C.

**Kinetics of the acetylation of cellulose fibres. V, VI.** Influence of solvent and the concentration of sulphuric acid on the acetylation velocity in the fibre bundle and the ratio of the catalytic action of sulphuric and perchloric acids. I. SAKURADA and M. MIYAGUTI (J. Soc. Chem. Ind. Japan, 1936, 39, 91-94B; cf. A., 1935, 42).—The velocity of acetylation is given by  $x = kt^m$  ( $x$ =mols.  $\text{AcOH}$  per 100 mols.  $\text{C}_6\text{H}_{10}\text{O}_5$ ).  $m$  is approx. const. with increasing  $[\text{H}_2\text{SO}_4]$  but  $k$  increases according to  $k = pc^{1/q}$  where  $p$  and  $q$  are consts. The catalytic activity of  $\text{HClO}_4$  is 10 times that of  $\text{H}_2\text{SO}_4$  but the influence of different solvents is small. R. S.

**Catalytic reduction of carbon monoxide to methane.**—See B., 1936, 531.

**[Catalytic] decomposition of methane and petroleum hydrocarbons with steam.**—See B., 1936, 532.

**[Catalytic] synthesis of ethyl acetate.**—See B., 1936, 536.

**Catalytic oxidation of benzene.**—See B., 1936, 536.

**Catalytic properties of rhenium. II.**—See this vol., 820.

**Catalytic action of colloidal ferric hydroxide at different degrees of dispersion. I.** S. TELETOV and A. V. T. TJUTJUNKINA (Ukrain. Chem. J., 1936, 11, 1-3).—The velocity of catalytic decomp. of  $\text{H}_2\text{O}_2$  by  $\text{Fe}(\text{OH})_3$  sols is a function of the degree of dispersion of the latter. R. T.

**Decomposition of nitrous oxide on the surface of platinum. II.** The effect of foreign gases. E. W. R. STEACIE and J. W. McCUBBIN (Canad. J. Res., 1936, 14, B, 84-89; cf. A., 1934, 1182).—Preliminary addition of  $\text{N}_2$  diminishes the rate of decomp. of  $\text{N}_2\text{O}$  on sponge Pt by filling up the pores, but is without effect in the case of Pt gauze. The retarding effect of  $\text{He}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  has also been studied and the adsorption isotherm of  $\text{O}_2$  on Pt at  $570^\circ$  has been determined.  $\text{O}_2$  formed by decomp. of  $\text{N}_2\text{O}$  gives the same isotherm, whilst adsorption of  $\text{N}_2\text{O}$  is small. It is concluded that  $\text{O}_2$  does not retard the decomp. R. S.

**Decomposition of hydrogen sulphide and water on molybdenum filaments.** F. E. T. KINGMAN (Trans. Faraday Soc., 1936, 32, 903-907).— $\text{H}_2\text{S}$  decomposes at  $400-685^\circ$  and 0.1 mm. by a first-order reaction with  $E$  25,000 g.-cal., giving  $\text{H}_2$  and  $\text{S}$ .  $\text{H}_2\text{O}$  decomposes at  $800-1200^\circ$ , giving  $\text{H}_2$  and  $\text{Mo}$  oxide, which retards the reaction below  $1000^\circ$ .

Above  $1000^\circ$ , H atoms are formed and react with the  $\text{Mo}$  oxide.  $E=43,000$  g.-cal. L. J. J.

**Reaction mechanism. VII. Rate of catalytic hydrogenation of doubly linked carbon in chain molecules in solution.** O. SCHMIDT (Z. physikal. Chem., 1936, 176, 237-259; cf. A., 1933, 913).—The rate of hydrogenation at  $20^\circ$  of various aliphatic and aromatic hydrocarbons, alcohols, carboxylic acids, and esters having an ethenoid double linking in  $\text{MeOH}$  and other solvents with Ni, Pt, and Co as catalysts has been determined. Hydrogenation occurs in the micropores of the metal phase into which the org. mols. diffuse as far as their size allows. The rate of reaction is determined by the rate of this diffusion. The  $\text{H}_2$  dissolves in the catalyst and is activated by being converted into protons. In general, the more substituents there are in the unsaturated mol. and the larger or less compact they are the slower is hydrogenation. Chain-branching retards diffusion and with it the reaction. With compounds of the type  $\text{CH}_2\text{:CHR}$  the time for half reaction,  $\tau$ , falls only slightly as the chain length of R increases. In some cases the Ph group has a powerful retarding action.  $\tau$  is particularly high for compounds of the type  $\text{CR'R''CHR}$ . For an acid  $\tau$  is  $>$  for its Me or Et ester, suggesting that  $\text{CO}_2\text{H}$  retards diffusion more than  $\text{CO}_2\text{Me}$  and  $\text{CO}_2\text{Et}$ . If the double linking is at the end of the chain the length and position of the substituents have little effect on the velocity.  $\tau$  runs approx. parallel with the viscosity and heat of adsorption of the solvent and increases with its mol. wt. R. C.

**Catalytic activity of palladium and overvoltage of hydrogen.** C. A. KNORR and E. SCHWARTZ (Z. physikal. Chem., 1936, 176, 161-168).—Extension of a previous investigation (A., 1934, 258) shows that the val. of  $b$  in the logarithmic relation between overvoltage and c.d. falls with increasing catalytic activity of the Pd electrode. On pure active Pd  $b$  would probably approach the val. required by Tafel's theory of overvoltage, and it is inferred that here it is the slowness not of the discharge of the  $\text{H}^+$  ions but of the process  $2\text{H} \rightarrow \text{H}_2$  which is responsible for overvoltage (cf. A., 1935, 705). R. C.

**Catalytic action of Japanese acid clay. II. Promotive action of Japanese acid clay on [the] catalytic action of mercuric sulphate [in the] condensation of acetylene and acetic acid.** T. KUWATA and O. KATO (J. Soc. Chem. Ind. Japan, 1936, 39, 127-128B; cf. B., 1936, 138).—The efficiency of  $\text{HgSO}_4$  in affecting condensation of  $\text{C}_2\text{H}_2$  and  $\text{AcOH}$  is increased if it is pptd. on Japanese acid clay (I). Optimum conditions (79.5% yield) are: (I) (9.6 g.), leached with hot 18%  $\text{HCl}$  and dried at  $150-200^\circ$ , is added to  $\text{HgO}$  (2.88 g.) in  $\text{AcOH}$  (29 c.c.), to which 50% oleum (1.2 g.) is then added. Addition of (I) to a previously prepared catalyst or use of C has no effect. S. C.

**Electrolysis of manganous salts.** M. GELOSO and (MLE.) C. ROUILLARD (Compt. rend., 1936, 202, 1418-1421).—Current-anode potential curves show two ascending branches, corresponding with deposition of  $\text{MnO}_n$ ,  $n\text{MnO}$ , and evolution of  $\text{O}_2$ , respectively,



and separated by a flat portion. Data are recorded for the variation of  $\eta$  with the conditions of electrolysis. Part of the current must be carried by  $\text{OH}'$ .

L. J. J.

**Electrochemical isolation of light metals from non-aqueous solutions. I. Alkali metal salts.** M. A. KLOTSCHKO (J. Appl. Chem. Russ., 1936, 9, 420—433).—The alkali halide is fused with  $\text{AlCl}_3$  or  $\text{AlBr}_3$ , and a solution of the melt in  $\text{PhNO}_2$  is electrolysed (Ag anode, Pt cathode, with electrode diaphragms). The yield of metal varies inversely with the c.d., max. vals. being obtained using 0.0002—0.001 amp. per sq. cm. The process consists of  $\text{MAlX}_4 \rightleftharpoons \text{M}' + \text{AlX}_4'$ ;  $\text{AlX}_4' \rightarrow \text{AlX}_3 + \text{X}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ).

R. T.

**Electrolysis of molten antimony sulphide.**—See B., 1936, 552.

**Electrolytic deposition of aluminium.**—See B., 1936, 552.

**Electro-deposition of nickel-cobalt alloys from solutions containing triethanolamine.**—See B., 1936, 551.

**Removal of sulphate from nickel hydroxide by electrodialysis.**—See B., 1936, 555.

**Electrolytic reduction of organic compounds. II. Catalytic hydrogenation of sorbic acid at prepared cathodes of nickel and platinum.** E. ISAACS and C. L. WILSON (J.C.S., 1936, 574—576; cf. this vol., 454).—Electro-deposition of spongy Ni or Pt-black on the metals converts them into efficient reducing agents for sorbic acid (I). These cathodes differ from other metals in causing reduction of (I) mainly to  $\Delta^6$ -hexenoic acid and hexoic acid, similar to the course of hydrogenation of (I) in EtOH solution with Adams' catalyst.

J. W. S.

**Electrolysis of magnesium methyl halides.**—See this vol., 830.

**Electrolytic oxidation of proline and  $\gamma$ -aminobutyric acid.**—See this vol., 828.

**Oxidation of sulphur dioxide in the high-voltage arc discharge.** S. M. GOLYAND (J. Phys. Chem. U.S.S.R., 1934, 5, 1471—1472).—A criticism of Kolodkina and Netschaeva's work (cf. A., 1935, 712).

CH. ABS. (e)

**Oxidation of sulphur dioxide in the high-voltage arc discharge.** N. NETSCHEVA and L. KOLODKINA (J. Phys. Chem. U.S.S.R., 1934, 5, 1473—1474; cf. preceding abstract).—A reply.

CH. ABS. (e)

**Behaviour of gases under the influence of high-frequency discharge. Ammonia and hydrogen.** B. S. SRIKANTAN (J. Indian Chem. Soc., 1936, 13, 79—85).— $\text{NH}_3$  is greatly adsorbed by the walls of highly evacuated glass tubes. When the walls are saturated with respect to  $\text{NH}_3$ , any further addition of  $\text{NH}_3$  is immediately decomposed by the discharge into  $\text{H}_2$  and  $\text{N}_2$  which are adsorbed, leaving a residue of  $\text{NH}_3$  in equilibrium with the adsorbed  $\text{NH}_3$ . Further discharge expels the  $\text{N}_2$  from the walls.

C. R. H.

**Mechanism of the photochemical reaction between bromine and water.** H. A. PAGEL and

W. W. CARLSON (J. Physical Chem., 1936, 40, 613—617).—The kinetics of the reaction have been investigated at 25°. The reaction appears to take place as follows: (1)  $\text{Br}_2 + \text{H}_2 \rightleftharpoons \text{H}' + \text{Br}' + \text{HOBr}$ , (2)  $\text{HOBr} + h\nu \rightarrow \text{H} + \text{Br}' + \frac{1}{2}\text{O}_2$ .

E. S. H.

**Oxidation of nitrites to nitrates in sunlight.** N. R. DHAR and S. P. TANDON (J. Indian Chem. Soc., 1936, 13, 180—184).—A study of the catalytic effect of  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and soil on the photo-oxidation of aq. solutions of  $\text{NaNO}_2$  shows that in dil. solutions oxidation is complete but that in conc. solutions the equilibrium  $2\text{NaNO}_2 + \text{O}_2 \rightleftharpoons 2\text{NaNO}_3$  is attained. It is suggested that the conversion of  $\text{NH}_4$  salts into nitrates in soil may be due more to photochemical than to bacterial action.

C. R. H.

**Photochemical peroxide formation. I. Oxidation of methyl alcohol by molecular oxygen in ultra-violet light.** R. CANTIENI (Ber., 1936, 69, [B], 1101—1106).—Aq. MeOH in presence of  $\text{O}_2$  is oxidised with formation of peroxide in ultra-violet light of long and short  $\lambda$ . Peroxide formation from  $\text{MeOH}-\text{O}_2$  also occurs in absence of  $\text{H}_2\text{O}$ , the presence of which retards its formation. The peroxide becomes less stable as its concn. increases. Its formation is about 120 times as rapid in unfiltered ultra-violet light as in that which has been filtered through glass. The hypothesis that  $\text{H}_2\text{O}_2$  is produced from  $\text{H}_2\text{O}$  during the photochemical oxidation of MeOH is untenable and it is improbable that  $\text{H}_2\text{O}_2$  arises by oxidation of H formed by photolysis. The production of  $\text{OMe}\cdot\text{OH}$  is assumed which, in ultra-violet light, oxidises MeOH.  $\text{CH}_2\text{O}$ , as primary oxidation product, is present in traces when the concn. of peroxide is small.  $\text{HCO}_2\text{H}$  cannot be detected by reason of its ready oxidisability by peroxide in ultra-violet light.

H. W.

**Theory of densensitisation.** K. WEBER (Z. wiss. Phot., 1936, 35, 124—128; cf. A., 1935, 1331).—The author's theory, that desensitisers act by oxidising the optical or chemical sensitisers present, is brought into agreement with the observations of Blau and Wambacher (this vol., 37) and Arens and Eggert (A., 1929, 277) by the assumption that the process is reversible in the absence of  $\text{O}_2$ . The reactions are treated mathematically, and are shown to be in agreement with various known data.

J. L.

**Action of light on catalytic oxidation by some metallic complex salts.** Y. SHIBATA and S. GODA (Iwata Inst. Plant Biochem., Publ. 2, 1936, 175—179).—By the use of suitable light filters the influence of light of different  $\lambda$  between infra-red and 3300 Å. on the oxidation of *d*-catechin in presence of  $r\text{-[Co(en)}_2\text{NH}_3\text{Cl)]Br}_2$  (I) ( $\text{en}$  = ethylenediamine) has been examined. Aq. (I) has absorption bands at  $\lambda$  5000 and 3640 Å., but light in this region is less active than the light of longer  $\lambda$  absorbed by  $\text{H}_2\text{O}$ . This confirms the theory previously put forward that oxidation takes place through the medium of activated  $\text{H}_2\text{O}$ . The following reaction scheme is proposed:  $\text{R} + 2\text{H}\cdot\text{OH} + 0.5\text{O}_2 = \text{R}(\text{OH})_2 + \text{H}_2\text{O}$  and  $\text{R}(\text{OH})_2 = \text{RO} + \text{H}_2\text{O}$ . The mechanism of activation of  $\text{H}_2\text{O}$  by the complex salt is still obscure.

M. S. B.

**Photochemical activation of the oxidising action of complex metal salts.** A. WATANABE



(Iwata Inst. Plant Biochem., Publ. 2, 1936, 129—158).—The catalytic oxidation of KI, pyrogallol, benzidine,  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ , and Nadi reagent, and the catalytic decomp. of  $\text{H}_2\text{O}_2$  by complex metal salts is accelerated by ultra-violet or visible light radiation. Photochemical reaction may take place even where there is no appreciable dark reaction. The infra-red radiation is active in the case of pyrogallol oxidation only. Preliminary irradiation of the separate constituents has no effect. The most active  $\lambda$  in the Hg arc is 366 m $\mu$ . Of the Co amines containing  $\text{NO}_2$  the most sensitive to light is  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ , and of the two stereoisomerides the *trans*- is more sensitive than the *cis*-form. The action is ascribed to the increased instability of the complex metal salt under the action of light. M. S. B.

**Photochemical sensitisation in solutions. I. Sensitisation of an Eder solution with eosin.** E. V. SCHPOLSKI and N. I. KOLESNIKOVA (J. Phys. Chem. U.S.S.R., 1934, 5, 1199—1209).—For light of  $\lambda\lambda$  5200 and 5460, 5760 Å. there was a short induction period, after which the reaction proceeded linearly with time. Its rate was  $\propto$  the light intensity. At concns. of  $5 \times 10^{-7}$  to  $10^{-5}$  g. per c.c. the rate  $\propto$  the concn. At concns. of  $3 \times 10^{-5}$  to  $10^{-4}$  g. per c.c. the rate was const., and at higher concns. it decreased. The concn. thresholds for the decrease in sensitisation and the damping of fluorescence coincided. The rate  $\propto$   $[\text{HgCl}_2]$  and was independent of  $[\text{C}_2\text{O}_4^{2-}]$  for concns.  $> 0.01$  g. per c.c. The temp. coeff. was 2.6 at 5—15° and 1.9 at 15—25°. The dark reaction became appreciable at  $> 30^\circ$ . The quantum yield for  $\lambda\lambda$  5470, 5760 Å., in presence of  $\text{O}_2$ , was 12.5.

CH. ABS. (e)

**Photochemical bleaching of chlorophyll.**—See this vol., 867.

**Photochemical reaction of chlorophyll with ferrous ions.**—See this vol., 907.

**Study of solid reactions by the emanation method.** R. JAGITSCH (Monatsh., 1936, 68, 1—9).—The following changes have been observed, at the temp. indicated, on heating the respective materials containing Rd—Th as a source of Tn:  $\alpha \rightarrow \beta\text{-SiO}_2$  575°;  $\beta\text{-SiO}_2 \rightarrow \beta\text{-tridymite}$  870°;  $\text{SiO}_2 + \text{CaCO}_3 \rightarrow \text{CaSiO}_3$  about 900°;  $\gamma\text{-Al}_2\text{O}_3 \rightarrow \text{corundum}$  840—950°;  $\text{Al}_2\text{O}_3 + \text{CoCO}_3 \rightarrow \text{Co}(\text{Ca})\text{Al}_2\text{O}_4$  complete at about 900°;  $\text{Fe}_2\text{O}_3 + \text{CaCO}_3 \rightarrow \text{CaFe}_2\text{O}_4$  550—600°.

F. L. U.

**Properties of sodium hexametaphosphate.** R. T. THOMSON (Analyst, 1936, 61, 320—323).—A no. of insol. salts of Ca, Ba, etc. readily dissolve in aq.  $\text{Na}_6\text{P}_6\text{O}_{18}$ . Portland cement is attacked, most of the Ca and part of the  $\text{SiO}_2$  being dissolved. E. C. S.

**Crystallisation and loss of water from copper hydroxide.** E. HAYEK (Monatsh., 1936, 67, 352—356).—Pure cryst.  $\text{Cu}(\text{OH})_2$  has been prepared by slow evaporation of  $\text{NH}_3$  from a cold solution of  $\text{CuO}$  in conc. aq.  $\text{NH}_3$  and shown to have a crystal structure identical with known forms. The relatively higher stability of this product, and of amorphous  $\text{Cu}(\text{OH})_2$  prepared by dilution of the  $\text{CuO-NH}_3$  solution, compared with  $\text{Cu}(\text{OH})_2$  obtained by pptn. with alkali, indicates that adsorbed alkali is the cause of the dehydration process at lower temp. J. W. S.

**Cuprous iodide.** R. HUERRE (J. Pharm. Chim., 1936, [viii], 23, 594—605).—The formation of  $\text{Cu}_2\text{I}_2$  from KI and  $\text{CuSO}_4$  in  $\text{H}_2\text{O}$  is inhibited in dil. solution. HCl has no effect, but excess of KI and  $\text{Na}_2\text{S}_2\text{O}_3$  favour the reaction. J. L. D.

**Preparation of the complex salt,  $\text{Cu}_2\text{HgI}_4$ .** P. G. POPOV (Ukrain. Chem. J., 1936, 11, 11—12).—8.3 g. of KI in 20 ml. of  $\text{H}_2\text{O}$  are added to 6.8 g. of  $\text{HgCl}_2$  in 100 ml. of  $\text{H}_2\text{O}$ , the washed ppt. is dissolved in 20 ml. of 41.5% KI, and the solution is added to a solution of 5 g. of  $\text{CuCl}$  in 40 ml. of 50% HCl. The ppt. of  $\text{Cu}_2\text{HgI}_4$  is washed with 50% HCl and  $\text{H}_2\text{O}$ , and dried at 100°. R. T.

**Calcium metaphosphates.** A. BOULLE (Compt. rend., 1936, 202, 1434—1435).—Data are recorded for the X-ray spectra of  $\text{Ca}(\text{PO}_3)_2$  prepared by ignition of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  at different temp. Ignition below 400° gives a new cryst. form, converted at higher temp. into a different modification, m.p.  $1010 \pm 5^\circ$ . Thermal analysis data are in agreement. L. J. J.

**Hexamethylenetetramine compounds.**—See this vol., 828.

**Potentiometric study of complex thiosulphates.**

**I. Strontium silver thiosulphate.** R. PORTILLO and J. G. TANAGO (Z. anorg. Chem., 1936, 227, 124—128).—The compounds  $[\text{Ag}_2(\text{S}_2\text{O}_3)_2]\text{Sr} \cdot \text{H}_2\text{O}$  and  $[\text{Ag}_2(\text{S}_2\text{O}_3)_3]\text{Sr} \cdot 6\text{H}_2\text{O}$  are described. Their formation is indicated by potentiometric titration of  $\text{SrS}_2\text{O}_3$  with  $\text{AgNO}_3$ , both 0.1N. F. L. U.

**Preparation of luminescent zinc orthosilicate.** J. V. GOLBREICH and I. V. EGOROVA (J. Appl. Chem. Russ., 1936, 9, 446—450).—Max. cathodal luminescence is obtained when  $\text{Zn}_2\text{SiO}_4$  containing 1% of Mn as  $\text{MnCl}_2$  or  $\text{MnSO}_4$  is heated for 30 min. at 1200°. R. T.

**Ammoniates of simple salts. II. Ammoniates of zinc salts.** G. SPACU and P. VOICHESCU (Z. anorg. Chem., 1936, 227, 129—144; cf. this vol., 573).—The existence of ammoniates of Zn salts of the following acids has been established by tensimetric methods (figures indicate no. of mols. of  $\text{NH}_3$  per mol. of anhyd. salt):  $\text{HCNS}$  8, 6, 4, 2;  $\text{HCO}_2\text{H}$  10, 6, 4, 2;  $\text{AcOH}$  8, 6, 4, 2, 1;  $\text{OH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  6, 4, 2;  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  5, 2, 1;  $(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$  6, 5, 3, 2, 1;  $[\text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}]_2$  2, 1;  $\text{BzOH}$  8, 6, 4, 2; salicylic 8, 4, 2; *o*-aminobenzoic 10, 6, 4, 2; 5-sulphosalicylic 8, 4, 2. The stability of corresponding ammoniates increases with the strength of the acid. The influence of the mol. vol. of the metal and of the acid radical is discussed. F. L. U.

**Preparation of crystalline aluminium hydroxide from chromate-aluminate solutions by precipitation with carbon dioxide.** F. F. VOLF and A. E. MOROCHOVETZ (J. Appl. Chem. Russ., 1936, 9, 412—419).—Cryst.  $\text{Al}(\text{OH})_3$  is pptd. from Na aluminate—chromate solutions at 80–90 by saturation with  $\text{CO}_2$ ; the product is readily filterable, and contains  $> 0.03\%$  of  $\text{Cr}_2\text{O}_3$  after washing. R. T.

**Activation of redwood and ash-free sugar charcoal in a current of air.** J. W. MCBAIN and R. F. SESSIONS (J. Physical Chem., 1936, 40, 603—611).—The best conditions for activating C in air



have been examined in relation to temp., duration of heating, and type of furnace. A peak of activation is observed at 350—450°, and a more pronounced peak at 920—960°. When kept for a long period, even in sealed tubes, a decrease in activity of 17—63% occurs. A higher degree of activity is attained by activating in air than by heating in N<sub>2</sub> or He.

E. S. H.

$\alpha$ - $\beta$  Transition in zirconium in the presence of hydrogen. J. H. DE BOER and J. D. FAST (Rec. trav. chim., 1936, 55, 350—356).—The solubility of H<sub>2</sub> in Zr decreases with rise of temp. except through the transition point when H<sub>2</sub> is rapidly absorbed.

C. R. H.

Lead chlorocarbonate and its applications as intermediary in the preparation of alkali nitrates. G. AUSTERWEIL and B. KOURAKINE (Bull. Soc. chim., 1936, [v], 3, 898—905).—The prep. of PbCO<sub>3</sub>.PbCl<sub>2</sub> from PbCl<sub>2</sub> and CaCO<sub>3</sub> is described. When KNO<sub>3</sub> is prepared by interaction of Pb(NO<sub>3</sub>)<sub>2</sub> and KCl, dissolved PbCl<sub>2</sub> can be removed by adding PbCO<sub>3</sub>.

E. S. H.

Nature of active nitrogen. C. R. DHODAPKAR (J. Univ. Bombay, 1935, 4, Part II, 190—199).—The production and properties of active N<sub>2</sub> are described. The first positive system of N<sub>2</sub> ( $B^3\Pi \rightarrow A^3\Sigma$ ) is due to the N<sub>2</sub> mol. The mechanism of the production and decomp. of active N<sub>2</sub> and the effects of impurities are discussed.

J. W. S.

Reaction of ammonia with phosphorus pentachloride. Amides of phosphorus and phospham. I, II. H. MOUREU and P. ROCQUET (Bull. Soc. chim., 1936, [v], 3, 821—828, 829—841).—Published work is described (cf. A., 1935, 945, 1057).

E. S. H.

Basicity of phosphorous acid. I. J. SPERBER and J. F. BODMER (Ber., 1936, 69, [B], 974—977).—Although only 2 H of H<sub>3</sub>PO<sub>3</sub> can be replaced by metal it gives esters Et<sub>3</sub>PO<sub>3</sub> and the view is expressed that it has exclusively the structure P(OH)<sub>3</sub>. Attempts to prepare K<sub>3</sub>PO<sub>3</sub> by fusion of K<sub>4</sub>PO<sub>4</sub> with CuCN lead to a product with the reactions of PO<sub>3</sub>'''. H. W.

Disproportionation of sulphurous acid by hydrogen bromide-acetic acid to sulphuric acid and sulphur. F. KROHNKE and H. TIMMLER (Ber., 1936, 69, [B], 1140—1142; cf. this vol., 592).—SO<sub>2</sub> and HBr in AcOH at room temp. slowly yield S and H<sub>2</sub>SO<sub>4</sub>: 3SO<sub>2</sub>+2H<sub>2</sub>O  $\rightarrow$  2H<sub>2</sub>SO<sub>4</sub>+S. The reaction appears complicated and the intermediate production of SOBr<sub>2</sub> and SBr<sub>4</sub> is assumed. S<sub>8</sub>Br<sub>2</sub> can be isolated and this with H<sub>2</sub>SO<sub>4</sub> are the products if the action takes place in an anhyd. medium or if dehydrating agents (Ac<sub>2</sub>O, AcBr) are present. Reaction does not occur in the presence of > about 20% of H<sub>2</sub>O.

H. W.

Sexavalent tellurium derivatives. I. Telluric acids. M. PATRY (Bull. Soc. chim., 1936, [v], 3, 845—860; cf. A., 1935, 1090).—Only two forms of telluric acid are recognised as definite compounds, viz., orthotelluric acid Te(OH)<sub>6</sub>, and polymetatelluric acid (H<sub>2</sub>TeO<sub>4</sub>)<sub>11±1</sub>. These forms exist in equilibrium in aq. solution; rise of temp. or concn. favours an increase in (H<sub>2</sub>TeO<sub>4</sub>)<sub>11±1</sub>. By heating Te(OH)<sub>6</sub> in a

sealed tube for a long time at 300°,  $\beta$ -TeO<sub>3</sub> ( $d$  6.22) is formed as a hard, grey, chemically inert mass.

E. S. H.

Preparation of chromic sulphide. S. M. VELLER (Ukrain. Chem. J., 1936, 11, 23—27).—The upper of the two layers formed when NH<sub>4</sub> hexahydrobenzoate is shaken with aq. Cr alum is (C<sub>6</sub>H<sub>11</sub>·CO<sub>2</sub>)<sub>3</sub>Cr, a boiling benzene solution of which yields Cr<sub>2</sub>S<sub>3</sub> with dry H<sub>2</sub>S. Cr<sub>2</sub>S<sub>3</sub> is also formed as an intermediate product from aq. Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as follows: Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>+3(NH<sub>4</sub>)<sub>2</sub>S  $\rightarrow$  Cr<sub>2</sub>S<sub>3</sub>+3(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; Cr<sub>2</sub>S<sub>3</sub>+6H<sub>2</sub>O  $\rightarrow$  2Cr(OH)<sub>3</sub>+3H<sub>2</sub>S.

R. T.

Action of molybdic acid on lævorotatory  $\alpha$ -glycerophosphoric acid.—See this vol., 821.

Constitution of  $\beta$ -iron oxide monohydrate. I. M. KOLTHOFF and B. MOSKOVITZ (J. Amer. Chem. Soc., 1936, 58, 777—779).—When the  $\beta$ -oxide is shaken with dil. HCl in aq. NaCl, the [HCl] decreases continuously. The results show that the  $\beta$ -oxide has the structure  $\beta$ -FeO(OH), and is isomorphous with FeOCl, with which it forms mixed crystals.

E. S. H.

Ferrites. I. A. E. VAN ARKEL, E. J. W. VERWEY, and M. G. VAN BRUGGEN. II. E. J. W. VERWEY, A. E. VAN ARKEL, and M. G. VAN BRUGGEN (Rec. trav. chim., 1936, 55, 331—339, 340—347).—I. X-Ray diagrams of mixtures of Fe<sub>2</sub>O<sub>3</sub> and oxides of bivalent metals which have been heated to various high temp. indicate the formation of a ferrite phase which, at about 1300°, can dissolve considerable amounts of Fe<sub>2</sub>O<sub>3</sub>. The fusion points of several ferrites, most of which exhibit cubic spinel structure, were determined.

II. X-Ray investigations were extended to mixtures containing an excess of the bivalent metallic oxide. The influence of the oxide on the properties of the binary system is more marked than is the case when the Fe<sub>2</sub>O<sub>3</sub> is in excess.

C. R. H.

Complex compounds of iridium. IV. (SIR) P. C. RAY and N. P. GHOSH (J. Indian Chem. Soc., 1936, 13, 138—140).—IrCl<sub>3</sub>.3Et<sub>2</sub>S and NH<sub>3</sub> at 100° form IrCl<sub>3</sub>.2Et<sub>2</sub>S.NH<sub>3</sub>, m.p. 155°. At 130—140°, in addition to IrCl<sub>3</sub>.Et<sub>2</sub>S.2NH<sub>3</sub> and (IrCl<sub>3</sub>.5NH<sub>3</sub>)Cl<sub>2</sub> (A., 1934, 1209), a viscous liquid was obtained which, by the action of Ag<sub>2</sub>SO<sub>4</sub>, yielded (Ir.Et<sub>2</sub>S.5NH<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.2H<sub>2</sub>O. Et<sub>2</sub>S and (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub> at 80° form IrCl<sub>3</sub>.3Et<sub>2</sub>S (+1CHCl<sub>3</sub>), m.p. 171°.

C. R. H.

Chromatographic analysis and its application. G. HESSE (Angew. Chem., 1936, 49, 315—320).—A review of the technique and applications of chromatographic analysis, and of the relation of degree of adsorption to structure of adsorbate.

J. S. A.

Chelidonine: a fluorescent principle. M. DÉRIBÉRE (Ann. Chim. Analyt., 1936, [iii], 18, 119—120).—Practical applications of the brilliant fluorescence of chelidonine are discussed.

J. S. A.

Neville and Winther's acid as fluorescent indicator. M. DÉRIBÉRE (Ann. Chim. Analyt., 1936, [iii], 18, 120).—The acid shows a sharp change from no fluorescence to intense blue at  $p_H$  6—6.5.

J. S. A.



Determination of deuterium content of hydrogen mixtures by Farkas' micro-thermal conductivity method. K. WIRTZ (Z. physikal. Chem., 1936, B, 32, 334—340).—The difficulties in the method are discussed and ways of overcoming them described. An accuracy of  $\pm 0.1\%$  is attainable. R. C.

Drying of substances decomposing when heated. V. F. MALACHOV (J. Appl. Chem. Russ., 1936, 9, 775—777).—The substance ( $\text{NH}_4\text{NO}_3$ ) is dried until the loss in wt. in unit time becomes const., and the part of the drying curve representing this period is produced back to zero time, giving the original dry wt. R. T.

Determination of dry substance content.—See B., 1936, 527.

Drop reaction for hydrogen peroxide. L. KULBERG and L. MATVEEV (J. Appl. Chem. Russ., 1936, 9, 754—755).—A drop each of 1% *o*-tolidine in EtOH, acetate buffer at  $p_H$  4, 1% aq.  $\text{FeSO}_4$ , and of the solution under examination are placed on filter-paper; a blue coloration develops in presence of  $2.5 \times 10^{-8}$  g. of  $\text{H}_2\text{O}_2$ . R. T.

Phenosafranine, tartrazine, and rose-Bengal as adsorption indicators. A. J. BERRY (Analyst, 1936, 61, 315—319; cf. A., 1932, 1009).—A method for determining the constituents of mixtures containing  $\text{CN}'$ ,  $\text{I}'$ , and  $\text{Cl}'$  is described. Since AgBr is intermediate between AgCl and AgI in solubility and adsorption capacity for dyes, Br' cannot be determined by this method in presence of other halides. The use of adsorption indicators in titrating Ag' in acid solution with KBr and in systems such as  $\text{Ti}^{\text{IV}}$ — $\text{Ti}^{\text{III}}$  halides is described. The particular conditions for which the three indicators are best adapted are discussed. E. C. S.

Determination of hypochlorite and chlorate.—See B., 1936, 541.

Determination of bromine.—See this vol., 914.

Detection and determination of hydrobromic acid in hydrochloric acid. L. CHELLE (Ann. Falsif., 1936, 29, 229—231).—The presence of Br (120 mg. per litre; determined by the method of Denigès and Chelle, B., 1913, 141) in samples of "pure" HCl is noted. E. H. S.

Acidimetric determination of iodine. R. I. ALEXEEV (J. Appl. Chem. Russ., 1936, 9, 547—551).—10 ml. of 13%  $\text{AgNO}_3$  are shaken with 25 ml. of approx. 0.1N-I in KI, the ppt. is collected and washed, and the filtrate+washings are titrated with 0.1N-NaOH. The [I] is calc. from  $6\text{I} + 3\text{H}_2\text{O} + 6\text{AgNO}_3 \rightarrow 5\text{AgI} + \text{AgIO}_3 + 6\text{HNO}_3$ . R. T.

Determination of iodine in basic slag and mineral fertiliser.—See B., 1936, 541.

Determination of small quantities of fluorine in dicalcium phosphate. S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 306—310).—F is isolated as  $\text{H}_2\text{SiF}_6$  by distillation with  $\text{HClO}_4$  and determined colorimetrically by the fading effect on Zr alizarin lake. F. O. H.

Determination of fluorine. I. A. A. VASILIEV (J. Appl. Chem. Russ., 1936, 9, 747—750).—50 ml. of

$\text{H}_2\text{O}$ , 2 ml. of 2N- $\text{HNO}_3$ , 10 drops of AcOH, and 25 ml. of 2.84% KBr are added to 50 ml. of neutral aq. NaF (containing 0.1 g. of NaF), the mixture is heated to  $40^\circ$ , and 25 ml. of a solution of 5.6%  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  in 1% AcOH are added. The ppt. of PbFBr is collected after 12—18 hr., washed successively with  $\text{H}_2\text{O}$ , aq.  $\text{PbBr}_2$ , and  $\text{H}_2\text{O}$ , and dissolved in 100 ml. of  $\text{H}_2\text{O}$  containing 5 ml. of  $\text{HNO}_3$ . 50 ml. of 0.1N- $\text{AgNO}_3$  are added, the solution is heated at  $100^\circ$  for 30 min., filtered, and the ppt. of AgBr is washed. Excess of  $\text{AgNO}_3$  is determined in the filtrate+washings by titration with 0.1N- $\text{NH}_4\text{CNS}$ . Alternatively, the ppt. of PbFBr is dried at  $105^\circ$  and weighed. R. T.

Instrument for automatic quantitative indication of hydrogen sulphide in the atmosphere. R. KRAUS (Chem. Fabr., 1936, 9, 241—242).—A continuous record of  $\text{H}_2\text{S}$  in the air is made by traversing  $\text{Pb}(\text{OAc})_2$  paper past a slit. The tint may be calibrated by exposure to the gas liberated by acid from measured amounts of aq.  $\text{Na}_2\text{S}$ . J. S. A.

Determination of small amounts of hydrogen sulphide in air. I. S. SCHERESCHEVSKAJA (J. Appl. Chem. Russ., 1936, 9, 572—575).— $\text{H}_2\text{S}$  is absorbed by 1% aq.  $\text{AgNO}_3$ , the ppt. of  $\text{Ag}_2\text{S}$  is treated with KCN, and the coloration given with Na plumbite by the  $\text{K}_2\text{S}$  formed is compared with those given by a series of standards prepared analogously from  $\text{Ag}_2\text{S}$  obtained by adding 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$  to aq.  $\text{AgNO}_3$ . The method serves for the determination of  $< 0.01$  mg. of  $\text{H}_2\text{S}$ . R. T.

Gravimetric determination of selenates. (MME.) RIPAN-TILICI (Bull. Soc. chim., 1936, [v], 3, 881).—A claim for priority (cf. Spacu, this vol., 442). E. S. H.

Gravimetric determination of selenates. P. SPACU (Bull. Soc. chim., 1936, [v], 3, 881).—A reply (cf. preceding abstract). E. S. H.

Determination of selenium in steel.—See B., 1936, 548.

[Determination of nitrogen by the] Kjeldahl method. LE TOURNEUR-HUGON and CHAMBIONNAT (Ann. Falsif., 1936, 29, 227—229).—Digestion is completed in about 30 min. if  $\text{HClO}_4$  is gradually added to the boiling liquid when the material has dissolved, i.e., after about 12 min. using Gunning's technique. E. H. S.

Alkalimetry in presence of nitrite. A. S. VETROV (J. Appl. Chem. Russ., 1936, 9, 772—774).—2 g.-mol. of  $\text{H}_2\text{O}_2$  per g.-mol. of  $\text{HNO}_2$  present are added to 20 ml. of the alkaline solution at  $50$ — $60^\circ$ , 50 ml. of 0.1N- $\text{H}_2\text{SO}_4$  are added, followed by 3 drops of 0.2% Me-red, and the solution is titrated with 0.1N-NaOH. R. T.

Photometric study of the diphenylamine reaction for determining small amounts of nitrates in water. A. V. TROFIMOV (J. Appl. Chem. Russ., 1936, 9, 756—771).—Max. sensitivity is obtained when the final solution contains 73 g. of  $\text{H}_2\text{SO}_4$  per 100 ml., and 100 mols. of  $\text{NHPh}_2$  per mol. of  $\text{HNO}_3$ ; under these conditions 5 mg. of  $\text{HNO}_3$  per cu. m. of  $\text{H}_2\text{O}$  may be determined. The most satisfactory reagent for low  $[\text{HNO}_3]$  is one containing 10 mg. of  $\text{NHPh}_2$  per litre of 89%  $\text{H}_2\text{SO}_4$ , taking 5 ml. of reagent to



2 ml. of  $\text{H}_2\text{O}$ . High or low results are obtained, according to whether the  $\text{Cl}^-$  content of the standard is  $>$  or  $<$  that of the  $\text{H}_2\text{O}$ .  $\text{SO}_4^{2-}$  ( $>$  10% of  $\text{MgSO}_4$  or  $\text{Na}_2\text{SO}_4$ ),  $\text{HCO}_3^-$  ( $>$  0.1%), and  $\text{HgCl}_2$  ( $>$  0.3%) do not interfere. The rate of development of colour increases with rising temp., and that of fading still more so; using the above reagent, however, the coloration remains const. at  $25^\circ$  for  $<$  20 hr. R. T.

**Distillation and separation of arsenic, antimony, and tin.** J. A. SCHERRER (J. Res. Nat. Bur. Stand., 1936, 16, 253—259).—The sulphates are distilled in an all-glass apparatus with  $\text{HCl}$  ( $d$  1.18), in a stream of  $\text{CO}_2$ .  $\text{AsCl}_3$  distils up to  $112^\circ$ ;  $\text{H}_3\text{PO}_4$  is then added and  $\text{SbCl}_3$  distilled at  $155$ – $165^\circ$ ;  $\text{Sn}$  is distilled at  $140^\circ$  from a 75%  $\text{HCl}$  ( $d$  1.18)–25%  $\text{HBr}$  (40%) mixture.  $\text{Ge}$ ,  $\text{Re}$ , and  $\text{Mo}$ , but not  $\text{Bi}$ , interfere. L. J. J.

**Salts of silicomolybdic acid with organic bases: gravimetric determination of small amounts of silica as pyramidone silicomolybdate.** E. J. KING and J. L. WATSON (Mikrochem., 1936, 20, 49—56).—In dil. acid solution  $\text{SiO}_2$  (1 mol.) combines with  $\text{MoO}_3$  (12 mols.) to form a stable complex which yields insol. compounds (silicomolybdates) with org. bases (e.g., coniine,  $\text{C}_5\text{H}_5\text{N}$ , and pyramidone). Since 1 mol. of complex combines with 3 mols. of pyramidone, conversion of  $\text{SiO}_2$  into the heavy pyramidone silicomolybdate yields a weighable ppt. from a very small amount of  $\text{SiO}_2$ . J. W. S.

**Determination of silica by means of 8-hydroxyquinoline.** M. I. VOLINETS (Ukrain. Chem. J., 1936, 11, 18—22).—0.25 g. of the substance is melted with 5 g. of  $\text{NaOH}$ , the melt is extracted with 200 ml. of  $\text{H}_2\text{O}$ , 30 ml. of conc.  $\text{HCl}$  are added, the solution is boiled, cooled, and made up to 1 litre. 20 ml. of 20%  $(\text{NH}_4)_2\text{MoO}_4$  are added to 100 ml. of the solution, excess of 50%  $\text{HCl}$  is added, and an amount of 8-hydroxyquinoline (I) given by  $0.024153P + 0.21$  g., where  $P$  is the expected  $\text{SiO}_2$  content of 1 g. of substance. The mixture is heated at  $60$ – $70^\circ$ , cooled, made up to a known vol., filtered, and excess of (I) in 100 ml. of filtrate is determined bromometrically. Alternatively, the ppt. of  $\text{SiO}_2 \cdot 12\text{MoO}_3 \cdot 4\text{C}_8\text{H}_8\text{N}_2\text{O}_2$  is collected, washed, and weighed. R. T.

**Spectrographic method of measuring carbon dioxide concentration.** E. D. McALISTER (Physical Rev., 1936, [ii], 49, 704).—An accurate and rapid method, independent of humidity and of the presence of other gases, and having very small temp. and pressure corrections, is described. It depends on the high opacity of  $\text{CO}_2$  to radiation in the region of one of its fundamental absorption bands ( $4.2$ – $4.3 \mu$ ); this, isolated from a Nernst filament, falls on a vac. thermocouple after passing through a known optical path length of air containing  $\text{CO}_2$ . The method is sensitive to 0.0001%. N. M. B.

**Determination of carbon dioxide in gas mixtures.**—See B., 1936, 541.

**Colorimetric determination of atmospheric carbon dioxide.**—See B., 1936, 493.

**Micro-determination of potassium.** P. WENGER, C. CIMERMAN, and C. J. RZYMOWSKA (Mikro-

chem., 1926, 20, 1—28).—Emich's method (pptn. with  $\text{H}_2\text{PtCl}_6$ ), with modified washing treatment, enables about 0.5 mg. of  $\text{K}$  to be determined in presence of 5 mg.  $\text{Na}$ . A micro-method has also been developed involving conversion into  $\text{KClO}_4$  before pptn. with  $\text{H}_2\text{PtCl}_6$ . The use of Pregl tubes for filtration was unsatisfactory. The  $\text{K}_2\text{PtCl}_6$  ppt. can be treated with  $\text{KI}$  and titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ , this method being advantageous for determination of  $\text{K}$  in biological media. Examples relate to blood sera and cerebrospinal fluid, which are preferably mineralised with a mixture of conc.  $\text{HNO}_3$  (5 vols.) and  $\text{HClO}_4$  ( $d$  1.67, 2 vols.). Ignition of the media causes loss of  $\text{K}$ . Micro-hot plates, filters, and water-baths are described. J. W. S.

**Micro-determination of potassium.** C. CIMERMAN and C. J. RZYMOWSKA (Mikrochem., 1936, 20, 129—143).—A review.

**Gravimetric determination of the titre of silver nitrate solutions.** E. N. TARAN (J. Appl. Chem. Russ., 1936, 9, 520—525).—2 ml. of 15% aq.  $\text{NH}_3$  and 1 ml. of 40% aq.  $\text{CH}_3\text{O}$  are added to 50 ml. of aq.  $\text{AgNO}_3$ , the solution is heated at  $100^\circ$  for 20 min., and the pptd.  $\text{Ag}$  is collected, ignited, and weighed. R. T.

**Micro-detection of beryllium with alkannin and naphthazarin.** J. V. DUBSKÝ and E. KRAMETZ (Mikrochem., 1936, 20, 57—58).—Addition of 2 drops of quinalizarin reagent [30 drops of 0.05% solution of quinalizarin in  $\text{EtOH}$  with 5 drops of 10%  $(\text{CH}_2\text{NH}_2)_2$ ] to 3 drops of test solution yields a blue colour with  $> 0.135 \times 10^{-6}$  g.  $\text{Be}$ . Similar addition of 1 drop of naphthazarin or alkannin reagent [30 drops of 0.03% naphthazarin solution in  $\text{EtOH}$  or 0.05% alkannin solution, with 5 drops of 10%  $(\text{CH}_2\text{NH}_2)_2$ ] gives reddish-violet colours with  $> 1.3 \times 10^{-6}$  g.  $\text{Be}$ . Use of  $\text{NH}_3$  or  $\text{NaOH}$  in place of  $(\text{CH}_2\text{NH}_2)_2$  reduces the sensitivity to  $2 \times 10^{-6}$  g. J. W. S.

**Coloured and dyed crystalline precipitates.** L. ROSENTHALER (Mikrochem., 1936, 20, 85—90).—The ppts. obtained on adding a 1% solution of Orange II in 0.1N- $\text{HCl}$  to solutions of various alkaloids, and on adding an  $\text{NH}_3$  solution of rhodamine GH to  $\text{NH}_3$  solutions of various derivatives of barbituric acid, are described. In  $\text{NH}_3$  solution Orange II also gives ppts. with  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Th}^{+++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ , and  $\text{Cd}^{++}$ , and in 0.1N- $\text{HCl}$  with alkaline-earth metals and many heavy metals. J. W. S.

**Microchemical detection of magnesium by means of 8-hydroxyquinoline.** M. V. GAPTSCHENKO and O. G. SCHEINTZIS (J. Appl. Chem. Russ., 1936, 9, 541—543).—A drop of aq.  $\text{NH}_3$  is added to a drop of 10%  $\text{Na}$  citrate in 2N- $\text{NaOH}$ , and a drop of solution is added, followed by a drop of 5% hydroxyquinoline in  $\text{EtOH}$ ; characteristic crystals of the  $\text{Mg}$  salt are obtained when the solution contains  $<$  3.76 mg. of  $\text{Mg}$  per 100 ml. R. T.

**Detection of cupric ion.** B. M. BOGOSLOVSKI and V. S. KRASNOVA (J. Appl. Chem. Russ., 1936, 9, 751—753).—1—2 ml. of 0.5%  $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-OH}$  (I) and 25—30 ml. of saturated aq.  $\text{NaCl}$  are added to 200 ml. of solution; a violet coloration appears in



presence of  $\leq 0.6$  mg. of  $\text{Cu}^{II}$ . The method also serves for detection of (I). R. T.

**Nephelometric determination of copper with salicylaldoxime in lead-free substances.** F. ALTEN, B. WANDROWSKY, and E. KNIPPENBERG (*Mikrochem.*, 1936, 20, 77—84).—The test and standard solutions, neutralised with  $\text{NH}_3$ , are treated with 3 c.c. of 30%  $\text{AcOH}$ , 1 c.c. of 20%  $\text{K}$  citrate, 2 c.c. of saturated aq.  $\text{KH}_2\text{PO}_4$ , and 0.5 c.c. of saturated aq.  $\text{NaOAc}$ , stirred, and brought into temp. equilibrium in a water-bath. 1 c.c. of 1% salicylaldoxime solution is added, and then after 1.5—2.5 hr. 1 c.c. of  $\text{AcOH}$ . The relative opacities are observed after a further 30 min. J. W. S.

**Microgravimetric determination of small amounts of mercury vapour in air.** V. A. PIANKOV (*J. Appl. Chem. Russ.*, 1936, 9, 580—582).—The air is passed over crystals of  $\text{I}$ , the  $\text{HgI}$  condensing in a cooled glass spiral is washed with  $\text{Et}_2\text{O}$ , the extract is conc. to 1—2 ml., filtered through asbestos, the filtrate + washings are evaporated to dryness at  $40^\circ$ , and the residue of  $\text{HgI}$  is weighed. Trustworthy results are obtained for concns. of  $\leq 0.385$  mg. of  $\text{Hg}$  per cu. m. of air (0.077 mg. of  $\text{Hg}$ ). R. T.

**Separation of aluminium from manganese, nickel, cobalt, and zinc.** T. KÔZU (*J. Chem. Soc. Japan*, 1935, 56, 683—688; cf. A., 1935, 1338).— $\text{Al}$  is pptd. quantitatively from sulphate solution at room temp. by adding saturated aq.  $\text{NH}_2\text{Ph}$ .  $\text{Zn}$  interferes, but  $\text{K}$ ,  $\text{Mn}$ ,  $\text{Ni}$ , and  $\text{Co}$  do not.

CH. ABS. (e)

**Solution of the manganese problem in analysis of silicate rocks.** O. HACKL (*Z. anal. Chem.*, 1936, 105, 81—95).—The mineral is fused with  $\text{Na}_2\text{CO}_3$ , and  $\text{SiO}_2$  is removed by a twofold separation.  $\text{Fe}$ ,  $\text{Al}$ ,  $\text{Mn}$ ,  $\text{Ti}$ , etc. are pptd. by aq.  $\text{NH}_3 + \text{H}_2\text{O}_2$ . The ppt. is partly dissolved in cold 40—50%  $\text{HNO}_3$ , and repptd. with  $\text{NH}_3 + \text{H}_2\text{O}_2$ . The solution is conc., and  $\text{Al} + \text{Fe}$  completely separated by addition of  $\text{NH}_3$ . The united oxide ppt. is fused with  $\text{KNaS}_2\text{O}_7$ , and the melt is dissolved in 10%  $\text{H}_2\text{SO}_4$ ; dissolved  $\text{Pt}$  is removed by  $\text{H}_2\text{S}$ . To the solution, 2—5% aq.  $\text{Ag}_2\text{SO}_4$  is added, and then solid  $\text{K}_2\text{S}_2\text{O}_8$ . The solution is warmed at  $75\text{--}80^\circ$  for  $\geq 5$  min., cooled rapidly, and colorimetrically for  $\text{Mn}$ .  $\text{H}_2\text{O}_2$  is then added, and  $\text{Ti}$  so determined colorimetrically. Finally  $\text{H}_2\text{O}_2$  is destroyed by heating at  $100^\circ$ ,  $\text{Fe}^{+++}$  is reduced by means of  $\text{H}_2\text{S}$ , and  $\text{Fe}$  is determined volumetrically. For the accurate colorimetry of  $\text{Mn}$ , solutions must be matched by dilution at equal thicknesses. J. S. A.

**Formation of hydrogen peroxide in the silver reductor: micro-analytical method for iron.** C. F. FRYLING and F. V. TOOLEY (*J. Amer. Chem. Soc.*, 1936, 58, 826—831).—Determination of small amounts of  $\text{Fe}$  by reduction with  $\text{Ag}$  followed by titration with  $\text{Ce}(\text{SO}_4)_2$  is complicated by the formation of  $\text{H}_2\text{O}_2$ . The procedure is applicable to the determination of about 1.5 mg. of  $\text{Fe}$  when the reduction is performed in an atm. of  $\text{H}_2$  and a correction is applied for the indicator. E. S. H.

**Oxidation-reduction indicators.** I. *N*-Phenylanthranilic acid. A. KIRSSANOV and V.

TSCHERKASSOV (*Bull. Soc. chim.*, 1936, [v], 3, 817—821).—The use of *N*-phenylanthranilic acid in the titration of  $\text{Fe}$ ,  $\text{V}$ , and  $\text{Cr}$  solutions is described. The oxidation-reduction potential is 1.08 volt.

E. S. H.

**Detection of cobalt in presence of other cations.** A. T. TSCHERNI (*Ukrain. Chem. J.*, 1936, 11, 13—14).—The solution is made acid with  $\text{HCl}$ ,  $\text{NH}_4\text{CNS}$  is added, and the mixture is shaken with  $\text{EtOH-Et}_2\text{O}$ ; the upper layer is coloured blue in presence of  $\text{Co}$ . If  $\text{Fe}$  is present  $\text{NH}_4\text{F}$  is added to discharge the red coloration obtained. R. T.

**Determination of chromium and chromates in waste water.**—See B., 1936, 574.

**Determination of chromium in chromite.**—See B., 1936, 541.

**Determination of tin in alloys with antimony and lead (antimony less than 2%).** H. F. HOVRIGAN (*Analyst.*, 1936, 61, 328—333).— $\text{Sn}$  and  $\text{Pb}$  in the alloy are dissolved in conc. aq.  $\text{HCl}$  in absence of  $\text{O}_2$ ,  $\text{Sb}$  is removed by filtration, and  $\text{SnCl}_2$  determined by titration with  $\text{KIO}_3$ . In presence of  $\text{Sb}^{III}$  in solution, the latter titration gives erratic results. E. C. S.

**Colorimetric determination of titanium in presence of bromine compounds.** H. A. LIEBHAFSKY (*Z. anal. Chem.*, 1936, 105, 113—114; cf. this vol., 45).—Contrary to the statement of Lutschinski and Lichatscheva,  $\text{Br}$  is best removed as  $\text{AgBr}$  by treating the acid solution with an excess of  $\text{H}_2\text{O}_2$ , followed by  $\text{AgNO}_3$ . J. S. A.

**Colorimetric detection of titanium and vanadium in steel.**—See B., 1936, 548.

**Drop reaction for zirconium.** N. A. TANANAEV and A. V. TANANAEVA (*J. Appl. Chem. Russ.*, 1936, 9, 526—531).— $\text{Zr}$  is detected in presence of other elements (except  $\text{Si}$ ) by pptn. as phosphate from solutions containing 25—30% of  $\text{H}_2\text{SO}_4$  or 20—22% of  $\text{HCl}$  or  $\text{HNO}_3$ . Directions are given for the detection and approx. determination of  $\text{Zr}$  in minerals, involving fusion with  $\text{NaOH}$ , elimination of  $\text{SiO}_2$  from the extract of the melt, pptn. of  $\text{Zr}$  as above, and ignition of the washed ppt., which is weighed as pyrophosphate. R. T.

**Determination of small amounts of germanium.** N. S. POLUEKTOV (*Z. anal. Chem.*, 1936, 105, 23—26).— $\text{Na}_2\text{GeO}_3$  solutions are acidified, freed from  $\text{CO}_2$ , and neutralised with  $\text{NaOH}$  (phenolphthalein + *p*-nitrophenol). Mannitol (I) is added, and the monobasic (I)- $\text{GeO}_2$  complex acid thereby formed is titrated with 0.1*N*- $\text{NaOH}$ .  $\leq 1$  mg. of  $\text{Ge}$  is determined colorimetrically as Mo-blue by the reduction of germanomolybdic acid by  $\text{FeSO}_4$ .  $\text{Ge}$  is first separated as  $\text{GeS}_2$ , which is dissolved in  $\text{NaOH} + \text{H}_2\text{O}_2$ , and treated with aq.  $(\text{NH}_4)_2\text{MoO}_4$  containing  $\text{FeSO}_4$  in presence of  $\text{NaOAc}$ . J. S. A.

**Detection of vanadium.** E. I. KRETSCH (*Ukrain. Chem. J.*, 1936, 11, 28—31).—The substance, containing  $\leq 0.2$  mg. of  $\text{V}_2\text{O}_5$ , is mixed with an equal wt. of  $\text{C}$ ,  $\text{Cl}_2$  is passed over the mixture at  $300\text{--}400^\circ$  and the issuing gases are passed through glass wool moistened with conc.  $\text{H}_2\text{SO}_4$ ;  $\text{V}$  is indicated by a yellow to orange coloration. R. T.



Quantitative spectral analysis, detection [and determination] of vanadium in steel, and investigation of minerals from the Dreiser Weiher (Eifel) and the Finkenberg, near Beuel-on-Rhine. W. SIEMEISTER (Z. anal. Chem., 1936, 105, 1—22).—

(a) Sensitive lines of V in the condensed spark discharge in presence of Fe are given. In presence of  $> 1\%$  of C, Mn, P, or Si, the photometric method of Hartley and de Gramont may be employed for determining V. In high alloy steels, owing to abnormal intensity relationships, the homologous line-pair method of Gerlach and Schweitzer is applicable. Where inhomogeneities (inclusions or segregations) occur, the material is first dissolved chemically. (b) Olivine, augite, and accompanying minerals from olivine bombs have been analysed spectrographically for Ni, Co, Mn, and Cr.  $\text{SiO}_2$  and Fe must first be removed chemically, Fe being extracted quantitatively by  $\text{Et}_2\text{O}$  from the HCl solution of the mineral. Ni, Mn, Co, and Cr are pptd. with  $(\text{NH}_4)_2\text{S}$ , and the arc spectrum of the ppt., on C electrodes, is matched against samples of known composition. J. S. A.

Microchemical detection of bismuth by means of quinoline thiocyanate. M. V. GAPTSCHENKO and O. G. SCHEINTZIS (J. Appl. Chem. Russ., 1936, 9, 544—546).—A drop of solution (made acid with  $\text{HNO}_3$ ) is added to a drop of reagent (1 g. of  $\text{NH}_4\text{CNS}$  in 100 ml. of saturated aq. quinoline) on a slide; characteristic yellow crystals, of the composition  $\text{C}_9\text{H}_7\text{N}.\text{HCNS}.\text{Bi}(\text{CNS})_3$ , are obtained in presence of  $< 0.3 \times 10^{-6}$  g. of Bi. Zn,  $\text{Sn}^{\text{II}}$ ,  $\text{Sb}^{\text{III}}$ ,  $\text{Hg}^{\text{I}}$ , Ag, and Cu interfere. R. T.

Micro-determination of m.p. R. C. RAY and V. DAYAL (Trans. Faraday Soc., 1936, 32, 741—743).—The angle of a V-shaped electrically heated Pt wire is brought in contact with a minute quantity of the powdered solid on a mica platform, and melting is observed microscopically. The method is rapid and fairly accurate. F. L. U.

Laboratory thermoregulator. J. S. BUCK (J. Chem. Educ., 1936, 13, 131). L. S. T.

Thermocouples for psychrometric purposes. R. W. POWELL (Proc. Physical Soc., 1936, 48, 406—414).—Factors affecting the wet-bulb depression are investigated. N. M. B.

Installation at the Bellevue Electromagnetic Laboratory of apparatus for helium liquefaction and production of temperatures below  $1^\circ \text{ abs.}$ , by the magnetic method. N. KURTI, P. LAINE, B. V. ROLLIN, and F. SIMON (Compt. rend., 1936 202, 1421—1423).—The apparatus is described. Certain paramagnetic salts become ferromagnetic at very low temp. L. J. J.

Focussing effect of double-crystal spectrometer. R. C. SPENCER (Physical Rev., 1936, [ii], 49, 704; cf. A., 1931, 1205; Barnes, A., 1933, 993).—An extension of the discussion by Parratt (cf. this vol., 181). N. M. B.

Heterochromatic photometry of the ultra-violet region. E. J. BOWEN (Proc. Roy. Soc., 1936, A, 154, 349—353).—A quartz cell containing aesculin solution, placed before a K photo-electric cell, can

be used as a relative quantum counter for  $\lambda$  3665—2500 Å. with a sensitivity much  $>$  that of a thermopile-galvanometer combination. L. L. B.

Technique of the far infra-red investigations. N. R. TAWDE, Y. G. NAIK, and D. D. DESAI (J. Univ. Bombay, 1935, 4, Part II, 181—189).—The apparatus is described. J. W. S.

X-Ray tubes with rotating anti-cathode. V. LINNITZKI and V. GORSKI (Tech. Phys. U.S.S.R., 1936, 3, 220—222).—The rotating anti-cathode simultaneously functions as a mol. Gaede pump, thus avoiding the presence of Hg vapour and giving compactness. R. S. B.

Starting the Daniels-Heidt capillary mercury-arc lamp. L. D. WILSON (J. Amer. Chem. Soc., 1936, 58, 856—857).—A magnetic device is described. E. S. H.

Stand for spark gap and interrupted arc. A. SCHLEICHER and N. KAISER (Z. anal. Chem., 1936, 105, 114—115).—Arc or spark gap and interrupter are mounted as a single rigid unit. J. S. A.

Voltage sources and amplifiers for Geiger counters. N. S. GINGRICH (Rev. Sci. Instr., 1936, [ii], 7, 207—210).—A description is given of a modified pentode stabiliser in which a Ne lamp replaces the usual battery for maintaining a const. grid bias, a simpler stabiliser in which a bank of Ne lamps supplies the stabilised voltage directly, and a new amplifier using two standard radio tubes and a small Ne lamp. A brief report is made of the use of a "Strobotron" in counter circuits. N. M. B.

Thin windows for photo-electric cells and counters. G. P. HARNWELL (Rev. Sci. Instr., 1936, [ii], 7, 216).—A method of blowing from glass tubing a very thin window of uniform thickness and capable of withstanding large pressure differences is described. N. M. B.

Determination of coefficient of magnetisation of solids. C. COURTY (Bull. Soc. chim., 1936, [v], 3, 929—933).—Good results are obtained, using the magnetic balance, when the solid is immersed in a non-solvent liquid. E. S. H.

Charts for determining  $p_H$  values when using quinhydrone and hydrogen electrodes and saturated calomel cell. G. N. PULLEY (Food Res., 1936, 1, 141—144).—Corrections for temp. between  $16^\circ$  and  $32^\circ$  are recorded graphically. E. C. S.

Apparatus for the micro-electrolysis of large volumes of solution. B. L. CLARKE and H. W. HERMAN (Mikrochem., 1936, 20, 126—128; cf. A., 1932, 492).—Improvements in the previous apparatus are described. J. W. S.

Properties of the immersion objective when used with rapid electrons. R. BEHNE (Ann. Physik, 1936, [v], 26, 372—384). A. J. M.

Blocking layer in a selenium valve photo-electric cell. S. FREIVERT (Tech. Phys. U.S.S.R., 1936, 3, 266—267).—The sensitivity of Se valve photo-cells decreases when the cell is placed in a vac., and reaches zero in 3—4 hr. The sensitivity is not regained by keeping in air. The resistance of the cell is reduced and the rectifying properties



are lost, the Se changing from grey to bluish. A shellac coating almost stops the decay in a vac. and it is suggested that the blocking layer is one either of gas or of  $\text{SeO}_2$ , which is volatile. R. S. B.

**Automatic potentiometer for thermal analysis.** R. J. M. PAYNE (J. Sci. Instr., 1936, 13, 158—161).—Improvements on an apparatus previously described (this vol., 45) are recorded. C. W. G.

**Flask with graduated neck for the rapid adjustment of titrated solutions.** J. BOUILLOT (J. Pharm. Chim., 1936, [viii], 23, 557—558).—A 925-c.c. flask with narrow neck graduated up to 1200 c.c. is described. E. W. W.

**Micro-volumetric analysis with weight burettes.** L. SZEDELLEDY and O. CLAUDER (Z. anal. Chem., 1936, 105, 26—31).—The use of hypodermic syringes as wt. burettes for precision micro-titrations is described. J. S. A.

**Accurate automatic mercury pipette.** P. H. BIGG (J. Sci. Instr., 1936, 13, 156—157).—The flow of Hg ceases automatically after filling and after delivery of  $0.3125 \pm 0.003$  ml. C. W. G.

**Apparatus with two thermionic vacuum tubes for automatic titration.** T. TASHIRO and Y. KATO (J. Chem. Soc. Japan, 1935, 56, 757—766).

CH. ABS. (e)

**Pregl's absorption apparatus for the micro-determination of carbon and hydrogen.** Influence of the nature of the capillary on the constancy of the increase in weight. H. LIEB and A. SOLTYS (Mikrochem., 1936, 20, 59—64).—The capillary constriction in Pregl's absorption apparatus must have a length of 4—6 mm. and cross-section of 0.2—0.3 mm. or inaccurate results are obtained. J. W. S.

**Atomising apparatus.** B. CLAUS (Z. tech. Phys., 1935, 16, 202—205; Chem. Zentr., 1935, ii, 1411).—The apparatus operates by the attuned piezoelectric vibrations of two  $\text{SiO}_2$  plates, and is applicable to the dispersion of substances deposited electrolytically. J. S. A.

**Absorption tube.** K. WAGENMANN (Chem.-Ztg., 1936, 60, 469).—A compact  $\text{CaCl}_2$  or soda-lime tube, with externally ground tap-stopper, is described. J. S. A.

**Fundamentals of vacuum technique for chemical laboratories.** G. MONCH (Chem.-Ztg., 1936, 60, 465—468).—A review of general technique and apparatus. J. S. A.

**Small multiple still.** F. R. PRATT (Rev. Sci. Instr., 1936, [iii], 7, 211—213).—The construction of, and performance data for, a simplified, economical, automatic still are given. N. M. B.

**Apparatus with ground-glass joints.** H. LEE (Analyst, 1936, 61, 334).—The apparatus figured is suitable for the determination of  $\text{NH}_3$  in  $\text{H}_2\text{O}$  and for the oxidation of org. matter with  $\text{HNO}_3$ — $\text{H}_2\text{SO}_4$ .

**Measurement of streaming of structure-viscous liquids.** W. PHILIPPOFF (Kolloid-Z., 1936, 75, 155—161).—Experiments with cellulose trinitrate in  $\text{BuOAc}$

show that viscosimeters of the capillary or Couette type give concordant results. E. S. H.

**Manometer of small volume.** R. A. HULL (J. Sci. Instr., 1936, 13, 165—166).—Tetralin is a satisfactory liquid for use in simple U-tube manometers. C. W. G.

**Vacuum joints in metal apparatus.** R. M. ARCHER (J. Sci. Instr., 1936, 13, 161—165).—Instructions are given for making metal-metal tube, metal-glass tube, metal-metal equatorial, and metal tube-spun nipple joints. C. W. G.

[Ultrafiltration.] H. J. C. TENDELOO (Chem. Weekblad, 1936, 33, 294).—Cyclostyle paper backed by a piece of filter-paper makes a satisfactory rapid ultrafilter medium. S. C.

**Collodion membranes.** Preparation, physical properties, and dialysis measurements in solutions. V. NOWATKE (Kolloid-Z., 1936, 75, 269—284).—The influence of method of prep. on the thickness,  $\text{H}_2\text{O}$  content, and  $\text{H}_2\text{O}$ -permeability of collodion membranes has been determined. With increasing  $\eta$  of the collodion solution, the membranes formed become thinner, more elastic, and stronger. Max. permeability is attained when a definite amount of air is used to remove the solvent. The extent to which the permeability of the membrane is altered by adding different org. compounds to the collodion solution has been determined. Dialysis measurements with alkali chloride and  $\text{CO}(\text{NH}_2)_2$  solutions are reported. The dialysis consts. tend to rise with increasing at. wt. of the cation and are in agreement with the lyotropic series (except Cs). Diffusion coeffs. have been calc. from the dialysis consts. E. S. H.

**Emulsifier.** K. FISCHER (Kolloid-Z., 1936, 75, 285—287).—Laboratory apparatus is described. E. S. H.

**Immersion pycnometer.** W. JUNG (J. Indian Chem. Soc., 1936, 13, 136—137).—A pycnometer specially adapted for obtaining the  $d$  of powders is described. The usual difficulty of weighing under  $\text{H}_2\text{O}$  is met by evacuating the pycnometer in a desiccator and allowing  $\text{H}_2\text{O}$  to flow into the desiccator until the pycnometer is filled. C. R. H.

**Surface tension.** C. C. PATEL, K. V. DESAI, and S. M. MEHTA (J. Univ. Bombay, 1935, 4, Part II, 132—139).—Methods of measuring surface tension are discussed critically. A modification of Ferguson's method (A., 1932, 828) which increases accuracy is described, and is illustrated with data for  $\text{CaCl}_2$  solutions. J. W. S.

**Impulse vacuum meter.** A. BUTSCHINSKI (Tech. Phys. U.S.S.R., 1936, 3, 223—228).—An apparatus for measuring pressures of  $10^{-4}$ —approx.  $2 \times 10^{-3}$  mm. by means of the impulse frequency of a thyratron is described. The frequency is a linear function of the pressure. R. S. B.

**Reaction vessels of variable capacity.** L. RAMBERG (Z. physikal. Chem., 1936, 176, 289—294).—These consist of two flat-bottomed glass tubes sliding one within the other. R. C.



Combustion experiment. S. C. BLACKTIN (Chem. and Ind., 1936, 402—403). D. K. M.

Weights and balances in ancient Egypt. ANON (Nature, 1936, 137, 890—892). L. S. T.

Thirty years of chromatography. L. ZECHMEISTER and L. VON CHOLNOKY (Monatsh., 1936, 68, 68—80).—A historical and descriptive summary. F. L. U.

## Geochemistry.

Temperatures and constituents of the upper atmosphere. D. F. MARTYN and O. O. PULLY (Proc. Roy. Soc., 1936, A, 154, 455—486; cf. Proc. Phys. Soc., 1935, 47, 340).—Temp. between the *E'* and *F* regions of the ionosphere are found, from consideration of the electron collision frequencies, to reach vals. of the order 1000° abs., both in summer and in winter daytime. Considerable cooling of the upper atm. occurs during the night, and from the observed rate of cooling it is found that an average concn. of 1 part in 6000 by vol. of H<sub>2</sub>O vapour is present in the ionosphere. The high temp. found are attributed mainly to the absorption of solar ultra-violet energy by O<sub>3</sub>. The attachment of electrons to neutral particles is the chief process by which free electrons are renewed from the ionised regions. L. L. B.

Abalach soda lake in Jakutia. A. D. EGOROV and V. I. NIKOLAEV (J. Appl. Chem. Russ., 1936, 9, 665—669).—The H<sub>2</sub>O contains Na<sub>2</sub>CO<sub>3</sub> 3.46, NaHCO<sub>3</sub> 2.20, and NaCl 3.22%. It can be exploited by pumping out the H<sub>2</sub>O before the ice melts in the spring, and further concn. by a combination of freezing and evaporation. R. T.

Can the difference in density between sea- and fresh water be accounted for by fractional distillation of the isotopic forms of water? K. NEUMANN and G. TOHMFOR (Z. physikal. Chem., 1936, 176, 226—228).—It is calc. that the *d* of sea-H<sub>2</sub>O will exceed that of the first fraction on isothermal distillation at 20°, which may be regarded as equiv. to fresh H<sub>2</sub>O, by  $4.3 \times 10^{-6}$ . A *d* difference of  $2.9 \times 10^{-6}$  between sea- and fresh H<sub>2</sub>O has been observed experimentally (cf. A., 1935, 600). R. C.

Heavy metals in mineral waters. II. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1935, 6, 217—234).—Natural H<sub>2</sub>O containing U or its degradation products is characteristic of the earlier, and those containing Co and Ni of the later, Archean folding. R. T.

Conductivity of mineral waters. II. Mineral water of Rogaska Slatina. P. S. TUTUNDZIC (Bull. Soc. Chim. Yougoslav., 1935, 6, 205—215).—Conductivity and other data are recorded. R. T.

Arsenic, nickel, cobalt, silver, bismuth, and uranium ores in calcite veins in the Riesengebirge. K. HOEHNE (Chem. Erde, 1936, 10, 432—474).—Chemical analyses of the ores from different veins in the Bergfreiheit mine at Oberschmiedeberg in Silesia are given, and the several minerals present are identified in polished sections. L. J. S.

Nature of the calcium content of Thuringian iron ores. J. HOLZNER (Chem. Erde, 1936, 10, 409—431).—Analyses of different fractions of two oolitic ores from Schmiedefeld show that the chloritic

mineral is thuringite. Ca is present as a silicate with the approx. formula Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>, seen in micro-sections as a colourless (orthorhombic?) granular aggregate, which cannot be identified with any known mineral species. P is present mainly as Fe phosphate. L. J. S.

Metamorphosed Devonian phyllites in the Altvatergebirge. R. FABIAN (Chem. Erde, 1936, 10, 343—408; Diss., Breslau, 1936).—Geological and petrographical description with chemical analyses of the rocks. L. J. S.

Formation of kaolin and alumina from granite and gneiss. F. W. FREISE (Chem. Erde, 1936, 10, 311—342).—The weathering of granite and gneiss in Brazil by the action of CO<sub>2</sub> and humic acids gives rise to both kaolin and bauxite or laterite. The action of CO<sub>2</sub> and formic, lactic, and acetic acids on these materials was examined. L. J. S.

Petrological classification of the basic intrusives of Danta state (H. Gujrat). N. L. SHARMA and N. C. NANDY (Proc. Indian Acad. Sci., 1936, 3, B, 366—376). A. G. P.

New synthesis of langbeinite, vanthoffite, and polyhalite. K. H. IDE (Kali, 1935, 29, 83—86, 93—96, 103—105; Chem. Zentr., 1935, ii, 1522—1523).—K, Na, and Ca sulphates react in the solid state with MgSO<sub>4</sub> at temp. < 80°, giving langbeinite, vanthoffite, and polyhalite, respectively, in amounts recognisable by X-ray methods. The reaction is promoted by compressing the mixture. KCl similarly reacts with MgSO<sub>4</sub>, giving either langbeinite or anhydrokainite, but formation of glauberite or glaserite was not detected. J. S. A.

Geochemistry of selenium. II. V. M. GOLDSCHMIDT and L. W. STROCK (Nachr. Ges. Wiss. Gottingen, 1935, [ii], 1, 123—142; Chem. Zentr., 1935, ii, 1522; cf. A., 1934, 53).—The S:Se ratio in meteorites, deep-seated basic rocks, sulphide and arsenide ores, sedimentary rocks, and marine and lacustrine salt deposits is discussed. Pneumatolytic and high hydrothermal sulphides and arsenides contain relatively more Se than the deeper-seated ores. An enrichment of Se is found with Cu in sulphide ore deposits, and with Fe and Mn in oxidic sediments, but FeS<sub>2</sub> from sedimentary rocks is very poor in Se. J. S. A.

Selenium content of European and Japanese slates. E. MINAMI (Nachr. Ges. Wiss. Gottingen, 1935, [ii], 1, 143—145; Chem. Zentr., 1935, ii, 1522).—Data are recorded. J. S. A.

Occurrence of selenium in natural phosphates, superphosphates, and phosphoric acid.—See B., 1936, 493.



**Native blue rock-salt. IV. Rate of growth and colour.** K. PRZIBRAM (Sitzungsber. Akad. Wiss. Wein, IIa, 1934, 143, 489—497; Chem. Zentr., 1935, ii, 1504).—Blue native NaCl crystals have a deeper blue colour in the portions giving evidence of most rapid growth, and a lighter more violet colour in regions of slower growth. The effect is attributed to lattice distortion, more impurities, causing the inclusion of layer Na particles, being included where growth was rapid. A similar effect is given by artificially coloured crystals. J. S. A.

**Characterisation of nontronite ferrisilicates. Marinsk nontronites.** I. J. MIKEI (Ukrain. Chem. J., 1936, 11, 56—66).—Most of the  $H_2O$  in nontronite (I) is adsorbed on colloidal constituents; the chemically bound  $H_2O$  is eliminated at 550—660°. Adsorption by (I) of different dyes is studied. R. T.

**Disthene (cyanite) from Prilepec in the Selecka mountains.** L. BARIĆ (Z. Krist., 1936, 93, 57—92).—Mineralogical. Different specimens of the mineral are described, and goniometric data, refractive index, double refraction, extinction, pleochroism, twinning, and chemical composition are given in detail. B. W. R.

**Mineralisation of the Virginia titanium deposits.** C. S. ROSS (Amer. Min., 1936, 21, 143—149).—The deposits occur within a rock of the anorthosite type introduced as a mush of crystals. The ores and associated gangue minerals were deposited by invading solutions probably derived from a highly ferromagnesian rock which was a differentiate from the same primary magma as the anorthosite. The outstanding chemical factors of mineralisation are indicated. L. S. T.

**Helium ratios of rocks and minerals from the diamond pipes of South Africa.** A. HOLMES and F. A. PANETH (Proc. Roy. Soc., 1936, A, 154, 385—413).—He ratios have been obtained for 20 specimens of rocks and minerals with the object of determining the relative ages of the inclusions found in kimberlite. The technique of He determination and of U and Th determinations is described. The He ratio of kimberlite, corresponding with an age of  $58 \times 10^6$  years, is consistent with the late Cretaceous age assigned to the diamond pipes. Xenoliths of the amphibolite group, known to be of Pre-Cambrian age, have He ratios of a higher order than kimberlite. Xenoliths of the peridotite suite (including zircons) give low He ratios. The bearing of the results on theories of petrogenesis is discussed. L. L. B.

**Viscosity of molten lavas from Mount Alaghez.** M. P. VOLAROVITSCH, D. M. TOLSTOI, and L. I. KORTSCHEMKIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 333—336).—of basalt, andesite-basalt, andesite, dacite, and alkaline dacite was determined by the rotating-cylinder method. The effect of temp. on  $\eta$  was also determined.  $\eta$  increases with increase of acidity of the rocks. A. J. M.

**Spectrum analysis of blende by pyroelectric concentration.** S. PINA DE RUBIES and J. M. LOPEZ DE AZCONA (Anal. Fis. Quim., 1936, 34, 307—314).—Analysis of blende from Picos de Europa (cf. Llord *et al.*, A., 1911, ii, 733) by the author's

procedure (A., 1934, 1323) reveals the presence of Ni, Co, Mn, Mo (?), Mg, Al, Si, Ca, Na, P, Cr, Ti, V, Ba, and Be. The procedure is more rapid than chemical methods, and avoids the possibility of detecting elements arising from impure reagents. Previous work on the analysis of blends is summarised.

F. R. G.

**Cleavage of ionic minerals.** M. D. SHAPPELL (Amer. Min., 1936, 21, 75—102).—Mineral cleavage is resolved into two components, viz., optical effect and cleavability which is the chief component and for which a quant. expression has been deduced. Application to minerals the constituent atoms of which have inert-gas cores gives good agreement with observation. L. S. T.

**Dickite in Missouri.** W. A. TARR and W. D. KELLER (Amer. Min., 1936, 21, 109—114).—Dickite (I) occurs in three localities near Columbia, Missouri, and in the Pb ores at Flat River, S.E. Missouri. Two of the former localities are limestone quarries in which (I) occurs in chert in association with millerite, chalcopryrite, galena (II), pyrite, and wurtzite. The associated country rock contains sphalerite and barite. (I) from the Pb ores is associated with marcasite and (II), and is a replacement of the dolomite country rock. Optical properties are recorded. L. S. T.

**Crystal form of sternbergite.** M. A. PEACOCK (Amer. Min., 1936, 21, 103—108).—Remeasurement of crystals of sternbergite,  $AgFe_2S_3$ , from Joachimsthal, Bohemia, shows that the classical data are inadequate. The crystals are orthorhombic, dipyramidal with  $a : b : c = 0.5913 : 1 : 0.6250$ . The morphology is similar to that of cubanite,  $CuFe_2S_3$ , but a close systematic relation between the two species has yet to be established. L. S. T.

**Composition of clay substance.** R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1936, 227, 179—183).—Very pure Zettlitz kaolin (I) still contains at least 10% of admixed feldspar and mica which can be converted into kaolin by hydrothermal treatment. The  $H_2O$  content of a specimen of (I) has thus been raised to 1.76 mol. per formula-wt., and the inference drawn by Körner and others (this vol., 50) from the results of isothermal dehydration of (I) is therefore invalid. F. L. U.

**Fluorescent minerals.** M. DERIBERÉ (Ann. Chim. Analyt., 1936, [iii], 18, 117—119).—The characteristic fluorescence of autunite, blende, willemite, chalcocite, celestine, scapolite, calcite, gypsum, aragonite, sodalite, sylvine, fluorite, and rock-salt is described. J. S. A.

**Plagioclase and its determination in pegmatites.** D. BELJANKIN and V. ONISIMO-JANOVSKI (Trans. Res. Inst. Ceram., 1934, No. 43, 10—19).—The occurrence of plagioclase and methods for its microscopic determination in pegmatites are discussed. CH. ABS. (e)

**Dioritic intrusive rocks and contact metamorphism in the Cascade Range in Oregon.** A. F. BUDDINGTON and E. CALLAGHAN (Amer. J. Sci., 1936, [v], 31, 421—449).—Petrographical descriptions and chemical analyses of augite-diorite,



augite-dacite-porphyry, aplite, granite, etc. are given. These rocks are intrusive into volcanic rocks which in places are changed into tourmaline-hornfels.

L. J. S.

**Fluorite in Aberdeenshire and Banffshire.** A. RUSSELL (Min. Mag., 1936, 24, 307—317).—Details are given of the occurrence of fluorite at several localities.

L. J. S.

**Baryte from Manvers Main colliery, Yorkshire.** A. RUSSELL (Min. Mag., 1936, 24, 318—320).—A crystallographic description is given of well-developed crystals from a cavity in sandstone. Analysis by C. P. FINN (1930) gave  $\text{BaSO}_4$  98.50,  $\text{CaSO}_4$  0.65,  $\text{SrSO}_4$  0.18, ignition loss 0.33%.

L. J. S.

**Wulfenite from Cumberland and leadhillite from Kirkcudbrightshire.** A. RUSSELL (Min. Mag., 1936, 24, 321—323).—New occurrences of these rare minerals are noted.

L. J. S.

**Ettringite from Scawt Hill, Co. Antrim.** F. A. BANNISTER [with M. H. HEY and J. D. BERNAL] (Min. Mag., 1936, 24, 324—329).—Minute crystals of ettringite from the larnite-rock in the contact-zone of chalk and dolerite (A., 1934, 1197) have a hexagonal unit cell,  $a$  11.24,  $c$  21.45 Å. ( $c/a$  1.908), containing  $\text{Ca}_{12}\text{Al}_4(\text{OH})_{24}(\text{SO}_4)_6 \cdot 52\text{H}_2\text{O}$ . They are identical with crystals from the original locality (Ettringen, Laacher See, Rhine) and with artificial crystals from Portland cement.  $\omega$  1.4655,  $\epsilon$  1.4618,  $d$  1.772. The space-group is  $D_{2h}^2$ , and a structure of the zeolitic type with  $48\text{H}_2\text{O}$  in channels parallel to the  $c$ -axis is suggested. At 110° 34.4%  $\text{H}_2\text{O}$  is lost and the structure partly collapses, leaving an oriented pseudomorph of cell dimensions  $a$  8.4,  $c$  10.21 Å. and the same space-group.

L. J. S.

**Petrochemistry of granites of Tarpatak Valley of High Tatra.** E. LENGYEL (Fold. Kozlony, 1935, 65, 120—126).—Granitic rocks are characterised by the changeable ratio of the contents of alkali or alkali-lime feldspars. Some granites approach the Si-rich granitic magma in composition.

CH. ABS. (e)

**Phosphatic limestone of the lower Eocene of the East Fergana (Middle Asia).** A. V. PEIYE (Bull. soc. nat. Moscou, Sect. geol., 1933, 11, 385—404).—The most probable explanation is that the phosphates are due to bacterial activity in sea- $\text{H}_2\text{O}$  with a low  $[\text{P}_2\text{O}_5]$ .

CH. ABS. (e)

**Distribution and mineralogical classification of the decomposed pumices in the north-western part of Kwanto district, Japan.** M. HARADA (J. Sci. Soil Manure, 1935, 9, 54—62, 189—201).—Soils from the decomp. of pumice are classified into 4 groups, according to the kind and quantity of hypersthene, augite, hornblende, quartz, and small pieces of lava.

CH. ABS. (e)

**Study of [petroleum] source beds in late Mesozoic rocks on the west side of the Sacramento Valley, California.** P. D. TRASK and H. E. HAMMAR (Bull. Amer. Assoc. Petr. Geol., 1934, 18, 1346—1373).—Analytical data are recorded.

CH. ABS. (e)

**Metamorphism of organic sediments and derived oils.** D. WHITE (Bull. Amer. Assoc. Petr. Geol., 1935, 19, 589—617).—A discussion.

CH. ABS. (e)

**Carbon ratios in part of Arkansas-Oklahoma coal field.** T. A. HENDRICKS (Bull. Amer. Assoc. Petr. Geol., 1935, 19, 937—947).

CH. ABS. (e)

**Highly polymerised compounds. CXXXX.** Development of macro-molecular chemistry. H. STAUDINGER (Ber., 1936, 69, [B], 1168—1185).—Mainly historical. Reply is made to Meyer *et al.* (this vol., 586).

H. W.

**Synthesis of hydrocarbons of the aliphatic series.** A. D. PETROV (Uspechi Chim., 1934, 3, 1050—1077).—A review.

CH. ABS. (r)

**Initial formation of alcohols during slow combustion of methane and ethane.**—See this vol., 801.

**Slow combustion of methane, methyl alcohol, formaldehyde, and formic acid.**—See this vol., 801.

**Catalytic cyclisation of aliphatic hydrocarbons.** B. MOLDAVSKI and H. KAMUSCHER (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 355—359).—Paraffins are cyclised and dehydrogenated to the corresponding aromatic hydrocarbons (% yields in parentheses) by passing them over  $\text{Cr}_2\text{O}_3$  (prep. described) at  $>400^\circ$ . Very little olefine formation occurs, the gaseous products consisting mainly of  $\text{H}_2$  (74—94%) and some  $\text{C}_n\text{H}_{2n}$ . Thus  $n\text{-C}_6\text{H}_{14}$ ,  $n\text{-C}_8\text{H}_{18}$ ,  $n\text{-C}_{10}\text{H}_{22}$ ,  $n\text{-C}_{12}\text{H}_{26}$ ,  $n\text{-C}_{14}\text{H}_{30}$ ,  $n\text{-C}_{16}\text{H}_{34}$ ,  $n\text{-C}_{18}\text{H}_{38}$ ,  $n\text{-C}_{20}\text{H}_{42}$ ,  $n\text{-C}_{22}\text{H}_{46}$ ,  $n\text{-C}_{24}\text{H}_{50}$ ,  $n\text{-C}_{26}\text{H}_{54}$ ,  $n\text{-C}_{28}\text{H}_{58}$ ,  $n\text{-C}_{30}\text{H}_{62}$ ,  $n\text{-C}_{32}\text{H}_{66}$ ,  $n\text{-C}_{34}\text{H}_{70}$ ,  $n\text{-C}_{36}\text{H}_{74}$ ,  $n\text{-C}_{38}\text{H}_{78}$ ,  $n\text{-C}_{40}\text{H}_{82}$ ,  $n\text{-C}_{42}\text{H}_{86}$ ,  $n\text{-C}_{44}\text{H}_{90}$ ,  $n\text{-C}_{46}\text{H}_{94}$ ,  $n\text{-C}_{48}\text{H}_{98}$ ,  $n\text{-C}_{50}\text{H}_{102}$ ,  $n\text{-C}_{52}\text{H}_{106}$ ,  $n\text{-C}_{54}\text{H}_{110}$ ,  $n\text{-C}_{56}\text{H}_{114}$ ,  $n\text{-C}_{58}\text{H}_{118}$ ,  $n\text{-C}_{60}\text{H}_{122}$ ,  $n\text{-C}_{62}\text{H}_{126}$ ,  $n\text{-C}_{64}\text{H}_{130}$ ,  $n\text{-C}_{66}\text{H}_{134}$ ,  $n\text{-C}_{68}\text{H}_{138}$ ,  $n\text{-C}_{70}\text{H}_{142}$ ,  $n\text{-C}_{72}\text{H}_{146}$ ,  $n\text{-C}_{74}\text{H}_{150}$ ,  $n\text{-C}_{76}\text{H}_{154}$ ,  $n\text{-C}_{78}\text{H}_{158}$ ,  $n\text{-C}_{80}\text{H}_{162}$ ,  $n\text{-C}_{82}\text{H}_{166}$ ,  $n\text{-C}_{84}\text{H}_{170}$ ,  $n\text{-C}_{86}\text{H}_{174}$ ,  $n\text{-C}_{88}\text{H}_{178}$ ,  $n\text{-C}_{90}\text{H}_{182}$ ,  $n\text{-C}_{92}\text{H}_{186}$ ,  $n\text{-C}_{94}\text{H}_{190}$ ,  $n\text{-C}_{96}\text{H}_{194}$ ,  $n\text{-C}_{98}\text{H}_{198}$ ,  $n\text{-C}_{100}\text{H}_{202}$ ,  $n\text{-C}_{102}\text{H}_{206}$ ,  $n\text{-C}_{104}\text{H}_{210}$ ,  $n\text{-C}_{106}\text{H}_{214}$ ,  $n\text{-C}_{108}\text{H}_{218}$ ,  $n\text{-C}_{110}\text{H}_{222}$ ,  $n\text{-C}_{112}\text{H}_{226}$ ,  $n\text{-C}_{114}\text{H}_{230}$ ,  $n\text{-C}_{116}\text{H}_{234}$ ,  $n\text{-C}_{118}\text{H}_{238}$ ,  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$n\text{-C}_{714}\text{H}_{1430}$ ,  $n\text{-C}_{716}\text{H}_{1434}$ ,  $n\text{-C}_{718}\text{H}_{1438}$ ,  $n\text{-C}_{720}\text{H}_{1442}$ ,  $n\text{-C}_{722}\text{H}_{1446}$ ,  $n\text{-C}_{724}\text{H}_{1450}$ ,  $n\text{-C}_{726}\text{H}_{1454}$ ,  $n\text{-C}_{728}\text{H}_{1458}$ ,  $n\text{-C}_{730}\text{H}_{1462}$ ,  $n\text{-C}_{732}\text{H}_{1466}$ ,  $n\text{-C}_{734}\text{H}_{1470}$ ,  $n\text{-C}_{736}\text{H}_{1474}$ ,  $n\text{-C}_{738}\text{H}_{1478}$ ,  $n\text{-C}_{740}\text{H}_{1482}$ ,  $n\text{-C}_{742}\text{H}_{1486}$ ,  $n\text{-C}_{744}\text{H}_{1490}$ ,  $n\text{-C}_{746}\text{H}_{1494}$ ,  $n\text{-C}_{748}\text{H}_{1498}$ ,  $n\text{-C}_{750}\text{H}_{1502}$ ,  $n\text{-C}_{752}\text{H}_{1506}$ ,  $n\text{-C}_{754}\text{H}_{1510}$ ,  $n\text{-C}_{756}\text{H}_{1514}$ ,  $n\text{-C}_{758}\text{H}_{1518}$ ,  $n\text{-C}_{760}\text{H}_{1522}$ ,  $n\text{-C}_{762}\text{H}_{1526}$ ,  $n\text{-C}_{764}\text{H}_{1530}$ ,  $n\text{-C}_{766}\text{H}_{1534}$ ,  $n\text{-C}_{768}\text{H}_{1538}$ ,  $n\text{-C}_{770}\text{H}_{1542}$ ,  $n\text{-C}_{772}\text{H}_{1546}$ ,  $n\text{-C}_{774}\text{H}_{1550}$ ,  $n\text{-C}_{776}\text{H}_{1554}$ ,  $n\text{-C}_{778}\text{H}_{1558}$ ,  $n\text{-C}_{780}\text{H}_{1562}$ ,  $n\text{-C}_{782}\text{H}_{1566}$ ,  $n\text{-C}_{784}\text{H}_{1570}$ ,  $n\text{-C}_{786}\text{H}_{1574}$ ,  $n\text{-C}_{788}\text{H}_{1578}$ ,  $n\text{-C}_{790}\text{H}_{1582}$ ,  $n\text{-C}_{792}\text{H}_{1586}$ ,  $n\text{-C}_{794}\text{H}_{1590}$ ,  $n\text{-C}_{796}\text{H}_{1594}$ ,  $n\text{-C}_{798}\text{H}_{1598}$ ,  $n\text{-C}_{800}\text{H}_{1602}$ ,  $n\text{-C}_{802}\text{H}_{1606}$ ,  $n\text{-C}_{804}\text{H}_{1610}$ ,  $n\text{-C}_{806}\text{H}_{1614}$ ,  $n\text{-C}_{808}\text{H}_{1618}$ ,  $n\text{-C}_{810}\text{H}_{1622}$ ,  $n\text{-C}_{812}\text{H}_{1626}$ ,  $n\text{-C}_{814}\text{H}_{1630}$ ,  $n\text{-C}_{816}\text{H}_{1634}$ ,  $n\text{-C}_{818}\text{H}_{1638}$ ,  $n\text{-C}_{820}\text{H}_{1642}$ ,  $n\text{-C}_{822}\text{H}_{1646}$ ,  $n\text{-C}_{824}\text{H}_{1650}$ ,  $n\text{-C}_{826}\text{H}_{1654}$ ,  $n\text{-C}_{828}\text{H}_{1658}$ ,  $n\text{-C}_{830}\text{H}_{1662}$ ,  $n\text{-C}_{832}\text{H}_{1666}$ ,  $n\text{-C}_{834}\text{H}_{1670}$ ,  $n\text{-C}_{836}\text{H}_{1674}$ ,  $n\text{-C}_{838}\text{H}_{1678}$ ,  $n\text{-C}_{840}\text{H}_{1682}$ ,  $n\text{-C}_{842}\text{H}_{1686}$ ,  $n\text{-C}_{844}\text{H}_{1690}$ ,  $n\text{-C}_{846}\text{H}_{1694}$ ,  $n\text{-C}_{848}\text{H}_{1698}$ ,  $n\text{-C}_{850}\text{H}_{1702}$ ,  $n\text{-C}_{852}\text{H}_{1706}$ ,  $n\text{-C}_{854}\text{H}_{1710}$ ,  $n\text{-C}_{856}\text{H}_{1714}$ ,  $n\text{-C}_{858}\text{H}_{1718}$ ,  $n\text{-C}_{860}\text{H}_{1722}$ ,  $n\text{-C}_{862}\text{H}_{1726}$ ,  $n\text{-C}_{864}\text{H}_{1730}</$



to isobutene was obtained. In all pyrolyses liquid products and C were formed in varying amounts. The severe conditions of pyrolysis completely masked the primary products because of extensive decomp., but experimental data and theoretical considerations indicate that the decomp. of olefines is preceded by polymerisation and that the gaseous products are produced by secondary reaction.

H. C. M.

**Catalytic hydration of olefines. II. Hydration of propylene over liquid catalysts at atmospheric pressure.** E. K. REMIZ (J. Appl. Chem. Russ., 1936, 9, 703—710).— $\text{Pr}^{\beta}\text{OH}$  is obtained in 21% yield from  $\text{CH}_2\text{:CHMe}$ , in presence of 54%  $\text{H}_2\text{SO}_4$  containing 3% of  $\text{Ag}_2\text{SO}_4$ , at  $110^\circ$ . Apparatus for the continuous production of  $\text{Pr}^{\beta}\text{OH}$  by the above method is described.

R. T.

**Polymerisation of propylene. Catalytic action of zinc chloride.** O. L. BRANDES, W. A. GRUSE, and A. LOWY (Ind. Eng. Chem., 1936, 28, 554—559).—The formation of liquid polymerides when  $\text{C}_3\text{H}_6$  is heated in presence of  $\text{ZnCl}_2$  depends on the pressure, temp., and duration of reaction. A max. yield of 81.5% is obtained at  $260\text{--}270^\circ$  and 3225 lb. per sq. in. during 75 min.; very little reaction occurs in the absence of  $\text{ZnCl}_2$ . At lower temp., the fraction of b.p.  $< 200^\circ$  increases (up to 92% of the total liquid), the tripolymeride being the main product together with smaller amounts of  $\text{C}_{10\text{--}12}$  hydrocarbons. The product obtained at  $290\text{--}310^\circ$  contains considerable amounts of  $\text{C}_{5\text{--}12}$  hydrocarbons, principally olefines and paraffins. The presence of naphthalenes is suspected.

J. L. D.

**Kinetics of *cis-trans* isomerisations.**—See this vol., 802.

**Preparation and physical constants of  $\beta$ -methyl- $\Delta^{\alpha}$ -butene.** M. L. SHERRILL and G. F. WALTER (J. Amer. Chem. Soc., 1936, 58, 742—745).— $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{OEt}$  and  $\text{MgMeCl}$  give  $\beta$ -ethoxypropyl bromide, b.p.  $28.6\text{--}28.8^\circ/10$  mm.,  $138\text{--}138.1^\circ/760$  mm., converted by a large excess of  $\text{KOH}$  at  $110\text{--}150^\circ$  into  $\text{CH}_2\text{:CMe}\cdot\text{OEt}$ , b.p.  $61.2\text{--}61.8^\circ/760$  mm. Successive treatment of this with  $\text{Br}$  and  $\text{MgEtBr}$  in  $\text{Et}_2\text{O}$  affords  $\beta$ -ethoxy- $\beta$ -methylbutyl bromide, b.p.  $53.4\text{--}53.6^\circ/9.5$  mm., which with  $\text{Zn}$  dust +  $\text{Zn}\cdot\text{Cu}$  in 95%  $\text{EtOH}$  affords  $\beta$ -methyl- $\Delta^{\alpha}$ -butene (I), b.p.  $31.05\pm 0.05^\circ/760$  mm. (dibromide, b.p.  $47.4\text{--}48^\circ/8.5\text{--}9$  mm.). The ultra-violet absorption spectra of (I),  $\text{CHMe:CMe}_2$ , and  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -pentene are given. Physical data for these hydrocarbons and  $\text{CH}_2\text{:CHPr}^{\beta}$  are recorded.

H. B.

**Raman spectra of  $\beta$ -methyl- $\Delta^{\alpha}$ - and - $\Delta^{\beta}$ -butene.** D. D. THOMPSON and M. L. SHERRILL (J. Amer. Chem. Soc., 1936, 58, 745—747; cf. Bourguet and Piaux, A., 1932, 1189).—Comparison of the spectra of  $\beta$ -methyl- $\Delta^{\alpha}$ -butene (I) and the low (A) and high (B) fractions of the hydrocarbon obtained by dehydration of *tert.*-amyl alcohol shows that (B) is practically pure  $\beta$ -methyl- $\Delta^{\beta}$ -butene (II) whilst (A) is a mixture of (I) and (II).

H. B.

**Fission and isomerisation of olefines involving a tertiary radical.** I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 329—332).—The following are prepared from  $\text{MgRX}$  and the appropriate

ketone:  $\text{CMePr}^{\beta}\text{Bu}\cdot\text{OH}$  (Whitmore *et al.*, A., 1933, 1140),  $\beta\beta\delta$ -trimethyl- $\gamma$ -ethyl-*n*-pentan- $\gamma$ -ol, b.p.  $188\text{--}191^\circ$ ,  $\beta\beta\gamma$ -trimethyl-*n*-hexan- $\gamma$ -ol, b.p.  $170\text{--}172^\circ$ ,  $\gamma$ -*tert.*-butyl-*n*-pentan- $\gamma$ -ol, b.p.  $172\text{--}175^\circ$   $\text{CMeEtBu}\cdot\text{OH}$ , and  $\text{CMe}_2\text{Bu}\cdot\text{OH}$ . They are converted by dehydration ( $2\cdot\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$  or I), respectively, into  $\text{CPr}^{\beta}\text{Bu}\cdot\text{CH}_2$  (I),  $\delta\delta$ -dimethyl- $\gamma$ -isopropyl- $\Delta^{\beta}$ -pentene (II), b.p.  $153\text{--}158^\circ$ ,  $\beta\beta\gamma$ -trimethyl- $\Delta^{\gamma}$ -hexene (III), b.p.  $130\text{--}132^\circ$ ,  $\gamma$ -*tert.*-butyl- $\Delta^{\gamma}$ -pentene (IV), b.p.  $124\text{--}132^\circ$ ,  $\text{CMeBu}\cdot\text{CHMe}$  (V), and  $\text{CMeBu}\cdot\text{CH}_2$  (VI). Fission of (I) with  $1:4\cdot\text{C}_{10}\text{H}_6\text{Br}\cdot\text{SO}_3\text{H}$  at  $130^\circ$  affords  $\text{CMe}_2\cdot\text{CH}_2$  and  $\text{CHMe:CMe}_2$ ; (II) similarly gives  $\text{CMe}_2\cdot\text{CH}_2$ ,  $\text{CHMe:CHPr}^{\beta}$ , and  $\text{CHEt:CMe}_2$ , the assumed mechanism being the isomerisation of a liberated substituted vinyl radical. (III)–(VI) do not undergo fission.

J. W. B.

**Condensation of acetylene and acetic acid.**—See this vol., 807.

**Preparation of dialkylacetylenes from acetylenic Grignard reagents and alkyl sulphates.** S. D. THORN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 796—797).— $\text{CMe}\cdot\text{CAlk}$  and  $\text{CEt}\cdot\text{CAlk}$  are prepared in good yield from  $\text{CAlk}\cdot\text{C}\cdot\text{MgBr}$  (I) (1 mol.) and  $\text{Me}_2\text{SO}_4$  and  $\text{Et}_2\text{SO}_4$  (2 mols.), respectively. The following are described: methyl-butyl-, b.p.  $110\text{--}111^\circ/747$  mm., and -hexyl-, b.p.  $155\text{--}156^\circ/747$  mm.; ethyl-butyl-, b.p.  $129\text{--}130^\circ/747$  mm., -amyl-, b.p.  $153\text{--}155^\circ/745$  mm., and -vinyl-, b.p.  $83^\circ/747$  mm., -acetylenes. (I) do not react with alkyl halides; reaction could not be catalysed by various metals and/or their salts.

H. B.

**Raman spectra of solid ethylene halides.**—See this vol., 776.

**Photochemical formation of ethylene iodide.**—See this vol., 688.

**Decomposition of ethylene oxide.**—See this vol., 802.

**Preparation of  $\alpha$ -chloro- $\gamma$ -bromopropane, and the velocity of addition of hydrogen bromide to allyl chloride.** M. S. SCHOSTAKOVSKI (J. Appl. Chem. Russ., 1936, 9, 681—683).— $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  (I) and  $\text{CHMeCl}\cdot\text{CH}_2\text{Br}$  are obtained in equal amount from  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl}$  and  $\text{HBr}$  at  $0^\circ$ ; at  $-19^\circ/1.5\text{--}2$  atm. (I) alone is obtained, in 90% yield.

R. T.

**Substitution and inversion of configuration.**—See this vol., 803.

**Catalytic esterification of alcohols.**—See this vol., 806.

**Exchange reactions between heavy water and hydrogen compounds.** E. OGAWA (Bull. Chem. Soc. Japan, 1936, 11, 310—320).—A substance, RH, is dissolved in  $\text{H}_2\text{O}$  containing 49 mol.-% of  $\text{D}_2\text{O}$ , allowed to come to equilibrium (some RD formed), distilled, and the *d* of the distillate measured. Thus are calc.  $K_m = [\text{RD}][\text{H}_2\text{O}]/[\text{RH}][\text{HDO}]$ .  $K_m$  are 10—16% too high owing to fractionation and further reaction during distillation. Determinations with 24 substances give the following  $K_m$  at  $100^\circ$ : OH (alcoholic) 1.55 or 0.72 (1.19 at  $50^\circ$ ),  $(\text{NH}_2\text{OH}, \text{HCl})$  0.8,  $(\text{H}_3\text{BO}_3)$  0.46,  $(\text{H}_3\text{PO}_4)$  0.34; NH  $(\text{NH}_4\text{Cl})$  0.52



(0.45 at 50°),  $[\text{CO}(\text{NH}_2)_2]$  0.50 (0.71 at 50°);  $\text{CO}_2\text{H}$  ( $\text{H}_2\text{C}_2\text{O}_4$ ) 0.51 (0.62 at 50°), (succinic) 0.42, (maleic) 0.66, ( $\text{NaHC}_2\text{O}_4$ ) 0.91, ( $\text{Na H succinate}$ ) 0.4;  $\text{HSO}_4'$  0.1;  $\text{OH}'$  ( $\text{NaOH}$ ) 0.2.  $K_m$  gives a measure of the differences of zero point energies or of the chemical binding forces of RH and RD. The results do not favour co-ordination between OH and  $\text{CO}_2\text{H}$  of OH-acids nor the usual betaine formula of  $\text{NH}_2$ -acids.

R. S. C.

**Catalytic properties of rhenium. II. Dehydrogenation of the propyl alcohols.** M. S. PLATONOV, S. B. ANISSIMOV, and V. M. KRASCHE-NINNIKOVA (Ber., 1936, 69, [B], 1050—1053; cf. A., 1935, 830).—Dehydrogenation of  $\text{Pr}^\alpha\text{OH}$  is effected as efficiently by Re at 400° as by an equal column of Cu at 300°. Re causes only very slight decomp. of the  $\text{EtCHO}$  produced and does not dehydrate  $\text{Pr}^\alpha\text{OH}$ . The formation of solid or liquid by-products could not be detected. The catalyst retains its activity well.  $\text{Pr}^\beta\text{OH}$  is more efficiently dehydrogenated to  $\text{COMe}_2$  by Re than by Cu and only slight decomp. of  $\text{COMe}_2$  is observed at > 500°.

H. W.

**Isomeric forms of the optically active  $\alpha\gamma$ -dimethylallyl alcohols [ $\Delta^7$ -penten- $\beta$ -ols].** H. W. J. HILLS, J. KENYON, and H. PHILLIPS (J.C.S., 1936, 576—583).—The H phthalate, m.p. 90—90.5°, of *dl*- $\text{CHMe}:\text{CH}:\text{CHMe}:\text{OH}$  gives the brucine salt, m.p. 169—169.5°,  $[\alpha]_{5461}^{20} -15.2^\circ$  in EtOH, and thence the H ester (I), m.p. 82—84°,  $[\alpha]_{5893}^{20} +38.75^\circ$  in  $\text{Et}_2\text{O}$ , of the (+)-alcohol (II); the mother-liquors give the brucine salt, m.p. 157—159°, and thence the H phthalate (III), m.p. 82—84°,  $[\alpha]_{5893}^{20} -24.1^\circ$  in  $\text{CHCl}_3$ , of the (—)-alcohol (IV). Hydrolysis of (I) and (III) gives (II) and (IV) of varying  $\alpha$ .  $[\alpha]$  of (III) is recorded in 7 solvents; (III) is usually dextrorotatory, about  $[\alpha]_{5461}^{20} +0.84^\circ$ , but  $\alpha$  changes with time often to negative;  $[\alpha]$  also has a very high temp. coeff., changing to negative at about 30—40°. (IV) behaves similarly when kept,  $\alpha$  often decreasing numerically. The changes with time are very erratic and could not be controlled. The optical behaviour of the esters and ethers is, however, quite normal; the following are prepared from (II): *formate*, b.p. 122—123°,  $[\alpha]_{5461}^{20} -72.8^\circ$ ; *acetate*, b.p. 136—137°,  $[\alpha]_{5461}^{20} -76.1^\circ$ ; *benzoate*, b.p. 126°/13 mm.,  $[\alpha]_{5461}^{20} +26.5^\circ$ ; *o-*, b.p. 124—125°/0.1 mm.,  $[\alpha]_{5461}^{20} +29.9^\circ$ , *m-*, b.p. 126—127°/0.1 mm.,  $[\alpha]_{5461}^{20} +27^\circ$ , and *p-nitrobenzoate*, m.p. 48°,  $[\alpha]_{5461}^{20} +57.3^\circ$  in  $\text{H}_2\text{O}$ ; *Me* (by MeI on the K salt in  $\text{Et}_2\text{O}$ ), b.p. 90°,  $[\alpha]_{5461}^{20} -56^\circ$ , *Bu*, b.p. 149—150°,  $[\alpha]_{5461}^{20} -30.4^\circ$ , and *CH}\_2\text{Ph ether}*, b.p. 107°/11 mm.,  $[\alpha]_{5461}^{20} -145.6^\circ$ . (IV) with  $\text{MeOH}-\text{H}_2\text{SO}_4$  gives a *Me ether*, b.p. 90—91°,  $[\alpha]_{5461}^{20} -1^\circ$ , but with  $\text{Bu}^\alpha\text{OH}-\text{H}_2\text{SO}_4$  the *dl-Bu* ether, b.p. 150—151°. The parachor of (II), (IV), and the *dl*-alcohol varies, but is always very low;  $\text{CH}_2:\text{CH}:\text{CH}(\text{Et})\text{OH}$ ,  $\text{CH}_2:\text{CH}:\text{CH}(\text{Bu}^\alpha)\text{OH}$ , and  $\text{CHPh}:\text{CH}:\text{CH}_2\text{OH}$  also have very low parachors, but that of  $\text{CH}_2:\text{CH}:\text{CH}_2\text{OH}$  is normal. The above and some other abnormalities are mostly explained by assuming that (II), (IV), etc. are in equilibrium with large but varying amounts of the cyclic form,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CHMe}$  (or its analogues). This, however, does not explain many other facts, notably that

(II) gives esters of normal, or almost normal,  $[\alpha]$  after "mutarotation" has occurred. *Cis-trans* isomerism explains only a few of the abnormalities. Hydrogenation ( $\text{PtO}_2$ ) of (II) in  $\text{Et}_2\text{O}$  affords (+)-pentan- $\beta$ -ol, b.p. 118—119° (H phthalate, m.p. 34°,  $[\alpha]_{5893}^{20} +35.9^\circ$  in  $\text{CHCl}_3$ ). (II) gave a (—)-chloride, b.p. 20°/13 mm., which with  $\text{CaCO}_3$  in  $\text{H}_2\text{O}$  gives a (—)-alcohol, but it is impossible to state whether this is related to (II) or to (IV).

R. S. C.

**Dehydration of dimethylcyclobutylcarbinol.** B. A. KASANSKI (Ber., 1936, 69, [B], 950—954).—Dimethylcyclobutylcarbinol, from Et cyclobutylcarboxylate or acetylcyclobutane (I) and  $\text{MgMeI}$ , is dissolved in decahydronaphthalene and treated successively with K,  $\text{CS}_2$ , and MeI and the solution is heated. The product contains isopropylidenecyclobutane (oxidised to  $\text{COMe}_2$ ),  $\alpha$ -methylvinylcyclobutane [oxidised to (I)], a glycol, and possibly succinic acid. Catalytic hydrogenation of the mixture affords isopropylcyclobutane, b.p. 90.5—91.5°/750 mm.

H. W.

**Secondary acyclic alcohols with seven to ten carbon atoms.** M. TUOT (Compt. rend., 1936, 202, 1339—1340).—The appropriate aldehydes (prep. from the alcohols by Cu reduced very slowly at 250—265°) and Grignard reagents give 60—85% yields of heptan- $\delta$ -ol, b.p. 70°/25 mm.,  $\beta$ -methylhexan- $\epsilon$ -ol, b.p. 74°/28 mm., octan- $\delta$ -ol, b.p. 81°/17 mm.,  $\beta$ -methylheptan- $\gamma$ -ol, b.p. 73°/19 mm.,  $\beta\epsilon$ -dimethylhexan- $\gamma$ -ol, b.p. 64°/15 mm., nonan- $\gamma$ -ol, b.p. 93°/18 mm.,  $\beta$ -methyloctan- $\delta$ -, b.p. 91°/23 mm., and  $\epsilon$ -ol, b.p. 79°/15 mm.,  $\beta\zeta$ -dimethylheptan- $\gamma$ -, b.p. 88°/25 mm., and  $\delta$ -ol, b.p. 79°/15 mm., and  $\beta\eta$ -dimethyloctan- $\delta$ -ol, b.p. 96°/18 mm. Other physical data are given.

R. S. C.

**Reaction of etherates of tin and titanium tetrachloride. I. Action of thionyl chloride on the etherates.** J. L. GOLDFARB and L. M. SMORGONSKI (Ber., 1936, 69, [B], 1036—1039).— $\text{SnCl}_4$  or  $\text{TiCl}_4$  is added to a mixture of the ether and  $\text{SOCl}_2$  at 0° followed by warming on the water-bath.  $\text{Et}_2\text{O}$  affords  $\text{EtCl}$  (1.5 mols.), reaction proceeding:  $\text{Et}_2\text{O} + \text{SOCl}_2 \rightarrow \text{EtCl} + \text{OEt} \cdot \text{SOCl}$  (I) and (I)  $\rightarrow \text{EtCl} + \text{SO}_2$ . Diisooamyl ether yields  $\text{C}_5\text{H}_{11}\text{Cl}$ , but side reactions cause evolution of HCl and production of a substance containing S.  $\text{CH}_2\text{Ph} \cdot \text{OEt}$  gives EtCl, much HCl, and an amorphous substance devoid of S or Cl.  $\text{PhOEt}$  yields  $\text{SO}_2$ , much HCl, EtCl, and a material containing S which is sol. in alkali.  $\text{Et}_2\text{O}$  and  $\text{S}_2\text{Cl}_2$  afford EtCl,  $\text{SO}_2$ , and S.

H. W.

**Thermal decomposition of ethylene oxide.** H. W. THOMPSON and M. MEISSNER (Nature, 1936, 137, 870—871).—Results of a more detailed investigation (cf. A., 1929, 1243) are summarised. Over the range 435—505°, CO and  $\text{CH}_4$  are the main products of the reaction, but  $\text{H}_2$  and  $\text{C}_2\text{H}_6$  are also formed. The variation of  $k$  with pressure indicates that the reaction involves the superposition of several independent quasi-unimol. processes. The existence of appreciably long reaction chains is improbable.

L. S. T.

**Dioxan series. III. Use of zinc and cadmium chlorides in Grignard synthesis of alkyl-substituted dioxans.** R. K. SUMMERBELL and L. N. BAUER (J. Amer. Chem. Soc., 1936, 58, 759—761).—

Improved yields of 2:3-dialkyldioxans (cf. this vol., 341) are obtained from 2:3-dichlorodioxan (I) and MgAlkBr when the latter is first treated with 1 mol. of anhyd.  $\text{ZnCl}_2$  or  $\text{CdCl}_2$  and the  $\text{Et}_2\text{O}$  replaced by PhMe. The following are described: 2:3-dimethyl- (? 2 forms), b.p. 127.7—129.7/750.8 mm. and 132.2—132.7°/750.8 mm., 2:3-diethyl-, b.p. 166.5—168.5°/739 mm., 2:3-di-n-propyl-, b.p. 87°/12 mm., 202—205°/744 mm., 2:3-di-n-butyl-, b.p. 129—130°/22 mm., 238—240°/744 mm., and 2:3-diallyl-, b.p. 90.2—90.7°/16 mm., -dioxans. The gases evolved in the reaction of (I) with  $\text{Et}_2\text{O}$ -MgMeBr are  $\text{CH}_4$  (5.4%),  $\text{C}_2\text{H}_6$  (94%), and  $\text{C}_2\text{H}_4$  (0.6%). H. B.

Effect of propyl alcohol on hydrolysis of sulphuric acid esters.—See this vol., 804.

Action of molybdic acid on laevorotatory  $\alpha$ -glycerophosphoric acid. P. FLEURY (J. Pharm. Chim., 1936, [viii], 23, 541—545).—The laevorotation of  $\alpha$ -glycerophosphoric acid depends on the  $p_{\text{H}}$ ; it is max. at  $p_{\text{H}}$  8.0. In presence of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , the rotation becomes positive, with a max. at  $p_{\text{H}}$  4.3—4.5, at which acidity glycerophosphomolybdates are most stable (cf. A., 1932, 143). E. W. W.

Esters of thiosulphurous acid  $\text{S}_2(\text{OR})_2$ . A. MEUWSEN (Ber., 1936, 69, [B], 935—937; cf. A., 1935, 326).—In agreement with Stamm (A., 1935, 729) the greenish-yellow series of esters is regarded as non-existent, but isomerides  $\text{OR}\cdot\text{S}\cdot\text{S}\cdot\text{OR}$  and  $\text{R}\cdot\text{SO}\cdot\text{SR}$  exist. The production of colourless  $\text{S}_2(\text{OEt})_2$  from  $\text{S}_2\text{Cl}_2$  necessitates the use of an excess of NaOEt.  $\text{S}(\text{OEt})_2$  is stable towards air and  $\text{SeO}_2$  at room temp., whereas  $\text{NO}_2$ ,  $\text{O}_3$ , or  $\text{H}_2\text{O}_2$  causes separation of S. MgEtBr causes production of a little  $\text{Et}_2\text{S}_2$  without separation of S. Hydrolysis by cold  $N\text{-KOH}$ -MeOH produces S and  $\text{K}_2\text{S}_2\text{O}_3$ . Thermal decomp. probably occurs thus:  $\text{S}_2(\text{OEt})_2 \rightarrow \text{H}_2\text{S} + \text{S} + \text{EtOAc}$ . H. W.

Sulphur monoxide diethylacetal,  $\text{S}(\text{OEt})_2$  [ethyl sulphoxylate]. A. MEUWSEN and H. GEHARDT (Ber., 1936, 69, [B], 937—946).—Catalytic decomp. of  $\text{S}_2(\text{OEt})_2$  by NaOEt in EtOH affords *Et*<sub>2</sub> sulphoxylate,  $\text{S}(\text{OEt})_2$ , b.p. 35°/32 mm., 117°/733 mm., readily autoxidised at room temp. to  $\text{Et}_2\text{SO}_3$ , also obtained by use of  $\text{NO}_2$  in abs.  $\text{Et}_2\text{O}$ ,  $\text{KMnO}_4$  in  $\text{COMe}_2$ , or  $\text{SeO}_2$ ; even  $\text{O}_3$  does not produce  $\text{Et}_2\text{SO}_3$ . Hydrolysis by  $\text{KOH}$ -MeOH proceeds mainly thus:  $2\text{S}(\text{OEt})_2 + 3\text{KOH} = \text{K}_2\text{S}_2\text{O}_3 + 3\text{EtOH} + \text{KOEt}$ , small amounts of  $\text{K}_2\text{S}$  and  $\text{K}_2\text{SO}_3$  being also produced. With  $\text{Cu}_2\text{O}$  at 110°  $\text{S}(\text{OEt})_2$  affords a mixture of oxides and sulphides of Cu with some MeCHO. In a sealed tube at 130°  $\text{S}(\text{OEt})_2$  becomes carbonised with production of S and  $\text{SO}_2$ . For comparison, Mg ethylsulphinate, from  $\text{SO}_2$  and MgEtBr in  $\text{Et}_2\text{O}$ , is transformed by HCl in light petroleum of low b.p. into ethylsulphinic acid, which with cold  $\text{SOCl}_2$  affords ethylsulphinyll chloride, b.p. 53°/15—16 mm. This with cold EtOH gives *Et* ethylsulphinate, b.p. 60°/13—14 mm., which is not autoxidisable, does not yield Se with  $\text{SeO}_2$ , and converts  $\text{KMnO}_4$  into  $\text{MnO}_2$  without apparent stoichiometric relationship. It is hydrolysed to *K* ethylsulphinate. H. W.

Esters of titanium. J. S. JENNINGS, W. WARDLAW, and W. J. R. WAY (J.C.S., 1936, 637—640).—

$\text{TiCl}_4$  with NaOMe-MeOH or NaOEt-EtOH, but not with the alcohol alone (cf.  $\text{SiCl}_4$ ), gives  $\text{Ti}(\text{OMe})_4$ , sublimes at 300°/18 mm., and  $\text{Ti}(\text{OEt})_4$ , b. p. 142°/18 mm.  $\text{TiCl}_4$  and dry MeOH give dimethoxydichlorotitanium, + MeOH, a solid.  $\text{Ti}(\text{OEt})_4$  and AcCl at 70—80° yield triethoxychlorotitanium, anhyd., b.p. 176°/18 mm., and + EtOH, cryst., unaffected by HCl, which with AcCl gives diethoxydichlorotitanium, anhyd., b.p. 142°/18 mm., + MeOH and + EtOH, cryst., also obtained from  $\text{TiCl}_4$  and EtOH at 80—100° and by the method of Demarçay (A., 1875, 441), whose formulation of the compound is erroneous. Similarly are obtained diisopropoxy-, anhyd., b.p. 160°/18 mm., solid, and +  $\text{Pr}^n\text{OH}$ , cryst., and diisobutoxy-dichlorotitanium, anhyd., b.p. 184°/18 mm., solid, and + MeOH, + EtOH, and +  $\text{Bu}^n\text{OH}$  (also obtained from  $\text{TiCl}_4$  and  $\text{Bu}^n\text{OH}$  at 100—110°), cryst. R. S. C.

Complex compounds of iridium.—See this vol., 810.

Action of anhydrous ferric chloride on anhydrous acetic and formic acids.—See this vol., 691.

Mechanism of organic reactions. IV. Pyrolysis of esters and acetals. E. M. BILGER and H. HIBBERT (J. Amer. Chem. Soc., 1936, 58, 823—826).—The nos. quoted after the following compounds denote the mols. of olefine and acid, respectively, produced during their decomp. at 470—500°: EtOAc 0.174, 0.176; glycol ethylidene ether 0.023, 0.005;  $\text{Pr}^n\text{CO}_2\text{Et}$  0.139, 0.14; Et *n*-butyral (? glycol *n*-butylidene ether) 0.048, 0.029;  $\text{HCO}_2\text{Et}$  0.122, 0.026; glycol methylene ether 0.008, 0.003;  $\text{Pr}^n\text{OAc}$  0.097, 0.14; propylene acetal 0.021, 0.024; propylene *n*-heptal, b.p. 204°, 0.04, 0.015; trimethylene glycol *n*-butylidene ether 0.04, 0.009;  $\text{Bu}^n\text{OAc}$  0.151, 0.157;  $\text{Bu}^n\text{OAc}$  0.141, 0.155; *sec*.- $\text{BuOAc}$  0.177, 0.18;  $\text{Pr}^n\text{OAc}$  0.181, 0.181. The cyclic acetals are more stable than the isomeric esters and cannot be intermediates in the decomp. of the latter. Pyrolysis of  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OAc}$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$  gives 38.1% of  $\text{CH}_2\cdot\text{CHCl}$  and 58.2% of  $\text{C}_2\text{H}_4$ , respectively. De-comp. of EtBr (at 482°) and  $\text{Bu}^n\text{Br}$  (at 484°) affords 58.7% of  $\text{C}_2\text{H}_4$  and 41.6% of  $\text{C}_4\text{H}_8$ , respectively. The olefine produced during decomp. of esters arises solely from Oalk. The results are best explained by the intermediate production of free radicals. H. B.

Exchange of hydrogen atoms in the methyl group of heavy acetic acid. A. DADIEU and W. ENGLER (Naturwiss., 1936, 24, 318).—Acetic acid prepared by the action of  $\text{H}_2\text{SO}_4$  on  $(\text{CD}_3\cdot\text{CO}_2)_2\text{Ba}$  gave a Raman line corresponding to a C-H linking. The substitution of D by H may have taken place either through the intermediate formation of  $\text{SO}_3\text{H}\cdot\text{CD}_2\cdot\text{CO}_2\text{H}$  with subsequent hydrolysis, or through an enol form of  $\text{CD}_3\cdot\text{CO}_2\text{H}$ . W. O. K.

Catalytic preparation of esters of glycol and acetic acid. II. M. B. TUROVA-POLAK and V. F. DZIOMA (J. Appl. Chem. Russ., 1936, 9, 696—702).  $(\text{CH}_2\cdot\text{OAc})_2$  (I) is obtained in 70% yield from AcOH and glycol, at 160—170°, in presence of wood-C heated at 200° with an equal wt. of  $\text{H}_3\text{PO}_4$ . Only



traces of  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$  are obtained from 1:1  $\text{AcOH}$ -glycol mixtures, the chief product being (I).

R. T.

**Organic deuterium compounds.** Acetic, malonic, and succinic acids. J. O. HALFORD and L. C. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 736—740; cf. Wilson, A., 1935, 731).— $\text{CD}_3(\text{CO}_2\text{D})_2$ , m.p.  $130\text{--}131^\circ$  [from  $\text{C}_2\text{O}_2$  and  $\text{D}_2\text{O}$  or by successive crystallisation of  $\text{CH}_3(\text{CO}_2\text{H})_2$  from  $\text{D}_2\text{O}$ ], heated at  $150^\circ$  gives  $\text{CD}_3\cdot\text{CO}_2\text{D}$  (I), m.p.  $15\cdot8\text{--}16^\circ$ , converted by dry  $\text{HCl}$  into trideuteracetic acid (II),  $\text{CD}_3\cdot\text{CO}_2\text{H}$ , m.p.  $17\cdot2^\circ$ . Anhyd.  $\text{KOAc}$  and conc.  $\text{D}_2\text{SO}_4$  in  $\text{D}_2\text{O}$  afford acetic deuteracid (III),  $\text{CH}_3\cdot\text{CO}_2\text{D}$ , m.p.  $15\cdot4^\circ$  (cf. Lewis and Schutz, A., 1934, 391). V.p. of (I)—(III) between  $21^\circ$  and  $83\cdot6^\circ$  are recorded. Successive treatment of  $(\text{C}\cdot\text{CO}_2\text{K})_2$  with  $\text{Na-Hg}$  in  $\text{D}_2\text{O}$  and  $\text{D}_2\text{O}$ - $\text{DBr}$  gives tetradeuterosuccinic deuteracid,  $(\text{CD}_2\cdot\text{CO}_2\text{D})_2$ , m.p.  $178\text{--}179\cdot1^\circ$ , which when crystallised from  $\text{D}_2\text{O}$  affords tetradeuterosuccinic acid,  $(\text{CD}_2\cdot\text{CO}_2\text{H})_2$ , m.p.  $181\text{--}182\cdot6^\circ$ . Succinic deuteracid,  $(\text{CH}_2\cdot\text{CO}_2\text{D})_2$ , m.p.  $179\text{--}180^\circ$ , is obtained from succinic acid and  $\text{D}_2\text{O}$ . The relationship between m.p. and D content is discussed.

H. B.

**Wall effect in the thermal polymerisation of unsaturated esters.** J. W. BRETTENBACH and R. RAFF (Ber., 1936, 69, [B], 1107—1110).—Polymerisation of Me acrylate and vinyl acetate occurs fairly rapidly, but quite irregularly, when they are heated in glass vessels, and is greatly influenced by the nature and pre-treatment of the glass. In pure Ni vessels only slight polymerisation is observed after several days at  $100^\circ$ ; it is readily induced by powdered glass and, particularly, by  $\text{Na}_2\text{SiO}_3$ . Similar differences are not observed with styrene. The phenomena are attributed to the alkali of the glass towards which esters, but not hydrocarbons, are very sensitive.

H. W.

**Electrolysis of mixtures of *n*-butyrates with nitrates.** F. FICHTER and F. METZ (Helv. Chim. Acta, 1936, 19, 597—606).—By electrolysis a mixture of  $4N\text{-PrCO}_2\text{Na}$  and  $2N\text{-NaNO}_3$  at  $18\text{--}20^\circ$  with a c.d. of  $0\cdot166$  amp. per sq. cm. an oil was obtained comparable with that from the corresponding propionate electrolysis (A., 1935, 472). It contained  $\text{Pr}^a\text{NO}_2$ ,  $n\text{-C}_6\text{H}_{14}$ ,  $\text{Pr}^a\text{NO}_3$ ,  $\text{Pr}^a\text{CO}_2\text{Pr}^a$ ,  $\text{CHMeBu}^a\cdot\text{O}\cdot\text{NO}_2$ ,  $\text{CHMePr}^a\cdot\text{O}\cdot\text{NO}_2$ ,  $\text{NO}_3\cdot\text{CHMeCH}_2\cdot\text{NO}_3$ ,  $\text{NO}_3\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{NO}_3$ , and glyceryl esters. The results are discussed with reference to previous observations (cf. loc. cit.; A., 1935, 730, 1105).

M. S. B.

**Catalytic hydrogenation of sorbic acid.**—See this vol., 808.

**Hydrogenation of  $\Delta^9$ -octadecenyl  $\Delta^9$ -octadecenoate (oleyl oleate).** T. P. HILDITCH and H. PAUL (J.C.S., 1936, 664—667).—Hydrogenation (Nikieselguhr) of oleyl oleate at  $180^\circ$  is largely non-selective, but there is slight preferential reaction of the oleyl ethylenic linking and slightly more formation of  $\text{C}_{17}\text{H}_{35}\cdot\text{CO}_2\cdot\text{C}_{18}\text{H}_{37}$  (I) than is calc. from probability data. The proportions of the products in the reaction mixture after varying times of hydrogenation are determined by the I val., oxidation by  $\text{KMnO}_4$  and isolation of unattacked (I), followed by hydrolysis and isolation of the  $\text{C}_{18}\text{H}_{37}\cdot\text{OH}$ . Other oxidation products could not be isolated quantitatively.

R. S. C.

**Higher aliphatic compounds. VI. Existence of compounds in binary systems from palmitic, margaric, stearic, tricosanoic, and tetracosanoic acids.** J. C. SMITH (J.C.S., 1936, 625—627; cf. A., 1933, 1271).—Mixed m.-p. diagrams of the pure acids indicate formation of 1:1 compounds of tricosanoic with tetracosanoic, palmitic (I) with margaric (II), stearic (III) with (II), and palmitic with stearic acid, with formation of complete solid solutions. Liquidus curves show the possibility also of compounds, 3(II):1(I), 3(II):1(III), and 1(II):3(III). Previous reports that acids with an odd no. of C do not form compounds with acids with an even no. of C were due to use of impure acids. It is suggested that the 3:1 compounds may be due to alternate layers of  $\text{RC}\begin{matrix} \text{O} \rightarrow \text{HO} \\ \text{OH} \quad \text{O} \end{matrix} \text{CR}$  and  $\text{RC}\begin{matrix} \text{O} \rightarrow \text{HO} \\ \text{OH} \leftarrow \text{O} \end{matrix} \text{CR}'$ .

R. S. C.

**Soap solutions. XI. Reactions between the systems: stearic acid-sodium oleate and oleic acid-sodium stearate.** J. MIKUMO (J. Soc. Chem. Ind. Japan, 1936, 39, 98—100b).—The reactions have been studied in  $\text{MeOH}$ ,  $\text{EtOH}$ , and  $\text{MeOH-C}_6\text{H}_6$  mixtures. The compound  $\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}\cdot\text{C}_{19}\text{H}_{36}\text{O}_2$ , m.p.  $119\text{--}120^\circ$ , is produced in each case and its crystallographic properties are described.

R. S.

**Lipins of wheat embryo. I, II.**—See this vol., 912.

**Naming of the highly unsaturated acid of the kernel fat of "akarittom," *Parinarium laurinum*.** M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 116—117b).—The name *parinaric acid* (I) is suggested for the unsaturated acid  $\text{C}_{18}\text{H}_{28}\text{O}_2$  (Farmer et al., A., 1935, 1041) isolated from the kernel fat of *P. laurinum* (B., 1933, 476). (I) is not identical with coueupic acid.

J. W. B.

**Determination of hydroxyl number of hydroxy fatty acids.** K. HINSBERG (Biochem. Z., 1936, 285, 125—129).—The acid (0.6 g. of dihydroxystearic acid) is acetylated with a known amount of dry  $\text{C}_5\text{H}_5\text{N-Ac}_2\text{O}$  and an aliquot of the reaction product distilled in vac. in a described apparatus, the  $\text{Ac}_2\text{O}$  remaining and the  $\text{AcOH}$  formed being absorbed in standard  $\text{KOH}$  and the OH val. being calc. by difference.

P. W. C.

**Optical properties of fermentation lactic acid. III.**—See this vol., 899.

**M.-p. curves of optical isomerides.** J. D. M. ROSS (J.C.S., 1936, 718—723).—Mixed setting-point curves of the *d*- and *l*-forms of  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$  (I:  $\text{R}=\text{H}$ . II:  $\text{R}=\text{Me}$ ) and  $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{R}$  (III;  $\text{R}=\text{Me}$  or  $\text{Et}$ ) show formation of the racemate in all cases. Kremann's method shows dissociation of the racemates as follows: (I) 10, (II) 16, (III) 20%; van Laar's method gives erroneous results.  $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  decomposes slightly at the m.p.

R. S. C.

**Behaviour of laevulyl chloride and acetyl-laevalic acid in the Friedel-Crafts reaction.** J. H. HELBERGER (Annalen, 1936, 522, 269—277).—Laevalyl chloride (I) (1 mol.) (from the acid and  $\text{SOCl}_2$ ),  $\text{C}_6\text{H}_6$  (excess), and  $\text{AlCl}_3$  (1 mol.) at  $50^\circ$  give 58% of phenacetylacetone (II), b.p.  $158^\circ/12\text{ mm.}$

m.p. 28—29°, and some of the diphenylvaleric acid (III), m.p. 116—118°, of Eykman (A., 1908, i, 22); in presence of  $\text{PhNO}_2$ , about the same amount of (III) but little (II) result. The formation of (II) shows that (I) can react as  $\text{CH}_2\text{Ac}\cdot\text{CH}_2\cdot\text{COCl}$ . Acetyl-lævulic acid [ $\gamma$ -acetoxy- $\gamma$ -valerolactone],  $\text{C}_8\text{H}_8$ , and  $\text{AlCl}_3$  (3 mols.) at 45—50° afford (II) (60%), (III) (trace), and a little  $\text{COPhMe}$ ; with  $\text{PhMe}$  and  $\text{PhOMe}$ , *p*-methyl-, b.p. 168°/12 mm., m.p. 53°, and *p*-methoxyphenacylacetone, respectively, are formed.  $\text{NH}_2\text{Ph}$  and (II) with a little  $\text{AcOH}$  at 100° give 1:5-diphenyl-2-methylpyrrole, m.p. 83°; *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  similarly affords a pyrrole,  $\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}_2$ , m.p. 103°; *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  yields a pyrrole,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_2$ , m.p. 184° (becoming red); *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  furnishes pyrroles,  $\text{C}_{17}\text{H}_{16}\text{N}_2$ , m.p. 137°, and  $\text{C}_{28}\text{H}_{21}\text{N}_2$ , m.p. 230° [from 1 and 2 mols. of (II), respectively]; benzidine gives a pyrrole,  $\text{C}_{31}\text{H}_{23}\text{N}_2$ , m.p. 229°.

H. B.

Raman spectrum of oxalic acid.—See this vol., 777.

Detection of oxalate ion by decolorisation of indigotin solution according to Tananaev and Budkevitch. A. S. KOMAROVSKI and V. A. NASHARENKO (Z. anal. Chem., 1936, 104, 413—416; cf. this vol., 190).—The reaction is not sp. Other org. acids,  $\text{NO}_2$ , and small amounts of  $\text{Fe}^{++}$  produce the same effect, whilst Mo, W, or Zr inhibit the action by complex formation.

J. S. A.

Tetradeterosuccinic acid and derivatives. A. McLEAN and R. ADAMS (J. Amer. Chem. Soc., 1936, 58, 804—810).— $(\text{C}\cdot\text{CO}_2\text{Me})_2$  is reduced ( $\text{D}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOAc}$ ) to *Me tetradeterosuccinate*, b.p. 190.3°/743 mm., m.p. 17°, hydrolysed (very dil.  $\text{HNO}_3$ ) to *tetradeterosuccinic acid*, m.p. 180—180.5° (anhydride, m.p. 119.3—119.6°). Other physical data are given. Reduction occurs more slowly with  $\text{D}_2$  than with  $\text{H}_2$ . Apparatus for (i) the production of  $\text{D}_2$ , (ii) reduction, and (iii) determination of *d* for solids which melt without decomp., is described.

H. B.

Mol. wts. of polymeric substances in pyrocatechol and their bearing on the nature of coal and derived products. R. C. SMITH and H. C. HOWARD (J. Amer. Chem. Soc., 1936, 58, 740—742).—Mol. wt. determinations (f.-p. method) of various polymeric substances (e.g.,  $\text{C}_2\text{H}_4$  succinate, adipic anhydride, lactide, tetraethylene glycol, synthetic resins) in *o*- $\text{C}_6\text{H}_4(\text{OH})_2$  and  $\text{Ph}_2$  (when sol.) indicate that (except when chemical degradation occurs) the anomalous behaviour exhibited by the products derived from coal (B., 1935, 534) is generally absent. The latter products must be built up of relatively small units.

H. B.

Constitution of the reduction product of trichloromethylparaconic acid. A. N. MEDRUM and R. D. KOTWAL (J. Indian Chem. Soc., 1936, 13, 213—216).—The reduction product of trichloromethylparaconic acid ( $\text{Me}_2$ , m.p. 77°,  $\text{Et}_2$ , b.p. 173°/10 mm., and  $\text{Et H}$  esters, b.p. 190°/20 mm.; anilide, m.p. 165—166°; *p*-toluidide, m.p. 173—174°; anilic acid, m.p. 121—122°) is not

et al., A.,

251) but is *8,8-dichloro-n-butane- $\alpha,\beta$ -dicarboxylic acid* [ $\text{Me}_2$ , b.p. 135°/11 mm., and  $\text{Et}_2$ , b.p. 215°/50 mm., esters; anhydride, m.p. 70—77°; acid chloride, b.p. 123°/5 mm. (not pure); dianilide, m.p. 176—177°; *di-p*-toluidide, m.p. 209—210°], converted by conc.  $\text{H}_2\text{SO}_4$  at 100° into tricarballic acid.

J. W. B.

Active methyldiglycollic acid and its derivatives. M. GODCHOT and P. VIELLES (Compt. rend., 1936, 202, 1358—1360).—*d*-Lactic acid (1 mol.), anhyd.  $\text{CuSO}_4$  (1 mol.), and the alcohol (4 mols.) when heated for 16 hr. give the *Me*, b.p. 49°/20 mm.,  $[\alpha]_D^{20}$  -9.61 and *Et* esters, b.p. 58°/20 mm.,  $[\alpha]_D^{20}$  +12°. These with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{R}$  give *methyldiglycollic* [ $\alpha$ -carballoxy-methoxypropionic] esters, in which (a)  $\text{R}=\text{R}'$  *Me*, b.p. 118°/20 mm.,  $[\alpha]_D^{20}$  -4.47°, and *Et* (I), b.p. 127°/20 mm.,  $[\alpha]_D^{20}$  -9.77°, (b)  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ , b.p. 124°/20 mm.,  $[\alpha]_D^{20}$  -2.07°, and (c)  $\text{R}=\text{Et}$ ,  $\text{R}'$  *Me*, b.p. 125°/20 mm.;  $[\alpha]_D^{20}$  -11.96°. Hydrolysis of (I) by  $\text{NaOH}$   $\text{EtOH}$  gives the *l*-acid, m.p. 70°,  $[\alpha]_D^{20}$  -6.71° in  $\text{Et}_2\text{O}$ , which with hot  $\text{Ac}_2\text{O}$  gives the *anhydride*, b.p. 118°/17 mm.,  $[\alpha]_D^{20}$  in  $\text{Et}_2\text{O}$ , easily hydrolysed to the active acid.

R. S. G.

Constitution of some tartaric complexes and their physico-chemical applications. I. Tungsto-, II. Molybdo-, III. Boro-, IV. Alumino-, V. Antimonio-tartaric complexes. T. K. HENG (J. Chim. phys., 1936, 33, 356—377, 377—383, 383—403, 403—413).—A polarimetric study has been made of the complexes formed by some compounds of W, B, Mo, Al, and Sb with tartaric acid ( $\text{H}_2\text{T}$ ), tartaric acid ( $\text{H}_2\text{T}$ ), tartramide [ $(\text{NH}_2)_2\text{T}$ ] in aq. solution, in order to determine which parts of the  $\text{H}_2\text{T}$  mol. are involved in each case.

I. (Cf. Gernez, A., 1888, 938; Grossmann and Potter, A., 1906, ii, 211; Henderson and Barr, J.C.S., 1896, 69, 1451).  $\text{H}_2\text{WO}_4$  gives with  $\text{H}_2\text{T}$ ,  $\text{H}_2\text{WO}_4\cdot 2\text{H}_2\text{T}$  (I), and with  $\text{HNH}_2\text{T}$ ,  $\text{H}_2\text{WO}_4\cdot 2\text{HNH}_2\text{T}$ , hence only 1  $\text{CO}_2\text{H}$  of each  $\text{H}_2\text{T}$  mol. in (I) is fixed.  $\text{NaHWO}_4$  gives with  $\text{H}_2\text{T}$  [ $\text{H}_2\text{T}\cdot 2\text{WO}_3$ ] $\text{Na}_2$ , and with  $\text{HNH}_2\text{T}$ , [ $\text{HNH}_2\text{T}\cdot 2\text{WO}_3$ ] $\text{Na}_2$ .  $\text{Na}_2\text{WO}_4$  gives with  $\text{H}_2\text{T}$ , [ $\text{H}_2\text{T}\cdot \text{WO}_3$ ] $\text{Na}_2$  (II); with  $\text{NaHT}$ ,  $(2\text{H}_2\text{T}\cdot \text{WO}_3)\text{Na}_4$  (III); with  $\text{HNH}_2\text{T}$ , [ $\text{HNH}_2\text{T}\cdot 2\text{WO}_3$ ] $\text{Na}_2$ ; with  $\text{NaNH}_2\text{T}$ , no compound, indicating that in (II), both  $\text{CO}_2\text{H}$  of the  $\text{H}_2\text{T}$  mol. are fixed. (III) can be obtained cryst. in very small quantity. With malic acid ( $\text{H}_2\text{M}$ ),  $\text{H}_2\text{WO}_4$  gives  $\text{NaHWO}_4$  gives [ $\text{H}_2\text{M}\cdot 2\text{WO}_3$ ] $\text{Na}_2$  (cryst. powder hydrated);  $\text{Na}_2\text{WO}_4$  gives [ $2\text{H}_2\text{M}\cdot \text{WO}_3$ ] $\text{Na}_2$  (very easily cryst.,  $\alpha_D^{20}$  -34.5). No compound [ $\text{H}_2\text{M}\cdot \text{WO}_3$ ] $\text{Na}_2$  exists.

II. (Cf. Gernez, A., 1887, 540; Rosenheim and Itzig, A., 1900, i, 272; Grossmann and Potter, loc. cit.).  $\text{H}_2\text{MoO}_4$  gives with  $\text{H}_2\text{T}$ ,  $2\text{H}_2\text{T}\cdot \text{H}_2\text{MoO}_4$ , but with  $\text{HNH}_2\text{T}$ ,  $\text{HNH}_2\text{T}\cdot \text{H}_2\text{MoO}_4$ .  $\text{NaHMoO}_4$  gives with  $\text{H}_2\text{T}$ , [ $\text{H}_2\text{T}\cdot 2\text{MoO}_3$ ] $\text{Na}_2$  (IV); with  $\text{NaHT}$ , (V).  $\text{Na}_2\text{MoO}_4$  and  $\text{H}_2\text{T}$  give [ $\text{H}_2\text{T}\cdot \text{MoO}_3$ ] $\text{Na}_2$  (VI). Corresponding with these three Na compounds with  $\text{H}_2\text{T}$ , only one, [ $2\text{HNH}_2\text{T}\cdot \text{MoO}_3$ ] $\text{Na}_2$  (VII), with  $\text{HNH}_2\text{T}$  exists. Structural formulae for (IV)—(VII) are advanced.

III. (Cf. Darmon, A., 1926, 251, 457; 1930, 854; Lowry, J.C.S., 1929, 2853; Jones, J.C.S., 1933,



952). Gradual addition of  $\text{KBO}_2$  to  $\text{H}_2\text{T}$  gives at first  $\text{H}_2\text{T} \cdot \text{KBO}_2$ , and later  $\text{BTK}_2$ ; finally (considerable excess of  $\text{KBO}_2$ )  $\text{BTK}$ . The complex  $2\text{H}_2\text{T} \cdot \text{KBO}_2$  (or  $\text{BT}_2\text{K}$ ) described by Lowry does not exist in aq. solution.  $\text{Me}_2\text{T}$  gives with  $\text{KBO}_2$ , at first  $\text{Me}_2\text{T} \cdot \text{BO}_2\text{K}$ , but after 2 months  $\text{H}_2\text{T} \cdot \text{KBO}_2$ , and not  $2\text{H}_2\text{T} \cdot \text{KBO}_2$ , as found by Darmois (A., 1927, 448) by hydrolysis of  $\text{Et}_2\text{T}$  with  $\text{KBO}_2$ .  $\text{NaBO}_2$  gives with  $(\text{NH}_2)_2\text{T}$ ,  $(\text{NH}_2)_2\text{T} \cdot \text{NaBO}_2$ ,  $\alpha_D^{20} + 69.5^\circ$ , analogous to the spirans, and with  $\text{HNH}_2\text{T}$ ,  $2\text{NH}_2\text{HT} \cdot \text{NaBO}_2$ .

IV. (Cf. Quadrat and Korecky, A., 1909, i, 762).  $\text{Al}(\text{OH})_3$  dissolves in aq.  $\text{H}_2\text{T}$  to give  $\text{H}_2\text{T} \cdot \text{Al}(\text{OH})_3$  which is levorotatory in conc., and dextrorotatory in dil., solution.  $\text{HNH}_2\text{T}$  gives  $\text{HNH}_2\text{T} \cdot \text{Al}(\text{OH})_3$ , which is levorotatory in all concns.  $(\text{NH}_2)_2\text{T}$  gives no compound. Addition of  $\text{NaOH}$  to a mixture of  $\text{Na}_2\text{T}$  and  $\text{Al}_2(\text{SO}_4)_3$  gives a very basic solution of  $(\text{AlT}_3)\text{Na}_3$ , from which  $\text{Al}$  cannot be pptd. by  $\text{Na}_2\text{HPO}_4$ . The mechanism of formation of this compound is discussed.  $(\text{AlT}_3)\text{K}_3$  can be obtained by hydrolysis of  $\text{Me}_2\text{T}$  with  $\text{KAlO}_2$ . From these results a polarimetric method of studying the corrosion of  $\text{Al}$  by  $\text{NaOH}$  is suggested.

V. (Cf. Darmois, A., 1927, 448). A mixture of  $\text{SbF}_3$  and  $\text{H}_2\text{T}$  when gradually neutralised gives a ppt. of tartar emetic at the correct concn. Similar compounds are obtained when  $\text{H}_2\text{T}$  is replaced by any of its salts, inorg. or org. Since aq.  $\text{SbF}_3$  attacks glass (by hydrolysis), a polarimetric method of studying the corrosion of glass by  $\text{HF}$  is indicated and developed.

R. C. M.

**Determination of citric acid by conversion into acetone.** II. K. TAUFEL and K. SCHOERER (Z. Unters. Lebensm., 1936, 71, 297—310; cf. A., 1933, 807).—Citric acid is pptd. by aq.  $\text{Bi}(\text{NO}_3)_3$ -mannitol, and oxidised either with  $\text{KMnO}_4$  to  $\text{COMe}_2$ , which is determined by the  $\text{CHI}_3$  method, or with  $\text{Fe}_2(\text{SO}_4)_3$  in presence of light to acetonedicarboxylic acid, which is determined by pptn. with Deniges'  $\text{HgSO}_4$  reagent. An improved procedure is described for the removal of substances which interfere in the former method.

E. C. S.

**Polarimetric study of the formation of complex molybdosaccharates.**—See this vol., 691.

**Synthesis of aldobionic acid of gum acacia.** R. D. HOTCHKISS and W. F. GOEBEL (J. Amer. Chem. Soc., 1936, 58, 858—859).—Me acetobromoglycuronate (A., 1935, 1483), 1:2:3:4-dusopropylidenegalactose, and  $\text{Ag}_2\text{O}$  in  $\text{Et}_2\text{O}$  give 1:2:3:4-dusopropylidenegalactose-6- $\beta$ -triacetylglucuronide Me ester, m.p. 112.5—114°,  $[\alpha]_D^{25} - 68^\circ$  in  $\text{CHCl}_3$ , hydrolysed [first  $\text{Ba}(\text{OH})_2$  then dil.  $\text{H}_2\text{SO}_4$ ] to galactopyranose-6- $\beta$ -glucuronopyranoside (I), which is identical with the aldobionic acid (II) from gum acacia (Heidelberg and Kendall, A., 1930, 66; cf. Challinor *et al.*, A., 1931, 465). (I) and (II) with  $\text{CH}_2\text{N}_2$  give the same Me ester, m.p. 119° (decomp.),  $[\alpha]_D^{25}$  (in  $\text{H}_2\text{O}$ )  $-2.9^\circ \rightarrow -9.1^\circ$  (Ac. derivative, m.p. 202—203°,  $[\alpha]_D^{25} - 17.5^\circ$  in  $\text{CHCl}_3$ ).

H. B.

**Synthesis of the hepta-acetyl methyl ester of gentiobiuronic acid.** R. D. HOTCHKISS and W. F. GOEBEL (Science, 1936, 83, 353—354).—Condensation of  $\beta$ -glucose 1:2:3:4-tetra-acetate, with Me 1-

bromotriacetylglucuronate in  $\text{CHCl}_3$  in presence of  $\text{Ag}_2\text{O}$  yields the  $\beta$ -hepta-acetyl Me ester (I) of the aldobionic acid, glucose-6- $\beta$ -glucuronide. (I), m.p. 198—199° has  $[\alpha]_D^{25} - 11.0$  in  $\text{CHCl}_3$ , and is converted into the  $\alpha$ -isomeride, m.p. 201—202°,  $[\alpha]_D^{25} + 48.4^\circ$  in  $\text{CHCl}_3$ , by the action of  $\text{ZnCl}_2$  in  $\text{Ac}_2\text{O}$ . L. S. T.

**Disulphoacetic acid.** H. J. BACKER and N. BENNINGA (Rec. trav. chim., 1936, 55, 370—373).—Oxidation of  $\text{CH}(\text{SO}_3\text{H})_2 \cdot \text{CHO}$  with either  $\text{AcO}_2\text{H}$ -aq.  $\text{H}_2\text{O}_2$  at  $50^\circ$  or  $\text{Ag}_2\text{O}$  on a water-bath affords disulphoacetic acid + 2.5  $\text{H}_2\text{O}$ , sinters  $78^\circ$ , m.p. 85—86°, isolated as its  $\text{Ag}_3 + \text{H}_2\text{O}$  salt ( $\text{Ba} + 9\text{H}_2\text{O}$ ,  $\text{K} + \text{H}_2\text{O}$ ,  $\text{NH}_2\text{Ph}$ , strychnine + 8 $\text{H}_2\text{O}$ , and quinine + 5 $\text{H}_2\text{O}$  salts). When heated at 110—130° it decomposes into  $\text{CO}_2$  and  $\text{CH}_2(\text{SO}_3\text{H})_2$ . J. W. B.

**Compounds of thiol-acids with aldehydes.** M. P. SCHUBERT (J. Biol. Chem., 1936, 114, 341—350).—Aldehydes,  $\text{RCHO}$ , and  $\text{SH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$  (I) in  $\text{EtOH}$  give  $\alpha$ -hydroxyalkylthiolglycolanilides (II),  $\text{OH} \cdot \text{CHR} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , which, although they can be recrystallised, are more or less dissociated in solution, but give rather more stable Ac derivatives.  $\text{AcCO}_2\text{H}$ , benzoquinone, and isatin give similar compounds, but  $\text{COMe}_2$ ,  $\text{COPhMe}$ ,  $\text{Ac}_2$ , and  $\text{Bz}$ , do not. Cysteine and aldehydes in  $\text{EtOH}$  or  $\text{H}_2\text{O}$  give thiazole derivatives,  $\text{CHR} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$

which dissociate to a smaller extent;  $\text{AcCO}_2\text{H}$ , however, gives ( $\beta$ -lactic acid)thiolalanine,  $\text{CO}_2\text{H} \cdot \text{CMe}(\text{OH}) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$  (III), which is of type (II). The following derivatives of (II) are described, in which  $\text{R} = \text{H}$ , m.p. 91—92° (Ac derivative, m.p. 91—92°),  $\text{Pr}$ , m.p. 73—75°,  $\text{CCl}_3$ , m.p. 111—112° (Ac derivative, m.p. 133—134°), and compounds,  $\text{OH} \cdot \text{CR} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , in which  $\text{R}$  is a residue from benzoquinone, m.p. 165—166°, and isatin, m.p. 101°, and ( $\beta$ -lactic acid)thiolacetanilide (from  $\text{AcCO}_2\text{H}$ ), m.p. 90—92°. These OH-compounds give a colour with Na nitroprusside (IV) in aq.  $\text{NaHCO}_3$  [although less strongly than does (I)] and can be titrated with I [1 atom consumed to give ( $\text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ )]]; the Ac derivatives consume I only very slowly and give no colour with (IV). (I) reacts with the compound (V) from  $\text{CHO} \cdot \text{COPh}$  and  $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  to ppt. the less sol. hydroxybenzoyl-methylthiolacetanilide,  $\text{COPh} \cdot \text{CH}(\text{OH}) \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , m.p. 148°. 4-Carboxytetrahydrothiazole, m.p. 195° (decomp.), and its 2- $\text{CCl}_3$  (VI), cryst., - $\text{Pr}$  (VII), m.p. 167—168°, - $\text{Ph}$  (VIII), m.p. 159—160° (Ac derivative, m.p. 202°), and 2'-furyl (IX) derivative, m.p. 125—126°, are described; they liberate  $\text{CO}_2$  from  $\text{NaHCO}_3$  and dissolve in aq.  $\text{NaOAc}$ . Only (VI) gives a colour with (IV) in aq.  $\text{NaHCO}_3$ , but in dil. aq.  $\text{NH}_3$  (VI), (VII), and (IX) give the test strongly and (VIII) weakly. Even if the test is negative, some dissociation occurs, since in  $\text{NaHCO}_3$  (VIII) and  $\text{CH}_3\text{I} \cdot \text{CO}_2\text{Na}$  produce  $\text{PhCHO}$  and  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , and  $\text{CHPh} \cdot \text{N} \cdot \text{NHPh}$  is obtained from (VIII) and  $\text{NH}_2 \cdot \text{NHPh}$  in 2M-aq.  $\text{KOAc}$ . The thiazoles, but not the Ac derivative, absorb I readily to give cystine. (III), m.p. 150—151°, but not its  $\text{Ac}_2$  derivative (prep. by  $\text{AcOH} \cdot \text{C}_2\text{H}_5\text{N}$ ), m.p. 201—202° (decomp.), can be titrated with I; neither gives a colour with

(IV), even in dil. aq.  $\text{NH}_3$ . (I) and (V) give *Ac* derivatives, m.p.  $91^\circ$  and  $202^\circ$ , respectively.

R. S. C.

**Preparation of carboxylic acids of organic selenides.** A. FREDGA (Svensk Kem. Tidskr., 1936, 48, 91—98).—Selenolcarboxylic acids  $\text{SeR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  are prepared by interaction (air excluded) of  $\text{Hg}(\text{Se}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2$  and  $\text{Na}_2\text{S}$  in  $\text{H}_2\text{O}$  to give  $\text{SeNa}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ , and treatment of the resulting solution with the alkyl halide in  $\text{MeOH}$  or  $\text{EtOH}$ . Thus from the appropriate halide are obtained *benzyl*-, m.p.  $71$ — $72^\circ$  (*Cu* salt), *methylenebis*-, m.p.  $122.5$ — $123^\circ$  (*Cu* salt), *ethane- $\alpha\beta$ -di*-, m.p.  $153$ — $154^\circ$  (only 2% yield, much  $\text{C}_2\text{H}_4$  formed) (*Cu* salt), and *propane- $\alpha\gamma$ -di-selenolacetic acid*, m.p.  $77$ — $78^\circ$  (*Cu* salt). Similarly from  $\text{Hg}(\text{Se}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H})_2$  are prepared  *$\beta$ -benzylselenolpropionic acid*, m.p.  $75$ — $76^\circ$  (*Cu* salt), and  *$\beta$ -carboxymethylselenolpropionic acid*, m.p.  $91$ — $92^\circ$ .

J. W. B.

**Slow combustion of formaldehyde.**—See this vol., 801.

**Reaction of formaldehyde with hydrogen peroxide in heavy water.**—See this vol., 688.

**Thermal decomposition of acetaldehyde and ethylene oxide: existence of short-lived intermediates.** M. W. TRAVERS and R. V. SEDDON (Nature, 1936, 137, 906—907).—The rates of decomp. are accelerated initially, the acceleration being more marked in the case of  $(\text{CH}_2)_2\text{O}$ , which exhibits an induction period. The processes involved are evidently more complex than hitherto supposed. With  $\text{MeCHO}$  at  $360$ — $500^\circ$  over a wide range of concn., decomp. follows alternative courses either into (i)  $\text{CH}_4$  and  $\text{CO}$  or (ii) propylene and  $\text{CO}$ . (i) is dominant in unpacked and (ii) in packed tubes. Some propylene is always formed in (i) and it undergoes some condensation to produce a 6-carbon hydrocarbon and more complex products. Although packing retards (i) and accelerates (ii) the total rate of decomp. is independent of the nature or dimensions of the reaction tube. The formation of a short-lived intermediate is probable.

L. S. T.

**Electrolytic reduction of aliphatic ketones.**—See this vol., 687.

**Action of bromine on acetone in presence of various solvents.** T. TOMONARI (Z. physikal. Chem., 1936, B, 32, 222—228).—The bromination is retarded by  $\text{H}_2\text{O}$  and to a smaller extent by alcohols, the effect falling and ultimately changing in sign with increasing chain length. This phenomenon is ascribed to the  $\text{COMe}_2\cdot\text{H}_2\text{O}$  or  $\text{COMe}_2\cdot\text{alcohol}$  complex retarding the enolisation of the  $\text{COMe}_2$ . In  $\text{COMe}_2\text{--CS}_2$  and  $\text{COMe}_2\text{--C}_6\text{H}_{14}$  mixtures and in pure  $\text{COMe}_2$  the rate is determined primarily by the amount of catalyst.

R. C.

**Metal ketyls of the aliphatic series. IV. Action of sodium on *tert*.-butyl *tert*.-amyl and on *tert*.-butyl *tert*.-hexyl ketones.** I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 71—75).— $\text{COBu}^\gamma\cdot\text{CMe}_2\text{Et}$  (I) (from  $\text{COPr}^\delta\text{Bu}^\gamma$ ,  $\text{NaNH}_4$ , and  $\text{EtI}$ ) in  $\text{Et}_2\text{O}$  with  $\text{Na}$  for 26 days affords (I) and *tert*.-butyl-*tert*. amylcarbinol (II), b.p.  $186$ — $190^\circ$ . From the above reaction mixture and  $\text{EtI}$ , (I), (II),

and  $\text{NH}_2\cdot\text{CO}_2\text{Ph}$  are obtained. Using  $\text{BzBr}$  instead of  $\text{EtI}$  the main product is *benzoyl-tert*.-butyl-*tert*.-amylcarbinol, b.p.  $182$ — $186^\circ/22\text{ mm.}$ , partly converted by  $6N\cdot\text{KOH}\text{--EtOH}$  during 7 hr. into (II). Reaction between  $\text{COBu}^\gamma\cdot\text{CMe}_2\text{Et}$  (III) (from  $\text{COBu}^\gamma\cdot\text{CHEt}_2$ ,  $\text{NaNH}_4$ , and  $\text{MeI}$ ) and  $\text{Na}$  in  $\text{Et}_2\text{O}$  was incomplete after 4 months. Decomp. of the reaction mixture affords (III) and *tert*.-butyl-*tert*.-hexylcarbinol (IV), b.p.  $190$ — $208^\circ$  (*phenylurethane*, m.p.  $97$ — $98^\circ$ ). (III) and (IV) are also obtained from the above reaction mixture and  $\text{EtI}$ .

P. G. C.

**Crystalline constituent of essential oil of matsubasa.**—See this vol., 651.

**Diacyetyl.** J. PIEN, J. BAISSÉ, and R. MARTIN (Ann. Falsif., 1936, 29, 204—225).—The prep. of  $\text{Ac}_2$  from  $\text{CMeEt}\cdot\text{N}\cdot\text{OH}$ , its recognition by formation of the yellowish-brown xyloquinone, and the characterisation by means of the phenylhydrazone and particularly by its reaction with 3 : 4-tolylenediamine and  $\text{H}_2\text{SO}_4$  are described. The yellow colour of the quinoxaline is appreciable at dilutions of 1 : 100,000 and for the determination,  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions may be used as colour standards. Conversion into the dioxime and treatment with a  $\text{Ni}$  salt is not sensitive. The formation of  $\text{Ac}_2$  in milk products and its isolation and determination are discussed.

E. H. S.

**Cobalt salts of glyoximes. I. II. Diglyoxime and sesquiglyoxime cobaltic salts.** L. CAMBI and (SIGNA.) C. CORISELLI (Gazzetta, 1936, 66, 81—91, 91—99).—I. The red series of complex Co derivatives of glyoximes represents  $\text{Co}^{\text{II}}$ , whilst the green series (A., 1924, i, 20) represents  $\text{Co}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$  salts being very readily oxidised in presence of glyoximes. The magnetic susceptibilities ( $\chi$ ) at  $84$ — $294^\circ\text{ abs.}$  of a no. of complexes are tabulated. In simple additive compounds of the type  $(\text{DH}_2)_2\text{Co}^{\text{II}}\text{X}_2$  ( $\text{DH}_2 = \text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ ),  $\chi$  is additive; salts of the red series (A., 1931, 938) belong to this type. Those of the green series are diamagnetic, and thus have the structure  $[(\text{DH})(\text{DH}_2)\text{Co}^{\text{III}}\text{X}_2]$  or  $[(\text{DH}_2)_2\text{Co}^{\text{III}}\text{X}_2]\text{H}$ ; they are obtained in  $\text{EtOH}$  from  $\text{CoX}_2$  and  $(\text{DH}_2)$ , in presence of acid and of  $\text{O}_2$ . With  $\text{NH}(\text{CH}_2\text{Ph})_2$ , and of other *sec.* amines,  $[(\text{DH})(\text{NH}_2)\text{CoBr}]$  (I) forms salts of type  $[(\text{DH})_2\text{CoBr}_2]\text{NH}_2(\text{CH}_2\text{Ph})_2$ , which are reconverted into (I) by  $\text{HBr}$ . With  $\text{NH}_3$ , the complex  $[(\text{DH})_2\text{Co}(\text{NH}_3)_2]\text{Br}$  is formed, or, using  $\text{NH}_4\text{OAc}$ ,  $[(\text{DH})_2\text{Co}(\text{NH}_3)_2]\text{Br}$ . With  $\text{AgNO}_2$  and  $\text{NaOAc}$ , (I) yields the complex  $[(\text{DH})_2\text{Co}(\text{NO}_2)_2]\text{Na}\cdot\text{H}_2\text{O}$ , in which  $\text{Na}$  can be replaced by the ion  $\text{NH}_2\text{Bu}^\delta$ , or by  $\text{H}$ . With  $\text{KOH}$ , (I) gives the salt  $[(\text{DH})_2\text{Co}(\text{OH})_2]\text{K}$ . Action of  $\text{KOAc}$  on (I) yields the diamagnetic complexes  $[(\text{DH})_2\text{Co}(\text{OH})]$  and  $[(\text{DH})\text{Co}(\text{D})]$ , which are reconverted into (I) by  $\text{HBr}$ .

II.  $\text{Co}(\text{OAc})_2 + \text{AcOH}$  and  $\text{DH}_2$  in boiling  $\text{EtOH}$  absorb  $\text{O}_2$  to form the complex  $[\text{Co}_2(\text{D})_3]$  (II), also obtained from  $[(\text{DH})\text{Co}(\text{D})]$  and  $\text{DH}_2$ , or from  $\text{Co}$  and  $\text{DH}_2$ ; (II) with  $\text{HBr}$  yields  $[(\text{DH})(\text{DH}_2)\text{CoBr}_2]$ . The *p*-tolylmethyl- and diphenyl-glyoxime analogues of (II) behave similarly.  $\chi$  of (II) varies according to method of prep. The structures of  $[(\text{DH})\text{Co}(\text{D})]$  and of (II) are discussed.

E. W. W.

**Methylalkoxyglyoximes as chelate groups.** E. SHARRATT and W. WARDLAW (J.C.S., 1936, 563—



567).—When  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$  (I) (*Ni* derivative, decomp.  $243^\circ$ ) and  $\text{CuCl}_2$  react in  $\text{EtOH}$  and the complex (I) produced (this vol., 410) is removed, the filtrate slowly deposits *Cu methylethoxyglyoxime dichloride* (III), m.p.  $165^\circ$  (decomp.), decomposed by  $\text{H}_2\text{O}$ ,  $\kappa=3.471\times 10^{-5}$  at  $25^\circ$ ; it is produced from (II) and  $\text{EtOH}$  by oxidation and its structure is proved by the following reactions. (III) is not obtained from (II) in the absence of air, with aq.  $\text{Na}_2\text{S}$  gives *methylethoxyglyoxime* (IV), m.p.  $142^\circ$  (*Ni* derivative, m.p.  $197^\circ$ ), and with  $\text{H}_2\text{S}$ -aq.  $\text{EtOH}$  gives  $\text{OH}\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , m.p.  $95^\circ$  [produced from (IV) by the  $\text{HCl}$  liberated; modified prep.]. (I) and  $\text{CuCl}_2$  in  $\text{MeOH}$  do not ppt. a complex analogous to (II), but slowly yield *Cu methylethoxyglyoxime dichloride* (V), m.p.  $176^\circ$  (decomp.), which with  $\text{Na}_2\text{S}$  and  $\text{H}_2\text{S}$  gives *methylmethoxyglyoxime*, m.p.  $148^\circ$  (*Ni* derivative, m.p.  $223^\circ$ , decomp.  $285^\circ$ ), and  $\text{OH}\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{Me}$ , m.p.  $71^\circ$  (lit.  $69^\circ$ ), respectively. When heated in  $\text{EtOH}$  or  $\text{MeOH}$  in air, (II) gives (III) and (V), respectively. Dimethyl-, methyl-ethyl- (*Ni* derivative, decomp.  $260^\circ$ ), and benzyl-methyl-glyoxime yield no such compounds, since they do not possess an oxidisable H. R. S. C.

**Harding sugar reagent.** E. J. KING, G. A. D. HASLEWOOD, and G. A. GRANT (*Nature*, 1936, 137, 872).—The Harding-Downs factor for glucose (A., 1933, 964) can be consistently reproduced when reagents of a sufficiently high grade are used. Van der Plank's results (this vol., 650) may be due to the use of inferior reagents. L. S. T.

**Enolisation of sugars under the action of different bases.** A. KUSIN (*Ber.*, 1963, 69, [B], 1041–1049).—Solutions of glucose (I) and  $\text{Ca}(\text{OH})_2$  when acidified after 1 hr. at  $30^\circ$  immediately decolorise dichloroindophenol and absorb I from acid solution, thus showing the presence of enolic OH. In similar circumstances solutions of (I) and  $\text{NaOH}$  or  $\text{NaOH}\cdot\text{Na}_2\text{HPO}_4$  ( $p_{\text{H}}$  12) have no reducing properties in acid solution. The existence of enolic OH is further established by the rapid disappearance of the reducing action and a fugitive coloration with  $\text{FeCl}_3$ . After 24 hr. at room temp. mannose (II) is present in appreciable amount in solution of (I) and  $\text{Ca}(\text{OH})_2$ , whereas after 48 hr. fructose (III) can scarcely be detected. In solutions of (I) and  $\text{NaOH}$  (III) can be isolated as *Ca fructosate* after 24 hr., whereas (II) is present only in traces. It is considered that the enolic form is produced from (I) by  $\text{Ca}(\text{OH})_2$  without rupture of the pyranose ring, whereas the much less stable enol formed by the action of  $\text{NaOH}$  has the open-chain structure. H. W.

**Optical rotation of *l*-threose.** V. DEULOFEV (*J. Amer. Chem. Soc.*, 1936, 58, 855; cf. Hockett, this vol., 191).—*d*-Threosediacetamide triacetate, prepared by the method (A., 1933, 147) used for the *l*-erythrose derivative, has m.p.  $176\text{--}177^\circ$   $[\alpha]_{\text{D}} +38^\circ$  in  $\text{H}_2\text{O}$ . The compounds of the *l*-threose series (A., 1930, 68) need correction for sign and vals. H. B.

**Monomethylhexoses. II. Revision of the constitutions of the supposed 4-methylgalactose and 4-methylmannose of Pacsu, and their for-**

**mulation as 6-methylgalactose and 2-methylmannose, respectively.** J. MUNRO and E. G. V. PERCIVAL (*J.C.S.*, 1936, 640–644; cf. A., 1935, 1108).—The so-called 4-methylgalactose of Pacsu and Lob (A., 1930, 197) is 6-methylgalactose (I). The experiments of Pacsu and von Kary (A., 1930, 70) on the methylation of diisopropylidenemannose-dibenzylmercaptal (II) could not be repeated; the supposed 4-methylmannose was probably 2-methylmannose (III) mixed with mannose and some polymethylated derivatives. (I) was recognised by (a) comparison with authentic specimens of the sugar, m.p.  $122\text{--}123^\circ$ ,  $[\alpha]_{\text{D}} +112^\circ$  (4 min.)  $\rightarrow +66^\circ$  in 6 hr. in  $\text{H}_2\text{O}$ , its phenylosazone, m.p.  $200\text{--}201^\circ$ ,  $[\alpha]_{\text{D}} +144^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and phenylhydrazone, m.p.  $179^\circ$ ,  $[\alpha]_{\text{D}} +24^\circ \rightarrow +14.8^\circ$  in 24 hr. in  $\text{C}_5\text{H}_5\text{N}$ , (b) formation of the  $\text{Ac}_3$  derivative, triacetyl-methylgalactosidyl bromide, methyltriacetyl-methylgalactoside, reaction with  $\text{Me}_2\text{SO}_4\text{--NaOH}$ -aq.  $\text{COME}_2$  and then with  $\text{MeI}\text{--Ag}_2\text{O}$ , and finally hydrolysis by 8%  $\text{HCl}$  at  $100^\circ$  to 2:3:4:6-tetramethylgalactose, (c) oxidation by  $\text{Br}$  at  $35^\circ$  to a  $\gamma$ -lactone, and (d) formation of a mixture of methyl-furanoside and -pyranoside with 0.5%  $\text{HCl}\text{--MeOH}$ . (II), when heated, gives mannosedi-benzylmercaptal,  $[\alpha]_{\text{D}} +79^\circ$  in  $(\text{CHCl}_3)_2$ . Pacsu and von Kary's conditions of methylation gave a syrup, yielding a mixture ( $\text{OMe}$  2.4%), m.p.  $118^\circ$  (sharp),  $[\alpha]_{\text{D}} -48^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ; with  $\text{HgCl}_2$ , the syrup gave only an oil (IV), which afforded a mixture ( $\text{OMe}$  11.1%) of methyl-tetra-acetyl- and -triacetyl-methyl-mannosides. More drastic methylation gives products with higher  $\text{OMe}$  contents which are, however, always mixtures. These syrups all give mannose-phenylhydrazone ( $<20\%$ ) and after removal thereof glucosazone (which must owe its formation to the presence of 2-methylmannose) and small amounts of methylated by-products. The structures of Pacsu's glucose-, galactose-, and mannose-dibenzylmercaptals need revision. R. S. C.

**Syntheses with 5:6-anhydroisopropylidene-glucose; *d*-glucosyl-6-phthalimide.** H. OHLE and E. EULER (*Ber.*, 1936, 69, [B], 1022–1026; cf. this vol., 192).—5:6-Anhydroisopropylideneglucose and pure  $\text{o-C}_6\text{H}_4(\text{CO})_2\text{NH}$  do not interact at  $140\text{--}150^\circ$ , but in presence of a suitable catalyst, notably  $\text{C}_5\text{H}_5\text{N}$ , isopropylidene-*d*-glucosyl-6-phthalimide (I) m.p.  $174^\circ$ ,  $[\alpha]_{\text{D}} +14.38^\circ$  in  $\text{COME}_2$ , is formed in 80% yield. The constitution of (I) follows from its conversion by  $\text{COME}_2$  containing  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$  into isodisopropylidene-*d*-glucosyl-6-phthalimide, m.p.  $124.5\text{--}125.5^\circ$ ,  $[\alpha]_{\text{D}} +18.92^\circ$  in  $\text{CHCl}_3$ , also obtained from isodisopropylideneglucose 6-*p*-toluenesulphonate through isodisopropylidene-*d*-glucosyl-6-amine, b.p.  $120^\circ$  (bath)/0.08 mm.,  $[\alpha]_{\text{D}} +39.9^\circ$  in  $\text{CHCl}_3$ . The  $\text{NH}_2$  in the isopropylideneglucosylamine of Ohle *et al.* (A., 1928, 870) is shown to occupy position 6, since the compound is converted by  $\text{o-C}_6\text{H}_4(\text{COCl})_2$  into a non-homogeneous product transformed by alkaline hydrolysis into isopropylidene-*d*-glucosyl-6-phthalamic acid, m.p.  $183^\circ$  (decomp.), also obtained from (I) and boiling dil.  $\text{NaOH}$ . (I) is hydrolysed by 50%  $\text{AcOH}$  at  $100^\circ$  to *d*-glucosyl-6-phthalimide, m.p.  $192^\circ$ ,  $[\alpha]_{\text{D}} +105.13^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , which strongly reduces Fehling's solution and gives approx. correct

results when titrated with I. When warmed with  $\text{NHPh}\cdot\text{NH}_2$  (3 mol.) and  $\text{AcOH}$  (3 mol.) at  $100^\circ$  it gives a (?) *phenylhydrazone*, m.p.  $171^\circ$ ,  $[\alpha]_D^{20} +81.66^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , whereas addition of it to a solution of  $\text{NHPh}\cdot\text{NH}_2$  (3 mol.) in excess of 25%  $\text{AcOH}$  at  $100^\circ$  affords a "semiosazone,"  $\text{C}_{46}\text{H}_{12}\text{O}_{10}\text{N}_8$ , m.p.  $177^\circ$ ,  $[\alpha]_D^{20} +80^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . H. W.

**Mechanism of carbohydrate oxidation. XIX. Preparation of disaccharide antipodes.** L. C. KREIDER and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 797—800).—The appropriate acetobromopentose (1 mol.) added in 10 portions to a stirred mixture of  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{OAc}$  (2 mols.),  $\text{Ag}_2\text{CO}_3$  (1 mol.), and "Drierite" (4 mols.) in  $\text{C}_6\text{H}_6$  (25 mols.) gives  $\beta$ -d- (I), m.p.  $102^\circ$  (all m.p. are corr.),  $[\alpha]_D^{21} +9.04^\circ$  in  $\text{CHCl}_3$ , and  $\beta$ -l- (II), m.p.  $102^\circ$ ,  $[\alpha]_D^{21} -9.07^\circ$  in  $\text{CHCl}_3$ , -arabinosido- and  $\beta$ -d-, m.p.  $117^\circ$ ,  $[\alpha]_D^{22} -60.3^\circ$  in  $\text{CHCl}_3$ , and  $\beta$ -l-, m.p.  $117^\circ$ ,  $[\alpha]_D^{23} +60.2^\circ$  in  $\text{CHCl}_3$ , -xylosido-dihydroxyacetone tetra-acetates in yields of 20—35%. The  $\beta$ -dl-arabinosido-derivative, from (I) and (II), has m.p.  $116^\circ$ . Acetobromo-1-xylose, m.p.  $102^\circ$ ,  $[\alpha]_D +212.2^\circ$ , is prepared in 28% yield by Levene and Raymond's method (A., 1931, 336). The contribution of the group  $\text{OAc}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}$  towards the mol. rotation is calc. to be about  $\pm 33,600$  according to the position of the O ring. H. B.

**Carbohydrates. XX. New syntheses of gentiobiose and 1- $\beta$ -glucosidofructose.** P. BRIGL and O. WIDMAIER (Ber., 1936, 69, [B], 1219—1227).—The constitution of the 5:6-benzylidene-1:2-isopropylideneglucose (I) of Levene *et al.* (A., 1923, i, 92; 1933, 378) is confirmed by converting it into the acetate, m.p.  $104$ — $105^\circ$ , which passes when kept in 80%  $\text{AcOH}$  or catalytically hydrogenated into 1:2-isopropylideneglucose 3-acetate. The dibenzylidenefructose of Brigl *et al.* (A., 1932, 1115) is 2:3:4:5-dibenzylidenefructopyranose (II) since it readily affords a 1-p-toluenesulphonate, m.p.  $171^\circ$  (decomp.),  $[\alpha]_D -34.9^\circ$  in  $\text{CHCl}_3$ , and is converted by  $\text{MeI}$  and  $\text{Ag}_2\text{O}$  into 2:3:4:5-dibenzylidene-1-methylfructose, m.p.  $113$ — $114^\circ$ ,  $[\alpha]_D^{20} -30.5^\circ$  in  $\text{CHCl}_3$ , hydrolysed to non-cryst. 1-methylfructose, which affords 1-methyl-2:3:4:5-diisopropylidenefructose, m.p.  $48$ — $49^\circ$ . The possibility that the  $\text{CHPh}$  and  $\text{CMe}_2$  residues are not similarly placed is excluded since the condensation of fructose with  $\text{PhCHO}$  in presence of  $\text{ZnCl}_2$  gives also 2:3-benzylidenefructose, m.p.  $181^\circ$ ,  $[\alpha]_D^{20} -183.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  (triacetate, m.p.  $112^\circ$ ,  $[\alpha]_D^{20} -158.9^\circ$  in  $\text{CHCl}_3$ ; tribenzoate,  $[\alpha]_D^{20} -327.1^\circ$  in  $\text{CHCl}_3$ ), which does not reduce Fehling's solution, is oxidised by  $\text{Pb}(\text{OAc})_4$ , and is converted by  $\text{PhCHO}$  and  $\text{ZnCl}_2$  into (II). Condensation of (I) with acetobromoglucose (III) and  $\text{Ag}_2\text{O}$  in  $\text{CHCl}_3$  (free from  $\text{EtOH}$ ) followed by regulated catalytic hydrogenation of the product leads to 3:5-benzylidene-1:2-isopropylidene-6- $\beta$ -glucosidoglucose tetra-acetate, m.p.  $166^\circ$ ,  $[\alpha]_D^{20} -20.7^\circ$  in  $\text{CHCl}_3$ , hydrolysed (Zemplen) to 3:5-benzylidene-1:2-isopropylidene-6- $\beta$ -glucosidoglucose, m.p.  $219^\circ$ ,  $[\alpha]_D^{21} -13.9^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , whence gentiobiose. Similarly (II) and (III) afford 2:3:4:5-dibenzylidene-1- $\beta$ -glucosidofructose tetra-acetate, m.p.  $144^\circ$ ,  $[\alpha]_D^{20} -4.5^\circ$  in  $\text{CHCl}_3$ , converted by  $\text{NH}_3$ - $\text{MeOH}$  into 2:3:4:5-dibenzylidene-1- $\beta$ -glucosidofructose, m.p.  $176$  after softening at  $166^\circ$ ,  $[\alpha]_D^{21} -40.5^\circ$  in  $\text{CHCl}_3$ ,

which is catalytically hydrogenated to 1- $\beta$ -glucosidofructose, m.p.  $134$ — $138^\circ$ ,  $[\alpha]_D^{20} -59.4^\circ$  in  $\text{H}_2\text{O}$  (octa-acetate, m.p.  $128$ — $129^\circ$ ,  $[\alpha]_D^{20} -13.91^\circ$  in  $\text{CHCl}_3$ ).

H. W.

**Catalytic hydrogenation of sucrose. I. Hydrogenation with reduced nickel as catalyst.** T. TANNO (Bull. Chem. Soc. Japan, 1936, 11, 204—207).—Hydrogenation of sucrose at 100 atm. in presence of reduced Ni (prep. described) consists of a rapid reaction at  $155$ — $175^\circ$  and a slow one at about  $225^\circ$ . In one experiment  $3\text{H}_2$  were absorbed at  $170$ — $175^\circ$ , giving *d*-mannitol (I) (0.5 mol.) and *d*-sorbitol (II) (0.5 mol.) with a mixture (III) of  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$  and glycerol. In a second experiment  $2\text{H}_2$  were absorbed at  $155$ — $160^\circ$  giving (I) and (II) and a resinous mixture, which was further reduced at  $170$ — $175^\circ$  to (III). Fructose gives similarly (I) and (II), but no (III), whence it is inferred that (III) is derived from the glucose portion of the mol. R. S. C.

#### Glycoside fissions in non-aqueous media.

**I. Alcoholysis of phenylglucosides.** W. VOSS and W. WACHS. **II. Alcoholysis of disaccharides.** W. VOSS, H. HEISIG, and W. WACHS (Annalen, 1936, 522, 240—261, 261—268).—I. The reaction between various phenylglucosides and  $\text{MeOH}\cdot\text{HCl}$  (0.5*N*) in presence of about 10% of  $\text{MeCl}$  at  $25\pm 0.05^\circ$  is followed by titration of the  $\text{PhOH}$  formed with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  (Chapin, A., 1920, ii, 563). The mean vals. of  $k\times 10^5$  are:  $\alpha$ - and  $\beta$ -phenylglucosides, 82.8 and 49, respectively [corresponding vals. for hydrolysis with aq. 0.5*N*- $\text{HCl}$  are 1.48 and 0.43, respectively];  $\alpha$ - and  $\beta$ -phenylglucoside tetra-acetates, 122 and 44.9, respectively [vals. for acetolysis with  $\text{AcOH}\cdot\text{HCl}$  (0.5*N*) are 112 and 7.5, respectively]; tetramethyl- $\alpha$ -, b.p.  $132.5$ — $133^\circ/0.05$  mm.,  $145$ — $146^\circ/0.19$  mm.,  $[\alpha]_D^{22} +158.5^\circ$  in  $\text{MeOH}$ , and - $\beta$ -, m.p.  $78$ — $78.5^\circ$ ,  $[\alpha]_D^{22} -65.8^\circ$  in  $\text{MeOH}$ , -phenylglucosides (prepared from the acetates and  $\text{Me}_2\text{SO}_4$  in  $\text{MeOH} + 50\%$   $\text{NaOH}$  at  $55^\circ$ ), 29.8 and 7.6, respectively. Polarimetric data for the methanolyses show that Walden inversion occurs, i.e.,  $\alpha$ - and  $\beta$ -methylglucosides are formed from  $\beta$ - and  $\alpha$ -phenylglucosides, respectively; subsequent equilibration may take place. Much  $\alpha$ - and a little  $\beta$ -methyl-*d*-glucoside are isolable from the reaction product from the above  $\beta$ -tetra-acetate. The first stage in the methanolysis is considered to be the addition of 1 mol. of  $\text{HCl}$  to give an oxonium-like compound.

**II. Methanolysis (as above) of heptamethyl- $\beta$ -methylcellobioside (I) and -methylmaltoside** is followed polarimetrically. The data for (I) show that inversion occurs, i.e., tetramethyl- $\alpha$ - and 2:3:6-trimethyl- $\beta$ -methylglucosides are formed. The conclusions of Hess *et al.* (A., 1928, 1359) are thus invalidated.

H. B.

**Synthetic nucleosides. IV. Theophylline-5-methyl-*l*-rhamnofuranoside.** P. A. LEVENE and J. COMPTON (J. Biol. Chem., 1936, 114, 9—26; cf. A., 1931, 940).—Theophylline-5-methyl-*l*-rhamnofuranoside (I) is prepared and certain aspects of rhamnose derivatives are discussed. Methyl- $\beta$ -5-methyl-*l*-rhamnofuranoside, b.p.  $58$ — $60^\circ/0.3$  mm.,  $[\alpha]_D^{25} +6.3^\circ$  in  $\text{H}_2\text{O}$ , is obtained from isopropylidene-*l*-rhamnose (II), m.p. 92 93, by



Mel- $\text{Na}_2\text{SO}_4$ - $\text{Ag}_2\text{O}$ , which proves the  $\beta$ -structure of (II). The  $\alpha$ -glucoside (impure), b.p.  $58-60^\circ/0.3$  mm.,  $[\alpha]_D^{24} -21.6^\circ$  in  $\text{H}_2\text{O}$ , is obtained similarly from the isopropylidene compound (III), m.p.  $79-81^\circ$ , which proves the  $\alpha$ -structure of (III). Both glucosides are hydrolysed by 1.5%  $\text{H}_2\text{SO}_4$  to syrupy 5-methyl-1-rhamnofuranose (IV), the phenylhydrazone, m.p.  $162-163^\circ$ ,  $[\alpha]_D^{24} -18.4^\circ \rightarrow +8.1^\circ$  in 7 days in  $\text{C}_5\text{H}_5\text{N}$ , of which with PhCHO affords the furanose with m.p.  $102-103^\circ$ ,  $[\alpha]_D -4.3^\circ$  (const.) in  $\text{H}_2\text{O}$ , and with  $\text{NHPh}\cdot\text{NH}_2$  gives the phenylosazone, m.p.  $123-124^\circ$ ,  $[\alpha]_D +65.3^\circ \rightarrow +44.4^\circ$  in 3 days in  $\text{C}_5\text{H}_5\text{N}$ -abs. EtOH (3:2). (IV) with cold  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  gives the  $\alpha$ - $\text{Ac}_3$  derivative (V), m.p.  $115-116^\circ$ ,  $[\alpha]_D^{25} -76.3^\circ$  in dry MeOH, and the  $\beta$ - $\text{Ac}_3$  compound, b.p.  $128-132^\circ/0.8$  mm.,  $[\alpha]_D^{24} -13.6^\circ$  in dry MeOH. (IV) with MeOH-HCl gives amongst other substances methyl- $\alpha$ -5-methyl-1-rhamnopyranoside (VI), m.p.  $59-60^\circ$ ,  $[\alpha]^{23} -89.2^\circ$  in  $\text{H}_2\text{O}$ . (V) and liquid HBr at room temp. (25 mm.) give the furanosidyl bromide, which with Ag theophylline in PhMe gives (I), m.p.  $212-213^\circ$ ,  $[\alpha]_D -46.3^\circ$  in  $\text{H}_2\text{O}$ . The crude mixture of 4- and 5-methyl-1-rhamnose triacetates with HBr-AcOH at  $0^\circ$  gives readily acetyl-4-methyl-1-rhamnosidyl bromide (VII) (previously considered to be the 5-Me compound), m.p.  $104-105^\circ$ ,  $[\alpha]_D^{25} -184.2^\circ$  in  $\text{CHCl}_3$  [also obtained from the pure 4-Me compound (VIII)], which with Ag theophylline in xylene at  $80-90^\circ$  gives theophylline- $\beta$ -4-methyl-1-rhamnopyranoside (IX), m.p.  $179-180^\circ$ ,  $[\alpha]^{23} -71.8^\circ$  in  $\text{H}_2\text{O}$ , also obtained by condensation of (VII) and hydrolysis of the resulting amorphous  $\text{Ac}_3$  compound. (VII) with  $\text{Ag}_2\text{O}$ -MeOH or its  $\text{Ac}_2$  derivative with  $\text{Ba}(\text{OMe})_2$ -MeOH gives methyl- $\beta$ -4-methyl-1-rhamnopyranoside, b.p.  $105-106^\circ/0.3$  mm.,  $[\alpha]_D^{24} -13.9^\circ$  in  $\text{H}_2\text{O}$ . Deacetylation of (VIII) affords about equal amounts of  $\beta$ - (XI), m.p.  $125-126^\circ$  [phenylosazone, m.p.  $162-163^\circ$ ,  $[\alpha]_D^{24} -25.8^\circ \rightarrow +14.3^\circ$  in 2 weeks in  $\text{C}_5\text{H}_5\text{N}$ -EtOH (3:2)], and  $\alpha$ -4-methyl-1-rhamnose, a syrup; the latter crude ether gives methyl- $\alpha$ -4-methyl-1-rhamnopyranoside (X), b.p.  $104-105^\circ/0.3$  mm.,  $[\alpha]^{23} -50.2^\circ$  in  $\text{H}_2\text{O}$ . Theophylline- $\beta$ -1-triacetyl-rhamnopyranoside and  $\text{Ba}(\text{OMe})_2$ -MeOH at  $0^\circ$  gives theophylline- $\beta$ -1-rhamnopyranoside, m.p.  $190-191^\circ$ ,  $[\alpha]^{25} -89.3^\circ$  in  $\text{H}_2\text{O}$ . (I) and (IX) are hydrolysed by 0.03N-HCl at  $100^\circ$  at about equal rates, but this is due to some peculiarity of the purine substituent, since (VI) is hydrolysed much faster than is (X). Mutarotation of (IV) could not be observed, but is assumed to occur very rapidly, since the presence of free CHO is contradicted by the absorption spectra. Mutarotation of (XI) in  $\text{H}_2\text{O}$  is rapid, resembling that of  $\beta$ -1-rhamnose.

R. S. C.

Colloid behaviour of starch, cellulose, and glycogen.—See this vol., 795.

Highly polymerised compounds. CXXXVIII. Tearing of the thread molecules of cellulose by grinding. H. STAUDINGER and E. DREHER (Ber., 1936, 69, [B], 1091-1098).—Intensive grinding of cellulose (I) under  $\text{H}_2\text{O}$  in an agate ball mortar causes degradation of the thread mols.; after 12 hr. the material has a mean degree of polymerisation about 300. The degraded cellulose nitrates obtained from the partly depolymerised materials form a

polymeric-analogous series; on further grinding they suffer marked degradation. The non-degraded eucolloidal celluloses are tenacious and long-fibred, dissolve with marked swelling, and give highly viscous solutions. The degraded mesocolloidal celluloses of degree of polymerisation 300 are friable and readily sol. without swelling to solutions of low viscosity. The degradation of eucolloidal polystyrene when ground under  $\text{H}_2\text{O}$  is more pronounced than that of (I); it is also degraded when its solutions are forced through very fine holes in a Pt foil, whereas cellulose nitrate in amyl acetate is not greatly changed.

H. W.

Hexamethylenetetramine compounds. P. BOUCHEREAU (J. Pharm. Chim., 1936, [viii], 23, 549-556).—The compounds  $M(\text{CaCl}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $M(\text{MgCl}_2)_2 \cdot 2\text{H}_2\text{O}$ , and  $M(\text{MgSO}_4)_2 \cdot 2\text{H}_2\text{O}$  [ $M = (\text{CH}_2)_6\text{N}_4$ ] are described. Their antiseptic action is ascribed to free  $\text{CH}_2\text{O}$ .

E. W. W.

Reaction of carbonyl chloride with hexamethylenetetramine.—See this vol., 689.

Characterisation and determination of tri-(hydroxyethyl)amine. D. FLORENTIN and (MME.) I. RUIZ (Ann. Falsif., 1936, 29, 197-204).—The isolation of  $\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_3$  from its preps. and characterisation by means of the platinichloride, aurichloride, and silicotungstate, and its gasometric determination by decomp. with hypobromite are described.

E. H. S.

Amino-acids and related compounds. IX. Electrolytic oxidation of proline and  $\gamma$ -aminobutyric acid. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1936, 11, 138-141; cf. A., 1935, 92).—Electrolytic oxidation of proline gives mainly succinimide with a little  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  and a solution, which with hot  $\text{Ba}(\text{OH})_2$  gives  $\text{NH}_3$ , pyrrolidine, and  $\text{NH}_2\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$  (I) and which thus probably contained pyrrolidone. Similar oxidation of (I) gives  $\text{NH}_3$  and  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ . (I) is considered to be the primary product indicating preferential attack at the *tert*-C.

R. S. C.

Delayed oxidation of cysteine and ascorbic acid.—See this vol., 685.

Condensation products of glucidic acid derivatives with amines. O. VON SCHICKH (Ber., 1936, 69, [B], 976-974).— $\alpha\beta$ -Oxido- $\beta$ -methyl-n-butyramide (I), m.p.  $121^\circ$ , is obtained by the action of conc. aq.  $\text{NH}_3$  on the corresponding Et ester or, preferably, by the action of Na on  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$  in  $\text{COMe}$ , at  $0-2^\circ$ .  $\alpha\beta$ -Oxido- $\beta$ -phenyl- $\alpha$ -methylpropionamide, m.p.  $134^\circ$ , and -methylamide, m.p.  $116^\circ$ , are derived from the corresponding Et ester.  $\alpha\beta$ -Oxido- $\beta$ -phenyl-n-valeramide has m.p.  $119-121^\circ$ ,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NEt}_2$ ,  $\text{NaNH}_2$ , and  $\text{COMe}_2$  at  $0-5^\circ$  affords  $\alpha\beta$ -oxido- $\beta$ -methyl-n-butyrdiethylamide, b.p.  $122-124^\circ/12$  mm. Et  $\alpha\beta$ -oxido- $\beta$ -phenyl- $\alpha$ -methylpropionate and  $\text{NH}_2\text{Me}\cdot\text{H}_2\text{O}$  at  $100^\circ$  give  $\beta$ -methylamino- $\alpha$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionmethylamide hydrochloride, m.p.  $240-242^\circ$  (decomp.), hydrolysed by HCl (*d* 1.19) at  $150^\circ$  to  $\beta$ -methylamino- $\alpha$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylpropionic acid hydrochloride, m.p.  $224-225^\circ$  (decomp.).  $\text{NH}_2\text{Ph}$  and (I) at  $120^\circ$  afford  $\alpha$ -anilino- $\beta$ -hydroxy- $\beta$ -methylbutyramide, m.p.  $102^\circ$ , whilst Et  $\alpha$ -anilino- $\beta$ -

hydroxy- $\beta$ -methylbutyrate, b.p. 171—175°/11 mm., m.p. 70—71°, is derived from the requisite Et ester and  $\text{NH}_2\text{Ph}$  at 170°. Et  $\alpha$ -methylanilino- $\beta$ -hydroxy- $\beta$ -methylbutyrate has b.p. 172—174°/8 mm. When heated with the requisite amine (I) affords  $\alpha$ -p-phenetidino-, m.p. 105°,  $\alpha$ -p-allyloxyanilino-, (+ $\text{H}_2\text{O}$ ), m.p. 70—72°,  $\alpha$ -4-aminoantipyril-, m.p. 151°, and  $\alpha$ -2-aminopyridyl-, m.p. 182—183°, - $\beta$ -hydroxy- $\alpha$ -methylbutyramide.  $\alpha$ -6-Methoxy-8-quinolylamino- $\beta$ -hydroxy- $\beta$ -methylbutyrdiethylamide has m.p. 170—171° (decomp.).  $\text{NHPh}\cdot\text{NH}_2$  and (I) at 150—180° give 4-hydroxy-1-phenyl-3:3-dimethylpyrazolid-5-one, m.p. 182—183°, transformed by  $\text{Me}_2\text{SO}_4$  and alkali into 4-hydroxy-1-phenyl-2:3:3-trimethylpyrazolid-5-one, m.p. 109°. With  $\text{CO}(\text{NH}_2)_2$  at 150—200° (I) yields 5-hydroxy-2:6-diketo-4:4-dimethylhydro-pyrimidine, m.p. 196—197°. H. W.

**Condensation of chloral with acid amides. Properties of  $\text{CH}(\text{OH})\cdot\text{CCl}_3$  group.** A. N. MELDRUM and M. G. BHOJRAJ (J. Indian Chem. Soc., 1936, 13, 185—186; cf. Yelburgi *et al.*, A., 1934, 770).—Condensation of  $\text{CCl}_3\cdot\text{CHO}$  with the appropriate  $\text{R}\cdot\text{CO}\cdot\text{NH}$ , affords chloral-propion-, m.p. 166—167°, -isobuty-, m.p. 156—157°, -n-valer-, m.p. 142°, -n-hexo-, m.p. 139°, -n-hepto-, m.p. 125—126°, and -phenylacet-, m.p. 141°, -amide. Reduction of these with  $\text{Zn}\cdot\text{AcOH}$  at <40° affords  $\beta\beta$ -dichlorovinyl-acet-, m.p. 88—89°, -propion-, m.p. 100—101°, -isobuty-, m.p. 84—85°, -n-valer-, m.p. 65—66°, -n-hexo-, m.p. 62—64°, -n-hepto-, m.p. 38—39°, and -phenylacet-, m.p. 90—92°, -amide. J. W. B.

**Determination of carbamide by the Folin distillation method. Determination by steam-distillation.** F. H. L. TAYLOR and M. A. ADAMS (J. Lab. Clin. Med., 1935, 20, 983—985).—Steam-distillation is preferred to the original direct distillation. CH. ABS. (p)

**Preparation of carbamides.** J. S. BUCK and C. W. FERRY (J. Amer. Chem. Soc., 1936, 58, 854).—*N*-Phenyl-*N*-n-butyl-, *N*-o-tolyl-*N*-n-propyl- and -n-butyl-, *N*-m-tolyl-*N*-ethyl- and -n-propyl-, and *N*-p-tolyl-*N*-n-propyl-carbamides are best prepared (61—91% yields) (cf. A., 1935, 1488) by cautious warming of  $\text{NHArAlk}$  (1 mol.) with  $\text{NO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  (1.15 mols.) in 95% EtOH (4—5 vols.). H. B.

**Dialkylaminoacetylcarbamides.** T. C. DANIELS (J. Amer. Pharm. Assoc., 1936, 25, 285—286).—The following aminoacetylcarbamides were prepared: diethyl m.p. 102°, di-n-propyl-, m.p. 123°, di-n-butyl-, m.p. 122°, diisobutyl-, m.p. 68°, di-n-amyl-, m.p. 97°, and diisoamyl-, m.p. 99°. None possesses hypnotic properties. F. O. H.

**Aliphatic carbimides and their conversion into  $\alpha$ -aryl- $\beta$ -alkylcarbamides.** J. W. BOEHMER (Rec. trav. chim., 1936, 55, 379—391).—Alkyl-carbimides are rapidly prepared (50—95% yields) by slow addition of  $\text{R}\cdot\text{COCl}$  to activated  $\text{NaN}_3$  (Nelles, A., 1932, 1118) in  $\text{C}_6\text{H}_6$  or PhMe and then boiling until the theoretical vol. of  $\text{N}_2$  has been evolved. Thus are obtained methyl-, ethyl-, n- and iso-propyl- and -butyl-carbimide. By addition of the appropriate  $\text{NH}_2\text{Ar}$  s-arylalkylcarbamides are obtained of

which the following are new: s-p-methoxy-, m.p. 178°, p-acetyl-, m.p. 184°, m-, m.p. 119° and p-chloro-, m.p. 200°, and m-bromo-phenyl-, m.p. 134°, o-phenyl-, m.p. 170°,  $\beta$ -naphthyl-, m.p. 187°, and 5-, m.p. 221°, and 8-quinolyl-, m.p. 192°, -methylcarbamide; s-p-tolyl-, m.p. 123°, p-methoxy-, m.p. 136°, p-ethoxy-, m.p. 147°, p-acetyl-, m.p. 123°, m-, m.p. 107°, and p-chloro-, m.p. 189°, m-, m.p. 110° and p-bromo-phenyl-, m.p. 197°, o-phenyl-, m.p. 126°,  $\alpha$ -, m.p. 177° and  $\beta$ -naphthyl-, m.p. 177°, 2-pyridyl-, m.p. 103°, and 5-, m.p. 186° and 8-quinolyl-, m.p. 167°, -n-propyl-carbamide; s-p-tolyl-, m.p. 157°, p-methoxy m.p. 154°, p-ethoxy-, m.p. 183°, p-acetyl-, m.p. 153°, m-, m.p. 135°, and p-chloro-, m.p. 217°, m-, m.p. 133° and p-bromo-phenyl-, m.p. 212°, o-, m.p. 157°, and p-phenyl-, m.p. 214°,  $\alpha$ -, m.p. 200° and  $\beta$ -naphthyl-, m.p. 192°, 2-pyridyl-, m.p. 104°, 5-, m.p. 232°, and 8-quinolyl-, m.p. 184°, -isopropylcarbamide, s-phenyl-, m.p. 130°, p-tolyl-, m.p. 119°, p-methoxy-, m.p. 116°, p-ethoxy-, m.p. 146°, p-acetyl-, m.p. 125°, m-, m.p. 83°, and p-chloro-, m.p. 173°, m-, m.p. 75°, and p-bromo-phenyl-, m.p. 185°, o-phenyl-, m.p. 120°,  $\alpha$ -, m.p. 149°, and  $\beta$ -naphthyl-, m.p. 175°, 2-pyridyl-, m.p. 88°, 5-, m.p. 179°, and 8-quinolyl-, m.p. 134°, -n-butylcarbamide; s-p-tolyl-, m.p. 154°, -p-methoxy-, m.p. 114°, -p-ethoxy-, m.p. 137°, -p-acetyl-, m.p. 72°, -m-, m.p. 114°, and -p-chloro-, m.p. 168°, -m-, m.p. 106°, and -p-bromo-phenyl-, m.p. 167°, -o-, m.p. 128°, and -p-phenyl-, m.p. 191°,  $\alpha$ -, m.p. 178°, and  $\beta$ -naphthyl-, m.p. 152°, 5-, m.p. 167°, and 8-quinolyl-, m.p. 164°, -isobutylcarbamide. With  $\text{NHPhMe}$  are obtained  $\alpha$ -phenyl- $\alpha$ -methyl- $\beta$ -n-, m.p. 46°, and - $\beta$ -isobutylcarbamide, m.p. 54°. With  $\text{H}_2\text{O}$  RNCO gives  $\text{CO}(\text{NHR})_2$  and thus are obtained s-di-n-, m.p. 100°, and -di-iso-propyl-, m.p. 192°, -di-n-, m.p. 71°, and -di-iso-butyl-, m.p. 134°, -carbamide. J. W. B.

**Complex compounds of semicarbazides.**—See this vol., 692.

**Synthesis of  $\beta\gamma$ -dihydropropylguanidine.** S. KAWAI and N. SUGIYAMA (Bull. Chem. Soc. Japan, 1936, 11, 141—143).—Heating  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OBz})\cdot\text{CH}_2\cdot\text{OBz}$  with  $\text{CN}\cdot\text{NH}_2$  or O-methyl- $\phi$ -carbamide in dry EtOH or  $\text{C}_2\text{H}_5\text{N}$  at 120—130° causes only migration of Bz to yield  $\text{NHBz}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OBz}$ , but  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$  and S-methyl- $\phi$ -thiocarbamide hydriodide in EtOH at 100° give  $\beta\gamma$ -dihydroxypropylguanidine, an oil (picrate, m.p. 126°). R. S. C.

**Reduction of nitroguanidine.** V. Synthesis of  $\gamma$ -amino- $\alpha$ -methyl-, - $\alpha$ -ethyl-, and - $\alpha$ -n-butyl-guanidine. G. W. KIRSTEN and G. B. L. SMITH (J. Amer. Chem. Soc., 1936, 58, 800—801).— $\gamma$ -Amino- $\alpha$ -methylguanidinium iodide, m.p. 121—122° [corresponding sulphate, m.p. 229—230° (decomp.)], and picrate, m.p. 162—163°, is prepared from  $\text{SMe}\cdot\text{C}(\text{NH})\cdot\text{NHMe}\cdot\text{HI}$  and  $\text{N}_2\text{H}_4$  or from  $\text{SMe}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HI}$  and  $\text{NH}_2\text{Me}$ .  $\gamma$ -Amino ethylguanidinium iodide, m.p. 84.5—86° (corresponding sulphate, m.p. 161—163°, and picrate, m.p. 113—114.5°), and  $\gamma$ -amino- $\alpha$ -n-butylguanidinium iodide, m.p. 51—52°, are similarly obtained from  $\text{SMe}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{Et}\cdot\text{HI}$  and S-methyl-n-butylisothiocarbamide hydriodide, m.p. 88—89° (from  $\text{NH}_2\cdot\text{CS}\cdot\text{NHBu}^\alpha$



and EtOH-MeI), respectively.  $\gamma$ -Amino- $\alpha$ -phenylguanidine could not be similarly prepared. H. B.

**Dyes from furfuraldehyde.** T. BOEHM and (FRL.) M. GROHNWALD (Arch. Pharm., 1936, 274, 318—326).—Hydrofurfuramide,  $\text{CHR}\cdot\text{N}\cdot\text{CHR}\cdot\text{N}\cdot\text{CHR}$  ( $\text{R}=\text{2-furyl}$ ), and  $\text{CH}_2(\text{CN})_2$  (I) in EtOH give  $\text{NH}_3$  and  $\gamma$ -hydroxy- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienyl  $\alpha\alpha\eta$ -tetracyanide (II), violet, decomp.  $225^\circ$ , anhyd. (from MeOH),  $+0.66\text{EtOH}$  (0.33 mol. retained at  $120^\circ/0.1$  mm.),  $+0.5\text{Pr}^{\text{B}}\text{OH}$ ,  $+C_5H_5N$ , and  $+AcOH$ . The liberated  $\text{NH}_3$  plays a part in the reaction, for (II) is also obtained from furfurylidene malonitrile (III) and  $\text{NH}_2\text{R}\cdot\text{EtOH}$ , R being H, Me, Et, Ph, or, best,  $\text{CH}_2\text{Ph}$ , or  $\text{NHMe}_2$  or  $\text{NHEt}_2\cdot\text{EtOH}$ . The presence of a free OH in (II) is shown by formation ( $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ ) of an Ac derivative (IV), decomp.  $210^\circ$ ,  $+C_5H_5N$  and anhyd. (III) and  $\text{NH}_2\cdot\text{CH}_2\text{Ph}$  give also as by-product N- $\delta$ -hydroxy- $\zeta\zeta$ -dicyanohexatrienylbenzylamine (V), blue, m.p.  $161^\circ$ , decomposes when recrystallised (hydrochloride,  $+MeOH$ , m.p.  $140^\circ$  after decomp. from about  $140^\circ$ ), which with  $\text{NHPh}\cdot\text{NH}_2$  in a little EtOH gives N- $\delta$ -hydroxy- $\zeta\zeta$ -dicyano- $\Delta^{\alpha\gamma\epsilon}$ -hexatrienyl-N'-phenylhydrazine, m.p.  $186^\circ$  after sintering at  $176^\circ$ , and with (I) yields (III) immediately. (II) is thus formed by primary reaction to (V) or its analogous amine and further reaction thereof with (I). Furfurylidene cyanoacetamide and  $\text{NH}_2\cdot\text{CH}_2\text{Ph}$  in hot EtOH give similarly  $\gamma$ -hydroxy- $\alpha\eta$ -dicyano- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienedicarbonamide,  $+H_2O$ , m.p.  $240\text{--}244^\circ$  (decomp.). (II) and cold conc. HCl give a substance, possibly the monoamide,  $C_{11}H_8O_2N_4$ , m.p.  $250\text{--}255^\circ$  (decomp.),  $+1.5AcOH$  and  $+EtOH$  [Ac derivative (by  $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ ), decomp.  $215\text{--}220^\circ$ ]. Hydrogenation of (II) gives mixtures; if that (2% Pd-BaSO<sub>4</sub>) of (IV) in  $\text{COMe}_2$  is stopped after adsorption of  $2H_2$ , there is obtained a substance, possibly an amide,  $C_{13}H_{12}O_2N_4$ , m.p.  $94\text{--}96^\circ$ , which is sol. in KOH, from which after some hours HCl ppts. an acid,  $C_{13}H_{11}O_5N_3$ , m.p.  $86^\circ$ . R. S. C.

**Arsinocarboxylic acids.** H. J. BACKER and C. H. K. MULDER (Rec. trav. chim., 1936, 55, 357—370).—Arsinocarboxylic acids are prepared by the reaction  $K_3AsO_3 + \text{CHBr}\cdot\text{CO}_2K \rightarrow \text{AsO}_3K_2\cdot\text{CHR}\cdot\text{CO}_2K + KBr$ , and are isolated from their Pb salts. Kinetic studies in the case  $\text{R}=\text{Me}$  show that the rate increases with increasing concn. of reactants more rapidly than is required by a bimol. reaction and optimum yields (in parenthesis) are obtained when the mol. ratio  $\text{KOH}/\text{As}_2\text{O}_3=6:1$ . Thus are prepared arsinoacetic,  $\alpha$ -arsino-propionic (I), m.p.  $134^\circ$  (71%) ( $\text{Ag}$ ,  $\text{Ba}_3+5H_2O$ , and  $\text{Pb}$  salts),  $n$ -butyric, m.p.  $127^\circ$  (68%) ( $\text{Ag}$ ,  $\text{Ba}+H_2O$ ,  $\text{Ba}_3+7H_2O$ , and  $\text{Pb}$  salts),  $\alpha$ -valeric, m.p.  $116\text{--}117^\circ$  (40%) ( $\text{Ba}+H_2O$  and  $+2H_2O$ ,  $\text{Ba}_3$ , and  $\text{Pb}$  salts),  $n$ -hexoic, m.p.  $96^\circ$  (33%),  $n$ -heptoic, m.p.  $82\text{--}83^\circ$  (19%) (together with  $\alpha$ -hydroxy- $n$ -heptoic acid, m.p.  $63^\circ$ ),  $n$ -octoic, m.p.  $114^\circ$  (12%) (with  $\alpha$ -hydroxy- $n$ -octoic acid, m.p.  $79^\circ$ ), and  $n$ -nonoic acid, m.p.  $115^\circ$ . Similarly  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2K$  gives  $\beta$ -arsinopropionic acid (II), m.p.  $145^\circ$  (56%) ( $\text{Na}_2+5H_2O$ ,  $\text{Ag}$ , and  $\text{quinine}+6H_2O$  salts). Reduction ( $H_3PO_2$ ) of (I) and (II) affords respectively  $\alpha$ -, ( $\text{As}\cdot\text{CHMe}\cdot\text{CO}_2H$ )<sub>2</sub>, decomp.  $85\text{--}90^\circ$ , and  $\beta$ -arsenopropionic acid, m.p.  $155\text{--}157^\circ$ .  $K_3AsO_3$  with either  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}_2K$  or

$\text{CH}_2\cdot\text{CBr}\cdot\text{CO}_2K$  gives  $\alpha$ -arsinoacrylic acid, m.p.  $159^\circ$  (43%—50%) ( $\text{quinine}+6H_2O$  salt), reduced to  $\alpha$ -arsenoacrylic acid, m.p.  $180^\circ$  (decomp.). Phenyl-arsinoacetic acid, sinters  $100^\circ$ , m.p.  $110^\circ$ , is similarly prepared. These acids titrate as dibasic acids to phenolphthalein. Some crystallographic data are given. J. W. B.

#### Organic reactions with silicon compounds.

**I. Use of silicon tetrafluoride in formation of esters and absorption reactions.** J. A. GIERUT, F. J. SOWA, and J. A. NIEWLAND (J. Amer. Chem. Soc., 1936, 58, 786—787).—Quant. yields of  $\text{MeOAc}$  and  $\text{EtOAc}$  and 20—60% yields of  $\text{Pr}^{\text{B}}\text{OAc}$ ,  $\text{Bu}^{\text{O}}\text{Ac}$ , and  $\text{Bu}^{\text{B}}\text{OAc}$  are obtained from  $\text{SiF}_4$  (from  $\text{Na}_2\text{SiF}_6$ ,  $\text{SiO}_2$ , and conc.  $\text{H}_2\text{SO}_4$ ),  $\text{AcOH}$ , and the appropriate alcohol (which forms an unstable 4:1 additive compound with  $\text{SiF}_4$ );  $\text{NH}_2\text{Ac}$  (for  $\text{AcOH}$ ) similarly gives 13—20% of ester. With  $\text{BzOH}$ , the yield of ester is much smaller.  $\text{Bu}^{\text{B}}\text{OH}$  and  $\text{AcOH}$  similarly afford 4.3% of  $\text{Bu}^{\text{B}}\text{OAc}$ . Stable additive compounds are formed from  $\text{SiF}_4$  and  $\text{NH}_3$ ,  $\text{NBu}_3$ , and  $\text{NH}_2\text{Ac}$ .  $\text{SiF}_4$  is not absorbed by  $\text{PhOH}$ ,  $\text{PhOPr}^{\text{B}}$ ,  $\text{Et}_2\text{O}$ ,  $\text{EtOAc}$ , or  $\text{AcOH}$ . H. B.

**Etherates of iodobismuthous and iodoantimonious acids.**—See this vol., 690.

**Electrolysis of magnesium methyl halides in ether solutions.** W. V. EVANS and E. FIELD (J. Amer. Chem. Soc., 1936, 58, 720—724; cf. A., 1934, 517).—Electrolysis (apparatus described) of  $\text{Et}_2\text{O}\cdot\text{MgMeHal}$  gives (mainly)  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , together with small amounts of  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  and (after hydrolysis)  $\text{EtOH}$ ,  $\text{Pr}^{\text{B}}\text{OH}$ , and a non-volatile halogen-free saturated substance;  $\text{H}_2$  and isobutene are not produced (cf. *loc. cit.*). The ratio  $\text{CH}_4:\text{C}_2\text{H}_6$  decreases rapidly with increase in c.d. to a limiting val. which is unaffected by concn. The efficiency of the electrolysis is, however, inversely  $\propto$  the concn. above a limiting val. and decreases in the order  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ . The following reactions occur:  $\text{Me}+\text{H}$  (from  $\text{Et}_2\text{O}$ , which also gives rise to the above minor products)  $\rightarrow \text{CH}_4$ ;  $2\text{Me} \rightarrow \text{C}_2\text{H}_6$ . The mechanism of formation of Me is:  $\text{Me}_2\text{Mg}\cdot\text{MgX}_2 \rightarrow [\text{MeMgX}_2]^- + [\text{MgMe}]^+$ ;  $[\text{MeMgX}_2]^- - e \rightarrow \text{Me} + \text{MgX}_2$ ;  $[\text{MgMe}]^+ + e \rightarrow 1/2\text{Mg} + 1/2\text{MgMe}_2$ . H. B.

**Catalysed reaction of magnesium ethyl bromide with ethyl bromide.** C. B. LINN and C. R. NOLLER (J. Amer. Chem. Soc., 1936, 58, 816—819).—In agreement with Jolibois (A., 1927, 233) and contrary to Job and Dubien (*ibid.*, 233), the reaction between  $\text{EtBr}$  and  $\text{MgEtBr}$  in presence of  $\text{Cu}_2\text{Cl}_2$  is heterogeneous; no conclusions concerning the mechanism can, therefore, be reached from rate measurements. The catalyst is Cu (formed by reduction of the  $\text{Cu}_2\text{Cl}_2$  with  $\text{MgEtBr}$ ). Ordinary Cu does not catalyse the reaction; Cu prepared by reduction ( $\text{H}_2$ ) of powdered CuO is fairly active. Solutions of  $\text{MgEt}_2$  behave in exactly the same manner as  $\text{MgEtBr}$ . The following reactions are considered to occur:  $2\text{Cu} + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{MgBr}_2 + \text{MgCl}_2 \rightarrow \text{Cu}_2\text{Cl}_2 + 2\text{MgEtBr} \rightarrow 2\text{Cu} + 2\text{C}_2\text{H}_4 + \text{H}_2 + \text{MgBr}_2 + \text{MgCl}_2$ . H. B.

**Catalysts for autoxidation of saturated cyclic hydrocarbons.**—See this vol., 685.

**cycloPropane.** Raman spectrum and polymerisation by ultra-violet light.—See this vol., 777.

**Ultra-violet absorption of cyclopropane and propylene; their preparation and b.p.** A. A. ASHDOWN, L. HARRIS, and R. T. ARMSTRONG (J. Amer. Chem. Soc., 1936, 58, 850—852).—*cycloPropane* (I), b.p.  $-32.89 \pm 0.05^\circ/755.9$  mm. [prep. (cf. Gustavson (A., 1888, 240) from  $(\text{CH}_2)_3\text{Br}_2$  (3 mols.) and Zn wool (4 mols.) in EtOH with exclusion of  $\text{H}_2\text{O}$ , thus practically eliminating reduction to  $\text{C}_3\text{H}_8$ ], and  $\text{C}_3\text{H}_6$ , b.p.  $-47.67 \pm 0.1^\circ/759.1$  mm. (from  $\text{Pr}^\beta\text{OH}$  and  $\text{H}_3\text{PO}_4$ , whereby a considerable amount of  $\text{Pr}_2^\beta\text{O}$  is produced), show continuous absorption in the ultra-violet; mol. extinction coeffs. are determined. (I) resembles a paraffin hydrocarbon. H. B.

**Synthesis of monosubstituted cyclopentane homologues with branched side chains.** B. A. KASANSKI, A. F. PLATE, and K. M. GNATENKO (Ber., 1936, 69, [B], 954—960).—The action of Grignard's reagents on *cyclopentanone* and subsequent dehydration of the *tert.* alcohols thus produced does not afford monosubstituted *cyclopentanes* in satisfactory yield. Hydrogenation of dimethylfulvene, b.p.  $45-47^\circ/12$  mm., from *cyclopentadiene* and  $\text{COMe}_2$ , proceeds slowly in EtOH with Pd-Ni, more rapidly in AcOH (Pd-black) giving *isopropylcyclopentane*, b.p.  $123-124^\circ/731.6$  mm. Similarly methyl-ethyl- and diethyl-fulvene afford *sec.-butylcyclopentane*, b.p.  $152.5-153.5^\circ/763.7$  mm., and *sec.-amylcyclopentane*, b.p.  $174-176^\circ$ , respectively. Hydrogenation of diphenylfulvene (I) (Ni-EtOH) at  $100-120^\circ/40$  atm. gives a substance  $\text{C}_{18}\text{H}_{18}$ , m.p.  $62.5-63^\circ$ , which becomes liquid when exposed to air. In EtOH (Pt or Pd) (I) absorbs 2 H very readily and a further 2 H more slowly, after which reaction nearly ceases. The crude product is, however, converted by Na in EtOH into *diphenylmethylcyclopentane*, m.p.  $32.5-33^\circ$ . H. W.

**Multiplanar isomerism of cyclohexanes.** R. F. MILLER and R. ADAMS (J. Amer. Chem. Soc., 1936, 58, 787—791).—Assuming that multiplanar forms of the *cyclohexane* ring are possible, the theoretical no. of isomerides of the types  $aa\text{C}_6\text{H}_8bb$ ,  $aa\text{C}_6\text{H}_8bc$ , and  $ab\text{C}_6\text{H}_8cd$  is 4 (3 "C," 1 "Z"), 8 (6 "C," 2 "Z"), and 16 (12 "C," 4 "Z"), respectively. Fractional crystallisation of 4-methyl- and 4:4-dimethyl-*cyclohexane-1:1-diacetic acids* and 4:4-dimethyl-*cyclohexane-1-carboxylic-1-acetic acid*, their  $\text{NH}_4$  salts, and anhydrides has failed to reveal the existence of more than one form (cf. Qudrat-i-Khuda, A., 1931, 1055; 1935, 1236; Goldschmidt and Grafinger, A., 1935, 489; Desai and Hunter, *ibid.*, 1495).

Reduction of 4-methyl-4-dichloromethyl- $\Delta^{2:5}$ -*cyclohexadienone* with  $\text{H}_2$  and Raney Ni in EtOH-NaOH (calc. amount to neutralise HCl produced) gives 4:4-dimethyl-*cyclohexanol*, b.p.  $68^\circ/7$  mm., m.p.  $37^\circ$ , oxidised (method: von Auwers and Keil, A., 1903, i, 100) to 4:4-dimethyl-*cyclohexanone* (I), m.p.  $40-42^\circ$ .  $\beta\beta$ -Dimethylglutaric acid is reduced [ $\text{H}_2$  (250 atm.), Cu-Cr oxide] to  $\gamma\gamma$ -dimethylpentane- $\alpha$ -diol, b.p.  $132^\circ/1$  mm., converted by  $\text{SOCl}_2$  into  $\alpha$ -dichloro-, b.p.  $135^\circ/80$  mm., and thence by NaCN

in 50% EtOH into  $\alpha\epsilon$ -dicyano- $\gamma\gamma$ -dimethylpentane, b.p.  $155-157^\circ/7$  mm., which is hydrolysed (EtOH-conc.  $\text{H}_2\text{SO}_4$ ) to *Et*  $\gamma\gamma$ -dimethylpimelate, b.p.  $135^\circ/7$  mm. Hydrolysis of this with aq.  $\text{Ba}(\text{OH})_2$ , evaporation of the reaction mixture to dryness, and subsequent heating to  $300^\circ$  (bath) gives (I). *Et* 4:4-dimethyl-*cyclohexylidenecyanoacetate*, b.p.  $155^\circ/7$  mm., m.p.  $50^\circ$  [from (I),  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (II), and piperidine], with aq. EtOH-KCN followed by hydrolysis (conc. HCl) of the resultant K salt, affords 4:4-dimethyl-*cyclohexane-1-carboxylic-1-acetic acid*, m.p.  $189^\circ$  (bloe Maquenne) (*anhydride*, m.p.  $124^\circ$ ). (I), (II), and  $\text{NH}_3$  in EtOH give 4:4-dimethyl-*cyclohexane-1:1-dicyanoacetic acid imide*, m.p.  $230^\circ$  (decomp.), hydrolysed (70%  $\text{H}_2\text{SO}_4$ ) to 4:4-dimethyl-*cyclohexane-1:1-diacetic acid*, m.p.  $213-218^\circ$  (tube),  $230^\circ$  (bloe) (*anhydride*, m.p.  $86^\circ$ ). H. B.

**Ring enlargement during the catalytic dehydrogenation of a cyclopentane derivative.** C. D. NENITZESCU and E. CIORANESCU (Ber., 1936, 69, [B], 1040—1041).—Methylcyclopentane is unchanged when passed over Pt-C at  $310^\circ$  or  $350^\circ$ . Under similar conditions small amounts of  $\text{C}_{10}\text{H}_8$  are obtained from 1-methylhydrindene or 1-methylhexahydrohydrindene, b.p.  $182-183^\circ$ . H. W.

**Kinetics of formation and decomposition of dicyclopentadiene.**—See this vol., 684.

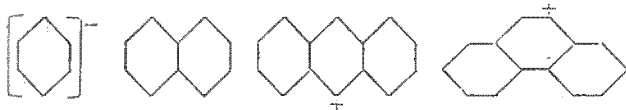
**Fused carbon rings. X. Fundamental properties of 0:3:3-dicyclooctane ring.** J. W. BARRETT and R. P. LINSTAD (J.C.S., 1936, 611—616).—Reduction of pure samples of *cis*- (I) and *trans*- $\beta$ -0:3:3-dicyclooctanone (Clemmensen or Kishner-Wolff methods) affords *cis*- (II) and *trans*- (III), m.p.  $-29^\circ$  (corr.) (A., 1935, 750 gives m.p.  $-36^\circ$ ). 0:3:3-dicyclooctane, the heats of combustion of which are 1197.7 and 1203.8 kg.-cal. per mol. for liquid at const. vol. (Becker). (II) is not dehydrogenated by Pt-asbestos (active to decalin) at  $300-320^\circ$  ( $\text{H}_2$  atm.). (I) and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  afford 2-benzyl-*cis*-0:3:3-dicyclooctan-2-ol, m.p.  $66-67^\circ$ , and a liquid stereoisomeride, both dehydrated by  $\text{H}_2\text{C}_2\text{O}_4$  at  $120^\circ$  to 2-benzylidene-*cis*-0:3:3-dicyclooctane, b.p.  $126-127^\circ/3$  mm.; this with Se at  $300-330^\circ$  is partly decomposed and partly unchanged. Under the same conditions *trans*-2-benzyl-octalin (by dehydration of *trans*-2-benzyl-2-decalol, b.p.  $170^\circ/3$  mm.) readily gives 2- $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Ph}$ . Reduction of (I) with Na-moist  $\text{Et}_2\text{O}$  or catalytically (Adams) gives *cis*-0:3:3-dicyclooctan-2-ol, b.p.  $85-86^\circ/10$  mm. (*H* phthalate, m.p.  $72^\circ$ ; phenylurethane, m.p.  $116^\circ$ ), which is a mixture of stereoisomerides, unchanged by Se at  $300-310^\circ$ , conditions under which *trans*- $\beta$ -decalol is also stable. With  $\text{AlCl}_3$  at room temp. (II) is converted mainly into (the more strained) 1:2:3-dicyclooctane, identical with a synthetic specimen (Komppa *et al.*, this vol., 333). (III) is unchanged by passage with  $\text{H}_2$  over Pt-asbestos (active to  $\text{C}_6\text{H}_6$ ) at  $200^\circ$ . J. W. B.

**Reactivity of aromatic hydrogen atoms.** O. ZWECKER (Ber., 1936, 69, [B], 993—997; cf. A., 1935, 1112).—The general hypothesis is that an aromatic H under the influence of an *o*-substituent, B, reacts more rapidly or more slowly with a given



reagent than when under the influence of a substituent *C* according as the compound *HB* reacts more rapidly or more slowly than *HC*. In this connexion the following changes are considered: chlorination, sulphonation, and nitration of  $\text{NH}_2\text{Ph}$  and its *N* derivatives; nitration of  $\text{PhMe}$ ,  $\text{CH}_2\text{PhCl}$ ,  $\text{CHPhCl}$ ,  $\text{CPhCl}_2$ ,  $\text{PhCHO}$ , and  $\text{BzOH}$  in comparison with the corresponding  $\text{CH}_3$  compounds; chlorination of  $\text{PhNO}_2$  and nitration of  $\text{PhCl}$ . H. W.

**Influence of solvent on the course of chemical reactions. VIII. Evidence of the ionoid course of substitution. Formulation of aromatic hydrocarbons.** K. LAUER and R. ODA (Ber., 1936, 69, [B], 1061—1065).—Evidence in favour of the view that the aromatic hydrocarbons have the annexed, dynamic limiting constitutions (in which — and +



denote the anionoid and cationoid nature of a position) is found in the observation that the chlorination of  $\text{C}_6\text{H}_6$  in  $\text{AcOH}$  is greatly hampered by  $\text{HCl}$  or chlorides whereas that of the condensed aromatic hydrocarbons is greatly accelerated. H. W.

**Condensation of benzene with unsaturated hydrocarbons and their halogen derivatives in presence of acid catalysts.** R. TRUFFAULT (Compt. rend., 1936, 202, 1286—1289).—With  $\text{P}_2\text{O}_5$  much polymerisation occurs in the condensation of unsaturated hydrocarbons with  $\text{C}_6\text{H}_6$ .  $\text{C}_6\text{H}_4$  and  $\text{C}_3\text{H}_6$  give, respectively, some  $\text{PhEt}$  and  $\text{PhPr}^a$ , but  $\text{C}_5\text{H}_{10}$  gives only  $(\text{C}_5\text{H}_{10})_2$ , and cyclohexene (I) gives mainly its dimeride and some phenylcyclohexane (II). No such polymerisation occurs when  $\text{H}_2\text{SO}_4$  at room temp. is used. Thus (I) gives a 70% yield of (II) and 25% of  $\text{C}_{18}$  hydrocarbons, mainly *p*-dicyclohexylbenzene.  $\text{C}_6\text{H}_6$  and  $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Cl}$  afford  $\beta$ -chloroisopropylbenzene (III), converted by  $\text{KCN}$  into the nitrile, hydrolysed to the amide of  $\beta$ -phenyl- $\beta$ -methylpropionic acid, which is readily obtained by the action of  $\text{CO}_2$  on the  $\text{Mg}$  compound of (III).

J. W. B.

**Addition and additive products of halogens and benzene derivatives. V. Addition of chlorine to three trichlorobenzenes.** T. VAN DER LINDEN (Rec. trav. chim., 1936, 55, 315—324).—The rate of addition of liquid  $\text{Cl}_2$ , at room temp. in sunlight, to 1:2:3- (I), 1:2:4- (II), and 1:3:5- (III)- $\text{C}_6\text{H}_3\text{Cl}_3$  decreases in this order. (I) affords only one isomeride of 1:1:2:2:3:3:4:5:6-nonachloro-cyclohexane, m.p.  $80^\circ$ . (II) gives a series of (unseparable) mixed crystals, m.p.  $112$ — $114^\circ$ ,  $120^\circ$ ,  $135^\circ$ , and  $82^\circ$ , of two isomerides of 1:1:2:2:3:3:4:4:5:6- $\text{C}_6\text{H}_3\text{Cl}_9$  (stable to boiling  $\text{EtOH}$ ), and 1:2:2:3:3:4:4:5:6-octachloro- $\Delta^6$ -cyclohexene, m.p.  $107$ — $108^\circ$ , obtained by loss of  $\text{HCl}$  from a third unstable isomeride. (III) affords one isomeride of 1:1:2:3:3:3:4:5:5:6-nonachlorocyclohexane, m.p.  $116^\circ$ . Addition is assumed to occur most readily at double linkings unsubstituted in both Kekule forms, and these and previous results, and the substitution of  $\text{PhCl}$ , are discussed on this basis. J. W. B.

**Tin vanadate as catalyst in the oxidation of toluene.**—See this vol., 686.

**Halogenation. XIV. Iodination of aromatic hydrocarbons and bromotoluenes.** P. S. VARMA and C. SREENIVASMURTHYACHAR. XV. Chlorination and bromination of cumene and *p*-cymene. P. S. VARMA and M. K. SRINIVASAN. XVI. Bromination and iodination of mesitylene. P. S. VARMA and T. S. SUBRAHMANYAN (J. Indian Chem. Soc., 1936, 13, 187—188; 189—191; 192—193).—XIV. Iodination of several aromatic hydrocarbons is effected by heating with I-fuming  $\text{HNO}_3$ -conc.  $\text{H}_2\text{SO}_4$  on a water-bath.

XV. Passage of  $\text{Cl}_2$  into cumene containing 15% I-AcOH in diffused sunlight affords *p*-chlorocumene and *p*-chloro- $\alpha$ -chloroisopropylbenzene, m.p.  $181^\circ$ . By similar methods are obtained *p*-bromo-, m.p.  $226^\circ$ , and *p*-chloro- $\alpha$ -bromoisopropylbenzene, m.p.  $207^\circ$ . 2-Chloro-*p*-cymene with  $\text{Br-Fe}$  affords its 5-*Br*-derivative, b.p.  $247^\circ$ . The products obtained using various halogen-carriers are tabulated.

XVI. Mesitylene (I) with Br-fuming  $\text{HNO}_3$  gives its 2-*Br*-derivative, and, with Br-AcOH-fuming  $\text{HNO}_3$ , its 2:4- $\text{Br}_2$ - and 2:4:6- $\text{Br}_3$ -derivatives. (I) and I-AcOH- $\text{NO}_2\text{SO}_3\text{H}$  give the 2:4- $\text{I}_2$ -derivative further iodinated to the 2:4:6- $\text{I}_3$ -derivative. 2-Bromomesitylene similarly gives 2-bromo-4-iodomesitylene, m. p.  $175$ — $176^\circ$ . J. W. B.

**Toluene series. V. Sulphinic and sulphonic acids of the mono- and di-chlorotoluenes.** W. A. SILVESTER and W. P. WYNNE. VI. Nitration of the 4-chlorotoluene-2- and -3-sulphonic acids, 3-chlorotoluene-6-sulphonic acid, and their sulphonyl chlorides. W. P. WYNNE. VII. Nitration of 2-chlorotoluene-4- and -5-sulphonic acids and their sulphonyl chlorides. (Miss) E. G. TURNER and W. P. WYNNE (J.C.S., 1936, 691—696, 696—707, 707—716; cf. J.C.S., 1898, 73, 730).—V. The orientation of the sulphonation products of the isomerides,  $\text{C}_6\text{H}_4\text{MeCl}_2$  (J.C.S., 1892, 61, 1042; Proc. C.S., 1895, 11, 151), is established by synthesis. In all cases orientation is normal, except that 2:3- $\text{C}_6\text{H}_3\text{MeCl}_2$  gives 89% of 6- and 11% of 5-sulphonic acid (cf. 10% of 6- and 90% of 4- $\text{NO}_2$ -derivative) and that *p*- $\text{C}_6\text{H}_4\text{MeCl}$  gives 86% of 2- and 14% of 3-sulphonic acid (cf. 42% of 2- and 58% of 3- $\text{NO}_2$ -derivative). *m*- $\text{C}_6\text{H}_4\text{MeNHAc}$  with  $\text{Cl}_2$  (1 mol.) in  $\text{AcOH}$  gives mixtures of  $\text{Cl-}$  with 4:6- and 2:6- $\text{Cl}_2$ -derivatives, and with  $\text{Cl}_2\text{-H}_2\text{O}$  a poor yield of 6-chloro-*m*-toluidine;  $\text{S}_2\text{Cl}_2$  (1 part) in  $\text{CS}_2$  (5 parts) gives, however, 80% of 6-, 12% of 4-, and 8% of 2- $\text{Cl}$ -derivative, and further reaction with  $\text{S}_2\text{Cl}_2$  (0.8 part) in  $\text{CS}_2$  gives a mixture containing much 4:6- and some 2:6- $\text{Cl}_2$ -compound. The diazonium sulphite of 3-chloro-*p*-toluidine with Cu-bronze gives a good yield of 3-chlorotoluene-4-sulphinic acid, m.p.  $110^\circ$  (*Ba* salt,  $+4\text{H}_2\text{O}$ ), oxidised by  $\text{KMnO}_4$  to the sulphonic acid (*K* salt; chloride, m.p.  $46^\circ$ ; amide, m.p.  $186^\circ$ ). Similar reactions give 3-chlorotoluene-6-sulphinic (*Ba* salt,  $+4\text{H}_2\text{O}$ ) and sulphonic acid [chloride, m. p.  $54^\circ$ ; amide, m.p.  $185^\circ$ ; obtained (*loc. cit.*) from *m*- $\text{C}_6\text{H}_4\text{MeCl}$ ], 2:3-dichlorotoluene-6-sulphinic, m.p.  $133^\circ$  (*Ba* salt,  $+4\text{H}_2\text{O}$ ), and -sulphonic acid (chloride, m.p.  $51$ — $52^\circ$ ; amide, m.p.  $228^\circ$ ),

-4-sulphinic, m.p. 142° (*Ba* salt, +H<sub>2</sub>O), and -sulphonic acid (*K* salt; *chloride*, m.p. 40–41°; *amide*, m.p. 237°), 2 : 4-dichlorotoluene-5-sulphinic, m.p. 132° (*K* salt), and sulphonic acid [*K* salt, +2H<sub>2</sub>O (only one lost at 190°); *chloride*, m.p. 72°; *amide*, m.p. 176°; obtained from 2 : 4-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>], 2 : 6-dichlorotoluene-3-sulphinic (poor yield), m.p. about 105° (*Ba* salt, +4H<sub>2</sub>O), and -sulphonic acid (*chloride*, m.p. 59°; *amide*, m.p. 203°; obtained from 2 : 6-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>), 3 : 5-dichlorotoluene-4-, m.p. about 127°, and -2-sulphinic acid, m.p. 115–116° (*Ba* salt, +4H<sub>2</sub>O), and -4- (*K* salt, +H<sub>2</sub>O; *chloride*, m.p. 56°; *amide*, m.p. 154–155°) and -2-sulphonic acid (*chloride*, m.p. 43°; *amide*, m.p. 168°; obtained from 3 : 5-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>). 5 : 6-Dichloroacet-*o*-toluidide, m.p. 143°, with 50% H<sub>2</sub>SO<sub>4</sub> at 90° gives 5 : 6-dichloro-toluidine, m.p. 33°, b.p. 288–290°/739 mm. (sulphate). 3-Chloro-*o*-toluidine-5-sulphonic acid (*Ba* salt, +3H<sub>2</sub>O) with 75% H<sub>2</sub>SO<sub>4</sub> at 160° gives 3-chloro-*o*-toluidine, an oil (Ac derivative, m.p. 163°), which affords (Sandmeyer) 1 : 2 : 3 : 5-C<sub>6</sub>H<sub>2</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H (97% yield; *chloride*, m.p. 88°; *amide*, m.p. 184–185°; *Ba*, +3H<sub>2</sub>O, and *Na*, +0.5H<sub>2</sub>O, salts). Nitration of 2 : 3-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub> is best effected by H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> (*d* 1.42) at <50° and gives a mixture, reduced to a mixture of 2 : 3-dichloro-*p*-, m.p. 40°, b.p. 271–276°/40 mm. (Ac derivative, m.p. 131°), and -*o*-toluidine (10%), which is best separated by fractional neutralisation of the hydrochlorides; similar nitration of 2 : 6-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>, b.p. 199–200°, gives the 3-NO<sub>2</sub>-compound, m.p. 50°, and on reduction solely 2 : 6-dichloro-*m*-toluidine, m.p. 57°, b.p. 266–268°. If Cl<sub>2</sub> (1 mol.) is passed into 5-chloroacet-*o*- or 3-chloroacet-*p*-toluidide in cold AcOH and the solution is warmed to 75° after some hr. and diluted with H<sub>2</sub>O, there are formed the 3 : 5-, m.p. 180°, and 2 : 3-Cl<sub>2</sub>-, m.p. 198°, -compounds, respectively, which are hydrolysed to the bases, m.p. 45° and b.p. 249°/772 mm., respectively.

[With J. KENNER.] The formation of 6- and 5-SO<sub>3</sub>H derivatives from 2 : 3-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub> is confirmed (cf. J.C.S., 1902, 81, 1334).

VI. The products of nitration of 1 : 4 : 2- (I), 1 : 4 : 3- (II), and 1 : 3 : 6- (III), -C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H can be separated only by way of the acid chlorides (obtained from the *Na* salts by PCl<sub>5</sub>-POCl<sub>3</sub>). Orientations are determined by the reactions, NO<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H + NH<sub>2</sub>·C<sub>6</sub>H<sub>2</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H →

C<sub>6</sub>H<sub>2</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H → C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub> → C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CO<sub>2</sub>H. (II) is remarkable in giving 31% of 5-, 15% of 6-, and 54% of 2-NO<sub>2</sub>-compound (although only 64% of the total material is accounted for), whereas the corresponding acid chloride gives 78% of 5-, 22% of 2-, and no 6-NO<sub>2</sub>-compound. All nitrations are effected by fuming HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> at or about room temp. (II) gives 4-chloro-5- [*Ba*, +2H<sub>2</sub>O, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 62.5° (crystallographic data given); *amide*, m.p. 196°], -6- (*Ba*, +2H<sub>2</sub>O, *K*, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 92°; *amide*, m.p. 188°), and -2-nitrotoluene-3-sulphonic acid (*Ba*, +8H<sub>2</sub>O, *K*, and *Na*, +3H<sub>2</sub>O, salts; *chloride*, m.p. 122°; *amide*, m.p. 177°; with conc. H<sub>2</sub>SO<sub>4</sub> at 220° affords 4 : 2-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>·NO<sub>2</sub>), which gives ("reduced" Fe-dil. H<sub>2</sub>SO<sub>4</sub>) 4-chloro-5-, +H<sub>2</sub>O (*Ba*, +1.5H<sub>2</sub>O, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O,

salts), -6- (*Ba*, +9H<sub>2</sub>O, *K*, +H<sub>2</sub>O, and *Na*, +5H<sub>2</sub>O, salts), and -2-aminotoluene-3-sulphonic acid (*Ba*, +0.5H<sub>2</sub>O, decomp. 140°, *K*, and *Na*, +1.5H<sub>2</sub>O, salts), and thence 4 : 5- (*Ba*, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 64°; *amide*, m.p. 158°), 4 : 6- (*Ba*, +2H<sub>2</sub>O, *K*, and *Na*, +1.5H<sub>2</sub>O, salts; *chloride*, m.p. 72°; *amide*, m.p. 178°), and 2 : 4-dichlorotoluene-3-sulphonic acid (*Ba*, +H<sub>2</sub>O, *K*, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 19.5°; *amide*, m.p. 188°), respectively, converted by H<sub>3</sub>PO<sub>4</sub> and steam at about 240° into the dichlorotoluenes. (I) or its chloride gives mainly 4-chloro-6- [*Ba*, +4H<sub>2</sub>O, *K*, +0.5H<sub>2</sub>O, and *Na*, +1.5H<sub>2</sub>O, salts; *chloride*, m.p. 60° (crystallographic data given); *amide*, m.p. 167°] with some -3-nitrotoluene-2-sulphonic acid (*Ba* salt, +5H<sub>2</sub>O, *K*, and *Na*, +4H<sub>2</sub>O, salts; *chloride*, m.p. 154°; *amide*, m.p. 183°), converted into 4-chloro-6-, +H<sub>2</sub>O (*Ba*, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O, salts), and -3-amino- (*Ba*, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O, salts), 4 : 6- (*Ba*, *K*, +H<sub>2</sub>O, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 54°; *amide*, m.p. 186°) and 3 : 4-dichloro-toluene-2-sulphonic acid (*Ba*, *K*, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 49°; *amide*, m.p. 186°). (III) or its chloride (IV) gives mainly 3-chloro-4- (*Ba*, +3H<sub>2</sub>O, *K*, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 116°; *amide*, m.p. 170°) and a very little -2-nitrotoluene-6-sulphonic acid (*Ba*, *K*, and *Na* salts; *chloride*, m.p. 96°; *amide*, m.p. 176°), converted into 3-chloro-4- (*Ba*, +2H<sub>2</sub>O, *K*, and *Na*, +H<sub>2</sub>O, salts) and -2-amino-, +H<sub>2</sub>O, 3 : 4- (optical data of chloride given) and 2 : 3-dichloro-toluene-6-sulphonic acid (*Na*, +H<sub>2</sub>O, salt; *chloride*, m.p. 54°), respectively. (IV) is obtained with a little 4 : 4'-dichloro-3 : 3'-dimethyldiphenylsulphone, m.p. 130°, from *m*-C<sub>6</sub>H<sub>4</sub>MeCl and ClSO<sub>3</sub>H in CS<sub>2</sub>.

VII. Nitration (as above) of 1 : 2 : 4-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H gives 95% of 5- and 5% of 6-NO<sub>2</sub>-derivative, 80% and 20%, respectively, being obtained from the chloride. 1 : 2 : 5-C<sub>6</sub>H<sub>3</sub>MeCl<sub>2</sub>·SO<sub>3</sub>H and its chloride give 67 and 98% of the 3- and 33 and 2% of the 4-NO<sub>2</sub>-derivative, respectively. *K* chloronitrotoluenesulphonates, in which the NO<sub>2</sub> has both an *o*-SO<sub>3</sub>K and a *p*-Cl, give with PCl<sub>5</sub>-POCl<sub>3</sub> poor yields of sulphonyl chloride with much dichloronitrotoluenesulphanyl chloride. Orientations are established as above. The following are described. 2-Chloro-5- (*K* salt; crystallographic data of chloride given) and -6-nitro- (*K* salt), -5- (*Ba*, +H<sub>2</sub>O, and *K*, +2H<sub>2</sub>O, salts) and -6-amino- (*K* salt), and 2 : 6-dichlorotoluene-4-sulphonic acid (*K* salt). 2-Chloro-5-nitro- (*Ba*, +H<sub>2</sub>O, and *Na* salts) and -amino-, +0.33H<sub>2</sub>O (*Na* salt), and 3 : 5-dichloro-toluene-6-sulphonic acid (*Ba*, *K*, and *Na*, +H<sub>2</sub>O, salts; *chloride*, m.p. 38°; *amide*, m.p. 180°). 2-Chloro-3- (*Ba*, +3.5H<sub>2</sub>O, *K*, and *Na* salts; *chloride*, m.p. 52°; *amide*, m.p. 201°) and -4-nitro- (*Ba*, +2H<sub>2</sub>O, *K*, and *Na*, +1.5H<sub>2</sub>O, salts; *chloride*, m.p. 97°; *amide*, m.p. 172°), -3- (*K* salt) and -4-amino- (*Na* salt) and 2 : 4-dichloro-toluene-5-sulphonic acid (*Na* salt, +H<sub>2</sub>O). 2 : *x*-Dichloro-5-nitrotoluene-4-, decomp. 128° (darkening at 95–100°), and -6-sulphanyl chloride, m.p. 119° (decomp.); the former is oxidised by dil. HNO<sub>3</sub> to a sulphonic acid (*K* salt); both react with AgNO<sub>3</sub> in dil. HNO<sub>3</sub> (1Cl removed), 1% aq. NaOH, and Fe(OH)<sub>3</sub>.



[Addendum. G. M. BENNETT.] Summary of the above results shows the high *o*- and less high *p*-directing power of Me and SO<sub>3</sub>H diminished as expected by conversion of SO<sub>3</sub>H into SO<sub>2</sub>Cl owing to the higher electron-attracting power of SO<sub>2</sub>Cl, inability of SO<sub>2</sub>Cl to ionise, and lesser attraction of SO<sub>2</sub>Cl for HNO<sub>3</sub>. Similarly PhSO<sub>3</sub>Cl gives 90% of *m*-NO<sub>2</sub>-derivative, whereas PhSO<sub>3</sub>H gives 27% of *o*-compound.

R. S. C.

**Reaction between triarylmethyl halides and magnesium phenyl bromide. II.** C. S. SCHOEFFLE and S. G. TREFF (J. Amer. Chem. Soc., 1936, 58, 791—794; cf. A., 1932, 1240).—MgPhBr (in Et<sub>2</sub>O) and CPh<sub>3</sub>Cl or CPh<sub>3</sub>Br (in C<sub>6</sub>H<sub>6</sub>) afford 5—7.5% of CPh<sub>4</sub> and 50—77% of diphenyldiphenylmethane (I). With Et<sub>2</sub>O-free MgPhBr and CPh<sub>3</sub>Cl (in C<sub>6</sub>H<sub>6</sub>, PhMe, PhBr, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, or dioxan) 20—25% of CPh<sub>4</sub> is obtained; (I) could not be isolated. In the latter case there appears to be a smaller tendency to favour the quinonoid form (cf. *loc. cit.*) of the CPh<sub>3</sub>Cl. The rate of reaction of the benzenoid form is very slow in comparison with the quinonoid. Other products isolated in the first-named (?) reaction are CHPh<sub>3</sub> (5%), phenyldi(diphenyl)- (3%), tri(diphenyl)- (trace), and *p*-phenyltetraphenyl- (0.6%) -methanes; reaction mechanisms are discussed briefly. 4 : 4' : 4''-Tribromo-, m.p. 234—235° (43—45% yield), 4 : 4' : 4''-trichloro-, m.p. 207—207.5° (38—49%), and 4 : 4' : 4''-trimethyl-, m.p. 177—178° (31—41%), -tetraphenylmethane are prepared from MgPhBr (in Et<sub>2</sub>O) and CAr<sub>3</sub>Cl (in C<sub>6</sub>H<sub>6</sub>); the higher yields (cf. above) are ascribed to the lessened tendency of the CAr<sub>3</sub>Cl to become quinonoid.

H. B.

**Influence of solvent on the course of chemical reactions. VII.** Spectra of aromatic hydrocarbons in solution. K. LAUER (Ber., 1936, 69, [B], 986—993).—The absorption spectrum of C<sub>10</sub>H<sub>8</sub> has been observed for the vapour and cryst. states and in *n*-hexane, Et<sub>2</sub>O, EtOH, MeOH, cyclohexene, and C<sub>6</sub>H<sub>6</sub>. The displacements show that the bands of longest  $\lambda$  are due in the first place to the polar, cationoid positions of the mol. which must be an  $\alpha$ -position. Such polar atoms not only attract the polar positions of the solute indirectly but also cause production of associates, solvates, or mol. compounds. Further bands are due to the entire mol. and show the peculiarities observed with C<sub>6</sub>H<sub>6</sub>. The second part of the spectrum, in the region of shorter  $\lambda$ , is due to the aromatic nucleus and the displacements correspond qualitatively with those of C<sub>6</sub>H<sub>6</sub>. To C<sub>10</sub>H<sub>8</sub>

the constitution (I) is therefore assigned, this being regarded as a limiting formula. Similar limiting formulae are proposed for anthracene indicating the strong cationoid polarity of the 9:10 positions.

(I) In general the displacements observed with phenanthrene are similar to those with C<sub>6</sub>H<sub>6</sub>. The first band is more markedly displaced towards the red in alcohols than in hexane and is therefore due to the 9 and 10 positions both of which are cationoid but weakened in comparison with anthracene, in consequence of their *o*-position to one

another. The displacement of the limits of absorption by linear annelation of C<sub>6</sub>H<sub>6</sub> nuclei is discussed.

H. W.

**Influence of solvent on the course of chemical reactions. VI.** Bromination of aromatic compounds. K. LAUER and R. ODA (Ber., 1936, 69, [B], 978—985).—The bromination of C<sub>10</sub>H<sub>8</sub> is accompanied by rapid diminution of the reaction const. In the cases of Me oleate and cyclohexene halogenation proceeds rapidly at first but very slowly towards the end of the change; addition of unsaturated material immediately restores the rate. With C<sub>10</sub>H<sub>8</sub> this is not the case so that the decay in rate is not attributable to the C<sub>10</sub>H<sub>8</sub> mol. Retardation appears due to HBr and the production of polybromides which have no brominating action. The phenomena are complex. Similar retardation is caused by bromides and to a smaller extent by alkali chlorides but not by HCl. I accelerates greatly due to union with HBr. The bromination of C<sub>6</sub>H<sub>6</sub>, anthracene (I), phenanthrene, *lm*-benzanthracene (II), 9-bromoanthracene, dihydroanthracene, *o*-xylene, and Ph<sub>2</sub> usually in hexane and (or) AcOH has been studied. The rate of bromination is dependent on the concn. due to the formation of polybromides and of associates of the aromatic mols. The aromatic hydrocarbons do not appear to be present in two forms one of which has a diradical nature; this is shown by the course of bromination after addition of fresh solution and by the observation that (II) is halogenated more slowly than (I).

H. W.

**Fused carbon rings. XI.** Action of aluminium chloride on decahydronaphthalene. R. L. JONES and R. P. LINSTAD (J.C.S., 1936, 616—621; cf. this vol., 713).—The low-boiling products of the action of AlCl<sub>3</sub> on decahydronaphthalene at 130° probably contain 1:4- (or, less probably, 2:5-) dimethyl-0:3:3-dicyclooctane (I); other fractions yield by dehydrogenation C<sub>6</sub>H<sub>6</sub>, PhMe, and mesitylene, proving the presence of cyclohexane, methyl- and 1:3:5-trimethyl-cyclohexane; formation of the last-mentioned product must have involved drastic degradation and resynthesis. A methylhyrindane may also have been present. (I), b.p. 158—163°, is stable to Br and KMnO<sub>4</sub>, and hardly affected by Ni-Al dehydrogenating catalysts; it gives a (?1)-Cl-derivative, b.p. 88—91°/16 mm., and thence (NH<sub>2</sub>Ph or *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>Ag) 1:4-dimethyl- $\Delta^{1,1,0}$ :3:3-dicyclooctene (II), b.p. 54—60°/20 mm., oxidised by KMnO<sub>4</sub> to ? 3-acetyl-1-methylcyclopentane-2-acetic acid, m.p. 120° (semicarbazone, m.p. 195°; gives CHI<sub>3</sub>). The structure of (I) is not certain, but is probable from the above reactions and from correspondence of *n* and *d* for (I) and (II) with those of analogous compounds described below; the above compounds are probably *trans*. The Na derivative of Et 5-methylcyclopentanone-2-carboxylate (modified prep.; 70—80% yield) and CHMeBr·CO<sub>2</sub>Et give Et 5-methylcyclopentanone-2-carboxylate-2- $\alpha$ -propionate, b.p. 171—175°/19 mm. (with some open-chain ester, b.p. 180—190°/20 mm.), which with hot HCl yields 5-methylcyclopentanone-2- $\alpha$ -propionic acid, m.p. 76° (phenylhydrazone, m.p. 192°), the Et ester, b.p. 127—128°/12 mm., of which could not be condensed with

CN·CH<sub>2</sub>·CO<sub>2</sub>Et. Et 4-methylcyclopentanone-2-carboxylate, b.p. 123—125°/24 mm., is obtained in 30% yield from 4-methylcyclohexanol by way of crude β-methyladipic acid and its Et ester, b.p. 138—144°/16—17 mm.; its Na derivative with CH<sub>2</sub>Cl·CO<sub>2</sub>Et affords Et<sub>2</sub> 4-methylcyclopentanone-2-carboxylate-2-acetate (65% yield), b.p. 180—183°/24 mm., converted by conc. HCl into methylcyclopentanone-2-acetic acid (crude), b.p. 183—190°/24 mm., the Et ester, b.p. 130—133°/23 mm. (semicarbazone, m.p. 141°), of which with CN·CHK·CO<sub>2</sub>Et affords Et<sub>2</sub> 4-methylcyclopentylidene-1-cyanoacetate-2-acetate, b.p. 194°/4 mm. (35% yield). Hydrogenation (Adams) in EtOH gives Et<sub>2</sub> 4-methylcyclopentane-1-cyanoacetate-2-acetate, b.p. 205°/17 mm., which with HCl affords 38% of 4-methylcyclopentane-1:2-diacetic acid (III), m.p. 173—174°, and a little 5-methyl-0:3:3-dicyclooctan-2-one (IV), b.p. 104°/26 mm. (semicarbazone, m.p. 183°), obtained in 32% yield from (III) and Ba(OH)<sub>2</sub> at 270—280°. (IV) and MgMeI give a carbinol, dehydrated by NH<sub>2</sub>Ph·HBr to 2:5-dimethyl-Δ<sup>1</sup>-0:3:3-dicyclooctene (70% yield), b.p. 167°, which is hydrogenated (Adams; no solvent) to 2:5-dimethyl-0:3:3-dicyclooctane, b.p. 165—167°. R. S. C.

**Syntheses of 1-phenylnaphthalenes.** W. N. HOWELL and A. ROBERTSON (J.C.S., 1936, 587—589). —1-Keto-1:2:3:4-tetrahydronaphthalene and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·MgBr in Et<sub>2</sub>O give 1-*p*-anisyl-3:4-dihydronaphthalene, b.p. 198—200°/12 mm., m.p. 76°, dehydrogenated by Se at 280—300° to 1-*p*-anisyl-naphthalene, m.p. 116.5° (NO<sub>2</sub>-derivative, m.p. 129°). 6:7-Dimethoxy-1-keto-1:2:3:4-tetrahydronaphthalene and MgPhBr give similarly 6:7-dimethoxy-1-phenyl-3:4-dihydronaphthalene, b.p. 215—217°/14 mm., m.p. 68.5°, and 6:7-dimethoxy-1-phenylnaphthalene (I), m.p. 110°, and thence by HI·Ac<sub>2</sub>O at 140—145° the (OH)<sub>2</sub>-compound, m.p. 167—168°. Similar reactions give 7-methoxy-1-phenyl-, m.p. 42.5—43.5°, and 1-*p*-anisyl-2-methyl- (with *pp'*-dianisyl), m.p. 91—92°, 3:4-dihydronaphthalene, and 7-methoxy-1-phenyl-, m.p. 48—50°, b.p. 214—215°/19 mm., and 1-*p*-anisyl-2-methyl-naphthalene, m.p. 108°. The Na derivative of CH<sub>2</sub>Bz·CH<sub>2</sub>·CO<sub>2</sub>Et and veratraldehyde (II) give the

lactone (III), 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH·C<math display="block">\begin{array}{c} \text{CO}\cdot\text{O} \\ \text{CH}\cdot\text{C}\_6\text{H}\_4 \end{array}, m.p. 131°, converted by hot MeOH into *Me* β-benzoyl-α-veratrylidene-*propionate* (IV), m.p. 96°, and thence by cold NaOMe into the corresponding acid, m.p. 168°. (III) with I in CHCl<sub>3</sub> at room temp. (5 days) yields 6:7-dimethoxy-1-phenylnaphthalene-3-carboxylic acid, m.p. 265° [also obtained by boiling (III) or (IV) with HCl·MeOH and hydrolysing the resulting *Me* ester, m.p. 124°], which with Cu-bronze in boiling quinoline affords (I). The Na derivative of *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et and PhCHO with Ac<sub>2</sub>O at 100° yield the lactone, m.p. 174°, analogous to (II), and thence β-*p*-anisoyl-α-benzylidene-*propionic acid*, +0.5C<sub>6</sub>H<sub>6</sub>, m.p. 170° (*Me* ester, m.p. 74—75°); none of these products could be cyclised. (OMe)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>·CO·CHN<sub>2</sub> and HCl·Et<sub>2</sub>O at 0° give ω-chloro-3:4:5-trimethoxyacetophenone, m.p. 86—87°, giving with KOAc·EtOH and a trace of I the *c*-derivative, m.p. 85—86°, and with CHNa(CO<sub>2</sub>Et)<sub>2</sub> 3:4:5-trimethoxybenzoylmalonic acid,

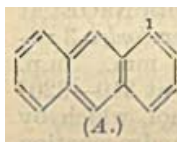
m.p. 167—168°, and thence (160°) 3:4:5-trimethoxybenzoylpropionic acid (V), dimorphic, m.p. 116° and 122°; the Na derivative of (V) with (IV) affords the γ-lactone, m.p. 172—173°, of β-3:4:5-trimethoxybenzoyl-α-veratrylidene-*propionic acid*. R. S. C.

**Aromatic fluoro-compounds. XXI. "ortho-Effect" in the "2-fluoro-1-nitronaphthalene"** of Willstaedt and Scheiber. G. SCHIEMANN and E. LEY (Ber., 1936, 69, [B], 960—964; cf. A., 1935, 856).—Repetition of the work of Willstaedt *et al.* (A., 1934, 522) shows that diazotisation of 1:2-NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NH<sub>2</sub> in conc. HCl is accompanied by replacement of NO<sub>2</sub> by Cl. The "2-fluoro-1-nitronaphthalene" is therefore 1-chloro-2-fluoronaphthalene, m.p. 62.5°. The isolation of 2:1-C<sub>10</sub>H<sub>6</sub>F·NO<sub>2</sub> from the products of the nitration of 2-C<sub>10</sub>H<sub>7</sub>F is very difficult, but the crude product can be reduced by the usual methods. H. W.

**Structure of anthracene.** L. F. FIESER and W. C. LOTHROP (J. Amer. Chem. Soc., 1936, 58, 749—753; cf. A., 1935, 1230).—Structure (A) (cf. Fries *et al.*, *ibid.*, 761) is indicated by the observation that 1:5-disubstituted-2:6-dihydroxyanthracenes do not couple with diazotised *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H or *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>. The position of equilibrium between the tautomeric forms of unsymmetrical derivatives (e.g., 2-OH-, 2-NH<sub>2</sub>-, 1-NO<sub>2</sub>-, 1:2-benz-) can be inferred from oxidation-reduction potential data for quinones.

6-Hydroxy-*o*-toluic acid (I) (from Na β-naphthylamine-4:8-disulphonate and 50% NaOH at 250—275°) is methylated (Me<sub>2</sub>SO<sub>4</sub>, alkali) to the 6-*OMe*-acid, m.p. 145—146°; the chloride, m.p. 40°, of this with AlCl<sub>3</sub> in CS<sub>2</sub> gives 4—10% of 2:6-dimethoxy- (II), m.p. about 305° (decomp.), and 3—7% of 2:6-dihydroxy-, decomp. about 330° (diacetate, m.p. 253°), -1:5-dimethylantraquinone. Reduction of (II) with SnCl<sub>2</sub> and AcOH·conc. HCl affords the hydroxyanthrone (?), decomp. about 295°, which is further reduced (method: Hall and Perkin, J.C.S., 1923, 123, 2029) to 2:6-dimethoxy-1:5-dimethylanthrane, m.p. 250° (decomp.), demethylated (48% IIBr, AcOH) to 2:6-dihydroxy-1:5-dimethylanthrane, decomp. from about 340° [diacetate, m.p. 266° (decomp.)]. An anthraquinone could not be obtained from (I) and ZnCl<sub>2</sub> (cf. G.P. 87,620), H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>·B<sub>2</sub>O<sub>3</sub>, or P<sub>2</sub>O<sub>5</sub>. (I) and SOCl<sub>2</sub> in Et<sub>2</sub>O give the *deside*, OH·C<sub>6</sub>H<sub>3</sub>Me·CO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·OH, m.p. 211°. 2:6-Diallyloxylantraquinone, m.p. 149° [from the (OH)<sub>2</sub>-derivative, allyl bromide, and K<sub>2</sub>CO<sub>3</sub> in COMe<sub>2</sub>], is reduced [as for (II)] to 2:6-diallyloxylanthrane, m.p. 201°, which when heated in NPhEt<sub>2</sub>·Ac<sub>2</sub>O and N<sub>2</sub> at 160—180° affords 2:6-diacetoxy-1:5-diallylanthrane, m.p. 179° [the 2:6-(OH)<sub>2</sub>-derivative could not be obtained cryst.]. H. B.

**Polycyclic aromatic hydrocarbons. XIV. Synthesis of 3:4-benzphenanthrene.** C. I. HEWETT (J.C.S., 1936, 596—599; cf. A., 1935, 1359).—A 7.3% over-all yield of 3:4-benzphenanthrene (I) is obtained from CO<sub>2</sub>H·CH<sub>2</sub>·CH(CHPh<sub>2</sub>)·CO<sub>2</sub>H (II). Difficulty of ring-closure in the last stage indicates resistance to formation of ring-structure of





(I), possibly due to steric hindrance. (II) and  $\text{AcCl}$  give the anhydride, which (crude) with  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at  $0^\circ$  gives 4-keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid, m.p. 208—209° (*Et* ester, m.p. 122—123°). Ordinary Clemmensen reduction gives poor yields, but reaction in boiling  $\text{PhOMe}$  and purification by way of the ester gives a 78% yield of 1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid, m.p. 148—148.5°, b.p. 200°/0.8 mm.; the *Et* ester, b.p. 170—173°/0.8—1 mm., thereof with  $\text{Na-EtOH}$  gives 1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthylcarbinol, b.p. 175—180°/1 mm., m.p. 93—94°, and thence ( $\text{SOCl}_2$ ) the chloride, m.p. 71—72°, b.p. 168°/0.8 mm.; the Grignard reagent with  $\text{CO}_2$  affords 1-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-acetic acid (III), m.p. 138—139° after sintering (*Et* ester, m.p. 55—56°), with a little 1-phenyl-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m.p. 46—47°, and  $\alpha\beta$ -bis-(1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthyl)ethane, m.p. 169.5—170.5°. Cyclisation of (III) was effected only by the action of  $\text{AlCl}_3$  in  $\text{CS}_2$  on the chloride (obtained by  $\text{SOCl}_2$ ) and yielded 2-keto-1 : 2 : 9 : 10 : 11 : 12-hexahydro-3 : 4-benzphenanthrene (IV), m.p. 154—155° (oxime, m.p. 191—192°), the semicarbazone, m.p. 235°, of which with  $\text{NaOEt}$  at 175—180° gives 1 : 2 : 9 : 10 : 11 : 12-hexahydro-3 : 4-benzphenanthrene, b.p. 148—153°/0.2 mm., m.p. 47.5—48°, dehydrogenated by  $\text{Pd-black}$  at 310—320° to (I). (IV) and  $\text{MgMeI}$  yield a carbinol, which by dehydration by  $\text{KHSO}_4$  at  $100^\circ$  and dehydrogenation by  $\text{Pd-black}$  at 300—310° gives 2-methyl-3 : 4-benzphenanthrene, m.p. 69.5—70°. R. S. C.

**Preparation of amino- and halogeno-phenanthrenes.** W. E. BACHMANN and C. H. BOATNER (J. Amer. Chem. Soc., 1936, 58, 857—858).—Hydrolysis of the products obtained by Beckmann rearrangement of the oximes of 1-, m.p. 112—113°, 2-, 3-, and 9-acetylphenanthrenes gives 1-, m.p. 145—146°, 2-, 3-, and 9-aminophenanthrenes, respectively. The following have been prepared: 1-, m.p. 120—120.5°, 2-, m.p. 85.5—86°, and 3-, m.p. 80.5—81.5°, chloro-; 1-, m.p. 109.5—110°, 2-, m.p. 95—96°, and 3-, m.p. 83—84°, bromo-; 1-, m.p. 112.5—113°, 2-, m.p. 116—116.5°, and 3-, m.p. 83.5—84°, iodo-phenanthrene. H. B.

**Diradical formula of rubenes.** C. DUFRAISSE (J. Amer. Chem. Soc., 1936, 58, 858).—Schonberg's claim (this vol., 326) to priority is disputed. H. B.

**[Reversible chemical absorption of free oxygen by organic compounds.]** C. DUFRAISSE (Ber., 1936, 69, [B], 1228).—A reply to Schonberg (this vol., 600). H. W.

**Catalytic condensation of acetylene with aromatic amines.** I. Condensation of acetylene with aniline in presence of cuprous and cupric chlorides. N. S. KOZLOV and P. N. FEDOSEEV (J. Gen. Chem. Russ., 1936, 6, 250—258).— $\text{NH}_2\text{Ph}$  and  $\text{C}_2\text{H}_2$  in presence of  $\text{CuCl}_2$  yield a product, from which quinaldine (I) and tetrahydroquinaldine (II) are obtained by distillation. In presence of excess of  $\text{NH}_2\text{Ph}$  *cis-trans*- $\text{NHPh}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPh}$  (III), also affording (I) and (II) when heated, is obtained. In presence of  $\text{CuCl}$  the products isolated after 1—10 days were (I) (50% yield), (II), (III), and  $\text{NHPhEt}$ ;

$\text{NPhEt}_2$  and  $\text{NHPhBu}$  were not found. The process is represented:  $2\text{NH}_2\text{Ph} + \text{C}_2\text{H}_2 \rightarrow \text{CHMe}(\text{NHPh})_2$  (IV);  $2(\text{IV}) \rightarrow 2\text{NH}_2\text{Ph} + (\text{III})$ ;  $\text{NH}_2\text{Ph} + \text{C}_2\text{H}_2 \rightarrow \text{NPh}\cdot\text{CHMe}$  (V);  $2(\text{V}) \rightarrow (\text{III}) \rightarrow (\text{I}) + \text{NH}_2\text{Ph} + \text{H}_2$ ;  $(\text{I}) + 2\text{H}_2 \rightarrow (\text{II})$ . The catalytic action of  $\text{CuCl}$  and  $\text{CuCl}_2$  appears to depend on formation of triple salts with  $\text{NH}_2\text{Ph}$  and  $\text{C}_2\text{H}_2$ . R. T.

**Reactivity and structure of primary aromatic amines.** G. VAVON and L. BOURGEOIS (Compt. rend., 1936, 202, 1446—1448).— $\text{CH}_3\text{PhBr}$  and 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\text{Br}$  with aromatic amines afford derivatives, the times of half formation of which are measured by the  $\text{HBr}$  liberated. When no steric factors are involved, the less basic amines react more slowly. *o*-Derivatives react more slowly than *p*-, the dimensions of the *o*-substituent being the determining factor. J. L. D.

**Rates of reaction and energies of activation of 1 : 2 : 4-chlorodinitrobenzene with aromatic primary amines.**—See this vol., 802.

**Stereochemistry of tervalent nitrogen compounds.** I. Attempted resolution of substituted derivatives of aniline. E. V. MENON and D. H. PEACOCK (J. Indian Chem. Soc., 1936, 13, 104—108).— $\text{NPhEt}\cdot\text{CH}_2\text{Ph}$  and 20% oleum at  $80^\circ$  give sulphobenzylethylaniline, the *brucine* salt, m.p. 164—165°, of which (after 5 crystallisations) yields an inactive Na salt. *N-Benzyl-p-toluenesulphon-m-nitroanilide* (I), m.p. 118° [from *p*-toluenesulphon-m-nitroanilide (modified prep.) and  $\text{CH}_2\text{PhCl}$  in  $\text{EtOH-NaOH}$ ], is reduced ( $\text{Sn}$ , conc.  $\text{HCl}$ ,  $\text{EtOH}$ ) to the -*m*-aminoanilide, m.p. 137° (*H tartrate*, m.p. 136°,  $[\alpha]^{25} + 4.57^\circ$  in  $\text{COMe}_2$ ;  $\gamma$ -phenoxy- $\alpha$ -methylbutyryl derivative, m.p. 117°), methylated ( $\text{MeI}$ , aq.  $\text{Na}_2\text{CO}_3$ ) to the -*m*-dimethylaminoanilide, m.p. 101° (methiodide, m.p. 111—112°, which affords a non-cryst. product with  $\text{Ag bromocamphorsulphonate}$ ). *N-Benzyl-p-toluenesulphon-p-nitroanilide*, m.p. 128° [obtained similarly to, but less readily than, (I)], is reduced to the -*p*-aminoanilide, m.p. 162° ( $\gamma$ -phenoxy- $\alpha$ -methylbutyryl derivative, m.p. 143°), which does not form a tartrate. The dry Na salt of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NHPh}$  and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$  at 140—150° give *N-m-nitrobenzyl-p-toluenesulphonanilide*, m.p. 95°, reduced to *N-m-aminobenzyl-p-toluenesulphonanilide*, m.p. 129° (*H tartrate*, m.p. 133°,  $[\alpha]^{25} + 4.6^\circ$  in  $\text{COMe}_2$ ;  $\gamma$ -phenoxy- $\alpha$ -methylbutyryl derivative, m.p. 111°). None of the above  $\text{NH}_2$ -derivatives shows signs of dissymmetry. H. B.

**Mesomeric effect of the dimethylamino-group in dimethylaniline, and the nature of its interaction with halogen groups.** R. J. B. MARSDEN and L. E. SUTTON (J.C.S., 1936, 599—606).—The dipole moments of  $\text{NPhMe}$ , and its *p*-Me, -Cl, -Br, -I, - $\text{NO}_2$ , and - $\text{NH}_2$ -derivatives, measured in  $\text{C}_6\text{H}_6$  solution at  $25^\circ$ , are 1.58, 1.29, 3.29, 3.37, 3.24, 6.87, and  $1.42 \times 10^{-18}$  e.s.u., respectively. On the assumption that the interaction between  $\text{Me}$  and  $\text{NMe}_2$  is zero the mesomeric effect of the latter group is calc. to be 1.55, the angle between the moment of  $\text{NPhMe}_2$  and the  $\text{C-NMe}_2$  linking being  $38^\circ$  (cf.  $33.5^\circ$ , the smaller of the two possible vals. obtained by Hertel *et al.*, this vol., 12). The interaction moment  $\mu_{\text{int}}$  (that moment parallel to the axis passing through the two

substituent-bearing C atoms necessary to convert the calc. to the observed val.) between  $\text{NMe}_2$  and substituent groups are calc. to be Cl 0.34, Br 0.46, I 0.69, and  $\text{NO}_2$  1.86:  $\text{NMe}_2$  thus reduces the mesomeric effect of the halogens, suppressing it almost completely in the I-derivative: decreases in the order  $\cdot\text{NMe}_2 > (\cdot\text{NH}_2, \cdot\text{OPh}, \cdot\text{OMe}) > \cdot\text{OH}$ , and is always positive relatively to the main group for any of the substituent groups used (cf. also Bennett *et al.*, A., 1934, 831). The nature of mesomeric effects and their mutual interaction are fully discussed especially in relation to excited structures, the increase or decrease in the relative importance of which may be produced not only by similar or dissimilar requirements of valency arrangements of the two groups, but also by the fields of the groups, and an attempt to assess the relative importance of such "valency" and "polar" effects is made. J. W. B.

**De-ethylation of diethylaniline.** G. I. GERSCHON and G. BERENSCHTEIN (J. Appl. Chem. Russ., 1936, 9, 496—501).—A mixture of  $\text{NH}_2\text{Ph}$ ,  $\text{NPhEt}$ , and  $\text{NPhEt}_2$  is obtained by heating  $\text{NH}_2\text{Ph}$  and  $\text{NPhEt}_2$  in presence of  $\text{HCl}$  or  $\text{C}_6\text{H}_5\text{Me}(\text{SO}_3\text{H})_2$ .  $\text{EtCl}$  and  $\text{C}_2\text{H}_4$  are obtained as by-products. R. T.

**Catalytic synthesis of diphenylamine.** G. I. GERSCHON and R. P. LASTOVSKI (J. Appl. Chem. Russ., 1936, 9, 502—504).— $\text{NHPh}_2$  is obtained in good yield from  $\text{NH}_2\text{Ph}\cdot\text{HCl}$  (I) (2 mols.) and  $\text{AlCl}_3$  (0.43 mol.) (220—240°; 20 hr.). The reaction is represented as  $3\text{NH}_2\text{Ph} + \text{AlCl}_3 \rightarrow \text{Al}(\text{NH}_2\text{Ph})_3$  (II); (II) + 3(I)  $\rightarrow$   $3\text{NHPh}_2 + 3\text{NH}_4\text{Cl} + \text{AlCl}_3$ . R. T.

**Preparation of di- $\alpha$ -naphthylmethylamine.** H. RUPE and W. BRENTANO (Helv. Chim. Acta, 1936, 19, 581—588).—Hydrogenation (Ni) of  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CN}$  (I) in  $\text{EtOH-EtOAc-H}_2\text{O}$  at 75°/70 atm. gives 71.1% of  $\text{NH}(\text{CH}_2\text{-C}_{10}\text{H}_7\text{-}\alpha)_2$  (II) and 5% of  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{OH}$ , m.p. 59—60°. Mostly  $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_{10}\text{H}_7\text{-}\alpha$  (III) is obtained at 75°/1 atm., room temp./75 atm., or room temp./1 atm. Other methods give poor yields of (II). 15 g. of  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\text{Cl}$  (IV), m.p. 31—32°, b.p. 150—155°/10 mm. (modified prep. by  $\text{CH}_3\text{O-HCl}$ ), and  $\text{NH}_3\text{-EtOH}$  at 160° give 5 g. of (III), 5.1 g. of (II), and 1.5 g. of tri-( $\alpha$ -naphthylmethyl)amine, m.p. 300° [hydrochloride, nitrate, phosphate, sulphate, and acetate, more sol. than the salts of (II)]. 10 g. of  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br}$  (improved prep. by Br at 190° in ultra-violet light) and  $\text{NH}_3\text{-EtOH}$  at 100° give 1.5 g. of (II) and 4.8 g. of (III), at 150° 6 g. of (III). (I) (prep. by diazo-reaction with  $\text{K}_2\text{Ni}(\text{CN})_4$  in 75—78% yield), b.p. 147—148°/12 mm., and  $\text{NH}_3\text{-H}_2\text{S-EtOH}$  at 100° give a very poor yield of (III).  $\alpha$ -Naphthylmethylphthalimide, m.p. 174—175°, with conc.  $\text{HCl}$  at 100° gives 86% of (II), 10 g. of which with (IV) give 1.8 g. of (II). (IV),  $p\text{-C}_6\text{H}_4\text{Me-SO}_2\text{-NH}_2$ , and hot  $\text{KOH-EtOH}$  give a good yield of  $p$ -toluenesulphon-di-( $\alpha$ -naphthylmethyl)amide, m.p. 134° (obtained also in 50—55% yield by hot  $\text{NaOBu}^t\text{-Bu}^t\text{OH}$ ), with conc.  $\text{HCl}$  at 100° gives a poor yield of (I).  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CHO}$  [prep. from (IV) by  $(\text{CH}_2)_6\text{N}_4$  in 48% yield], b.p. 158—159°/14 mm., and (III) give  $\alpha$ -naphthylidene- $\alpha$ -naphthylmethylamine, m.p. 105°, giving by hydrogenation (Ni) in  $\text{EtOH-H}_2\text{O}$  10% of (II).

R. S. C.

[Pharmacology of] quaternary ammonium iodides.—See this vol., 892.

**Reduction of nitro-compounds by hydrazine.** [Preparation of 4:4'-azoxyphenetole.] B. M. BOGOSLOVSKI (J. Appl. Chem. Russ., 1936, 9, 725—727).—A 100% excess of  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  added to 4-nitrophenetole (I) in hot  $\text{NaOEt-EtOH}$  gives 4:4'-azoxyphenetole in 62% yield. With 4-nitrotoluene in place of (I), the chief product is an unidentified substance, m.p. 265°, together with some 4:4'-azoxytoluene. R. T.

**Action of Grignard compounds on phenylhydrazones.** Preparation of  $s$ -alkylphenylhydrazines. P. GRAMMATIKAKIS (Compt. rend., 1936, 202, 1289—1291).—Contrary to Busch *et al.* (A., 1905, i, 519) arylphenylhydrazones react with  $\text{MgRX}$ :  $\text{CHAr}\cdot\text{N}\cdot\text{NHPh} + \text{MgRX} \rightarrow \text{CHRAr}\cdot\text{NH}\cdot\text{NHPh}$ . Thus  $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$  and  $\text{MgEtBr}$  give  $s$ -phenyl- $\alpha$ -phenyl- $n$ -propylhydrazine (I), b.p. 210°/15 mm. [hydrochloride, m.p. 217° (decomp.);  $\text{Ac}_1$  derivative, m.p. 138°; phenylurethane, m.p. 140°], reduced by  $\text{Zn-AcOH}$  quantitatively to  $\text{NH}_2\text{Ph}$  and  $\text{NH}_2\cdot\text{CHPhEt}$ , which, with  $\text{COPhPr}^a$ , are also obtained as secondary products in the formation of (I). (I) has the usual basic and reducing properties of  $s$ -alkylphenylhydrazines. J. W. B.

**Velocity of diazotisation.**—See this vol., 802.

**Mechanism of diazotisation.** J. BOESEKEN and H. SCHOUTISSEN (Rec. trav. chim., 1935, 54, 956—958).—The conclusions of Reilly *et al.* (A., 1935, 1232), who have overlooked previous work by the authors and others, are criticised. Attention is drawn to the conclusion of Schoutissen (A., 1934, 67) that substituents in the  $\text{C}_6\text{H}_5$  nucleus exert a twofold opposing influence on the velocity of diazotisation, by affecting the basicity of the amine and the rate of transformation of the  $\text{NH}_2$ -group. H. G. M.

**Double salts of aryldiazonium chlorides with heavy-metal chlorides.** K. A. KOTSCHESCHKOV and A. N. NESMEJANOV (J. Gen. Chem. Russ., 1936, 6, 144—160).—128 double salts of  $o$ -,  $m$ -, and  $p$ - $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  ( $\text{R}=\text{H}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{Me}, \text{OMe}, \text{OH}$ ) with  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{TiCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ ,  $\text{BiCl}_3$ ,  $\text{AuCl}_3$ ,  $\text{PtCl}_4$ , and  $\text{FeCl}_3$  are described. R. T.

**Double salts of lead halides and benzene-diazonium halides, and their decomposition.** K. A. KOTSCHESCHKOV, A. N. NESMEJANOV, and N. K. GIPP (J. Gen. Chem. Russ., 1936, 6, 172—175).—The double salts  $\text{PhN}_2\text{Cl}\cdot\text{PbCl}_2$ ,  $\text{PhN}_2\text{Br}\cdot\text{PbBr}_2$ , and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Br}\cdot\text{PbBr}_2$  are described. The above salts, as well as  $2\text{PhN}_2\text{Cl}\cdot\text{PbCl}_4$  (I), react with Zn or Cu in boiling  $\text{COMe}_2$ ,  $\text{AcOEt}$ , or  $\text{Et}_2\text{O}$  to yield  $\text{C}_6\text{H}_6$ ,  $\text{Ph}_2$  or  $(\text{C}_6\text{H}_4\text{R})_2$ ,  $\text{PhX}$ ,  $\text{PhOH}$ , and tarry products; in the case of (I),  $\text{PbPh}_3\text{Cl}$  is also obtained in small yield. R. T.

**Nature of the reaction between diazotised sulphanilic acid and proteins.** H. EAGLE and P. VICKERS (J. Biol. Chem., 1936, 114, 193—197).— $p\text{-SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  (I) at  $p_H$  7.2—7.6 is inactivated by glycine, alanine, lysine, ornithine, phenylalanine, proline, hydroxyproline, and indole, but not by diketopiperazine,  $\text{NH}_2\text{Ac}$ , or arginine. Each  $\text{NH}_2$



inactivates about 2 mols. of (I). This explains why proteins commonly inactivate more (I) than can be accounted for by the histidine- and tyrosine-Ph components, since free  $\text{NH}_2$  and  $\text{NH}$  and indole groups also react.

R. S. C.

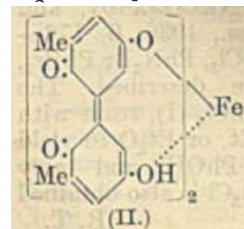
**Condensation of oximes with aromatic diazo-compounds.** A. MANGINI (Atti R. Accad. Lincei, 1935, [vi], 22, 452—457).—Structures proposed for these compounds (cf. A., 1892, 163, 1079; 1906, i, 421; 1907, i, 567) are examined. The products from acetoxime and *p*-toluene- and *p*-nitrobenzene-diazo-compounds are hydrolysed by acid to  $\text{COMe}_2$ , *p*-toluidine or *p*-nitroaniline, and *p*-toluene- or *p*-nitrobenzene-diazoimide. The *p*-toluene compound with  $\text{BzCl}$  or  $\text{C}_6\text{H}_4\text{Br}\cdot\text{COCl}$  yields benz- or bromobenz-*p*-toluidine, and with  $\text{PhNCO}$  yields *N*-phenyl-*N'*-*p*-tolylcarbamide. The *p*-nitrobenzene compound with  $\text{PhNCO}$  gives the same product as the latter and acetoxime, viz.,  $\text{CMe}_2\cdot\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ . These reactions are in agreement with Bamberger's formulæ (A., 1899, i, 589), viz.,  $\text{CMe}_2\cdot\text{N}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{N}(\text{OH})\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{X}$  ( $\text{X}=\text{p-Me}$  or  $\text{p-NO}_2$ ), if the tautomeric formula  $\cdot\text{N}(\text{O})\cdot\text{N}\cdot\text{NH}\cdot$  is also admitted. Acetoxime Me ether and *p*-toluenediazo-compounds do not give  $\text{CMe}_2(\text{OH})\cdot\text{N}(\text{OMe})\cdot\text{N}\cdot\text{R}$ , but only *p*-toluenediazo-*p*-cresol.

E. W. W.

**Aliphatic diazo-compounds. II. Phenyl- $\alpha$ -naphthylhydrazomethane.** G. C. HARROLD and M. G. HEMPHILL [with F. E. RAY] (J. Amer. Chem. Soc., 1936, 58, 747—749).—*dl*-Phenyl- $\alpha$ -naphthylmethylamine, prepared by reduction of  $\text{Ph}\cdot\alpha\text{-C}_{10}\text{H}_7$  ketoxime (modified prep.), is resolved by *d*-camphorsulphonic acid (cf. Berlingozzi, A., 1920, i, 480) into the *l*-form,  $[\alpha]_D -56.8^\circ$  in  $\text{Et}_2\text{O}$ , which with  $\text{ClCO}_2\text{Et}$  in  $\text{Et}_2\text{O}+5\%$   $\text{NaOH}$  gives *Et phenyl- $\alpha$ -naphthylmethylcarbamate*, m.p.  $125^\circ$ ,  $[\alpha]_D -28^\circ$  in  $\text{EtOH}$ . The *NO*-derivative, m.p.  $87-89^\circ$  (decomp.),  $[\alpha]_D^{25} +9.2^\circ$  in  $\text{EtOH}$ , of this with  $\text{KOMe}$  in  $\text{COMe}_2$  at  $-20^\circ$  affords inactive *phenyl- $\alpha$ -naphthylhydrazomethane* (I), m.p.  $58^\circ$  (decomp.), together with an active by-product. The inactivity of (I) may be due to its rapid racemisation or to the symmetrical structure of the diazo-group.

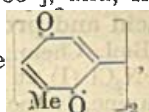
H. B.

**Reaction between cresols and hydrogen peroxide in presence of ferrous sulphate.** K. ONO and T. OYAMADA (Bull. Chem. Soc. Japan, 1936, 11, 132—137).—Oxidation of *o*-cresol with 2%  $\text{H}_2\text{O}_2$ -aq.  $\text{FeSO}_4$  under various conditions affords *p*-toluquinol (I) [ $1:2:5\text{-C}_6\text{H}_3\text{Me}(\text{OH})_2$ ] and a black substance, separated into  $\text{Et}_2\text{O}$ -sol. (A) and  $\text{Et}_2\text{O}$ -insol. (B) portions. Fractional pptn. of A with ligroin affords an insol. substance (II)  $\text{C}_{23}\text{H}_{20}\text{O}_8\text{Fe}$ , reduced by  $\text{Zn-EtOH-HCl}$  to  $2:5:2':5'$ -tetrahydroxydi-*m*-tolyl, m.p.  $202^\circ$ .



[converted into the known  $\text{Ac}_2$  derivative (III), m.p.  $135^\circ$ ], and, from the mother-

liquor, ditolyldiquinone



converted by

reduction-acetylation into (III). B is a black substance, (?)  $\text{C}_{23}\text{H}_{22}\text{O}_8\text{Fe}$ , possibly identical with the

complex of Majima *et al.* (A., 1920, i, 837), converted in small yield by  $\text{Zn-Ac}_2\text{O-NaOAc}$  into an acetate, m.p.  $193-195^\circ$ , probably  $4:4':5:5'$ -tetra-acetoxydi-*m*-tolyl. Oxidation of *m*- and *p*-cresol gives (I) (only from *m*-) and similar black substances containing Fe not definitely identified.

J. W. B.

**Mobility of the nitro-group. I. Nitro-group mobility in 3:4-dinitroanisole. II. Preparation of 3:4-dinitroanisole.** K. S. TOPTSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 201—204, 204—106).—I. 3:4-Dinitroanisole when heated ( $140-150^\circ$ ; 8 hr.) with  $\delta$ -amino- $\alpha$ -diethylaminopentane gives  $\delta$ -(2-nitro-5-methoxyanilino)- $\alpha$ -diethylaminopentane, b.p.  $205^\circ/2$  mm. The constitution of this was confirmed by reduction ( $\text{SnCl}_2\text{-HCl}$ ) to the corresponding 2- $\text{NH}_2$ -compound, b.p.  $190-192^\circ/3$  mm., which when heated with  $\text{H}_3\text{AsO}_4$ , glycerol, and  $\text{H}_2\text{SO}_4$  (Skraup) gives 8-diethylamino-6-hydroxy-*sec*-amylaminoquinoline, also obtained when the corresponding 6- $\text{OMe}$ -derivative is heated with  $\text{HCl}$  (sealed vessel) (cf. lit.).

II. Nitration of  $1:4\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$  gives the 3- $\text{NO}_2$ -derivative, which when successively hydrolysed, diazotised in presence of excess of  $\text{H}_2\text{SO}_4$ , and then treated with  $\text{CuSO}_3\cdot\text{Cu}_2\text{SO}_3$  (cf. "Abegg's Handbuch, Kupfer," p. 462)- $\text{NaNO}_2\text{-H}_2\text{O}$  gives 3:4-dinitroanisole in good yield.

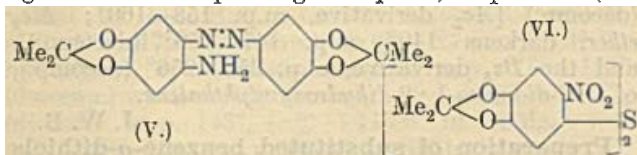
H. G. M.

**Condensation of polyhydric phenols with acetone.** C. H. FISHER, R. W. FURLONG, and M. GRANT (J. Amer. Chem. Soc., 1936, 58, 820—822).—In agreement with Baker (A., 1935, 80), the compound obtained from  $\alpha\text{-C}_6\text{H}_4(\text{OH})_2$  and  $\text{COMe}_2$  (method: *loc. cit.*) is considered to be  $5:6:5':6'$ -tetrahydroxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene (I). Guaiacol and  $\text{COMe}_2$  similarly yield the 6:6'-dihydroxy-5:5'-dimethoxy-derivative, m.p.  $266-267^\circ$ , methylated ( $\text{Me}_2\text{SO}_4$ , 20%  $\text{KOH}$ ) to the  $\text{Me}_4$  ether (II), m.p.  $155-156^\circ$ , of (I). (II) could not be oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ).  $1:2:4\text{-C}_6\text{H}_3(\text{OAc})_3$  and  $\text{COMe}_2$  or phorone in  $\text{AcOH}$ -conc.  $\text{HCl}$  give  $4:6:7:4':6':7'$ -hexahydroxy-3:3:3':3'-tetramethylbis-1:1'-spirohydrindene, m.p.  $265-267^\circ$  (decomp.). Oily products were obtained from  $\text{COMe}_2$  and quinol or toluquinol.

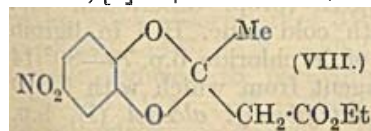
H. B.

**Cyclic ethers by condensation of pyrocatechol with aldehydes and ketones.** G. SLOOF (Rec. trav. chim., 1935, 54, 995—1010).—Pyrocatechol (I) with  $\text{COMe}_2\text{-P}_2\text{O}_5$  gives isopropylidenepyrocatechol (II), b.p.  $182^\circ/760$  mm. [ $4\text{-NO}_2$ , m.p.  $92^\circ$ ,  $4:5\text{-(NO}_2)_2$ , (III), m.p.  $161^\circ$ ,  $4\text{-Cl}$ , b.p.  $223^\circ/760$  mm.,  $4:5\text{-Cl}_2$ , m.p.  $88^\circ$ ,  $4\text{-Br}$ , m.p.  $12^\circ$ , b.p.  $122^\circ/20$  mm.,  $4:5\text{-Br}_2$ , m.p.  $92^\circ$ , b.p.  $166^\circ/20$  mm.,  $4\text{-chloro-5-bromo}$ , m.p.  $78^\circ$ ,  $4\text{-NH}_2$  (IV), m.p.  $35^\circ$ , b.p.  $135^\circ/11$  mm.,  $4\text{-I}$ , m.p.  $47^\circ$ , b.p.  $130^\circ/12$  mm.,  $4\text{-chloro-5-nitro}$ , m.p.  $118^\circ$ ,  $4\text{-bromo-5-nitro}$ , m.p.  $130^\circ$ ,  $4\text{-iodo-5-nitro}$ , m.p.  $114^\circ$ , derivatives].  $4\text{-Chloro-5-bromo}$ , m.p.  $90^\circ$  ( $\text{Ac}_2$  derivative, m.p.  $104^\circ$ ),  $4\text{-chloro-5-nitro}$ , m.p.  $169^\circ$  ( $\text{Ac}_2$  derivative, m.p.  $119^\circ$ ), and  $4\text{-bromo-5-nitro}$ , m.p.  $172^\circ$  ( $\text{Ac}_2$  derivative, m.p.  $122^\circ$ ), -pyrocatechol are described. Diazotised (IV) couples with (IV) giving the red-brown compound (V), m.p.  $179^\circ$ , from which the  $\text{CMe}_2$  is readily hydrolysed by  $\text{H}_2\text{SO}_4$ . (III) with a little  $\text{NH}_3\text{-H}_2\text{O-H}_2\text{S-EtOH}$  gives the

sulphide (VI), m.p. 230°, with more of this reagent gives the corresponding disulphide, m.p. 247° (de-



comp.), and with excess gives 5-nitro-4-aminopyrocatechol, m.p. 127°. The condensation products of (I) with the following ketones are described (b.p./20 mm. are given in parenthesis): COMeEt (94°); COMePr<sup>a</sup> (107°); COMeBu<sup>a</sup> (114.5°); COMe-C<sub>6</sub>H<sub>13</sub> (118°); COEt<sub>2</sub> (105°); COEtPr<sup>a</sup> (121°); CPr<sup>a</sup><sub>2</sub> (131.5°); CH<sub>2</sub>Ac·CO<sub>2</sub>Et (155°); cyclopentanone (124°); and cyclohexanone (141°). Hydrolysis of the product from (I) and CH<sub>2</sub>Ac·CO<sub>2</sub>Et gives an acid, m.p. 61° [the 4-NO<sub>2</sub>-derivative (VII), m.p. 125°, crystallises from PhMe and CHCl<sub>3</sub> with 1 mol. of solvent and has m.p. 41° from CHCl<sub>3</sub>], decomposed by heat into (II). (VII) is resolved by cinchonine and then has m.p. 117.5°, [α]<sub>D</sub><sup>15</sup> +41.0° in EtOH (cinchonine salt of the d-acid has [α] +167°).



The Et ester (VIII), m.p. 71°, of (VII) with KOH-EtOH at room temp. gives Et β-(2-hydroxy-5-nitrophenoxy)crotonate (IX), m.p. 127° (Ac derivative, m.p. 59°; Me ether, m.p. 120°), as the K salt, which when heated passes irreversibly into a second form which yields an isomeride of (IX), m.p. 137° [Ac derivative, m.p. 67°; Me ether (X), m.p. 106°]. (IX) and its isomeride are converted by heat into (VIII), and with Ag<sub>2</sub>O-MeI give the same ether (X); this change of configuration is avoided by the use of CH<sub>2</sub>N<sub>2</sub>. With H<sub>2</sub>SO<sub>4</sub> both the foregoing Me ethers give the same nitroguaiacol. (VIII) when boiled (1 hr.) with KOH-EtOH gives a mixture of the two forms of β-(2-hydroxy-5-nitrophenoxy)crotonic acid, decomp. 167° and 170°, respectively (corresponding Me<sub>2</sub> derivatives, m.p. 92° and 130°, obtained with CH<sub>2</sub>N<sub>2</sub>; Ag<sub>2</sub>O-MeI gives the latter derivative with both acids); the former acid is less sol. than the latter in EtOAc. The two forms of the foregoing compounds are *cis-trans*-isomerides. (I) when heated with MeCHO and P<sub>2</sub>O<sub>5</sub> gives a little ethyldienepyrocatechol, b.p. 75—79°/20 mm. (4-NO<sub>2</sub>-derivative, m.p. 82°); in the cold, however, the compound

$\text{o-C}_6\text{H}_4\left\langle \begin{array}{c} \text{O-CHMe} \\ \text{O-CHMe} \end{array} \right\rangle \text{O}$ , m.p. 34°, b.p. 118°/20 mm (4-NO<sub>2</sub>-derivative, m.p. 111—112°), is formed. Only resins were obtained from (I) and CH<sub>2</sub>O. The equilibrium const. for the reaction (I)+COMe<sub>2</sub> cyclic acetal+H<sub>2</sub>O is ±0.001, and is much < would be expected from the parallelism between this quantity for other diols and the formation of boric acid complexes. A stereochemical explanation for this divergence is given.

H. G. M.

**Synthesis of vanillin from cresols.** I. Synthesis of homopyrocatechol. K. OXO and M. IMORO (Bull. Chem. Soc. Japan, 1936, 11, 127—131).—Rearrangement of *m*- and *p*-C<sub>6</sub>H<sub>4</sub>Me·OAc with AlCl<sub>3</sub> at 130—160° gives, respectively, 2-hydroxy-4-methyl- and 6-hydroxy-3-methyl-aceto-

phenone, both oxidised by 3% H<sub>2</sub>O<sub>2</sub>-NaOH at room temp. to homopyrocatechol [1:3:4-C<sub>6</sub>H<sub>3</sub>Me(OH)<sub>2</sub>] [Ac<sub>2</sub> derivative, m.p. 57—58°, oxidised by 0.5*N*-H<sub>2</sub>SO<sub>4</sub>-2% KMnO<sub>4</sub> to 1:3:4-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>(OAc)<sub>2</sub>], methylation of which gives homoveratrole and creosol, oxidised by EtO·NO to veratric acid and vanillin, respectively. *o*-C<sub>6</sub>H<sub>4</sub>Me·OAc rearranges to 2-hydroxy-3-methylacetophenone, which gives no definite product by Dakin's oxidation.

J. W. B.

**Synthesis of 4-hydroxy-3-ethoxy-1-allylbenzene (eugenol).** N. HIRAO (Bull. Chem. Soc. Japan, 1936, 11, 179—184).—Eugenol Me ether and MgMeI in xylene at 160—180° give chavibetol (I) and eugenol, separated by fractional crystallisation of their benzoates and isomerised (KOH at 220°) to isochavibetol (II) [1:3:4-CHMe·CH·C<sub>6</sub>H<sub>3</sub>(OH)·OMe]. *iso*Eugenol Me ether similarly gives *isoeugenol* and (I); eugenol and *isoeugenol* Et ether give, respectively saфро- and *isosaфро*-eugenol. (II) with KEtSO<sub>4</sub>-KOH at 150—160° gives its Et ether, converted by MgMeI into *isohomogenol* [1:3:4-CHMe·CH·C<sub>6</sub>H<sub>3</sub>(OEt)·OH] (III). Chavibetol with EtBr-KOH at 80—90° gives its Et ether, b.p. 114°/6.5 mm. (oxidised to 4-methoxy-3-ethoxyallylbenzoic acid), converted by MgMeI into 4-hydroxy-3-ethoxyallylbenzene (*homogenol*), b.p. 112°/6.5 mm. (*phenylurethane*, m.p. 93.5—94.5°; *benzoate*, m.p. 45.5°), which is isomerised (KOH at 170—220°) to (III).

J. W. B.

**Raman spectra and decomposition reactions of ozonides; ozonides of *isoeugenol* methyl ether, *eugenol* methyl and ethyl ether, ethyl maleate and fumarate.** E. BRINER, E. PERROTTET, H. PAILLARD, and B. SUSZ (Helv. Chim. Acta, 1936, 19, 558—568).—When a substance is ozonised, the O<sub>3</sub> absorbed (taking account of a blank on the solvent) gives the max. (a), and determination of a product gives the min. (b) amount of ozonide formed. *iso*-Eugenol Me ether gives (a) 45, (b) 38%, eugenol Me and Et ethers (a) 30 and 47, (b) 20 and 38%, respectively, of ozonide, (b) being determined by yields of aldehyde. Et<sub>2</sub> maleate and fumarate give (a) 31 and 33, (b) 30 and 27%, respectively, (b) being determined by yields of Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; Et<sub>2</sub> maleate reacts very slowly, Et<sub>2</sub> fumarate very quickly. The eugenol and *iso*-eugenol ether ozonides retain the Raman spectra of the Ph but have lost those of the unsaturated side-chain which are replaced by new bands characteristic of the ozonide linking. The ozonides of Et<sub>2</sub> maleate and fumarate differ from those of the esters themselves only by an additional new band at 1821 cm.<sup>-1</sup>

R. S. C.

**Raman spectra of compounds belonging to the anethole, safrole, and eugenol groups.**—See this vol., 777.

**Condensation of ethylene chlorohydrin with resorcinol.** D. C. MOTWANI and T. S. WHEELER (J. Univ. Bombay, 1935, 4, Part II, 104—105).—*m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, CH<sub>2</sub>Cl·CH<sub>2</sub>·OH, and 40% KOH at 100° give, according to the relative amounts, *resorcinol* β-*hydroxyethyl*, b.p. 185—195°/10 mm. (*diacetate*, m.p. 75°; *dibenzoate*, m.p. 90—91°), or *di-β-hydroxyethyl ether*, m.p. 95—96° (*diacetate*, m.p. 75—76°; *dibenzoate*, m.p. 110°). The ethers with



$\text{PCL}_5$  afford *m*-chlorophenyl  $\beta$ -hydroxyethyl ether, m.p. 78—79°, and *resorcinol di- $\beta$ -chloroethyl ether*, m.p. 63—64°, b.p. 130—150°/1 mm. R. S. C.

**C-Alkylresorcinols. I. 4 : 6-Diethylresorcinol and its reactions.** R. C. SHAH and P. R. MEHTA (J. Univ. Bombay, 1935, 4, Part II, 109—113).—5-Ethylresacetophenone (prep. by the Nencki-Sieber and Hoesch methods), m.p. 118—119° ( $\text{Bz}_2$ , m.p. 91—92°, 3-Br-, m.p. 123—125°, and 3 : *x* : *x*-Br<sub>3</sub>-derivative, m.p. 144—145°; phenylhydrazone, m.p. 232—233°; oxime, m.p. 141—143°; semicarbazone, m.p. 300—302°), is reduced (activated Zn-Hg; HCl) to 4 : 6-diethylresorcinol, unstable, b. p. 150—151°/7 mm., m.p. 65—67° after softening at 55° (*di-p*-nitrobenzoate, m.p. 163—165°;  $\text{CO}_2\text{Me}$ -derivative, m.p. 83—85°), which with  $\text{PhN}_2\text{Cl}$  gives the 2-benzeneazo-compound, m.p. 89°, with  $\text{Hg}(\text{OAc})_2$  in EtOH yields the 2-acetoxymethyl-derivative, decomp. 200°, with 40%  $\text{CH}_2\text{O}$  and 2*N*-HCl gives *di*-(2 : 6-dihydroxy-3 : 5-diethylphenyl)methane, m.p. 119°, and with  $\text{H}_2\text{SO}_4$  and malic acid or  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  affords 5-hydroxy-6 : 8-diethyl-, m.p. 148—149°, or 5-hydroxy-4-methyl-6 : 8-diethyl-coumarin, m.p. 169—170°, respectively. R. S. C.

**Mechanism of formation of benzaldehyde-resorcinol resins.** E. MERTENS and M. FONTEYN (Bull. Soc. chim. Belg., 1936, 45, 186—188).—Equimol. amounts of  $\text{PhCHO}$  and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$  in 0.5%  $\text{NaOH}$ -EtOH at 100° in an inert atm. gives 2 : 4-dihydroxydiphenylcarbinol (cf. J.C.S., 1910, 97, 78), which with  $\text{PhCHO}$  in 10%  $\text{NaOH}$ -EtOH affords the same resin as is obtained from *m*- $\text{C}_6\text{H}_4(\text{OH})_2$  and excess of  $\text{PhCHO}$ . J. L. D.

**Nitration of 1 : 8-dihydroxynaphthalene.** F. CALVET and (in part) (MISS) M. C. CARNERO (J.C.S., 1936, 556—560).—With  $\text{HNO}_3$  (*d* 1.4) at 25—30° 1 : 8- $\text{C}_{10}\text{H}_6(\text{OAc})_2$  gives the 8-*O*-Ac derivative, m.p. 200° (decomp.) [*Me* ether (I), m.p. 115—117°], of 2 : 4-dinitro-1 : 8-dihydroxynaphthalene (II), m.p. 180—182° [*Me*<sub>2</sub> ether (III), m.p. 137—139°], obtained as its *K* salt (IV) by  $\text{KOH}$ -MeOH hydrolysis. Hydrolysis of (I) with cold  $\text{KOH}$ -MeOH affords some (IV) and 2 : 4-dinitro-8-hydroxy-1-methoxynaphthalene, m.p. 170—171°, hydrolysed to (II). Hydrolysis of (III) with boiling 2*N*-NaOH affords 2 : 4-dinitro-1-hydroxy-8-methoxynaphthalene, m.p. 179—180° (decomp.), reduced ( $\text{Sn}$ -HCl) to the dihydrochloride of the 2 : 4-( $\text{NH}_2$ )<sub>2</sub>-derivative, oxidised by  $\text{HNO}_3$  to 3-methoxyphthalic acid. Similar reduction of (II) affords the dihydrochloride of 2 : 4-diamino-1 : 8-dihydroxynaphthalene [ $\text{Bz}_4$  derivative, m.p. 257—258° (decomp.)]. Nitration of 1 : 8-methylenedioxy-naphthalene with  $\text{AcOH}$ - $\text{HNO}_3$  (*d* 1.5) affords its (?) 2 : 7- (V), m.p. 198—200°, and 4 : 5-( $\text{NO}_2$ )<sub>2</sub>-derivative (VI), m.p. 177—179°. Hydrolysis of (V) with boiling 2*N*-NaOH affords (?) 2 : 7-dinitro-1 : 8-dihydroxynaphthalene (VII) +  $\text{H}_2\text{O}$  and anhyd., m.p. 171—173° (decomp.) [ $\text{Ac}_1$ , m.p. 125—170° (decomp.) and  $\text{Ac}_2$  derivative, m.p. about 228° (decomp.)]; *Me*<sub>2</sub> ether, m.p. 268—270° (decomp.)]. With boiling  $\text{KOH}$ -MeOH (V) gives (?) 2 : 7-dinitro-1-hydroxy-8-methoxynaphthalene, m.p. 218—220° (*Ac* derivative, m.p. 183—185°). Reduction of (VII) gives the hydrochloride of the 2 : 7-( $\text{NH}_2$ )<sub>2</sub>-derivative [ $\text{Bz}_4$  derivative, m.p. about 300°

(decomp.)]. By similar methods (VI) affords 4 : 5-dinitro-1 : 8-dihydroxynaphthalene, m.p. about 225° (decomp.) [ $\text{Ac}_2$  derivative, m.p. 158—160°; *Me*<sub>2</sub> ether, darkens 140°, m.p. 147—150° (decomp.)], and the  $\text{Bz}_4$  derivative, m.p. 255—256° (decomp.), of 4 : 5-diamino-1 : 8-dihydroxynaphthalene.

J. W. B.

**Preparation of substituted benzene-*o*-dithiols for use as specific reagents for tin.** R. E. D. CLARK (Tech. Publ. Internat. Tin Res. and Dev. Council, 1936, A, No. 41, 7 pp.).—The prep. of toluene- and 1-chlorobenzene-3 : 4-dithiol is described. These reagents give an intense red coloration with  $\text{Sn}^{\text{II}}$  salts. E. S. H.

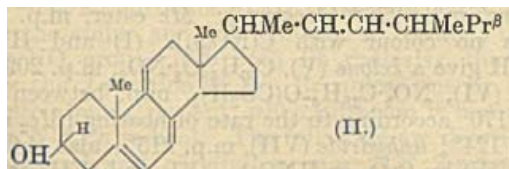
**Synthesis of 2 : 3-di- and 2 : 3 : 4-tri-methylbenzyl alcohol. Anomalous reactions.** T. REICHSTEIN, A. COHEN, M. RUTH, and H. F. MELDAHL (Helv. Chim. Acta, 1936, 19, 412—418).—Reaction of  $\text{MgCl}\cdot\text{CH}_2\text{R}$  ( $\text{R}=\text{Ph}$ ,  $\text{C}_6\text{H}_4\text{Me}$ , or  $\text{C}_6\text{H}_3\text{Me}_2$ ) with  $\text{CH}_2\text{O}$  results in introduction of *o*- $\text{CH}_2\text{OH}$  with reduction of the original  $\text{CH}_2\text{Cl}$  to *Me* (cf. A., 1903, i, 48). *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{OH}$  (prep. described), b.p. 115—120°/14 mm., with cold conc. HCl in ligroin gives an 85—92% yield of the chloride, b.p. 76—80°/14 mm., the Grignard reagent from which with  $\text{CH}_2\text{O}$  gives 50% of 2 : 3-dimethylbenzyl alcohol (I), b.p. about 125°/12 mm., m.p. 64° (oxidised to 2 : 3- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$ ), and (*o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2$ )<sub>2</sub>, b.p. about 170—180°/12 mm., m.p. 65°. (I) gives similarly a 90% yield of the chloride, b.p. 99°/12 mm., and thence a poor yield of 2 : 3 : 4-trimethylbenzyl alcohol, m.p. 49—50° (*H* phthalate; oxidised to 2 : 3 : 4- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ ), and probably 2 : 2' : 3 : 3'-tetramethyldibenzyl, m.p. 111—112°, and 1 : 2 : 3- $\text{C}_6\text{H}_3\text{Me}_3$ . R. S. C.

**Reduction of  $\gamma$ -phenyl- $\alpha$ -methylallyl alcohol with deuterium.** J. B. M. COPPOCK and S. M. PARTRIDGE (Nature, 1936, 137, 907).—There is no change in b.p.,  $\mu$ , or optical rotatory power in the reduction products of this alcohol with  $\text{H}_2$  and  $\text{D}_2$ . The results indicate that an asymmetric system of the type  $\text{CHDRR}'$  has no optical rotatory power, and that the electrical fields associated with H and D in combination with C are approx. equiv. L. S. T.

**Synthesis of 3-nitro-4-methoxybenzyl alcohol and of its alkyl ethers.** R. QUELET and (Mlle.) Y. GERMAIN (Compt. rend., 1936, 202, 1442—1444; cf. A., 1921, i, 23).—*o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$  with  $\text{CH}_2\text{O}$ ,  $\text{ZnCl}_2$ , and HCl (gas) at 80—90° affords 3-nitro-4-methoxybenzyl chloride (I), m.p. 85.5—86° (free from 3 : 3'-dinitro-4 : 4'-dimethoxyphenylmethane; cf. A., 1934, 999), which when boiled with aq. NaOAc gives 3-nitro-4-methoxybenzyl acetate, m.p. 37°, hydrolysed ( $\text{KOH}$ ) to 3-nitro-4-methoxybenzyl alcohol (phenylurethane, m.p. 129°), which with  $\text{KMnO}_4$  gives 3-nitro-4-methoxybenzoic acid. (I) reacts with Na alkoxides to give ethers. The following are prepared: 3-nitro-4-methoxybenzyl *Me*, m.p. 30°, *Et*, b.p. 181°/16 mm., and *Pr*<sup>*n*</sup> ether, b.p. 190°/15 mm. (decomp.). J. L. D.

**Lumisterol.** K. DIMROTH (Ber., 1936, 69, [B], 1123—1129).—Lumisteryl acetate with  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$  gives the corresponding oxide (I),  $\text{C}_{30}\text{H}_{48}\text{O}_3$ , m.p. 133°,  $[\alpha]_D^{20} +119.2^\circ$  in  $\text{COMe}_2$ , hydrolysed by

cautious treatment with KOH-MeOH to *lumisterol oxide*, m.p. 132°,  $[\alpha]_D^{25} +173^\circ$  in  $\text{CHCl}_3$ . (I) is converted by hot  $\text{H}_2\text{O}$  into *lumistadienetriol acetate*, m.p. 178—179° (decomp.),  $[\alpha]_D^{25} +27.8^\circ$  in  $\text{CHCl}_3$ , hydrolysed to *lumistadienetriol*, m.p. 180—183° (decomp.) when rapidly heated,  $[\alpha]_D^{25} +37.9^\circ$  in  $\text{CHCl}_3$  (*diacetate*, m.p. 143°,  $[\alpha]_D^{25} +113.6^\circ$  in  $\text{COMe}_2$ ), isomeric with the compounds of Heilbron *et al.* (A., 1935, 1493). Lumisterol has thus the same structural formula as ergosterol; in the initial stages, therefore, irradiation causes only steric transformations, prob-



ably at  $\text{C}_{(9)}$  or  $\text{C}_{(10)}$ . Dehydrolumisterol (Heilbron, *loc. cit.*) has the same absorption spectrum as dehydroergosterol and hence is probably (II). Catalytic hydrogenation of its acetate (III) (Pt in AcOH) ceases after absorption of  $3\text{H}_2$  and yields a product, m.p. 142—143°,  $[\alpha]_D^{25} -69.2^\circ$  in  $\text{CHCl}_3$ , which is further reduced to perhydropyrocalficeryl acetate, m.p. 135—136°,  $[\alpha]_D^{25} +26.38^\circ$  in  $\text{CHCl}_3$ , hydrolysed to perhydropyrocalfiferol. The identity of the products proves that no further steric transformations in other parts of the mol. occur during the conversion of lumisterol into tachysterol and vitamin-D. Ultraviolet light causes primarily fission between  $\text{C}_{(9)}$  and  $\text{C}_{(10)}$  and subsequently a displacement of the double linkings. Exposure to sunlight of (III) and eosin in EtOH affords a compound  $\text{C}_{60}\text{H}_{86}\text{O}$ , m.p. 183—184°. H. W.

#### Synthesis of sterols with modified side-chains and their $\alpha$ -derivatives from lithocholic acid.

F. REINDEL and K. NIEDERLANDER (Annalen, 1936, 522, 218—239).—Norepicoprostan-3:24-diol (I) (A., 1935, 1494) is converted by boiling  $\text{Ac}_2\text{O}$  into norepi- $\Delta^{24}$ -coprostenyl acetate (II) (not characterised), which is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH) to norepicoprostan-3-one-24-ol (III), m.p. 83—84° (cf. Ruzicka and Goldberg, *ibid.*, 749). Energetic hydrolysis (5% EtOH-NaOH) of (III) affords norepicoprostan-3-one-24-ol (IV), m.p. 147—148° (cf. *loc. cit.*), whilst mild hydrolysis (0.1% MeOH-NaOH) gives a 1:1-compound (+ $2\text{H}_2\text{O}$ ), m.p. 110—112°, of (III) and (IV). Oxidation [ $\text{CrO}_3$  (=60), AcOH] of (II) yields the Ac derivative (V), m.p. 145—146°, of *norlithocholyl Me ketone* (VI), m.p. 157—158° [semicarbazone, m.p. 226—227° (decomp.)]. Reduction (as above) of (V) affords the Ac derivative, m.p. 91—92°, of *norlithocholylmethylcarbinol* (+ $0.5\text{H}_2\text{O}$ ), m.p. 155—157°, also formed by Wolff-Kishner reduction (V) semicarbazone, m.p. 217—218° (decomp.). (IV) is oxidised ( $\text{CrO}_3$ , AcOH) to norcoprostan-3-one [semicarbazone, m.p. 167—168° (decomp.)], reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH-conc. HCl) to *norcoprostan-3-ol* (VII), m.p. 117—118° (acetate, m.p. 122—123°), which is pptd. by digitonin. Similar reduction of *norcoprostan-3-one-24-ol*, m.p. 80—81° [semicarbazone, m.p. 168—169° (decomp.)] [from (I) and  $\text{CrO}_3$ -AcOH], gives a product containing some 24-

chlorocoprostan-3-ol, since subsequent treatment with EtOH-NaOH affords some  $\Delta^{24}$ -*norcoprostan-3-ol* (+ $0.5\text{H}_2\text{O}$ ), m.p. 92—93°; (VII) is obtained from the non-cryst. material by successive treatment with  $\text{Ac}_2\text{O}$ , reduction, and hydrolysis. Et lithocholate and  $\text{MgPr}^{\text{Br}}\text{Cl}(\text{Br})$  (6 mols.) give a little *epicoprostan-3-ol-24-one* (VIII), m.p. 177—178° [Ac derivative, m.p. 179—180°; semicarbazone, m.p. 241—242° (decomp.)]; *hydrazone*, m.p. 135—140° (decomp.), and (mainly) 24-isopropylepicoprostan-3:24-diol (+ $0.5\text{H}_2\text{O}$ ) (IX), m.p. 106—107°, m.p. (anhyd.) 150—152° (*diacetate*, m.p. 82—83°). (VIII) is oxidised ( $\text{CrO}_3$ , AcOH) to coprostan-3:24-dione, m.p. 184—186°, whilst (IX) (as acetate) gives (VIII). Wolff-Kishner reduction of (VIII) affords a pinacol,  $\text{C}_{54}\text{H}_{94}\text{O}_4\cdot\text{H}_2\text{O}$ , m.p. 140—145°, m.p. (anhyd.) 182—183°, acetylated ( $\text{Ac}_2\text{O}$ ) to a *diacetate*, m.p. 175—176° (X); an isomeric *diacetate*, m.p. 145—147° (XI), is obtained by reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH) of the acetate of (VIII). (XI) is converted into (X) by boiling  $\text{Ac}_2\text{O}$ , whilst hydrolysis (EtOH-NaOH) of (X) and (XI) gives the pinacol. Clemmensen reduction of (VIII) affords a bimol. compound,  $\text{C}_{54}\text{H}_{92(94)}\text{O}_3$ , m.p. 196—197° (*diacetate*, m.p. 150—151°).  $\text{MgMeI}$  and (VIII) yield  $\psi$ -epiergostane-3:24-diol (+ $0.5\text{H}_2\text{O}$ ), m.p. 212—214°, m.p. (anhyd.) 223—224° also prepared from (VI) and  $\text{MgPr}^{\text{Br}}\text{Br}$ , which with  $\text{Ac}_2\text{O}$  gives the *diacetate*, m.p. 165—166°, of  $\psi$ -epiergostanediol 24:24'-ether, m.p. 208—209°.  $\text{MgEtI}$  and (VIII) yield  $\psi$ -epistigmastane-3:24-diol, m.p. 240—241° [24:24'-ether, m.p. 186—188° (*diacetate*, m.p. 160—161°)]. Biscoprocoprostan-3:23-diol (XII) (A., 1935, 1494) is converted by  $\text{Ac}_2\text{O}$  into the acetate (not characterised) of *biscoprocoprostan-3-ol* (+ $0.5\text{H}_2\text{O}$ ), m.p. 120—123°, which is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH) to the acetate, m.p. 93—94°, of *biscoprocoprostan-3-ol*, m.p. 134—135°. The latter is oxidised to *biscoprocoprostanone* [semicarbazone, m.p. 158—161° (decomp.)], which is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH-conc. HCl) to *biscoprocoprostan-3-ol* (XIII), m.p. 126—127° (acetate, m.p. 103—104°). Similar reduction of *biscoprocoprostan-3-one-23-ol*, m.p. 161—163° [semicarbazone, m.p. 173—175° (decomp.)], prepared by oxidation of (XII), gives a product (pptd. by digitonin) which on successive treatment with  $\text{Ac}_2\text{O}$ , reduction, and hydrolysis affords (XIII).

Comparison of the m.p. of various sterols and bile acids shows that the form pptd. by digitonin is more fusible than the *epi*-derivative in both the *cis*- and *trans*-series; shortening of the side-chain is generally accompanied by an increase in m.p. H. B.

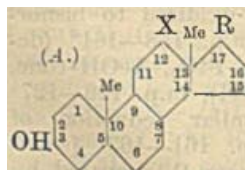
**Detection of oxysterol and its behaviour in the organism.** K. YAMASAKI (Fukuoka Acta med., 1935, 28, 109).—Oxysterol gives a blue colour with conc.  $\text{H}_2\text{SO}_4$ . Cholesterol exposed to solar radiation gives the blue colour and the m.p. is lowered. NUTR. ABS. (m)

**Action of selenium dioxide on sterols and bile acids. II. Formation of isomeric dihydroxycholadienic acids from apocholic acid and dihydroxycholenic acid; oxidation products of dihydroergosterol.** R. K. CALLOW (J.C.S., 1936, 462—469).—Prep. of the dihydroxycholadienic acids



(I) obtained by action of Br on *apocholic acid* (II) or on *dihydroxycholenic acid* (A., 1922, i, 1027; 1931, 957) or by other methods (A., 1931, 841; 1932, 615; 1933, 158) is repeated. Variation of  $[\alpha]$  is due to (I) being varying mixtures of  $\alpha$ -*dihydroxycholadienic acid* (III), m.p. 252—255°,  $[\alpha]^{20}_D$  —35.3°,  $[\alpha]^{20}_{4401}$  —47.7° (in EtOH), absorption max. at 243 m $\mu$  (broad) [obtained by action of BzO<sub>2</sub>H on (II)], with  $\beta$ -*dihydroxycholadienic acid* (IV), m.p. 253—255°,  $[\alpha]^{20}_D$  +71.0°,  $[\alpha]^{20}_{4401}$  +82.1°, absorption max. at 249 m $\mu$  (sharp), with subsidiary max. at 242 m $\mu$  [obtained by action of aq. SeO<sub>2</sub> on (II) in EtOH]. Catalytic reduction of (III) yields (II); (IV) is reduced to  $\beta$ -*apocholic acid*, m.p. 163—165°,  $[\alpha]^{20}_D$  +78.5°,  $[\alpha]^{20}_{4401}$  +92.4° [AcOH compound (V), m.p. 150—155°,  $[\alpha]^{20}_D$  +73.5°,  $[\alpha]^{20}_{4401}$  +86.5°; *xylene* compound, m.p. 156.5—161°;  $[\alpha]^{20}_D$  +69.7°,  $[\alpha]^{20}_{4401}$  +82.5°; *Me* ester (+1.5H<sub>2</sub>O), m.p. 84—87°,  $[\alpha]^{20}_D$  +79°,  $[\alpha]^{20}_{4401}$  +90°, prepared from the *Ag* salt]. When (V) is treated with SeO<sub>2</sub>, the resulting  $\beta$ -*dihydroxycholadienic acid* has m.p. 233—240°,  $[\alpha]^{20}_D$  +77.7°,  $[\alpha]^{20}_{4401}$  +92.8° (absorption max. at 250 m $\mu$ ). When these are taken as the vals. for  $[\alpha]^{20}_D$  and  $[\alpha]^{20}_{4401}$  of (IV), and theoretical vals. of each for mixtures of (III) and (IV) are plotted against composition, observed  $[\alpha]^{20}_D$  and  $[\alpha]^{20}_{4401}$  for specimens of (I) from various sources indicate that these are a series of mixtures of (III) and (IV), the same composition being deduced for any one prep. from either  $[\alpha]^{20}_D$  or  $[\alpha]^{20}_{4401}$ .

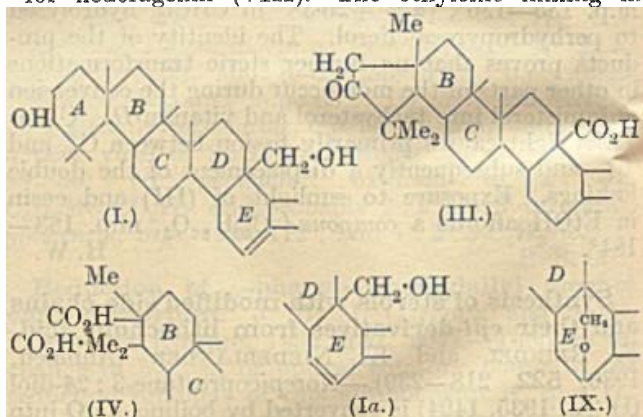
The  $\Delta^{7:8}$ -formula proposed by Wieland and Dane (A., 1932, 615; 1933, 158) for *dihydroxycholenic acid* (VI) is similar to that for  $\gamma$ -ergosterol, but since the latter is isomerised by Pt to non-reducible  $\alpha$ -ergosterol, whilst (VI) is reduced normally, (VI) is now re-formulated as the  $\Delta^{14:15}$ -compound [*A*; X=OH, R=C<sub>4</sub>H<sub>8</sub>·CO<sub>2</sub>H (cf.  $\beta$ -ergosterol)]. As (II) and (VI) are directly interconvertible, (II) is regarded as the  $\Delta^{8:14}$  compound.



Of the six conceivable positions of the ethylenic linkings in the dienic acids, absorption spectra and general chemical grounds eliminate all but the  $\Delta^{7:8:14:15}$  structures. As the latter would be expected to have the higher absorption at longer  $\lambda$ , (III) is regarded as the  $\Delta^{7:8:14:15}$  and (IV) as the  $\Delta^{9:8:14:15}$  compound.  $\alpha$ - and  $\beta$ -*apocholic acids* differ in the position of H at C<sub>9</sub>; SeO<sub>2</sub> attacks the latter position, BzO<sub>2</sub>H the C<sub>17</sub>. Ergosterol-*D* (A., 1933, 605) is regarded as the analogue of (IV), and thus formulated as the  $\Delta^{9:8:14:15}$ -compound [*A*; X=H, R=C<sub>9</sub>H<sub>17</sub>], ergosterol-*B*<sub>3</sub> as the analogue of (III), with the  $\Delta^{7:8:14:15}$  structure, being derived from the decomp. of dihydroergosterol oxide, in which the oxide-bridge is in the 8:14-position.

$\alpha$ -Ergosterol and SeO<sub>2</sub> give dehydroergosterol (3:5-dinitrobenzoate, m.p. 163—166°,  $[\alpha]^{20}_D$  —3.0°,  $[\alpha]^{20}_{4401}$  —5.7° in C<sub>6</sub>H<sub>6</sub>), which is now formulated as the  $\Delta^{9:8:14:15}$ -compound; X=H, R=C<sub>9</sub>H<sub>19</sub>. *Me apocholate* and SeO<sub>2</sub> yield (IV), of which the *Ag* salt gives *Me*  $\beta$ -*dihydroxycholadienate*, m.p. 87—89°,  $[\alpha]^{20}_D$  +62.5°,  $[\alpha]^{20}_{4401}$  +71°. The oxidation of *Me* *dihydroxycholenate* (*bis*-3':5'-*dinitrobenzoyl* derivative, m.p. 209—210.5°) and of  $\beta$ -*apocholic acid* by SeO<sub>2</sub>, and by BzO<sub>2</sub>H is also studied. E. W. W.

**Polyterpenes and polyterpenoids. CVI. Oxidation of dihydrobetulin and dihydrobetulonic acid by nitric acid.** L. RUZICKA and O. ISLER (Helv. Chim. Acta, 1936, 19, 506—509; cf. this vol., 607).—The prep. of betulin (I), dihydrobetulin (II), and dihydrobetulonic acid (III) is modified. (III) and fuming HNO<sub>3</sub> in AcOH at —5° to 0° give an acid (IV), C<sub>27</sub>H<sub>46</sub>(CO<sub>2</sub>H)<sub>3</sub>, m.p. 275° (*Me*<sub>3</sub> ester, m.p. 145°, liberates only 1 CO<sub>2</sub>H with *N*-KOH-EtOH), which at 330°/high vac. gives CO<sub>2</sub> (1 mol.), H<sub>2</sub>O (1 mol.), and a *keto-acid*, C<sub>29</sub>H<sub>46</sub>O<sub>3</sub>, m.p. 259° [*oxime*, m.p. 278° (decomp.); *Me* ester, m.p. 178°, gives no colour with C(NO<sub>2</sub>)<sub>4</sub>]. (I) and HNO<sub>3</sub>-AcOH give a *ketone* (V), C<sub>30</sub>H<sub>48</sub>O<sub>2</sub>·NO<sub>2</sub>, m.p. 209°, an acid (VI), NO<sub>2</sub>·C<sub>28</sub>H<sub>47</sub>O(CO<sub>2</sub>H)<sub>2</sub>, m.p. between 158° and 170° according to the rate of heating [*Me*<sub>3</sub> ester, m.p. 124°; *anhydride* (VII), m.p. 215°; also obtained from (V) by CrO<sub>3</sub> or HNO<sub>3</sub>]. (VI) and (VII) at 330° give CH<sub>2</sub>O, also obtained from (V) at 260—300° along with a substance, ? C<sub>28</sub>H<sub>46</sub>O, m.p. about 200—204° (1 active H). The anhydride of the acid, C<sub>30</sub>H<sub>46</sub>O<sub>6</sub>, from hydroxymethylencallobetulinone has m.p. 193° (lit. 293°). These and previously recorded reactions lead to the formulæ shown, based on that (*loc. cit.*) for hederagenin (VIII). The ethylenic linking in



(I) may be as in (Ia), in which case *allobetulin* has the grouping (IX); but (I) is preferable, because the similar differences in  $[\alpha]$  between the diols and diol acetates from (a) (I) and (II) and (b) *hederabetulin* and *dihydrohederabetulin* indicate a close relationship between (I) and (VIII).

[With M. FURTER] *d* and *n* are determined for the diacetates of (I) and (II) above the m.p. R. S. C.

**s-Di-*p*-anisylpinacol.** C. W. SHOPPEE (J.C.S., 1936, 506—507).—Di-*p*-anisyl ketone (I) (2:4-dinitrophenylhydrazone, m.p. 197°) is reduced by Al-Hg in EtOH to 4:4'-dimethoxybenzhydrol (II) and *s*-di-*p*-anisylpinacol, new m.p. 183° (cf. A., 1933, 68) [decomp. to (I) and (II)]. The last with AcOH and a trace of I forms anisyl trianisylmethyl ketone (*loc. cit.*). Attempts to obtain the pinacol from Mg anisyl bromide and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (cf. Bouvet, Bull. Soc. chim., 1915, [iv], 17, 209) gave an oil consisting mainly of (*p*-OMe·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C(OH)·CO<sub>2</sub>Et. Anisil and Mg *p*-anisyl bromide yield *anisoyldianisylcarbinol*, m.p. 117.5°. E. W. W.

**Olivil.** P. DREYFUSS (Gazzetta, 1936, 66, 98—99).—Olivil *Me*, ether is oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-AcOH to

the lactone of 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (A., 1935, 860), to tetramethoxy-benzoylbenzoic acid and -phenylphthalide, and to a small amount of 2:3:6:7-tetramethoxyanthraquinone, apparently formed by way of an internal anhydro-compound. These results support the formulæ proposed (A., 1934, 1099) for olivil and for isoolivil. E. W. W.

**Nitration of benzanilide and its derivatives.** W. B. VAN HORSSEN (Rec. trav. chim., 1936, 55, 245—262).—The action of abs.  $\text{HNO}_3$  on several benzanilides (from the amine and acid chloride in tetralin) introduces  $\text{NO}_2$ -groups into both Ph radicals; the  $\text{NO}_2$  enters the 3-position of the Bz unless one or more  $\text{NO}_2$  are already present, when nitration is restricted to the  $\text{NH}_2$ Ph radical. The following are described: 3:5-dinitrobenz-2':4'-dinitro-, m.p. 213°, 2-nitrobenz-4'-nitro-, m.p. 212°, 4-nitrobenz-4'-nitro-, m.p. 269°, 3:5-dinitrobenz-4'-nitro-anilide, m.p. 280°; 3-nitrobenz-2':6'-dinitro-, m.p. 213°, 4-nitrobenz-2':6'-dinitro-, m.p. 227°, 3:5-dinitrobenz-2':6'-dinitro-p-toluidide, m.p. 275°; 3-nitrobenz-, m.p. 176°, 3-nitrobenz-2':6'-dinitro-, m.p. 213°, 4-nitrobenz-, m.p. 231°, 4-nitrobenz-2':6'-dinitro-, m.p. 210°, 3:5-dinitrobenz-, m.p. 237°, 3:5-dinitrobenz-2':6'-dinitro-4'-chloroanilide, m.p. 265°; 3-nitrobenz-, m.p. 182°, 3-nitrobenz-2':6'-dinitro-, m.p. 226°, 4-nitrobenz-, m.p. 247°, 4-nitrobenz-2':6'-dinitro-, m.p. 214°, 3:5-dinitrobenz-p-bromoanilide, m.p. 251°. P. G. C.

**Condensations by sodium. V. Preparation of acids. Dicarboxylic acids from monohalogen compounds.** A. A. MORTON, W. J. LEFEVRE, and I. HECHENBLEIKNER (J. Amer. Chem. Soc., 1936, 58, 754—757; cf. A., 1932, 158).— $\text{PhCl}$ , *m*- and *p*- $\text{C}_6\text{H}_4\text{MeCl}$ , *p*- $\text{C}_6\text{H}_4\text{PhCl}$ , and *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$  with  $\text{CO}_2$  (40—400 lb. pressure), and Na in  $\text{C}_6\text{H}_6$  give  $\text{BzOH}$  (max. yield 78%), *m*- (88%) and *p*- (95%)  $\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ , *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$  (67%), and *o*- $\text{CHO}\cdot\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$  (47%), respectively. With *n*-amyl chloride,  $\text{CO}_2$ , and Na in light petroleum, the following reactions occur: (i) Wurtz (predominates at pressures up to 100 lb.); (ii)  $\text{C}_5\text{H}_{11}\text{Cl} + \text{CO}_2 + 2\text{Na} \rightarrow \text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{Na} + \text{NaCl}$ ; (iii)  $\text{C}_5\text{H}_{11}\text{Cl} + 2\text{CO}_2 + 4\text{Na} \rightarrow 2\text{NaCl} + \text{C}_5\text{H}_{12} + \text{CHBu}(\text{CO}_2\text{Na})_2$  (appreciable at 200—400 lb. pressure); (iv) formation of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{C}_2\text{O}_4$  (major products at higher pressures). The use of  $\text{C}_6\text{H}_6$  as solvent leads to some *m*- and *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ .  $\text{AlkCO}_2\text{H}$  and  $\text{CHAlk}(\text{CO}_2\text{H})_2$  or  $\text{CAlkAlk}'(\text{CO}_2\text{H})_2$  are formed (yields recorded) from  $\text{EtCl}$ ,  $\text{Bu}^n\text{Cl}$ , *n*-hexyl and cetyl chlorides,  $\beta$ -chloropentane and  $\gamma$ -methylbutane, and  $\text{CH}_3\text{PhCl}$ . H. B.

**Differential reduction of the nitro-group by means of glucose.** G. BACHARACH and R. WEINSTEIN (Rec. trav. chim., 1935, 54, 931—933).—Reduction of *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  with  $\text{NaOH}\cdot\text{H}_2\text{O}$ -glucose at 50° gives *p*-azoxybenzoic acid, decomp. above 355°, and at 75° gives *p*-azobenzoic acid, decomp. above 300°. The consens. of the reagents in the two cases are specified. H. G. M.

**Iodo-silver nitrobenzoate complex and its action on some allyl derivatives.** R. JACQUEMAIN and A. MUSKOVITS (Compt. rend., 1936, 202, 497—

499).—*o*-, *m*-, and *p*- (I)  $\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Ag}$  when treated in dry  $\text{C}_6\text{H}_6$  with I yield the corresponding *I*-complexes (cf. A., 1933, 711), which convert ethylene derivatives into the diester of the corresponding  $\alpha$ -glycol. Thus allyl *p*-nitrobenzoate and the complex obtained from (I) yield glycerol tri-*p*-nitrobenzoate. The following derivatives of glycerol  $\alpha$ -benzoate were similarly prepared in good yield from allyl benzoate:  $\alpha'\beta$ -di-*o*-, m.p. 93°,  $\alpha'\beta$ -di-*m*-, m.p. 103° and  $\alpha'\beta$ -di-*p*-, m.p. 153°, -nitrobenzoate. H. G. M.

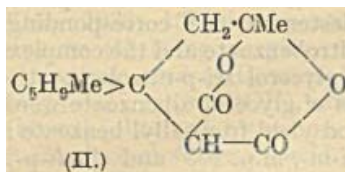
**Two new dichloro-*o*-nitrobenzoic acids.** P. RUGGLI and H. ZAESLIN (Helv. Chim. Acta, 1936, 19, 434—439).—4:5-Dichloro-2-nitrotoluene and  $\text{CrO}_3\cdot\text{H}_2\text{SO}_4$  at  $\Delta$   $-15^\circ$  give 4:5-dichloro-2-nitrobenzoic acid, m.p. 165°, possibly identical with the acid, m.p. 160°, of Claus *et al.* (A., 1887, i, 828). 2:4:6- $\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_3$  and  $\text{NH}_4\text{HS}\cdot\text{EtOH}$  give an 85% yield of 2-nitro-4:6-diaminotoluene, m.p. 135° (lit. 132°), converted, best (70%) by addition of aq.  $\text{NaNO}_2$  to its solution with  $\text{CuCl}$  in conc.  $\text{HCl}$  at 50—70°, to 4:6-dichloro-2-nitrotoluene, m.p. 60° (obtained also much less well by other methods), oxidised with 15%  $\text{HNO}_3$  at 150—160° (not by other methods) into 4:6-dichloro-2-nitrobenzoic acid, m.p. 189—190°. *p*- $\text{C}_6\text{H}_4\text{MeCl}$  and fuming  $\text{HNO}_3$  give a mixture of 2- and 3- $\text{NO}_2$ - and 2:5-, 3:5-, and 2:6- $(\text{NO}_2)_2$ -compounds (cf. lit.). 4-Chloro-2-nitrotoluene and fuming  $\text{HNO}_3$  at 10—15° give 66% of 2:5- and 33% of 2:6- $(\text{NO}_2)_2$ -compounds (cf. lit.). R. S. C.

**Synthesis of 1:9-dimethyltetrahydrophenanthrene-2-carboxylic acid and of 1:9-dimethylphenanthrene.** G. DARZENS and A. LÉVY (Compt. rend., 1936, 202, 427—428; cf. A., 1935, 975).—1:4- $\text{C}_{10}\text{H}_6\text{Me}\cdot\text{CH}_2\text{Cl}$  gives  $\text{Et}_2$  4-methyl-1-naphthylmethylmalonate, b.p. 201—203°/2.5 mm., and thence  $\text{Et}_2$  4-methyl-1-naphthylmethylallylmalonate ( $\alpha$ -4-methyl-1-naphthyl- $\Delta^5$ -pentene-3,3-dicarboxylate), hydrolysed to the corresponding acid, m.p. 184.5°, which decomposes at about 190° into  $\alpha$ -4-methyl-1-naphthylmethyl- $\Delta^7$ -pentenoic acid, m.p. 93.5°, and about 4% of the  $\gamma$ -lactone, b.p. 204°/2 mm. This acid is cyclised by  $\text{H}_2\text{SO}_4\cdot\text{AcOH}$  (40°, 3 days) to 4:9-dimethyl-1:2:3:4-tetrahydrophenanthrene-2-carboxylic acid, m.p. 201°; about 40% of the  $\delta$ -lactone, m.p. 91°, is also formed. The acid with S at 230—300° yields 4:9-dimethylphenanthrene-2-carboxylic acid, m.p. 266°, but dehydrogenation with Se at 340—350° is accompanied by decarboxylation giving 1:9-dimethylphenanthrene [picrate, m.p. 163.5° (lit. 160°); styphnate, m.p. 181°]. All yields are good. H. G. M.

**Keto-lactol tautomerism. V. Influence of methylcyclohexane rings on the tautomerism of  $\delta$ -ketonic acids.** M. QUDRAT-I-KHUDA and A. MUKHERJI (J.C.S., 1936, 570—573).—4-Methylcyclohexenylacetone (a mixture of  $\Delta^5$ -30-3, and  $\Delta^5$ -69-7%, isomerides obtained from  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}\cdot\text{NaOEt}\cdot\text{EtOH}$ -4-methylcyclohexanone) heated with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2\cdot\text{NaOEt}\cdot\text{EtOH}$  gives 4-methylcyclohexane-1:4-spiro-2'-hydroxy-6'-keto-5'-cyano-2-methylpiperidine (I), m.p. > 300°, hydrolysed (conc.  $\text{HCl}$ ) to the dilactone (II), m.p. 172°, converted by 10%  $\text{NaOH}$  and acidification at 0° into 1-acetonyl-



4-methylcyclohexane-1-malonic acid (*Ag* salt) which slowly reverts to (II), and is decarboxylated at 170°



to the corresponding -1-acetic acid (III), b.p. 183°/6 mm. [*Ag* salt; semicarbazone, m.p. 195° (decomp.); *Me* ester, b.p. 120°/2 mm. (semicarbazone, m.p. 155°]. The anhydride of 4-methylcyclohexane-1:1-diacetic acid with boiling EtOH gives the *Et H* ester (*Ag* salt), converted by successive treatment with SOCl<sub>2</sub> and ZnMeI into *Et* 1-acetonyl-4-methylcyclohexane-1-acetate, b.p. 133°/3 mm. (semicarbazone, m.p. 140°), hydrolysed by KOH-aq. EtOH to (III). Reduction of (III) with Na-boiling EtOH affords the lactone (IV)

$C_5H_9Me > C \begin{matrix} \diagup CH_2 \cdot CRMe \\ \diagdown CH_2 \cdot CO \end{matrix} O$  (R=H), b.p. 142°/3 mm. By similar methods 3-methylcyclohexenyl-acetone affords the imide, m.p. > 300° [as (I)], hydrolysed to the dilactone [as (II)], m.p. 144°, hydrolysed to 1-acetonyl-3-methylcyclohexane-1-malonic acid (*Ag* salt), decarboxylated to the -1-acetic acid (V), b.p. 161°/2 mm. {semicarbazone, m.p. 212°; *Me* ester, b.p. 135—136°/13 mm. [semicarbazone, m.p. 162° (decomp.)]}. Similarly from 3-methylcyclohexane-1:1-diacetic anhydride are obtained the *Et H* ester (*Ag* salt), *Et* 1-acetonyl-3-methylcyclohexane-1-acetate (VI), b.p. 129°/5 mm. [semicarbazone, m.p. 105° (decomp.)], hydrolysed to (V), and converted by NaOEt into 3-methylcyclohexanespirocyclohexane-3':5'-dione. (VI) and MgMeI afford the lactone [as (IV), R=Me], b.p. 159°/10 mm. Reduction of (V) gives the lactone [as (IV), R=H], b.p. 187°/4 mm. The relative proportions of (III) and (II) formed in the 4- and 3-Me series are, respectively, 35.7:58 and 25:67%.

J. W. B.

**Derivatives of salicylic acid. IX. Stability of the sulphonic acid group in 4-sulphosalicylic acid. I. Nitration of 4-sulphosalicylic acid. X. II. Bromination of 4-sulphosalicylic acid.** N. W. HIRWE and M. R. JAMBHEKAR (Proc. Indian Acad. Sci., 1936, 3, A, 236—239, 261—264).—IX. 4-Sulphosalicylic acid (I) and HNO<sub>3</sub> (*d* 1.4)—Ac<sub>2</sub>O at < 5° give a mixture of its 3:5-(NO<sub>2</sub>)<sub>2</sub>- (II), decomp. > 261° (*K*, *K H*, and *Ba*, +2H<sub>2</sub>O salts), and its 5-NO<sub>2</sub>-derivative +2H<sub>2</sub>O (III), m.p. 166—167° (isolated as its *K H* salt by addition of conc. aq. KCl to the mother-liquor: *Ba* salt, +H<sub>2</sub>O). When heated with HNO<sub>3</sub> (*d* 1.4) at 100° (I) gives 2:4:6-trinitrophenol-3-sulphonic acid +4H<sub>2</sub>O, m.p. 105° (replacement of CO<sub>2</sub>H by NO<sub>2</sub>). Reduction of (III) with (NH<sub>4</sub>)<sub>2</sub>S-EtOH affords *o*-amino-4-sulphosalicylic acid, decomp. > 260°. Similar reduction of (II) gives 3-nitro-5-amino-4-sulphosalicylic acid, decomp. > 280°, and with Fe-HCl the 3:5-(NH<sub>2</sub>)<sub>2</sub>-acid, decomp. > 290°, is obtained.

X. Passage of Br vapour into an aq. solution of (I) affords a mixture of its 5-Br-, +4H<sub>2</sub>O, m.p. 210° (*Ba*, +4H<sub>2</sub>O, and *K H* salts), 3:5-Br<sub>2</sub>-, +4H<sub>2</sub>O, m.p. 83° (*Ba*, +H<sub>2</sub>O, and *K H* salts), and 3:5:6-Br<sub>3</sub>-derivative, m.p. 115° (*Ba* salt). The non-replacement of CO<sub>2</sub>H or SO<sub>3</sub>H by Br results from the

combination of the directing influences of OH and CO<sub>2</sub>H, and of Br and SO<sub>3</sub>H. J. W. B.

**Condensation of chloral with salicylic acid.** F. CALVET and M. N. MEJUTO (J.C.S., 1936, 554—556).—Condensation of CCl<sub>3</sub>·CH(OH)<sub>2</sub> and *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H in presence of conc. H<sub>2</sub>SO<sub>4</sub> gives (after esterification) the *Me* ester (I), m.p. 200—202° (*Ac*<sub>2</sub> derivative, m.p. 207—209°), of βββ-trichloro-4:4'-dihydroxy-3:3'-dicarboxy-α-diphenylethane (II), m.p. 290—292°, and 2-hydroxy-5-βββ-trichloro-α-hydroxyethylbenzoic acid (III), m.p. 180—182° [*Ac*<sub>2</sub> derivative, m.p. 190—192°, which gives a colour with FeCl<sub>3</sub>; *Me* ester, m.p. 97—99° (*Ac*<sub>2</sub> derivative, m.p. 90—92°, giving no FeCl<sub>3</sub> colour)]. Condensation of (III)-*o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H-H<sub>2</sub>SO<sub>4</sub> also gives (II). When boiled with KOH-MeOH (I) affords ββ-dichloro-4:4'-dihydroxy-3:3'-dicarboxy-α-diphenylethane, m.p. 295—297° (*Me* ester, m.p. 120—122°), and (III) similarly treated gives 6-hydroxyisophthalaldehydic acid (IV), oxidised to 4-hydroxyisophthalic acid which is also obtained by KMnO<sub>4</sub>-NaOH oxidation of (III). Hydrolysis of (III) with conc. H<sub>2</sub>SO<sub>4</sub> also gives (IV). Reduction of (III) with Zn-HCl-EtOH affords (?) 2-hydroxy-5-ββ-dichlorovinylbenzoic acid, m.p. 170—172°. J. W. B.

**Isomeric, optically inactive menthyl mandelates. New type of racemism.** A. MCKENZIE and E. M. LUIS (Ber., 1936, 69, [B], 1118—1123).—Esterification of (+)-mandelic acid with (+)-menthol in presence of HCl at 100° yields (+)-menthyl (+)-mandelate (I), m.p. 81—82°, [α]<sub>D</sub><sup>25</sup> +138.1°, [α]<sub>D</sub><sup>25</sup> +164.8° in EtOH. (+)-Menthyl *r*-mandelate, m.p. 85—86°, [α]<sub>D</sub><sup>25</sup> +73.2° in EtOH, is obtained by direct esterification or mixing equal amounts of (I) and (+)-menthyl (−)-mandelate in COMe<sub>2</sub> and removing the solvent at room temp. dl-Menthyl (+)-mandelate, m.p. 76—77°, [α]<sub>D</sub><sup>25</sup> +64.4° in EtOH, prepared by mixing equal amounts of (I) and (−)-menthyl (+)-mandelate in COMe<sub>2</sub> and removing the solvent, suffers partial resolution when recryst. successively from EtOH and light petroleum. dl-Menthyl *r*-mandelate (provisional nomenclature), m.p. 103—704°, is derived from equal amounts of (I) and (−)-menthyl (−)-mandelate, by esterification of *r*-mandelic acid by dl-menthol in presence of HCl, or from equal wts. of (+)- and (−)-menthyl *r*-mandelate. It is isomeric with *r*-menthyl *r*-mandelate, m.p. 80—81° (A., 1934, 777). The forms differ from one another in appearance. Each can be recryst. without change. The possibility of dimorphism appears excluded. Both isomerides can be isolated by fractional crystallisation from dil. alcohol of the product derived by mixing dl-menthyl (+)- with (−)-mandelate in equal proportions. Fractional esterification of dl-menthol with (−)-mandelic acid by Marekwald and McKenzie's method gives a laevorotatory unesterified alcohol. H. W.

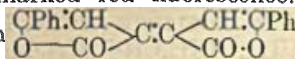
**Synthesis of 3-hydroxynaphthyl-2-acetic acid and of acylcarbinols.** B. EISTERT (Ber., 1936, 69, [B], 1074—1079; cf. A., 1935, 858).—Gradual addition of 3-acetoxy-2-naphthoyldiazomethane (I) to a suspension of Ag<sub>2</sub>O in EtOH at 60° gives *Et* 3-acetoxy-2-naphthylacetate (II), b.p. 187—189°/4 mm., hydrolysed by 2*N*-NaOH to 3-hydroxy-2-naphthylacetic acid, m.p. 178—180° (decomp.), which passes

when heated above its m.p. or, better, when boiled with  $\text{Ac}_2\text{O}$ , into 5:6-benzo-2-coumaranone (III). The "hydroxynaphthylacetic acid hydrate" (*loc. cit.*) is identified as the *K H* salt,  $\text{C}_{12}\text{H}_{10}\text{O}_3 \cdot \text{C}_{12}\text{H}_9\text{O}_3\text{K}$ , decomp. 243—244°. (II) and boiling  $\text{NH}_2\text{Ph}$  give 3-hydroxynaphthyl-2-acetanilide, m.p. 220—222°, converted by boiling  $\text{Ac}_2\text{O}$  into 3-acetoxynaphthyl-2-acetanilide, m.p. 196°, also obtained from (I),  $\text{NH}_2\text{Ph}$ , and  $\text{Ag}_2\text{O}$  in hot  $\text{EtOH}$ . (I) suspended in dioxan is transformed by  $2\text{N-H}_2\text{SO}_4$  at room temp. into 3-acetoxy-2-naphthoylecarbinol, m.p. about 120—124° (slight decomp.), transformed by boiling  $\text{EtOH}$  containing conc.  $\text{HCl}$  into (III), also obtained from (I) and  $2\text{N-H}_2\text{SO}_4$  in boiling  $\text{EtOH}$ . 1-Acetoxy-2-naphthoic acid, m.p. 158°, is converted by  $\text{SOCl}_2$  in light petroleum at 80—90° into 1-acetoxy-2-naphthoyle chloride, m.p. 113—114° (gradual decomp.).

H. W.

**Addition of aromatic hydrocarbons to maleic anhydride and green radicals from diaryldihydrofuranones.** R. PUMMERER and E. BUCHTA (*Ber.*, 1936, 69, [B], 1005—1017).—It appears impossible to conduct the action between  $\text{C}_6\text{H}_6$ , maleic anhydride, and  $\text{AlCl}_3$  so that phenylsuccinic anhydride and thence phenylmaleic anhydride are produced, the products being  $\beta$ -benzoyl- or, with  $\text{PhMe}$ ,  $\beta$ -toluoyl- (I) -acrylic acid. If, however, hydrocarbon and  $\text{AlCl}_3$  are used in large excess  $\beta$ -toluoyl- $\alpha$ -tolyl-propionic acid (II), m.p. 151°, is obtained in 20% yield, also prepared from (I),  $\text{PhMe}$ , and  $\text{AlCl}_3$ . (II) is stable to  $\text{ClSO}_3\text{H}$  at 15—20° but is converted by boiling  $\text{AcCl}$  containing a little conc.  $\text{H}_2\text{SO}_4$  into the dilactone (III),  $\text{C}_{36}\text{H}_{30}\text{O}_4$ , decomp. 263° after softening and darkening, and by  $\text{Ac}_2\text{O}$  at 100° into (III) and the monolactone (IV),  $\text{C}_{18}\text{H}_{16}\text{O}_2$ , m.p. 104°. (IV) is transformed into (III) by  $\text{Br}$  in warm  $\text{AcOH}$ , by  $\text{FeCl}_3$  in  $\text{AcOH}$ , or by warm  $\text{Ac}_2\text{O}$  containing a little  $\text{H}_2\text{SO}_4$ . (III) is converted into (IV) by reduction with  $\text{Zn-Hg}$  and boiling  $\text{AcOH}$  whereas  $\text{Zn}$  dust and  $\text{AcOH}$  convert it into a substance,  $\text{C}_{36}\text{H}_{32}\text{O}_3$ , m.p. 98°. (III) appears unchanged by hydrazobenzene in boiling  $\text{PhCl}$ . Oxidation of (III) by  $\text{CrO}_3$  in  $\text{AcOH}$  affords  $p$ - $\text{C}_6\text{H}_4\text{MeCO}_2\text{H}$ . (IV) is hydrolysed in the usual manner by  $\text{KOH-MeOH}$  whereas (III) is converted with difficulty into di-( $\beta$ -toluoyl- $\alpha$ -tolyl)propionic acid,  $\text{C}_{36}\text{H}_{34}\text{O}_6$ , m.p. 166°. (III) and anhyd.  $\text{AlCl}_3$  in  $\text{PhCl}$  at 120° yield a lactonic acid,  $\text{C}_{36}\text{H}_{34}\text{O}_5$ , m.p. 163°, reconverted into (III) when heated in  $\text{Ac}_2\text{O}$  at 100°. (II) and boiling  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  or (IV) and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  in boiling  $\text{EtOH}$  afford 1:3-ditolyl-2:3:4:5-tetrahydropyridazol-4-one, m.p. 165°. 3:3'-Di-(5-N-phenyl-1:3-ditolyl-2:3:4:5-tetrahydropyridazin-4-one, m.p. 160°, is prepared from (III) and  $\text{NHPhNH}_2$  in boiling xylene. When warmed in media of b.p. > 100° (III) dissociates into green radicals with marked red fluorescence.

By analogy the constitution



is ascribed to Pechmann's dye.  $\text{CHBz:CHCO}_2\text{H}$ ,  $\text{AlCl}_3$ , and  $\text{PhMe}$  at 100° give  $\beta$ -benzoyl- $\alpha$ -tolylpropionic acid, m.p. 149°. Fumaric acid is obtained from maleic anhydride,  $m\text{-C}_6\text{H}_4(\text{OH})_2$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$ .

H. W.

**Derivatives of benzoylbenzoic acids.** M. HAYASHI, S. TURUOKA, I. MORIKAWA, and H. NAMIKAWA

(*Bull. Chem. Soc. Japan*, 1936, 11, 184—200).—3-Methylphthalic anhydride (I) (*imide*, m.p. 188.5—189°) condenses ( $\text{AlCl}_3$ ) with  $\text{C}_6\text{H}_6$  to give a substance (II),  $\text{C}_{21}\text{H}_{16}\text{O}_2$ , m.p. 116—117° (structures suggested), 2-benzoyl-3- (III), m.p. 171—172° (*Me* ester, m.p. 106.5—107.5°), and 2-benzoyl-6-methylbenzoic acid, m.p. 126.5—127.5° (*Me* ester, m.p. 122.5—123°) (also by the action of conc.  $\text{H}_2\text{SO}_4$  on the -3-acid), oxidised by 1%  $\text{KMnO}_4$  to benzophenone-2:6-, m.p. 255—256°, and -2:3-dicarboxylic acid,  $+\text{H}_2\text{O}$ , m.p. indefinite 121—146°, and anhyd., m.p. 140—141° (decomp.), respectively. (I) is converted by the usual methods into its 1-*Me* 2-*H*,  $+\text{H}_2\text{O}$  and anhyd. (IV), m.p. 114.5—115°, *Me*<sub>2</sub> b.p. 169°/21 mm., and 1-*Et* 2-*H*,  $+\text{H}_2\text{O}$ , m.p. 75—85°, and anhyd., m.p. 86—87°, esters, and 4-methylphthalic anhydride (*imide*, m.p. 194.5—195°) into its 2-*Me* 1-*H*,  $+\text{H}_2\text{O}$  and anhyd. (V), m.p. 89—90°, and *Et*<sub>2</sub> esters, b.p. about 193—195°/27 mm. The acid chloride of (IV) and  $\text{C}_6\text{H}_6 \cdot \text{AlCl}_3$  give (II) and (III), and the acid chloride of (V) similarly affords 2-benzoyl-5-methylbenzoic acid (cf. below). (I) condenses with  $\text{PhOH}$  to give 2-(2'-hydroxybenzoyl)-, m.p. 220—221°, and 2-(4'-hydroxybenzoyl)-3-methylbenzoic acid, m.p. 197—198°, isomerised by conc.  $\text{H}_2\text{SO}_4$  at room temp. to 2-(2'-hydroxybenzoyl)-, m.p. 141—142°, and 2-(4'-hydroxybenzoyl)-6-methylbenzoic acid, m.p. 183—184°, respectively. (I) and  $\text{PhCl}$  give (?) 2-(4'-chlorobenzoyl)-3-methylbenzoic acid, m.p. 175.5—176°. Contrary to Lawrance (A., 1920, i, 741) 3-nitrophthalic anhydride and  $\text{C}_6\text{H}_6$  give only 3-nitro-2-benzoylbenzoic acid (VI), m.p. 236—237°. Condensation of the acid chloride of 1-*Me* 2-*H* 3-nitrophthalate with  $\text{C}_6\text{H}_6$  gives only (VI), whereas the 2-*Me* 1-*H* ester gives mainly 6-nitro-2-benzoylbenzoic acid, m.p. 160—161°, and a little (VI). 2-Amino-6-, -3-, -5-, and -4-methylbenzoic acid and boiling  $\text{Ac}_2\text{O}$  afford, respectively, 6-, m.p. 84°, 3- (VII), m.p. 136—137°, 5- (VIII), m.p. 123—124°, and 4-methylacetoanthranil, m.p. 102—103° (all of type  $\text{C}_6\text{H}_3\text{Me} < \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{N} = \text{CMe} \end{array}$ ).

Acetoanthranil and  $\text{C}_6\text{H}_6$  give 2-anilino-, m.p. 121.5—122° [*hydrochloride*, m.p. 165—167° (decomp.)], and 2-amino-benzophenone, m.p. 109—110° [*hydrochloride*, m.p. 179—180° (decomp.)]; (VII) similarly gives only 2-anilino-3-methylbenzophenone, m.p. 123—123.5° [*hydrochloride*, m.p. 166—173° (decomp.)], and (VIII) gives 2-amino- (IX) and 2-anilino-5-methylbenzophenone, m.p. 163.5°. Diazotisation of (IX), treatment with  $\text{Cu}_2(\text{CN})_2$  [substance, m.p. 189—190°, possibly di-(2-benzoyl-*p*-tolyl)amine, obtained], and hydrolysis of the crude nitrile affords 2-benzoyl-4-methylbenzoic acid, m.p. 150—150.5° [described in Part II (A., 1930, 1183) as the 5(or 4)-*Me* acid]; hence the 4(or 5)-*Me* acid, m.p. 145—145.5°, is 2-benzoyl-5-methylbenzoic acid. The following corrections to Parts III and IV (*loc. cit.*) are proposed: 2-(5'-chloro-2'-hydroxybenzoyl)-5-, m.p. 239.5—240.5° becomes -4-, and -4-, m.p. 227—228.5°, becomes -5-methylbenzoic acid. In all cases where the alternative 3(or 6)- and 6(or 3)-methylbenzoic acid occurs the first no. is correct.

J. W. B.

**Synthesis of *cis*- and *trans*-*dl*-norcaryophyllenic acids and of dehydronorcaryophyllenic acid.**



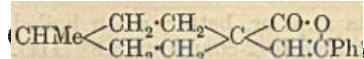
H. N. RYDON (J.C.S., 1936, 593—596).— $\beta\beta$ -Dimethyladipic acid (improved prep.) is converted by  $\text{SOCl}_2$ -Br into *Et*  $\alpha\alpha'$ -dibromo- $\beta\beta$ -dimethyladipate, b.p. 178—182°/12 mm., converted by NaCN-boiling EtOH and hydrolysis of the product with conc. HCl at 180° into *dl-trans*-3:3-dimethylcyclobutane-1:2-dicarboxylic acid (I), m.p. 148—149°, identical with the *dl*-norcaryophyllenic acid (Ramage *et al.*, A., 1935, 489, 756, who describe it as *cis*) and converted by the method of these authors into 3:3-dimethyl- $\Delta^1$ -cyclobutene-1:2-dicarboxylic acid, m.p. 195°, identical with dehydronorcaryophyllenic acid. When heated with  $\text{Ac}_2\text{O}$  at 220° (I) affords (through the crude anhydride) the *dl-cis*-acid, m.p. 149—150°, converted by  $\text{AcCl}$  into the *cis*-anhydride, m.p. 40—41°, b.p. 100—102°/1 mm., identical with norcaryophyllenic anhydride (Ruzicka *et al.*, A., 1935, 351). The stereochemistry of norcaryophyllenic acid is still doubtful but (I) is certainly the *trans*-acid and the *dl*-acid, m.p. 149—150°, of Ruzicka *et al.* is the *dl-cis*-acid. The natural *d*-acid is probably *cis*. Neither  $\alpha$ -isopropylglutaric acid (improved prep.) nor  $\alpha$ -isobutylglutaric acid, m.p. 68° [from  $\text{CH}_3\text{Bu}^\beta(\text{CO}_2\text{Et})_2$ -NaOEt- $\text{CH}_2\text{Cl}$ - $\text{CH}_2$ - $\text{CO}_2\text{Et}$  and hydrolysis], could be oxidised by  $\text{CrO}_3$  to the  $\alpha$ -OH-acid.  $\gamma$ -Carboxy- $\gamma$ -isheptolactone with  $\text{PBr}_2$ - $\text{PBr}_3$  affords *Et*  $\alpha$ -bromo- $\alpha$ -isopropylglutarate, b.p. 138—142°/11 mm., and a substance, m.p. 126—127°, which contains Br.

J. W. B.

**Valency-deflexion hypothesis.** R. D. DESAI (J. Univ. Bombay, 1935, 4, Part II, 206—214).—Mostly a brief review. 1-Carboxy-4-methylcyclohexane-1-acetic acid exists in only two forms (cf. A., 1931, 1055; 1935, 489). Attempts to isolate "extra" forms of six similar cyclohexane derivatives failed. These and other data show failure of the usual methods to prove strain in the methylcyclohexane ring.

R. S. C.

**Isomeric 1-carboxy-4-, -3-, and -2-methylcyclohexane-1-acetic acids.** R. D. DESAI, R. F. HUNTER, G. KHAN, and G. S. SAHARIA (J.C.S., 1936, 416—419).—Hydrolysis of *Et* 1-cyano-4-methylcyclohexane-1- $\alpha$ -cyanoacetate, b.p. 162—164°/15 mm. (obtained by action of  $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$  on 1-hydroxy-1-cyano-4-methylcyclohexane, b.p. 128°/20 mm., prepared from 4-methylcyclohexanone by  $\text{NaHSO}_3$  and KCN), yields two 1-carboxy-4-methylcyclohexane-1-acetic acids, m.p. 137° (I) and 173° (II), identical with those obtained by oxidation of the two  $\alpha$ -keto-4-methylcyclohexane-1:1-diacetic acids (A., 1932, 741). Repetition of the work of Quadrat-i-Khuda (A., 1931, 1055) shows that his *A* and *C* acids are identical with (I) and (II), but that his "*B*" is a mixture of *A* and *C* (cf. A., 1935, 489); "*D*" was not obtained. The anhydride (III), m.p. 104°, derived from (II) forms an *imide*, m.p. 171°, an *amic acid*, m.p. 195°, a *p-toluidinic acid*, m.p. 168—169°, a *p-tolylimide*, m.p. 160°,  $\alpha$ - and  $\beta$ -naphthylamic acids, m.p. 140° and 185°, and  $\alpha$ - and  $\beta$ -naphthylimides, m.p. 163° and 185°. The anhydride (IV), m.p. 77°, from (I) forms an *imide*, new m.p. 130°. In presence of  $\text{AlCl}_3$ , (III) and  $\text{C}_6\text{H}_6$  yield 1-benzoyl-4-methylcyclohexane-1-acetic acid *A* (V), m.p. 165° (semicarbazone, m.p. 165°), and a neutral substance,  $\text{C}_{16}\text{H}_{18}\text{O}_2$ , m.p. 160°, formulated as



(V) is reduced (Zn—

Hg) to 1-benzyl-4-methylcyclohexane-1-acetic acid *A*, m.p. 98°. (IV) and  $\text{C}_6\text{H}_6$  yield 1-benzoyl-4-methylcyclohexane-1-acetic acid *B* (VI), m.p. 140—141° (semicarbazone, m.p. 150°), with a neutral substance, m.p. 89°. Reduction of (VI) gives 1-benzyl-4-methylcyclohexane-1-acetic acid *B*, m.p. 127°, with a neutral substance,  $\text{C}_{11}\text{H}_{20}\text{O}_2$ , m.p. 250°. 1-Hydroxy-1-cyano-3-methylcyclohexane, b.p. 120°/15 mm., prepared from 3-methylcyclohexanone, yields  $(\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et})$  *Et* 1-cyano-3-methylcyclohexane-1- $\alpha$ -cyanoacetate, b.p. 185°/15 mm., which is hydrolysed (HCl) to 1-carboxy-3-methylcyclohexane-1-acetic acid, m.p. 163° (decomp.) (VII), identical with that obtained by Desai (A., 1932, 741), and to a second form (VIII), m.p. 108° (*Ag* salt). The "third form" claimed by Desai and Hunter (A., 1935, 618) is a mixture of (VII) with (VIII). Treatment of *Et* 3-methylcyclohexylidenecyanoacetate with KCN followed by HCl yields (VII) and (VIII). (VII) forms an anilic acid, new m.p. 176° (decomp.), an anil, new m.p. 143°, an *imide*, m.p. 180—181°, a *p-toluidinic acid*, m.p. 180° (decomp.), *p-tolylimide*, m.p. 145°,  $\alpha$ - and  $\beta$ -naphthylamic acids, m.p. 150° and 192° (decomp.), and  $\alpha$ - and  $\beta$ -naphthylimides, m.p. 142° and 189°. (VIII) forms an anhydride, m.p. 50°, b.p. 145—148°/15 mm.; anilic acid, m.p. 207°; anil, m.p. 107°; *imide*, m.p. 92°; *p-toluidinic acid*, m.p. 185°; *p-tolylimide*, m.p. 102—103°;  $\alpha$ - and  $\beta$ -naphthylamic acids, m.p. 207° and 183°;  $\alpha$ - and  $\beta$ -naphthylimides, m.p. 115° and 116°. 1-Hydroxy-1-cyano-2-methylcyclohexane, b.p. 114—116°/15 mm., prepared from 2-methylcyclohexanone (IX), yields *Et* 1-cyano-2-methylcyclohexane-1- $\alpha$ -cyanoacetate, b.p. 180°/15 mm., hydrolysed to two 1-carboxy-2-methylcyclohexane-1-acetic acids, m.p. 170° (decomp.) [anhydride, b.p. 142—143°/12 mm.; anilic acid, m.p. 148°], and m.p. 160° [anhydride, b.p. 141—142°/12 mm.; anilic acid, m.p. 161—162°]. With  $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ , (IX) yields *Et* 2-methylcyclohexylidenecyanoacetate, b.p. 150—160°/15 mm., which with KCN yields the above pair of acids; since the m.p. of each of these differs from those of Quadrat-i-Khuda's "*B*" and "*D*" acids, Thorpe's suggestion (J.C.S., 1931, 1023) that the latter arose from (IX) in the starting material is eliminated. E. W. W.

**Fused carbon rings. VIII. Dehydration of 2-methyl-1- $\Delta^7$ -butenylcyclohexanol.** D. C. HIBBIT, R. P. LINSTEAD, and A. F. MILLIDGE. IX. Synthesis of stereoisomeric 1-methylcyclohexane-1:2-dicarboxylic acids and of various methylcyclohexanecarboxylic-acetic acids. Influence of the angular methyl group on the stability of their anhydrides. R. P. LINSTEAD and A. F. MILLIDGE (J.C.S., 1936, 476—478, 478—486).—VIII.  $\text{CH}_2\text{CH}[\text{CH}_2]_2\text{MgBr}$  and 2-methylcyclohexanone readily react in  $\text{Et}_2\text{O}$  to form 2-methyl-1- $\Delta^7$ -butenylcyclohexanol, b.p. 104—108°/18 mm. When heated with  $\text{H}_3\text{PO}_4$ , this is dehydrated to 2-methyl-1- $\Delta^7$ -butenylcyclohexene, b.p. 75—78°/10 mm., or, on prolonged heating, to *cis*-9-methyl- $\Delta^2$ -octahydronaphthalene (cf. this vol., 713), oxidised ( $\text{KMnO}_4$ ) to two 1-methylcyclohexane-1:2-diacetic acids as

before. The acid of m.p. 163—165° gives (MeOH-H<sub>2</sub>SO<sub>4</sub>) a Me<sub>2</sub> ester, b.p. 122—125°/1 mm., and with Ba(OH)<sub>2</sub> yields 8-methyl-2-hydrindone.

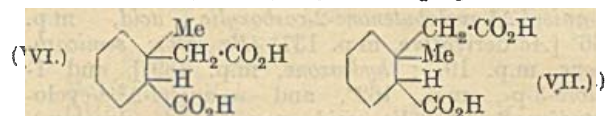
IX. The two forms of 1-methylcyclohexane-1:2-dicarboxylic acid are prepared. Et 1-methylcyclohexan-2-one-1-carboxylate, prepared by action of MeI on the Na derivative of Et cyclohexan-2-one-1-carboxylate, is converted (HCN) into Et 2-cyano-1-methylcyclohexan-2-ol-1-carboxylate, b.p. 148—149°/12 mm., which on prolonged treatment with HCl gives 1-methylcyclohexan-2-ol-1:2-dicarboxylic acid, m.p. 166—167°. This with Ac<sub>2</sub>O gives the anhydride, m.p. 86—87°, of 2-acetoxy-1-methylcyclohexane-1:2-dicarboxylic acid, m.p. 168°. The above cyanohydrin with SOCl<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N yields Et 2-cyano-1-methyl-Δ<sup>2</sup>-cyclohexene-1-carboxylate, b.p. 140—141°/9 mm. (not reduced by Al-Hg), hydrolysed to 1-methyl-Δ<sup>2</sup>-cyclohexene-1:2-dicarboxylic acid, m.p. 229—230° (decomp.) (anhydride, m.p. 67—68°; Ag<sub>2</sub> salt; Me<sub>2</sub> ester, b.p. 140°/11 mm.), which with 5% MeOH-H<sub>2</sub>SO<sub>4</sub> gives 2-carbomethoxy-1-methyl-Δ<sup>2</sup>-cyclohexene-1-carboxylic acid, m.p. 112—114°. When the Me<sub>2</sub> ester is heated with KOH-MeOH, 1-carbomethoxy-1-methyl-Δ<sup>2</sup>-cyclohexene-2-carboxylic acid, m.p. 119—120°, is formed. The Me<sub>2</sub> ester is hydrogenated (Adams) to a mixture of saturated esters, b.p. 122—129°/9 mm. [hydrolysed to a mixed acid (I), m.p. about 170°], which is treated with K in Et<sub>2</sub>O, followed by dil. acid; hydrolysis of the resulting ester, b.p. 124—126°/10 mm., with HCl gives a mixture, m.p. 200°, containing 40% of *cis*-acid, recrystallised to give *cis*-1-methylcyclohexane-1:2-dicarboxylic acid (II), m.p. 213°. The mixture (I) treated with conc. HCl at 190° gives 85% of *cis*-acid, recrystallised to *cis*-1-methylcyclohexane-1:2-dicarboxylic acid (III), m.p. 160°. The composition of mixtures of (II) and



(III) is determined by thermal analysis. (II) forms (AcCl) the *trans*-anhydride, m.p. 80°. (III) with Ac<sub>2</sub>O gives an anhydride, m.p. 60—65°, b.p. 144—146°/19 mm., hydrated to an 80% *cis*-acid. (II) and (III) are both racemates; their constitutions are based on analogy and are not certain. (III) and (II) are considered to be *cis* and *trans* since their anhydrides are low- and high-melting, respectively, resembling those of *cis*- and *trans*-hexahydrophthalic acid; also the anhydride of (III) is the more stable; this evidence is preferred to that of the action of HCl on (I). The action of angular Me is to stabilise the *cis*-form.

Both forms of 1-methylcyclohexane-1-carboxylic-2-acetic acid have been synthesised from Et 2-methylcyclohexanone-2-carboxylate, which with CN-CH<sub>2</sub>-CO<sub>2</sub>Et and C<sub>5</sub>H<sub>11</sub>N at room temp. gives no condensation products, but at very high pressure forms Et<sub>2</sub> 2-methylcyclohexylidene-1-cyanoacetate-2-carboxylate (IV), b.p. 160—165°/1 mm., which deposits a small amount of solid, m.p. 85—86°. (IV) reduced (Al-Hg) and hydrolysed yields *cis*-1-methylcyclohexane-1-carboxylic-2-acetic acid, m.p. 174—175°. The *cis*-configuration is assigned by analogy with previous results;

(V) differs from the isomeride obtained by Chuang *et al.* (A., 1935, 859), which is therefore the *trans*-form, identical with that obtained from 8-methyl-2-hydrindanone (this vol., 713). Attempted prep. of (V) from 1-methylcyclohexanol-2-acetic acid lactone, b.p. 140—141°/15 mm. (obtained from Et cyclohexanone-2-acetate and MgMeI), is unsuccessful. Both forms of 1-methylcyclohexane-2-carboxylic-1-acetic acid are prepared. 1-Carbethoxy-9-methyl-decahydronaphthalene-2:4-dione is hydrolysed to 9-methyldecahydronaphthalene-2:4-dione, which with NaOBr gives a mixture of *cis*- (VI), m.p. 171.5°, and *trans*-1-methylcyclohexane-2-carboxylic-1-acetic acid (VII), m.p. 131—132°. Mixtures are determined by thermal analysis. (VII) with Ac<sub>2</sub>O gives the *trans*-



anhydride, b.p. 163—165°/19 mm.; (VI) an anhydride, m.p. 50°, b.p. 152—154°/19 mm., hydrolysed to 45% of *cis*-acid, from which (VII) is isolated. (VII) is almost unchanged by HCl at 190—200°, but (VI) gives 90% of (VII). (VI) with 20% Ba(OH)<sub>2</sub> at 350° gives the *cis*-anhydride (no ketone). Arguments for the *cis*- and *trans*-structures of (VI) and (VII) are discussed. (VI) is synthesised from the lower homologue. With H<sub>2</sub> and Ni at 220—240°, the anhydride of (III) gives only a hydrocarbon, b.p. 130—140° (1:2-dimethylcyclohexane?), but with EtOH and Na, it yields a lactone, b.p. 129—132°/12 mm., which is probably a mixture of 2-methylol-1-methylcyclohexanecarboxylic acid lactone with the 2-Me isomeride, and with KCN at 280—290° yields a CN-acid hydrolysed to (VI).

Two forms of 1-methylcyclohexane-2-carboxylic-3-acetic acid are synthesised. The cyanohydrin of 2-methylcyclohexanone is obtained as a semi-solid mixture of stereoisomerides, b.p. 122—123°/10 mm., dehydrated by SOCl<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>N to tetrahydro-*o*-toluonitrile, b.p. 85—86°/10 mm. This is probably a mixture of the Δ<sup>1</sup>- and Δ<sup>6</sup>-forms, but only the latter reacts with Na, EtOH, and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, forming Et<sub>2</sub> 2-cyano-1-methylcyclohexane-3-malonate, b.p. 180—188°/11 mm., hydrolysed to a mixture of “*cis*” m.p. 164—165°, and “*trans*”-1-methylcyclohexane-2-carboxylic-3-acetic acid, m.p. 138—140° (Ba salts). With HCl at 200°, the former gives the latter. α-Methylglutaconic acid (improved prep.) forms a Me<sub>2</sub> ester, b.p. 117°/13 mm. Attempted condensation of butadiene with this or with Me<sub>2</sub> β-methylglutaconate, b.p. 109—110°/12 mm., to give methylcyclohexane-carboxylic-acetic acids was unsuccessful. E. W. W.

Condensation of phenols and phenolic ethers with acetonedicarboxylic acid. II. β-Substituted cyclobutenonecarboxylic acids. V. M. DIXIT (J. Univ. Bombay, 1935, 4, Part II, 153—160; cf. A., 1932, 512).—The keto-acids obtained (*loc. cit.*) from CO(CH<sub>2</sub>-CO<sub>2</sub>H)<sub>2</sub> and PhOH, *o*- and *p*-C<sub>6</sub>H<sub>4</sub>Me-OMe are 3-aryl-Δ<sup>2</sup>-cyclobutenone-2-carboxylic acids, because of the following reactions. The 3-*p*-hydroxyphenyl-acid, m.p. 224°, more readily obtained by a modified method, is monobasic (Ba salt), is



obtained from  $\beta$ -*p*-hydroxyphenylglutaconic acid (I) by heating alone at 195° or with AcCl at 100°, and is converted into (I) by 10% NaOH; it gives *Ac*<sub>2</sub> (II), m.p. 123° (*Ba* salt), and *Ac* derivative (III), m.p. 171°; with PCl<sub>3</sub> at 100° it affords 1-chloro-3-*p*-hydroxyphenyl- $\Delta^2$ :4-cyclobutadiene-2-carboxylic acid (IV), m.p. 143°; it gives a semicarbazone, m.p. 258° (decomp.), hydrazone, m.p. 193°, and oximino-derivative, m.p. 201° (decomp.). (III) gives a semicarbazone, m.p. 279°, and oximino-derivative, m.p. 212°, with Ac<sub>2</sub>O yields (II), with PCl<sub>3</sub> the *Ac* derivative, m.p. 126°, of (IV), and with dil. NaOH the *Ac* derivative of (I). *p*- and *o*-Cresol afford similarly 3-*p*-, m.p. 160° (*Ac* derivative, m.p. 118°; semicarbazone, m.p. 213°; hydrazone, m.p. 188°), and -*o*-anisyl- $\Delta^2$ -cyclobutenone-2-carboxylic acid, m.p. 166° [*Ac* derivative, m.p. 137° (*Ba* salt); semicarbazone, m.p. 197°; hydrazone, m.p. 189°], and 1-chloro-3-*p*-, m.p. 162°, and -*o*-anisyl- $\Delta^2$ :4-cyclobutadiene-2-carboxylic acid, m.p. 176° (decomp.). The "anhydride" obtained (J.C.S., 1912, 107, 859) from  $\beta$ -phenylglutaconic acid and AcCl is considered to be a similar cyclic compound. R. S. C.

**Dehydrogenation.** III. Dehydrogenation of hydroaromatic carboxylic acid derivatives and ketones by selenium. L. RUZICKA (Helv. Chim. Acta, 1936, 19, 419—423; cf. A., 1935, 738).—Hydroaromatic substances containing groups derived from CO<sub>2</sub>H may give with Se aromatic acids or methylated hydrocarbons. Hydroaromatic ketones may give phenols. Et  $\Delta^1$ -tetrahydro-*o*-toluate with Se at 360° gives PhMe and *o*-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>H. Me<sub>2</sub> 1:3:3-trimethyl- $\Delta^1$ -cyclohexene-4:5-dicarboxylate at 360° gives *m*-xylene-4:5-dicarboxylic anhydride, m.p. 115—116°, sublimes at 100°/0.1 mm. [corresponding acid, m.p. 183° (loss of H<sub>2</sub>O)], also obtained, but only at 400°, from Me<sub>2</sub> 1:3:3-trimethylcyclohexene-4:5-dicarboxylate. 1:1-Dimethyloctahydronaphthalene-6:7-dicarboxylic anhydride [from myrcene (I) and maleic anhydride] at 330—350° gives 1:6:7-C<sub>10</sub>H<sub>5</sub>Me<sub>3</sub>, which proves conclusively the position of the ethylenic linkings in (I). *trans*- $\beta$ -Decalone at 260° gives 3-C<sub>10</sub>H<sub>7</sub>·OH and a substance, C<sub>20</sub>H<sub>12</sub>Se, m.p. 307—308°, whilst 3-methyl- $\Delta^2$ -cyclohexenone gives *m*-cresol. R. S. C.

**Oxidation of isosafrole.** M. IMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 132B; cf. A., 1934, 403).—The yield of piperonylic acid obtained from isosafrole and the theoretical amount of KMnO<sub>4</sub> is increased by various catalysts, most (to 62.8%) by active C. R. S. C.

**Synthesis of  $\alpha$ -substituted glutaconic acids.** N. L. PHALNIKAR and K. S. NARGUND (J. Univ. Bombay, 1935, 4, Part II, 106—108).—Esters, CH<sub>2</sub>R·CO<sub>2</sub>Et (R=Me, CH<sub>2</sub>Ph, or Ph), with HCO<sub>2</sub>Et and "mol." Na give the  $\alpha$ -aldehydo-acids, which are condensed without isolation with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> and piperidine to give Et H glutaconates; purification by way of the Et<sub>2</sub> esters and subsequent hydrolysis then affords *trans*- $\alpha$ -methyl-, m.p. 144° (Et<sub>2</sub> ester, b.p. 180—185°/120 mm.), -benzyl-, and -phenyl-glutaconic acid, m.p. 164° (Et<sub>2</sub> ester, b.p. 220°/80 mm.). R. S. C.

**Condensation of phenylpyruvic acid with acetophenone.** P. CORDIER (Compt. rend., 1936, 202, 1440—1442).—Interaction of CH<sub>2</sub>Ph·CO·CO<sub>2</sub>H with CPhMe in aq. KOH-EtOH affords, after treatment with dil. HCl,  $\alpha$ -hydroxy- $\beta$ -benzoyl- $\alpha$ -benzylpropionic acid, m.p. 140°, which is unchanged by cold HCl, but with hot HCl in AcOH is converted into  $\beta$ -benzoyl- $\alpha$ -benzylidenepropionic acid (I), m.p. 160—165° (decomp.), and 2-keto-5-phenyl-3-benzylidene-2:3-dihydrofuran, m.p. 149—150°, easily hydrolysed to (I). J. L. D.

**Syntheses in the thujane group. I. Synthesis of ketopolymethylene-1:3-dicarboxylic esters.** P. C. GUHA and N. K. SESHADRIENGAR (Ber., 1936, 69, [B], 1207—1212).—CH<sub>2</sub>(CH<sub>2</sub>Br)<sub>2</sub> and the Na derivative of CO(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> give the compound CH<sub>2</sub>< $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \\ \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \end{array}$ >C·CH<sub>2</sub>·CO<sub>2</sub>Et (obtained by Perkin in alcoholic solution) and compounds obtained by the action of Na on CO(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub>·CH<sub>2</sub>(CH<sub>2</sub>Br)<sub>2</sub> and the Mg derivative of CO(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub> in boiling EtOH afford Et<sub>2</sub> cyclohexanone-1:3-dicarboxylate, b.p. 142°/2 mm., hydrolysed by boiling H<sub>2</sub>SO<sub>4</sub> (1:1) to cyclohexanone, unchanged material, CH<sub>2</sub>Ac·CO<sub>2</sub>Et, and Et cyclohexanonecarboxylate. Under similar conditions C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> gives Et<sub>2</sub> cyclopentanone-2:5-dicarboxylate, b.p. 143°/4 mm. (Cu derivative, m.p. 200°), hydrolysed to cyclopentanone, whilst CH<sub>2</sub>Br<sub>2</sub> affords Et<sub>2</sub> cyclobutanone-2:4-dicarboxylate and two compounds, m.p. 102° and 286°, respectively. H. W.

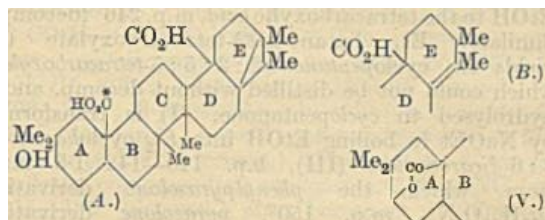
**Degradation of  $\beta$ -anisyl- and  $\beta$ -halogenoanisylglutaric acids to succinic acids through  $\gamma$ -butyrolactones and other reactions [thereof].** D. B. LIMAYE and R. G. CHITRE (J. Univ. Bombay, 1935, 4, Part II, 94—103).—Ag salts of 3-*p*-anisyl-(I) [anhydride, m.p. 152°; monoanilide, m.p. 157°; Et<sub>2</sub>, b.p. 206°/14 mm., EtH, m.p. 78°, and (COPh·CH<sub>2</sub>)<sub>2</sub> ester, m.p. 95°] and  $\beta$ -3-halogeno-*p*-anisylglutaric acids with I at 150° do not give butyrolactones. Ag  $\beta$ -3:5-dihalogeno-*p*-anisylglutarates, however, give CO<sub>2</sub> and butyrolactones, which with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> give the substituted succinic acids. (I) is substituted, yielding the 3-*I*-derivative, m.p. 160° [anhydride, m.p. 148°; monoanilide, m.p. 182°; Et<sub>2</sub>, m.p. 83°, Me<sub>2</sub>, m.p. 79°, and (COPh·CH<sub>2</sub>)<sub>2</sub> ester, m.p. 131°], also obtained by I and HIO<sub>3</sub> in hot H<sub>2</sub>O. The substituted Et<sub>2</sub> glutarates with Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and "mol." Na (not NaOEt) give cyclopentadione derivatives. The following are described; direct halogenation, where recorded, is effected in AcOH.  $\beta$ -3-Bromo- [from (I)], m.p. 147° [anhydride, m.p. 143°; monoanilide, m.p. 150°; Et<sub>2</sub>, m.p. 66°, Me<sub>2</sub>, m.p. 74°, and (COPh·CH<sub>2</sub>)<sub>2</sub> ester, m.p. 125°], -3-chloro- [from (I)], m.p. 157° [anhydride, m.p. 128°; monoanilide, m.p. 143°; Et<sub>2</sub>, m.p. 40.5°, and Me<sub>2</sub> ester, m.p. 59°], -3:5-dichloro- [from (I)], m.p. 195° [anhydride, m.p. 182°; monoanilide, m.p. 172°; Et<sub>2</sub>, b.p. 320° (decomp.), Me<sub>2</sub>, m.p. 63.5°, and (COPh·CH<sub>2</sub>)<sub>2</sub> ester, m.p. 120°], and -3:5-dibromo-*p*-anisylglutaric acid, m.p. 211° [anhydride, m.p. 233°; monoanilide, m.p. 180°; Et<sub>2</sub>, b.p. 315° (decomp.), and Me<sub>2</sub> ester, m.p. 62°].  $\beta$ -3:5-Di-chloro-, m.p. 72°, and -bromo-*p*-anisyl- $\gamma$ -butyrolactone, m.p. 98°. 3:5-Di-chloro- [also

obtained from  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CO}_2\text{H}$  (II) and  $\text{Cl}_2\text{-AcOH}$ , m.p.  $173^\circ$ , and *-bromo-* [also obtained from (II) and dry Br at  $100^\circ$ ], m.p.  $198^\circ$  (*anhydride*, m.p.  $110^\circ$ ), and *3-bromo-p-anisylsuccinic acid*, m.p.  $175^\circ$  (*anhydride*, m.p.  $168^\circ$ ). *Et\_2* 1-*p-anisyl-*, m.p.  $123^\circ$ , 1-3'-*chloro-*, m.p.  $126^\circ$ , *-bromo-*, m.p.  $129^\circ$ , *-iodo-*, m.p.  $133^\circ$ , 3':5'-*dichloro-*, m.p.  $164^\circ$ , and *-dibromo-p-anisyl-cyclopentadione-2:5-dicarboxylate*, m.p.  $168^\circ$ . 3:5-Dibromo-*p-anisaldehyde* [*semi-carbazone*, m.p.  $236^\circ$  (decomp.)]; *phenylhydrazone*, m.p.  $135^\circ$ ] could not be condensed with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ . 3:5-Dibromo-4-hydroxybenzaldehydesemicarbazone has m.p.  $233^\circ$  (decomp.). R. S. C.

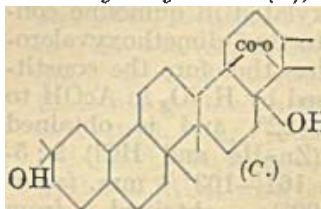
**Methoxylated o-benzoylbenzoic acids.** C. WEIZMANN and E. BERGMANN (J.C.S., 1936, 567—569).—Demethylation by  $\text{AlCl}_3$  in condensations occurs only if the reaction is slow. Thus phthalic anhydride (I) with  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OMe}$ , and 1:5- $\text{C}_{10}\text{H}_6(\text{OMe})_2$  and  $\text{AlCl}_3$  at room temp. afford, respectively, *o*-4'- and *o*-2'-methoxy- [also from (I) and the Mg compound of 1:2- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{OMe}$ ] and *o*-1':5'-dimethoxy-4'-naphthoylbenzoic acid. Pyrogallol  $\text{Me}_3$  ether and 2:3- $\text{C}_{10}\text{H}_6(\text{CO})_2\text{O}$  or hemipinic anhydride (II) with  $\text{AlCl}_3$  in  $\text{CS}_2$  give, respectively 3-(4'-hydroxy-2':3'-dimethoxybenzoyl)-2-naphthoic acid and 6-(4'-hydroxy-2':3'-dimethoxybenzoyl)-2:3-dimethoxybenzoic acid. *o*-(2':3':4'-Trimethoxybenzoyl)benzoic acid, m.p.  $196^\circ$ , is obtained by the action of (I) on 4-lithio-1:2:3-trimethoxybenzene ( $\text{N}_2$ ), the product, m.p.  $169^\circ$  (Bentley *et al.*, J.C.S., 1908, 93, 436) being partly demethylated. (II) and  $\text{MgPhBr}$  afford 2-benzoyl-3:4-dimethoxybenzoic acid, cyclised by  $\text{H}_2\text{SO}_4$  to alizarin 1:2- $\text{Me}_2$  ether and a substance, m.p.  $192^\circ$ . (II) and  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  give 2- $\alpha$ -naphthoyl-3:4-dimethoxybenzoic acid, cyclised to 1:2-dimethoxy-7:8-benzanthraquinone; (II) and the Mg compound of 2:6- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{OMe}$  give 2-(6'-methoxy- $\beta$ -naphthoyl)-3:4-dimethoxybenzoic acid, dimorphous, m.p.  $237^\circ$  and  $240^\circ$ . J. W. B.

**Dyes derived from acetylenedicarboxylic acid.** R. N. MISRA and S. DUTT (J. Indian Chem. Soc., 1936, 13, 98—103).— $(\text{C}\cdot\text{CO}_2\text{H})_2$  (I) condenses with some phenols and amines, preferably in presence of  $\text{SnCl}_4$  or a little conc.  $\text{H}_2\text{SO}_4$ , to yield dyes which are more deeply coloured (generally pink in alkali) and possess higher absorption max. than analogous compounds containing C:C (cf. A., 1927, 969). The following are described: *phenol-* (II), m.p.  $119$ — $120^\circ$  (decomp.) (softens at  $115^\circ$ ), *resorcinol-*, decomp.  $185^\circ$  [ $\text{Br}_4$ -derivative, m.p.  $115$ — $117^\circ$  (decomp.)], *phloroglucinol-*, m.p.  $>310^\circ$ , *orcinol-*, m.p.  $155$ — $157^\circ$  (decomp.), *m-dimethyl-*, m.p.  $126^\circ$  (decomp.), and *m-diethyl-*, m.p.  $109^\circ$  (decomp.), *-aminophenol-*, and *m-phenylenediamine-*, decomp.  $260^\circ$ , *-acetylenein*. Solutions of these [except (II)] show strong fluorescence. Condensation does not occur with *o*- and *p*-cresol, *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , and *o*-, *m*-, and *p*-xylenols; pure products could not be isolated from (I) and *o*- $\text{C}_6\text{H}_4(\text{OH})_2$  or pyrogallol. H. B.

**Quinovic acid.** V. H. WIELAND, A. HARTMANN, and H. DIETRICH (Annalen, 1936, 522, 191—217).—*o*-dehydrogenation (Se at  $350$ — $360^\circ$ ; Pd-C at  $340$ — $350^\circ$ ) of quinovic (I) or pyroquinovic (II) acid gives a hydrocarbon (III),  $\text{C}_{24}\text{H}_{24}$  or  $\text{C}_{26}\text{H}_{26}$ , m.p.  $202$ — $203^\circ$ , together with the trimethylpicene (IV), m.p.  $306^\circ$  (corr.) [previously described (A., 1932, 945) as a hydrocarbon  $\text{C}_{20}\text{H}_{16}$ ], obtained by Ruzicka *et al.* (cf. A., 1934, 530) from various sapogenins. Siarensinic acid is also dehydrogenated (Se at  $310$ — $320^\circ$ ) to a little (IV); the main products are [unlike (I) or (II)]  $\text{C}_{10}\text{H}_8$  derivatives. (IV) is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to an *o*-quinone,  $\text{C}_{25}\text{H}_{18}\text{O}_2$  (?), m.p.  $252$ — $255^\circ$  (decomp.), purified by adsorption on activated  $\text{Al}_2\text{O}_3$ ; (III) similarly gives non-cryst. material. Structure (A) is now assigned to (I); (II) is formulated as (B) with  $\text{CO}_2\text{H}=\text{H}$ .



Oxidation (2%  $\text{KMnO}_4$ , 0.5%  $\text{KOH}$ ,  $60^\circ$ ) of novic acid (V) gives a *hydroxyketo-acid* (VI),  $\text{C}_{30}\text{H}_{42}\text{O}_6$ , m.p.  $237$ — $238^\circ$  ( $\text{Me}_1$  ester, m.p.  $198^\circ$ ), and a little of an *isomeride*, m.p.  $262^\circ$  [also formed in small yield by oxidation of (V) with  $\text{CrO}_3$  in  $\text{AcOH}$ ]. (VI) is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to novicquinone (A., 1930, 600) (structure suggested), which is further oxidised (30%  $\text{H}_2\text{O}_2$ ,  $\text{AcOH}$ ) to a dilactonic dicarboxylic acid,  $\text{C}_{30}\text{H}_{42}\text{O}_8$ , m.p.  $287$ — $288^\circ$  (decomp.) ( $\text{Me}_2$  ester, m.p.  $242^\circ$ ). Thermal decomp. of (VI) at  $260^\circ$  affords a 3:2 mixture of two isomeric neutral substances,  $\text{C}_{29}\text{H}_{40}\text{O}_3$ , m.p.  $218^\circ$  and  $242$ — $243^\circ$ . Oxidation ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) of diacetylpyroquinovic acid is now considered (cf. *loc. cit.*) to give the  $\text{Ac}_1$  derivative, m.p.  $289^\circ$  ( $\text{Me}$  ester, m.p.  $220^\circ$ ), of a  $\text{OH}$ -acid,  $\text{C}_{29}\text{H}_{42}\text{O}_5$ ; the latter is then similarly oxidised to a  $\text{CO}$ -acid (VII),  $\text{C}_{29}\text{H}_{40}\text{O}_5$ , m.p.  $290^\circ$  (decomp.) [ $\text{Me}_1$  ester, m.p.  $219^\circ$ ;  $\text{Br}$ -derivative, m.p.  $192$ — $194^\circ$  (decomp.)]. (II), which gives a violet colour with  $\text{Ac}_2\text{O}$ -conc.  $\text{H}_2\text{SO}_4$ , is similarly oxidised at  $20^\circ$  or  $60^\circ$  to (VII), an acid,  $\text{C}_{29}\text{H}_{42}\text{O}_6$ , m.p.  $318^\circ$  (decomp.) ( $\text{Me}_1$  ester, m.p.  $195^\circ$ ), and (VIII) (below); oxidation at  $100^\circ$  affords a non-cryst. product which when distilled in a high vac. yields a neutral substance,  $\text{C}_{29}\text{H}_{36}\text{O}_5$ , m.p.  $273$ — $274^\circ$ . (II) absorbs 1 O when treated with  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$ , but the *dihydroxylactone* (C), m.p.  $267^\circ$  (decomp.) [ $\text{Ac}_1$  derivative, m.p.  $298$ — $300^\circ$  (decomp.)], is produced; this is identical with the compound previously obtained (A., 1931, 1158) by ozonolysis of (II) and it is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to the *hydroxyketolactone* (VIII), m.p.  $286$ — $288^\circ$  (cf. *loc. cit.*).



Anhydroquinovic acid (simplified prep.) loses  $\text{CO}_2$  at  $245^\circ$  to give pyroanhydroquinovic acid, m.p.  $188$ — $189^\circ$ , which is converted by  $\text{ZnCl}_2$  in  $\text{AcOH}$  into the same lactone as is similarly obtained (A., 1932, 954) from (II). (I) and cold conc.  $\text{H}_2\text{SO}_4$  give (cf. A., 1927, 562) quinochromin (IX), m.p.  $249^\circ$ , and isoquinochromin,  $\text{C}_{29}\text{H}_{42}\text{O}_2$ , m.p.  $205$ — $206^\circ$ . (IX) is unsaturated (catalytic reduction; Br in  $\text{AcOH}$ - $\text{NaOAc}$ ;



cryst. products not isolable) and is reduced (Na, EtOH) to a *dihydro*-derivative, m.p. 177—178°. H. B.

**Syntheses in the thujane group. II. Synthesis of northujone-2:6-dicarboxylic esters.** P. C. GUHA and N. K. SESHADRIENGAR (Ber., 1936, 69, [B], 1212—1218).—Addition of  $\text{COBr}_2$  in  $\text{Et}_2\text{O}$  to the Na derivative of  $\text{Et}_4$  pentane- $\alpha\alpha\alpha\epsilon$ -tetracarboxylate (I) [prep. from  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and  $\text{CH}_2(\text{CH}_2\text{Br})_2$  described] yields  $\text{Et}_4$  cyclohexanone-2:2:6:6-tetracarboxylate, b.p. 177°/1 mm. (corresponding *tetranilide*, m.p. 305°), hydrolysed and decarboxylated by  $\text{H}_2\text{SO}_4$  to cyclohexanone and by cold, 10% KOH-EtOH to the tetracarboxylic acid, m.p. 246° (decomp.). Similarly  $\text{Et}_4$  butane- $\alpha\alpha\delta\delta$ -tetracarboxylate (II) yields  $\text{Et}_4$  cyclopentanone-2:2:5:5-tetracarboxylate, which could not be distilled without decomp. and is hydrolysed to cyclopentanone. (I) is transformed by NaOEt in boiling EtOH into  $\text{Et}_2$  cyclohexanone-2:6-dicarboxylate (III), b.p. 140—142°/1.3 mm., from which the *phenylpyrazolone* derivative,  $\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_2$ , m.p. 150°, *pyrazolone* derivative,  $\text{C}_{10}\text{H}_{14}\text{O}_3\text{N}_2$ , m.p. 156—157°, the corresponding *dianilide*, m.p. 259—260°, and the *amide*, m.p. 225°, are obtained. The successive action of Na and Br on (III) in  $\text{Et}_2\text{O}$  leads to  $\text{Et}_2$  dicyclo-[0:1:3]-hexan-1-one-2:6-dicarboxylate, which could not be distilled without decomp.; its structure is established by its oxidation to cyclopentane-1:2-dicarboxylic acid. (II) and NaOEt in boiling EtOH afford  $\text{Et}_2$  cyclopentanone-2:5-dicarboxylate, b.p. 143°/3 mm. (Cu derivative, m.p. 200°), and a substance, m.p. 82°, which does not form a Cu compound. H. W.

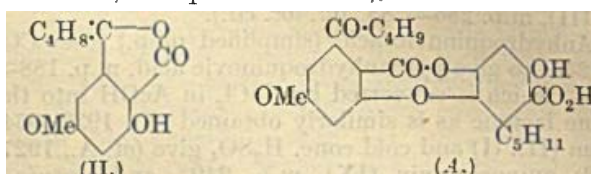
**Lichen substances. LXVI. Constitution of lobaric acid. II.** Y. ASAHINA and M. YASUE (Ber., 1936, 69, [B], 643—649; cf. A., 1935, 1366).—Thermal decomp. of lobaric acid (I) at 200—300°/1 mm. affords *lobaritonide* (II), m.p. 127—128°, *n*-amylquinol (III), m.p. 87°, and an impure material, m.p. 70—75°, which resembles 2:3:5-trihydroxy-1-methyl- or -1:4-dimethyl-benzene in its behaviour towards  $\text{NH}_3$  and  $\text{CaOCl}_2$  in EtOH. (II) gives a *Me* ether, m.p. 99°, oxidised by  $\text{KMnO}_4$  in  $\text{COMe}_2$  to 3:5-dimethoxyphthalic anhydride and  $\text{Pr}^+\text{CO}_2\text{H}$ . Hydrolysis of (II) by conc. HCl in  $\text{COMe}_2$  at 50° gives *lobaritononic acid*,  $\text{C}_{13}\text{H}_{16}\text{O}_5$ , m.p. 120°, converted by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  or  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  in EtOH into the *hydrazine anhydride*,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$ , m.p. 151°; the corresponding *Me* ether, m.p. 134°, is decarboxylated in quinoline containing Cu-bronze at 215° to 3:5-dimethoxyvalerophenone, m.p. 42—43°. (II) has therefore the constitution shown. (III) is oxidised by  $\text{HNO}_3$  in AcOH to *n*-amyl-*p*-benzoquinone, m.p. 22°, and is obtained synthetically by reducing (Zn-Hg and HCl) 2:5-dihydroxyvalerophenone, b.p. 161—163°/4 mm. (semicarbazone, m.p. 189—190°), obtained from

and subsequent acidification into *lobariolide* (V),  $\text{C}_{24}\text{H}_{30}\text{O}_6$ , m.p. 87° after softening at 83°, or (+ $\text{1H}_2\text{O}$ ), m.p. (indef.) about 75°. *Lobariol Me* ether, m.p. about 138°, from (IV),  $\text{Me}_2\text{SO}_4$ , and NaOH, is reduced by Na-Hg to *lobariolide Me* ether, also obtained from (V) and  $\text{CH}_2\text{N}_2$ , which is oxidised by  $\text{Na}_2\text{Cr}_2\text{O}_7$  in AcOH to the quinone (VI),  $\text{C}_{25}\text{H}_{30}\text{O}_7$ , m.p. 139°, obtained previously (*loc. cit.*) from permethylated norlobariolide; 6-methoxy-2-*n*-amyl-*p*-benzoquinone, b.p. 163°/3 mm., m.p. 1.3°, is also obtained. Reduction of (VI) with  $\text{H}_2\text{SO}_3$  affords the colourless *quinol*, m.p. 151—152° (*diacetate*, m.p. about 100° after softening at 80°). The structure A is assigned to (I). H. W.

**Oxidation of acetaldehyde and benzaldehyde by hydrogen peroxide in presence of selenium oxychloride.** J. B. FIRTH and H. H. GETHING (J.C.S., 1936, 633—634).—Oxidation of MeCHO or PhCHO to the acids by  $\text{H}_2\text{O}_2$  is greatly accelerated by addition of  $\text{SeOCl}_2$  (max. at 0.1—0.2 c.c. per 0.5 g. MeCHO) and by rise of temp. HCl alone does not catalyse the oxidation. J. W. B.

**Catalytic hydrogenation of nitriles with nickel. Hydrogenation of hydroxybenzonitriles and their methyl ethers.** H. RUPE and W. BRENTANO (Helv. Chim. Acta, 1936, 19, 588—596).—The yield of aldehyde obtained in the hydrogenation (Ni) of nitriles in  $\text{EtOAc-EtOH-H}_2\text{O}$  is increased by the presence of  $\text{NHPh}\cdot\text{NH}_2$ , although the rate of reaction is greatly reduced. Some of the aldehyde is obtained free and some as phenylhydrazone; much  $\text{NH}_2\text{Ph}$  is formed. *p*- and *o*-OH- $\text{C}_6\text{H}_4\cdot\text{CN}$  (I) and *p*- and *o*-OMe- $\text{C}_6\text{H}_4\cdot\text{CN}$  give 40–66, 40, 14–66, and 40–5%, respectively, of aldehyde without and 54–25, 50, 27–33, and 66%, respectively with  $\text{NHPh}\cdot\text{NH}_2$ . *Di-p*- and *o*-methoxybenzylamine have m.p. 35–37°, b.p. 225–230°/10 mm., and b.p. 200–210°/10 mm., respectively. *o*-Methoxybenzylamine has b.p. 120–125°/10 mm. The prep. of (I) from *o*-OH- $\text{C}_6\text{H}_4\cdot\text{NO}_2$  by way of the *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_2$  derivative, reduction by Fe-AcOH, hydrolysis, and Sandmeyer reaction is impracticable owing to poor yields in the last reaction. R. S. C.

**Conversion of acids into aldehydes.** J. S. McFADYEN and T. S. STEVENS (J.C.S., 1936, 584—587).—Benzenesulphonylacylhydrazides are prepared thus: (a)  $\text{R}\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 + \text{PhSO}_2\text{Cl} + \text{C}_5\text{H}_5\text{N} \rightarrow \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$  (I) or (b)  $\text{R}\cdot\text{COCl} + \text{PhSO}_2\cdot\text{NH}\cdot\text{NH}_2 + \text{C}_5\text{H}_5\text{N} \rightarrow$  (I): (a) is better since (b) favours diacylation and thus *benzenesulphondibenzoylhydrazide*, m.p. 198—200° (decomp.), is obtained. The following are prepared usually by method (a): *benzenesulphonyl-benzoyl*, m.p. 192—194° (decomp.), *-o-hydroxy-*, m.p. 161—162°, *-p-methoxy-*, m.p. 187—189° (decomp.), *-3:4-methylene-dioxy-*, m.p. 166—168°, *-m*, m.p. 222—223° (decomp.), and *-p-nitro-benzoyl*, m.p. 197—199° (decomp.), *-isobutyl-*, m.p. 156—158°, and *-diphenylacetyl-*, m.p. 191—193°, *-hydrazide*; 2:*o*-dichlorobenzenesulphonyl-benzoyl, m.p. 186—188° (decomp.), *-p-chlorobenzoyl*, m.p. 235—237° (decomp.), and *-o-hydroxybenzoyl*, m.p. 229—230° (decomp.), *-hydrazide*. Cinnamoylhydrazide and  $\text{PhSO}_2\text{Cl}$  give a compound, m.p. 169—171° (decomp.). Addition of alkali to a solution of (I) in hot glycol affords good

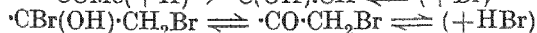
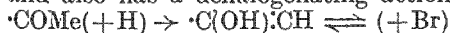


$\text{Bu}^+\text{CO}_2\text{H}$  and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$  in presence of  $\text{ZnCl}_2$ . Lobariol (IV) is converted by reduction with Na-Hg

yields (42–87%) of aromatic aldehydes: (I)  $\rightarrow$   $\text{PhSO}_2\text{K} + (\text{R}\cdot\text{CO}\cdot\text{N}\cdot\text{NH}) \rightarrow \text{R}\cdot\text{CHO} + \text{N}_2$ , but fails in the aliphatic series. The yield is best when a considerable excess of alkali (best  $\text{Na}_2\text{CO}_3$ ) at  $160^\circ$  is used, and is unaffected by the quantity of solvent: prolonged heating ( $>75$  sec.) gives poor results. The reaction can be applied to the replacement of reactive halogen in the benzene ring by H; thus picryl chloride and  $\text{PhSO}_2\cdot\text{NH}\cdot\text{NH}_2$  afford *benzenesulphon-2':4':6'-trinitrophenylhydrazide*, m.p.  $210\text{--}220^\circ$  (decomp.), which gives  $1:3:5\text{-C}_6\text{H}_3(\text{NO}_2)_3$ , and the  $2':4'\text{-dinitrophenylhydrazide}$ , dimorphous, laminæ and needles, both m.p.  $196\text{--}198^\circ$  (decomp.), gives  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ . *Piperonylhydrazide* has m.p.  $171\text{--}172^\circ$ . J. W. B.

**Derivatives of *p*-homosalicylaldehyde.** K. CHANG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 80–83).—*p*-Homosalicylaldehyde (5-methyl-2-hydroxybenzaldehyde; cf. A., 1878, 875) with hydrazines, or semicarbazides in boiling 95% EtOH affords cryst. derivatives. The following are prepared: *phenyl*-, m.p.  $148.5\text{--}149.5^\circ$ , *o*-, m.p.  $149\text{--}150^\circ$  and *p*-tolyl-, m.p.  $153.5\text{--}155.5^\circ$ , and  $\beta$ -naphthylhydrazone, m.p.  $201.5\text{--}202.5^\circ$ ; *o*-nitro-, m.p.  $232\text{--}233^\circ$ , and 2-bromo-4-methyl-phenylhydrazone, m.p.  $128\text{--}129^\circ$ ; 3-, m.p.  $253\text{--}254^\circ$  (uncorr.), 4-nitro-, m.p.  $269\text{--}270^\circ$ , 3:5-dinitro-, m.p.  $259.5\text{--}260.5^\circ$ ; *p*-chloro-, m.p.  $247\text{--}248^\circ$  (decomp.), and *p*-bromobenzoylhydrazone, m.p.  $246.5\text{--}247.5^\circ$ ; *o*-, m.p.  $208\text{--}209^\circ$ , and *p*-tolylsemicarbazone, m.p.  $212\text{--}213^\circ$ . J. L. D.

**Theory and practice of the halogenation of active methyl and methylene groups.** F. KROHNKE (Ber., 1936, 69, [B], 921–935; cf. this vol., 592).—When Br (1 mol.) acts on  $\text{COPhMe}$  in 15 different media and the action is interrupted immediately after disappearance of the colour of the halogen the proportions of  $\text{COPh}\cdot\text{CH}_2\text{Br}$ ,  $\text{COPh}\cdot\text{CHBr}_2$ , and  $\text{COPhMe}$  in the product vary with the solvent; if the reaction is interrupted after a further 1.5–2 hr. the ratio  $\text{COPh}\cdot\text{CH}_2\text{Br}:\text{COPh}\cdot\text{CHBr}_2$  (80:20) is independent of the medium. Similar observations are recorded for other Me ketones, the constitution of which controls the position of equilibrium. For max. utilisation of Br in production of monobromo-ketones it is necessary to use an excess of ketone;  $\text{AcOH}$ ,  $\text{CCl}_4$ , and  $\text{CS}_2$  are unsuitable as media since in them the “time equilibrium” is very rapidly established whereas  $\text{CHCl}_3$  and  $\text{EtBr}$  are well adapted to the purpose. HBr activates the Me and  $\text{CH}_2\text{Br}$  ketone and also has a dehalogenating action, thus:



$\cdot\text{CO}\cdot\text{CHBr}_2$ . There is no apparent relationship between the effect of medium and its physical nature. Since further bromination of  $\text{CHBr}$  ketones is difficult, equilibrium is generally in favour of the  $\text{Br}_1$  compound. The  $\text{CBr}_2$  ketones in presence of HBr readily and almost completely undergo the change, e.g.,  $\text{COPh}\cdot\text{CMeBr}_2 + \text{COPhEt} \rightleftharpoons 2\text{COPh}\cdot\text{CHMeBr}$  and analogously the  $\text{CBr}$  compounds give the reaction  $\text{COPh}\cdot\text{CBr}_3 + 2\text{COPhMe} \rightarrow 3\text{COPh}\cdot\text{CH}_2\text{Br}$ . Unexpectedly bromination of  $\text{COPhMe}$  in presence of

$\text{KOAc}$  (as catchment for HBr) is accompanied by production of more  $\text{COPh}\cdot\text{CHBr}_2$  than in its absence; owing to non-activation of  $\text{COPhMe}$  by acid the reaction necessitates a higher temp. whilst  $\text{COPh}\cdot\text{CH}_2\text{Br}$  is regarded as activated by HBr in its immediate vicinity previous to the reaction with  $\text{KOAc}$ .  $\text{CaCO}_3$  behaves similarly. Bromination is preceded by the formation of red additive compounds, e.g.,  $\text{CORMe}\cdot\text{Br}_2$ . The separation of mono- and di-bromoketones is effected by  $\text{C}_5\text{H}_5\text{N}$  in hot EtOH in which the former rapidly produce salts,  $\text{COR}\cdot\text{CH}_2\cdot\text{N}(\text{C}_5\text{H}_5)\text{Br}$  whereas the latter react only after expulsion of EtOH at  $100^\circ$  thus:  $\text{COR}\cdot\text{CHBr}_2 + 2\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} = \text{R}\cdot\text{CO}_2\text{H} + \text{CH}_2(\text{NC}_5\text{H}_5\text{Br})_2$ . The following appear new:  $\omega$ -tribromoacetophenone, m.p.  $65\text{--}66^\circ$ , b.p.  $176^\circ/16$  mm.; *pinacolynilpyridinium bromide*, m.p.  $203\text{--}204^\circ$ ; 3-phenanthracylpyridinium bromide, m.p.  $233^\circ$  (decomp.); 4-*p*-chlorophenacylpyridinium bromide, m.p.  $206^\circ$  (decomp.) after softening at  $203^\circ$ , and the corresponding *enolbetaine*  $\text{C}_{13}\text{H}_{10}\text{ONCl}$ , m.p.  $135\text{--}136^\circ$  (decomp.) after becoming discoloured at  $132^\circ$ ; 3:4-dichlorophenacylpyridinium bromide, m.p.  $222^\circ$  (decomp. commencing at  $220^\circ$ ), and the *enolbetaine*  $\text{C}_{13}\text{H}_9\text{ONCl}_2$ , m.p.  $130\text{--}135^\circ$  (decomp.); *p*-iodophenacylpyridinium bromide, m.p.  $252\text{--}253^\circ$  (decomp. beginning at  $248^\circ$ ), and the *enolbetaine*  $\text{C}_{13}\text{H}_{10}\text{ONI}$ , m.p.  $147^\circ$  (decomp.) after becoming discoloured at  $140^\circ$ ; *m*-nitrophenacylpyridinium bromide, m.p.  $244\text{--}245^\circ$  (decomp.), and the corresponding *picrate*. H. W.

**Halogen analogues of adrenaline and ephedrine. II. Derivatives of acetophenone.** R. P. EDKINS and W. H. LINNELL (Quart. J. Pharm., 1936, 9, 75–109; cf. A., 1932, 1245).—3-Amino-4-hydroxyacetophenone (an oil) obtained by reduction of the 3- $\text{NO}_2$ -derivative gave 3-bromo-4-hydroxyacetophenone (I), m.p.  $112^\circ$ , by the Sandmeyer method. (I) in  $\text{Et}_2\text{O}$  saturated with HCl gave with  $\text{BuNO}_2$  the *oximino*-derivative, and reduction *in situ* with  $\text{SnCl}_2$  gave 3-bromo- $\omega$ -amino-4-hydroxyacetophenone hydrochloride, m.p.  $236^\circ$ . In a similar way the hydrochloride, m.p.  $235^\circ$ , of the 3-Cl-derivative was obtained. 3-Chloro-5-nitroso-4-hydroxyacetophenone, m.p.  $110^\circ$ , was obtained from the chlorohydroxyketone and  $\text{BuNO}_2$  in  $\text{AcOH}$ . The hydrochlorides of 3-chloro-, 3-bromo-, 4-chloro-, and 4-bromo- $\omega$ -aminoacetophenones, m.p.  $222^\circ$ ,  $236^\circ$ ,  $290^\circ$ , and  $306^\circ$ , respectively, were obtained by reduction of the corresponding *oximino*-compounds with  $\text{SnCl}_2$  in  $\text{Et}_2\text{O}$  saturated with HCl. Reduction of these halogenated  $\omega$ -aminoacetophenones in aq. solution with  $\text{H}_2$  (Pd) gave excellent yields of  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ , halogen being eliminated, whilst in EtOH with or without  $\text{H}_2$ , but in presence of Pd, hydrolysis occurred, and theoretical yields of the halogenobenzoic acids were obtained. J. N. A.

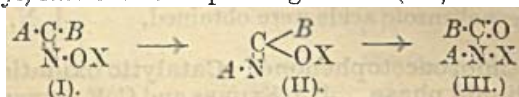
**4-Chloroacetophenone. Catalytic oxidation in the liquid phase.** J. J. STUBBS and C. E. SENSEMAN (Ind. Eng. Chem., 1936, 28, 559–560).—4-Chloroacetophenone with  $\text{O}_2$  in  $\text{AcOH}$  containing  $\text{MnO}_2$  at  $110\text{--}112^\circ$  during 3 hr. affords 91%  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$  (I). In the absence of  $\text{MnO}_2$  no (I) is formed. J. L. D.



**Organo-magnesium derivative of pentamethylbenzene.** H. CLÉMENT (Compt. rend., 1936, 202, 425—427; cf. A., 1934, 526).—Xylene and MeCl in presence of  $\text{AlCl}_3$  (24 hr.) afford an easily separable mixture of  $\text{C}_6\text{HMe}_5$  and  $\text{C}_6\text{Me}_6$ .  $\text{C}_6\text{Me}_5\cdot\text{MgBr}$  (I), prepared in presence of EtBr (*loc. cit.*), and AcCl yield *pentamethylacetophenone*, m.p.  $110^\circ$  (oxime; semicarbazone), and some *pentamethylphenylmethylethylcarbinol*, m.p.  $52^\circ$ . Similarly (I) (containing EtBr) with BzCl or EtOBz affords *pentamethylbenzophenone*, m.p.  $125^\circ$  (oxime; semicarbazone), and some *pentamethylphenylphenylethylcarbinol*, m.p.  $49^\circ$ , and with  $\text{HCO}_2\text{Et}$  affords *pentamethylbenzaldehyde*, m.p.  $130.5^\circ$  (oxime; semicarbazone). H. G. M.

**ar-Turmerone from curcuma oil.** H. RUPE and A. GASSMANN [with (in part) R. HAECKER] (Helv. Chim. Acta, 1936, 19, 569—581).—*ar*-Turmerone (I),  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}_2$ , and *dl*-*dihydroar-turmerone* (II) are synthesised. Crude curcuma oils had  $[\alpha]_D -9^\circ$  to  $+7.54^\circ$ , but various samples of rhizome gave to  $\text{C}_6\text{H}_6$  only dextrorotatory mixtures,  $[\alpha]_D +0.82^\circ$  to  $+20.48^\circ$ . The oil gave crystalline compounds with  $\text{H}_4\text{Fe}(\text{CN})_6$  and  $\text{H}_3\text{Fe}(\text{CN})_6$ , but treatment with these reagents does not give pure products. Oxidation of the oil with Pd-C, Se,  $\text{SeO}_2$ ,  $\text{FeCl}_3$ , and  $\text{O}_2\text{-FeCl}_3$  gives oils enriched in (I), but pure (I), b.p.  $159\text{--}160^\circ/10\text{ mm.}$ ,  $[\alpha]_D^{20} +82.21^\circ$ ,  $[\alpha]_{3461}^{20} +101.06^\circ$ , is best obtained by controlled oxidation with  $\text{CrO}_3$ , prep. of the *dinitrophenylhydrazones* (III), m.p.  $133\text{--}134^\circ$ , and hydrolysis thereof with hot HCl-EtOH. When pure, (I) gives a *semicarbazone*, m.p.  $108\text{--}109^\circ$ , an *oxime*, b.p.  $179\text{--}180^\circ/10\text{ mm.}$ , and *hydroxylamino*-compound, m.p.  $112^\circ$  (stable to acid). (III), but not (I), with conc. acid may give *d-curcuminone* (IV) (*dinitrophenylhydrazone*, m.p.  $89.5^\circ$ ). Hydrogenation (Ni) of (I) in 70% EtOH gives *dihydroar-turmerone*, b.p.  $146\text{--}147^\circ/10\text{ mm.}$ ,  $[\alpha]_D^{20} +44.25^\circ$ ,  $[\alpha]_{3461}^{20} +54.3^\circ$  (*dinitrophenylhydrazone*, m.p.  $121\text{--}122^\circ$ ; *oxime*, b.p.  $169\text{--}170^\circ/10\text{ mm.}$ ). (II), b.p.  $145\text{--}155^\circ/10\text{ mm.}$  (*dinitrophenylhydrazone*, m.p.  $127\text{--}128^\circ$ , not depressed by admixture with the *d*-compound; *oxime*, b.p.  $169\text{--}170^\circ/10\text{ mm.}$ ), is best obtained from  $\beta$ -*p*-tolylpropionpiperidide, b.p.  $205\text{--}208^\circ/10\text{ mm.}$ , and  $\text{MgBu}^{\text{I}}$ , and, less well, from  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COCl}$  and  $\text{ZnBu}^{\text{I}}$  or  $\text{CPr}^{\text{II}}\text{Na}(\text{CO}_2\text{Et})_2$ . (IV) and  $\text{COMe}_2$  with cold NaOEt (not other reagents) gives (I). R. S. C.

**Beckmann change. IV. Effects of substitution on the rate of rearrangement of ketoxime picryl ethers. Suggested mechanism of the transformation.** A. W. CHAPMAN and F. A. FIDLER (J.C.S., 1936, 448—453; cf. A., 1935, 1498).—Velocities of Beckmann rearrangement of *p*-substituted benzophenoneoxime picryl ethers (I) ( $\text{X} = \text{picryl}$ ) into the corresponding amides (III):



are measured in  $\text{CCl}_4$  for compounds in which A and B = Ph, in which  $\text{A} = p\text{-Y}\cdot\text{C}_6\text{H}_4$  ( $\text{Y} = \text{Cl}$ ,  $\text{NO}_2$ , or Me) and B = Ph, and vice versa, and in which A and B =  $p\text{-Y}\cdot\text{C}_6\text{H}_4$  ( $\text{Y} = \text{Cl}$ ,  $\text{NO}_2$ , Me, or OMe). It is suggested that the activity of reagents promoting the Beckmann

rearrangement of ketoximes depends on the formation of ethers of type (I) ( $\text{X} = \text{acyl etc.}$ ), in which the change is spontaneous, its velocity depending on the polar character of the solvent. There is no evidence that ions are formed. The attraction for electrons exerted by  $\cdot\text{OX}$  creates a dipole at  $\text{N}\cdot\text{O}$ , its positive end being at N. If the mol. acquires sufficient energy, N becomes attached to A and OX migrates. The process is facilitated by electron-repelling groups on A or B. The following are prepared. *Ph p-tolyl  $\alpha$ - and  $\beta$ -ketoxime picryl ethers*, m.p.  $103^\circ$  and  $83^\circ$ , converted respectively into *p-toluoyl-N-picrylanilide*, m.p.  $209^\circ$  [also obtained from *p*-toluanilide-imidochloride and  $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{ONa}$ ], and *benz-N-picryl-p-toluidide*, m.p.  $180\text{--}185^\circ$  (also obtained from *benz-p-toluidideimidochloride*). *p-Nitrobenzophenone- $\alpha$ -oxime picryl ether*, m.p.  $134^\circ$ , when heated in  $(\text{CH}_2\text{Cl})_2$  for 5 hr. at  $100^\circ$  gives *p-nitrobenz-N-picrylanilide*, m.p.  $214\text{--}215^\circ$ ; the  $\beta$ -oxime picryl ether, m.p.  $154\text{--}155^\circ$ , is unchanged under the same conditions. The picryl ether, m.p.  $189^\circ$ , of *pp'*-*dipitrobenzophenoneoxime*, m.p.  $195^\circ$  (decomp.), is similarly unchanged, as is *benzophenoneoxime 2:4-dinitrophenyl ether*, m.p.  $173\text{--}174^\circ$ ; the isomeric *benz-N-2:4-dinitrophenylanilide*, m.p.  $155\text{--}156^\circ$ , is obtained from *benzanilideimidochloride* and Na 2:4-dinitrophenoxide. *p*-Chlorobenzophenone- $\beta$ -oxime picryl ether has m.p.  $116\text{--}118^\circ$  (cf. A., 1933, 952). Attempts to prepare di-*p*-anisylketoxime picryl ether, even in a freezing mixture, give *p*-anisoyl-*p*-aniside. Improved methods of separating isomeric *p*-chloro- and *m*-methyl-benzophenoneoximes are described.

E. W. W.

**Action of alkalis on aromatic ketones.** N. S. KOZLOV, P. N. FEDOSEEV, and L. E. OLIFSON (J. Gen. Chem. Russ., 1936, 6, 259—264).—Ketones of the type  $\text{C}_6\text{H}_4\text{R}\cdot\text{COPh}$  decompose when heated at  $250\text{--}300^\circ$  for 50 min. with KOH, to yield  $\text{C}_6\text{H}_4\text{R}\cdot\text{CO}_2\text{H} + \text{C}_6\text{H}_6$ , whilst with  $\text{C}_6\text{H}_5\text{R}_2\cdot\text{COPh}$  the products are  $\text{C}_6\text{H}_5\text{R}_2$  and BzOH. Thus *o*- and *p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{COPh}$  yield *o*- and *p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{CO}_2\text{H}$  and  $\text{C}_6\text{H}_6$ , *p*- $\text{C}_6\text{H}_4\text{Pr}^{\text{II}}\cdot\text{COPh}$  affords *p*- $\text{C}_6\text{H}_4\text{Pr}^{\text{II}}\cdot\text{CO}_2\text{H}$  (I) and  $\text{C}_6\text{H}_6$ , 4:4'-*diisopropylbenzophenone*, b.p.  $195\text{--}196^\circ/1\text{ mm.}$  (from  $\text{PhPr}^{\text{II}}$  and  $\text{COCl}_2$  in presence of  $\text{AlCl}_3$ ), gives (I) and  $\text{PhPr}^{\text{II}}$ , and 4:4'-*diethylbenzophenone*, b.p.  $344^\circ$  (from  $\text{PhEt}$ ,  $\text{COCl}_2$ , and  $\text{AlCl}_3$ ), yields *p*- $\text{C}_6\text{H}_4\text{Et}\cdot\text{CO}_2\text{H}$  and  $\text{PhEt}$ , whilst 2:4'-*diisopropylbenzophenone*, b.p.  $334\text{--}335^\circ$  [from *m*- $\text{C}_6\text{H}_4\text{Pr}^{\text{II}}$  (II) and BzCl, in presence of  $\text{AlCl}_3$ ], gives (II) and BzOH, and  $\text{C}_6\text{H}_3\text{MePr}^{\text{II}}\cdot\text{COPh}$  yields  $\text{C}_6\text{H}_3\text{MePr}^{\text{II}}\cdot\text{CO}_2\text{H}$ , BzOH,  $\text{C}_6\text{H}_6$ , and *p*-cymene. R. T.

**Synthetical experiments with benzhydrylsodium.** E. BERGMANN (J.C.S., 1936, 412—413; cf. A., 1930, 1585).— $\text{CHPh}_2\text{Na}$  usually undergoes 1:4-addition to  $\Delta^{\alpha}$ -unsaturated CO-compounds.  $\text{CPh}_2\cdot\text{C}\cdot\text{CO}_2\text{Et}$ , however, gives a carbinol,  $\gamma$ -phenyl- $\alpha$ -bis(diphenylmethyl)propargyl alcohol, m.p.  $178\text{--}179^\circ$ .  $\text{CHPh}_2\text{Na}$  reacts with enolisable esters partly in the normal way, and partly is converted into  $\text{CH}_2\text{Ph}_2$  by the enolic form. Acyl chlorides of corresponding type react exclusively in the enolic form.  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$  condenses normally, forming  $\alpha\alpha\delta\delta$ -tetraphenyl- $\gamma$ -methylbutan-3-one, m.p.  $130\text{--}131^\circ$  (hydrolysed to  $\beta\beta$ -diphenylisobutyric acid, m.p.  $160\text{--}$

161°). With Et fluorene-9-carboxylate, the enolic reaction prevails, giving  $\text{CH}_2\text{Ph}_2$ . The condensation product with  $\text{CPh}_2\cdot\text{COPh}$  decomposes spontaneously into  $\text{CHPh}_3$  and  $\text{COPh}\cdot\text{CHPh}_2$ . The following are also prepared. From  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHPh}_2$ ; from  $\text{CHPhMeCl}$ ,  $\text{CHPhMe}\cdot\text{CHPh}_2$ ; from  $\text{CH}_2\text{Cl}\cdot\text{OMe}$ ,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{OMe}$ ; from  $\text{CH}_2\text{PhO}$ ,  $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{OH}$ ; from  $\text{COMe}_2$  or  $\text{CO}(\text{CH}_2\text{Ph})_2$ ,  $\text{CH}_2\text{Ph}_2$ ; from  $(\text{COPh})_2$ ,  $(\text{CHPh}_2)_2$  and  $\text{COPh}\cdot\text{CHPh}\cdot\text{OH}$ ; from  $\text{COPh}\cdot\text{CHPh}\cdot\text{OEt}$ ,  $\alpha$ -ethoxy- $\alpha\beta\gamma\gamma$ -tetraphenylpropan- $\beta$ -ol, m.p. 140°; from benzylideneacetophenone oxide,  $\gamma\delta$ -epoxy- $\alpha\alpha\beta\delta$ -tetraphenylbutan- $\beta$ -ol, m.p. 179—180°; from  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COMe}$ ,  $\beta\beta$ -diphenyl- $\alpha$ - $p$ -chlorophenylethanol, m.p. 176—178°, dehydrated (AcCl) to  $p$ -chlorotetraphenylethylene, m.p. 166—167° (cf. Norris and Tibbetts, A., 1920, i, 831); from  $(p\text{-C}_6\text{H}_4\text{Cl})_2\text{CO}$ ,  $\beta\beta$ -diphenyl- $\alpha$ -bis-( $p$ -chlorophenyl)ethanol, m.p. 183—184°, dehydrated (AcCl) to an anomalous product,  $\text{C}_6\text{H}_5\text{O}_3\text{Cl}_2$ , m.p. 185—186°; from  $(p\text{-C}_6\text{H}_4\text{Br})_2\text{CO}$ ,  $\beta\beta$ -diphenyl- $\alpha$ -bis-( $p$ -bromophenyl)ethanol, m.p. 197°, dehydrated to  $pp'$ -dibromotetraphenylethylene, m.p. 205°; from  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ ,  $\alpha\beta\beta$ -triphenyl- $\alpha$ - $p$ -anisylethanol, dehydrated to  $p$ -methoxytetraphenylethylene, m.p. 131—132°; from  $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$ ,  $\text{CH}_2\text{Ph}_2$  and  $Me\ \beta\gamma\gamma$ -triphenyl- $n$ -propyl ketone, m.p. 137°; from  $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$ ,  $Ph\ \beta\gamma\gamma$ -triphenyl- $n$ -propyl ketone, m.p. 182—184°; from  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ ,  $Ph\ \gamma\gamma$ -diphenyl- $\beta$ - $p$ -anisyl- $n$ -propyl ketone, m.p. 146—148°; from  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ ,  $Ph\ \delta$ -phenyl- $\beta$ -benzyl- $\Delta^2$ -butenyl ketone, m.p. 151—152°; from  $\text{CPh}_2\cdot\text{N}\cdot\text{NPhMe}$ ,  $N$ -phenyl- $N'$ - $\alpha\alpha\beta\beta$ -tetraphenylethyl- $N$ -methylhydrazine, m.p. 149—151°, with some  $(\text{CHPh}_2)_2$ ; from  $\text{CH}_2\text{Ph}\cdot\text{OBz}$  or  $\text{PhCN}$ ,  $\text{CHPh}_2\cdot\text{COPh}$ ; from  $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ ,  $o$ -anisyl benzhydryl ketone, m.p. 86—87°; from  $o\text{-C}_6\text{H}_4\text{F}\cdot\text{CO}_2\text{Me}$ ,  $o$ -fluorophenyl benzhydryl ketone, m.p. 84—85°; from AcCl or  $\text{CH}_2\text{Ph}\cdot\text{COCl}$ ,  $\text{CH}_2\text{Ph}_2$ ; from  $\text{Pr}^i\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{Ph}_2$  and benzhydryl isopropyl ketone, m.p. 75—76°; from  $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{Ph}_2$  and benzhydryl  $\beta$ -phenylisopropyl ketone, b.p. 250—252°/16 mm.; from  $(\text{CH}_2\text{Ph})_2\text{CH}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\text{Ph}_2$  and benzhydryl  $\beta$ -phenyl- $\alpha$ -benzylethyl ketone, m.p. 107—108°; and from  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ ,  $Me\ \beta\gamma\gamma$ -triphenylbutyrate, m.p. 126—127°.

E. W. W.

**Action of amines on indandione derivatives.** G. WANAG and V. WALBE (Ber., 1936, 69, [B], 1054—1060).—2-Phenylindan-1:3-dione (I) and  $\text{NH}_2\text{Ph}$  in boiling EtOH give 1-anilo-2-phenylindan-3-one, m.p. 212—213°, hydrolysed by boiling 2N-HCl to (I) and  $\text{NH}_2\text{Ph}\cdot\text{HCl}$ . The following 2-phenylindan-3-ones are obtained similarly: -1- $p$ -tolylimino-, m.p. 242°, identical with the "phenylindandione-toluidide" of Liebermann; -1- $p$ -anisylimino-, m.p. 239—240°; -1-2'-naphthylimino- (II), m.p. 274—275° (block). 2-Methylindan-1:3-dione and  $\text{NH}_2\text{Ph}$  afford 1-anilo-2-methylindan-3-one (III), m.p. 153°. The compounds are generally stable towards  $\text{H}_2\text{O}_2$  in boiling EtOH with the exception of (III), which is slowly transformed into phthalanil. 2-Bromo-2-phenylindan-1:3-dione and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  in boiling EtOH yield 2- $p$ -toluidino-2-phenylindan-1:3-dione, m.p. 187°.  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  similarly affords 2- $p$ -anisidino-2-phenylindan-1:3-dione, m.p. 165°.

whereas  $\beta\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$  affords 2-2'-naphthylimino-2-phenylindan-1:3-dione, m.p. 201—203°, and some (II). 2-Anilino-2-phenylindan-1:3-dione is converted by  $\text{NaNO}_2$  and HCl into nitroso-2-anilino-2-phenylindan-1:3-dione, m.p. 187°. 2-Methylanilino-2-phenylindan-1:3-dione has m.p. 119°. Condensation with aliphatic amines is effected in  $\text{Et}_2\text{O}$ . Thus are obtained 2-isobutylamino-, m.p. 95°; 2-propylamino-(hydrochloride, decomp. 239°; nitroso-2-propylamino-2-phenylindan-1:3-dione, m.p. 139—140°; propylammonium bromide, m.p. 182°); 2-ethylamino- [hydrochloride, m.p. 237° (decomp.)]; 2-methylamino- (hydrochloride, decomp. 235°), 2-phenylindan-1:3-dione. 2-Anilino-2-methylindan-1:3-dione has m.p. 190°.

H. W.

**2-Nitroindan-1:3-dione and its salts.** G. WANAG (Ber., 1936, 69, [B], 1066—1074).—Indan-1:3-dione is transformed by fuming  $\text{HNO}_3$  in AcOH into  $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (I). If the experiment is performed with efficient cooling 2-nitroindan-1:3-dione (II), m.p. 110°, or (+2H<sub>2</sub>O), m.p. 113° (decomp.), is obtained in 78% yield. It is converted by conc. NaOH or conc.  $\text{H}_2\text{SO}_4$  into (I) and  $\text{NH}_3$  (derived from  $\text{MeNO}_2$ ). (II) and  $\text{Br}\cdot\text{H}_2\text{O}$  afford 2-bromo-2-nitroindan-1:3-dione, m.p. 115—116°. (II) is about as strong as HCl and hence in solution exists in the form,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C}(\text{OH}) \\ \text{CO} \end{smallmatrix}\rangle\text{C}\cdot\text{NO}_2$  or  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{C}\cdot\text{NO}\cdot\text{OH}$ . The  $\text{NH}_4$ , m.p. 222°, Na, K, Ba, Sr, Ca, Mg, Ag, Pb, Hg<sup>I</sup>, Cd, and Cu salts are described. The dark violet  $\text{Fe}^{II}$  salt (+4H<sub>2</sub>O and +2H<sub>2</sub>O) is very characteristic. Salts from the following org. bases are described:  $\text{NH}_2\text{Ph}$ , m.p. 209° after softening at 203°;  $o$ -,  $m$ -, and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ , m.p. 197—198°, 193—194°, and 192—193°, respectively;  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\text{Ph}$ , m.p. 199°;  $\text{NPhMe}$ , m.p. 186°;  $\text{NPhMe}_2$ , m.p. 133°. (II) appears suitable for the isolation and characterization of org. bases, thus resembling picric, picrolonic, and styphnic acid; the group  $\text{OH}\cdot\text{C}\cdot\text{C}\cdot\text{NO}_2$  or  $\text{O}\cdot\text{C}\cdot\text{C}\cdot\text{NO}\cdot\text{OH}$ , which readily forms an internal complex, is common to all.

H. W.

**Condensation of indan-1:3-dione with acetone.** A. CIRULIS (Annalen, 1936, 522, 278—284).—Indan-1:3-dione (I) and  $\text{COMe}_2$ +piperidine give resinous products, di-indone, and  $s$ -di-(3-indenonyl)acetone (II),  $(\text{CO}\langle\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix}\rangle\text{C}\cdot\text{CH}_2)_2\text{CO}$ , m.p. 199—200° [Na, Ag, and Ba salts;  $\text{Me}_2$ , m.p. 251° (from MeI and  $\text{MeOH}\cdot\text{NaOMe}$ ), and  $\text{Br}_2$ , m.p. 195°, derivatives; monoxime, m.p. 216° (decomp.); tri(phenylhydrazine), m.p. 248—249° (decomp.); nitrate, m.p. 233—235° (decomp.; evolution of NO), converted by  $\text{MeOH}\cdot\text{NaOMe}$  into (II)]. (II) contains 2 active  $\text{CH}_2$  groups and 2 enolisable H; it exists in yellow (keto) and bluish-green (enol) forms. (II) is produced by elimination of 2H<sub>2</sub>O from 2 mols. of the enolic form of (I) and 1 mol. of  $\text{COMe}_2$ . The di-indandionylpropane of Radulescu and Georgescu (A., 1925, i, 1285) is impure (II). The presence of a little  $\text{COMe}_2$  in  $\text{COMeEt}$  is demonstrated by treatment with (I) (as above); (II) is isolable.

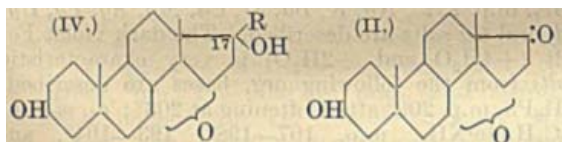
H. B.

**Dimesityl diketones and their derivatives.** III.  $\alpha\eta$ -Dimesitylheptane- $\alpha\eta$ -dione and  $\beta\zeta$ -dibromo- $\alpha\eta$ -dimesitylheptane- $\alpha\eta$ -dione. T. Y. KAO



and C. K. CHANG (J. Chinese Chem. Soc., 1936, 4, 103—104).— $\alpha\eta$ -Dimesitylheptane- $\alpha\eta$ -dione, m.p. 72—73.5° ( $\beta\zeta$ -Br<sub>2</sub>-derivative, m.p. 132—134°), is synthesised from pimelic acid (cf. A., 1935, 862). J. L. D.

**Constituents of the adrenal gland. IV. T. REICHSTEIN** (Helv. Chim. Acta, 1936, 19, 402—412; cf. this vol., 704).—Substances A, C, and D with CrO<sub>3</sub> give a diketone (I), C<sub>19</sub>H<sub>28</sub>(O<sub>2</sub>)<sub>3</sub>, m.p. 178—180° (corr.), sublimes at 165°/0.1 mm. [dioxime, m.p. 274—276° (corr.; decomp.), sublimes at about 220—250°/high vac.], and are thus closely related. Substance E is probably of a different type, since with CrO<sub>3</sub> it gives a substance (possibly impure), m.p. 211—216° (corr.), sublimes at 180°/0.1 mm. Substance A absorbs 2.5 O from Pb(OAc)<sub>4</sub>, giving a ketone (II), C<sub>19</sub>H<sub>28</sub>(O<sub>2</sub>)<sub>3</sub>, m.p. 235—238° (corr.),  $[\alpha]_D^{20} + 84.5 \pm 3^\circ$  in dry EtOH [semicarbazone, m.p. 317—322° (corr.; decomp.), hygroscopic], and an acid, C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, m.p. 256—258° (corr.; decomp.); it absorbs 2 O from KIO<sub>3</sub> to give (II) only. (II) with a little CrO<sub>3</sub> gives a substance (possibly impure) (III), C<sub>19</sub>H<sub>28</sub>O<sub>3</sub>, m.p. 156.5—158° (corr.), sublimes at 180—190°/0.02 mm. [dioxime, m.p. 262—273° (decomp. from 230°)], oxidised by CrO<sub>3</sub> to (I), which is also obtained directly from (II) by more CrO<sub>3</sub>. (II) is pptd. by digitonin in 90% EtOH, confirming its relation to *trans*-androsterone. These results lead to the provisional formulæ shown, substance A being (IV) [R=CH(OH)·CH<sub>2</sub>·OH] and



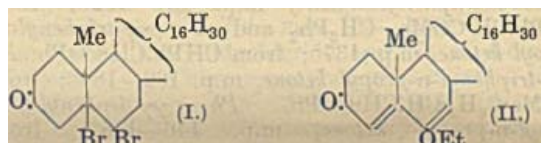
substances C and D stereoisomerides of (IV) (R=CO·CH<sub>2</sub>·OH) with respect to C<sub>17</sub>. These relations are strengthened by the fact that (II), (I), and (III) have one thirtieth, third, and seventh, respectively, of the activity of androsterone by the capon test. The sensitivity of the digitonin test is greater in 50% MeOH than in 90% EtOH; in 50% MeOH androstanedione, but not 3-epihydroxyætiocolan-17-one, gives a ppt. The O in the formulæ given may be a *tert*.-OH or ethereal. R. S. C.

**Synthesis of  $\Delta^4$ -dehydroandrosterone (3-hydroxy- $\Delta^4$ -ætiocolan-17-one) directly from cholesterol. I. A. REMESOV** (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 261—263).—Cholesteryl acetate dibromide is converted by oxidation with CrO<sub>3</sub> and subsequent reduction and hydrolysis into  $\Delta^4$ -dehydroandrosterone, m.p. 144—146°, which exhibits high biological activity (cocks). J. W. B.

**$\Delta^1$ -Androstene-3 : 17-dione. A. BUTENANDT** and H. DANNENBERG (Ber., 1936, 69, [B], 1158—1162).—Androstanedione is transformed by Br in AcOH-HBr into 2-bromoandrostanedione, m.p. 213—214° (decomp.), converted by KOAc in AcOH at 200° into  $\Delta^1$ -androstene-3 : 17-dione (I), m.p. 139—140°,  $[\alpha]_D^{20} + 6.8^\circ$  in EtOH [dioxime, gradual decomp. 225—252°]. The absorption spectrum of (I) proves

the double linking to be in conjugation with CO, and further evidence in favour of the assigned constitution is obtained as follows. *iso*Androstanediol diacetate is partly hydrolysed to the 17-monoacetate, m.p. 147—148°, oxidised by CrO<sub>3</sub> in AcOH to androstan-17-ol-3-one acetate, m.p. 156—157°. This is hydrolysed to androstan-17-ol-3-one, m.p. 178°, transformed by Br in AcOH into 2-bromoandrostan-17-ol-3-one, m.p. 180—181° (decomp.), oxidised to (I). (I) has physiological activity similar to that of the follicular hormone. H. W.

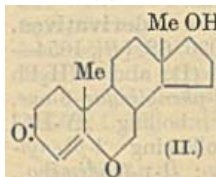
**Peculiar mode of formation of  $\Delta^4$ ·5-cholestene-3 : 6-dione ethyl ether. H. H. INHOFFEN** (Ber., 1936, 69, [B], 1134—1139).—Treatment of cholesterol with Br followed by oxidation of the product with CrO<sub>3</sub> in AcOH gives the ketone dibromide (I), decomp. 68—69°, debrominated to cholestenone. (I) and Br in Et<sub>2</sub>O-AcOH at 20° afford the bromoketone dibromide, C<sub>27</sub>H<sub>43</sub>OBr<sub>3</sub>, decomp. 137—138°, which when boiled with abs. EtOH under defined conditions passes into  $\Delta^4$ ·5-cholestene-3 : 6-dione Et ether (II), m.p. 164—165°, hydrolysed by boiling AcOH containing Zn(OAc)<sub>2</sub> to cholestenedione. (II) and Br in CHCl<sub>3</sub>-



AcOH yield cholestenedione tribromide, m.p. 192—193° (decomp.). The mode of formation and inability of (II) to react with maleic anhydride at 140° suggest the annexed formula for it. H. W.

**Absorption spectra of œstrone and related compounds.**—See this vol., 776.

**6-Ketotestosterone and related compounds. A. BUTENANDT and B. RIEGEL** (Ber., 1936, 69, [B], 1163—1168).—Oxidation of androstanediol monoacetate with CrO<sub>3</sub> (= 6 O) in AcOH yields 6-ketotestosterone acetate (I), m.p. 198—201°,  $[\alpha]_D^{25} + 47.2 \pm 1.4^\circ$  in COMe<sub>2</sub>, and (?) androstane-5 : 17-diol-3 : 6-dione 17-monoacetate, m.p. 239—241° after softening at 229—231°,  $[\alpha]_D^{25} - 29.9 \pm 1.3^\circ$  in COMe<sub>2</sub>. Cautious treatment of (I) with HCl-MeOH affords 6-ketotestosterone (II), m.p. 203—205°,  $[\alpha]_D^{25} - 58^\circ$  in COMe<sub>2</sub>. Dehydroandrosterone is oxidised to  $\Delta^4$ -androstene-3 : 6 : 17-trione (III), m.p. 216—217°,  $[\alpha]_D^{25} + 42.1 \pm 1.4^\circ$  in COMe<sub>2</sub> [trioxime, m.p. 235—237° (decomp.) after softening at 188°], an acid, m.p. 239—241°,  $[\alpha]_D^{25} - 12.5^\circ$



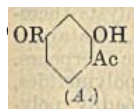
in COMe<sub>2</sub>, and (?) androstan-5-ol-3 : 6 : 17-trione, m.p. 248—249° after becoming discoloured at 225°,  $[\alpha]_D^{25} + 54.6^\circ$  in COMe<sub>2</sub>. The physiological activity of the original materials is so changed by the introduction of a further CO in conjugation with the double linking that (II) and (III) resemble the members of the œstrone group. H. W.

**Action of acetic anhydride on 2-acetylresorcinol. Synthesis of  $\gamma$ -resorcylic acid. D. B. LIMAYE and G. R. KELKAR** (J. Indian Chem. Soc., 1935, 12, 788—790).—2-Acetylresorcinol (cf. A., 1934,

298) with  $\text{Ac}_2\text{O}$  at 140—150° (3 hr.) gives the *diacetate*, b.p. 175—180°/10 mm., but with  $\text{Ac}_2\text{O}$ - $\text{NaOAc}$  at 160° (5 hr.) gives 5-hydroxy-3-acetyl-2-methylchromone (I), m.p. 122° (*Ac* derivative, m.p. 109°), together with a trace of a compound, m.p. 261—262°, probably the corresponding coumarin.  $\gamma$ -Resorcylic acid is obtained in good yield by hydrolysis of (I) with 0.5*N*- $\text{NaOH}$  for 0.5 hr.

H. G. M.

**Glycerol ethers of resacetophenone.** D. R. NADKARNI and T. S. WHEELER (J.C.S., 1936, 589—591).—Resacetophenone (I) and glycerol  $\alpha$ -chlorohydrin with aq.  $\text{KOH}$  at 100° afford 2-hydroxy-4-( $\beta$ -dihydroxypropoxy)acetophenone [A; R=



$\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2$ ], m.p. 88° (*hydrazone*, m.p. 98°; *azine*, m.p. 292—294°; *phenylhydrazone*, m.p. 119—120°), and glycerol  $\alpha$ -bis-(3-hydroxy-4-acetylphenyl) ether, m.p. 161° (*hydrazone*, m.p. 184°;

*azine*, m.p. > 300°; *phenylhydrazone*, m.p. 206°), the proportion of which is increased by use of higher [ $\text{KOH}$ ]. (I) and epichlorohydrin with aq.  $\text{NaOH}$  at room temp. give 2-hydroxy-4- $\beta$ -epoxypropoxyacetophenone (II) (A; R= $\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2$ ), m.p. 78° (*Ac* derivative, m.p. 198—200°), and (?) 2:4-bis-( $\beta$ -epoxypropoxy)acetophenone (*azine*, m.p. > 300°) which could not be purified. When only a trace of 10%  $\text{NaOH}$  is used as a catalyst 2-hydroxy-4- $\gamma$ -chloro- $\beta$ -hydroxypropoxyacetophenone, + $\text{H}_2\text{O}$ , (III), m.p. 68° (softens 58°), is formed, converted by aq.  $\text{NaOH}$  and reacidification with  $\text{AcOH}$  into (II), which with hot conc.  $\text{HCl}$  gives (III).

J. W. B.

**Synthesis of 2:5-dibenzoylquinol; 2:5-dibenzoylbenzoquinone.** R. PUMMERER and E. BUCHTA (Ber., 1936, 69, [B], 1018—1021).—Quinol-2:5-dicarboxylic acid is converted by  $\text{Ac}_2\text{O}$  containing conc.  $\text{H}_2\text{SO}_4$  at 100° into the  $\text{Ac}_2$  derivative and thence by  $\text{PCl}_5$  in boiling  $\text{C}_6\text{H}_6$  into the corresponding *dichloride*, m.p. 149° after slight softening, which with  $\text{AlCl}_3$  and  $\text{C}_6\text{H}_6$  affords 2:5-dibenzoylquinol (I), m.p. 199°. (I) is not dehydrogenated by  $\text{CrO}_3$  in boiling  $\text{AcOH}$ , alkaline  $\text{K}_3\text{Fe}(\text{CN})_6$ , or  $\text{PbO}_2$  in boiling  $\text{o}-\text{C}_6\text{H}_4\text{Cl}_2$  but is transformed by  $\text{Ag}_2\text{O}$  in boiling  $\text{C}_6\text{H}_6$  into 2:5-dibenzoyl-p-benzoquinone (II), m.p. 228° when placed in bath preheated to 227°. (II) differs entirely from Pechmann's dye.

H. W.

**Hydrolysis of 2-hydroxyanthraquinone- $\beta$ -d-glucoside.** J. H. GARDNER and W. H. DEMAREE (J. Amer. Chem. Soc., 1936, 58, 757—758).—2-Hydroxyanthraquinone- $\beta$ -d-glucoside (+ $\text{H}_2\text{O}$ ) (I), m.p. (anhyd.) 244.4—244.7° (corr.), obtained by hydrolysis (method: Robertson, A., 1930, 895) of its  $\text{Ac}_4$  derivative, m.p. 170—170.3° (corr.) (prep.: Müller, *ibid.*, 71), is hydrolysed (in suspension under identical conditions) by 0.05*N*- $\text{KOH}$ , 0.05*N*- $\text{HCl}$ , and approx. 10% borax at 100° with decreasing ease in the order quoted. Hydrolysis occurs less readily than with 1-hydroxyanthraquinone- $\beta$ -d-glucoside and -arabinoside (A. 1935, 983). The rate of hydrolysis of (I) by emulsin at 37° is in accordance with the  $\beta$ -glucoside formulation.

H. B.

**Additive product of carotene with maleic anhydride.** Z. NAKAMIYA (Bull. Inst. Phys. Chem.

Res. Japan, 1936, 15, 286—287).—Carotene and maleic anhydride give in  $\text{C}_6\text{H}_6$  an *anhydride*,  $\text{C}_{40}\text{H}_{56}(\text{C}_4\text{H}_2\text{O}_3)_5$ , m.p. 285—286°, of which the absorption spectrum shows no remaining double linkings. The corresponding *acid* (*Ba* and *Ag* salts), and a compound  $\text{C}_{40}\text{H}_{56}(\text{C}_4\text{H}_2\text{O}_3)\text{Br}_{10}$ , decomp. 250—260°, are prepared.

E. W. W.

**Catalytic reduction of pulegone.** B. N. RUTOVSKI, T. A. KOLOBLOTZKAJA, and Z. A. JAROSLAVTZEVA (J. Appl. Chem. Russ., 1936, 9, 684—689).—Pulegone (I) is converted into menthol (90% yield) by hydrogenation at 180°, in presence of a catalyst prepared by washing 27:73  $\text{Ni-Al}$  with aq.  $\text{NaOH}$  for 25—45 min., and then with  $\text{H}_2\text{O}$ , and drying the product in a stream of  $\text{H}_2$ . Impure (I), from the essential oil of *Ziziphora clinopodioides*, L., may be used for the process.

R. T.

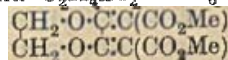
**Optically active 2-deuteroamphane.** E. BILLMANN, K. A. JENSEN, and E. KNUTH (Ber., 1936, 69, [B], 1031—1035).—Treatment of *l*-bornyl chloride with  $\text{Mg}$  and then with  $\text{H}_2\text{O}$  gives a mixture of camphane (I), *l*-camphene, and *d*-dihydrocamphene from which the last-named is removed by distillation; crystallisation of the residue from  $\text{MeOH-Et}_2\text{O}$  affords (I), m.p. 153—154°,  $[\alpha]_D^{20} \pm 0^\circ$ . If  $\text{D}_2\text{O}$  is used in place of  $\text{H}_2\text{O}$ , 2-deuteroamphane (II), m.p. 153.5—154°,  $[\alpha]_D^{20} +0.40 \pm 0.05^\circ$  in  $\text{Et}_2\text{O}$ , is obtained which does not depress the m.p. of (I). Treatment of (II) with  $\text{H}(\text{Pt-C})$  causes inactivation whereas (I) remains unchanged.

H. W.

**Pinane group. I. Synthesis of pinononic acid and "ketonopinone" [4:6-diketopinane].** P. C. GUHA and K. GANAPATHI (Ber., 1936, 69, [B], 1185—1194; cf. A., 1935, 975; this vol., 206).—*trans*-Norpinic acid is converted by  $\text{Ac}_2\text{O}$  into *cis*-norpinic anhydride (I) (corresponding *anilic acid*, m.p. 218—219°, and *monoamide*, m.p. 197—198°), (I) and  $\text{NaOMe}$  in  $\text{MeOH}$  at 0° afford *Me H cis-norpinate*, m.p. 69—71°, converted by the successive action of  $\text{SOCl}_2$  and  $\text{NH}_2\text{Ph}$  into the corresponding *anilide*, m.p. 174°, and by  $\text{SOCl}_2$  followed by  $\text{ZnMeI}$  into *Me<sub>2</sub> pinononate*, b.p. 127°/13 mm. (*semicarbazone*, m.p. 177—178°), hydrolysed to *cis-pinononic acid*, m.p. 129° [*semicarbazone*, m.p. 208° (decomp.)]; *oxime*, m.p. 175—176°]. The synthesis of 4:6-diketopinane (*loc. cit.*) is described in greater detail. *cis-Norpinyl dichloride*, m.p. about 80° (corresponding *dianilide*, m.p. 269—270°), gives a neutral product with terpene-like odour with  $\text{MgMeI}$  and a mixture of compounds with  $\text{ZnMeI}$ .

H. W.

**Syntheses in the camphane group. I. Attempted synthesis of apocamphorquinone.** P. C. GUHA and S. K. RANGANATHAN (Ber., 1936, 69, [B], 1195—1198).—Condensation of  $\text{Me}_2$  diketapocamphorate with  $\text{Na}$  and  $\text{C}_2\text{H}_4\text{Br}_2$  in  $\text{C}_6\text{H}_6$  or  $\text{MeOH}$  affords the substance

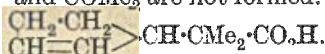


164—165°, which does not react with ketonic reagents or give a coloration with  $\text{FeCl}_3$ . It is hydrolysed by  $\text{KOH-MeOH}$  to the corresponding dicarboxylic acid, m.p. 274—275° (decomp.), and hydrolysed and decarboxylated by boiling dil.  $\text{H}_2\text{SO}_4$  (1:3) to 3:4-diketo-1:1-dimethylcyclopentane. The latter



substance could not be condensed with  $\text{NaNH}_2$  and  $\text{C}_2\text{H}_4\text{Br}_2$  in  $\text{Et}_2\text{O}$ . H. W.

**Camphor series. Structure of camphene-lauroic acid.** O. ASCHAN (Soc. Sci. Fenn., Comment. phys.-math., 1935, 8, No. 1, 13 pp.; Chem. Zentr., 1935, ii, 1555—1556; cf. A., 1916, i, 53).—Distillation of camphenic acid in a stream of  $\text{CO}_2$  at atm. pressure affords camphenic acid and camphene-lauroic acid (I),  $\text{C}_{15}\text{H}_{14}\text{O}_2$ , b.p.  $129^\circ/7$  mm.,  $[\alpha]_D^{25} +2.51^\circ$  (Na, Ba, and Ca salts; amide, m.p.  $139^\circ$ ,  $142$ — $143^\circ$ ). (I) does not add  $\text{N}_2\text{O}_3$ , is not hydrolysed by 95%  $\text{HCO}_2\text{H}$  at  $160$ — $170^\circ$ , it yields a readily decomposed Br additive product, and, on oxidation ( $\text{KMnO}_4$ ), cyclopentanone-3-carboxylic acid and  $\text{COMe}_2$  are not formed. It is concluded that (I) is



H. N. R.

**Optical activity and chemical constitution. Optically active acids and bases. II.** MAHAN SINGH and MANOHAR SINGH (J. Indian Chem. Soc., 1935, 12, 768—770; cf. A., 1935, 1127).— $[\alpha]_D^{25}$ ,  $[\alpha]_{5780}$ , and  $[\alpha]_{491}$  of *p*-diethylaminoanilcamphor (I), m.p.  $102.5^\circ$ , prepared by heating camphorquinone with *p*- $\text{NH}_2\text{C}_6\text{H}_4\text{NET}_3$ ,  $\text{EtOH}$ , and anhyd.  $\text{Na}_2\text{SO}_4$ , have been determined in several solvents. (I) and the corresponding  $\text{Me}_2$  compound (*loc. cit.*) are both photo- and thermo-tropic. The two forms of these compounds have different  $[\alpha]_D^{25}$ . The changes in  $[\alpha]_D^{25}$  of the two forms of (I) in  $\text{EtOH}$  solution indicate an equilibrium. H. G. M.

**Salts of camphor-10-sulphonic acid (Reychler's acid).** S. BERLINGOZZI and R. LENOCI (Boll. Chim. farm., 1936, 75, 270, 273—276).—Hexamethylenetetramine, m.p.  $165$ — $166^\circ$ ,  $[\alpha]_D^{20} +13.2^\circ$  (in  $\text{H}_2\text{O}$ ), piperazine, decomp. about  $250^\circ$ ,  $[\alpha]_D^{25} +17.5^\circ$ , antipyrine, m.p.  $164^\circ$ ,  $[\alpha]_D^{25} +11.9^\circ$ , and pyridone, m.p. about  $180^\circ$  (decomp.),  $[\alpha]_D^{25} +10.4^\circ$ , camphor-10-sulphonates are prepared. E. W. W.

**Camphor series. II. Synthesis of oximinothiocamphor and its application as an indicator in acidimetry and alkalimetry.** D. C. SEN (J. Indian Chem. Soc., 1935, 12, 751—755).—Thiocamphor, isomyl nitrite,  $\text{Et}_2\text{O}$ , and  $\text{NaNH}_2$  give oximinothiocamphor, m.p.  $148^\circ$  (Ni and Co salts), suitable as an indicator in acid- and alkalimetry. ( $p_K=8.8$ ;  $p_H$  range  $8.6$ — $9.0$ .) It is a sensitive reagent for Co, detecting 1 part in 50,000 of  $\text{H}_2\text{O}$ . H. G. M.

**Syntheses in the camphane group. II. Synthesis of ketohomonorcamphor [dicyclo-[1:2:3]-octane-2:4-dione].** P. C. GUHA and S. K. RANGANATHAN (Ber., 1936, 69, [B], 1199—1206).—Mainly an extended account of work already reported (A., 1935, 1245). The following appears new. Acetylcyclopentane-3-carboxylic acid is oxidised by  $\text{KOBBr}$  to *cis*-cyclopentane-1:3-dicarboxylic acid. Condensation of methylenedimalonic ester with  $\text{C}_2\text{H}_4\text{Br}_2$  and  $\text{NaOEt}$  gives after hydrolysis and decarboxylation of the product, glutaric anhydride. *cis*-cyclopentane-1:3-dicarboxylic anhydride and  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  do not appear to yield the ketonic acid. *Me*, *cis*-cyclopentane-1:3-dicarboxylate,  $\text{Me}_2\text{C}_4\text{O}_4$ , and  $\text{NaOMe}$  give unchanged material and *trans*-cyclopentane-1:3-dicarboxylic acid.

*Et*, 1:3-dibromocis-cyclopentane-1:3-dicarboxylate and  $\text{C}_2\text{Na}_2(\text{CO}_2\text{Et})_4$  do not react in boiling  $\text{C}_6\text{H}_6$ . H. W.

**The santene inversion of fenchyl alcohol and its conditions.** N. J. TOIVONEN (Suomen Kem., 1936, 9, B, 15—16).—Al salts and other catalysts are divided into those which catalyse the conversion of fenchyl alcohol (I) into 1-methylsantene (II) and into fenchenes, respectively (cf. this vol., 338). The santene inversion seems to be favoured by influences which increase the ionisation of esters of (I), e.g., cresol,  $\beta\text{-C}_{10}\text{H}_7\text{OH}$ . Using  $\text{AlPO}_4$ ,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and cyclofenchene are obtained. Fenchenes are more readily polymerised than (II); polymerising catalysts therefore give terpene mixtures richer in (II). Catalysts which yield (II) also give monocyclic terpenes. *iso*Fenchyl alcohol and kaolin give mainly polymerides, but also (II). *cuclo*Fenchene is very readily polymerised. E. W. W.

**$\alpha$ -Cyperone, a sesquiterpene ketone from the oil of *Cyperus rotundus*.** A. E. BRADFELD, B. H. HEGDE, B. S. RAO, J. L. SIMONSEN, and (in part) A. E. GILLAM (J.C.S., 1936, 667—677).—The higher-boiling fractions of the oil, treated with semicarbazide acetate, give  $\alpha$ -cyperonesemicarbazone (I), m.p.  $216^\circ$ ,  $[\alpha]_{5461}^{25} +178^\circ$  in  $\text{CHCl}_3$ , hydrolysed to  $\alpha$ -cyperone,  $\text{C}_{15}\text{H}_{22}\text{O}$  (II), b.p.  $177^\circ/20$  mm.,  $[\alpha]_{5461}^{25} +138^\circ$  (oxime, m.p.  $150.5^\circ$ ,  $[\alpha]_{5461}^{25} +134^\circ$  in  $\text{EtOH}$ ; 2:4-dinitrophenylhydrazones, m.p.  $209$ — $210^\circ$ ; nitroguanyldiazones, decomp.  $203$ — $204^\circ$ ,  $[\alpha]_D^{25} +196^\circ$ ). (II) with Na and amyl formate yields hydroxymethylene- $\alpha$ -cyperone (2:4-dinitrophenylhydrazones, m.p.  $159$ — $160^\circ$ ). Reduction of (II) with  $\text{Pd-H}_2$  affords tetrahydro- $\alpha$ -cyperone (III), b.p.  $151$ — $152^\circ/14$  mm.,  $[\alpha]_{5461}^{25} +14.8^\circ$  (semicarbazones, decomp.  $173$ — $175^\circ$ ; oxime, m.p.  $116$ — $117.5^\circ$ ; 2:4-dinitrophenylhydrazones, m.p.  $151$ — $152^\circ$ ), and with Na-EtOH gives dihydro- $\alpha$ -cyperol (IV), b.p.  $167$ — $168^\circ/15$  mm.,  $[\alpha]_{5461}^{25} +17.7^\circ$  in  $\text{EtOH}$  (3:5-dinitrobenzoate, m.p.  $157$ — $158^\circ$ ), dehydrogenated (Se) to eudalene. Hydroxymethylenetetrahydro- $\alpha$ -cyperone forms a 2:4-dinitrophenylhydrazones, m.p.  $182$ — $183^\circ$ . Oxidation of (II) with  $\text{O}_3$  gives  $\text{CH}_2\text{O}$ , and a dibasic keto-acid,  $\text{C}_{13}\text{H}_{20}\text{O}_5$  ( $\text{Me}_2$  ester, b.p.  $190$ — $197^\circ/11$  mm., and its semicarbazones, decomp.  $245$ — $246^\circ$ ), and with  $\text{H}_2\text{O}_2$ -NaOH yields 6-acetyl-1-methyl-4-isopropenylcyclohexane-1-carboxylic acid, m.p.  $112^\circ$ ,  $[\alpha]_{5461}^{25} +62.6^\circ$  in  $\text{MeOH}$  (semicarbazones, decomp.  $180$ — $181^\circ$ ; phenylsemicarbazones, decomp.  $200^\circ$ ). Ozonisation of (I) leads to a semicarbazones, decomp.  $185$ — $187^\circ$ . (IV) is ozonised to a neutral oil, which is oxidised ( $\text{H}_2\text{CrO}_4$ ) to a diketone (dioxime, decomp.  $258$ — $259^\circ$ ; disemicarbazones, decomp.  $251$ — $252^\circ$ ) (using an impure specimen containing  $\alpha$ -cyperol, a substance forming a di- or tri-phenylsemicarbazones, decomp.  $222$ — $223^\circ$ , has been obtained). Ozonolysis of dihydro- $\alpha$ -cyperyl 3:5-dinitrobenzoate gives  $\text{CH}_2\text{O}$  and a ketone,  $\text{C}_{21}\text{H}_{26}\text{O}_7\text{N}_2$ , m.p.  $148$ — $149^\circ$ , from which  $\text{CHI}_3$  is derived by oxidation with Fuson's reagent. (III) and  $\text{MgMeI}$  afford a mixture, which is dehydrogenated (Se) to 1:2-dimethyl-7-isopropyl-naphthalene (V), b.p.  $149$ — $151^\circ/9$  mm. (picrate, m.p.  $92$ — $93^\circ$ ; *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$  derivative, m.p.  $107$ — $109^\circ$ ). Reduction of hydroxymethylene- $\alpha$ -cyperone with  $\text{Pd-H}_2$  followed by Na-EtOH leads to an oil,

dehydrogenated (Se) to a hydrocarbon,  $C_{15}H_{18}$  (picrate, m.p. 102–5–104°;  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  derivative, m.p. 116–118°). (I) with  $\text{NaOEt}$  affords  $\alpha\text{-cyperene}$ , b.p. 132–133°/15 mm., which could not be reduced by  $\text{Na}$ . (III) is 1:10-dimethyl-7-isopropyldecal-2-one and (II) is represented as

$\text{CH}_2\text{:CH}_2\text{:CH}\text{---}\text{CH}\text{:CH}$   
 $\text{CH}_2\text{:CMe}\text{---}\text{CH}_2\text{:CH}\text{---}\text{CHMe}\text{:CO}$  (II) is isomerised by  $\text{H}_2\text{C}_2\text{O}_4$ , aq. or  $\text{MeOH}\text{---}\text{KOH}$  to  $\beta\text{-cyperone}$ , b.p. 175–176°/16 mm.  $[\alpha]_{5461}^{20} + 239^\circ$  (semicarbazone, decomp. 207°; oxime, m.p. 138°,  $[\alpha]_{5461}^{20} + 217^\circ$  in  $\text{EtOH}$ ; 2:4-dinitrophenylhydrazine, decomp. 218–219°; nitroquanylhydrazine, m.p. 197°,  $[\alpha]_{\text{D}}^{20} + 220^\circ$  in  $\text{CHCl}_3$ ), which must differ only stereochemically from (II). Homocuminy alcohol, b.p. 129°/10 mm. (p-xenylcarbamate, m.p. 144–145°), obtained from the corresponding Et ester, is converted into the bromide, b.p. 136°/14 mm., which with Et methylpotassium malonate forms Et homocuminy methylmalonate, b.p. 200°/13 mm. The ester with  $\text{H}_2\text{SO}_4$  yields 2-methyl-7-isopropyl-1:2:3:4-tetral-1-one, b.p. 155–160°/12 mm. (phenylsemicarbazone, m.p. 180–181°; 2:4-dinitrophenylhydrazine, m.p. 177–178°), which with  $\text{MgMeI}$  forms an oil, dehydrogenated (Se) to (V). Tetrahydroeremophilone and  $\text{MgMeI}$  give a substance, dehydrogenated (Se) to 1:3:7- $\text{C}_{10}\text{H}_5\text{Me}_2\text{Pr}^8$  (picrate, m.p. 113–114.5°;  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  derivative, m.p. 141–142°).

$\alpha\text{-Methylbenzyl Pr}^8$  ketone, b.p. 125–126° (semicarbazone, m.p. 128–129°; phenylsemicarbazone, m.p. 183°), with  $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$  and  $\text{Zn}$  affords Et  $\gamma\text{-o-tolyl-}\alpha\text{-methyl-}\beta\text{-isopropylbutyrate}$ , b.p. 165°/13 mm., which with  $\text{H}_2\text{SO}_4$  gives 2:5-dimethyl-3-isopropyl-1:2:3:4-tetral-1-one, b.p. 185–190°/22 mm. (phenylsemicarbazone, m.p. 222–223°). The ketone is reduced and dehydrogenated to 1:6-dimethyl-7-isopropyl-naphthalene, b.p. 154–158°/13 mm. (picrate, m.p. 124–126°; styphnate, m.p. 141–142°). Et homocuminy malonate, b.p. 198°/13 mm., is converted with  $\text{H}_2\text{SO}_4$  into 7-isopropyl-1:2:3:4-tetral-1-one, b.p. 158–160°/17 mm. (2:4-dinitrophenylhydrazine, m.p. 223–224°), which with  $\text{MgEtI}$  followed by dehydrogenation affords 1:7- $\text{C}_{10}\text{H}_6\text{EtPr}^8$  (picrate, m.p. 65–67°;  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  derivative, m.p. 79–81°). The absorption spectrum of (II) indicates an  $\alpha\beta$ -unsaturated ketone.

F. R. S.

**Colouring matter in the wood of "Hinoki" tree.** I. Hinokitin and hinokitiol. T. HOZOE (Bull. Chem. Soc. Japan, 1936, 11, 295–298).—Discrepancies in earlier work by Hirao (J. Chem. Soc. Japan, 1926, 47, 666, 743) and Tsuchihashi *et al.* (Rep. Gov. Res. Inst. Formosa, 1920, 1) are investigated. From the ethereal oil of the wood of the "Hinoki" tree (*Chamaecyparis obtusa*, Lieb. and Zucc.) are isolated l-rhodinic acid,  $\text{C}_{10}\text{H}_{18}\text{O}_2$ , and a phenolic substance hinokitiol,  $\text{C}_{10}\text{H}_{12}\text{O}_2$  (I) (no OMe; gives liquid products with CO reagents), converted by  $\text{FeCl}_3$  into hinokitin,  $\text{C}_{10}\text{H}_{33}\text{O}_6\text{Fe}$ , m.p. 251° (absorption max. 584, 540  $\mu$ ) (II) (A;  $\text{M}=\text{Fe}$ ,  $n=3$ ), an Fe complex salt of (I). The interconversion  $3(\text{I}) + \text{FeX}_3 \rightleftharpoons (\text{II}) + 3\text{HX}$  is realised. (I) also forms complex salts (all of type A) with  $\text{Cr}^{+++}$ , m.p. 230°,  $\text{Co}^{+++}$ , m.p. 208°,  $\text{Cu}^{++}$ , m.p. 177°,  $\text{Ni}^{++}$ , m.p. 242°,  $\text{Co}^{++}$ , m.p. 210°,  $\text{Mn}^{+}$ , m.p. > 300°,  $\text{Cd}^{++}$ , m.p. > 300°,  $\text{Zn}^{++}$ ,

and  $\text{Mg}^{++}$ , m.p. > 300° those with bivalent metals form cryst. compounds with 2 mols. of org. bases. By catalytic reduction (I) absorbs 3–4  $\text{H}_2$ , and the product no longer forms complex salts.

J. W. B.

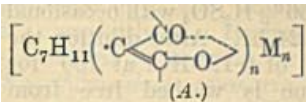
**Limonin, the bitter principle of orange kernels.** G. KOLLER and H. CZERNY [with K. LOCKER and W. MAAS] (Monatsh., 1936, 67, 248–268).—The air-dried material is extracted successively with light petroleum and EtOH. The syrupy residue is treated with  $\text{H}_2\text{O}$  and much  $\text{Et}_2\text{O}$ , which induces crystallisation of a mixture of bitter principles. Limonin (I) is isolated therefrom by dissolution in dil. NaOH or KOH, acidification of the solution at 0°, and suspension of the pptd. OH-acids in EtOH, when (I) slowly crystallises. Alternatively the mixture is treated with  $\text{Ac}_2\text{O}$  in  $\text{C}_6\text{H}_6\text{-N}$ , whereby (I) remains unchanged whereas isolimonin (II) is transformed into a more freely sol. Ac derivative. (II) is best isolated by regulated extraction of the mixture with boiling  $\text{C}_6\text{H}_6$ , which removes more freely sol. (I). (I), m.p. 280° (vac.; decomp.), is probably  $\text{C}_{23}\text{H}_{36}\text{O}_7$ . The presence of CO could not be established. Under drastic conditions acetylation occurs to only a slight extent. With cold  $\text{MgMeI}$  little  $\text{CH}_4$  is evolved, but in boiling solution the vol. of gas is equiv. to about 1 OH. One lactone group is certainly, a second probably present. Catalytic hydrogenation (Pd-C) of (I) in abs. EtOH leads to absorption of 3  $\text{H}_2$  and production of an amorphous product which passes on contact with  $\text{H}_2\text{O}$  into the cryst. hexahydrolimonin acid (III),  $\text{C}_{23}\text{H}_{34}\text{O}_8$ , decomp. 175–178° (vac.). When kept over  $\text{P}_2\text{O}_5$  at 140°/vac. (III) loses  $\text{H}_2\text{O}$  with apparent formation of polymerised material. It is unchanged by  $\text{CaCl}_2$  in  $\text{C}_6\text{H}_6$ .  $\text{Ac}_2\text{O}$  transforms it into a non-cryst. Ac derivative from which it is regenerated by EtOH- $\text{H}_2\text{O}$ . Its non-cryst. Me ester appears to be  $\text{C}_{24}\text{H}_{34}\text{O}_8$ . During hydrogenation small amounts of tetrahydrolimonin,  $\text{C}_{23}\text{H}_{30}\text{O}_7$ , m.p. 282° (vac.), appear to be produced. Treatment of (I) with molten KOH affords partly hydrogenated alkyl-naphthalenes from which by treatment with Se at 300° 1:2:5- $\text{C}_{10}\text{H}_5\text{Me}_3$  and possibly a  $\text{C}_{10}\text{H}_6\text{Me}_2$  are isolated; the acidic products contain  $m\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ . Oxidation of (I) with  $\text{KMnO}_4$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{O}_2$  gives ill-defined products whereas  $\text{MnO}_2$  and boiling 57%  $\text{H}_2\text{SO}_4$  give  $\text{C}_6\text{H}(\text{CO}_2\text{H})_5$ . (II), probably  $\text{C}_{23}\text{H}_{32}\text{O}_7$ , m.p. 264° (vac.; decomp.), contains 2 OH (Zerevitinov) and appears to give a diacetate.

H. W.

**Capsanthol, a reduction product of capsanthin.** P. KARRER and H. HÜBNER (Helv. Chim. Acta, 1936, 19, 474–479).—Capsanthin (I) and  $\text{Al}(\text{OPr}^8)_3$  in  $\text{Pr}^8\text{OH}\text{---}\text{C}_6\text{H}_6$  gives capsanthol (II),  $\text{C}_{40}\text{H}_{57}(\text{OH})_3$ , m.p. 175–176° (photomicrograph), isolated by adsorption on  $\text{CaO}$ . (II) absorbs 10  $\text{H}_2$  on micro-hydrogenation and its adsorption spectrum (max. at 5080 and 4770 Å. in  $\text{CS}_2$ ) closely resembles that of (I), confirming the presence of a CO in (I) at the end of a series of 10 ethylenic linkings.

R. S. C.

**Formation of lignin in wood.** P. KLASON (Ber., 1936, 69, [B], 676–678).—For the determination of lignin in wood the finely-divided sample is extracted





with  $\text{Et}_2\text{O}$  and dried at  $100^\circ$ . 1—1.3 g. is kept in contact with 50 c.c. of 65—66%  $\text{H}_2\text{SO}_4$  with occasional shaking at room temp. for 24 hr. After dilution the ppt. is heated with 50 c.c. of 0.1N-HCl at  $100^\circ$  for about 12 hr. The residue is washed free from mineral acid, dried at  $75^\circ$  and then at  $100^\circ$ , weighed, and incinerated. The possible formation of lignin in plants from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through  $\text{CH}_2\text{O}$  is discussed. The part played by  $\text{H}_3\text{PO}_4$  is considered. The "lignin fermentation" appears invariably associated with the production of pentoses. H. W.

**Dioxan-lignin and the pigment of ebony wood.** R. S. HILPERT and S. WISSELINCK (Ber., 1936, 69, [B], 680—684).—Xylose is transformed by HCl-dioxan into a pitch-like mass converted by  $\text{H}_2\text{O}$  into a black powder. Under like conditions, fructose gives a brown solution from which  $\text{H}_2\text{O}$  ppts. a similar material. Glucose does not become discoloured but its chemical properties are altered. In composition, which varies somewhat with the [HCl] used, the solid products are closely allied to the lignins, from which they differ mainly in the absence of OMe. The assumption that HCl-dioxan simply removes lignin and incrustations from wood and leaves cellulose is of doubtful validity. Wedekind's method (this vol. 207) for the isolation of the pigment of ebony wood is criticised. H. W.

**Further resinol from matai (*Podocarpus spicatus*).** L. H. BRIGGS and D. A. PEAK (J.C.S., 1936, 724).—From the mother-liquors of matai-resinol, condendrin, m.p.  $254\text{--}255^\circ$ , has been isolated (cf. Haworth *et al.*, this vol., 80). F. R. S.

**Pigments of *Lactarius deliciosus*, L. II.** H. WILLSTAEDT (Ber., 1936, 69, [B], 997—1001; cf. A., 1935, 495).—The material is extracted with  $\text{EtOH}$  and then with  $\text{COMe}_2$ . The  $\text{COMe}_2$  extract is treated with  $\text{H}_2\text{O}$  and light petroleum. The latter extract is chromatographed with  $\text{Al}_2\text{O}_3$  thus giving *lactarazulene* (I), b.p.  $155\text{--}160^\circ/2.5\text{--}3$  mm. [additive compound,  $\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}_3$ , m.p.  $122\text{--}123^\circ$ , with 1 : 3 : 5- $\text{C}_6\text{H}_3(\text{NO}_2)_2$ ]. (I) is closely similar to but not identical with the azulene from camomile oil. Both sources contain a second azulene and also a green product. H. W.

**Red gossypol.**—See this vol., 912.

**Catalytic transformations of heterocyclic compounds. II. Conversion of 2-methylfuran into 2-methylpyrrole and 2-methylthiophen. III. Reciprocal transformations of the simplest five-membered heterocyclic compounds.** J. K. JURIEV (Ber., 1936, 69, [B], 1002—1004; cf. this vol., 481).—2-Methylfuran gives 2-methylpyrrole when passed with  $\text{NH}_3$  over  $\text{Al}_2\text{O}_3$  at  $450^\circ$  and 2-methylthiophen when passed with  $\text{H}_2\text{S}$  over the catalyst at  $350^\circ$ . The conversion of furan (I) into pyrrole (II) and thiophen (III) takes place with good yields, but yields are poor in the changes (II)  $\rightarrow$  (III), (III)  $\rightarrow$  (II), (II)  $\rightarrow$  (I), and (III)  $\rightarrow$  (I). H. W.

**Resolution of  $\alpha$ -furylmethylcarbinol.** D. I. DUVEEN and J. KENYON (J.C.S., 1936, 621—623).—dl- $\alpha$ -Furylmethylcarbinol (p-xenylurethane, m.p.  $114^\circ$ ; acetate, b.p.  $177^\circ/760$  mm.) with o- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  gives dl- $\alpha$ -furylmethylcarbinyl H phthalate, m.p.  $80^\circ$ , which

is resolved through the quinidine salts, m.p.  $81^\circ$ ,  $[\alpha]_{\text{D}}^{20} +76.8^\circ$ , and  $[\alpha]_{\text{D}}^{20} +13.4^\circ$  in  $\text{CHCl}_3$ , into d- and l- $\alpha$ -furylmethylcarbinyl H phthalate, m.p.  $61^\circ$ ,  $[\alpha]_{\text{D}}^{20} +39.6^\circ$  and  $-39.3^\circ$  in  $\text{CHCl}_3$ . d- and l-Furylmethylcarbinol have b.p.  $70^\circ/15$  mm.,  $\alpha_{\text{D}}^{20} +10.29^\circ$  and  $-40.07^\circ$ , and are obtained by hydrolysis of the H phthalates with NaOH; hydrolysis with  $\text{Na}_2\text{CO}_3$  or steam leads to inactive alcohols. F. R. S.

**Condensation of acetone and mesityl oxide with furfuraldehyde.** P. P. SURMIN (J. Gen. Chem. Russ., 1935, 5, 1642—1644).— $\text{COMe}_2$  and furfuraldehyde (I) in presence of 3% of NaOH at  $0^\circ$  yield mono- and di-furfurylideneacetone (phenylhydrazones, m.p. respectively  $123^\circ$  and  $121\text{--}122^\circ$ ). Mesityl oxide and (I) in presence of 50% of NaOH afford furfurylidene-mesityl oxide, m.p.  $140\text{--}145^\circ$ , not yielding a phenylhydrazone. R. T.

**Identity of isopsoralene, a component of the seeds of *Psoralea corylifolia*, L., with angelicin from the roots of *Archangelica*, L.** H. S. JOIS and B. L. MANJUNATH (Ber., 1936, 69, [B], 964—967).—The solid which crystallises from the oil from the seeds of *P. corylifolia*, L., is separated by  $\text{EtOH}$  into psoralene and isopsoralene (I), m.p.  $142^\circ$ , identical with angelicin (Spath, A., 1934, 779, 899). (I) is oxidised by alkaline  $\text{H}_2\text{O}_2$  to furan-2 : 3-dicarboxylic acid. Reduction of (I) by Na-Hg in alkaline solution affords 3-hydroxy-4- $\beta$ -carboxyethylcoumarone (II), m.p.  $124.5^\circ$ , which passes at  $155^\circ$  vac. into the corresponding lactone, m.p.  $74.5^\circ$ . Methylation ( $\text{Me}_2\text{SO}_4$ ) and subsequent hydrolysis of (I) gives 3-methoxy-4- $\beta$ -carboxyvinylcoumarone (III), m.p.  $142\text{--}144^\circ$ , converted into an isomeride, m.p.  $214^\circ$ , by repeated sublimation in high vac., and reduced to the corresponding saturated acid, m.p.  $77^\circ$ , also obtained by methylation of (II). Oxidation of (III) by  $\text{KMnO}_4$  yields an acid,  $\text{C}_9\text{H}_8\text{O}_4$ , m.p.  $107^\circ$ . H. W.

**6-Methylcoumarin and its methylation products.** K. CHANG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 84—88).—5-Methylsalicylaldehyde with anhyd. NaOAc and  $\text{Ac}_2\text{O}$  containing some I at  $180\text{--}190^\circ$  affords 6-methylcoumarin, m.p.  $76.5\text{--}77.5^\circ$  (lit.,  $74.5^\circ$ ), which with MeI in  $\text{EtOH}$ -NaOEt at room temp. affords Me cis-5-methyl-o-methoxycinnamate (cf. A., 1908, i, 441), whereas with NaOH- $\text{Me}_2\text{SO}_4$ , the trans-isomeride (cf. A., 1911, i, 295) is formed. J. L. D.

**Relation between odour and constitution of alkoxy coumarins. New product with a celery odour.** A. S. PFAU (Riechstoffind., 1935, 10, 57—58; Chem. Zentr., 1935, ii, 1457).—The odours of the following are described: 6-methoxy- (odourless), 6-, m.p.  $106\text{--}107^\circ$ , and 7-ethoxy-coumarin, m.p.  $89^\circ$ ; 6-methoxy-, m.p.  $163\text{--}164^\circ$ , 6-ethoxy-, m.p.  $113\text{--}114^\circ$ , 7-methoxy-, 7-ethoxy-, m.p.  $114.5^\circ$  (strong celery odour), 7-n-propoxy-, m.p.  $72\text{--}73^\circ$ , 7-isobutoxy-, m.p.  $55\text{--}56^\circ$ , and 7-allyloxy-, m.p.  $103^\circ$  (odourless), 4-methylcoumarin; 7-ethoxy-4-methyldihydrocoumarin, m.p.  $30^\circ$ . H. N. R.

**Synthesis of coumarins from phenols and  $\beta$ -ketonic esters. V. Constitution of chlororesorcinol and chlororesorcylaldehyde.** D. CHAK-

RAVARTI and B. GHOSH (J. Indian Chem. Soc., 1935, 12, 791—797).—The diazo-anhydride of 8-amino-7-hydroxy-4-methylcoumarin is converted (Sandmeyer) into 8-chloro-7-hydroxy-4-methylcoumarin, m.p. 267° (*Ac* derivative, m.p. 188—189°), which is different from the condensation product of  $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et}$  and 4-chlororesorcinol (I), (cf. A., 1935, 1503). Nitration of 7-hydroxy-3:4-dimethylcoumarin gives the 8- $\text{NO}_2$ -derivative (*loc. cit.*), reduced by  $\text{SnCl}_2\text{--HCl--EtOH}$  to the corresponding 8- $\text{NH}_2$ -derivative, m.p. 272°. This is converted into the corresponding diazo-anhydride, m.p. 172°, and then (Sandmeyer) into 8-chloro-7-hydroxy-3:4-dimethylcoumarin, m.p. 272°, which is different from the condensation product of (I) and  $\text{CHMeAc} \cdot \text{CO}_2\text{Et}$  (cf. *loc. cit.*). These comparisons confirm the constitution of (I) (cf. A., 1933, 270). Nitration of umbelliferone yields its 6-, m.p. 220° (*Ac* derivative, m.p. 180°), and 8-, m.p. 245° (*Ac* derivative, m.p. 185°)- $\text{NO}_2$ -derivatives (cf. J.C.S., 1910, 97, 1400). The constitution of the latter is confirmed by reduction to 8-amino-7-hydroxycoumarin, converted (Sandmeyer) into 8-chloro-7-hydroxycoumarin, m.p. 263°, which is different from the condensation product (II) of (I) and malic acid (*loc. cit.*). (I) with anhyd.  $\text{Zn}(\text{CN})_2$  and dry  $\text{HCl}$  in  $\text{Et}_2\text{O}$  gives 5-chlororesorcyaldehyde (III), which with  $\text{NaOH--ClCO}_2\text{Me}$  gives chlorodicarbomethoxyresorcyaldehyde, m.p. 58°, this with  $\text{CH}_2(\text{CO}_2\text{H})_2\text{--AcOH}$  yields chlorocarbomethoxy-7-hydroxycoumarincarboxylic acid and a trace of 2:4-dicarbomethoxycinnamic acid (cf. A., 1934, 775). The former when boiled with  $\text{Na}_2\text{CO}_3$  gives 6-chloro-7-hydroxycoumarin-3-carboxylic acid, m.p. 284°, decomposed by heat into 6-chloro-7-hydroxycoumarin, identical with (II). H. G. M.

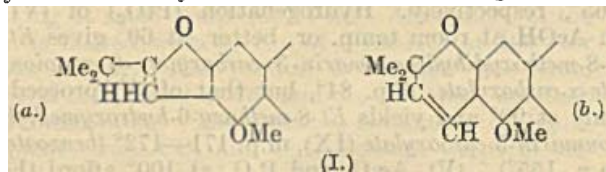
[Attempted] synthesis of furocoumarins from 4-hydroxy-5-methoxyisophthaldialdehyde. K. W. MERZ and J. HOTZEL (Arch. Pharm., 1936, 274, 292—310).—Attempts to prepare xanthotoxin or an isomeride thereof failed. Guaiacol-4:6-dialdehyde (I) with  $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$  gives the *Ac* derivative, m.p. 145—146°, and with  $\text{P}_2\text{O}_5\text{--Ac}_2\text{O}$  at 100° gives acetylguaiacol-4:6-dialdehyde tetra-acetate, m.p. 136.5°. With  $\text{NH}_2\text{OH}$  these give the dioxime of (I), which with  $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$  gives acetylguaiacol-4:6-dialdoxime diacetate (II), m.p. 148—149°, but with hot  $\text{Ac}_2\text{O}$  yields acetylguaiacol-4:6-dinitrile, m.p. 143°. 4-Aldehydoacetylguaiacol-6-aldoxime with  $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$  gives the acetate (III), m.p. 134—135°, and with hot  $\text{Ac}_2\text{O}$  affords 4-aldehydoacetylguaiacol-6-nitrile, m.p. 117°. Attempts to hydrolyse the nitriles gave resins. (I) with  $\text{NH}_3\text{--EtOH}$  or  $\text{NH}_2\text{Ph--EtOH}$  yields 4-aldehydoguaiacol-6-aldimine, m.p. 211°, or 6-aldehydeimine (IV), m.p. 132°, respectively, and attempts to induce both  $\text{CHO}$  to react failed. (IV) with  $\text{Ac}_2\text{O--C}_5\text{H}_5\text{N}$  gives the *Ac* derivative, m.p. 170°, hydrolysed by aq.  $\text{EtOH}$ . Attempts to nitrate (I) failed; fuming  $\text{HNO}_3$  in  $\text{EtOH}$  gives 4:6-dinitroguaiacol, m.p. 121—122°. (I), piperidine, and  $\text{CH}_2(\text{CO}_2\text{Et})_2$  give a mixture, m.p. 189°, of nitrogenous substances, which with hot  $\text{AcOH}$  yields *Et* 6-aldehydo-8-methoxycoumarin-3-carboxylate (V), m.p. 209—210° (*phenylhydrazone*, m.p. 215°), and a little *Et* 8-methoxycoumarin-3-carboxylate-6-methylenemalonate (VI), m.p. 148—149°. Hydrolysis of (V) and (VI) by 5%  $\text{NaOH}$  gives the corre-

sponding acids (VII), m.p. 243° (decomp.) [*phenylhydrazone*, m.p. 250° (decomp.)], and (VIII), m.p. 265°, respectively. Hydrogenation ( $\text{PtO}_2$ ) of (VI) in  $\text{AcOH}$  at room temp. or, better, at 60° gives *Et* 3- $\beta$ -8-methoxydihydrocoumarin-3-carboxylate-6-propionate- $\alpha$ -carboxylate, m.p. 84°, but that of (V) proceeds only at 90° and yields *Et* 8-methoxy-6-hydroxymethylcoumarin-3-carboxylate (IX), m.p. 171—172° (*benzoate*, m.p. 155°). (V),  $\text{Ac}_2\text{O}$ , and  $\text{P}_2\text{O}_5$  at 100° afford the diacetate, m.p. 127—129°, hydrogenation ( $\text{PtO}_2$ ) of which in  $\text{AcOH}$  gives the *Ac* derivative, m.p. 139°, of (IX). (VI),  $\text{H}_2\text{SO}_4$ , and  $\text{KNO}_3$  at  $\approx -5^\circ$  give a poor yield of 5- or 7- $\text{NO}_2$ -derivative, m.p. 152—154°, which could not be hydrolysed to the acid and gave amorphous products when hydrogenated; the  $\text{NO}_2$ -acid could also not be obtained directly from (VIII). Similar nitration of (V) affords the 5- and 7- $\text{NO}_2$ -esters, m.p. 185—186° [*phenylhydrazone*, m.p. 256° (decomp.)] and 124° [*phenylhydrazone*, m.p. 227.5° (decomp.)], respectively, or vice versa, which decompose when hydrolysed, but with  $\text{H}_2\text{--Pt}$  or  $\text{H}_2\text{--Pd--BaSO}_4$  in  $\text{AcOH}$  absorb 2  $\text{H}_2$  to yield benzisooxazoles, m.p. 208—210° and 246° (decomp.), respectively, both resistant to further reduction. (VII) with 65%  $\text{HNO}_3$  in conc.  $\text{H}_2\text{SO}_4$  at 0° gives the 5- and 7- $\text{NO}_2$ -acids, m.p. 145° [*phenylhydrazone*, m.p. 236° (decomp.)] and 178° [*phenylhydrazone*, m.p. 269° (decomp.)], respectively, or vice versa. The  $\text{NO}_2$ -esters with  $\text{Ac}_2\text{O--P}_2\text{O}_5$  afford the diacetates, m.p. 197° and 131—132°, respectively, which are hydrogenated ( $\text{Pd}$  or  $\text{PtO}_2$ ) in  $\text{AcOH}$  to *Et* 5- and 7-hydroxylamino-8-methoxy-6-acetoxymethylcoumarin-3-carboxylate, m.p. 164—165° and 116°, respectively, or vice versa. Attempts to decarboxylate (VII) failed. R. S. C.

Constituents of the bark of *Zanthoxylum Americanum* (Mill). I. Xanthoxyletin. (MISS) J. C. BELL, A. ROBERTSON, and T. S. SUBRAMANIAM (J.C.S., 1936, 627—633).—Xanthoxyletin,  $\text{C}_{14}\text{H}_{11}\text{O}_3 \cdot \text{OMe}$  (I), m.p. 133°, has been isolated and is the same compound as xanthoxylin *N* (cf. Gordin, A., 1907, i, 68). (I) is hydrolysed ( $\text{NaOH}$ ) to phloroglucinol *Me* ether (*di-p-nitrobenzoate*, m.p. 199—200°) and  $\text{COMe}_2$ , and oxidation with  $\text{KMnO}_4\text{--NaOH}$  leads to  $\alpha$ -hydroxyisobutyric acid. With  $\text{NaOH--Me}_2\text{SO}_4$ , (I) is converted into *O*-methylxanthoxyletinic acid (II), m.p. 179.9—180.5° (*Me* ester, m.p. 78.5—79.5°), an unsaturated acid. Hydrogenation ( $\text{Pd--H}_2$ ) of (I) gives dihydroxanthoxyletin, m.p. 144.5—145.5°, which with  $\text{NaOH--Me}_2\text{SO}_4$  forms *O*-methyl-dihydroxanthoxyletinic acid, m.p. 171—172°, reduced to the tetrahydro-acid, m.p. 150.5—151.5°, also obtained from (II). Ozonisation of (I) affords apoxanthoxyletin, m.p. 217—218° [*phenylhydrazone*, m.p. 251° (decomp.)]; *Ac* derivative, m.p. 151—152°, reduced ( $\text{Pd--H}_2$ ) to deoxyapoxanthoxyletin (III), m.p. 197—198°, the *Me* ether, m.p. 138—139°, of which with  $\text{Me}_2\text{SO}_4$  gives 2:4:6-trimethoxy-3-methylcinnamic acid (IV), m.p. 163—164°, reduced ( $\text{Pd--H}_2$ ) to 2:4:6-trimethoxy-3-methyldihydrocinnamic acid, m.p. 139—140°. 2-Hydroxy-4:6-dimethoxy-3-methylbenzaldehyde,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , and  $\text{NaOH}$  yield 4:6-dimethoxy-3-methylsalicylideneacyanoacetic acid, hydrolysed and cyclised to 5:7-dimethoxy-8-methylcoumarin-3-carboxylic acid, which is decarboxylated to 5:7-



*dimethoxy-8-methylcoumarin*, m.p. 187—188°. Hydrolysis and methylation of this coumarin give (IV).



Hence (III) must be either 7-hydroxy-5-methoxy- or 5-hydroxy-7-methoxy-6-methylcoumarin and (I) has the structure of type (a) or (b). F. R. S.

**Natural coumarins. XVI. Coumarins of the root of *Heracleum sphondylium*, L.** E. SPATH and A. F. J. SIMON (Monatsh., 1936, 67, 344—351).—The dried material is extracted with Et<sub>2</sub>O and the extract is washed with dil. alkali. The neutral portion remaining in the Et<sub>2</sub>O is hydrolysed, the unsaponifiable matter is removed, and ring-closure of the lactones is effected by addition of acid. The lactone mixture is separated into its components by fractional distillation in high vac. combined with suitable crystallisation. Thus are isolated *isopimpinellin*, m.p. 147—149°, *pimpinellin*, m.p. 117—119°, *isobergaptin*, m.p. 217—219°, *sphondylin* (I), C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>, m.p. 161—163°, and *sphondin* (II), C<sub>12</sub>H<sub>8</sub>O<sub>4</sub>, m.p. 189—191°. (I) and (II) contain 1 OMe and are isomeric with *bergapten*; when oxidised with H<sub>2</sub>O<sub>2</sub> they give furan-2:3-dicarboxylic acid. H. W.

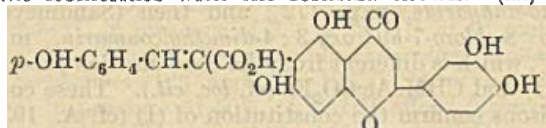
**Antiseptics and anthelmintics. II. Synthesis of 7-hydroxy-6-benzyl- and -6-*n*-hexyl-flavone.** D. R. DHINGRA, H. L. UPPAL, and K. VENKATARAMAN (Proc. Indian Acad. Sci., 1936, 3, A, 206—210).—2:4-Dihydroxydiphenylmethane (Klarman, A., 1926, 515) is converted (Hoesch) into 5-benzylresacetophenone (I), m.p. 153° (*dinitrophenylhydrazone*, m.p. 221°), benzylated to the 4-O-CH<sub>2</sub>Ph derivative, m.p. 111°, converted by PhCHO-50% NaOH into 2-hydroxy-4-benzyl-5-benzylchalcone, oxidised (SeO<sub>2</sub>-C<sub>5</sub>H<sub>11</sub>OH at 150°) to 7-benzyl-6-benzylflavone, m.p. 222°, debenzylated by HBr-AcOH to 7-hydroxy-6-benzylflavone, m.p. 267° (*Ac* derivative, m.p. 191°), also obtained together with its 3-Bz derivative, m.p. 229°, from (I) and Bz<sub>2</sub>O-NaOBz and subsequent hydrolysis with 10% KOH-EtOH. By similar reactions from α-2:4-dihydroxyphenyl-*n*-hexane are obtained 5-*n*-hexylresacetophenone, m.p. 85°, b.p. 195—200°/3—4 mm. (*dinitrophenylhydrazone*, m.p. 183—184°); 2-hydroxy-4-benzyl-5-*n*-hexylacetophenone, m.p. 94°; 2-hydroxy-4-benzyl-5-*n*-hexylchalcone, m.p. 92°; 7-benzyl-5-*n*-hexylflavone, m.p. 120°, and 7-hydroxy-6-*n*-hexylflavone, m.p. 191—192° (*Ac* derivative, m.p. 104°). J. W. B.

**Constitution of oroxylin-A, a yellow colouring matter from the root-bark of *Oroxylum indicum*, Vent.** R. C. SHAH, C. R. MEHTA, and T. S. WHEELER (J.C.S., 1936, 591—593).—Oroxvlin-A (probably identical with oroxylin; cf. Naylor and Dyer, J.C.S., 1901, 79, 954) has been isolated in 0.86% yield, and from its reactions appears to be 6-*O*-methylbaicalein (5:7-dihydroxy-6-methoxyflavone). It forms 5:7-diacetoxy-, m.p. 131—132°, and 5-hydroxy-7-benzoyloxy-6-methoxyflavone, m.p. 211°; hydrolysis with KOH gives BzOH and demethylation gives baicalein.

Monomethyloroxvlin-A corresponds in properties with 5-hydroxy-6:7-dimethoxyflavone [*platinichloride*, m.p. 185—187° (decomp.); 5-*Ac* derivative, m.p. 130—131°; 5-*Bz* derivative, m.p. 206—207°].

F. R. S.

**Fukugenetin, a rearrangement product of fukugetin.** M. MURAKAMI and T. IRIE (Bull. Chem. Soc. Japan, 1936, 11, 288—292).—Fukugetin and hot 30% aq. KOH in H<sub>2</sub> give a mixture (I) of fukugetin (II) and isofukugetin (III), m.p. > 380°, which are *cis-trans* isomerides with the formula shown. (II) and



(III) cannot be separated directly from (I), but methylation gives the *Me*<sub>6</sub> ethers, m.p. 204—206°, and (IV), m.p. 199—200°, of (II) and (III), respectively, separable by fractionation from EtOH; (IV) shows only 5 OMe by a Zeisel determination, but a sixth under the conditions used for NMe and is obtained from the *Me*<sub>5</sub> ether (V) described below by further methylation. Further, (I) and H<sub>2</sub>SO<sub>4</sub>-EtOH give (II), which is unaffected, and *anhydroisofukugetin* (VI), C<sub>24</sub>H<sub>14</sub>O<sub>8</sub>, m.p. > 380°, also obtained from pure (III); the *Ac*<sub>3</sub> derivative, m.p. 267°, is obtained from (VI) or from (I) by hot Ac<sub>2</sub>O-NaOAc, and, since (II) is isomerised to (III) by this reagent, the yield from (I) is excellent. Hydrolysis of (VI) by 10% KOH at room temp. gives (III). Methylation of (VI) gives (V), m.p. 178.5—179° (1 active H); (IV) and 10% KOH give an acid, C<sub>28</sub>H<sub>21</sub>O<sub>9</sub>, m.p. 258—260°, which proves the presence of CO<sub>2</sub>H in (II) and (III). The loss of one active H (*Ac*<sub>3</sub> derivative only) in the formation of (VI) is noted. R. S. C.

**Chromone group. XIX. Synthesis of genkwanin.** H. S. MAHAL and K. VENKATARAMAN (J.C.S., 1936, 569—570).—Condensation of 2:4:6-trimethoxyacetophenone and *p*-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me with Na at 120° affords ω-4'-benzyl-2:4:6-trimethoxyacetophenone, m.p. 101—102°, which with AlCl<sub>3</sub>-PhNO<sub>2</sub> gives only a poor yield of (I) (below). 2-Hydroxy-4:6-dimethoxyacetophenone with *p*-CH<sub>2</sub>Ph·O·C<sub>6</sub>H<sub>4</sub>·CHO and NaOH-EtOH affords 2-hydroxy-4'-benzyl-4:6-dimethoxychalcone, m.p. 159°, oxidised by SeO<sub>2</sub> in boiling C<sub>5</sub>H<sub>11</sub>OH to 4'-benzyl-5:7-dimethoxyflavone (I), m.p. 178°, converted by HCl-AcOH into genkwanin 5-*Me* ether, m.p. 298° (*Ac* derivative, m.p. 220°), partly demethylated by AlCl<sub>3</sub>-PhNO<sub>2</sub> to genkwanin (5:4'-dihydroxy-7-methoxyflavone) identical with the natural product (cf. Tseng, J. Pharm. Soc. Japan, 1935, No. 636, 30).

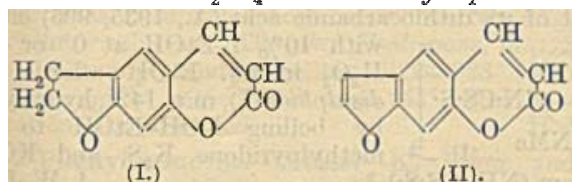
J. W. B.

**Constitution of awobanin and awobanol, the colouring matter of awobana and its co-pigment.** (Miss) C. KURODA (Bull. Chem. Soc. Japan, 1936, 11, 265—271).—Details are given for the isolation of awobanin chloride (I), +5H<sub>2</sub>O, and picrate, +5H<sub>2</sub>O (cf. A., 1935, 1290), its decomp. by cold NaOH to give *p*-coumaric acid (II), its hydrolysis by cold 20% aq. HCl to glucose and awobanin-A (III) chloride, +3H<sub>2</sub>O, and by hot acid to delphinidin chloride, and its fusion with NaOH to gallic acid

and phloroglucinol. (III) is shown to be delphinidin-3:5-diglucoside and (I) a compound of this glucoside and (II). A co-pigment, *awobanol*, isolated as *chloride*, m.p. 216° (*Ac* derivative, m.p. 148—156°), is obtained, which on NaOH fusion gives *p*-C<sub>6</sub>H<sub>4</sub>·Ac·OH and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H. R. S. C.

**Constitution of natural colouring matters, kuromanin, shisonin, and nasunin.** (Miss) C. KURODA and M. WADA (Bull. Chem. Soc. Japan, 1936, 11, 272—287).—Details are given of the isolation of kuromanin from the H<sub>2</sub>O-sol. and -insol. portions of "kuromane" from 4 sources and of the proof of its identity with chrysanthemin (cf. A., 1935, 1040). Details are given of the isolation from the leaves of "shiso" (cf. A., 1935, 674) of *shisonin-A* (I) and -B (II); (I) is proved to be a cyanin and (II) a compound thereof with *p*-coumaric acid (III). "Nasu," the fruit of *Solanum melongena*, L., var. *erculentum*, Ness, yields to MeOH-HCl *nasunin chloride* (IV), +10H<sub>2</sub>O (*picrate*, +4H<sub>2</sub>O), purified by Pb(OAc)<sub>2</sub> etc., which with cold aq. HCl gives *nasunin-A chloride* (V), decomp. 197°, and yields delphinidin chloride; these pigments are probably not identical with the awobana pigments. Probably (V) is delphinidin-3-disaccharide and (IV) contains (III) attached to the sugar nucleus. R. S. C.

**Synthesis and constitution of psoralene.** E. SPATH, B. L. MANJUNATH, M. PAILER, and H. S. JOIS (Ber., 1936, 69, [B], 1087—1090).—6-Hydroxycoumarone is hydrogenated (Pd-C in AcOH) to 6-hydroxycoumarone, m.p. 61°, which is condensed with malic acid and conc. H<sub>2</sub>SO<sub>4</sub> at 120° to *dihydropsoalene*

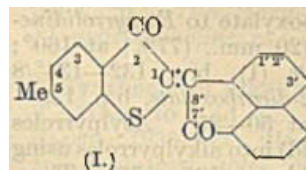


(I), m.p. 204°. Dehydrogenation of (I) with Pd-sponge at 170° gives psoralene (II), m.p. 171°, identical with the natural substance. Methylation, oxidation, and renewed methylation of (II) gives Me<sub>2</sub> 2:4-dimethoxybenzene-1:5-dicarboxylate, m.p. 147—148°, thus confirming the assigned structure. H. W.

**Partial oxidation of metathioxen.** I. J. RINKES (Rec. trav. chim., 1935, 54, 940—942).—The conclusion of Steinkopf *et al.* (A., 1935, 354) that partial oxidation of metathioxen (I) gives 2-thiotolen-4-carboxylic acid is criticised. Repetition of the prep. of the acid there described as 4-bromo-3-methylthiophen-5-carboxylic acid, m.p. 195°, gave 4-bromo-3-methylthiophen-*x*-carboxylic acid, m.p. 219—220° (*Me* ester, m.p. 76°, which regenerates the acid on hydrolysis), reduced by Na-Hg to 3-methyldihydrothiophen-*x*-carboxylic acid, m.p. 79° (cf. *loc. cit.*). The author maintains that the *α*-Me is converted into CO<sub>2</sub>H in the partial oxidation of (I) (cf. A., 1934, 81). H. G. M.

**Dyes derived from acenaphthenequinone.** 5-Methyl-1:8'-thionaphthenacenaphthenyl-indigos. S. K. GUHA (J. Indian Chem. Soc., 1936, 14, 94—97).—2-Hydroxy-5-methylthionaphthen with acenaphthenequinone and its derivatives in AcOH-

conc. HCl gives 5-methyl-1:8'-thionaphthenacenaphthenylindigo (I), m.p. 305°, and its 3'-Cl-, m.p. 297°, 3'-Br-, m.p. 302°, and 1'-OMe-, m.p. 300° (softens at 298°), derivatives. These dye wool (from acid bath) and cotton (from Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> vat) with lighter shades (of red) than the isomeric 4-Me compounds (A., 1934, 534). H. B.



**Bimolecular reduction of thioindigotindisulphonate.**—See this vol., 800.

**Phenoxthionine. I. Comparison of directive influences of oxygen and sulphur.** C. M. SUTER, J. P. MCKENZIE, and C. E. MAXWELL (J. Amer. Chem. Soc., 1936, 58, 717—720).—Phenoxthionine (I), m.p. 57.5—58°, obtained (cf. Ferrario, A., 1911, i, 555) from Ph<sub>2</sub>O (10.4 mols.), S (8 mols.), and AlCl<sub>3</sub> (3.84 mols.) at 100° in 67—72% yield, with Br in CCl<sub>4</sub> gives the 2-Br-derivative (II), m.p. 59—60° (which could not be prepared from *p*-C<sub>6</sub>H<sub>4</sub>Br·OPh and S), and then the 2:8-Br<sub>2</sub>-derivative, m.p. 92—93° [oxidised (30% H<sub>2</sub>O<sub>2</sub>, AcOH) to the 10:10-dioxide (III), m.p. 185—186°]. 4:4'-Dibromodiphenyl ether (IV) and ClSO<sub>3</sub>H (1 mol.) in CCl<sub>4</sub> followed by H<sub>2</sub>O give the 2-sulphonic acid (*Na* salt), the *chloride*, m.p. 128—129°, of which with AlCl<sub>3</sub> in *s*-C<sub>2</sub>H<sub>5</sub>Cl<sub>4</sub> affords (III). (IV) and an excess of ClSO<sub>3</sub>H give the 2:2'-disulphonyl chloride, m.p. 241—243°, hydrolysed to the disulphonic acid (*Na* salt). (I), AcCl, and AlCl<sub>3</sub> in CS<sub>2</sub> afford 2-acetylphenoxthionine, m.p. 111—112° (phenylhydrazone, m.p. 93.5—94.5°; oxime, m.p. 142—143°), oxidised (CaOCl<sub>2</sub>, dil. NaOH) to phenoxthionine-2-carboxylic acid, m.p. 260—262°, which was also obtained (in 8% yield) from the Grignard reagent (prepared only once) from (II) and CO<sub>2</sub>. 2-Benzoyl-, m.p. 96—97°, and 2:8-dibenzoyl-, m.p. 197°, -phenoxthionines are prepared from (I), BzCl (1 mol.), and AlCl<sub>3</sub> in CS<sub>2</sub>. (I) with 1 and 4 mols. of ClSO<sub>3</sub>H in CCl<sub>4</sub> gives phenoxthionine-2-sulphonic acid (*Na* salt; *chloride*, m.p. 127—128°; *amide*, m.p. 177—178°) and -2:8-disulphonic acid [*Na* and *Ag* salts; *chloride* (V), m.p. 142—143°, also obtained directly from (I) and ClSO<sub>3</sub>H], respectively. (V) heated with PCl<sub>5</sub> affords a little of (probably) 2:8-dichlorophenoxthionine, m.p. 134—135° (Hilditch and Smiles, J.C.S., 1911, 99, 408). In all the above reactions with (I), O has a greater directive influence than S. Contrary to Ferrario (*loc. cit.*), (I) could not be converted into diphenylene oxide by Cu at 250° or 285—290°. H. B.

**Reactions of hydrogen with derivatives of pyrrole.** F. K. SIGNAIGO and H. ADKINS (J. Amer. Chem. Soc., 1936, 58, 709—716).—Pyrroles are more resistant to hydrogenation [H<sub>2</sub> (usually 200—300 atm.); Raney Ni or Cu-Cr oxide; EtOH, dioxan, methylcyclohexane, or no solvent] than any of the unsaturated ring compounds hitherto examined; reduction is, however, facilitated by an *N*-substituent (*e.g.*, Ph, CO<sub>2</sub>Et). The following reductions are done with Ni: pyrrole to pyrrolidine (47% yield) at 180°; 3:5-dimethyl-2:4-diethylpyrrole to 3:5-dimethyl-2:4-diethylpyrrolidine, b.p. 186—188°, (70%) at 180°; 1-phenylpyrrole to 1-phenyl- (63%) and 1-cyclohexyl-



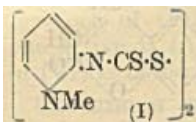
pyrrolidine (30%) at 135° (0 and 84%, respectively, at 180°); Et pyrrole-1-carboxylate to Et pyrrolidine-1-carboxylate, b.p. 98—99°/20 mm., (77%) at 160°; Et pyrrole-1:2-dicarboxylate (I), b.p. 132—134°/8 mm., to Et pyrrolidine-1:2-dicarboxylate, b.p. 133—134°/7.5 mm., (97—98%) at 50—85°. Acylpyrroles are converted (65—95% yield) into alkylpyrroles using Ni or (usually) Cu—Cr oxide at 135—175°. Thus, Et 4-acetyl-3:5-dimethylpyrrole-2-carboxylate gives Et 3:5-dimethyl-4-ethylpyrrole-2-carboxylate; Et and Bu<sup>r</sup>, m.p. 154—155° (prep. as A., 1933, 1303). *o*-acetyl-2:4-dimethylpyrrole-3-carboxylate afford Et and Bu<sup>r</sup> (II), m.p. 128—129°, 2:4-dimethyl-5-ethylpyrrole-3-carboxylate, respectively; Et 5-benzoyl-2:4-dimethylpyrrole-3-carboxylate furnishes Et 5-benzyl-2:4-dimethylpyrrole-3-carboxylate (III), m.p. 119—121°; 2:4-diacetyl-3:5-dimethylpyrrole (IV) (prep. as *loc. cit.*) yields 3-acetyl-2:4-dimethyl-*o*-ethylpyrrole, m.p. 157—158°, which then gives 3:4-dimethyl-2:4-diethylpyrrole. *C*-Carbomethoxypyrroles undergo hydrogenolysis to the methylpyrroles with Cu—Cr oxide at 210—225°; further reduction to the methylpyrrolidines may then occur (with 3-CO<sub>2</sub>Et, but not 2-CO<sub>2</sub>Et, reduction precedes hydrogenolysis). Thus, Et 3:5-dimethyl-4-ethylpyrrole-2-carboxylate (V) gives 2:4:5-trimethyl-3-ethylpyrrole (VI) (30%) and -pyrrolidine (VII) (15%); Et 3:5-dimethylpyrrole-2:4-dicarboxylate (VIII) affords (according to H<sub>2</sub> absorbed) Et 2:4:5-trimethylpyrrole-3-carboxylate (IX) (33—55%) and 2:3:4:5-tetramethylpyrrole (X) (trace—13%) and -pyrrolidine (XI) (5—25%); (IX) furnishes (X) (2%) and (XI) (33%); Et 2:4-dimethyl-5-ethylpyrrole-3-carboxylate (XII) yields 3:4:5-trimethyl-2-ethylpyrrolidine (XIII), b.p. 147—151° (30%); Et 4-acetyl-3:5-dimethylpyrrole-2-carboxylate gives (V) (36%), (VI) (23%), and (VII) (29%); (I) affords 2-methylpyrrole (42%). Reduction of the above esters is also accompanied by *N*-ethylation (with EtOH produced during hydrogenolysis); this is better accomplished by reduction at (usually) 250° with Ni or Cu—Cr oxide in EtOH. Thus, Et pyrrole-2-carboxylate furnishes 1-ethyl- (10%; Ni) or 2-methyl-1-ethylpyrrolidine, b.p. 119—120° (90%; Cu); (XII) yields (XIII) (0—35%) and 3:4:5-trimethyl-1:2-diethylpyrrolidine, b.p. 183—184° (35—88%); (V) gives (according to H<sub>2</sub> consumed and catalyst) (VII) (0—8%), 4:5-dimethyl-1:3-diethyl- (37%), and 2:4:5-trimethyl-1:3-diethylpyrrolidine, b.p. 184—185° (37—80%); (VIII) affords 2:3:4:5-tetramethyl-1-ethylpyrrolidine, b.p. 163—165° (70%); (III) furnishes 3:4:5-trimethyl-1-ethyl-, b.p. 52—55°/23 mm. (17%) (hydrochloride), and 2-benzyl-3:4:5-trimethyl-1-ethylpyrrolidine, b.p. 139—141°/12 mm. (52%); (II) yields (XIII) (80%) (*N*-ethylation does not occur); (IV) gives 3:5-dimethyl-1:2:4-triethylpyrrolidine, b.p. 200—201° (50%); Et pyrrole-1-carboxylate affords 1-methyl- (27%) and 1-ethyl- (37%) -pyrrolidines. Further reduction [Cu—Cr oxide, EtOH, 200—250°, H<sub>2</sub> (varying amounts)] of Et pyrrolidine-1:2-dicarboxylate gives 2-methyl-1-ethyl- (XIV) (2—27%) and 1-ethyl-2-hydroxymethylpyrrolidine (XV), b.p. 82—84°/24 mm. (23—34%), and Et 2-hydroxymethylpyrrolidine-1-carboxylate, b.p. 134—135°/8 mm. (0—62%) [also reduced further to

(XIV) (7%) and (XV) (32%)]. Much better yields of many of the above compounds are obtained by hydrogenolysis than by other methods. H. B.

**Interaction of alkyl chlorosulphates and pyridine in ethereal solution.** W. GERRARD (J.C.S., 1936, 688—691).—When an alkyl chlorosulphate, RO·SOCl, is mixed with C<sub>5</sub>H<sub>5</sub>N in Et<sub>2</sub>O, an oily mixture of 1-alkylpyridinium chloride and 1-alkylpyridinium chlorosulphate separates in quantity, leaving in the Et<sub>2</sub>O about a 40% yield of alkyl chloride. With 1 mol. of chlorosulphate per mol. of C<sub>5</sub>H<sub>5</sub>N, nearly one third of the base remained in the Et<sub>2</sub>O, but with 0.5 mol. of the base, no C<sub>5</sub>H<sub>5</sub>N remained in the Et<sub>2</sub>O, and the yield of alkyl chloride was somewhat larger. Two mechanisms for the reaction are suggested. The isolation and identification of the alkylpyridinium compounds have been effected through the ferrocyanides, (C<sub>5</sub>H<sub>5</sub>NR)<sub>2</sub>H·Fe(CN)<sub>6</sub>·2H<sub>2</sub>O: ferrocyanide; R=Me; Et m.p. 150—151° (decomp.); Pr, m.p. 143° (decomp.); Bu, decomp. 165°; isoamyl; Pr<sup>β</sup>, decomp. 145°; Bu<sup>β</sup>, decomp. 150°; derivatives of C<sub>5</sub>H<sub>5</sub>NR: R=Me, picrate, m.p. 109°, aurichloride, m.p. 247°; Et, picrate, m.p. 89°, aurichloride, m.p. 141—142°, platinichloride, m.p. 201°; Pr, aurichloride, m.p. 128°; Bu, platinichloride, m.p. 202°, aurichloride, m.p. 117°; isoamyl, platinichloride, m.p. 203°, aurichloride, m.p. 139°; Pr<sup>β</sup>, aurichloride, m.p. 144°; and Bu<sup>β</sup>, aurichloride, m.p. 139—140°.

F. R. S.

***N*-Methylpyridinethiouram disulphide.** K. S. TOPTSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 115—118).—Oxidation of the methylpyridoneimide salt of its dithiocarbamic acid (A., 1935, 995) either with 10% I-EtOH at 0° or 3% H<sub>2</sub>O<sub>2</sub> in aq. EtOH affords the disulphide (I), m.p. 142°, hydrolysed by boiling KOH-EtOH to *N*-methylpyridone, K<sub>2</sub>S, and KCNS [from (NH<sub>2</sub>·CS·S)<sub>2</sub>].



J. W. B.

**Nicotinamide methiodide.** P. KARRER and O. WARBURG (Biochem. Z., 1936, 285, 297—298).—The hydrochloride, m.p. 233°, of the iminoethyl ether, the methylamide, m.p. 100°, the *N*-methylamidine, decomp. 235°, and the methoxymethochloride of the amide of nicotinic acid do not react (at *p*<sub>H</sub> 8 and room temp.) with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>; glucosido-1-pyridinium iodide reacts slowly yielding a substance not identical with reduced H-transporting co-enzyme (I). The methiodide of nicotinamide (II) reacts as quickly as does (I) yielding a substance identical with reduced (I). (I) contains 13.3% of (II).

W. McC.

**Synthesis in the indole group.** XV. **Synthesis of bufotenin methyl ether (5-methoxy-*NN*-dimethyltryptamine) and bufotenin.** T. HOSHINO and K. SHIMODAIRA (Bull. Chem. Soc. Japan, 1936, 11, 221—224).—Bufotenin Me ether (I) is synthesised in a manner similar to that used for its Et ether (A., 1935, 1378). 5-Methoxy-3-indolylacetic acid, m.p. 146—147° (from the nitrile), gives its Et ester, b.p. 202—203°/4 mm., m.p. 97—98°, reduced to 5-methoxytryptophol, b.p. 194°/4 mm. (picrate, m.p. 117—118°), from which are obtained 5-methoxy-3-β-bromoethylindole and 5-methoxy-*NN*-dimethyltryptamine (I), m.p. 66—67° [picrate, m.p. 176—177°; mono-,

m.p. 170—171°, and *di-picrate*, m.p. 103—104° (lit. m.p. 84°), of the methiodide], demethylated by  $\text{AlCl}_3$  to bufotenin. When heated with  $\text{MeI-EtOH}$ -anhyd.  $\text{Na}_2\text{CO}_3$  5-methoxytryptamine affords the methiodide of (I), converted by  $\text{AgCl}$  into the *methochloride*, m.p. 144°, which gives (I) when heated at 240—250°.

J. W. B.

**Stereoisomerism of 6-methyldecahydroquinoline.** S. FUJISE and M. IWAKIRI (Bull. Chem. Soc. Japan, 1936, 11, 293—294).—Reduction of 6-methylquinoline ( $\text{PtO}_2\text{-H}_2$  in  $\text{AcOH}$ , 50°) affords *trans*-(I), m.p. 68—69°, b.p. 211.5—212° (*hydrochloride*, m.p. 265°; *hydrobromide*, m.p. 244—245°; *aurichloride*, m.p. 117—119°; *platinichloride*, m.p. 171.5—172.5°; *Bz*, m.p. 95—99°, and *p-nitrobenzoyl*, m.p. 124.5—125°, derivatives), and *cis*-6-methyldecahydroquinoline, b.p. 212—212.5° [*hydrochloride*, m.p. 263—264°; *hydrobromide*, m.p. 252—253°; *aurichloride*, m.p. 152—153°; *platinichloride*, m.p. 230° (decomp.); *p-nitrobenzoyl*, m.p. 138—139°, and liquid *Bz* derivative]. Resolution of (I) with *d*-bromocamphorsulphonic acid gives the *d-trans*-form, m.p. 92—93°,  $[\alpha]_D^{25} +4.8^\circ$  in  $\text{EtOH}$ . The reduced 6-methylquinoline, m.p. 44° (Finger *et al.*, A., 1909, i, 512), must be impure (I).

J. W. B.

**4-Hydroxyquinoline-3-aldehyde.** Preparation of 4-hydroxyquinoline (*kynurine*). B. BOBRANSKI (Ber., 1936, 69, [B], 1113—1117).—4-Hydroxyquinoline (prep. from quinoline through the oxide and 4-chloroquinoline described) is converted by  $\text{NaOH}$  and  $\text{CHCl}_3$  into 4-hydroxyquinoline-3-aldehyde, m.p. 273° (decomp.), in about 10% yield. It is a very weak base which does not reduce  $\text{NH}_3\text{-Ag}_2\text{O}$  or Fehling's solution. The *phenylhydrazone*, m.p. 244—245° (decomp.), and *oxime*, m.p. 222—223° (decomp.) when rapidly heated and m.p. 241° after re-solidification, are described.

H. W.

**2-Phenylquinoline series.** K. FEIST and M. KUKLINSKI (Arch. Pharm., 1936, 274, 310—315; cf. this vol., 735).—The  $\text{NH}_2$  of 4-amino-2-phenylquinoline (I) is relatively unreactive. (I) and  $\text{NH}_4\text{CNS}$  in very dil.  $\text{HCl}$  give the *thiocarbamide*, m.p. 277°, but  $\text{C}_3\text{H}_5\text{-CNS}$  and  $\text{PhCNS}$  give only poor yields of *allyl*-, m.p. 279°, and *phenyl-carbamide*, derivatives, m.p. 150°. (I),  $\text{S}$ , and  $\text{NaOH}$  in hot  $\text{CS}_2\text{-EtOH}$  give only a little 2-phenylquinolyl-4-thiourethane, m.p. 151°, and probably  $\text{H}_2\text{S}$ ; 6-amino-2-methylpyridine gives mainly *thiocarbamide* with a little thiourethane. (I) and the aldehyde, when melted together, afford the *o-methoxybenzylidene*, m.p. 136° and *salicylidene* derivative (II), m.p. 138°, but *o*- (III) and *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-CHO}$  (IV) and *p*- $\text{NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$  do not react. (II) yields ( $\text{H}_2\text{-Pd-black}$  in  $\text{Et}_2\text{O}$ ) 4-benzylamino-2-phenylquinoline, m.p. 204°. (I) also does not react with (III), (IV),  $\text{PhCHO}$ ,  $\text{o-OH-C}_6\text{H}_4\text{-CHO}$ , or piperonal in anhyd.  $\text{HCO}_2\text{H}$ .

R. S. C.

**Catalytic dehydrogenation of 3-phenyltetrahydroisoquinolines.** B. REICHERT and W. HOFFMANN (Arch. Pharm., 1936, 274, 281—283).—6:8-Methylenedioxy-3-phenyl- and -3:4':5'-methylenedioxyphenyl-, 6-methoxy- and 6:7-dimethoxy-3-phenyl-1:2:3:4-tetrahydroisoquinoline are quantitatively dehydrogenated by 10—25% of  $\text{Pd-black}$

at 170—210°, the reaction being favoured by the 3-Ph. 6:7-Dimethoxy-, m.p. 128°, and 6-methoxy-3-phenylisoquinoline, m.p. 101°, are described.

R. S. C.

**Synthesis of alkoxy- and hydroxy-carbazoles.** T. HOSHINO and K. TAKIURA (Bull. Chem. Soc. Japan, 1936, 11, 218—220).—Dehydrogenation of tetrahydrocarbazoles, prepared by Borsche's method (A., 1908, i, 365), is best effected with  $\text{Pd-black-CHPh:CH-CO}_2\text{H}$  at 150—200°, and thus are obtained carbazole, 3-ethoxy-, m.p. 106—107° (converted by  $\text{NH}_2\text{Ph.HCl}$  at 220° in  $\text{CO}_2$  into 3-hydroxy-, m.p. 256—257°), 7-ethoxy-1:2:3:4-tetrahydro-, m.p. 120°, 2-ethoxy-, m.p. 216—217°, converted into 2-hydroxy-, m.p. 273—274°, -carbazole. *cycloHexanone-p*-phenetylhydrazine has m.p. 77° and 6-ethoxy-1:2:3:4-tetrahydrocarbazole, m.p. 105—106° (*loc. cit.*, m.p. 87—88°).

J. W. B.

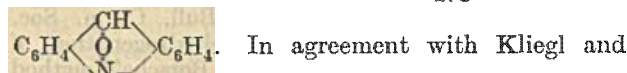
**4:5-Di-m-aminophenylcarbazole.** S. SAKO (Bull. Chem. Soc. Japan, 1936, 11, 144—157).—3-Nitro-2-acetamidodiphenyl with  $\text{H}_2\text{SO}_4\text{-HNO}_3$  (*d* 1.52)  $< 2^\circ$  gives its 4'- $\text{NO}_2$ -derivative, m.p. 207.5°, hydrolysed (boiling  $\text{EtOH-conc. HCl}$ ) to 3:4'-dinitro-2-amino-, m.p. 196—197° (oxidised to *p*- $\text{CO}_2\text{H-C}_6\text{H}_4\text{-NO}_2$ ), converted through its diazo-compound into 2-iodo-3:4'-dinitro-, m.p. 139—140°, and reduced by  $\text{Na}_2\text{S-aq. EtOH}$  to 3-nitro-2:4'-diamino-diphenyl, m.p. 156—157°, converted by  $\text{Ac}_2\text{O-C}_6\text{H}_6$  into its 4'-*Ac* derivative, m.p. 174—175°, converted (Sandmeyer) into the 4'-*Ac* derivative, m.p. 239°, of 2-iodo-3-nitro-4'-aminodiphenyl (I), m.p. 126—127° [*hydrochloride*; *p*-toluenesulphonyl derivative (II), m.p. 136—137°], which is obtained by hydrolysis with  $\text{EtOH-conc. HCl}$ . Addition of (I) to  $\text{HNO}_3$  (*d* 1.456, essential) at 0° affords 2-iodo-3:3':5'-dinitro-4'-acetamidodiphenyl, m.p. 196—197°, hydrolysed to the 4'- $\text{NH}_2$ -compound (III), m.p. 178—178.5°. (I) with  $\text{HNO}_3$  (*d* 1.52) gives the 3:3':5'-( $\text{NO}_2$ )<sub>3</sub> derivative, m.p. 263—264°, hydrolysed to 2-iodo-3:3':5'-trinitro-4'-aminodiphenyl, m.p. 220—221°, also obtained by nitration of (II) and subsequent hydrolysis. Deamination of (III) by the diazo-reaction affords 2-iodo-3:3'-dinitrodiphenyl, m.p. 130—131°, b.p. 239°/6 mm., converted by  $\text{Cu}$  powder at 190—195° into 2:2'-dinitro-6:6'-di-m-nitrophenyl-, m.p. 259.5—260°, reduced ( $\text{SnCl}_2\text{-AcOH-HCl}$ ) to 2:2'-diamino-6:6'-di-m-aminophenyl-diphenyl, m.p. 169—170°, converted by 0.5*N*- $\text{HCl}$  ( $\text{N}_2$  atm.) at 200—205° into 4:5-di-m-aminophenylcarbazole (IV), softens 175°, m.p. 180—182° [*dihydrochloride*,  $+2\text{H}_2\text{O}$ ;  $\text{Ac}_2$ , m.p. 257—258°, and *di-l-menthoxyacetyl* derivative (V), m.p. 190—191°,  $[\alpha]_D^{25} -22.27^\circ$  in  $\text{EtOH}$ ,  $+14.2^\circ$  in  $\text{C}_6\text{H}_6$ ]. Spatial considerations suggest that (IV) should exist in *cis*- and *trans*-forms, the latter being resolvable, but attempts to resolve (IV) with *d*-camphorsulphonic acid or *d*-tartaric acid failed, and hydrolysis of the *l*-menthoxyacetyl group from (V) was unsuccessful.

J

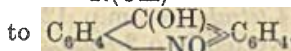
**Acridine. XIII. *ms*-Acridine derivatives.** IV. "Acridol" and the tautomerism, *N*-hydroxyacridone-5-hydroxyacridine 10-oxide. K. LEHMSTEDT and H. KLEE (Ber., 1936, 69, [B], 1155—1158; cf. A., 1935, 1251).—Acridine *N*-oxide identical



with "acridol" is converted by  $\text{NaHSO}_3$  and  $\text{HCN}$  into acridine (I) and 5-cyanoacridine, respectively; since in these reactions it behaves similarly to (I) it must be formulated  $\text{C}_6\text{H}_4\langle\text{CH}\rangle\text{C}_6\text{H}_4$  not



In agreement with Kliegl and Brosamle (this vol., 343) the hydroxyacridone of Kliegl and Fehrle (A., 1914, i, 867) is regarded as  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4$  which can become tautomerised



H. W.

**Synthesis of substituted acridines as possible antimalarials.** G. R. CLEMO and W. HOOK (J.C.S., 1936, 608—609).—The *p*-toluenesulphonamide of 1-methylamino-5:10-dihydroacridine, m.p. 170°, is hydrolysed ( $\text{H}_2\text{SO}_4$ ) to 1-methylaminoacridine, m.p. 75°. 1-( $\beta$ -Diethylaminoethyl)aminoacridine, b.p. 180°/1 mm. [dipicrate, m.p. 192°; monopicrate, m.p. 151°; dihydrochloride (+2 $\text{H}_2\text{O}$ ), m.p. 104°], is obtained from 1-aminoacridine,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{N}(\text{Et})_2\cdot\text{HCl}$ , and  $\text{NaOAc}$ , and also by hydrolysing the *p*-toluenesulphonamide of 1-( $\beta$ -diethylaminoethyl)amino-5:10-dihydroacridine, m.p. 88°.  $\alpha$ -Diethylamino- $\delta$ -hydroxypentane and  $\text{SOCl}_2$ , followed by  $\text{NaOH}$  give  $\delta$ -chloro- $\alpha$ -diethylaminopentane (methiodide, m.p. 116°), which is isomerised to a solid [picrate, m.p. 270° (decomp.)]. 1-Aminoacridine (monopicrate, m.p. 220°), *p*-nitrobenzyl bromide, and  $\text{NaOAc}$  give 1-(*p*-nitrobenzyl)-aminoacridine, m.p. 170°, reduced to the 1-*p*- $\text{NH}_2$ -compound [dihydrochloride (+2 $\text{H}_2\text{O}$ ), m.p. 168°; dipicrate, m.p. 178° (decomp.)]. F. R. S.

**Manufacture of acridine derivatives [pharmaceuticals].**—See B., 1936, 524.

**Creatinine derivatives.** II. W. R. CORNTHWAITE, S. LAZARUS, R. H. SNELLINGS, jun., and C. E. DENOON, jun. (J. Amer. Chem. Soc., 1936, 58, 628—629; cf. A., 1935, 352).—Creatinine and the appropriate  $\text{RCHO}$  at 150—180° give 5-*o*- (I), m.p. 241°, and -*p*-, m.p. 248—249° (decomp.), -*anisylidene*-, 5-*o*-ethoxybenzylidene- (II), m.p. 236° (decomp.), 5-*p*-hydroxybenzylidene-, m.p. 289° (cf. Deulofeu and Mendivelzua, A., 1935, 850), 5-*p*-tolylidene- (III), m.p. 285° (decomp.), 5-*o*-chlorobenzylidene- (IV), m.p. 242° (decomp.; sealed tube), 5-*p*-piperonylidene- (V), m.p. 274° (decomp.; sealed tube), and 5- $\gamma$ -phenylpropylidene-, m.p. 225—230°, -*creatinine*. (I)—(V) are accompanied by products, m.p. 292°, 297°, 309°, 270°, and 327°, respectively, which are (probably) triarylidenecreatinines; that from *o*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  is also produced from (II) and an excess of the aldehyde at 175°. H. B.

**Tertiary alkylbarbituric acids.** A. W. DOX and W. G. BYWATER (J. Amer. Chem. Soc., 1936, 58, 731—732).— $\text{CHBu}^t(\text{CO}_2\text{Et})_2$ , b.p. 205—210°/750 mm. [obtained in 6.4% yield from  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and  $\text{Bu}^t\text{Br}$  in  $\text{EtOH}$  at 5°—room temp.], and  $\text{CEtBu}^t(\text{CO}_2\text{Et})_2$ , b.p. 244—248° [formed in 3.8% yield from  $\text{CHEt}(\text{CO}_2\text{Et})_2$  (I),  $\text{Bu}^t\text{Br}$ , and  $\text{Na}$  powder in dry  $\text{PhMe}$ ], with  $\text{CO}(\text{NH}_2)_2$  in  $\text{EtOH}\text{--NaOEt}$  give 5-*tert*-butyl- (II), m.p. 230—231°, and impure

5-ethyl-5-*tert*-butyl- (III), m.p. 191.5—192.5°, -*barbituric acid*, respectively. 5-Ethyl-5-*tert*-amylbarbituric acid (IV), m.p. 196.5—197.5°, is similarly prepared from  $\text{Et}$  ethyl-*tert*-amylmalonate, b.p. 93—96°/1.5 mm. [formed in 4.6% yield from (I), *tert*-amyl bromide, and  $\text{EtOH}\text{--NaOEt}$  at room temp.]. Contrary to expectation, (III) and (IV) are not more active than the isomeric 5-*sec*-alkyl derivatives. (II) is inactive. H. B.

**Nitrogen-substituted barbituric acids.** D. NIGHTINGALE and C. H. ALEXANDER (J. Amer. Chem. Soc., 1936, 58, 794—796).—1-Aryl- and 1:3-diarylbarbituric acids are prepared from  $\text{CH}_2(\text{COCl})_2$  and  $\text{NH}_2\cdot\text{CO}\cdot\text{NHar}$  or  $\text{CO}(\text{NHar})_2$  (Whiteley, J.C.S., 1907, 91, 1330); their 5:5-di-*p*-nitrobenzyl derivatives are obtained by Lyons and Dox's method (A., 1929, 453), whilst the 5-anilinomethylene derivatives, which are recommended for identification, are formed from the acids and  $\text{NHPh}\cdot\text{CH}\cdot\text{NPh}$  in  $\text{EtOH}$ . The following are described: 1-phenyl- (5-cinnamylidene, decomp. 271°, 5:5-di-*p*-nitrobenzyl, m.p. > 295°, and 5-anilinomethylene, m.p. 271°, derivatives); 1-*p*-tolyl-, m.p. 244° (5-cinnamylidene, decomp. 275°, 5:5-di-*p*-nitrobenzyl, m.p. 245°, and *o*-anilinomethylene, m.p. 290°, derivatives); 1-*p*-phenetyl-, m.p. 211° (5-cinnamylidene, decomp. 258°, 5:5-di-*p*-nitrobenzyl, m.p. 240°, and 5-anilinomethylene, m.p. 248°, derivatives); 1:3-diphenyl- (5:5-di-*p*-nitrobenzyl, m.p. > 300°, and 5-anilinomethylene, m.p. 228°, derivatives); 1:3-di-*o*-tolyl-, m.p. 171° (5-cinnamylidene, decomp. 223°, 5:5-di-*p*-nitrobenzyl, m.p. > 300°, and *o*-anilinomethylene, m.p. 198°, derivatives); 1:3-di-*p*-tolyl-, m.p. 213° (5-cinnamylidene, decomp. 260°, 5:5-di-*p*-nitrobenzyl, m.p. > 300°, and 5-anilinomethylene, m.p. 258°, derivatives); 1:3-di-*p*-phenetyl-, m.p. 167° (5-anilinomethylene derivative, m.p. 207°); 1:3-diphenyl-2-thio- (5-anilinomethylene derivative, m.p. > 300°), and 1:3-di-*o*-tolyl-2-thio-barbituric acid, m.p. 217° (5-cinnamylidene, decomp. 248°, and 5-anilinomethylene, m.p. 237°, derivative). H. B.

**Synthesis of glyoxaline derivatives from  $\alpha$ -amino-acids.** III. Synthesis of two homologues of histamine. S. AKABORI and T. KANEKO. IV. Synthesis of histamine. S. AKABORI and S. NUMANO (Bull. Chem. Soc. Japan, 1936, 11, 208—213, 214—217).—III. Reduction of arginine  $\text{Et}$  ester dihydrochloride with  $\text{Na}\text{--Hg}\text{--EtOH}\text{--}5N\text{--HCl}$  at  $-12^\circ$  to  $-17^\circ$  and treatment of the product with  $\text{NH}_4\text{SCN}$  affords 2-thiol-5- $\gamma$ -guanidinopropylglyoxaline hydrochloride (I), m.p. 236.5—237.5° (decomp.), converted by aq.  $\text{FeCl}_3$ -phosphotungstic acid into 5- $\gamma$ -guanidinopropylglyoxaline [picrate, m.p. 258° (decomp.); flavianate, m.p. 248° (decomp.)], isolated as its dinitrate (II), m.p. 183.5—184° (decomp.). Hydrolysis of (I) with  $\text{Ba}(\text{OH})_2$  gives 2-thiol-5- $\gamma$ -aminopropylglyoxaline (not isolated), converted by  $\text{FeCl}_3$ -phosphotungstic acid into 5- $\gamma$ -aminopropylglyoxaline (III), isolated as its picrate, m.p. 244—244.5° (decomp.), also obtained by hydrolysis of (II). Similarly lysine  $\text{Et}$  ester dihydrochloride is converted successively into 2-thiol-5- $\delta$ -amino-*n*-butyl-, m.p. 220.5—221.5° (decomp.) [hydrochloride, m.p. 212—214° (decomp.)]; picrate, m.p. 154—155° (decomp.)], and 5- $\gamma$ -amino-*n*-butyl-glyoxaline (IV), b.p. 204°/6 mm.,

m.p. 51—53° [oxalate, m.p. 168.5—170° (decomp.); picrate, m.p. 197.5—198.5° (decomp.)]. The physiological action (non-pregnant dogs) of (III) is <, and that of (IV), that of histamine (V).

IV. *Et hydantoinpropionate*, m.p. 78—82°, is converted through the *hydrazide*, m.p. 164—167°, *azide*, decomp. 69—70°, into *Et β-hydantoinylethylcarbamate*, m.p. 82—88°, hydrolysed by Ba(OH)<sub>2</sub> to α-diaminobutyric acid hydrochloride, the *Et* ester, m.p. 173—175° (decomp.), of which is converted as above into 2-thiolhistamine hydrochloride, m.p. 245.5—247°, and (V).  
J. W. B.

**Ethylene oxamide (2 : 3-diketopiperazine).** J. VAN ALPHEN (Rec. trav. chim., 1935, 54, 937—939).—2 : 3-Diketopiperazine (I), m.p. 285°, is obtained when Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and ethylenediamino hydrate [corresponding dioxalate, m.p. 207° (decomp.)] are added very gradually to much abs. EtOH (cf. lit.). In H<sub>2</sub>O they give β-aminoethyloxamic acid, m.p. about 320° (decomp.). (I) forms the 1 : 4-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. about 150° (decomp.).  
H. G. M.

**Pyrimidines.** (A) Molecular rearrangement of 2-ethylthiol-6-thiocyano-4 : 5-dimethylpyrimidine. (B) Synthesis of 4 : 5-dimethylcytosine. Y. F. CHI and Y. S. KAO. (C) Molecular rearrangement of 2-ethylthiol-6-thiocyano-4-phenylpyrimidine. Y. F. CHI, Y. S. KAO, and Y. T. HUANG (J. Amer. Chem. Soc., 1936, 58, 769—771, 772, 773—774; cf. A., 1934, 85).—(A) 6-Hydroxy-4 : 5-dimethyl-2-thiopyrimidine (I), m.p. 279—280° [from CS(NH<sub>2</sub>)<sub>2</sub> and CHMeAc·CO<sub>2</sub>Et in EtOH-NaOEt], with EtI, MeI, and CH<sub>2</sub>Cl·CO<sub>2</sub>Et in EtOH-NaOEt gives 2-ethylthiol- (II), m.p. 155—156°, 2-methylthiol-, m.p. 225—227°, and 2-carbethoxymethylthiol-, m.p. 132—133° [and thence 2-carboxymethylthiol- (+H<sub>2</sub>O), m.p. 128—129°], 4 : 5-dimethyluracil, respectively. 4 : 5-Dimethyluracil, m.p. 294—296°, is obtained from (I) and aq. CH<sub>2</sub>Cl·CO<sub>2</sub>H or from (II) and aq. HBr. (II) and POCl<sub>3</sub> give 6-chloro-2-ethylthiol-4 : 5-dimethylpyrimidine (III), b.p. 142—144°/10 mm., which with KCNS in EtOH affords 2-ethylthiol-6-thiocyano-4 : 5-dimethylpyrimidine (IV), b.p. 160°/1.5 mm., m.p. 64.5—65.5°, converted by SH·CH<sub>2</sub>·CO<sub>2</sub>H into 2-ethylthiol-4 : 5-dimethyl-6-thiopyrimidine, m.p. 187—188° [also formed from (III) and NaHS]. (IV) heated in xylene for 20 hr. at the b.p. rearranges partly into 2-ethylthiol-6-thiocarbimido-4 : 5-dimethylpyrimidine (V), b.p. 150—152°/1.5 mm., m.p. 29.5—30°, which with NH<sub>2</sub>Ph and conc. aq. NH<sub>3</sub> in light petroleum gives the 6-phenylthiocarbimido-, m.p. 139—141°, and 6-thiocarbamido-, m.p. 209—210°, derivatives, respectively. (V) with MeOH, EtOH, and Pr<sup>o</sup>OH affords the corresponding thiourethanes, m.p. 75—76°, 129—130°, and 61—63°, respectively.

(B) 6-Amino-2-ethylthiol-4 : 5-dimethylpyrimidine, m.p. 92—93° [from (III) (above) and conc. EtOH-NH<sub>3</sub> at 140—150°], is hydrolysed (48% HBr) to 4 : 5-dimethylcytosine (+H<sub>2</sub>O), m.p. >300° [hydrobromide, m.p. 291° (decomp.) (sinters at 278°)].

(C) 2-Ethylthiol-6-thiocyano-4-phenylpyrimidine (VI), b.p. 204°/1.5 mm., m.p. 88—89° [from the 6-Cl-derivative (VII) and KCNS in EtOH], is converted by SH·CH<sub>2</sub>·CO<sub>2</sub>H into 2-ethylthiol-4-phenyl-6-thiopyrimidine, m.p. 206—207°, also prepared from (VII)

and EtOH-NaHS. (VI) heated in PhMe at 160—170° (sealed tube) for 10 hr. rearranges to 2-ethylthiol-6-thiocarbimido-4-phenylpyrimidine (VIII), b.p. 215—218°/2 mm., which with NH<sub>2</sub>Ph and NH<sub>3</sub> (as above) gives the 6-phenylthiocarbimido-, m.p. 215—216°, and 6-thiocarbamido-, m.p. 212—213°, derivatives, respectively. (VIII) with MeOH, EtOH, Pr<sup>o</sup>OH, and Bu<sup>o</sup>OH affords the corresponding thiourethanes, m.p. 130—131°, 115—116°, 97—98°, and 89—90°, respectively. (IV) and (VI) do not react with NH<sub>3</sub>, NH<sub>2</sub>Ph, or alcohols.  
H. B.

**1-Arylindazoles.** II. W. BORSCHKE and L. BUTSCHLI (Annalen, 1936, 522, 285—298).—The p-tolylhydrazone, m.p. 178—179°, p-acetylphenylhydrazone, m.p. 163—164°, p-carboxyphenylhydrazone, m.p. 262° (decomp.), 2 : 4-dichlorophenylhydrazone, m.p. 204°, 2 : 4 : 6-trichlorophenylhydrazone, m.p. 173—174°, and mesitylhydrazone, m.p. 137—138°, of Me 2 : 4-dinitrophenylglyoxylate are prepared (method : A., 1934, 784) from ArN<sub>2</sub>Cl and 2 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>Me and converted (*loc. cit.*) into 6-nitro-1-p-tolyl-, m.p. 268° (decomp.) (*Me* ester, m.p. 191—192°), -1-p-acetylphenyl-, m.p. 233° (decomp.), -1-p-carboxyphenyl-, m.p. 300° (decomp.), -1-2' : 4'-dichlorophenyl-, m.p. 262° (decomp.), -1-2' : 4' : 6'-trichlorophenyl-, decomp. 236° (*Me* ester, m.p. 190°), and -1-mesityl- (*Me* ester, m.p. 164°) -indazole-3-carboxylic acids, respectively. 6-Nitro-1-p-tolyl- (I), m.p. 134—135°, and -1-mesityl-, m.p. 109—110°, -indazoles are described. PhN<sub>2</sub>Cl and 2 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH<sub>2</sub>·COPh (A., 1909, i, 232) in MeOH-C<sub>5</sub>H<sub>5</sub>N give α-Ph β-2 : 4-dinitrophenyl diketone-β-phenylhydrazone, m.p. 209° (decomp.) [corresponding anisylhydrazone, m.p. 175—176° (decomp.)], convertible into 6-nitro-3-benzoyl-1-phenylindazole, m.p. 212—214° (1-4'-OMe-derivative, m.p. 199—200°), also obtained from the chloride, m.p. 191°, of 6-nitro-1-phenylindazole-3-carboxylic acid (*anilide*, m.p. 220—221°), C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>. A phenylhydrazone could not be prepared from 2 : 4-dinitrobenzophenone, m.p. 172° [from 2 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·COCl, C<sub>6</sub>H<sub>6</sub>, and AlCl<sub>3</sub>]. 2 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H could not be prepared by oxidation (CrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) of 2 : 4-C<sub>6</sub>H<sub>3</sub>Me(NO<sub>2</sub>)<sub>2</sub>; in one case, some 2 : 4-dinitrophenyl 2 : 4-dinitrobenzyl ketone (?) was obtained. Reduction (H<sub>2</sub>, Pd-C, MeOH) of (I) gives 6-amino-1-p-tolylindazole (hydrochloride, decomp. 255—257°; *Bz* derivative, m.p. 213—214°) [converted by diazotisation and subsequent treatment with H<sub>3</sub>PO<sub>2</sub> into 1-p-tolylindazole (II), m.p. 70°] and some of the azoxy-derivative, m.p. 200°. 6-Amino-3-acetyl-1-phenylindazole, m.p. 226—228° (*Bz* derivative, m.p. 192°), prepared from the 6-NO<sub>2</sub>-compound, is similarly converted into 3-acetyl-1-phenylindazole, m.p. 84—85° (*oxime*, m.p. 137°; 2 : 4-dinitrophenylhydrazone, m.p. 263°), which with PhCHO in MeOH-NaOH gives 3-cinnamoyl-1-phenylindazole, m.p. 149—150°. *Me* 6-nitro-1-phenylindazole-3-carboxylate (III) (modified prep.) is similarly reduced to the NH<sub>2</sub>-ester, m.p. 115° (*Bz* derivative, m.p. 201°), deaminated (as above) to the *Me* ester (IV), m.p. 81°, of 1-phenylindazole-3-carboxylic acid, m.p. 181° (*anilide*, m.p. 127—128°); the chloride, m.p. 147—148°, of this with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub> affords 3-benzoyl-1-phenylindazole, m.p. 148—149° (2 : 4-dinitrophenyl-



hydrazone, m.p. 215°). 1-Phenylindazole (V) and 86%  $\text{HNO}_3$  give  $(\text{NO}_2)_4$ -derivatives, m.p. 226—228° and 238—241°; with  $\text{KNO}_3$ +conc.  $\text{H}_2\text{SO}_4$  (method a) a  $(\text{NO}_2)_2$ -derivative, m.p. 253°, results. (II) affords (a) a  $(\text{NO}_2)_2$ -derivative, m.p. 215°. 6-Nitro-1-phenylindazole and fuming  $\text{HNO}_3$  give a  $(\text{NO}_2)_4$ -compound, m.p. 220—223°; (a) leads to 6:4'-dinitro-1-phenylindazole, m.p. 265° [also obtained by decarboxylation of (VI) (below)], which is reduced (as above) to the  $(\text{NH}_2)_2$ -derivative, m.p. 207—209° (becoming red). Contrary to Strassmann (A., 1890, 781), a  $(\text{NO}_2)_4$ -compound, m.p. 225—226°, is formed from (III) and fuming  $\text{HNO}_3$ ; (a) affords the Me ester, m.p. 269—270°, of 6:4'-dinitro-1-phenylindazole-3-carboxylic acid (VI), m.p. 275° (decomp.). (V) and Br in AcOH at room temp. give (probably) the 3:5:4'- $\text{Br}_3$ -derivative, m.p. 181°; (II) and (IV) similarly yield the 3:5- $\text{Br}_2$ -, m.p. 132—134°, and 5:4'- $\text{Br}_2$ -, m.p. 182—183°, derivatives, respectively. Reduction ( $\text{SnCl}_2$ , AcOH-HCl) of (III) affords some 6-amino-1-phenylindazole-3-carboxylic acid (cf. Schulhofer, A., 1891, 1231), also obtained from the 6- $\text{NO}_2$ -acid and alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ . An  $\alpha$ -oxy-compound, m.p. 243—244° (decomp.), is formed by reduction ( $\text{H}_2$ , Pd-C, MeOH) of Me 2:4-dinitrophenylglyoxylate phenylhydrazone. H. B.

**Pyrogenic rearrangement of 3-2-pyridylpyrrole.** A. G. OOSTERHUIS and J. P. WIBAUT (Rec. trav. chim., 1936, 55, 348—349).—Under the conditions of pyrolysis of N-2-pyridylpyrrole (I) to 2- (II) and 3-2-pyridylpyrrole (III) (A., 1926, 1260; Tschitschibabin *et al.*, A., 1925, i, 1174), (III) is converted into (II) but not (II) into (III). Hence no (III) is found in the products if the vapour of (I) is passed too slowly through the reaction tube.

J. W. B.

**Quinoxaline colours.** K. YAMADA, T. NOGUCHI, and K. OTWA (Bull. Chem. Soc. Japan, 1936, 11, 225—231).—The solubility, colour reactions, and dyeing properties of the quinoxaline dyes obtained by condensation (in AcOH) of phenanthraquinone with *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}$  (I) (chloride, +0.5 $\text{ZnCl}_2$ , bromide, and iodide, all m.p. > 285°) and *o*- $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\text{NHMe}$  (chloride, +0.5 $\text{ZnCl}_2$ , decomp. 200—205°; bromide, decomp. 216—217°; iodide, decomp. 195—200°), and of naphthoquinone with (I) (chloride, +0.5 $\text{ZnCl}_2$ , decomp. 278—279°; bromide, decomp. 281—282°; iodide, decomp. 220—221°) are tabulated.

J. W. B.

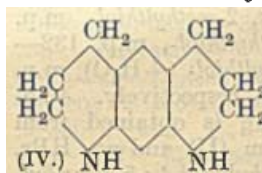
**Synthesis of  $\alpha$ -picolylisoquinolines as possible antimalarials.** I. G. R. CLEMO, H. MCLWAIN, and W. MCG. MORGAN (J.C.S., 1936, 610—611).—Et pyridyl-2-acetate and 3:4-methylenedioxy- $\beta$ -phenylethylamine condense to pyridyl-2-aceto-3':4'-methylenedioxy- $\beta$ -phenylethylamide, m.p. 89°, which with  $\text{POCl}_3$  forms 6:7-methylenedioxy-1- $\alpha$ -picolyl-3:4-dihydroisoquinoline, m.p. 105° [dihydrochloride (+EtOH), m.p. 210°; picrate, m.p. 210°]. This compound is reduced with  $\text{Zn-H}_2\text{SO}_4$  to 6:7-methylenedioxy-1- $\alpha$ -picolyl-1:2:3:4-tetrahydroisoquinoline (I), b.p. 215°/1 mm. [picrate, m.p. 175°; hydrochloride (+ $\text{H}_2\text{O}$ ), m.p. 205°], and with  $\text{PtO}_2\text{-H}_2$  to the  $\alpha$ -pipecolyl compound, b.p. 210°/1 mm. (picrate, m.p. 236°; hydrochloride, m.p. 293°). (I) is dehydrogen-

ated (Pd-C) to  $\alpha$ -picoline and 6:7-methylenedioxyisoquinoline, isolated as the picrate, m.p. 206°.

F. R. S.

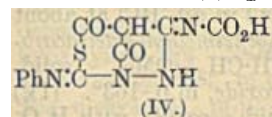
**Nitrogenous heterocyclic rings. XXIII. Reduced *lm-m*-benzodipyridine.** P. RUGGLI and A. STAUB (Helv. Chim. Acta, 1936, 19, 439—448; cf. this vol., 614).— $\text{m-C}_6\text{H}_4(\text{CH}_2\text{CH}\cdot\text{CO}_2\text{H})_2$  (I) and  $\text{HNO}_3$  1:51 at 0° give only 4-nitrophenylene-1:3-diacrylic acid (II), m.p. 268—269° (decomp.), reduced by  $\text{FeSO}_4\text{-aq. NH}_3$  or, better,  $\text{H}_2\text{-Ni}$  in AcOH at 40—50° to the 4- $\text{NH}_2$ -acid, decomp. > 300°. Absence of ring-closure proves the *trans*-nature of the ethylenic linking. The Me<sub>2</sub> ester (III) of (I) with  $\text{HNO}_3$  at -5° to 0° gives the Me<sub>2</sub> ester, m.p. 162° (Ac derivative, m.p. 215°), of (II), hydrogenation (Ni; aq. EtOH; 75°) of which gives 70% of Me 3-dihydrocarbostyryl-6-propionate, m.p. 134°, hydrolysed by acid or alkali to the corresponding acid, m.p. 234°. Hydrogenation (Ni; EtOH-EtOAc- $\text{H}_2\text{O}$ ) of (III) gives 95% of Me<sub>2</sub> *m*-phenylenedipropionate, m.p. 50—52°, converted by  $\text{HNO}_3$  (d 1:52) at > 0° into the 4:6- $(\text{NO}_2)_2$ -ester, m.p. 71°, which with  $\text{H}_2\text{-Ni}$  in EtOH-EtOAc- $\text{H}_2\text{O}$  gives by partial ring-closure Me 3-7-aminodihydrocarbostyryl-6-propionate, cryst. (Ac derivative, m.p. 245—246°). When heated at 250—270° or, better (90—100%), with conc. HCl, this gives 2:7-diketo-1:2:3:4:5:6:7:8-octahydro-*lm-m*-benzodipyridine [1':2':3':4'-tetrahydro-2'-pyridono-5':6'-6:7-dihydrocarbostyryl], sublimes at about 300°, which with HI-red P (not other reagents) at 185° yields 1:2:3:4:5:6:7:8-octahydro-*lm-m*-benzodipyridine [1':2':3':4'-tetrahydropyridino-5':6'-6:7-ar-tetrahydroquinoline] (IV), m.p. 114°, b.p. 210°/vac. [hydriodide, m.p. 307°; hydrochloride; Ac., m.p. 143°; Bz<sub>2</sub>, m.p. 209°, and  $(\text{NO}_2)_2$ -derivative, m.p. 187°; picrate, m.p. 210—215° (decomp. from 164—170°)], or, if less P is used, mainly the 2-keto-derivative of (I) [1':2':3':4'-tetrahydropyridino-5':6'-6:7-dihydrocarbostyryl], m.p. 234—235°.

R. S. C.



**Formation of heterocyclic compounds from thioacetocarbamic acid derivatives.** I. T. N. GHOSH (J. Indian Chem. Soc., 1936, 13, 86—93).—Dicarbethoxythioacetocarbamic acid (I) (A., 1934, 400) and  $\text{NHPh}\cdot\text{NH}_2$  (II) in EtOH give Et 3-keto-2-phenyl-2:3-dihydro-1:2:4-triazolyl-5-malonate, m.p. 203°, hydrolysed by 15% EtOH-KOH to the 5-acetic acid, m.p. > 300° (darkens at 280°), and thence by aq. 20% KOH to 3-keto-2-phenyl-5-methyl-2:3-dihydro-1:2:4-triazole, m.p. 210—212° (decomp.). (I) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  afford Et 3-carboxylimino-5-pyrazolone-4-carboxylate (+1.5 $\text{H}_2\text{O}$ ), m.p. 181°, hydrolysed (10% EtOH-KOH) to 3-carboxylimino-5-pyrazolone (+2 $\text{H}_2\text{O}$ ), m.p. > 300° (darkens at 250°) [4-CHPh derivative (+2 $\text{H}_2\text{O}$ ), resinifies slowly at > 280° (softens at 180°)], whilst acetylcarbethoxythioacetocarbamic acid (*loc. cit.*) and (II) give the pyrazolone,  $\text{NPh}\langle\text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{CO}_2\text{H}$  185 186° (decomp.). Diacetylthioacetocarbamic acid (III) (*loc. cit.*) and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  yield 3-keto-5-diacetylmethyl-

m.p. 70—71°, and thence (hydrolysis with 15% EtOH-KOH) 3-keto-5-acetylmethyl-, m.p. 228—230°, -2:3-dihydro-1:2:4-triazole. 4-Phenylthiosemicarbazide and (I) give the thioheptadiazine (IV),



m.p. 183° (decomp.), which with  $\text{Ac}_2\text{O}$  affords  $\text{PhNCS}$  and tar; S is not removed from (IV) by yellow  $\text{HgO}$ .  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$  and (I) in  $\text{AcOH}$  give *Et* 2-benziminazolylmalonate, m.p. 218°, hydrolysed (15% EtOH-KOH) to 2-methylbenziminazole; (III) similarly affords 2-diacetylmethylbenziminazole, m.p. 138—139° [hydrochloride, m.p. 243—244° (decomp.; turning green)], whilst (I) and  $\text{C}_2\text{H}_4(\text{NH}_2)_2$  yield *Et* 4:5-dihydro-2-glyoxalinylmalonate, m.p. 100—101°. H. B.

**Synthesis of glyoxaline derivatives from  $\alpha$ -oximinoketones.** 4-3'-Piperidylglyoxaline. E. OCHIAI and S. IKUMA (Ber., 1936, 69, [B], 1147—1151).—Production of glyoxaline derivatives by reduction of oximinoketones (I) in presence of KCNS is not practicable, since the catalyst becomes poisoned, but addition of KCNS to the reduced solution of (I) effects the desired change. Thus  $\text{OH}\cdot\text{N}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$  affords *Et* 2-thiol-4-methylglyoxaline-5-carboxylate, decomp. 229°, whilst  $\text{CMeAc}\cdot\text{N}\cdot\text{OH}$  gives 2-thiol-4:5-dimethylglyoxaline, m.p. about 270°. Replacement of  $\text{CNS}'$  by  $\text{CNO}'$  gives, respectively, *Et* 4-methylglyoxal-2-one-5-carboxylate, m.p. 220°, and 4:5-dimethylglyoxal-2-one, darkens at about 210°. *Et* oximinonicotylacetate yields *Et* 2-thiol-4-3'-pyridylglyoxaline-5-carboxylate (II), decomp. 230—231° (picrate, decomp. 192°; hydrochloride, decomp. 116°). *Et* 4-3'-pyridylglyoxal-2-one-5-carboxylate, decomp. 258°, is described. (II) is converted by 3%  $\text{H}_2\text{O}_2$  in presence of dil.  $\text{H}_2\text{SO}_4$  at 40° into *Et* 4-3'-pyridylglyoxaline-5-carboxylate, m.p. 198°; the corresponding acid, decomp. 248°, is decarboxylated at 260° to 4-3'-pyridylglyoxaline, m.p. 40—41° (hydrobromide, decomp. > 320°), the hydrochloride of which is hydrogenated (Pt) under pressure to non-cryst. 4-3'-piperidylglyoxaline, b.p. 200—250° (bath)/0.001 mm. (platinichloride, decomp. > 330°; monobenzoate, m.p. 192°). H. W.

**[Relation between] constitution and fluorescence of flavins.** P. KARRER and H. FRITZSCHE (Helv. Chim. Acta, 1936, 19, 481—483).—8-Methyl- and 6:8-dimethyl-9- $\beta$ -hydroxyethylisalloxazine (I) in  $\text{H}_2\text{O}$  or  $\text{COMe}_2$  show brownish-yellow fluorescence in ultra-violet light, but none in daylight, and thus differ markedly from the alloxazines, although Me next to the N-ring has the same qual. effect in both series. Diazotisation of 5-nitro-*m*-4-xylylidine at 0° and treatment with Cu first at room temp. and then at 100° gives 67.8% of 4-chloro-5-nitro-*m*-xylene, m.p. 51°, which with  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  in hot  $\text{C}_5\text{H}_5\text{N}$  gives 5-nitro-N- $\beta$ -hydroxyethyl-1:3:4-xylylidine, m.p. 51°. Reduction with  $\text{Na}_2\text{S}_2\text{O}_4$  in aq. EtOH, followed by reaction with alloxan, affords (I), m.p. 268° (uncorr.; decomp.) after sintering from 258°. R. S. C.

**Syntheses in the flavin series.** P. KARRER and F. M. STRONG (Helv. Chim. Acta, 1936, 19, 483—493).—Attempts to synthesise flavins with 2 Me in positions other than 6 and 7 failed. 4-Nitro-N-carb-

ethoxy-1:2:3-xylylidine (prep. by  $\text{ClCO}_2\text{Et}$  in  $\text{CHCl}_3$ ), m.p. 115°, with  $\text{H}_2$ -Pt-black in EtOH gives 3-carb-ethoxyamino-1:2:4-xylylidine, m.p. 127—129°, which by condensation with *l*-arabinose (I) in dry MeOH, followed by hydrogenation (Ni; 80°/25 atm.) gives 4-1-1'-arabamino-N-carboethoxy-1:2:3-xylylidine, m.p. 182°. With 2.5*N*-KOH at 70° this gives nearly quantitatively 2-hydroxy-1-*l*-arabityl-4:5-dimethylbenziminazole, m.p. 247—248°. 5-Nitro-*m*-xylene (modified prep.) with  $\text{H}_2$ -PtO<sub>2</sub> in EtOH gives *s*-m-xylylidine, b.p. 97—98°/12 mm., converted by conc.  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  at 0—5° into 6- (II), m.p. about 45° (lit. 54°; converted by reduction and condensation with alloxan into a fluorescent solution of an alloxazine), and 4-nitro-*s*-m-xylylidine, m.p. 136° (gives no alloxazine). The  $\text{CO}_2\text{Et}$ -derivative, m.p. 61.5°, of (II) is hydrogenated ( $\text{PtO}_2$ ; EtOH) to 5-carboethoxy-amino-1:3:4-xylylidine, m.p. 116°, which gives only a trace of N-*d*-ribityl derivative, m.p. 164°, whence no flavin could be obtained. N-*d*-1'-Arabityl-1:3:4-xylylidine, m.p. 145°, and  $\text{PhN}_2\text{Cl}$  give the phenyldiazamino-compound, decomp. 150°. (I) and (II) in MeOH at 105—115° give the Schiff's base, m.p. 165—166°, which by hydrogenation (Ni; 60°; MeOH) and condensation with alloxan and  $\text{H}_3\text{BO}_3$  gives only a trace of flavin. R. S. C.

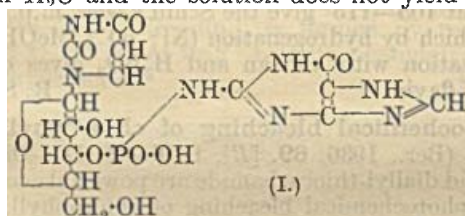
**Photochemical bleaching of chlorophyll.** K. WEBER (Ber., 1936, 69, [B], 1026—1031).—Diethyl-allyl- and diallyl-thiocarbamide are powerful acceptors in the photochemical bleaching of chlorophyll (I) in presence of air; phenylallylthiocarbamide and allylthiosemicarbazide are about as efficient as thiosinamine, whereas hydrazine-*NN'*-dithiocarbonyl-amine is less powerful.  $\text{FeSO}_4$  is active in neutral or feebly acid solution. In absence of acceptor the rate of bleaching is slow; it increases rapidly in the presence of small amounts of acceptor, attains a max., and then diminishes approx. logarithmically with increasing acceptor concn. In all cases there is a marked induction period. The rate depends little on temp. Bleaching is greatly inhibited by quinol, toluquinol, *p*-benzoquinone, toluquinone, thymoquinone, *p*- $\text{C}_6\text{H}_4(\text{OMe})_2$ ,  $\text{PhOH}$ , *m*- $\text{C}_6\text{H}_4(\text{OH})_2$ , *o*- $\text{C}_6\text{H}_4(\text{OH})_2$ , *s*- $\text{C}_6\text{H}_3(\text{OH})_3$ , thymol, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ ,  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ ,  $\text{NHPh}_2$ ,  $\text{NH}_2\text{Ph}$ , and KI. Acceptors and inhibitors, except KI, do not extinguish fluorescence. The phenomena are explained by the hypothesis that the mol. of (I) activated by a light quantum brings the acceptor into an active state in which it combined with a mol. of  $\text{O}_2$  giving a peroxide which then oxidises (I). Induction and photochemical after-effect are due to the long life-period of the intermediate peroxide. With high concn. of acceptor (I) is stabilised by the reaction  $\text{AO}_2 + \text{A} \rightarrow 2\text{AO}$ . H. W.

**Magnetic properties and structure of hæmoglobin, oxyhæmoglobin, and carboxyhæmoglobin.** L. PAULING and C. D. CORYELL (Proc. Nat. Acad. Sci., 1936, 22, 210—216; cf. this vol., 616).—Magnetic measurements show that the two last-named contain no unpaired electrons; thus the  $\text{O}_2$  mol., with two unpaired electrons, undergoes a profound change in electronic structure on attachment to hæmoglobin (I). The magnetic susceptibility of (I) corresponds



with an effective magnetic moment of 5.46 Bohr magnetons per heme (Fe-porphyrin complex). This shows the presence of 4 unpaired electrons per heme, and indicates that the heme-heme interaction tends to stabilise the parallel configuration of the moments of the 4 hemes in the mol. The linkings from Fe to surrounding atoms are ionic in (I), and covalent in the other two compounds. N. M. B.

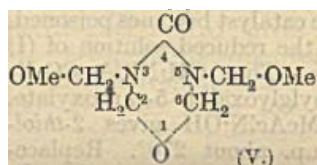
**Nucleic acids. V. Hydrolytic fissions of yeast nucleic acid.** H. BREDERECK and G. RICHTER (Ber., 1936, 69, [B], 1129—1133).—Hydrolysis of yeast nucleic acid with boiling  $H_2O$  gives *guanine-uridylic acid* (I),  $C_{14}H_{16}O_8N_4P$ , the individuality of which is established by analysis, production essentially of guanine (II) when treated with HCl in MeOH, hydrolysis by 3.8%  $H_2SO_4$  to guanine sulphate and uridylic acid (III) (isolated as the brucine salt) and by 3% NaOH to (II) and (III), and separation of (II) under the action of almond emulsin at  $pH$  4.9. The possibility of the presence of a mixture of (II) and (III) is excluded, since the material is relatively freely sol. in  $H_2O$  and the solution does not yield guanine



picrate or brucine uridylylate. Since (I) is monobasic acid (phenolphthalein) the union of (II) and (III) must occur through the  $PO_4$  group. Further, since de-amination of (I) and subsequent hydrolysis with dil.  $H_2SO_4$  affords (II) and (III), the  $NH_2$  of (II) is not free, but linked to the  $PO_4$  of (III). Hence (I) has the above constitution. Examination of the filtrate from (I) shows the presence of (II), adenine, (III), cytidylic acid, ribose, and  $H_3PO_4$ . H. W.

**Carbamide-formaldehyde condensation products.** H. KADOWAKI (Bull. Chem. Soc. Japan, 1936, 11, 248—261).—Many cryst. condensation products are isolated.  $CH_2O$  (1 mol.) and  $CO(NH_2)_2$  (8 mols.) in dil. HCl under defined conditions give *methylenebiscarbamide* (I),  $CH_2(NH-CO-NH_2)_2$ , m.p. 218° (decomp.) (Ac. derivative, m.p. 156°), which with a trace of HCl in  $H_2O$  gives *trimethylenetetra-*, m.p. 230° (decomp.), and *pentamethylenehexa-carbamide*, m.p. 236° (decomp.),  $NH_2-CO-NH-[CH_2-NH-CO-NH]_x-H$  ( $x=3$  and 5, respectively). (I) and  $CH_2O$  with a trace of  $Ba(OH)_2$  give, according to the conditions,  $\omega$ -*hydroxymethyl-* ("methylolmethylenedicarbamide"), solid, and  $\omega\omega'$ -*di(hydroxymethyl)-methylenedicarbamide* ("methylenebismethylolcarbamide") (II), m.p. 228° (decomp.),  $OH-CH_2-NH-CO-NH-CH_2-NH-CO-NHR$  ( $R=H$  and  $-CH_2-OH$ , respectively). Methylcarbamide,  $CH_2O$ , and HCl give similarly the  $\omega\omega'$ - $Me_2$  derivative, m.p. 184° of (I) ("methylenebismethylcarbamide"). *N*-Hydroxymethylcarbamide ("methylolcarbamide") (III) with MeOH or EtOH and a trace of HCl gives the *Me*, m.p. 91°, and *Et ether*, m.p. 111°. *NN'*-*Di*(hydroxymethyl)carbamide ("dimethylolcarbamide") (IV) gives similarly the *Me*., m.p. 101°, *Et*., m.p. 124°, *Pr*., m.p. 95°, *Bu*.,

m.p. 93°, *di-n-amyl*, m.p. 84°, and *dibenzyl ether*, m.p. 112°, and with SHEt and a little HCl *NN'*-*di*(ethylthiolmethyl)carbamide, m.p. 108.5°. (II) gives similarly the *Me\_2 ether*, m.p. 240° (decomp.).  $CH_2O$  (1 mol.) and carbamide (8 mols.) in dil. HCl at about  $-5^\circ$  give  $\omega\omega'$ -*di*(methoxymethyl)trimethylenetetra-carbamide,  $OMe-CH_2-[NH-CO-NH-CH_2]_3-OMe$ , solid. (III) and acid  $H_2O_2$  give a *peroxide*, m.p. 163°. (IV) with neutral  $H_2O_2$  gives a liquid *peroxide*, with  $H_2O_2$  and acid a cryst. *peroxide*, but with slightly acid  $H_2O_2$  a polymeric, amorphous *peroxide*,  $CO(NH-CH_2-O_2-CH_2-NH-CO-NH-CH_2-O_2H)_2$ . When  $CH_2O$  (4 mols.) and carbamide (1 mol.) are condensed in aq.  $Ba(OH)_2$  and then treated with MeOH and HCl, there is obtained 3 : 5-*di*(methoxymethyl)urone [4-*keto*-3 : 5-*di*(methoxymethyl)tetrahydro-1 : 3 : 5-oxadiazine] (V), b.p. 82—83°/0.1 mm. (the hypothetical 4-*keto*-tetrahydro-1 : 3 : 5-oxadiazine,  $O<\begin{smallmatrix} CH_2-NH \\ CH-NH \end{smallmatrix}>CO$ , is termed "urone"), which with SHEt and a little HCl gives 3 : 5-*di*(ethylthiolmethyl)urone [4-*keto*-3 : 5-*di*(ethylthiolmethyl)tetrahydro-1 : 3 : 5-oxadiazine], m.p. 59°. *N*-Methyl- and -ethyl-carbamide lead similarly to 3-methyl-5-methoxymethyl-, b.p. 89—90°/0.2 mm., and -5-ethylthiolmethyl-, b.p. 122—125°/1 mm., 3-ethyl-5-methoxymethyl-, b.p. 91—93°/1 mm., and -5-ethylthiolmethyl-urone, m.p. 15.5°, b.p. 110—113°/1 mm. [4-*keto*-3-methyl-5-methoxymethyltetrahydro-1 : 3 : 5-oxadiazine etc.];  $CO(NHMe)_2$  gives 3 : 5-*dimethyl*-urone [4-*keto*-3 : 5-*dimethyl*tetrahydro-1 : 3 : 5-oxadiazine], m.p. 38.5°, and tetramethyldimethylenediureide,  $CO<\begin{smallmatrix} NMe-CH_2-NMe \\ NMe-CH_2-NMe \end{smallmatrix}>CO$ , m.p. 258° (also obtained in acid solution);  $NH_2-CO-NMe_2$  gives *N,N*-dimethyl-*N'*-methoxymethylcarbamide, m.p. 65°; (I) gives 3 : 3'-methylenebis-5 : 5'-dimethoxymethylurone [*bis*-4-*keto*-5 : 5'-*di*(methoxytetrahydro-1 : 3 : 5-oxadiazine)],



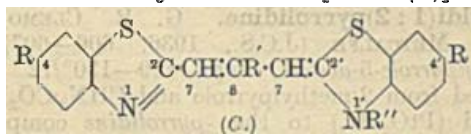
$CH_2\left[N<\begin{smallmatrix} CH_2-O \\ CO-N-CH_2-OMe \end{smallmatrix}>CH_2\right]$ , a gum. (II), its  $Bu_n$ , diamyl, and  $(CH_2Ph)_2$  ethers, when heated, give transparent resins with great resistance to  $H_2O$ . 20 photomicrographs are given. R. S. C.

**Thiazolinephenols. Synthesis and proof of structure.** J. B. NIEDERL, W. F. HART, and J. V. SCUDI (J. Amer. Chem. Soc., 1936, 58, 707—708).—Allylthiocarbimide (0.5 mol.), PhOH (1 mol.), and conc.  $H_2SO_4$  (1 mol.) at 0—5° (24 hr.) and then at room temp. (3 days) give 2-*p*-hydroxyphenyl-5-methylthiazoline, m.p. 166—168° (hydrochloride, m.p. 187°; picrate, m.p. 178°), oxidised ( $KClO_3$ , dil. HCl) to *p*-OH-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>H and  $NH_2-CH_2-CHMe-SO_3H$ . 2-4'-Hydroxy-2'-methylphenyl-, m.p. 131° (hydrochloride, m.p. 175°; picrate, m.p. 154°), 2-4'-hydroxy-3'-methoxyphenyl-, m.p. 142° (hydrochloride, m.p. 187°; picrate, m.p. 159—160°), and 2-2' : 4'-dihydroxyphenyl-, m.p. 184° (hydrochloride, m.p. 251°; picrate, m.p. 190°), -5-methylthiazolines are similarly prepared from *m*-cresol, guaiacol, and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, respectively. H. B.

**Thiazoles. XXII. Synthesis of some 6-methoxy- and 5:6-dimethoxy-benzthiazoles and of certain dyes obtainable therefrom.** M. G. ASF and M. T. BOGERT (Rec. trav. chim., 1935, 54, 917—930).—*p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>·HCl and S<sub>2</sub>Cl<sub>2</sub> give a condensation product, m.p. 168—168.5° (corr.) (decomp.), hydrolysed by NaHCO<sub>3</sub>·Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to 2-amino-5-methoxythiophenol, m.p. 110° [Na and Zn (I) salt; Bz<sub>2</sub> derivative, m.p. 162—162.5° (corr.)], yields 1-phenyl-5-methoxybenzthiazole, m.p. 114—114.5° (cf. lit.). (I) with AcOH and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COCl (II) gives 1-*p*-nitrophenyl-5-methoxybenzthiazole (III), m.p. 215—216.5° (corr.). The corresponding *m*-NO<sub>2</sub>-compound, m.p. 161.5—162.5° (corr.), similarly prepared, was obtained together with a trace of 1-*m*-nitrophenyl-5-methoxychlorobenzthiazole, m.p. 199.5—200.5° (corr.). (I) and *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO give a compound, m.p. 123.5—124.5° (corr.), reduced by SnCl<sub>2</sub> to a compound, m.p. 108.5—109.5° (corr.); these were not investigated further. (III) when refluxed with SnCl<sub>2</sub>·AcOH·HCl yields 1-*p*-aminophenyl-5-methoxybenzthiazole, m.p. 195—196° [corresponding *m*-NH<sub>2</sub>-derivative, m.p. 128.5—129.5° (corr.)]. (I) with *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO·AcOH affords 1-*p*-dimethylaminophenyl-5-methoxybenzthiazole (III), m.p. 181.5—182.5° (corr.). 6:6'-Dinitro-3:4:3':4'-tetramethoxydiphenyl disulphide (V), m.p. 232—232.5° (corr.) (cf. lit.), prepared from 4:5-dinitroveratrole, Na<sub>2</sub>S, S, and MeOH, when treated with Zn·AcOH gives a solution of Zn 2-amino-4:5-dimethoxyphenyl mercaptide (VI), which with (II) gives an amorphous product (VII), m.p. 238.5—239.5° (corr.), reduced by SnCl<sub>2</sub>·HCl·AcOH to 1-*p*-amino-4:5-dimethoxybenzthiazole, m.p. 224.5—225.5° (corr.) [the corresponding *o*-, m.p. 196.5—197.5° (corr.), and *m*-amino-compound, m.p. 206—206.5° (corr.)]. (VI) and (II) with anhyd. NaOAc gives a cryst. product, which on heating to 190—195° or attempted crystallisation is converted into (VII). (V) when boiled with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, NaOH, and H<sub>2</sub>O and then treated with BzCl at room temp. gives dibenzoyl-2-amino-4:5-dimethoxythiophenol, m.p. 149.5—150° (corr.), converted by hot AcOH·NaOAc into 1-phenyl-4:5-dimethoxybenzthiazole, m.p. 149—150°; 1-*o*-, m.p. 162—163.5° (corr.), and 1-*m*-, m.p. 186—187° (corr.), -nitrophenyl-4:5-dimethoxybenzthiazole were similarly prepared. (VI) and *p*-NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO give 1-*p*-dimethylaminophenyl-4:5-dimethoxybenzthiazole, m.p. 231—232°. This and (IV) when methylated yield 1-*p*-dimethylamino-4:5-dimethoxy-, m.p. 221—224° (corr.), and -5-methoxy-, m.p. 217.5—218.5° (corr.), -benzthiazole methiodide, respectively, which are thioflavine dyes, unstable to light or washing. Chloramine-yellows were obtained by treating the aminobenzthiazoles described with H<sub>2</sub>SO<sub>4</sub>·SO<sub>3</sub> and the resulting sulphonic acid with NaOCl. The tinctorial properties of the dyes are described. H. G. M.

**Cyanine dyes. VIII. Synthesis of 8-methyltrimethinethiocyanine derivatives and the reactivity of the 8-methyl group.** T. OGATA (Bull. Chem. Soc. Japan, 1936, 11, 262—264).—The following are prepared from the appropriate 2-methylbenzthiazole ethiodide and Ac<sub>2</sub>O·HCO<sub>2</sub>K (A) or Ac<sub>2</sub>O·KOAc (B) at 150—165°, the data in parentheses being,

respectively, method, yield, and sensitisation max. in mμ: 1:1'-diethyl- (A, 1934, 422) (A), 1:1'-diethyl-8-methyl- (B, 30%), m.p. 286° (decomp.) (580), 1:1':4:4':8-pentamethyl- (B, 20%), m.p. 279° (decomp.) (580), and 8-methyl-1:1'-diethyl-3:4:3':4'-dibenzo- (B, 70%), m.p. 293° (decomp.) (600), -trimethinethiazolocyanine iodide [all as (C)]. The 8-Me



derivatives condense with aldehydes and piperidine to give the corresponding 8-2-substituted vinyl compound, and thus are obtained: 1:1'-diethyl-8-β-furylvinyl-, m.p. 277° (decomp.) (C, R'=CH:CH·C<sub>4</sub>H<sub>3</sub>O), -8-styryl- (R'=CH:CHPh), m.p. 266° (decomp.) (600), and -8-*p*-dimethylaminostyryl-, m.p. 252° (decomp.) (600), -trimethinethiazolocyanine iodide; 1:1'-diethyl-8-styryl-, m.p. 265° (decomp.), and -8-*p*-dimethylaminostyryl-, m.p. 288°, -3:4:3':4'-dibenzotrimethinethiazolocyanine iodide, and 1:1':4:4'-tetramethyl-8-*p*-dimethylaminostyryltrimethinethiazolocyanine iodide, m.p. 292° (decomp.). J. W. B.

**Alkaloids of Heliotropium lasiocarpum. V. Lasiocarpine.** G. MENSCHIKOV and J. SCHDANOVITSCH (Ber., 1936, 69, [B], 1110—1113; cf. A., 1932, 865).—Lasiocarpine (I) is hydrolysed by boiling 2% NaOH to heliotridine and angelic acid. Hydrogenation (PtO<sub>2</sub> in 0.5*N*-HCl) of (I) affords lasiocarpic acid, C<sub>8</sub>H<sub>16</sub>O<sub>5</sub>, m.p. 95—97°, [α]<sub>D</sub>+10.6° in EtOH, which contains 2 OH (Zerevitinov) and 1 OMe, and a non-cryst. base, C<sub>13</sub>H<sub>23</sub>O<sub>2</sub>N, b.p. 123—125°/8 mm., [α]<sub>D</sub>+3.8° in EtOH (picrate, m.p. 157—159°), hydrolysed by KOH·EtOH to hydroxyheliotridane and CHMeEt·CO<sub>2</sub>H. H. W.

**Electrolytic reduction of vasicine.** K. S. NARANG and J. N. RAY (J.C.S., 1936, 686—688).—In reply to Spath and Platzer (this vol., 489), the reduction of *B* (cf. A., 1935, 765) for 5 hr. gives a base, C<sub>11</sub>H<sub>12</sub>ON<sub>2</sub>, m.p. 115°, whilst similar reduction of vasicine (I) gives a base, C<sub>11</sub>H<sub>14</sub>ON<sub>2</sub> [picrolonate, m.p. 165—168° (decomp.)], the first addition of H taking place at N:C in the middle ring. Reduction of (I) for a longer period yields a base, C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>, m.p. 92° [picrolonate, m.p. 224—228° (decomp.)]. The constitution of the various reduction products of (I) is discussed, and the structure assigned previously to (I) is confirmed. F. R. S.

**Identity of tazettine from Narcissus tazetta, L., with "base VIII," from Lycoris radiata, Herb.** E. SPATH, H. KONDO, and F. KUFFNER (Ber., 1936, 69, [B], 1086—1087).—Tazettine is identical with Kondo's "base VIII" (J. Pharm. Soc. Japan, 1932, 52, 51) which is therefore, C<sub>18</sub>H<sub>21</sub>O<sub>5</sub>N; it has [α]<sub>D</sub><sup>18</sup>+165.1° in CHCl<sub>3</sub>. Their identity with unergine (Norkina et al., this vol., 618) is probable. H. W.

**Tobacco alkaloids. VII. New synthesis of di-anabasine.** E. SPATH and L. MAMELI (Ber., 1936, 69, [B], 1082—1085).—1-Benzoylpiperidone, m.p. 110—112°, from piperidone and Bz<sub>2</sub>O at 180°, is condensed with Et nicotinate by NaOEt in C<sub>6</sub>H<sub>6</sub> at 110—115° to anabaseine, C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>, b.p. 110—120°



(bath)/1 mm. [*dipicrate*, m.p. 174° (vac.; slight decomp.)], which is reduced (Pd-C in 3% AcOH) to *dl*-anabasine, identical with that obtained by racemisation of the natural base. The *dipicolonate* has m.p. 258—259°. H. W.

**Lupin alkaloids. IX. Synthesis of 5:5'-dimethylidi(1:2)pyrrolidine.** G. R. CLEMO and T. P. METCALFE (J.C.S., 1936, 606—607).—*Et* 2-methylpyrrole-5-acetate, b.p. 129—130°/12 mm., obtained from 2-methylpyrrole and  $\text{CHN}_2 \cdot \text{CO}_2\text{Et}$ , is reduced ( $\text{PtO}_2\text{--H}_2$ ) to the *-pyrrolidine* compound, b.p. 98°/12 mm. (*picrate*, m.p. 112°; *picolonate*, m.p. 194°), which condenses with  $\text{CHMeBr} \cdot \text{CO}_2\text{Et}$  to *Et* 2-methylpyrrolidine-5-acetate-1- $\alpha$ -propionate, b.p. 150—151°/12 mm. This ester with K forms 4-keto-5:5'-dimethylidi(1:2)pyrrolidine, b.p. 65°/1 mm. (*picrate*, m.p. 186°; *picolonate*, m.p. 217°), which is reduced (Zn-HCl) to the 4-hydroxy-compound, b.p. 68—70°/1 mm. (*picolonate*, m.p. 205°) but with  $\text{N}_2\text{H}_4$  affords 5:5'-dimethylidi(1:2)pyrrolidine, b.p. 25°/1 mm. (*picrate*, m.p. 249°; *picolonate*, m.p. 180°).

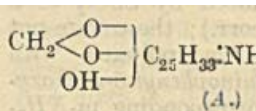
F. R. S.

**Hydrobromoquinine.** J. K. PODLEWSKI and J. SUSZKO (Rec. trav. chim., 1936, 55, 392—400; cf. this vol., 490).—Quinine hydrochloride with 38% HBr-AcOH at 80° affords a partly racemised mixture of *hydrobromoquinine dihydrobromide* (A), m.p. 223—225° (decomp.),  $[\alpha]_D^{20}$  -140° to -150° in  $\text{H}_2\text{O}$  (*dinitrate*, decomp. 180—210°,  $[\alpha]_D^{20}$  -150° to -170° in  $\text{H}_2\text{O}$ ). With 48% aq. HBr-10%  $\text{NaNO}_2$  or 10%  $\text{NaOAc}$  (A) gives the *monohydrobromide*, m.p. 200—210° (decomp.). Crystallisation from  $\text{C}_6\text{H}_6$  of the bases liberated by the action of aq.  $\text{NH}_3$  on (A) affords plates of  $\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}_2\text{Br}$ ,  $+\text{C}_6\text{H}_6$ , m.p. 103°, resolidifying and decomp. at 140°,  $[\alpha]_D^{20}$  -130° to -150°, and needles, decomp. 140°,  $[\alpha]_D^{20}$  -115° to -140°, of the solvent-free base. Both cryst. forms give a mixture of  $\beta$ -isoquinine and niquine when hydrolysed with KOH-EtOH. Separation of the stereoisomerides is effected by fractional crystallisation of the  $\text{Et}_2\text{O}$  extract of (A) basified with 10% NaOH, which affords *hydrobromoquinine-II*, m.p. 166—167° (decomp.),  $[\alpha]_D$  -200° in EtOH- $\text{CHCl}_3$  [*metho-p-toluenesulphonate*, m.p. 145—155° (decomp.),  $[\alpha]_D^{20}$  -114° in EtOH, and  $\text{CH}_3\text{PhBr}$  additive salt, m.p. 185—190° (decomp.),  $[\alpha]_D$  -142° in EtOH], and, from the  $\text{Et}_2\text{O}$  mother-liquor, *hydrobromoquinine-I*, solvent-free, m.p. 160—162° (decomp.),  $[\alpha]_D^{20}$  -182° to -186°, and  $+\text{C}_6\text{H}_6$ ,  $[\alpha]_D^{20}$  -50° in EtOH- $\text{CHCl}_3$  [*metho-p-toluenesulphonate*,  $+\text{H}_2\text{O}$  and anhyd., m.p. 193—194° (decomp.),  $[\alpha]_D^{20}$  -59° in EtOH, and  $\text{CH}_3\text{PhBr}$  additive salt, m.p. 185—190° (decomp.),  $[\alpha]_D^{20}$  -95° in EtOH]. When heated with 3% KOH-EtOH, base-I gives only  $\beta$ -isoquinine, and base-II gives only niquine. Base-I and -II are stereoisomeric *tert.* bases. J. W. B.

**Alkaloids of white hellebore. II. Isolation of alkaloids from the so-called resinous matters.** K. SAITO and H. SUGINOME. **III. Constitution of jervine.** K. SAITO and M. TAKAOKA (Bull. Chem. Soc. Japan, 1936, 11, 168—171, 172—176).—II. Extraction of the resin remaining after EtOH-extraction of the roots (A., 1934, 422) with dil. AcOH affords a sol. portion from which jervine (I) is isolated,

and an insol. portion (2.5% of roots). Prolonged  $\text{Et}_2\text{O}$ -extraction of the latter removes 18%, from which ligroin (b.p. 40—60°) dissolves 19% of fats leaving an insol. *substance*, m.p. 262° (decomp.). From the  $\text{Et}_2\text{O}$ -insol. residue are isolated phenolic substances, sol. acids including angelic and an *acid*, m.p. 102°, and alkaloids from which more (I) (total yield 0.6% of roots) is obtained.

III. Pure (I), m.p. 243.5—244.5° (bath preheated to 180°),  $[\alpha]_D^{20}$  -150° in EtOH, with  $\text{CH}_2\text{N}_2$  or MeI-KOH-EtOH gives its N-Me derivative,  $+\text{H}_2\text{O}$  and anhyd., m.p. 201—202° [*methiodide*, m.p. about 247°, by MeI at 100°; *methochloride*, m.p. 252° (decomp.); Ac derivative, m.p. 186—187°, and with  $\text{NaNO}_2$ -AcOH a NO-derivative, m.p. 251—252° (decomp.). (I) with  $\text{Ac}_2\text{O}$  at room temp. affords its N-Ac derivative,  $+\text{H}_2\text{O}$  and anhyd. (II), m.p. 161—162° (decomp.), and with boiling  $\text{Ac}_2\text{O}$  an ON-Ac<sub>2</sub> derivative, m.p. 176—177°, hydrolysed by 0.1N-NaOH-EtOH to (II). In agreement with these data (I) contains 2 active H (Zerevitinov) and is represented by the partial formula (A).

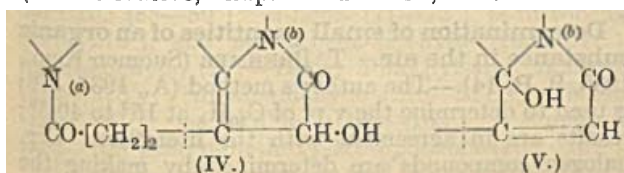


**Alkaloids of *Holarrhena antidysenterica*. IV. Occurrence of two further new bases in the bark of Indian *Holarrhena* and their relationship to conessine and holarrhimine.** S. SIDDIQUI. **V. Holarrhimine.** S. SIDDIQUI and R. H. SIDDIQUI (Proc. Indian Acad. Sci., 1936, 3, A, 249—266; 257—260).—IV. From the mother-liquor of holarrhimine sulphate (A., 1933, 289) are isolated (insolubility of their hydrochlorides in 10% HCl and fractional crystallisation from ligroin) *conamine* (I),  $\text{C}_{22}\text{H}_{36}\text{N}_2$ , probably  $\text{C}_{21}\text{H}_{31}(\text{NMe})\text{NH}_2$ , m.p. 130°,  $[\alpha]_D^{20}$  -19° in EtOH, converted by heating to dryness into a *substance*, m.p. 220—240°, and *conarrhimine* (II), (?)  $\text{C}_{21}\text{H}_{31}(\text{NH})\text{NH}_2$ . The latter was not obtained pure since it forms eutectic mixtures, of sharp m.p. 160° and m.p. 175°, with holarrhimine (III), into which they are converted completely by heating with moist EtOAc. These observations may explain the isolation of kurchicine (Ghosh *et al.*, A., 1928, 1265). The presence of (II) was established by the isolation of *nitrosohydroxyapoconarrhimine*,  $\text{C}_{21}\text{H}_{31}(\text{N}\cdot\text{NO})\cdot\text{OH}$ , sinters 145°, m.p. 160—163° [together with  $\text{C}_{21}\text{H}_{31}(\text{OH})\text{NMe}$  from (I) and  $\text{C}_{21}\text{H}_{31}(\text{OH})_3$  from (III)], by the action of  $\text{HNO}_2$  on the mother-liquor from (I). Contrary to earlier statements (*loc. cit.*) (III) contains 5 active H atoms,  $\text{C}_{22}\text{H}_{31}(\text{NH}_2)_2(\text{OH})$ , and is converted by 40%  $\text{CH}_3\text{O}\cdot\text{HCO}_2\text{H}$  into *tetra-N-methylholarrhimine*, m.p. 233—235°,  $[\alpha]_D^{20}$  -45.5° in EtOH (also obtained by direct methylation of the total bases from *Holarrhena* bark) [*hydrochloride*, m.p. 315—316° (decomp.); *hydriodide*, m.p. 302—303° (decomp.); *hydrobromide*, m.p. 306—307°; *picrate*, sinters 225°, m.p. 272—275°; *platinichloride*, m.p. 251—252°; *monomethiodide*, m.p. 286—287° (decomp.); Bz, m.p. 176° [*hydrochloride*, shrinks 163°, m.p. 237—238° (decomp.); *picrate*, evolves  $\text{H}_2\text{O}$  at 105—160°, decomp. 205—210°], and Ac derivative, softens 134°, m.p. 139—140° [*hydrochloride*, decomp. 230—273°; *picrate*, evolves  $\text{H}_2\text{O}$  at 105°, m.p. 160°, decomp. 202—205°]]. (II) is pro-

bably the parent of the alkaloid constituents of *H. antidyenterica*.

V. With  $\text{BzCl}$  (4 mols.)- $\text{C}_5\text{H}_5\text{N}$  (III) gives a  $\text{Bz}_3$  derivative, m.p. 269—270°, and, from the mother-liquor, a  $\text{Bz}_2$  derivative, decomp. 115°, and with  $\text{Ac}_2\text{O}$ - $\text{NaOAc}$ , a  $\text{Ac}_3$  derivative,  $+\text{H}_2\text{O}$  and anhyd., m.p. 249—250°. (III) contains 1 double linking and with  $\text{Br}-\text{CHCl}_3$  a dibromide, m.p. 290—295° [m.p. 226—228° (decomp.) after liberation from its solution in  $\text{AcOH}$  by  $\text{NaOH}$ ], is obtained. With  $\text{MeI}-\text{CHCl}_3$  (III) gives a dimethiodide, m.p. 279°, converted (loss of  $\text{HI}$  and  $\text{MeOH}$ ) by aq.  $\text{NH}_3$ ,  $\text{NaOH}$ , or  $\text{AgOH}$  into methylholarrhimine, m.p. 170° [hydrochloride, m.p. 266° (decomp.)]; platinichloride, m.p. 245° (decomp.); picrate, m.p. 205°]. J. W. B.

**Structure of strychnine. III. Strychninolone and its derivatives.** M. KOTAKE and T. MITSUWA (Bull. Chem. Soc. Japan, 1936, 11, 231—238).—Oxidation of strychnine ( $\text{KMnO}_4$ - $\text{COMe}_3$ ) affords dihydrostrychnine,  $+\text{MeOH}$ ,  $+2.5\text{H}_2\text{O}$ , and solvent-free, decomp. 100°, resolidifies, shrinks at 155°, m.p. 240° (hydrochloride, decomp. 212°; methiodide, m.p. 322°). Fractional crystallisation of Leuchs' strychninolone- $\alpha$  (I), m.p. 228—230°, from  $\text{MeOH}$  separates it into strychninolone- $\alpha$  (II), m.p. 224° ( $\text{Ac}$  derivative, m.p. 240—243°), and - $\beta$ , m.p. 240° (less sol.) ( $\text{Ac}$  derivative, m.p. 253°), both  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$  (different positions of double linking) and both reduced by  $\text{Pd}-\text{H}_2$  to the same  $\text{H}_2$ -derivative m.p. 274°. (II) with 10%  $\text{KOH}$  gives isomeric strychninolone- $\gamma$  (III), m.p. 254° ( $\text{Ac}$  derivative, m.p. 260°), which gives a different  $\text{H}_2$ -derivative, and is probably formed by  $\text{OH}$ -migration. (I) with  $\text{NaOEt}-\text{EtOH}$  gives strychninolone- $\delta$  (IV),  $+3\text{H}_2\text{O}$ , and anhyd., m.p. 285—286° (decomp.) ( $\text{Ac}$  derivative,  $+\text{H}_2\text{O}$ , m.p.  $>340^\circ$ ; not reduced by  $\text{Pd}-\text{H}_2$ ), and (I) with  $\text{NH}_3$ - $\text{MeOH}$  gives, by fractional crystallisation of the product from  $\text{H}_2\text{O}$ , (III) and strychninolone- $\epsilon$  (V),  $+\text{H}_2\text{O}$  and anhyd., m.p. 240—243° ( $\text{Ac}$  derivative, m.p. 214—215°;  $\text{H}_2$ -derivative,



m.p. 257°). Oxidation of (I) with  $\text{CrO}_3$ - $\text{AcOH}$  gives strychninone, m.p. 273° (yellow solution in alkali, repptd. by  $\text{CO}_2$ ), and dihydrostrychninolone- $\alpha$  similarly gives dihydrostrychninone, m.p. 314° (colourless solution in alkali, not repptd. by  $\text{CO}_2$ ). The structural implications of these results are discussed, the partial formulæ above being suggested. J. W. B.

**Iodo-derivatives of brucine.** G. SOLLAZZO (Boll. Chim. farm., 1936, 75, 213—219).—The compounds  $\text{C}_{23}\text{H}_{27}\text{O}_4\text{N}_2\text{I}_3$ , new m.p. 239—241°, and  $\text{C}_{23}\text{H}_{27}\text{O}_4\text{N}_2\text{I}_4$ , and the compound  $\text{C}_{23}\text{H}_{27}\text{O}_4\text{N}_2\text{I}_3 \cdot 3\text{H}_2\text{O}$ , are prepared from brucine and I in  $\text{EtOH}$  under varying conditions. E. W. W.

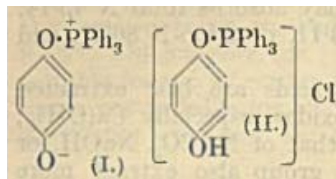
**Organic compounds of germanium.** K. BURSCHKIES (Ber., 1936, 69, [B], 1143—1146).—Sulphides,  $\text{S}(\text{GeR}_3)_2$ , are obtained by heating the appropriate bromide with  $\text{Na}_2\text{S}$  alone or in  $\text{EtOH}$ ;

$\text{R}=\text{Ph}$ , m.p. 138°; *tolyl*, m.p. 156—157°;  $\text{CH}_2\text{Ph}$ , m.p. 124°;  $\text{C}_6\text{H}_4\text{Ph}$ , m.p. 238°, cyclohexyl, m.p. 87—88°; *Et*, b.p. 148—150°/12 mm. They are well-cryst. compounds with sharp m.p. and completely insol. in alkali. *Ge tetra- $\beta$ -phenylethyl*, m.p. 56—57°, is obtained from  $\text{CH}_2\text{Ph}-\text{CH}_2-\text{MgBr}$  and  $\text{GeCl}_4$  in  $\text{Et}_2\text{O}$ .  $\text{Ge}(\text{CH}_2\text{Ph})_4$  is unattacked by  $\text{HNO}_3$  (*d* 1.52) in  $\text{AcOH}$  at 15—20° or 50—60° and decomposed at the b.p. into  $\text{Ge}$  and  $\text{NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ . Di-*p*-dimethylamino-phenylgermanic anhydride is transformed by  $\text{HNO}_3$  (*d* 1.52)-conc.  $\text{H}_2\text{SO}_4$  at room temp. into the 3- $\text{NO}_2$ -derivative. Tolylgermanic anhydride is oxidised by  $\text{KMnO}_4$  in boiling  $\text{H}_2\text{O}$  to di-*p*-carboxyphenylgermanic anhydride. H. W.

**Mercury acetamide as a mercurating agent. II. Mercuration of phenols.** K. G. NAIK and B. V. MEHTA (J. Indian Chem. Soc., 1935, 12, 783—787).— $\text{Hg}$  acetamide when heated with the appropriate phenol in  $\text{EtOH}$  gives rise to  $\text{OH-Hg}$ -derivatives, the constitution of which was established by conversion by means of  $\text{Br}$  into the corresponding Br-derivatives. The following have been prepared: 2-nitro-4-hydroxymercuriphenol, m.p.  $>285^\circ$ , unaffected by dil.  $\text{HCl}$ ,  $\text{KI}$ ,  $\text{H}_2\text{S}$ , or  $(\text{NH}_4)_2\text{S}$ , but when heated with conc.  $\text{HCl}$  gives  $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-OH}$ ; 4-nitro-2-hydroxymercuriphenol, m.p.  $>285^\circ$ , converted by hot  $\text{AcOH}$  into 4-nitro-2-acetoxymercuriphenol, m.p.  $>285^\circ$ , which with  $\text{Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$  gives 2 : 2'-mercuribis-4-nitrophenol, m.p.  $>285^\circ$ ; 1-hydroxymercuri- $\beta$ -naphthol (I), m.p. 210° (decomp.), which with hot dil.  $\text{HCl}$  gives  $\beta\text{-C}_{10}\text{H}_7\text{-OH}$ , with  $\text{H}_2\text{S-H}_2\text{O}$  gives  $\text{HgS}$ , and with  $\text{KI}$  gives  $2\text{KOH}$  quantitatively, and is converted by hot  $\text{AcOH}$  into 1-acetoxymercuri- $\beta$ -naphthol, m.p. 185°; 4-hydroxymercuri- $\alpha$ -naphthol, m.p.  $>285^\circ$ ; trihydroxymercuriphenol, m.p.  $>285^\circ$ . (I) with dil.  $\text{NaOH}$  and  $\text{CS}_2$  gives 1-thiolmercuri- $\beta$ -naphthol, m.p.  $>285^\circ$ ; *o*-, m.p.  $>285^\circ$ , and thiolmercuriphenol were similarly prepared from the appropriate chloromercuriphenol. H. G. M.

**Manufacture of heterocyclic mercury compounds.**—See B., 1936, 572.

**Quinonephosphines. I. Benzoquinone-triphenylphosphine.** A. SCHONBERG and R. MICHAELIS (Ber., 1936, 69, [B], 1080—1082).—*p*-Benzoquinone and  $\text{PPh}_3$  in  $\text{C}_6\text{H}_6$  afford *p*-benzoquinone-triphenylphosphine (I) decomp.  $>270^\circ$ , hydrolysed by boiling 50%  $\text{KOH}$  to  $\text{PPh}_3\text{O}$  and quinol. (I) is converted by boiling  $2\text{N-HCl}$  into the hydrochloride (II), decomp. (indef.) 290—300°, and by  $\text{EtI}$  in  $\text{EtOH}$  into the ethiodide [(II) with  $\text{OEt}$  for  $\text{OH}$  and  $\text{I}$  for  $\text{Cl}$ ], m.p. about 235° (decomp.). H. W.



**Synthesis of selenophen derivatives. I. Action of chlorine and bromine on selenophen.** H. SUGINOME and S. UMEZAWA (Bull. Chem. Soc. Japan, 1936, 11, 157—167).—Selenophen (I) with  $\text{Cl}_2$  at 50—60° gives its 2-*Cl*-, b.p. 42°/12.5 mm., and 2 : 5-*Cl*\_- (II) -derivative, b.p. 67°/12 mm., and (best with excess of  $\text{Cl}_2$ ) 2 : 2 : 3 : 4 : 5 : 5-hexachlorotetrahydroselenophen, m.p. 55°, oxidised by fuming  $\text{HNO}_3$



at  $-21^{\circ}$  to  $15^{\circ}$  to its 1-oxide, m.p.  $172-172.5^{\circ}$  (decomp.). (I) with  $\text{Cl}_2\text{-CS}_2$  at  $-15^{\circ}$  gives 2 : 3 : 4 : 5-tetrachlorotetrahydroselenophen, m.p.  $97^{\circ}$  (decomp.), decomposed at  $95^{\circ}$  to (II) and 2 : 2 : 5 : 5-tetrachlorotetrahydroselenophen, m.p.  $96-98^{\circ}$  [oxidised to its 1-oxide, m.p.  $149-150^{\circ}$  (decomp.)]. (I) with 20%  $\text{Br-CS}_2$  at  $-15^{\circ}$  gives the 1 : 1-dibromide (III), m.p.  $152^{\circ}$  (decomp.), of 2 : 2 : 5 : 5-tetrabromotetrahydroselenophen (IV), m.p.  $97^{\circ}$ , which is obtained, together with its 1-oxide (V), m.p.  $128.5-130^{\circ}$  (decomp.), by decomp. with  $\text{H}_2\text{O}$ , and is reconverted into (III) by  $\text{Br-CS}_2$  at room temp. (V) is also obtained by oxidation of (IV) with fuming  $\text{HNO}_3$ , and is reconverted into (IV) by either hot cyclohexanol or hot  $\text{PhMe}$ . A 10% solution of (I) in  $\text{CS}_2$  with cold 10%  $\text{Br-CS}_2$  gives 2-bromoselenophen, b.p.  $59^{\circ}/13\text{ mm.}$ , the 2 : 5- $\text{Br}_2$  (VI), b.p.  $42^{\circ}/0.02\text{ mm.}$ , and 2 : 3 : 5- $\text{Br}_3$ -derivative, b.p.  $94^{\circ}/0.12\text{ mm.}$ , m.p.  $38^{\circ}$ , being obtained when excess of Br is used. Excess of Br and (I) without solvent give tetrabromoselenophen, m.p.  $102^{\circ}$ , oxidised by fuming  $\text{HNO}_3$  to  $(\text{CBr-CO}_2\text{H})_2$ . Excess of  $\text{Cl}_2$  and a  $\text{CS}_2$  solution of (VI) give 2 : 5-dibromo-2 : 3 : 4 : 5-tetrachlorotetrahydroselenophen, m.p.  $70-72^{\circ}$ . J. W. B.

Preparation of dibenzanthronyl, mixed benzanthrone-anthraquinone, dianthraquinonyl, and benzanthrone selenoethers.—See B., 1936, 489.

X-Ray studies of protein structure. W. T. ASTBURY (Nature, 1936, 137, 803-805).—A summary of three lectures. L. S. T.

Nature of ostacin-ovo-ester from lobsters. P. KARRER and H. HUBNER (Helv. Chim. Acta, 1936, 19, 479-480).—In spite of its hypophasic behaviour on partition, the ostacin ester from lobster eggs ("ovo-ester") (prop. detailed) is shown by analysis to be  $\text{C}_{40}\text{H}_{47}\text{O}_4\cdot\text{CO}\cdot\text{C}_{5-7}\text{H}_{11-15}$  or an ester of a similar, but unsaturated, acid. R. S. C.

Separation of amino-acids. III. Adsorption of amino-acids by Japanese clay from protein hydrolysate. IV. Dissolving out of amino-acids adsorbed by Japanese clay. M. MASHINO and N. SHIKAZONO (J. Soc. Chem. Ind. Japan, 1936, 39, 88B).—III. Of the various forms of N in the hydrolysate of soya-bean protein after removal of glutamic acid. Japanese clay adsorbs total N 45.14,  $\text{NH}_3\text{-N}$  21.77, humin-N 63.11, diamino-N 86.21, and monoamino-N 20.16%.

IV. The adsorbed  $\text{NH}_4$ -acids are best extracted with alkaline-earth hydroxides, especially  $\text{Ca(OH)}_2$ ; its dissolving power is < that of  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ , or aq.  $\text{NH}_3$ , but the latter group also extract more colouring matter and render the clay colloidal, unless  $\text{Ca(OH)}_2$  or  $\text{EtOH}$  is also added. J. W. B.

Constituents of acid globulins. Protein-C.—See this vol., 875.

Apparatus for drying organic compounds decomposed by heat. J. BOUILLLOT (J. Pharm. Chim., 1936, [viii], 23, 605-607).—Apparatus for drying under reduced pressure at  $30-60^{\circ}$  is described. J. L. D.

Ashing of organic matter with nitric acid. H. KAUNITZ (Mikrochem., 1936, 20, 104-106).—Vessels are described for avoiding loss of material

by spurting during ashing with  $\text{HNO}_3$ , which can be done in 3 hr. J. W. S.

Pregl's absorption apparatus for micro-determination of carbon and hydrogen.—See this vol., 815.

Structure in relation to chromic oxidation of nitrogenous substances. C. N. ACHARYA (Biochem. J., 1936, 30, 1026-1032; cf. this vol. 352).—In the determination of N by the  $\text{K}_2\text{CrO}_4\text{-H}_2\text{SO}_4$  oxidation method with substances containing C-2N and C-3N linkings and  $\text{NH}_2\text{OH}$  derivatives the low vals. obtained are due to the formation of  $\text{N}_2\text{O}$ ; with  $\text{N}_2\text{H}_4$  and azo-derivatives, to the formation of  $\text{N}_2$ . The method is modified by collecting the gases evolved after absorption of  $\text{CO}_2$  and determining the  $\text{O}_2$  by pyrogallol absorption and the  $\text{N}_2\text{O}$  by explosion with  $\text{H}_2$ . H. D.

Determination of nitrogen by the Kjeldahl method.—See this vol., 811.

Micro-analytical determination of active hydrogen by the Tschugaev and Zerevitinov method. Simultaneous determination of the active hydrogen atom and of the Grignard reagent consumed. A. SOLTYS (Mikrochem., 1936, 20, 107-125).—Sufficient material to yield about 1 c.c. of  $\text{CH}_4$  is weighed, 0.5 c.c. of anethole added, and introduced into a micro-gas-evolution apparatus in which the air is displaced by  $\text{N}_2$ . A known vol. of Grignard reagent is introduced and the  $\text{CH}_4$  evolved is measured. Excess of  $\text{NH}_2\text{Ph}$  is then added and the amount of  $\text{CH}_4$  now produced indicates the amount of reagent unconsumed. Details of apparatus and procedure are described. J. W. S.

Micro-analytical determination of oxygen in organic substances. H. HENNIG (Chem. Fabr., 1936, 9, 239-241).—The material is hydrogenated by combustion in  $\text{H}_2$ , freed from  $\text{O}_2$  by hot Cu, in presence of a Ni catalyst carried on pumice at  $400-420^{\circ}$ . J. S. A.

Determination of small quantities of an organic substance in the air. T. BREHMER (Suomen Kem., 1936, 9, B, 14).—The author's method (A., 1935, 876) is used to determine the v.p. of  $\text{C}_{10}\text{H}_8$  at  $15^{\circ}$  to  $40.5^{\circ}$ ; results are in agreement with the literature. Org. halogen compounds are determined by making the compound react with a metal or metallic oxide (of which the corresponding carbonate has low  $\text{CO}_2$  pressure), or with a metallic carbonate (of high  $\text{CO}_2$  pressure). On applying the necessary corrections, the vals. of the v.p. of  $p\text{-C}_6\text{H}_4\text{Br}_2$  at  $17.8^{\circ}$  to  $23^{\circ}$  given by the two methods are concordant. E. W. W.

Coloured crystalline precipitates.—See this vol., 812.

Determination of citric acid in presence of certain organic substances. A. I. KOGAN and S. D. SCHTEIPELMAN (J. Appl. Chem. Russ., 1936, 9, 568-571).—3-4 ml. of buffer solution (49 g. of  $\text{H}_3\text{PO}_4$  and 68 g. of  $\text{KH}_2\text{PO}_4$  per litre) are added to 100 ml. of solution in a flask fitted with a condenser, and 0.05%  $\text{KMnO}_4$  is added drop by drop to the boiling solution to the appearance of a permanent coloration.  $\text{MeCHO}$  (from lactic or tartaric acid, glucose, or tannins)

is removed from the distillate by adding 5 ml. of 25%  $\text{H}_2\text{SO}_4$  and 5 ml. of 5%  $\text{KMnO}_4$ , excess of which is eliminated by adding  $\text{FeSO}_4$ , excess of  $\text{NaOH}$  is added, the vol. is made up to 300 ml., and the solution is filtered. Excess of 0.1N-I in KI is added to 100 ml. of filtrate, the solution is shaken for 15 min., made acid with  $\text{H}_2\text{SO}_4$ , and excess of I is titrated. The method depends on the reactions: citric acid  $\rightarrow \text{COMe}_2$ ;  $6\text{NaOH} + 6\text{I} \rightarrow 3\text{NaI} + 3\text{NaOI}$ ;  $\text{COMe}_2 + 3\text{NaOI} \rightarrow \text{CHI}_3 + \text{NaOAc} + 2\text{NaOH}$ . R. T.

$\beta$ -Naphthoylhydrazine as a reagent for the identification of aldehydes and ketones. H. CHEN and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 62—68).— $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{Et}$  with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in boiling EtOH affords  $\beta$ -naphthoylhydrazine (cf. A., 1932, 847) which with the theoretical amount of aldehyde or ketone in 95% EtOH containing a little AcOH gives the hydrazone.  $\beta$ -Naphthoylhydrazones (m.p. in parenthesis) of the following are prepared: MeCHO (109—110°); EtCHO (165—166°); PrCHO (187—188°);  $\text{Pr}^i\text{CHO}$  (146—147°); BuCHO (158—159°) *n*-hex- (96—97°) and *n*-heptaldehyde (114—115°); PhCHO (213—214°); *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (234—235°); 5-methylsalicylaldehyde (196—197°); furfuraldehyde (199—200°);  $\text{COMe}_2$  (145—146°); Me hexyl ketone (84—85°); COPhMe (201—202°); *p*-bromo- (219—220°), *p*-methyl- (181—182°), and *p*-methoxy-acetophenone (210—211°); Et (135—136°) and benzyl laevulate (111—112°), and laevulic acid (142—143°). Primary and *sec.* alcohols are identified after oxidation. J. L. D.

*m*-Bromobenzhydrazide as a reagent for the identification of aldehydes and ketones. CHUNG-HSI KAO, T. TAO, CHENG-HENG KAO, and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 69—74; cf. A., 1934, 790).—*m*-Bromobenzhydrazide (A., 1899, i, 136) with aldehydes or ketones in boiling 95% EtOH gives *m*-bromobenzoylhydrazones. Derivatives (m.p. in parenthesis) are prepared from: MeCHO (160—161°); EtCHO (135—136°); PrCHO (97—98°); BuCHO (88—89°); *n*-hept- (71—72°), *m*-nitrobenz- (217—218°), and *p*-nitrobenz-aldehyde (240—241°); furfuraldehyde (197—198°); 5-methylsalicylaldehyde (222—223°); cinnamaldehyde (210—211°);  $\text{CH}_3\text{Ac}_2$  (126—127°); COPhMe (162—163°); *p*-methyl- (188—189°) and *p*-methoxy-acetophenone (163—164°); COPh<sub>2</sub> (128—129°); laevulic acid (155—156°); benzyl laevulate (102—103°). J. L. D.

Reduction of silver nitrate by cuprous oxide applied to the determination of reducing sugars. V. HARLAY (J. Pharm. Chim., 1936, [viii], 23, 589—594).—Glucose with an alkaline Cu salt ppts.  $\text{Cu}_2\text{O}$  which is determined with  $\text{AgNO}_3$ . J. L. D.

Analytical uses of Nessler's reagent. M. GOSWAMI and B. C. DAS-PURKAYASTHA (J. Indian Chem. Soc., 1936, 13, 73).—Fructose and sucrose have been determined by the method previously described (this vol., 745). E. E. A.

Azides. V. 3-Nitrobenzazide as a reagent for the identification of amines. K. MENG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 75—79; cf. A., 1934, 997; 1935, 207).—3-Nitrobenzazide with an amine in dry hot PhMe gives a carbamide.

Carbamides are prepared (m.p. in parenthesis) from the following: *o*- (227—228°) and *p*-nitro- (270—271°), *p*-chloro- (212—213°), and *p*-bromo-anilino (257°); NHPPhEt (104—105°); *o*- (214—215°), *m*- (191—192°), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  (202—203°); *m*-nitro-*p*-toluidine (213—214°);  $\alpha$ - (238—239°) and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  (245—246°); NHPPhAc (135—136°); *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NHAc}$  (152°); acet-*o*- (233—234°) and *p*-toluidide (241—242°); *m*-bromo-*p*-toluidine (192—193°). J. L. D.

Reactions of cystine and materials containing cystine. A. STEIGMANN (Phot. Ind., 1935, 33, 445—446; Chem. Zentr., 1935, ii, 1486).—A reaction is given, in conjunction with the Feigl and albumin reactions, for the sp. identification of cystine, keratoses, albumins, and albumoses. J. S. A.

Precipitation of cystine.—See this vol., 881.

Separation of amino-acids. V. Recovery of Japanese acid clay [after use for adsorption of] amino-acids. M. MASHIMO and N. SHIKAZONO (J. Soc. Chem. Ind. Japan, 1936, 39, 136B; cf. this vol., 561).—The  $\text{NH}_3$ -acid is removed with CaO and the clay washed with the theoretical amount of HCl and then with  $\text{H}_2\text{O}$ . The total N, but not the protein-N, adsorbed decreases with repeated use of the clay. Recovery of the protein by CaO is complete after the first adsorption. R. S. C.

Determination of camphor as 2:4-dinitrophenylhydrazone in concentrated and dilute alcoholic solutions of camphor. M. M. JANOT and M. MOUTON (J. Pharm. Chim., 1936, [viii], 23, 547—549).—The method of Hampshire and Page (B., 1935, 253) is examined and modified, and is compared with that of Bougault and Leroy (B., 1928, 690). E. W. W.

Micro-determination of uric acid. N. L. EDSON and H. A. KREBS (Biochem. J., 1936, 30, 732—735).—A method for conversion of uric acid (I) by way of allantoin and allantoic acid into a mixture of  $\text{CO}(\text{NH}_2)_2$  (II) and  $\text{CHO}\cdot\text{CO}_2\text{H}$  (III) is described. Either end product can then be determined, (III) either colorimetrically or by  $\text{HSO}_3^-$ -titration and (II) by various methods. In determinations of 0.1—2.0 mg. of (I), (II) is determined manometrically using urease, the method being sp. and having a const. error of  $8 \pm 3\%$  which is corr. for. The method is particularly suitable for use in conjunction with tissue slice work but is not suitable for blood analysis or for solutions containing  $< 0.1$  mg. of (I) per 5 ml. of fluid. P. W. C.

The Vitali reaction: new technique permitting micro-determination of substances giving the reaction. C. MORIN (J. Pharm. Chim., 1936, [viii], 23, 545—547).—When atropine or hyoscyamine is evaporated with fuming  $\text{HNO}_3$  and the residue dissolved in anhyd.  $\text{COMe}_2$  and treated with 10% MeOH-KOH, an intense and comparatively stable violet coloration results, by means of which small quantities of the alkaloid may be determined colorimetrically. E. W. W.

Determination of the number of replaceable hydrogen atoms in strychnine, vomicine, and phloroglucinol. H. ERLNMEYER, A. EPPRECHT,



and H. LOBECK (Helv. Chim. Acta, 1936, 19, 543—545).—Strychnine nitrate, vomicine nitrate, and phloroglucinol exchange 1, 3, and 6 H, respectively, for D, when cryst. from 99.6% D<sub>2</sub>O. R. S. C.

Determination of total basic amino-acids in gelatin by titration in glacial acetic acid. J.

RUSSELL and A. E. CAMERON (J. Amer. Chem. Soc., 1936, 58, 774—775).—Titration of a gelatin (dissolved in a little H<sub>2</sub>O and then diluted with AcOH) with 0.0119N-HClO<sub>4</sub> using a H electrode indicates the presence of  $9.6 \times 10^{-4}$  equiv. of dibasic NH<sub>2</sub>-acids per g. Titration curves for lysine and arginine in AcOH are given. H. B.

## Biochemistry.

Relations between oxygen consumption, carbon dioxide production, and expired air during respiration in man. J. JOANID and F. NEPVEUX (Compt. rend. Soc. Biol., 1936, 121, 1618—1620).—CO<sub>2</sub> production  $\propto$  ventilation, but O<sub>2</sub> consumption is const. R. N. C.

Determination of basal metabolism in the adult pigeon during nutritional studies. R. LECOQ and J. M. JOLY (Compt. rend. Soc. Biol., 1936, 122, 193—195).—The R.Q. can be determined by direct measurement of O<sub>2</sub> consumed and CO<sub>2</sub> produced. A coeff. is given to determine the surface area of the body. R. N. C.

Absorption of dust through respiration. II. Absorption of pyrolusite dust. O. EHRSIMANN (Z. Hyg., 1935, 117, 662—678).—MnO<sub>2</sub> is adsorbed by rabbits and cats exposed to pyrolusite dust, but there is no essential increase of Mn in the organs, particularly the lungs. R. N. C.

Permeability of the mammalian erythrocyte to deuterium oxide (heavy water). A. K. PARPART (J. Cell. Comp. Physiol., 1935, 7, 153—162).—The rate of penetration of ox and rat erythrocytes by 99.5% D<sub>2</sub>O is about 44% < that by H<sub>2</sub>O; the permeability is apparently uninjured by D<sub>2</sub>O. R. N. C.

Permeability of erythrocytes to deuterium oxide (heavy water). S. C. BROOKS (J. Cell. Comp. Physiol., 1935, 7, 163—171).—The rate of hæmolysis of sheep erythrocytes by solutions containing D<sub>2</sub>O is < that by H<sub>2</sub>O alone, given equal concn. gradients. This is due largely to differences in fugacity. R. N. C.

Osmotic properties of the erythrocyte. VII. Temperature coefficients of certain hæmolytic processes. M. H. JACOBS, H. N. GLASSMAN, and A. K. PARPART (J. Cell. Comp. Physiol., 1935, 7, 197—225).—The temp. coeff. of hæmolysis of human, rat, mouse, rabbit, and guinea-pig erythrocytes in isotonic glycerol solution is low. Hæmolysis is rapid, and is retarded by CO<sub>2</sub>, acids, and traces of Cu, the temp. coeff. being increased. Ox, sheep, swine, horse, dog, and cat erythrocytes show slow hæmolysis, high temp. coeff., and often acceleration of hæmolysis by acids and Cu. R. N. C.

Permeability of red blood corpuscles to organic anions. R. HÖBER (J. Cell. Comp. Physiol., 1936, 7, 367—391).—Penetration of anions across a collodion membrane is > that expected from the migration velocity, due to surface activity in the case of fatty acids, and the hydrotropic properties in the case of sulphonates and aromatic anions. Anions of

OH- and polybasic acids lack these properties and are rather inactive. The permeability of the red cell membrane is similar, but the presence of lipins facilitates the entrance of fatty and aromatic anions, particularly with sheep and ox corpuscles. R. N. C.

Magnetic properties and structure of hæmoglobin, oxyhæmoglobin, and carboxyhæmoglobin.—See this vol., 867.

Hæmocuprin from hæmocyanins. J. ROCHE and P. DUBOULOZ (Compt. rend. Soc. Biol., 1936, 122, 234—236).—Hæmocuprin is a polypeptide containing tyrosine, arginine, and leucine. R. N. C.

Isoelectric point of fibrinogen. E. KYLIN and F. PAULSEN (Biochem. Z., 1936, 285, 159—174).—Fibrinogen (I) yields an acid and two basic fractions on subjection to cataphoresis. One basic fraction (min. stability at  $p_H$  7.3 and < 12.4) is colourless, is coagulated by heat at 55°, and is pptd. on 28% saturation with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, saturation with MgSO<sub>4</sub>, and half saturation with NaCl. The other (min. stability at  $p_H$  7.3) is white, is coagulated by heat at 37°, and is pptd. on 16% saturation with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, half saturation with MgSO<sub>4</sub>, and 33% saturation with NaCl. The isoelectric points are: acid fraction  $p_H$  5.4, basic fractions 12.4 and 8.5, respectively. The theory of ideal ampholytes does not hold for (I). (I) of exudates consists entirely of the second basic fraction. W. McC.

Viscosity of fibrinogen. E. WOHLISCH and A. KIESGEN (Biochem. Z., 1936, 285, 200—206; cf. this vol., 562).—Fibrinogen (I) (from horse plasma) exhibits anomalous  $\eta$ , the deviation from normal decreasing with rising temp. High concns. of urea reversibly inhibit coagulation of (I) solutions by heat, EtOH, and thrombin (II) and increase  $\eta$ , greatly reducing the abnormality. After extraction with Et<sub>2</sub>O the temp. of denaturation of (I) is raised; denaturation with EtOH and heat and coagulation with (II) are more difficult, and  $\eta$  is normal. These results confirm the view that (I) has a fibrous mol. structure. W. McC.

Protein equilibrium of serum during sensitisation and serum shock. AUBRY, THIODET, and RIBERE (Compt. rend. Soc. Biol., 1936, 122, 209—212).—The albumin/globulin ratio increases during sensitisation, falls rapidly at the crisis, and rises again at the end of the reaction. R. N. C.

Precipitation of serum-proteins by ammonium sulphate: arterial hypertension. A. ROCHE, M. DORIER, and L. SAMUEL (Compt. rend. Soc. Biol.,

1936, 122, 231—233).—In cases of hypertension, pptn. does not separate albumin (I) and globulin (II), and the (I)/(II) ratio has no significance. The modifications are associated with the nature of the proteins rather than with the (I) and (II) contents of the serum. R. N. C.

**Constituents of acid globulins. Protein C.** M. DOLADILHE (Compt. rend., 1936, 202, 1385—1387).—The serum of human, ox, or sheep blood is aged under sterile conditions for 4—5 days at 0°; the acid globulins therefrom are dissolved in physiological aq. NaCl (1/10 vol. of the serum); CO<sub>2</sub> then ppts. protein *B* and a new protein *C*. The mixed ppt. is redissolved in aq. NaCl and centrifuged at 45° for 15 min., whereby protein *A* is pptd.; *C* separates on cooling. *C* dissolves in H<sub>2</sub>O at higher temp. and is repptd. on cooling, unless the solution has been heated above a certain temp. This crit. temp. is usually 55°, but is higher if the ageing of the serum has been prolonged (e.g., 8—15 days) or slightly less if *B* has been heated at too high a temp. (which also decreases the pptn. of *C* by CO<sub>2</sub>). *C* is a constituent of group *B* and a probable factor of complement. Ageing and heat diminish the physiological effects of the latter in serum at the same time as affecting the physical properties of the former. R. S. C.

**Biochemistry of choline and its derivatives. I. Acetylcholine in blood.** E. KAHANE. II. Biological determination of acetylcholine. J. LÉVY and L. OLSZYCKA. III. Determination of acetylcholine in biological material. IV. Action of blood on esters of quaternary ammonium compounds. E. KAHANE and J. LÉVY (Bull. Soc. Chim. biol., 1936, 18, 479—489, 490—504, 505—528, 529—555).—I. Introductory.

II. The method makes use of the fact that 0.03—0.2 × 10<sup>-6</sup> g. of acetylcholine (I) may be detected by the fall in blood pressure produced on intravenous injection into chloralised dogs. The effect of the material to be determined is compared with that produced by (I) chloride. Eserine sulphate (II) may be used to increase the reaction of the animals.

III. The above method is applied to the determination of (I) added to serum and blood. The technique of chemical methods of determining (I) involving hydrolysis and pptn. as phosphotungstate, silicotungstate, Reineckate, and periodate is described. The pharmacological method may also be applied to these ppts.

IV. Propionyl-, formyl-, and acetyl-choline are rapidly hydrolysed by serum; betaine Et ester, acetyl-β-methylcholine, and benzoylcholine are slowly attacked, and bromocholine and the nitric and carbamic esters of choline are not hydrolysed. Injections of (II) only increase the hypotensive action of those esters which are rapidly hydrolysed. A. L.

**Acetylcholine-like substance dissimulated in normal blood.** E. KAHANE and J. LEVY (Compt. rend., 1936, 202, 1210—1212).—The fluid obtained when blood is treated with boiling H<sub>2</sub>O and then EtOH contains an acetylcholine-like substance (0.01—1.5 × 10<sup>-5</sup> g. per c.c.) which is not ultrafilterable and may be the precursor of acetylcholine. J. L. D.

**Blood-glutathione and pulmonary respiration.** L. BINET and S. BARRET (Compt. rend. Soc. Biol., 1936, 122, 16—18).—Perfusion of a dog's lung ventilated with O<sub>2</sub> diminishes the reduced glutathione (I) content of the blood. In N<sub>2</sub> (I) increases, subsequent ventilation with O<sub>2</sub> decreasing it again. R. N. C.

**Determination of indole in blood.** P. MAZZOCCO (Rev. soc. argentina biol., 1935, 11, 31—37).—Oxalated blood (1 c.c.) is extracted successively with 3, 2, 2, and 1 c.c. of Et<sub>2</sub>O and the combined extract is diluted to 12 c.c. with EtOH. *p*-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO (10 drops of 5% EtOH solution) followed by 2 c.c. of conc. HCl are added and the colour is matched against a standard. Blood-urobilinogen interferes since it gives a red colour.

CH. ABS. (p)

**Extraction of blood-lipins.** E. M. BORD (J. Biol. Chem., 1936, 114, 223—234).—The limitations of the Bloor lipin extractions (A., 1915, ii, 805) are investigated. For aliquots > 3 c.c. 20 vols. of EtOH-Et<sub>2</sub>O for plasma and 30 vols. for whole blood are required; warming and variation of the EtOH : Et<sub>2</sub>O ratio were without influence. Oxalated plasma had higher vals. than defibrinated serum. H. D.

**Relationship between total and free cholesterol in human blood-serum.** W. M. SPERRY (J. Biol. Chem., 1936, 114, 125—133).—In 126 samples of serum from 91 healthy adults, the min. amount of free in total cholesterol (I) was 24.3% (max. 30.1%; average 26.9%). Most samples taken after sudden death gave vals. within the same range. Similar results were obtained in healthy children and in 80% of diseased children. The % of free (I) in total (I) may be of val. in the study of (I) metabolism and in pathology. J. N. A.

**Blood-cholesterol in rabbits painted or injected with benzopyrene.** Y. POURBAIX and N. DENISOFF (Compt. rend. Soc. Biol., 1936, 122, 128—130).—There is no appreciable variation. R. N. C.

**Normal blood-sugar in domestic animals.** A. S. CAMPORI (Rev. Med. vet. Buenos Aires, 1935, 17, 47—75).—The vals. were: cows 40—70, horses 50—100, asses 40—100, cats 50—120, dogs 50—100, poultry 100—214 mg. per 100 ml. NUTR. ABS. (m)

**Fasting blood-sugar in rats.** E. M. GREISHEIMER, E. GEORGE, and L. GILMAN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1669).—The rate of decrease of blood-sugar in females is > in males, and is greatest in both sexes between 12 and 24 hr. R. N. C.

**Rapid methods of blood-sugar determination with potassium ferricyanide.** C. H. HAGEDORN, F. HALSTRÖM, and N. JENSEN (Hospitalstidende, 1935, 78, 1193—1202).—To 0.1 or 0.05 ml. of blood are added 1 ml. of 0.1N-NaOH and 5 ml. of 0.45% aq. ZnSO<sub>4</sub>, the mixture is heated at 100° for 4 min., and after cooling, filtered through purified cotton wool. Then 2 ml. of alkaline 0.005N-K<sub>3</sub>Fe(CN)<sub>6</sub> are added and the mixture is heated for 5 min. at 100°. When cold, KI is added, then 1 ml. of citric acid and ZnSO<sub>4</sub> reagent, and the I liberated titrated with 0.005N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Rapidity is increased by heating in an open flask and using tablet reagents.

NUTR. ABS. (m)



**Widmark's method of blood-alcohol determination.** H. ELBEL (Deut. Z. ges. gerichtl. Med., 1935, 25, 124—129; Chem. Zentr., 1935, ii, 1585).—Methods for increasing the accuracy are described.

H. N. R.

**Variations of blood-copper in normal children at different ages.** F. LESNÉ, P. ZIZINE, and S. B. BRISHKAS (Compt. rend. Soc. Biol., 1936, 121, 1582—1583).—Blood-Cu falls after birth, fluctuates at < 1 mg. per litre in the first 10 days, and then increases to a steady val. of 1.35 mg. per litre in the first or second month.

R. N. C.

**Determination of total iron in blood.** F. B. SHORLAND and E. M. WALL (Biochem. J., 1936, 30, 1047—1048).—The blood (0.5 ml.) is digested with  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$  and the Fe determined by a modification of the 2:2'-dipyridyl method.

J. N. A.

**Action of certain reagents on the "loosely bound" iron in blood.** F. B. SHORLAND and E. M. WALL (Biochem. J., 1936, 30, 1049—1052).—Thioacetic acid has a definite action on haemoglobin-Fe (I) and cannot be used for determination of non-haemoglobin-Fe (II).  $\text{Na}_4\text{P}_2\text{O}_7$  does not attack (I) and gives a good recovery of inorg. Fe added to blood. The vals. obtained for (II) by use of  $\text{Na}_4\text{P}_2\text{O}_7$  are much lower than those obtained by Starkenstein and Weden's method (A., 1928, 1275).

J. N. A.

**Iron content and oxygen capacity of blood.** M. JOHNSON and M. E. HANKE (J. Biol. Chem., 1936, 114, 157—170).—An iodometric method by which the Fe in blood may be determined to  $10^{-6}$  g. per litre of blood is described. To obtain this accuracy, complete oxidation of the blood, removal of  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , and control of the concn. of acid and salts for the  $\text{Na}_2\text{S}_2\text{O}_3$  titration are essential. The conversion factor for  $\text{Na}_2\text{S}_2\text{O}_3$  must be determined with standard  $\text{FeCl}_3$ , as it varies with the amount of Fe. The end-point must be determined under standardised conditions as regards amounts of KI and time intervals. The Fe content and  $\text{O}_2$  capacity of blood agreed within 1%.

J. N. A.

**Determination of lead in blood.** AXON. (Chem. Ztg., 1936, 60, 368).—Various methods are described.

F. O. H.

**Iodometric determination of chloride in small amounts of blood.** A. D. HASLEWOOD and E. J. KING (Biochem. J., 1936, 30, 902—905).—The method uses the fact that on adding  $\text{AsIO}_3$  in aq.  $\text{NH}_3$  solution to solutions containing  $\text{Cl}^-$  an amount of  $\text{IO}_3^-$  equiv. to the  $\text{Cl}^-$  passes into solution, which on determination iodometrically liberates 6I for each  $\text{Cl}^-$  originally present. The method is used for determinations of pure  $\text{NaCl}$  and of  $\text{Cl}^-$  in  $\text{Zn}(\text{OH})_2$  nitrates of 0.2 ml. of blood or plasma, the results in the latter case agreeing within 1% amongst themselves and with gravimetric analyses.

P. W. C.

**Effect of diet on blood-phosphorus partition of rats with or without insulin.** N. VAN CLEVE and A. F. MORGAN. Proc. Soc. Exp. Biol. Med., 1935, 32, 1636—1641).—Insulin evokes a decrease of inorg. P only in animals on a high-fat diet. Other determined P fractions vary only slightly: total P is unchanged and org. P tends to increase.

R. N. C.

**Distribution of phosphorus compounds in human and animal blood.** H. NISSEN (Z. Kinderheilk., 1935, 57, 289—320; Chem. Zentr., 1935, ii, 1571).—Analytical vals. are given for the different P fractions in the blood of man and a no. of animals.

R. N. C.

**Acid-base condition of blood.** V. Influence of protein concentration on the colorimetric  $p_{\text{H}}$  determination of blood-serum. H. W. ROBINSON, J. W. PRICE, and G. E. CULLEN (J. Biol. Chem., 1936, 114, 321—340).—The influence of the protein concn. on the correction to be applied to the determined val. of serum- $p_{\text{H}}$  by Cullen's method (A., 1922, ii, 672) is studied by comparing the  $p_{\text{H}}$  vals. of sera conc. by ultrafiltration and diluted with the ultrafiltrate. The correction  $\propto$  log protein concn.

H. D.

**Determination of the  $p_{\text{H}}$  of blood with the glass electrode.** G. HAUGAARD and E. LUNDSTEEN (Biochem. Z., 1936, 285, 270—281).—Methods of determining the  $p_{\text{H}}$  of venous and capillary blood are described. Determinations must be made  $> 5$  min. after drawing the blood. Part of the titration curve of venous blood has been plotted.

W. McC.

**Anion and cation contents of normal and anæmic blood.** M. MAIZELS (Biochem. J., 1936, 30, 821—830).—The concn. of anions and cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$ ) in erythrocytes is < that in plasma, the resulting deficiency in cellular osmotic pressure indicating binding of approx. 8% of the cell- $\text{H}_2\text{O}$ . The excess of base over  $\text{Cl}^- + \text{HCO}_3^- + \text{Hb}^+$  in the cells indicates the presence of another anion which is increased in anæmia but not in acholuric jaundice. Concn. of cell-cation is relatively const. despite wide variations in cell-Hb and in blood regeneration and destruction. Cellular changes in acholuric jaundice are discussed.

F. O. H.

**Ionisation and buffers of the internal medium of the parasitised sacculenised crab (*Carcinus maenas*).** A. DRILHON and E. A. PORA (Compt. rend., 1936, 202, 1309—1311).—The parasite causes a disappearance of the buffering substances of the serum, whereas the presence of the large amount of  $\text{CO}_2$  in the hæmolymph maintains a high alkaline reserve and lowers the  $p_{\text{H}}$ .

H. G. R.

**Composition of arterial blood after ingestion of saline solution.** P. CAMBIER and G. BARDOS (Compt. rend. Soc. Biol., 1936, 122, 130—132).—Ingestion of Priestley's solution causes dilution of the blood with only feeble diuresis compared with that from ingestion of  $\text{H}_2\text{O}$ .

R. N. C.

**Water content of the blood of the normal human adult.** Correlation between the water content of blood from the ear lobe and that from the median vein. T. RYÖ (Keijo J. Med., 1935, 6, 9—22).—Average vals. were 79.25% for the ear and 79.74% for the median vein.

CH. ABS. (p)

**Water content of the blood of chicken during the course of development.** K. KURODA (Keijo J. Med., 1935, 6, 23—29).—Max. vals. were observed at hatching; a min. at 2 weeks was followed by a second max. and a subsequent decline to a const. level.

CH. ABS. (p)

**Lipin films in relation to the structure of the plasma membrane.** J. F. DANIELLI (J. Cell. Comp. Physiol., 1936, 7, 393—407).—Continuous lipin and mosaic films are all metastable, the lipin films being the more stable. The prep. of shell-lipin films is described. R. N. C.

**Spontaneous reversibility of the gelation of serum.** I. KOPACZEWSKA, W. KOPACZEWSKI, and S. MARCZEWSKI (Compt. rend., 1936, 202, 1212—1214).—Normal human serum in  $H_2O$  gels in presence of 0.1—0.3*N*-NaOH. The optimum rate of gelation for any concn. of serum occurs with only one [NaOH]. The gel liquefies, the rate being greatest when [NaOH] is high and the serum is very dil. J. L. D.

**Gelation of human serum by bases.** S. MARCZEWSKI (Compt. rend., 1936, 202, 510—511; cf. A., 1935, 374).—The period of gelation by NaOH and various org. bases decreases with rising temp. Certain bases (toluidine, PhOH) have no direct action, but accelerate gelation by other bases. Still other bases, even at high concns., are ineffective. Factors other than  $[OH^-]$  are concerned in gelation. A. G. P.

**Relations between electric charge and hydration of flocculation of blood-serum.** R. JONNARD (Compt. rend. Soc. Biol., 1936, 122, 48—50).—The curve of the EtOH/acid ratio for flocculation to begin and the acid concn. is almost a rectangular hyperbola. The ratio at any given acid concn. is const. and independent of the serum concn. R. N. C.

**Nature of agglutinogens.** G. BRUYNOGHE (Compt. rend. Soc. Biol., 1936, 122, 94—95).—The A and B isoagglutinogens are proteins, whilst the M and N supplementary agglutinogens are lipins. R. N. C.

**Mode of formation of aggregates in bacterial agglutination.** W. W. C. TOPLEY, J. WILSON, and J. T. DUNCAN (Brit. J. Exp. Path., 1935, 16, 116—120).—Experimental data throw doubt on the view that flocculation occurs in two stages, one sp. and one non-sp., but accord well with Marrack's lattice theory. CH. ABS. (p)

**Relation between the complement and opsonin of normal serum.** J. GORDON and F. C. THOMPSON (Brit. J. Exp. Path., 1935, 16, 101—108).—Treatment of serum with  $NH_3$ , Congo-red, acid, alkali, or with hypertonic solutions of certain Na or K salts, or long storage at room temp. may inactivate the complement without affecting the concn. of opsonin. The latter is non-sp. and thermolabile, and resembles the complement in many respects, but is probably an independent system. Modified complement may possibly function as an opsonin. CH. ABS. (p)

**Specificity of hybrid proteins.** A. G. ZOET (Proc. Soc. Exp. Biol. Med., 1935, 32, 1469—1470).—Hybridised protein from horse and swine serum is serologically different from the serum-proteins of both species. R. N. C.

**Reactivation of ammonia-inactivated complement by leucocytes.** E. MALTANER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1555—1558). R. N. C.

**Nature of tuberculous antibodies: some properties peculiar to the guinea-pig.** K. MEYER

(Compt. rend. Soc. Biol., 1936, 122, 26—28).—The production of lipin (I) and protein antibodies (II) in normal guinea-pigs by the Besredka antigen (III) or extracts of tubercle bacilli is similar to that in rabbits, but in tuberculous animals (I) are often absent, whilst (II) react only feebly with the protein antigens, although strongly with (III). R. N. C.

**Mechanism of immunity to filterable viruses.** I. Does the virus combine with the protective substance in immune serum in the absence of tissue? II. Fate of the virus in a system consisting of susceptible tissue, immune serum, and virus and the role of tissue in the mechanism of immunity. A. B. SABIN (Brit. J. Exp. Path., 1935, 16, 70—84, 84—100).—I. There is no apparent union between the virus and the protective substance *in vitro*.

II. Immunity to virus intimately concerns the cell. Both protective substance and virus are fixed by the tissue. If fixation of the virus precedes that of protective substance infection is not prevented. Fixation in the reverse order or simultaneously prevents infection. CH. ABS. (p)

**Diffusion potentials in scallop muscles.** H. B. STEINBACH (J. Cell. Comp. Physiol., 1935, 7, 271—289).—The concn.  $E$  is the same at the injured and uninjured surfaces, the more dil. solution being positive for KCl but negative for NaCl,  $MgCl_2$ , or  $CaCl_2$ .  $Ca^{++}$  increases the  $[KCl]$   $E$  at the injured, but not the uninjured surface.  $E$  may be termed a diffusion concn. if the tissue is considered as a solution of a colloidal electrolyte. R. N. C.

**Nature and permeability of the grasshopper egg membrane.** I. E.m.f. across membranes during early diapause. T. L. JAHN (J. Cell. Comp. Physiol., 1935, 7, 23—46).—The apparent relative ionic mobilities of univalent cations across membranes increase in the same order as  $\Lambda_r$  in solution, but the differences are less. Those of bivalent cations fall very rapidly as concn. increases. The concn. effect is reversed by conc. solutions of bivalent ions ( $-\log c = 1.3$  approx.), and by HCl solutions at  $p_H < 2.1$ ; the membrane can recover from reversal by  $Ca^{++}$ , but only incompletely from reversal by HCl. The anion does not influence the concn. effect.  $E$  across the membrane in  $M$ - and  $0.1M$ -KCl is not affected by  $p_H$  between 4 and 6, but below  $p_H$  4 it falls rapidly, reaching zero at  $p_H$  2.2 and then becoming negative; equilibrium is established only slowly below  $p_H$  3. The exochorion and one of the cuticle layers of the egg are semipermeable, the former probably being responsible for  $E$  changes.  $E$  shows a definite correlation with the expected changes in potential for a protein surface. R. N. C.

**Electrical conductivity of yolk, albumin, and allantoic and amniotic fluids of developing birds' eggs.** A. L. ROMANOFF and H. J. GROVER (J. Cell. Comp. Physiol., 1936, 7, 425—431). R. N. C.

**Behaviour of the electrical conductivity of the yolk of the hen's egg with change of temperature.** A. ORRU (Atti R. Accad. Lincei, 1935, [vi], 22, 458—463).—Egg-yolk does not exhibit the hysteresis of  $\kappa$  at rising and falling temp. observed



with gelatin (A., 1930, 993). At 16—18° to 60° a straight-line graph of  $\kappa$  against temp. is obtained on heating the uncoagulated or coagulated yolk. At higher temp., changes of  $\kappa$  indicate a max. (72—76°) due to the coagulation of lecitho-vitellin, a second due to that of livetin, whilst a third is ascribed to a third protein, as suggested by Jukes and Kay (A., 1932, 957). E. W. W.

**Relation between acids and bases in the human brain cortex.** A. PETRUNKINA and M. PETRUNKIN (J. Physiol. Path. gén., 1935, 33, 1102—1113).—Grey matter of human brain cortex contains a large excess of base combined with the  $\text{CO}_2$  and colloids. The isoelectric point of the colloids is at  $p_H$  4.35. NUTR. ABS. (m)

**Calcium and phosphorus content of the body of the brook trout in relation to age, growth, and food.** C. M. McCAY, A. V. TUNISON, M. CROWELL, and H. PAUL (J. Biol. Chem., 1936, 114, 259—263).—The increases of body-Ca are chiefly due to absorption from  $\text{H}_2\text{O}$ . In the eggs and fry  $[\text{P}]$  is  $> [\text{Ca}]$ ; as soon as the fry start to feed the  $[\text{Ca}]$  increases rapidly. H. D.

**Primary calculi of the smaller intestine.** G. BLIX (Acta chirurg. Scand., 1935, 76, 25—34; Chem. Zentr., 1935, ii, 1391).—The calculi contain 58% of  $\text{CaC}_2\text{O}_4$ , 11% of choleic acid, and 1.4% of  $\text{ZnS}$ . The  $\text{ZnS}$  is formed from sol. Zn compounds by bacterial action. A. G. P.

**Histo-chemical detection of lead in bones.** E. SIEBER (Arch. exp. Path. Pharm., 1936, 181, 273—280).—Fixation by 70%  $\text{EtOH}$  or aq.  $\text{CH}_2\text{O}$  and decalcification by 30%  $\text{HCO}_2\text{H}$  (both saturated with  $\text{H}_2\text{S}$ ) indicates the distribution of Pb in bone-tissue of Pb-poisoned guinea-pigs. Variations of Pb distribution with age of Pb-poisoned animals are described. F. O. H.

**Chemical composition of the minerals of bone.** J. MAREK, O. WELLMANN, and L. URBANYI (Mezőg. kutat., 1935, 8, 217—225).— $\text{H}_2\text{O}$ , glycerol (I), aq.  $\text{KOH}$ ,  $\text{KOH}$  in (I), and aq.  $\text{K}_2\text{CO}_3$  hydrolyse the Ca-P compound of bones in the same way as they hydrolyse  $\text{Ca}_3(\text{PO}_4)_3$ . Hence bone-phosphate must be composed chiefly of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$  with small amounts of  $\text{Mg}_3(\text{PO}_4)_2$  and Ca alkali phosphates. NUTR. ABS. (m)

**Chemical determination of the age of fossilised bones.** J. GANGL (Oesterr. Chem.-Ztg., 1936, 39, 79—82).—Examination by ultra-violet light does not differentiate between fresh and 2000-year-old bones. The nature of the fats (as with "bog-butter") indicates, however, that with increasing age (2500—5500 years) the m.p., sap. val., and, more especially, the acid val. increase, whilst the I val. and glycerol content decrease. These changes are due to initial enzymic action and, to a greater extent, subsequent oxidation. F. O. H.

**X-Ray examination of tooth structure.** J. TREWLIS (Nature, 1936, 137, 828).—Enamel which is smooth and free from pigmentation contains much preferentially oriented apatite. A tooth is entirely enclosed by a thin layer of hypercalcified tissue which may act as a protecting layer against caries.

The arrangement of crystallites at the surface of the enamel generally differs from that of the interior.

L. S. T.

**Teeth. III. Variations in chemical composition in relation to dental structure.** J. H. BOWES and M. M. MURRAY (Biochem. J., 1936, 30, 977—984).—With increased hyperplasia the apatite content of the enamel decreased from 92 to 86% with a corresponding increase in some other P compound; in the dentine the val. decreased from 53 to 49%, but the variations were less regular. H. G. R.

**Copper content of the embryonic calf liver.** Z. GRUZEWSKA and G. ROUSSEL (Compt. rend. Soc. Biol., 1936, 122, 13—14).—Cu is equally distributed between the sol. and insol. ash, but is apparently contained in a complex which is decomposed only by inorg. acids. The liver-Cu curve is analogous to the Fe curve throughout embryonic development. The Fe/Cu ratio increases with the age of the embryo. R. N. C.

**Fatty acids of chrysalis oil.** W. BERGMANN (J. Biol. Chem., 1936, 114, 27—38).—Commercial chrysalis oil of *Bombyx mori* slowly deposits glyceryl  $\alpha$ -dipalmitate, which is, however, not formed from the oil from living chrysalides. The acids from both oils contain palmitic 20, stearic 4, palmitoleic 2, oleic 35, linoleic 12, and linolenic acid 28%, with  $< 1\%$  of other saturated and 1—2% of unsaturated acids with  $> 18^\circ\text{C}$ . The oils contain  $< 1\%$  of  $\text{COMe}_2$ -insol. matter. Chrysalis oil from *Malacosoma americana* has a similar composition but contains 7.1% of  $\text{COMe}_2$ -insol. phosphatide. R. S. C.

**Lipins of retina, brain, and blood.** P. J. LEINFELDER and P. W. SALIT (Amer. J. Ophthalm., 1934, 17, 619—624).—Methods of sampling and analysis are described. The lipin content of the retina is  $<$  of brain but  $>$  that of blood. Retinal tissue contains more  $\text{H}_2\text{O}$  and lecithin (%) but less protein and cholesterol than the other two tissues. Glycolipins have equal concn. in retina and brain. The I vals. of extracts of brain and of retina are similar, suggesting a similar rate of metabolism. CH. ABS. (p)

**Application of Fujita's method of blood-sugar determination to tissue-sugar.** R. WETZEL (Arch. exp. Path. Pharm., 1936, 181, 259—264).—The method (A., 1932, 75) is modified so as to be applicable to 0.05—1.50 mg. of glucose. Deproteinisation of tissue hydrolysates by phosphotungstic acid is permissible when excess of reagent is pptd. (as  $\text{K}_2\text{WO}_4$ ) by  $\text{KCl}$ . F. O. H.

**Production of glycogen in the liver from sugars.** Y. OTOMO (Tohoku J. Exp. Med., 1935, 27, 420—433).—In rabbits all sugars caused an increase in liver-glycogen as follows: glucose  $>$  fructose  $>$  galactose  $>$  sucrose  $>$  maltose  $>$  lactose. Intravenous injection gave in most cases higher vals. than did oral administration. NUTR. ABS. (m)

**Osmotic pressure of glycogen solutions.** H. B. OAKLEY and F. G. YOUNG (Biochem. J., 1936, 30, 868—876; cf. A., 1935, 297).—Solutions of glycogen from rabbit liver and muscle and methylated rabbit-liver glycogen in 0.1N- $\text{CaCl}_2$  gave osmotic pressures

indicating a mean particle wt. of the order of  $2 \times 10^6$ . A solution of methylglycogen in  $C_6H_6$  contained particles of the same order of magnitude ( $3.4 \times 10^6$ ). The significance of these results is discussed.

J. N. A.

**Determination of muscle-glycogen.** H. BERRY, B. GOUZON, and C. MAGNAN (Compt. rend. Soc. Biol., 1936, 122, 4—6).—The tissue is dissolved in 30% KOH by autoclaving at  $110^\circ$ , and glycogen (I) is pptd. with hot EtOH and removed by centrifuge. (I) is then hydrolysed with HCl at  $120^\circ$ , the solution is neutralised and deproteinised with  $Hg(NO_3)_2$ , excess of Hg being removed with Cu, and glucose determined by the micro-Bertrand method.

R. N. C.

**Carbohydrate groups of submaxillary mucin.** G. BLIX (Z. physiol. Chem., 1936, 240, 43—54).—The mucin (I) yields only traces of  $H_2SO_4$  on hydrolysis, indicating absence of mucoitinsulphuric acid as prosthetic group. Digestion of EtOH-dried (I) with boiling  $H_2O$ , extraction of the  $H_2O$ -sol. fraction with MeOH, and fractionation of the extract with  $Et_2O$  and light petroleum affords two carbohydrates. One [cryst. and forming 20—25% of (I)] contains hexosamine (1 mol.), an acidic (not hexuronic) group, and two Ac groups and gives a positive Ehrlich reaction; the other [forming 5% of (I)] is neutral, contains hexosamine (1 mol.) and hexose (2 mols.; probably mannose), and is probably of the same type as that from ovo- and serum-mucin.

F. O. H.

**Carbohydrate groups of some glucoproteins.** O. KARLBERG (Z. physiol. Chem., 1936, 240, 55—58).—Mucins from umbilical cord, cornea, and vitreous humour yield only traces of  $H_2SO_4$  on hydrolysis (indicating a low content of mucoitinsulphuric acid) and contain hexose and glucosamine approx. 1:1 (mol.).

F. O. H.

**Amino-acids in human skin.** H. C. ECKSTEIN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1573—1574).—Analytical vals. are given.

R. N. C.

**Basic amino-acids of human skin.** R. J. BLOCK (Proc. Soc. Exp. Biol. Med., 1935, 32, 1574—1575).—The analytical results agree closely with those of Eckstein (see preceding abstract).

R. N. C.

**Amino-acid content of cod muscle-protein.** E. ABDERHALDEN, E. BAERTICH, and W. ZIESECKE (Z. physiol. Chem., 1936, 240, 152—162).—All known  $NH_2$ -acids (including alanine 5.7, valine 3.7, leucine 7.5, glutamic acid 7.5, arginine 6.8, lysine 8.0, histidine 4.8%) are obtained on hydrolysis of the protein. Glycine (I) [but not other  $NH_2$ -acids or polypeptides containing (I)] gives a bluish-violet colour with pyrocatechol.

W. McC.

**Separation of amino-acids. III—V.**—See this vol., 872, 873.

**Choline in the animal organism.** J. GAUTRELET (Bull. Soc. Chim. biol., 1936, 18, 449—478).—A review of published work.

A. L.

**Composition of muscle of normal adult pigeons at rest.** R. LECOQ and R. DUFFAU (Compt. rend. Soc. Biol., 1936, 122, 180—182).— $H_3PO_4$ , total acid-sol. P, and adenyolphosphoric acid show const.

vals. for all the birds tested. Lactic acid and total reducing substances vary over a small range, whilst the readily hydrolysed phosphoric esters, particularly creatinephosphoric acid, vary considerably.

R. N. C.

**Bence-Jones proteinuria.** L. MEYLER (Arch. Int. Med., 1936, 57, 708—713).—Bence-Jones protein is present in normal bone-marrow probably in the lymphocytes and other leucocytes.

H. G. R.

**Crystalloids of the mammary gland.** J. GRYNFELT (Compt. rend., 1936, 202, 1300—1302).—These are present in the gland when colostrum is secreted and appear to be due to pptn. of protein.

H. G. R.

**Determination of particle weight and shape from diffusion and viscosity data.** A. POLSON (Nature, 1936, 137, 740).—Mol. wt. and shape of proteins have been determined from the diffusion const. and  $\eta$  by the formulæ given. For ovalbumin, lactoglobulin, serum-albumin, amandin, thyroglobulin, and octopus haemocyanin the particle wts. are approx. 0.71 of those obtained from sedimentation data.

L. S. T.

**Carotenoids of human serum and liver. I.** H. WILLSTAEDT and T. LINDQVIST (Z. physiol. Chem., 1936, 240, 10—18).—Chromatographic separation of serum-carotenoids indicated, in addition to that of  $\beta$ -carotene, the occasional presence of lycopene, zeaxanthin, and xanthophyll; these and, in one case, violaxanthin also occurred in the liver. Two unknown pigments with absorption max. at respectively 498, 468, 422, and 478, 559 in light petroleum, and 512 (?), 498, 470, and 493, 472 m $\mu$  in  $CS_2$  occurred in serum and liver; their probable nature is discussed.

F. O. H.

**Colouring matter of the shell of the cassowary's egg.** D. DYNELI (Atti R. Accad. Lincei, 1936, [vi], 22, 464—467).—The residue after treating the powdered shells with 5% HCl is extracted by MeOH, and the solution treated with MeOH-HCl. The green pigment obtained on evaporation is taken up in  $Et_2O$  and extracted with 0.5% aq. HCl. The neutralised product yields a mixture, decomp. 90—100°, which gives an absorption band at 650 m $\mu$ , but does not fluoresce after treatment with  $NH_3$  and  $Zn(OAc)_2$  (cf. A., 1931, 1066). The residue after the original MeOH extraction is also green: treated with 10% NaOH and acidified, it evolves  $H_2S$  and yields a green chromoprotein (N 14.3%).

E. W. W.

**Cytochrome-c. II. Preparation and properties.** H. THEORELL (Biochem. Z., 1936, 285, 207—218; cf. A., 1935, 1277).—Simplified methods of purification involving pptn. with  $(NH_4)_2SO_4$  and adsorption on  $BaSO_4$  and Cellophane followed by elution with HCl and pptn. with  $COMe_2$  are described. Purest cytochrome-c (I), mol. wt. 16,500, contains C 49.18, H 7.73, O 27.5, N 14.4, S 1.18, Fe 0.34%, and has isoelectric point  $p_H$  9.82 (borate buffer) and 9.86 (glycine-NaOH). At  $p_H$  7.0—9.3 the ionic mobility is independent of  $[H^+]$ . Dried (I) does not deteriorate on keeping and is not destroyed by N-HCl and N-NaOH. Reduced (I) exhibits absorption max. at 550, 540, 520, 470, and 415 m $\mu$  and bands at 345 (weak), 316 (strong), and 275 m $\mu$ , whilst



oxidised (I) exhibits bands at 520—550, 407, 364, and 276  $\mu$ . In  $H_2O$  at  $p_H < 2.5$  oxidised (I) exhibits one band only at 515—545  $\mu$  and at  $p_H > 13$  it exhibits bands at 570—580, 525—545  $\mu$ , the changes which produce these spectroscopically different forms of (I) being reversible. The change to the acid form is accompanied by a red-brown colour change. W. McC.

Constituents of the adrenal gland. III, IV.—See this vol., 704, 854.

Ostacin-ovo-ester from lobsters.—See this vol., 872.

Substance P, the atropine-resistant, intestine-stimulating, and vaso-dilating substance from intestine and brain. U. S. VON EULER (Arch. exp. Path. Pharm., 1936, 181, 181—197).—The active principle (cf. Gaddum and Schild, A., 1935, 780), extracted from tissues by  $EtOH-H_2SO_4$  and purified by half-saturation with  $(NH_4)_2SO_4$  and fractional pptn. from  $EtOH$  solution with  $COMe_2$  until active in dilutions of  $1:3 \times 10^6$  on the isolated rabbit's intestine, is unstable to  $0.1N-NaOH$  at  $100^\circ$  and tryptic hydrolysis, but relatively stable to acids. Electrodialysis etc. indicate an albumose nature. Its physiological activity and reactions to base-precipitants are discussed. F. O. H.

"Methæmoglobin-production" test for assaying antianæmic potencies of liver extracts. W. DEUTSCH and J. F. WILKINSON (Brit. J. Exp. Path., 1935, 16, 33—39).—No correlation exists between results of clinical tests of hæmopoietic potency and ability to form methæmoglobin as determined spectroscopically or by the respirometer. The antianæmic principle of liver is not identical with, and occurs independently of, the methæmoglobin-producing factor. CH. ABS. (p)

Action of ultra-violet light on villikinin. G. VON LUDANY (Biochem. Z., 1936, 285, 192—194; of this vol., 518).—Secretin (I) and villikinin (II) are not identical, since (I) but not (II) is destroyed by ultra-violet light. W. McC.

Physiology of milk and butter-fat secretion. I. Milk pressure in the udder. II. Development and evolution of milk secretion. J. HAMMOND (Vet. Rec., 1936, 16, 519—527, 528—535).—II. During the development of milk secretion the composition of the milk changes. Globulin (I) and albumin (II) appear first, but decrease as the rate of secretion increases; at the same time  $H_2O$ , lactose (III), casein (IV), and ash increase. (III) increases faster than (IV). The milks of different species generally show the same proportional composition as that of cow's milk in course of development at similar (I) and (II) levels. A parallel can be drawn between changes in the development of constitution of milk in the individual and the changes that have occurred during the course of evolution in different species. R. N. C.

Electrical resistance of milk and its constituents. B. LUYET (Compt. rend. Soc. Biol., 1936, 122, 64—65).— $R$  is a property of the whey, cream or casein increasing it without altering it essentially. R. N. C.

Ultracentrifugal and electrophoretic studies on the milk-proteins. I. Preliminary results with fractions from skim-milk. II. Lactoglobulin of Palmer. K. O. PEDERSEN (Biochem. J., 1936, 30, 948—960, 961—970).—I. A method for calculating sedimentation equilibrium concn. from  $n$  data by the method of Lamm (A., 1929, 129, 1234) is described. In milk-plasma, the caseinogen (I) is present as a coarse polydisperse system, and the degree of dispersity in solution in  $PO_4'''$  buffer depends on the concn. of (I). Milk-serum contains the low-mol. wt. protein of Kekwick, Palmer's lactoglobulin (II) (A., 1924, 434), and lactoglobulin.

II. (II) is homogeneous, mol. wt. about 39,000 and isoelectric point in OAc' buffer  $p_H$  5.19. The mol. wt. is const. between  $p_H$  1 and 9, but the sedimentation const. indicated a change in the mol. frictional const. at  $p_H$  5 and 7.5. H. G. R.

Variations in lactose content of milk. W. R. BROWN, W. E. PETERSEN, and R. A. GORTNER (J. Dairy Sci., 1936, 19, 81—92).—Hourly samples show considerable variations in blood-sugar and in lactose contents of milk. Correlation between sugar vals. of blood and milk is highest when milk samples taken 1 hr. after blood samples are considered. A. G. P.

Thiol compounds of milk. C. J. JACKSON (J. Dairy Res., 1936, 7, 29—30).—No sol.  $-SH$  compounds occur in cow's milk. The positive nitroprusside test is attributed to cystine in the protein complex. A. G. P.

Iron and copper content of milk throughout the season, as related to anæmia development in rats. W. E. KRAUSS and R. G. WASHBURN (J. Biol. Chem., 1936, 114, 247—252).—Nutritional anæmia was produced in rats fed exclusively on milk obtained from cows fed on a variety of diets, indicating that the variation of the cow's diet was insufficient to cause profound modifications in the Fe and Cu contents of its milk. H. D.

Alleged occurrence of acetylcholine and adrenaline in cat's saliva. J. SECKER (J. Pharm. Exp. Ther., 1936, 56, 464—465).—Polemical against Larson (A., 1935, 1146). H. D.

Hormone content of saliva. A. I. WEISMAN and C. C. YERBURY (Endocrinol., 1936, 20, 103—104).—Anterior pituitary-like and œstrogenic hormones are not present in saliva. R. N. C.

Diastatic activity of rat saliva. E. W. COHN and M. H. BROOKES (J. Biol. Chem., 1936, 114, 139—145).—Rat saliva contains an enzyme capable of hydrolysing starch to reducing sugars. The amount of these produced was determined in terms of  $Cu_2O$  by a photo-electric method. J. N. A.

Determination of bile salts in human bile. R. GOIFFON, F. NEPVEUX, and CHALEIL (J. Pharm. Chim., 1936, [viii], 23, 499—513).—After removal of protein with the Folin-Wu reagent, decolorisation with  $FeCl_3$ , and subsequent purification, the determination is carried out nephelometrically in  $(NH_4)_2SO_4$  suspension. H. G. R.

Differential quantitative analysis of bile acids in bile and in duodenal drainage. H. DOUBILET

(J. Biol. Chem., 1936, **114**, 289—308).—The bile acids conjugated with taurine and glycine are determined by the Schmidt-Dart method (A., 1921, ii, 284), the cholic acid by the Gregory-Pascoe reaction (A., 1929, 1114) modified by addition of EtOH to the coloured solutions before comparison, and the total bile acids by pptn. with  $\text{FeCl}_3$  and determination of the pptd. Fe. From these vals. the concns. of deoxycholic and total free bile acids may be calc.

H. D.

**Gastric secretion of infants with special reference to pepsin and rennin.** B. ANDERSEN (Diss., Copenhagen, 1935, 94 pp.).—Methods of distinguishing between rennin (I) and pepsin (II) and possible sources of error are discussed. (I) is not present in the gastric juice of infants and coagulation of milk is due to (I) alone.

NUTR. ABS. (m)

**Gastric secretion. V. Achlorhydria following partial gastrectomy for ulcer: histamine and the transplanted gastric pouch.** E. KLEIN (Arch. Surg., 1935, **30**, 162—170; cf. this vol., 99).—Phases of gastric secretion are discussed. Partial gastrectomy eliminates the secondary phaso due to chemical stimulation of the antrum. In some cases there is true anacidity which does not disappear with histamine, as well as a pseudoanacidity.

CH. ABS. (p)

**Demonstration of adrenaline in the amniotic liquid and extract of the amniotic membrane in different periods of pregnancy.** O. MACCHIARULO (Arch. Gynakol., 1935, **159**, 355—359; Chem. Zentr., 1935, ii, 1570).—Adrenaline cannot be detected in human amniotic extract or fluid or Wharton's gelatin. Traces occur after the 9th month of pregnancy. The hyperglycaemic action of amniotic fluid and extract is due to other active principles.

R. N. C.

**Micro-test for acetone in urine.** J. F. BARRETT (Biochem. J., 1936, **30**, 888—889).—About 0.2 ml. of urine (or 2 ml. of blood-filtrate after pptn. with tungstic acid) mixed with 3 ml. of sulphosalicylic acid (5% in 1% aq.  $\text{Na}_2\text{SO}_4$ ) is boiled and the vapour passed into dil. Nessler's reagent.  $\text{COMe}_2$  in concns.  $\leq 0.01$  mg. per ml. produces a creamy ppt. Volatile reducing substances (e.g.,  $\text{CH}_2\text{O}$ ) interfere, and when such are present 1 drop of 1% aq.  $\text{NaOCl}$  is added to the reagent, the test being then less sensitive.

W. McC.

**Experimental variations of sulphur elimination in dogs.** J. GOSSET and S. DELAUNEY (Compt. rend. Soc. Biol., 1936, **121**, 1616—1617).—The post-operative increase in urinary S excretion is due to muscular trauma; anaesthesia and hyperthermia are without influence.

R. N. C.

**Canine cystinuria. II. Analysis of cystine calculi and sulphur distribution in the urine.**

F. GREEN, M. L. MORRIS, G. F. CAHILL, and E. BRAND (J. Biol. Chem., **114**, 91—94).—The calculi contained 0.14—0.26% of allantoin and approx. 0.5% of unidentified N. Only 30% of the neutral present in the urine was cystine-S.

H. G. R.

**Sulphur metabolism. I. Precipitation of cystine from solutions by mercuric and cuprous chlorides and its recovery, as preliminary to its**

**quantitative determination in urine.** G. MEDES and K. E. PADIS (Biochem. J., 1936, **30**, 941—947).—Recovery of cystine (I) from  $\text{HgCl}_2$  and  $\text{Cu}_2\text{Cl}_2$  pptn. by decomp. with  $\text{H}_2\text{S}$  yields 69 and 95%, respectively. If the Cu is pptd with  $\text{KSCN}$  and  $\text{C}_5\text{H}_5\text{N}$  the val. is raised to 100%, but the filtrate is not suitable for determination of (I) with Folin's reagent. Using 8 ml. of solution, 0.24 mg. of (I) may be determined by this method.

H. G. R.

**Composition of urine in the seal.** H. W. SMITH (J. Cell. Comp. Physiol., 1936, **7**, 465—473).—Urea is the principal N compound, but  $\text{NH}_3$ , creatinine (I), and creatine (II) are present, (II) being apparently of exogenous origin, since the quantity after a meal of herring is  $>$  after a meal of clams. There is no evidence that the seal swallows much sea- $\text{H}_2\text{O}$ . Simultaneous inulin and (I) clearances are essentially identical, showing the absence of renal (I) secretion.

R. N. C.

**Determination of creatine in urine.** W. D. LANGLEY, M. ROSENBAUM, and M. G. ROSENBAUM (J. Lab. Clin. Med., 1935, **20**, 972—974).—To the urine (1—2 c.c.) is added 1 c.c. of  $\text{H}_2\text{SO}_4$  (dropwise with mixing) and the mixture left 2—5 hr. at room temp. A standard solution of creatinine (1 mg. per c.c.) is treated similarly. Subsequently, 20 c.c. of saturated picric acid and sufficient 10% aq.  $\text{NaOH}$  to neutralise the acid with 1.5 c.c. excess are added. The solutions are compared colorimetrically after dilution to 100 c.c. The method is not applicable to diabetic urines.

CH. ABS. (p)

**Histidine in human urine.** (A) F. FOLDES. (B) R. KAPPELLER-ADLER (Biochem. Z., 1936, **285**, 294—296, 296; cf. this vol., 362).—(A) Polemical.

(B) A reply. Foldes' method is based on the detection of a substance other than histidine itself and hence is untrustworthy.

W. McC.

**Metabolism of guanyltaurine. Occurrence of glycocyamine in urine.** D. ACKERMANN (Z. physiol. Chem., 1936, **239**, 231—235).—When guanyltaurine (I) is fed to dogs about 8% is recovered unchanged in the urine but no asterubin is produced. The glycocyamine (II) in the urine occurs preformed and is not derived from (I). Allantoin (III) is adsorbed by Lloyd's reagent, but gives no red colour with  $\text{NaOBr}$  in Sakaguchi's test. Hence (III) can be distinguished from (II).

W. McC.

**Determination of morphine in urine of opium and morphine addicts: practical applications of the reaction.** S. To (Japan. J. Med. Sci., IV, 1935, **8**, 93—115).—The min. intake of morphine (I) which gives a positive Frohde test was 0.01 g. in normal cases and 0.017 g. in addicts. Use of (I) or smoking of opium is readily detected by testing the urine.

CH. ABS. (p)

**Presence of anti-pernicious anaemia principle in normal human urine.** G. E. WAKERLIN (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1607—1610).

R. N. C.

**Occurrence of a new breakdown product of blood pigments (pentdyopent) in the urine.** F. WIMPLINGER (Deut. med. Woch., 1935, **61**, 1072—1074).—Pentdyopent appears regularly in the urine



in conditions that lead to elimination of bile pigments. It can appear independently from bilirubin and urobilin. Its absence is diagnostically important, as it indicates absence of liver disease. R. N. C.

**Origin of natural crystalline urobilin (stercobilin).** C. J. WATSON (J. Biol. Chem., 1936, 114, 47—57).—A cryst. urobilin, not identical with stercobilin, has been obtained from mesobilirubinogen *in vitro*, and the existence of a second urobilinogen in excreta is indicated. H. G. R.

**Uropterin**, a yellow pigment from human urine. W. KOSCHARA (Z. physiol. Chem., 1936, 240, 127—151; cf. A., 1935, 774; Schopf *et al.*, A., 1933, 1311).—The "purine fraction" of normal human urine contains uropterin (I) (concn. 1 : 10<sup>6</sup>), which is probably identical with the xanthopterin of the wings of the brimstone butterfly (*Gonepteryx rhamni*). (I) is isolated by adsorption on fuller's earth and elution with aq. C<sub>5</sub>H<sub>5</sub>N with const. observation of the fluorescence in ultra-violet light. H<sub>2</sub>S reduces (I), the leuco-compound produced being re-oxidised by atm. O<sub>2</sub>. Xanthopterins occur also in the rabbit, horse, and ox and in hay. W. McC.

**Human foot perspiration; nature and inter-reactions with footwear.** A. COLIN-RUSS (J. Hyg., 1935, 35, 198—206). CH. ABS. (p)

**Cure of anaemia by ingestion of mammalian liver.** E. LEMAIRE (Bull. Soc. d'Encour., 1936, 135, 330—332).—A review. H. G. R.

**Anaemia in pregnancy.** J. A. BOYCOTT (Lancet, 1936, 230, 1165—1172).—The common anaemia of pregnancy is of the hypochromic type and is due apparently to Fe deficiency. It responds to Fe treatment. L. S. T.

**Hypochlorhydria in asthma with special reference to the age incidence.** M. GILLESPIE (Quart. J. Med., 1935, 4, 397—405).—Low free acidity of the gastric contents was present in 51% and low total acidity in 41% of 109 cases of asthma. Subacidity (74% of cases) was most marked in the age group under 15 years. After 6 months' treatment, 16 of 46 cases showed increased acid content of the juice. NUTR. ABS. (m)

**Treatment of Basedow's disease with large doses of vitamin-A (Vogan).** H. WENDT (Munch. med. Woch., 1935, 82, 1160—1162).—The body gains in wt. and basal metabolism falls almost to normal. R. N. C.

**Treatment of tuberculous lung-bleeding with vitamin-C (Cebion-Merck).** F. HASSELBACH (Fortschr. Therap., 1935, 11, 407—411; Chem. Zentr., 1935, ii, 1573). R. N. C.

**Treatment of gynaecological bleeding with vitamin-C.** E. JUNGHANS (Klin. Woch., 1935, 14, 899). R. N. C.

**Biochemical factors of cancer.** M. COPISAROW (Chem. and Ind., 1936, 422).—The metabolic significance of enzymes, vitamins, and hormones in cancer and the curative effect of methylene-blue, cystine disulphoxide, and vitamin-E treatments support the author's views on the aetiology of cancer (cf. B., 1934, 1032; 1935, 107). F. O. H.

**Cancer. I. Influence of parenteral administration of certain sugars on the  $p_H$  of malignant tumours.** C. VOEGTLIN, R. H. FITCH, H. KAHLER, J. M. JOHNSON, and J. W. THOMPSON. II. Influence of [H<sup>+</sup>] on the reversal of proteolysis in oxygenated extracts of normal and neoplastic tissues. M. E. MAVER, J. M. JOHNSON, and C. VOEGTLIN (Nat. Inst. Health Bull., 1935, No. 164, 1—14, 29—45).—I. Administration of *d*-glucose decreased the  $p_H$  of Jensen rat sarcoma, Walker rat sarcoma, Flexner-Jobling rat carcinoma, and a spontaneous adenocarcinoma in albino mice. *d*-Fructose, *d*-mannose, and maltose, and to a smaller extent *d*-xylose, affected Jensen sarcoma and Flexner-Jobling carcinoma tissue similarly whereas *l*-arabinose, *d*-galactose, lactose, and sucrose were ineffective. The active sugars increase lactic acid in the tumours.

II. Protein synthesis in digests of both tissues reached max. at neutrality under the high [O<sub>2</sub>] used. At  $p_H$  6.0—6.5 and 7.3—7.5 slight protein synthesis was followed by proteolysis. The cystine content of the protein increased during digestion and regained its original val. during oxidation. Protein synthesis is not due to non-enzymic oxidation of ·SH in protein cleavage products. Org. S has no sp. role in digestion and oxidation. CH. ABS. (p)

**Chemotherapy of cancer. I. Lead.** J. A. BARGEN, B. T. HORTON, and A. E. OSTERBERG (Amer. J. Cancer, 1935, 23, 762—770).—Use of colloidal Pb phosphate is described. CH. ABS. (p)

**Therapy of enzymes in experimental rat tumours.** B. OTTENSTEIN and S. VON PASTINSZKY (Z. Krebsforsch., 1935, 42, 1—8; Chem. Zentr., 1935, ii, 1563). R. N. C.

**Relation of glycaemia to adrenal capsules and growth of tumours.** A. H. ROFFO and L. M. CORREA (Bol. inst. med. exp., 1931, 8, 132—146).—Adrenaline regulates glycaemia and stimulates growth of tumours. CH. ABS. (p)

**Oestrogenic hormones and mammary adenocarcinoma of the mouse.** A. LACASSAGNE (Compt. rend. Soc. Biol., 1936, 122, 183—184). R. N. C.

**Independence of malignant growths and type of metabolism.** A. REIS and L. KLUGE (Arch. exp. Path. Pharm., 1936, 181, 281—284).—Data of metabolic processes in rat sarcomata before and after general and local (growth-inhibiting) X-irradiation indicate their independence of growth; this is exemplified by the increase (32—48%) in uric acid content. F. O. H.

**Chlorine and cholesterol metabolism of animals suffering from cancer.** Hepatorenal symptom complex. S. SUMEGI (Frankfurter Z. Path., 1935, 48, 386—397).—During the growth of a transplanted rat carcinoma, cholesteryl ester in blood was low and the rise and fall in blood-Cl' following NaCl administration was > normal. Later blood-Cl' was greatly increased and diuresis and Cl' excretion were reduced. These changes were accompanied by a rise in total blood-cholesterol. They are ascribed to changes in liver and kidney due to toxic degradation products of tumour-protein. NUTR. ABS. (m)

**Tobacco and cancer.** O. SCHURCH and A. WINTERSTEIN (Z. Krebsforsch., 1935, 42, 76—92; Chem. Zentr., 1935, ii, 1563).—Tobacco-tar obtained from burning cigars contains 9% of nicotine, > 5% of hentriacontane,  $C_{31}H_{64}$ , m.p. 66°, a higher (possibly dipalmityl) ketone, m.p. 79°, a phytosterol, m.p. 135°, and about 2% of a substance,  $C_{10}H_{14}O$ , b.p. 50—55°/1 mm., which is responsible for the odour of tobacco-smoke, and is possibly a furan derivative; the odour is destroyed by catalytic hydrogenation. No product of the tar exhibits carcinogenic activity.

R. N. C.

**Effect of interference with the vascular supply on the induction of dibenzanthracene tumours.** J. W. ORR (Brit. J. Exp. Path., 1935, 16, 121—126).—Fibrosis of subcutaneous tissue produced by insertion and removal of linen threads accelerated tumour induction in mice by 1:2:5:6-dibenzanthracene. Injection of adrenaline hydrochloride further accelerated the tumours. Ephedrine sulphate had no effect.

CH. ABS. (p)

**Effect of methylene-blue on oxygen consumption and respiratory quotient of normal and tumour tissue.** J. J. JARES (Amer. J. Cancer, 1935, 24, 80—89).—Addition of methylene-blue (I) in concns. of > 0.01% to normal and tumour tissues causes an initial increase followed by a decrease in  $O_2$  consumption. The R.Q. of spleen, kidney, liver, and cerebral cortex are increased and that of testis and tumour tissues are lowered by (I) in final concn. of 0.01%. Injection of (I) and  $CH_2Br\cdot CO_2H$  into rats bearing Jensen sarcoma does not affect the rate of tumour growth.

CH. ABS. (p)

**Purine-nitrogen content of the organs of rats on various diets and suffering from avitaminosis and Jensen sarcoma.** S. EDLBACHER and P. JUCKER (Z. physiol. Chem., 1936, 240, 78—98).—Purine-N/total N ratios are given for liver, kidney, muscle, and spleen. A-Avitaminosis does not affect the vals., whilst sarcomatous rats have a high liver-purine content.

F. O. H.

**Natural sources of fluorine and "mottled teeth" in Maldon, Essex.** J. H. BOWES and M. M. MURRAY (Nature, 1936, 137, 828).—Pond- $H_2O$ , well- $H_2O$ , grass, and rabbit's teeth from this "mottled teeth" area contain much more F than similar substances from other localities.

L. S. T.

**Possible role of the anterior pituitary in human diabetes.** O. L. V. DE WESSELOW and W. J. GRIFFITHS (Lancet, 1936, 230, 991—994).—Injection of the blood-plasma of elderly, obese, glycosuric patients into rabbits diminishes the hypoglycaemic action of insulin in a manner closely resembling that obtained with extracts of the anterior pituitary gland. The plasma of young diabetic and normal subjects produces no alteration in the blood-sugar response of the rabbit to insulin. These results are discussed in relation to the pathogenesis of human diabetes.

L. S. T.

**Influencing of diphtheric circulation weakness by cortical hormone and vitamin-C.** P. BAMBERGER and L. WENDT (Klin. Woch., 1935, 14, 846—847).

R. N. C.

**Pathogenesis of galactorrhoea: hormonal processes in physiological lactation.** E. J. KRAUS (Arch. Gynakol., 1935, 159, 380—394; Chem. Zentr., 1935, ii, 1568).

R. N. C.

**Treatment of gapeworm disease.** P. A. CHAPMAN (J. Helminthology, 1935, 13, 3—8).—The eggs and adults of the parasite were killed by allyl sulphate in linseed oil (0.33 minim, 3 times daily).

CH. ABS. (p)

**Ascorbic acid in paroxysmal hæmoglobinuria.** L. ARMENTANO (Nature, 1936, 137, 910).—Paroxysmal hæmoglobinuria is accompanied by a marked deficiency in ascorbic acid, administration of which causes it to disappear.

L. S. T.

**Chronic hypoglycæmia.** M. A. GOLDZIEHER (Endocrinol., 1936, 20, 86—92).

R. N. C.

**Biochemical aspects of canine hysteria treatment.** J. McGREE (Vet. Rec., 1936, 16, 416).—The condition is due to deficiency of blood-Mg rather than -Ca.

R. N. C.

**Relative values of urea-stibamine and neo-stibosan in treatment of kala-azar.** C. U. LEE and C. F. CHU (Chinese Med. J., 1935, 49, 328—329).—Urea-stibamine is the more potent and also the more toxic.

CH. ABS. (p)

**Iodine values and total lipins of leprous human blood-sera.** H. H. ANDERSON and J. VAN D. ANDERSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1470—1473).—The I val. is low and total lipins (I) are high in early cuta-neural leprosy. Chaulmoogra (II) therapy increases the I val. and lowers (I), but the large amount of (II) given may be responsible for this.

R. N. C.

**Fat metabolism in liver disease.** S. M. LEITES, L. S. LIFSCHITZ, and A. I. ODINOV (Méd. exp. Ukraine, 1935, No. 1, 44—54).—In patients suffering from affections of the liver the curve of the alimentary lipæmia following a meal of 75 g. of butter and 20 g. of bread did not differ greatly from normal, but the ketones in the blood were > normal. In very severe cases the amount of ketones was reduced.

NUTR. ABS. (m)

**Blood-purine derivatives in migraine.** J. BRAZELL and L. A. CRANDALL, jun. (Proc. Soc. Exp. Biol. Med., 1935, 32, 1450—1451).—Adeninonucleotide-N and purine-N show no deviation from the normal vals.

R. N. C.

**Chemistry of muscle in myopathy.** R. DEBRÉ, J. MARIE, and D. NACHMANSON (Compt. rend., 1936, 202, 520—522).—In myopathy the lactic acid and glycogen contents of muscle remain within normal ranges but the proportion of P compounds is much reduced.

A. G. P.

**Insulin hypoglycæmia in myxœdema.** A. BAUDOUIN, E. AZÉRAD, and J. LEWIN (Compt. rend. Soc. Biol., 1936, 122, 170—171).—The hypoglycæmia is abnormally prolonged, the abnormality disappearing on treatment with thyroid.

R. N. C.

**Nephritis in the dog: differential diagnosis with special reference to urine analysis.** N. S. KING (Vet. Rec., 1936, 16, 445—459).—A lecture and discussion.

R. N. C.



**Congo-red test in nephropathics.** I. E. E. FERNANDEZ (*Dia Méd.*, 1932, 4, 681).—Retention of dye is shown especially in renal disease.

CH. ABS. (p)

**Paget's disease. II. Effect of adreno-cortical extract treatment on blood-phosphatase in Paget's disease.** L. BERMAN (*Endocrinol.*, 1936, 20, 226—227).—The phosphatase is reduced.

R. N. C.

**Secondary pellagra.** S. L. SIMPSON (*Quart. J. Med.*, 1935, 4, 191—201).—Pellagra following gastrectomy was cured by vitamin-B<sub>3</sub>. Gastrectomy may deprive the patient of an essential dietary factor which is derived from or bound up with protein. Adrenal hypofunction and pellagra are related.

CH. ABS. (p)

**Copper content of blood in pregnancy.** S. L. THOMPSETT and D. F. ANDERSON (*Brit. J. Exp. Path.*, 1935, 16, 67—69).—Blood-Cu increases during the last 3 months of pregnancy and is not greatly affected by associated anaemias. Milk is deficient in Cu and Fe. In foetal life a reserve of these metals is laid down, notably in liver, to be utilised in the period between birth and weaning. Cu feeding during pregnancy lowers the Fe content of liver and tissues and increases that in blood. Cu is essential for blood formation even when excess of Fe is present.

CH. ABS. (p)

**Influence of pregnancy on histamine sensitivity.** I. KARÁDY and F. STRÓBL (*Orvosi Het.*, 1935, 79, 589—590).—Changes in sensitivity occur from the third or fourth month.

CH. ABS. (p)

**Streptococcal complement-fixing reaction in rheumatic diseases.** A. BECK and F. COSTE (*Brit. J. Exp. Path.*, 1935, 16, 20—25).—Tuberculous and pregnancy sera frequently react with streptococcal lipin antigens; positive reaction with these occurs only in cases of rheumatic disease in which, clinically, a connexion with streptococcal infection is probable.

CH. ABS. (p)

**Experimentally rachitic rats after injection of porphyrin.** E. EMMINGER and B. BÜCHELE (*Virchow's Archiv*, 1935, 295, 46—56; *Chem. Zentr.*, 1935, ii, 1395).—Porphyrin deposition in the bones is apparently unrelated to rickets.

R. N. C.

**Silicosis.** W. E. COOK (*J. Hyg.*, 1935, 35, 207—218).—A review.

CH. ABS. (p)

**Action of iodine-containing saline atmosphere on thyroid hyperplasia.** H. UFFENORDE (*Z. ges. exp. Med.*, 1934, 93, 547—569; *Chem. Zentr.*, 1935, ii, 1570).

R. N. C.

**Use of nitric acid in the serological diagnosis of cattle trypanosomiasis.** E. R. JONES (*Vet. Rec.*, 1936, 16, 602—605).—HNO<sub>3</sub> gives a sp. serological reaction for trypanosome infections, the reaction being a modification of the xanthoproteic reaction.

R. N. C.

**Cholesterolaemia and tuberculosis.** L. LLOPIS (*Cron. med. Valenciana*, 1934, 28, No. 809).—Blood-cholesterol is unrelated to the course of pulmonary tuberculosis.

CH. ABS. (p)

**Value of urine examination in disease of the urinary tract in the dog.** J. MCGHEE (*Vet. Rec.*, 1936, 16, 570—574).

R. N. C.

**Metabolism of cold-blooded animals in different latitudes.** H. M. FOX (*Nature*, 1936, 137, 903—904).—The O<sub>2</sub> consumption of English marine invertebrates is > that of related northern species each at the temp. of their habitat. Since locomotory activities are approx. equal, non-locomotory metabolism appears to be higher in the warmer-H<sub>2</sub>O species. Ciliary activity parallels O<sub>2</sub> consumption, but in crustaceans the respiratory movements of the warmer- and colder-H<sub>2</sub>O species are equal.

L. S. T.

**Effects of complete and incomplete hypophysectomy on basal metabolism of pigeons.** O. RIDDLE, G. C. SMITH, and C. S. MORAN (*Proc. Soc. Exp. Biol. Med.*, 1935, 32, 1614—1616).—Basal metabolism falls after both complete and incomplete hypophysectomy, to extents which are influenced by the temp. of measurement.

R. N. C.

**Respiratory metabolism of the seal and its adjustment to diving.** L. IRVING, O. M. SOLANDT, D. Y. SOLANDT, and K. C. FISHER (*J. Cell. Comp. Physiol.*, 1935, 7, 137—151).

R. N. C.

**Fumarate and tissue-respiration. I. Effect of dicarboxylic acids on oxygen consumption.** G. D. GREVILLE (*Biochem. J.*, 1936, 30, 877—887; cf. *Annau et al.*, A., 1935, 1406).—The effects of malonate (I) and fumarate (II) on the respiration of tissues (pigeon's breast-muscle, rat diaphragm) are the more pronounced the greater is the degree of damage which they have suffered. (I) inhibits carbohydrate respiration in rat's brain-cortex and retina and respiration, accelerated by dinitro-*o*-cresol, in brain-cortex and tumour. (II) partly counteracts the inhibition. (I) does not inhibit respiration, accelerated by brilliant-cresyl-blue, in tumour.

W. McC.

**Determination of the respiratory quotient of tissues in Ringer's solution containing phosphate.** E. CLARANFI (*Biochem. Z.*, 1936, 285, 238—240).—The amount of preformed CO<sub>2</sub> in tissues  $\propto$  their wt. if determined in unbuffered Ringer's solution after the const. of proportionality has been determined. The respiration of tissues is subsequently measured in a vessel described, the *p<sub>H</sub>* of the solution being adjusted as required.

W. McC.

**Metabolism of normal and tumour tissues. XVI. Action of some oxidation-reduction systems.** F. DICKENS (*Biochem. J.*, 1936, 30, 1064—1074; cf. this vol., 629).—Thionine (I) and brilliant-cresyl-blue (II) considerably increase rat kidney oxidation in HCO<sub>3</sub>' and PO<sub>4</sub>' media, whilst pyocyanine (III) produces an increase in PO<sub>4</sub>'—Ringer's solution. All three dyes increase the respiration of kidney in lactate medium, whilst methylene-blue has a progressive toxic action and gallocyanine is without effect. With tumour-tissue, the max. increase (200%) in respiration in glucose occurs with (I) and (II), and these also increase the oxidation of brain-tissue in glucose. Phenosafranine greatly increases aerobic glycolysis in both brain and tumour tissue. (III) increases respiration and decreases aerobic and

anaerobic glycolysis of tumour. Phenazine mothiodide and *NN'*-dimethyldihydrophenazine have similar but less marked actions. J. N. A.

Low-temperature blood meals as a source of essential amino-acids for nutritive purposes. W. C. MILLER (Vet. Rec., 1936, 16, 311—321).—A lecture and discussion. R. N. C.

Oxidative deamination of amino-acids. M. NEBER (Z. physiol. Chem., 1936, 240, 59—69).—The principal  $\text{NH}_2$ -acids are oxidatively deaminated (by the same enzyme; glycine most readily) to decreasing extents by liver, kidney, and intestinal mucosa. The isolated organs, unlike those *in situ* (as indicated by feeding experiments), deaminate the naturally-occurring optical forms more slowly than the corresponding non-natural isomerides. Deamination of tryptophan and *d*(+)-histidine by kidney occurs to only a small extent; that of alanine by liver is accompanied by disappearance of part of the resultant  $\text{NH}_3$  which is not converted into urea, but probably utilised for purine synthesis. F. O. H.

Nutritive value of canavanine (amino-acid). M. OGAWA (J. Agric. Chem. Soc. Japan, 1936, 12, 256—259; cf. A., 1935, 1407).—Canavanine is not essential for growth in the later part of the growing period of animals. J. N. A.

Conversion of histidine into histamine in the animal organism. W. BLOCH and H. PINOSCH (Z. physiol. Chem., 1936, 239, 236—240).—The histamine (I) content (0.0015—0.0025%) of the lungs of guinea-pigs is doubled following subcutaneous injection of histidine (II) (1.0 g. per kg of body-wt.). No increase follows injection of other  $\text{NH}_2$ -acids or of 0.9% aq. NaCl, or fasting. Organs other than the lungs contain very little (I) and no definite increase in their content of (I) follows injection of (II).

W. McC.

Inactivation of histamine *in vivo*. C. A. DRAGSTEDT and F. B. MEAD (Proc. Soc. Exp. Biol. Med., 1935, 32, 1435—1437).—Histamine injected in almost lethal doses in the dog disappears in 30—40 min.; in smaller doses the time is proportionately less.

R. N. C.

Metabolism of betaine and allied tertiary nitrogenous bases in the ruminant. W. L. DAVIES (J. Dairy Res., 1936, 7, 14—24).—The principal tertiary N metabolite of all *tert.* N bases examined is  $\text{NMe}_3\text{O}$  (I). Traces of  $\text{NMe}_3$ ,  $\text{NHMe}_2$ , and  $\text{NH}_2\text{Me}$  also occur in cow's urine. The N of simple bases [ $\text{NMe}_3$  and (I)] is rapidly and almost quantitatively excreted as (I). From 14 to 43% of the N of betaine (II), choline, and  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  is excreted as (I), the rate of excretion varying with the nature and amount of the bases fed. No unchanged (II) was found in the urine. A. G. P.

Fission of proline in the animal organism. M. NEBER (Z. physiol. Chem., 1936, 240, 70—77).—Decomp. of *l*(-)-proline and -hydroxyproline by liver and kidney tissue is accompanied by formation of  $\cdot\text{NH}_2$ , but not of  $\text{NH}_3$ . From the products of decomp. were isolated *l*(+)-glutamic (I) and  $\alpha$ -ketoglutaric acid (II). The decomp. of pyrrolidonecarboxylic (III) and  $\alpha$ -amino- $\delta$ -hydroxyvaleric acid (IV) (the latter

yielding  $\delta$ -hydroxy- $\alpha$ -ketovaleric acid) indicates that the route is proline  $\rightarrow$  (III) + (IV)  $\rightarrow$  (I)  $\rightarrow$  (II), (II) being further catabolised. F. O. H.

Tryptophan metabolism. VIII. Growth and kynurenic acid production on carboxylic acid derivatives of tryptophan. L. C. BAUGUENESS and C. P. BERG (J. Biol. Chem., 1936, 114, 253—257; cf. A., 1934, 1252).—*Me*, m.p. 149—150°, *Et*, m.p. 105—106°, *Pr*, m.p. 124—125°, *Ph*, m.p. 151° (decomp.), and  $\text{CH}_2\text{Ph}$  tryptophancarboxylate, m.p. 122—124°, were all inactive in promoting growth or kynurenic acid production in tryptophan-deficient rats.

Metabolism of sulphur. XXIII. Influence of ingestion of cystine, cysteine, and methionine on the excretion of cystine in cystinuria. H. B. LEWIS, B. H. BROWN, and F. R. WHITE (J. Biol. Chem., 1936, 114, 171—184; cf. A., 1935, 1008).—When cystine (I) isolated from urine or obtained from human hair was fed to a cystinuric, no extra (I) was excreted in the urine, but there was a large increase in urinary  $\text{SO}_4^{--}$ . When cysteine hydrochloride was fed, there was an increase in the amounts of (I) and  $\text{SO}_4^{--}$  excreted. When *dl*-methionine (II) was fed, extra (I) but not  $\text{SO}_4^{--}$  was excreted. If the cystinuric received a high-protein diet, the extra excretion of (I) after feeding (II) was < when a moderate protein diet was fed. There was no evidence of the presence in the urine of a readily decomposed complex containing (I). J. N. A.

Metabolism of argininic acid. K. FELIX and H. MÜLLER (Z. physiol. Chem., 1936, 240, 1—9).—Argininic acid (A., 1928, 744) is harmless to fed animals (e.g., 10—30 g., daily in man, the blood-sugar being unaffected), but doses of 0.5 g. per kg. are toxic and occasionally lethal to starved animals. In animals and men suffering from muscular dystrophy (but not from myasthenia), it increases excretion of (partly nowly formed) creatine, whilst in diabetics it is converted mainly into urea and sugar. F. O. H.

Comparative studies on the concentrating power of the liver and kidney with respect to cholalic acid. E. CHABROL, J. COTTET, and J. SALLET (Compt. rend. Soc. Biol., 1936, 122, 184—186).—Slow continuous intravenous injection of cholalic acid (I) in the dog does not increase blood-(I); most of the injected (I) is removed by the liver, very little being eliminated in the urine. Increase of the rate of injection causes a rise of blood-(I) through inability of the liver to remove the increased supply; renal elimination is not increased in this case, nor if the bile duct is ligatured. In dogs poisoned with tolylenediamine, (I) is removed during injection as in normal dogs, but blood-(I) rises after injection has ceased.

R. N. C.

Increase in cholalic acid in the liver and muscle during experimental cholalæmia. E. CHABROL, J. COTTET, and J. SALLET (Compt. rend. Soc. Biol., 1936, 122, 186—188).—Cholalic acid (I) injected into normal dogs is removed by the liver but not stored in the muscles. With the bile duct ligatured, (I) is stored in both liver and muscles, their content continuing to increase after injection has



coased. In dogs intoxicated by tolylenediamine, storage of (I) is reduced in both liver and muscles.

R. N. C.

**Origin and fate of urea in the developing hen's egg.** J. NEEDHAM, J. BRACHET, and R. K. BROWN (J. Exp. Biol., 1935, 12, 321—336).—The urea produced during development of the embryo is not derived from the  $\text{NH}_3$  of protein catabolism, or from uric acid (I) by means of uricase. Its source appears to be an arginine-arginase system present from the 2nd day of incubation onward. Arginase (II) activity falls very regularly as development proceeds, reaching a min. about the 12th day, but the quantity of activators present does not decrease. (II) occurs in the yolk sac, but in much smaller quantity than in the embryo. Results of injection of urea and tartronic acid show that Werner's urea conjugation hypothesis of (I) synthesis is untenable. Injection of  $(\text{NH}_4)_2\text{CO}_3$  markedly increases the (I) content of the embryo.

NUTR. ABS. (m)

**Pigment metabolism during and after a fifty-day period of starvation.** G. G. GASENKO and N. P. BLAGOVESTOVA (Folia Hæmatol., 1935, 53, 283—290).—Changes in the pigment of internal organs were slow. Urobilin excretion reached a min. normal. Decreased formation of red cells followed only at the end of the period and during recovery.

CH. ABS. (p)

**Biological degradation of chlorophyll. V. Dihydropyrophæophorbide-a and pyrophæophorbide-b from the fæces of sheep.** H. FISCHER and F. STADLER (Z. physiol. Chem., 1936, 239, 167—178; cf. A., 1933, 627, 1173; 1934, 317).—Probo-phorbide-a is a mixture of pyrophæophorbide-a. (I) and its  $\text{H}_2$ -derivative (II). (I) and (II) are partly separated by adsorption on talc. Probo-phorbide-b probably consists chiefly of methyl-phæophorbide-a or contains chlorin- $c_8$ . In the sheep, after the Mg of chlorophyll is eliminated in the stomach, part of the phæophytin produced passes through the intestine unchanged, but most is converted into (I) and small amounts of pyrophæophorbide-b, together with a little phæophorbide. Enzymic hydrogenation of (I) yields (II),  $\text{CH}:\text{CH}_2$  being reduced to Et. According to the conditions which prevail in the intestine (I) and (II) are excreted or converted into phylloerythrin.

W. McC.

**Cholesterol content of different organs during digestion and fasting.** K. YAMASAKI (Fukuoka Acta med., 1935, 28, 106—107).—During digestion of food the cholesterol (I) content of the adrenals was increased but that of other organs remained const. In fasting animals the (I) content of the adrenals was decreased and that of the liver increased. Increased liver-(I) was noted, together with hypercholesterolaemia, after oral administration of (I).

NUTR. ABS. (m)

**Cholesterol ratio in living and necrotic neoplastic tissue.** A. H. ROFFO (Bol. inst. med. exp., 1932, 9, 503—510).—Increased cholesterol occurs in neoplastic tissue.

CH. ABS. (p)

**Phosphorus metabolism. V. Relation between urinary phosphate and blood-phospholipin during absorption of fats.** G. E. YOUNG-

BURG (J. Lab. Clin. Med., 1935, 20, 920—922; cf. A., 1933, 178).—Increased blood-phospholipin (I) occurring after ingestion of a high-fat meal is not accompanied by a decrease in urinary  $\text{PO}_4'''$  (II). The P of (I) and (II) is not drawn from the same immediate source.

CH. ABS. (p)

**Fat metabolism. XVII. Biological degradation of hydrogen esters. I. Metabolism of ethyl hydrogen sebacate in dogs.** B. FLASCHENTRAGER and K. BERNHARD (Z. physiol. Chem., 1936, 240, 19—22).—Of 30 g. of Et H sebacate ingested, 91.8% is apparently metabolised and 5.2% is excreted unchanged, 2.1% as sebacic acid and 0.63% as Et H suberate. This confirms the enhanced catabolism of  $(\text{CO}_2\text{H})_2$ -acids by blocking a  $\cdot\text{CO}_2\text{H}$  (cf. A., 1935, 1015, 1151; Verkade and van der Lee, this vol., 234).

F. O. H.

**Influence of food-fat of varying degrees of unsaturation on blood-lipins and milk-fat.** L. A. MAYNARD, C. M. MCCAY, and L. L. MADSEN (J. Dairy Sci., 1936, 19, 49—53).—Changes in the I val. of milk-fat appear 18—24 hr. after changes in the ration and reach max. in 2—4 days. Similar though less marked changes occur in blood-lipins.

A. G. P.

**Effect of various fats in the production of dietary fatty livers.** H. J. CHANNON and H. WILKINSON (Biochem. J., 1936, 30, 1033—1039).—Rats fed on a diet containing 5% of protein supplemented with butter or beef fat or palm, coconut, or olive oil all developed fatty livers. The differences in accumulation were accounted for by the differences in the content of glycerides, and the degree of accumulation was inversely  $\propto$  the I val. of the dietary fat, and, except in the case of olive and cod-liver oils, ran parallel with the % of  $\text{C}_{14}$ — $\text{C}_{18}$  saturated acids. The data indicate that the nature of the stored fat depends, both in the glyceride and phosphatide fraction, on that of the dietary fat.

H. D.

**Effect of dietary caseinogen in the prevention of fatty livers.** A. W. BEESTON, H. J. CHANNON, J. V. LOACH, and H. WILKINSON (Biochem. J., 1936, 30, 1040—1046).—1 g. of caseinogen (I) is equiv. to 7—8 mg. of choline (II) in preventing liver-fat deposition in rats receiving diets containing 40% of fat. The presence of marmite in the diet has no further effect on liver-fat accumulation than that due to its (II) content. With diets containing 5% of (I) and 40% of fat, 3 mg. of (II) per day reduced the liver-fat from 20 to 10%, but amounts varying from 8.8 to 79.8 mg. did not prevent some fat accumulation. Edestin has lipotropic action.

J. N. A.

**Serum-lipin changes in relation to the intermediary metabolism of fat.** A. E. HANSEN, W. R. WILSON, and H. H. WILLIAMS (J. Biol. Chem., 1936, 114, 209—222).—Serum-lipins (I) were determined in dogs, which were fasted to deplete the fat depots, and then fed a complete diet, including linseed oil or coconut oil as sources of fat. After regaining wt., the dogs were fasted for 7 days and then fed a diet in which carbohydrate replaced the fat. This was followed by a fast of 4 days. The highest vals. for total lipins were found during the ingestion of fat, and the lowest during feeding of

carbohydrate, with approx. equal vals. at the end of the two fasts. The level of (I) varied with the intensity of fat metabolism. All the principal fractions of the total lipin were concerned with the transport and utilisation of fat. Dogs receiving coconut oil had higher (I) vals. than those receiving linseed oil. The difference was greatest in the neutral fat. The I vals. of the total fatty acids and, to a smaller extent, those of the phospholipin fatty acids reflected the characters of the diet during the feeding, and of the depot fat during fasting. J. N. A.

**Physiology of pyrimidines. VIII. Metabolism of isobarbituric acid in the rabbit.** W. J. CONWAY and L. R. CERECEDO (Proc. Soc. Exp. Biol. Med., 1935, 32, 1600—1601).—Feeding with isobarbituric acid (I) results in a decrease of inorg. S and increases in sulphuric esters and urea; hence (I) is metabolised as in the dog and man. R. N. C.

**Fate of phenol after intravenous injection in the dog.** G. BARAC (Compt. rend. Soc. Biol., 1936, 122, 74—75).—PhOH diffuses into the organs, the liver and kidneys taking up slightly > the remaining organs. R. N. C.

**Blood-sugar equilibrium in simultaneous portal and arterial perfusion of the liver.** N. FIESSINGER, H. BENARD, M. HERBAIN, and L. DERMER (Compt. rend. Soc. Biol., 1936, 122, 32—33).—Liver-glycogen (I) in the dog falls considerably, particularly if initially high, whilst blood-sugar rises proportionally, falling again when (I) is exhausted. R. N. C.

**Metabolism of the frog's egg in course of development. IV. Glycogen content of the egg from segmentation to hatching.** J. BRACHET and J. NEEDHAM (Arch. Biol., 1935, 46, 821—825).—Glycogen (I) is steady until gastrulation, afterwards falling progressively. The % of desmoglecogen also falls. (I) is reduced by anaerobiosis at segmentation, but not at neurulation. R. N. C.

**Digestion and utilisation of starch by the honey bee.** R. LOTMAR (Arch. Bienenk., 1935, 16, 195—204).—Starch (I) is digested by bees and utilised almost as well as sugar. Cooked (I) is less readily digested, but intact (I) grains are not digested, being protected by amylopectin against the action of bee-diastase (II). Pollen-(I) is not attacked by pollen-(II) but by bee-(II). NUTR. ABS. (m)

**Biochemistry and physiology of glycuronic acid. VI. Excretion of ethereal sulphate by the rabbit following administration of phenylglucosides. VII. Conjugation of borneol in man.** J. PRYDE and R. T. WILLIAMS (Biochem. J., 1936, 30, 794—798, 799—800; cf. A., 1934, 442).—VI. Phenyl- $\alpha$ - and - $\beta$ -glucosides, orally or subcutaneously administered to rabbits, are not excreted as glycuronides, but as (the equiv. amount of)  $\text{Ph}_2\text{SO}_4$ , indicating hydrolysis to PhOH and glucose.

VII. Following ingestion of borneol (2 g.), up to approx. 80% is excreted as glycuronide within 10—12 hr. F. O. H.

**Effect of low-carbohydrate diet on glucose tolerance in spontaneous hypoglycæmia.** B. B.

CLARK and J. A. GREENE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1459—1462).—Glucose tolerance is increased. R. N. C.

**In-vitro studies on lactic acid metabolism in tissues from polyneuritic chicks.** W. C. SHERMAN and C. A. ELVEHJEM (Biochem. J., 1936, 30, 785—793).—Determinations of  $\text{O}_2$  uptake, lactic acid (I) removal, and reduction of methylene-blue by normal and polyneuritic chick tissues indicate that diminished  $\text{O}_2$  uptake and removal of (I) occur in heart- but not brain-tissue, the deficiency being remedied by addition of vitamin- $B_1$ . Inhibition of (I) dehydrogenase by  $\text{AcCO}_2\text{H}$  in avitaminous heart and kidney is > that in normal tissues. The influence of - $B_1$  on the dehydrogenation of (I) and the bearing of the data on those of Birch and Mann (A., 1934, 705) are discussed. F. O. H.

**Post-mortal formation of lactic acid in muscles of seals, ducks, and hens.** J. F. MANERY, M. S. WELCH, and L. IRVING (J. Cell. Comp. Physiol., 1935, 7, 131—135).—The anaerobic reserves of the skeletal muscle of the seal are not different from those of other animals, nor those of the duck from those of the hen. Post-mortal formation of lactic acid is the same in muscles of hens and ducks without buffers, and is high in the pectoral muscles. The  $\text{CO}_2$  contents of the muscles are also similar in the two species. R. N. C.

**Degradation of butyric acid by surviving liver.** E. CIARANFI (Biochem. Z., 1936, 285, 228—237).—The respiration and production of ketones by surviving guinea-pigs' liver in presence of  $\text{Pr}^c\text{CO}_2\text{Na}$  and the ratio  $\beta$ -hydroxybutyric acid (I) to  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$  (II) produced are greater when the Ringer's solution employed contains  $\text{NaH}_2\text{PO}_4$  as buffer than when it contains  $\text{NaHCO}_3$ . The liver oxidises (I) slightly with production of (II), and partly reduces and partly oxidises (II), free  $\text{O}_2$  being consumed. In Ringer's solution the reaction (I)  $\rightarrow$  (II) proceeds equally rapidly in both directions when  $\text{NaHCO}_3$  is the buffer but (II) $\rightarrow$ (I) is more rapid when  $\text{NaH}_2\text{PO}_4$  is buffer. Consumption of  $\text{O}_2$  and production of  $\text{CO}_2$  by the liver are increased by addition of  $\text{Pr}^c\text{CO}_2\text{Na}$ , indicating that degradation proceeds beyond the stage of (I) and (II). W. McC.

**Variations in magnesium content of the normal white rat with growth and development.** D. M. GREENBERG and E. V. TUFTS (J. Biol. Chem., 1936, 114, 135—138; cf. A., 1927, 894).—The Mg content of normal rats is least in the foetus and increases rapidly to a max. val. of 40 mg. per 100 g. at 4 weeks of age. This is followed by a const. level for 11 weeks, and a subsequent reduction of about 20%. There is no significant difference in the Mg content of the two sexes. The  $\text{H}_2\text{O}$  content progressively decreases from birth. J. N. A.

**Sulphur and sulphate balance experiments with sheep.** F. J. WARTH and T. S. KRISHNAN (Indian J. Vet. Sci., 1935, 5, 319—331).—A loss (intake less that recovered in excreta and estimated to be present in live-wt. increase and wool) of total S and  $\text{SO}_4$  always occurred in sheep receiving a diet low in S and in those receiving the same diet supple-



mented with  $\text{SO}_4^{''}$ , but there was a gain in org. S. The org. S of the urine increased after feeding inorg.  $\text{SO}_4^{''}$ .  
NUTR. ABS. (m)

**Response of the kidney to an alkalosis during salt deficiency.** R. A. McCANCE and E. M. WIDDOWSON (Proc. Roy. Soc., 1936, 120, B, 228—239).—Overbreathing by normal persons produced alkaline urine with increased excretion of  $\text{Na}^+$  and  $\text{K}^+$  and diuresis. In salt-deficient cases, oliguria with no change in  $p_{\text{H}}$  or excretion of  $\text{Na}^+$  and  $\text{K}^+$ , but with a generalised lowering of functional renal activity, occurred, administration of  $\text{CO}_2$  preventing the latter.  
H. G. R.

**Physiology of digestion in ruminants. I. Acid and enzyme content of the abomasum of the sheep.** F. W. KRZYWANIEK and W. BUSS (Arch. wiss. pr. Tierheilk., 1935, 69, 321—328).—In the abomasum acidity and  $p_{\text{H}}$  were not closely correlated, the discrepancy being due to the presence of org. acids. In a pregnant sheep,  $\text{HCl}$  fell to a very low level 1 month before lambing and gradually rose to normal at lambing. Pepsin was the only enzyme of importance.  
NUTR. ABS. (m)

**Denaturation of proteins by sound waves of audible frequencies.** L. A. CHAMBERS and E. W. FLOSDORF (J. Biol. Chem., 1936, 114, 75—83).—Ovalbumin and plastein, but not horse serum-albumin, are denatured by intense sonic vibration sufficient to produce vigorous cavitation of the solutions, except in an atm. of  $\text{N}_2$  or  $\text{H}_2$  or in vac. The solubility of the products equals that of the heat-denatured products.  
H. G. R.

**Modifications of the state of oxidation-reduction of tissues *in vivo* during photo-sensitisation.** P. DUBOULOZ and J. ROCHETTE (Compt. rend. Soc. Biol., 1936, 122, 221—222).—Irradiation of the skin of the guinea-pig injected with methylene-blue decolorises it irreversibly. The skin of the frog similarly coloured is decolorised in darkness, but the colour is restored on irradiation.  
R. N. C.

**Determination of oxidation-reduction potentials [in biological media].** L. P. DUGAL (Natural. Canad., 1936, 63, 113—133).—Data are recorded for the survival of specimens of *Gammarus locusta* and of the larvæ of coastal plankton in media of varying  $p_{\text{H}}$  and  $r_{\text{H}}$ .  
H. J. E.

**Oxidation-reduction potential of  $\alpha$ -amino-ketobutyric ester and of reductone.** C. MARTIUS and F. KNOOP (Z. physiol. Chem., 1936, 240, 195—197).—The average potential,  $E_0$ , of the ester (I) at 25° and  $p_{\text{H}}$  4.53—8.68 is 0.077, whilst the vals. for reductone and ascorbic acid are approx. equal. (I) readily decolorises indigotindisulphonate, Janus-green, phenosafranin, safranin VE, and (chiefly irreversibly) neutral-red.  
W. McC.

**Effect of certain environmental conditions on skin and body temperatures and rate of oxygen consumption.** H. FREEMAN (Refrig. Eng., 1935, 30, 27—30).—Effects of temp. and R.H. are examined.  
CH. ABS. (p)

**Physiological basis of the sensation of cold. IV. Influence of temperature and of thyroid extract on oxygen consumption of the anæsthet-**

**ised rabbit. V. Relation between basal metabolism, regulation of temperature, and sensation of cold.** J. M. O'CONNOR (Proc. Roy. Irish Acad., 1936, 43, B, 23—33, 34—42).—IV. The influence of temp. on the basal metabolic rate in normal and in thyrotoxic rabbits is the same, the vals. at all temp. being raised 50% in the latter.

V. The onset of shivering between 22° and 38° corresponds with a change in the basal metabolic rate with temp.  
H. G. R.

**Effects of fractional doses of prolactin and X-rays in association on the morphology of the ovary of the adult rabbit.** P. DESAIVE (Arch. Biol., 1935, 46, 669—694).  
R. N. C.

**Interpretation of the action of X-rays and prolactin on the ovary of the adult rabbit.** P. DESAIVE (Arch. Biol., 1935, 46, 695—715).  
R. N. C.

**Exogastrulation in amphibia after X-ray exposure.** W. C. CURTIS, J. A. CAMERON, and K. O. MILLS (Science, 1936, 83, 354).  
L. S. T.

**Absorption of radium emanation by the human body through the skin.** R. WAGNER (Sitzungsber. Akad. Wiss. Wien, II, A, 1934, 143, 521—531).—Rn from radioactive baths is absorbed through the skin and lungs, the latter being the more important route. The permeability of the skin to Rn is about 0.01%, but is increased with large skin surface and excessive hypodermal fat tissue. Absorption in warm  $\text{H}_2\text{O}$  baths is > in ordinary air-baths.  
R. N. C.

**Electromotive force in biological systems. IV. Effect of various nitrogen-oxygen and carbon monoxide-oxygen mixtures on the electromotive force and oxygen consumption of frog skin.** A. B. TAYLOR (J. Cell. Comp. Physiol., 1935, 7, 1—21).— $[\text{O}_2]$  of < 20% in  $\text{N}_2$ - $\text{O}_2$  mixtures lower both  $E$  and  $\text{O}_2$  consumption, the fall of  $E$  being > that of  $\text{O}_2$  consumption, which  $\propto$  the  $[\text{O}_2]$ . Pure  $\text{O}_2$  stimulates  $E$  and increases  $\text{O}_2$  consumption slightly. The decline of  $E$  and of respiration in  $\text{CO}$ - $\text{O}_2$  mixtures depends partly on the  $[\text{CO}]$ , the fall of  $E$  being the greater in certain limits. Complete recovery after treatment with either mixture depends on the time of exposure and the composition of the mixture. The effect of  $\text{CO}$  is unaffected by light.  
R. N. C.

**Ionic antagonism in the water-permeability of sea-urchin eggs.** T. R. FUKUDA (J. Cell. Comp. Physiol., 1935, 7, 301—312).—The rate of swelling of the eggs in hypotonic solutions depends on the ionic composition of the solution. The permeability changes caused by two-salt mixtures containing chlorides of bivalent cations are simple if both cations are bivalent, but more complicated if one only is bivalent; the changes are characteristic of the mixed ratio.  $\text{Na}^+$ - $\text{Ca}^{++}$  mixtures show max. at 99.5% and 50%  $\text{Na}^+$ , and min. at 5% and 100%  $\text{Ca}^{++}$ ;  $\text{Na}^+$ - $\text{Mg}^{++}$  mixtures show max. at 30% and 75%  $\text{Na}^+$  and a min. at 100%  $\text{Mg}^{++}$ .  
R. N. C.

**Permeability of the egg of *Arbacia punctulata* to certain solutes and water.** D. R. STEWART and M. H. JACOBS (J. Cell. Comp. Physiol., 1936, 7, 333—350).—The permeability consts. for a no. of glycols and  $\text{H}_2\text{O}$  are given. They are doubled after

fertilisation of the egg.  $\text{CaCl}_2$  in the solution decreases the permeability of the cell to  $\text{H}_2\text{O}$ , but does not affect that to glycol. R. N. C.

**Distribution of penetrating ammonium salts between cells and their surroundings.** M. H. JACOBS and D. R. STEWART (J. Cell. Comp. Physiol., 1936, 7, 351—365).—The rate of penetration of cells by  $\text{NH}_4$  salts of weak acids is  $>$  that by salts of strong acids, the mechanism probably being by means of the hydrolysis products. The *Arbacia* egg does not swell in isotonic  $\text{NH}_4\text{Cl}$  or hypertonic  $\text{KCl-NH}_4\text{OAc}$  mixture, but ultimately swells in hypertonic  $\text{NH}_4\text{Cl-NH}_4\text{OAc}$  mixture; swelling is caused in  $\text{NH}_4\text{Cl}$  by addition of  $\text{NaOAc}$ , but not by  $\text{Na}_3\text{BO}_3$ , although the cell is apparently permeable to  $(\text{NH}_4)_3\text{BO}_3$ . This suggests that in a mixture of a penetrating and a non-penetrating  $\text{NH}_4$  salt the former may distribute itself so as to raise the internal concn. above the equilibrium concn., but that sufficiently weak acids may prevent this increase. R. N. C.

**Phosphocreatine and lactic acid changes in potassium chloride contractions of frog's muscle in acid solution.** S. R. TIPTON (J. Cell. Comp. Physiol., 1936, 7, 433—443).—Muscles in solution buffered at  $p_{\text{H}}$  6.0 are contracted by 0.04% of K. The contraction is accompanied by a sudden rise in  $\text{O}_2$  consumption, and by hydrolysis of phosphocreatine (I), but lactic acid (II) does not begin to accumulate until  $[\text{K}]$  reaches 0.08%. At this concn. (I) resynthesis is increased. Anaerobic (I) hydrolysis with high  $[\text{K}]$  is  $>$  aerobic hydrolysis. In presence of  $\text{O}_2$  (I) is resynthesised even if (II) formation is not increased. R. N. C.

**Effect of cations on the velocity of the extinguishing action of animal and vegetable organs.** G. RUSSO (Boll. Soc. ital. Biol. sperim., 1935, 10, 805—807).—The velocity of extinction in the presence of cations in the alkaline  $p_{\text{H}}$  zone decreases in the order  $\text{Li} > \text{K} > \text{Na} > \text{Sr} > \text{Mg}^{++}$ ,  $\text{Ba}^{++} > \text{Ca}^{++} > \text{NH}_4^+$ , whilst in the acid zone it increases in the order  $\text{K} < \text{Ba}^{++} < \text{Ca}^{++} < \text{Sr}^{++} < \text{Mg}^{++} < \text{Na}^+$ ,  $\text{NH}_4^+ < \text{Li}^+$ . R. N. C.

**Effect of inorganic salts on the diuretic action of salyrgan.** C. B. ETHRIDGE, D. W. MYERS, and M. N. FULTON (Arch. Int. Med., 1936, 57, 714—728).—Diuresis is increased by the addition of salts which produce acidosis and diminished by those producing alkalosis. H. G. R.

**Inorganic salts in nutrition. Changes in kidneys of rats fed a diet poor in inorganic constituents.** P. P. SWANSON, C. A. STORVICK, and A. H. SMITH (J. Biol. Chem., 1936, 114, 309—319).—Rats on a salt-deficient diet showed enlarged kidneys for 45 days, followed by a regression in kidney size. The proportions of ash, Ca, and P did not decrease, and at the end of 3 weeks the  $[\text{Ca}^{++}]$  was abnormally high. H. D.

**Influence of arsenic on basal metabolism, blood-residual nitrogen, and reticulocytes in man.** E. KNEEL (Arch. exp. Path. Pharm., 1936, 292—300).—Administration of single therapeutic doses of org. or inorg. As preps. lowers the basal metabolism and blood-residual N (I), the latter subsequently increasing and, with inorg. As, exceeding

normal vals. Prolonged dosage increases (I) and the reticulocyte count, the course of the latter together with those of haemoglobin and erythrocytes resembling (and hence indicating the non-specificity of) those due to anti-anæmic preps. F. O. H.

**Value of carbon dioxide in counteracting oxygen lack.** E. GELLHORN (Nature, 1936, 137, 700—701).—The presence of 3% of  $\text{CO}_2$  in the air prevents or alleviates the effect of a low  $[\text{O}_2]$  (8—9%) on brain-stem reflexes in the rabbit and on vision, muscular co-ordination, and mental processes in man. L. S. T.

**Mineral metabolism. XXXIII. Iodine in the nutrition of sheep.** II. A. I. MALAN, P. J. DU TOIT, and J. W. GROENEWALD (Onderstepoort J. Vet. Sci., 1935, 5, 189—200).—There was no significant difference in wt. or wool production between merino ewes receiving KI daily and those receiving none. NUTR. ABS. (*m*)

**Action of lithium on sea-urchin development.** J. RUNNSTRÖM (Biol. Bull., 1935, 68, 378—384).—Effects of  $\text{Li}^+$ , to which the eggs are very sensitive, are described. Pyocyanine counteracts the action of Li which affects the structure of the protoplasm and respiration. CH. ABS. (*p*)

**Effect of uranium nitrate on insulin hypoglycæmia and glycolysis in the blood.** R. WEEKERS (Compt. rend. Soc. Biol., 1936, 122, 78—80).— $\text{UO}_2(\text{NO}_3)_2$  does not appreciably modify the reduction of blood-sugar and  $-\text{PO}_4$  caused by insulin, but it slackens, without inhibiting, blood-glycolysis. R. N. C.

**Effect of sulphur on the bone-marrow.** A. H. MÜLLER (Klin. Woch., 1935, 14, 917—918).—Stimulation of the bone-marrow by thioalbumin (I) is not more productive than that by S-free proteins. Pure S and inorg. S compounds do not affect blood-formation. The action of (I) on the haemopoietic system is due probably to the presence of Fe and Cu as impurities. The effect of Cu on the marrow is not strengthened by S. R. N. C.

**Effect of dietary supplements of different forms of sulphur on the wool of merino sheep.** C. M. VAN WYK, M. L. BOTHA, and J. G. BEKKER (Onderstepoort J. Vet. Sci., 1935, 5, 177—188).—The daily supplements were: 0.45 g. of cystine, 0.7 g. of a mixture of sulphates, 0.36 g. of KCNS, 5.0 g. of S, and 0.12 g. of S. They had no effect on grease wt., clean wt. and % yield of fleece, mean length, thickness, and fibre wt. NUTR. ABS. (*m*)

**Dipolar theory of sense of odour.** A. MÜLLER (Perf. Essent. Oil Rec., 1936, 27, 202—205).—An attempt to explain the odour of organic compounds in relation to their structure by consideration of the theory of dipole moments. P. G. M.

(A) Second eclosion of the infective larvæ of certain *Trichostrongylidae* in solutions of sodium sulphide and of organic compounds containing sulphur. (B) Behaviour of sterilised exsheathed infective *Trichostrongylid* larvæ in sterile media resembling their environment in ovine hosts. G. LAPAGE (J. Helminthol., 1935, 13, 103—114,



115—128).—(A) Effects of garlic,  $\text{Na}_2\text{S}$ , cysteine, sulphonol, and  $\text{Na}_2\text{S}_2\text{O}_3$  are compared.  $\text{NaOCl}$  was more toxic than these.

(B) The larvæ had a wide  $p_{\text{H}}$  tolerance (3.6—9.6). In media containing sheep serum the longevity of the larvæ was not affected by lactose, fructose, glucose, vitamins, or  $\text{NH}_2$ -acids. Yeast and liver extracts were toxic. CH. ABS. (p)

**Blood-chloride and the renal secretion of urea in mice.** P. FEYEL (Compt. rend., 1936, 202, 507—509).—Increased secretion of urea (I) in the brush-bordered cells following intraperitoneal injection of (I) is accompanied by increased secretion of  $\text{Cl}'$ . Similarly, injection of  $\text{NaCl}$  leads to increased secretion of both (I) and  $\text{Cl}'$ . A. G. P.

**Influence of dietary factors on renal secretion of urea in mice.** P. FEYEL (Compt. rend., 1936, 202, 687—689).—Interrelationships between urea and  $\text{Cl}$  excretion are further examined (cf. preceding abstract). A. G. P.

**Influence of renal secretion of urea on the functioning of the chloride resorption mechanism in the mouse.** P. FEYEL (Compt. rend., 1936, 202, 871—874).—The special cells of the Schweigger-Seidel segment of the kidney of a mouse after a meat diet for 15 days contained more  $\text{Cl}'$  than those of a similar mouse which had received an injection of urea just before examination. The renal secretion of urea is accompanied both by secretion and resorption of  $\text{Cl}'$ . J. N. A.

**Physiological effects of certain aliphatic thiocyanates on the isolated heart preparation from the roach, *Blatta orientalis*.** J. F. YEAGER, A. HAGER, and J. M. STRALEY (Ann. Entom. Soc. Amer., 1935, 28, 256—264).—Thiocyanates are grouped in three classes according to their action in inhibiting the contraction rate of the heart prep.: (i) Me and Et, (ii)  $\text{Pr}^a$ ,  $\text{Pr}^b$ , and Bu, (iii) trimethylene, "butylcarbitol," and diethylene glycol thiocyanates,  $\beta\beta$ -dithiocyanodiethyl ether, and diethylene glycol dithiocyanacetate. Relative activity of the groups is (iii) > (ii) > (i). CH. ABS. (p)

**Pharmacological action and pathological effects of alkyl thiocyanates in relation to chemical constitution and physical-chemical properties.** W. F. VON OETTINGEN, W. C. HUEFER, and W. DEICHMANN-GRUEBLER (J. Ind. Hyg., 1936, 18, 310—336).—Of 8 alkyl thiocyanates studied the lower homologues (Me, Et, etc.) cause stimulation and subsequent paralysis of the medullary centres following subcutaneous injection, whilst octyl and decyl thiocyanate are active only in very large doses, and lauryl and myristyl thiocyanate are almost inactive. The higher homologues irritate the mucous membrane. P. G. M.

**Action of acetone and of ketones present in diabetic blood on the heart.** M. M. BAGOURY (Brit. J. Exp. Path., 1935, 16, 25—33).—Toxicity of  $\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{H}$  is > that of  $\text{COMe}_2$ .  $\beta$ -Hydroxybutyric acid (> 1%) has no effect on the heart, its action being attributed to the changes in acid-base equilibrium in the blood. Administration of glucose

and of insulin does not modify the action of the three substances. CH. ABS. (p)

**Action of methylglyoxal on acetoacetic acid.** VI. Liver- and muscle-glycogen after feeding of the ketol and simultaneous injection of insulin. R. STÖHR (Z. physiol. Chem., 1936, 240, 23—25; cf. A., 1935, 1412).—Glycogen (I) formation from  $\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{H}$  (II) in the liver of starving rats is inhibited by insulin (III). Compensatory (I) formation in muscle does not occur, the level being diminished. Parallel results with  $\text{AcCHO}$  indicate that (II) is degraded into two 3-C compounds ( $\text{AcCHO?}$ ). (II) does not inhibit (III)-hypoglycæmia. F. O. H.

**Physiological behaviour of trioses and related compounds.** VI. Liver- and muscle-glycogen after feeding of methylglyoxal and simultaneous injection of insulin. R. STÖHR (Z. physiol. Chem., 1936, 240, 26—28; cf. A., 1934, 919).—See preceding abstract. F. O. H.

**Fat and calcium metabolism.** II. Effect of tributyrin on the excretion of calcium by the intestine in the growing rat. A. WESTERLUND (Lantbruks-Högskolans Ann., 1933—1934, 4, 21—31; Chem. Zentr., 1935, ii, 1574).—Tributyrin does not affect Ca excretion. R. N. C.

**Increased cardiac output [after administration of dinitrophenol].** J. V. GALGANI and M. L. TAINTER (J. Pharm. Exp. Ther., 1936, 56, 451—463).—The increased  $\text{O}_2$  consumption of dogs injected with the drug is only partly due to increased cardiac output. H. D.

**Sensitising action of antioxygenic phenols after post-ganglionic enervation of the nictitating membrane.** Z. M. BACQ (Compt. rend. Soc. Biol., 1936, 122, 112—114).—The sensitising action is inhibited by antioxygenic phenols and aminophenols, but not by non-phenolic antioxygens or amines. The action takes place in the tissues. R. N. C.

**Characterisation of the sympathomimetic and parasympathomimetic substances in the blood by dialysis *in vivo*.** J. GAUTRELET, D. BROUN, H. SCHEINER, and E. CORTEGGIANI (Compt. rend., 1936, 202, 1302—1304).—The parasympathomimetic action of carotid or jugular blood is due to the presence of acetylcholine and the sympathomimetic action of the adrenal vein blood to adrenaline. H. G. R.

**Inhibition of autoxidation of adrenaline by the aqueous humour.** F. BONHOMME (Compt. rend. Soc. Biol., 1936, 122, 110—112).—The inhibition is feebler than that exerted by plasma; the inhibiting agents are proteins and ascorbic acid. R. N. C.

**Choline as a factor in the elaboration of adrenaline.** R. L. STEHLE, J. I. MELVILLE, and F. K. OLDHAM (J. Pharm. Exp. Ther., 1936, 56, 473—481).—A possible genetic relationship between choline (I) and adrenaline (II) is investigated by determining the effects on the blood pressure of possible intermediates in the synthesis of (II) from (I). Methyl- $\beta$ -acetoxyethylammonium chloride, m.p. 105°, and  $\beta$ -3 : 4-dihydroxyphenyldimethyl- $\beta$ -hydroxyethylammonium iodide, m.p. 186°, are described. H. D.

**Comparative action of sodium oleate and ricinoleate on lecithin.** G. VALLETTE (Compt. rend. Soc. Biol., 1936, 122, 150—152).—Na ricinoleate clarifies lecithin suspensions at  $p_H$  7.0—9.0, the clarifying power increasing with  $p_H$ . Na oleate only clarifies the suspension at  $p_H > 9.8$ . R. N. C.

**Dephosphorylation processes during phloridzin diabetes in the dog.** A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, 122, 72—73).—There is no evidence of inhibition by phloridzin of the action of phosphatases. R. N. C.

**Pharmacodynamics of dyes with distinct electrical charges.** A. H. ROFFO and R. L. RAMIREZ (Bol. inst. med. exp., 1931, 8, 99—104).—The action of electro-positive dyes (malachite-green, neutral-red, methylene-blue) on blood pressure and respiration is not appreciably modified by admixture with electro-negative dyes (acid-fuchsin, phenolsulphonephthalein). CH. ABS. (p)

**Toxic action of percutaneously-applied irradiated wool-fat preparations in the sense of hyper-*vitaminosis-D*.** M. SCHIEBLICH and G. PALLASKE (Deut. med. Woch., 1935, 61, 957—960).—Crude wool-fat, lanolin, and eucerin do not generate vitamin-D when irradiated with ultra-violet light, nor do they after irradiation cause calcification of the inner organs when rubbed on the dorsal skin of guinea-pigs. R. N. C.

**Methæmoglobin test for the determination of anti-anæmic efficiency of liver-extracts.** J. F. WILKINSON and W. DEUTSCH (Klin. Woch., 1935, 14, 926—928; Chem. Zentr., 1935, ii, 1586).—The methæmoglobin test is no real indication of the anti-anæmic efficiency and cannot replace clinical methods. H. N. R.

**Ornitho-callicrein.** I. E. WERLE and J. HURTER (Biochem. Z., 1936, 285, 175—191).—Callicrein (I), injected into birds (hen, goose, pigeon, duck), has no effect on the blood pressure, but the fæces and pancreas of birds contain *ornitho-callicrein* (II) which closely resembles (I), having a powerful reducing effect on the blood pressure of birds, but none on that of mammals. (II) is inactivated by heat, *N*-HCl, *N*-NaOH, I,  $H_2O_2$ , and the serum of birds and mammals. In the fæces of birds (II) is accompanied by small amounts of a substance, probably histamine. W. MCC.

**Effect of adrenal and splanchnic denervation on sugar tolerance of dogs.** G. DE TAKATS and F. P. CUTHBERT (Arch. Surg., 1935, 30, 150—161).—The sugar tolerance increased under both conditions. Dogs are more responsive to insulin and less to the hyperglycæmic action of adrenaline. Bilateral vagotomy does not diminish the increased sugar tolerance obtained in these operations. Interruption of the sympathico-adrenal mechanism may cause increased storage or fixation of glycogen in the liver. CH. ABS. (p)

**Fixation of alcohol on the encephalon of rats with experimental alkalosis.** J. LEVY (Compt. rend., 1936, 202, 440—441).—The min. anæsthetic dose of EtOH for normal rats is sufficient for rats with alkalosis produced by NaOH, but insufficient

for those with alkalosis produced by  $Na_2CO_3$ . The hyposensitivity to EtOH of the latter is discussed. H. G. M.

**Blood-alcohol and its relation to intoxication in man.** R. G. TURNER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1548—1552).—Blood-EtOH must be  $> 0.2\%$  to cause noticeable intoxication;  $0.31$ — $0.4\%$  causes marked intoxication,  $0.41$ — $0.5\%$  stupor, and  $> 0.5\%$  coma or death. R. N. C.

**Specific dynamic action and toxicity of synthetic alcohol and fermentation alcohol.** J. KRIZENECKY and F. DIAKOV (Z. Unters. Lebensm., 1936, 71, 149—159).—No important difference was observed, but the synthetic EtOH appeared to contain an impurity with narcotic properties. E. C. S.

**Activity of anæsthetics and their partition in blood.** N. LAZAREV (Compt. rend. Acad. Sci., U.R.S.S., 1936, 1, 237—238).—In the blood of frogs and mammals those anæsthetics which are most powerful exist almost entirely "bound," whilst those which are weak exist chiefly in aq. solution. Probably the hæmoglobin shares in binding the anæsthetics. W. MCC.

**General narcosis with gases, cyclopropane, carbon dioxide, nitrous oxide, ethylene, and oxygen.** A. CHUECO (Semana méd., 1935, I, 1793—1799). CH. ABS. (p)

**Summation of the action of two soporifics on molecular combination.** H. J. FUCHS (Arch. exp. Path. Pharm., 1936, 181, 215—218).—Mol. combinations of diethylbarbituric acid (I) and bromoisovalerylcarbamide have a soporific action  $>$ , and a toxicity  $<$ , that of (I). F. O. H.

**Sodium propylmethylcarbonylallylbarbiturate, a short-acting hypnotic.** E. E. SWANSON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1563—1565). R. N. C.

**Effects of phenacetin and aspirin, respectively, on action of phenobarbital.** A. GILMAN and H. G. BARBOUR (Proc. Soc. Exp. Biol. Med., 1935, 32, 1634—1636). R. N. C.

**Cinchophen (atophan) therapy and the liver.** T. BRUGSCH (Semana méd., 1935, I, 1907—1910).—Cinchophen mobilises uric acid, reduces inflammation, and stimulates hepatic secretion. CH. ABS. (p)

**Ocular reactions due to arsphenamine.** J. J. SKIRBALL and F. M. THURMAN (Amer. J. Syphilis, 1935, 19, 197—209).—Substitution of I', Bi, or Hg for arsphenamine does not affect the return of the eye condition to normal. CH. ABS. (p)

**Purgative constituent of castor oil.** G. VALETTE and R. SALVANET (Compt. rend. Soc. Biol., 1936, 122, 68—70).—Ricinoleic acid prepared by way of the Li salt exerts a purgative action, but not that prepared by way of the Et ester and saponification with LiOH. R. N. C.

**Pharmacological actions of indolyl-N-methyl-harmine.** I. BAKHSH (Quart. J. Pharm., 1936, 9, 37—47; cf. Gunn, A., 1912, ii, 857).—The min. lethal dose of indolyl-N-methylharmine hydrochloride (I) per kg. by subcutaneous injection is  $0.11$  (frog),  $0.038$  (guinea-pig), and  $0.1$  g. (mouse). Toxic doses



cause a descending paralysis of the central nervous system. Small doses increase whilst large doses diminish blood pressure. (I) dilates the coronary vessels in the isolated rabbit's heart. Conc. solutions cause contraction of frog's skeletal muscle, whilst smooth muscle is first stimulated. (I) kills *Paramaecium caudatum* and *Amoeba proteus* in concn. of 1 in 320,000 and 1 in 1,280,000, respectively, in 24 hr. Judged by toxicity (I) is approx. three times as active as harmine. J. N. A.

Relative values of caffeine and hypertonic glucose and saline solutions in reducing cerebrospinal fluid pressure. A. BLAU (Arch. Int. Med., 1936, 57, 749—757).—Reductions obtained on intravenous injection of hypertonic aq. glucose or caffeine-NaOBz were inconsistent and transient, whereas those with 15% saline were uniform and more persistent. H. G. R.

Pharmacology of caffeine and of tea and coffee. G. R. LYNCH (Analyst, 1936, 61, 300—302).—The action of caffeine on the central nervous system, muscular tissue, and kidney is discussed. E. C. S.

[Pharmacology of] twenty-three quaternary ammonium iodides. H. M. LEE, A. M. VANARENDONK, and K. K. CHEN (J. Pharm. Exp. Ther., 1936, 56, 466—472).—The nicotine- and muscarine-like activities of the compounds are compared. d-, m.p. 206.5—207°, and dl-*Methylephedrine methiodide*, m.p. 230—230.5°, d-, m.p. 212—213°, l-, m.p. 211—212°, and dl-*Methyl- $\psi$ -ephedrine methiodide*, m.p. 168.5—169°,  $\beta$ -hydroxy- $\beta$ -phenylisopropyl-dimethyl-ethyl-, m.p. 166—167°, and -benzyl-dimethyl-ammonium iodide, m.p. 188—189°,  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -ethyl-, m.p. 162—163°, and  $\beta$ -1:2-diethoxyphenyl-ethyl-trimethylammonium iodides, m.p. 245°, *dendrobine methiodide*, m.p. 246°, *tetrandrine dimethiodide*, m.p. 273°, 4- $\beta$ -ethoxyethyl-, m.p. 93—95°, and 4- $\beta$ -acetoxyethyl-morpholine methiodide, m.p. 123.5—124.5°, are described. H. D.

Absorption of drugs through the oral mucosa. II. III. Fat-water solubility coefficient of alkaloids. R. P. WALTON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1486—1488, 1488—1492).—III. Absorption of drugs with high oil-H<sub>2</sub>O solubility coeffs. is > of those with relatively low coeffs. R. N. C.

[Pharmacology of] morphine, codeine, and their derivatives. XII. Isomerides of morphine and dihydromorphine. N. B. EDDY (J. Pharm. Exp. Ther., 1936, 56, 421—431; cf. A., 1936, 517).—The pharmacological activities of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomorphine and of their H<sub>2</sub>-derivatives were compared among themselves and with those of analogous codeine derivatives. H. D.

Pharmacology and therapeutics of curare and its constituents. R. WEST (Proc. Roy. Soc. Med., 1935, 28, 565—578).—Fractionation of the active constituents is described. Tubocurarine and curine are examined. CH. ABS. (p)

Eupaverine in relation to papaverine and visammin. K. SAMAAAN (Quart. J. Pharm., 1936, 9, 23—36).—Eupaverine (I) and papaverine (II), injected intravenously into dogs, have a min.

lethal dose of 60 and 40 mg. per kg., respectively. In the toad, rabbit, and dog, (I) depresses the heart and relaxes all types of smooth muscle by direct action on the muscle fibres, but the degree of action varies greatly. The relative actions of (I), (II), and visammin of antagonising the effect of Ba<sup>++</sup> vary with different types of plain muscle. The low toxicity of (I) compared with (II) is offset by its insolubility. J. N. A.

Analgesic and respiratory action of the morphine group. W. KEIL and F. H. POHLS (Arch. exp. Path. Pharm., 1936, 181, 285—291).—The course and extent of analgesic and respiratory action (the latter being produced by smaller doses than is the former) of morphine alkaloids (I) in rabbits were determined. Morphinised animals have a diminished sensitivity to (I). F. O. H.

Emetic action of lobelanine and lobelanidine. A. CLEMENTI (Arch. exp. Path. Pharm., 1936, 181, 265—272).—Toxicity and emetic and respiratory action were determined in dogs, rabbits, and frogs. F. O. H.

Respiratory stimulating action of lobeline and carbon dioxide on the morphinised respiratory centre in rabbits. B. BEHRENS and W. GRAUBNER (Deut. med. Woch., 1934, 60, 1675—1677). R. N. C.

Relation between nicotine and the sexual hormone I. Lethal dose of nicotine and sexual difference. II. Effect of castration and sexual hormone on nicotine activity. III. Effect of nicotine on morphological and histological changes of female sex organs after injections of female sexual hormones. IV. Antidotal action of luteohormone on nicotine toxicity during anaphylaxis. (A) Effect of nicotine on blood-sugar, blood pressure, and anaphylaxis. (B) Effect of luteohormone on anaphylaxis. (C) Effect of nicotine with luteohormone on anaphylaxis. V. Discussion and conclusion. Y. C. LEE (J. Severance Union Med. Coll., 1935, 2, 80—86, 87—107, 108—127, 128—155, 156—159).—The greater resistance of female animals to the action of nicotine is due to the production of luteohormone. CH. ABS. (p)

Role of glycaemic response to nicotine. Tobacco smoking and blood-sugar. W. J. McCORMICK (Amer. J. Hyg., 1935, 22, 214—220).—Injection of adrenaline into rabbits prior to administration of nicotine reduces the toxic action of the latter. Hyperglycaemia caused by smoking is a protective response and results in decreased potential muscular energy, through lowering the body-reserve of glycogen. CH. ABS. (p)

Determination of the average lethal dose in the biological assay of digitalis by the frog method. K. O. MÖLLER (Quart. J. Pharm., 1936, 9, 7—22).—A method by which the average lethal dose (LD 50) can be determined on 30—40 frogs (kept at a const. temp.) by means of a mortality curve is described. The statistical determination of LD 50 is discussed. "Summer frogs" are much more resistant to digitalis than "winter frogs." J. N. A.

**Antagonistic effect of iodides in baldness and toxicity due to thallium acetate.** O. V. HYKES and F. A. DIAKOV (Nature, 1936, 137, 871).—In addition to KI (cf. A., 1935, 1533), LiI, NaI, and  $MgI_2$  largely counteract the toxic effects in rats due to  $TlOAc$ . L. S. T.

**Influence of diet on the toxicity of mercurochrome and of nearsphenamine.** R. WIEN (Quart. J. Pharm., 1936, 9, 48—59; cf. Burn and Elphick, B., 1930, 881).—The sensitivity of mice towards mercurochrome and nearsphenamine varies with different diets which, however, have no influence on liver-glycogen. J. N. A.

**Ability of rats to discriminate between diets of varying degrees of toxicity.** K. W. FRANK and V. R. POTTER (Science, 1936, 83, 330—332).—Rats are able to detect and differentiate between small quantities of Se in foodstuffs. Sub-lethal injections of  $Na_2SeO_3$  cause a voluntary starvation even when normal diets are offered. L. S. T.

**Toxic wheat grown on soils containing selenium.**—See B., 1936, 515.

**Toxicity of carbon tetrachloride; animal exposures and field studies.** H. F. SMYTH, H. F. SMYTH, jun., and C. P. CARPENTER (J. Ind. Hyg., 1936, 18, 277—298).—100 p.p.m. of  $CCl_4$  vapour are safe for continuous daily exposure of workmen. At a level of 50—400 p.p.m., damaged liver and kidney cells regenerate with increased resistance. P. G. M.

**Toxicity and potential dangers of phenylhydrazine zinc chloride.** W. F. VON OETTINGEN, W. DEICHMANN-GRUEBLER, and W. C. HUEPER (J. Ind. Hyg., 1936, 18, 301—309).—This double salt is less toxic than  $NHPh \cdot NH_2$  (I) as judged by subcutaneous injection in rats; the min. lethal dose is 0.25 mg. as opposed to 0.18 mg. per g. and its effect is more prolonged. Unlike (I), it does not evolve toxic vapours when heated to 100—170°. It destroys red cells and reduces the hæmoglobin content of the blood, but to a smaller degree than (I). It produces more pronounced skin irritation than (I). P. G. M.

**Influence of diet on toxicity of ethylhydrocupreine hydrochloride.** A. J. NEDZEL (J. Lab. Clin. Med., 1935, 20, 944—945).—Rabbits fed exclusively on oats are more, and those on a diet of carrots less, sensitive to ethylhydrocupreine than are those on a mixed diet. Differences are attributed to variations in acid/base ratio resulting from the diets. CH. ABS. (*p*)

**Chronic poisoning by aniline. Acute poisoning by *p*-phenylenediamine.** A. BUZZO, R. CARRATALA, and C. MARTINEZ (Rev. crim. psychiat. med. legal, 1931, 18, 427—433).—Cases are described. Methods of detecting  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  are given. CH. ABS. (*p*)

**Hypoglycæmia as a result of agaric (*Amanita phalloides*) poisoning.** L. BINET and J. MAREK (Compt. rend., 1936, 202, 1219—1220).—Aq. extracts, subcutaneously (10 mg. per kg.) or orally administered to dogs, cause a marked hypoglycæmia and uræmia followed by death in several hr. Rabbits show convulsions, and the liver is rendered glycogen-

free. Extracts of non-toxic agarics do not produce these effects. J. L. D.

**Snake venom.** F. MICHEEL and F. JUNG (Z. physiol. Chem., 1936, 239, 217—230).—The dried venom of *Naja flava* when purified by ultrafiltration, dialysis, and fractional pptn. with  $\text{COMe}_2$  at the isoelectric point ( $p_H$  about 7.0) yields an extremely active ( $0.12 \times 10^{-6}$  g. is min. lethal dose per g. for mice) neurotoxin (I), mol. wt. 2500—4000, containing C, H, O, N, S, and combined mineral matter. (I) is stable at  $p_H$  2—8, especially if glycerol is present, but is inactivated by  $O_2$  and reactivated by cysteine at  $p_H$  2—3. (I), which is related to the proteins, probably contains a thiolactone group, but no free  $\cdot\text{SH}$ . The venom also contains a poison having about 12% of the activity of (I). The poison from the venom of vipers *Crotalus adamanteus*, *C. terrificus*, *Bothrops jararaca*, and *Ancistrodon piscivorus* also contains S, has mol. wt.  $\gg$  that of (I), and is more sensitive to attack by acid and alkali. Its stability is greatest at  $p_H$  5.8—6.0. In the venom it is accompanied by a dialysable activator. Albumin, albumose, and (in greater amount) peptone also activate the poison to the same extent. W. McC.

**Ascorbic acid oxidase from drumstick, *Moringa pterygosperma*.** M. SHRINIVASAN (Current Sci., 1935, 4, 407—408).—Drumstick press juice contains an enzyme system (prep. described) which is capable of oxidising ascorbic acid (I) and is inactivated when boiled or treated with  $\text{CCl}_3\text{CO}_2\text{H}$  (cf. Szent-Gyorgi's hexoxidase; A., 1931, 533). The oxidation of (I) occurs best at  $p_H$  5.3 and 37°, and is unimol.; the rate  $\propto$  the quantity of enzyme and is independent of (I) concn. The reaction is inhibited by  $\text{CN}^-$  and  $\text{H}_2\text{S}$  (0.001*M*). Guaiacum, pyrocatechol, pyrogallol, and  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  are not oxidised except in presence of  $\text{H}_2\text{O}_2$ . EtOH and  $\text{COMe}_2$  destroy the (I)-oxidising constituent, but leave the peroxidase unaffected. The conclusions of Tauber *et al.* (A., 1935, 1023) concerning the existence of a sp. enzyme capable of oxidising (I) are thus confirmed. H. G. M.

**Mechanism of oxidation processes. XLIV. Dehydrogenating enzyme system of *Acetobacter peroxydans*.** I. H. WIELAND and H. J. PISTOR (Annalen, 1936, 522, 116—137).—EtOH (0.11—0.67*M*) is dehydrogenated to  $\text{MeCHO}$  and a little  $\text{AcOH}$  by *A. peroxydans* (I) in  $O_2$  at  $p_H$  4.5—7 (reaction is retarded considerably at higher  $p_H$ );  $\text{CO}_2$  is not produced. Reaction with 0.05*M*-EtOH is almost completely inhibited by KCN (*M*/4000—*M*/8000) and  $\text{H}_2\text{O}_2$  (*M*/160—*M*/230; *M*/800 has little effect) and retarded by  $\text{NaN}_3$  (*M*/2000—*M*/4000) and  $\text{CN}\cdot\text{ONa}$  (*M*/5000—*M*/10000). Little conversion of  $\text{MeCHO}$  into  $\text{AcOH}$  occurs in  $\text{N}_2$ , indicating absence of mutase.  $\text{H}_2\text{O}_2$  formed during dehydrogenation could not be detected. Since EtOH is also dehydrogenated by (I) +  $\text{H}_2\text{O}_2$  in  $\text{N}_2$  or air, and (I) is free from catalase, the  $\text{H}_2\text{O}_2$  formed is probably used immediately in the respiratory process. When suspensions of (I) are shaken with  $\text{H}_2$  a small amount is absorbed; subsequent addition of  $\text{H}_2\text{O}_2$  (*M*/270) causes rapid consumption of the  $\text{H}_2$  until all  $\text{H}_2\text{O}_2$  has disappeared, but the residue is still able to effect aerobic dehydrogenation of EtOH. The enzyme system prob-



ably contains peroxidase and dehydrogenase. The organism contains cytochrome but no porphyrins.

H. B.

**Amino-acid dehydrogenase. I. Proline dehydrogenase.** N. B. DAS (Biochem. J., 1936, 30, 1080—1087).—A purified dehydrogenase from pig's kidney oxidises *dl*-proline more readily than *d*-alanine, *dl*-phenylalanine, or leucine. Codehydrogenases I and II, flavin-enzyme, glutathione, adenylyl pyrophosphate, and ascorbic acid do not activate the dehydrogenase. When the enzyme solution is heated at 80° at  $p_H$  8 for 5 min. and then added to the original enzyme prep., there is an activation of the oxidation of proline.

J. N. A.

**Liver enzymes. VI. Citric acid dehydrogenase.** L. REICHEL and A. NEEFF (Z. physiol. Chem., 1936, 240, 163—178; cf. A., 1935, 1162; this vol., 242).—The dehydrogenase (I) is purified by fractional pptn. with  $COMe_2$  and with  $COMe_2-Et_2O$ -light petroleum (3:1:1). Adsorption on kaolin and  $Al_2O_3$  followed by elution is not advantageous but electrodialysis is satisfactory. The activity, which is measured, after removal of protein with  $p-C_6H_4Me-SO_3H$ , by determination of residual citric acid as Ca salt, is optimal at  $p_H$  7.6 (pptn. and inactivation at 3.4) with 0.0033*M*-substrate, the max. effect being attained in 3 hr. (I) acts in presence and absence of  $O_2$ . No activity is lost on dialysis and addition of cozymase is without effect, a coenzyme being probably not required.

W. McC.

**Oxidase-like action of certain complex metal salts.**—See this vol., 805.

**Flavins and metabolism. I. Flavins and amylolysis.** A. J. CHARIT. II. Flavins and proteolysis. A. J. CHARIT and N. V. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 215—218, 219—224).—I. Lactoflavin and a flavin-containing liver extract exert no influence on amylolysis by diastase or salivary amylase outside the cell, when used alone or in presence of Fe salts or aspartic acid.

II. The oxidised form of flavin under aerobic conditions does not activate the digestion of proteins by trypsin, the action of papain, or the autolytic process of muscle-tissue.

H. G. M.

**Free and bound amylase of barley.** K. MYRBACK and S. MYRBACK (Biochem. Z., 1936, 285, 282—289; cf. this vol., 245).—In general, the liberation of bound amylase (I) in barley is caused only by proteolytic enzymes and is increased by substances (e.g., HCN) which activate these enzymes. Prolonged action of papain (II) on ungerminated barley does not cause destruction of (I). Probably the  $\beta$ -amylase of barley exists partly free and partly bound, the action of (II) consisting in liberating more (I) not in activation.

W. McC.

**Hydrolysis of starch by vegetable amylases. I.** K. MYRBACK (Biochem. Z., 1936, 285, 290—293).—Starch (I), oxidised with I, is hydrolysed by  $\alpha$ -(II) and  $\beta$ -amylase (III) to the same extent as is untreated (I). Malt-amylase (IV) has a more powerful action than have (II) and (III), the action of (II) being slight. Dextrin obtained from (I) by the action of (III) is very slightly affected by (III), is first rapidly

(up to 30% hydrolysis), then slowly attacked by (IV), and is rapidly and extensively attacked by (II). Hence (III) leaves unattacked a component of (I) which is hydrolysed by (II).

W. McC.

**Effect of acetylcholine hydrochloride on the amylolytic activity of pancreatin.** F. CAUJOLLE and R. MONNET (Compt. rend. Soc. Biol., 1936, 121, 1570—1572).—The activity of pancreatic amylase *in vitro* is increased.

R. N. C.

**Malt diastases. II.**—See B., 1936, 565.

**Emulsin. XXVI. Action of osmium tetroxide on sweet almond-emulsin.** B. HELFERICH and F. VORSATZ (Z. physiol. Chem., 1936, 239, 241—256; cf. A., 1935, 783; this vol., 243).—The  $\beta$ -glucosidase (1 unit) of the emulsin (I) is inactivated by  $OsO_4$  (25 mg.), the effect not being due to oxidation, which proceeds much more slowly. Aq.  $H_2S$  and cysteine (II) (1 mol. for each equiv. of active O from  $OsO_4$  has max. effect) if added before oxidation has gone far restore much of the activity. Probably (II) acts by reducing  $OsO_4$ , and no inactivation occurs if (II) and  $OsO_4$  are mixed before adding to (I). The action of  $OsO_4$  is not affected by *l*-proline, indole, and *d*-alanine, but *l*-histidine and ascorbic acid have a slight protective effect. Tryptophan (approx.  $\propto$  its amount) intensifies the action of  $OsO_4$ , the effect being partly counteracted by  $H_2S$  and (II).

W. McC.

**Liberation of the zymase system from the yeast cell by autolysis.** R. NILSSON and F. ALMR (Z. physiol. Chem., 1936, 239, 179—187).—The zymase (I) is extracted partly from fresh and almost completely from dried brewer's yeast by shaking with  $H_2O$  if the extraction is preceded by a sufficiently long period of autolysis. No (I) is liberated by plasmolysis with sugar or glycerol.

W. McC.

**Activator of zymohehexase.** E. BAUER (Z. physiol. Chem., 1936, 239, V; cf. Meyerhof *et al.*, A., 1934, 927).—The activator occurs in dialysed muscle extract. Thermodynamic equilibrium in the reaction hexosediphosphoric acid + 2 dihydroxyacetonephosphoric acid is not attained with dil. solutions of zymohehexase chiefly because of the absence of the activator.

W. McC.

**Nature of cozymase.** K. MYRBACK (Svensk Kem. Tidskr., 1936, 48, 100—103; cf. A., 1935, 1278).—The behaviours of cozymase (I), ouabain, and  $\Delta^2$ -angelicalactone towards oxidising agents indicate that (I) contains a lactone ring, probably 6-membered with two double linkings.

M. H. M. A.

**Cozymase as a phosphate carrier.** R. VESTIN (Z. physiol. Chem., 1936, 240, 99—112).—In dialysed extract of rat's muscle, cozymase (I) and (I) inactivated by heat hydrolyse phosphopyruvic acid (II) and phosphocreatine and act as phosphate carriers in the transfer of  $PO_4$  from (II) to creatine. Heat-inactivated (I) is usually more effective than (I), and is sometimes as effective as adenylic or adenosinetriphosphoric acid.

W. McC.

**Chemistry of highly purified cozymase.** H. VON EULER, H. ALBERS, and F. SCHLENK (Z. physiol. Chem., 1936, 240, 113—126).—Methods of puri-

fication are described. The products of acid-hydrolysis include adenine, nicotinamide, and a pentose-phosphoric acid which together constitute about 60% of the purest material. Cozymase is a dibasic acid each mol. of which takes up 6 I from alkaline solution. W. McC.

**Inhibition of glycolysis by heavy metals. Re-activation by Warburg's co-enzyme and Euler's cozymase.** T. WAGNER-JAUREGG and H. W. RZEPPA (Z. physiol. Chem., 1936, 240, I—IV).—Low concns. of Cu, Fe<sup>++</sup>, and Fe<sup>+++</sup> (but not Zn or Cd) inhibit production of lactic acid (I) from hexose-phosphoric acid in dialysed frog's muscle extract containing MgCl<sub>2</sub> and adenosine triphosphate (II). Warburg's co-enzyme (III) and Euler's cozymase (IV) (75 mol. to 1 of metal) counteract the effect, the amount of (I) then produced being > double that produced with (II) and (III) or (II) and (IV) alone. Cysteine and glutathione counteract much less effectively than do (III) and (IV), whilst adenylic acid from muscle and KCN are inactive. W. McC.

**Mechanism of cerebral glycolysis.** F. P. MAZZA and C. MALAGUZZI-VALERI (Boll. Soc. ital. Biol. sperim., 1935, 10, 725—727).—Brain extract induces the four reactions of the Embden-Meyerhof glycolysis cycle, and, like muscle extract, contains zymohexase and a dialysable co-enzyme, apparently the same as that of muscle. F<sup>-</sup> inhibits breakdown of phosphoglyceric acid (I); it does not interfere with formation of lactic acid (II) from  $\alpha$ -glycerophosphoric acid (III) and AcCO<sub>2</sub>H (IV), but inhibits liberation of H<sub>3</sub>PO<sub>4</sub>. CH<sub>2</sub>I-CO<sub>2</sub>H partly inhibits formation of (II) from (I) and (III), or from (IV) and (III), but does not inhibit breakdown of (I). R. N. C.

**Control of the enzymic action of lipase.** R. ITOH (Nature, 1936, 137, 783).—A substance (I), m.p. 130°, [ $\alpha$ ]<sub>D</sub><sup>18</sup> -77°, which controls the reversible action of lipase, has been isolated from *Ricinus* seed. The EtOH solution exhibits blue-violet fluorescence and two absorption bands with max. at 314 and 285 m $\mu$ . The Liebermann-Burchardt sterol reaction, the Cuboni reaction for oestrogenic hormone, and the vanillin-H<sub>3</sub>PO<sub>4</sub> reaction for bile acid are positive, but the Salkowski reaction for sterol and the Gregory reaction for bile acid are negative. The reduced form of (I) activates the hydrolysis of fat by the *Ricinus* lipase and inhibits the synthesis from glycerol and oleic acid. The oxidised form acts in the reverse manner. L. S. T.

**Castor bean lipase and its activator.** E. TAKAMURA (Proc. Imp. Acad. Tokyo, 1936, 12, 73—74).—From castor seeds have been isolated (a) a highly active lipase giving no reactions with Molisch, biuret, and sterol reagents but an active Millon test, and (b) an activator (I) in the form of needles. The enzyme catalyses both the synthesis and the hydrolysis of oils. (I) has a moderate effect on both processes, but after air oxidation it has an increased action on synthetic but not on the hydrolytic process. After oxidation with H<sub>2</sub>O<sub>2</sub> (I) strongly retards both processes. W. O. K.

**Role of bile acids in the enzymic synthesis of cholesterol.** S. V. NEDSVEDSKI (Z. physiol. Chem.,

1936, 239, 165—166; cf. A., 1935, 1416).—In absence of salts of bile acids, pancreatic lipase (in H<sub>2</sub>O) is destroyed in 24 hr. When Na glycocholate is added, the lipase remains almost unaltered for  $\leq$  10 days.

W. McC.

**Glyoxalase and its co-enzyme. II. Kidney-glyoxalase.** K. NAGAYA, S. YAMAZOYE, and S. NAKAMURA (J. Biochem. Japan, 1936, 23, 41—56).—The difference between kidney- and other tissue-glyoxalases is due to an inhibitory substance (I) in kidney tissue. The inhibition occurs after reaction of (I) with glutathione (II), the reaction product combining with AcCHO at the same rate as does free (II), the respective final products being differentiated by only that from free (II)-AcCHO decompose with glyoxalase to give lactic acid and (II). F. O. H.

**Enzymic hydrolysis of acetylcholine by serum.** E. KAHANE and J. LEVY (Compt. rend., 1936, 202, 781—783).—The "activity" (defined) of serum is const. when there is < 5% of serum in a 0.18—1.8% solution of acetylcholine chloride; it decreases with  $p_H$ , is zero at  $p_H$  6, and increases with rise of temp. to 38°. Serum is inactivated at 70° and by pptn. (EtOH, COMe<sub>2</sub>) of the proteins: dialysates and ultrafiltrates are inactive. J. L. D.

**Variations of the proteolytic activity of kinase-activated pancreatic juice as a function of the quantity of kinase.** M. GUILLAUMIE (Compt. rend. Soc. Biol., 1936, 122, 51—53).—The quantity  $T$  of trypsin produced by a quantity  $x$  of kinase is given by  $T = 70x^{0.49}$ . R. N. C.

**Enzymic histochemistry. XIII. Distribution of enzymes in the stomach of pigs as a function of its histological structure.** K. LINDERSTRÖM-LANG, H. HOLTER, and A. S. OHLSEN (Compt. rend. Trav. Lab. Carlsberg, 1935, 20, No. 11, 66—127).—The enzyme contents of the different portions of the stomach, and curves of the variation of the enzyme content with the distance below the inner surface, are given. HCl is found chiefly in the parietal cells of the fundus at 0.5 mm. depth, pepsin in the chief cells at 2 mm., peptidase in the chief cells of the stomach and the cylinder and Brunner cells of the duodenum, and esterase in the epithelial cells and interstitial tissues.

R. N. C.

**Digestive enzymes in cephalopods.** C. ROMIJN (Acta Brev. neerl. Physiol., 1935, 5, 14—15; Chem. Zentr., 1935, ii, 1385—1386).—The salivary glands of *Sepia officinalis* contain no digestive enzymes. The combined digestive juices of the liver and pancreas at  $p_H$  5.4 contain amylase, tributyrinesterase, proteinase, carboxy- and amino-polypeptidases, and dipeptidase, but no disaccharase, and cannot hydrolyse castor oil. The pancreatic but not the liver-protease requires activation by enterokinase, which can be replaced by extract of the caecum walls, but not by glutathione or H<sub>2</sub>S. The enzymes show optimum activity at neutral or weakly acid  $p_H$ . R. N. C.

**Phosphatases. I. Reaction mechanism of phosphatase from bone.** M. LORA Y TAMAYO and F. SEGOVIA. II. New preparation of a phosphatase from bone. M. LORA Y TAMAYO and J. R. BLANCO (Anal. Fis. Quím., 1936, 34, 363—375,



376—382).—I. The rate of hydrolysis at 38° of Na  $\beta$ -glycerophosphate (I) by phosphatase (II) isolated by the method of Martland *et al.* (A., 1929, 603) from the bones of a young rabbit  $\propto$  the sq. root of the time and the sq. root of the concn. of (II). Optimum conditions are 0.05M solution, at 40°, and  $p_H$  9.7. Ultra-violet irradiation slightly retards the hydrolysis. The optimum  $p_H$  for the hydrolysis of Na  $\alpha$ -glycerophosphate is the same for (I).

II. Agitation of the bones of young rabbits with aq. EtOH containing EtOAc and PhMe yields a new phosphatase more active than (II). F. R. G.

**Accelerant effect of  $\alpha$ -amino-acids on the activity of bone-phosphatase.** O. BODANSKY (J. Biol. Chem., 1936, 114, 273—288).—Low concns. of  $\alpha$ -NH<sub>2</sub>-acids prevent the rapid diminution of the rate of hydrolysis of Na  $\beta$ -glycerophosphate by bone phosphatase (I); the optimal concns. differ for the various acids. Mg<sup>++</sup> has a similar influence, but also increases the initial rate of hydrolysis. With optimal concns. of Mg<sup>++</sup> and glycine (II) the reaction velocity  $\propto$  (I) concn. (II) retards the inactivation of (I) at room temp. H. D.

**Serum-phosphatase in normal young rabbits.** P. D. ROSAHN (Proc. Soc. Exp. Biol. Med., 1935, 32, 1601—1603).—Between 15 and 71 days serum-phosphatase falls linearly with increasing age and wt. R. N. C.

**Separation of  $\alpha$ -glycerophosphatase and pyrophosphatase from bottom yeast.** E. BAUER (Z. physiol. Chem., 1936, 239, 195—206; cf. this vol., 380). The phosphatases of bottom yeast contain 10 times as much pyrophosphatase (I) as  $\alpha$ -glycerophosphatase (II). (I) and (II) differ as regards effect of [H<sup>+</sup>], substrate concn., and activation by Mg<sup>++</sup>. (II) is freed from (I) by adsorption on Al<sub>2</sub>O<sub>3</sub> at  $p_H$  8.6. W. McC.

**Kinetics of cell respiration. I. Rate of oxygen consumption by *Saccharomyces Wanching* as a function of  $p_H$ .** P. S. TANG (J. Cell. Comp. Physiol., 1936, 7, 475—493).—The effect of  $p_H$  varies with the buffer employed. O<sub>2</sub> consumption falls logarithmically in the OAc<sup>-</sup> buffers, but less rapidly in the PO<sub>4</sub><sup>---</sup> and phthalate buffers until a limiting [H<sup>+</sup>] is reached beyond which O<sub>2</sub> consumption falls steeply to zero. In BO<sub>3</sub><sup>---</sup> buffer, respiration falls linearly from  $p_H$  7.7 to 8.9, then increasing to 9.8. The difference of the effects of  $p_H$  in the acid and alkaline ranges suggests the existence of two different respiratory systems in the yeast cells. Respiration is inhibited at high [H<sup>+</sup>] and partly restored on returning to low [H<sup>+</sup>] after an induction period depending on the magnitude of [H<sup>+</sup>] and the time of exposure. R. N. C.

**Selective fermentation. III. Fermentation of hexose-pentose mixtures.** H. SOBOTKA, M. HOLZMAN, and M. REINER (Biochem. J., 1936, 30, 933—940).—Fermentation by brewer's yeast of glucose and to a greater extent of fructose is retarded in the presence of xylose and to a smaller extent of arabinose, the effect being observed in all sugar concns. tested (0.8—6.7%) and with yeast concns. from 0.16 to 15.0% under aerobic and anaerobic conditions. The effect ran parallel with the ratio of the concns. of pentose to hexose, leading sometimes to almost complete sup-

pression of fermentation. The fermentation, although slower, proceeds further, the total CO<sub>2</sub> evolved being often greater. Competitive diffusion of these sugars into the yeast cell is the major factor in the mechanism of this effect. Studies of diffusion permit the differentiation of extracellular, intracellular, and chemically bound H<sub>2</sub>O in yeast. P. W. C.

**$\beta$ -Alanine and "bios."** R. J. WILLIAMS and E. ROHRMAN (J. Amer. Chem. Soc., 1936, 58, 695).—The growth of various yeasts (Wildiers; "Gebrüder Mayer"; Lash Miller; "Rasse M") on a medium containing inositol (5 mg. per litre) in addition to sugar and salts, is stimulated by  $\beta$ -alanine (I) (10<sup>-6</sup> g. per 12 c.c. of culture; with 10<sup>-10</sup> g. inhibition is often found); "old process" yeast responds similarly but requires vitamin-B<sub>1</sub> as a necessary supplement. (I) is effective only in the absence of asparagine. H. B.

**Influence of crystalline hormones on the growth of certain yeasts.** A. P. WEBER (Compt. rend., 1936, 202, 517—519).—*Rhodotorula suganii* and *R. glutinis* var. *Sailoi* are stimulated by folliculin and dihydrofolliculin benzoate and inhibited by heteroauxin. Six other yeasts examined were unaffected by either substance. A. G. P.

**Pharmacological and therapeutic action of fresh yeast. I. Effect on blood-indican. II. Effect on blood-sugar.** U. SAMMARTINO (Arch. Farm. sperim., 1936, 61, 13—23, 24—33).—I. Fresh Fleischmann's yeast diminishes blood-indican in digestive or entero-hepatic disorders, previous dieting not affecting the result.

II. Oral administration of yeast gradually reduces the hyperglycæmia occurring during skin disease etc. R. N. C.

**Inhibition of the Pasteur effect.** K. C. DIXON (Nature, 1936, 137, 742).—A discussion. L. S. T.

**Mechanism of enzyme action. XIII. Phosphorylation and alcoholic fermentation of sugars. Biochemistry of *Fusarium lini*.** B. I. F. F. NORD, E. DAMMANN, and H. HOFSTETTER [with V. SENFTNER and E. ROSDORFF] (Biochem. Z., 1936, 285, 241—269; cf. A., 1933, 982).—In the fermentation of pentoses and hexoses and in the dehydrogenation of alcohols by *F. lini* (living and dried) inorg. P begins to disappear usually 2—5 days after the action and CO<sub>2</sub> is liberated. *F. lini* ferments *d*-xylose (no phosphorylation occurring) and *d*-arabinose. In the absence of inorg. P fermentation is slight, but reaches rates comparable with those of yeast fermentation on addition of inorg. P. No phosphorylation occurs. Accompanying morphological changes indicate that P is involved in rebuilding and buffering the cells. W. McC.

**Alleged necessity for initial phosphorylation in alcoholic carbohydrate degradation.** F. F. NORD, E. DAMMANN, and H. HOFSTETTER (Naturwiss., 1936, 24, 297).—The fermentation of hexoses and pentoses by both living and dried *Fusarium lini*, B., is not necessarily preceded (although it may be accompanied) by esterification of inorg. PO<sub>4</sub><sup>---</sup>. W. O. K.

**Role of formic acid in the biochemical formation of oxalic acid.** B. S. BUTKEVITSCH and L. K.

OSNIZKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 361—364).—Proof that the  $\text{H}_2\text{C}_2\text{O}_4$  (I) produced by moulds is derived from the mycelium (A., 1934, 1263) is given by the following observations. The amount of (I) formed by films of *A. niger* at 30° is not affected by varying the  $[\text{HCO}_2\text{Na}]$  in the solution, and only slightly by replacing this salt completely by  $\text{NaHCO}_3$ . In 6%  $\text{Na}_2\text{HPO}_4$  solution (I) accumulates rapidly at first, but ceases after 2—3 days in the case of 2 day-old films, and after 5 days with films 3 days old, the accumulated (I) amounting to 70% of the loss in wt. of the mycelium. Such exhausted films no longer produce (I) in 1%  $\text{HCO}_2\text{Na}$  or 1.23%  $\text{NaHCO}_3$ , but readily do so (without change in wt.) from 2%  $\text{NaOAc}$ . J. W. B.

**Metabolism of *Aspergillus niger*. I. Effect of phytin on the metabolism.** W. BRAUN and A. FREY (Biochem. Z., 1936, 285, 219—227).—The wt. of the mycelium and the amount of sugar consumed by *A. niger* increase with increasing inorg. and org. P [ $\text{KH}_2\text{PO}_4$  and phytin (I) with 20% of P] content of the medium. Very small amounts of P suffice for max. production of acid by *A. niger*, the P being completely utilised. Acid production varies with the form in which N is given, decreasing with increasing supply of P if the N supply is partly org., but the form in which the N is given has less effect than has that in which P is given. Unconsumed (I) is for the most part hydrolysed by phytase which passes into the solution. When (I) is supplied the P consumption is always > that when inorg. P is given. W. McC.

**Citric acid fermentation. I. Carbon balance.** P. A. WELLS, A. J. MOYER, and O. E. MAY (J. Amer. Chem. Soc., 1936, 58, 555—558).—A C-balance for a strain of *A. niger* grown on a medium containing glucose (I) as the sole source of C is prepared; the final distribution of the C is given. The ratio wt. of citric acid (II) : wt. of  $\text{CO}_2$  produced is that required by a process involving the breakdown of (I) in a manner analogous to that occurring in alcoholic fermentation. The wt. yields of (II) are also the max. obtainable by any process involving decarboxylation of  $\text{AcCO}_2\text{H}$  as one stage (cf. Bernhauer *et al.*, A., 1932, 1168); Emde's mechanism (A., 1935, 407) is similarly excluded. H. B.

**Production of kojic acid from xylose by *Aspergillus flavus*.** H. N. BARHAM and B. L. SMITS (Ind. Eng. Chem., 1936, 28, 567—570).—The fermentation of xylose (I) by *A. flavus* was carried out over 4 years, with only moderate change in kojic acid (II) production. Using a medium containing (I),  $\text{NH}_4\text{NO}_3$ ,  $\text{KH}_2\text{PO}_4$ , and  $\text{MgSO}_4$ , yields of > 20% of (II) were obtained. The effect of variation  $\text{PO}_4^{'''}$ ,  $\text{NH}_4\text{NO}_3$ , (I), and Mg concns. and of  $p_{\text{H}}$  has been investigated. Fe and Ca usually inhibit and Zn has no effect on the fermentation. P. W. C.

**Chemistry of mould tissue. XI. Isolation of leucine and isoleucine from *Aspergillus sydowi*.** D. W. WOOLLEY and W. H. PETERSON (J. Biol. Chem., 1936, 114, 85—90).—Leucine and isoleucine [*p*-toluenesulphonate, m.p. 124° (corr.)] have been obtained by extraction of the dried, defatted mycelium with  $\text{COMe}_2$ . H. G. R.

**Fungicidal power of phenol derivatives. II. Strength in presence of proteins.** G. J. WOODWARD, L. B. KINGERY, and R. J. WILLIAMS (J. Lab. Clin. Med., 1935, 20, 950—953; cf. A., 1935, 409).—Activity of many fungicides in aq. or broth suspensions is lowered by the presence of proteins. The action of I,  $\text{BzOH}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , salicylic acid, hexylresorcinol, and chlorothymol is reduced or inhibited by vesicle fluid, blood-serum, or hide powder. Thymol is active in presence of hide powder, but is inhibited by serum or vesicle fluid.  $\text{NaOCl}$  retains its activity in high concns. of proteins. CH. ABS. (p)

**Composition of plankton. I. Plankton from the Ekaterininski pond at Detskoie Selo.** A. VINOGRADOV (Trav. lab. biogeochem. Acad. Sci. U.R.S.S., 1, 33—48).—Analyses are given. CH. ABS. (p)

**Growth curves of *Polytoma uvella*: effect of oxygenation.** P. B. ROTTIER (Compt. rend. Soc. Biol., 1936, 122, 65—68).—The rate of growth is increased by oxygenation. R. N. C.

**Action of various organic antimony compounds on *Schistosoma japonicum* in vitro.** C. M. LEE and H. L. CHUNG (Proc. Soc. Exp. Biol. Med., 1935, 32, 1400—1403).— $\text{Sb}^{\text{III}}$  compounds are more effective than  $\text{Sb}^{\text{V}}$ , and tartar emetic than Fouadin. R. N. C.

**Action of chemotherapeutics on the trypanosome cell.** E. SINGER (Z. Hyg., 1936, 117, 752—756). R. N. C.

**Effect of ethylurethane on bacterial respiration and luminescence.** G. W. TAYLOR (J. Cell. Comp. Physiol., 1936, 7, 409—415). R. N. C.

**Variability in the activity of bacterial enzymes. I. Effect of age of culture.** W. R. WOOLDRIDGE, R. KNOX, and V. GLASS (Biochem. J., 1936, 30, 926—931).—The dehydrogenase activity of many bacterial cells varies considerably with the period between inoculation and reaping of the organism, increasing at first and subsequently decreasing. The max. activity usually occurs within the first 24 hr. of growth but it could not be definitely correlated with the logarithmic phase of growth. P. W. C.

**Oxidation-reduction potentials of some non-sporulating obligate anaerobes.** G. M. DACK and W. BURROWS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1441—1443).—The  $E_h$  curve shows only moderate falls, never reaching  $-300$  mv.; it rises directly lysis begins. R. N. C.

**Relation between respiration and the growth of aerobic bacteria.** J. HIRSON (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 44—60).—During the linear phase of growth of aerobic bacteria the  $\text{O}_2$  uptake  $\propto$  the increasing bacterial concn. in the culture. During the following period of diminishing growth the  $\text{O}_2$  consumption, after reaching a max., decreases and finally becomes const. at a very low val. during the stationary phase. The increase of  $\text{O}_2$  consumption associated with growth may be made the basis of a manometric method of measuring growth rates. W. O. K.

**Effect of electrolytes added to growth medium on electrophoretic potential of *Esch. coli*.** G. W.



PEARCE, M. W. LISSE, and R. P. TITSLER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1572—1573).—The migration velocity is slightly reduced by  $\text{CaCl}_2$ , increased by  $\text{Na}_2\text{SO}_4$ , and scarcely affected by  $\text{NaCl}$ ,  $\text{AlCl}_3$ , or  $\text{Na}_3\text{PO}_4$ . Adjustment of the initial  $\mu\text{H}$  over the range  $0.8 \pm 1.9$  does not alter the electrophoretic velocity of organisms by  $> 2.5\%$ . R. N. C.

Isolation of the growth factor of pathogenic bacteria. S. HOSOVA, Y. KUWASHIMA, S. KAYO, M. ODA, and K. KAGABE (Proc. Imp. Acad. Tokyo, 1936, 12, 67—69).—From a commercial syrupy condensed extract of the fish, scumbar, a non-hygroscopic grey-white granular substance has been separated which stimulates the growth of *Staphylococcus aureus* and *B. botulinus* on a medium containing alkali hydrolysate of peptone or gelatin, arginine, cysteine hydrochloride, glucose, and salts. Other substances were obtained which acted on *S. aureus* only. W. O. K.

Microbial variants of *B. aertryke* and possible variation in the chemical constitution of its complete somatic antigen. M. CIUCA, L. MESROBIANU, and G. BADENSKI (Compt. rend., 1936, 202, 1314—1316).—On macerating a culture with its metabolic products, a variant obtained yields an antigen serologically identical, but with a different stability in  $\text{H}_2\text{O}$ . H. G. R.

Dehydrogenase of the S and R forms of *B. coli*. E. SORU (Compt. rend. Soc. Biol., 1936, 121, 1647—1649).—When acting as H donor, the rate of decolorisation of methylene-blue by the S form is  $>$  that by the R form. R. N. C.

Hæmatoxins in gas gangrene. J. CELAREK and S. STETKIEWICZ (Compt. rend. Soc. Biol., 1936, 122, 143—144).—Toxins of *B. perfringens* and *B. autematis* purified by pptn. with  $(\text{NH}_4)_2\text{SO}_4$  or adsorption from COMe, with  $\text{BzOH}$  are less toxic to animals than in the crude state; the hæmolytic titre is unchanged. Adsorption with  $\text{BzOH}$  gives better yields of both toxins and hæmolysins than pptn. with  $(\text{NH}_4)_2\text{SO}_4$ . R. N. C.

Immuno-chemistry. I. Preparation and properties of a specific polysaccharide from *B. dysenteriae*, Shiga. W. T. J. MORGAN (Biochem. J., 1936, 30, 909—925).—A modified method is described for the isolation from the "smooth" form of *B. dysenteriae*, Shiga, and purification of a sp. polysaccharide (I) which accounts completely for the serological specificity of the organism and has the following properties:  $[\alpha]_D^{20} + 98^\circ$ , N 1.61%, mol. wt. calc. from NaOI titre 5100, yields 97% of reducing sugars on acid hydrolysis with complete loss of sp. immunological properties, acid equiv. about 9000, negative oreinol, phloroglucinol, naphthorescinol, and protein-tests,  $\text{Ac}$ ,  $[\alpha]_D^{20} + 71^\circ$  and Bz derivative,  $[\alpha]_D^{20} + 63^\circ$ , from both which the original (I) can be regenerated. The N of (I) does not react with  $\text{HNO}_3$  and is therefore probably present as substituted  $\text{NH}_2$ . (I) contains 5% of  $\text{Ac}$ , isolated after acid hydrolysis as  $\text{AcOAg}$ , and this and the N content both fit the requirements of a basic unit consisting of  $\frac{1}{2}$  mol. of hexose with 1 mol. or acetamidohexose (II), such unit appearing from the 1 reduction to be repeated 6 times in the (I) mol.

Colour reactions are used to follow quantitatively the liberation of (II) during acid hydrolysis and the subsequent deacetylation and these indicate that the whole of the N in the hydrolysis products is present as aminohexose. The crude (I) contains, in addition to (I), agar-like polysaccharides, (a)  $[\alpha]_D^{20} - 60^\circ$ , N 5.2%, (b)  $[\alpha]_D^{20} - 20^\circ$ , N 0.6%, which react with anti-agar bodies of immune horse serum, a polysaccharide,  $[\alpha]_D^{20} + 195^\circ$ , identified as glycogen and a substance,  $[\alpha]_D^{20}$  N 14.1%, sol. in 96%  $\text{AcOH}$ . P. W. C.

Analysis of the hydrophile colloids in *B. paratyphosus* colonies. L. BIRCH-HIRSCHFELD (Z. Hyg., 1935, 117, 626—634).—The mucous growth on the colonies is due to a sol. colloidal substance containing acid groups but no N, that can be hydrolysed to 40% of glucose (I) and other weakly- or non-reducing substances. It forms a stable viscous solution in  $\text{H}_2\text{O}$ . Cultures grown at  $37^\circ$  contain small quantities of another hydrophile substance, which can be hydrolysed to a N-rich protein, and a polysaccharide giving 80% of (I) by further hydrolysis. R. N. C.

Cultural studies in the *Salmonella* group, with particular reference to organic acids. F. KAUFFMANN and F. A. BURON (Z. Hyg., 1935, 117, 660—661).—The organisms fall into distinctive fermentative types according to their action on tartrate, citrate, and mucate. R. N. C.

Staphylococcal leucocidin (Neisser-Wechsberg type) and antileucocidin. J. WRIGHT (Lancet, 1936, 230, 1002—1004). A modification of the Neisser-Wechsberg technique for the determination of these substances is described. Their relationship to hæmolysis and antihæmolysis has also been investigated. L. S. T.

Medium for production of staphylococcal toxins. G. RAMON, A. BRETHERLOT, and G. AMOUT (Compt. rend., 1936, 202, 515—516).—Preps. from veal-broth cultures have high toxicity and antigenic activity. A. G. P.

Bacteriophage phenomena in cultures of lactic Streptococci. H. R. WHITEHEAD and G. A. COX (J. Dairy Res., 1936, 7, 55—62).—The isolation of bacteriophages from "starter" cultures is described. Aeration stimulates development of the phage. A. G. P.

Bacterial flora of foremilk and of rennet extract with special reference to acid proteolytic types. N. R. KNOWLES (J. Dairy Res., 1936, 7, 63—74).—Proteolytic cocci are more abundant in old than in fresh rennet samples or in foremilk. These strains probably contribute to the final breakdown of protein degradation products in ripening cheese. A. G. P.

A lactobacillus from Californian wine: *Lactobacillus hilgardii*. H. C. DOUGLAS and W. V. CRESS (Food Res., 1936, 1, 113—119).—The organism, isolated from  $> 20$  samples of dry, red and white wines, ferments glucose, fructose, and xylose with production of acid (mainly lactic and  $\text{AcOH}$ ) but not  $\text{CO}_2$  gas. The optimum temp. of growth is  $31\text{--}37^\circ$ , death occurring within 1 min. at  $63^\circ$ . The max. tolerated  $[\text{EtOH}]$  is 18%. R. C.

Optical properties of fermentation lactic acid.  
 III. Action of inactive lactic acid-producing organisms on optically active lactic acids added to fermentation liquids. H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 281—283; cf. this vol., 247).—Differences in rates of racemisation of *d*- and *l*-lactic acids by *Lactobacillus plantarum* and *L. pentoceticus* are examined.  
 A. G. P.

Biology of *B. cellulosa dissolvens*. Y. KHOUVINE and K. SOETERS (Compt. rend. Soc. Biol., 1936, 122, 59—61).  
 R. N. C.

Enzyme formation and polysaccharide synthesis by bacteria. II. A. CARRUTHERS and E. A. COOPER (Biochem. J., 1936, 30, 1001—1009; cf. A., 1935, 1419).—*B. lactis* synthesises a fructosan polysaccharide from sucrose (I) only. When *Leuconostoc dextranicum* is incubated with (I) the resulting solution, after removal of the formed dextran (II), contained fructose, yet incubation with glucose alone gave little or no (II). Small quantities of EtOH extracts of molasses accelerate growth and (II) formation; this effect is not explained by the added N. The large-scale prep. of (II) from 20% (I) is described.  
 H. D.

Curve of production of glyoxalines related to histamine in some bacterial cultures. M. LEGER, L. DUCHON, A. LESURE, and A. THOMAS (Compt. rend. Soc. Biol., 1936, 121, 1591—1593).—Glyoxaline production by *B. pyocyaneus* (particularly young cultures) and *B. putrificus* is high; it is lower by *B. typhosus*, and almost negative by *B. coli*. It reaches a max. in the first few weeks, afterwards falling; proteins at the same time fall to a steady min. val.  
 R. N. C.

Occurrence of sterols in bacteria. R. H. SIFFERD and R. J. ANDERSON (Z. physiol. Chem., 1936, 239, 270—272; cf. Hecht, A., 1935, 663). The unsaponifiable part of the fat of *Azotobacter chroococcum* yielded a mixture (0.13% of the fat), m.p. 156—158°,  $[\alpha]_D -16^\circ$  in  $\text{CHCl}_3$ , of sterols. The properties of the mixture resembled those of ergosterol rather than those of the usual animal and vegetable sterols.  
 W. McC.

Oxidation of amino-acids by *Bacillus pyocyaneus* (*Pseudomonas aeruginosa*). M. D. WEBSTER and F. BERNHEIM (J. Biol. Chem., 1936, 114, 265—271).—The  $\text{NH}_2$ -acids studied fell into three classes: (a) leucine, isoleucine, and histidine, only the natural isomerides of which were attacked; (b) phenylalanine and valine, of which non-natural isomerides increased the  $\text{O}_2$ -uptake of the bacteria without undergoing de-amination, whilst the natural isomerides were attacked; (c) alanine, serine, tyrosine, and proline, both isomerides of which were rapidly attacked. 0.005*M*-KCN inhibited oxidation and de-amination, whilst 1% NaF or urethane was without influence.  
 H. D.

Lipins of tubercle bacilli. XLIV. Comparative study of lipins of human tubercle bacillus. J. A. CROWDER, F. H. STODOLA, M. C. PANGBOON, and R. J. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 636—642).—Cultures of four recently isolated

strains (A10, A12, A13, A14) and a new batch of H37 (cf. A., 1927, 1111), grown under identical conditions, are extracted with EtOH and  $\text{Et}_2\text{O}$ ; the extracted material is then separated into sol. [further separated into fat (I) and -insol. phosphatide (II)] and  $\text{H}_2\text{O}$ -sol. fractions [containing the polysaccharide previously described *cit.*]. Further extraction with  $\text{CHCl}_3$  followed by EtOH- $\text{Et}_2\text{O}$  removes wax (that from H37 contains little or no sterol). Combined lipins are then isolated from the bacterial residue with EtOH- $\text{Et}_2\text{O}$  containing 1% HCl; these are sterol-free. The amounts of the various fractions obtained vary considerably. All the (II) isolated have low N contents and generally resemble that previously described (*loc. cit.*). The const. of the (I) show considerable variation and indicate the presence of 26 of free fatty acids. The (I) from A12 and H37 contain small amounts of phthocol (III); hydrolysis gives (III), trehalose (but no glycerol), anisole, stearic, tuberculo-stearic, and phthoic acids, and an optically active OII-acid of high mol. wt. The (I) contain 2.47—17.7% of unsaponifiable matter; that from A12 appears to contain a little sterol.  
 H. B.

Influence of temperature on nitrogen fixation by *Azotobacter*.—See B., 1936, 562.

Nodule bacteria. V. Influence of plant extract as accessory substance on the growth of the bacteria. A. ITANO and A. MITSURU (Ber. Ohara Inst. landw. Forsch., 1936, 7, 185; cf. A., 1935, 530).—Growth of the organisms was accelerated by extracts of seedlings and of germinated and ungerminated seeds in the (descending) order named. Optimum concns. differed with the species of plants examined, being greater for nodule-bearing than for non-nodule-bearing legumes, with non-legumes exhibiting an intermediate effect. The action of the extracts is ascribed to the presence in them of growth-accessory substances rather than to their N or inorg. matter contents.  
 A. G. P.

Hypothesis concerning bacteriophage. J. G. WILLIAMS (J. Physiol. Chem., 1936, 40, 477—479). The theory is advanced that phage is a suspension of extremely small crystals of one or more of the compounds in the homologous bacteria. Bacteriophage is thus the seedling of these amorphous compounds by phage particles and their subsequent crystallisation.  
 M. H. H.

Cultivation of poliomyelitis virus. R. JOHNSON (Science, 1936, 83, 324—325). A discussion.  
 L. H. P.

Bacteriocidal effects of vapours from crushed garlic. L. WALTON, M. L. MORGAN, and O. C. LANDERSON (Food Res., 1936, 1, 163—169). The bacteria were grown on agar subjected for various periods to the vapour. Growth of *B. subtilis* (spores) was inhibited after 4 hr. treatment, that of *Serratia marcescens* after 2 hr., and that of *Mycobacterium butyricum* and *M. smegmatis* after 32 min. Boiled and autoclaved garlic were ineffective.  
 B. C. B.

Comparison of resistance of bacteria and embryonic tissue to germicidal substances. V. Iodine. A. J. HALL and A. R. LAZARUS (Proc.



Soc. Exp. Biol. Med., 1935, 32, 1481—1483).—I has the min. toxicity index and max. PhOH coeff. of all the germicides studied (cf. A., 1935, 1421).

R. N. C.

Bactericidal action of mercury on *B. coli* in continuously flowing water. M. LISBONNE and R. SEIGNEURIN (Compt. rend. Soc. Biol., 1936, 122, 18—20).

R. N. C.

Is the pressor effect of a glycerol extract of adrenal glands due to adrenaline? R. G. HOSKINS and J. S. GOTTLIEB (Endocrinol., 1936, 20, 188—191).—The amount of adrenal medullary material extracted has no effect on the pressor effect of the extract, which suggests that the agent responsible is not adrenaline. It is considered to be different from cortin.

R. N. C.

Local adrenaline effect after sympathectomy. I. Peripheral vessels. A. M. WRIGHT, J. H. MULHOLLAND, K. L. MCCLOSKEY, and F. W. COTUI (J. Lab. Clin. Med., 1935, 20, 947—949).

CH. ABS. (p)

Vagotonin and adrenalinæmia. D. SANTENOISE, L. MERKLEN, C. FRANCK, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1936, 121, 1567—1569).—Vagotonin increases adrenalin secretion.

R. N. C.

Effect of various cortico-adrenal extracts on diphtheria toxin *in vivo* and *in vitro*. R. L. ZWEMER and C. W. JUNGBLUT (Proc. Soc. Exp. Biol. Med., 1935, 32, 1583—1588).

R. N. C.

Effect of cortico-adrenal extract on the course of bacterial intoxications in guinea-pigs. R. W. WHITEHEAD and C. A. FOX (Endocrinol., 1936, 20, 93—99).

R. N. C.

Effects of cattle anterior pituitary extracts and potassium iodide on liver-glycogen in guinea-pigs. R. HOLDEN and E. W. THURSTON (Proc. Soc. Exp. Biol. Med., 1935, 32, 1417—1419).—The depression of liver-glycogen (I) by intraperitoneal injections of anterior pituitary extracts is not modified by previous or simultaneous oral administration of KI. KI alone reduces (I) moderately.

R. N. C.

Effects of human anterior pituitary gland on sex organs and thyroid gland of the guinea-pig. P. KUNKEL and L. LOEB (Proc. Soc. Exp. Biol. Med., 1935, 32, 1413—1417).

R. N. C.

Effect of various anterior pituitary gland preparations on thyroidectomised guinea-pigs. K. C. MORRIN and L. LOEB (Proc. Soc. Exp. Biol. Med., 1935, 32, 1425—1427).

R. N. C.

Effect of an alkaline extract of the anterior pituitary on the weight of the spleen and adrenal glands and on the blood-calcium level. H. B. FRIEDGOOD (Endocrinol., 1936, 20, 159—169).—The spleen and cortex are increased in wt. and blood-Ca rises.

R. N. C.

Calorigenic action of extracts of the anterior lobe of the pituitary in man. W. O. THOMPSON, S. G. TAYLOR, 3rd., P. K. THOMPSON, S. B. NADLER, and L. F. N. DICKIE (Endocrinol., 1936, 20, 55—63).—Thyrotropic hormone increases basal metabolism in every group of patients where the thyroid tissue can still function. Thyroxine and desiccated thyroid

produce calorogenic effects in patients who have become refractory to pituitary extracts. R. N. C.

Action of anterior pituitary hormones on basal metabolism of normal and hypophysectomised pigeons and a paradoxical effect of temperature. O. RIDDLE, G. C. SMITH, R. W. BATES, C. S. MORAN, and E. L. LAHR (Endocrinol., 1936, 20, 1—16).—Prolactin (I), like thyrotropic hormone (II), exhibits calorogenic action, but does not act through the thyroid. Follicle-stimulating hormones and prolactin are without effect, as are also luteinising and adrenotropic hormones when free from (I) and (II). (I) and (II) injected simultaneously act synergistically to one another on O<sub>2</sub> consumption. "Growth-hormone" preps. usually contain (I) and (II). The calorogenic effect is reduced by decreasing the temp. from 32° to 20°.

R. N. C.

Effect of injections of antuitrin-S on the sexually inactive male ground squirrel. B. L. BAKER and G. E. JOHNSON (Endocrinol., 1936, 20, 219—223).

R. N. C.

Substances affecting the ovary from the anterior pituitary and from pregnancy urine. H. W. NIEMEIER (Klin. Woch., 1935, 14, 576).—A follicle-stimulating but non-luteinising substance (I) is obtained from the urine of cancer. Another principle that is inactive *per se* but causes luteinisation when combined with (I) is obtained from pregnancy urine or the anterior pituitary.

R. N. C.

Relation of potency of anterior pituitary-like hormone to hydrogen-ion concentration. C. A. ELDEN and M. D. FELLOWS (Proc. Soc. Exp. Biol. Med., 1935, 32, 1597—1599).—Potency is max. at  $p_H$  6.1—7.3; it is scarcely affected by acid, but varies with the alkali content, being greatly reduced by addition of NaOH, but less changed by an alkaline  $p_H$  which develops on storage for 3 months in the cold. The hormone may be protein-like in nature, or carried down with foreign protein at the isoelectric point,  $p_H$  6.1.

R. N. C.

(A) Habituation to the anterior pituitary hormone. (B) Production of antihormone in serum of resistant animals. E. GUYENOT, E. HELD, and A. MOSZKOWSKA (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 10—12, 12—14).—(A) When guinea-pigs are treated for 30—40 days with anterior pituitary extracts, they become resistant to the action of the hormones which affect the thyroid and the adrenal cortex and to the crinogenic action (which results in the inhibition of œstrus). The auxogenic action on the development of the ovarian follicle and probably the luteinising action does not show this phenomenon of habituation.

(B) The action of anterior pituitary hormone on the thyroid, adrenal cortex, and the crinogenic action on the ovary of the guinea-pig is inhibited by the serum of another guinea-pig made resistant by prolonged treatment with the hormone, the action on the ovary being less complete than that on the other organs. Antibodies are probably formed in the blood of the resistant animals. No evidence could be obtained of the formation of antibodies

against the luteinising or auxogenic actions of the hormone.

W. O. K.

**Chemical changes in the muscle of the hypophysectomised toad.** A. D. MARENZI (Endocrinol., 1936, 20, 184—187).—Asthenia following removal of the whole pituitary or anterior lobe is accompanied by fall of glycogen, inorg. P, phosphocreatine, and glutathione in skeletal muscle, and by reduced production of lactic acid during tetanic stimulation. Grafts or extracts of the glandular or intermedio-neural lobe of the pituitary relieve asthenia, and cause increases of the above constituents that do not usually reach normal.

R. N. C.

**Oxytocic hormone of posterior lobe of pituitary gland.** J. M. GULLAND and S. S. RANDALL (Chem. and Ind., 1936, 442—443).—The evidence adduced by Sealock and du Vigneaud (A., 1935, 1275) that the oxytocic principle contains a reducible ·S·S· is not conclusive because the agent employed, cysteine, is not sp. for ·S·S·. It is possible that the redox system with  $E_0' - 0.190$  volt at  $p_H$  6.0 is actually a ·S·S· ·SH system and that the second redox system with  $E_0' - 0.025$  volt at  $p_H$  6.0 is due to a group of as yet unknown nature (cf. Gulland and Randall, *ibid.*, 542).

W. O. K.

**Depressor substances in the posterior lobe of the pituitary.** E. LARSON (J. Pharm. Exp. Ther., 1936, 56, 396—416).—Histamine (I) was present in aq. extracts of the COMe<sub>2</sub>-sol. and -insol. material of the posterior lobe; EtOH extracts of the latter contained (I) whilst aq. extracts with EtOH gave a ppt. which exhibited oxytocic but not depressor activity.

H. D.

**Antagonism between posterior lobe pituitary hormones and insulin.** H. C. ELLSWORTH (J. Pharm. Exp. Ther., 1936, 56, 417—420).—Small doses of the oxytocic hormone depress, and large doses completely inhibit, insulin hypoglycaemia in dogs; the pressor fraction has little or no effect.

H. D.

**Absence of follicle-stimulating hormone in pituitaries of young pigeons.** O. RIDDLE and J. P. SCHOOLEY (Proc. Soc. Exp. Biol. Med., 1935, 32, 1610—1614).—The hormone appears 1.8 months after hatching in pigeons and 2.5 months after in ring-doves.

R. N. C.

**Uterine response to pitocin.** M. R. WHITE and J. P. PRATT (Endocrinol., 1936, 20, 17—23).

R. N. C.

**Reaction of fish to sex hormones.** S. E. OWEN (Endocrinol., 1936, 20, 214—218).

R. N. C.

**Relation of sex hormones to calcium metabolism in the bone marrow.** O. ARNOLD, F. HOLTZ, and H. MARX (Naturwiss., 1936, 24, 314—317).—The hypocalcaemia and tetany, which accompanies parathyroid deficiency, may be counteracted by administration of the ergosterol derivative contained in the prep. "A.T. 10." During pregnancy and lactation the quantity of "A.T. 10" required increases several-fold, due, probably, to the presence in the body of increased amounts of sex hormone.

W. O. K.

**Effect of endocrine gland preparations on allergic reactions (anterior pituitary extract, pregnancy urine extract, follicular hormone).** B. SOLOMONICA and R. KURZROK (Endocrinol., 1936, 20, 171—173).

R. N. C.

**Pathological conditions induced by oestrogenic compounds in the coagulating gland and prostate of the mouse.** H. BURROWS (Amer. J. Cancer, 1935, 23, 490—512).—Application of ketohydroxy- and trihydroxy-cestrin to the skin of the interscapular region caused lesions in the coagulating gland and the prostate in mice.

CH. ABS. (p)

**Effects of cestrin injections on accessory reproductive organs of the male ground squirrel (*Citellus tridecemlineatus*).** L. J. WELLS (Anat. Rec., 1936, 64, 475—497).

R. N. C.

**Effect of cestrin on the pituitary gland.** W. CRAMER and E. S. HORNING (Lancet, 1936, 230, 1056—1057; cf. this vol., 504).

L. S. T.

**Lack of effect of theelin on somatogenic, thyrotropic, and adrenotropic activity of pituitary.** H. B. SHUMACKER, jun., and A. LAMONT (Proc. Soc. Exp. Biol. Med., 1935, 32, 1568—1570).

R. N. C.

**Induction of an acid vaginal secretion in the immature macaque by injections of cestrin.** B. V. HALL and R. M. LEWIS (Endocrinol., 1936, 20, 210—213).—The  $p_H$  of the fluid is depressed at least 2 units.

R. N. C.

**Folliculin and carbohydrate metabolism.** J. A. COLLAZO and F. B. MARTI (Ann. Méd., 1935, 38, 383—388).—Injection of pure folliculin into bitches caused a 30% increase in blood-sugar and a 96% increase in lactic acid.

NUTR. ABS. (m)

**Paradoxical action of folliculin (menformone) in male animals; effect of male hormone.** S. E. DE JONGH (Arch. int. Physiol., 1935, 50, 348—378; Chem Zentr., 1935, ii, 1569).

R. N. C.

**Preparation of the gonadotropic hormone of pregnant mare's blood.** E. L. GUSTUS, R. K. MEYER, and O. R. WOODS (J. Biol. Chem., 1936, 114, 59—63).—The hormone has been obtained from citrated plasma by selective adsorption on Al(OH)<sub>3</sub>, elution at  $p_H$  3.5, and filtration through a Pasteur-Chamberland filter at  $p_H$  8.3.

H. G. R.

**Two gonadotropic substances in mare serum.** F. J. SAUNDERS and H. H. COLE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1476—1478).—The serum contains a stable luteiniser and a gonadotropic hormone which is destroyed by treatment with H<sub>2</sub>S and incubation, and has not been identified as the follicle-stimulating hormone of Fevold and Hisaw.

R. N. C.

**Effect of oestrogenic hormones on lactation in the cow.** S. J. FOLLEY (Nature, 1936, 137, 741—742).—Administration of oestrogenic hormone to a lactating cow produces a marked diminution in the daily milk yield, but increases the non-fatty solids content and the milk-phosphatase concn. Secretion of milk-fat is a process not closely related to that of other milk-solids.

L. S. T.



**Excretion of ovarian hormone by sows during pregnancy.** M. STRUCK (Deut. tierärztl. Woch., 1935, 43, 260—263; Chem. Zentr., 1935, ii, 1568).—Ovarian hormone excretion in the urine occurs in the 3rd and 4th week, ceases at the 5th, and reappears in the 11th or 12th, thence increasing until parturition, after which it disappears for 14 days. R. N. C.

**Extraction of both œstrin and gonadotropic hormones from a single blood sample.** S. C. FREED (Endocrinol., 1936, 20, 224—225).—Citratd blood is poured into 5 vols. of  $\text{COMe}_2$ , and the ppt. is removed by centrifuging and washed with  $\text{COMe}_2$ . The combined filtrate and washings are evaporated, the residue is extracted with  $\text{Et}_2\text{O}$ , and the  $\text{Et}_2\text{O}$  evaporated off after addition of oil as solvent; the solution contains œstrin. Gonadotropic hormones (I) are extracted from the  $\text{COMe}_2$  ppt. with 50%  $\text{EtOH}$  at  $p_H$  4.4, pptd. with 95%  $\text{EtOH}$ , and extracted twice with a buffer solution at  $p_H$  4.4, which is pptd. twice with 95%  $\text{EtOH}$ , (I) being removed by centrifuging. R. N. C.

**Specificity of the oviduct test for follicular hormone.** W. FLEISCHMANN and S. KANN (Klin. Woch., 1935, 14, 644).—The positive reaction given by male hormone (I) preps. such as Testosan is due to their contents of female hormone; cryst. (I) is inactive. R. N. C.

**Problem of standardisation of follicular hormone and its derivatives.** W. SCHOELLER, M. DOHRN, and W. HOHLWEG (Klin. Woch., 1935, 14, 826—827). R. N. C.

**Excretion of prolan in essential hypertension.** M. SCARF and S. L. ISRAEL (Endocrinol., 1936, 20, 180—183). R. N. C.

**Gonadotropic substance from teratoma of the testis.** S. C. FREED and A. COPPOCK (Proc. Soc. Exp. Biol. Med., 1935, 32, 1589—1591). R. N. C.

**Testicular hormone and Sebright plumage.** C. H. DANFORTH (Proc. Soc. Exp. Biol. Med., 1935, 32, 1474—1476). R. N. C.

**Synthesis of  $\Delta^1$ -dehydroandrosterone.**—See this vol., 854.

**Purification of galactin, the lactogenic hormone.** W. H. MCSHAN and C. W. TURNER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1655—1656).—The isoelectric ppt. at  $p_H$  5.5—6.5 from the alkaline digest, after dehydration with  $\text{COMe}$ , and drying, is extracted repeatedly with  $\text{AcOH}$  and the extract poured into  $\text{Et}_2\text{O}$ , the ppt. being washed with  $\text{COMe}$ , and dried. The ppt. gives the biuret reaction and is active in pigeons in doses of 3 mg. daily. R. N. C.

**Insulin and blood-lactic acid.** J. A. COLLAZO and J. ALMELA (Ann. Med., 1935, 38, 371—382).—The rise in blood-lactic acid (I) in the dog after lactate ingestion was increased by simultaneous insulin (II) injection. (II) injection alone produced a rise in (I) > that after lactate ingestion alone. This (II) effect is attributed to a compensatory secretion of adrenaline. NUTR. ABS. (m)

**Role of insulin in metabolism in non-diabetic patients. I. Transitory hyperglycæmia and**

**glycosuria following discontinuation of insulin.** B. B. CLARK, R. B. GIBSON, and W. D. PAUL (J. Lab. Clin. Med., 1935, 20, 1008—1016).—Effects are ascribed to the action of administered insulin in causing a compensatory inhibition of the normal islet secretion. CH. ABS. (p)

**Continuous intravenous injection of insulin in man: limiting dose.** A. BAUDOUIN and J. LEWIN (Compt. rend. Soc. Biol., 1936, 121, 1594—1596).—The limiting hypoglycæmic dose in man is 0.01—0.02 international unit per kg. per hr. R. N. C.

**Preparation of crystalline insulin free from vagotonin.** D. SANTENOISE, T. BRIEU, G. FUCHS, and E. STANKOFF (Compt. rend. Soc. Biol., 1936, 121, 1565—1567).—Commercial insulin (I) is dissolved in  $\text{HCl}$  at  $p_H$  3, impurities are removed by centrifuging, and (I) and vagotonin (II) are pptd. with  $\text{LiCl}$  and dried. (I) is then repeatedly pptd. isoelectrically at  $p_H$  5.2. (II) is finally destroyed by incubation for 12 hr. in  $\text{HCl}$  solution at  $p_H$  1 and  $55^\circ$ , after which  $p_H$  is restored to 5.2 with  $\text{LiOH}$ ; after another pptn. at  $p_H$  5.2 (I) is dehydrated and crystallised by Scott's method. R. N. C.

**Electrometric titration of insulin. Iodinated insulin.** C. R. HARRINGTON and A. NEUBERGER (Biochem. J., 1936, 30, 809—820).—Titrations of cryst. insulin in aq. and 80%  $\text{EtOH}$  solution indicate acid- and base-binding capacities of respectively  $43 \pm 2$  and 60—70 groups per mol. (cf. Harvey *et al.*, A., 1934, 602). Iodination gives a product [15.4% I, corresponding with 24 tyrosine (I) groups] in which the (I) groups only are substituted (probably in the 3:5 position) and exhibiting 5—10% of the initial hypoglycæmic action (mice, rabbits); partial removal of I by hydrogenation ( $\text{Pd}-\text{BaSO}_4$  in 50% aq.  $\text{C}_2\text{H}_5\text{N}$ ) produces reactivation approx.  $\propto$  the amount of I removed. F. O. H.

**Action of various reagents on insulin.** H. JENSEN, E. A. EVANS, jun., W. D. PENNINGTON, and E. D. SCHOCK (J. Biol. Chem., 1936, 114, 199—208).—Treatment with 0.033N- $\text{NaOH}$ , aldehydes,  $\text{HNO}_2$ ,  $\text{Ac}_2\text{O}$ , acid- $\text{EtOH}$ ,  $\text{CH}_3\text{N}_2$ ,  $\text{MeI}$ , or I caused partial or complete inactivation of insulin (I) and a change in either cystine (II) or  $\text{NH}_2$ -N content, with the exception of acid- $\text{EtOH}$  which had no effect on (II). The physiological activity of (I) cannot be attributed to a localised portion of the mol., but the hypoglycæmic property may be associated with certain  $\cdot\text{S}\cdot\text{S}\cdot$  groups, and also with certain  $\text{NH}_2$  groups, both being present probably as (II). J. N. A.

**Mechanism of the action of parathormone on urinary elimination of phosphorus.** L. BRULL (Compt. rend. Soc. Biol., 1936, 122, 76—77).—Parathormone (I) increases P excretion in the urine of the dog without affecting plasma- $\text{PO}_4'''$ . Isolated normal kidneys perfused with the blood of a (I)-injected dog also excrete more P, but if this is interrupted for 3 hr. with perfusion from a control animal, the isolated kidneys do not re-establish the high P excretion if perfusion from the injected animal is resumed, although the latter's kidneys still show a high P excretion, being no doubt saturated with (I). R. N. C.

**Influence of parathormone on the magnesium, calcium, and phosphorus content of human blood.** G. MELLI and N. KORADIMOVA (Policlinico, 1935, 42, 629—636).—The average effects of 200 units of parathormone on the blood constituents of 10 patients were: Ca rose after 4 hr. to a max. of 13.4 mg. per 100 ml. at the 9th and returned to normal at the 15th hr.; Mg rose from the 1st hr. to a max. of 4.8 mg. at the 3rd and fell to normal at the 4th hr.; P remained practically const. NUTR. ABS. (m)

**Influence of infection on action of parathyroid hormone in man.** G. C. LINDER (Quart. J. Med., 1935, 4, 131—137).—Serum-Ca was low and the response to injection of parathyroid hormone small during typhoid fever but increased on recovery. In pulmonary tuberculosis serum-Ca was normal and response to the hormone was greater in active than in quiescent phases, but increased when basal metabolism was raised by thyroid extract. CH. ABS. (p)

**Effect of thyroxine on glycolysis of muscular tissue.** P. E. GREGOIRE (Compt. rend. Soc. Biol., 1936, 122, 103—105).—Thyroxine (I) depresses glycolysis by tissues in presence of glucose alone, but if glycogen (II) is added, glycolysis increases to vals. of the same order as the increased vals. due to addition of (II) to normal tissue without (I). The max. limit of carbohydrate concn. for glycolysis to occur is raised to infinity by (I). R. N. C.

**Site and manner of action of thyroxine in the organism.** G. MANSFELD (Orvosi Hetilap, 1935, 79, 491—497).—Thyroxine migrates through the nerves into muscular cells and increases their O<sub>2</sub> consumption. CH. ABS. (p)

**Action of the thyroid on blood formation.** J. VON BOROS and G. CZONICZER (Klin. Woch., 1935, 14, 573—575). R. N. C.

**Metabolism of isolated surviving tissues from animals rendered hyperthyroid with thyroxine.** D. McEACHERN (Bull. Johns Hopkins Hosp., 1935, 56, 145—179).—Tissue from hyperthyroid animals showed increased O<sub>2</sub> consumption but < that anticipated from the total consumption of the animal. Increased tissue glycolysis was not the cause of the increased O<sub>2</sub> consumption. CN', F', and CH<sub>2</sub>I-CO<sub>2</sub>' reduced the respiration of hyperthyroid tissue without affecting the mechanism which necessitates an increased O<sub>2</sub> supply. I had no effect. In hyperthyroid animals hepatic and renal tissues retained their ability to oxidise lactate, pyruvate, and succinate. The oxidising capacity of muscle was > normal. CH. ABS. (p)

**Thyroglobulin. II. The Van Slyke nitrogen distribution and tyrosine and tryptophan analyses for normal and goitrous human thyroglobulin.** J. W. CAVETT (J. Biol. Chem., 1936, 114, 65—73).—The NH<sub>2</sub>-acid content of thyroglobulin with the exception of thyroxine (I), di-iodotyrosine (II), and tyrosine (III) is the same in all cases. (III) in the mol. is capable of conversion into (I) or (II), being observed during I medication in pathological cases. H. G. R.

**Analyses of thyroglobulin.** A. WHITE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1558—1560).—Vals. are given. R. N. C.

**Non-thyroid substances with thyroid action. IV. Thyroid-like substances from artificially iodinated protein.** J. ABELIN (Arch. exp. Path. Pharm., 1936, 181, 250—258; cf. A., 1934, 814, 1409).—Iodinated proteins, like active thyroid gland substance, are separable into < two fractions. Removal of inactive material is achieved by hydrolysis with alkalis (but not with enzymes or acids), especially with 40% Ba(OH)<sub>2</sub>. Thus iodinated caseinogen (5.17% I) yields preps. (42.2% I), 2 × 10<sup>-5</sup> g. of which has an action on the metabolism and resistance to MeCN poisoning of mice characteristic of thyroid preps. F. O. H.

**Reid Hunt reaction and the thyrotropic hormone.** H. WIESBADER (Endocrinol., 1936, 20, 100—102).—The resistance of mice to MeCN is not increased by normal serum, but it is increased by pregnancy serum, follutein from pregnancy urine, and thyrotropic hormone. R. N. C.

**Anti-thyrotropic activity.** I. W. ROWLANDS and A. S. PARKES (Proc. Roy. Soc., 1936, 120, B, 114—125).—Normal serum of goat, horse, sheep, cow, or rabbit does not show any anti-thyrotropic activity. This may be induced in rabbits in 4 weeks by daily injection of thyrotropic extract and rises to a max. in 10 weeks. H. G. R.

**Vitamin deficiency, passage of infection, and resistance to disease.** L. OELRICHS (Z. Hyg., 1935, 117, 684—710). R. N. C.

**Experimental calcification in avitaminosis-A.** A. ESCUDERO and P. BOSQ (Semana méd., 1935, 42, 1283—1286; Chem. Zentr., 1935, ii, 1572).—Microscopic intraparenchymatous calcification of the kidneys occurs in avitaminosis-A in the rat. R. N. C.

**Effect of vitamin-A deficiency on development of the retina and on the first appearance of visual purple.** K. TANSLEY (Biochem. J., 1936, 30, 839—844).—Only a moderate deficiency of vitamin-A could be developed in young rats during the suckling period. The development of visual purple was retarded and in some cases prevented, whilst the effect on the structure and development of the rods was not so marked. The part played by -A in the visual purple system is discussed. J. N. A.

**Vitamin-A metabolism and liver in experimental phosphorus poisoning.** F. LASCH (Klin. Woch., 1935, 14, 1070—1073).—Vitamin-A (I) in the liver of rats and guinea-pigs is unaffected by fatal P poisoning. Parenteral administration of (I) to guinea-pigs simultaneously with poisoning by P results in quant. storage of (I) in the injured liver as in normal animals. R. C.

**Carotene and vitamin-A contents of human serum.** E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1935, 14, 670—673).—Carotene (I) and vitamin-A (II) can be demonstrated in serum, but not in corpuscles. A life-curve of serum-(II) can be defined, from which the presence of hypovitaminosis can be determined; such hypovitaminosis when



the diet is complete is due to liver injury. (I) and (II), but not ascorbic acid, increase glycolysis.

R. N. C.

**Vitamin-A content of West Indian shark (*Carcharinus* sp.) liver oil.** C. F. ASENJO, L. M. DALMAU, and J. H. AXTMAYER (Puerto Rico J. Publ. Health, 1935, 11, 158—162).—The vitamin-A val. of the oil from sharks caught during July was about 13,300 Sherman units per g. NUTR. ABS. (m)

**Determination of vitamin-A by means of its influence on the vaginal contents of the rat.** W. HOHLWEG and M. DOHRN (Biochem. J., 1936, 30, 932).—Claim of priority as to this method over Coward *et al.* (this vol., 253). P. W. C.

**Determination of vitamin-A.** G. BALASSA and G. SZANTÓ (Z. physiol. Chem., 1936, 240, 29—32).—Addition of guaiacol may be omitted from Rosenthal's test for vitamin-A (A., 1934, 225, 1145), 0.2% aq. para-brown Z extra being a suitable comparison standard. Cholesterol and tissue extracts give unstable red solutions with the  $\text{SbCl}_3$  reagent. Photometric data of light absorption by the reacted solution are discussed. F. O. H.

**Correlation of vitamin-A and -B with the calcinosis factor.** F. WIDENBAUER (Klin. Woch., 1935, 14, 901).—Calcinosis poisoning in mice by vigantol or "A.T. 10" is checked by simultaneous large doses of vitamin-A and -B. R. N. C.

**Avitaminosis-B and muscular glycolysis.** P. E. GRÉGOIRE (Compt. rend. Soc. Biol., 1936, 122, 101—103).—Total inorg. and hydrolysable  $\text{PO}_4^{4-}$  in the rat are both depressed in avitaminosis-B. Mg is increased in avitaminosis-B but not in starvation. R. N. C.

**Variations of the respiratory quotient and basal metabolism during avitaminosis-B.** J. M. JOLY (Compt. rend. Soc. Biol., 1936, 122, 196—199).—The R.Q. in pigeons is lowered, but basal metabolism is increased. R. N. C.

**Production of avian polyneuritis by the addition of lactic acid to diets rich in sugar, protein, or fat, containing considerable quantities of the B vitamins.** R. LÉCOQ (Compt. rend., 1936, 202, 1304—1307).—Even with an excess of vitamin-B, development of polyneuritis is caused by accumulation of lactic acid in the tissues, when 10% is present in the diet. H. G. R.

**Requirements of the flour-beetle (*Tribolium confusum*, Duval) for vitamins in the B group.** H. R. STREET and L. S. PALMER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1500—1501).—The larvae require vitamin-B<sub>1</sub> and also a thermostable factor which is destroyed by autoclaving at  $p_H$  13. R. N. C.

**B-Vitamins in human urine.** M. H. ROSCOE (Biochem. J., 1936, 30, 1053—1063).—Vitamin-B<sub>1</sub> and -B<sub>2</sub> were determined in the urine of 3 controls and one case of "alcoholic" polyneuritis. All cases received a known diet for 12 days, and then the same diet + a known daily amount of B-vitamins for 12 days. The conc. urine was fed to rats deprived of -B<sub>1</sub> and -B<sub>2</sub>, respectively. -B<sub>1</sub> was determined by the power to cure neuritis and -B<sub>2</sub> by promoting growth. -B<sub>1</sub> was not present in the urine of the controls in the first

period, but addition of 720 international units daily caused a daily excretion of 167—333 units. -B<sub>2</sub> was present in small amounts, and feeding of -B<sub>2</sub> increased the amount excreted. In the case of "alcoholic polyneuritis," the initial excretions of -B<sub>1</sub> and -B<sub>2</sub> were comparable with those of the controls. With added -B<sub>1</sub> and -B<sub>2</sub> the retentions were respectively slightly < and slightly > those of the controls.

J. N. A.

**Effect of some reagents on the "filtrate factor" (water-soluble vitamin belonging to the vitamin-B complex and preventing a dietary dermatitis in chicks).** S. LEPKOVSKY and T. H. JUKES (J. Biol. Chem., 1936, 114, 109—116).—The factor can be conc. from aq. rice bran extract by pptn. of inert matter with fuller's earth and MeOH. It is slightly inactivated by warming with NaOH and completely with NaOH and  $\text{FeCl}_3$  and is not appreciably adsorbed from acid solution or pptd. by  $\text{Pb}(\text{OAc})_2$ . H. G. R.

**Distribution of the "filtrate factor" (water-soluble vitamin belonging to the vitamin-B complex and preventing a dietary dermatitis in chicks) in certain feeding stuffs.** T. H. JUKES and S. LEPKOVSKY (J. Biol. Chem., 1936, 114, 117—121).—On suboptimal levels the growth of the chicks approx.  $\propto$  the quantity of the factor fed. The relative vals. of common feeding stuffs are given. H. G. R.

**Biochemical lesion in vitamin-B<sub>1</sub> deficiency. Application of modern biochemical analysis in its diagnosis.** R. A. PETERS (Lancet, 1936, 230, 1161—1165).—A lecture. L. S. T.

**Vitamins in human nutrition. Excretion of vitamin-B<sub>1</sub> in human urine and its dependence on the dietary intake.** L. J. HARRIS and P. C. LEONG (Lancet, 1936, 230, 886—894).—The daily excretion of vitamin-B<sub>1</sub> in human urine has been measured by the Harris bradycardia method. Healthy adults on normal diets excrete 12—35 international units with an average of 20 per day (approx. 5—8% of the daily intake). The proportion of -B<sub>1</sub> excreted is markedly < that of -C under comparable conditions. With a diet containing comparatively large or small amounts of -B<sub>1</sub> the amounts excreted increase or decrease proportionally. In hypovitaminosis-B<sub>1</sub> in rats the amount excreted is negligible. In avitaminosis (beri-beri) in man excretion of -B<sub>1</sub> may almost cease. A daily intake of 200 units for a man of 10 stone wt. may be fixed as a provisional min. allowance and an excretion of < 12 units indicates a diet containing < the normal allowance of -B<sub>1</sub>. -B<sub>1</sub> is absorbed from urine by shaking with acid clay and if dried, the activated clay retains its full activity after 3 months' storage in a refrigerator. L. S. T.

**Adsorption and elution of vitamin-B<sub>1</sub>.** W. H. SCHOPFER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 6—10).—Vitamin-B<sub>1</sub>, adsorbed on fuller's earth as in the international standard powder, is eluted but slightly when treated at 115° for 15 min. with buffer solution of low  $p_H$ , but is extracted at higher  $p_H$  with a max. at  $p_H$  6—7. When the powder is added to a culture of *Phycomyces* growth is stimu-

ated apparently as a result of the elution and utilisation of the vitamin in the cold. W. O. K.

**Measurement of vitamin- $B_1$  activity by means of a micro-organism (*Phycomyces*).** W. H. SCHOPFER and A. JUNG (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 22—25).—Assay of vitamin- $B_1$  preps. by means of their action on the growth of *Phycomyces* yields results in general agreement with those obtained by the usual rat method. Divergences sometimes occur, more especially in the case of crude preps. W. O. K.

**Crystalline torulin (as vitamin- $B_1$ ) and the international vitamin- $B_1$  standard.** H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1936, 30, 985—991).—1 International unit of vitamin- $B_1$  is approx. equiv. to  $2 \times 10^{-6}$  g. of cryst. - $B_1$  hydrochloride, the val. being the same whether given orally or by injection. The day dose method for pigeons by injection may be used for impure but not for cryst. specimens. H. G. R.

**Vitamin- $B_1$  and - $B_2$  content of Arizona-grown grapefruit and broccoli.** G. H. ROEHM (J. Home Econ., 1935, 27, 663—666).—Grapefruit peel and pulp contained  $\approx 0.28$  Sherman units of - $B_1$ , but the fresh peel contained 1.0 unit of - $B_2$  and the boiled peel 0.5 unit. Broccoli leaf and flowers contained 4.0 and 3.0 units, respectively, of - $B_2$  and 0.66 and 0.5 unit, respectively, of - $B_1$ . NUTR. ABS. (m)

**Water-soluble B-vitamins. V. Two types of skin lesion occurring in vitamin- $B_2$  deficiency in the rat in relation to deficiency of flavin and vitamin- $B_6$ , respectively. VI. Flavin and vitamin- $B_6$  in cereals.** A. M. COPPING (Biochem. J., 1936, 30, 845—848, 849—856; cf. A., 1935, 544).—V. With young rats maintained on diets lacking only one constituent of vitamin- $B_2$ , those deprived of flavin (I) developed the (b) type of skin lesions, whilst those deprived of - $B_6$  developed the florid (a) type of dermatitis. Cures were effected in the first case by feeding pure (I), and in the second by administration of - $B_6$  as an EtOH extract of whole maize or wheat.

VI. Wheat and maize are good sources of vitamin- $B_6$ , 25—33% of which could be extracted by cold 80% EtOH. Wheat contains more (I) than maize, but none is extracted by cold 80% EtOH. The germ and integuments of wheat and maize contain more - $B_6$  than the endosperm. Maize and its extracts may contain a deleterious substance which is extracted by cold 80% EtOH, and this possibly is related to endemic pellagra. J. N. A.

**(A) Vitamin- $B_2$  complex in distiller's yeast, No. 12. V. V. EFREMOV and N. JARUSOVA. (B) Vitamin- $B_2$  complex in millet. V. V. EFREMOV (Problems of Nutrition, Moscow, 1935, 4, No. 6, 137—139, 139—141).—(A) The yeast contained about 40,000 Sherman units of - $B_2$  per kg. (B) The amount of - $B_2$  per kg. in millet was  $> 300$  and  $< 1000$  Sherman units. NUTR. ABS. (m)**

**Vitamin- $B_2$ .** W. VON DRIGALSKI (Klin. Woch., 1935, 14, 773—775).—Vitamin- $B_2$  (I) is present in cow's, goat's, and human milk, in "campolon" (II), but not "hepracton" liver extract, and in cerebrospinal fluid; it is frequently demonstrable in blood-

serum, in which it is increased by (II) treatment. It is probably not identical with the exogenous factor for pernicious anaemia therapy. Contrary to -A, blood-(I) exhibits only small upward fluctuations. R. N. C.

**Effect of *Capsicum annuum* on serum-protein.** S. LEE (J. Severance Union Med. Coll., 1935, 3, 31—32).—The feeding to rabbits of 1 g. daily of *C. annuum*, which is very rich in vitamin-C, reduced the protein content of the serum. NUTR. ABS. (m)

**Action of ascorbic acid on metabolism and on blood.** L. ARMENTANO, A. BENTSATH, A. HAMORI, and A. KORANYI (Z. ges. exp. Med., 1935, 96, 321—327; Chem. Zentr., 1935, ii, 1573).—Ascorbic acid does not play an essential part in carbohydrate metabolism, and does not affect the composition, catalytic effect, or basal exchange of blood. R. N. C.

**Ascorbic acid and blood-catalase. III. Hormonal relations.** G. TOROK, M. HEDRY, and R. NEUFELD (Klin. Woch., 1935, 14, 673—675).—Ascorbic acid (I) reduces the temporary increase of blood-catalase (II) caused by unilateral adrenalectomy, and increases the fall of (II) caused by thyroidectomy in rabbits. Its effect after removal of the sex glands or spleen is variable. (I) does not increase (II) in animals given vitamin-free diets after removal of any of the above glands. R. N. C.

**Ascorbic acid as a precursor of serum complement.** E. S. HORGAN (Nature, 1936, 137, 872).—The results of Marsh (this vol., 765) are supported. L. S. T.

**Effect of incomplete diets on the concentration of ascorbic acid in the organs of rats.** S. S. ZILVA (Biochem. J., 1936, 30, 857—867; cf. A., 1935, 262).—The total amounts of ascorbic acid (I) in the liver and intestines of rats on a stock diet increased as the rats grew, but the concns. remained approx. the same. In rats starved for 48 hr. the concn. of (I) in the liver was the same, but the intestines showed a rise, due possibly to a loss in wt. of the intestine. A carbohydrate diet had a detrimental effect, but the concn. of (I) in the livers and intestines was similar to those for normal rats. Rats on a protein-fat diet thrive worse than on a carbohydrate diet, but there was no increase of (I) in the liver or intestines. The hypothesis of Hopkins and Slater (this vol., 254) is not fully supported by experimental evidence. J. N. A.

**Histochemistry. VII. Concentration of vitamin-C in the thymus in relation to its histological changes at different stages of development and regression.** D. GLICK and G. R. BISKIND (J. Biol. Chem., 1936, 114, 1—7).—The concns. in the whole gland for the foetus and calf, steer, and cow and bull are 0.35—0.52, 0.23—0.36, and 0.04—0.17 mg. per g., respectively. These vals. are approx. the same on the fat- and connective tissue-free basis. H. G. R.

**Amount of vitamin-C required to maintain the normal reducing power of animal tissues.** L. DE CARO (Z. physiol. Chem., 1936, 240, 179—190). In guinea-pigs on scorbutic diets, ascorbic acid (I) disappears almost completely from the adrenals in 10—13 days, the curve expressing the rate of



disappearance being approx. exponential. The amounts (12 mg. or 10 g. of cabbage) of (I) which must be given daily in order to maintain normal reducing power in the adrenals and liver are much > those required for prevention and cure of scurvy. Naturally-occurring (I) in food is better utilised than isolated (I) and injected (I) than (I) given orally. The preventive and curative effects of daily injections of 12 mg. of "Maurer's acid" (A., 1933, 936) are equiv. to daily injections of 5 mg. of (I). The (I) of tissues not required for prevention of scurvy is less a reserve than a factor for maintaining optimal functioning of the cells.

W. McC.

**Ascorbic acid content of blood.** C. J. FARMER and A. F. ABT (Proc. Soc. Exp. Biol. Med., 1935, 32, 1625—1629).—To determine ascorbic acid (I) oxalated blood is centrifuged and the plasma deproteinised with  $\text{H}_2\text{WO}_4$  and titrated with 2:6-dichlorophenol-indophenol. Oxidised (I) cannot be determined by reduction with  $\text{H}_2\text{S}$ , as colloidal  $\text{WS}_2$  interferes.  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ -deproteinisation gives slightly higher vals. owing to a less definite end-point, but permits the determination of oxidised (I). R. N. C.

**Content of vitamin-C in normal and pathological [human] cerebrospinal fluid.** G. MARINESCO, G. ALEXIANU-BUTTU, and I. OLTEANU (Bull. Acad. Sci. Roumaine, 1936, 17, 129—137).—The normal content increases with increasing age; considerable variations occur in pathological conditions.

H. G. R.

**Vitamin-C in saliva.** O. H. STUTEVILLE (Proc. Soc. Exp. Biol. Med., 1935, 32, 1454—1455).—The vitamin is present in concn. 0.0025 mg. per c.c.

R. N. C.

**Ascorbic acid content of the ovary and corpus luteum at different stages of the oestrous cycle.** A. A. POLICARD and M. FERRAND (Compt. rend. Soc. Biol., 1936, 122, 200—202).—The ascorbic acid content of the corpus luteum at various stages of formation is approx. const. and equals that of the ovary. The content of the residual ovarian tissue is also relatively const.

R. N. C.

**Fresh vegetables rich in vitamin-C.**—See B., 1936, 568.

**Vitamin-C content of apples and its relation to human welfare.** W. F. DOVE and E. MURPHY (Science, 1936, 83, 325—327).—As with the fruits, the vitamin-C content of the leaves of the Northern Spy apple is > that of the McIntosh apple.

L. S. T.

**Vitamin studies on apples.** I. A. MANVILLE, A. S. MCMINIS, and F. G. CHUINARD (Food Res., 1936, 1, 121—140; cf. A., 1935, 414).—The vitamin-A and -C contents of Arkansas Black apples were 36 and < 2.5 units per oz.; of Baldwin, 15 and 2.5—3.0; of Jonathan, 24 and 1.5—2.0; of Winesap, 36 and 3.0; of Delicious, 24 and < 2.5; of Gravenstein, 14—17 and 3.75; of Spitzenberg, 36 and 7. The three last-named do not form a good source of -B. During storage, -A is destroyed < -C, the decomp. of the latter varying with the type of apple. Careful removal of the peel does not markedly decrease the -C content. A new (biological) method for the determination of -A is proposed. E. C. S.

**Specific reaction for the detection and determination of ascorbic acid in serum.** H. LUND and H. LIECK (Nature, 1936, 137, 784).—The addition of small amounts of ascorbic acid to a solution of methylene-blue results in complete decolorisation in < 30 sec. on exposure to strong light. This reaction is not produced or inhibited by glutamine, ergothionine, creatine, creatinine, urea, adenine, guanine, hypoxanthine, xanthine, uric acid, cystine, haemoglobin, and PhOH.

L. S. T.

**Determination of vitamin-C in various foods and in human urine.** R. CASAZZA (Arch. Ist. Biochim. Ital., 1936, 8, 39—62).—Data are given and discussed for the ascorbic acid (I) content (determined iodometrically) of *Citrus* fruits and of human urine following ingestion of (I)-free and -rich meals and intravenous injection of (I).

F. O. H.

**Influence of milk constituents on the effectiveness of vitamin-D.** G. C. SUPPLEE, S. ANSBACHER, R. C. BENDER, and G. E. FLANIGAN (J. Biol. Chem., 1936, 114, 95—107).—A "symplex" (A., 1934, 913) of vitamin-D and lactalbumin is formed when the latter is pptd. from solution containing the vitamin. The biological activity of the system is > that of its components and is increased still further if lipin-free lactalbumin is used.

H. G. R.

**Colour reaction for the detection and determination of vitamin-D.** W. HALDEN (Naturwiss., 1936, 24, 296—297; cf. following abstract).—A solution of the prep. (oils are first saponified and extracted) in anhyd. petrol,  $\text{C}_6\text{H}_6$ , or  $\text{CHCl}_3$  is treated with 1% pyrogallol in abs. EtOH, 10%  $\text{AlCl}_3$  in abs. EtOH is added to the conc. solution, and the mixture is heated at 100° for 4 min.

W. O. K.

**Colour reaction for the detection and determination of vitamin-D.** W. HALDEN and (Mrs.) H. TZONI (Nature, 1936, 137, 909; cf. preceding abstract).—The reaction detects < 0.002 mg. of vitamin-D. -A and related products must be absent, but cholesterol, ergosterol, and lumisterol do not react. Suprasterol II gives a fainter tint.

L. S. T.

**Vitamin-E. III.** S. UENO, Y. OTA, and Z. UEDA (J. Soc. Chem. Ind. Japan, 1936, 39, 110—112b).—Feeding experiments (albino rats) with a basic sterility diet to which the vitamin-E fraction from rice oil (A., 1935, 1037) had been added confirm the anti-sterility action of the latter.

J. W. B.

**Vitamin-E and the gonads.** W. SAPHIR (Endocrinol., 1936, 20, 107—108).—Commercial preps. of wheat-germ oil exhibit no oestrogenic, gonadotropic, or luteinising effects in rats.

R. N. C.

**Mode of action of vitamin-K.** H. DAM, F. SCHÖNHEYDER, and E. TAGE-HANSEN (Biochem. J., 1936, 30, 1075—1079; cf. this vol., 907).—Prothrombin (I) can be pptd. from the plasma of normal chicks by  $\text{COMe}_2$  or  $\text{AcOH}$ , whilst the ppts. from the plasma of K-avitaminous chicks are inactive. The ppt. of (I) from normal chicks is still active after removal of lipins by  $\text{COMe}_2$  and  $\text{Et}_2\text{O}$ , and the lipins so obtained are inactive. A concentrate of -K does not accelerate *in vitro* clotting of plasma+thrombokinase. (I) pptd. by  $\text{AcOH}$  and washed with  $\text{COMe}_2$  and  $\text{Et}_2\text{O}$  contains -K.

J. N. A.

**Occurrence and chemical nature of vitamin-K.** H. DAM and F. SCHÖNHEYDER (Biochem. J., 1936, 30, 897—901).—The vitamin-K (antihæmorrhagic factor) content of numerous substances is determined and green vegetables are shown to be a particularly rich source. Cold saponification of hog-liver fat destroys one third and hot the whole of the -K content. The fatty acid fraction is inactive but enhances the activity of the unsaponifiable fraction. -K is thermostable.  $\text{COMe}_2$  is the most efficient solvent for extraction of -K from lucerne leaves. Various methods of purification of the extracted material were tried.  $\text{Al}_2\text{O}_3$  adsorbed -K but elution was unsuccessful. Using the  $\text{CaCO}_3$  and cane sugar methods, concns. of  $6 \times 10^5$ — $10^6$  units per g. were obtained. P. W. C.

**Purification of the antihæmorrhagic vitamin.** H. J. ALMQUIST (J. Biol. Chem., 1936, 114, 241—245; cf. A., 1935, 1401).—The hexane extract of lucerne meal is treated with MgO and C to remove pigments, then conc., fats and sterols are separated by chilling, the filtrate is evaporated to dryness, and the residue extracted with MeOH; further impurities are removed by chilling. A yellow oil, active in a daily dose of 2 mg. per kg. of diet, was separated by dilution with  $\text{H}_2\text{O}$ . The residue from the aq. MeOH solution was inadequate at twice this level. The vitamin is stable to heat and light but is alkali-labile. H. D.

**Determination of vitamin-K.** I. F. SCHÖNHEYDER (Biochem. J., 1936, 30, 890—896; cf. Dam, A., 1935, 903).—The delay in clotting is not due to lack of thrombokinase, insufficiency of fibrinogen, or accumulation of anti-coagulants. In diseased chicks serum-Ca is usually low and inorg. P always high. Addition of  $\text{Ca}^{++}$  to the plasma of diseased chicks does not shorten the clotting time. The  $p_{\text{H}}$  and salt content of the plasma are normal. After addition of thrombokinase, the amount of thrombin produced in diseased is much < in normal plasma. Normal plasma contains excess of material which accelerates clotting in the blood of chicks deficient in -K. K-Avitaminosis is prevented by giving dried pig's liver as 20% of the diet (10% affords partial protection) and is cured by giving 11.3 mg. of the liver per g. of chick daily for 3 days. Degree of -K deficiency is expressed by the ratio of the concns. of coagulant (1 drop to 5 drops of plasma) required to clot diseased and normal plasma in 3 min. at  $40^\circ$ . 1 unit of -K is contained in the min. daily dose of substance per g. of chick which reduces the ratio to 1 in 3 days. W. McC.

**Photochemical reaction of chlorophyll with ferrous ions.** K. WEBER (Nature, 1936, 137, 870).—Critical (cf. this vol., 11). The bleaching action of  $\text{FeSO}_4$  on chlorophyll (I) in neutral and in  $\text{H}_2\text{SO}_4$  solution is not affected by irradiation with a strong C arc. The photochemical reaction between (I) and  $\text{FeSO}_4$  does not occur according to the equation given by Weiss, and it is not analogous to the photochemical reduction of vat dyes. L. S. T.

**Number of chlorophyll molecules acting as an absorbing unit in photosynthesis.** H. I. KOHN (Nature, 1936, 137, 706).—Measurements of the  $\text{O}_2$  liberated by a thin suspension of *Chlorella pyrenoidosa*

in intermittent light from a Ne discharge tube indicate that the absorption unit within the plant is equiv. to approx. 500 chlorophyll mols. per quantum. The unit is not a rigid structure, and quanta absorbed by a no. of units are pooled in order to reduce 1 mol. of  $\text{CO}_2$ . L. S. T.

**Photoperiodism and changes in the enzymic system [of plants].** N. KRASSINSKI, A. A. KONDRASHOVA, and N. I. VINOGRADOVA (Ann. Bot., 1936, 50, 293—304).—An artificially shortened day period increased the catalase and peroxidase activity of bean leaves and pods and of chrysanthemum leaves, decreased that of amylase (I) and invertase (II) in beans, and decreased (I) and increased (II) in chrysanthemum. No definite changes occurred in cineraria leaves. Relations between these changes and photoperiodic effects are discussed. A. G. P.

**Rate of increase of fluorescence of living leaves.** H. KAUTSKY and A. MARX (Naturwiss., 1936, 24, 317).—The fluorescence in the leaves of *Ageratum mex.*, *Parietaria officinale*, and *Piper nigrum* following illumination after being kept in the dark has been accurately measured with a photo-electric cell. The activation of the chlorophyll- $\text{O}_2$  complex by light follows a unimol. course. W. O. K.

**Isotopic fractionation of water by physiological processes.** M. DOLE (Science, 1936, 83, 351).—A correction applied to Washburn and Smith's data indicates a preferential rejection rather than selection of D (cf. A., 1934, 570). L. S. T.

**Absorption and accumulation of solutes by living plant cells. VIII. Effect of oxygen on respiration and salt accumulation.** F. C. STEWARD, W. E. BERRY, and T. C. BROYER (Ann. Bot., 1936, 50, 345—366; cf. A., 1934, 708).—The previously observed influence of  $[\text{O}_2]$  on the absorption of  $\text{K}^+$  and  $\text{Br}^-$  by potato discs is confirmed in carrot and artichoke. Respiratory changes are affected only when the  $[\text{O}_2]$  of the air current is < that of the atm. Aerobic but not anaerobic metabolic processes are concerned in salt accumulation. A. G. P.

**Vital oxidation of plant cells by complex cobaltamines.** A. WATANABE (Iwata Inst. Plant Biochem., Publ. 2, 1936, 88—96).—The oxidation of various natural OH-compounds, such as myricetin, quercetin, etc., in presence of complex Co ammine salts, is accompanied by a rise in  $p_{\text{H}}$  due to the liberation of  $\text{NH}_3$ . The increasing alkalinity causes an autocatalytic increase in reaction velocity. M. S. B.

**Transport of nitrogenous substances under the influence of differences of humidity.** M. P. BOTH (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 531—540).—Transport from leaf to leaf through the sieve tubes is established. A. G. P.

**Nitrogen metabolism of the pea seedling.** P. MCKIE and J. BARNETT (Biochem. J., 1936, 30, 1010—1013).—During 32 days' growth from seed, insol., protein-, and  $\text{NH}_2\text{-N}$  represent > 95% of the total N in the plant of *P. sativum*.  $\alpha\text{-NH}_2$ -acids increase from 2% in the seed to 25% on the 18th day. After an initial decrease, protein-N rises to a const.



val. of 40%. In etiolated seedlings, amide is produced at the expense of  $\text{NH}_2$ -acids. H. D.

**Plant nutrition. IV. Nitrogen metabolism in relation to nutrient deficiency and age in leaves of barley.** F. J. RICHARDS and W. G. TEMPLEMAN (Ann. Bot., 1936, 50, 367-402; cf. A., 1936, 3, 249-265).

Comparison of the N contents of successively developing leaves of sand-cultured barley indicates that deficiency of N supplies although lowering the general N level of the plants involved no fundamental change in the N cycle. Deficiency of P causes a decline in the protein content of leaves from the early stages of development, marked accumulation of amide-N, and smaller accumulation of  $\text{NH}_2$ -N and of  $\text{NO}_3$  in later leaves. Protein synthesis is probably checked at the stage of asparagine production. Deficiency of K is marked by disappearance of protein from older leaves, increased proportions of amide- and  $\text{NH}_2$ -N, and, in later leaves, an accumulation of  $\text{NO}_3$ . K is not primarily concerned in protein formation, but is essential to the maintenance of the protoplasmic complex, the breakdown of which leads to rapid proteolysis. Relations between the increase in  $\text{NO}_3$  following P and K deficiency, the proportion of  $\text{NH}_2$ -N, and reductase activity in leaves are discussed. A. G. P.

**Changes in the nitrogenous fractions in stored apples.** J. P. HOWARTH, W. R. PHILLIPS, and R. WRIGHT (Proc. Leeds Phil. Soc., 1936, 3, 249-265). Structural breakdown in stored apples follows the period when the sol. N content is a min., and hence cannot be related to hydrolysis of protoplasmic protein. Loss of N from the cortex is considerable in the early period of storage. Changes in N fractions are retarded at low temp. A. G. P.

**Phosphorus metabolism of aconia during germination in la knes** E. MICHEL-DURAND (Compt. rend., 1936, 202, 503-505). At the beginning of germination 2/3 of the total P of the seed is in acid-sol. forms of which a half is inorg. After 80 days 70% of the total P has passed into the seedling. Translocation of all forms of P occurs, but that of phytin P is the most complete. (I) and inorg. P are localised mainly in roots, and lipin-P in the aerial organs. A. G. P.

**Fat metabolism in plants, with special reference to sterols. II. Differential changes in the cotyledons, roots, stems, and leaves.** P. L. MACHLISIAN (J. Biol. Chem., 1936, 114, 185-191; cf. this vol., 1936, 3, 249-265). During germination of soya beans, the total fat of the cotyledons decreased, the effect being more marked in light than in darkness. The roots, stems, and leaves synthesised fat equally well in the light and dark. The degree of saturation of the fatty acids was the same in cotyledons and seeds, but was greater in the newly formed acids of roots, stems, and leaves. There was an increase of sterol (I) in roots, stems, and leaves, whilst (I) esters were present in the cotyledons. A close relation probably exists between the metabolism of (I) and the utilisation of fat in the cotyledons. (I) is a vital constituent of roots, stems, and leaves. J. N. A.

**Metabolism of the colourless alga, *Prototheca zopfii*, Krüger.** H. A. BARKER (J. Cell. Comp. Physiol., 1935, 7, 73-93).—The alga cannot develop in absence of complex org. compounds such as are present in yeast autolysate. It can utilise N from both  $\text{NH}_3$  and more complex N compounds, the N content of the cells varying from 1 to 10% according to the amount of N available. The alga can utilise fatty acids, hexoses, and some alcohols, but not OH-, keto-, or dibasic acids. Glucose is converted aerobically into cell material and  $\text{CO}_2$ ; anaerobically it is fermented quantitatively to lactic acid. R. N. C.

**Vitamins and plants.** A. I. VIRTANEN (Nature, 1936, 137, 779-780).—Vitamin-C is essential to the growth of pea seedlings. By removing the cotyledons at a suitable stage, the seedlings are deprived of 90% of their -C and die or remain dwarfed. The addition of -C to the cotyledon-less seedlings assists development and the production of normal blossoms. L. S. T.

**Formation of vitamin-C in germinating seeds.** A. I. VIRTANEN and L. V. EEROLA (Suomen Kem., 1936, 9, B, 13).—Production of vitamin-C by germinating seeds is independent of light, but is greater when the temp. of germination is relatively low, and is inversely  $\propto$  the rate of germination. The -C content of seedlings is relatively high when the  $\text{H}_2\text{O}$  supply is low, is influenced by the  $p_{\text{H}}$  of the seed (optimum 6.3-6.6), and is increased by addition of  $\text{PO}_4^{3-}$  (but not by that of sugar) to the nutrient medium. A. G. P.

**Germination of leguminous seeds and urease activity.** B. N. SASTRI and B. A. S. IYENGAR (Current Sci., 1936, 4, 107).—The activities of germinated are always > those of the ungerminated seed extracts. In powdered seed materials differences are small. Part of the urease exists in seeds in an unextractable condition (desmo-urease), converted during germination into an extractable lvo-form. H. G. M.

**Physiology and chemistry of the plant hormones.** K. V. THIMANN (Current Sci., 1936, 4, 716-721).—A review.

**Influence of glucose on auxin production by the root-tip of *Vicia faba*.** M. H. VAN RAALTE (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 261-265).—Glucose favours the accumulation of auxin and may also induce the formation of additional auxin in the root-tips. A. G. P.

**Interaction of factors in growth of *Lemna*.** H. L. WHITE (Ann. Bot., 1936, 50, 403-417; cf. this vol., 1936, 3, 249-265).—The effects of varying levels of N supply on the rates of multiplication and of respiration, on dry matter production, and on the starch, protein, and chlorophyll contents are examined. Accumulation of carbohydrates in N-deficient plants results from retarded multiplication associated with lowered carbohydrate consumption in growth, and is accentuated by decreased respiration leading to a high net assimilation rate. Decreasing N supply is associated with low amylolytic activity. Changes during recovery from N-starvation are examined. A. G. P.

**Action of alkaline extract of the anterior pituitary on A. growth of plants, B) germin-**

ation. E. C. D. PASCAL (Rev. soc. argentina biol., 1935, 11, 57—67, 68—94).—(A) Small doses of the extract accelerated the growth of some but not all plants examined. Large doses caused root damage and inhibited growth.

(B) Pre-soaking seeds in the extract accelerated germination in some cases. The extract probably contains two active factors. Chr. Ans. (p)

Effect of X-irradiation on auxins and plant growth. F. SKOOG (J. Cell. Comp. Physiol., 1935, 7, 227—270). Auxin (I) in solution is inactivated by moderate irradiation in presence of  $O_2$ , which is required for formation of the oxidisers responsible for the inactivation. Inactivation also takes place in white light in presence of eosin. Extracted hetero-auxin and indolylacetic acid are also inactivated in aq. solution. Irradiation inactivates the (I) normally present in plants; it inhibits (I) formation in young *Pisum* and *Vicia*, but not in *Avena* coleoptile, and does not affect (I) transport. (I) applied to irradiated plants causes renewed growth. Lateral bud development caused by irradiation is correlated with loss of (I). The inhibition of growth is due largely to interference with (I) formation. R. N. C.

Effects of ethylene on the plant growth hormone. F. F. NORD (Science, 1936, 83, 284).—A Discussion. L. S. T.

Effect of ascorbic acid and indolylacetic acid on regeneration of willow branches and germination. W. DAVIES, G. A. ATKINS, and P. C. B. HUDSON (Nature, 1936, 137, 618).—Dil. solutions of ascorbic (I),  $\beta$ -indolyl-acetic (II) and -propionic (III) acids stimulate root and shoot regeneration in willow branches, but at concns. of 1 in 2500 regeneration is retarded by (I) and practically prevented by (II) and (III). (II) and (III) apparently retard the germination and growth of oats and mustard and cress seeds, but (I) stimulates in dil. solutions. At higher concns. (1:10<sup>3</sup>), (I) shows a retarding effect, whilst (II) and (III) are practically lethal. L. S. T.

Stimulation of root-hair growth in legumes by sterile secretions of nodule bacteria. H. G. THORNTON and H. NICOL (Nature, 1937, 137, 494—495).—Addition of a sterile filtrate containing secretions of nodule bacteria deforms and increases the no. and length of the root hairs of lucerne seedlings. L. S. T.

Stimulation of development of plants and of ripening of their fruit by ethyl alcohol and by temporary asphyxia of the roots.—See B., 1936, 467.

Factors affecting nodule formation on seedlings of leguminous plants. C. A. LUDWIG and F. E. ALLISON (J. Amer. Soc. Agron., 1935, 27, 895—902).—In sand cultures nodulation of lucerne and soya bean was increased in many cases by the presence of other plants, including maize and wheat. In the absence of older plants additions of sugar and, in some instances, of small amounts of available N were beneficial. Cold- $H_2O$  extracts of sand in which lucerne, maize, or wheat seedlings had been growing did not affect nodulation of lucerne when added to sand cultures. Presence of other plants may produce con-

ditions in the rhizosphere (including liberation of bacterial growth-promoting substance) more favourable to bacterial development. A. G. P.

Growth, chemical composition, and efficiency of normal and mosaic potato plants in the field. W. E. STONE (J. Agric. Res., 1936, 52, 295—309). Infected plants had lowered % of sugar and starch and an increased % of ash (dry matter basis). Assimilation per unit leaf area was smaller. A. G. P.

Determination of potassium carbonate in sunflower ash. V. K. ZOLARENCH (J. Appl. Chem. Russ., 1936, 9, 552—554). 1 g. of ash is extracted with 150–200 ml. of boiling  $H_2O$  for 10 min., the cooled solution is diluted to 250 ml., and 50 ml. of the filtered solution are titrated with 0.1N-HCl. A deduction of 0.3 ml. of acid per 100 ml. of solution is made, to correct for solubility of  $CaCO_3$ . R. T.

Comparison between the Benedict Denis and Parr bomb methods for determining total sulphur in plants and proteins. P. PAINTNER and K. W. FRANKE (J. Biol. Chem., 1936, 114, 235—239). The Parr bomb method gave higher vals. for total S in cereal and proteins than the Benedict Denis method (A., 1911, ii, 66); the latter gave particularly low vals. with cystine and methionine. The  $Na_2O_2$  fusion method gave good vals. in all cases. H. D.

Cyanophoric plants of the Maquiling region. V. J. B. JULIANO and M. GUERRERO (Philippine Agric., 1935, 24, 22—26). HCN is recorded in a large no. of species. Chr. Ans. (p)

Recovery of hydrocyanic acid from fumigated Citrus leaves. E. T. BARTHOLOMEW and E. C. RANX (J. Biol. Chem., 1936, 113, 655—660). HCN was determined by a photo-electric nephelometric method sensitive to  $5 \times 10^{-5}\%$ . Part of the HCN which enters the leaves during fumigation is rapidly and permanently fixed, probably not entirely by aldehydes, sugars, or citral. HCN could not be recovered from the leaves by distillation with 2% tartaric acid owing to combination with some substance in the distillate. J. N. A.

Determination of the forms of calcium and oxalic acid in leaves of sugar-beet. A. P. LEHNEDEVA and K. N. PORCHENOK (Nauch. Zap. Sakh. Prom., 1931, 11, Book 46—48, No. 8, 10, 31—40). A small portion of Ca in the leaves is not extractable by HCl. This fraction is higher in younger leaves. No  $H_2O$ - or  $AcOH$  sol. Ca is present. The  $H_2O$  sol.  $CaC_2O_4$  varies in different parts—the leaf is greater in the younger leaves, and is 1.5–2 times the quantity of  $CaC_2O_4$  present. Chr. Ans. (p)

Subtropical fruit trees of Azerbaidzhan. A. KERIMOV (Bull. Appl. Bot. U.S.S.R., 1934, [III], No. 5, 325—347). Juice of cultivated pomegranates contains 11–19% of sugars and 0.4–0.6% of citric acid. Wild varieties have 12–18 and up to 8–9%, respectively. In olives the sugar content decreases as ripening progresses and again increases in over-ripe fruit. Changes in oil content are in the reverse order. The 1 val. of the oil increases with advancing ripeness. The oil content of almonds and pistachio nuts grown in different localities is recorded.

Chr. Ans. (p)



**Flavour of shoyu. II.** K. SHOJI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 29, 166—170; cf. A., 1935, 1540).—A  $\text{CHCl}_3$  extract after treatment with 10% NaOH affords hexoic acid,  $\text{C}_1$  to  $\text{C}_6$  primary alcohols, methyl-*n*-nonylcarbinol, and an unidentified product with the odour of shoyu. J. L. D.

**Flavour of shoyu. III.** K. SHOJI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 223—229).—An  $\text{Et}_2\text{O}$  extract of shoyu (not sterilised) yielded  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ , guaiacol, and Et vanillate. J. N. A.

**Coumarins of root of *Heracleum sphondylium*, L.**—See this vol., 860.

**Kuromannin, shisonin, and nasunin.**—See this vol., 861.

**Constituents of bark of *Zanthoxylum americanum*.**—See this vol., 859.

**Oroxylin-A.**—See this vol., 860.

**Limonin, the bitter principle of orange kernels.**—See this vol., 857.

**Change of hesperidin content of peel of the mandarin orange during ripening:** hesperidin content of juice, embedded fibre (white fibre on segments), and endocarp of ripened fruit. Y. IWASAKI (J. Agric. Chem. Soc. Japan, 1936, 12, 279—280).—Hesperidin (I) was determined by extraction of the dried substance with MeOH. The amount of (I) in the peel gradually decreased with advancing maturity; that in the dried white fibre of the segments was < that of the dried peel. Juice contained only a very small amount. J. N. A.

**Preparation of sinigrin.** S. MORELL and K. P. LINK (J. Biol. Chem., 1936, 114, 123—124).—Sinigrin cannot be obtained from *Brassica nigra* by Gadamer's method (A., 1897, i, 360), but good results can be obtained by the methods of Herissey and Boivon (A., 1928, 207) and of Sandberg and Holly (A., 1932, 776). J. N. A.

**Active principle of *Myrsine africana*, Linn.** S. KRISHNA and B. S. VARMA (J. Indian Chem. Soc., 1936, 13, 115—116).—Embelic acid (embelin) is extracted (yield 3%) by  $\text{CHCl}_3$  from the fat-free berries; subsequent extraction with EtOH affords quercitol (I) (1%) and colouring matter. (I) is also isolable from the berries of *Embelia ribes*. H. B.

**Constituents of *Evodia danielli*, Hemsl.** S. MAYEDA (J. Pharm. Soc. Japan, 1935, 55, 531—537).—The following are isolated from the  $\text{COMe}_2$  extract: a substance, m.p. 80—80.5°, not reacting with  $\text{BzCl}$  or  $\text{NH}_4\text{OH}$ ; *evodin*,  $\text{C}_{26}\text{H}_{30}\text{O}_8$ , m.p. 292—293°,  $[\alpha]_D^{25}$  —129.4° in  $\text{CHCl}_3$ , also from *E. ruteacarpa*, Benth and Hook; *evodol*,  $\text{C}_{26}\text{H}_{30}\text{O}_8$  or  $\text{C}_{26}\text{H}_{30}\text{O}_{10}$ , m.p. 281° (*Me* derivative, m.p. 279°). a terpenic oil. CH. ABS. (r)

**Presence of norstictic acid in the tree lichen *Lobaria pulmonaria* (L.), Hoffm.** H. SCHINDLER (Ber. deut. bot. Ges., 1936, 54, 240—246).—Production of red crystals with alkali is characteristic of norstictic (I) and  $\alpha$ -methylethylsalazic as well as of salazic acid (A., 1934, 189, 891). (I) and stictic acid occur in *L. pulmonaria*. Asahina's diamine reaction is more sensitive than the KOH test. A. G. P.

**Aromatic compounds of "Kasutorishochu."** K. SHOJI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 230—233; cf. B., 1933, 328).—Treatment of Kasutorishochu with NaOH yielded  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$  (*phenylurethane*, m.p. 79—80), octoic acid, and *p*-cresol. J. N. A.

**Formation of potassium eugenoxide crystals during examination of plant ashes in violet oil.** H. TZONI (Mikrochem., 1936, 19, 208—213).—During use of violet oil as a medium for the microscopic investigation of the structure of the ash of plant tissues, crystals of K eugenoxide (I) form, especially along the leaf nerves. Highly siliceous tissues give no (I) crystals, owing to the formation of  $\text{K}_2\text{SiO}_3$  during ashing. J. S. A.

**Determination of carbohydrates in the leaves of *Euphrasia stricta* and of *Trifolium pratense*.** N. SALAGEANU (Compt. rend. Soc. Biol., 1936, 121, 1531—1533).—Analytical vals. are given. R. N. C.

**Hexose phosphates produced by higher plants.** B. TANKÓ (Biochem. J., 1936, 30, 692—700).—The nature of the hexose phosphates produced by incubation of pea flours with added inorg. P is investigated. > 90% of the phosphorylated product consisted of 1:6-diphosphofructofuranose; the monophosphate complex was purified with brucine and was similar to the Robison ester but had a lower  $[\alpha]$ ; oxidation with Br left a non-aldose residue, possibly fructose 1-phosphate. Phosphohexokinase (A., 1935, 660) is present in pea flour and converts fructose 6-phosphate into a mixture of 62% of aldose and 38% of non-aldose esters. H. D.

**Glucoside in *Pardanthus chinensis*, shekanin.** Y. H. WU (J. Chinese Chem. Soc., 1936, 4, 89—92).—Extraction of resin-free roots with 96% EtOH affords *shekanin*, m.p. 245—250° (*Ac* derivative, m.p. 182°, contains 4 *Ac* and 1 *OMe* groups), which is hydrolysed to a pentose and *shekangenin*,  $\text{C}_{16}\text{H}_{16}\text{O}_8$ , m.p. 257° (decomp.). J. L. D.

**A new digitalic: *Menabea venenata*, Baillon.** R. HAMET (Compt. rend. Soc. Biol., 1936, 121, 1327—1329).—The roots contain two glucosides with digitalin-like action; the name *menabein* is applied to the (apparently) more active of the two. R. N. C.

**Gum from lemon trees.** E. ANDERSON, F. H. RUSSELL, and L. W. SEIGLE (J. Biol. Chem., 1936, 113, 683—690).—The purified gum,  $[\alpha]_D^{25}$  +20.7°, is a compound of methylated uronic acid (2 mols.) + *d*-galactose (4 mols.) + *L*-arabinose (4 mols.)— $\text{H}_2\text{O}$  (10 mols.). The gum, the structure of which is discussed, is not formed from pectic substances or hemicelluloses, but from sugars or polysaccharides in the inner part of the bark. J. N. A.

**Separation of hydratopectin into calcium and magnesium pectinates and araban by means of water-alcohol-ether.** T. K. GAPONENKOV and V. N. MIMRIKOVA (J. Appl. Chem. Russ., 1936, 9, 505—508).—Ca and Mg pectinates are pptd., whilst araban remains in solution, when 100 ml. of EtOH and 16.5 ml. of  $\text{Et}_2\text{O}$  are added to 50 ml. of 2% aq. hydratopectin. R. T.

**Tea tannin.** M. NIERENSTEIN (Analyst, 1936, 61, 294).—The constitution of tea tannin is discussed in relation to the products of hydrolysis after methylation, and also to those resulting from the action of tannase (cf. B., 1922, 907A). E. C. S.

**Constitution of tannins including those of tea and coffee.** P. MATTLAND (Analyst, 1936, 61, 288—293).—The probable constitution of a no. of hydrolysable and condensed tannins is discussed.

E. C. S.

**Tannin from the Indian gooseberry (*Phyllanthus emblica*) with a protective action on ascorbic acid.** M. DAMODARAN and K. R. NAIR (Biochem. J., 1936, 30, 1014—1020).—A tannin, m.p.  $> 360^\circ$ , containing gallic and ellagic acids and glucose, which inhibits the oxidation of ascorbic acid in air is prepared from the Indian gooseberry by extraction with MeOH and pptn. with EtOAc. A second tannin, decomp.  $120^\circ$ , without this inhibiting effect was also isolated.

H. D.

**Constituents of seeds of *Blepharis edulis*,** Pers. I. J. B. LAL (J. Indian Chem. Soc., 1936, 13, 109—114).—Extraction of the oil-free ( $C_6H_6$ ) seeds with EtOH gives *dl*-allantoin (2.1%), a bitter glucoside (*blepharin*) (1.2%),  $C_{15}H_{20}O_{11}$ , m.p.  $222^\circ$  (softens at  $220^\circ$ ), glucose,  $\alpha$ - $C_6H_4(OH)_2$ , tannins, and saponins.

H. B.

**Failure of iodine-starch reaction.** E. MANGOLD and H. JANSCH (Sitzungsber. Ges. naturf. Fr. Berl., 1935, Feb., 35—40).—Potato that had been treated with saliva gave no blue colour but there was a yellow or brown coloration which could be removed by washing. Thereafter (I) produced a blue colour which could not be washed out.

NUTR. ABS. (m)

**Diastatic decomposition of intercellular cement.** H. COLIN and A. CHANDUN (Compt. rend., 1936, 202, 973—975).—Digestion of sugar-beet pulp at  $15^\circ$  with the digestive juice of *Helix* effects 50% greater decomp. of pectic substances than hot  $H_2O$  extraction, as measured by the reducing-sugar content.

P. G. M.

**Biochemical characteristics of variety in vegetables.** B. A. RUBIN and L. I. NAUMOVA (Compt. rend. Acad. Sci., U.R.S.S., 1935, 4, 341—344; cf. A., 1935, 658).—In roots and leaves of early radishes the catalase (I), invertase (II), and amylase contents are  $>$  those in late radishes, the differences being very pronounced in the cases of (I) and (II). Differences in wt. and sugar content between early and late varieties are also observed.

W. McC.

**Influence of climatic conditions on the resin content of the needles of coniferous trees.** G. V. PIGULEVSKI (J. Gen. Chem. Russ., 1935, 5, 1634—1638).—The resin content of the needles of different species of pine, larch, and fir is greatest in those growing in cold or temperate climates.

R. T.

**Properties of the secretion of *Primula obconica*.**

HOCQUETTE (Compt. rend., 1936, 202, 1089—1091).—Differences (solubility in org. and inorg. solvents, colour reactions) between the fluid in the cells and the excreted matter may be due to the presence in the latter of fatty acids and/or neutral fats.

W. McC.

**Composition of the secretion of *Primula obconica*,** Hance. M. HOCQUETTE (Compt. rend., 1936, 202, 436—438).—The secretion of the hairs of *Primula obconica* probably contains saponosides or related compounds and phytosterols.

H. G. M.

**Composition of the oil of *Primula auricula*, L.** A. GORIS and H. CANAL (Compt. rend., 1936, 202, 1351—1352).—Steam-distillation of the crushed and steeped roots of this plant give 0.8% of distillate consisting of paeonol and some *Me methoxyquinol-carboxylate*, an oil. The acid, m.p.  $143^\circ$ , therefrom gives 2 : 5- $C_6H_3(OH)_2 \cdot CO_2H$ , m.p.  $200^\circ$  [obtained from  $p$ - $C_6H_4(OH)_2$ ,  $CO_2$ , and  $KHCO_3$  in glycerol at  $180^\circ$ ], and is prepared from this acid by  $Me_2SO_4$  (2 mols.) and boiling NaOH (2 mols.).

R. S. C.

**Essential oil of parasite-infested flower stems of marjoram.** R. SALGUES (Compt. rend. Soc. Biol., 1936, 121, 1074—1076).—Phenols, particularly thymol, in the oil are decreased by infection of the stems with *Eriophyes thomasi*.

R. N. C.

**Constituents of flowering dogwood (*Cornus florida*).** C. E. SANDO, K. S. MARKLEY, and M. B. MATLACK (J. Biol. Chem., 1936, 114, 39—45).—The fresh flowers and bracts (79.6—16.3 kg. dry) of dogwood yielded 825 g. of Et<sub>2</sub>O-sol. extract (I) and then a further EtOH-sol. extract (II). Ligroin (b.p.  $30$ — $60^\circ$ ) removed 330 g. from (I); after being shaken with 25% HCl, this was saponified by 3% KOH-EtOH, yielding palmitic and stearic (3 : 7), oleic, and some linolenic acids, a crude hydrocarbon, m.p.  $62$ — $62.5^\circ$ , setting point  $61.2$ — $60.9^\circ$  (probably a ternary mixture containing much  $C_{25}H_{50}$ ), and a phytosterol,  $C_{26}H_{43} \cdot OH$ , +  $H_2O$ , m.p.  $124^\circ$  (acetate, m.p.  $110$ — $111^\circ$ ). The ligroin-insol. part of (I) gives ursolic acid. (II) yields inositol, scyllitol, campherol, gallic acid, and quercitin.

R. S. C.

**Chemical examination of seed of *Abies balsamea* (L.),** Miller. S. R. BENSON and H. N. CALDERWOOD (J. Amer. Chem. Soc., 1936, 58, 523—525).—The seeds contain crude fibre 35.13, protein 9.42, ash 1.88, oleoresin (I) (extracted by 75% EtOH at room temp.) 19.1, and oil (by extraction of the (I)-free endosperm with light petroleum) 11.7% on a  $H_2O$ -free basis. The oil has  $d_{25}^{25}$  0.9279,  $n_D^{25}$  1.4783, f.p.  $-37^\circ$ , acid val. 0.88, I val. (Hanus) 141, sap. val. 185.6, Ac val. 15.4, Reichert-Meissl val. 0.53, Polenske val. 0.21, contains 4.8% of unsaponifiable matter, and consists of the glycerides of stearic (small amount), oleic 33—40, linoleic (II) 54.6—59.7, and linolenic ( $\Delta^{9,12}$ -octadecatrienoic) 3.1—5% acids. (II) appears to be a mixture of two isomerides, which when oxidised (aq.  $KMnO_4$ ) give tetrahydroxystearic acids of m.p.  $152^\circ$  and  $173^\circ$ .

H. B.

***Sium latifolium*, L., seeds.** G. V. PIGULEVSKI and E. L. KARASIK (J. Appl. Chem. Russ., 1936, 9, 284—286).—The seeds contain monoses 3.48, cellulose 21.31, protein 16.84, fatty oils 24.2, essential oils 7.01%. The fatty oil contains 2.2% of saturated acids; linoleic and oleic acids were also identified.

R. T.

**Constitution of certain nutshells. I. Seed-coat of *Bertolletia excelsa* (Brazil nut).** J. G. BOSWELL (Biochem. J., 1936, 30, 971—976).—The



fat of the shell was identical with that of the endosperm, and the hemicellulose and lignin were similar to those of other lignified tissues. The cellulose (furfuraldehyde yield high) was similar to that of peanut hull.

H. G. R.

**Unsaturated acid of kernel fat of "akarittom."**  
—See this vol., 822.

**Chemical constitution and biological properties of lipins in the carrot.** D. ROMOLI-VENTURI and A. PUGLIESE (Biochim. Terap. sper., 1935, 22, 421—457).—The carrot, *Daucus carota*, contained: protein 1.2, fat 0.6, sugar reducing substances 6.5, non-N extractives 3.3, cellulose 1.6%. From the oil there were isolated a phospholipin with vitamin-A and -D reactions and containing Ca, N, and org. P, carotene, and material with the physicochemical properties of -A and -E.

NUTR. ABS. (m)

**Relation between ascorbic acid and carotenoids [in plants].** A. GIROUD, A. R. RATSEMAMANGA, C. P. LEBLOND, CHALOPIN, and RABINOWICZ (Bull. Soc. Chim. biol., 1936, 18, 573—589; cf. this vol., 391).—With few exceptions, in plants where carotenoid compounds are present, significant quantities of vitamin-C are also found.

A. L.

**Lipins of wheat embryo.** I. Fatty acids. II. Unsaponifiable fraction. B. SULLIVAN and C. H. BAILEY (J. Amer. Chem. Soc., 1936, 58, 383—390, 390—393).—I. EtOH-extracts of the fresh germ yield a mixture of carbohydrates containing sucrose, a little glucose, and an unidentified sugar (*acetate*, m.p. 229°,  $[\alpha]_D^{25}$  —16.7° in  $\text{CHCl}_3$ ). The oil (13.68% of germ) has  $d_{20}^{25}$  0.9326,  $n_D^{20}$  1.4800, acid val. 6.95 sap. val. 184, I val. (Rosenmund) 125, SCN-val. 84.7, Ac val. 16.7, Reichert-Meissl val. 0.77, Polenske val. 0.44, Hehner val. 89, ester val. 177.05, and contains 1.44% of sol. acids (as  $\text{Pr}^{\text{C}}\text{CO}_2\text{H}$ ). Hydrolysis gives palmitic 11.76, stearic 3.05, lignoceric 1.19, oleic 28.14,  $\alpha$ -22.32 and  $\beta$ -29.99 -linoleic, and  $\alpha$ -1.83 and  $\beta$ -linolenic acid 1.72%. Little or no fully saturated glyceride is present. Oxidation (1%  $\text{KMnO}_4$ , dil. NaOH) of the mixed unsaturated acids gives di-,  $\alpha$ -, m.p. 155—155.5° (lit. 153—157°), and  $\beta$ -, m.p. 172.5°, -tetra-, and hexa-, m.p. 173° and 201—202°, -hydroxystearic acids.

II. The unsaponifiable matter (4% of oil) consists of about 70% of free (56.2%) and combined (43.8%) sterols (sitosterols, dihydrositosterol, and a sterol with  $\leq 2$  double linkings) and an almost N-free oil containing (cf. Drummond *et al.*, A., 1935, 418) polyene hydrocarbons, xanthophyll, and an alcohol. Determination of the unsaturation of sterols by I vals. (Hanus; Rosenmund) is untrustworthy.

H. B.

**Occurrence of ergosterol and vitamin-D in reindeer lichen.** G. BLIX and H. RYDIN (Upsala Läkeforen Forhandl., N.F., 1932, 37, 333—340; Chem. Zentr., 1935, ii, 1398).—*Cladonia rangiferina*, L. Hoffm., contains small quantities of ergosterol, the content increasing in autumn. The vitamin-D content of the lichen is insignificant.

R. N. C.

**Sulphur-containing pigments of plant origin.** P. HAAS, T. G. HILL, and B. RUSSELL-WELLS (Nature, 1936, 137, 783—784).—The blue compound formed

on drying the actively growing shoots of *Mercurialis perennis* changes on keeping, or more rapidly on heating aq. solutions, into a red product which can be separated into a series of glucosidic pigments containing N and S.

L. S. T.

**Red gossypol.** M. PODOLSKAJA (Biochem. Z., 1936, 284, 401—411).—Cotton seeds contain, in addition to a yellow pigment (I), a red cryst. compound (II),  $\text{C}_{30}\text{H}_{30}\text{O}_8$ , containing 2  $\cdot\text{CO}_2\text{H}$  groups; (I) and (II) are distinguished by pleochroism and extinction and absorption spectra but both yield the same derivative with  $\text{AcOH}$  and  $\text{NH}_2\text{Ph}$ . In EtOH, (II) changes to (I) whilst  $\text{CHCl}_3$  solutions are relatively stable (cf. B., 1935, 732; Schmid and Margulies, A., 1935, 984).

F. O. H.

**Pigment of the flowering currant (*Ribes sanguineum*, vars. *splendens* and *atrosanguineum*).** T. J. NOLAN and T. G. BRADY (Proc. Roy. Irish Acad., 1936, 43, B, 1—12).—The pigment of these two varieties is isolated and identified as antirrhinin (kercyanin) (cf. A., 1930, 967).

E. W. W.

**Mandarin pigment.** II. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1936, 240, 191—194; cf. A., 1934, 121).—The fruit contains carotene, cryptoxanthin in the proportion 1:10—25, xanthophyll, and probably violaxanthin and zeaxanthin.

W. McC.

**Carotenoids of fresh-water algæ.** I. *Euglenarhodone* and other carotenoids of a red *Euglena*. J. FISCHER (Z. physiol. Chem., 1936, 239, 257—269; cf. Kylin, A., 1927, 703).—In addition to chlorophyll-a and -b,  $\beta$ -carotene, esterified zeaxanthin and lutein, xanthophyll, fatty acids (palmitic), and glycerol, *E. heliorubescens* contains two esters of *euglenarhodone* (I),  $\text{C}_{40}\text{H}_{48}\text{O}_4$ , m.p. 227—228° (corr.) [*dioxime* (II) (absorption max. at 512 m $\mu$  in  $\text{C}_5\text{H}_5\text{N}$ ); *tetraoxime*]. (I), which is probably 4:6:4':6'-tetra keto- $\beta$ -carotene, exhibits an absorption band at 480—535 m $\mu$  (max. at 505 m $\mu$ ) in  $\text{C}_5\text{H}_5\text{N}$  and when pure is very stable in air. (I) and (II) yield salts with heavy metals.

W. McC.

**Awobanin and awobanol.**—See this vol., 860.

**Colouring matter in the wood of "Hinoki" tree.** I.—See this vol., 857.

**Tanganyika arrow poisons.**—See B., 1936, 475.

**Chemical investigation of Indian medicinal plants.** V. *Cryptocoryne spiralis*. S. N. CHAKRAVARTI and T. S. KUPPUSWAMY (J. Annamalai Univ., 1936, 5, 269—270).—No org. active principle is detected in the root of this plant.

E. W. W.

**Detection of scopoletin in gelsemium and belladonna roots.** R. FISCHER and H. EHRLICH (Arch. Pharm., 1936, 274, 268—273).—The method of isolating scopoletin from gelsemium and its extract is improved. Micro-sublimation at 125°/12 mm. (2—3 mm. distance) gives stable, m.p. 204—205° (mostly six-sided; angle 137°), and unstable forms, m.p. 193—195° (often twinned; shape variable). Partly purified extracts, but not the powdered roots, give recognisable sublimates.

R. S. C.

**"Lofout," a Saharan lily containing colchicine.** E. PERROT (Compt. rend., 1936, 202,

1088—1089).—All parts of the plant (*Androcymbium gramineum*) contain colchicine (seeds 0.37, bulbs, 0.29, flowers 0.1%). W. McC.

**Alkaloid content of infusions and decoctions of seeds of *Lupinus albus*.** D. TORRISI (Boll. Soc. ital. Biol. sperim., 1935, 10, 807—809).—Prolonged roasting slightly reduces the lupanine (I) content of the seeds, and, by increasing the imbibing power of the seeds, increases the quantity of (I) that can be extracted by decoction or infusion. R. N. C.

**Presence of alkaloids in *Sambucus*.** H. YARDIN (Compt. rend. Soc. Biol., 1936, 122, 155—156).—Choline and other bases giving alkaloid reactions are present in extracts of the bark; cicutine is absent. R. N. C.

**Nicotinamide methiodide.**—See this vol., 862.

**Alkaloids of white hellebore.**—See this vol. 870.

**Alkaloids of *Holarrhena antidysenterica*.** IV. —See this vol., 870.

**Amino-acid content of root nodules.** A. I. VIRTANEN and M. TORNIAINEN (Suomen Kem., 1936, 9, B, 13—14).—Proteins of nodules yielded tryptophan, arginine, tyrosine, aspartic acid (I), and  $(\text{NH}_4)_2$ -acids. Excretion of (I) and lysine by nodules is not due to fission of protein. These  $\text{NH}_4$ -acids represent primary products of N fixation. A. G. P.

**Non-protein-nitrogen of pulses.** K. BHAGVAT and M. SREENIVASAYA (Current Sci., 1936, 4, 651—652).—Differentiation of the non-protein-N indicates that *P. mungo* is very rich in proline, whilst *P. aconitifolius* (I) and *C. arietinum* are rich in arginine and arginine-like compounds. The % of dicarboxylic N in (I) is high. F. A. A.

**Constituents of mulberry leaves, especially proteins.** XI. Distribution of amino-acids in leaf proteins. XII. Solubility of leaf proteins and its application. Y. KISHI (J. Agric. Chem. Soc. Japan, 1936, 12, 348—362, 363—378; cf. A., 1935, 1146).—XI. The N distribution of the protein sol. in 60% EtOH containing 0.3% of NaOH is examined. This fraction constitutes the major portion of the protein in dried leaves and is distinct from globulin, glutelin, and albumin present.

XII. The N distribution of the  $\text{H}_2\text{O}$ -sol. protein of dried leaves differs from that of fresh leaves. The latter consists largely of the alkaline-EtOH-sol. protein obtained from dried leaves. Fractionation of the proteins with other solvents is examined. A. G. P.

**Globulin from the cashew nut (*Anacardium occidentale*).** M. DAMODARAN and T. G. SIVASWAMY (Biochem. J., 1936, 30, 604—608).—The fat-free seed yields 17—18% of a globulin, *anacardein* (N 19.3, S 0.75—0.78%; P nil; Molisch test negative). W. O. K.

**Proteins of Indian foodstuffs.** VII. Globulins of the aconite bean (*P. aconitifolius*, Jacq.). VIII. Heat-coagulation of globulins from *Vigna catieng*, Walp., and *P. aconitifolius*, Jacq. K. BHAGVAT. IX. Digestibility of globulins from cow-pea and aconite bean. K. BHAGVAT and M. SREENIVASAYA (J. Indian Inst. Sci., 1935, A, 18,

137—144, 145—151; 1936, A, 19, 9—18).—VII. The globulins (I) of aconite bean were fractionated by  $\text{COMe}_2$  and  $(\text{NH}_4)_2\text{SO}_4$  pptn. and by a dilution technique.  $\text{CHCl}_3$  extracted more org. P than other lipin solvents.

VIII. The (I) were fractionated by heat-coagulation.

IX. The tryptic digestion of (I), measured by direct N determinations and by a dilatometric technique which gave good agreement, was much slower than that of caseinogen. Preliminary treatment of (I) with pepsin increased the rate of digestion. The viscosimetric determination of digestibility was obscured by ppt. formation. H. D.

**Methylene-blue technique for permanent preparations.** E. C. COLE (Stain Tech., 1936, 11, 45—47).—Tissues stained intravitaly with methylene-blue are best fixed with  $(\text{NH}_4)_2\text{MoO}_4$ , washed in  $\text{H}_2\text{O}$ , and dehydrated with EtOH—Bu<sup>o</sup>OH (1:1) followed by pure BuOH and finally by Me salicylate-xylene (1:4). W. O. K.

**Physical chemistry of silver staining.** L. ZON (Stain Tech., 1936, 11, 53—67).—Silk fibres in aq.  $\text{NH}_3$ -AgOH adsorb Ag, but the amount of Ag deposited in the fibres on addition of  $\text{CH}_2\text{O}$  is > that originally adsorbed. It is concluded that during Ag staining actual deposition of Ag takes place in the tissues as opposed to simple reduction of Ag already adsorbed. Various factors influencing Ag reduction, e.g., adsorption of AgOH and  $\text{NH}_3$ , affinity of Ag for proteins, and the protective power of the gel structures, are discussed and the conclusions reached are applied to modified methods of Ag staining. W. O. K.

**[Differential] staining with safranin and fast-green FCF.** J. A. MOORE (Stain Tech., 1936, 11, 69—70). W. O. K.

**Feulgen reaction.** J. A. DE TOMASI (Stain Tech., 1936, 11, 70).—Improvements in the Feulgen staining reaction (cf. A., 1924, i, 905) are described. W. O. K.

**Micro-extraction apparatus for determining alcohol-ether-soluble lipins.** J. ERDOS and L. POLLAK (Mikrochem., 1936, 19, 245—247).—The material is supported on a filter cone beneath the reflux condenser. J. S. A.

**Sensitivity and stability of the nickel nitroprusside reaction for reduced glutathione.** D. ZIMMET and H. D. FERRIERE (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 44—48).—When one or two drops of a solution containing  $\text{NiCl}_2$  (5 g.) and  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$  (0.5 g.) in  $\text{H}_2\text{O}$  (100 c.c.) are added to a solution of reduced glutathione a rose-violet ppt. is formed, a greenish turbidity being obtained with distilled  $\text{H}_2\text{O}$ . The reaction is highly sensitive, being positive with 0.25 p.p.m., and is not given by  $\text{COMe}_2$ , creatinine, or cysteine. W. O. K.

**Determination of paraldehyde (A) in the tissues and fluids after intravenous injection of this substance, (B) in the respiratory air of paraldehyde-anæsthetised animals.** I. I. NITZESCU, I. D. GEORGESCU, and D. TIMUS (Compt. rend. Biol., 1936, 121, 1657—1659, 1660—1661).—(A) Paraldehyde (I)



is determined by boiling the tissue in 10%  $\text{H}_2\text{SO}_4$ , the depolymerised  $\text{MeCHO}$  being absorbed in aq.  $\text{NaHSO}_3$ , excess of which is determined iodometrically. (I) injected into the dog is stored in most organs, particularly the heart, but a large quantity remains in the blood and is eliminated in the urine and expired air.

(B) The expired air is passed through hot 10%  $\text{H}_2\text{SO}_4$  to depolymerise (I), and then through aq.  $\text{NaHSO}_3$  in which  $\text{MeCHO}$  is absorbed and determined. R. N. C.

**Determination of fats in biological material.** P. A. SESHAN (Indian J. Vet. Sci., 1935, 5, 355—363).—With ragi straw, earthnut cake, and dried faeces, extraction with  $\text{Et}_2\text{O}$  or light petroleum for 16 hr. is inadequate. The extract in the later stages differs materially (e.g., in sap. val. and fatty acid content) from that obtained in the early stage of the extraction. The alkali hydrolysis method also gives unsatisfactory results owing to its destructive nature.

NUTR. ABS. (m)

**Enzymic histochemistry. XVII. Micro-determination of nitrogen.** M. LEVY (Z. physiol. Chem., 1936, 240, 33—42).—A method, applicable to approx. 0.1 mg. of N and based on digestion of the tissue-extract with  $\text{H}_2\text{SO}_4$ — $\text{K}_2\text{SO}_4$ —Se and subsequent nesslerisation, is described. F. O. H.

**Adsorption of nitrogenous substances from aqueous solutions.** D. ACKERMANN and H. G. FUCHS (Z. physiol. Chem., 1936, 240, 198).—Lloyd's reagent (in 5%  $\text{H}_2\text{SO}_4$ ) is as effective as, and in some ways preferable to, phosphotungstic acid as an adsorbent for substances containing N. Adsorbed material is recovered by long-continued elution with aq.  $\text{Ba}(\text{OH})_2$ . W. McC.

**Micro-determination of uric acid.**—See this vol., 873.

**Microchemical detection of arsenic in forensic investigations.** A. MARTINI and B. BERISSO (Mikrochem., 1936, 19, 181—182).—Animal tissues etc. are decomposed with alkaline  $\text{H}_2\text{O}_2$ . The solution is acidified with  $\text{HCl}$ , and treated with conc. aq.  $\text{NaI}$  + a drop of quinoline. In presence of  $> 4 \times 10^{-10}$  g. of As a microscopically characteristic yellow cryst. ppt. is obtained. Alternatively, 20% aq.  $\text{CsCl}$ , saturated aq.  $\text{Na}_2\text{HPO}_4$ , and  $\text{C}_5\text{H}_5\text{N}$  are added, giving a characteristic ppt. J. S. A.

**Determination of boron in soils and plants.** E. V. BOBKO and T. V. MATVEEVA (J. Appl. Chem. Russ., 1936, 9, 532—540).—Bertrand and Agulhon's method (A., 1914, ii, 217) is preferred. The B content of moist is < that of dry soils. The B content of apple leaves is < that of the blossoms, in which the stigmata are richest in B. The B content of plants may be increased 3—4-fold by raising the B content of the nutritive solution. R. T.

**Determination of halogen absorption of oils.**—See B., 1936, 461.

**Bromine in the body.** H. UCKO (Biochem. J., 1936, 30, 992—1000).—A colorimetric method for determination of Br and of the Br and Cl content of

various tissues (normal and after Br intake) is described. H. G. R.

**Determination of bromine.** G. E. BATRAK (Med. exp. Ukraine, 1935, No. 2, 100—104).—In the colorimetric method using Schiff's reagent, the depth of colour of the lilac rings developing when drops of aq.  $\text{Cl}_2$  are added is measured by ocular observation.

NUTR. ABS. (m)

**Determination of iodine in biological material.** G. J. FASHENA and V. TREVORROW (J. Biol. Chem., 1936, 114, 351—355; cf. A., 1935, 1182).—Reduction of  $\text{IO}_3^-$  by  $\text{HPO}_3^{2-}$  is increased by dilution of the reaction mixture. H. D.

**Ionisable iron in foods.** L. SHACKLETON and R. A. McCANCE (Biochem. J., 1936, 30, 582—591).—The ionisable Fe in various foodstuffs, determined by the 2:2'-dipyridyl method and expressed as a % of the total Fe, appears more const. and characteristic of the foodstuff than the total Fe. Cereals contain 75—100, vegetables and fruits 50—100, beef and mutton 10—25, other flesh foods > 25, most white fish 100, and herring, mackerel, and sardines about 60% of their Fe in ionised form. W. O. K.

**Micro-determination of potassium in substances of biological origin.** A. CAHEN (Bull. Soc. chim., 1936, [v], 3, 640—643).—The substance is oxidised by  $\text{HNO}_3$ — $\text{HClO}_4$ , and K obtained as  $\text{K}_2\text{PtCl}_6$  by evaporation with  $\text{PtCl}_4$ .  $\text{K}_2\text{PtCl}_6$  is reduced by  $\text{H}_2$ , and the KCl titrated by standard methods. The error is < 2%. E. S. H.

**Micro-determination of potassium.**—See this vol., 812.

**Colorimetric determination of inorganic sulphate in serum and urine.** T. V. LETONOFF and J. G. REINHOLD (J. Biol. Chem., 1936, 114, 147—156).—A method based on the colour-producing reaction between benzidine sulphate and Na  $\beta$ -naphthoquinone-4-sulphonate is described.  $\text{PO}_4^{3-}$  and proteins are removed simultaneously by uranyl acetate prior to the analysis. The inorg. S of normal human serum is approx. 1.04 mg. per 100 c.c. Additional  $\text{SO}_4^{2-}$  is liberated when serum is treated with  $\text{CCl}_3\text{CO}_2\text{H}$ .  $\text{SO}_4^{2-}$  added to serum is rendered partly non-precipitable by benzidine. J. N. A.

**Determination of sulphur for sulphur-balance experiments with cattle and sheep.** F. J. WARTH and T. S. KRISHNAN (Indian J. Vet. Sci., 1935, 5, 210—215).—The method, which is applicable to urine, faeces, and foodstuffs, consists in oxidation with  $\text{HNO}_3$  followed by fusion of the evaporated filtrate with  $\text{NaOH}$  in a Ag basin. NUTR. ABS. (m)

**Sulphur metabolism. Sulphur and protein metabolism in infants and children.** A. BLAZSO (J. Physiol. Path. gén., 1935, 33, 1076—1092).—S is determined in urine, faeces, serum, and milk, by oxidising with fuming  $\text{HNO}_3$  and removing phosphates with  $\text{Ca}(\text{OH})_2$ . After neutralisation, excess of  $\text{BaCrO}_4$  is added and then  $\text{Ca}(\text{OH})_2$  to ppt. the excess. The  $\text{H}_2\text{CrO}_4$  liberated is determined colorimetrically in the filtrate with *s*-diphenylcarbazide. NUTR. ABS. (m)

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

AUGUST, 1936.

### General, Physical, and Inorganic Chemistry.

**Dissymmetry of intensity in the longitudinal Stark effect of the Balmer series.** H. BOMKE (Physikal. Z., 1936, 37, 417—427).—The effect of pressure and application of a magnetic field on the dissymmetry of intensity of the longitudinal Stark components of the Balmer series has been investigated. The dissymmetry is different for the different components and varies with pressure, being a max. at approx.  $8 \times 10^{-3}$  mm. An additional magnetic field affects the intensity distribution in a manner dependent on the relative directions of the electric and magnetic fields. A. J. M.

**Dependence of polarisation of light emission of positive rays [on pressure etc.].** J. STARK and M. SCHÖN (Physikal. Z., 1936, 37, 431—435).—The effect of pressure, nature of gas, and the type of series of the lines emitted by the positive rays on the polarisation of the light from such rays has been investigated. The polarisation of the  $H_\alpha$  and lines obtained from H positive rays varies considerably with the pressure, and with the nature of the gas in the tube, being much smaller for H positive rays in  $O_2$  and in  $N_2$  than in He. The polarisation of He lines of different series, obtained from He positive rays in  $H_2$ , was determined. A. J. M.

**$1X$ -level of the hydrogen molecule.** G. H. DIEKE (Nature, 1936, 137, 944—945).—Observations on the near infra-red spectra of  $H_2$ , HD, and  $D_2$  are discussed. Effective moments of inertia are 0.871, 1.156, and  $1.725 \times 10^{-40}$ , respectively, and the effective internuclear distance is  $1.019 \times 10^{-8}$  cm. L. S. T.

**Emission spectrum of  $D_2$  in the extreme ultra-violet.** C. R. JEPPESEN (Physical Rev., 1936, [ii], 49, 797—803; cf. A., 1934, 575).—Full data are tabulated and analysed for 37 bands in the  $2p^1\Sigma-1s^1\Sigma$  system and 29 bands in the  $2p^1\Pi-1s^1\Sigma$  system photographed in the extreme ultra-violet with a grazing-incidence vac. spectrograph. Consts. for the three observed electronic states of the mol. are given and data are compared with those for  $H_2$ . Electronic shifts of 4 and 23  $cm^{-1}$  are observed in the respective systems. N. M. B.

**Simultaneous action of electrical and magnetic fields on line spectrum of helium.** W. STEUBING (Sitzungsber. preuss. Akad. Wiss., 1935, 150—159; Chem. Zentr., 1935, ii, 1830).—Data are given for parallel and perpendicular observation under parallel and crossed fields for the region 3800—5100 Å. J. S. A.

**Effect of magnetic field on the polarisation of stationary and moving light emission of positive rays.** J. STARK, R. RITSCHL, and H. BOMKE (Physikal. Z., 1936, 37, 427—431).—A magnetic field up to 30,000 gauss exerts no appreciable effect on the polarisation of the stationary light emission of He lines in the transverse Stark effect. There is, however, some effect on the polarisation of the moving light emission for both H and He positive rays. A. J. M.

**Zeeman effect of induced lines in the helium spectrum.** L. JANSON (Bull. Acad. Polonaise, 1935, A, 16—21).—Combined Zeeman and Stark effects of the forbidden He lines  $2^1P_1-5^1P_1$ ,  $2^1P_1-5^1F_3$ , and  $2^1P_1-5^1G_4$  are described. O. D. S.

**Band spectrum of sulphur.** E. OLSSON (Z. Physik, 1936, 100, 656—664).—The energy of dissociation of the ground level is probably  $<3.6$  volts. A. B. D. C.

**Nebular spectra due to elements of the second period.** H. A. ROBINSON (Nature, 1936, 137, 992).—The singlet systems of S III and K VI have been partly classified from new data in the Schumann region which also show the presence of S III and A V in nebulae. L. S. T.

**Band spectra of halogens in point discharge.** A. CAMPETTI (Atti R. Accad. Sci. Torino, 1934—1935, 70, I, 618—631; Chem. Zentr., 1935, ii, 2026).—The emission spectra of the point discharge in Cl, Br, and I consist of 2, 4, and 3 somewhat ill-defined bands, respectively. The position of the bands moves from short to longer  $\lambda$ , and their breadth decreases regularly from Cl to I, following the decrease in ionisation potential. The spectra are considered to be recombination spectra between ions, or between ions and neutral atoms. J. S. A.

**Absorption spectrum of rare gases at the limit of the argon spectrum.** U. FANO (Nuovo Cim., 1935, [ii], 12, 154—161; Chem. Zentr., 1935, ii, 1830).—Theoretical. The intensities in the absorption spectrum, in presence of superposed Rydberg terms, are calc. Agreement is found with Beutler's experimental data (A., 1935, 271). J. S. A.

**Na I-like spectra of the elements potassium to copper, K IX—Cu XIX.** B. EDLÉN (Z. Physik, 1936, 100, 621—635). A. B. D. C.

**New type of absorption bands of potassium vapour.** B. K. CHAKRABORTY (Indian J. Physics, 1936, 10, 155—162).—In the absorption spectrum of K vapour photographed in the range 4100—2800 Å. at temp.  $>600^\circ$  and pressures  $>20$  cm. of Hg, each



principal series line from 4047 to 2894 Å. is associated with diffuse lines on both the short- and long- $\lambda$  sides. The lines corresponding with the 4th, 5th, and 6th members of the principal series form a regular series of band heads; full data and a provisional classification are tabulated, and a probable explanation is given. The bands have no fine structure. A new ultra-violet absorption band extending over 2950–2890 Å. was observed at pressures beyond 20 cm. N. M. B.

**Structure of the *D* and *F* terms in potassium.** O. MASAKI and K. KOBAYAKAWA (J. Sci. Hiroshima Univ., 1936, A, 6, 217–226).—The combined doublet of the first subordinate series and the Bergmann series of K are analysed. From a consideration of the vibrational distances in the Bergmann series, and of the intensity ratios in the doublet, it is shown that the *F* and *D* terms are all inverted. W. R. A.

**Structure of the spectrum of neutral cobalt.** M. A. CATALAN and M. T. ANTUNES (Anal. Fis. Quím., 1936, 34, 103–145).—An extension of earlier work (A., 1928, 338). The classification of the spectrum of Co I is critically considered and 96 new levels are discovered. The spark limit determined by three methods is 63,312–14 cm.<sup>-1</sup> F. R. G.

**Arc spectrum of cobalt between 2450 and 1960 Å.** M. T. ANTUNES (Anal. Fis. Quím., 1935, 33, 319–349).—The lines observed have been compared with those previously recorded and are assigned to Co I and Co II (cf. this vol., 769). F. R. G.

**Spectrum of doubly-ionised zinc.** K. C. MAZUMDER (Indian J. Physics, 1936, 10, 171–187; cf. Basu, A., 1935, 1437; Bloch, A., 1934, 1051).—Full data and classifications for 222 new lines of Zn III, in the range 2600–400 Å., and identifications of 53 new terms are tabulated. Term vals. are calc. The ionisation potential is approx. 40 volts. N. M. B.

**Arc and spark spectra of niobium.** W. F. MEGGERS and A. S. KING (J. Res. Nat. Bur. Stand., 1936, 16, 385–419).—The  $\lambda\lambda$  of 5700 lines of the arc and spark spectra of Nb in the region 2100–12,000 Å. are recorded, with an average probable error <0.005 Å. From comparisons of intensity the lines are separated into the Nb I, Nb II, Nb III, and Nb IV spectra. J. W. S.

**Measurement of the spark spectrum of molybdenum between 2195 and 2000 Å.** M. A. CATALAN and J. H. ROMAN (Anal. Fis. Quím., 1936, 34, 146–164).—Mo powder on C electrodes was used. Known lines and 181 new lines between 2195 and 2081 Å. are recorded, and 156 lines are recorded between 2081 and 2000 Å. The lines of Mo I are separated from those of Mo II. F. R. G.

**Hyperfine structure of the resonance lines of silver.** D. A. JACKSON and H. KUHN (Nature, 1936, 137, 1030).—The nuclear spin of <sup>107</sup>Ag and <sup>109</sup>Ag is  $\frac{1}{2}$ . L. S. T.

**Influence of temperature on the absorption of excited cadmium vapour containing neon.** O. MASAKI, Y. MORIMOTO, and K. SAKUMA (J. Sci. Hiroshima Univ., 1936, A, 6, 227–236).—The absorption of the lines 5086, 4800, and 4678 Å., corresponding with <sup>23</sup>P.,  $^0-2^3S_1$ , is investigated. W. R. A.

**Anomalies in the fine structure of the first spark spectrum of iodine.** K. MURAKAWA (Nature, 1936, 137, 1030–1031). L. S. T.

**New lines in the ultra-violet spectrum of atomic iodine.** J. H. McLEOD (Physical Rev., 1936, [ii], 49, 804–807; cf. Kalia, A., 1935, 272).—Data are tabulated for 250 lines in the range 1900–800 Å. for the arc and first spark spectrum of I photographed with a vac. grating spectrograph. The spectrum was produced in A–I mixture and, eliminating a fluorite window, I was prevented from entering the spectrograph by an outward flow of A circulated through the whole system. N. M. B.

**Mechanical nuclear moment of caesium.** T. FOLSCHIE (Naturwiss., 1936, 24, 297).—Investigation of the Paschen-Back effect with the hyperfine structure of the Cs resonance line  $\lambda$  8943 Å. gives  $\nu = (7/2)h/2\pi$ . A. J. M.

**Spectrum of tungsten I.** F. POGGIO (Anal. Fis. Quím., 1935, 33, 171–202).—The arc spectrum of W between 1980 and 2248 Å. has been measured and new lines observed between 2248 and 8500 Å. One even and 54 odd levels are calc., and from these and the levels calc. by Laporte (A., 1926, 1071), 1066 lines are classified. F. R. G.

**Emissivity of tungsten as a function of wavelength from 0.23–2.0  $\mu$  in the region of temperature 1600–3000° abs.** ANON. (Physica, 1936, 3, 561–562).—Combined data are given in tabular form. The coeffs. determined for W of different origins and heat-treatments show no systematic differences. J. W. S.

**Hyperfine structure of platinum isotopes. II. Hyperfine structure scheme for the platinum isotope 195 and its mechanical nuclear moment.** (FRL.) B. JAECKEL (Z. Physik, 1936, 100, 513–528; cf. this vol., 654).—The nuclear spin of <sup>195</sup>Pt is  $\frac{1}{2}$ . A. B. D. C.

**Luminous discharges [in a gas] at pressures less than 10<sup>-1</sup> mm. of mercury in a magnetic field.** T. V. IONESCU (Compt. rend., 1936, 202, 1842–1843).—Longitudinal magnetic fields >100 gauss cause a violet discharge between an annular grid and the plate of an ionisation tube. J. G. A. G.

**Spectral line intensity in the far ultra-violet and estimation of temperatures and pressures in vacuum arc spectra.** H. A. ROBINSON (Z. Physik, 1936, 100, 636–643). A. B. D. C.

**Electron temperature and daily variation in the *F*-region of the ionosphere.** J. FUCHS (Naturwiss., 1936, 24, 429). A. J. M.

**Corona rotation effect in different gases at various pressures.** A. GÜNTHER-SCHULZE and H. BETZ (Z. Physik, 1936, 100, 269–272).—This effect has been studied for air, CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. A. B. D. C.

**Spectroscopic investigations on flames in relation to ionisation potentials.** M. PIERUCCI and L. B. SILVA (Nuovo Cim., 1935, [ii], 12, 269–272; Chem. Zentr., 1935, ii, 2343).—In a mixture, the spectrum of the element with the lowest ionisation potential *P* is excited preferentially; where the

difference is great, the spectrum of the element of lowest  $P$  appears alone and intensified. J. S. A.

Dark bands in the spectra from acoustic and optical double gratings. P. CERMAK and H. SCHOENECK (Ann. Physik, 1936, [v], 26, 465—473).—The spectrum of light which has passed through two similar gratings shows dark bands of which the separation is  $\propto$  grating const. and inversely  $\propto$  distance apart of the gratings and the order of the spectra. Similar results are obtained with ultrasonic waves acting as gratings. A. J. M.

Method for obtaining soft X-rays in gases and particularly the  $K$  spectrum of neon. J. M. BACKOVSKY (Compt. rend., 1936, 202, 1671—1672).—A method for determining the  $K$  spectrum of Ne, using Al electrodes and a layer of Li borate on the anticathode, is described.  $\lambda$  for the ray  $K\alpha_{1,2}$  is 14.61 Å., in good agreement with the calc. val. M. S. B.

Intensity of  $L$  lines of gold. L. PINCHERLE (Nuovo Cim., 1935, [ii], 12, 162—170; Chem. Zentr., 1935, ii, 1658).—The intensity of a Röntgen line corresponding with a transition  $m \rightarrow n$  depends on (1) the probability of excitation of the state  $n$ , (2) the Auger effect, (3) the probability of the spontaneous transitions. The intensities so calc. for the Au  $L\alpha_1$ ,  $L\alpha_2$ , lines agree with the similar experimental vals. for Pt. J. S. A.

Number of  $L$ -dispersion electrons. H. NITKA (Physikal. Z., 1936, 37, 445—446).—The effective no. of dispersion electrons in the  $L_I$ ,  $L_{II}$ , and  $L_{III}$  shells can be obtained from the  $L$ -partial absorption coeffs. for X-rays determined by Schwarz (this vol., 262). The vals. obtained are in good agreement with those of Hönl (Z. Physik, 1933, 84, 1). A. J. M.

Form of the Compton line. G. BURKHARDT (Ann. Physik, 1936, [v], 26, 567—584).—The form of the Compton line is calc. from the impulse distribution by means of the semi-classical corpuscular process of du Mond. The impulse distribution is calc. according to the at. models of Thomas and Fermi, Schrödinger and Slater, and Hartree, respectively. The effect of the binding of the electrons and of relativity is to cause a slight asymmetry and displacement of the max. of the line. The calculations are compared with Kappeler's experimental values for Ne. Agreement is good except when the calculation is based on the Thomas-Fermi model. A. J. M.

Auger effects. L. PINCHERLE (Nuovo Cim., 1935, [ii], 12, 81—92; Chem. Zentr., 1935, ii, 1658).—Theoretical. The probability of Auger transitions with excited  $K$  and  $L$  levels is calc. as of the same order of magnitude. Calc. vals. for the fluorescence yield agree with experimental vals. J. S. A.

Determination of the Townsend ionisation coefficient  $\alpha$  for pure argon. A. A. KRUTHOF and F. M. PENNING (Physica, 1936, 3, 515—533).—An apparatus which can be evacuated at high temp. is described and has been used for the determination of  $\alpha$  for A between  $E/p_0$  vals. of 5—400 ( $E$ =electric field in volts per cm.;  $p_0$ =mm. gas pressure reduced to 0°). For low  $E/p_0$  vals.  $\alpha$  is  $\ll$  indicated by Avres (A., 1923, ii, 111). J. W. S.

Determination and analysis of the thermionic constants of thoriated tungsten. A. ROSE (Physical Rev., 1936, [ii], 49, 838—847).—The slopes and intercepts of Richardson plots were obtained for states of activation from a flashed to a completely thoriated surface, and for applied fields up to  $3 \times 10^4$  volts per cm. Observations on the work function, effect of positive ion bombardment, ageing, proportionalities, emission lag effects, and temp. dependence of the anomalous Schottky effect are described and analysed in terms of a patch distribution theory of adsorbed atoms. N. M. B.

Photo-electron effect of white-hot metals. C. M. I. VERCELLI (Atti R. Accad. Sci. Torino, 1935, 70, I, 462—471; Chem. Zentr., 1935, ii, 2180).—Theoretical. J. S. A.

Energy transmission by high-energy electrons. W. F. G. SWANN (Physical Rev., 1936, [ii], 49, 829—830).—Mathematical. Oppenheimer's postulate (cf. A., 1935, 278) follows from previous results (cf. A., 1934, 236). N. M. B.

Velocity distribution of electrons in gas-discharges in helium. J. A. SMIT (Physica, 1936, 3, 543—560).—Mathematical. The velocity distribution of electrons in gaseous discharges is derived and the parts played by each factor changing the velocity of an electron in maintaining this distribution are deduced. Numerical data are calc. for discharges in He. J. W. S.

Time coincidence of secondary rays in the Compton effect. A. PICCARD and E. STAHEL (Naturwiss., 1936, 24, 413—414).—An experiment is described which shows that there is no delay in the emission of secondary electrons in the Compton effect (cf. Shankland, this vol., 265). A. J. M.

At. wt. of hydrogen. E. MOLES (Anal. Fis. Quim., 1935, 33, 721—728).—A revision, taking account of the known amounts of D, in the  $H_2$  used for at. wt. determination. The most probable conversion factor between the chemical scale of at. wts. based on  $O_2$  containing the normal mixture of isotopes and the physical scale of nuclear masses based on  $^{16}O$  is considered to be 1.00022. At. wt. determinations (cf. A., 1925, ii, 346) employing electrolytic  $H$ , probably containing 1 part of D, in 30,000 give the accepted average val. of 1.0078, whence the nuclear mass of H is  $1.0080 \pm 0.00005$ , slightly  $<$  the val. from mass spectroscopy data (Aston, A., 1935, 677). The most probable D:H ratio in distilled  $H_2O$  is considered to be 1:5500 so that the "normal" at. wt. of H (i.e., that of the mixture of H and D in  $H_2O$ ) is  $1.0082 - 0.00005$ , in agreement with vals. previously obtained (cf. Thomsen, A., 1896, ii, 244) for H prepared by the action of metals on acid or alkaline solutions. F. R. G.

Element 87. H. HULTBEI (Compt. rend., 1936, 202, 1927—1929).—Lines attributed to 87  $L\alpha_1$  and 87  $L\alpha_2$  were observed in the alkali concentrate from pollucite. H. J. E.

Isotope effect in evaporation of lithium, potassium, and rubidium ions. A. K. BREWER J. Chem. Physics, 1935, 4, 350—353).—A correction for change in abundance ratios during evaporation of the



source is required in computing the at. wt. of Li, but not for K or Rb. The final vals. are: Li 6.939, K 39.094, Rb 85.46 (cf. this vol., 400). F. L. U.

**Existence of  $^{22}\text{Na}$ .** A. K. BREWER (Physical Rev., 1936, [ii], 49, 856).—Mass spectra observations show a small peak at 22, and approx. abundance ratio  $^{23}\text{Na}/^{22}\text{Na}=5000\pm500$ . N. M. B.

**Isotope corrections in molecular spectra.** J. H. VAN VLECK (J. Chem. Physics, 1936, 4, 327—338; cf. A., 1935, 9).—Small corrections due to various causes are calc. F. L. U.

**Radioactivity of glasses.** A. TROST (Z. Physik, 1936, 100, 549—552).—Counters moulded into glasses show the presence of a readily absorbed radioactive radiation. A. B. D. C.

**Measurement of strong polonium preparations by their ionisation in pure nitrogen.** R. GROSSMANN (Sitzungsber. Akad. Wiss. Wien, 1934, IIA, 143, 563—577; Chem. Zentr., 1935, ii, 1918—1919).—In pure  $\text{N}_2$  the negative carriers are free electrons, and all ions are readily collected by moderate fields. H. J. E.

**Supposed radioactivity of lanthanum, yttrium, and antimony.** Z. KLEMENSIEWICZ and Z. BODNAR (Acta. phys. polon., 1934, 3, 187—190; Chem. Zentr., 1935, ii, 2492—2493).—La and Y compounds show some activity, which is traced to admixed Ac and Th materials. Sb compounds are completely inactive. J. S. A.

**Irregular distribution of thorium-C''.** J. ZIRKLER (Z. Physik, 1936, 100, 203—204).—A fractional separation experiment showed linear distribution of Th-C'' according to the  $\text{Th}^{100}$  mass (cf. this vol., 282, 540). A. B. D. C.

**Emission of  $\gamma$ -radiation during the  $\beta$ -decay of nuclei.** J. K. KNIPP and G. E. UHLENBECK (Physica, 1936, 3, 425—439).—Mathematical. It is shown that most, if not all, of the  $\gamma$ -radiation accompanying disintegration of Ra-E arises from the creation of the electron and its loss of energy as it leaves the nucleus. J. W. S.

**Determination of the energy distribution of recoil atoms during  $\beta$  decay and the existence of the neutrino.** A. I. LEPIENSKI (Proc. Camb. Phil. Soc., 1936, 32, 301—303).—The results suggest that neutrinos are probably emitted during  $\beta$  decay. T. G. P.

**Intensity of the  $\gamma$ -rays emitted by the active deposit of thorium.** F. OPPENHEIMER (Proc. Camb. Phil. Soc., 1936, 32, 328—335).—The energies of the  $\gamma$ -rays from Th-C and Th-Pb have been determined. The excitation probabilities of Th-C and its products have been calc., and a level system for Th-Pb is proposed. T. G. P.

**Scattered and secondary radiation of hard  $\gamma$ -rays.** W. GENTNER (Z. Physik, 1936, 100, 445—455).—Scattered and secondary radiation from Th-C'' rays have been determined for Al and Pb. A. B. D. C.

**Efficiency of neutrons for  $\gamma$ -ray excitation.** Appendix: recoil radiation of slow neutrons. R. FLEISCHMANN (Z. Physik, 1936, 100, 307—320).—The intensity of  $\gamma$ -radiation excited in Cd, Cu, Fe, H.,

Pb, and Ag by slow neutrons has been determined (cf. this vol., 131). A. B. D. C.

**Nuclear spectra of some light atoms.** W. BOTHE (Z. Physik, 1936, 100, 273—285).—Energy spectra of electrons released by nuclear  $\gamma$ -radiation were obtained for Li, F, and Be. A. B. D. C.

**Artificial radioactivity giving continuous  $\gamma$ -radiation.** E. C. G. STUECKELBERG (Nature, 1936, 137, 1070—1071).—Every emission of positive electrons should be accompanied by weak  $\gamma$ -radiation, but in only 1 out of 137 cases of decay is  $\gamma$ -radiation emitted. L. S. T.

**Apparently general rule for nuclear transformations.** B. WALTER (Naturwiss., 1936, 24, 429—430).—The rule states that where the new element formed in a nuclear transformation is an isotope of the bombarded one, slow neutrons (e.g., neutrons which have passed through  $\text{H}_2\text{O}$ , paraffin, etc.) possess sufficient energy to bring about the change. When, however, the new element possesses a different at. no. from the bombarded one, rapid neutrons are necessary. A. J. M.

**$\beta$ -Ray spectra of several slow neutron-activated substances.** E. R. GAERTTNER, J. J. TURIN, and H. R. CRANE (Physical Rev., 1936, [ii], 49, 793—797).—In, Ag, Rh, Mn, and Dy have been rendered radioactive by exposure to slow neutrons from a 200 millicurie Rn-Be source surrounded by paraffin, and their  $\beta$ -ray spectra obtained by the cloud-chamber method. The plots of energy distributions were transformed into straight lines on the Konopinski-Uhlenbeck formula and extrapolated to find the upper energy limits, in good agreement with theory; these limits are In (54 min. period) 1.3, In (13 sec. period) 3.2, Ag 2.8, Rh 2.8, Mn 2.8, and Dy 1.4 m.e.v. N. M. B.

**Lightest nuclei.** H. DOLCH (Z. Physik, 1936, 100, 401—439).—Theoretical. Mass defects of nuclei of masses 2, 3, and 4, and the collision cross-section for disintegration of  $\text{D}^+$  by  $\text{D}^1$  and for elastic collision of neutrons on protons are calc. A. B. D. C.

**Disintegration of  $^7\text{Li}$  bombarded by slow protons.** H. D. DOOLITTLE (Physical Rev., 1936, [ii], 49, 779—782).—The no. of  $^7\text{Li}$  atoms disintegrated by protons in the energy range 23.6—72.5 e.k.v. was determined; results agree satisfactorily with those calc. from the probability formula, and are compared with those at higher voltages (cf. Herb, A., 1935, 1186). There are no indications of resonance or of a min. voltage. N. M. B.

**Variation of range with angle of the disintegration  $\alpha$ -particles of  $^7\text{Li}$ .** A. ROBERTS, T. ZANDSTRA, R. CORTELL, and F. E. MYERS (Physical Rev., 1936, [ii], 49, 783—788).—The range of  $\alpha$ -particles from  $^7\text{Li}$  under 200 and 240 kv. proton bombardment was measured and plotted for various angles relative to the incident proton beam. Results agree with the predictions of the principles of conservation of energy and momentum when the straggling due to the penetration of the target by the proton beam is taken into account, and show that if  $^4\text{He}$  is formed and disintegrates into two  $\alpha$ -particles without the emission of a  $\gamma$ -ray its mean life is  $>3\times10^{-14}$  sec. N. M. B.

**Structures of light nuclei and the existence of Be.** W. H. WELLS and E. L. HILL (Physical Rev., 1936, [ii], 49, 858).—Mechanisms for dispensing with  ${}^6\text{Be}$  as a stable nucleus, for the probable structures of  ${}^{10}\text{B}$  and  ${}^{11}\text{B}$ , and for disintegration reactions giving the observed two-homogeneous groups of  $\alpha$ -particles are proposed and discussed. N. M. B.

**Variation of wave-length and the nuclear photo-effect of beryllium.** R. FLEISCHMANN and W. GENTNER (Z. Physik, 1936, 100, 440—444).—The  $\gamma$ -ray efficiency for disintegration of Be decreases with increasing quantum energy. A. B. D. C.

**Excitation of the  ${}^{17}\text{O}$  nucleus.** G. STETTER (Z. Physik, 1936, 100, 652—655).— ${}^{17}\text{O}$  in an unstable level is obtained from disintegration of N by Ra-C'. A. B. D. C.

**New radioelement.** M. DANYSZ and M. ŻYŹ (Acta. phys. polon., 1934, 3, 485—492; Chem. Zentr., 1935, ii, 2019).—By the irradiation of most elements with  $\alpha$ -rays from Po or Rn, an activity of half-life 1 min. is produced, which is traced to the N of the surrounding air. The action is considered to be  ${}^1_0\text{N} + {}^4_2\text{He} = {}^5_0\text{F} + {}^1_0\text{n}$ , followed by  ${}^{17}\text{F} = {}^{17}_8\text{O} + e^+$ . The same activity is produced intensely by bombardment of  $\text{NaN}_3$ . J. S. A.

**Transmutation of platinum by deuterons.** J. M. CORK and E. O. LAWRENCE (Physical Rev., 1936, [ii], 49, 788—792).—Chemical separation of the radioactive substances induced in Pt by 5 mv. deuterons and analysis of the decay curves show that radioactive isotopes, probably  ${}^{193}\text{Pt}$  and  ${}^{197}\text{Pt}$  and  ${}^{194}\text{Ir}$  and  ${}^{196}\text{Ir}$ , are formed with approx. decay periods 28 min., 8.5 hr., 49 min., and 14.5 hr., respectively. The first pair are formed probably by neutron capture and the second pair by reactions involving deuteron capture and  $\alpha$ -particle emission. The transmutation functions for the reactions leading to Ir isotopes show max. indicating resonance penetration of the Pt nucleus by the deuteron. N. M. B.

**Correlation of nuclear disintegration processes.** R. D. EVANS and S. M. LIVINGSTON (Rev. Mod. Phys., 1935, 7, 229—236).—A summary and discussion. CH. ABS. (e)

**Nuclear chemistry, the neutron, and artificial radioactivity.** W. D. HARKINS (Science, 1936, 83, 533—543).—A lecture. L. S. T.

**Exact measurement of cosmic rays by the uranium compensation method.** K. H. STRAUSS (Z. Physik, 1936, 100, 237—249).—This method utilising  $\beta$ -rays of U is well adapted to prolonged measurement of cosmic-ray intensities. A. B. D. C.

**Statistical derivation of barometer effect on cosmic radiation.** J. A. PRIEBSCH (Sitzungsber. Akad. Wiss. Wien, 1935, II, 144, 65—75; Chem. Zentr., 1935, ii, 1829). J. S. A.

**Variation of cosmic ray intensity with height in the atmosphere.** S. ZIEMECKI and K. NARKIEWICZ-JODKO (Nature, 1936, 137, 944). L. S. T.

**Wilson chamber studies of penetrating radiation on the Hafelkar (2300 m.), near Innsbruck.**

F. RIEDER (Sitzungsber. Akad. Wiss. Wien, 1934, 143, 499—502; Chem. Zentr., 1935, ii, 2493—2494). J. S. A.

**Cosmic-ray measurements at great water depths and radioactivity of dry batteries.** E. REGENER (Z. Physik, 1936, 100, 286—292).—Radioactive impurities in the dry batteries used for Lake Constance measurements (A., 1932, 440) gave false residual ionisation. A. B. D. C.

**Cosmic-ray observations on the Atlantic Ocean.** K. NARKIEWICZ-JODKO and S. ZIEMECKI (Acta. phys. polon., 1934, 3, 297—300; Chem. Zentr., 1935, ii, 2021—2022). J. S. A.

**Soft recoil radiation effects of cosmic rays.** R. HOSEMANN (Z. Physik, 1936, 100, 212—220).—Recoil radiation from cosmic-ray bursts is absorbed by a few mm. of Al. A. B. D. C.

**Properties of cosmic corpuscles of the penetrating group.** P. AUGER and A. ROSENBERG (Compt. rend., 1936, 202, 1923—1925).—After traversing 30 m. of  $\text{H}_2\text{O}$  the cosmic radiation is reduced to a group of ultra-penetrating rays, which produce secondary rays of low penetrating power (several mm. of Pb). H. J. E.

**Specific ionisation of cosmic-ray particles as determined by Geiger-Müller counter efficiency.** W. E. DANFORTH and W. E. RAMSEY (Physical Rev., 1936, [ii], 49, 854).—Efficiency measurements may be used for determining primary ionisation along the path of the particles. Results for air-filled and  $\text{H}_2$ -filled counters at different gas pressures are approx. intermediate between available data by other methods. N. M. B.

**Neutrons and other heavy particles in cosmic radiation of the stratosphere.** L. H. RUMBAUGH and G. L. LOCHER (Physical Rev., 1936, [ii], 49, 855).—Examination of free and shielded photographic plates from a stratosphere balloon shows no primary  $\alpha$ -particles, but proton tracks due to recoils from neutron collisions, indicating that neutrons are primary constituents of cosmic radiation. Results are analysed and discussed. N. M. B.

**Critical review of the present theories of the active modification of nitrogen.** M. N. SAHA and L. S. MATHUR (Proc. Nat. Acad. Sci. India, 1936, 6, 120—127).—Existing theories are regarded as inadequate. It is concluded that at. N has nothing to do with the active modification and that the mol. of the latter is raised a state composed of two  ${}^2\text{D}$  atoms probably located at 9.77 volts. N. M. B.

**Reconstruction of the mass-defect curve and the stability of  ${}^9\text{Be}$ .** N. K. SAHA (Proc. Nat. Acad. Sci. India, 1936, 6, 110—119).—The mass-defect curve for the nuclei  ${}^4\text{He}$ ,  ${}^6\text{Be}$ ,  ${}^{12}\text{C}$ ,  ${}^{16}\text{O}$ ,  ${}^{20}\text{Ne}$ ,  ${}^{24}\text{Mg}$ ,  ${}^{28}\text{Si}$ ,  ${}^{32}\text{S}$ ,  ${}^{36}\text{Ar}$ , and  ${}^{40}\text{Ca}$  is constructed on the new corr. mass scale, and shows that the nuclei of light elements are more stable than by Aston's curve, and that the most stable nucleus is  ${}^{20}\text{Ne}$ . The mass defect of  ${}^9\text{Be}$  is almost zero. The stability of this nucleus and its possible connexion with the origin of He deposits in beryl are discussed. N. M. B.

**Transmutation of phosphorus, sulphur, chlorine, and potassium, and the masses of light**



atoms. E. POLLARD and C. J. BRASEFIELD (*Nature*, 1936, 137, 943—944).—Vals. obtained for the nuclear energy change for the transmutation of S, Cl, and K suggest that the energy levels are closer in nuclei of the type  $4n$  than in those which are more complex. Masses are derived for most of the nuclei from Ne to A. When the departure of mass from whole no. is plotted against nuclear mass no., min. indicating extra stability appear at each repetition of 4 units until  $^{40}\text{A}$ , which is exceptional, is reached. This extra stability is ascribed to the existence of  $\alpha$ -particles in the nucleus and not merely to shells of four particles irrespective of charge. L. S. T.

Theory of the Stern-Gerlach effect. (SR) A. S. EDDINGTON (*Nature*, 1936, 137, 1029).

Radioactive  $\beta$ -decay and nuclear exchange force as a consequence of a unitary field theory. E. C. G. STUECKELBERG (*Nature*, 1936, 137, 1032).—The hypothesis that the positive electron, neutrino, positive proton, and neutron are four different quantum states of one elementary particle is advanced. Permitted transitions are positive electron or proton neutrino or neutron. L. S. T.

Consequences of Fermi's theory of  $\beta$ -radioactivity. B. KAHN (*Physica*, 1936, 3, 495—502).—Mathematical. Wick's explanation (*A.*, 1935, 679) of the magnetic moment of the proton and neutron on the basis of Fermi's theory of  $\beta$ -radioactivity is criticised. With the Fermi interaction "Ansatz" the magnetic moment due to the electron-neutrino field is zero. An estimate is made of the neutron-neutron forces relative to the proton-neutron interaction. J. W. S.

Selection rules in nuclear radiation. H. M. TAYLOR (*Proc. Camb. Phil. Soc.*, 1936, 32, 291—300).—Mathematical. T. G. P.

Constancy of nuclear bond energies. W. M. LATIMER (*J. Amer. Chem. Soc.*, 1936, 58, 1061—1062).—Recent data for the masses of the lighter elements are used to check the assumption that the energies of nuclear reactions can be calc. as the sum of changes in the energies of the nuclear linkings and the coulombic fields. E. S. H.

Analytical form of eigen-functions of electrons in light atoms. S. ROZENTAL (*Bull. Acad. Polonaise*, 1935, A, 501—506).—Mathematical. O. D. S.

Light quantum and neutrino. II. Three-dimensional radiation field. P. JORDAN and R. DE L. KRONIG (*Z. Physik*, 1936, 100, 569—583; cf. this vol., 543). A. B. D. C.

Neutrinos and light quanta. N. S. N. NATH (*Proc. Indian Acad. Sci.*, 1936, 3, A, 448—458).—Theoretical. The introduction of neutrino spin in the neutrino theory of light enables the correct Planck formula for energy density to be derived. R. S. B.

Self-consistent field for tungsten. M. F. MAN-NING and J. MILLMAN (*Physical Rev.*, 1936, [ii], 49, 848—853).—Calc. results are tabulated. N. M. B.

Band spectra of boron hydride and deuteride. S. F. THUNBERG (*Z. Physik*, 1936, 100, 471—477). A. B. D. C.

Band spectra of NiH and CoH. A. HEIMER (*Naturwiss.*, 1936, 24, 413).—A new band system  ${}^2\Delta_{21}$ — ${}^2\Delta_{21}$  has been found in the violet of the NiH spectrum. The bands show isotopic components due to  ${}^{58}\text{NiH}$  and  ${}^{60}\text{NiH}$ . A band system in the blue showing R, P, and Q branches is ascribed to CoH. A. J. M.

The C system of barium hydride. G. W. FUNKE and B. GRUNDSTRÖM (*Z. Physik*, 1936, 100, 293—306).—Two new band systems with predissociation are recorded. A. B. D. C.

Band spectra of CaF and CaCl. K. H. HELL-WEGE (*Z. Physik*, 1936, 100, 644—651).

A. B. D. C.

Absorption spectra of complex compounds of tervalent cobalt. J. KRANIG (*Keem. Teated*, 1934, 2, 4—6; *Chem. Zentr.*, 1935, ii, 2335).—In the series  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_3(\text{C}_2\text{O}_4)_2]\text{NH}_4$ ,  $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$  the two chief absorption bands show a progressive displacement towards longer  $\lambda\lambda$ . J. S. A.

Absorption spectrum and the ground state of the Ce IV ion. S. DATTA and M. M. DEB (*Indian J. Physics*, 1936, 10, 163—170).—Ultra-violet absorption curves are given for different concns. of  $\text{CeCl}_3$  in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and conc.  $\text{HCl}$ , and absorption max., intensities, and transitions giving rise to the bands are considered. A detailed discussion of the probable ground state of Ce IV leads to  $4F$  rather than  ${}^3\text{d}$ , the absorption bands in the ultra-violet arising from  $4^2F$ — $5^2D$  transitions, and the  ${}^2D$  state being further split up by the inhomogeneous cryst. electric field (cf. Freed, *A.*, 1932, 211). N. M. B.

Rotational constants of SnS. E. N. SHAWHAN (*Physical Rev.*, 1936, [ii], 49, 810—812; cf. *A.*, 1935, 1299).—Vals. for the lowest state of the mol. and for the upper state of the visible system were determined from the (0, 0) and (1, 0) bands of the visible system. N. M. B.

Absorption spectra and linking of inorganic nitrates and sulphates in the vapour state. M. I. HAQ and R. SAMUEL (*Proc. Indian Acad. Sci.*, 1936, 3, A, 487—511; cf. this vol., 661, 775).—The absorption spectra of vapours of the nitrates of H, K, Ag, Mg, Cd, Pb,  $\text{NH}_4$ , and Na, and the sulphates of H, K, Ag, Zn, and  $\text{NH}_4$  have been determined. The transition from covalency to electrovalency is discussed with reference to Franck-Condon diagrams. All compounds are covalent as vapours, presumably because of the small electron affinity of  $\text{NO}_3'$  and  $\text{SO}_4''$ ; nitrites are probably covalent as vapours. In  $\text{NH}_4\text{NO}_3$  both N atoms are quinque-covalent in the vapour state, in agreement with the absorption spectra of  $\text{R}_4\text{NI}$  (cf. this vol., 921) and the existence of  $\text{NF}_5$ . Photo-dissociation processes are discussed. R. S. B.

$\text{A}^1\Pi \rightarrow \text{X}^1\Sigma$  (IV pos.) carbon monoxide bands. II. L. GERO (*Z. Physik*, 1936, 100, 374—388; cf. this vol., 661). A. B. D. C.

Group resonators. XXII. General law of frequencies of the fine structure bands. D. RADULESCU (*Bul. Soc. Chim. Romania*, 1935, 17, 193—222; cf. *A.*, 1935, 1302).—The frequencies of

the fine structure bands for absorption, fluorescence, phosphorescence, and Tesla luminescence spectra of vapours and solutions can be represented accurately by  $F_y = F_0 u^y$ , where  $y$  is an integer (+ or -) and  $\mu$  a universal const. = 1.000110998. The formula is applied to the spectra of the vapours of benzoquinone,  $C_{10}H_8$ ,  $C_6H_6$ ,  $C_6H_2$ , glyoxal, and acraldehyde.

R. S. B.

**Light absorption of adsorbed *p*-nitrophenol.** J. F. H. CUSTERS and J. H. DE BOER (*Physica*, 1936, 3, 407—417; cf. *A.*, 1934, 715).—*p*-Nitrophenol mols. adsorbed on a vac.-sublimed  $BaF_2$  surface form two films. The mols. of the first film are adsorbed electrostatically with the -OH dipoles next the  $F'$  ions of the surface, and yield an absorption spectrum shifted further towards the red than in the case of films on  $CaF_2$ . The second film is held to the first by van der Waals forces and its absorption spectrum also shows a shift towards the red which becomes less with increasing density of adsorbed film.

J. W. S.

**Ultra-violet radiation in the Reboul effect.** O. VIKTORIN (*Coll. Czech. Chem. Comm.*, 1936, 8, 207—218; cf. this vol., 664).—Ultra-violet radiation is emitted only from the positive end of the tablet of semi-conductor subjected to an electric current; the intensity is a function of the voltage and varies irregularly with time and with the thickness of the tablet. Results are given for black paper, NaCl, NaF,  $PbI_2$ , and  $KNO_3$ .

N. M. B.

**Spectra of aromatic hydrocarbons in solution.**—See this vol., 834.

**Absorption spectra of tetra-alkylammonium salts. Theory of the co-ordinate linking.** IX. S. N. ALI and R. SAMUEL (*Proc. Indian Acad. Sci.*, 1936, 3, A, 399—419).—The absorption spectra of 0.00001—0.01*M* and 0.1—1*M* aq. solutions of  $NR_4X$  ( $R=Me, Et, Pr^a, Bu^s$ , and *n*- and *iso*- $C_5H_{11}$ ;  $X=Cl, Br$ , and  $I$ ) have been determined, alone and in some cases in presence of other electrolytes. The absorption max. are interpreted by Franck-Condon diagrams. Selective max. are the stronger the heavier is the radical and the lighter the halogen. There is evidence from the more dil. solutions of  $(C_5H_{11})_4NI$  for decreasing  $[I']$  with increasing concn. of salt owing to the formation of a small amount of the undissociated quinqu-covalent N compound. The five covalent linkings, one of which is more readily polarisable than the other four, are formed from the  $2s^22p^3$  outer electrons of N, in contradiction to the octet theory and in harmony with the authors' views (cf. *A.*, 1934, 1058).

R. S. B.

**Absorption and fluorescence spectra of derivatives of pyrene and 1:2-benzpyrene.** C. SANNIE and V. POREMSKI (*Bull. Soc. chim.*, 1936, [v], 3, 1139—1155).—Characteristic regularities in the structure of the spectra have been noted. The ultra-violet absorption and fluorescence spectra are related as mirror images.

E. S. H.

**Normal frequencies of vibration of benzene compounds in ultra-violet absorption.** K. MASAOKI (*Bull. Chem. Soc. Japan*, 1936, 11, 346—348).—Data for PhMe, PhCl, PhBr, PhOH,  $NH_2Ph$ , PhCHO, and PhCN are recorded.

T. G. P.

**Absorption and fluorescent spectra of naphthalene derivatives.** H. BELA (*Acta Phys. Polon.*, 1932, 1, 339—344).—Absorption bands of  $C_{10}H_8$ , acenaphthene, and diacenaphthylidene, and a new fluorescence band of the last-named substance, are described.

CH. ABS. (e)

**Tautomerism of toluene, from its absorption spectra at different temperatures.** J. J. MICHAILENKO and A. P. KRESCHKOV (*J. Gen. Chem. Russ.*, 1936, 6, 102—106).—The absorption spectrum of PhMe in  $n-C_6H_{14}$  ( $\lambda=2200$ —2780 Å.) has been determined at 18°; at 67° the absorption bands become wider, and a new band appears at 2400—2500 Å. The formation of an extra-nuclear double linking is suggested to account for this.

R. T.

**Nuclear vibration bands of solid hydrogen bromide and iodide near their transition points.** J. ZUNINO (*Z. Physik*, 1936, 100, 335—344).—Nuclear vibration bands of solid HBr and HI appear at 4.1 and 4.7  $\mu$ , displaced towards longer  $\lambda\lambda$  compared with gaseous absorption; this displacement decreases with rising temp.

A. B. D. C.

**Infra-red absorption band in fused quartz.** J. W. ELLIS and W. K. LYON (*Nature*, 1936, 137, 1031—1032).—The band at 2.7  $\mu$  attributed to quartz, is absent from certain specimens, and may be due to traces of impurities such as  $H_2O$  vapour or  $CO_2$ .

L. S. T.

**Infra-red absorption of aqueous solution.** A. CARRELLI (*Nuovo Cim.*, 1935, [ii], 12, 65—72; *Chem. Zentr.*, 1935, ii, 1657).—Aq. solutions of  $NaNO_3$  and  $Na_2SiO_3$  show the same alterations of the 3  $\mu$  absorption band of  $H_2O$  as of the Raman band, the absorption band showing a similar complex structure.

J. S. A.

**Photographic infra-red spectrum of some simple carbon compounds in the gaseous state.** G. HERZBERG and H. VERLEGER (*Physikal. Z.*, 1936, 37, 444—445).—The near infra-red absorption spectra of the vapours of HNCN,  $HCO_2H$ , and MeOH have been photographed. HNCN gives a band with very complicated fine structure, showing the mol. to have an asymmetric structure. The  $\cdot NCO$  group is either considerably bent, or has a triangular structure. The fine structure of the  $HCO_2H$  band is much simpler, and the mol. is therefore probably approx. symmetrical. The evidence is, however, not sufficiently conclusive to decide between the structures  $H\cdot C(\cdot O)\cdot O\cdot H$  and  $H\cdot C(\cdot O\cdot)_2H$ . The MeOH band is also simple, and the mol. is approx. symmetrical.

A. J. M.

**Infra-red absorption spectra and modes of vibration of organic compounds.** J. LECOMTE (*Compt. rend.*, 1936, 202, 1918—1920).—Data for the vibrational frequencies of mols. of the type  $Pr^aX$ ,  $CH_2Cl\cdot CH_2X$ ,  $X\cdot [CH_2]_3\cdot Y$ , and  $Bu^aY$  ( $X, Y=OH, CN, Cl, Br, I$ , etc.) are recorded. The no. of frequencies  $<1100\text{ cm.}^{-1}$  suggests the existence of several mol. forms.

J. E.

**Comparison of the infra-red absorption and Raman spectra of some primary aliphatic and aromatic amines.** (MME.) M. FREYMANN (*Compt. rend.*, 1936, 202, 1674—1676).—Absorption bands have been determined between 0.8 and 1.2  $\mu$ . Three



components have been observed in the NH band for primary aliphatic amines, whilst the Raman spectrum and the first infra-red harmonic have only two components. Except for  $\text{NH}_2\text{Me}$  (determined in  $\text{H}_2\text{O}$ ) the intensities of the components of the NH band are const. in the homologous series for both types of spectrum. The displacement of the NH band towards high frequencies is similar to that observed for both spectra in the case of  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$ . The NH band of aromatic amines is displaced towards higher frequencies. The absorption spectrum of  $\text{CH}_3\text{Ph}\cdot\text{NH}_2$  is almost identical with that of aliphatic amines. The mean distance apart of the lower-frequency components is practically const.

M. S. B.

**Infra-red absorption spectra and Raman spectra of amides and anilides and the structure of these compounds.** (MME.) M. FREYMANN and R. FREYMANN (Compt. rend., 1936, 202, 1850—1852).—Amides and primary and sec. amines have strong absorption bands near  $1.04 \mu$  due to the NH, but in monosubstituted amides the NH band is very feeble.  $\text{NHAcBu}$  does not give a Raman frequency at  $3200\text{—}3400 \text{ cm}^{-1}$ . The absence of frequencies anticipated from classical structural formulæ is interpreted in terms of chelation through H (cf. A., 1935, 563).

J. G. A. G.

**Simple relations between vibrational frequencies of isotopic molecules.** H. TOMPA (Nature, 1936, 137, 951).—Two formulæ relating vibrational frequencies that affect Raman spectra to the masses of isotopic mols. are given.

L. S. T.

**Depolarisation factor of Raman lines in nitrogen, oxygen, and carbon dioxide.** J. CABANNES and A. ROUSSET (Compt. rend., 1936, 202, 1825—1828).—The depolarisation factors of the Raman frequencies  $\text{N}_2$ ,  $2331 \text{ cm}^{-1}$ ,  $\text{O}_2$ ,  $1556$ , and  $\text{CO}_2$ ,  $1286\text{—}1389$ , are  $0.16$ ,  $0.26$ , and  $0.20$ , respectively.

J. G. A. G.

**Raman spectrum of solid hydrogen sulphide at low temperature.** S. C. SIKKAR and J. GUPTA (Indian J. Physics, 1936, 10, 227—231).—At liquid air temp., lines at  $2523$ ,  $2547$ , and  $2558 \text{ cm}^{-1}$  and a broad band at  $80 \text{ cm}^{-1}$ , present also on the anti-Stokes side, were observed. The first line is identified with the fundamental vibrational frequency  $\omega_2$ , and the other two with  $\omega_1$ ; the  $80 \text{ cm}^{-1}$  band is assigned to loosely bound mol. complexes in the solid state. The angle between the two HS linkings is about  $108^\circ$ , compared with  $90^\circ$  in the liquid or gaseous states. Provisional arrangement of the mols. in the unit cell is suggested so that the field of the crystal lattice splits up the vibrational level without splitting up  $\omega_3$ .

N. M. B.

**Raman effect of gaseous and liquid sulphur trioxide and of mixtures of the trioxide with the dioxide.** H. GERDING, W. J. NIJVELD, and G. J. MULLER (Nature, 1936, 137, 1033).—On dilution of liquid  $\text{SO}_3$  with liquid  $\text{SO}_2$ , the relative intensity of the Raman lines ascribed to  $(\text{SO}_3)_1$  increases, whilst that of others ascribed to  $(\text{SO}_3)_2$  decreases. This agrees with the conception of an inner equilibrium in liquid  $\text{SO}_3$  between single and polymerised mols., in the sense of Smits' theory.

L. S. T.

**Raman spectrum of the ice-like form of sulphur trioxide.** H. GERDING and N. F. MOERMAN (Nature, 1936, 137, 1033—1034; cf. preceding abstract).—The presence of a large proportion of  $(\text{SO}_3)_2$  mols. with a small no. of  $(\text{SO}_3)_1$  mols. is indicated.

L. S. T.

**Raman spectrum of gaseous and liquid sulphur dioxide and its solutions in water.** H. GERDING and W. J. NIJVELD (Nature, 1936, 137, 1070).—The Raman spectrum of gaseous  $\text{SO}_2$  at 12 atm. shows only one strong frequency  $1150.5 \pm 0.5$  (cf. A., 1931, 145). With the liquid, only a small displacement of the strong, sharp line occurs at  $30^\circ$  and  $80^\circ$ . For  $\text{SO}_2$  in  $\text{H}_2\text{O}$  no lines attributable to  $\text{SO}_3^{''}$  or  $\text{HSO}_3'$  were found; the majority of  $\text{SO}_2$  mols. in the solution are present as such, the frequency of the stronger Raman line agreeing with that of gaseous  $\text{SO}_2$ .

L. S. T.

**Raman spectrum of sulphuric acid.** M. A. CATALAN and L. YZU (Anal. Fis. Quim., 1936, 34, 26—47).—A review of the literature. The results of Woodward *et al.* (A., 1934, 473) are confirmed. The continuous background is considered to arise partly from suspended and fluorescent matter, and partly from the constitution of the acid.

F. R. G.

**Raman effect and structure of glasses. II.** T. G. KUJUMZELIS (Z. Physik, 1936, 100, 221—236; cf. this vol., 137).—Measurements have been extended to  $\text{SiO}_2\text{—PbO}$  glasses. The continua are ascribed to vibrations of a lattice, whilst the discrete lines cannot be exclusively ascribed to the  $\text{SiO}_4$  group, and indicate the presence of complex groups of definite types.

A. B. D. C.

**Raman spectra of oxalates in solution and the structure of the oxalate ion.** J. GUPTA (Indian J. Physics, 1936, 10, 199—204; cf. this vol., 663).—The Raman spectra of aq.  $\text{H}_2\text{C}_2\text{O}_4$  and aq. K and  $\text{NH}_4$  oxalates show differences from those of the pure substances similar to those previously reported for  $\text{HCO}_2\text{H}$  and formates. Results confirm previous conclusions on the behaviour of the  $\text{CO}_2\text{H}$  group before and after ionisation.

N. M. B.

**Raman effect of two complex borotartrates in solution.** (MLLE.) M. THEODORESCO (Compt. rend., 1936, 202, 1676—1678).—Raman spectra have been determined for aq. solutions of the borotartrates KBT, and KBT, tartaric acid (I),  $\text{H}_3\text{BO}_3$ , K borate, and borax. One new line,  $934 \text{ cm}^{-1}$ , was found in both aq. KBT<sub>2</sub> and KBT. Slightly displaced lines of (I) also appeared in both these solutions. The results support the theory, put forward by other investigators, that KBT, does not exist in aq. solution but is split up into KBT and (I).

M. S. B.

**Interpretation of Raman line of benzene at  $984 \text{ cm}^{-1}$ .** O. SPECCHIA and G. SCANDURRA (Nuovo Cim., 1935, [ii], 12, 129—133; Chem. Zentr., 1935, ii, 1859—1860).—Studies of fine structure support the view that the  $984 \text{ cm}^{-1}$  line corresponds to the  $992 \text{ cm}^{-1}$  line, but is due to mols. containing  $^{13}\text{C}$  in place of  $^{12}\text{C}$ .

J. S. A.

**[Raman] spectra of o-dideuterobenzene and N-deuteropyrrole.** O. REDLICH and W. STRICKS (Monatsh., 1936, 68, 47—50).—Frequencies are

recorded for pyrrole, *N*-deuteropyrrole (from K pyrrole and D<sub>2</sub>O), and *o*-C<sub>6</sub>H<sub>4</sub>D<sub>2</sub> [obtained by distillation of *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)<sub>2</sub>Ca with CaO + Ca(OD)<sub>2</sub>].

H. B.

**Raman effect of organic substances. V. Raman effect of homocyclic compounds.** K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1936, 11, 321—345).—Data for C<sub>6</sub>H<sub>6</sub>, cyclohexane, phenylcyclohexane, indene, C<sub>10</sub>H<sub>8</sub>, tetralin, decalin, tetra- and deca-hydroacenaphthene, deca- and per-hydro-pyrene, and dicyclohexyl are recorded and discussed.

T. G. P.

**Raman effect and organic chemistry. Comparison of Raman spectra of ethylenic alcohols and their *cis* and *trans* derivatives. Classification of radicals R in compounds CHPh·CHR. (MILE.)** B. GREDY (Bull. Soc. chim., 1936, [v], 3, 1101—1107).—Determinations of Raman spectra reveal a close similarity between the spectra of the alcohols and their derivatives.

E. S. H.

**Raman spectra of molten organic acids and their derivatives.** V. N. THATTE and D. Y. ASKHEDKAR (Z. Physik, 1936, 100, 456—462).—Raman displacements are tabulated for molten NaOAc, CH<sub>2</sub>Cl·CO<sub>2</sub>H, CHCl<sub>2</sub>·CO<sub>2</sub>H, CCl<sub>3</sub>·CO<sub>2</sub>H, citric acid, and BzOH.

A. B. D. C.

**Scattered spectrum of CD<sub>2</sub>Br<sub>2</sub>.** B. TRUMPY (Z. Physik, 1936, 100, 250—252).—The Raman spectrum of CD<sub>2</sub>Br<sub>2</sub> is given; the CD<sub>2</sub> frequencies are 1023, 2195, and 2235 cm.<sup>-1</sup> as compared with 1390, 2988, and 3054 for the CH<sub>2</sub> group.

A. B. D. C.

**Raman spectra of carbon disulphide, benzene, chloroform, and carbon tetrachloride in different states and at different temperatures.** S. C. SIRKAR (Indian J. Physics, 1936, 10, 189—198).—Some new lines in the neighbourhood of the Rayleigh line were observed in the Raman spectra of solid CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> at liquid air temp. Changes in the intensities, widths, and frequency shifts of some of the lines of single mols. of these substances with lowering of temp. were observed. The properties of some of the Raman lines of C<sub>6</sub>H<sub>6</sub> liquid and vapour at different temp. were examined. Results are discussed in relation to theory.

N. M. B.

**Raman spectra of isoeugenol and the safrole series.** B. SZUSZ and E. PERROTTET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 29—33; cf. A., 1935, 807).—Raman frequencies are recorded for safrole, isosafrole, and heliotropin. Discrepancies with the results of previous investigators are probably due to the presence of a mixture of isomerides. The frequencies due to the ethylenic linking are particularly intense.

J. W. S.

**Glow of the barrier anodes of aluminium.** K. GUMINSKI (Bull. Acad. Polonaise, 1936, A, 145—163).—The glow at an Al anode in aq. solution shows no direct relation to the chemical nature of the electrolyte, but generally solutions which yield a thick oxide layer give the most intense glow. The glow is very intense in 3% H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and has a continuous spectrum from 5875 to 3705 Å., with a max. at about 4590 Å. At 111 volts the spectrum tends to spread and its

max. to move towards longer λ, especially in presence of impurity (Cu, Mn, Tl, Bi, or Cd) in the Al.

J. W. S.

**Photo-luminescence of felspar.** S. IIMORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 79—110).—Quant. photoluminographic investigations on Naegi felspars, which exhibit photoluminescence when exposed to the light of a quartz Hg lamp, give results concordant with radioluminescence data on fluorites, and strongly support the transformation theory previously proposed (cf. A., 1931, 1111), and the view of the existence of temporary and permanent luminescence centres.

N. M. B.

**Extinction of the luminescence of phosphorescent substances activated by organic activators.** L. VINOKUROV and V. LEVSHIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 135—138).—The decay of the phosphorescence of H<sub>3</sub>BO<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O, heated to 170° and 135°, respectively, and activated by uranine, eosin, erythrosin, aesculin, or naphthionic acid, follows the exponential law (for λλ 4600—4950 and for 5500—6200 Å.). With high activator concns. the luminescence becomes feebler and changes to longer λλ. The spectrum of the fluorescence resembles that of the phosphorescence.

H. J. E.

**Direct proof of the bimolecular process in the luminescence of zinc phosphors.** V. ANTONOV-ROMANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 97—100).—Measurements on single crystals of ZnS activated with Cu gave results in agreement with the bimol. law.

H. J. E.

**Purification and fluorescence spectrum of chlorophyll-*b*.** C. DHERÉ and O. BIERNACHER (Compt. rend. Soc. Biol., 1936, 122, 591—594).—The band at 6720 Å., attributed by Zscheile (A., 1935, 905) to chlorophyll-*b*, is due to an impurity.

H. G. R.

**Structure of electrolytic oxide layers.** T. RUMMEL (Z. Physik, 1936, 100, 665—666).—Thin valve layers are porous (cf. this vol., 668).

A. B. D. C.

**Elementary theory of the critical field of a dielectric.** F. CERNUSCHI (Proc. Camb. Phil. Soc., 1936, 32, 276—280).—Theoretical.

T. G. P.

**Continuous absorption and photo-electric effect.** H. RAKSHIT (Z. Physik, 1936, 100, 396—400).—Theoretical.

A. B. D. C.

**Quantum yield of formation of colour centres in KBr crystals.** R. HILSCH and R. W. POHL (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 209—214; Chem. Zentr., 1935, ii, 1663—1664).—The quantum yield of the formation of *U* centres rises from a few % at -100° to 100% at 500° according to an exponential law. The transformation of *U* centres into *F* centres involves electron displacements of mol. dimensions, and so gives rise to no measurable transfer of electricity.

J. S. A.

**Thermo-potential of the element, metal-semiconductor-metal. I. Various samples of cuprous oxide.** G. MONCH (Ann. Physik, 1936, [v], 26, 481—494).—The effect of temp. on the thermo-potential and conductivity of the element



Cu-Cu<sub>2</sub>O-Cu was determined for different samples of Cu<sub>2</sub>O. The theory of the phenomenon is summarised.

A. J. M.

**Breakdown potential of electrolytic barrier layers.** A. GUNTHER-SCHULZE and H. BETZ (Z. Physik, 1936, 100, 539—542).—The breakdown potential of an electrolytic barrier layer increases logarithmically with electrolyte dilution.

A. B. D. C.

**Breakdown of compressed nitrogen in a non-uniform electric field. II.** I. GOLDMAN and B. VUL (Tech. Phys. U.S.S.R., 1936, 3, 16—27).—Data are recorded for the breakdown voltage (*V*) at pressures up to 50 kg. per sq. cm., using electrodes of various shapes. Under certain conditions rise in temp. raises *V*, due to an increase in ionic diffusion.

H. J. E.

**Volta effect and Peltier effect.** F. O'DONE (Nuovo Cim., 1935, [ii], 12, 273—284; Chem. Zentr., 1935, ii, 2500).—A theory of the internal and external Volta effect, and of the Peltier effect, is based on Duhem's theory of metallic conduction.

J. S. A.

**Determination of specific electrical resistance of substances in powder form.** Z. SPECHT (Acta phys. polon., 1934, 2, 393—407; Chem. Zentr., 1935, ii, 2153).—Component factors of the resistance of compressed powders are discussed. The formation of layers between which exist high contact resistances does not occur with sufficiently short columns.

J. S. A.

**Influence of conductivity in determination of dipole moments.** A. PARTS (Keem. Teated, 1934, 2, 27—29; Chem. Zentr., 1935, ii, 2337).—Expressions are derived for calculating the error in dipole moment measurements due to neglect of conduction, and for calculating the conductivity of the fluid.

J. S. A.

**Experimental determination of quadrupole moments.** O. FUCHS (Z. ges. Naturwiss. Naturphil. Gesch. Naturwiss. Med., 1935, 1, 69; Chem. Zentr., 1935, ii, 2509).—For a mol. containing quadrupoles  $\epsilon$  in a non-homogeneous field is  $> \epsilon$  in a homogeneous field, owing to orientation. The difference depends, *inter alia*, on the magnitude of the quadrupole moment and it may be possible to determine this in such a manner. Data are given per C<sub>2</sub>Cl<sub>4</sub>.

H. N. R.

**Dielectric constants of gases and vapours. IV.** M. KUBO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 122—128; cf. A., 1935, 1304).—The dielectric consts. of the vapours of EtSH, Et<sub>2</sub>S, and thiophen were measured and used to calculate the dipole moments and at. polarisations of the mols. Results are discussed in relation to available data for dil. solutions.

N. B.

**Dielectric constant of helium.** F. J. WIŚNIEWSKI (Acta phys. polon., 1934, 2, 383—391; Chem. Zentr., 1935, ii, 1666).—The val. calc. from the Bohr atom model agrees with the experimental val.

J. S. A.

**Dipole moments of alkali halides.** W. H. RODEBUSH, L. A. MURRAY, jun., and M. E. BIXLER (J. Chem. Physics, 1936, 4, 372—376).—The following dipole moments have been determined by the mol. beam method (A., 1933, 1105): KCl 9.5, KBr 10.9,

KI 11.1, CsI 12.1  $\times 10^{-18}$ . The actual moment of the mols. is uncertain owing to the possibility of association.

F. L. U.

**Dielectric polarisation of alums.** T. PIECH (Bull. Acad. Polonaise, 1936, A, 108—122; cf. A., 1933, 1000).—The dielectric consts. ( $\epsilon$ ) and densities of KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, and KCr(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (I) have been measured at 10—60° and the polarisability of the mols. calc. They all show dispersion of  $\epsilon$  at room temp., explained by the rotation of these mols., which contain loosely bound H<sub>2</sub>O. For (I) the  $\epsilon$ -*T* curve shows a max. at about 45°.

J. W. S.

**Influence of magnetic fields on the dielectric constant of liquids.** S. D. CHATTERJEE (Indian J. Physics, 1936, 10, 233—236).—In a field of the order 26 k.-gauss PhNO<sub>2</sub> showed an increase in dielectric const. for both parallel and perpendicular fields. No change was observed with C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, and Pr<sup>n</sup>OH at 2 k.-gauss.

N. M. B.

**Dipole moments of certain polynitro-compounds.** H. O. JENKINS (J.C.S., 1936, 862—867).—Dielectric consts. and densities have been found for dil. solutions of C<sub>6</sub>H<sub>5</sub> in CHCl<sub>3</sub>, 1 : 3 : 5-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (I) in CHCl<sub>3</sub>, trinitromesitylene in C<sub>6</sub>H<sub>6</sub>, and 2 : 4 : 6 : 1 : 3 : 5-C<sub>6</sub>Et<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub>. C<sub>6</sub>H<sub>5</sub> in CHCl<sub>3</sub> gives a total polarisation of 27.5  $\pm$  0.5, in agreement with Smyth *et al.* (A., 1933, 339). (I) has no moment in CHCl<sub>3</sub>. The pyramidal structure for the :C:NO<sub>2</sub> group suggested by Le Fevre *et al.* (A., 1935, 1056) is untenable, since it involves single linkings between N and O, whereas the N—O distance in the above group is 1.22 Å., which is essentially a double linking distance. The structure is a resonating one, requiring a coplanar arrangement. The moment shown by some symmetrical, and therefore “non-polar,” substances in solution, and the invariance of the polarisation of such mols. with temp., are explained by assuming a fluctuation of link moments about a most probable val., that changes in the moment of any one mol. are slow relative to its time of relaxation in the medium, and that each group moment is independent. The moment of *p*-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> in solution can be related to the most probable val. for that of PhNO<sub>2</sub> in the same solvent. It is suggested that at. polarisations determined by the dil. solution method are too high.

A. J. M.

**Raman effect and dipole moment in relation to free rotation. IV. Molecular structure of acetylene tetrachloride.** S. MIZUSHIMA, Y. MORINO, and K. KOZIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 111—121; cf. this vol., 776).—Measurements of the dipole moment of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> in hexane, C<sub>6</sub>H<sub>6</sub>, and Et<sub>2</sub>O in the temp. range 50° to —25° show that the moment changes considerably with the solvent, but, contrary to the case of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, is almost const. over the temp. range. The Raman spectra of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> were investigated in the solid and liquid state and in dil. hexane and Et<sub>2</sub>O solutions. Results are discussed in relation to mol. structure.

N. M. B.

**Refraction and dispersion of deuterium. T.** LARSEN (Z. Physik, 1936, 100, 543—546).—Refraction and dispersion data are given between 2300 and

5790 Å.; refraction values are  $<$  for  $H_2$ , and the dispersion curve is flatter. Inequality of zero point energies accounts for these differences. A. B. D. C.

**Rotatory dispersion and circular dichroism of 2:2-dinitrocamphane in the ultra-violet.** S. MITCHELL and R. R. GORDON (J.C.S., 1936, 853—856).—The rotation of 2:2-dinitrocamphane in EtOH falls to a negative max. at approx. 3020 Å., and passes through zero at 2762 Å. The solution absorbs strongly beyond 2666 Å., thus preventing the determination of the rotation at lower  $\lambda$ . The graph of mol. ellipticity against  $\lambda$  is symmetrical, with a negative max. at 2770 Å. The dissymmetry factor is approx. const. down to 2778 Å., after which it decreases. The contribution of the  $NO_2$  groups accounts for essentially the whole of the observed rotation. A. J. M.

**Magneto-optical rotation and natural dispersion in gases.** R. T. LAGEMAN and F. G. SLACK (Physical Rev., 1936, [ii], 49, 807—809).—Formulae are tested by the use of experimental data for  $C_2H_2$ ,  $C_2H_4$ , and  $CO_2$ . Agreement is found for dispersion and Verdet const. formulae. N. M. B.

**Debye effect and lag of the Kerr effect in pure nitrobenzene.** I. RANZI (Nuovo Cim., 1935, [ii], 12, 285—289; Chem. Zentr., 1935, ii, 2337).— $PhNO_2$  shows a high dispersion at long  $\lambda$ ,  $n$  being 3.6 and 2.7, respectively, for 7.2- and 3.8-cm. waves. The time of relaxation of the mol. is calc. as  $2 \times 10^{-10}$  sec. J. S. A.

**Electronic configuration and bond energy.** R. K. ASUNDI and R. SAMUEL (Proc. Indian Acad. Sci., 1936, 3, A, 466—481).—Theoretical. A survey has been made of the spectroscopic data for diat. mols. Results are stated to support the electronic pair-linking theory of valency and to contradict the identification of promoted and non-promoted with non- or anti-linking and linking electrons, respectively. R. S. B.

**Intensity of valency and the structure of molecules.** V. RASUMOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 101—105).—A discussion. H. J. E.

**Latent and active polarity of molecules.** V. RASUMOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 63—66).—A discussion of the relation between electronic mobility, polarity, and valency electrons. H. J. E.

**Stereochemistry of quadricovalent atoms: copper and silver.** E. G. COX, W. WARDLAW, and K. C. WEBSTER (J.C.S., 1936, 775—781).—The high birefringence of Ag picolinate shows that it has a planar configuration, confirmed by its isomorphism with the corresponding Cu compound, demonstrated by X-ray powder photographs. X-Ray analysis of Cu picolinate dihydrate gives a planar configuration. The complex in the anhyd. salt has the same structure as in the hydrate. Quadricovalent  $Ag^I$  and  $Cu^I$  derivatives have a tetrahedral structure, revealed by X-ray examination of  $K_3[Cu(CN)_4]$ , tetrakis-thioacetamide-cuprous chloride, and tetrakis-thioacetamide-argentous chloride. The structure of the thioacetamide derivatives is given in detail. The prep. of all

the above compounds, and the picolates of Ni, Pt, and Pd are described. The effect of the principal valency of a metal atom in determining the configuration of its quadricovalent derivatives is emphasised. A. J. M.

**Potential curves of the hydrogen molecule ion.** G. STEENSHOLT (Z. Physik, 1936, 100, 547—548).—Curves for various levels are obtained by calculation. A. B. D. C.

**Polarisability of molecular hydrogen  $H_2$ .** C. E. EASTHOPE (Proc. Camb. Phil. Soc., 1936, 32, 260—264).—Theoretical. T. G. P.

**Quantum-mechanical treatment of helium hydride molecule-ion  $HeH$ .** J. Y. BEACH (J. Chem. Physics, 1936, 4, 353—357).—The equilibrium nuclear distance, force const., and fundamental vibration frequency are calc. The doubly charged mol.-ion is unstable. F. L. U.

**Metallic binding. II.** P. GOMBAS (Z. Physik, 1936, 100, 599—614; cf. this vol., 781).—Previous calculations are extended to include heat of sublimation, and the crystal consts. are given for K, Rb, and Co. A. B. D. C.

**General theory of molecular co-ordination.** G. URBAIN (Rev. univ. Mines, 1935, [viii], 11, 124—133; Chem. Zentr., 1935, ii, 2486).—The constitution of compounds of  $CH(NO_2)_3$  and  $CHCl_3$  involving  $C^{III}$  is discussed. J. S. A.

**Diffraction and selective adsorption of atoms at crystal surfaces.** J. E. LENNARD-JONES and A. F. DEVONSHIRE (Nature, 1936, 137, 1069—1070).—An explanation of the observed (A. 1933, 994) anomalous reflexion and diffraction of He atoms by LiF is suggested. Under certain conditions, atoms incident on a solid surface may be diffracted along and not away from it. The atom is captured by the surface field of the solid, by "selective adsorption." Energy levels for an adsorbed He atom on LiF are deduced. L. S. T.

**Quantum theory of temperature variation of the magnetisation curve.** N. AKULOV (Z. Physik, 1936, 100, 197—202). A. B. D. C.

**Application of "eks" to determining crystal lattice energy.** A. E. FERSMAN (Bull. Acad. Sci. U.R.S.S., 1935, 1425—1430).—Application of the conception of eks (energy coeffs. of ions in a lattice) permits the approx. evaluation of the energy of crystal lattices of complex compounds. R. T.

**Determination of the efficiency of X-ray fluorescence by means of the counter tube.** W. NIENS (Ann. Physik, 1936, [v], 26, 513—532).—The counter-tube provides a sensitive method of determining the efficiency ( $u$ ) of X-ray fluorescence (ratio of no. of emitting atoms to the no. of excited atoms). The vals. for K-fluorescence,  $u_K$ , are V 0.21, Cr 0.25, Fe 0.30, in satisfactory agreement with results of other methods.

**Determinations with the complete reflexion system of a crystal lattice.** W. KOSSEL (Ann. Physik, 1936, [v], 26, 533—553).—The multi-periodic structure of a crystal lattice, providing, as it does, a series of diffracting systems in mutually opposite



positions, may be employed in the precision determination of crystal structure, or  $\lambda$  of X-rays, by a compensation process. The method involves the determination of a small angle, and  $\lambda\lambda$  can be determined by observations made directly on the plate, and not involving the distance from the plate to the lattice. The lattice const. of Cu is found to be  $a=3.6075\pm0.0005$  A. A. J. M.

Graphical method of studying crystal structure by means of the Weissenberg X-ray goniometer. Application to specimens of aluminium foil. J. GARCIA DE LA CUEVA and J. PALACIOS (Anal. Fis. Quím., 1936, 34, 165—172).—The method previously described (A., 1935, 433) is amplified.

F. R. G.

Interpretation of Weissenberg diagrams. J. GARRIDO (Anal. Fis. Quím., 1936, 34, 399—401).—A graphical method for the interpretation of the diagrams is described (cf. preceding abstract).

F. R. G.

New spectrographic measurements for the quality and homogeneity of X-rays. I. Technique. H. TELLEZ PLASENCIA (Anal. Fis. Quím., 1936, 34, 402—413).—Employing the data of Glocker (A., 1927, 999) the photographic blackening obtained in a Cu X-ray diagram is translated into terms of ionisation and energy, which are plotted against  $\lambda$ .

F. R. G.

Principles of crystal chemistry, and physico-chemical analysis. A. F. KAPUSTINSKI (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 103—114).—Theoretical.

R. T.

Non-ambiguous system of crystallography. B. N. DELONE (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 91—101).—Mathematical.

R. T.

Crystal structure of Spanish graphite. A. LASTOWIECKI (Acta. phys. polon., 1934, 3, 33—38; Chem. Zentr., 1935, ii, 1858).—Lattice dimensions and intensities of reflexion agree with those of graphite from other sources.

J. S. A.

Crystal structure and composition of intermediary phases in non-tungsten and non-molybdenum alloys. H. ARNFELT and A. WESTGREN (Jernkont. Ann., 1935, 119, 185—196; Chem. Zentr., 1935, ii, 1944).—The hexagonal phase in  $\text{Fe}_2\text{W}$  has  $a$  4.727,  $c$  7.704 A., with 8 Fe and 4 W per unit cell; space-group  $D_{6h}$ . The phases saturated with Fe, usually designated  $\text{Fe}_3\text{W}_2$  and  $\text{Fe}_3\text{Mo}_2$ , are rhombohedral, the elementary rhombohedra having the edge 9.02 A., angle  $30^\circ 30' 5''$  and edge 8.97 A. angle  $30^\circ 38' 6''$ , respectively. Both have 13 atoms per unit cell and must be actually  $\text{Fe}_7\text{W}_6$  and  $\text{Fe}_7\text{Mo}_6$ , belonging to space-group  $D_{3d}^5$ . Technical Fe-W with 85% W consists only of Fe<sub>7</sub>W and W, indicating that  $\text{Fe}_7\text{W}_6$  is unstable at low temp. No intermediary phases other than  $\text{Fe}_7\text{Mo}_6$  could be detected in Fe-Mo after prolonged heating at 500—700°. J. S. A.

Crystal structure of  $\text{MgNi}$ , and its relations to the types of  $\text{MgCu}$ , and  $\text{MgZn}_2$ . F. LAVES and H. WITTE (Metallwirts., 1935, 14, 645—649; Chem. Zentr., 1935, ii, 2023).— $\text{MgNi}_2$  is hexagonal,  $a$  4.805,  $c$  15.77 A., with 8 mols. per unit cell; space-group  $D_{6h}$ . Compared with  $\text{MgZn}_2$  the  $c$  axis is

doubled in length: the structure is similar in type to, and intermediate in the disposition of the atoms between, those of  $\text{MgCu}$ , and  $\text{MgZn}_2$ . J. S. A.

Model of polymerised molecule of silicic acid in a melt. G. G. LAEMMLEIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 139—142).—A discussion. The tetrahedral configuration of  $\text{SiO}_2$  breaks down on melting, chain-like  $\text{SiO}_2$  mols. being formed.

H. J. E.

Transitions of solid hydrogen sulphide. E. JUSTI and H. NITKA (Physikal. Z., 1936, 37, 435—438).—The cryst. structure of solid  $\text{H}_2\text{S}$  has been investigated by the Debye-Scherrer method. All its three phases have a face-centred cubic lattice, the lattice const. ( $5.77\pm0.03$  A.) being almost unaltered by change of temp. between  $20^\circ$  and  $150^\circ$  abs. For 4 mols. in the unit cell,  $d=1.17$  g. per c.c. The  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  transitions are transitions of the third order (rotational transitions). It is shown that such transitions can occur with integral energies  $> RT$  g.-cal. per g.-mol.

A. J. M.

Orientation of crystals of potassium borofluoride by mica and barytes, and of sodium sulphite crystals by mica. L. ROYER (Compt. rend., 1936, 202, 1687—1689).—If conc. aq.  $\text{KBF}_4$  is allowed to crystallise on a fresh mica cleavage face most of the crystals are oriented by the mica so that planes become coincident. A similar phenomenon may be observed with aq.  $\text{KBF}_4$  on barytes or aq.  $\text{Na}_2\text{SO}_3$  on mica.

M. S. B.

Application of the three-dimensional Patterson method and crystal structures of proustite,  $\text{Ag}_3\text{AsS}_3$ , and pyrrargyrite,  $\text{Ag}_3\text{SbS}_3$ . D. HARKER (J. Chem. Physics, 1936, 4, 381—390).—Patterson's method (A., 1935, 1193) is simplified and applied to determine the positions of the atoms in proustite and pyrrargyrite, the structures of which are described.

F. L. U.

Interstitial chemical compounds. Structure of antimony pentoxide hydrate and of some antimonates. G. NATTA and M. BACCAREDDA (Gazzetta, 1936, 66, 308—316; cf. A., 1933, 692).— $\text{Sb}_2\text{O}_5\cdot\text{H}_2\text{O}$  has a cubic structure, with unit cell containing 8 mols.,  $a$  10.21—10.25 A., space-group  $O_h^1$ ,  $d_{\text{calc}}$  4.15,  $d_{\text{obs}}$  3.5—4. The structure belongs to the same space-group as those of the antimonates of Ca, Pb, and  $\text{Sb}_2\text{O}_4$ . The ageing of  $\text{Sb}_2\text{O}_5\cdot\text{H}_2\text{O}$  is described.

O. J. W.

Crystals of lead chromate produced in various inorganic and organic substances. N. MATSUMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 180B).— $\text{PbCrO}_4$ , pptd. in the presence of proteins and starches, is tetragonal, having axes  $a=b=6.74$ ,  $c=13.97$  A. The unit cell contains 8 mols.

C. R. H.

Isomorphism and its dependence on the spatial structure of organic compounds. J. FIRSCH (Ber., 1936, 69, [B], 1323—1330).—Examination of many org. compounds shows that the similar mode of space fulfilment of the mol. and not structural similarity is the decisive factor for the occurrence of isomorphism. With mols. of approx. spherical space utilisation, in contrast with other spatial types, this factor is so important that addition of Me groups or

rings does not inhibit isomorphism if the mol. form remains almost unchanged. Therefore, at least for mols. with equally pronounced space extension, the form rather than the magnitude of the space demand is decisive for the formation of solid solutions.

H. W.

**Crystallography and structure of hexamethylenetetramine salicylate.** A. LASZKIEWICZ (Arch. Chem. Farm., 1935, 2, 219—233; Chem. Zentr., 1935, ii, 2353—2354).—Full crystallographic data are given.

H. N. R.

**Crystal structure of acetylnaphthazarin.** L. RIVOIR and R. SALVIA (Anal. Fís. Quím., 1935, 33, 314—318).—The triclinic crystals of 1:4-diacetoxynaphthoquinone have  $a_0=b_0=8.02$ ,  $c_0=10.94$  Å.;  $\alpha=\beta=112^\circ 2'$ ,  $\gamma=86^\circ 13'$ ; 2 mols. in unit cell; space-group  $C_i^1$  or  $C_i^2$ .

F. R. G.

**X-Ray study of the structure of some dibenzyl derivatives.** M. MILONE (Z. Krist., 1936, 93, 113—115).—Space-groups and cell data are given for  $\alpha$ -diphenylglyoxime, diphenylfurazan, and diphenylglyoxime peroxide.

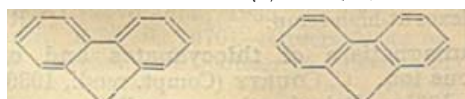
B. W. R.

**Stereochemistry of fluorene.** J. W. COOK and J. IBALL (Chem. and Ind., 1936, 467—468).—X-Ray crystallographic examination of pure fluorene shows that the crystals are orthorhombic (unit cell  $a$  8.47,  $b$  5.70,  $c$  18.87 Å.). It is concluded that the mol. is not planar, the planes of the six-membered rings being inclined at an angle of  $20^\circ$  to the plane of the five-membered ring and at about  $40^\circ$  to each other.

S. C.

**Spatial configuration of fluorene and its derivatives.** E. D. HUGHES, C. G. LE FEVRE, and R. J. W. LE FEVRE (Chem. and Ind., 1936, 545—546, 581; cf. preceding abstract).—Dipole moments of fluorenone, 2-nitro- and 2:7-dinitro-fluorenones (3.35, 6.04, and 4.80, respectively) suggest that fluorene and fluorenone derivatives exist in solution as flat mols. mesomeric between the unreal structures (I) and (II).

(I.)



F. N. W.

**Crystallographic study of  $\gamma$ -oximino- $\beta$ -keto- $\alpha$ -phenylbutane.** E. SANERO (Period. Min., 1935, 6, 31—41; Chem. Zentr., 1935, ii, 2353).—The crystals are monoclinic-prismatic ( $a$  10.95,  $b$  15.83,  $c$  5.67 Å.; 4 mols. in unit cell). Goniometric measurements are given.

H. J. E.

**X-Ray crystallographic measurements on phrenosinic (cerebronic) acid and its oxidation product.** (Miss) D. M. CROWFOOT (J.C.S., 1936, 716—718).—Phrenosinic acid (I), its oxidation product (II), the synthetic acids  $C_{21}H_{48}O_2$  (III) and  $C_{23}H_{46}O_2$  (IV), and the K salts of (II), (III), and (IV) were examined. The  $d_{001}$  vals. for (II) are near those of pure tricosanoic acid (V); (II) is probably (V) contaminated with acids of longer chain length. The  $c$  spacing of (I) suggested that it is more nearly  $C_{24}H_{48}O_3$ .

W. R. A.

**Crystalline structure of the sugars. III. Ascorbic acid and related compounds.** E. G.

COX and T. H. GOODWIN (J.C.S., 1936, 769—775; cf. A., 1935, 1484).—A crystallographic examination of ascorbic acid (I) and several related compounds has been made. (I) crystallises in the monoclinic system, the elementary cell consisting of two asymmetric units each of two mols., which are probably connected by a pseudo-glide plane of symmetry. The mol. possesses a plane of symmetry perpendicular to the ring. X-Ray evidence suggests a mol. in which most of the atoms lie in one plane. The positions of the four mols. in the unit cell and of the 12 atoms in each mol. have been ascertained by comparison of the vals. of the structure factors obtained from X-ray reflexion intensity results and those calc. by assuming all the possible vals. for the parameters, which were reduced to three by the assumption of various interat. distances etc. Both  $d$ - and  $l$ -synthetic (I) have been examined and are identical in cryst. structure with the natural  $l$ -compound. X-Ray data are also recorded for  $d$ -galactoscorbic acid monohydrate,  $d$ -imino-galactoscorbic acid, and dimethyl- $d$ -glucoscorbic acid.

F. R.

**Long spacings in macromolecular solids.** R. B. COREY and R. W. G. WYCKOFF (J. Biol. Chem., 1936, 114, 407—414).—Using a set-up capable of showing mol. spacings as long as 150 Å. in the X-ray diffraction spectrum it is shown that all the well-cryst. proteins examined, except silk fibroin (I), have numerous sharply-defined large spacings with large mol. units. (I) gave a typical polysaccharide pattern with a continuous band of scattering reaching to the shortest measurable angles.

H. D.

**Fibrous structure of native cellulose in Japanese Kozo and Ganpi (*Broussonetia* sp. and *Wikstroemia* sp.).** T. FUJIWARA and Y. IMAKAWA (J. Sci. Hiroshima Univ., 1936, A, 6, 237—238).—X-Ray patterns are reproduced and discussed.

W. R. A.

**Images of foils with the immersion objective.** R. BEHNE (Ann. Physik, 1936, [v], 26, 385—397).—The examination of foils by the electron microscope using the immersion objective (cf. this vol., 814) is described.

A. J. M.

**Determination of molecular structure by electron diffraction.** P. G. AOKERMANN and J. E. MAYER (J. Chem. Physics, 1936, 4, 377—381).—Apparatus using 6.4-kv. electrons for studying mol. structure is described. Interat. distances and configurations of  $(CH_2)_2O$ ,  $S_2Cl_2$ ,  $MeCHO$ , and paraldehyde have been determined.

F. L. U.

**Electron interference of aluminium oxide.** E. BELWE (Z. Physik, 1936, 100, 192—196).—Electrolytic oxide layers are fine cryst.  $\gamma$ - $Al_2O_3$ , whilst those obtained in a flame are coarse crystals of the same  $\gamma$ -oxide containing small Al single crystals.

A. B. D. C.

**Inverse piezo-electric properties of Rochelle salt at audio frequencies.** O. NORGORDEN (Phys. Rev., 1936, [ii], 49, 820—828).—Results of measurements of the variation of the inverse piezo-electric dilation with the temp. and with the frequency and intensity of the applied field, for temp. above and below the Curie point, are given and discussed.

N. M. B.



**Piezo-electricity of quartz in liquid air.** H. DOBBERSTEIN (Naturwiss., 1936, 24, 414).—Experiments are described which show, contrary to Osterberg (this vol., 672), that quartz will oscillate piezo-electrically at temp.  $< -190.5^\circ$ . A. J. M.

**Temperature variation of crystal plasticity.** W. BOAS and E. SCHMID (Z. Physik, 1936, 100, 463—470).—Flow experiments recorded for Zn, Cd, Bi, and Sn at temp. down to  $90^\circ$  abs. do not agree with the Becker-Orowan theory (cf. this vol., 145).

A. B. D. C.

**Effect of titanium on polymorphic transformations in iron.** V. N. ŠVERŠCHNIKOV and V. N. GRIDNEV (Domez, 1935, No. 2, 41—43).—Pure Fe containing 0.17, 0.36, and 0.59% Ti was heated at the rate of  $6-7^\circ$  per min. and studied dilatometrically and micrographically. The  $\gamma$ -field is closed at approx. 0.6% Ti.

CH. ABS. (e)

**Polymorphism of potassium pentaborate,  $K_2O_5B_2O_3$ .** A. P. ROLLET (Compt. rend., 1936, 202, 1863—1865; cf. A., 1935, 824).— $K_2O_5B_2O_3$  exists in three forms. The transition points are  $\alpha \rightarrow \beta$   $720^\circ$  and  $\alpha \rightarrow \gamma$  (metastable)  $690^\circ$ .  $\alpha$ , at the m.p. ( $780^\circ$ ), decomposes  $\alpha \rightarrow \text{liq.} + K_2O_4B_2O_3$  and  $\beta$ , m.p.  $760^\circ$  (metastable), behaves similarly.

J. G. A. G.

**Lattice constitution and growth of polymorphic substances, especially potassium nitrate, in the transition range.** J. LEONHARDT and W. BORCHERT (Naturwiss., 1936, 24, 412—413).—A single crystal of the rhombic ( $\beta$ )  $KNO_3$  heated above  $128^\circ$  becomes a mass of small crystals of the high-temp. trigonal form ( $\alpha$ ). At  $< 195^\circ$  there is the possibility of re-forming a distorted single crystal of the  $\beta$ -form on cooling. At  $> 195^\circ$  there is recrystallisation on cooling. If a single crystal of the  $\alpha$ -form is cooled to  $123-113^\circ$  the distorted trigonal form is retained. Cooling below  $113^\circ$  gives the  $\beta$ -form. The existence of a third (monotropic) modification (cf. Cohen *et al.*, A., 1929, 498) could not be demonstrated. A. J. M.

**Two coexistent electronic lattices in iron and alloys of the  $\beta$ -brass type.** M.-p. law. R. FORRER (Ann. Physique, 1936, [xi], 5, 719—756; cf. A., 1935, 1305).—An investigation of the m.-p. law and electronic lattice theory as applied to  $\alpha$ -Fe,  $\beta$ -brass, alloys of analogous constitution, and to Heusler's alloy shows that these substances possess two independent electronic lattices, the supplementary lattice, stable up to the anomalous ferromagnetic point ( $465^\circ$ ) in  $\beta$ -brass, and to the Curie point in Fe, and the principal lattice, stable up to the  $\beta$ - $\gamma$  transition point in Fe, and to the m.p. in alloys. The above points correspond with the rupture of the respective lattices. The principal electron valency of  $\alpha$ -Fe and  $\beta$ -brass is 4; the supplementary vals. are 3 and  $3/2$ , respectively. The latter vals. agree with the Hume-Rothery law in the case of the cubic-centred lattice.

N. M. B.

**Inversion of polymorphism in the series of normal saturated diacids.** F. D. LA TOUR (Compt. rend., 1936, 202, 1935—1937; cf. A., 1935, 1351).—For the acids with 7 and 9 C rise of temp. tends to convert the  $\alpha$ - into the  $\beta$ -form. For higher acids the

reverse is true. The transition temp. is nearer to the m.p. for higher members of the series. H. J. E.

**Determination of thermo-electrical force of metals in a vacuum by a photographically recording double galvanometer.** E. ROSENBOHM and F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 469—477; cf. this vol., 672).—The apparatus and method are described. Measurements for Fe-Cu ( $200-950^\circ$ ) and for Ni-Cu ( $300-400^\circ$ ) are recorded.

H. J. E.

**Hypothesis of spontaneous magneto-galvanic and thermo-electric forces.** A. PERRIER and L. MEYLAN (Helv. phys. Acta, 1935, 8, 320—322; Chem. Zentr., 1935, ii, 2500).—Former results are confirmed.

J. S. A.

**Peltier heat for the element copper-cuprous oxide-copper.** G. MÖNCH (Z. Physik, 1936, 100, 321—325).—The thermo-electric potential due to the Peltier effect  $\propto$  abs. temp. (cf. this vol., 148).

A. B. D. C.

**Crystal structure and diamagnetic susceptibility.** R. N. MATHUR and M. B. NEVGI (Z. Physik, 1936, 100, 615—620).—Diamagnetic susceptibility has been measured for allotropic forms of S, Hg oxides, Pb, Sb, and As; it varies with crystal structure.

A. B. D. C.

**Diamagnetic susceptibility of heavy water.** V. C. G. TREW and J. F. SPENCER (Nature, 1936, 137, 998).—The mean val. for two samples of 99.95%  $D_2O$  is  $0.638 \times 10^{-6}$  in agreement with the previous val. (this vol., 786).

L. S. T.

**Diamagnetic susceptibilities of tin in the bi- and quadri-valent states.** S. S. BHATNAGAR, M. B. NEVGI, and R. L. SHARMA (J. Indian Chem. Soc., 1936, 13, 273—280).—The  $\chi$  of Sn salts in solution and in the solid state have been measured and the vals. of  $\chi$  for Sn<sup>++</sup> and Sn<sup>++++</sup> calc. Whilst for the solid state  $\chi$  increases with rise of temp., for solutions the reverse is the case, and is attributed to the breakdown of complexes at high temp.

C. R. H.

**Diamagnetism of thiocyanates and of the cuprous ion.** C. COURTNY (Compt. rend., 1936, 202, 1929—1931).—Vals. for the susceptibility agree with those calc. for the formulæ  $S:C:N \cdot Ag$  and  $S:C:N \cdot Cu$ .

H. J. E.

**Magnetic susceptibilities of some organic compounds in different physical states.** K. C. SUBRAMANIAM (Proc. Indian Acad. Sci., 1936, 3, A, 420—427).—The following diamagnetic susceptibilities have been observed in the solid, dissolved (MeOH), and liquid states, respectively;  $COPh_2$ , 0.600, 0.616, 0.629;  $p\text{-C}_6\text{H}_4\text{Me} \cdot NO_2$ , 0.518, 0.483, 0.492. Supercooling was observed with  $COPh_2$ . The changes on melting and dissolution are attributed to the breakdown of polymerides.

R. S. C.

**Magnetic studies of sulphur and some sulphur compounds.** P. S. VARADACHARI and K. C. SUBRAMANIAM (Proc. Indian Acad. Sci., 1936, 3, A, 428—434).—The magnetic susceptibility ( $\chi$ ) of solutions of S in  $CS_2$  shows small departures from additivity owing to the breakdown of  $S_{16}$  mols. In  $S_2Cl_2$  solutions of S vals. of  $\chi$  suggest that no  $S_2$  mols. are formed even on heating to  $120^\circ$ . Vals. of  $\chi$  determined are:

$\text{CS}_2$  —0.556,  $\text{S}_2\text{Cl}_2$  —0.461,  $\text{SCl}_2$  —0.467,  $\text{SOCl}_2$  —0.372,  $\text{SO}_2\text{Cl}_2$  —0.365. For the halides vals. agree with those calc. for the structures  $\text{S}:\text{SCl}_2$ ,  $\text{O}:\text{SCl}_2$  and  $(\text{O})_2\text{SCl}_2$ . The val. for the "iodide" (—0.329) shows that no compound is formed. R. S. B.

Magnetic properties and structure of hæmoglobin, oxyhæmoglobin, and carboxyhæmoglobin.—See this vol., 867.

Paramagnetism of the octahydrated sulphates of the rare earths. I. Terbium, dysprosium, holmium, and erbium. S. VELAYOS (Anal. Fis. Quím., 1935, 33, 297—313).— $\chi$  for  $\text{M}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  has been measured over the range 80—300° abs. whence the magneton nos. of Tb, Dy, Ho, and Er are 48.3<sub>6</sub>, 52.0<sub>5</sub>, 51.7<sub>8</sub>, and 46.9<sub>4</sub>. F. R. G.

Paramagnetic relaxation. C. J. GORTER (Physica, 1936, 3, 503—514; cf. this vol., 417).—The heat liberated ( $H$ ) under the action of an alternating magnetic field at high frequency and low temp. has been studied for Ti, V, Cr, Fe, and Al alums, mixed crystals of ferro-magnetic alums with Al alum, and for  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . In each case  $H \propto A/T$  ( $A$  = amplitude of magnetic field;  $T$  = abs. temp.). In some cases  $H$  diminishes when a continuous field is superimposed, either parallel or perpendicular to the alternating field.  $H$  increases more rapidly with frequency for strongly magnetic alums than for weakly magnetic compounds. J. W. S.

Magnetic and electrical properties of the binary systems  $\text{MO}-\text{Fe}_2\text{O}_3$ . J. L. SNOEK (Physica, 1936, 3, 463—483; cf. A., 1935, 1451; this vol., 421, 810).—The magnetisation curves and electrical conductivities have been measured for the binary systems of  $\text{Fe}_2\text{O}_3$  with FeO, MnO, CuO, NiO, and MgO, and for some ternary systems of those oxides with  $\text{Fe}_2\text{O}_3$ . The data are in accord with  $X$ -ray measurements. J. W. S.

Alteration of conductivity of thin metal sheets. M. PIERUCCI (Nuovo Cim., 1935, [ii], 12, 73—75; Chem. Zentr., 1935, ii, 1670).—Observations on W foil confirm the results of Deubner (A., 1934, 1061). J. S. A.

Variation of resistance and structure of cobalt with temperature and a discussion of its photo-electric emission. L. MARICK (Physical Rev., 1936, [ii], 49, 831—837).— $X$ -Ray diffraction patterns for Co, obtained in a camera designed for high-temp. work, showed no crystallographic change in the region of the reported temp. of change of photo-electric emission (cf. Cardwell, A., 1933, 105). The  $\alpha$ - $\beta$  transformation temp. at 492° is unchanged by heating at 875° for 55 hr. The variation of electrical resistance with temp., extended to 1200°, shows a change of slope at the Curie point at 1100°. An expansion of approx. in the lattice edge is observed as Co is heated through the Curie temp. There is no evidence of reversion to the hexagonal form at 1015°. The temp. coeff. of expansion is  $0.143 \times 10^{-4}$  per degree, agreeing with the macroscopic coeff. N. M. B.

Electrical resistance of gold and silver at low temperatures. W. J. DE HAAS and G. J. VAN DEN BERG (Physica, 1936, 3, 440—449; cf. A., 1935, 154).—It is confirmed that Au wires containing  $<10^{-3}\%$

impurity, of different origins and annealed to different extents, all show a min. in their resistance-temp. curves. The temp. of the min. is the lower the lower is the residual resistance. For the region above the min., the "ideal" resistance, calc. from Matthiessen's rule,  $\propto T^{4.2}$ . One Ag wire tested also showed a min. The ideal resistance of Ag  $\propto T^{4.1}$ . J. W. S.

Electrical resistance of gold at low temperatures in a transverse magnetic field. II. E. JUSTI and H. SCHEFFERS (Physikal. Z., 1936, 37, 475—481).—There is strong anisotropy with respect to the electrical resistance of Au crystals at 14° abs. in a transverse magnetic field, when the field is variously oriented in relation to the crystal. Al, Cu, and Ag (not specially pure) also show this anisotropy, but to a much smaller extent. A. J. M.

Electrodynamics of macroscopic fields in superconductors. F. LONDON (Nature, 1936, 137, 991—992).—Theoretical. L. S. T.

Transition of a tin sphere from the non-superconductive state to the superconducting state. W. J. DE HAAS and O. A. GUINAU (Physica, 1936, 3, 534—542; cf. this vol., 556).—The changes of magnetic field strength measured by Bi wires through a central canal and around the equator of a Sn sphere during transition from non-superconducting to superconducting state ( $a$ ) at const. temp. and ( $b$ ) at const. magnetic field are analogous to those occurring during the reverse change. The phenomenon is not completely reversible, however. Lippmann's rule is not valid at the centre of the sphere. J. W. S.

Magnetic fields in superconductors. F. LONDON (Physica, 1936, 3, 450—462).—Mathematical. A theory of the intermediate stage of superconductivity has been developed. J. W. S.

Ultrasonic velocities in organic liquids. III. Esters and ethers. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 3, A, 482—486; cf. this vol., 787).—Ultrasonic velocities ( $v$ ) have been determined for a frequency of  $7.382 \times 10^6$  kc. at 25.5—28°. For the substituent groups of ethers  $v$  is in the order Me and OMe > Et and OEt, aromatic > aliphatic. For esters  $v$  decreases with increasing mol. wt., but increases on introduction of Cl as in  $\text{CH}_3\text{Cl}-\text{CO}_2\text{Et}$ . R. S. B.

Regulated behaviour of the magnitude of mol. depression of the m.p. of mixtures of solvents from isomorphous organic compounds. J. PIRSCH (Ber., 1936, 69, [B], 1330—1332).—Examination of mixtures of  $\alpha$ -dicyclopentadiene, dihydro- and tetrahydro- $\alpha$ -dicyclopentadiene shows that the law of additivity of mol. depression of the m.p. holds also for ternary solvent mixtures. H. W.

M.p. of vanadium oxytrichloride and vanadium tetrachloride. Thermal analysis of the system chlorine-vanadium tetrachloride. A. MORETTE (Compt. rend., 1936, 202, 1846—1847).—The m.p. are:  $\text{VOCl}_3$  —77 $\pm$ 2°,  $\text{VCl}_4$  —28 $\pm$ 2°. There are no discontinuities in the f.-p. and m.-p. curves of the system  $\text{Cl}_2$ - $\text{VCl}_4$  over the entire range of composition. J. G. A. G.

Exact measurement of the specific heats of metals at high temperatures. XXIII. Calori-



metrical, electrical, and thermo-electrical behaviour of ductile titanium. I—III. F. M. JAEGER, E. ROSENBOHM, and R. FONTEYNE (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 442—452, 453—461, 462—469; cf. this vol., 672).—The sp. heat of Ti, plotted as a function of temp., shows minor discontinuities at 297—300°, 298—400°, approx. 554°, 640°, and 817°. There is no change in the X-ray diagram at these points.  $\beta$ -Ti is formed above 950°. Its at. heat is 7.525 g.-cal., and is independent of temp. The minor discontinuities are connected with the presence of O or oxides. They may be at the transition points of the modifications of  $\text{TiO}_2$ . Measurements of the electrical resistance (15—1000°) are recorded. The hysteresis effects are discussed. Vals. for the c.m.f. of a Ti—Au thermocouple (15—1000°) are recorded.

H. J. E.

Transition of hexagonal  $\alpha$ -titanium into regular  $\beta$ -titanium at a high temperature. J. H. DE BOER, W. G. BURGERS, and J. D. FAST (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 515—519).—The transition temp. of  $\alpha$   $\beta$ -Ti (from measurements of electrical resistance) is  $882 \pm 20^\circ$ .  $\beta$ -Ti is cubic body-centred ( $a$  at  $900^\circ = 3.32 \text{ \AA}$ ). When Ti has taken up N or O it shows a transition range instead of a transition temp.

H. J. E.

Temperature variation of properties used to measure temperature. V. JACYNA (Z. Physik, 1936, 100, 205—211).—Theoretical. A. B. D. C.

Determination of vapour pressure. D. RADULESCU and S. TILENSCHI (Bul. Soc. Chim. Romania, 1935, 17, 323—327).—Pure electrolytic  $\text{H}_2$  is passed over the substance and the amount entrained determined by adsorption on active charcoal. The v.p. of  $\text{CH}_2\text{PhCl}$  at  $170^\circ$  is 0.523 mm.

R. S. B.

Vapour-pressure curve of thallium at very low densities. F. MÜLLER (Helv. phys. Acta, 1935, 8, 152—164; Chem. Zentr., 1935, ii, 1840; cf. A., 1935, 438).—The v.p. of Tl between  $350^\circ$  and  $500^\circ$  is calc. from abs. measurements of the max. absorption of the 3776  $\text{\AA}$ . resonance line, the abs. intensity of which is calc. Vals. found ( $1.2 \times 10^{-6}$  to  $7.4 \times 10^{-4}$  mm.) accord well with the high-temp. measurements of Gibson and von Wartenberg.

J. S. A.

Vapour pressure measurements on indium halides. C. ROBERT and M. WEHRLI (Helv. phys. Acta, 1935, 8, 322—324; Chem. Zentr., 1935, ii, 2501).—The v.p. of  $\text{InCl}$ ,  $\text{InBr}$ ,  $\text{InI}$ ,  $\text{InCl}_2$ , and  $\text{InBr}_2$  between  $300^\circ$  and  $600^\circ$  are recorded. Between  $500^\circ$  and  $700^\circ$ ,  $\text{InCl}_2$  and  $\text{InBr}_2$  form undissociated simple mols.

J. S. A.

Vapour pressure of certain substances. V. A. KIREEV and V. A. NIKIFOROVA (J. Gen. Chem. Russ., 1936, 6, 75—77).—V.p. data are recorded for  $\text{CH}_2\text{Cl}\cdot\text{CHMeCl}$  ( $16$ — $95^\circ$ ),  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$  ( $17.5$ — $127.5^\circ$ ), and  $\text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{OH}$  ( $43.8$ — $126^\circ$ ). Empirical formulæ connecting v.p. with temp. are given.

R. T.

Determination of the thermodynamical temperature scale below  $1^\circ$  abs. W. J. DE HAAS and E. C. WIERSMA (Physica, 1936, 3, 491—494; cf. A., 1935, 815).—When  $\text{Cs}_2\text{SO}_4\cdot\text{Ti}_2(\text{SO}_4)_3\cdot 24\text{H}_2\text{O}$  is magnetised in a field of 24,075 gauss at  $1.20^\circ$  abs. and

demagnetised down to  $104.6$  gauss, its magnetisation remains const. It is shown that for such salts the thermodynamic temp. scale can be determined for a large interval below  $1^\circ$  abs. by magnetic measurements only.

J. W. S.

Relation between critical data and atomicity. M. PEDRERO (Anal. Fís. Quím., 1936, 34, 173—178).—The relation  $T/p + 0.1p = 1 + i + (3i - 2)T/31i^2$  where  $T$  is the abs. crit. temp.,  $p$  the crit. pressure, and  $i$  the no. of atoms in the mol. is calc. for 79 substances. Other relations containing variable atomicity factors are considered and summarised as  $f(p, T, i) = 0$ .

F. R. G.

General equation of state. G. WOOLSEY (J. Amer. Chem. Soc., 1936, 58, 984—987).—The formula  $PV + (4.555V + 7.427)/(T^{1/2}V^2 + 0.9382T^{2/3}V + 2.140/[T^{3/2}]) = 3.25T + 0.2837P + 1.343 \log(P + 1)$  is put forward.

E. S. H.

Verification of the laws of Knudsen and of Reynolds by means of radon. W. MUND and A. LUYCKX (Ann. Soc. Sci. Bruxelles, 1936, B, 56, 196—219).—Knudsen's cosine law for the directional distribution of mols. leaving a vessel wall and Reynolds' law for the flow of gas mols. through an orifice are discussed. Data for the flow of Rn through an orifice are applied to the verification of these laws.

C. R. H.

Critical relation and molecular association. R. LAUTIFÉ (Bull. Soc. chim., 1936, [v], 3, 1136—1139).—The expression  $xP_c V_c/T_c = 25.2 + 4.0617 \times 10^{-4} T_c^2 / (1 + 1.925 \times 10^{-5} T_c^2)$  is derived.  $x$ , the degree mol. association, can thus be calc. from crit. data.

E. S. H.

Nernst theorem. R. BRUNNER (Z. Physik, 1936, 100, 584—593).—The entropy of a substance is obtained from pressure characteristics.

A. B. D. C.

Phaseequilibria in hydrocarbons. XIV. Joule-Thomson coefficients of *n*-butane and *n*-pentane. E. R. KENNEDY, B. H. SAGE, and W. N. LACEY (Ind. Eng. Chem., 1936, 28, 718—720; cf. this vol., 788).—Joule-Thomson coeffs. were determined for *n*- $\text{C}_4\text{H}_{10}$  and *n*- $\text{C}_5\text{H}_{12}$  at temp.  $70$ — $220^\circ \text{F}$ . and pressures from 1 atm. to nearly saturation pressure and compared with vals. for  $\text{C}_3\text{H}_8$ . The vals. of  $C_p$  and isothermal changes of heat content with change of pressure were also calc.

D. M. M.

Joule-Thomson coefficient of carbon monoxide. T. C. HUANG, F. LIN, and C. Y. FU (Z. Physik, 1936, 100, 594—598).—This coeff. is calc. from the Beattie-Bridgman equation of state.

A. B. D. C.

Bismuth crystals. I. Thermal and electrical conductivity in transverse magnetic fields. E. GRUNEISEN and J. GIELESSEN (Ann. Physik, 1936, [v], 26, 449—464).—The effect of a magnetic field, in various directions, on the thermal and electrical conductivity of single Bi crystals at  $-183^\circ$  and  $-195^\circ$  has been examined. The thermal conductivity decreases slowly with increasing field strength, irrespective of the direction. A similar, but more rapid, decrease of the electrical conductivity was found. Both thermal and electrical conductivity vary with the direction of the field. Except at high field strengths, there is an

approx. linear relationship between the two conductivities. The electronic conductivity derived from this relationship is somewhat < that obtained from the Wiedemann-Franz-Lorenz equation. A. J. M.

Effect of a magnetic field on thermal conductivity and viscosity of paramagnetic gases. II. M. VON LAUE (Ann. Physik, 1936, [v], 26, 474—480).—Corrections in the method of an earlier paper (A., 1935, 923) are made, but the results are unaffected. A. J. M.

Viscosity and diffusion coefficients of atomic hydrogen and atomic deuterium. I. AMDUR (J. Chem. Physics, 1936, 4, 339—343; cf. A., 1935, 827).—The viscosity of at. H, recalcd. from Harteck's experimental data, is  $\eta = 4.746 \times 10^{-6} \sqrt{T/(1+30.6/T)}$  between 0° and 100°. Expressions for the diffusion coeffs. of H and D in binary mixtures of H, D, H<sub>2</sub>, and D<sub>2</sub> are given. F. L. U.

Viscosity of air. W. N. BOND (Nature, 1936, 137, 1031).—The val. obtained,  $\eta_{23} = (1834.7 \pm 0.8) \times 10^{-7}$ , agrees with that found by Kellstrom (A., 1935, 1455), and gives  $e = (4.800 - 4.816 \pm 0.005) \times 10^{-10}$  e.s.u. L. S. T.

Penetration of copper and gold ions into transparent crystals of NaCl and KCl. S. A. ARZIBISCHEV, M. N. BOGOMOLOVA, N. V. BORISOV, and I. C. REPSE (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 95—96).—Mobility data are recorded. The diffusion of the Cu ion in NaCl was less during electrolysis than in absence of the field. The Au colloids were pptd. by cooling the crystal to 300—350°. H. J. E.

Correlations between curves of inverse properties in binary systems. V. J. ANOSOV (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 69—75).—Theoretical. R. T.

Shape of curves representing properties in binary systems in the case of formation of an undissociated chemical compound, when the property in question is represented in an ideal system by a straight line. II. V. J. ANOSOV (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 77—89).—Theoretical. R. T.

Refractivity and magnetic birefringence of liquid mixtures. M. RAMANADHAM (Proc. Indian Acad. Sci., 1936, 3, A, 384—397).—The deviations of observed vals. (cf. Chinchalkar, A., 1933, 889) from those calc. by the Langevin theory are quantitatively explained by the new idea of a varying set of anisotropic polarisation field coeffs. The actual variations of the coeffs. with changing concn. have been determined from observed refractivities of mixtures of the requisite composition in the case of CCl<sub>4</sub>-C<sub>6</sub>H<sub>6</sub>, -PhMe, -PhNO<sub>2</sub>, -CS<sub>2</sub>; C<sub>6</sub>H<sub>6</sub>-CS<sub>2</sub>, CS<sub>2</sub>-PhCl, and CS<sub>2</sub>-PhBr. N. M. B.

Diamagnetism of some organic binary mixtures at different temperatures. S. SEELY (Physical Rev., 1936, [ii], 49, 812—819; cf. Pal, A., 1930, 1245).—Results obtained by use of the improved Wills-Boeker manometric balance (cf. A., 1933, 212) are recorded for binary mixtures of CCl<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and PhNO<sub>2</sub> over the temp. range 10—50°. For C<sub>6</sub>H<sub>6</sub>-PhNO<sub>2</sub> mixtures, each constituent of which shows no variation of mass susceptibility with temp., additive

relations are shown, but systematic deviations, depending on concn. and temp., are found for C<sub>6</sub>H<sub>6</sub>-CCl<sub>4</sub> or PhNO<sub>2</sub>-CCl<sub>4</sub> mixtures. N. M. B.

Variation of vapour pressure of the isotopic mixture of hydrogen with time at 20.38° abs. A. FARKAS, L. FARKAS, and P. HARTECK (Physikal. Z., 1936, 37, 447—448).—The explanation of this phenomenon given by Steiner (A., 1935, 1456) is not the same as that suggested for the variation of thermal conductivity of the isotopic mixture at low temp. by Farkas *et al.* (A., 1934, 608). A. J. M.

Vapour pressure of the binary mixtures (A) PbCl<sub>2</sub> + CuCl<sub>2</sub> and ZnCl<sub>2</sub> + CuCl<sub>2</sub>, (B) ZnCl<sub>2</sub> + PbCl<sub>2</sub>, in an atmosphere of chlorine. D. N. TARASENKOV and A. V. BABAeva (J. Gen. Chem. Russ., 1936, 6, 305—310, 311—314).—(A) The v.p. of PbCl<sub>2</sub> at 500—700° in a Cl<sub>2</sub> atm. is > in N<sub>2</sub>. Dissociation of CuCl<sub>2</sub> in Cl<sub>2</sub> at 760 mm. becomes evident at 520°. The partial pressure of CuCl<sub>2</sub> in the systems CuCl<sub>2</sub>-PbCl<sub>2</sub> and -ZnCl<sub>2</sub> is at a max. for 1 : 1 mixtures.

(B) V.-p. data are recorded for ZnCl<sub>2</sub> and for the system ZnCl<sub>2</sub>-PbCl<sub>2</sub> in a stream of Cl<sub>2</sub>, at 398°, 516°, and 604°. R. T.

Orthobaric azeotropes. M. LECAT (Ann. Soc. Sci. Bruxelles, 1936, B, 56, 221—234).—A further list is given of 452 orthobaric or normal azeotropic mixtures together with their b.p. and compositions (cf. this vol., 675). C. R. H.

Binary systems of organic compounds. Thermal analyses and specific refractivities. W. R. BURNHAM and W. M. MADGIN (J.C.S., 1936, 789—793).—F.-p. and *n* data show that the binary mixtures *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>-*p*-C<sub>6</sub>H<sub>4</sub>Cl-OH, C<sub>5</sub>H<sub>5</sub>N-PhCl, and AcOH-PhCl are of the simple eutectic type, and that *p*-C<sub>6</sub>H<sub>4</sub>Me-NH<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>Cl-OH, *p*-C<sub>6</sub>H<sub>4</sub>Me-NH<sub>2</sub>-*p*-C<sub>6</sub>H<sub>4</sub>Cl-OH, and *p*-C<sub>6</sub>H<sub>4</sub>Cl-OH-C<sub>5</sub>H<sub>5</sub>N form stable 1 : 1 compounds. Deviations from a straight line in the *n*-composition curve for AcOH-PhCl are attributed to the presence of dimeric AcOH and, possibly, of higher polymerides. C. R. H.

*p*-Toluidine in binary systems with certain phenols. K. HRYNAKOWSKI and M. SZMYTÓWNA (Rocz. Chem., 1936, 16, 113—118).—Fusion diagrams for PhOH,  $\alpha$ - and  $\beta$ -C<sub>10</sub>H<sub>7</sub>-OH, and *m*-, *o*-, and *p*-NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-OH indicate the existence of 1 : 1 compounds in all but the last two systems. R. T.

Systems : sulphur dioxide and mono-olefines. I. Caprylene and sulphur dioxide. W. F. SEYER and L. HODNETT (J. Amer. Chem. Soc., 1936, 58, 996—998).—Miscibility relations and f.-p. data for octene-SO<sub>2</sub> mixtures have been determined. Octene absorbs O<sub>2</sub> from the air, apparently forming a peroxide. E. S. H.

Formation of molecular swarms in binary liquid mixtures. V. S. VRKLJAN and M. KATALINČ (Physikal. Z., 1936, 37, 482—487).—Theoretical. Gans' theory (this vol., 144) is applied to the Krishnan effect of anomalous depolarisation in binary liquid mixtures at the crit. solution temp. (or slightly above). A. J. M.

Electrical resistance of dilute solid solutions. N. F. MOTT (Proc. Camb. Phil. Soc., 1936, 32, 281—290).—Theoretical. T. G. P.



**Dependence of hardness of Ag-Zn alloys on their composition.** G. I. PETRENKO and E. E. TSCHERKASCHIN (Z. anorg. Chem., 1936, 227, 415—416).—The hardness-composition curve for Ag-Zn alloys exhibits max. corresponding with the compounds  $\text{AgZn}$ ,  $\text{Ag}_2\text{Zn}_3$ , and  $\text{Ag}_5\text{Zn}_8$ . F. L. U.

**Incubation of alloys.** K. HONDA and K. TAMARU (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 315—319).—Measurements of hardness, electrical resistance, and  $d$  for Cu-Be alloys and duralumin lead to an explanation of incubation in terms of differential hardening and lattice distortion. N. M. B.

**Crystallisation of ternary eutectics.** A. A. BOTSCHVAR and K. V. GOREV (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 283—290).—The components of the ternary eutectics of the systems Cd-Pb-Bi, Cd-Pb-Sn, and Cd-Sn-Bi crystallise out successively, with the result that the concn. of each constituent in the liquid eutectic varies during the process of solidification. Simultaneous crystallisation takes place only when centres of crystallisation for each component co-exist. R. T.

**Density and refractive index of the ternary systems water-methyl alcohol-*n*-propyl alcohol and water-*n*-propyl alcohol-isobutyl alcohol.** R. RIGAMONTI (Annali Chim. Appl., 1936, 26, 143—151).—The composition of ternary  $\text{H}_2\text{O}$ -MeOH-PrOH mixtures may be derived from measurements of  $d$  and  $n$ , but this is not possible in the case of ternary  $\text{H}_2\text{O}$ -PrOH-BuOH mixtures. Miscibility relations in the latter system have been studied at 15—120°. L. A. O'N.

**Homogenising properties of binary liquid mixtures.** I. Water-aniline-pyridine-piperidine. II. Water-aniline-pyridine-acetic acid. III. Water-aniline-piperidine-acetic acid. IV. Water-dimethylaniline-piperidine-allylthiocarbimide. V. F. UST-KATSCHKINTZEV and R. V. MERTZLIN (J. Gen. Chem. Russ., 1936, 6, 15—21, 22—26, 27—31, 32—36).—Phase diagrams have been constructed for the systems at 0—50°. Homogenising power is an additive property for the systems in I and IV. R. T.

**"Antagonism" and "synergism" of ions in heterogeneous equilibrium in liquid systems of three components. Two co-existing phases.** X. A. K. VLCEK (Chem. Obzor, 1935, 10, 88—90; Chem. Zentr., 1935, ii, 1822).—Equilibrium relations for the systems  $\text{H}_2\text{O}$ -Et<sub>2</sub>O-COMe<sub>2</sub>,  $\text{H}_2\text{O}$ -Et<sub>2</sub>O-EtOH,  $\text{H}_2\text{O}$ -Et<sub>2</sub>O-AcOH, and  $\text{H}_2\text{O}$ -C<sub>6</sub>H<sub>6</sub>-COMe<sub>2</sub>, in presence of pairs of salts, have been determined and compared with the relations which are exhibited when a single salt is present. J. S. A.

**Equilibria in liquid mixtures and solutions. Solubility in different solvents, at less than atmospheric pressure.** IX. Acetylene and vinyl chloride, at 0°. X. Hydrogen and methane at -20° to 40°. V. A. KIREEV and M. A. ROMANTSCHUK (J. Gen. Chem. Russ., 1936, 6, 78—80, 81—84).—IX. Data are recorded for C<sub>2</sub>H<sub>2</sub> and CH<sub>2</sub>:CHCl (I) in kerosene at -20° to 20° (100—760 mm.) and in heavy solvent oil, "solar oil," EtOH, and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> at 0° (100—760 mm.). Small deviations from Henry's

law are found in all cases, the greatest differences being shown by (I) at low temp. The best solvent for (I) is C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

X. Data are given for H<sub>2</sub> and CH<sub>4</sub> in xylene, kerosene, and "cracking benzine" at -20° to 40° (50—760 mm.) and in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and heavy solvent oil at 0° (500—760 mm.). Henry's law is followed in all cases. The solubility of H<sub>2</sub> in xylene rises with temp. over the range -20° to 40°. R. T.

**Solubility of mono-, di-, and tri-olein in some organic solvents.** C. ARTOM and L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 880—882).—Solubility and partition data (with H<sub>2</sub>O as the second medium) are given at 20—25° for CHCl<sub>3</sub>, light petroleum, Et<sub>2</sub>O, CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, EtOAc, EtOH (also at 50°, 80°, and 90°), and COMe<sub>2</sub> (also at 50° and 80°). The hydrophilic character of mono-olein is noteworthy. F. O. H.

**Solubility of silver nitrate in ethyl and isopropyl alcohols.** C. L. M. BROWN (Pharm. J., 1936, 136, 618).—The solubility of AgNO<sub>3</sub> in 90% aq. EtOH is 10.73 g. per 100 at 15.5° and 5.67 g. at 20°. The corresponding vals. for PrOH are 31.17 and 30.91 g., respectively. A. L.

**Solubility of calcium oxide in water and in aqueous sucrose.** K. SMOLEŃSKI and W. ŻERO (Rocz. Chem., 1936, 16, 24—36, and Bull. Acad. Polonaise, 1935, A, 586—601).—The solubility of CaO in H<sub>2</sub>O and 1.5—36% sucrose (I), at 0—80°, rises with (I) concn. and falls with rising temp. The final  $p_H$  is the same in presence or absence of (I). R. T.

**Solubility measurement. Solubilities in the system SrCl<sub>2</sub>-H<sub>2</sub>O from 20° to 200°.** A. W. C. MENZIES (J. Amer. Chem. Soc., 1936, 58, 934—937).—Apparatus and procedure requiring the use of only 1 c.c. of solvent are described. Solubilities of SrCl<sub>2</sub> in H<sub>2</sub>O are recorded for the range 20—200°. Transition temp. at 61.4° and 134.4° are reported. E. S. H.

**Heteropoly-compounds. V. Solubility of certain heteropoly-compounds.** A. V. RAKOVSKI and E. A. NIKITINA (J. Gen. Chem. Russ., 1936, 6, 50—54).—The solubility of phosphomolybdic (P<sub>2</sub>O<sub>5</sub>.24MoO<sub>3</sub>) and phosphotungstic (P<sub>2</sub>O<sub>5</sub>.24WO<sub>3</sub>) acids, and of their Na<sub>2</sub> and Na<sub>3</sub> salts, has been determined at 0—98°. The existence of definite crystal hydrates is not indicated. The solubility of Na phosphotungstate is greatly depressed in presence of NaCl. R. T.

**Adsorption of zinc sulphide by copper sulphide.** A. DEL CAMPO and A. HOYOS DE CASTRO (Anal. Fis. Quím., 1935, 33, 754—764).—In the pptn. of CuS from aq. HCl by H<sub>2</sub>S in presence of Zn<sup>2+</sup>, ZnS is partitioned between the CuS gel and the aq. layer, unless the pptn. is accompanied by mechanical stirring. CuS pptd. in presence of Pb<sup>2+</sup> cannot be entirely freed from PbS by stirring. F. R. G.

**Adsorption of electrolytes on crystal surfaces.** L. DE BROUCKÈRE (Chem. Weekblad, 1936, 33, 420—423).—A reply to Kolthoff (this vol., 792). D. R. D.

**Influence of indole on the adsorption of indican by various adsorbents.** J. GARCÍA-BLANCO and F. ALDAYA (Anal. Fis. Quím., 1935, 33, 463—465).—

The adsorption of indican (I) by blood charcoal is decreased in amount by the presence of indole (II), but the smaller adsorption of (I) by sheep-blood corpuscles, bone charcoal, talc, and kaolin is increased in presence of (II). F. R. G.

**Measurement of the adsorption of oils by metallic surfaces.** J. J. TRILLAT and R. VAILLÉ (Compt. rend., 1936, 202, 2134—2136).—The adsorption of acids, *e.g.*, oleic acid, from mineral oil by a metallic surface has been followed by measuring the interfacial tension between the oil and  $H_2O$  before and after contact with the metal. C. R. H.

**Adsorption of binary mixtures of acetic acid and alcohols in aqueous solution [by animal charcoal].** R. AMIOT (Compt. rend., 1936, 202, 1852—1854).—The order of the adsorption of the single substances is  $MeOH < EtOH < AcOH < Pr^iOH < Pr^oOH < Bu^iOH < Bu^oOH < isoamyl$  alcohol. With the binary mixtures, each solute depresses the adsorption of the other. The order of the adsorbability of the alcohols is independent of  $[AcOH]$  but the adsorption decreases with rise of  $[AcOH]$  and the adsorption of  $AcOH$  decreases as the adsorbability of the alcohol rises. J. G. A. G.

**Adsorption of glucose by albumin.** E. GOU-BAREV and G. MOISEENKO (Bull. Soc. Chim. biol., 1936, 18, 769—779).—The adsorption of glucose by solutions of albumin increases with increase of  $p_H$ , and for any  $p_H$  val. is represented by the ordinary adsorption formula. A. L.

**Adsorption of alkali and alkaline-earth cations by a colloidal clay medium.** A. DELFORGE (Chim. et Ind., 1936, 35, 1276—1279).—Approx. equimol. quantities are adsorbed as a result of neutralisation, but in the case of the alkaline earths there is an additional adsorption. Reasons for this are discussed. The adsorption effects are reversible and equilibrium is attained more rapidly with excess of alkaline earth. With small amounts of  $CaO$ , corresponding with the usual conditions for the liming of soil, equilibrium may take several months. C. R. H.

**Adsorption of lime on silica gels.** A. MAFFEI (Gazzetta, 1936, 66, 197—204).—The chemisorption of  $CaO$  on  $SiO_2$  gel has been studied. The initial process is one of true adsorption, but  $Ca$  silicate is gradually formed. J. W.

**Validity of Mecklenburg's formula. New viewpoint on the dynamics of adsorption.** D. RADULESCU and S. TILENSCHI (Bul. Soc. Chim. Romania, 1935, 17, 313—321).—Mecklenburg's formula (cf. A., 1931, 298) is criticised. Observations on the adsorption of  $H_2$ ,  $N_2$ , and  $O_2$  by charcoal suggest that for primary adsorption the v.p. is approx. 0, and that this is followed by capillary condensation and the appearance of concave surfaces in the liquid. R. S. B.

**Simultaneous adsorption of two adsorbates which react together.** E. ANGELESCU and D. CISMARU (Bul. Soc. Chim. Romania, 1935, 17, 229—247).—The adsorption by charcoal of acids ( $AcOH$ ,  $EtCO_2H$ ,  $Pr^iCO_2H$ ) and bases ( $NH_2Ph$ , *o*-, *m*-, and *p*- $C_6H_4MeNH_2$ ) from aq. solutions has been examined. The observations are discussed in relation to the constitution of the aq. solutions. R. S. B.

**Formation of unimolecular films on thin foils of metals and of cellulose.** H. MARK and H. MORZ (Chem. Eng. Cong. World Power Conf., 1936, M/1, 13 pp.).—The formation of films of org. substances on metals and on cellulose has been studied by photographing an electron beam reflected from the surface. The org. substance is placed on a support connected with the metal or cellulose film by a wire or band along the surface of which the org. substance diffused. The rate of formation of a cryst. film depends on the rates of diffusion, nucleus formation, and crystal growth. These in turn depend on the nature of the substance, temp., etc. In some cases diffusion consists of a series of jumps between active spots which require a definite activation energy. Diffusion is most rapid for neutral substances and slowest for highly polar substances, but the latter form nuclei more readily; crystal growth is generally relatively rapid. Diffusion is slower on metals than on glass, cellulose, etc. A. G.

**Electrical changes in interfacial films.** T. TEORELL (Nature, 1936, 137, 994—995).—The d.c. conductance of films of  $CCl_4$ , olive oil, etc. changes abruptly as the film becomes thinner from a barely detectable to a measurable val. which increases in definite steps until the bubble bursts. The a.c. conductance also varies but in a more continuous manner. Other liquids, *e.g.*,  $PhNO_2$ , develop an "asymmetry potential" which changes in a characteristic manner as the interfacial non-aq. film becomes thinner. L. S. T.

**Surface ionisation of caesium on tungsten.** M. J. COPLEY and J. GLASSER (J. Amer. Chem. Soc., 1936, 58, 1057—1058).—Below  $2000^\circ$  abs. the % ionisation agrees with theory, but above  $2000^\circ$  abs. the experimental vals. are lower. E. S. H.

**Influence of hydrogen ions on the dielectric potential and surface tension of some alkaloids and other organic substances in aqueous solutions.** B. KAMIENSKI and W. GOSLAWSKI (Bull. Acad. Polonaise, 1935, A, 515—530).—The influence of  $[H^+]$  on the surface tension and on the dielectric potential at the air-solution interface of aq. solutions of veratrine, cevadine, amarine, quinine, quinidine, citronellol, and citral is described. A parallelism between the two effects is observed. O. D. S.

**Dielectric potential and surface tension of  $\beta$ -eucaine, procaine, and orthocaine solutions at different hydrogen-ion concentrations.** B. KAMIENSKI and B. ZAPIÓR (Bull. Acad. Polonaise, 1936, A, 133—144; cf. A., 1935, 931).—The influence of  $p_H$  on the dielectric potential ( $V$ ) and surface tension ( $\sigma$ ) of solutions of  $\beta$ -eucaine, procaine, and orthocaine salts has been investigated. The change of  $V$  and  $\sigma$  at the interface depends on the size of mol. adsorbed and the dissociation const. The mono-bases  $\beta$ -eucaine and procaine show only one break in the  $V$ - $p_H$  curve, instead of two for bivalent bases (quinine and quinidine); both  $V$  and  $\sigma$  begin to rise rapidly at  $p_H$  8 and reach a max. rate of increase above  $p_H$  10. J. W. S.

**Measurement of transient resistance as a method of physico-chemical analysis.** P. P.



PORFIROV (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 135—140).—The importance of transient resistance measurements for the study of surface films is emphasised.  
R. T.

Significance of electrical surface phenomena for the stability of hydrophobic dispersions. H. EILERS and J. KORFF (Chem. Weekblad, 1936, 33, 358—362).—From a mathematical consideration of Donnan's hypothesis, it is shown that the protective action of the double layer in hindering collision between the particles is represented by  $A = c\zeta^2/K$ , where  $\zeta$  is the crit. potential and  $K$  the mean diameter of the ionic sphere (Debye-Hückel) and is not a simple function of  $\zeta$  as is usually supposed. The formula is in good agreement with the more important data in the literature.  
S. C.

Determination of the thickness of the albumin membrane formed between water and benzene and properties of this membrane. H. DEVAUX (Compt. rend., 1936, 202, 1957—1960).—The thickness of albumin membranes formed at a  $H_2O-C_6H_6$  interface is determined by reducing the area until the membrane becomes turbid, due to a process of folding. Membranes formed in contact with air are much more elastic and form more slowly than those between two liquid phases.  
H. J. E.

Liesegang periodicity and concentration of the reagent in the drop. (MLLE.) S. VEIL (Compt. rend., 1936, 202, 2078—2079).—A linear relationship was observed in the distribution const. of the rings formed by adding drops of  $AgNO_3$  to  $Cr_2O_7^{2-}$  in gelatin, and the  $[AgNO_3]$ .  
H. J. E.

[Use of] pyrosulphuric acid as a solvent. C. R. DE ROBLES and E. MOLES (Anal. Fis. Quím., 1935, 33, 643—654).—For solutions of sulphonal, veronal, trional, and  $PhNO_2$  in  $H_2S_2O_7$  the mol. f.-p. depression is 111.5, in agreement with the calc. val. of Auerbach (A., 1926, 791). The addition of  $H_2SO_4$ ,  $H_2O$ , or  $SO_3$  produces an anomalous depression of the m.p. (cf. this vol., 798).  
F. R. G.

Cryoscopic determination of the hydration of hydrochloric acid ions. F. BOURION and O. HUN (Compt. rend., 1936, 202, 2149—2152).—Cryoscopic data for solutions of resorcinol in 0.5*N*-HCl indicate a degree of hydration corresponding with  $HCl \cdot 14.5H_2O$ .  
C. R. H.

Determination of osmotic pressure.—See this vol., 969, 972.

Membrane method and method of isothermal distillation with highly polymerised compounds.—See this vol., 972.

Dialysis and diffusion coefficients of alkali chlorides. W. NOWATKE (Rocz. Chem., 1936, 16, 49—56).  
R. T.

Determination of dielectric constants of aqueous solutions of electrolytes by the Fürth ellipsoid method. T. LIN (Ann. Physik, 1936, [v], 26, 495—512).—The dielectric consts. of aq. solutions of NaCl, LiCl, NaI, HCl,  $Mg(NO_3)_2$ ,  $LaCl_3$ , and  $MgSO_4$  have been determined by the Fürth method with a frequency of  $2.5 \times 10^5$ .  
A. J. M.

Suspended matter in gases. A. WINKEL (Angew. Chem., 1936, 49, 404—410).—A review of recent work on the formation, sedimentation, particle size, optical properties, electrical discharge, and structure of aerosols.  
J. S. A.

Viscosity of suspensions of asbestos and yeast. R. F. GARCIA (Anal. Fis. Quím., 1936, 34, 414—418).—The val. of the const. in Einstein's formula is found to increase with the vol. of the suspended particles.  
F. R. G.

Colloidal solutions. A. LANGIEN and M. PIVO-TEAU (Bull. Sci. pharmacol., 1934, 41, 660—666; Chem. Zentr., 1935, ii, 2502).—The mean particle size of Rh sols has been calc. (a) from the extent of the deviation from Lambert's absorption law, (b) from the  $\lambda$  of scattered light, and (c) from the degree of polarisation of scattered light.  
J. S. A.

Electric double layer of colloids, particularly silver iodide, metals, and carbon. E. J. W. VERWEY (Chem. Weekblad, 1936, 33, 414—420).—The double layer theory is discussed and illustrated by a consideration of the properties of sols of AgI, noble metals, and C.  
D. R. D.

[Properties of] a colloidal solution prepared from resorcinol-formaldehyde resins. M. ENGELDER (Compt. rend., 1936, 202, 1854—1856).—In aq. suspension, the particles are negatively charged. Quantities of LiCl insufficient to cause flocculation retard flocculation by subsequent additions of LiCl.  
J. C. A. G.

Effect of adsorbed layers on the dielectric constant of a disperse system. D. I. SHURAVLEV (J. Phys. Chem. U.S.S.R., 1934, 5, 784—789).—A formula is derived for the dielectric const. as a function of particle size. The calc. thickness of the adsorbed layer on particles of the emulsified  $H_2O-EtOH$  mixture in paraffin oil is approx.  $3.5 \times 10^{-5}$  cm.  
CH. ABS. (e).

Relation between low-temperature research and colloid chemistry. F. F. NORD (Chem. Eng. Cong. World Power Conf., 1936, M5, 24 pp.).—The effect of freezing on the state of aggregation of lyophilic biocolloids has been examined by determining the rate of diffusion of frozen and unfrozen solutions of Na oleate, ovalbumin, polyacrylic acid (I), and myosin. The effect of freezing on electrical conductivity and cataphoresis was also determined. In solutions of concn. <1% there is a disaggregation on freezing, and in solutions more conc. than 1.5% there is an aggregation, which increases with concn. and may become a coagulation. Freshly prepared (I) does not show the effect. These observations may explain the transient increase in activity of frozen solutions of zymases, peroxidases, and tyrosinase in connexion with the carrier theory of enzymic activity, and also the increase in soil activity after freezing.  
A. J. M.

Influence of non-electrolytes on the velocity of coagulation of ferric hydroxide. K. JABECZYNSKI and J. HELWICH (Rocz. Chem., 1936, 16, 141—145).—Coagulation of  $Fe(OH)_3$  sols is accelerated by MeOH, EtOH, PrOH, and  $CO_2Me$ , and retarded by glycol, glycerol, mannitol, and  $CH_2O$ ; MeCHO is without effect.  
R. T.

**Thermo-ageing of colloids. I. Variation of refractivity.** S. S. JOSHI and P. V. J. RAO (J. Indian Chem. Soc., 1936, 13, 217—223).—After heating at about 100° for 2.5 hr. the val. of  $n$  for 19 colloids was found to increase. Diminution of particle size is suggested as the simplest explanation. C. R. H.

**Action of clay stabilisers.** A. FOLDVARI (Kolloid-Beih., 1936, 44, 125—170).—Clay stabilisers act (1) by charging the particles with OH' (alkalis), (2) by reacting with the pptg. electrolytes normally present in the clay, especially Ca<sup>++</sup> (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), or (3) by forming a protective sheath around the clay particles (Na<sub>2</sub>SiO<sub>3</sub>). The degree of effectiveness of a given stabiliser depends on the composition of the suspension. In general, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> gives the finest dispersions, but when the clay contains CaCO<sub>3</sub>, CaSO<sub>4</sub>, or considerable amounts of electrolytes, Na<sub>2</sub>SiO<sub>3</sub> is the best stabiliser. E. S. H.

**Silica gels and other dehydrating agents.** J. CAILLAUD and J. BEAUFILS (Chim. et Ind., 1936, 35, 1280—1292).—The theory of desiccation is discussed and applied to the action of SiO<sub>2</sub> gels. C. R. H.

**Action of ultra-violet irradiation on surface tension and viscosity of gelatin solutions.** W. DUCE (Boll. Soc. ital. Biol. sperim., 1935, 10, 978—979).—Irradiation slightly lowers  $\gamma$  and  $\eta$  for equiv.  $p_H$  vals. F. O. H.

**Method of observation of gelation.** T. FUJWARA and T. HUDITA (J. Sci. Hiroshima Univ., 1936, A, 6, 239—243).—The influence of stirring during a sol-gel transformation on the "hardness" of the resulting gel is discussed. W. R. A.

**Syneresis. II.** G. ROSSI and A. MARESCOTTI (Gazzetta, 1936, 66, 223—227; cf. A., 1933, 568).—In the liquid resulting from the syneresis of agar-agar gels containing both NaCl and NaI the molar concn. of both salts is < that for the original gel. The [NaCl]/[NaI] ratio is also smaller and approaches a const. val. as the concn. of the two salts in the original gel decreases. O. J. W.

**Stability of lyophilic bio-colloids.** H. P. TEUNISSEN (Chem. Weekblad, 1936, 33, 362—363).—Differences in stability of lyophilic bio-colloids depend on the nature and the no. of ionogenic groups present in the mol. Such colloids can be divided into three groups according to the types of grouping they contain. S. C.

**Influence of vitamin-D and certain carcinogenic hydrocarbons on the hydrophilic coefficient of lipins.** A. KLING and G. LECORDIER (Compt. rend., 1936, 202, 1535—1538).—The hydrophilic activity of ergosterol (I) in vaseline is > that of cholesterol and the product obtained by irradiation is more active than pure vitamin-D. Carcinogenic hydrocarbons diminish the activity of (I) etc. whilst non-carcinogenic hydrocarbons do not. The carcinogenic hydrocarbons have no hydrophilic activity towards pure vaseline. R. S.

**Interchange equilibrium between acetylene and heavy water.** K. HIROTA and G. OKAMOTO (Bull. Chem. Soc. Japan, 1936, 11, 349—351).—Equilibrium consts. are calc. from spectroscopic data. T. G. P.

**Ionic equilibrium in solutions. I. I. SASLAVSKI** (Z. Physik, 1936, 100, 345—359).—Methods of determining the degree of ionisation are critically reviewed. A. B. D. C.

**Hydration of ions.** H. BRINTZINGER (Z. anorg. Chem., 1936, 227, 341—346; cf. A., 1935, 579, 824).—Reply to criticisms by Schmitz-Dumont (this vol., 289).

[Hydration of ions.] O. SCHMITZ-DUMONT (Z. anorg. Chem., 1936, 227, 347—350).—Reply to Brintzinger.

[Hydration of ions.] H. BRINTZINGER (Z. anorg. Chem., 1936, 227, 351—352).—Reply to Schmitz-Dumont. F. L. U.

**Hydration and change in water equilibrium in electrolytic solutions.** C. S. RAO (Current Sci., 1936, 4, 650; cf. A., 1935, 295).—The intensity curves of the Raman band for H<sub>2</sub>O in the pure solvent and in solutions of NaNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HCl have been determined. The influence of the dissolved electrolytes on the 1-, 2-, 3-H<sub>2</sub>O equilibrium is discussed. N. M. B.

**Electrolytic dissociation processes. I. Dipole moment of iodine monochloride in solution.** F. FAIRBROTHER (J.C.S., 1936, 847—853).—The increase in the dipole moment of ICl in CCl<sub>4</sub> and cyclohexane to approx. double the val. for gaseous ICl is ascribed to an increase in the ionic character of the valency linking of the ICl. In solvents of less non-polar character, e.g., PhCl, CH<sub>2</sub>Cl<sub>2</sub>, this increase in ionic character is sufficient for the ICl to behave as an extremely weak electrolyte. The data are also discussed in relation to the energy of solvation of the ions. C. R. H.

**Ionisation constant of glycollic acid from 0° to 50°.** L. F. NIMS (J. Amer. Chem. Soc., 1936, 58, 987—989).—The ionisation const. and the free energy, heat content, and entropy change have been obtained. E. S. H.

**Formation of polyiodides in dark solutions.** G. HERRERO ORTIZ (Anal. Fis. Quim., 1936, 34, 48—65). F. R. G.

**Polyhalides. I. Solubility of iodine in hydrobromic acid.** F. H. LEE and K. H. LEE (J. Chinese Chem. Soc., 1936, 4, 126—130).—The const. for the equilibrium HBr—I<sub>2</sub> ⇌ HBrI<sub>2</sub> has been determined between 15° and 45°.  $\Delta H = -1602$  g.-cal. R. S.

**Raman effect and dissociation of KHSO<sub>4</sub>.** W. M. SHAFFER and D. M. CAMERON (J. Chem. Physics, 1936, 4, 392—393).—Raman spectra of aq. solutions of KHSO<sub>4</sub> show that progressive dissociation of HSO<sub>4</sub>' with dilution occurs between 34 and 13% concn. No lines attributable to undissociated KHSO<sub>4</sub> are present even at the highest concn. F. L. U.

**Complex fluorides. I. Hydrolysis of the silicofluoride ion.** J. G. RYSS and N. P. BARINA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 21—25).—According to  $p_H$  measurements of Na<sub>2</sub>SiF<sub>6</sub> solutions the hydrolysis const. of SiF<sub>6</sub>' is  $1.2 \times 10^{-2}$  at 20°. T. G. P.

**Complex fluorides. II. Hydrolysis of borofluoride ions.** J. G. RYSS and N. P. BARINA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 107—110).—The



val. of  $K$  for the equilibrium  $\text{BF}_4' + 3\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{BO}_3 + 4\text{F}' + 3\text{H}'$  ( $18^\circ$ ) is  $2.51 \times 10^{-19}$  according to  $p_H$  data for aq. solutions of KF saturated with  $\text{KBF}_4$  and  $\text{H}_3\text{BO}_3$ . Titration of  $\text{HBF}_4$  in dil. solution does not give satisfactory results. H. J. E.

**Hydrolysis of solutions of quinquivalent vanadium sulphate.** G. GIRE and F. RIVENQ (Compt. rend., 1936, 202, 2081—2083).—The degree of hydrolysis of aq.  $\text{V}_2\text{O}_5(\text{SO}_3)_2$  has been measured at  $0$ – $75^\circ$  in presence of varying amounts of  $\text{H}_2\text{SO}_4$ . H. J. E.

**Equilibrium between isopropyl alcohol and acetone in presence of alcohol-dehydrogenase.** R. WURMSER and (MME.) S. FILITTI-WURMSER (Compt. rend., 1936, 202, 1848—1849; cf. A., 1935, 658).—The normal potential of the system at  $p_H$  7 is  $-0.247$  volt at  $35^\circ$ . The free energy of the reaction is 8300 g.-cal. J. G. A. G.

**B.-p. lowering by non-volatile substances in ternary systems. I. Influence of potassium chloride on the b.p. of aqueous solutions of calcium chloride.** M. CENTNERSZWER and (MISS) M. SWIERCZEWSKA (Bull. Acad. Polonaise, 1935, A, 551—558).—Addition of KCl to aq. solutions of  $\text{CaCl}_2$  causes a lowering of the b.p. at high  $[\text{CaCl}_2]$  and an elevation at low  $[\text{KCl}]$ . At an intermediate concn., the "indifferent solution," the b.p. is unchanged by KCl. Similar effects are observed on addition of glucose and fructose to solutions of  $\text{CaCl}_2$ . The composition of the indifferent solution is sp. for the added substance and independent of its concn. O. D. S.

**Calculation of isoelectric zones and isoelectric points.** D. I. HITCHCOCK (J. Biol. Chem., 1936, 114, 373—379).—A method for calculating the breadth of the isoelectric zone of a simple ampholyte as a function of  $K_1/K_2$  is described and a general equation is given for the isoelectric point of a multivalent ampholyte in terms of the several  $K$  vals. H. D.

**Thermodynamic law of action and reaction.** L. MALIS and V. JACYNA (Bull. Acad. Polonaise, 1935, A, 507—514).—A thermodynamic treatment of irreversible change. O. D. S.

**Thermodynamic properties of nitric oxide [as] an example of an associated liquid.** O. K. RICE (J. Chem. Physics, 1936, 4, 367—372; cf. this vol., 294).—The heat of dissociation of  $(\text{NO})_2$  in the liquid phase, calc. from sp. heat data, is 3.91 kg.-cal. per mol. at the b.p. It is estimated to be about 1 kg.-cal. lower in the gas phase. The sp. heat of the completely associated liquid and the entropy of vaporisation are also calc. F. L. U.

**Free energy of iodine and hydrogen iodide from spectroscopic data.** G. M. MURPHY (J. Chem. Physics, 1936, 4, 344—350).—Thermodynamic quantities relating to the dissociation of I, and of HI are calc. F. L. U.

**Influence of dipole fields between solute molecules. III. Thermodynamic properties of non-electrolytes.** R. M. FUOSS (J. Amer. Chem. Soc., 1936, 58, 982—984; cf. A., 1934, 728).—Theoretical. For solute mols. which may be represented as spheres containing a point dipole, there is a linear relation at

limiting low concns. between (a) the osmotic deviation function  $j$  of Lewis and Randall and the concn., and (b) the partial mol. heat capacity and concn. E. S. H.

**Thermodynamics of hydrobromic acid in aqueous solution from electromotive force measurements.** H. S. HARNED, A. S. KESTON, and J. G. DONELSON (J. Amer. Chem. Soc., 1936, 58, 989—994).—E.m.f. of the cells  $\text{H}_2|\text{HBr}(m)|\text{AgBr}-\text{Ag}$  at  $0$ – $60^\circ$  and  $0.001$ – $1M$  have been determined. The standard potential is given by  $E_0 = 0.06846 - 0.0005185(t-30) - 2.973 \times 10^{-6}(t-30)^2$ . The activity coeff., relative partial mol. heat content, and sp. heat of HBr have been calc. E. S. H.

**Thermodynamic study of zinc bromide.** F. ISHIKAWA, Y. FERUI, and T. TAKAI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 339—346).—From e.m.f. data for the cell  $\text{Zn}-\text{Hg}(10\%)|\text{ZnBr}_2, \text{HgBr}|\text{Hg}$  and v.p. of  $\text{ZnBr}_2$  solutions, differential and integral free energies have been calc. N. M. B.

**Activity coefficients of bivalent metal sulphates in aqueous solution from vapour-pressure measurements.** R. A. ROBINSON and R. S. JONES (J. Amer. Chem. Soc., 1936, 58, 959—961).—Osmotic and activity coeffs. for  $\text{CuSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CdSO}_4$ ,  $\text{MnSO}_4$ , and  $\text{NiSO}_4$  in aq. solution at  $25^\circ$  have been determined. With  $\text{CdSO}_4$  the activity coeff. does not agree with that derived from e.m.f. measurements. E. S. H.

**Quantum mechanics and the third law of thermodynamics.** L. PAULING and E. D. EASTMAN (J. Chem. Physics, 1936, 4, 393—394).—A discussion of a paper by Rodebush (A., 1934, 1306). F. L. U.

**Topological properties of phase diagrams.** A. B. MŁODZIEJEWSKI (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 57—68).—Theoretical. R. T.

**Topology of diagrams of chemical equilibria.** N. S. KURNAKOV (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 15—55).—Theoretical. R. T.

**Micro-structures of some calcium aluminate melts.** D. S. BELJANKIN and N. A. TOROPOV (Zentr. Min., 1935, A, 174—182; Chem. Zentr., 1935, ii, 2034).—Micrographic and equilibrium data for the  $\text{CaO}-\text{Al}_2\text{O}_3$  system are recorded, and the results applied to magmatic rocks. J. S. A.

**Existence of the complex  $\text{MnSO}_4 \cdot x\text{SO}_2$ .** L. I. KASCHTANOV and G. A. GULJANSKAJA (J. Gen. Chem. Russ., 1936, 6, 227—231).— $\text{SO}_2$  is adsorbed by  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , to yield a product of the composition  $\text{MnSO}_4 \cdot \text{SO}_2$ , but not by  $\text{MnSO}_4 \cdot 4$  or  $7\text{H}_2\text{O}$ . R. T.

**Physico-chemical analysis of the system iron-oxygen. Revision of earlier studies, applying semi-permeable diaphragms.** E. V. BRITZKE, A. F. KAPUSTINKSI, and T. I. SCHASCHKINA (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 141—149).—The partial  $\text{H}_2\text{O}$  and  $\text{H}_2$  pressures over a mixture of Fe and FeO at  $800$ – $1200^\circ$  have been measured separately by use of a Pd diaphragm. The dissociation pressure of FeO is given by  $\log p = -29078/T + 3.5 \log T - 0.00165(T-600) - 1.68$ . R. T.

**Thermal analysis of mixtures containing ammonium, sodium, potassium, and calcium**

nitrate. T. URBANSKI and S. KOŁODZIEJCZYK (Rocz. Chem., 1936, 18, 119—125).—The system  $\text{NH}_4\text{NO}_3\text{--Ca}(\text{NO}_3)_2$  (eutectic, 71% of  $\text{NH}_4\text{NO}_3$ , 111°) belongs to Rooseboom's type V. Thermal diagrams for the systems  $\text{NH}_4\text{NO}_3\text{--NaNO}_3\text{--KNO}_3$  and  $\text{NH}_4\text{NO}_3\text{--NaNO}_3\text{--Ca}(\text{NO}_3)_2$  have been determined.

R. T.

**System: aluminium sulphate-potassium sulphate-water.** L. TS'AI and W. YEN (J. Chinese Chem. Soc., 1936, 4, 178—182).—Equilibrium data for the system at 0° are recorded.

R. S.

**Partial solubility isotherm of the system  $\text{NH}_3\text{--MoO}_3\text{--H}_2\text{O}$  at 25°.** H. W. FOOTE and W. M. BRADLEY (J. Amer. Chem. Soc., 1936, 58, 930—931).—The conditions for the existence of

$3(\text{NH}_4)_2\text{MoO}_4, 4\text{MoO}_3, 4\text{H}_2\text{O}$  and  $3(\text{NH}_4)_2\text{MoO}_4, 5\text{MoO}_3, 4\text{H}_2\text{O}$  have been determined.

E. S. H.

**Fusion diagram of the ternary system  $\text{Na}_2\text{SiO}_3\text{--PbSiO}_3\text{--PbO}$ .** K. A. KRAKAU (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 331—350).—The cryst. phases are  $\text{Na}_2\text{O}, \text{SiO}_2$ ,  $\text{PbO}$ ,  $3\text{PbO}, \text{SiO}_2$ ,  $2\text{PbO}, \text{SiO}_2$ , and  $\text{PbO}, \text{SiO}_2$ .

R. T.

**Acid salts of monobasic organic acids. II. *r*-Mandelic acid.** J. D. M. ROSS and T. J. MORRISON (J.C.S., 1936, 867—872).—Previous work (A., 1933, 1013) on the system *r*-mandelic acid-metal mandelate- $\text{H}_2\text{O}$  has been extended to Cs, Rb, Tl,  $\text{NH}_4$ , and Mg mandelates. The following acid salts have been isolated:  $\text{RbM}, \text{HM}$ ;  $\text{RbM}, 3\text{HM}$ ;  $\text{CsM}, \text{HM}$ ;  $\text{NH}_4\text{M}, \text{HM}$ ;  $\text{NH}_4\text{M}, 3\text{HM}$ ;  $\text{TlM}, \text{HM}$ ;  $2\text{MgM}_2, \text{HM}, 2\text{H}_2\text{O}$  ( $\text{M}=\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2$ ).

C. R. H.

**Systems zirconium oxalate-alkali oxalates-water.** J. BOULANGER (Compt. rend., 1936, 202, 2156—2159).—The following solid phases were obtained:  $2\text{MCs}_2, \text{MZrO}, \text{MH}_2, 4\text{H}_2\text{O}$ ;  $2\text{MRb}_2, \text{MZrO}, \text{MH}_2, 2\text{H}_2\text{O}$ ;  $2\text{MK}_2, \text{MZrO}, \text{MH}_2, 4\text{H}_2\text{O}$ ;  $\text{MK}_2, \text{MZrO}, \text{MH}_2, \text{H}_2\text{O}$ ;  $\text{MRb}_2, \text{MZrO}, \text{MH}_2, 3\text{H}_2\text{O}$  ( $\text{M}=\text{C}_2\text{O}_4$ ).

C. R. H.

**Quaternary system  $\text{CaO--MgO--2CaO}, \text{SiO}_2\text{--5CaO}, 3\text{Al}_2\text{O}_3$ .** H. F. MCMURDIE and H. INSLEY (J. Res. Nat. Bur. Stand., 1936, 16, 467—474).—Vol. measurements afford no evidence of ternary or quaternary compounds, and there is no detectable solid solution formation. The amount of  $\text{MgO}$  required to be added to the system  $\text{CaO--2CaO}, \text{SiO}_2\text{--5CaO}, 3\text{Al}_2\text{O}_3$  to render it the primary phase varies from 5 to 33%.

J. W. S.

**Entropy of organic compounds from calorimetric data. Lack of equilibrium in crystalline tetramethylmethane.** J. G. ASTON and G. H. MESSERLY (J. Chem. Physics, 1936, 4, 391—392).—Comparison of calorimetric and spectroscopic data indicates zero-point entropy of about 8 e.u. in ordinary crystals of  $\text{CMe}_4$  at 0° abs., due to randomness caused by lack of equilibrium.

F. L. U.

**Heat capacity of lead sulphate.** E. G. HAAS [with G. STEGEMAN] (J. Amer. Chem. Soc., 1936, 58, 879—880).—A low-temp. calorimeter is described. Data are recorded for  $\text{PbSO}_4$  between 83° and 298° abs.

E. S. H.

**Heat capacity and entropy of  $\beta$ -lactose.** E. F. FURTSCH [with G. STEGEMAN] (J. Amer. Chem. Soc.,

1936, 58, 881—882).—Heat capacities between 83° and 298° abs. are recorded. The entropy and free energy of formation have been calc.

E. S. H.

**Heat of reaction of binding substances.** P. P. BUDNIKOV and L. GULINOVA (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 357—372).—The heat evolved when  $\text{H}_2\text{O}$  is added to fired gypsum rises to a max. at 200° with rise in temp. of firing and falls to a min. at 750°, thereafter rising uninterruptedly to 1200°; this corresponds with the production of anhydrite (200°), of inactive  $\text{CaSO}_4$  (750°), and with the dissociation to  $\text{CaO}$  and  $\text{SO}_3$ . The inactive form may be activated by addition of aq.  $\text{NaHSO}_4$ .

R. T.

**Influence of molecular size on activity.** C. G. BOISSONNAS (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 40—42).—The heats of dilution of solutions of related substances in the same solvent are said to depend only on the wt. composition of the solution.

J. W. S.

**Thermochemistry of aqueous solutions of electrolytes. I. Heat of dissolution, and specific heat of aqueous potassium sulphate.** K. P. MISCHTSCHENKO and M. Z. PRONINA (J. Gen. Chem. Russ., 1936, 6, 85—101).—Heats of dissolution of  $\text{K}_2\text{SO}_4$  and sp. heats, have been determined at 25° for solutions over a wide range extending to saturation, and the integral heats of dilution are calc. Different types of integral heat of dissolution-concn. curves are discussed.

R. T.

**Integral free energy of dissolution of (A) sodium bromide. F. ISHIKAWA and T. TAKAI. (B) Potassium chloride. F. ISHIKAWA and K. MORIWAKI** (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 333—335, 336—338).—(A) The integral free energy change has been calc. from differential free energy data for dissolution and dilution.

(B) The free energy change for  $\text{KCl}$  has been derived similarly from heats of dissolution and v.-p. data.

N. M. B.

**Heats of combustion of organic compounds of selenium.** H. MERTEN and H. SCHLÜTER (Ber., 1936, 69, [B], 1364—1366).—The following vals. at const. vol. and pressure, respectively, have been determined:  $\text{CSe}_2$ ,  $240.6 \pm 1.0$  and  $241.8 \pm 1.0$ ;  $\text{Et}_2\text{Se}$ ,  $747.7 \pm 0.7$  and  $749.7 \pm 0.7$ ;  $(\text{CH}_2\text{Ph})_2\text{Se}$ ,  $1846.9 \pm 5.7$  and  $1849.5 \pm 5.7$  kg.-cal. per mol.; polymeride A,  $124.2$  and  $124.8$  kg.-cal. per Se atom.

H. W.

**Conductivity of solutions in iodine. II.** V. A. PLOTNIKOV, J. A. FIALKOV, and V. P. TSCHALI (J. Gen. Chem. Russ., 1936, 6, 273—278).—The conductivity of solutions of  $\text{HgI}_2$ ,  $\text{SnI}_4$ ,  $\text{SbI}_5$ ,  $\text{AlI}_3$ , and  $\text{PI}_3$  in I has been determined, at 130° and 140°. Conductivity is due to dissociation of associated mols. as represented by  $(\text{MI})_n \rightleftharpoons \text{MI}_n - m + m\text{I}$ ; the formation of polyiodides is not indicated.

R. T.

**Mobility of bromine and iodine ions.** M. HLASKO and A. SIEMIASZKO (Rocz. Chem., 1936, 16, 92—100).—The transport nos., calc. from conductivity data, are  $\text{Br}^-$  78.4, and  $\text{I}^-$  78.9.

R. T.

**Metaphosphoric acids. I. Changes in electrical conductivity during transformation of the acids in aqueous solution.** S. GLIXELLI, R.



CHYZANOWSKA, and K. BORATYNSKI (*Z. anorg. Chem.*, 1936, 227, 402—412).—The mol. conductivity ( $\lambda$ ) of aq.  $\text{HPO}_3$  is  $>$  that of  $\text{H}_3\text{PO}_4$  (when referred to equal  $[\text{P}_2\text{O}_5]$ ) at all concns., the difference decreasing with increasing dilution. It is also  $>$  that of  $\text{H}_4\text{P}_2\text{O}_7$  above  $[\text{P}_2\text{O}_5]=0.015M$ , below which the difference is reversed. The alteration of  $\text{HPO}_3$  solutions with time consists of two processes, viz., (1) hydration to  $\text{H}_3\text{PO}_4$ , favoured by high concn., and (2) depolymerisation of  $(\text{HPO}_3)_n$  to simpler mols., favoured by rise of temp. These changes are respectively indicated by decrease and increase of  $\lambda$ . F. L. U.

**Electrochemistry of aqueous glycerol and aqueous glycol solutions.** I. I. I. SHUKOV and I. F. KARPOVA (*J. Gen. Chem. Russ.*, 1936, 6, 161—166).—The  $p_H$  of 0.01—0.1N-HCl or  $\text{H}_2\text{SO}_4$  is unaffected by dilution with glycerol, glycol, or erythritol. R. T.

**Oxidation potential of thalious and thallic salts.** M. S. SHERRILL and A. J. HAAS, jun. (*J. Amer. Chem. Soc.*, 1936, 58, 952—959).—In mixtures of  $\text{TiClO}_4$ ,  $\text{Ti}(\text{ClO}_4)_3$ , and  $\text{HClO}_4$  the oxidation potential is determined by the ionic strength  $\mu$  of the solution and by the concn. ratio  $(\Sigma\text{Ti}^{III})/(\Sigma\text{Ti}^{IV})$ , as given by  $E=E_0+0.02957 \log (\Sigma\text{Ti}^{III})/(\Sigma\text{Ti}^{IV})$  and  $E_0=1.2466+0.0076\mu+0.00482\mu^2$ , in which  $E_0$  is the formal oxidation potential of the reaction  $\text{Ti}^{III}+2e=\text{Ti}^{IV}$ . In  $\text{Ti}_2\text{SO}_4\text{—Ti}_2(\text{SO}_4)_3\text{—H}_2\text{SO}_4$  mixtures the formal electrode potential calc. as above varies appreciably at the lower concn. ratios, but is nearly const. when  $(\Sigma\text{Ti}^{III})/(\Sigma\text{Ti}^{IV})=1$ . The solubility of moist  $\text{Ti}(\text{OH})_3$  in aq.  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  at  $25^\circ$  has been determined. The solubility product of  $\text{Ti}(\text{OH})_3$  is  $1.5 \times 10^{-44}$ . E. S. H.

**Double electrode potential and oxidation-reduction potential.** T. T. CHEN (*J. Chinese Chem. Soc.*, 1936, 4, 117—125).—The double electrode potentials for pairs of benzoquinone-quinol mixtures are approx. equal to the oxidation-reduction potentials which would be obtained if the two pairs were combined to produce a single solution. In the case of pure, unstirred benzoquinone and quinol solutions, more or less stable mixtures are at once formed around the electrodes; if these are dispersed by stirring, a steady potential is not obtained. R. S.

**Luciferin-oxy luciferin system.** I. M. KORR (*J. Amer. Chem. Soc.*, 1936, 58, 1060—1061).—The oxidation-reduction potential of the system (which is partly reversible, is active at an electrode, and is unusually  $+$  for a biological compound) lies near that for quinihydrone. H. B.

**Mechanism of the Becquerel effect of organic molecules.** C. STORA (*Compt. rend.*, 1936, 202, 2152—2154).—From data for coloured org. compounds it is concluded that the Becquerel effect at any instant is the resultant of the positive and negative effects due to the oxidisability of the reduced form and the reducibility of the oxidised form, respectively. C. R. H.

**Potentials at liquid-liquid phase boundaries.** I, II. K. KARCZEWSKI (*Rocz. Chem.*, 1936, 16, 69—75, 126—129).—I. The potentials ( $-$ ) between  $\text{EtOAc}$  (I) and 0—0.1N-KCNS, (I) saturated with

$\text{H}_2\text{O}$  and KCNS in aq. (I), and the same system at equilibrium, have been measured, at  $17^\circ$ . In the last case, a min.  $\pi$  is found for 0.005N-KCNS, at which concn. the most stable emulsions are obtained. No correlation is found between  $-$  and surface tension.

II. The vals. of  $\pi$  have been determined for the systems  $\text{Bu}^\circ\text{OH}$ —0.0001—0.1N-KCNS, in presence of different concns. of KCl (0—1N) equal to those in the electrolyte of the standard (AgCl) electrodes.

R. T.

**Thermo-electric potentials in salt crystals with colour centres.** O. STASIŃ (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 199—202; *Chem. Zentr.*, 1935, ii, 1837).—The thermo-electric potential between clear KCl and coloured KCl crystals, with the "hot junction" at  $700^\circ$ , has been measured. From its variation with temp. the mobility of the positive ions is calc. J. S. A.

**Decomposition potentials of Grignard reagents in ether solution.** F. H. LEE and C. H. LI (Nanking J., 1934, 4, 1—3; cf. A., 1934, 517).—Relative vals. recorded for different groups are: Ph 2.17, Me 1.94,  $\text{Pr}^\circ$  1.42,  $\text{Bu}^\circ$  1.32, Et 1.28,  $\text{Bu}^\beta$  1.24,  $\text{Pr}^\beta$  1.07,  $\text{Bu}^\gamma$  0.97, allyl 0.86. CH. ABS. (r)

**Acoustic electrochemical phenomena.** II. L. V. NIKITIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 2, 67—69; cf. A., 1935, 306).—Certain cells with Pt electrodes are said to be sensitive to sound waves. H. J. E.

**Passivity of iron and steel in nitric acid solution.** Y. YAMAMOTO (*Bull. Inst. Phys. Chem. Res. Japan*, 1936, 15, 350—383).—The p.d. between active Fe in dil.  $\text{HNO}_3$  and passive Fe in conc.  $\text{HNO}_3$  is about 0.33—0.39 volt, corresponding with the difference between the electrode potentials  $\text{Fe}/\text{Fe}^{II}$  (−0.43 volt) and  $\text{Fe}/\text{Fe}^{III}$  (−0.04 volt). When Fe in  $\text{HNO}_3$  becomes passive, the p.d. between Fe and Pt is lowered, and the difference between the max. (p.d. between active Fe and Pt) and the min. (p.d. between passive Fe and Pt) is about 0.75—0.78 volt, corresponding with the standard potential for  $\text{Fe}^{III}+e\rightleftharpoons\text{Fe}^{II}$  (+0.748 volt). Results indicate that the surface of passive Fe is in the ferric, and that of active Fe in the ferrous, condition. N. M. B.

**Structure and properties of the insulating layers formed on aluminium electrodes during anodic polarisation.** I. ZŁOTOWSKI (*Bull. Acad. Polonaise*, 1936, A, 164—194).—A method is developed for measuring the changes in resistance ( $R$ ), capacity ( $C$ ), and dielectric losses during anodic formation of Al at const. c.d. The influence of c.d., temp., and concn. for aq.  $\text{H}_2\text{C}_2\text{O}_4$  suggests that the insulating layer comprises a very thin and almost non-porous film of solid dielectric next to the Al, and an outer, relatively thick, porous layer impregnated with electrolyte. The thin film determines  $R$  and  $C$ . Assuming the dielectric const. of this film to be 7.45, the thickness of the films formed at 1—25 volts is  $10^{-7}$ — $10^{-6}$  cm., and  $R$  is  $10^{10}$ — $10^{11}$  ohms per  $\text{cm}^2$ .  $R$  increases exponentially with increasing temp. of polarisation. The results are in accord with X-ray measurements. J. W. S.

**Free energy and rate of chemical reactions. Relation between rate and oxidation-reduction potentials.** H. GERSHINOWITZ (J. Chem. Physics, 1936, 4, 363—366; cf. A., 1935, 1205).—A theoretical explanation of the connexion between rates of oxidation-reduction reactions and the potentials of the reagents is given. F. L. U.

**Rate of reaction of deuterium with iodine.** K. H. GEIB and A. LENDLE (Z. physikal. Chem., 1936, B, 32, 463—470; cf. this vol., 567).—At 710—780° abs. the velocity coeff. for the reaction of  $H_2$  with I is on the average 2.2 times that of the reaction of 95%  $D_2$  with I. If this difference is due not only to difference in collision no. but also to a difference in the heats of activation the latter amounts to ~0.75 kg.-cal. R. C.

**Thermal decomposition of acetone.** A. O. ALLEN (J. Amer. Chem. Soc., 1936, 58, 1052—1053).—Thermal decomp. of  $COMe_2$  to  $CH_2=CO$  and  $CH_4$  is investigated by the usual static method; the results indicate a chain mechanism (cf. Rice and Herzfeld, A., 1934, 369; Winkler and Hinshelwood, A., 1935, 827). H. B.

**Kinetics of cyclopentadiene.** G. B. KISTIAKOWSKY and W. H. MEARS (J. Amer. Chem. Soc., 1936, 58, 1060).—Polymerisation of cyclopentadiene (I) and depolymerisation of dicyclopentadiene in the gas phase are second- and first-order reactions, respectively; the consts. differ somewhat from those found by Khambata and Wasserman (this vol., 684) but the abs. rates are nearly the same. Dimerisation of liquid (I) is a reaction of nearly first order; no chains are involved. H. B.

**Application of the theory of chain reactions to the slow combustion of benzene.** A. AMIEL (Compt. rend., 1936, 202, 1509—1511; cf. A., 1933, 1249).—The slow combustion of  $C_6H_6$  exhibits a region of const. velocity and belongs therefore to the  $C_2H_2$ -aldehyde class of oxidation reactions (Semenov, "Chain Reactions and Chemical Kinetics," 1935, p. 338). The theory of interacting branched chains accounts qualitatively for the results. Certain products inhibit the reaction and diminish the period of const. velocity. R. S.

**Detection of reaction chains by small amounts of nitric oxide. Thermal decomposition of acetaldehyde and of propaldehyde.** L. A. K. STAVELEY and C. N. HINSHELWOOD (J.C.S., 1936, 812—818; cf. this vol., 803).—The decomp. of  $MeCHO$  is approx. independent of  $[NO]$  up to 1.0 mm., whilst further additions accelerate the rate. It is inferred that the reaction is of the non-chain type. In the case of  $EtCHO$ , the rate of decomp. is reduced by addition of  $NO$ , the min. velocity occurring when  $[NO]=2$  mm., but the position of the end-point is unaffected. The energy of activation of the inhibited reaction is approx. 5000 g.-cal. < that of the uninhibited, the inhibition occurring chiefly in the initial region of rapid decomp., whilst the rate of the subsequent decomp. is equal to that of the inhibited reaction. It is suggested that short chains may arise only from a certain type of activated  $EtCHO$  mol. which is formed in the early stages. R. S.

**Kinetics of thermal polymerisation of indene.** H. DOSTAL and R. RAFF (Z. physikal. Chem., 1936, B, 32, 417—429).—The rate of polymerisation of the liquid in a high vac. and under  $CO_2$  and of the  $PhMe$  solution has been determined at 120—200°, and the results have been worked out in relation to the theory previously advanced (this vol., 164). The velocity of the nucleus-forming reaction is  $0.92 \times 10^{-4}$  and the steric factor  $5 \times 10^{-10}$ . Owing to the exceptionally high velocity of the process of isomeric change which terminates the growing chains only a low degree of polymerisation is achieved. R. C.

**Kinetics and mechanism of decomposition of hydrocarbons. III. Relation between velocity and extent of decomposition of *n*-hexane and *n*-octane.** A. I. DINTZES and A. V. SHERKO (J. Gen. Chem. Russ., 1936, 6, 68—74).—The velocity of thermal decomp. of  $n-C_6H_{14}$  or  $-C_8H_{18}$  does not conform to that of a reaction of the first order, or to any other simple scheme. The velocity coeff. is given, for 50—70% decomp., by  $k t - \log 1/(1+x)$ —where  $\delta$  is a const. for a given hydrocarbon and temp., and  $x$  is extent of decomp. at time  $t$ . R. T.

**Kinetics of thermal *cis-trans* isomerisations.** R. W. HARKNESS (J. Amer. Chem. Soc., 1936, 58, 1058—1059).—The results of Kistiakowsky and Smith (this vol., 802) are consistent with the hypothesis of a bimol. mechanism. E. S. H.

**Velocity of the reaction between organic peracids and cyclohexene.** S. MEDVEDEV and O. BLOCH (J. Phys. Chem. U.S.S.R., 1933, 4, 721—730).—The reactions of perbenzoic, *p*-methoxyperbenzoic (I), *p*- (II) and *m*-nitroperbenzoic,  $\alpha$ - and  $\beta$ -pernapththoic, peracetic, and phenylperacetic acids with cyclohexene at 25° follow the bimol. law. The velocity coeff.  $k$  depends on the initial peroxide concn. but not on that of cyclohexene. The ratio of  $k$  in  $C_6H_6$  to  $k$  in xylene was 1.76. The reactivity of the acyl radicals was of the same order as in the corresponding acyl halides. The activation energy was approx. 14,000 g.-cal. in each case. The Arrhenius coeff.  $\beta$  varied from  $2 \times 10^8$  for (I) to  $4 \times 10^{11}$  for (II).

CH. ABS. (c)

**Oxidising action of ferric chloride. I. Statics and dynamics of the reaction.** C. N. IONESCU and A. BARDEANU (Bul. Soc. Chim. Romania, 1935, 17, 297—307; cf. A., 1934, 521).—The reaction between  $\beta-C_{10}H_7 \cdot OH$  and  $FeCl_3$  has been studied in aq. solution, when  $2C_{10}H_7 \cdot OH + 2FeCl_3 = (C_{10}H_6 \cdot OH)_2 + FeCl_2 + 2HCl$ . Owing to hydrolysis of  $FeCl_3$  the reaction is not quant., but becomes so in presence of 0.1N-HCl;  $Fe(OH)_3$  has no influence on  $C_{10}H_7 \cdot OH$ . The reaction is unimol. with respect to both reactants, indicating the existence of intermediate reactions. R. S. B.

**Elucidation of the course of reactions and of rates of reaction by modern conductometric methods.** G. JANDER and H. IMMOG (Ber., 1936, 69, [B], 1282—1292).—A conductometric method for measuring rates of reaction is described. The great sensitivity of measurement of conductivity allows the rate of ester hydrolysis ( $OH \cdot CHPh \cdot CO_2Me$  and  $Pr^aCO_2Me$ ) to be determined in buffered solutions. The dependence of the coeff. on temp. and  $p_H$  is



confirmed and the marked catalytic influence of liver esterase on the hydrolysis of  $\text{Pr}^{\text{CO}_2}\text{Me}$  is established. In buffered solutions, the unimol. course of hydrolysis is transformed by the catalyst into a reaction of zero order. The method is also applied to the fission of  $\text{CCl}_3\text{-CO}_2\text{H}$ , which is greatly accelerated by sulphates.

H. W.

**Kinetics of the reaction between iodoacetic acid and glycine.** R. BRDIČKA (J. Gen. Physiol., 1936, 19, 843—866).—The reaction, being of the ionic type and showing a positive salt catalysis, proceeds in two steps in which H of the  $\text{NH}_2$  are replaced by Ac, the velocity coeff. being in the ratio 2 : 1. Since only the anionic form of glycine reacts there is evidence for the existence of an unbonded pair of electrons on the N in the  $\text{NH}_2$ .

H. G. R.

**Hydrolysis of acetyl and chloroacetyl chlorides.** J. RODRÍGUEZ VELASCO and J. R. DE LA BORBOLLA (Anal. Fis. Quím., 1936, 34, 179—197).—The velocity coeffs. of hydrolysis, in  $\text{PhMe}$ , of the chlorides at  $25^\circ$  are inversely  $\propto$  the square root of the dissociation consts. of the corresponding acids.

F. R. G.

**Kinetics of racemisation of 2:2'-diamino-6:6'-dimethyldiphenyl.** G. B. KISTIAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1936, 58, 1043—1045).—The reaction in  $\text{Ph}_2\text{O}$  solution or in the gaseous phase is homogeneous and unimol., and has an activation energy of 45,100 g.-cal. The rate coeffs. have been determined.

E. S. H.

**Ease of formation of cyclic imines. III. Kinetics of the formation of polymembered rings.** G. SALOMON (Helv. Chim. Acta, 1936, 19, 743—793; cf. A., 1934, 902).—Formation of  $[\text{CH}_2]_n\text{NH}$  from  $\text{NH}_2\text{[CH}_2\text{]}_x\text{Br}$  differs from the accompanying polymerisation and hydrolysis in being unimol. The rate of liberation of  $\text{Br}'$  under various conditions thus allows detection of the conditions under which unimol. ring-formation is the chief reaction and is determined in aq.  $\text{PrOH}$ . Ease of formation of 17-, 15-, and 14-membered rings is in the ratio, 2 : 1 : 1; that of the 12-membered ring is very much less, as hydrolysis is in this case the main reaction under comparable conditions. The kinetic measurements show that this hydrolysis is partly a bimol. reaction with  $\text{OH}'$  and partly reaction with the solvent. The data of Stoll *et al.* (A., 1934, 1201) show that formation of poly-esters occurs by various routes, so that his figures give relative accessibility and not relative ease of formation.

R. S. C.

**Thermal decomposition of silver oxalate. I. Experimental. II. Theoretical.** J. Y. MACDONALD (J.C.S., 1936, 832—838, 839—947; cf. A., 1926, 134).—I. The period of attainment of the max. rate of decomp. of  $\text{Ag}_2\text{C}_2\text{O}_4$  in vac. increases with increasing  $[\text{NO}_3']$  or  $[\text{SO}_4'']$  in the pptg. solutions, and in some cases the fraction decomposed at the max. diminishes. Dispersion of the  $\text{Ag}_2\text{C}_2\text{O}_4$  in gelatin has little effect, but in presence of air the rate = that in vac. up to 3% of decomp., after which it decreases. When the salt is suspended in paraffin, the behaviour resembles that in air with the addition of a second and greater max. Exposure to ultra-violet light produces two rate max., viz., (a) corresponding with the first

paraffin max. and (b) corresponding with the max. in vac. The reaction is catalysed by Hg. Microscopical examination has shown that decomp. proceeds uniformly throughout and not from crystal to crystal. Three mechanisms are suggested. Process I concerns only the initial 3% of decomp. and is associated with the first paraffin max. Process II is a surface reaction which appears in vac. but is absent in presence of air or paraffin, whilst process III is responsible for the second paraffin max. Experiments with large crystals are in agreement with these views.

II. The ways in which a single crystallite may decompose have been studied in relation to the experimental results and the following conclusions have been reached. Process I is due to decomp. starting from a fixed no. of initial centres and propagating in two dimensions in thin plates across the crystal planes, whence  $dx/dt \propto kt$ . The energy of activation is 32,700 g.-cal. Process II depends on the formation of fresh planes of decomp. by branching at the crystal surface, and  $dx/dt \propto \frac{1}{2}\pi K^2 n(e^{p'} - 1)/p$ , where  $p$  is the rate of branching. In the case of vac. decomp.,  $p \propto -\log [\text{NO}_3']$ , i.e., the rate of branching depends on the concn. of ions on the surface. Finally a plane may branch at any point along its edge. This process (III), which is much slower than II, becomes important when the no. of active planes is only a small fraction of the total no. of planes. Here  $dx/dt \propto bwne^{bt}$  where  $b$  is the no. of new planes generated per sec. by each decomp. plane.

R. S.

**Velocity of dissolution of magnesium in acids.** J. V. DURDIN and A. M. MARKEVITSCH (J. Gen. Chem. Russ., 1936, 6, 236—249).—The velocity of dissolution,  $V$ , of Mg in aq.  $\text{HCl} \propto [\text{H}']$ , whilst in aq.  $\text{AcOH-NaOAc}$  buffers it is independent of the  $[\text{H}']$ , but  $\propto [\text{AcOH}]$ ; it is unaffected by the presence of  $\text{MgCl}_2$  or  $\text{Mg}(\text{OAc})_2$ . At const. temp.  $V$  rises rapidly with increasing rate of stirring; the temp. coeff. falls with rise in temp., in contrast to the behaviour of Cr. In the case of  $\text{HCl}$ , the val. of  $V$ , with const. rate of stirring, varies with temp. parallel with variation in the  $\eta$  of the medium ( $V \propto k/\eta$ ), whilst in  $\text{AcOH}$   $V \propto T/\eta$ . The process is concluded to be exclusively one of diffusion in the case of  $\text{HCl}$ , and dominantly so in the case of  $\text{AcOH}$ .

R. T.

**Corrosion of magnesium.**—See B., 1936, 600.

**Theories of corrosion. III.** W. J. MULLER (Korros. u. Metallschutz, 1935, 11, 35—34; Chem. Zentr., 1935, ii, 2118; cf. B., 1934, 324).—Intercryst. corrosion and the relation of corrosion to the electrode potential of a metal are considered in terms of a porous oxide skin theory of passivity.

J. S. A.

**Kinetics of hydration of some cobalt complexes.** J. BRULL (Compt. rend., 1936, 202, 1584—1586).—Conductometric determinations of velocity have been made for the reaction of  $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  (I),  $[\text{Co en}_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}$  (II), and  $[\text{Co en}_2\text{ClO}(\text{H})]\text{Cl}$  with  $\text{H}_2\text{O}$ . Differences in rate were observed with the isomeric forms of (I) and (II).

H. J. E.

**Adsorption of gases by glass walls. XIII. Sulphur dioxide on Jena glass. Kinetics of the adsorption.** M. CRESPI and V. ALEXANDRE (Anal. Fis. Quím., 1935, 33, 350—359).—The adsorption

of  $\text{SO}_2$  by Jena glass is between 0.33 and 0.5 of that by ordinary glass. The vol. adsorption by 1 sq. cm. of Jena glass wall is given by  $1.3 \times 10^{-5} p^{0.35}$ , where  $p$  is the pressure in mm. for vals. of  $p$  between 50 and 710. The velocity ( $v$ ) at const. pressure is given by  $dy/dt = Kp(y_e - y)/y$ , where  $y_e$  is the equilibrium velocity,  $y$  is the velocity at time  $t$ , and  $K$  varies but slightly from 0.0076 for vals. of  $p$  from 50 to 710. Corrections are given for the wt. of a given vol. of  $\text{SO}_2$  at  $16^\circ$  and pressures between 100 and 710 mm. when contained in Jena glass. F. R. G.

**Quantum theory of catalysis.** A. A. SCHUCHOVITZKI (Acta Physicochim. U.R.S.S., 1934, 1, 901—912).—The calc. activation energy for the ortho-para- $\text{H}_2$  conversion was 7 kg.-cal. < the val. of Eyring and Polanyi. CH. ABS. (e)

**Influence of hydrogen on unimolecular reactions involving short chains.** C. N. HINSHELWOOD and L. A. K. STAVELEY (J.C.S., 1936, 818—820; cf. A., 1927, 630, 1036).—The addition of  $\text{H}_2$  to  $\text{EtCHO}$  or  $\text{Et}_2\text{O}$  (35 mm.), containing  $\text{NO}$ , increases the rate of decomp. to that prevailing at high initial pressures as in the absence of  $\text{NO}$ . It is inferred that only the primary activation process is affected by  $\text{H}_2$ . R. S.

**Catalytic action of salts on the velocity of ionic reactions.** II. E. BEKIER (Rocz. Chem., 1936, 16, 64—68).—The catalytic action of different ions in the reaction  $\text{CH}_3\text{Cl} \cdot \text{CO}_2' + \text{S}_2\text{O}_3'' \rightarrow \text{S}_2\text{O}_3 \cdot \text{CH}_3 \cdot \text{CO}_2'' + \text{Cl}'$  varies in the series  $\text{K}' > \text{Na}' > \text{Li}'$ ;  $\text{Ba}'' > \text{Sr}'' > \text{Ca}'' > \text{Mg}''$ ;  $\text{Br}' > \text{Cl}' > \text{NO}_3' > \text{OAc}'$ . The same order holds for the mobility of the ions, and the inverse order for their hydration. The heat of activation of the reaction is 18,500 g.-cal. R. T.

**Influence of alkyl groups on reaction velocities in solution. I. Acid-catalysed prototropy of phenyl alkyl ketones.** D. P. EVANS (J.C.S., 1936, 785—789; cf. A., 1935, 828, 1206; this vol., 35).—The acid-catalysed prototropy of a series of ketones  $\text{CH}_3\text{R} \cdot \text{COPh}$  has been studied. The velocity coeffs. decrease in the order  $\text{R} = \text{H}, \text{Me}, \text{Et}, \text{Pr}^a, \text{Bu}^a$ , tending towards a const. val. There is an increase in the energy of activation of 2000 g.-cal. and a tenfold increase in the  $P$  factor in passing from  $\text{R} = \text{H}$  to  $\text{R} = \text{Me}$ , after which  $E$  and  $P$  decrease. Since  $E$  is about the same in the case of  $\text{COPhPr}^a$  and  $\text{COPhEt}$ , it is inferred that the increase is due to the co-ordination of a  $\beta\text{-H}$  with  $\text{O}$ , whilst the increase in  $P$  is attributed to the greater inductive effect due to co-ordination. R. S.

**Formation of intermediate compounds in the oxidation of sulphur dioxide by oxygen in presence of catalysts and anti-catalysts.** L. I. KASCHTANOV and V. P. RISHOV (J. Gen. Chem. Russ., 1936, 6, 549—554).—The yield of  $\text{H}_2\text{S}_2\text{O}_6$  falls, and that of  $\text{H}_2\text{SO}_4$  rises, with increasing  $[\text{H}']$  when air containing small amounts of  $\text{SO}_2$  is bubbled through  $\text{H}_2\text{O}$  at  $0\text{--}20^\circ$ , whilst at  $40\text{--}60^\circ$  the opposite effects are observed. In presence of  $\text{MnSO}_4$  increasing  $[\text{H}']$  favours  $\text{H}_2\text{SO}_4$  formation at  $0\text{--}60^\circ$ , whilst  $\text{PhOH}$ , alone or in presence of  $\text{MnSO}_4$ , favours  $\text{H}_2\text{S}_2\text{O}_6$  production. Flue gases are best desulphurised by passing the gas mixture through aq.  $\text{MnSO}_4$  at  $0\text{--}20^\circ$ .

**Olefine-benzene condensation with sulphuric acid catalyst.**—See this vol., 975.

**Destructive alkylation with a hydrogenating catalyst.**—See this vol., 975.

**Phosphoric acid as catalyst for destructive alkylation of hydrocarbons.**—See this vol., 976.

**Dehydrogenating enzyme system of *Acetobacter peroxydans*.**—See this vol., 893.

**Significance of surface of glass and of salts in certain homogeneous gas reactions.** M. PRETTE (Document. sci., 1935, 4, 33—41; Chem. Zentr., 1935, ii, 2174).—The ignition temp. of  $\text{H}_2\text{--CO}$ -air mixtures on a Pyrex glass vessel was not appreciably raised by coating the glass with  $\text{KCl}$ . The combustion of  $\text{H}_2$  proceeded much more slowly at a  $\text{KCl}$  surface. In the latter case the wall is considered to initiate reaction chains. J. S. A.

**Heterogeneous catalysis of gas reactions.** M. POURBAIX (Rev. univ. Mines, 1935, [viii], 11, 367—370; Chem. Zentr., 1935, ii, 2488).—A theory of heterogeneous catalysis is outlined, whereby the catalyst consists (e.g., for oxidation reactions) of two materials in oxidation-reduction equilibrium. Any oxide pair may thus function catalytically for which the equilibrium pressure of  $\text{O}_2$ , as calc. from the Nernst formula, =  $\text{O}_2$  pressure of the gas mixture. J. S. A.

**Ageing of thin-layered palladium catalysts.** D. P. DOBUTSCHIN and A. V. FROST (J. Phys. Chem. U.S.S.R., 1934, 5, 1031—1038, and Acta Physicochim. U.R.S.S., 1934, 1, 503—510).—During ageing of a  $\text{Pd}$  catalyst, obtained by sublimation, the crystal nuclei increase in size from  $<40$  to  $250\text{--}1000$  Å. The total adsorption of  $\text{H}$  is unchanged, but the rate of adsorption and desorption is reduced. Ageing was effected by heating in vac. at  $0\text{--}100^\circ$  for  $0\text{--}20$  hr. Its rate was reduced by the presence of  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , or air. No ageing occurred in vac. at  $-185^\circ$ . Desorption from the fresh layer occurred very rapidly. Sintering took place only after desorption (cf. Bastow, A., 1931, 1120; Muller and Schwab, A., 1933, 36).

CH. ABS. (e)

**Catalytic decomposition of  $\text{N}_2\text{O}$ .** J. SANCHO (Anal. Fis. Quím., 1935, 33, 854—860).—The reaction coeff. for the decomp. of  $\text{N}_2\text{O}$  by bauxite having  $1.5 \times 10^{19}$  active centres per g. at temp. from  $180^\circ$  to  $300^\circ$  and 10 to 15 mm. has a zero temp. coeff. between  $214^\circ$  and  $280^\circ$ . The vol. remains const., and it is concluded that the reaction is unimol.,  $\text{O}_2$  being adsorbed by the catalyst, which it poisons. A mixture of  $\text{N}_2\text{O}$  with  $\text{O}$ , is not decomposed.

F. R. G.

**Platinised silver gauze, and silver-platinum alloys, in the oxidation of ammonia.** I. E. ADADUROV, J. M. DEITSCH, and N. A. PROZOROVSKI (J. Appl. Chem. Russ., 1936, 9, 807—812).—Platinised  $\text{Ag}$  gauze gives satisfactory results, without corrosion, at temp.  $<750^\circ$ ; at higher temp. the gauze fuses.  $\text{Pt--Ag}$  alloys are less fusible, but are comparatively inactive, even with a  $\text{Pt}$  content of 90%. 96% conversion is given by 8 : 1 : 1  $\text{Pt--Ag--Rh}$  alloy at  $935^\circ$ . R. T.

**Catalysis by alloys. I. Decomposition of formic acid vapour on copper-gold and silver-**



gold alloys. G. RIENACKER (Z. anorg. Chem., 1936, 227, 353—375; cf. A., 1934, 974).—Energies of activation ( $E$ ) of the reaction  $\text{HCO}_2\text{H} \rightarrow \text{H}_2 + \text{CO}_2$  have been determined, using as catalysts Au, Ag, Cu, and Ag-Au and Cu-Au alloys. With Ag-Au at 180°  $E$  is approx. the same as with the pure components. With Cu-Au  $E$  retains the val. (about 24 kg.-cal.) observed with pure Cu up to Au 75 at.-%, but shows a marked decrease (21.3 kg.-cal.) when the crystals of composition  $\text{Cu}_3\text{Au}$  have an ordered structure (non-statistical distribution of atoms). F. L. U.

Reactions in concentrated sulphuric acid. I. Carbon disulphide. J. MILBAUER and J. DOŠKAR (Chem. Obzor, 1935, 10, 65—69; Chem. Zentr., 1935, ii, 2045).— $\text{CS}_2$  reacts with  $\text{H}_2\text{SO}_4$  ( $\text{N}_2$  atm.) at temp.  $> 190^\circ$  with formation of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , and S. The effect of catalysts is described; Pd-black reduces the min. reaction temp. to  $105^\circ$ , with production of COS. The primary reaction is  $\text{CS}_2 + \text{H}_2\text{O} = \text{COS} + \text{H}_2\text{S}$ , followed by oxidation. H. N. R.

Pumice as a support for copper-chromium oxide catalysts in dehydrogenations. R. E. DUNBAR, D. COOPER, and R. COOPER (J. Amer. Chem. Soc., 1936, 58, 1053—1054).—The prep. of supported catalysts, which give a high yield of aldehyde from alcohols at  $330\text{--}350^\circ$ , is described. E. S. H.

Properties of zinc-chromium catalysts for methyl alcohol synthesis.—See B., 1936, 631.

Enhancement of thermostability of chromium catalysts.—See B., 1936, 640.

Preparation of catalyst for ammonia synthesis from Ural magnetite.—See B., 1936, 639.

Nickel catalysts. I. Effect of temperature of preparation on the crystal size and composition of nickel oxide. M. C. BOSWELL and R. K. ILER (J. Amer. Chem. Soc., 1936, 58, 924—928).—NiO, prepared at fairly low temp. from  $\text{Ni}(\text{OH})_2$ , is microcryst. When treated with aq.  $\text{NaOCl}$  the surface takes up active O, which can be determined iodometrically; assuming a unimol. layer, the particle size of NiO can be calc. X-Ray determination of particle size tends to show that there is 1 atom of active O to each atom of surface Ni. The diameter of the crystals,  $D$ , increases with rising temp. of prep.,  $T$ , according to  $\log D = kT + C$ , where  $k$  and  $C$  are consts. The presence of  $\text{Al}_2\text{O}_3$  retards the sintering of NiO at high temp. S. H.

Nickel contact catalyst for removal of carbon monoxide from hydrogen-nitrogen mixture.—See B., 1936, 640.

Formation of sulphuric acid in presence of nitrogen oxides.—See B., 1936, 638.

Catalytic condensation of benzines.—See B 1936, 581.

Catalytic synthesis of diphenylamine.—See this vol., 837.

Electrolytic production of alkali metals from non-aqueous solutions. N. P. FEDOTEEV and R. N. KINKULSKAJA (Coll. Trans. I U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 114—141).—Na is obtained in 60% yield on the current (2.5—3 volts)

from NaBr in  $(\text{CH}_3\text{NH}_2)_2$  at  $150^\circ$  (Ni electrodes). Preliminary experiments indicate the possibility of similarly producing K from KI. R. T.

Mechanism of electrolysis of manganese salts. M. GELOSO (Compt. rend., 1936, 202, 1573—1575; cf. this vol., 807).—A discussion. The composition of the pseudo- $\text{MnO}$ , deposited varies continuously with the conditions. The reactions are  $\text{Mn}^{++} \rightarrow \text{Mn}^{IV+} + 2e$ , and  $\text{Mn}^{IV+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+$ . H. J. E.

Water vapour discharge and hydrogen peroxide formation. K. H. GEIB (J. Chem. Physics, 1936, 4, 391; cf. A., 1934, 157).— $\text{H}_2\text{O}_2$  is formed from the products of discharge in  $\text{H}_2\text{O}$  vapour only below  $-100^\circ$ . The following mechanism is suggested ( $s$ =surface of glass,  $\text{H}_2\text{O}$ , or  $\text{H}_2\text{O}_2$ ):  $s + \text{H} = s\text{H}$ ;  $s\text{H} + \text{O}_2 \rightarrow s\text{HO}_2$ ;  $s\text{HO}_2 + \text{H} \rightarrow s + \text{H}_2\text{O}_2$ . F. L. U.

Action of colloids on the KG of cathode deposits. A. GLAZUNOV and E. DRESCHER (Chem. Listy, 1936, 30, 145—149).—The linear velocity of crystallisation of Ag at the cathode rises with increasing concn. of gelatin in the electrolyte to a max., thereafter falling. The significance of the phenomenon is discussed. R. T.

Cathodic reduction of oxides on iron surfaces as a method of estimating corrosion.—See B., 1936, 599.

Electrodeposition of (A) tungsten, (B) tungsten-nickel and tungsten-nickel-copper alloys, from aqueous solutions.—See B., 1936, 645.

Electrochemical reduction of europium. W. KAPFENBERGER (Z. anal. Chem., 1936, 105, 199—205).—Eu is separated as insol.  $\text{EuSO}_4$  by electrochemical reduction of rare earth chloride solutions (containing 60—100 g. of  $\text{H}_2\text{O}_2$  per litre) +  $\text{H}_2\text{SO}_4$  at a Hg cathode. A divided cell is employed, with  $N\text{-H}_2\text{SO}_4$  as anolyte. Some  $\text{SmSO}_4$  may be pptd. at high c.d. The  $\text{EuSO}_4$  is separated and oxidised with conc.  $\text{HNO}_3$ . Hg is pptd with  $\text{H}_2\text{S}$ , and Eu is converted into  $\text{Eu}_2(\text{C}_2\text{O}_4)_3$  and thence into  $\text{Eu}_2\text{O}_3$ . This is converted into  $\text{EuCl}_3$ , and re-electrolysed. From material containing 3% of Eu, 99.7% of Eu is recovered as  $\text{EuSO}_4$  from each reduction. Three reductions give a product containing 98% Eu + a little Sm; 99.9% Eu is obtainable with  $> 6$  reductions. J. S. A.

Electrolytic oxidation. VII. Electrolysis of acetates in non-aqueous solutions. S. GLASSTONE and A. HICKLING (J.C.S., 1936, 820—827; cf. A., 1934, 176).—The electrolysis of  $N\text{-KOAc} + N\text{-AcOH}$  in glycol has been studied. The efficiency of  $\text{C}_2\text{H}_6$  formation is a max. at  $50^\circ$  and decreases with decreasing c.d., total  $[\text{OAc}']$ , and  $[\text{AcOH}]$ , whilst the duration of the electrolysis and the nature of the anode material have little effect. In the case of an Au anode, the efficiency decreases linearly with increasing  $[\text{H}_2\text{O}]$ , becoming const. at 4.7% of  $\text{H}_2\text{O}$ . It is unaffected by the addition of  $\text{Mn}^{++}$ ,  $\text{Pb}$ ,  $\text{Co}$ ,  $\text{Cu}^{++}$ , and  $\text{Fe}^{++}$ , but is diminished by small  $[\text{OH}']$ . When the anode is coated with  $\text{PbO}_2$ , the efficiency is greatly reduced, but  $\text{MnO}_2$  is without effect. Various anode materials give approx. the same e.m.f., except  $\text{PbO}_2$ , with which it is less. It is suggested that the reactions  $2\text{OAc}' \rightarrow 2\text{OAc} \rightarrow (\text{OAc})_2$  occur and that

(OAc)<sub>2</sub> yields C<sub>2</sub>H<sub>6</sub>+CO<sub>2</sub> or reacts with the solvent to give CHO·CH<sub>2</sub>·OH. The latter has been shown to be a product of the anodic oxidation of (CH<sub>2</sub>·OH)<sub>2</sub>. The PbO<sub>2</sub> electrode is reduced to PbO by (CH<sub>2</sub>·OH)<sub>2</sub>, which then decomposes the (OAc)<sub>2</sub>, thus inhibiting the reaction. *Glyoxal-2:4-dinitrophenylhydrazone*, reddish-orange needles, m.p. 330°, has been prepared.

R. S.

**Electrolytic reduction and oxidation of aminoacetic acid and alanine.** E. BAUR (Z. Elektrochem., 1936, 42, 285—287).—The "redox" decomp. which NH<sub>2</sub>-acids undergo in contact with bone C (A., 1935, 1356) is separable into a reduction and an oxidation which can be realised electrolytically. Thus in N-H<sub>2</sub>SO<sub>4</sub> solution NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H gives NH<sub>2</sub>Me and HCO<sub>2</sub>H at the cathode and CH<sub>2</sub>O at the anode. With NH<sub>2</sub>·CHMe·CO<sub>2</sub>H the products are EtOH, NH<sub>3</sub>, and HCO<sub>2</sub>H at the cathode and MeCHO at the anode.

F. L. U.

**Electrolytic reduction of pyrrole.** B. SAKURAI (Bull. Chem. Soc. Japan, 1936, 11, 374—376).—Electrolytic reduction of pyrrole in presence of Ni or Pt affords pyrrolidine in 15.6% yield.

J. T. A.

**Dissociation of carbon dioxide in the electrodeless discharge.** W. C. SCHUMB and F. A. BICKFORD (J. Amer. Chem. Soc., 1936, 58, 1038—1043).—The influence of variation in frequency, current, and voltage on the % decomp. has been determined by the pressure change and by analysis of the gaseous products. The decomp. products under the experimental conditions are CO and O<sub>2</sub>, avoiding the formation of C<sub>3</sub>O<sub>2</sub>. A mechanism of decomp. is proposed.

E. S. H.

**Relationship between the critical pressure and the energy absorbed in the photochemical ignition of mixtures of hydrogen and chlorine.** F. A. LAVROV and A. V. SAGULIN (Acta Physicochim. U.R.S.S., 1934, 1, 979—984).—Stoichiometric H<sub>2</sub>-Cl<sub>2</sub> mixtures at various pressures were exploded by various intensities of light from a C arc. The same energy-crit. ignition pressure law holds for photochemical and for spark discharge ignition.

CH. ABS. (c)

**Photochemical reaction of mercury vapour with oxygen.** I. M. FRANK (J. Phys. Chem. U.S.S.R., 1934, 5, 1013—1030, and Acta Physicochim. U.R.S.S., 1934, 1, 833—854).—The oxidation of Hg under the action of the resonance line 2537 Å., and pressures of a few tenths mm. to several cm., was studied. Formation of O<sub>3</sub> was observed. The mechanism proposed is Hg\*+O<sub>2</sub>→Hg+O<sub>2</sub>\*; O<sub>2</sub>\*+O<sub>2</sub>→O<sub>3</sub>+O; Hg+O<sub>2</sub>→HgO+O<sub>2</sub>. Dickinson and Sherill's results are explained (cf. A., 1926, 485). The mechanism Hg\*+O<sub>2</sub>→HgO+O; Hg\*+O<sub>2</sub>→Hg'+O<sub>2</sub>, where Hg' is a metastable atom, is also possible.

CH. ABS. (c)

**Photochemical decomposition of azomethane.** G. GOLDFINGER (Compt. rend., 1936, 202, 1502—1504).—The relative velocity of the photo-decomp. of Me<sub>2</sub>N<sub>2</sub> in the full light of the Hg arc diminishes with increasing [Me<sub>2</sub>N<sub>2</sub>]. Addition of 5 mm. of A, N<sub>2</sub>, or CH<sub>4</sub> accelerates the rate but 100 mm. of A, N<sub>2</sub>, or CH<sub>4</sub> decreases it.

R. S.

**Electro-chemical theory of photographic development.** J. E. DE LANGHE (Physica, 1936, 3, 398—406).—On the basis of the supersaturation theory of photographic development a relationship is developed between the p.d. ΔE (ΔE=E<sub>Ag</sub>−E<sub>red.</sub>, where E<sub>Ag</sub> is the potential of the Ag electrode and E<sub>red.</sub> is the oxidation-reduction potential of the developer) and velocity of development. For univalent developer ions the relation is in accord with experiment.

J. W. S.

**Mechanism of photographic sensitisation and hypersensitisation for the red and infra-red.** G. SEMERANO (Gazzetta, 1936, 66, 154—162; cf. A., 1934, 975).—Infra-red sensitisers of the cyanine class reduce Ag<sup>+</sup> to Ag. With Ag halides the reduction is slow, but is greatly accelerated by the radiation absorbed by the dye. In neutral solution 1 mol. of sensitiser reduces 1 Ag; in alkaline solution 1 mol. reduces 4 Ag immediately and then more Ag slowly. The formation of Ag nuclei in the light absorption process and the mechanism of the sensitisation are discussed.

O. J. W.

**General photographic density law.** A. VAN KREVELD and L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 477—484).—Several expressions are obtained for mixed and for monochromatic colours.

H. J. E.

**Quantum theory and photography.** H. KEILICH (Z. wiss. Phot., 1936, 35, 134—152).—A detailed review and discussion of photographic processes in the light of the quantum theory.

J. L.

**General form of the relation between exposure and photographic density by exposure to Röntgen rays.** E. HOFER (Z. wiss. Phot., 1936, 35, 132—134).—Mathematical. The author's modification (A., 1935, 177) of the formula of Arens *et al.* (A., 1931, 579) is reconsidered in relation to the case of spaces occurring between grains. De Langhe's formula (B., 1935, 783) corresponds with a special case of the above formula.

J. L.

**Action of ordinary metals on the photographic plate and the electrometer.** J. REBOUL (Compt. rend., 1936, 202, 1920—1922).—Russell's explanation of the action of metals as due to formation of H<sub>2</sub>O<sub>2</sub> (cf. A., 1898, ii, 287) is questioned. The action on plates and the ionisation effects are attributed to the emission of soft X-rays by the metal.

H. J. E.

**Theories of the latent photographic image.** H. ARENS and F. LUFT (Veröff. wiss. Zentr.-Lab. phot. Abt. Agfa, 1935, 4, 1—14; Chem. Zentr., 1935, ii, 2005).—A review.

J. S. A.

**Photographic behaviour of colloid-free silver bromide layers.**—See B., 1936, 620.

**Colour indicator for ultra-violet light in the wave-length range 2650—3341 Å.** O. BAUDISCH and F. BENFORD (Naturwiss., 1936, 24, 361).—An ice-cold aq. solution of 2:7-diaminofluorene hydrochloride (I) is colourless in absence of air, but gives a blue colour in the presence of O<sub>2</sub> on exposure to light. If KNO<sub>3</sub> is added to (I), and the latter is then exposed to ultra-violet light (2650—3341 Å.), the at. O produced by the photochemical decomp. of the



$\text{KNO}_3$  ( $\text{KNO}_3 \rightarrow \text{KNO}_2 + \text{O}$ ) oxidises (I) giving a blue colour. A. J. M.

Oxidation of alcohols by molecular oxygen in ultra-violet light.—See this vol., 963.

Photochemical studies. XXII. Effect of radiation of wave-length 1980—1860 Å. on *cis*- and *trans*-dichloroethylene. H. E. MAHNCKE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1936, 58, 932—933; cf. A., 1935, 561).—The primary action of the radiation is to produce Cl atoms. A small amount of polymerisation product is also formed. E. S. H.

Photochemical chlorination of *tert*-butyl chloride etc.—See this vol., 962.

Production of hydrogen peroxide from hydrogen and oxygen. M. V. POLJAKOV and P. M. STADNIK (Trans. VI Mendeleev Congr. Theor. Appl. Chem., 1932, 1935, 2, Pt. 1, 202—206).— $\text{H}_2\text{O}_2$  may be formed in a homogeneous reaction.

CH. ABS. (e)  
Direct preparation of HD by a chemical method. H. BEUTLER, G. BRAUER, and H. O. JÜNGER (Naturwiss., 1936, 24, 347).—The reaction  $\text{LiH} + \text{D}_2\text{O} \rightarrow \text{HD} + \text{LiOD}$  may be used. The ultra-violet absorption spectrum of the product shows new bands due to HD, the intensity of which was about four times that of the sum of the intensities of lines due to  $\text{H}_2$  and  $\text{D}_2$ . The reaction is probably ionic. A. J. M.

Attempted enrichment of heavier water isotopes in ordinary water by fractional crystallisation. E. H. RIESENFELD and T. L. CHANG (Ber., 1936, 69, [B], 1302—1305).—To obviate, if possible, exchange reactions between solid and liquid phase an apparatus has been devised in which the  $\text{H}_2\text{O}$ , impoverished of HDO and  $\text{H}_2\text{O}^{18}$ , is very rapidly removed from the ice and replaced by fresh, normal  $\text{H}_2\text{O}$ . Enrichment of the cryst. phase in the heavy isotopes is not, however, observed. H. W.

Exchange reactions between heavy water and amino-acids and carbohydrates.—See this vol., 973.

Crystal hydrates of lithium ferrocyanide. V. I. NIKOLAEV and Z. E. BUROVAJA (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 351—356).—Tensimetric and analytical data suggest the hydrates  $\text{Li}_4\text{Fe}(\text{CN})_6$ , 8, 6, and  $3\text{H}_2\text{O}$ . R. T.

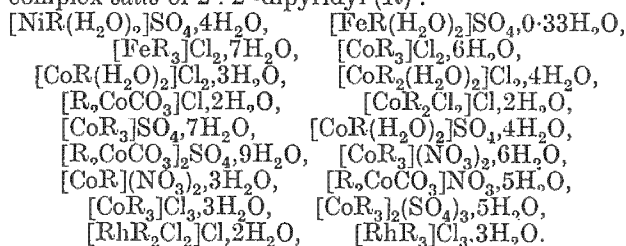
Preparation of sodium hydrogen carbonate. E. TOPORESCU (Compt. rend., 1936, 202, 1591; cf. A., 1922, ii, 642).—A reply to criticism by Neumann and Domke (A., 1928, 480). H. J. E.

Rubidium fluorides and silicofluorides. J. MEYER and W. TAUBE (Z. anorg. Chem., 1936, 227, 337—340).—The sparingly sol. salt obtained by treating  $\text{Rb}_2\text{CO}_3$  with excess of 40% HF is  $\text{Rb}_2\text{SiF}_6$ .  $\text{RbHF}_2$  and  $\text{RbH}_2\text{F}_3$  have been prepared from aq. HF free from  $\text{H}_2\text{SiF}_6$ . F. L. U.

Purification of solutions of copper sulphate. L. A. ROTINJANTZ and V. TARAJAN (J. Appl. Chem. Russ., 1936, 9, 813—818).— $\text{CaOCl}_2$  is added to the hot solution, when  $\text{FeSO}_4$  is pptd. as  $\text{Fe}(\text{OH})_3$ . Ca, Mg, and part of the Al and Zn present in the filtrate

are pptd. by HF, and the filtrate is evaporated, when practically pure  $\text{CuSO}_4$  crystallises out. R. T.

Different types of complex salts of 2:2'-dipyridyl with Cu, Zn, Cd, Fe, Ni, Co, and Rh. F. M. JAEGER and J. A. VAN DIJK (Z. anorg. Chem., 1936, 227, 273—327).—In addition to data for compounds previously prepared (cf. A., 1934, 1317; 1935, 167, 312, 714; this vol., 175), the prep. and crystallographic details are given for the following complex salts of 2:2'-dipyridyl (R):



and probably several more or less hydrolysed R derivatives of  $\text{RhCl}_3$ .  $[\text{NiR}_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$  has been split up into its two stereoisomerides. These salts vary very much in their stability towards  $\text{H}_2\text{O}$ ; aquo-salts may be formed or it may be impossible to separate the salts at all in presence of  $\text{H}_2\text{O}$ , as in the case of  $\text{R}_1$  and  $\text{R}_2$  salts of  $\text{FeSO}_4$  and  $\text{FeCl}_2$ . M. S. B.

Cupric salts of aminosulphonic acids. J. MEYER and W. TAUBE (Z. anorg. Chem., 1936, 227, 425—428).—The prep. of the compound  $(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{SO}_3)_2\text{Cu}$  is described. It is dark blue, insol. in but hydrolysed by  $\text{H}_2\text{O}$ , and is regarded as a complex salt analogous to  $(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2)_2\text{Cu}$ .  $\text{NH}_2 \cdot \text{CH}(\text{SO}_3\text{H})_2$  yields only a normal Cu salt. F. L. U.

Silver salts of aminosulphonic acid. (MLLE.) L. CHAUMETON (Compt. rend., 1936, 202, 1783—1786).—When  $\text{NH}_2 \cdot \text{SO}_3\text{H}$  ( $>1.75$  mol.), dissolved in aq. NaOH equiv. to this acid and the  $\text{AgNO}_3$  added, is treated with solid  $\text{AgNO}_3$  (1 mol.), complete dissolution occurs but a white deposit of the compound  $\text{AgNH} \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$  (I) slowly forms. When 1—1.75 mol. of  $\text{NH}_2 \cdot \text{SO}_3\text{H}$  is used the compound  $\text{AgNH} \cdot \text{SO}_3\text{Na} \cdot \text{Ag}_2\text{N} \cdot \text{SO}_3\text{Na} \cdot 4\text{H}_2\text{O}$  (II) is produced. Addition of  $\text{NH}_2 \cdot \text{SO}_3\text{H}$  to very conc.  $\text{AgNO}_3$  yields only  $\text{NH}_2 \cdot \text{SO}_3\text{Ag}$ . (I) and (II) dissolve in aq.  $\text{NH}_3$  but deposit birefringent crystals of the compound  $[\text{NH}_3\text{Ag}]_2\text{NSO}_3[\text{AgNH}_3] \cdot 2\text{H}_2\text{O}$ . J. W. S.

Basic magnesium sulphates. (MME.) L. WALTER-LÉVY (Compt. rend., 1936, 202, 1857—1859).—By prolonged boiling of conc. aq.  $\text{MgSO}_4$  with small quantities of  $\text{K}_2\text{CO}_3$ , the ppt.,  $4\text{MgO} \cdot 2\text{CO}_2 \cdot \text{SO}_3 \cdot 7\text{H}_2\text{O}$ , first formed is gradually converted into  $7\text{MgO} \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$ . J. G. A. G.

Formation and dissociation of peroxides of the alkaline-earth metals. M. CENTNERSZWER and M. BLUMENTHAL (Bull. Acad. Polonaise, 1935, A, 540—550).—The dissociation pressures of pure  $\text{MgO}_2$ ,  $\text{CaO}_2$ ,  $\text{SrO}_2$ , and  $\text{BaO}_2$  are measured. Their heats of dissociation are calc. to be, respectively, 12, 12.6, 13.5, and 26.93 kg.-cal. Hydrates are formed at room temp., the dissociation pressures of which are those of the dry compounds.  $\text{BeO}_2$  cannot be obtained free from hydrate. The dissociation of

MgO<sub>2</sub> and BeO<sub>2</sub> is irreversible. CaO<sub>2</sub> and SrO<sub>2</sub> each exist in two modifications. O. D. S.

**Calcium metaphosphates and pyrophosphates.** A. BOULLÉ (Compt. rend., 1936, 202, 1788—1790).—Addition of (NaPO<sub>3</sub>)<sub>6</sub> (I) to a neutral solution of CaCl<sub>2</sub> deposits a viscous amorphous mass retaining 20% H<sub>2</sub>O after drying cold in a vac. and dehydrated only on prolonged heating at 300°. It crystallises at 400° yielding α-Ca(PO<sub>3</sub>)<sub>2</sub> which at > 765° is irreversibly converted into Ca metaphosphate-β, identical with the product of dehydration of CaH<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub> at > 400°. The ppt. obtained on adding (I) to N/25 aq. Ca(OH)<sub>2</sub> has a P<sub>2</sub>O<sub>5</sub>/CaO ratio 1.85, but with N/3—N/60 aq. Ba(OH)<sub>2</sub> (II), the P<sub>2</sub>O<sub>5</sub>/BaO ratio is 1. A neutral solution of (NaPO<sub>3</sub>)<sub>3</sub> gives no ppt. with neutral Ca(NO<sub>3</sub>)<sub>2</sub>, Ba(NO<sub>3</sub>)<sub>2</sub>, or Sr(NO<sub>3</sub>)<sub>2</sub>. Amorphous ppts. with P<sub>2</sub>O<sub>5</sub>/MO ratio=2 (M=Ca, Ba, Sr, or Pb) are obtained on adding (II) to solutions of CaCl<sub>2</sub>, Ca(OAc)<sub>2</sub>, or Pb(OAc)<sub>2</sub> slightly alkaline to Me-orange, or to aq. Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, or Sr(OH)<sub>2</sub>. The Ca compounds all lose H<sub>2</sub>O at 300° and after keeping at 700° yield the same cryst. variety of Ca pyrophosphate identical with that obtained on heating the ppt. produced in a mixture of theoretical proportions of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and Ca(OH)<sub>2</sub>, or Ca(NO<sub>3</sub>)<sub>2</sub>. J. W. S.

**Ammoniates of simple salts. III. Ammoniates of cadmium salts.** G. SPACU and P. VOICCHESCU (Z. anorg. Chem., 1936, 227, 385—401; cf. this vol., 573).—The existence of ammoniates of Cd salts of the following acids has been established by tensimetric methods (figures indicate no. of mols. of NH<sub>3</sub> per mol. of anhyd. salt): HCNS 8, 6, 5, 4, 2; HCO<sub>2</sub>H 6, 4, 2; AcOH 8, 6, 4, 2, 1; OH·CH<sub>2</sub>·CO<sub>2</sub>H 4, 3, 1; NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H 5, 4, 2, 1; (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> 4, 3, 1; [·CH(OH)·CO<sub>2</sub>H]<sub>2</sub> 2, 1; BzOH 8, 6, 4, 2, 1; o-aminobenzoic 10, 6, 5, 2, 1; 5-sulphosalicylic 10, 6, 5, 4, 2, 1. The same general relations are found as with Zn salts. F. L. U.

**Double salts of mercuric cyanide with the azides of the alkali and alkaline-earth metals.** F. PIRRONE and P. ROSSONI (Gazzetta, 1936, 66, 235—244; cf. A., 1929, 1406).—The prep. and crystallographic properties of the following double salts are described: Hg(CN)<sub>2</sub>·LiN<sub>3</sub>·2H<sub>2</sub>O; Hg(CN)<sub>2</sub>·NH<sub>4</sub>N<sub>3</sub>·2H<sub>2</sub>O; Hg(CN)<sub>2</sub>·KN<sub>3</sub>; Hg(CN)<sub>2</sub>·MN<sub>3</sub>·3H<sub>2</sub>O (M=Ca, Sr, Ba). O. J. W.

**Boron hydrides. XXII. Conversion of diborane, B<sub>2</sub>H<sub>6</sub>, into other volatile boron hydrides. XXIII. Transformation of diborane, B<sub>2</sub>H<sub>6</sub>, into solid boron hydride (BH)<sub>x</sub>.** A. STOCK and W. MATHING (Ber., 1936, 69, [B], 1456—1469, 1469—1475).—XXII. A flow apparatus is described for the decomp. of the now readily accessible B<sub>2</sub>H<sub>6</sub> which can be guided along different paths by suitable choice of conditions. At 180°/0.2 atm. practical yields of B<sub>5</sub>H<sub>11</sub> with some B<sub>4</sub>H<sub>10</sub> are obtained, whilst at 250°/120 mm. with Hg as catalyst B<sub>5</sub>H<sub>9</sub> is produced. B<sub>5</sub>H<sub>11</sub> is obtained by warming B<sub>4</sub>H<sub>10</sub> with H<sub>2</sub>. Only for the prep. of B<sub>6</sub>H<sub>10</sub> in appreciable amounts is it necessary to use Mg<sub>3</sub>B<sub>2</sub> and acid.

XXIII. Exposure of B<sub>2</sub>H<sub>6</sub> under 11 mm. pressure to the silent electric discharge causes formation of (BH)<sub>x</sub> with B<sub>5</sub>H<sub>9</sub> and B<sub>5</sub>H<sub>11</sub>. In presence of excess

of H<sub>2</sub> the transformation is incomplete but no volatile hydrides are produced. In presence of A, B<sub>2</sub>H<sub>6</sub> is slowly but quantitatively converted into (BH)<sub>x</sub>, which forms a chrome-yellow, non-cryst. powder. It occasionally explodes on exposure to air. It cannot be volatilised or dissolved without decomp. H<sub>2</sub>O causes evolution of H<sub>2</sub> with odour of boranes, but hydrolysis does not continue to the formation of H<sub>3</sub>BO<sub>3</sub>. MeOH and EtOH decompose (BH)<sub>x</sub> with evolution of H<sub>2</sub>. With 2N-HNO<sub>3</sub>, (BH)<sub>x</sub> gives a persistent brownish-red colour and the solution when evaporated leaves a mixture of H<sub>3</sub>BO<sub>3</sub> and a (?) NO<sub>2</sub>-compound which explodes when gently heated or rubbed with a glass rod. H. W.

**Etherates of aluminium chloride.** N. KOZLOV, R. BOGDANOVSKAJA, and I. SOLOGUB (J. Gen. Chem. Russ., 1936, 6, 315—317).—Et<sub>2</sub>O and AcCl or Ac<sub>2</sub>O in presence of AlCl<sub>3</sub> or TiCl<sub>3</sub> react as follows: MCl<sub>3</sub>·Et<sub>2</sub>O (I) + AcCl EtOAc + EtCl + MCl<sub>3</sub>·(I) + Ac<sub>2</sub>O → 2EtOAc + MCl<sub>3</sub>. R. T.

**Aluminium iodide.** A. VIAN and E. MOLES (Anal. Fis. Quim., 1936, 34, 81—90).—AlI<sub>3</sub> is synthesised by the action of I in H<sub>2</sub> on Al at 420°. AlI<sub>3</sub> with H<sub>2</sub>O vapour gives dry HI. AlI<sub>3</sub> has m.p. 179.5°. Heat of vaporisation and v.p. from 310° to 370° are recorded and b.p. and crit. temp. are calc. F. R. G.

(A) Variations in m.p., and denaturation of cryolite when fused in contact with air. (B) Molecular state of oxides dissolved in cryolite. V. P. MASCHOVETZ (J. Appl. Chem. Russ., 1936, 9, 789—801, 802—806).—(A) The f.p. and f content of cryolite fall with increasing time of heating in contact with O<sub>2</sub> and H<sub>2</sub>O. The process is associated with a fall in NaF content, and a corresponding rise in Al<sub>2</sub>O<sub>3</sub> content.

(B) Reactions of the type 4CaO + 2Na<sub>2</sub>AlF<sub>6</sub> → 3CaF<sub>2</sub> + Ca(AlO<sub>2</sub>)<sub>2</sub> + 6NaF; 2Al<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>AlF<sub>6</sub> 3NaAlO<sub>2</sub> + 2AlF<sub>3</sub>; NaAlO<sub>2</sub> Na<sup>+</sup> + AlO<sub>2</sub><sup>-</sup> are shown to take place in molten cryolite in presence of CaO and Na<sub>2</sub>O. R. T.

**Polarimetric study of aluminium malate.** J. L. DELSAL (Compt. rend., 1936, 202, 1589—1591; cf. Quadrat and Korecky, A., 1930, 743).—The compound AlH<sub>5</sub>C<sub>4</sub>O<sub>6</sub> was prepared by dissolution of Al(OH)<sub>3</sub> in malic acid and drying the product at 100°. It yields Na and Na<sub>2</sub> derivatives. Polarimetric and electrometric measurements confirm the existence of these compounds. H. J. E.

**Double salts of indium and organic bases.** J. B. EKELEY and H. A. POTRATZ (J. Amer. Chem. Soc., 1936, 58, 907—909).—The prep. of InCl<sub>3</sub>·4NH<sub>3</sub>MeCl, m.p. > 300°, InCl<sub>3</sub>·4NH<sub>2</sub>Me<sub>2</sub>Cl, m.p. 215—217°, InCl<sub>3</sub>·3NH<sub>2</sub>Me<sub>2</sub>Cl, m.p. 196—198°, InCl<sub>3</sub>·2NMe<sub>4</sub>Cl, m.p. > 300°, InBr<sub>3</sub>·2NMe<sub>4</sub>Br, m.p. 236—238°, InCl<sub>3</sub>·2NEt<sub>4</sub>Cl, m.p. 275—277°, and InBr<sub>3</sub>·NEt<sub>4</sub>Br, m.p. 289—291°, is described. The double salts In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·(NH<sub>3</sub>Me)<sub>2</sub>SO<sub>4</sub>·4H<sub>2</sub>O, 2In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·2(NH<sub>3</sub>Et)<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O, 2In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·2(NH<sub>2</sub>Et)<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O, 2In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·2(NH<sub>2</sub>Et)<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·3(n-C<sub>5</sub>H<sub>11</sub>·NH<sub>2</sub>)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O, and In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·(NH<sub>3</sub>·CH<sub>2</sub>Ph)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O have been prepared; all have m.p. > 300°. The optical properties



of most of these compounds have been determined. The prep. of  $2\text{InCl}_3 \cdot 4\text{SMe}_3\text{Cl} \cdot 3\text{H}_2\text{O}$ , m.p. 203–204° (decomp.),  $\text{InI}_3 \cdot \text{SMe}_3\text{I}$ , m.p. 149–150°, and  $\text{InI}_3 \cdot \text{SEt}_3\text{I}$ , m.p. 145–147°, is described. E. S. H.

**Preparation and properties of carbon selenide.** H. G. GRIMM and H. METZGER (Ber., 1936, 69, [B], 1356–1364).—Carbon diselenide cannot be prepared from  $\text{Al}_2\text{Se}_3$  and  $\text{CCl}_4$  but is obtained in 50% yield when a mixture of  $\text{H}_2\text{Se}$  and  $\text{CCl}_4$  is passed through a Jena glass tube at 500°. It is a golden-yellow liquid, b.p. 69.5°/130 mm., 124°/760 mm., m.p. –45.5°, which burns with difficulty in air or  $\text{O}_2$  and decomposes slowly in the dark, rapidly in daylight. It does not react with Zn or Ag, slowly blackens Cu, and immediately forms  $\text{HgSe}$  with Hg. With KOH in EtOH– $\text{CCl}_4$  it affords K selenoxanthate. When treated with  $\text{NH}_3$ –EtOH it yields polymeride A (I),  $\text{CHSe}$ , or  $\text{C}_4\text{H}_4\text{Se}_9$ , decomp. 190° after darkening at 170°, which is not affected by  $\text{SeO}_2$  or I in EtOH and is disintegrated by more powerful oxidants. When preserved in 96% EtOH it affords polymeride B, closely similar to (I). With  $\text{NH}_3$  in  $\text{CCl}_4$   $\text{CSe}_2$  yields a compound  $\text{C}_4\text{H}_4\text{Se}_8\text{N}$ . Gradual addition of  $\text{CSe}_2$  to  $\text{NH}_2\text{Ph}$  yields  $\text{H}_2\text{Se}$  and small amounts of diphenylselenocarbamide, also obtained with a yellow polymeride when  $\text{NH}_2\text{Ph}$  is added to  $\text{CSe}_2$ .  $\text{PhOH}$ ,  $\text{NHPh}_2$ ,  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and  $\text{MeCHO}$  do not react with  $\text{CSe}_2$  at room temp. whereas  $\text{NET}_3$  and  $\text{NPhMe}$ , give dark ppts.  $\text{CCl}_4$  and  $\text{TeH}_4$  give Te,  $\text{TeCl}_2$ , HCl, and  $\text{C}_2\text{Cl}_6$ .  $\text{Ag}_2\text{Te}$  and  $\text{CBr}$ , or  $\text{Cl}$ , in  $\text{CCl}_4$  at room temp. give  $\text{AgBr}$  or  $\text{AgI}$  and Te halides. Te and C do not react at 1000°. H. W.

**Synthesis of cyanic acid by the action of carbonyl chloride on ammonia.** R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1936, 202, 1544–1547).— $\text{HCNO}$  is formed by adding a PhMe solution of  $\text{COCl}_2$  to conc. aq.  $\text{NH}_3$  at 0° (A). It was identified by the formation of blue  $\text{K}_2\text{Co}(\text{CON})_1$  and by the isolation and analysis of  $\text{AgCNO}$ . No  $\text{CO}(\text{NH}_2)_2$  was formed under these conditions. It is formed on heating the solution (A) at 90° for 30 min. H. J. E.

**Silicon fluorobromides.** W. C. SCHUMB and H. H. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 994–996).—The prep. of  $\text{SiFBr}_3$ , m.p. –82.5±0.5°, b.p. 83.8±0.2°,  $\text{SiF}_2\text{Br}_2$ , m.p. –66.9±1°, b.p. 13.7±0.2°, and  $\text{SiF}_3\text{Br}$ , m.p. –70.5±0.5°, b.p. –41.7±0.2°, is described. V.p. have been determined. E. S. H.

**Preparation of disilicon hexachloride.** T. TORAL (Anal. Fis. Quím., 1935, 33, 225–228).—By the use of lower temp. and diffused light, the yield of  $\text{Si}_2\text{Cl}_6$  by chlorination of Ca–Mn–Si (cf. Schumb *et al.*, A. 1932, 482) is increased to 58%. The f.p. is –1°. F. R. G.

**Lead oxides.** E. RENCKER (Bull. Soc. chim., 1936, [v], 3, 981–988).—The thermal decomp. of  $\text{PbO}_2$  in the air yields  $\text{Pb}_2\text{O}_3$  and red lead, accompanied by a brown oxide, also of composition  $\text{Pb}_2\text{O}_4$ . The brown oxide can be obtained by heating  $\text{PbO}$ , in a vac. The two forms of  $\text{PbO}$  cannot be distinguished by colour; the  $\alpha$  form may vary from yellow to red. Dry methods of prep. yield the  $\alpha$  form below 530°; at higher temp. it is converted into the  $\beta$  form, but the

reverse transformation has not been observed. Both forms may be obtained by wet methods of prep. E. S. H.

**Formation of  $\text{N}_2\text{O}_3$  by reduction of nitric acid with aluminium.** W. GELLER (Z. anorg. Chem., 1936, 227, 413–414).— $\text{HNO}_3$  (sp. gr. 1.210), left undisturbed in contact with pure Al for 30 days at room temp., assumes an intense blue colour, and is shown by titration with  $\text{KMnO}_4$  to contain about 0.7% of  $\text{N}_2\text{O}_3$ . Stirring prevents the formation of the blue colour and destroys it when formed, with evolution of  $\text{NO}$ . F. L. U.

**Volume-chemical evidence as to existence of orthonitric acid.** W. BILTZ [with O. HULSMANN and W. EICKHOLZ] (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 95–102; Chem. Zentr., 1935, ii, 1846–1847).—From measurements of the vol. increments and thermal expansions in the  $\text{HNO}_3$ – $\text{H}_2\text{O}$  system,  $\text{HNO}_3 \cdot \text{H}_2\text{O}$  is regarded as actually  $\text{H}_3\text{NO}_4$ , and  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  as its dihydrate  $\text{H}_3\text{NO}_4 \cdot 2\text{H}_2\text{O}$ . J. S. A.

**Dynamics of preparation of red phosphorus.** I. A. J. ZVORIKIN (J. Appl. Chem. Russ., 1936, 9, 779–788).—Complete conversion of white into red P is attained in 15–30 min. at 400–500°. Red P,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{U}_3\text{O}_8$ , and Se are without catalytic action. R. T.

**Mutual reactions of phosphates and soils. III. Monocalcium hydrogen phosphate and calcium carbonate, alone or in presence of variable quantities of lime.** J. CLARENS and H. MARGULIS (Bull. Soc. chim., 1936, [v], 3, 1053–1060; cf. this vol., 39).—When  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is pptd. by  $\text{Ca}(\text{OH})_2$  in presence of small amounts of  $\text{CO}_2$ , a certain amount of  $\text{Ca}_2(\text{HPO}_4)_2$  is found in the ppt. Dil. solutions of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  do not attack pptd.  $\text{CaCO}_3$ . The pptn. of aq.  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , containing suspended  $\text{CaCO}_3$ , by progressively increasing amounts of  $\text{Ca}(\text{OH})_2$  has been studied. E. S. H.

**Alteration of properties of vanadium pentoxide brought about by cold-working.** C. KROGER (Z. anorg. Chem., 1936, 227, 376–384).—Cold-working of  $\text{V}_2\text{O}_5$ , by compression or by grinding in a mortar, effects a change of colour from yellow to green. At the same time  $d$  is reduced from 3.32 to 2.83, and the adsorptive capacity for  $\text{SO}_2$  and reactivity with CO are increased. X-Ray examination shows slight broadening of the lines, but no essential change in cryst. structure. The effects are attributed to disturbance of the atoms in the outer lattice planes. Similar behaviour is shown by  $\text{CuVO}_3$ . F. L. U.

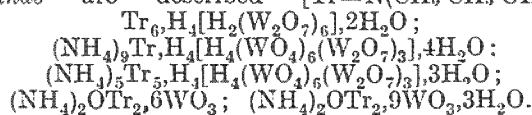
**Bismuth bromide,  $\text{BiBr}_2$ .** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 1082–1084).—Properties and reactions of  $\text{BiBr}_2$ , prepared by the action of Br on pptd. Bi, are described. E. S. H.

**Sulphide, selenide, and thioselenide of thiocyanogen.** A. BARONI (Atti R. Accad. Lincei, 1936, [vi], 23, 139–142).—The compounds  $\text{Se}_2(\text{SCN})_2$  and  $\text{SeS}(\text{SCN})_2$  have been prepared by the action of  $\text{Hg}(\text{SCN})_2$  on  $\text{Se}_2\text{Cl}_4$  and  $\text{SeSCL}_2$ , respectively.  $\text{S}(\text{SCN})_2$  can be obtained in an analogous way from  $\text{SCl}_2$ . All three substances polymerise readily at room temp. giving non-fusible and insol. products.

**Potassium tellurates.** Analogy with the sulphates and selenates. M. PATRY (Compt. rend., 1936, 202, 1516—1519; cf. A., 1935, 1090).— $K_2TeO_4 \cdot 2H_2O$  is not isomorphous with  $K_2H_4OsO_6$  (Retgers, A., 1893, ii, 161). Of the compounds  $KHTeO_4 \cdot 1.5H_2O$ ,  $KHTeO_7 \cdot 1.5H_2O$ , and  $K_2Te_3O_{10} \cdot 5H_2O$  reported in the literature, only the amorphous  $KHTeO_4 \cdot 1.5H_2O$  could be prepared.  $K_2TeO_4$ ,  $K_2SeO_4$ , and  $K_2SO_4$  have been shown by X-rays to be isomorphous. R. S.

**Chromic picrate.** H. J. S. KING (J.C.S., 1936, 861—862).—Excess of  $Ag_2O$  with picric acid affords Ag picrate +  $1H_2O$  (I) (cf. J.C.S., 1908, 93, 486), which loses  $1H_2O$  at  $85^\circ$ . Hexa-aquochromic chloride (II) (cf. A., 1904, ii, 565) with (I) at  $0^\circ$  gives chromic picrate +  $8H_2O$  (III) (the aq. solution is probably an equilibrium mixture as shown by conductivity measurements; boiling  $H_2O$  affords a basic picrate), converted at  $85^\circ$  into the anhyd. salt, sinters with decomp. at  $94^\circ$ , which with cold  $H_2O$  gives picric acid and basic chromic picrate, and with liquid  $NH_3$  affords a mixture of chromiammine picrates in which 1 Cr is associated with 3.5  $NH_3$ . (III) (1 mol.) with hexamminochromic nitrate (1.5 mols.) in cold  $H_2O$  gives immediately hexa-amminochromic dipicrate (cf. A., 1924, i, 1060). Dichlorotetra-aquochromic chloride with (I) gives mainly (III), and (II) with  $AgNO_3$  evolves N oxides and affords no  $Cr(NO_2)_3$ . J. L. D.

**Behaviour of tri(hydroxyethyl)amine towards tungstic acid.** F. GARELLI and A. TETTAMANZI (Atti. R. Accad. Sci. Torino, 1935, 70, I, 588—594; Chem. Zentr., 1935, ii, 2035).—The following compounds are described  $[Tr=N(CH_2 \cdot CH_2 \cdot OH)_3]$ :



J. S. A.

**Preparation of hydrobromic acid in the laboratory.** C. N. IONESCU and V. RADULESCO (Bul. Soc. Chim. Romania, 1935, 17, 309—312).—Pure HBr is prepared by slowly dropping Br on to lighting petroleum in presence of  $AlBr_3$  at room temp. at first and at a higher temp. towards the end. The yields with and without  $AlBr_3$  are 80—90 and 45%.

R. S. B.

**Dissociation of excited iodine molecules.** E. RABINOWITCH and W. C. WOOD (J. Chem. Physics, 1936, 4, 358—362; cf. this vol., 437).—Using  $I_2$  vapour diluted with He, A,  $N_2$ , or  $H_2$ , it is shown that all excited  $I_2$  mols. dissociate by collision with foreign mols. With He  $\leq 10$  collisions are required, whilst with the other gases the first collision is effective.

F. L. U.

**Preparation of iodic acid.** A. PÉREZ-VITORIA (Anal. Fis. Quím., 1935, 33, 795—803).—Further details (cf. A., 1932, 352) are given. The action of samples of fuming  $HNO_3$  containing from 84.7 to 98.3%  $HNO_3$  ( $d$  1.476 to 1.511) on I is described; a minimum concn. of 89%  $HNO_3$  is essential. A solution of  $HIO_3$  in  $HNO_3$  yields crystals of  $HIO_3$  or  $3I_2O_5 \cdot H_2O$  (cf. Moles *et al.*, A., 1934, 617) according as the  $HNO_3$  is dil. and cold, or conc. and hot.

F. R. G.

**Metallic iodochlorides. II.** M. G. DE CELIS (Anal. Fis. Quím., 1935, 33, 203—224).— $MCl_4I$  ( $M=NH_4$ , Rb, Cs), and  $M(Cl_4I)_2 \cdot 8H_2O$  ( $M=Be$ , Mn, Co, Ni, Zn) have been prepared by the author's method (A., 1932, 1215). The  $d$  of these salts and their m.p. together with the m.p. of the salts previously prepared (*loc. cit.*) are recorded. The mol. vol. of the anion is influenced by the nature of the cation.

F. R. G.

**Internal complex salts of bivalent manganese and univalent copper.**—See this vol., 968.

**Amorphous and crystalline oxide hydrates and oxides. XXVI.** Structure and catalytic properties of crystalline ferric hydroxides which give amorphous X-ray patterns. A. KRAUSE and S. KRZYŻANSKI (Z. anorg. Chem., 1936, 227, 417—422; cf. this vol., 686, 691).—The prep. of two microcryst. varieties of hydrated  $Fe_2O_3$  by means of conc. KOH is described (cf. A., 1935, 314). Both belong to the ortho-hydroxide type and give amorphous X-ray diagrams. When heated with  $H_2O$  or aq. KOH in an autoclave they yield  $\alpha$ - $Fe_2O_3$ .

F. L. U.

**Barium ferric fluorides.** A. H. NIELSEN (Z. anorg. Chem., 1936, 227, 423—424; cf. this vol., 441).—The prep. and properties of the compound  $Ba_3Fe_2F_{13} \cdot H_2O$  are described. Attempts to prepare the anhyd. salt were unsuccessful.

F. L. U.

**Reaction of ferric salts with pyrimidone in the presence of complex cyanides of iron.** J. V. DUBSKY, E. KRAMETZ, and J. TRTÍLEK (Publ. Fac. Sci. Univ. Masaryk, 1936, 223, 7—10).—Reduction of  $Fe^{III}$  salts by pyrimidone (I) in aq. solution accounts for the different constitution,  $[Fe^{III}(CN)_5NO]Fe^{II}6aq.$  of the ppt. obtained with Na nitroprusside in the presence of  $Fe^{III}$  salts, to that obtained with antipyrine. Only with KCNS and  $Fe^{III}$  salts in aq. solution (I) gives purple-red ppts.,  $2Fe(SCN)_3 \cdot 3pyram.$ , analogous to those obtained with antipyrine, whilst in alcoholic solution in which antipyrine gives  $Fe(SCN)_3 \cdot 0.3antip.$ , no satisfactory result was obtained.  $Fe^{III}$  salts and (I) with  $[Fe^{III}(CN)_5NO]Na_3$  and  $[Fe^{III}(CN)_5NH_2]Na_2$  give respectively blue ppts. of  $[Fe^{III}(CN)_5NO]_2Fe^{II}$  and  $[Fe^{III}(CN)_5NH_2]Fe^{II}$ ; with  $[Fe^{II}(CN)_5NH_3]Na_3$  and  $[Fe^{II}(CN)_5NO]Na_4$  they give respectively blue ppts. of  $[Fe^{II}(CN)_5NH_3]Fe^{III}$  and  $[Fe^{II}(CN)_5NO]_3Fe^{II}_4$ .

F. R.

**Temperature of the iron thermite reaction.** H. VON WARTENBERG and G. WEHNER (Z. Elektrochem., 1936, 42, 293—298; cf. A., 1932, 913).—The temp. of a Fe-thermite mass, determined spectrographically, is  $2400 \pm 50^\circ$ .

F. L. U.

**Complexes of sodium nitroprusside.** V. L. MASALSKI and A. T. TSCHERNI (J. Gen. Chem. Russ., 1936, 6, 37—41).— $Na_2[Fe(CN)_5NO]$  yields complexes of the probable structures  $Na_3[Fe(CN)_4NO_2NO]$  (I),  $Na[Fe(CN)_2NO_2 \cdot 3NO]$  (II), and  $[Fe(CN)_4NO][NO_2]$  (III), when treated with NaOH. Titration with  $KMnO_4$  in acid solution at room temp. converts (I) into  $Na_2[Fe^{III}(CN)_4NO_2NO]$ , (II) into  $Na_2[Fe^{III}(CN)_2NO_2 \cdot 3NO \cdot SO_4]$ , and (III) into  $[Fe^{III}(CN)_4NO_2NO_2][H]$ . At  $75^\circ$   $Fe^{II}$  is oxidised to  $Fe^{III}$ , and then  $NO_2^-$  to  $NO_3^-$ .

R. T.



**Insoluble nitroprussides of metals.** J. V. DUBSKY and E. KRAMETZ (Publ. Fac. Sci. Univ. Masaryk, 1936, 223, 1—8).—Na nitroprusside precipitates  $\text{Fe}^{\text{II}}\text{X}_2 \cdot 6\text{H}_2\text{O}$  (chocolate),  $\text{CdX}_2 \cdot 2\text{H}_2\text{O}$  (flesh-pink),  $\text{ZnX}_2 \cdot 3\text{H}_2\text{O}$  (flesh),  $\text{CoX}_2 \cdot 4 \cdot 5\text{H}_2\text{O}$  (pink),  $\text{Hg}^{\text{I}}\text{X}_2 \cdot 0 \cdot 5\text{H}_2\text{O}$  (white),  $\text{Hg}^{\text{II}}\text{X}_2 \cdot 2\text{H}_2\text{O}$  (white), and  $\text{Ag}_2\text{X}$  (white), from solutions of salts of these metals [ $\text{X} = \text{Fe}^{\text{III}}(\text{CN})_5\text{NO}$ ]. Antipyrine when present in the pptns. forms a complex only with  $\text{Fe}^{\text{II}}$  nitroprusside. F. R.

**Gmelin's reaction (sulphides and nitroprussides).** F. E. RAURICH-SAS (Anal. Fis. Quím., 1936, 34, 419—494).—Solutions of  $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NO})]$  (I) with  $\text{M}_2\text{S}$  ( $\text{M} = \text{alkali metal or NiI}_2$ ) give a deep red compound,  $\text{Na}_3\text{M}_2[\text{Fe}(\text{CN})_4(\text{HS})_2]$  (II), which, in presence of the  $\text{NO}_2^-$  formed, yields an indigo compound,  $\text{Na}_2\text{M}_2[\text{Fe}(\text{CN})_4(\text{S} \cdot \text{S}(\text{S})_2)]$  (III); this is the sole product of the reaction of (I) with tetrasulphides (IV), which are formulated  $\text{S}' \cdot \text{S}(\text{S}) \cdot \text{S}'$ . The variation of colour obtained in the reaction is due to formation of (II) and (III) in differing proportions together with  $\text{Na}_4[\text{Fe}(\text{CN})_5(\text{NO})_2]$  and  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ . The following analogues of (IV) give a colour reaction:  $\cdot\text{O} \cdot \text{SO} \cdot \text{O} \cdot$ ,  $\cdot\text{O} \cdot \text{CS} \cdot \text{O} \cdot$ ,  $\cdot\text{S} \cdot \text{CS} \cdot \text{S} \cdot$ ,  $\cdot\text{O} \cdot \text{CO} \cdot \text{O} \cdot$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{CS}(\text{NH}_2)_2$ . The blue ppt. given by  $\text{Na}_2\text{S}_2\text{O}_4$  with (I) (cf. Comanducci, A., 1918, ii, 248) is regarded as  $\text{Na}_3\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ . Evidence is adduced for the formulæ  $\cdot\text{O} \cdot \text{SO} \cdot \text{O} \cdot \text{S} \cdot \text{O} \cdot$  and  $\cdot\text{O} \cdot \text{SO} \cdot \text{O} \cdot \text{S}'$  for the hypsulphite and thiosulphate ions. F. R. G.

**Nitrites. III. Ammines of cobaltous nitrite.** L. LE BOUCHER (Anal. Fis. Quím., 1936, 34, 66—71).— $\text{Co}(\text{NO})_2 \cdot 2 \cdot 3\text{C}_5\text{H}_5\text{N}$  (A., 1929, 781), after alternate treatment with  $\text{NH}_3$  and evacuation over  $\text{H}_2\text{SO}_4$ , yields the *hexammoniate*, which at  $50^\circ$  12 mm. loses  $\text{NH}_3$  to give the *tetrammoniate* which again loses  $\text{NH}_3$  at lower pressures.  $d_{40}^{25}$  are recorded. F. R. G.

**Complex cobalti-oxalates. II.** G. SPACU and M. VANCEA (Bul. Soc. Stiințe Cluj, 8, 228—236; Chem. Zentr., 1935, ii, 2795—2796; cf. A., 1934, 1321).—The following salts are described:  $\text{A}[\text{Co}(\text{NH}_3)_5\text{X}]\cdot\text{H}_2\text{O}$  ( $\text{A} = [(\text{C}_2\text{O}_4)_2, \text{Co}(\text{OH})(\text{H}_2\text{O})]$ ,  $\text{X} = \text{Cl, Br, CNS, NO}_2, + 2\text{H}_2\text{O, NO}_3 + 2\text{H}_2\text{O}$ );  $\text{A}[\text{Co en}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ;  $\text{A}[\text{Co}(\text{NH}_3)_6] \cdot 9\text{H}_2\text{O}$ ;  $\text{A}[\text{Co}(\text{NH}_3)_5\text{Co}_2] \cdot 2\text{H}_2\text{O}$ ;  $\text{A}_3[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ ;  $\text{A}[\text{Co en}_2(\text{OH})(\text{H}_2\text{O})]$ . J. S. A.

**Substitution of water for chlorine in the dichloro-trans-ethylenediaminecobaltic ion.** O. BINDER and P. SPACU (Compt. rend., 1936, 202, 1586—1588).—The X-ray spectra of *cis*- and *trans*-dichloro-, *cis*-monoquo- and *cis*-diaquo-diethylenediaminecobaltic chlorides are distinct. Interaction of *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  with  $\text{H}_2\text{O}$  yields only *cis*- $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ . H. J. E.

**Action of malonic acid on dichloro-trans-diethylenediaminecobaltic chloride.** O. BINDER and P. SPACU (Compt. rend., 1936, 202, 1786—1787).—X-Ray spectra indicate that *trans*- $[\text{Co en}_2\text{Cl}_2]\text{Cl}$  treated with malonic acid yields the violeo-compound and not the monoquo-salt (A., 1929, 780). J. W. S.

**Thiocyanate co-ordination compounds.** R. J. McILROY, A. C. ESPINER, and A. D. MONRO (J. New Zealand Inst. Chem., 1936, 1, 10—14).—The following compounds prepared by the action of the amine+

$\text{NH}_4\text{CNS}$  on the metal salts are described:  $\text{Co}[p\text{-C}_6\text{H}_4(\text{NH}_2)_2]_2(\text{CNS})_2$ ;  $\text{NiX}_2(\text{CNS})_2$  [ $\text{X} = o\text{-, } m\text{-, and } p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ;  $o\text{-, } m\text{-, and } p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ ;  $\text{NH}_2\text{Ph}$ ; and benzidine]. Cu salts yield  $2\text{CuCNS}$ ,  $o\text{-}$  or  $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ .  $\text{NH}_3$  displaces the amines from the Ni compounds at room temp., yielding  $[\text{Ni}(\text{NH}_3)_6](\text{CNS})_2$ . From their greater solubility in associated solvents, it is considered that the Ni compounds are electrolytes, e.g.,  $[\text{Ni}(\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2)_2](\text{CNS})_2$ . J. S. A.

**Iodates. I. Copper and nickel.** J. MARTINEZ-CROS and L. LE BOUCHER. II. Cobalt and zinc. J. MARTINEZ-CROS (Anal. Fis. Quím., 1935, 33, 229—240; 1936, 34, 72—80).—I. A green form of  $\text{Ni}(\text{IO}_3)_2$  has been isolated, as well as the yellow form, by dehydration of  $\text{Ni}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ .  $\text{Ni}(\text{IO}_3)_2$  with  $\text{NH}_3$  under pressure gives  $\text{Ni}(\text{IO}_3)_2 \cdot 6\text{NH}_3$ , which, when left at reduced pressure over  $\text{H}_2\text{SO}_4$ , yields  $\text{Ni}(\text{IO}_3)_2 \cdot 2\text{NH}_3$  and this, when heated at  $120^\circ$ , gives  $\text{Ni}(\text{IO}_3)_2 \cdot \text{NH}_3$ .  $\text{Cu}(\text{IO}_3)_2$  has been obtained in a colourless form by dehydration of  $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ , which with  $\text{NH}_3$  gives  $\text{Cu}(\text{IO}_3)_2 \cdot 5\text{NH}_3$  whence  $\text{Cu}(\text{IO}_3)_2 \cdot 2\text{NH}_3$  and  $\text{Cu}(\text{IO}_3)_2 \cdot \text{NH}_3$  are obtained as above.  $d_{40}^{25}$  have been determined.

II. The observations of Meusser (A., 1901, ii, 555) on the hydrates of  $\text{Co}(\text{IO}_3)_2$  are confirmed.  $\text{Co}(\text{IO}_3)_2$  with  $\text{NH}_3$  under pressure gives the *hexammoniate* which, when left in vac. over  $\text{H}_2\text{SO}_4$ , yields the *diammoniate*.  $\text{Zn}(\text{IO}_3)_2 \cdot 4\text{NH}_3$  (cf. Ephraim *et al.*, A., 1915, ii, 166), when heated at  $125^\circ$ , yields the *di-ammoniate*.  $d_{40}^{25}$  and mol. vol. are recorded for  $\text{Co}(\text{IO}_3)_2$ ,  $\text{Zn}(\text{IO}_3)_2$ , their hydrates and ammoniates. F. R. G.

**Oxidising agents for nickel solutions.** W. A. WESLEY (Metal Ind., N.Y., 1935, 33, 290).—A discussion (cf. A., 1935, 45, 1467). L. S. T.

**Luteo- and purpureo-salts of ruthenium. Ruthenammines. I.** K. GLEU and K. REHM (Z. anorg. Chem., 1936, 227, 237—248).—The following stable complex *ammines* of  $\text{Ru}^{\text{III}}$ , with co-ordination no. 6, have been obtained: luteo-salts (I)  $[\text{Ru}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $[\text{Ru}(\text{NH}_3)_6]_2(\text{H}_2\text{SO}_4)_2$ ; purpureo-salts (II)  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Ru}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ . The compounds are analogous with the corresponding Co and Cr compounds, but (I) are colourless like Rh hexammines. (I) are stable to dil. mineral acids, but not to conc. alkalis, which give a yellow colour with liberation of  $\text{NH}_3$ . By treating this yellow product with conc.  $\text{HCl}$  a blue compound is obtained which is an oxidation-reduction indicator, being colourless in the oxidised stage. With dil. alkali both (I) and (II) give a deep red colour. (I) are not readily oxidised in acid solution in the cold, but are completely decomposed on heating, giving  $\text{RuO}_4$ . They form insol. ppts. with a no. of anions, e.g.,  $\text{I}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ , and  $\text{ClO}_4^-$ . (II) are obtained by boiling (I) with conc.  $\text{HCl}$  or  $\text{HBr}$  giving, respectively, yellow and orange-red ppts. They are dissolved by gentle warming with excess of aq.  $\text{NH}_3$  giving the ion  $[\text{Ru}(\text{NH}_3)_5\text{OH}]^+$  in solution from which a white cryst. roseo-salt,  $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]\text{X}_3$ , is probably pptd. by carefully acidifying. All the compounds are paramagnetic, in accordance with

theory, and have a moment of 2 Bohr magnetons at 20°.  
M. S. B.

Interaction of pyridine with the chloride and bromide of Blomstrand salt.—See this vol., 998.

Artificial preparation of radioactive elements. (MME.) I. JOLIO-CURIE and F. JOLIO (Angew. Chem., 1936, 49, 367—369).—Nobel lecture. J. W. S.

Microchemical methods. T. A. THOMSON (J. New Zealand Inst. Chem., 1936, 1, 21—26).—A review. J. S. A.

Raman effect in analytical chemistry. J. GOUBEAU (Z. anal. Chem., 1936, 105, 161—182).—The application of the Raman effect to the detection and determination of org. compounds is discussed, with special reference to the analysis of hydrocarbon fuel mixtures. The intensity  $I$  of the Raman lines is measured by their persistence through a series of standardised exposures decreasing in geometrical progression, and is compared with  $I$  for the pure substance: quant. results are inaccurate for lines of small  $I$ .  $H_2O$  and fluorescent impurities are first removed by shaking with  $CaSO_4$  and active C.

Importance of the absorption of light in chemistry. H. FROMHERZ (Chem.-Ztg., 1936, 60, 445—448).—Applications of absorption spectra methods to the determination of the presence and concn. of substances possessing absorption bands, and to the elucidation of problems of constitution, are illustrated by examples drawn from the lit.

Electrometric analysis. Attempt at a general classification. J. GUZMÁN (Anal. Fis. Quím., 1935, 33, 109—113).—A survey of the methods in use.

Magneto-optic method of chemical analysis. I. History and present status of the method. II. Construction, adjustments and operation of the apparatus; physical measurements; unknowns. S. S. COOPER [with T. R. BALL] (J. Chem. Educ., 1936, 13, 210—215, 278—283).—I. From a review of evidence for and against the method, it is concluded that min. exist and are characteristic of the substance or substances under examination.

Crystallo-chemical analysis. G. B. BOXI (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 115—124).—Descriptive.

Methods of physico-chemical analysis. V. A. KISTIakovSKI (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 5—13).—Descriptive.

Systematic qualitative analysis of anions. E. W. FLOSDORF and C. HENRY (J. Chem. Educ., 1936, 13, 274—277).—Details are given for the separation of 19 of the commoner anions into 4 groups. Sensitivities of the tests are recorded.

Hydrogen carbonate method of qualitative chemical analysis for cations. A. B. LEVIN (Z. anal. Chem., 1936, 105, 328—331).—A scheme for the group separation of the common cations, avoiding the use of  $H_2S$ , is outlined.

New oxidation-reduction indicators. I. Phenylanthranilic acid (diphenylamine-*o*-carboxylic acid). W. S. SYROKOMSKY and V. V. STIEPIN (J. Amer. Chem. Soc., 1936, 58, 928—929).—Phenylanthranilic acid gives sharp, reversible colour changes with the usual oxidising solutions used in volumetric analysis, and is more stable in presence of excess of oxidant than  $NHPh_2$  and its derivatives. The normal oxidation potential, referred to the  $H_2$  electrode, is +1.08 volt. The indicator error, determined potentiometrically, is negligible.

Micro-method for accurate determination of  $D_2O$  in water. K. FENGER-ERIKSEN, A. KROGH, and H. USSING (Biochem. J., 1936, 30, 1264—1269).—The precautions for the removal and purification of  $H_2O$ - $D_2O$  mixtures from tissues, and a pipette for producing drops of the same vol. in the  $d$  determinations, are described.

Measurement of  $p_H$  values. L. G. GROVES (J. Sci. Instr., 1936, 13, 209—214).—A discussion of the methods available, especially of the glass electrode.

Accuracy of  $p_H$  measurements. F. LIENEWEG (Arch. tech. Mess., 1935, 4, 774—775, 4 pp.; Chem. Zentr., 1935, ii, 2248—2249).—The accuracy of the customary colorimetric and electrometric methods is reviewed.

Determination of hydrogen-ion concentration. T. T. COCKING (Ind. Chem., 1936, 12, 299—301).—An apparatus for the prep. and storage of  $H_2O$  for use in  $p_H$  determinations, and an accurate method of determining  $p_H$  so as to avoid the error due to the buffering action of the indicator, are described.

Borax as an acidimetric standard. F. H. HURLEY, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 220—221).—The drying of  $Na_2B_4O_7 \cdot 10H_2O$  with  $EtOH$  and  $Et_2O$  is described. The rate of loss of  $H_2O$  of crystallisation by exposure to air has been determined. The stability is such that borax may be used satisfactorily.

Action of 4-nitropyrocatechol as a titration indicator. S. R. COOPER and V. J. TULANE (Ind. Eng. Chem. [Anal.], 1936, 8, 210—211).—4-Nitropyrocatechol is useful for titrations of strong acids with strong bases, or strong acids with weak bases, but not for weak acids.

Oximinothiocamphor as an indicator.—See this vol., 856.

Titration of weak acids and bases in water-alcohol mixtures. H. BAGGESGAARD-RASMUSSEN (Z. anal. Chem., 1936, 105, 269—282).—The theories of Bjerrum and Bronsted are applied to the titration of weak acids and bases in  $H_2O$ - $EtOH$  mixtures. The  $p_A$  of weak acids, as also of most indicators except Me-orange, is elevated with increasing  $[EtOH]$ , the  $p_A$  of weak bases being similarly progressively lowered. Weak acids may therefore be titrated accurately in aq.  $EtOH$ , using phenolphthalein, but no advantage is obtained other than increased solubility of org. acids. The titration of weak bases is less practicable than in  $H_2O$ , but the salts of weak bases



(e.g., alkaloid hydrochlorides) may be titrated with much enhanced accuracy in conc. aq. EtOH.

J. S. A.

**Universal indicator for the range  $p_H$  1.2—12.7, and its use in volumetric analysis.** F. ČUTA and K. KÁMEN (Chem. Listy, 1936, 30, 22—24, 129—133).— $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$  1.125, phenolphthalein 0.0355,  $o$ -cresolphthalein 0.03, bromothymol-blue 0.1, Me-red 0.022, Me-orange 0.0085, and 2':4':2'':4'':2'''-penta-methoxytriphenylcarbinol 0.5 g. are dissolved in a litre of MeOH, and the solution is made exactly neutral with aq. NaOH. The indicator is unstable when made up in EtOH instead of MeOH. Examples of its application to volumetric analysis are given, and a colour scale is appended, enabling  $p_H$  vals. from 1.2 to 12.7 to be read with an error of  $\pm 0.2$ . R. T.

**Determination of free acid in dark coloured liquids.** M. DE MINGO and H. THALER (Anal. Fis. Quim., 1935, 33, 376—380).—Electrometric titration is preferred to the use of outside indicators.

F. R. G.

**Titration of hydrogen peroxide in presence of oxalic acid (alkali oxalates).** A. SIMON and T. REETZ (Z. anal. Chem., 1936, 105, 321—323).— $\text{H}_2\text{O}_2 + \text{H}_2\text{C}_2\text{O}_4$  is titrated with  $\text{KMnO}_4$ .  $\text{H}_2\text{O}_2$  in a second portion is destroyed by boiling with NaOH or  $\text{NH}_3$  in presence of  $\text{FeCl}_3$ , and  $\text{H}_2\text{C}_2\text{O}_4$  is then titrated alone.

J. S. A.

**Determination of active chlorine in bleach liquors.**—See B., 1936, 589.

**[Use of] benzidine acetate in the determination of bromides by silver.** F. BURRIEL (Anal. Fis. Quim., 1935, 33, 692—695).—The method previously described (A., 1932, 825) for the determination of  $\text{I}'$  is suitable for determination of  $\text{Br}'$  between  $N$  and  $0.02N$  with an error  $< 0.5\%$ , but is unsuitable for determination of  $\text{Cl}'$ .

F. R. G.

**Ultra-violet light as an aid in the fluorescence test for bromine.** J. GRANT (Analyst, 1936, 61, 400—401).—The sensitiveness of the Baubigny test for Br (cf. B., 1936, 254) is increased by examination of the stains in ultra-violet light.

E. H. S.

**Micro-determination of iodine.** F. GONZALEZ NUNEZ and P. P. REGIDOR (Anal. Fis. Quim., 1935, 33, 445—456).—The solution (10 c.c.) containing about  $5 \times 10^{-6}$  g. I with an equal amount of 28%  $\text{K}_2\text{CO}_3$  is evaporated and calcined and the residue lixiviated; the solution is evaporated, this residue extracted with 95% EtOH, which is boiled with a few drops of 20%  $\text{H}_2\text{SO}_4$  and 1 c.c. of  $\text{Br-H}_2\text{O}$ , with subsequent addition of a little KI and starch, and titrated with 0.002*N*- $\text{Na}_2\text{S}_2\text{O}_3$ . The method is used for the determination of I in blood with an error of about 5%.

F. R. G.

**Volumetric determination of iodides by ceric sulphate.** Application of the indicator  $o$ -phenanthroline ferrous ion. D. LEWIS (Ind. Eng. Chem. [Anal.], 1936, 8, 199—200).—A satisfactory visual end-point is obtained in presence of  $\text{CoMe}$ , and  $\text{H}_2\text{SO}_4$ . Moderate amounts of neutral chloride do not interfere. If  $\text{Br}'$  is present, more  $\text{Ce}(\text{SO}_4)_2$  is required.

E. S. H.

**Quantitative distillation of fluorine.** D. DAHLE and H. J. WICHMANN (J. Assoc. Off. Agric.

Chem., 1936, 19, 313—320).—The effect of varying the amount of non-volatile acid used, the distillation temp., the vol. of distillate collected, and the size of flask used in the Willard and Winter method is investigated. The retarding effect of Al salts and gelatinous  $\text{SiO}_2$  on the distillation is confirmed.

E. C. S.

**Determination of fluorine in presence of a large excess of aluminium ions.** D. DAHLE and H. J. WICHMANN (J. Assoc. Off. Agric. Chem., 1936, 19, 320—327; cf. preceding abstract).—The Willard and Winter method is modified (a) by raising the distillation temp. to  $162^\circ$ , (b) by increasing the vol. of distillate collected to 300—350 c.c., and (c) by evaporating and redistilling the distillate. 2 p.p.m. of F can be detected in  $\text{Al}_2(\text{SO}_4)_3$  and alum.

E. C. S.

**Determination of fluorine.** S. SHINKAI (J. Soc. Chem. Ind. Japan, 1936, 39, 162B).—Fluorides are decomposed by conc.  $\text{H}_2\text{SO}_4$  and Si, the liberated  $\text{SiF}_4$  being absorbed in powdered NaF.

C. R. H.

**Conductometric determination of fluorine down to minimal quantities.** J. HARMS and G. JANDER (Z. Elektrochem., 1936, 42, 315—319; cf. A., 1935, 1092).—Conductometric titration of NaF in dil. AcOH with  $\text{AlCl}_3$  gives good results for quantities of F from 20 mg. to  $12 \times 10^{-6}$  g. No disturbance is caused by  $\text{Cl}'$ ,  $\text{NO}_3'$ ,  $\text{SO}_4''$ , or  $\text{SiO}_3''$ .

F. L. U.

**Determination of fluorine in artificial cryolite.**—See B., 1936, 640.

**Determination of fluorine in presence of beryllium.** A. A. VASILIEV (J. Appl. Chem. Russ., 1936, 9, 943—945).—The sample is fused with 2:1  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ , and F' is determined as  $\text{PbFCl}$  in the aq. extract of the melt.

R. T.

**Analysis of sulphide-hydrosulphide lyes.**—See B., 1936, 639.

**Volumetric determination of sulphate using sodium rhodizonate.** R. STREBINGER and L. VON ZOMBORY [with L. POLLAK] (Z. anal. Chem., 1936, 105, 346—350; cf. A., 1930, 53).—In acid solutions,  $\text{SO}_4''$  is pptd. with an excess of standard  $\text{BaCl}_2$ . Na rhodizonate is added as indicator, and the excess of Ba is then titrated with aq.  $\text{K}_2\text{SO}_4$ . The addition of  $\text{NH}_4\text{Cl}$  is advantageous.

J. S. A.

**Colorimetric determination of inorganic sulphate.**—See this vol., 914.

**Standardisation of sodium thiosulphate iodometrically against copper.** L. O. HILL (Ind. Eng. Chem. [Anal.], 1936, 8, 200).—After dissolving the Cu in  $\text{HNO}_3$ ,  $\text{HNO}_3$  is removed by boiling with  $\text{CO}(\text{NH}_2)_2$ . The usual procedure is then followed.

E. S. H.

**Micro-determination of nitrogen by Kjeldahl.** Z. ZAKRZEWSKI and H. J. FUCHS (Biochem. Z., 1936, 285, 390—406).—The technique of this determination is investigated critically in all its stages—burning, liberation and distillation of  $\text{NH}_3$ , and iodometric titration—and apparatus and modifications are introduced which lead to improved accuracy.

P. W. C.

**Colorimetric determination of nitrates in water in presence of chlorides.**—See B., 1936, 622.

**Reaction for hydroxylamine.**—See this vol., 1036.

**Removal of phosphate ion [in qualitative analysis].** L. J. CURTMAN and T. B. GREENSLADE (J. Chem. Educ., 1936, 13, 238—239).—The Sn, FeCl<sub>3</sub>, and ZrOCl<sub>2</sub> methods have been compared. All are efficient for removal of PO<sub>4</sub>''', but in the first two loss of cations is serious. The ZrOCl<sub>2</sub> method is the most rapid, efficient, and convenient. L. S. T.

**"Purity-testing" for arsenic by the method of the Swiss Pharmacopoeia V.** H. T. LIEM (Pharm. Tijds. Nederl.-Indie, 1935, 12, 81—85, 145—152; Chem. Zentr., 1935, ii, 2244).—The method is described and the results are discussed.

H. N. R.

**Determination of arsenic in steel, pig iron, and iron ores.**—See B., 1936, 598.

**[Determination of] carbon monoxide content of laboratory air.**—See B., 1936, 669.

**Systematic separation of anions.** E. UMBLIA (Keem. Teated, 1935, 2, 79—87; Chem. Zentr., 1935, ii, 2408).—A group separation is described. (1) acids detected in the original solution; CO<sub>3</sub>'', OAc', CrO<sub>4</sub>'', MnO<sub>4</sub>', NO<sub>2</sub>', S'', Fe(CN)<sub>6</sub>''', and Fe(CN)<sub>6</sub>'''. (2a) Anions with Ba salts insol. in mineral acids; SO<sub>4</sub>' and SiF<sub>6</sub>'; (2b) Ba salts insol. in AcOH; IO<sub>3</sub>', C<sub>2</sub>O<sub>4</sub>'', SO<sub>3</sub>'', F', S<sub>2</sub>O<sub>3</sub>'', and BrO<sub>3</sub>'; (2c) Ba salts insol. in H<sub>2</sub>O; PO<sub>4</sub>''', AsO<sub>3</sub>'', AsO<sub>4</sub>'', SiO<sub>3</sub>'', C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>'', BO<sub>2</sub>'. (3) Anions giving Zn salts insol. in AcOH; S'', Fe(CN)<sub>6</sub>''', Fe(CN)<sub>6</sub>'''. (4) Anions the Ag salts of which are insol. in HNO<sub>3</sub>; I', Br', Cl', CN', CNS', IO<sub>3</sub>', BrO<sub>3</sub>'. (5) ClO<sub>4</sub>', NO<sub>3</sub>', ClO<sub>3</sub>'. J. S. A.

**Use of direct and alternating current in effusion method of measuring radioactivity of air.** G. ALIVERTI and G. ROSA (Nuovo Cim., 1935, [ii], 12, 26—36; Chem. Zentr., 1935, ii, 2847—2848).—The apparent nos. of atoms of Rn found, using a.c. and d.c., are as 1 : 0.925. J. S. A.

**Determination of small amounts of potassium by means of silver cobaltinitrite.** R. J. ROBINSON and G. L. PUTNAM (Ind. Eng. Chem. [Anal.], 1936, 8, 211—213).—A modification of Breh and Gaebler's procedure (A., 1930, 944) permits the determination of 0.002 mg. of K. E. S. H.

**Reagent for potassium.** I. Qualitative. A. W. CLARK and C. O. WILLITS (Ind. Eng. Chem. [Anal.], 1936, 8, 209—210).—The use of 2% naphthol-yellow S is described. 1 part of K in 2500 parts of solution can be detected. Na and NH<sub>4</sub> do not interfere. E. S. H.

**Rapid detection of sodium and potassium in presence of ammonium and magnesium.** C. CANDEA and L. I. SAUCIUC (Bull. sci. École polytech. Timişoara, 1934, 5, 111—113; Chem. Zentr., 1935, ii, 2555).—Na and K, present as chlorides after volatilisation of NH<sub>4</sub> salts, are detected with H<sub>3</sub>Sb<sub>2</sub>O<sub>7</sub>+KOH, and NaOAc+tartaric acid respectively. J. S. A.

**Spectrographic detection of metal traces in experimentally produced current contact marks.** T. SCHMIDT (Deut. Z. ges. gerichtl. Med., 1935, 25, 164—166; Chem. Zentr., 1935, ii, 2848—2849).—

The spectrographic detection of traces of metals is applied in forensic examinations to the detection of the direction of passage of current. J. S. A.

**Microchemical detection of metal ions with picric acid.** C. FRANGOPOLO (Bul. Chim. Soc. rom. Stiinte, 1934, 37, 259—261; Chem. Zentr., 1935, ii, 2250).—Crystal forms given by NH<sub>4</sub>, Al, Ag, Ba, Ca, Fe, Mg, Mn, and Pb with picric acid are described.

J. S. A.

**Titration of silver with potassium iodide. Ceric ammonium sulphate and starch as indicators.** A. BLOOM and W. M. McNABB (Ind. Eng. Chem. [Anal.], 1936, 8, 167).—The procedure gives good results in presence of Cu'' or Fe'''. E. S. H.

**Identification of silver in opaque minerals by the method of imprints.** T. HILLER (Arch. Sci., phys. nat., 1936, [v], 18, Suppl., 54—57; cf. A., 1935, 1478).—A Cu-containing mineral is attacked electrolytically in contact with 50% HNO<sub>3</sub> imbibed on filter-paper above which is a layer of gelatinized paper. The filter-paper is then washed for 1 min. in 1% KBr and then in HNO<sub>3</sub> and distilled H<sub>2</sub>O. It is developed in a physical developer, when the intensity of darkening produced  $\propto$  the [Ag] in the mineral. In absence of Cu the filter-paper is soaked in a reagent comprising 5% aq. KCN (2 parts) and a saturated solution of *p*-dimethylaminobenzylidenerhodanine in COMe<sub>2</sub> (3 parts) and is applied to a polished surface of the mineral for 3—5 min. It is then immersed in dil. HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, when a violet-red colour indicates Ag. Presence of Cu is indicated by a violet-blue colour.

J. W. S.

**Micro-determination of zinc by means of 8-hydroxyquinoline.** C. CHERMAN, D. FRANK, and P. WENGER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 57—59).—The neutral solution containing 1—3 mg. Zn'' is treated with 1 drop of Merck's Universal Indicator, 2 drops of 10% AcOH, and 6—7 drops of 40% NaOAc to yield a *p*<sub>H</sub> of 5—6. It is heated to the b.p., and excess (0.1—1 c.c.) of freshly prepared EtOH solution of 8-hydroxyquinoline added. It is stirred and boiled for 1—2 min. and filtered through porcelain. The ppt. is washed 8 times with H<sub>2</sub>O (1—2 c.c.) and dried at 155—158°.

J. W. S.

**Anthranilic acid and its use in the determination of zinc, cadmium, cobalt, nickel, and copper.** R. J. SHENNAN, J. H. F. SMITH, and A. M. WARD (Analyst, 1936, 61, 395—400).—The conditions specified by Funk and Ditt (A., 1933, 924), i.e., pptn. of the anthranilate from neutral, unbuffered solution, are satisfactory and are not improved by the addition to the solution of NH<sub>4</sub>OAc, NaOAc, or Na tartrate. These increase the solubility of the ppt. For the volumetric determination of anthranilic acid, Day and Taggart's procedure (A., 1928, 660) is preferred. E. H. S.

**Indicator transformations of fuchsin.** V. N. SKVORTZOV and E. S. SCHEPELEVA (J. Gen. Chem. Russ., 1936, 6, 55—62).—The transition point of fuchsin (I) shifts in the direction of rising *p*<sub>H</sub> with increasing concn. of (I) and with rising temp.; the salt error is relatively small. (I) is a suitable indi-



cator for the titration of  $\text{ZnSO}_4$  with  $\text{NaOH}$  (at  $100^\circ$ , end-point at  $p_{\text{H}}$  11.5). R. T.

**Sodium diethyldithiocarbamate as a reagent for certain micro-crystal reactions.** J. GRANT and F. A. MEGGY (*Analyst*, 1936, 61, 401—402).—Characteristic micro-crystals of  $\text{Cd}$  (sensitiveness 1:20,000),  $\text{Hg}^{\text{II}}$  (1:2000), and  $\text{Mn}^{\text{II}}$  (1:20,000) diethyldithiocarbamate are formed and  $\text{Co}$  may easily be detected in the presence of  $\text{Ni}$ . The  $\text{Sb}$  and  $\text{Bi}$  salts form oily drops and the  $\text{Pb}$ ,  $\text{Zn}$ , and  $\text{Sr}$  salts have little practical significance. E. H. S.

**Separation of sulpho-bases from sulpho-acids and detection of individual elements of second analytical group. Detection and separation of elements of second group;  $\text{Pb}$ ,  $\text{Hg}$ ,  $\text{Bi}$ ,  $\text{Cd}$ , and  $\text{Cu}$ . Detection and separation of elements of third group.** C. CÂNDEA and L. I. SAUCIU (*Bull. sci. École polytech. Timişoara*, 1934, 5, 104—105, 106—107, 108—110; *Chem. Zentr.*, 1935, ii, 2554).—Modifications of the usual procedure are described. J. S. A.

**Photographic ripening accelerator ("thiocarbin") and sensitive analytical reagent.**—See B., 1936, 621.

**Spectrographic determination of small quantities of copper, lead, arsenic, and antimony in nickel and nickel sulphate solutions.**—See B., 1936, 599.

**Copper catalysis of the oxidation of thiol acids as a basis for the micro-determination of copper.** J. BJERRUM (*J. Biol. Chem.*, 1936, 114, 357—359).—Thiol acids, *e.g.*, thioglycollic acid (I), are oxidised by air in the presence of small quantities of  $\text{Cu}$ . The rate of reaction  $\propto [\text{Cu}]$  below a crit. concn.; hence quantities of  $\text{Cu}$  of the order of  $10^{-7}$  g. may be determined by observing the rate of oxidation of (I) in their presence. H. D.

**Quantitative spectral analysis of traces [of metallic impurities].** W. SMITH and A. KEIL (*Z. Elektrochem.*, 1936, 42, 299—302).—In the determination of minimal quantities of an impurity by spectrophotometric comparison with a reference substance, the relative intensities of the observed lines may be affected by the presence of the main substance; *e.g.*, excess of  $\text{Mg}$  thus affects the relative intensities of  $\text{Cu}$  3247 and  $\text{Zn}$  3282. Experiments are recorded to show that a quant. analysis is possible if due account is taken of the absorption of the lines concerned. F. L. U.

**Photo-electric micro-determination of copper.**—See this vol., 1038.

**Mercurimetry. Action of ammonia on mercuric chlorides and their determination.** M. SCHTSCHIGOL (*Ann. Chim. Analyt.*, 1936, [iii], 18, 149—151).—For the determination of  $\text{Hg}_2\text{Cl}_2$ , 0.3—0.4 g. is heated for 5—10 min. with 25—40 c.c. of 3*N*-aq.  $\text{NH}_3$  and the mixture is filtered and washed. The filtrate is acidified with  $\text{HNO}_3$  and the  $\text{NH}_4\text{Cl}$  is titrated according to the method previously described (this vol., 577). The same method, slightly modified, is used for  $\text{HgCl}_2$ . The reactions of the two compounds with aq.  $\text{NH}_3$  are:  $2\text{Hg}_2\text{Cl}_2 + 4\text{NH}_3\text{OH} =$

$[\text{Hg} + \text{Hg}_2\text{O} + \text{HgNH}_2\text{Cl}] + 3\text{H}_2\text{O} + 3\text{NH}_4\text{Cl}$ ,  $\text{Hg}_2\text{O} \rightarrow \text{Hg} + \text{HgO}$ ;  $\text{HgCl}_2 + 2\text{NH}_3 = \text{NH}_4\text{Cl} + \text{HgNH}_2\text{Cl}$ .

E. H. S.

**Anomalous valencies of the rare earths.** D. W. PEARCE and P. W. SELWOOD (*J. Chem. Educ.*, 1936, 13, 224—230).—The quadri- and bi-valency of certain rare earths metals are discussed, together with the application to methods of analysis and separation. L. S. T.

**Detection of lanthanum, yttrium, and ytterbium from spark in flame spectra.** O. S. PLANTINGA and C. J. RODDEN (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 232).—The limit of detection is in each case about 0.0001*M*, but is influenced by the presence of other rare earths or of large amounts of  $\text{Na}$ . E. S. H.

**Colorimetric determination of aluminium with alizarin S.** A. P. MUSSAKIN (*Z. anal. Chem.*, 1936, 105, 351—361).—The method of Atack (*A.*, 1915, ii, 842) is critically reviewed. The optimum acidity of the solutions is  $p_{\text{H}}$  3.6. The coloration does not follow Beer's law;  $\text{Fe}$ , if present, is best removed as  $\text{Fe}(\text{CNS})_3$  by extraction with  $\text{C}_5\text{H}_{11}\text{OH}$ . J. S. A.

**Separation and determination of gallium.** V. Separation of gallium from beryllium, titanium, zirconium, and thorium, and the determination of the gallium thus separated. S. ARO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, 29, 71—77; *cf. A.*, 1934, 1192).—A solution of the chlorides in 5.6*N*- $\text{HCl}$  is extracted with  $\text{Et}_2\text{O}$ , the extract is washed with 5.6*N*- $\text{HCl}$ , the washings are evaporated, and the aq. solution is treated with 2*N*- $\text{NH}_4\text{OAc} + 6\text{N}$ - $\text{NH}_3$  and filtered. The filtrate is combined with the washed  $\text{Et}_2\text{O}$  extract and the  $\text{Ga}$  pptd. with  $\text{Na}$  camphorate. Each stage has been quantitatively investigated. R. S.

**Solution of manganese problem in analysis of silicate rocks.** O. HACKL (*Z. anal. Chem.*, 1936, 105, 182—199).—Factors governing the choice and accuracy of the method previously described (this vol., 813) are exhaustively discussed. For the oxidation of  $\text{Mn}$ ,  $[\text{H}_2\text{SO}_4]$  should be  $> 2\%$  to prevent pptn. of  $\text{Ti}$ , and  $< 10\%$  to prevent oxidation of  $\text{Ti}$ . J. S. A.

**Last lines of rhenium in presence of large amounts of molybdenum.** S. A. BOROVIK and N. M. GUDRIS (*J. Appl. Chem. Russ.*, 1936, 9, 937—942).—The intensity of the lines at 3451.88, 3460.7, and 3464.72 Å. is unaffected by presence of 16—30% of  $\text{Mo}$ . The lines serve for the detection of  $\leq 0.002\%$  of  $\text{Re}$  in calcite or molybdenite.  $\text{Mn}$  interferes with the spectrometric detection of  $\text{Re}$ . R. T.

**Quantitative separation of iron from copper and nickel.** P. SPACU (*Bull. Soc. chim.*, 1936, [v], 3, 1061—1063).—The solution is treated with excess of  $\text{C}_5\text{H}_5\text{N}$ .  $\text{Fe}^{\text{III}}$  is pptd. as  $\text{Fe}(\text{OH})_3$ , ignited, and weighed as  $\text{Fe}_2\text{O}_3$ . The filtrate is treated with solid  $\text{KCNS}$ , which ppts.  $\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{SCN})_2$  or  $\text{Cu}(\text{C}_5\text{H}_5\text{N})(\text{SCN})_2$ , which are weighed as such. E. S. H.

**Application of 5:7-dibromo-8-hydroxyquinoline to determination of small amounts of iron, titanium, and aluminium in mixtures.** A. M.

ZANKO and A. J. BURSUK (J. Appl. Chem. Russ., 1936, 9, 895—898).—1 g. of tartaric acid and 3 ml. of  $\text{COMe}_2$  (I) are added to 100 ml. of solution, which is then made neutral with aq.  $\text{NH}_3$ , and 10 ml. of  $\text{AcOH}$  and 2% 8-hydroxyquinoline (II) in  $\text{AcOH}$  [0.6 mg. of (II) per mg. of Fe present] are added. The ppt. of Fe salt is collected, washed with  $\text{H}_2\text{O}$ , dried at  $110^\circ$ , and weighed. 2 ml. of 2*N*- $\text{HCl}$ , 2 g. of  $\text{NH}_4\text{NO}_3$ , and 15 ml. of (I) are added per 100 ml. of filtrate + washings, and 9 ml. of 0.2*N*- $\text{KBrO}_3$ - $\text{KBr}$  are added to the solution at  $50^\circ$ , thereby converting excess of (II) present into the 5:7- $\text{Br}_2$ -derivative (III), which then forms a ppt. with Ti. This is collected, washed successively with 200 ml. of 0.04*N*- $\text{HCl}$  containing 10% of (I), and with  $\text{H}_2\text{O}$ , and dried at  $185^\circ$ . 3 g. of  $\text{NH}_4\text{NO}_3$  and (I) to 15% are added to the filtrate (containing 6—8 mg. of Al), the solution is made feebly alkaline with aq.  $\text{NH}_3$ , and 5—20 ml. of a 1% solution of (III) in (I) are added, at  $100^\circ$ . The ppt. of Al salt is washed successively with 10% aq. (I) containing 1.5% of  $\text{NaOAc}$ , and with  $\text{H}_2\text{O}$ , and dried at  $190^\circ$ . R. T.

**Determination of ferrous oxide in ores containing manganese peroxides.**—See B., 1936, 640.

**Determination of very small amounts of iron in silicic acid, with special reference to quantitative spectral analysis.** H. SCHLEGEL (Angew. Chem., 1936, 49, 411—412).— $\text{SiO}_2$  is removed by evaporation with  $\text{HF} + \text{H}_2\text{SO}_4$ . The residue is dissolved in 0.2 c.c. of  $\text{HCl}$  and 0.2 c.c. of a standard solution of  $\text{CrSO}_4 + \text{NiSO}_4$  is added to provide spectral lines of standard intensity for comparison with the Fe lines. 0.02 c.c. of the solution, which should contain 0.00025—0.001 mg. of Fe, is transferred to a C electrode, and the spectrum excited by a condensed spark discharge. J. S. A.

**Colorimetric determination of cobalt.** G. SPACU and C. G. MACAROVICI (Bul. Soc. Ştiinţe Cluj, 8, 245—256; Chem. Zentr., 1935, ii, 2707—2708).—The method of Chiarottino (Ind. Chim., 1933, 8, 32) is modified by use of tolidine (Tld) in place of benzidine (Bzd). The solution is mixed with 5 c.c. of 1% dimethylglyoxine ( $\text{DH}_2$ ) + 2 c.c. of 1% tolidine, and colorimetric after 15 min. 0.0002 mg. of Co per c.c. may be determined. As possible sources of the reddish-brown colour, the following compounds have been obtained by the action of  $\text{DH}$  on Co-Bzd and Co-Tld salts:  $\text{Co}(\text{DH})(\text{NO}_3)(\text{DH}_2)(\text{Bzd})_2 \cdot 2\text{H}_2\text{O}$ ;  $[(\text{DH}_2)(\text{Bzd})\text{Cl} \cdot \text{Co} \cdot \text{D} \cdot \text{CoCl}(\text{Bzd})(\text{DH}_2)]_2 \cdot 6\text{H}_2\text{O}$ ;  $[(\text{DH}_2)(\text{Tld})(\text{H}_2\text{O})\text{ClCo} \cdot \text{D} \cdot \text{CoCl}(\text{H}_2\text{O}) \cdot \text{Tld} \cdot \text{DH}_2]$ . J. S. A.

**Method of preventing formation of colloidal nickel sulphide in qualitative analysis.** Z. H. PAN and C. C. TANG (Nanking J., 1934, 4, 33—39).—The test solution is neutralised with  $\text{HNO}_3$  and then made just alkaline with aq.  $\text{NH}_3$  before passing  $\text{H}_2\text{S}$  to ppt.  $\text{NiS}$ . CH. ABS. (e)

**Volumetric determination of nickel.** G. SPACU and V. ARMEANU (Bul. Soc. Ştiinţe Cluj, 8, 206—210; Chem. Zentr., 1935, ii, 2708).—A solution containing 2% of  $\text{KCN}$  + 1% of  $\text{C}_5\text{H}_5\text{N}$  is titrated with the Ni solution [as  $\text{Ni}(\text{NO}_3)_2$ , preferably in the absence of  $> 5\%$  of  $\text{NH}_4$  salts] until a permanent turbidity

forms.  $[\text{Ni}(\text{CN})_2(\text{H}_2\text{O})(\text{C}_5\text{H}_5\text{N})]$  is initially formed, and redissolves in excess of  $\text{KCN}$  forming  $\text{K}_2[\text{Ni}(\text{CN})_4]$ . J. S. A.

**Preparation and storage of standard chromous sulphate solutions.** H. W. STONE and C. BEESON (Ind. Eng. Chem. [Anal.], 1936, 8, 188—190).— $\text{CrSO}_4$  is prepared by reduction of violet chrome alum solutions in preference to  $\text{K}_2\text{Cr}_2\text{O}_7$ . Modified procedure for preventing oxidation by air is recommended. E. S. H.

**Determination of tungsten with hydroxyquinoline.** E. OTERO and R. MONTEQUI (Anal. Fis. Quím., 1935, 33, 132—139).—The method of Halberstad (A., 1933, 366) is performed in slightly acid solution and the ppt. dried by washing with  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ .  $(\text{NH}_4)_6\text{W}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$  can be determined by this method. With insufficient  $\text{C}_6\text{H}_5\text{N} \cdot \text{OH}$  a blood-red compound,  $\text{C}_6\text{H}_5\text{N} \cdot \text{OH} \cdot \text{WO}_3$ , is formed. F. R. G.

**Conductometric titration of tungstate with silver nitrate.** C. CANDEA and I. G. MURGULESCU (Bul. Soc. Chim. Romania, 1935, 17, 223—227).—Solutions of  $\text{Na}_2\text{WO}_4$  may be titrated conductometrically with  $\text{AgNO}_3$  in presence of  $\text{EtOH}$  (30% for 0.05*N*- and 50% for 0.05*N*- $\text{Na}_2\text{WO}_4$ ):  $\text{WO}_4^{2-} + 2\text{Ag}^+ = \text{Ag}_2\text{WO}_4$ . After the addition of  $\text{EtOH}$  the solution is kept for 0.75 hr. before titration. Results are accurate down to 0.005*N*- $\text{Na}_2\text{WO}_4$ . R. S. B.

**Volumetric determination of orthotungstates with fluorescent indicators.** A. DEL CAMPO and F. SIERRA (Anal. Fis. Quím., 1935, 33, 364—373).—The solution containing  $\text{WO}_4^{2-}$  is titrated with  $\text{Pb}(\text{NO}_3)_2$  using umbelliferone or quinine to give fluorescence with Wood light. F. R. G.

**Substituted benzene-*o*-dithiols as specific reagents for tin.**—See this vol., 840.

**Application of gravimetric methods of determination of thorium to its isolation and determination in small amounts.** L. E. KAUFMAN (J. Appl. Chem. Russ., 1936, 9, 918—924).—An equal vol. of a solution of 15 g. of  $\text{KIO}_3$  in 150 ml. of 33%  $\text{HNO}_3$  is added to 10—40 ml. of the solution, containing Th, Ce, and group III cations and 25% of its vol. of  $\text{HNO}_3$ , the mixture is heated at  $60$ — $80^\circ$  for 15 min., and 2 vols. of 0.8%  $\text{KIO}_3$  in 20%  $\text{HNO}_3$  are added. The ppt. of Th iodate is washed with the last-named solution, heated with 3—5 g. of  $\text{H}_2\text{C}_2\text{O}_4$  in 50 ml. of  $\text{H}_2\text{O}$ , to elimination of I, the solution is made acid with 0.3*N*- $\text{HCl}$ , and the ppt. is washed, calcined, and weighed as  $\text{ThO}_2$ . R. T.

**Micro-determination of bismuth compounds.** M. M. KIRILLOV (J. Appl. Chem. Russ., 1936, 9, 932—936).—The solution, containing 0.01—0.04 mg. of Bi per ml., is brought to  $p_H$  0.7 by means of  $\text{HNO}_3$  and 0.2 ml. of 20%  $\text{KIO}_3$  is added, the ppt. is washed 6—10 times on the centrifuge with  $\text{H}_2\text{O}$  (0.2 ml.), 1 ml. of 5%  $\text{KI}$  and 0.3 ml. of 5%  $\text{H}_2\text{SO}_4$  are added, and the I liberated is titrated with 0.01*N*- $\text{Na}_2\text{S}_2\text{O}_3$ . R. T.

**Titration of bivalent platinum and tervalent iridium at different temperatures.** A. A. GRUNBERG and B. V. PRIZYN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 17—19).— $[\text{PtCl}_4]^{2-}$ , in presence of  $[\text{IrCl}_6]^{3-}$ , may be titrated potentiometrically with



$\text{KMnO}_4$  (+ $\text{H}_2\text{SO}_4$ ) at 80–90°; or  $\text{KMnO}_4$  may be added until the Ir begins to oxidise, and the solution visually back titrated with aq. Mohr's salt until the reddish-brown colour just vanishes. The titrations are less satisfactory with  $\text{NaBrO}_3$  (+ $\text{HCl}$ ).

T. G. P.

Comparison of platinum resistance thermometers with the helium thermometer from –190° to –258°. W. H. KEESOM and A. BIJL (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 574–575, and Physica, 1936, 3, 418–423).—Determinations for 4 thermometers are described. H. J. E.

Production of temperatures below 1° abs. Heat capacities of water, gadolinium nitrobenzenesulphonate heptahydrate, and gadolinium anthraquinonesulphonate. D. P. MACDOUGALL and W. F. GIAUQUE (J. Amer. Chem. Soc., 1936, 58, 1032–1037).—The production of very low temp. by adiabatic demagnetisation is described. Heat capacity calculations show that increased dilution of the magnetic atoms results in a closer approach to the ideal magnetic situation than would result if the Gd atoms were controlled only by the external magnetic field. The heat capacity of  $\text{H}_2\text{O}$  between 0.2° and 4° abs. is zero within about 0.01 g.-cal. per degree per mol. The reversibility of the magnetic phenomena of the above Gd compounds is illustrated. E. S. H.

Lowest temperatures. E. WOLTHUIS (J. Chem. Educ., 1936, 13, 172–174).—A summary of the magnetic method. L. S. T.

Inorganic liquid mixture for temperature baths in the range 100–250°. B. E. CHRISTENSEN and A. E. KING (Ind. Eng. Chem. [Anal.], 1936, 8, 194).—Mixtures of  $\text{H}_3\text{PO}_4$  and  $\text{HPO}_3$  are recommended. E. S. H.

Simple thermostat for temperatures between 100° and 150°. H. C. S. SNETHLAGE (Chem. Weekblad, 1936, 33, 368–369).— $\text{CaCl}_2$  solutions of definite b.p. are boiled in an Al pan and evaporation is corr. by adding  $\text{H}_2\text{O}$  at a const. rate. S. C.

Ebulliometric investigation of the impurity contents of succinic acid, proposed as a secondary standard for calorimetric measurements. W. SWIENTOSLAWSKI, M. WOJCIECHOWSKI, and E. SAPIRO (Bull. Acad. Polonaise, 1935, A, 531–539).—The impurity content of specially purified samples is 0.002–0.02%. O. D. S.

Twin calorimeter for small heat effects. H. GAWLICK (Z. Ver. deut. Ing., 1935, 79, 1089; Chem. Zentr., 1935, ii, 2703).—A double calorimeter, enabling small effects to be measured by a null method, is described. J. S. A.

Determination of insulating power of Dewar vessels. J. GUERON (Document. sci., 1935, 4, 114–118; Chem. Zentr., 1935, ii, 2846).—The rate of evaporation of solid  $\text{CO}_2$  from a vessel, plugged with cotton wool, is determined gravimetrically. J. S. A.

Thermal balance-analyser with photographic recording. P. DUBOIS (Bull. Soc. chim., 1936, [v], 3, 1178–1181).—Apparatus and technique are described. E. S. H.

Apparatus for photometric and colorimetric measurements using the photometric law of distances. F. ANSELM and F. WÜRSTLIN (Z. tech. Phys., 1935, 16, 157–161; Chem. Zentr., 1935, ii, 1753–1754).—A photometer is described. J. S. A.

Precision photo-electric colorimeter. R. B. WITHROW, C. L. SHREWSBURY, and H. R. KRAYBILL (Ind. Eng. Chem. [Anal.], 1936, 8, 214–219).—The principles of design are discussed and apparatus based on these principles is described. E. S. H.

Photo-electric colorimeter. T. W. SCHMIDT (Z. Instrument., 1935, 55, 336–346, 357–367; Chem. Zentr., 1935, ii, 2552).—Apparatus is described. J. S. A.

Photo-electric colorimetry. VIII. Starch-iodine system. R. H. MÜLLER and M. H. MCKENNA (J. Amer. Chem. Soc., 1936, 58, 1017–1020; cf. A., 1935, 1097).—Photo-electric titrations with approx. monochromatic light show that Beer's law is obeyed beyond a preliminary dissociation stage. The system does not require the use of purely empirical correction. E. S. H.

Colorimeter for a series of determinations. HORMISDAS (Compt. rend., 1936, 202, 1925–1927).—The tube holding the solution under examination is mounted so that it can be moved horizontally, and compared in turn with a series of comparison tubes. H. J. E.

Recent developments in fluoroscopic screens. F. E. SWINDELLS (X-Ray Technician, 1935, 6, 162–164, 184).—A form of  $\text{ZnS}$  which is free from afterglow, and fluoresces more brightly than Cd tungstate, is described. CH. ABS. (e)

Light source for absorption spectroscopic investigations in the ultra-violet. H. KLUMB and R. ODENWALD (Z. tech. Phys., 1935, 16, 200–202; Chem. Zentr., 1935, ii, 1753).—A W-filament lamp running in  $\text{H}_2$  and giving a continuous spectrum down to 2200 Å. is described. J. S. A.

Colorimeter pipette cell. S. T. BOWDEN (J.S.C.I., 1936, 55, 180r).—A glass pipette cell which facilitates the examination of coloured solutions by tintometric or photo-electric methods is described. It may be readily adapted for measurements on reactive or hydrolysable solutions, and is also suitable for the observation of colour changes in a reaction system.

Determination of the refractive power of liquids.—See B., 1936, 623.

Individual determination of principal elastic stresses by X-rays. R. GLOCKER and E. OSSWALD (Z. tech. Phys., 1935, 16, 237–242; Chem. Zentr., 1935, ii, 2573–2574).—The X-ray method of determining total superficial stress from its effect on the X-ray reflexion lines is applied to the determination of the magnitude and direction of stresses. J. S. A.

Apparatus for making spectral flames of the alkali and alkaline-earth metals. J. F. BIRMINGHAM, jun., and W. H. WOOD (J. Chem. Educ., 1936, 13, 240–241). L. S. T.

Glass filters for isolating lines of mercury arc in photography of Raman spectra. L. AMY (Document. sci., 1935, 4, 97–103; Chem. Zentr.,

1935, ii, 2848).—For isolation of the 4358 Å. line, 0.27 mm. of Corning glass 38 is recommended, and for the 4047 Å. line, 3 mm. of Corning glass 597.

J. S. A.

**Photometric method suitable for spectrum analysis.** D. H. FOLLETT (J. Sci. Instr., 1936, 13, 221—228).—A stepped wedge of Pt deposited on fused  $\text{SiO}_2$  is used. Microphotometric readings are taken of the density of two consecutive steps on one line of a pair of two neighbouring lines, and a similar reading on a step of intermediate density on the other. The relative intensities of the two lines can then be calc. The probable error of a single determination is about 1.5%.

C. W. G.

**Production of silver mirrors by cathodic sputtering.** E. G. JONES and E. W. FOSTER (J. Sci. Instr., 1936, 13, 216—219).—An apparatus is described. Special attention must be paid to the cleanliness of the specimen to be silvered, the containing vessel, and the discharge atm.

C. W. G.

**Deposits of colloidal graphite.** B. H. PORTER (Nature, 1936, 137, 1034).—Homogeneous films of colloidal graphite can be used in the construction of  $\alpha$ -particle counters, the formation of guard rings for evacuated apparatus, coating of plate glass for electrostatic condensers, and electrodes in ionisation chambers, etc.

L. S. T.

**Photo-electric apparatus for delineating the size frequency curve of clays or dusts.** E. G. RICHARDSON (J. Sci. Instr., 1936, 13, 229—233).—While sedimentation is taking place in accordance with Stoke's law, the concns. at various heights are compared by means of a beam of light and a photo-electric cell.

C. W. G.

**Vacuum-tube voltmeter.** G. F. KINNEY and R. L. GARMAN (J. Chem. Educ., 1936, 13, 190—192).—A voltmeter suitable for electrometric titrations is described.

L. S. T.

**Tellurium electrode.** G. A. BRAVO (Annali Chim. Appl., 1936, 26, 162—166).—The Te electrode is not sufficiently accurate for ordinary  $p_{\text{H}}$  determinations, but may be used for potentiometric titrations if the solution is kept agitated by a current of air free from dust and  $\text{CO}_2$ .

L. A. O'N.

**Potentiometry of autoinversion.** J. GUZMAN and A. ARA (Anal. Fis. Quím., 1935, 33, 729—751).—In an apparatus for electrometric titration the comparison electrode Pt or  $\text{Pd|N-KCl}$  or  $\text{K}_2\text{SO}_4$  in a porous porcelain container is immersed in the solution being titrated. The application of the method to several types of titration is described.

F. R. G.

**Energy distribution in back-diffusing cathode rays.** J. O. BRAND (Ann. Physik, 1936, [v], 26, 609—624; cf. A., 1930, 269).—The velocity distribution of the back-diffusing electrons produced when a target is bombarded with cathode rays of 16, 24, and 32 kv. has been studied photographically in a special magnetic refraction apparatus. In the case of Al, Cu, Ag, and Pt anodes, the quality of the surface is without effect but the position of the velocity max. alters with the angle  $\varphi$  between the incident and emitted electron beams. Increase of  $\varphi$  broadens the

max. and displaces it towards greater energy loss in the case of Al and Cu, but less so with Ag and Pt.

R. S.

**Electron microscopic photographs (electron micrograms) of chitin objects.** E. DRIEST and H. MULLER (Z. wiss. Mikroskop., 1935, 52, 53—57; Chem. Zentr., 1935, ii, 2702).—An electron microscope technique permitting total linear exposures up to 25,000 diameters is described, revealing detail not perceptible with the optical ultramicroscope.

J. S. A.

**Apparatus for measuring ionic spectrum [of the atmosphere].** H. GRIEGER (Z. Instrument., 1935, 55, 116—122; Chem. Zentr., 1935, ii, 2847).—Apparatus is described.

J. S. A.

**Micro-electrode for determining  $p_{\text{H}}$ .**—See this vol., 1038.

**Apparatus for the measurement of magnetic susceptibility by Faraday's method.** B. CARRERA and J. M. TORROJA (Anal. Fis. Quím., 1936, 34, 5—25).—A new apparatus for the measurement of vals. of between  $-50^\circ$  and  $150^\circ$  employs a permanent Co-steel magnet tempered at  $950^\circ$ .

F. R. G.

**Pipette for titrating dark-coloured liquids in two phases.** M. M. HICKS-BRUN and L. W. CLAFFEY (Ind. Eng. Chem. [Anal.], 1936, 8, 229).

E. S. H.

**Gas analytical apparatus.** F. BUCHLER (Glückauf, 1935, 71, 641—643; Chem. Zentr., 1935, ii, 2407).—A gas burette of increased accuracy, and modified Orsat absorption vessels, are described.

J. S. A.

**Biburette.** J. GUZMAN (Anal. Fis. Quím., 1935, 33, 470—473).—Several modified forms of micro-burette, designed to increase the amount of liquid which can be measured accurately, are described.

F. R. G.

**Macro-micro-burette.** J. GUZMAN (Anal. Fis. Quím., 1935, 33, 241—243).—A combination of a graduated micro-pipette and micro-burette is described.

F. R. G.

**Gravimetric methods in use during the sixteenth century.** J. GUZMAN (Anal. Fis. Quím., 1936, 34, 495—500).—A description of the balance and aliquot wts. used by Alonso Barba.

F. R. G.

**Errors in micro-weighing due to the use of lead shot in tares.** R. J. WILLIAMS (Ind. Eng. Chem. [Anal.], 1936, 8, 229—230).—The use of Pb shot introduces considerable errors due to variations of temp., atm. pressure, and R.H.

E. S. H.

**Modification of Pregl's apparatus, permitting the carrying out of a series of micro-determinations of nitrogen.** P. BLANC (Bull. Soc. chim., 1936, [v], 3, 1019—1021).—Apparatus and procedure are described.

E. S. H.

**One-piece glass micro-Kjeldahl distillation apparatus.** P. L. KIRK (Ind. Eng. Chem. Anal., 1936, 8, 223—224).

E. C. S.

**Micro-determination of bromide.**—See this vol., 1009.

**Apparatus for measurement of surface tension.** L. D. MAHAJAN (J. Sci. Instr., 1936, 13, 189—191).—



A modification of Sutton's method (A., 1933, 250) is described. J. S. A.

**Hill method for solubility determinations.** T. W. EVANS (Ind. Eng. Chem. [Anal.], 1936, 8, 206—208).—The theoretical basis of the method is investigated and suitable apparatus described. E. S. H.

**Manipulator for glass blowing.** V. COLLIER, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 208). E. S. H.

**Apparatus for analytical laboratories.** Crucible support for desiccators, graduated cylinder, and flask cover. F. E. TUTTLE (Ind. Eng. Chem. [Anal.], 1936, 8, 230—231). E. S. H.

**Laboratory shaking machine.** S. H. HIGBERGER (Ind. Eng. Chem. [Anal.], 1936, 8, 227). E. C. S.

**Combination of continuous extractor and extract washer.** H. B. WYLIE and M. J. SCHMULOVITZ (Science, 1936, 83, 398). L. S. T.

**Electrical pressure dilatometer.** E. COHEN and A. K. W. A. VAN LIESHOUT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 596—603).—The expansion or contraction is measured by the change in resistance of a thin Pt wire dipping into Hg. The Hg meniscus is connected by a closed system with the substance under examination and records its vol. change. Measurements with Sn up to 200 atm. are described. H. J. E.

**Glass pump for circulation of gases against moderate pressures.** J. C. BALSBAUGH, R. G. LARSEN, and D. A. LYON (Ind. Eng. Chem., 1936, 28, 682—683).—An all-glass magnetically operated pump, which completely eliminates gas leakage between piston and cylinder wall, and can force air against a pressure of 210 mm. Hg, is described. C. R. H.

**Differential measurement of density by means of twin pycnometers.** E. R. SMITH and M. WOJCIECHOWSKI (Rocz. Chem., 1936, 16, 104—112).—A differential method, involving an error of  $\pm 1$  p.p.m., is described. R. T.

**Apparatus for catalytic micro-hydrogenation in liquid medium.** B. FORESTI (Annali Chim. Appl., 1936, 26, 207—217).—The apparatus for catalytic micro-hydrogenation which is described measures the velocity of hydrogenation to an accuracy of 10<sup>-4</sup> g.-mol. H<sub>2</sub>, determines at the same time the  $p_H$  of the medium, and enables the to be varied by addition of acid or alkali, or by anodic or cathodic polarisation, without interrupting the experiment. L. A. O'N.

**Light metal rotors for the molecular ultracentrifuge.** J. BISCOE, E. G. PICKELS, and R. W. G. WYCKOFF (Rev. Sci. Instr., 1936, [ii], 7, 246—250).—Tests of the range of usefulness of light metal rotors proved the superiority of duralumin 14ST; a shape of 7 in. diameter rotor can be used at speeds up to 900 r.p.s. (field at centre of cell=215,000 times gravity). For more intense fields, special steels or smaller diameter must be used. N. M. B.

**Measurement of viscosity at high temperatures, as a method of physicochemical analysis.** M. P. VOLAROVITSCH (Ann. Sect. Anal. Phys.-Chim., 1936, 8, 125—134).—A review. R. T.

**Bimetal high-vacuum manometer.** H. SEEMANN (Physikal. Z., 1936, 37, 446—447).—An instrument similar to that devised by Klumb *et al.* (this vol., 183) was patented in 1925. A. J. M.

**Preparation and measurement of adsorbing surfaces.** F. DURAU and G. TSCHOEPE (Z. Physik, 1936, 100, 145—165).—Reproducible surfaces were obtained for Pb, Sn, Zn, Bi, Cd, Wood's metal, NaNO<sub>3</sub>, KNO<sub>3</sub>, CdCl<sub>2</sub>, and PbCl<sub>2</sub> by passing the vapour through N, at several atm., and condensing. The effective adsorbing surface is roughly the geometrical surface. A. B. D. C.

**Separation of gas mixtures by diffusion in streaming mercury vapour.** H. BARWICH (Z. Physik, 1936, 100, 166—191).—Hertz's separation pump (cf. A., 1935, 59) is investigated, and a formula deduced for the separation factor. A. B. D. C.

**Spiral bubbler.** P. H. PEARCE and E. C. ROBERSON (Chem. and Ind., 1936, 543).—A spiral bubbler, giving a long contact time between gas and washing liquid, and suitable for use in Vandaveer trains for CO determination, is described. H. J. E.

**Precision manometer.** J. PREVOT (Document. sci., 1935, 4, 177—181; Chem. Zentr., 1935, ii, 2845—2846). J. S. A.

**Vapour-pressure hygrometer.** J. J. DOWLING (J. Sci. Instr., 1936, 13, 214—216).—An air sample of fixed vol. is exposed to a chemical drying agent and the consequent reduction in pressure observed. C. W. G.

**Use of the dilatometric method in chemistry.** E. RENCKER (Bull. Soc. chim., 1936, [v], 3, 978—981).—The application of the dilatometer to the study of chemical reactions involving vol. change is discussed. E. S. H.

**Apparatus with plane glass joints for fractional distillation in a vacuum.** L. PALFRAY (Bull. Soc. chim., 1936, [v], 3, 1175—1178).—An all-glass apparatus is described. E. S. H.

**Condenser system for fractional distillation.** E. A. MEANS and E. L. NEWMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 231). E. S. H.

**Bubble-cap columns of glass.** J. H. BRUUN (Ind. Eng. Chem. [Anal.], 1936, 8, 224—226).—Two laboratory all-glass columns, suitable for vapour velocities up to 31.3 and 65.5 cm. per sec., respectively, are described. E. S. H.

**Micro-distillation apparatus.** L. C. CRAIG (Ind. Eng. Chem. [Anal.], 1936, 8, 219—220). E. S. H.

**Micro-determination of mol. wt. in exaltone.** F. GIRAL (Anal. Fis. Quim., 1935, 33, 438—444).—*cyclopentadecanone* (I) is a suitable solvent for determination of mol. wt. of substances which decompose at the m.p. of camphor, as it is readily procurable and a good solvent for many substances including carotenoids and sterols. The mol. wt. of alkannin (C<sub>16</sub>H<sub>16</sub>O<sub>5</sub>) and calciferol (C<sub>28</sub>H<sub>44</sub>O) has been determined. The mol. m.p. depression and mol. latent heat of fusion of (I) are shown to differ from those

of  $\text{CO}(\text{C}_2\text{H}_{15})_2$  in accordance with the views of Pirsch (A., 1934, 79, 951). F. R. G.

**Nomographs for determining mol. wts. by the f.-p. and b.-p. methods.** W. S. GILFOIL (Ind. Eng. Chem. [Anal.], 1936, 8, 228). E. S. H.

**Isopiestic method for the determination of mol. wts.** C. M. MASON and H. M. GARDNER (J. Chem. Educ., 1936, 13, 188—190).—An apparatus for measuring the relative v.p. of aq. solutions is described. L. S. T.

**Accuracy of measurement of null method of dosage of radium.** P. KIPFER (Helv. phys. Acta, 1935, 8, 267—271; Chem. Zentr., 1935, ii, 2847).—The accuracy of  $\gamma$ -ray measurements over a given time is discussed. J. S. A.

**Leo Africanus on Alchemy.** F. B. DAINS (J. Chem. Educ., 1936, 13, 272). L. S. T.

**Ko Hung on the yellow and the white.** T. L. DAVIS and LU-CH'ANG WU (J. Chem. Educ., 1936, 13, 215—218).—Alchemical. L. S. T.

## Geochemistry.

**Ozone content of the lower layers of the atmosphere during winter at Abisko (Swedish Lapland).** D. BARBIER, D. CHALONGE, and E. VASSY (Compt. rend., 1936, 202, 1525—1527; cf. A., 1934, 626).—There is no direct connexion between the  $\text{O}_3$  content and meteorological or seasonal variations, whilst the mean thickness of the  $\text{O}_3$  layer is similar to that obtaining elsewhere. R. S.

**Neon content of natural gases.** N. P. PÉNTCHEFF (Compt. rend., 1936, 202, 1604—1606).—The gas from a spring at Kovanlik (Bulgaria) contained 0.003 vol.-% of Ne (based on  $d$  measurements). H. J. E.

**Distribution of the heavy water isotopes on the earth.** E. H. RIESENFELD and T. L. CHANG (Ber., 1936, 69, [B], 1308—1310).—The distribution is explained by the differing v.p. of the water isotopes. H. W.

**Content of  $\text{HDO}$  and  $\text{H}_2\text{O}^{18}$  in rain and snow.** E. H. RIESENFELD and T. L. CHANG (Ber., 1936, 69, [B], 1305—1307).— $\text{H}_2\text{O}$  obtained by melting snow collected at Potsdam and Uppsala is, as an average,  $2.7 \times 10^{-6}$  lighter than Berlin water and  $4.2 \times 10^{-6}$  lighter than that of the ocean. H. W.

**Hydrochemical study of River Tzna water.** N. E. KUSCHLIANSKI (J. Appl. Chem. Russ., 1936, 9, 899—912).—Hydrochemical data are recorded. R. T.

**Physico-chemical properties of Ui and Uvelka river water.** K. B. SHAGGARS (J. Appl. Chem. Russ., 1936, 9, 913—917).—Analytical data are recorded. R. T.

**Presence of gold in sea-water.** G. CLAUDE (Compt. rend., 1936, 202, 1885—1887).—Treatment of 168 cu.m. of sea- $\text{H}_2\text{O}$  (off the Californian coast) with pyrites gave no detectable pptn. of Au. The Au content of the  $\text{H}_2\text{O}$  was  $< 0.1$  mg. per cu.m. H. J. E.

**Spectrographic analyses of some Spanish medicinal waters.** III. S. PIÑA DE RUBIES and M. A. BARGUÉS (Anal. Fís. Quím., 1935, 33, 765—766).—Four samples have been analysed and determinations made of the Sr, Be, Pb, Li, Ag, when present, by the authors' method (A., 1934, 48). F. R. G.

**Iodine in Polish waters.** K. JABŁCZYNSKI, A. HARTMAN, and M. SALWIN (Rocz. Chem., 1936, 16, 19—23).—The I content of Vistula  $\text{H}_2\text{O}$  varies from 0.98 to  $27.5 \times 10^{-6}$  g. per litre, at different seasons.

Data are recorded for other Polish rivers ( $1-4 \times 10^{-6}$  g. per litre) and mineral springs ( $2.5-52,500 \times 10^{-6}$  g. per litre). R. T.

**Density of purified Nevada hot spring and surface water.** M. DOLE (Science, 1936, 83, 434).—The Nevada surface  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  from three different hot springs have the same  $d$ , which is  $<$  that of Lake Michigan  $\text{H}_2\text{O}$  by  $2.8 \pm 0.6$  p.p.m. The difference is due primarily to the O and not to the H in the two waters. L. S. T.

**Water of the mud volcanoes of Western Turkmenia.** A. I. KOSIGIN (Bull. Acad. Sci. U.R.S.S., 1935, 1029—1039).—Analysis of the  $\text{H}_2\text{O}$  from a no. of mud volcanoes indicates a high degree of mineralisation. R. T.

**Hyperthermal springs of Colli Euganei.** G. BRAGAGNOLO and E. CARRARO (Annali Chim. Appl., 1936, 26, 185—193).—Chemical and physico-chemical analyses of the hyperthermal waters of Abano, Montegrotto, Monteortone, and Battaglia have been made, and the radioactivity has been measured. The waters contain appreciable quantities of NaCl. History, geology, and pharmacological action are discussed. L. A. O'N.

**Mineral water of the "sulphurous spring" of Alfredena (Aquila).** M. TALENTI and A. RAGNO (Annali Chim. Appl., 1936, 26, 224—233).—The  $\text{H}_2\text{O}$  has an odour of  $\text{H}_2\text{S}$  and contains a notable quantity of  $\text{CaSO}_4$ . Chemical and physico-chemical analyses are given. Radioactivity is not appreciable. L. A. O'N.

**Geochemistry of alkaline magmas.** A. E. FERSMAN (Bull. Acad. Sci. U.R.S.S., 1935, 1419—1424).—Alkalinity is associated with high concn. of Na, K, Ca, Fe, or Mn, in conjunction with a high oxide content. R. T.

**Origin of the gold ore of Belaya Gora, on the southern coast of Ochotsk.** V. N. DANILOVITSCH (Bull. Acad. Sci. U.R.S.S., 1935, 1021—1027).—The ore contains sulphides, whence it is supposed that it represents the oxidised zone of a disseminated porphyritic pyrites deposit. R. T.

**Formula and structural scheme of attapulgitite.** J. DE LAPPARENT (Compt. rend., 1936, 202, 1728—1731; cf. A., 1935, 1346).—From the crystal structure of attapulgitite and its analogy with sepiolites it is concluded that its formula is



(OH)<sub>2</sub>H<sub>2</sub>(Mg<sub>2</sub>Al<sub>4/3</sub>)Si<sub>3</sub>H<sub>4</sub>O<sub>10</sub>, and a lattice structure is proposed. It is suggested that substitution of 2Al for 3Mg in this crystal enables H<sub>2</sub>O of composition to be included within a 10 Å elementary film, whereas in sepiolite it causes expansion to 12 Å. (A., 1935, 1099).

J. W. S.

(A) Instances of incrustations selective upon crystal forms. (B) Mineral incrustations upon the edges and corners of crystals. C. FRONDEL (Amer. Museum Nov., 1935, No. 695, 6 pp.; No. 759, 11 pp.).—(A) Examples of selective incrustations of stilbite on apophyllite and of marcasite on calcite, and of selective filming of hæmatite on calcite, are described.

(B) Various examples of edge and corner incrustations are described. The effect may be due to the greater absorptive power of these parts. CH. ABS. (e)

Oxidation of single crystals of zinc sulphide studied by electron diffraction. G. AMINOFF and B. BROOMÉ (Nature, 1936, 137, 995).—When a crystal of sphalerite is heated in air it is covered by a thin film, presumably of ZnO, which, when examined by electron diffraction, shows the properties of a single crystal in a crystallographically defined position relative to the ZnS structure. L. S. T.

Age of ferro-manganese concretions. L. M. KURBATOV (Nature, 1936, 137, 949—950; cf. this vol., 49).—Times of deposition calc. from the variation in Ra content of successive layers are 5300—5500 years for a specimen from the Kara Sea and 2000 years for one from Lake Uksche, Karelia. L. S. T.

Origin of a crystalline schist from Southern Katanga. M. GYSIN (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 52—54).—Schist from Mokambo (Katanga) contains labradorite (27.1%), epidote (30.1%), chlorite (17.5%), biotite (13.8%), magnetite (6.7%), and sphene (4.8%). Comparison with analysis of other schists suggests that it was produced from metamorphosed gabbroic rock. J. W. S.

Spectrophotometric study of smoky quartz. N. M. MOHLER (Amer. Min., 1936, 21, 258—263).—The absorption curve of smoky quartz (I) has been determined from 700 to 200 mμ and compared with the absorption after decolorisation by heat and exposure to Ra, and with clear cryst. and fused (I) coloured by the same exposure. Fluorescence effects were obtained. All show max. at 16,500, 20,000, 25,000, 33,000, and 38,000 (wave no. per cm.) with increased absorption beyond 42,000. Further irradiation by Ra in general increases absorption, but fused (I) shows a shift in importance of the bands with a superimposed lavender tint. The similarity in the curves confirms the theory of radioactive coloration. The change in energy due to transfer of an electron from an O to a Si ion is calc., and possible subsequent changes due to redistribution of such electrons. These changes correspond with amounts of energy indicated by positions of absorption bands. L. S. T.

Bertrandite and epistilbite from Bedford, New York. F. H. PUGH (Amer. Min., 1936, 21, 264—265).—Occurrences at Baylis Quarry are described. L. S. T.

Uraninite from Hottah Lake. F. H. BRUNER (Amer. Min., 1936, 21, 265—266).—The sample has U<sub>3</sub>O<sub>8</sub> 51.45, Fe<sub>2</sub>O<sub>3</sub> 41.51, Pb 2.31, SiO<sub>2</sub> 2.75, Al<sub>2</sub>O<sub>3</sub> 1.12, CaO 1.01, MgO trace, Mn present, S 0.14, CO<sub>2</sub> 0.42, total 100.71%. Th is absent. The Pb:U ratio 0.0529, gives an approx. age of 387×10<sup>6</sup> years. Weathering appears to be more selective to U than to Pb. L. S. T.

Fluorescence of Japanese hyalite in ultra-violet light. II. E. IWASE (Bull. Chem. Soc. Japan, 1936, 11, 377—379).—The fluorescence of Japanese hyalite has been compared with that of U compounds and several minerals. It may be due to UO<sub>3</sub> phosphate or sulphate. Other radioactive minerals may accompany deposits of fluorescent hyalite. J. T. A.

Nesquehonite from the Cogne mines, Val d'Aosta. M. FENOGLIO (Period. Min., 1935, 16, 1—17; Chem. Zentr., 1935, ii, 2507).—The crystals were rhombic (*a*<sub>0</sub> 7.68, *b*<sub>0</sub> 11.93, *c*<sub>0</sub> 5.39 Å.; 4 mols. MgCO<sub>3</sub>·3H<sub>2</sub>O in unit cell; space-group *V*<sub>h</sub><sup>1</sup>).

H. J. E.

New occurrences in oxidation zone of Rudabánya. G. KERTAI (Foldt. Kozlony, 1935, 65, 21—30; Chem. Zentr., 1935, ii, 2350).—Occurrences of petrological interest are described, including zoned crystals the composition of which grades from Cu through cuprite to malachite. J. S. A.

Copper occurrence in Studene, S. Serbia. T. GEDEON (Fold. Kozlony, 1935, 65, 50—52; Chem. Zentr., 1935, ii, 2192).—The deposits are described. H. J. E.

Vogesite from Ginepro (Island of Elba). M. FENOGLIO (Atti R. Accad. Lincei, 1936, [vi], 23, 77—82).—A vogesite rock of the hornblende type is described. Analysis gave SiO<sub>2</sub> 46.61, TiO<sub>2</sub> 2.26, Al<sub>2</sub>O<sub>3</sub> 12.23, Fe<sub>2</sub>O<sub>3</sub> 2.32, FeO 9.79, MgO 8.59, CaO 12.96, K<sub>2</sub>O 1.65, Na<sub>2</sub>O 2.31, H<sub>2</sub>O—0.12, H<sub>2</sub>O+ 1.41, P<sub>2</sub>O<sub>5</sub> 0.03, S 0.05, total 100.33%; traces of Cr<sub>2</sub>O<sub>3</sub>, MnO, BaO. O. J. W.

Monazite sand in the Arosa estuary (Galicia). I. PARGA-PONDAL (Anal. Fis. Quim., 1935, 33, 466—469).—The sand of a small beach at Palmeira (W. coast of Spain) contains 30% of monazite which consists of rare-earth oxides 67.97%, ThO<sub>2</sub> 3.14%, P<sub>2</sub>O<sub>5</sub> 28.89%. F. R. G.

Phosphate of iron and manganese from Olgiasca pegmatites. E. GRILL (Period. Min., 1935, 16, 19—23; Chem. Zentr., 1935, ii, 2651).—A new mineral, *repossite*, consisting essentially of an Fe<sup>II</sup> Mn<sup>II</sup> phosphate is described. J. S. A.

Iron ore deposits and mineral occurrences on the island of Serifos. C. PRAGER (Fortschr. Min. Krist. Petr., 1935, 19, 53—56; Chem. Zentr., 1935, ii, 2038).—Analytical data are given. J. S. A.

Spherosiderite and siderite from Felsőbánya. A. KOCH and L. VON ZOMBORY (Fold. Kozlony, 1935, 65, 18—20; Chem. Zentr., 1935, ii, 2038).—Analytical data are given. J. S. A.

Mineralogical and chemical composition of syenite-granite from Boekit Batoe near Palembang, Sumatra. W. VAN TONGEREN (Proc. K.

Akad. Wetensch. Amsterdam, 1936, 39, 670—673).—Data are given. H. J. E.

**Cobaltiferous oligon spar.** R. REISSNER (Zentr. Min., 1935, A, 170—173; Chem. Zentr., 1935, ii, 2037).—The mineral contains 14.44% of  $\text{CoCO}_3$ . J. S. A.

**Violet kainite containing hydrogen sulphide.** J. LEONHARDT and R. KÜHN (Zentr. Min., 1935, A, 193—194; Chem. Zentr., 1935, ii, 2037).—The occurrence and petrographical properties of the mineral are described. J. S. A.

**Cronstedite from Kisbánya.** B. GOSSNER (Zentr. Min., 1935, A, 195—201; Chem. Zentr., 1935, ii, 2037).—The mineral is an isomorphous mixture of  $\text{Si}_2\text{Fe}_2\text{O}_{10}\cdot\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_4(\text{OH})_8$  with  $\text{Si}_2\text{O}_{10}\text{Fe}^{\text{II}}_6(\text{OH})_8$  with an excess of  $\text{Fe}(\text{OH})_2$ , with  $a$  5.48,  $b$  9.45,  $c$  7.08 Å.;  $\beta = 90^\circ$ . J. S. A.

**Silicified aragonite twins from Uruguay related to Molina-Bastennes type.** K. WALTHER (Zentr. Min., 1935, A, 201—209; Chem. Zentr., 1935, ii, 2036).—Comparative geological and petrographical data are recorded. J. S. A.

**Photographs of axial figures of opaque minerals in infra-red.** D. MALMQUIST (Zentr. Min., 1935, A, 209—213; Chem. Zentr., 1935, ii, 2035).—Semi-conductors such as sulphide ores are transparent to infra-red light. The optic axial figures of Sb and Fe glance and arsenical pyrites have been so investigated with negative results. J. S. A.

**Wollastonite-urtite, and manner of formation of alkali rocks.** O. H. ERDMANNSDÖRFFER (Sitzungsber. Heidelberg. Akad. Wiss., 1935, No. 2, 19 pp.; Chem. Zentr., 1935, ii, 2798).—Mineralogical data are given for rocks from Lake Natron (Magadi), in the E. African rift valley region. J. S. A.

**Basalts of Guiliana and Contessa Entellina and their alteration; petrographic investigation.** A. SCHERILLO (Period. Min., 1935, 16, 61—84; Chem. Zentr., 1935, ii, 2797—2798).—Celadonite and lepto-chlorite are identified as products of basaltic alteration. J. S. A.

**Method of delineating a curve representing the manner of variation of chemical composition in a zoned plagioclase.** F. HOMMA (Proc. Imp. Acad. Tokyo, 1936, 12, 132—134).—The method of constructing a composition curve from an extinction curve for the various zones of a plagioclase is given. The formation of the rock is discussed. A. J. M.

**Age and origin of the Oberharz lead-zinc dykes.** E. BECKSMANN (Z. ges. Naturwiss., 1935, 1, 121—122; Chem. Zentr., 1935, ii, 2192—2193).—An upper carboniferous or lower Permian sandstone age is inferred. J. S. A.

**Structural and morphological relations between epidote and zoisite, and between epidote and ardennite.** H. STRUNZ (Z. Krist., 1936, 92,

402—407).—By a suitable choice of axes, close relationship is evident between these compounds. B. W. R.

**Electrical conductivity of the zeolites.** B. GROSS (Z. Krist., 1936, 92, 284—292).—The abnormal electrical behaviour of the zeolites is confirmed; Ohm's law is obeyed only for brief currents, and for long durations at a potential gradient exceeding 3000 volts per cm. the current increases and hysteresis effects appear. These are discussed on the basis of a heating effect. B. W. R.

**"Blue copper pyrites."** W. KURZ (Z. Krist., 1936, 92, 408—434).—This is a mixed crystal of  $\text{Cu}_2\text{S}$  with  $\text{CuS}$  in which the  $\text{CuS}$  content has delayed the transition  $\alpha \rightarrow \beta$ . B. W. R.

**Natural and synthetic emerald.** E. SCHIEBOLD (Z. Krist., 1936, 92, 435—473).—A detailed comparison by X-ray and microscopic methods. Whilst in general the natural and the synthetic products are identical, there are definite slight differences, e.g., in chemical purity, shape, and arrangement of layers and inclusions, lattice const. along the  $a$  axis, mosaic structure,  $d$ , cleavage,  $n$ , colour, dichroism, fluorescence, and resistance to etching. B. W. R.

**Synthetic emerald.** H. ESPIC (Z. Krist., 1936, 92, 387—391).—The synthetic is compared with the natural stone. B. W. R.

**Petrofabric analysis of gypsum.** H. W. FAIRBAIRN (Z. Krist., 1936, 92, 321—343).—General orientation and cleavage of the constituent grains in samples of gypsiferous schist are described.

**Bentonitic magnesian clay mineral from California.** W. F. FOSHAG and A. O. WOODFORD (Amer. Min., 1936, 21, 238—244).—A bentonitic clay from the Mojave Desert, near Hector, San Bernardino Co., California, is a hydrated Mg silicate (analysis given). X-Ray powder photographs show that it closely resembles saponite. The high  $\text{Na}_2\text{O}$  (3.00%) and  $\text{Li}_2\text{O}$  (1.12%) contents are unusual. When placed in  $\text{H}_2\text{O}$  the white clay swells immediately, and finally sets to a firm jelly 5 or 6 times the vol. of the original dry clay. Similar Mg clays are widespread in this desert region of California and Nevada. L. S. T.

**Constitution of Normandy flintstone clay.** B. BRAJNIKOV (Compt. rend., 1936, 202, 1595—1597).—Optical and analytical data are given. The essential minerals belong to the beidellite-nontronite series. H. J. E.

**Occurrence of beryllium in fossil coals.** A. SILBERMINZ and A. K. RUSANOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 27—31).—Of 604 Russian coals only 38 had  $\text{Be} > 0.001\%$ , and none  $> 0.1\%$ . T. G. P.

**Brown and red carbonated crust soils in Tunis.** V. AGAFONOV (Compt. rend., 1936, 202, 159, 1599).—A discussion.



## Organic Chemistry.

**Electronic structure of organic compounds.** E. OLIVIERI-MANDALA (Gazzetta, 1936, 66, 253—258).—A crit. review. E. W. W.

**Theory of organic reactions.** H. F. TSEOU (J. Chinese Chem. Soc., 1936, 4, 235—277).—Theoretical. A theory applicable to all org. reactions is put forward: the position of an element in the periodic table is determined by its electrical condition in the outermost sphere, the position being capable of displacement according to the affinity for electrons of the atoms joined to it, and the periodic table is represented not by isolated elements, but by a continuous function of the electrical forces of the different elements.

F. R. S.

**Empirical method for predicting configuration of optically active carbon compounds.** R. E. MARKER (J. Amer. Chem. Soc., 1936, 58, 976—978).—23 groups are tabulated in decreasing and 6 (more polar) in increasing order of levorotation. The resulting table is used to predict the configurative relationships of various compounds. H. B.

**Reactions of paraffins and naphthenes with olefines. Alkylation.** V. N. IPATIEV and A. V. GROSSE (J. Gen. Chem. Russ., 1936, 6, 423—432).—*n*-Paraffins in presence of  $\text{AlCl}_3$ , or *iso*-paraffins in presence of  $\text{AlCl}_3$  or  $\text{BF}_3$ , at 30—70°/1—15 atm., afford a mixture of higher paraffins; thus *n*- $\text{C}_6\text{H}_{14}$  and  $\text{C}_2\text{H}_4$  afford chiefly  $\text{C}_8\text{H}_{18}$  and  $\text{C}_{10}\text{H}_{22}$ , *iso*- $\text{C}_4\text{H}_{10}$  and  $\text{C}_2\text{H}_4$  yield chiefly  $\text{C}_6\text{H}_{12}$  and  $\text{C}_8\text{H}_{18}$ , *iso*- $\text{C}_4\text{H}_{10}$  and *iso*-butylene give  $\text{C}_8\text{H}_{18}$  and  $\text{C}_{12}\text{H}_{26}$ , and *iso*- $\text{C}_5\text{H}_{12}$  and  $\text{C}_2\text{H}_4$  afford  $\text{C}_7\text{H}_{16}$  and  $\text{C}_8\text{H}_{18}$ . R. T.

**Isomerism of hydrocarbons. III. Thermal isomerisation of *n*-hexane and *n*-octane.** B. L. MOLDAVSKI, M. V. KOBILSKAJA, and S. E. LIVSCHITZ (J. Gen. Chem. Russ., 1936, 6, 616—620).—*n*- $\text{C}_6\text{H}_{14}$  does not yield *iso*-paraffins when heated in presence of Fe,  $\text{SiO}_2$ , or  $\text{MoS}_3$  at temp. not involving cracking (370—609°). Analogous results are obtained with *n*- $\text{C}_8\text{H}_{18}$ ; under conditions involving production and condensation of unsaturated hydrocarbons (475°/70 atm., in a steel autoclave) the liquid products contain 40% of *iso*-paraffins. R. T.

**Structure of ceresin hydrocarbons.** S. S. NAMETKIN and S. S. NIFONTOVA (J. Appl. Chem. Russ., 1936, 9, 834—840).—Surachani ceresin consists chiefly of *n*- and *iso*-paraffins of mean mol. wt. corresponding with  $\text{C}_{43}\text{H}_{92}$ , with an admixture of hydrocarbons of low mol. wt. ( $\text{C}_{22}\text{H}_{46}$ ). R. T.

**Alkylation of paraffins with olefines in presence of aluminium chloride.** V. N. IPATIEV, A. V. GROSSE, H. PINES, and V. I. KOMAREVSKI (J. Amer. Chem. Soc., 1936, 58, 913—915; cf. A., 1935, 1348).—A mixture, b.p. 20—350° (mostly 45—235°), of paraffins is formed when  $\text{C}_2\text{H}_4$  is passed into *n*- $\text{C}_6\text{H}_{14}$  +  $\text{AlCl}_3$  at 30—40° and atm. pressure; after absorption of  $\text{C}_2\text{H}_4$  slows down, a little dry HCl and fresh  $\text{AlCl}_3$  are added. Reaction proceeds much faster with  $\text{AlBr}_3$ . *n*- $\text{C}_6\text{H}_{14}$  (1 mol.) and  $\text{C}_2\text{H}_4$  (2—2.5 mols.) with  $\text{AlCl}_3$  at 25° and 15 atm. give paraffins, b.p. 25—400° (mostly 50—330°);  $\text{CHMe}_3$  (1 mol.) and  $\text{C}_2\text{H}_4$  (3 mols.) similarly afford paraffins, b.p. 25—200°.

Side reactions are: (i) polymerisation of  $\text{C}_2\text{H}_4$ ; (ii) compound formation with  $\text{AlCl}_3$ ; (iii) "auto-destructive alkylation" of paraffins, i.e., fission to a lower paraffin and olefine (which then alkylates the original mol. to a higher paraffin). H. B.

**System octene-sulphur dioxide.**—See this vol., 931.

**Selective catalytic hydrogenation by cold nickel. I. Ethylenic linking. II. Acetylenic linking.** G. DUPONT (Bull. Soc. chim., 1936, [v], 3, 1021—1030, 1030—1035).—I. Hydrogenation of terminal  $\text{CH}:\text{CH}_2$  in presence of Raney Ni in EtOH at room temp. proceeds very rapidly and at an approx. const. rate until completion (examples cited:  $\Delta^a$ -heptene,  $\text{CHPh}:\text{CH}_2$ ,  $\text{CH}_2\text{Ph}:\text{CH}:\text{CH}_2$ , safrole, eugenol,  $\text{CH}_2:\text{CH}:\text{CH}(\text{CH}_2)_8\text{CO}_2\text{H}$ ).  $\text{CH}_2:\text{CH}_2:\text{CH}_2\text{OH}$  and  $\text{CH}_2:\text{CH}:\text{CHO}$  are rapidly reduced initially, but reaction soon stops, apparently due to temporary poisoning of the catalyst. Hydrogenation of  $\text{CH}:\text{CH}$  generally proceeds less rapidly than that of  $\text{CH}:\text{CH}_2$ , and the rate diminishes as the reaction proceeds (examples,  $\Delta^b$ -octene, maleic acid,  $\text{CHPh}:\text{CH}:\text{CH}_2\text{OH}$ , isosafrole, isoeugenol, cyclohexene). Double linkings in the aromatic nucleus or in furfuraldehyde are not appreciably affected, whilst Me oleate and elaidic acid are not reduced. The linking  $\text{CR}:\text{R}'\text{CH}_2$  or  $\text{CR}:\text{R}'\text{CHR}'$  is not usually hydrogenated (examples: dimethyloctene, methylcyclohexene, camphene, nopinene, pinene, carvomenthene,  $\Delta^b$ -menthene,  $\alpha$ -dihydro-linalol, citronellal, terpineol, methylheptenone, dihydroionone). Two or more double linkings reciprocally increase the ease of hydrogenation. If one is *tert.*, it usually remains unattacked; if two are *tert.*, one of them is reduced. If the linkings are conjugated, addition occurs partly in the  $\alpha\delta$  position (examples: alloocimene, geraniol, linalol, limonene,  $\alpha$ -terpinene,  $\alpha$ - and  $\beta$ -pyronene). CO or CHO conjugated to a primary or *sec.* double linking appears to reduce the rate of hydrogenation of the latter; otherwise they participate in the reaction, which does not cease after the absorption of 2 H (examples:  $\text{CHPh}:\text{CH}:\text{CHO}$ ,  $\text{COMe}:\text{CH}:\text{CHPh}$ ,  $\alpha$ - and  $\beta$ -ionone, citral, mesityl oxide).

II. Hydrogenation of heptinene proceeds at an approx. const. rate throughout its entire course, but interruption of the reaction after absorption of 2 H shows the process to be selective.  $\text{CPh}:\text{CH}$  is similarly hydrogenated. With disubstituted acetylenes the selectivity is satisfactory.  $\Delta^b$ -Octinene and  $\alpha$ -methoxy- $\Delta^b$ -octinene are rapidly reduced until 2 H have been absorbed, after which there is a sudden fall in the velocity of the change. Me heptinenyl carbonate behaves similarly.  $\text{C}_2\text{H}_2$  and  $\text{H}_2$  in equal vols. give  $\text{C}_2\text{H}_4$ , much  $\text{C}_2\text{H}_6$ , unchanged  $\text{C}_2\text{H}_2$ , and complex products;  $\text{C}_6\text{H}_2 + 2\text{H}_2$  yield  $\text{C}_6\text{H}_6$  quantitatively.

H. W.

**Polymerisation of ethylene with aluminium chloride.** V. N. IPATIEV and A. V. GROSSE (J. Amer. Chem. Soc., 1936, 58, 915—917).— $\text{C}_2\text{H}_4$  does not react with pure  $\text{AlCl}_3$  at 10—50° and 50 atm. except in presence of traces of  $\text{H}_2\text{O}$  or HCl. When reaction does occur, paraffins, b.p.  $-10^\circ$  to  $372^\circ$ , and

unsaturated cyclic hydrocarbons, b.p. 175—392° (which combine with  $\text{AlCl}_3$ ), are formed. The process is termed "conjunct polymerisation." H. B.

**Physical constants of polymerisation products of unsaturated hydrocarbons.** H. I. WATERMAN, J. J. LEENDERTSE, and J. P. MAKINK (J. Inst. Petroleum Tech., 1936, 22, 333—340; cf. A., 1935, 469).—The  $\eta$  and  $\eta$ -temp. curves of a series of polymeride fractions obtained from a mixture of branched pentenes ( $\text{CMeEtCH}_2$  and  $\text{CMe}_2\text{CHMe}$ ) have been compared graphically over the range 20—80° with unbranched  $\Delta^2$ -*n*-pentene polymerides. The latter are slightly more cyclic than the former. The properties of the polymerised fractions are independent of the chemical structure of the original pentenes, branching having no influence when polymerisation is carried out under similar conditions.

C. C.

**Alkylacetylenes and their additive products.**

## XII. Addition of methanol to alkenylacetylenes.

D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 892—894; cf. A., 1934, 1089).— $\text{CH}_2\text{:CH}\cdot\text{C}\equiv\text{CEt}$  and MeOH in presence of  $\text{BF}_3$ ,  $\text{Et}_2\text{O}$ ,  $\text{HgO}$ , and  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  give (probably)  $\alpha\gamma$ -trimethoxyhexane, b.p. 80—82°/19 mm.;  $\text{CH}_2\text{:CH}\cdot\text{COMe}$  similarly affords  $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ , b.p. 137—138°/745 mm., whilst divinylacetylene is polymerised. Butyl-, amyl-, and phenyl-alkylacetylenes similarly add MeOH at the C:C only to give the *Me*<sub>2</sub> acetals, b.p. 91—93°/18 mm., 104—106°/16 mm., and 117—118°/16 mm., respectively, of Bu, b.p. 75—77°/19 mm., amyl, b.p. 86—88°/16 mm., and Ph, b.p. 127—129°/21 mm.,  $\Delta^2$ -butenyl ketone, respectively. The conjugated system C:C-C appears to be necessary for addition of MeOH to the C:C of an alkenylacetylene. Physical data for the acetals are given.

H. B.

**Vinylacetylene as a primary product of polymerisation of acetylene under different conditions.** L. G. TZIURICH, E. M. EFREMOVA, V. A. BARTASHEV, and J. G. JAPPU (J. Gen. Chem. Russ., 1936, 6, 197—202).— $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}_2$  is identified amongst the gaseous products obtained when  $\text{C}_2\text{H}_2$  is passed over  $\text{CuCl}$ -pumice at 200—250° or  $\text{ZnCl}_2$ -pumice at 350°.

R. T.

**Formation of *s*-dibromoethylene from *s*-tetrabromoethane.** A. PONGRATZ (Ber., 1936, 69, [B], 1267—1269).—The ratio of *cis*- to *trans*-( $\text{CHBr}$ )<sub>2</sub> produced by treatment of ( $\text{CHBr}_2$ )<sub>2</sub> with Zn dust in abs. EtOH is conveniently deduced from the Raman spectrum.

H. W.

**Mercuric fluoride, a new fluorinating agent.** A. L. HENNE and T. MIDGLEY, jun. (J. Amer. Chem. Soc., 1936, 58, 884—887).—Anhyd.  $\text{HgF}_2$  is obtained in about 75% yield when F is passed into finely divided  $\text{HgCl}_2$  in a revolving Cu vessel at room temp.  $\text{HgF}_2$  is used for the replacement of Hal in aliphatic mono- and poly-halides by F; reaction is effected usually in Cu in absence or presence of solvents ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ; not alcohols, ethers, or esters) at 0—160°. The following are prepared: EtF from EtBr; AcF from AcCl;  $\text{CH}_2\text{Br}\cdot\text{CHBrF}$  and  $\text{CH}_2\text{Br}\cdot\text{CHF}_2$  from *s*- $\text{C}_2\text{H}_4\text{Br}_2$ ;  $\text{CHBr}_2\cdot\text{CHBrF}$  or

$\text{CHBr}_2\cdot\text{CHF}_2$  from *s*- $\text{C}_2\text{H}_4\text{Br}_4$ . EtOH gives about 2% of EtF and some  $\text{C}_2\text{H}_4$ . The fluorides from cyclohexyl bromide, 1:2-dibromocyclohexane, dichlorodioxan, and  $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$  eliminate HF to give almost quant. yields of the ethylenic compounds. PhHal,  $\text{C}_6\text{H}_6\text{Cl}_6$ , and  $\text{C}_6\text{Cl}_6$  do not react. Very little reaction occurs with acids or anhydrides.

H. B.

**Reactivity and influence of fluorine in aliphatic compounds.** A. L. HENNE and T. MIDGLEY, jun. (J. Amer. Chem. Soc., 1936, 58, 882—884).—Aliphatic compounds containing 1 F atom are unstable and show a marked tendency to liberate HF; those containing  $\text{CHalF}$  are more stable. The presence of  $\cdot\text{CRF}_2$  causes (i) a marked increase in the strength of the C-F linkings, (ii) strengthening of the C-R linking when R is Hal, and (iii) marked increase in the stability of any Hal atoms attached to adjacent C atoms.

H. B.

**Fluoro-derivatives of ethane and ethylene.**

IV, V. A. L. HENNE and M. W. RENOLL (J. Amer. Chem. Soc., 1936, 58, 887—889, 889—890).—IV. *s*- $\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$  and  $\text{SbF}_3$  give  $\alpha\beta$ -dichloro- $\alpha$ -bromo- $\beta$ -fluoroethane, b.p. 124.7—125.1°/736 mm.,  $\alpha$ -chloro- $\alpha$ -bromo- $\beta\beta$ -difluoroethane, b.p. 82.3—82.5°/743 mm., and small amounts of  $\text{CHCl}_2\cdot\text{CHClF}$ ,  $\text{CHCl}_2\cdot\text{CHF}_2$  (I),  $\text{CHCl}_2\cdot\text{CCl}_2\text{F}$ , and  $\text{CHCl}_2\cdot\text{CCl}_2\text{F}$  (I) and  $\text{SbF}_3$  under varying conditions afford some  $\alpha$ -chloro- $\beta\beta\beta$ -trifluoroethane, b.p. 6.1°;  $\text{CH}_2\text{Br}_2\cdot\text{CHF}_2$  (II) similarly gives some  $\text{CH}_2\text{Br}\cdot\text{CF}_3$  (?), v.p. 23—25°, and (III) (below). *s*- $\text{C}_2\text{H}_2\text{Br}_2$  and  $\text{HgF}_2$  at 150—160° afford a quant. yield of (II); this and  $\text{HgF}_2$  at 180—190° give  $\alpha$ -bromo- $\alpha\beta\beta$ -trifluoroethane (III), b.p. 40—41°/735 mm., and *s*-tetrafluoroethane, b.p. —23°.

V.  $\text{CMeCl}_3$  and  $\text{SbF}_3$ - $\text{SbF}_3\text{Cl}_2$  (9:1) at 0°—room temp. give  $\alpha\alpha$ -dichloro- $\alpha$ -fluoro-, b.p. 31.7—31.8° (this and following b.p. are at 760 mm.),  $\alpha$ -chloro- $\alpha\alpha$ -difluoro-, b.p. —9.6°, and  $\alpha\alpha\alpha$ -trifluoro-, b.p. —46.7°, -ethane according to amounts of reagents used.  $\text{CHMeCl}$  similarly affords  $\alpha$ -chloro- $\alpha$ -fluoro-, b.p. 16.1—16.2°, and  $\alpha\alpha$ -difluoro-, b.p. —24.7°, -ethane; the latter is better obtained from  $\text{CHMeBr}_2$  and  $\text{HgF}_2$ . *s*- $\text{C}_2\text{H}_4\text{Br}_2$  and  $\text{HgF}_2$  give  $\alpha$ -bromo- $\beta$ -fluoro-, b.p. 71.5—71.8° (50%),  $\alpha\beta$ -difluoro-ethane, b.p. 10—11° (10%), BuF (25—30%), and a mixture (10—15%) of butadiene and  $\text{C}_4\text{H}_8$ ; *s*- $\text{C}_2\text{H}_4\text{I}_2$  behaves similarly but  $\alpha$ -iodo- $\beta$ -fluoroethane, b.p. 98—102°, can be isolated in small amount as an intermediate.  $\text{CH}_2\text{Cl}\cdot\text{CHCl}_2$  and  $\text{HgF}_2$  at 140° afford  $\alpha\beta$ -dichloro- $\alpha$ -fluoro-, b.p. 73.7—73.9° (50%), and  $\beta$ -chloro- $\alpha\alpha$ -difluoro-ethane, b.p. 35.1° (8—10%); use of  $\text{SbF}_3$  with various catalysts is less satisfactory.  $\text{CH}_2\text{Br}\cdot\text{CHBr}_2$  and  $\text{HgF}_2$  give  $\text{CH}_2\text{Br}\cdot\text{CHBrF}$  and then  $\text{CH}_2\text{Br}\cdot\text{CHF}_2$  (which does not react further; successive treatment with EtOH- $\text{CaI}_2$  and  $\text{HgF}_2$  affords  $\alpha\alpha\beta$ -trifluoroethane, b.p. 5°).  $\alpha$ -Chloro- $\beta$ -bromo- $\alpha$ -fluoroethane, b.p. 96.6°, is obtained in almost quant. yield from  $\text{CH}_2\text{Br}\cdot\text{CHClBr}$  and  $\text{HgF}_2$ . The at. refraction of F calc. from  $\text{CMeCl}_2\text{F}$  is abnormal.

H. B.

**Action of sulphuric acid in the gas phase on alkyl chlorides and bromides.** J. B. SENDRENS and J. ABOULENC (Compt. rend., 1936, 202, 1548—1550; cf. A., 1935, 604).— $\text{Pr}^n\text{Cl}$ ,  $\text{Pr}^n\text{Br}$ ,  $\text{Bu}^n\text{Cl}$ ,  $\text{Bu}^n\text{Br}$ , and *s*- $\text{C}_2\text{H}_4\text{Cl}_2$  are decomposed by conc.  $\text{H}_2\text{SO}_4$  at 200—210°, 210—215°, 205—210°, 160°, and 225—230°, respectively, with the formation of CO and  $\text{CO}_2$



(from deposited C) in different proportions.  $\text{CHCl}_3$  and  $\text{CHBr}_3$  give gases rich in CO and there is but a slight deposit of C.  $\text{CCl}_4$  gives no CO. J. L. D.

**Liquid-phase photochemical chlorination of tert.-butyl chloride and related compounds.** A. O. ROGERS and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 1027—1029).—Chlorination of  $\text{Bu}^t\text{Cl}$  in light from incandescence lamps gives  $\alpha\beta$ -dichloro- $\beta$ -methyl- (I),  $\alpha\alpha\beta$ -trichloro- $\beta$ -methyl- (II), b.p. 144.5—145.4°, m.p.  $-6.5^\circ$  to  $-6^\circ$ ,  $\alpha\beta\gamma$ -trichloro- $\beta$ -methyl- (III), b.p. 162—163.1° (major product),  $\alpha\alpha\alpha\beta$ -tetrachloro- $\beta$ -methyl- (IV), b.p. 192°/1175 mm., m.p. 178.6—179.6° (trace),  $\alpha\alpha\beta\gamma$ -tetrachloro- $\beta$ -methyl- (V), b.p. 190.6—191.3°, m.p.  $-46^\circ$ , and  $\alpha\beta\gamma$ -trichloro- $\beta$ -chloromethyl-propane, b.p. 206—210°. All b.p. are corr. Similarly, (II) gives (IV); (I) affords (II) and (III);  $\text{CHMe}(\text{CH}_2\text{Cl})_n$  yields (III) and (V). Cl attached to C promotes further substitution on the same C. H. B.

**Effect of radiation of wave-length 1980—1860 Å. on cis- and trans-dichloroethylene.**—See this vol., 944.

**Study of the structure of polymerides of chloroprene by ozonolysis and oxidation by nitric acid.** I. A. L. KLEBANSKI and V. G. VASILIEVA (J. Gen. Chem. Russ., 1936, 6, 359—369).—The ozonide of  $\alpha$ -polychloroprene gives succinic acid (I) in 82.3% yield when treated with 30%  $\text{H}_2\text{O}_2$  at 100°; substitution of  $\text{H}_2\text{O}$ , an aq. suspension of  $\text{CaCO}_3$ , or 3% HCl in MeOH for  $\text{H}_2\text{O}_2$  leads to formation of tarry products. The ozonides of the  $\mu$ - and  $\omega$ -polymerides yield (I) in 87—90% yield when heated with  $\text{H}_2\text{O}$  at 100°. R. T.

**Mechanism of the allyl change.** A. KIRRMANN and P. RENN (Compt. rend., 1936, 202, 1934—1935).— $\alpha\alpha$ -Dibromo- $\Delta^2$ -propene (I), b.p. 29—31°/14 mm., is stable in a sealed tube, but in presence of dry HBr is converted into  $\text{CH}_2(\text{CH}_2\text{Br})_2$ , which supports the view that addition followed by removal of HBr is responsible for the change. (I) with HBr (liquid) at  $-80^\circ$  in a sealed tube affords mainly  $\text{CHBr}(\text{CH}_2\text{Br})_2$ , which loses HBr to give  $\alpha\beta$ -dibromo- $\Delta^2$ -propene. Acetaldehyde with HBr, followed by  $\text{PCl}_3\text{Br}_2$ , affords  $\alpha\gamma$ -tribromopropene (II), b.p. 84—85°/14 mm. which does not lose HBr with quinoline but gives (I) with anhyd. KOH at 200°, indicating that (II) is not an intermediate product of the change. J. L. D.

**$\alpha\delta$ -Dibromobutane from divinyl.** L. G. TZIURICH and I. A. ROTENBERG (J. Gen. Chem. Russ., 1936, 6, 203—205).—Divinyl and Br afford  $\text{CH}_2\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Br}$ , converted by NaOEt in EtOH into  $(\text{CH}\cdot\text{CH}_2\cdot\text{OEt})_2$ , which is hydrogenated (Pd-Ni) to  $\text{OEt}\cdot[\text{CH}_2]_4\cdot\text{OEt}$ , and this yields  $\alpha\delta$ -dibromobutane when heated with HBr (130°; 3 hr.). R. T.

**Reactions and derivatives of  $\alpha\beta\gamma$ -trichloro- $\beta$ -methylpropane.** A. O. ROGERS and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 1029—1032).—Alkaline hydrolysis of  $\alpha\beta\gamma$ -trichloro- $\beta$ -methylpropane (I) gives a good yield of  $\gamma$ -chloro- $\beta$ -methylallyl alcohol (II), two (*cis* and *trans*) forms, b.p. 160—162° (corr.) (3:5-dinitrobenzoate, m.p. 94.4—95.8°), and

160—168° (corr.) (3:5-dinitrobenzoate, m.p. 63.8—64.5°), which is readily oxidised (dil.  $\text{KMnO}_4$ ), adds Br very slowly, and could not be reduced (Na-Hg). Thermal decomp. of (I) at 450—550° affords a mixture (A) of  $\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Cl})_2$  and *cis*- and *trans*- $\text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CHCl}$ . (II) is obtained by alkaline or neutral hydrolysis of (A); acid conditions lead to an aldehyde as one of the main products. (A) and  $\text{Cl}_2$  at 0° in the dark give  $\alpha\alpha\beta\gamma$ -tetrachloro- $\beta$ -methyl- and  $\alpha\beta\gamma$ -trichloro- $\beta$ -chloromethyl-propane and some  $\text{Cl}_5$ -derivatives.  $\alpha$ -Chloro- $\gamma$ -phenyl- $\beta$ -methyl- $\Delta^2$ -propene, b.p. 125°/36 mm., is obtained from (A) and  $\text{MgPhBr}$ ; *Mg n*- and *iso*-amyl bromides similarly afford complex mixtures. H. B.

**Rearrangement of polyinenes. IX. Dimerides of tritert.-butylethynylmethyl halides.** W. J. SPARKS and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 865—870).—The chloride, new m.p. 176° (A., 1926, 43), and bromide, m.p. 177—178° (A., 1928, 988), previously obtained from  $(\text{CBu}^t)_2\text{C}\cdot\text{OH}$  (I) are dimerides,  $\text{C}_{38}\text{H}_{54}\text{Cl}_2$  (II) and  $\text{C}_{38}\text{H}_{54}\text{Br}_2$  (III), respectively, containing 1 reactive halogen. The compound (A., 1932, 496) from (I) and  $\text{TiCl}_3$  is also (II). (II) and (III) with Ag in  $\text{C}_6\text{H}_6$  give compounds,  $\text{C}_{76}\text{H}_{108}\text{Cl}_2$ , m.p. 241°, and  $\text{C}_{76}\text{H}_{108}\text{Br}_2$ , m.p. 244—246°, respectively; (III) and  $\text{AgOAc}$  in AcOH afford a compound,  $\text{C}_{38}\text{H}_{54}\text{Br}\cdot\text{OAc}$ , m.p. 108—110°. Tritert.-butylethynylmethyl chloride (IV), m.p. 73° [from (I) and  $\text{PCl}_3$  in light petroleum at room temp. or from (I) and aq. EtOH-HCl at 0°], is oxidised ( $\text{CrO}_3$ , warm AcOH) to  $\text{Bu}^t\text{CO}_2\text{H}$  and  $(\text{CBu}^t)_2\text{C}\cdot\text{CO}$  (V), m.p. 62—63°, indicating a preliminary rearrangement of (IV) into  $(\text{CBu}^t)_2\text{C}\cdot\text{C}:\text{C}:\text{CBu}^t\text{Cl}$  (VI). Similar oxidation of (II) gives a compound,  $\text{C}_{38}\text{H}_{54}\text{O}_{10}$  (VII), amorphous, m.p. about 65°; whilst  $(\text{CBu}^t)_2\text{C}\cdot\text{CH}\cdot\text{COBu}^t$  (A., 1928, 988) affords (V). (II) and  $\text{NaNH}_2$  in boiling xylene afford resinous products [the hydrocarbon, previously reported (A., 1932, 496) could not be isolated], whilst (II) and Mg in Et<sub>2</sub>O give a compound,  $\text{C}_{38}\text{H}_{56}\text{O}_2$ , m.p. 178°. (II) heated to 170° (in small amounts only) rearranges to an isomeride, m.p. 257°, which does not react with Ag, is oxidised ( $\text{KMnO}_4$ ,  $\text{COMe}_2$ ) to a compound,  $\text{C}_{38}\text{H}_{54}\text{O}_3$ , m.p. 260—263° [also obtained from (VIII) (below) and moist Ag<sub>2</sub>O in  $\text{C}_6\text{H}_6$ ], and absorbs  $\text{O}_2$  readily to give an oxide,  $\text{C}_{38}\text{H}_{54}\text{OCl}_2$  (VIII), m.p. 250° (decomp.). The Cl atoms of (VIII) are replaced by OAlk by heating with AlkOH; the (*OMe*)<sub>2</sub>, m.p. 250°, (*OEt*)<sub>2</sub>, m.p. 217°, (*OBu*)<sub>2</sub>, m.p. 132°, and (*O-C*<sub>12</sub>H<sub>25-n</sub>)<sub>2</sub>, m.p. 85°, derivatives are described. These acetals (?) and (VIII) are all hydrolysed (50%  $\text{H}_2\text{SO}_4$ ) to a compound,  $\text{C}_{38}\text{H}_{54}\text{O}_2$ , m.p. 169—170°, which is oxidised (conc.  $\text{HNO}_3$ ) to (probably) (VII). (II) is considered to be a cyclobutane derivative (structure suggested) formed by dimerisation of (VI). (VIII) is probably a furan. H. B.

**Catalysts promoting dehydrogenation and dehydration of alcohols.** N. N. MOVOILOVA (Sintet. Kautschuk, 1935, 4, No. 1, 44—49; No. 2, 25—40; No. 3, 24—38).—A review. CH. ABS. (r)

**Reaction between magnesium and alcohols in presence of certain alkyl halides.** M. N. VISCHN-JAKOV (J. Gen. Chem. Russ., 1936, 6, 107—128).—The reactivity of Mg with alcohols in presence of alkyl

halides rises in the order  $\text{MeOH} < \text{Pr}^n\text{OH} < \text{EtOH}$ ; the activating action of the halides increases in the series  $\text{RX} < \text{RX}_2 < \text{RX}_3$ ;  $\text{RCl} < \text{RBr} < \text{RI}$ ;  $\text{Pr}^n\text{X} < \text{EtX} < \text{MeX}$ . A limiting concn. exists for each activator, below which the reaction does not proceed, or commences after a prolonged induction period; in presence of high concns. of halides two max. are found on the velocity of reaction curve. The gaseous products consist of  $\text{H}_2$  and saturated hydrocarbons in presence of mono- and unsaturated hydrocarbons in presence of di-halides. The results are explained on the assumption that the first reaction is  $\text{ROH} + \text{Mg} + \text{R}'\text{X} \rightarrow \text{MgX} \cdot \text{OR} + \text{H}$ , and that the  $\text{MgX} \cdot \text{OR}$  catalyses the reaction  $2\text{ROH} + \text{Mg} \rightarrow \text{Mg} \cdot \text{OR} + \text{H}_2$ . R. T.

**Photochemical peroxide formation. II. Oxidation of ethyl, propyl, butyl, and amyl alcohol by molecular oxygen in ultra-violet light. Photochemical formation of peralcohols.** R. CANTENI (Ber., 1936, 69, [B], 1386—1394).— $\text{EtOH}$ ,  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^s\text{OH}$ ,  $\text{Bu}^n\text{OH}$ ,  $\text{Bu}^s\text{OH}$ , and fermentation amyl alcohol yield peroxides in the presence of  $\text{O}_2$  under the influence of ultra-violet light of the quartz-Hg lamp of short or long. Addition of  $\text{H}_2\text{O}$  to  $\text{EtOH}$  or  $\text{PrOH}$  retards peroxide formation. Production of peroxides occurs most rapidly with *iso*-alcohols, rapidly with  $\text{MeOH}$ , more slowly with the remaining *n*-alcohols. In ultra-violet light of long  $\lambda$ , the rate of formation of peroxides increases with increasing no. of C atoms ( $\text{MeOH}$  is an exception). The peroxides formed from the alcohols at a nearly const. rate decompose as their concn. increases until a balance is nearly attained. The production of peroxides from alcohols cannot be attributed to the formation of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}$  and  $\text{O}_2$  or from photolytically formed  $\text{H}$  and  $\text{O}_2$ , and the production of peralcohols,  $\text{R} \cdot \text{O} \cdot \text{OH}$ , is postulated. H. W.

**Action of calcium hypochlorite on organic compounds with hydroxyl and carbonyl groups. II. Calcium hypochlorite and secondary alcohols and ketones.** J. SUNEVIČ and A. TSCHILINGARJAN (Ber., 1936, 69, [B], 1537—1542).—The following general scheme is given for the action of  $\text{Ca}(\text{OCl})_2$  on ketones  $\text{COR}_2$  or the corresponding carbinols:  $\text{COEt} \rightarrow \text{OH} \cdot \text{CEt} \cdot \text{CHMe} \rightarrow$

$\text{CEt}(\text{OCl}) \cdot \text{CHMe} \rightarrow \text{COEt} \cdot \text{CHMeCl} \rightarrow \text{COEt} \cdot \text{CMeCl}$ , (I)  
 $\text{COMe} \cdot \text{COEt} \xrightarrow{\text{AcOH} + \text{EtCO}_2\text{H}} \text{(I)} \rightarrow$   
 $\text{CO}(\text{CMeCl}_2)_2 \rightarrow \text{COMe} \cdot \text{CO} \cdot \text{CMeCl} \rightarrow \text{AcOH} + \text{CMeCl}_2 \cdot \text{CO}_2\text{H}$  (II); (II)  $\rightarrow \text{AcCO}_2\text{H} \rightarrow \text{AcOH} + \text{CO}_2$ ;  
 (II)  $\rightarrow \text{CCl}_3 \cdot \text{CO} \cdot \text{CO}_2\text{H} \rightarrow \text{CHCl}_3 + \text{H}_2\text{C}_2\text{O}_4$ . The following transitions are illustrative;  $\text{COPr}^n \cdot \text{C}_6\text{H}_4\text{Me}$  to  $\text{CHCl}_3$ ,  $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ , and  $\text{AcOH}$ ;  $\text{CHEt}^n \cdot \text{OH}$  to  $\text{CHCl}_3$ ,  $\text{AcOH}$ , and  $\text{EtCO}_2\text{H}$ ;  $\text{COEt}^n$  to  $\text{CHCl}_3$ ,  $\text{AcOH}$ , and  $\text{EtCO}_2\text{H}$ ;  $\text{CHPr}^n \cdot \text{OH}$  to  $\text{CHCl}_3$ ,  $\text{EtCO}_2\text{H}$ , and  $\text{Pr}^n\text{CO}_2\text{H}$ ;  $\text{COPr}^s$  to  $\text{CHCl}_3$  with traces of acid;  $\text{COPr}^s$  to  $\text{CHCl}_3$ ,  $\text{AcOH}$ , and  $\text{Pr}^s\text{CO}_2\text{H}$ ;  $\text{CHPr}^n \cdot \text{OH}$  to  $\text{PrCO}_2\text{H}$ , and  $\text{BuCO}_2\text{H}$ ;  $\text{CHBu}^s \cdot \text{OH}$  to  $\text{EtCO}_2\text{H}$  and  $\text{CHMeEt} \cdot \text{CO}_2\text{H}$ ;  $\text{COMe} \cdot \text{CH}_2\text{Ph}$  to  $\text{BzOH}$ ,  $\text{PhCHO}$ , and  $\text{AcOH}$ .  $\text{Ac}_2$  yields  $\text{AcOH}$  exclusively.  $\text{CH}_3\text{Ac}_2$  gives  $\text{CHCl}_3$  and  $\text{AcOH}$ .  $\text{CH}_3\text{Cl} \cdot \text{CH}_2 \cdot \text{OH}$  affords little  $\text{CHCl}_3$  and very little unidentified acids. Propylene chlorohydrin gives  $\text{CHCl}_3$  and  $\text{AcOH}$ .  $(\text{CH}_2\text{OH})_2$  yields very little acid and no  $\text{CHCl}_3$  or  $\text{H}_2\text{C}_2\text{O}_4$ .  $\text{CHCl}_3$  and (?) aldehyde are obtained from

$\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{OH}$  whilst  $\text{CHCl}_3$  and a little  $\text{AcOH}$  are derived from  $(\text{CHMe} \cdot \text{OH})_2$ . H. W.

**$\alpha$ -Chloro-3-methylpropan-3-ol from  $\alpha$ ,5-dichloro-3-methylpropane.** C. E. SPARKS and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 1010—1011; cf. Pogorzelsky, A., 1905, i, 165).—Liquid-phase hydrolysis of  $\text{CH}_2\text{Cl} \cdot \text{CMe}_2\text{Cl}$  under neutral, slightly basic, or slightly acidic conditions gives 35—48% of  $\text{CH}_2\text{Cl} \cdot \text{CMe}_2 \cdot \text{OH}$ . H. B.

**Preparation of *cis*- and *trans*-ethylenic alcohols and their derivatives. Comparison of their physical properties.** (MLLE.) B. GREDY (Bull. Soc. chim., 1936, [v], 3, 1093—1101).—Treatment of acetaldehyde with  $\text{Mg}$  and  $n\text{-C}_2\text{H}_{11}\text{Br}$  affords vinylamylcarbinol, b.p.  $74^\circ/15$  mm., converted by excess of  $\text{PBr}_3$  in  $\text{C}_2\text{H}_5\text{N}$  into  $\alpha$ -bromo- $\Delta^8$ -octene (I), b.p.  $74$ — $75^\circ/14$  mm., which with  $\text{NaOAc}$  in  $\text{AcOH}$  gives  $\Delta^8$ -octenyl acetate, b.p.  $95.5$ — $96^\circ/14$  mm., hydrolysed to  $\Delta^8$ -octen- $\alpha$ -ol (II).  $\text{NaNH}_2$  and  $\text{Me}_2\text{SO}_4$  transform (II) into *trans*- $\alpha$ -methoxy- $\Delta^8$ -butene, b.p.  $69.5$ — $70^\circ/15$  mm. The following compounds are derived by semihydrogenation of the requisite acetylenic compounds (colloidal  $\text{Pd}$ ): *cis*- $\alpha$ -methoxy- $\Delta^8$ -butene (III), b.p.  $61^\circ/12$  mm.; *cis*- $\Delta^8$ -octen- $\alpha$ -ol, b.p.  $80$ — $12$  mm., whence *cis*- $\Delta^8$ -octenyl acetate, b.p.  $91.5$ — $92^\circ/10$  mm.; (III) is transformed by  $\text{HBr}$  followed by  $\text{H}_2\text{SO}_4$  mainly into (I). Technical cinnamyl alcohol, shown by the Raman spectrum to be the *trans*-derivative, is converted by boiling  $\text{Ac}_2\text{O}$  into *trans*-cinnamyl acetate, b.p.  $141$ — $142^\circ/14$  mm., by  $\text{NaNH}_2$  and  $\text{Me}_2\text{SO}_4$  into *trans*- $\alpha$ -methoxy- $\gamma$ -phenyl- $\Delta^8$ -propene, b.p.  $111.5$ — $112.5^\circ/15$  mm., and by  $\text{PBr}_3$  in  $\text{C}_5\text{H}_5\text{N}$  into *trans*- $\gamma$ -phenyl- $\Delta^8$ -propenyl bromide, b.p.  $128$ — $129^\circ/10$  mm., m.p.  $29^\circ$ . Partial hydrogenation of  $\gamma$ -phenyl- $\Delta^8$ -propinen- $\alpha$ -ol affords *cis*-cinnamyl alcohol, b.p.  $127$ — $128^\circ/?$  pressure; *cis*- $\alpha$ -methoxy- $\gamma$ -phenyl- $\Delta^8$ -propene, b.p.  $95$ — $96^\circ/9$  mm., and *cis*- $\gamma$ -phenyl- $\Delta^8$ -propenyl acetate, b.p.  $140$ — $15$  mm., are obtained similarly. The physical properties of the aliphatic *trans*- and *cis*-compounds are closely similar to one another, whereas marked differences are observed in the cinnamic series. H. W.

**Isolation from cottonseed oil of an alcohol resembling  $\alpha$ -tocopherol from wheat-germ oil.** O. H. EMERSON, G. A. EMERSON, and H. M. EVANS (Science, 1936, 83, 421; cf. this vol., 531).—The unsaponifiable matter of cottonseed oil yielded four allopphanates, m.p.  $240^\circ$  (I),  $158$ — $160^\circ$  (II),  $134$ — $135^\circ$ , and  $80^\circ$  (III), respectively. The regenerated alcohol from (III) is biologically inactive, that from (I) is inactive as vitamin-E, whilst the remainder are active. The alcohol from (II) appears identical with  $\alpha$ -tocopherol. L. S. T.

**Explosiveness of methylated ether.** P. S. ARUP (Chem. and Ind., 1936, 546—547).—Comments on the conditions under which  $\text{Et}_2\text{O}$  is likely to explode. F. N. W.

**Etherates of aluminium chloride.**—See this vol., 945.

**Carbohydrates and polysaccharides. XLVIII. Ethylene oxide and related compounds: synthesis of polyethylene glycols.** S. Z. PERRY and H. HIBBERT (Canad. J. Res., 1936, 14, B, 77—83).—Fractional distillation of the product obtained by



heating diethylene glycol with I at 190° affords *tri*-, b.p. 115.5—117°/0.1 mm., *tetra*- (I), b.p. 140.0—145.5°/0.1 mm. (*dichloride*, b.p. 107.5—108.5°/1 mm., by the action of  $\text{SOCl}_2$ ), and *penta-ethylene glycol*, b.p. 174.0—176.0°/0.14 mm. (total yield, 25%). Higher polyethylene glycols are best obtained by interaction of the  $\text{Na}_1$  derivative of a glycol (by the action of  $\text{NaOMe-MeOH}$ , or Na at a high temp. on an excess of the glycol) with an  $\omega\omega'$ - $\text{Cl}_2$ -derivative. Thus  $(\text{CH}_2\text{Cl-CH}_2)_2\text{O}$  and  $\text{OH-CH}_2\text{-CH}_2\text{-ONa}$  at 65° give (I), and by similar action with the appropriate Na derivative are obtained *hexa*-, b.p. 166—168°/0.015 mm. (*dichloride*, b.p. 146.5—148°/1 mm.), *octa*-, b.p. 206—209°/0.015—0.018 mm. (*dichloride*, b.p. 199.5—202°/3—4 mm.), and *deca-ethylene glycol*, b.p. 220—223°/0.01 mm. (*dichloride*, b.p. 205—208°/0.015 mm.). J. W. B.

**Preparation of  $\beta$ -ethoxy- $\Delta^{\gamma}$ -butadiene and  $\beta$ -methoxy- $\Delta^{\beta\gamma}$ -butadiene and their polymerisation.** I. A. ROTENBERG and M. A. FAVORSKAJA (J. Gen. Chem. Russ., 1936, 6, 185—189).— $\text{CH}_2\text{:C-CH:CH}_2$  in  $\text{EtOH}$  and  $\text{KOH}$  (140—150°; 10 hr.) afford  $\text{CH}_2\text{:CH-C(OEt):CH}_2$ , b.p. 113—117° (ozonolysis products  $\text{HCO}_2\text{H}$  and  $\text{H}_2\text{C}_2\text{O}_4$ ), oxidised by  $\text{KMnO}_4$  in aq.  $\text{K}_2\text{CO}_3$  at 30—35° to  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{AcOH}$ . When  $\text{MeOH}$  is substituted for  $\text{EtOH}$  in the above reaction (150°; 18 hr.), the product is  $\text{OMe-CMe:C:CH}_2$ ; in absence of  $\text{KOH}$  styrene is obtained. R. T.

**Polymembered heterocyclic compounds. IX. Polymembered cyclic ethers and keto-ethers.** M. STOLL and W. SCHERRER (Helv. Chim. Acta, 1936, 19, 735—743; cf. A., 1935, 1351).—Active, very fine Na powder (I) is obtained by dissolving Na in  $\text{PhMe}$  (in solid  $\text{CO}_2\text{-Et}_2\text{O}$ ) by  $\text{NH}_3$  and removing the  $\text{NH}_3$  by vigorous stirring. The Na in the resulting suspension is determined by removing all trace of  $\text{NH}_3$  by  $\text{N}_2$ , treating with aq.  $\text{EtOH}$ , and titrating the  $\text{NaOH}$  formed. Very dry reagents are required for the prep. and use of (I).  $\text{OH-[CH}_2\text{]}_{14}\text{-OH}$  and (I) in hot  $\text{PhMe}$  give slowly  $\text{OH-[CH}_2\text{]}_{14}\text{-ONa}$ , which with  $\text{PhSO}_2\text{Cl}$  gives  $\xi$ -hydroxytetradecyl benzenesulphonate, m.p. 47—48°; with (I) in hot  $\text{C}_6\text{H}_6$  this gives 5% of tetradecylene  $\alpha\xi$ -ether (II), m.p. 31.5—33°, with large amounts of highly sulphonated products.  $\text{OH-[CH}_2\text{]}_3\text{-O-[CH}_2\text{]}_{10}\text{-CO}_2\text{H}$  with  $\text{SOCl}_2$  in  $\text{CHCl}_3\text{-MeOH-H}_2\text{O}$  gives *Me  $\kappa$ - $\gamma'$ -chloropropoxyundecate*, b.p. 145—147°/0.2 mm., which with  $\text{CHNa(CO}_2\text{Me)}_2$  gives *Me $_2$   $\gamma$ - $\kappa'$ -carbomethoxydecoxypropylmalonate*, b.p. 172—175°/0.5 mm., and thence  $\delta$ -carboxybutyl  $\kappa$ -carboxydecyl ether, m.p. 94.5—95°, the Ce salt of which affords  $\epsilon$ -keto-n-pentadecylene  $\alpha\text{o}$ -ether (III), b.p. 120—121°/0.05 mm., and a substance,  $\text{CO-[CH}_2\text{]}_{10}\text{-O-[CH}_2\text{]}_4\text{-CO}$  or  $\text{CO-[CH}_2\text{]}_{10}\text{-O-[CH}_2\text{]}_4\text{-CO}$ , b.p. 220—230°/0.02 mm., separated by the semicarbazones, m.p. 171.5—172° (IV) and 182.5—183°, respectively. (IV) and  $\text{KOH-EtOH}$  give pentadecylene  $\alpha\text{o}$ -ether (V), m.p. 26°, b.p. 84—85°/0.02 mm., and the pinacone,  $\left| \text{O-[CH}_2\text{]}_4\text{-C(OH)-[CH}_2\text{]}_4\text{-C(OH)-[CH}_2\text{]}_4\text{-O} \right|$ , b.p. 230—233°/0.3 mm., m.p. 30—31°. The structure of (V) is proved by hydrolysis

to  $\text{Br-[CH}_2\text{]}_{15}\text{-Br}$ . (II), (III), and (V) have weak musk-like odours. R. S. C.

**Alkyl hypochlorites. I. Action on Schiff's bases.** R. FUSCO and C. MUSANTE (Gazzetta, 1936, 66, 258—264).— $\text{CMe}_2\text{Et-OCI}$ , prepared from  $\text{CMe}_2\text{Et-OH}$  (cf. J.C.S., 1923, 123, 3002), is extracted and used in  $\text{CCl}_4$ . It reacts with  $\text{NPh:CHPh}$  and with  $p\text{-C}_6\text{H}_4\text{Me:N:CHPh}$  to give *NN'*-diphenyl- and *NN'*-di-*p*-tolyl-benzamidine, respectively, presumably by addition of  $\text{ROCl}$  to  $\text{CH:N}$  in the direction  $\text{CHCl-N(OR)}$ , followed by reaction of  $\text{Cl}$  with the amine.  $\beta\text{-C}_{10}\text{H}_7\text{:N:CHPh}$ , however, gives exclusively its 2- $\text{Cl}$ -derivative, and  $\alpha\text{-C}_{10}\text{H}_7\text{:N:CHPh}$  its 2- and 4- $\text{Cl}$ -derivatives; here addition in the direction  $\text{C(OR)-NCl}$  is presumed. E. W. W.

**Relative mobility of alkyl radicals in their chlorosulphites and chloroformates.** P. CARRÉ (Bull. Soc. chim., 1936, [v], 3, 1064—1073; cf. A., 1935, 606).—The relative mobilities of the alkyl groups of chlorosulphites and chloroformates is deduced from their temp. of decomp. when heated in  $\text{C}_6\text{H}_5\text{N}$  or quinoline. With *n*-alkyl chlorosulphites the mobility diminishes from  $\text{C}_1$  to a min. at  $\text{C}_7$ ; between  $\text{C}_8$  and  $\text{C}_{15}$  alternation is marked, the groups with an odd no. of C atoms being more mobile than neighbouring groups with an even no. With the chloroformates the mobility decreases from  $\text{C}_1$  to  $\text{C}_4$ ; between  $\text{C}_7$  and  $\text{C}_{15}$  alternation is marked in the inverse order from that recorded for chlorosulphites. For simpler pairs containing the same no. of C atoms the mobilities of the *sec.* are > those of primary radicals; with the higher members the difference becomes less or disappears, and is inverted in the cases of *n*- and *sec.*-octyl chlorosulphite. Introduction of  $\text{Cl}$  or  $\text{Ph}$  into the alkyl of a chlorosulphite diminishes the mobility of the radical, but enhances it in the case of chloroformates. A double linking in the alkyl increases the mobility.  $\gamma$ -Chloropropyl, b.p. 111—112°/21 mm.,  $\beta\gamma$ -dichloropropyl, b.p. 110—111°/3 mm.,  $\beta$ -chloroisopropyl, b.p. 86—88°/20 mm.,  $\beta\beta'$ -dichloroisopropyl, b.p. 120°/20 mm., chlorosulphite and di- $\beta$ -chloroisopropyl sulphite, b.p. 155—158°/37 mm., are described. H. W.

**Attempted explanation of the principal differences in the properties of alkyl chloroformates and chlorosulphites.** P. CARRÉ (Bull. Soc. chim., 1936, [v], 3, 1073—1082; cf. this vol., 453).—An electronic explanation of the differing behaviour of alkyl chlorosulphites and chloroformates is advanced. The differing reactivities of elements directly united may be considered as corresponding with a difference in polarity which is the more pronounced as the electronic distance becomes greater. The latter depends qualitatively on the at. nos. of the directly united elements and their immediate substituents. H. W.

**Action of certain dihalogen derivatives of hydrocarbons on ethyl phosphite and on diethyl phosphites.** A. E. ARBUSOV and N. P. KUSCHKOVA (J. Gen. Chem. Russ., 1936, 6, 283—288).— $\text{P(OEt)}_3$  and  $\text{CH}_2\text{I}_2$  at 150° yield  $\text{CH}_2\text{I-PO(OEt)}_2$  (I), b.p. 133°/6 mm.,  $\text{OK-P(OEt)}_2$  and  $\text{CH}_2\text{I}_2$  in 90%  $\text{EtOH}$  afford  $\text{OH-CH}_2\text{-P(OEt)}_2$ , b.p. 72°/5 mm., from which

$OH\cdot CH_2\cdot P(OH)_2$ , m.p. 84.5—86°, is obtained by hydrolysis with 50% HCl (4 hr. at 150°). R. T.

Raman spectra of molten organic acids and their derivatives.—See this vol., 923.

Influence of structure on saponification. Analytical technique for esters. W. M. D. BRYANT and D. M. SMITH (J. Amer. Chem. Soc., 1936, 58, 1014—1017).—The esters are saponified by an excess of 2*N*-NaOH in 90% MeOH in a closed glass vessel at 60—100°, the temp. and time depending on the structure. The procedure has been applied to 34 esters, chiefly aliphatic, and the effect of steric hindrance is shown. The prep. of  $\beta\delta$ -dimethyl- $\gamma$ -amyl phthalate, b.p. 231°/20 mm., and  $\alpha\alpha$ -dimethylpropionate, b.p. 127.5—128°/95 mm., is described. E. S. H.

Detection of acetic acid by formation of acet-aldehyde. J. VAZQUEZ SANCHEZ (Anal. Fis. Quím., 1936, 34, 198—201).—AcOH is detected by distillation with 0.07 g. of  $Ca(OH)_2$  and a drop of 2%  $(HCO_2)_2Ca$ , the formation of MeCHO being confirmed by the Rimini-Simon reaction (cf. Dœuvre, A., 1934, 630). 15—20  $\times 10^{-6}$  g. of AcOH can be detected. The distillate obtained by heating lactic, butyric, or propionic acid with  $Ca(OH)_2$  also gives a positive reaction. F. R. G.

Electrolysis of acetates in non-aqueous solutions.—See this vol., 942.

Kinetics of the reaction between iodoacetic acid and glycine.—See this vol., 940.

Electrolysis of mixtures of isovalerates and nitrates. F. FICHTER and F. METZ (Helv. Chim. Acta, 1936, 19, 880—889).—Electrolysis of  $Bu^iCO_2Na$  in presence of  $NaNO_3$  gives  $Bu^i_2$ ,  $(CMe_2)_2$  (I), and  $(CHMe)_2$  (II) as primary products. (I) reacts further to yield  $Bu^iOH$  and  $Bu^iOH$  and thence  $Bu^iCO_2Bu^i$ , whilst (II) leads to (a)  $CHMeEt\cdot OH$  and thence  $Bu^iCO_2CHMeEt$ , (b)  $CHMeEt\cdot CHMe\cdot CHMe\cdot OH$ ,  $(CHMe\cdot OH)_2$ ,  $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$ , and  $OH\cdot CHMe\cdot CH(OH)\cdot CH_2\cdot OH$  (III). All these compounds, except (I) and (II), were isolated and identified, but the structure of (III) (urethane, m.p. 131°) is uncertain. Relatively small amounts of glycol nitrates are formed. R. S. C.

Electrolytic reduction of organic compounds. III.  $\beta$ -Vinylacrylic acid. E. ISAACS and C. L. WILSON (J.C.S., 1936, 810—812).—The electrolytic reduction of  $\beta$ -vinylacrylic acid using a spongy Ni cathode in EtOH-NaCl and 0.5*N*-NaOH gave, respectively, 25.1% and 15.6% of  $\Delta^a$ -*n*-pentenoic acid and 19.5% and 49.5% of  $Bu^aCO_2H$ , the remaining reduction product being  $\Delta^a$ . (I) +  $\Delta^v$ -*n*-pentenoic acids (cf. Muskat and Knapp, A., 1934, 631). A Cu cathode in 0.5*N*-NaOH gave 99.2% of (I), and Hg in  $NaHCO_3$  gave 75% of (I) and considerable quantity of pinacol-like dimeride. The ease of reduction of vinylacrylic acid and the three pentenoic acids is in the order: vinylacrylic  $\gg \Delta^a > \Delta^v > \Delta^v$ -*n*-pentenoic acid, in both acid and alkaline solution. F. R.

Alkylacetylenes and their additive compounds.

XI. Bromination of alkenyl esters. S. J. SLANINA, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 891—892).— $CH_2\cdot CAlk\cdot CO_2R$  (A., 1934, 1089) and Br in  $CHCl_3$  at

$< 0^\circ$  give unstable dibromides which undergo spontaneous fission to  $RCOBr$  and  $COAlk\cdot CH_2Br$ .  $\alpha$ -Butylvinyl chloroacetate thus affords  $CH_2Cl\cdot COBr$  and  $\alpha$ -bromohexan- $\beta$ -one, b.p. 86—88°/30 mm., whilst  $\alpha$ -amylvinyl acetate yields  $AcBr$  and  $\alpha$ -bromoheptan- $\beta$ -one, b.p. 109—110°/30 mm.  $CH_2\cdot CH\cdot OAc$  similarly gives  $\alpha\beta$ -dibromoethyl acetate, b.p. 94—95°/22 mm., the yield increasing with rise in temp. (30% at 5°; 42% at 70°). H. B.

Use of fractionating column for separation of fatty acids. S. LEPKOVSKY, G. V. FESKOV, and H. M. EVANS (J. Amer. Chem. Soc., 1936, 58, 978—981).—Octoic, deoic, lauric, and myristic acids can be obtained pure by fractional distillation of the mixed acids from coconut oil (I); an improved column (cf. A., 1930, 1153) is described. A better separation is effected through the Me esters; the composition of (I) is thus determined as hexoic 0.5, octoic 9, deoic 6.8, lauric 46.4, myristic 18, palmitic 9, stearic 1, oleic 7.6, and linoleic 1.6%. Erucic acid is obtained in 40% yield from the Me esters from rape-seed oil. H. B.

Comparative hydrogenation of different substances in one solution. H. I. WATERMAN and C. VAN VLODRUP (Rec. trav. chim., 1936, 55, 401—406).—Selective hydrogenation in mixtures of octadecenoic with more unsaturated esters (i.e., in partly hydrogenated linseed oil) is attributed to the active surface of the catalyst being occupied by the more unsaturated groups. The substances taken alone are hydrogenated with similar velocities. Selective hydrogenation is not observed with mixtures of  $C_{10}H_{18}$  and peanut oil, which at 180° with  $H_2$  at atm. pressure in presence of Ni-kieselguhr are hydrogenated simultaneously. E. W. W.

Transformation of oleic acid into elaidic acid and fission of fats with simultaneous increase of the solid fatty acids. G. RANKOFF (Ber., 1936, 69, [B], 1231—1238).—Treatment of oleic acid (I) with  $H_3PO_3$  in presence or absence of  $H_2O$  at 200—220° gives a crude product with solidifying point 26—30°; on further crystallisation the product attains the m.p. 49—51° or 61—62°, according to the ratio of the components, and hence does not contain elaidic acid (II). Under these conditions  $H_3PO_3$  does not give  $H_2$  or  $PH_3$ . (I) and  $H_3PO_2$  give a product of solidifying point 24—27° from which (II) can be isolated;  $H_3PO_2$  is decomposed with production of  $PH_3$ , and hence is possibly not the actual elaidinising agent. (I) and yellow P do not interact at 200—220°. In presence of  $H_2O$  (I) is transformed by yellow or red P into (II) in 60—70% yield;  $PH_3$ ,  $H_3PO_2$ ,  $H_3PO_3$ , and  $H_3PO_4$  are also produced. The yield of (II) is higher with P than with  $H_3PO_2$ . The bulk of the unused yellow P is recovered unchanged, whereas unattacked red P is transformed into bright red P. Treatment of olive oil, palm oil, tallow, or bone fat with S (1%) or P (3%) in  $H_2O$  (50%) at 220° causes almost complete hydrolysis into glycerol and a fatty acid mixture containing much more solid acid than is obtained from the fat by alkaline hydrolysis, owing to the formation of (II). Simultaneously pronounced bleaching is observed particularly when P is used. The acids are suitable for direct conversion into soaps of high detergent power. H. W.



**Diene synthesis with fats. I. Diene value of fats.** H. P. KAUFMANN and J. BALTES (*Fette u. Seifen*, 1936, **43**, 93—97).—Maleic anhydride (I) and  $\Delta^8$ -octadecadienecarboxylic acid give (?) 1-hexyl-4-carboxyheptyl- $\Delta^2$ -cyclohexene-5:6-dicarboxylic anhydride, m.p. 94.5°. With  $\alpha$ -elaeostearic ( $\Delta^8$ -octadecatrienecarboxylic) acid a substance, m.p. (impure) 62°, is formed (Morrell and Samuels, A., 1932, 1019). The "diene val.," suggested as a new const. for conjugated unsaturated fatty acids and fats, is determined by heating 0.1—0.15 g. of the unsaturated material with 10 ml. of a 1.0%  $\text{COMe}_3$  solution of (I) for 20 hr. at 100° in a sealed tube, adding  $\text{H}_2\text{O}$ , and titrating the excess of maleic acid with 0.1N-alkali. Vals. in good agreement with theory have been obtained for tri- $\beta$ -elaeostearin. F. C. B. M.

**Synthesis of normal  $\text{C}_{23}$ ,  $\text{C}_{25}$ ,  $\text{C}_{27}$ , and  $\text{C}_{29}$  saturated fatty acids, alcohols, and alkyl iodides.** S. SHIINA (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 180B).—Et erucate is catalytically hydrogenated to docosoic acid, which is converted by the usual methods [ $\text{R}\cdot\text{CO}_2\text{Et} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{OH}$   $\text{R}\cdot\text{CH}_2\cdot\text{I} \rightarrow \text{R}\cdot\text{CH}_2\cdot\text{CN}$ , and by the  $\text{CH}_2(\text{CO}_2\text{Et})_2$  synthesis; no prep. details given] into the  $\text{C}_{23}$ ,  $\text{C}_{25}$ , and  $\text{C}_{27}$  fatty acids and their Me and Et esters, and the  $\text{C}_{23}$ ,  $\text{C}_{25}$ , and  $\text{C}_{27}$  saturated alcohols and iodides. M.p. are given. P. G. C.

**X-Ray crystallographic measurements in phrenosinic (cerebronic) acid and its oxidation product.**—See this vol., 927.

**Pyruvyl chloride.** P. CARRE and P. JULLIEN (*Compt. rend.*, 1936, **202**, 1521—1523).— $\text{SOCl}_2$  and  $\text{AcCO}_2\text{H}$  at room temp. give a mixture  $\text{AcCl}$ ,  $\text{Ac}_2\text{O}$ ,  $\text{CHMeCl}$ , etc. When, however, they interact in  $\text{C}_5\text{H}_5\text{N}$ , and the product after pptn. of  $\text{C}_5\text{H}_5\text{N}$  by gaseous  $\text{HCl}$  is distilled, the fraction of b.p. 70—80° contains *pyruvyl chloride*, converted into pyruvanilide (*semicarbazone*, m.p. 268°). E. W. W.

**Ether-like compounds. XVII. Constitutive factors in esterification and hydrolysis.** M. H. PALOMAA and T. A. SIITONEN (*Ber.*, 1936, **69**, [B], 1338—1353).—Acids of the types,  $\text{OR}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ,  $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot[\text{CH}_2]_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{OR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{OR}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ , and fatty acids  $n\text{-C}_x\text{H}_{2x+1}\cdot\text{CO}_2\text{H}$  have been investigated. All  $n$ -fatty acid from  $\text{Pr}\cdot\text{CO}_2\text{H}$  onwards have the same or almost the same esterification const., and their esters the same hydrolysis const.  $\text{AcOH}$  and  $\text{EtCO}_2\text{H}$  also  $\text{HCO}_2\text{H}$  form peculiar groups. The influence of the position and nature of the O atoms is discussed in detail. H. W.

**Glycidic acids from chlorohydroxystearic acids.** K. HASHI (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 162—163B).—The chlorohydroxystearic acid prepared from oleic acid is converted by 4N-aq.  $\text{KOH}$  at 100° into *oxido-stearic acid*, m.p. 57.5—58.3°. The *isomeride* from chlorohydroxyelaidic acid has m.p. 54.5—55.3°; mixed m.p. and solubilities are given. P. G. C.

**Complex cobaltioxalates.**—See this vol., 948.

**Condensations by sodium VI. Malonic acids from mercury dialkyls.** A. A. MORTON and I.

HECHENBLEIKNER (*J. Amer. Chem. Soc.*, 1936, **58**, 1024—1026).— $\text{Hg}$  diamyl, b.p. 95—96°/3 mm. (obtained in 25% yield from amyl chloride, 2%  $\text{Na-Hg}$ , and a little  $\text{EtOAc}$  in light petroleum), with  $\text{Na}$  powder in  $\text{C}_5\text{H}_{12}$  followed by  $\text{CO}_2$ , gives hexoic (20—35%) and butylmalonic (40—50%) acids:  $\text{NaHg} + 2\text{C}_5\text{H}_{11}\text{Na} \xrightarrow{\text{Hg}(\text{C}_5\text{H}_{11})_2 + 3\text{Na}} \text{NaHg} + \text{C}_5\text{H}_{12} + \text{C}_5\text{H}_{10}\text{Na}_2$ .  $\text{C}_6\text{H}_6$  as solvent leads to  $\text{BzOH}$  and  $m$ - and  $p$ - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ;  $\text{PhMe}$  gives  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  and  $\text{CHPh}(\text{CO}_2\text{H})_2$ .  $\text{CHMe}(\text{CO}_2\text{H})_2$  is similarly formed from  $\text{HgEt}_2$  (obtained in 60—70% yield from  $\text{EtI}$ , 1%  $\text{Na-Hg}$ , and  $\text{EtOAc}$  in light petroleum). H. B.

**Action of malonic acid on dichloro-*trans*-diethylenediaminecobaltic chloride.**—See this vol., 948.

**Application of the indophenol reaction to the detection of certain organic polyacids.** J. VÁZQUEZ SÁNCHEZ (*Anal. Fis. Quím.*, 1935, **33**, 126—131).—Certain acids, which after neutralisation with  $\text{Na}_2\text{CO}_3$  and treatment with  $\text{P}_2\text{S}_5$  yield  $\text{C}_4\text{H}_4\text{S}$  or thiophthen, give a blue colour with isatin solution in Feigl's micro-apparatus. The following quantities of the acids may be detected: succinic (I) and fumaric, 25; maleic and malic, 50; methylsuccinic (II), 100; tartaric and citric,  $250 \times 10^{-6}$  g. (I) and (II) may be detected in presence of the remaining acids by preliminary oxidation of the mixture with a boiling solution of  $\text{KMnO}_4$  in 33%  $\text{H}_2\text{SO}_4$ . F. R. G.

**Formation of enolates from lactonic esters.** A. MICHAEL and N. WEINER (*J. Amer. Chem. Soc.*, 1936, **58**, 999—1004).—The production of  $\alpha$ -carbomethoxy- $\alpha$ -methyl- $\beta$ -isobutyrolactone (Ott, A., 1913, i, 1302) from the Ag salt of  $\alpha$ -carboxy- $\beta$ -isobutyrolactone (I) and  $\text{MeI}$  is considered to indicate that (I) forms an enolate. Attempted esterification [ $\text{Na}$  salt with  $\text{Me}_2\text{SO}_4$  in  $\text{MeOH}$ ;  $\text{EtOH-H}_2\text{SO}_4$  (trace)] of (I) results in retrogressive decomp. to  $\text{COMe}$ , and  $\text{CH}_2(\text{CO}_2\text{R})_2$ .  $\gamma$ -Butyrolactone (II) shows little or no tendency to form an enolate; the Na derivative obtained by Brecht (A., 1882, 34) from  $\gamma$ -isohexolactone is probably dimeric (cf. Fittig and Strom, A., 1892, 813).  $\alpha$ -Carbomethoxy- $\gamma$ -butyrolactone (III) and  $\text{NaOEt}$  give the enolate,  $\text{CH}_2\text{CH}_2 \begin{smallmatrix} \text{O} & \text{CO} \end{smallmatrix} \text{ONa}(\text{OEt})$ , also obtained by Traube and Lehmann's method (A., 1901, i, 501), which with  $\text{MeI}$  in  $\text{C}_6\text{H}_6$  affords  $\alpha$ -carbomethoxy- $\alpha$ -methyl- $\gamma$ -butyrolactone, b.p. 104.5—105°/2 mm., 264—265°/765.5 mm., and with I in  $\text{C}_6\text{H}_6$  gives two (probably) stereoisomeric  $\alpha\alpha'$ -dicarbomethoxy- $\alpha\alpha'$ -di- $\gamma$ -butyrolactones, b.p. 189°/2 mm. and m.p. 145°. These are hydrolysed [aq.  $\text{Ba}(\text{OH})_2$ ] to the same  $\alpha\alpha'$ -dicarboxy- $\alpha\alpha'$ -di- $\gamma$ -butyrolactone, m.p. 154—156° (decomp.), which when heated at 170° gives  $\alpha\alpha'$ -di- $\gamma$ -butyrolactone, m.p. 176°; (III) is similarly converted into (II).  $\delta$ -Chloro- $\alpha$ -carbomethoxy- $\gamma$ -valerolactone (Traube and Lehmann, *loc. cit.*) and  $\text{EtOH-NaOEt}$  give an enolate which when heated gives (by intramol. alkylation) the thermally stable 3-hydroxy-1-carbomethoxycyclobutane-1-carboxylic acid lactone, b.p. 135°/2 mm., which is hydrolysed (conc.  $\text{HCl}$ ) to  $\beta\gamma$ -dihydroxypropylmalonic acid dilactone (Leuchs and Spletstösser, A., 1907, i, 176). The lactone, m.p. 80—81°, of 3-hydroxycyclobutane-1:1-dicarboxylic acid (*Ba* salt) undergoes little decomp. at 200°; the stability of the

rings is not in harmony with Baeyer's strain theory.  $\delta$ -Lactonic esters could not be prepared. Thus,  $\text{CHNa}(\text{CO}_2\text{Et})_2$  (IV) and  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  give a product (?  $\alpha$ -carbethoxy- $\delta$ -valerolactone) (V), which on attempted distillation in a high vac. first polymerises to a rubber-like mass and then decomposes. A similar product is obtained from (IV) and  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OAc}$  in EtOH; in  $\text{C}_6\text{H}_6$  or dioxan *Et*  $\gamma$ -acetoxypromylmalonate, b.p. 143—145°/4 mm. (from which a lactone could not be obtained), results.  $\delta$ -Hydroxy- $\alpha$ -carbethoxy- $\gamma$ -valerolactone [from glycidol and (IV) in EtOH] also polymerises readily.  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  (VI) and  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{COCl}$  or (VI),  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and dry HCl give  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , *Et*  $\gamma$ -chloropropyl malonate (VII), b.p. 118°/3 mm., and  $\gamma$ -chloropropyl malonate, b.p. 164—165°/2 mm. (VII), and  $\text{EtOH}\cdot\text{NaOEt}$  afford (V). *Et*  $\beta$ -chloroethyl malonate (VIII), b.p. 105—106°/3 mm., and  $\text{CH}_2(\text{CO}_2\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$  are similarly formed from  $\text{CH}_2(\text{CO}_2\text{Et})_2$ ,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ , and dry HCl. (VIII) and Na in  $\text{C}_6\text{H}_6$  followed by dil. acid give (II).

H. B.

**Synthesis of cyclic derivatives of tartaric acid.** Y. TSUZUKI (Bull. Chem. Soc. Japan, 1936, 11, 362—366).—The following *Me*<sub>2</sub>-dioxysuccinates are obtained from *Me*<sub>2</sub> tartrate and the appropriate aldehyde or ketone in presence of a dehydrating agent: isopropylidene-, b.p. 139°/16 mm.,  $[\alpha]_D^{20} -53.13^\circ$  (*Et*<sub>2</sub> ester, b.p. 150°/19 mm.,  $[\alpha]_D^{25} -51.19^\circ$ ); ethylidene-, b.p. 142°/18 mm.,  $[\alpha]_D^{20} -82.17^\circ$  (*Et*<sub>2</sub> ester, b.p. 151°/19 mm.,  $[\alpha]_D^{20} -74.67^\circ$ ); methylene-, b.p. 145°/17 mm. (*Et*<sub>2</sub> ester, b.p. 153—154°/19 mm.,  $[\alpha]_D^{20} -78.54^\circ$ ).

J. T. A.

**Mechanism of the condensation of benzylmalonic ester with fumaric ester.** Michael's reaction. R. MALACHOWSKI, E. BILBEL, and M. BILIŃSKI-TABASOWICZ (Ber., 1936, 69, [B], 1295—1302).—Contrary to Duff and Ingold and to Rydon (A., 1935, 977), *Et*<sub>4</sub>  $\alpha$ -benzylpropane- $\alpha\beta\gamma$ -tetracarboxylate (I), b.p. 206—208°/1.5 mm., is the sole product of the condensation of NaOEt,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , and  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$  or of NaOEt,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , and *Et*<sub>2</sub> fumarate. Hydrolysis of (I) with boiling 20% HCl or with  $\text{H}_2\text{O}\cdot\text{H}_2\text{SO}_4\cdot\text{HCO}_2\text{H}$  (1 : 3 : 9 vol.) gives a mixture of  $\alpha$ -benzyltricarballic acids, m.p. 177° (anhydride, m.p. 120°) and m.p. 198° (anhydride m.p. 130°), respectively, separable by fractional crystallisation or, preferably, through the anhydrides. The interconversion of the acids is described.

H. W.

**Crystalline structure of sugars.** III.—See this vol., 927.

**Bismuth salts of gluconic acid.** W. M. LAUTER and H. A. BRAUN (J. Amer. Pharm. Assoc., 1936, 25, 497—499).— $\text{Bi}(\text{OH})_3$  with gluconic acid in dil. NaOH followed by pptn. with EtOH yields Na di- (Bi 59.6%) and tri-bismuthylgluconate (Bi 67.6%); the tetra-derivative could not be isolated.

F. O. H.

**Preparation of acetone derivatives of gluconic acid.** F. GARCÍA GONZÁLEZ and T. QUINTERO GUERRA (Anal. Fis. Quím., 1935, 33, 570—573; cf. A., 1932, 144).—K  $\alpha$ -ketodiiisopropylidenegluconate with 1 mol. of  $N\cdot\text{H}_2\text{SO}_4$  gives a compound, m.p. 155—

156°, and with  $N\cdot\text{H}_2\text{SO}_4$  at 100° yields K gluconate, the Ca salt of which with  $\text{COMe}_2$  and conc.  $\text{H}_2\text{SO}_4$  gives a compound,  $\text{C}_{27}\text{H}_{42}\text{O}_{14}\text{K}_2$  regarded as formed from 5 mols. of  $\text{COMe}_2$  with 2 mols. of gluconic acid.

F. R. G.

**Lactones in liquid ammonia.** J. W. E. GLATT-FELD and D. MACMILLAN (J. Amer. Chem. Soc., 1936, 58, 898—901).—*d*-Glucono- $\gamma$ -lactone (cf. A., 1935, 72) and benzylidenephthalide (I) are completely ammonolysed by anhyd. liquid  $\text{NH}_3$ ; (I) gives *o*- $\text{CO}\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ . Phthalide,  $\alpha$ -phenylphthalide, phthalophenone, coumarin, and the lactone of 2':4'-dihydroxydiphenyl-2-carboxylic acid do not react. Phenolphthalein is temporarily ammonolysed; the resulting product loses all its  $\text{NH}_3$  on prolonged evacuation yielding a pink hygroscopic compound. Me, Et, Pr, and Bu lactates, Et mandelate, and  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$  are partly or completely ammonolysed whilst BuOAc, EtOBz, *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OAc}$  are not.

H. B.

**Keten and acetylketen.** C. D. HURD and J. W. WILLIAMS (J. Amer. Chem. Soc., 1936, 58, 962—968).—*EtSH* and liquid keten (I) at  $-80^\circ$  (3 days) and then at room temp. give 92.6% of crude *EtS*Ac; little or none is obtained with gaseous (I). (I) with ZnMe<sub>2</sub> and ZnEt<sub>2</sub> in PhMe similarly affords about 40% of  $\text{COMe}_2$  and  $\text{COMeEt}$ , respectively; MgEt<sub>2</sub> gives a resin. (I) passed into  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ —anhyd. KOAc affords  $\beta$ -styrylacrylic acetic anhydride; intermediate production of a  $\beta$ -lactone is considered not to occur (cf. A., 1933, 274) since  $\beta$ -*m*-nitrophenyl- $\beta$ -propiolactone does not react with (I). Mixed anhydrides are not obtained from (I) and  $\text{Pr}^n\text{CHO}$ ,  $\text{COPhMe}$ ,  $\text{COMe}_2$ , or  $\text{CPh}_2\cdot\text{CO}$ . The production of styrene and  $\text{CO}_2$  during the Perkin reaction (cf. *loc. cit.*) is probably due to the decomp. of  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ . Benzilic acid and (I) in  $\text{COMe}_2$  give acetylbenzilic acetic anhydride, which is hydrolysed (aq.  $\text{COMe}_2$ ) to  $\text{OAc}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$  (II) (*anilide*, m.p. 176°), and converted by  $\text{NH}_4\text{Ph}$  in  $\text{COMe}_2$  into (II) and  $\text{NHAcPh}$ . Mandelic acid and (I) similarly afford acetylmandelic acetic anhydride, which undergoes thermal decomp. to  $\text{Ac}_2\text{O}$  and  $\text{PhCHO}$ , is hydrolysed ( $\text{H}_2\text{O}$ ) to  $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , and is converted by  $\text{NH}_4\text{Ph}$  into  $\text{NHAcPh}$  and  $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NHPh}$ . Acetylsalicylic acetic anhydride is similarly formed from *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . Contrary to the previous statement (*ibid.*, 259),  $\text{Bu}^n\text{OH}$  is not acetylated by (I). No reaction occurs between (I) and  $\text{CPh}_3$  in  $\text{C}_6\text{H}_6$ . Contrary to Angus *et al.* (this vol., 191), the dimeride (III) of (I) is considered to be  $\text{CHAc}\cdot\text{CO}$  or its resonance isomeride  $\beta$ -crotonolactone. Thus, (III) and  $\text{NH}_4\text{Ph}$  give  $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{NHPh}$ , whilst ozonolysis of (III) affords  $\text{AcCHO}$  [and  $\text{AcOH}$  but no  $\text{CH}_2(\text{CO}_2\text{H})_2$ ]. Pyrolysis of (III) at 550° gives C, dehydroacetic acid, resinous material, and the same gaseous products ( $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ) as are formed from (I) (Williamson, A., 1935, 67). Thermal decomp. of (I) probably occurs by way of (III).

H. B.

**Micro-determination of acetone.** A. LINDENBERG (Compt. rend. Soc. Biol., 1936, 122, 317—319).—The  $\text{COMe}_2$  is absorbed in aq.  $\text{NaHSO}_3$  and I added to oxidise both  $\text{NaHSO}_3$  and  $\text{COMe}_2$ , excess of I being



titrated with 0.005*N*-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The error for 0.01—0.05 mg. COMe<sub>2</sub> is  $\pm$  1%. F. O. H.

**Thermal decomposition of acetone.**—See this vol., 939.

**Action of phenylhydrazine on metallic acetylacetonates.** B. EMMERT and O. SCHNEIDER (Ber., 1936, 69, [B], 1316—1319).—Fe<sup>III</sup> acetylacetonate in abs. EtOH or C<sub>6</sub>H<sub>6</sub> is transformed by NHPh·NH<sub>2</sub> into the compound  $\left( \text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{O} \\ \text{CMe} \cdot \text{O} \end{smallmatrix} \right) \text{Fe}(\text{NH}_2\text{NHPh})_2$ , also obtained from Fe<sup>II</sup> acetylacetonate (+2C<sub>6</sub>H<sub>5</sub>N) and NHPh·NH<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>. Similar reduction is observed with Fe<sup>III</sup> benzoylacetonate, which affords the substance, C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>Fe·2C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>, with Mn<sup>III</sup> acetylacetonate, which yields the compound, C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Mn·2C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>, with Co<sup>III</sup> benzoylacetonate, which gives the substance, C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>Co·2C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>, and with Co<sup>III</sup> acetylacetonate, which yields the product, C<sub>28</sub>H<sub>40</sub>O<sub>5</sub>N<sub>6</sub>Co. Al acetylacetonate does not appear to react with NHPh·NH<sub>2</sub>. H. W.

**Internal complex salts of bivalent manganese and univalent copper.** B. EMMERT, H. GSOTT-SCHNEIDER, and H. STANGER (Ber., 1936, 69, [B], 1319—1321).—MnCl<sub>2</sub> and CH<sub>3</sub>Ac<sub>2</sub> in H<sub>2</sub>O in absence of air and presence of NaOH, NH<sub>3</sub>, NH<sub>2</sub>Me, C<sub>3</sub>H<sub>7</sub>(NH<sub>2</sub>)<sub>2</sub>, or piperidine give the compound, C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Mn·2H<sub>2</sub>O; if conc. NH<sub>3</sub> is used followed by treatment with NH<sub>3</sub> at 100—120° the product, C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Mn·2NH<sub>3</sub>, results; this passes when kept over P<sub>2</sub>O<sub>5</sub> in high vac. into C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>Mn. Analogously CH<sub>3</sub>AcBz, CH<sub>3</sub>Ac·CO<sub>2</sub>Et, CO(CH<sub>3</sub>·CO<sub>2</sub>Et)<sub>2</sub>, and o-OH·C<sub>6</sub>H<sub>4</sub>·CHO give the substances, C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>Mn·1.5H<sub>2</sub>O, C<sub>12</sub>H<sub>18</sub>O<sub>6</sub>Mn, C<sub>18</sub>H<sub>26</sub>O<sub>10</sub>Mn·1.5H<sub>2</sub>O, and C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>Mn·1.5H<sub>2</sub>O, respectively. The compound, C<sub>6</sub>H<sub>7</sub>O<sub>4</sub>Cu, results from CH<sub>3</sub>Ac<sub>2</sub> and NH<sub>3</sub>-Cu<sub>2</sub>O. H. W.

**Synthesis of tetrahydroartemisia ketone.** L. RUZICKA, T. REICHSTEIN, and R. PULVER (Helv. Chim. Acta, 1936, 19, 646—649).—CMc<sub>2</sub>Et·COCl, b.p. 23°/12 mm., and ZnBu<sup>II</sup>I give tetrahydroartemisia ketone, b.p. 65—68°/12 mm., the semicarbazone, m.p. 139—140° (corr.), of which is identical (mixed m.p., X-ray diagram, and crystallographic change at about 120°) with that of the H<sub>4</sub>-derivative of the natural product. Artemisia ketone is one of the rare, but increasingly frequent, compounds built up "irregularly" from isoprene units. R. S. C.

**Optical analysis and rotatory power of glycothiodiazolines.** H. WUYTS and R. VERSTRAETEN (Bull. Acad. roy. Belg., 1935, [v], 21, 415—431).—The condensation of β-thiobenzoyl-α-phenylhydrazine (I) with aldoses gives a mixture of isomeric glycothiodiazolines. Condensation products of (I) with arabinose, xylose, rhamnose, and fucose have been formed and vals. of  $[\alpha]_{780}^{20}$  and  $[\alpha]_{5461}^{20}$  are given and compared with previous data on glucose, mannose, and galactose. In each case the condensation product consists of two substances differing in solubility and in  $[\alpha]$ , the more sol. constituent being laevo- and the less sol. dextro-rotatory, except for rhamnose. W. R. A.

**Determination of acetyl in carbohydrate derivatives.** A. FRIEDRICH and H. STERNBERG (Biochem. Z., 1963, 286, 20—27; cf. A., 1932, 1051).—Accuracy

is increased and simplification achieved by half-neutralising with KOH the *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H used for hydrolysis. The average error is —4% and hence a correction is applied. W. McC.

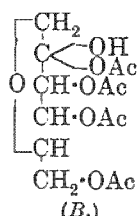
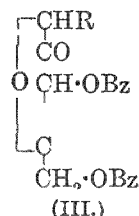
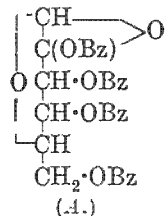
**Formation of hydrocyanic acid by the oxidation of sugars in presence of ammoniacal copper salts.** J. PARROD (Bull. Soc. chim., 1936, [v], 3, 1126—1136).—HCN is formed from sugars and HNO<sub>3</sub> or NH<sub>3</sub> in presence of *Pangium edule*. Oxidation of fructose by NH<sub>3</sub>-CuSO<sub>4</sub> by atm. O<sub>2</sub> at room temp. gives HCN and traces of CO(NH<sub>2</sub>)<sub>2</sub>. HCN is formed in considerable amount when the principal reducing sugars and their closely allied derivatives [glycer-aldehyde, CO(CO<sub>2</sub>H)<sub>2</sub>, tartaric acid (I), (CHO)<sub>2</sub>, CHO·CO<sub>2</sub>H] are oxidised by NH<sub>3</sub>-CuSO<sub>4</sub> at 60—80°; under these conditions, lactose, maltose, sucrose, rhamnose, gluconic acid, tartaric acid, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, CH<sub>2</sub>O, and pyrogallol do not yield HCN. If SO<sub>3</sub><sup>2-</sup> is replaced by other anions, CO(CO<sub>2</sub>H)<sub>2</sub> and (I) yield HCN in considerable quantity, whereas fructose gives small and variable yields. H. W.

**Crystalline 6-methylglucose. New synthesis.** D. J. BELL (J.C.S., 1936, 859—861).—*iso*Propylidene-glucose when shaken with freshly distilled PhCHO and P<sub>2</sub>O<sub>5</sub> gives 3 : 5-benzylidene-*isopropylidene*glucose 6-acetate, methylated and deacetylated with Me<sub>2</sub>SO<sub>4</sub>+NaOH to 3 : 5-benzylidene-6-methyl-*isopropylidene*glucose, m.p. 95—96°,  $[\alpha]_{D}^{20} +3.8^\circ$  in CHCl<sub>3</sub>, hydrolysed by EtOH-H<sub>2</sub>SO<sub>4</sub> to 6-methylglucose, m.p. 145°. F. R.

**Use of ceric salts in the micro-determination of glucose.** R. VANOSI and R. FERRAMOLA (Anal. Assoc. Quím. Argentina, 1935, 23, 162—180).—The authors' method (A., 1933, 138) employed for the determination of 0.003—0.3 mg. of glucose (I), particularly in blood, is 3—4 times as accurate as the iodometric method. A solution of glucose is heated under controlled conditions, varying with the amount of (I) present, with K<sub>2</sub>Fe(CN)<sub>6</sub> in Na<sub>2</sub>CO<sub>3</sub> solution and the Fe(CN)<sub>6</sub><sup>4-</sup> titrated in neutralised (H<sub>2</sub>SO<sub>4</sub>) solution with 0.00025*N*- or 0.0005*N*-Ce(SO<sub>4</sub>)<sub>2</sub>, using Me-violet as indicator. The influence of time of heating and concn. of the reagents on the accuracy of the method has been investigated. F. R. G.

**Glucosone. I. Halogenoses and glucosidic derivatives. II. Catalytic hydrogenation of osones.** K. MAURER and R. BOHME (Ber., 1936, 69, [B], 1399—1410).—I. Glucosone 2 : 3 : 4 : 6-tetra-benzoate (I) does not give a hydrate form. The presence of the anhydride ring is supported by the observations that it has 4 Bz groups, does not contain OH (Zerevitinov), and does not show mutarotation; it is converted by C<sub>6</sub>H<sub>5</sub>N into dibenzoylkojic acid (II), since C<sub>11</sub> is not esterified, and gives a *phenylosazone*, m.p. 201°,  $[\alpha]_D^{20} -45.1^\circ$  in C<sub>6</sub>H<sub>5</sub>N. (I) is therefore A. (I) is stable towards Ac<sub>2</sub>O, but reacts with technical AcCl or BzCl owing to presence of HCl. Hence it is converted by these reagents into 1-chloro-Δ<sup>4,5</sup>-glucosone 3 : 6-dibenzoate (III, R=Cl), m.p. 131°,  $[\alpha]_{D}^{20} +78^\circ$  in COMe<sub>3</sub>, and by AcOH-HBr in Et<sub>2</sub>O into the corresponding *Br-sugar*, m.p. 152°,  $[\alpha]_D^{20} +112.8^\circ$  in COMe<sub>3</sub>. The halogeno-sugars slowly reduce Fehling's solution at room temp., are transformed by AcOH and NaOAc into (II), very readily give the corresponding

phenylosazone (IV), m.p. 193°,  $[\alpha]_D^{20} -43.7^\circ$  in  $C_5H_5N$ , immediately react with  $C_5H_5N$ , and are not acetylated



by  $ZnCl_2$  and  $Ac_2O$ ; replacement of halogen by OH could not be effected. (III) and hot EtOH readily afford 1-ethyl- $\Delta^{4:5}$ -glucosonene 3:6-dibenzoate (III;  $R=Et$ ), m.p. 106°,  $[\alpha]_D^{20} -97.7^\circ$  in  $COMe_2$ ; the corresponding benzyl-, m.p. 113°,  $[\alpha]_D^{20} -92.8^\circ$  in  $COMe_2$ , methyl-, m.p. 112°,  $[\alpha]_D^{20} -91.7^\circ$  in  $COMe_2$ , anilino-, m.p. 101°,  $[\alpha]_D^{20} -161.0^\circ$  in  $COMe_2$ , ethylthiol-, m.p. 119°,  $[\alpha]_D^{20} -113^\circ$  in  $COMe_2$ , and acetyl-, m.p. 152°,  $[\alpha]_D^{20} -25^\circ$  in  $COMe_2$ , derivatives are described. The glucosonides reduce boiling Fehling's solution very slowly. They do not contain OH (Zerevitinov). With  $NHPh \cdot NH_2$ , they afford (IV) and with  $NaOAc$  in boiling AcOH they give (II). Br in  $CHCl_3$  or  $CCl_4$  is only very slowly absorbed by them with almost quantitative production of HBr, so that the halogen is used for oxidation. Mutual replacement of the glucosidic residues does not appear possible. The presence of C=O is established by the production of semicarbazones, m.p. 158°,  $[\alpha]_D^{20} -204.1^\circ$  in  $COMe_2$ , and m.p. 138°,  $[\alpha]_D^{20} -210.2^\circ$  in  $COMe$ , from the Et and  $CH_2Ph$  derivatives, respectively. The Et compound is transformed by long contact with cold  $C_5H_5N$  into a substance, m.p. 158°,  $[\alpha]_D^{20} \pm 0^\circ$ , probably

$\text{CO} \begin{array}{c} \text{CH} \cdot \text{C}(\text{OEt}) \\ \text{CH} \cdot \text{C}(\text{CH}_2 \cdot \text{OBz}) \end{array} \text{O}$ ; it is hydrolysed by  $NH_3$ -EtOH,  $NaOMe$ , or  $MeOH-Ba(OH)_2$  to non-cryst. products, but appears stable in acid media. It is not hydrogenated homogeneously, generally giving cryst. products, m.p. 131°,  $[\alpha]_D^{20} -18^\circ$  in  $COMe_2$ . Glucosone hydrate 2:3:4:6-tetra-acetate absorbs 2H (Pd in 50% AcOH), yielding a substance (V), m.p. 158°,  $[\alpha]_D^{20} -32^\circ$  in EtOH (monoacetate, m.p. 116°,  $[\alpha]_D^{20} -25^\circ$  in  $CHCl_3$ ); H does not appear to be absorbed, but to be utilised in the removal of O. (V) is probably B.

H. W.

Determination of osmotic pressure by isothermal distillation using solvents of low boiling point (glucose penta-acetate-acetone). M. ULMANN (Ber., 1936, 69, [B], 1437-1442).—An apparatus is figured and described which permits operations to be effected in the vac. of a  $H_2O$  pump. The mol. wt. of glucose penta-acetate (I) in  $COMe_2$  is normal only if the concn. is  $> 0.025\%$ ; in more conc. solution the observed vals. are markedly greater. The tendency of (I) towards association is greater in  $COMe_2$  than in AcOH. Further, if a 0.1% solution is diluted to 0.07%, after establishment of the corresponding osmotic pressure, a gradual increase of the latter is observed, indicating a slow dissociation of the previously associated mols.

H. W.

Solubility of calcium oxide in water and in aqueous sucrose.—See this vol., 932.

**Biose from methylbioside. Synthesis of 2- $\beta$ -glucosidoglucose.** K. FREUDENBERG and K. SOFF (Ber., 1936, 69, [B], 1245-1251; cf. A., 1933, 149).—In  $Ac_2O-H_2SO_4$  at 20° glucose  $\alpha$ - (I) shows slight downward and the  $\beta$ -penta-acetate (II) marked upward mutarotation; equilibrium [about 88% of (I) and 12% of (II)] is reached in 30 min.  $\beta$ -Glucosan triacetate is converted into (I) and (II) within 20 min. Maltose  $\beta$ -octa-acetate (III) and anhydromaltose hexa-acetate rapidly give an equilibrium mixture of (III) and the  $\alpha$ -octa-acetate (IV), but the degradation to glucose derivatives cannot be followed polarimetrically. The graph of  $\beta$ -methylmaltose hepta-acetate rises steeply owing to loss of Me and then passes through a flat max., pointing to the occurrence of a Walden inversion with production of (IV), and finally of an equilibrium mixture. The process is suitable for the isolation of bioses from methylbiosides. 4:6-Benzylidene- $\alpha$ -methylglucoside and acetobromoglucose give a methylbioside (V) (cf. A., 1930, 1412), converted by catalytic hydrogenation into 2- $\beta$ -glucosido- $\alpha$ -methylglucoside hepta-acetate, m.p. 132°,  $[\alpha]_D^{20} +50.2^\circ$  in  $CHCl_3$ . This is converted by acetolysis and subsequent treatment with  $AcOH-HBr$  into 2- $\beta$ -glucosidoglucose 1-bromohydrin hepta-acetate, m.p. 194° (decomp.),  $[\alpha]_D^{20} +95.6^\circ$  in  $CHCl_3$ , transformed by  $Tl(OAc)_2$  in AcOH, into 2- $\beta$ -glucosido- $\beta$ -glucose octa-acetate, m.p. 192°,  $[\alpha]_D^{20} -32.5^\circ$  in  $CHCl_3$ , which is hydrolysed ( $NaOMe$  in  $CHCl_3-MeOH$ ) to 2- $\beta$ -glucosido- $\alpha$ -glucose (+ $H_2O$ ), (anhyd.)  $[\alpha]_D^{20} +34.5^\circ$  to  $+19.9^\circ$  in  $H_2O$ . With  $NHPh \cdot NH_2$  it immediately yields glucosephenylosazone, establishing thus the union in position 2. It is hydrolysed by emulsin. The reducing power towards Fehling's solution is  $\frac{1}{2}$  that of glucose. A simplified prep. of acetochloroglucose from glucose penta-acetate,  $AcCl$ ,  $PCl_5$ , and  $AlCl_3$  is recorded.

H. W.

**$\beta$ -d-Fructosides of phenols.** B. HELFERICH and R. STREECK (Ber., 1936, 69, [B], 1311-1313).—o-Cresol, p- $C_6H_4Me \cdot SO_3H$ , and  $\beta$ -fructose penta-acetate at 100° afford o-tolyl- $\beta$ -d-fructoside tetra-acetate (I), m.p. 127-129° (corr.),  $[\alpha]_D^{20} -156^\circ$  in  $CHCl_3$ , hydrolysed by  $NaOMe$  in  $MeOH$  to o-tolyl- $\beta$ -d-fructoside, m.p. 167-170° (corr.),  $[\alpha]_D^{20} -223^\circ$  in  $H_2O$ , which slowly reduced boiling Fehling's solution and is not appreciably hydrolysed by sweet almond emulsin. (I) is transformed by the successive actions of  $Me_2SO_4$ ,  $NaOH$ , and  $MeI-Ag_2O$  into tetramethyl-o-tolyl- $\beta$ -d-fructoside, m.p. 57-59° (corr.),  $[\alpha]_D^{20} -163^\circ$  in  $CHCl_3$ , which does not reduce Fehling's solution previously to hydrolysis and is converted by 3%  $HCl$  at 90° into 1:3:4:5-tetramethylfructose.

H. W.

**Emulsin. XXVII. Synthesis of the  $\beta$ -d-cellobiose and  $\beta$ -d-maltoside of vanillin and the action of almond emulsin on these substances.** B. HELFERICH and E. WEBER (Ber., 1936, 69, [B], 1411-1414).—The action of acetobromocellobiose in  $COMe$ , on vanillin in  $KOH-H_2O$  gives vanillin- $\beta$ -d-cellobioside hepta-acetate, m.p. 206°,  $[\alpha]_D^{20} -48^\circ$  in  $CHCl_3$ , hydrolysed (Zemplen) to vanillin- $\beta$ -d-cellobioside (I), m.p. 214-216° (decomp.) after becoming discoloured at 170°,  $[\alpha]_D^{20} -73^\circ$  in  $H_2O$  [p-nitrophenylhydrazone, m.p. 251-252° (decomp.)]. Analogously, acetobromomaltose affords vanillin- $\beta$ -d-



*maltoside hepta-acetate*, m.p. 144—145°,  $[\alpha]^{20}_D +27.7^\circ$  in  $\text{CHCl}_3$ , whence *vanillin- $\beta$ -D-maltoside* (II), m.p. 153° and, after resolidification, m.p. 220° (decomp.), (+4H<sub>2</sub>O), m.p. 85°,  $[\alpha]^{20}_D +16.9^\circ$  in H<sub>2</sub>O [p-nitrophenyl-hydrazone, m.p. 208—209° (decomp.)]. Reductometric and polarimetric observation of the course of the hydrolysis of (I) or (II) by sweet almond emulsin (III) affords no evidence of the intermediate formation of cellobiose or maltose; the presence of maltosidases or cellobiosidases in (III) could not be detected.

H. W.

**New hesperidin.** F. KOLLE and K. E. GLOPPE (Pharm. Zentr., 1936, 77, 421—425).—Unripe bitter oranges extracted with  $\text{CHCl}_3$  and with EtOH yield, together with hesperidin (I) (A., 1931, 1041), *neo-hesperidin*, (C<sub>28</sub>H<sub>34</sub>O<sub>15</sub>) (II), m.p. 244°. (I) and (II) are not interconvertible. (II) differs from (I) in being easily hydrolysed by dil. H<sub>2</sub>SO<sub>4</sub>, giving rhamnose and *glucohesperitin*, C<sub>22</sub>H<sub>24</sub>O<sub>11</sub>·H<sub>2</sub>O, m.p. 206°, which is further hydrolysed to hesperitin and glucose. (II) is thus a *rhamnoglucosesperitin*. (II) is not found in ordinary oranges or in ripe bitter oranges.

E. W. W.

**Preparation of sinigrin.**—See this vol., 910.

**Glucoside in *Pardanthus chinensis*.**—See this vol., 910.

**Constituents of seeds of *Blepharis edulis*.**—See this vol., 911.

**Specific polysaccharide from *B. dysenteriae*, Shiga.**—See this vol., 898.

**Determination of nitrate groups in carbohydrate derivatives.** J. DEWAR and (Miss) G. W. BROUGH (J.S.C.I., 1936, 55, 207—208r).—The nitrate content of a sugar derivative may be accurately determined by heating with excess of Devarda's alloy and KOH-EtOH, the N being removed as NH<sub>3</sub> and determined volumetrically; the nitro-group is not affected by this reagent.

F. R. S.

**X-Ray structure of animal and plant polysaccharides.**—See this vol., 1011.

**Hydrolysis and acetolysis of starch and Schardinger's dextrins.** K. FREUDENBERG, G. BLUMQVIST, L. EWALD, and K. SOFF (Ber., 1936, 69, [B], 1258—1266).—Titrimetric and polarimetric observation of the rate of hydrolysis of amylopectin and amyloamylose in 51% H<sub>2</sub>SO<sub>4</sub> and polarimetric observation of the acetolysis of starch triacetate show that starch must be regarded as the  $\alpha$ -analogue of cellulose. Other linkings alternating with maltose unions are excluded and, if present at all, do not form > one of 30 linkings. The cause of slight deviations in the initial parts of the curves cannot yet be established. The graph of the hydrolysis of  $\alpha$ -dextrin (I) in 51% H<sub>2</sub>SO<sub>4</sub>, determined iodometrically, lies between that of starch and maltose; ultimately the reducing power corresponds exactly with that of an equivalent amount of glucose.  $\beta$ -Dextrin (II) shows unexplained reducing power immediately after dissolution in acid; subsequently other CHO groups are developed and the full reducing val. of glucose is attained. The polarimetric curve of (I) rapidly passes through a max., then follows the same course as that of starch, and finally has  $[\alpha]$  for glucose.

The possible presence of one or more rapidly hydrolysed  $\beta$ -linkings is suggested. The graph of (II) exhibits a rise, does not then follow that of starch, and finishes with  $[\alpha]$  of glucose. The presence of I-consuming groups is not here observed. During acetolysis,  $[\alpha]$  of (I), (II), and  $\gamma$ -dextrin increases, and finally attains the val. of glucose. The not very pronounced downward mutarotation of the  $\alpha$ -linkings is > compensated by a pronounced upward action of a linking which is developed at about the same small rate as the fission of the  $\beta$ -linkings in cellulose and cellobiose.  $\beta$ -Glucosan as termination of the chain of the dextrins is excluded. Anhydric or glucosidic termination becomes less probable, particularly since completely methylated (I) does not appear to afford a tetramethylhexose. The possibility of large rings is therefore very cautiously suggested.

H. W.

**Hydrolysis of starch by vegetable amylases.**—See this vol., 894.

**Degradation of starch by acetyl bromide.** K. FREUDENBERG and K. SOFF (Ber., 1936, 69, [B], 1252—1257).—The substance is treated with a mixture of Ac<sub>2</sub>O, AcBr, AcOH, and HBr; the product is poured into H<sub>2</sub>O and extracted with Et<sub>2</sub>O. The extract is shaken with Ag<sub>2</sub>CO<sub>3</sub>, and the maltose hepta-acetate (I) is weighed. Under these conditions starch triacetate gives 21% of (I) at 20° and 22% at 0°. At 0° or 20° the max. yield of (I) from maltose octa-acetate is 56—57%, whereas with AcOH-HBr the max. yield is > 90%. The yields of (I) from maltose anhydride hexa-acetate are 42% and 46% at 20° and 0°, respectively, whereas  $\beta$ -glucosan triacetate gives 83% of acetobromoglucose. Contrary to Karrer (A., 1921, i, 313), therefore, the behaviour of starch differs widely from that of maltose. Polarimetric, reaction-kinetic, and reaction-static observations show that starch is uniformly or greatly preponderantly formed by  $\alpha$ -linkings.

H. W.

**Reducing power and average molecular chain-length of starch and its hydrolysis products, and the constitution of their aqueous pastes.** W. A. RICHARDSON, R. S. HIGGINBOTHAM, and F. D. FARROW (J. Text. Inst., 1936, 27, T131—157).—In determinations of the Cu no. of starch a part of the Cu<sub>2</sub>O produced is lost owing either to its solubility or to accidental oxidation. This is avoided by adding a fixed wt. of glucose to each determination, and deducting the "blank" found with this alone. Cu nos. so determined are independent of the wt. of starch taken, and when starch is hydrolysed with dil. acids there is a linear increase of Cu no. with time, with no initial lag period. Unmodified starches have definite Cu nos. (2.8—8.9 mg. Cu per g.), and if it is assumed that each chain mol. terminates at one end in a reducing group, and that each of these groups reduces as much Cu as does the reducing group in maltose, the average chain-lengths of starches are 460—1470 glucose units. Prolonged acid hydrolysis results in a solution of reducing power equal to that of glucose. It is assumed that during hydrolysis glucosidic linkings are broken in a random manner along the chain mol., and in this case the fracture of a small proportion of the linkings will have a great effect on the average chain length and hence on the  $\eta$ .

Thus if 3% of the linkings in a chain of 1000 units are broken the average length becomes 32.3 units. The production of sol. starch represents this stage of a continuous hydrolytic process. By the cold storage or freezing of a paste a starch can be analysed into a pptd. insol. fraction of low Cu no. and great chain-length and a sol. fraction of high Cu no. and small chain-length. Analysis into amylose and amylopectin is a separation of this type. A. G.

**Fibrous structure of native cellulose in Japanese Kozo and Ganpi.**—See this vol., 927.

**Molecular size of cellulose from different sources.** I. J. K. CHOWDHURY and T. P. BARDHAN (J. Indian Chem. Soc., 1936, 13, 240—252).—Mol. wts. of purified cellulose are determined by the ultracentrifuge method. Cotton (I), jute (II), and bamboo cellulose (III) in Schweitzer's reagent contain 978, 516, and 189 anhydroglucose units, respectively, but above 0.042, 0.058, and 0.122%, respectively (called the "limiting concns."), the mol. wts. appear to rise with concn., indicating breakdown of the method. In viscose (I), (II), and (III) contain 894, 468, and 158 units, respectively, limiting concns. being 0.054, 0.072, and 0.185%, respectively. The triacetates of (I) and (II) in *m*-cresol contain 138 and 56 units, limiting concns. being 0.16 and 0.18%, respectively. After treatment with 42% HCl at 0° (I) and (II) in Schweitzer's reagent contain 13 and 9 units, respectively. The progressive breakdown of the mol. is clearly shown and also that (I), (II), and (III) are not identical. R. S. C.

**Reactions relating to carbohydrates and polysaccharides.** L. Chemical identity of cotton and wood cellulose. J. BARSHA and H. HIBBERT (J. Amer. Chem. Soc., 1936, 58, 1006—1007).—Repeated methylation ( $\text{Me}_2\text{SO}_4$ , 30% wt. NaOH) of spruce- and maple-pulps (dispersed in  $\text{COMe}_2$ ) gives products containing 43.32—43.54% OMe, which if pptd. from  $\text{CHCl}_3$  by light petroleum can be methylated further. The resultant methylcelluloses (44.39—44.63% OMe) are hydrolysed ( $\text{MeOH-HCl}$ ) to 2 : 3 : 6-trimethylmethylglucoside. Bell's assumption (A., 1932, 934) of a "resistant portion" in wood cellulose appears to be unwarranted. H. B.

**Chemical changes occurring during the dissolution of cellulose in Schweitzer's reagent.** W. TRAUBE and A. FUNK (Ber., 1936, 69, [B], 1476—1483).—The dissolution of cellulose (I) in Schweitzer's reagent is considered analogous to that of aliphatic polyhydroxy-compounds or biuret. The isolation of the compound  $[\text{C}_{12}\text{H}_{16}\text{O}_{10}\text{Cu}][\text{Cu en.}]$  (II) indicates also the formation of the substance.

$[\text{C}_{12}\text{H}_{16}\text{O}_{10}\text{Cu}][\text{Cu}(\text{NH}_3)_4]$  (III), although in different compounds the valency of  $[\text{C}_{12}\text{H}_{16}\text{O}_{10}\text{Cu}]$  varies between 1 and 2. The passage of Cu from Cu en. or  $\text{Cu}(\text{NH}_3)_4$  to the anion of a "cupriphile" compound necessitates the assumption that Cu is more firmly united in the latter than in the former; evidence in favour of this view is furnished by the behaviour of biuret. (II) and (III) in solution behave as salts and by double pptn. give salts of which *Tl* and *Ba cupricellulose* are described. For the dissolution of (III) it is necessary that Schweitzer's reagents supplies Cu to both anion and cation, and since the equilibrium

$\text{Cu}(\text{OH})_2 + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4](\text{OH})_2$  lies markedly towards the left, a solution obtained with conc.  $\text{NH}_3$  can *per se* dissolve only small amounts of (III) and the presence of solid  $\text{Cu}(\text{OH})_2$  is necessary for considerable dissolution. Indirectly (III) can be dissolved in solutions obtained with 5—6%  $\text{NH}_3$ . Addition of  $\text{NH}_3$  to  $\text{CuSO}_4$  gives  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  which with NaOH affords  $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ ; if addition of (III) is made simultaneously with NaOH and the mixture is vigorously agitated, dissolution is accomplished before the dissociation of the complex into  $\text{Cu}(\text{OH})_2$  and  $4\text{NH}_3$  has been realised: alternatively, the solution may be cooled to 0° or below, whereby dissociation is retarded and dissolution is more effectively achieved.

H. W.

**Behaviour of salts of cupricellulose towards alkylating agents.** I. W. TRAUBE, R. PIWONKA, and A. FUNK (Ber., 1936, 69, [B], 1483—1493).—*Tl* cupricellulose suspended in dil.  $\text{TlOH}$  is readily converted by MeI at 50° into *hemimethylcellulose* (I), which is freed from *Tl* by dissolution in Schweitzer's reagent and re-pptn. by acid. The product has OMe:cellulose C=1:12—16. It appears homogeneous. Hydrolysis with  $\text{MeOH-HCl}$  and separation of the methylglucoses by distillation in high vac. shows that (I) of lower OMe content contain > one Me per glucose residue, whereas those richer in OMe contain 2 Me in some glucose residues. The possibility of degradation of cellulose during the various reactions is lessened by using Na cupricellulose obtained by action of NaOH and  $\text{Cu}(\text{OH})_2$  on cellulose, or more simply by treating an intimate mixture of cellulose and powdered  $\text{CuCl}_2$  or  $\text{CuSO}_4$  with 16—18% NaOH. The products are readily methylated, and are partly sol. in  $\text{H}_2\text{O}$  when containing 13% OMe, completely sol. in hot and cold  $\text{H}_2\text{O}$  when 14—16% of OMe is present. The stability in boiling  $\text{H}_2\text{O}$  is not due to degradation of the cellulose mol., since the solutions are highly viscous and the products have a very low Cu no. Entry of Me into the mol. beyond the stage of (I) is less uniform, but in no case is the presence of 3 Me per glucose residue observed, so that one OH is shielded from attack. A single methylation does not proceed far beyond the Me stage, but these products can be converted into the Na-Cu derivatives, which with a large excess of NaOH and  $\text{Me}_2\text{SO}_4$  give products with 34.6% OMe in which singly, doubly, and trebly substituted glucose residues are present. The aq. solutions of these products are not stable to boiling. Initial entry of Me occurs in position 3 of the glucose residue, but a uniform entry of 1 Me per cellobiose unit does not occur.

H. W.

**Osmometric investigations of dilute solutions of polymeric carbohydrates.** IX. Mol. size of technical cellulose acetate (cellite) in acetone. M. ULMANN (Ber., 1936, 69, [B], 1442—1447).—Determinations of the mol. wt. of cellite II in  $\text{COMe}_2$  by the method of isothermal distillation gives va's. about 75,000 for the most dil. solutions to those of concn. 1.25%. If, on the basis of observations in  $\text{AcOH}$ , it is assumed that the complexes are formed of even multiples of  $(\text{C}_6)_n$ , a degree of polymerisation  $(\text{C}_6)_{256}$  is indicated. The behaviour of less viscous cellite fraction IV in  $\text{COMe}_2$  indicates a rupture of the mol.



dependent on concn., but even in the most dil. solution the aggregates are more complex than in AcOH at equal concn.

H. W.

**Determination of the osmotic pressure of cellulose derivatives by the membrane method.** M. ULMANN and K. HESS (Ber., 1936, 69, [B], 1426—1437).—Measurements are recorded for a cellite fraction II, m.p. 245°,  $[\alpha]_D^{25} + 6.5^\circ$  in  $\text{COMe}_2$ , in methylglycol acetate,  $\text{COMe}_2$ , and AcOH and of a cellite fraction IV, m.p. 225° (decomp.),  $[\alpha]_D^{25} + 4.8^\circ$  in  $\text{COMe}_2$ , in  $\text{COMe}_2$ . In the normal case the establishment of pressure difference is preceded by a more or less rapid increase of pressure, depending on concn., to the final value. Normal curves are usually obtained in those regions of concn. in which the osmotic pressure obeys van 't Hoff's law. Formation of well-marked max., great delay, and irregularities greatly restrict, the applicability of the method to cellulose esters in org. media. Even if these abnormalities are excluded, great differences ( $>$  experimental error) are observed in the systems when the concn. is  $> 0.6\%$ , so that the influence of the solvent cannot be evaluated. With solutions of medium concn. these differences tend to disappear, whilst in more dil. solution the phenomena are complicated by differences in the state of dissolution in one and the same solvent at a given concn.

H. W.

**Membrane method and method of isothermal distillation with highly polymerised compounds.** K. HESS and M. ULMANN (Ber., 1936, 69, [B], 1448—1456).—The results obtained by determination of the mol. wt. of cellite fractions in AcOH and  $\text{COMe}_2$  by the membrane and isothermal distillation methods are compared; the concordance observed establishes the validity of the latter method. A marked influence of the solvent on the state of dissolution or mol. size is observed. The anomalies observed, particularly at low concn., when the membrane method is used are not attributable to inherent errors of the method caused by the membrane; they occur also when the distillation method is employed, and are a very important indication of the condition of the dissolved substance. The generally accepted idea of the stability of the mols. of cellulose derivatives in org. media is not in harmony with the observations. Dependent on concn. and nature of solvent, the mols. suffer reversible fission, and the size is not const. It is characteristic that the changes in the mol. do not lead to mixtures of indefinite size as required by the kinetic considerations of chain-like unions of mol. groups (Freudenberg *et al.*), but occur in stoichiometric relationships (degradation into fractions which are integral multiples of  $\text{C}_{12}$ ). It is therefore doubtful whether it is advisable to regard the cellulose mol. as a chain in which the  $\text{C}_{10}$  groups are uniformly linked by strict main valencies: rather it must be assumed to be formed by polar or non-polar association of  $\text{C}_{12}$  groups. It appears unlikely that the state of dissolution of a cellulose ester in an org. medium is strictly reproducible. In consequence of retardation phenomena, appreciable variation under apparently comparable conditions may occur.

H. W.

**Reactivity and structure of the primary aliphatic amines.** G. VAVON and L. BOURGEOIS

(Compt. rend., 1936, 202, 1593—1595; cf. this vol., 836).—The rates of interaction of  $\alpha$ - and  $\delta$ -aminoheptane,  $\gamma$ -amino- $\beta\delta$ -dimethylpentane, and  $\gamma$ -amino- $\gamma$ -ethylpentane with  $\text{CH}_3\text{PhBr}$ , 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\text{CH}_2\text{Br}$ ,  $(\text{CH}_3\text{Ph})_2\text{C}_6\text{O}_4$ , and piperonal in PhMe or EtOH are found to decrease as the C chain branches and the hydrocarbon substituent interferes in space with  $\text{NH}_2$ .

J. L. D.

**Use of tetrachlorobenzoquinone for identification of the methylamines.** A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1936, 18, 649—651).—Improvements in the technique of the method are described.

A. L.

**Bouveault's method of preparing aldehydes from mixed organo-magnesium compounds and N-disubstituted formamides.** N. MAXIM and R. MAVRODINEANU (Bull. Soc. chim., 1936, [v] 3, 1084—1093).—By use of an excess of the Grignard reagent the reaction can be used for the prep. of *tert.* bases if aq.  $\text{NH}_4\text{Cl}$  is used in the final decomp.; if acid is used the bases are hydrolysed to the aldehyde. Thus formpiperidylamide (I) and  $\text{MgPr}^n\text{Br}$  (1 : 2 mols.) give 1- $\delta$ -n-heptylpiperidine, b.p. 220° (picrate, m.p. 74°), (I) and  $\text{Mg isobutyl chloride}$  (II) afford 1- $\delta$ - $\beta\gamma$ -dimethylheptylpiperidine, b.p. 230° (picrate, m.p. 129°), whilst (I) and  $\text{CH}_3\text{Ph.MgCl}$  give 1- $\beta$ - $\alpha\gamma$ -diphenylpropylpiperidine, b.p. 345°. (I) and  $\text{MgPhBr}$  (3 mols.) yield PhCHO and  $\text{C}_2\text{Ph}$ , if decomp. is effected with  $\text{H}_2\text{SO}_4$ , whereas 1-benzhydrylpiperidine, b.p. 189°/19 mm., results when aq.  $\text{NH}_4\text{Cl}$  is used. (II) and  $\text{HCO.NMe}_2$  yield dimethyl- $\beta\gamma$ -dimethyl- $\delta$ -heptylamine, b.p. 176° (picrate, m.p. 116°). With  $\text{Mg isoamyl bromide}$   $\text{HCO.NMe}_2$  gives isohexaldehyde and dimethyl- $\beta\delta$ -dimethyl- $\epsilon$ -octylamine, b.p. 198° (picrate, m.p. 104°), and with  $\text{MgPhBr}$  it yields, according to conditions, PhCHO,  $\text{CHPh}_2\text{OH}$ ,  $\text{C}_2\text{Ph}_4$ , or benzhydryldimethylamine, b.p. 265°/13 mm., m.p. 105°.  $\text{HCO.NEt}_2$  is converted by  $\text{MgPhBr}$  into PhCHO,  $\text{C}_2\text{Ph}_4$ , and benzhydryldiethylamine, b.p. 170°/17 mm., m.p. 56°.  $\text{HCO.NPhMe}$  and  $\text{MgPhBr}$  yield PhCHO and  $\text{CHPh}_2\text{OH}$  without  $\text{C}_2\text{Ph}_4$  or *tert.* base. Diphenyl- $\gamma$ -n-amyamine, b.p. 195°/12 mm., is derived from  $\text{HCO.NPh}_2$  and  $\text{MgEtBr}$  whereas PhCHO and  $\text{CHPh}_2\text{OH}$  without  $\text{C}_2\text{Ph}_4$  or *tert.* base are derived from  $\text{HCO.NPh}$ , and  $\text{MgPhBr}$ .

H. W.

**Choline as a factor in the elaboration of adrenaline.**—See this vol., 890.

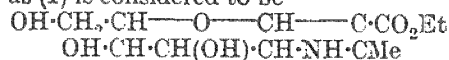
**Behaviour of tri(hydroxyethyl)amine towards tungstic acid.**—See this vol., 947.

**Action of ammonia on propylene oxide, and the synthesis of dimethylmorpholine.** K. KRASUSKI (J. Gen. Chem. Russ., 1936, 6, 460—469).—Propylene oxide and aq.  $\text{NH}_3$  at 0—20° afford  $\text{NH}_3\text{CH}_2\text{CHMeOH}$ , di- $\beta$ -hydroxypropylamine, b.p. 249—250°/745 mm. [platinichloride,  $+2\text{H}_2\text{O}$ , m.p. 120° (decomp.)]; picrate, m.p. 130—136°, from which 2 : 6-dimethylmorpholine is obtained by heating with 70%  $\text{H}_2\text{SO}_4$  (160—170°; 8 hr.), and tri- $\beta$ -hydroxypropylamine, b.p. 190°/23 mm., m.p. 52° (hydrochloride, m.p. 186—188°).

R. T.

**Constitution of the condensation product of glucosamine with ethyl acetoacetate.** F. GARCÍA GONZÁLEZ and R. TRUJILLO TORRES (Anal. Fís. Quím.,

1935, 33, 566—569).—Glucosamine hydrochloride (from the shells of crustaceans) exactly neutralised ( $\text{Na}_2\text{CO}_3$ ) with  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  yields *Et* 2-methyl-5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylpyrrole-3-carboxylate (I), m.p.  $142^\circ$ ,  $[\alpha]_D^{25} +49.7^\circ$ , oxidised ( $\text{KMnO}_4$ ) to 3-carbethoxy-2-methylpyrrole-5-carboxylic acid, m.p.  $200^\circ$  (decomp.), the *Et* ester of which appears to be identical with that of Fischer *et al.* (A., 1932, 281). The compound, m.p.  $128^\circ$ , described by Pauly *et al.* (A., 1922, i, 953) as (I) is considered to be



F. R. G.

Exchange reactions between heavy water and amino-acids and carbohydrates. E. OGAWA (Bull. Chem. Soc. Japan, 1936, 11, 367—374).—For the exchange reactions between heavy water and substances containing exchangeable radicals, expressions for the equilibrium const., where the exchanges are (a) random and (b) stepwise, are derived. Several types of exchange reactions are considered on the basis (a). It is thus shown that a Pt catalyst has no effect on the equilibrium in the case of glucose and heavy water. From a consideration of the equilibrium const. for glutamic acid and asparagine, the structure A is deduced for  $\text{NH}_2$ -acids, and from the electronic structures involved therein, a mechanism is suggested for reactions between aldehydes and ketones and  $\text{NH}_3$ ,  $\text{NH}_2\text{OH}$ ,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , and  $\text{NHPh}\cdot\text{NH}_2$  e.g.,  $-\text{C}\cdot\text{O}+\text{H}_3\text{N}\cdot\text{OH}_2 \rightarrow$

$-\text{C}\cdot\text{O}\cdot\text{H}_2+\text{HN}\cdot\text{OH}_2 \rightarrow -\text{C}(\text{NH})\cdot\text{OH}_2+\text{H}_2\text{O}$ . The equilibrium const. for exchange reactions between heavy water and glycerol, fructose, glucose, galactose, maltose, lactose, starch, and inulin are examined and suggestions are made as to the structure of some of the carbohydrates.

J. T. A.

Oxidation of amino-acids with sodium hypobromite. A. H. FRIEDMAN and S. MORGULIS (J. Amer. Chem. Soc., 1936, 58, 909—913).—Determinations of the  $\text{NaOBr}$  consumed and the  $\text{N}_2$  and  $\text{CO}_2$  produced during oxidation of various  $\text{NH}_2$ -acids lead to the following mechanisms: (a)  $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{NHBr}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  (I); (b) in neutral solution at room temp.: (I)  $\rightarrow \text{NBr}\cdot\text{CHR}\cdot\text{CO}_2\text{H} \rightarrow \text{RCN}+2\text{HBr}+\text{CO}_2$ ; (c) at higher temp. and in alkaline solution: (I)  $\rightarrow \text{NH}\cdot\text{CR}\cdot\text{CO}_2\text{H} \rightarrow \text{RCHO}+\text{CO}_2+\text{NH}_3$ ;  $2\text{NH}_3+3\text{NaOBr} \rightarrow \text{N}_2+3\text{H}_2\text{O}+3\text{NaBr}$ . Little or no  $\text{N}_2$  is produced from glycine, aspartic acid, cysteine hydrochloride, histidine dihydrochloride, and creatinine.

H. B.

Amino-acids. I. Application of Curtius reaction to the synthesis of glycine. P. P. T. SAH (J. Chinese Chem. Soc., 1936, 198—207).—By a modification of the Curtius reaction,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  is converted successively into cyanoacet-hydrazide and -azide and cyanomethylurethane, which is hydrolysed by  $\text{Ba}(\text{OH})_2$  to glycine.

F. R. S.

Electrolytic reduction and oxidation of amino-acetic acid and alanine.—See this vol., 943.

Action of hydroxylamine and phenylhydrazine on glycine anhydride and glycyglycine. A. SPIRIDONOVA (J. Gen. Chem. Russ., 1936, 6, 137—

139).—No reaction takes place, indicating that condensation with the  $\text{CO}$  group is inhibited by the adjacent  $\text{NH}$ .

R. T.

Preparation of  $\epsilon$ -trimethylhexobetaine. F. GIRAL (Anal. Fis. Quím., 1935, 33, 752—753).— $\epsilon$ -Aminohexoic lactam (cf. Ruzicka, A., 1921, i, 591) with 50%  $\text{HCl}$  yields the hydrochloride, m.p.  $131$ — $132^\circ$  (corr.), which with conc.  $\text{KOH}$  and  $\text{Me}_2\text{SO}_4$  gives  $\epsilon$ -dimethylaminohexoic acid methochloride, m.p.  $180^\circ$  (corr.), which with freshly pptd.  $\text{Ag}_2\text{O}$  gives the betaine obtained by Prelog (A., 1931, 204).

F. R. G.

Spontaneous decomposition of cystine dimethyl ether. R. D. COGHILL (J. Biol. Chem., 1936, 114, 419—424).—Cystine  $\text{Me}_2$  ether decomposes at room temp. usually completely in 6 weeks or more rapidly in hot  $\text{MeOH}$  into S (one third of the total amount),  $(\text{NH}_4)_2\text{SO}_4$ , *dl*-alanine anhydride (I), a solid substance (contains S), insol. in  $\text{H}_2\text{O}$ ,  $\text{Et}_2\text{O}$ , and  $\text{EtOH}$ , a solid substance (N 11.8—14.5: S 16—25%) (II), sol. in  $\text{EtOH}$ , insol. in  $\text{Et}_2\text{O}$ , and a liquid substance, about  $\text{C}_{14}\text{H}_{23}\text{O}_6\text{NS}_3$ , b.p.  $155^\circ/17$  mm. Decomposition probably occurs by formation of cystine anhydride, which is expected to be unstable and yield  $\text{CH}_2\cdot\text{C} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{C}\cdot\text{CH}_2$ , which would afford (I) by reduction and (II) by polymerisation and reaction with S.

R. S. C.

Synthesis of djenkolic acid. V. DU VIGNEAUD and W. I. PATTERSON (J. Biol. Chem., 1936, 114, 533—538).—The Na derivative of *l*-cysteine and  $\text{CH}_2\text{Cl}_2$  in liquid  $\text{NH}_3$  give djenkolic acid,  $[\alpha]_D^{25} -44.5^\circ$  in 1%  $\text{HCl}$ , identical with the natural product; the latter is, however, partly racemised during isolation by  $\text{Ba}(\text{OH})_2$ .

R. S. C.

$\alpha$ -Aminoketones. III.  $\beta$ -Ketoheptylamine hydrochloride. J. PASCUAL and J. GARCÍA BOADA. IV. Ethyl aminobutyrylacetate and 2-keto-n-amyamine hydrochlorides. J. PASCUAL and L. HALCÓN (Anal. Fis. Quím., 1935, 33, 804—807, 808—812).—III. The well-cooled oximino-derivative of  $n\text{-C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$  (obtained by hydrolysis of the *Me* ester, b.p.  $156$ — $160^\circ/10$ — $11$  mm., of  $\beta$ -diethylamino- $\beta$ -amylacrylic acid) reduced by  $\text{SnCl}_2$  in conc.  $\text{HCl}$ , followed by  $\text{Sn}$  foil, gives  $\beta$ -ketoheptylamine hydrochloride, decomp.  $157$ — $158^\circ$ .

IV. The oximino-derivative of  $\text{COPr}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  similarly yields *Et*  $\alpha$ -aminobutyrylacetate hydrochloride, decomp.  $126$ — $127^\circ$ , and  $\beta$ -keto-n-amyamine hydrochloride, decomp.  $155$ — $156^\circ$ .

F. R. G.

Derivatives of  $\epsilon$ -azidohexoic acid. E. GRISCHKIEVITSCH-TROCHIMOVSKI and A. SPORZYNSKI (Rocz. Chem., 1936, 16, 37—40).— $\epsilon$ -Bromohexonitrile and  $\text{NaN}_3$  in 50%  $\text{MeOH}$  yield  $\epsilon$ -azidohexonitrile (I), b.p.  $107$ — $108^\circ/3$  mm., from which the expected cyclopentanetetrazole was not obtained by heating at  $160$ — $200^\circ$ , alone, or with  $\text{HgCl}_2$ , or by ultra-violet light. (I) in  $\text{EtOH}$  and  $\text{HCl}$  at  $0^\circ$  afford *Et*  $\epsilon$ -azidohezoate, b.p.  $100^\circ/5$  mm., which with aq.  $\text{NH}_3$  and  $\text{EtOH}$  at  $100^\circ$  yields  $\epsilon$ -azidohezoamide, m.p.  $64.5$ — $65.5^\circ$ .

1.

Interaction of selenium oxychloride with substituted malonamides. R. K. TRIVEDI (J. Univ.



Bombay, 1935, 4, Part II, 114—117).— $\text{SeOCl}_2$  and  $\text{CH}_2(\text{CO}\cdot\text{NHPh})_2$  in dry  $\text{Et}_2\text{O}$  at room temp. give  $\text{CCL}_2(\text{CO}\cdot\text{NHPh})_2$ , but in hot dry  $\text{C}_6\text{H}_6$  mesoxanilide is obtained, probably by way of  $(\text{NHPh}\cdot\text{CO})_2\text{C}\cdot\text{SeO}$ .  $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$  gives similarly mesoxdi-o-, m.p.  $172^\circ$  [hydrate, m.p.  $127\text{--}130^\circ$  (decomp. from  $100^\circ$ )], and -p-toluidide, m.p.  $187^\circ$  (hydrate, m.p.  $122\text{--}130^\circ$ ).

R. S. C.

**Thiocarbamide as key reagent for preparation of aliphatic sulphonyl chlorides and bromides.** T. B. JOHNSON and J. M. SPRAGUE (Science, 1936, 83, 528).— $\text{CS}(\text{NH}_2)_2$  is used in place of P halides in the prep. of these aliphatic halides. The method is illustrated by the synthesis of  $\text{MeSO}_2\text{Cl}$ . L. S. T.

**Ethers of ethane- $\alpha\beta$ -dioxamic acid and their derivatives.** II. W. GAUDE (Rec. trav. chim., 1936, 55, 541—559).—Further esters of the type  $(\text{CO}_2\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2)_2$  are prepared from  $(\cdot\text{CH}_2\cdot\text{NH}_2)_2$  and  $\text{R}_2\text{C}_2\text{O}_4$  (cf. A., 1935, 202): *Pr*<sup>a</sup>, m.p.  $137^\circ$ , *Bu*<sup>a</sup>, m.p.  $142^\circ$ , *di-n-amyl*, m.p.  $137^\circ$ , *di-n-hexyl*, m.p.  $141^\circ$ , and *di-n-heptyl ethane-dioxamate*, m.p.  $139^\circ$ . The  $\text{Et}_2$  ester (I) (*loc. cit.*) reacts with  $\text{NH}_2\text{R}$  to form *Et ethylene- $\alpha$ -oxamate- $\beta$ -oxam-ethyl*, m.p.  $194^\circ$ , -n-propyl-, m.p.  $191^\circ$ , -n-butyl-, m.p.  $187^\circ$ , -n-amyl-, m.p.  $182^\circ$ , -n-hexyl-, m.p.  $181^\circ$ , -n-heptyl-, m.p.  $183^\circ$ , -n-octadecyl-, m.p.  $152^\circ$ , -isopropyl-, m.p.  $204^\circ$ , -isobutyl-, m.p.  $203^\circ$ , -isoamyl-, m.p.  $179^\circ$ , -isohexyl-, m.p.  $178^\circ$ , -allyl-, m.p.  $184^\circ$ , and -benzyl-amide, m.p.  $204^\circ$ , - $\beta$ -oxam-anilide, m.p.  $183^\circ$ , -o-, -m-, and -p-toluidides, m.p.  $190^\circ$ ,  $167^\circ$ , and  $204^\circ$ , and -p-aniside, m.p.  $199^\circ$ . *sec*-Amines do not react with (I). Diamines give compounds of type  $M(\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Et})_2$ ; thus  $\text{CH}_2(\text{CH}_2\cdot\text{NH}_2)_2$ ,  $\text{CH}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$  and o-, m-, and p- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  give *Et*, trimethylene-, m.p.  $330^\circ$  (+ $2\text{H}_2\text{O}$ ), pentamethylene-, m.p.  $285^\circ$ , and o-, m.p.  $250^\circ$ , m-, m.p.  $253^\circ$ , and p-phenylene-bis(oxamido-ethyleneoxamate), m.p.  $320^\circ$ . Treatment of  $(\text{CO}_2\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2)_2$  with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (or  $\text{NHR}'\cdot\text{NH}_2$ ) in ROH yields ester-hydrazides and dihydrazides. The following are described. *Pr*<sup>a</sup>, m.p.  $171^\circ$ , *Bu*<sup>a</sup>, m.p.  $170^\circ$ , -n-amyl, m.p.  $179^\circ$ , and -n-hexyl, m.p.  $178^\circ$ , ethylene- $\alpha$ -oxamate- $\beta$ -oxamhydrazides; *Et ethylene- $\alpha$ -oxamate- $\beta$ -oxam-phenyl*, m.p.  $196^\circ$ , -o-, m.p.  $193^\circ$ , -m-, m.p.  $163^\circ$ , and -p-tolyl-hydrazide, m.p.  $195^\circ$ ; and ethylene- $\alpha\beta$ -bis(oxamphenyl-, m.p.  $265^\circ$ , and -bis(oxam-o-, m.p.  $259^\circ$ , -m-, m.p.  $260^\circ$ , and -p-tolyl-hydrazide), m.p.  $261^\circ$ . The ester-hydrazides with RCHO give hydrazones, suitable for the identification of aldehydes. The following are prepared. Benzaldehyde *Me*, m.p.  $320^\circ$ , *Pr*<sup>a</sup>, m.p.  $216^\circ$ , *Bu*<sup>a</sup>, m.p.  $230^\circ$ , -n-amyl, m.p.  $213^\circ$ , and -n-hexyl, m.p.  $220^\circ$ , ethylene- $\alpha$ -oxamate- $\beta$ -oxamhydrazones; and *acet*-, m.p.  $245^\circ$ , *propion*-, m.p.  $221^\circ$ , -n-butyl-, m.p.  $218^\circ$ , -n-valer-, m.p.  $215^\circ$ , -n-hex-, m.p.  $213^\circ$ , -n-hept-, m.p.  $212^\circ$ , *phenylacet*-, m.p.  $218^\circ$ , o-, m.p.  $226^\circ$ , m-, m.p.  $223^\circ$ , and p-chlorobenz-, m.p.  $273^\circ$ , o-, m.p.  $237^\circ$ , m-, m.p.  $250^\circ$ , and p-nitrobenz-, m.p.  $267^\circ$ , p-tolu-, m.p.  $232^\circ$ , *anis*-, m.p.  $229^\circ$ , *cumin*-, m.p.  $228^\circ$ , *salicyl*-, m.p.  $241^\circ$ , *furfur*-, m.p.  $247^\circ$ , 5-methyl-, m.p.  $199^\circ$ , and 5-hydroxymethyl-furfur-, m.p.  $221^\circ$ , and piperon-aldehyde, m.p.  $254^\circ$ , and *vanillin*, m.p.  $221^\circ$ , *Et ethylene- $\alpha$ -oxamate- $\beta$ -oxamhydrazones*.  $\text{CH}_2\text{O}$ ,  $\text{COMe}$ ,  $\text{COEt}$ , glucose, and mannose, failed to react.

Treatment of ester-amides with  $\text{N}_2\text{H}_4$  gives the amide-hydrazides. *Ethylene- $\alpha$ -oxam*-, m.p. about  $300^\circ$

(impure), - $\alpha$ -oxam-ethyl-, m.p.  $297^\circ$ , -n-propyl-, m.p.  $288^\circ$ , -n-butyl-, m.p.  $287^\circ$ , -n-amyl-, m.p.  $283^\circ$ , -n-hexyl-, m.p.  $276^\circ$ , and -n-heptyl-amide- $\beta$ -oxamhydrazide, m.p.  $274^\circ$ , are prepared. *Ethylene- $\alpha$ -oxam-anilide- $\beta$ -oxamhydrazide*, m.p.  $309^\circ$ , is obtained from the ester-hydrazide and  $\text{NH}_2\text{Ph}$ . With  $\text{PhCHO}$  these give benzaldehyde ethylene- $\alpha$ -oxam-, m.p.  $340^\circ$ , - $\alpha$ -oxam-ethyl-, m.p.  $320^\circ$ , -n-propyl-, m.p.  $319^\circ$ , -n-butyl-, m.p.  $319^\circ$ , -n-amyl-, m.p.  $317^\circ$ , and -n-hexyl-amide- $\beta$ -oxamhydrazone, m.p.  $313^\circ$ , and - $\alpha$ -oxamanilide- $\beta$ -oxamhydrazone, m.p.  $330^\circ$ . p-Chlorobenzaldehyde ethylene- $\alpha$ -oxam-methylamide- $\beta$ -oxamhydrazone, m.p.  $> 340^\circ$ , is also prepared. Action of  $\text{NHPh}\cdot\text{NH}_2$  on the ester-hydrazide yields ethylene- $\alpha$ -oxamhydrazide- $\beta$ -oxamphenylhydrazide, m.p.  $261^\circ$ , from which benzaldehyde ethylene- $\alpha$ -oxamhydrazide- $\beta$ -oxamphenylhydrazide, m.p.  $310^\circ$ , is obtained.

E. W. W.

**Organic reactions with silicon compounds.** II. Reaction of silicon tetrafluoride with Grignard reagent. J. A. GIERUT, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 897—898).— $\text{SiF}_4$  and  $\text{MgAlkBr}$  or, better,  $\text{MgAlkCl}$  give 45—70% of  $\text{MgAlk}_3\text{F}$ , the F atom of which is unreactive. The following are described:  $\text{SiEt}_3\text{F}$ , b.p.  $109^\circ/745$  mm. (accompanied by an approx. equal amount of  $\text{SiEt}_4$ , b.p.  $153^\circ$ ); *Si tripropyl*, b.p.  $175^\circ/745$  mm., *tributyl*, b.p.  $224^\circ/745$  mm., and *triaryl*, b.p.  $267^\circ/745$  mm., fluorides.

H. B.

**Resolution of co-ordinated inorganic compounds into optical isomerides.** Co-ordinated cadmium compounds with racemic and active propylenediamine. P. NEOGI and K. L. MANDAL (J. Indian Chem. Soc., 1936, 13, 224—227).—*Cd r-tripropylenediamine chloride*, bromide, iodide, thiocyanate, camphornitronate,  $[\alpha]_D^{25} +195^\circ$ , camphorsulphonate,  $[\alpha]_D^{30} +23.5^\circ$ , bromocamphorsulphonate,  $[\alpha]_D^{30} +66^\circ$ , and tartrate,  $[\alpha]_D^{30} +27.5^\circ$ , have been obtained; no evidence of resolution was found. The corresponding chloride,  $[\alpha]_D^{30} -37.5^\circ$ , bromide,  $[\alpha]_D^{30} -25.8^\circ$ , iodide,  $[\alpha]_D -26^\circ$ , and thiocyanate,  $[\alpha]_D -23.5^\circ$ , of the *l*-base and chloride,  $[\alpha]_D +26^\circ$ , bromide,  $[\alpha]_D^{30} +26.5^\circ$ , iodide,  $[\alpha]_D^{30} +25^\circ$ , and thiocyanate,  $[\alpha]_D^{30} +24.7^\circ$ , of the *d*-base are described.

C. R. H.

**Triheptylstibine and its derivatives.** C. L. TSENG and W. Y. SHIH (J. Chinese Chem. Soc., 1936, 4, 183—186).—*Triheptylstibine*, b.p.  $229\text{--}231^\circ/50$  mm., is obtained in 18% yield from Mg n-heptyl bromide and  $\text{SbCl}_3$ , and forms *triheptylstibine iodide*, oxide, and metantimonite.

F. R. S.

**Reaction of thallous chloride with certain organic lithium compounds.** N. N. MELNIKOV and G. P. GRATSCHIEVA (J. Gen. Chem. Russ., 1936, 6, 634—635).—The reaction  $2\text{LiR} + \text{TlCl}_3 \rightarrow \text{TlR}_2\text{Cl} + 2\text{LiCl}$  ( $\text{R} = \text{Et}$ ,  $\text{Ph}$ , p- $\text{C}_6\text{H}_4\text{Me}$ ) takes place in  $\text{Et}_2\text{O}$ .

R. T.

**Double salts of indium and organic bases.**—See this vol., 945.

**Kinetics of cyclopentadiene.**—See this vol., 939.

**Phenylcyclopentane and its behaviour during catalytic hydrogenation.** J. I. DENISSENKO (Ber., 1936, 69, [B], 1353—1356).—*cyclopentanone* is converted by  $\text{MgPhBr}$  into phenylcyclopentanol, dehydrated to phenylcyclopentene, which is hydrogenated

to phenylcyclopentane (I), b.p. 216—218°/750 mm. (I) is very readily decomposed by Pt-C at 305—310° into  $\text{CH}_2\text{Ph}[\text{CH}_2]_4\text{Me}$ ,  $\text{CHMePr}^a\text{Ph}$ , and, possibly,  $\text{CHPhEt}$ . H. W.

**Polyatomic peroxides formed in the initial stages of combustion of cyclohexane.** K. I. IVANOV (J. Gen. Chem. Russ., 1936, 6, 470—477).—A non-volatile peroxide (I),  $\text{C}_6\text{H}_9(\text{O}_2\text{H})_2\cdot\text{O}_2\cdot\text{CH}_2\cdot\text{OH}$ , is obtained in 25% yield from atm.  $\text{O}_2$  and cyclohexane at 316°. (I) is probably formed by condensation of  $\text{CH}_2\text{O}$  with  $\text{C}_6\text{H}_9(\text{O}_2\text{H})_3$ . R. T.

**Velocity of the reaction between organic peracids and cyclohexene.**—See this vol., 939.

**Alkylation of naphthenes with olefines in presence of catalysts.** V. N. IPATIEV and A. V. GROSSE [with V. I. KOMAREVSKI] (J. Gen. Chem. Russ., 1936, 6, 433—438).—cycloHexane (I) and  $\text{C}_2\text{H}_4$  in presence of  $\text{AlCl}_3$  at 50—75°/1—15 atm. yield a mixture of 1:3-dimethyl-, 1:2:3:4- and 1:2:4:5-tetramethyl-cyclohexane, and hexaethylbenzene. Methyl- and isopropyl-cyclohexane combine with  $\text{C}_2\text{H}_4$  in presence of  $\text{AlCl}_3$  or  $\text{BF}_3$  at 30—80°/1—15 atm. to yield higher homologues (unidentified) of (I).  $\text{BF}_3$  catalyses condensation of  $\text{C}_2\text{H}_4$  only with hydrocarbons having a tert. C atom. R. T.

**Destructive alkylation with a hydrogenating catalyst.** V. N. IPATIEV and V. I. KOMAREVSKI (J. Amer. Chem. Soc., 1936, 58, 922—923).—Dehydrogenation of cyclohexane over a  $\text{NiO-Al}_2\text{O}_3$  catalyst (A., 1913, i, 65) at 350° is accompanied by "destructive alkylation" (this vol., 322);  $\text{CH}_4$  and  $\text{PhMe}$  are formed with  $\text{H}_2$  and  $\text{C}_6\text{H}_6$ . Ethylcyclohexane (I) or  $\text{PhEt}$  may be an intermediate. (I) similarly gives  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$ , and  $\text{PhMe}$  whilst  $\text{PhEt}$  affords  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , and  $\text{C}_{10}\text{H}_8$ . The  $\text{Al}_2\text{O}_3$  is considered to effect alkylation:  $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlO}(\text{OH})$ ;  $\text{AlO}(\text{OH}) + \text{C}_2\text{H}_4 \rightarrow \text{AlO}(\text{OEt})$ ;  $\text{AlO}(\text{OEt}) + \text{C}_6\text{H}_6 \rightarrow \text{PhEt} + \text{AlO}(\text{OH})$ . No alkylation occurs with Pt-C or Pd-asbestos. H. B.

**Addition and additive products of halogens and benzene derivatives.** VI. Addition of chlorine to the three tetrachlorobenzenes. T. VAN DER LINDEN (Rec. trav. chim., 1936, 55, 421—430).—1:2:3:4- $\text{C}_6\text{H}_2\text{Cl}_4$  (I) and liquid  $\text{Cl}_2$  in sunlight at room temp. give, after 1 month, 1:2:3:3:4:5:6:6-octachloro- $\Delta^1$ -cyclohexene (II), m.p. 178°, which with  $\text{MeOH-NaOH}$  eliminates  $\text{HCl}$ , giving  $\text{C}_6\text{Cl}_6$ , and is reduced by  $\text{Zn-EtOH}$  to (I). The structure of (II) is based on addition of  $\text{Cl}_2$  first to the unsubstituted positions, and then to the ends of the resulting conjugated system. (II) does not lose  $\text{HCl}$  when treated with  $\text{EtOH}$ , and crystallises unchanged from fuming  $\text{HNO}_3$ . As by-products with (II), substances of m.p. 101—104° and 89—93° are obtained, which at room temp. yield  $\text{C}_6\text{Cl}_6$ , and are reduced (Zn) to  $\text{C}_6\text{HCl}_5$ ; these are regarded as mixed crystals of 1:2:3:3:4:4:5:5:6- with 1:2:3:3:3:4:4:5:6:6-enneachloro- $\Delta^1$ -cyclohexene (III), the structures of which are discussed. Both with  $\text{MeOH-NaOH}$  form  $\text{C}_6\text{Cl}_6$ . 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$  and  $\text{Cl}_2$  give, after 3 months, two products. One is regarded as 1:2:3:3:4:4:5:6:6-enneachloro- $\Delta^1$ -cyclohexene (IV), m.p. 89—91°; it is reduced (Zn)

to  $\text{C}_6\text{HCl}_5$  with some  $\text{C}_6\text{Cl}_6$ , and differs from (III) in being converted by  $\text{MeOH-NaOH}$  into  $\text{C}_6\text{Cl}_8$ . The other product, m.p. 120—125°, is reduced to  $\text{C}_6\text{HCl}_5$  and 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$ , and is a mixture, probably of  $\text{C}_6\text{H}_2\text{Cl}_{10}$  and  $\text{C}_6\text{HCl}_9$ . The mother-liquors treated with  $\text{MeOH-NaOH}$  give *p*-quinonoid  $\text{C}_6\text{Cl}_8$ . 1:3:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$  and  $\text{Cl}_2$  in sunlight give, after 4 months, a mixture of  $\text{C}_6\text{Cl}_6$ , enneachloro-cyclohexenes [m.p. 94—95°, mainly (IV)]; converted by  $\text{MeOH-NaOH}$  into  $\text{C}_6\text{Cl}_6$  and  $\text{C}_6\text{Cl}_8$ . 1:2:3:3:4:5:5:6-octachloro- $\Delta^1$ -cyclohexene, and 1:1:2:3:3:4:4:5:5:6-decachlorocyclohexane, m.p. 178°, which is reduced to 1:3:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$ . E. W. W.

**Aromatic nitro-derivatives.** VII. Reactivity of substituents and nuclear substitution in benzene derivatives. A. MANGINI (Gazzetta, 1936, 66, 300—308).—Theoretical. Aromatic substitution, and especially the position of entry of further substituents in di- and tri-substituted  $\text{C}_6\text{H}_6$  derivatives, is considered in relation to Bonino's view that substituents stabilise one of the two possible "tricentric" linkings in  $\text{C}_6\text{H}_6$ . Multiple substituents are either in "concordance" or in "opposition," and the influence of this, and of dipole moments, on stability and on further substitution is discussed. E. W. W.

**Raman effect of homocyclic compounds.**—See this vol., 923.

**Normal frequencies of vibration of benzene compounds in ultra-violet absorption.**—See this vol., 921.

**Benzene rings.** P. LAROSE (Chem. and Ind., 1936, 547—548).—A plea for the consistent use of regular hexagons to represent  $\text{C}_6\text{H}_6$  rings in the literature. F. N. W.

**Interference measurements with benzene derivatives.** R. SCHOPPE (Z. ges. Naturwiss., 1935, 1, 122—124; Chem. Zentr., 1935, ii, 2041; cf. this vol., 976).—X-Ray measurements with  $\text{C}_6\text{H}_6$  and  $\text{PhCl}$  confirm the planar hexagonal structure of  $\text{C}_6\text{H}_6$ ; "buckled" models are excluded. The following distances are found:  $\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}=1.42$  Å.,  $\text{C}_{\text{Ar}}-\text{Cl}=1.65$  Å.,  $\text{C}_{\text{Ar}}-\text{Br}=1.86$  Å., and  $\text{Br}-\text{Br}=6.56$  Å. (in *p*- $\text{C}_6\text{H}_4\text{Br}_2$ ) and 3.80 Å. (in *o*- $\text{C}_6\text{H}_4\text{Br}_2$ ). H. N. R.

**Olefine-benzene condensation with the sulphuric acid catalyst.** H. L. WUNDERLY, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1007—1009; cf. A., 1935, 1358).—The effects of temp., time, amount of  $\text{H}_2\text{SO}_4$ , and  $\text{BF}_3$  on the reaction between  $\text{C}_6\text{H}_6$  and  $\text{C}_3\text{H}_6$  are studied. Contrary to Ipatiev *et al.* (see below),  $\text{BF}_3$  is a promoter.  $\text{C}_6\text{H}_6$  and  $\text{C}_2\text{H}_4$  with  $\text{H}_2\text{SO}_4 + \text{BF}_3$  (not with  $\text{H}_2\text{SO}_4$  alone) at 10—20° give some  $\text{PhEt}$  and  $\text{C}_6\text{H}_4\text{Et}_2$ . A reaction mechanism (involving an "activated" olefine) is discussed. H. B.

**Influence of sulphuric acid concentration on reaction between olefines and benzene.** V. N. IPATIEV, B. B. CARSON, and H. PINES (J. Amer. Chem. Soc., 1936, 58, 919—922).—Alkylation is the main reaction when  $\text{C}_6\text{H}_6$  is treated with  $\text{C}_3\text{H}_6$  in presence of cold 96%  $\text{H}_2\text{SO}_4$  and leads to  $\text{PhPr}^{\beta}$ , *p*- $\text{C}_6\text{H}_4\text{Pr}^{\beta}_2$ ,  $\text{C}_6\text{H}_3\text{Pr}^{\beta}_3$ , and 1:2:4:5- $\text{C}_6\text{H}_2\text{Pr}^{\beta}_4$ ;  $\text{PhPr}^{\beta}$  and



$C_6H_4Pr^s$  similarly give  $C_6H_3Pr^s$  and  $C_6H_2Pr^s$ . In 80%  $H_2SO_4$  alkylation and ester formation ( $Pr^s_2SO_4$ ) occur to about the same extent. *iso*Butene (I),  $C_6H_6$ , and 96%  $H_2SO_4$  give (mainly)  $PhBu^r$ ,  $p$ - $C_6H_4Bu^r_2$  (chief product under conditions used), and  $C_6H_3Bu^r_3$ ; (I) is largely polymerised by 80%  $H_2SO_4$ , whilst  $Bu^r_2SO_4$  is the sole product with 70%  $H_2SO_4$ .  $PhMe$ ,  $C_3H_6$ , and 96%  $H_2SO_4$  afford  $p$ - $C_6H_4MePr^s$  and (probably)  $C_6H_3MePr^s_2$ ;  $C_{10}H_8$  similarly gives  $C_{10}H_7Pr^s$  (?).  $C_6H_6$  with  $\Delta^o$ -butene, pentene, octene, nonene, and dodecene (mixtures) in 96%  $H_2SO_4$  gives (usually) mono- and di-alkylbenzenes; the following are described: mono- and di-*sec*.-butyl-, *tri*amyl-, b.p. 282–288° and 312–318°, *di*octyl-, b.p. 338–343°, *dinonyl*-, b.p. 153–163°/5 mm., and *didodecylbenzene*, b.p. 197–211°/5 mm. Alkylation is considered to occur through the intermediate  $Alk_2SO_4$ .  $BF_3$  is unnecessary for the reaction between  $C_6H_6$ ,  $C_3H_6$ , and  $H_2SO_4$  under the conditions used by Slanina *et al.* (A., 1935, 1358). H. B.

**Alkylation accompanying depolymerisation.** V. N. IPATIEV and H. PINES (J. Amer. Chem. Soc., 1936, 58, 1056).—*Diisobutene* (I),  $C_6H_6$ , and 96%  $H_2SO_4$  at 0° give  $PhBu^r$ ,  $p$ - $C_6H_4Bu^r_2$  (II), and  $C_6H_3Bu^r_3$ . (II) is similarly obtained from  $PhBu^r$  and (I) or *triisobutene*, whilst  $C_6H_6$  and *dibutene* afford *p*-di- and *tri-sec*.-butylbenzenes. The same type of reaction occurs with (I),  $C_6H_6$  or *cyclohexane*, and  $AlCl_3$ . The term “depolyalkylation” is proposed for such reactions. H. B.

**Phosphoric acid as catalyst for destructive alkylation of hydrocarbons.** V. N. IPATIEV, V. I. KOMAREVSKI, and H. PINES (J. Amer. Chem. Soc., 1936, 58, 918–919).—“Destructive alkylation” (this vol., 322) occurs when  $C_6H_6$  is treated with  $\beta\beta$ -trimethylpentane or  $n$ - $C_6H_{14}$  in presence of 100%  $H_3PO_4$  and  $N_2$ . The following reactions take place: (i)  $CMe_3 \cdot CH_2 \cdot CHMe_2 + C_6H_6 \rightarrow CHMe_3 + PhBu^r$ ; (ii)  $2C_6H_{14} + 2C_6H_6 \rightarrow C_3H_8 + C_2H_6 + PhBr^s + PhBu$ . H. B.

**Action of excess of bromine on benzene derivatives in presence of beryllium bromide.** R. PAJEAU (Compt. rend., 1936, 202, 1795–1796; cf. this vol., 461).— $C_6H_6$ ,  $PhMe$ , *o*-, *m*-, and *p*-xylene with excess of  $Br$  in presence of  $BeBr_2$  at room temp. afford  $p$ - $C_6H_4Br_2$ , 2:4:5- $C_6H_3MeBr_3$ , and the 3:4:5:6-, 2:4:5:6-, and 2:3:5:6-tetrabromoxylene, respectively.  $PhCl$  and  $PhI$  similarly afford  $p$ - $C_6H_4ClBr$  and  $p$ - $C_6H_4ClI$  on heating.  $o$ - $C_6H_4MeCl$  affords a  $Br_2$ -derivative, m.p. 98.5°, which is oxidised ( $HNO_3$ , *d* 1.2) to a chlorodibromobenzoic acid, m.p. 190°. *m*- and *p*- $C_6H_4MeCl$  similarly afford  $Br_2$ -derivatives, m.p. 96.5° and 99°, respectively; the latter is oxidised to an acid, m.p. 185°. J. L. D.

**“ortho-Effect” in dihalogenobenzenes.** R. SCHOPPE and K. L. WOLFF (Z. ges. Naturwiss., 1935, 1, 67–68; Chem. Zentr., 1935, ii, 2040–2041).—Possible modes of interaction of *o*-substituents are discussed. By X-ray measurements on the vapours, the Cl–Cl distance is found to be  $6.1 \pm 0.09$  Å. in *p*- and  $3.3 \pm 0.05$  Å. in *o*- $C_6H_4Cl_2$ . The latter val. is > that calc. for an angle of 60° between the C–Cl linkings. H. N. R.

**Behaviour of aromatic compounds at the anode in nitric acid solutions.** C. B. MEDINSKI (Acta Univ. Asiae Mediae (Tashkent), 1933, Ser. VI, No. 6, 5 pp.).—Experiments on the electrolytic nitration of  $OH \cdot C_6H_3(NO_2)_2$ ,  $PhSO_3H$ , and  $C_6H_6$  in presence of  $KNO_3$  and  $Na_2SO_4$  show that only the compounds insol. in  $H_2O$  were nitrated.  $H_2O$ -sol. compounds were predominantly oxidised.

CH. ABS. (e)

**Synthesis of *s*-tridiphenylbenzene and *s*-tri(benzylphenyl)benzene.** Z. SKROWACZEWSKA and E. SUCHARDA (Rocz. Chem., 1936, 16, 151–155).—*p*-Diphenylmethyl ketone and conc.  $HCl$  (180°; 34 hr.) or  $PhSO_3H$  (100°; 7 hr.) yield *s*-tridiphenylbenzene, m.p. 232°, oxidised by  $CrO_3$  in  $AcOH$  to  $p$ - $C_6H_4Ph \cdot CO_2H$ .  $CH_2Ph \cdot C_6H_4 \cdot COMe$  and conc.  $HCl$  (180°; 60 hr.) afford *s*-tri(benzylphenyl)benzene, m.p. 168–169°, oxidised similarly to  $p$ - $C_6H_4Ph \cdot CO_2H$ . R. T.

**Friedel and Crafts reaction. I. Polyhalogen derivatives of triphenylmethane.** S. D. WILSON and H. T. HUANG (J. Chinese Chem. Soc., 1936, 4, 142–148).— $p$ - $C_6H_4Cl_2$ ,  $CHCl_3$ , and  $AlCl_3$  in the absence of solvents give 2:5:2':5':2'':5''-hexachlorotriphenylmethane, m.p. 206–208°, and with  $p$ - $C_6H_4Br_2$ , the  $Br_6$ -compound, m.p. 225–227°, is obtained.  $p$ - $C_6H_4Cl_2$ ,  $CCl_4$ , and  $AlCl_3$  afford two isomeric substances, m.p. 179–180°, and m.p. 70–100°, probably forms of 1:4:7:9-tetrachloro-9-2':5'-dichlorophenylfluorene. F. R. S.

**Preparation of diphenyldiacetylene.** J. S. SALKIND and B. M. FUNDLER (J. Gen. Chem. Russ., 1936, 6, 530–533).— $CPh \cdot CH$  is added to  $CuCl$  in 30% aq.  $NH_4Cl$  containing 0.2% of  $HCl$ , at the b.p., and the salt,  $C_{16}H_{10}CuCl$ , separating out after 5–6 hr. is decomposed by  $Et_2O$  to give  $(CPh \cdot C)_n$  (18% yield). R. T.

**Anthracene derivatives. I.** B. P. FEDOROV (J. Gen. Chem. Russ., 1936, 6, 444–454).—9:10-Dichloroanthracene in  $PhNO_2$  and 20% oleum at 12–15° yield the 2-sulphonic acid (I), m.p. 212.1° (decomp.) [ $+2.5H_2O$ , m.p. 158–159°; *chloride* (II), m.p. 221–225° (decomp.); *amide*, m.p. 279°; *Et* ester, m.p. 159°; *anilide*, m.p. 247.8°], the Na salt of which yields Na anthrone-2-sulphonate when heated with 30%  $NaOH$  (190–200°; 10 hr.). (II) and Zn in  $PhMe$  (110°; 12 hr.) yield the corresponding Zn sulphinate, which with Zn and  $HCl$  (100°; 8 hr.) affords 9:10-dichloro-2-thiolanthracene, readily oxidised by atm.  $O_2$  to the *disulphide*, m.p. 235°. R. T.

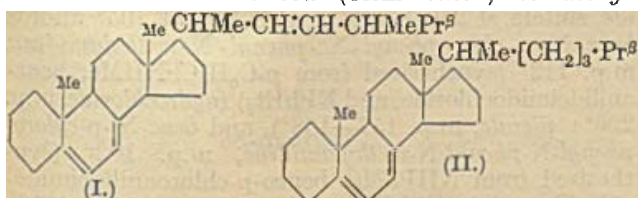
**1-Methylnaphthalene derivatives. III.** K. DZIEWONSKI and E. KOWALCZYK (Bull. Acad. Polonaise, 1935, A, 559–563; cf. A., 1935, 1116).—Treatment of 1- $C_{10}H_7Me$  with 100%  $H_2SO_4$  at 165–175° affords 1:3- and 1:6- $C_{10}H_6Me \cdot SO_3H$ , separated by means of the sparing solubility of their Ba salts in  $H_2O$ , and 1:7- $C_{10}H_6Me \cdot SO_3H$  isolated as the Ba salt (I) which is freely sol. in  $EtOH$ . The corresponding Na and  $NH_2Ph$ , m.p. 209–211°, salts, 1-methylnaphthalene-7-sulphonyl chloride, m.p. 88°, and -sulphonamide, m.p. 116°, are described. (I) is converted by  $KOH$  at 180° into 1:7- $C_{10}H_6Me \cdot OH$  (*Bz* derivative, m.p. 85–86°), transformed by  $(NH_4)_2SO_3 \cdot NH_3$  at 150–190° into 1:7- $C_{10}H_6Me \cdot NH_2$  (*Ac* derivative, m.p. 158–159°). H. W.

**Spatial configuration of fluorene and its derivatives.**—See this vol., 927.

**Action of sulphuryl chloride on polynuclear, aromatic hydrocarbons.** I. A. PONGRATZ and E. EICHLER (Ber., 1936, 69, [B], 1292—1294).—The reaction is studied under conditions which appear to exclude the possibility of dissociation of  $\text{SO}_2\text{Cl}_2$  into  $\text{SO}_2$  and  $\text{Cl}_2$ . Pyrene and  $\text{SO}_2\text{Cl}_2$  in  $\text{CCl}_4$  at room temp. slowly give chloropyrene, m.p. 119—120°, in small yield. Perylene in boiling  $\text{C}_6\text{H}_6$  gives a mixture of dichloroperylene. Chrysene does not react.  $\text{C}_{10}\text{H}_8$  affords 1:2:3:4-tetrachlorotetrahydronaphthalene, m.p. 187° (decomp.), and  $\text{SO}_2$ , probably amongst other products. A parallelism appears to exist between readiness of reaction with  $\text{SO}_2\text{Cl}_2$  and ease of hydrogenation. H. W.

**2-Methyl-1:9-aceanthrene.** A. DANSI and A. SEMPRONJ (Gazzetta, 1936, 66, 182—186).— $\beta$ -Methylanthracene with  $\text{C}_2\text{O}_2\text{Cl}_2$  in  $\text{CS}_2$  and  $\text{AlCl}_3$  yields a methylaceanthrenequinone, m.p. 258° [semicarbazone, m.p. 278—280° (decomp.)] [insol. in  $\text{NaHSO}_3$  and oxidised ( $\text{CrO}_3$ ) to 2-methylanthraquinone-1-carboxylic acid, m.p. 268°, isolated by Mayer (A., 1930, 1042)], and an isomeride, m.p. 206—208°, oxidised to anthraquinone-2-carboxylic acid, m.p. 295° (Butescu, A., 1913, i, 273). The quinones on distillation with Zn powder and sublimation of the product in a vac. yield methylaceanthrenes of m.p. 122° and 99°, respectively, the former being 2-methyl-1:9-aceanthrene. F. O. H.

**Ergostatriene and  $\Delta^7$ -dehydrocholestene.** K. DIMROTH and G. TRAUTMANN (Ber., 1936, 69, [B], 669—675).—The absorption spectra of ergostatriene (I) and  $\Delta^7$ -dehydrocholestene are precisely similar to that of ergosterol (III). The OH of (III) has therefore no significance with respect to the marked absorption bands between 260 and 290  $\mu$ ; these are due solely to the conjugated double linkings in ring B of the cyclopentanohydrophenanthrene skeleton. Ergosteryl acetate-maleic anhydride is oxidised by  $\text{CrO}_3$  in AcOH to ergoster-3-one-maleic anhydride, m.p. 178—179°, which is reduced (Clemmensen) to deoxy-



ergosterol-maleic anhydride, m.p. 176—177°, which passes when heated at 220°/12 mm. into (I), m.p. 99—100°. 7-Ketocholestene is reduced by  $\text{Al}(\text{OPr}^i)_3$  in boiling  $\text{Pr}^i\text{OH}$  to 7-hydroxycholestene (IV), m.p. 93—94°, which with boiling  $\text{Ac}_2\text{O}$  gives a hydrocarbon,  $\text{C}_{27}\text{H}_{44}$ , m.p. 91°. (IV) is transformed by  $\text{BzCl}$  in anhyd.  $\text{C}_6\text{H}_5\text{N}$  into the benzoate, m.p. 108—109°, which passes at 120—125°/high vac. into  $\text{BzOH}$  and (III), m.p. 88—89°,  $[\alpha]_D^{25}$  —127° in  $\text{CHCl}_3$ . H. W.

**Oxidation of cyclo-pentyl- and -propyl-amine.** N. J. DEMJANOV and Z. I. SCHUKINA (J. Gen. Chem. Russ., 1936, 6, 350—358).—cyclopentylamine in  $\text{H}_2\text{O}$  and  $\text{O}_2$  in presence of Cu or  $\text{OsO}_4$  afford cyclopentanone and  $\text{NH}_3$ . cyclopropylamine in  $\text{Et}_2\text{O}$  or  $\text{H}_2\text{O}$  and Cu yield  $\text{CH}_2\text{:CH}\cdot\text{CHO}$  (I) and  $\text{NH}_3$ ,

whilst in presence of  $\text{OsO}_4$ , cyclopropanone and its hydrate are formed as intermediate products, which isomerise to yield (I) and  $\text{EtCO}_2\text{H}$ . R. T.

**Action of primary aromatic amines on ethyl hypophosphate.** A. E. ARBUSOV and B. P. LUGOVKIN (J. Gen. Chem. Russ., 1936, 6, 394—403).— $\text{Et}_4$  hypophosphate yields the following compounds, of the probable structure  $\text{NR:P}(\text{OH})(\text{OEt})_2$ : with  $\text{NH}_2\text{Ph}$ , m.p. 70.5—71.5°; with *p*-toluidine, m.p. 74—75°; with 3:4-dimethylaniline, m.p. 94—95°; with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ , m.p. 67—68°. The products are sol. in  $\text{H}_2\text{O}$ , and are readily hydrolysed by aq.  $\text{NaOH}$ . R. T.

**Molecular dissymmetry due to symmetrically placed hydrogen and deuterium. I. Resolution of  $\alpha$ -pentadeuterophenylbenzylamine.** G. R. CLEMO and A. MCQUILLEN (J.C.S., 1936, 808—810).— $\text{C}_6\text{D}_6$  with  $\text{BzCl}$  in boiling  $\text{CS}_2$  containing  $\text{AlCl}_3$  affords pentadeuterobenzophenone, b.p. 160°/15 mm. (oxime, m.p. 140°, undepressed by benzophenoneoxime) (cf. A., 1935, 806; this vol., 604). The oxime in dil.  $\text{NaOH}$  at 100° with Na-Hg affords *dl*- $\alpha$ -pentadeuterophenylbenzylamine, which rapidly absorbs  $\text{CO}_2$ , and is resolved into *d*- $\alpha$ -pentadeuterophenylbenzylamine 1-*H* tartrate (I), m.p. 181°,  $[\alpha]_D^{25}$  —13.2°, and *l*- $\alpha$ -pentadeuterophenylbenzylamine *d*-*H* tartrate (II), m.p. 181°,  $[\alpha]_D^{25}$  +13.2°. (I) and (II) afford with  $\text{NaOH}$  and then  $\text{H}_2\text{C}_2\text{O}_4$ , oxalates,  $[\alpha]_D^{25}$  +2.2° and —2.5°, respectively, from which the free *d*-,  $[\alpha]_D^{25}$  +5.0°, and *l*-bases,  $[\alpha]_D^{25}$  —5.7° (cf. A., 1934, 832; this vol., 604), are prepared. J. L. D.

**Molecular compounds of acid anhydrides with amines.** R. KOJIMA (Sci. Rept. Tokyo Bunrika Daigaku, 1936, 3, 71—88).—The constitution of mol. compounds of acid anhydrides with amines has been determined by measurement of eutectic points, with the following results:  $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  (1:1);  $\text{C}_6\text{H}_2(\text{CO})_2\text{O}$ , with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  (2:1),  $\text{NHPH}_2$  (1:1), antipyrine (3:2), pyrimidone (1:1);  $\text{Bz}_2\text{O}$  with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  (1:1), antipyrine (1:1), pyrimidone (1:1); and  $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  with  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$  (1:1),  $\text{NHPH}_2$  (2:1). F. R. S.

***p*-Toluidine in binary systems with certain phenols.**—See this vol., 931.

**Manufacture of substituted aromatic amino-compounds [sulphones].**—See B., 1936, 488.

**Relative hypnotic effects of some aryl- and unsymmetrical arylalkyl-thiocarbamides.** E. J. DEBEER, J. S. BUCK, W. S. IDE, and A. M. HJORT (J. Pharm. Exp. Ther., 1936, 57, 19—33).—The following new *as*. thiocarbamide derivatives have been prepared by condensing the appropriate amine (1 mol.) with KCNS (1.1 mol.) in aq. solution containing conc.  $\text{HCl}$  (1.3 mol.), the *sec*. amines prepared by alkylation of the primary amines (I), being freed from unchanged (I) by treatment with a conc.  $\text{PhCHO}\cdot\text{NaHSO}_3$  solution; *m*-, m.p. 166°, and *p*-anisyl, m.p. 218°, *o*-, m.p. 109°, and *m*-tolylmethyl, m.p. 76°, *o*-, m.p. 104°, *m*-, m.p. 145°, and *p*-anisylmethyl, m.p. 148°, *o*-, m.p. 97°, *m*-, m.p. 111°, and *p*-phenetilmethyl, m.p. 144°, *o*-, m.p. 93°, *m*-, m.p. 108°, and *p*-tolylethyl, m.p. 101°, *o*-, m.p. 118°, *m*-, m.p. 128°, and *p*-anisylethyl, m.p. 140°, *o*-, m.p. 99°, *m*-, m.p. 152°, and *p*-



*phenylethyl*, m.p. 106°, *n-phenylpropyl*, m.p. 108°, *o-*, m.p. 87°, *m-*, m.p. 115°, and *p-tolyl-n-propyl*, m.p. 78°, *o-*, m.p. 85°, *m-*, m.p. 153°, and *p-anisyl-n-propyl*, m.p. 122°, *o-*, m.p. 124°, *m-*, m.p. 173°, and *p-phenetyl-n-propyl*, m.p. 103°, *phenyl-*, m.p. 89°, *o-*, m.p. 68°, *m-*, m.p. 66°, and *p-tolyl-n-butyl*, m.p. 98°, *o-*, m.p. 94°, *m-*, m.p. 106°, and *p-anisyl-n-butyl*, m.p. 129°, *o-*, m.p. 126°, *m-*, m.p. 126°, and *p-phenetyl-n-butyl*, m.p. 78°, *phenyl-*, m.p. 78°, *o-*, m.p. 73°, *m-*, and *p-tolyl-n-amyl*, m.p. 78°, *o-*, m.p. 80°, *m-*, m.p. 85°, and *p-anisyl-n-amyl*, m.p. 139°, *o-*, m.p. 122°, *m-*, m.p. 103°, and *p-phenetyl-n-amyl*, m.p. 123°. In a homologous series, the hypnotic effect on mice increases with increase in mol. wt. until the Pr or amyl member (according to the series) is reached, after which it remains approx. const. The lower members of the series are more potent than the corresponding carbamide analogue; the higher members are approx. equally active.

W. O. K.

**Optically active imides.** O. LUTZ (Ber., 1936, 69, [B], 1333—1337).—*l*-Anilinosuccinoanil has m.p. 211.5—212°,  $[\alpha]_D^{20}$  —12.4° in  $C_5H_5N$ . *p-Toluidine* *l-p-toluidinosuccinate*, m.p. 157°,  $[\alpha]_D^{20}$  +44.8°, +53.3°, and +57.8° in presence of 1, 4, and 39 mols. of HCl, respectively, obtained from *p-C\_6H\_4Me-NH\_2* and *l*-bromosuccinic acid under defined conditions, passes when slowly heated to 155° into *l-p-toluidinosuccino-p-tolil*, m.p. 215—215.5°,  $[\alpha]_D^{20}$  —11.2° in  $C_5H_5N$ . *m-Toluidine* *l-m-toluidinosuccinate*, m.p. 126—126.5°,  $[\alpha]_D^{20}$  +32.7°, +40.8° and +46.2° in presence of 1, 5, and 40 mols. of HCl, respectively, *l-m-toluidinosuccino-m-tolil*, m.p. 120—121°,  $[\alpha]_D^{20}$  —21.9° in  $C_5H_5N$ , *o-toluidine* *l-o-toluidinosuccinate*, m.p. 104°, and *l-o-toluidinosuccino-o-tolil*, m.p. 109—111°,  $[\alpha]_D^{20}$  —3.7°, are described.

H. W.

**Ethyl esters of  $\beta$ -arylaminoacrotonic acids.** S. COFFEY, J. K. THOMSON, and F. J. WILSON (J.C.S., 1936, 856—859).—Carefully purified  $CH_3Ac-CO_2Et$  (1 mol.) with  $NH_2Ph$  (1 mol.) and a little  $NH_2Ph.HCl$  at room temp. affords Et  $\beta$ -anilinocrotonate (cf. A., 1884, i, 302). A drop of HCl or I catalyses the reaction. The following are similarly prepared, with or without a catalyst: Et  $\beta$ -*p*-phenetidino-, m.p. 54—54.5° (lit., 60—61°),  $\beta$ -*m*-4-xyloidino-, b.p. 123—124°/2 mm. (cf. A., 1919, i, 453),  $\beta$ -*p*-xyloidino- (I), b.p. 132—133°/2—3 mm.,  $\beta$ -*p*-phenylaminoanilino-, m.p. 77—78°,  $\beta$ -*o*- (II), b.p. 141—143°/2 mm., and  $\beta$ -*m*-chloroanilino-crotonate, b.p. 145—148°/1—1.5 mm. Nitroanilines do not enter into reaction as above. (I) with *p*-xylidine in boiling petroleum (b.p. > 120°) affords  $\beta$ -*p*-xylidinocrotono-*p*-xylidine in poor yield. Similarly, (II) affords  $\beta$ -*o*-chloroanilinocrotono-*o*-chloroanilide. The other Et  $\beta$ -arylaminoacrotates do not react similarly, which indicates that they do not form an intermediate stage in the prep. of  $\beta$ -arylaminoacrotanoarylamides.

J. L. D.

**Amidines. I. Synthesis of symmetrical and unsymmetrical benzdiphenylamidines, and new reactions of amidines.** S. P. JOSHI, A. P. KHANOLKAR, and T. S. WHEELER (J.C.S., 1936, 793—797).—Many arylamines with benzotrichloride in  $PhNO_2$  at 165° afford *s*-benzdiphenylamidines. The following are prepared using the appropriate arylamine: *s-benzdi-p-nitrophenyl-* (I), m.p. 190° [also prepared

from benzo-*p*-nitroanilideimidochloride (which may be an intermediate product in the above reaction),  $-NO_2 \cdot C_6H_4 \cdot NH_2$ , and  $NPhEt_2$  at 100°] (*hydrochloride*, sinters at 265°; *Ac* and *N-Me* derivatives, m.p. 182—183° and 188°, respectively), *m-nitrophenyl-* (II), m.p. 147—148° (*hydrochloride*, m.p. 275°; *sulphate*, m.p. 196°; *Ac*, *Bz*, and *N-Me* derivatives, m.p. 135—136°, 195—196°, and 114—115°, respectively), *m-tolyl-* (III), m.p. 135° (*N-Me* derivative, m.p. 90°), *p-chlorophenyl-* (IV), m.p. 143° (*hydrochloride*, decomp. > 250°; *sulphate*, m.p. 201°; *Bz* and *N-Me* derivatives, m.p. 155—156°, and 153—154°, respectively), *s-tribromophenyl-amidine*, m.p. 196—197° (*Ac*, *Bz*, and *N-Me* derivatives, m.p. 173—174°, 235—237°, and 160—161°, respectively). *o-* and *m*-Nitro-*p*- and *p*-nitro-*o*-toluidine and 2:4-dinitroaniline will not react.  $CPhCl_3$  reacts with  $NHPhAc$  at 150° to give *s*-acetdiphenylamidine and  $NHPhBz$ .  $p-C_6H_4Cl-NHBz$  with  $NH_2Ph$  in dry boiling  $C_6H_6$  containing  $PCl_5$  (A., 1927, 144) affords *benz-N-p-chlorophenyl-N'-phenylamidine* (V), m.p. 120—122° (also obtained from  $CPhCl_3$ ,  $NH_2Ph$ ,  $p-C_6H_4Cl-NH_2$ , and  $PhNO_2$ ; and from benzo-*p*-chloroanilideimidochloride,  $NH_2Ph$ , and  $NPhEt_2$ ) (*hydrochloride*, m.p. 260—262°; *Bz* derivative, m.p. 155—156°). The following are prepared similarly: *benz-N-p-bromophenyl-N'-phenyl-* (VI), m.p. 123° (*hydrochloride*, m.p. 265—266°), *N-p-chlorophenyl-N'-p-methoxyphenyl-*, m.p. 117—119° (*hydrochloride*, m.p. 260°; *picrate*, m.p. 165—166°), *N-p-chlorophenyl-N'-p-ethoxyphenyl-*, m.p. 95—98° (*hydrochloride*, m.p. 242—244°; *picrate*, m.p. 147—148°), *N-p-chlorophenyl-N'-p-tolyl-*, m.p. 134° [*hydrochloride*, m.p. 283° (decomp.); *picrate*, m.p. 189—190°], *N-p-nitrophenyl-N'-m-nitrophenyl-*, m.p. 170° (*hydrochloride*, sinters at 238°), *p-nitrophenyl-N'-p-tolyl-*, m.p. 159—160° (*hydrochloride*, sinters at 258°), *N-p-nitrophenyl-N'-m-4-xylyl-*, m.p. 143—144° (*hydrochloride*, sinters at 237°), *N'-p-chlorophenyl-N-p-nitrophenyl-*, m.p. 174—175° (*hydrochloride*, sinters at 272°), *N'-p-bromophenyl-N-p-nitrophenyl-amidine*, m.p. 170—171° (*hydrochloride*, sinters at 270°), and *p-nitrobenz-N-p-nitrophenyl-N'-phenylamidine*, m.p. 223° (*hydrochloride*, sinters at 250°). (III) with  $MeI$  at 105° affords *benz-N-p-chlorophenyl-N'-phenyl-N-methylamidine*, m.p. 112° (synthesised from  $p-C_6H_4Cl-NHMe$ , benzoanilideimidochloride, and  $NPhEt_2$ ) (*hydrochloride*, m.p. 226°; *picrate*, m.p. 157—158°), and *benz-N'-p-chlorophenyl-N-phenyl-N-methylamidine*, m.p. 102° (synthesised from  $NHPhMe$ , benzo-*p*-chloroanilideimidochloride, and  $NPhEt_2$ ) (*picrate*, m.p. 150—151°). (IV) similarly affords *benz-N-p-bromophenyl-N'-phenyl-N-methylamidine*, m.p. 123—124° (*picrate*, m.p. 179—180°), and *N'-p-bromophenyl-N-phenyl-N-methylamidine*, m.p. 120—121° (*picrate*, m.p. 158—159°). *s*-Benzdiphenylamidine with  $KMnO_4$  in dil.  $H_2SO_4$  at 100° affords *s-diphenyldi(phenyliminobenzyl)hydrazine*, m.p. 112°. (I) and (II) similarly afford *s-di-p-nitrophenyldi(p-nitrophenyliminobenzyl)hydrazine*, m.p. 236°, and *s-di-m-nitrophenyldi(m-nitrophenyliminobenzyl)hydrazine*, m.p. 262—264°, respectively. (II) in  $C_6H_6$  containing  $ClCO_2Et$  with  $NaHCO_3$  at room temp. affords *N-carbethoxy-s-benzdi-m-nitrophenylamidine*, m.p. 153°, also obtained from (II) and  $COCl_2$  in  $PhMe$  at room temp. (I), (III), and (IV) similarly yield *N-carbethoxy-s-benzdi-p-nitrophenyl-*, m.p. 169—170°,

-*m*-tolyl-, m.p. 94–95°, and -*p*-chlorophenyl-amidine, m.p. 118–119°.

J. L. D.

Attempts to prepare [optically] active complex salts containing an asymmetric nitrogen atom. Y. NAKATSUKA and H. INUMA (Bull. Chem. Soc. Japan, 1936, 11, 353–357; cf. this vol., 598).—Attempts were made to prepare complex salts of the type  $[\text{CoA}_2(\text{DH})_2]\text{X}$  ( $\text{DH}$ =dimethylglyoxime,  $\text{A}$ =*sec.* or *tert.* base), the optical activity of which would depend on *as*-N centres only. Using  $\text{NPhMe}_3$ , no compound could be obtained, and with  $\text{NPhMe}$  the salt  $[\text{CoA}(\text{DH})_2]\text{X}$  resulted. Attempts to prepare  $[\text{CoA}'(\text{DH})_2]\text{X}$  ( $\text{A}'=\text{NPhMe}$ :  $\text{A}'$ =primary base) failed when  $\text{A}'$  was  $\text{NH}_3$  or  $\text{NH}_2\text{Ph}$ , but succeeded when  $\text{A}'$  was  $\alpha$ - or  $\beta$ - $\text{C}_{10}\text{H}_7\text{-NH}_2$ . Definite proof of the resolution of the compounds, using optically active acids, could not be obtained. The prep. and properties of the following salts are described: *di-dimethylglyoxime- $\alpha$ -naphthylamine-methylanilinecobaltic chloride*, acetate, *d-camphorsulphonate*, *d- $\alpha$ -bromo--camphorsulphonate*, *d-tartrate*, and *d-camphornitroso-compound*. The corresponding  $\beta$ - $\text{C}_{10}\text{H}_7\text{NH}_2$  acetate, *d-camphorsulphonate*, and *d-camphornitroso-compound* were prepared.

J. T. A.

Theory of oxidative dyeing. II. Oxidation of *p*-phenylenediamine at different  $p_{\text{H}}$ . III. Colloidal properties of oxidative dyeing baths. V. PTSCHELIN (J. Appl. Chem. Russ., 1936, 9, 846–854, 855–861).—II. The velocity of oxidation of  $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$  (I) by  $\text{H}_2\text{O}$  at  $p_{\text{H}}$  4.45 and 8.05 is  $>$  at  $p_{\text{H}}$  3.05 and 10.35; the amount of sol. oxidation products formed is greatest at  $p_{\text{H}}$  4.45. Production of  $\text{NH}_3$  is at a min. at  $p_{\text{H}}$  8.05.

III. During oxidation of (I) by atm.  $\text{O}_2$ , colloidal and sol. products are formed at  $p_{\text{H}}$  3–11, both of which have dyeing properties, and both are produced in greatest amounts at  $p_{\text{H}}$  4.45 and 8. The colloidal particles have a positive charge at  $p_{\text{H}}$  3, and a negative one at  $p_{\text{H}}$  11; the magnitude of the charge is small, and is of no importance in the process of dyeing. Bandrowski's base (II), but not the above oxidation products, is rapidly coagulated at high  $p_{\text{H}}$ . The dyeing power of (II) is intensified in presence of (I). The oxidation processes are retarded in gelatin, which is only very faintly dyed by the products.

R. T.

Thiocyanate co-ordination compounds.—See this vol., 948.

Azoxycarboxylic derivatives. E. JOLLES (Atti R. Accad. Lincei, 1936, [vi], 23, 67–72).—The views of Oddo and Indovina (this vol., 328–329, Part XI), and their experimental findings, are criticised. Benzeneazoxycarboxylamide (I) and Br give a substance of m.p. 107–110°, not 102–103°; the “benzeneazoxycarboxylic acid” of m.p. 142° (*loc. cit.*) is impure (I). The protective action of the group  $\cdot\text{NO}$  is shown by the fact that benzeneazoxycarboxyanilide and Br give the monosubstituted *p*-bromoanilide, whilst benzeneazocarboxyanilide yields 2 : 4-dibromobenzeneazocarboxy-*p*-bromoanilide. The velocity of hydrolysis of azoxy-esters in  $\text{PhNO}_2$  and  $\text{NH}_3$  is infinitely greater than that of formation of diazo-hydroxides, whilst with the amides the reverse is the case. Benzene-, m.p. 163°, and *p*-chlorobenzene-

azoxycarboxydiphenylamide, m.p. 162°, are prepared; neither of these gives  $\text{RNO}$ , on hydrolysis.

E. W. W.

Azo-dyes. II. A. MIRONESCU and I. V. NICOLIESCU (Bul. Soc. Chim. Romania, 1935, 17, 293–296; cf. A., 1933, 1286).—Arylideneamines couple normally with diazonium salts, halogenoarylideneamines unusually readily. Benzylidenediamines give vat dyes. Diazotised benzidine and  $\text{NPh}:\text{CH}:\text{C}_6\text{H}_4\text{Cl-}p$  with  $\text{NaOAc}$  in hot  $\text{EtOH}$  give 4-*p*-chlorobenzylidenaminobenzeneazo-4'-hydroxydiphenyl, m.p. 112°;  $\alpha\text{-C}_{10}\text{H}_7\text{N}:\text{C}_6\text{H}_4\text{Cl-}p$  gives 4-*p*-chlorobenzylidenaminonaphthaleneazo-4'-hydroxydiphenyl, m.p. 173°.  $\text{NPh}:\text{CHPh}$  with the appropriate diazonium salts gives *Na* 2-(benzylidenaminobenzeneazo)naphthalene-4-sulphonate, m.p. 137°, and  $\alpha$ -benzylidenaminobenzeneazonaphthalene, m.p. 194°. Diazotisation of  $m\text{-NH}_2\text{C}_6\text{H}_4\text{N}:\text{CHPh}$  in very dil.  $\text{HCl}$  and coupling gives *m*-benzylidenaminobenzeneazo-dimethylaniline hydrochloride, m.p. 290°, and -resorcinol, m.p. 322°. All the dyes are hydrolysed by  $\text{HCl}$  to  $\text{NH}_2$ -compounds. The compounds containing the  $\text{C}_{10}\text{H}_8$  ring have great stability.

R. S. C.

Action of amines on esters. I. H. IRVING (J.C.S., 1936, 797–801).— $\beta\gamma\gamma$ -Tetrachloro- $\alpha$ -nitropropane (I) with  $\text{NPh}:\text{NH}_2$ ,  $p\text{-C}_6\text{H}_4\text{Me}:\text{NH}_2$ , or dry  $\text{NH}_3$  in  $\text{EtOH}$  affords  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -phenylhydrazino-,  $\beta$ -*p*-toluidino-, and  $\beta$ -amino-propane, respectively, but  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -hydroxypropane is unreactive, unlike the corresponding  $\beta$ -OAc-compound (cf. this vol., 595). Picryl acetate, in which the  $\text{C}_{(1)}$  is definitely cationoid, gives neither picramide with  $\text{NH}_3$  nor  $\beta$ -picrylphenylhydrazine with  $\text{NPh}:\text{NH}_2$  (cf. A., 1895, i, 140; 1920, i, 99).  $\beta\beta\beta$ -Trichloro- $\alpha$ -acetoxypromionamide,  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -acetamido- $\beta$ -acetoxypromion,  $\gamma\gamma\gamma$ -trichloro- $\beta$ -acetoxypromion,  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxypromion, and chloral diacetate do not react readily with  $\text{NH}_3$  or  $\text{NPh}:\text{NH}_2$ , in spite of the electron-restraining  $\cdot\text{CCl}_3$  in the mol. *O*-Acetylchloral cyanohydrin, *O*-acetylchlorolactic acid, or the dimeride of  $\text{AcCN}$  does not react with  $\text{NH}_3$ ,  $\text{NH}_2\text{Ph}$ , or  $\text{NPh}:\text{NH}_2$  to give amines, in spite of the presence of two electron-restraining groups (cf. this vol., 595). The mechanism of amination probably involves loss of  $\text{HCl}$  or  $\text{AcOH}$ , followed by addition of the amine to the double linking.

J. L. D.

Anomalous decomposition of the tetrazo-derivative of 2 : 2'-diamino-1 : 1'-dinaphthyl. III. A. CORBELLINI, C. BOTRUGNO, and P. VILLA (Gazzetta, 1936, 66, 186–196).—1 : 2- $\text{C}_{10}\text{H}_6\text{Bz}:\text{NH}_2$  (Dziwonski *et al.*, A., 1935, 336), diazotised and treated with  $\text{SnCl}_2\text{-HCl}$  at 0° and the  $\text{Et}_2\text{O}$ -sol. part treated with  $\text{HCl}$ , yields a hydrochloride which with aq.  $\text{NH}_3$  gives 3-phenyl-4 : 5-1' : 2'-naphthopyrazole [1-phenyl- $\beta$ -naphthindazole] (I), m.p. 199–5° (picrate, m.p. 154–155°; Ac derivative, m.p. 159–5°). 1-Phenyl- $\beta$ -naphthindazole-2'-acrylic acid (II) (A., 1932, 524) fused with  $\text{KOH}$  and treated with  $\text{HCl}$  yields the corresponding carboxylic acid (*loc. cit.*), m.p. 269–270–5° (decomp.) [*Me* ester (impure), m.p. 110–120° (picrate, m.p. 168–171°); *Et* ester (impure), m.p. 85–90° (picrate, m.p. 148–149°); lactam, m.p. 230°], decarboxylated to (I). The constitution



of (II) from tetrazotised 2:2'-diamino-1:1'-dinaphthyl (A., 1931, 966), is thus confirmed. Oxidation ( $\text{Na}_2\text{O}_2$ ) of naphthisatin affords 2:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$  (Friedlander and Littner, A., 1915, i, 246) [*Bz*, m.p. 196° (decomp.), and *CHPh*: derivative, m.p. 197.5—198° (decomp.)], the former with  $\text{SOCl}_2$  yielding benzoylbenzoanthranil,  $\text{C}_{10}\text{H}_6\text{N} \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \text{N}=\text{CPh} \end{smallmatrix}$  or  $\text{C}_{10}\text{H}_6\text{N} \begin{smallmatrix} \text{CO} \\ \text{NBz} \end{smallmatrix}$ , m.p. 187—187.5°. F. O. H.

**Diazo-resins.** III. E. JOLLES (Gazzetta, 1936, 66, 204—208).—Recent papers by Oddo and Indovina (cf. this vol., 328) are criticised. E. W. W.

**Nitro-amino-hydroxy-derivatives of benzene.** G. I. GERSCHZON (J. Appl. Chem. Russ., 1936, 9, 879—884).—The prep. of 4-nitro-2-aminophenol from 1:2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$ , picramic acid from picric acid, 2-aminophenol-4-sulphonic acid (I) from 2-nitrophenol-4-sulphonic acid, and 6-nitro-2-aminophenol-4-sulphonic acid from (I) are described. R. T.

**Preparation of thymol from *m*-cresol [by the phosphoric acid method].** I and II. K. ONO and M. IMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 170—171B).—The method of B.P. 200,151 (cf. A., 1923, i, 1006), using *m*-cresol (I),  $\text{Pr}^\beta\text{OH}$ , and  $\text{H}_3\text{PO}_4$ , affords thymol (II) (identified as 1:4:3- $\text{C}_6\text{H}_3\text{MePr}^\beta\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ), an isomeride (III) of (II), m.p. 114°, diisopropyl-*m*-cresol (IV), b.p. 260—266°, *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OPr}^\beta$  (V), thymol isopropyl ether (VI), b.p. 210—220°, and an isomeride, b.p. 220—230°. Steam-distillation of the reaction mixture leaves (V) (insol. in 10% aq. KOH), (IV) and probably the  $\text{Pr}^\beta$  ether of (IV); the distillate contains (I), (II), (III) (all three sol. in 10% aq. KOH), (V), (VI), and (IV). P. G. C.

**Effect of halogen substituents on rearrangement of aryl alkyl ethers.** I. Ethers which rearrange normally. C. D. HURN and C. N. WEBB (J. Amer. Chem. Soc., 1936, 58, 941—942).—*o*-Bromophenyl allyl ether, b.p. 130—134°/20 mm., heated to about 220° in  $\text{N}_2$  or  $\text{CO}_2$  rearranges exothermally to 82% of 6-bromo-2-allylphenol, b.p. 87—88°/2 mm. 2:4-Dibromophenyl allyl ether, b.p. 127—134°/0.5 mm., heated in tetrahydronaphthalene gives 69% of 4:6-dibromo-2-allylphenol, b.p. 118—122.5°/1 mm., and 11% of phenolic material, b.p. 109.5—118°/1 mm. Contrary to Raiford and Howland (A., 1931, 615), 3:5- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2$  rearranges exothermally to 72% of 3:5-dibromo-2-allylphenol, b.p. 138—139°/2 mm., and 6% of (probably) 3:5-dibromo-1-methylcoumarone, b.p. 143—147°/1 mm. 4:6-Dibromo-2-allylphenoxyacetic acid has m.p. 115—117.5°. The above ethers are prepared by Claisen's method (A., 1913, i, 1175). H. B.

**Action of organo-magnesium compounds on phenolic ethers.** V. GRIGNARD and J. RITZ (Bull. Soc. chim., 1936, [v], 3, 1181—1184).—The scission of phenolic ethers  $\text{ArOR} + \text{MgR}'\text{X} \rightarrow \text{ArO}\cdot\text{MgX} + \text{RR}'$  is accompanied by the production of mixtures of hydrocarbons. Thus  $\text{PhOEt}$  and  $\text{MgEtHal}$  afford  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{C}_4\text{H}_{10}$  and with  $\text{MgMeI}$  yields  $\text{C}_2\text{H}_6$ ,

$\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_8$ . The formation of  $\text{MeI}$  from  $\text{MgPr}^\beta\text{I}$  and  $\text{PhOMe}$  is due to secondary change:  $2\text{Pr}^\beta\text{I} + \text{Mg} = \text{MgI}_2 + \text{CHMe}\cdot\text{CH}_3 + \text{C}_3\text{H}_8$  and  $\text{PhOMe} + \text{MgI}_2 \rightarrow \text{OPh}\cdot\text{MgI} + \text{MeI}$ ; gas is not evolved. The change is better explained on the basis of Grignard's formulation than by that of Baeyer and Villiger. Iodides are greatly superior to bromides for the conversion of phenolic ethers into phenols. H. W.

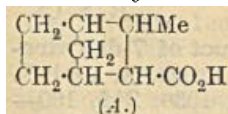
**Action of chloroacetic acid on naphthols.** R. SHIBATA and M. OKUYAMA (Tech. Rep. Tohoku, 1936, 12, 119—135).— $\alpha$ -Naphthyloxyacetic acid (Spitzer, A., 1901, i, 715; Ingham *et al.*, A., 1931, 737) with  $\text{HNO}_3$  at 20—30° gives its 4- $\text{NO}_2$ -derivative [unstable  $\text{NH}_2\text{Ph}$  salt, converted by heat into the anilide (I), m.p. 181.5°, also obtained from  $\text{NH}_2\text{Ph}$  and the acid chloride, m.p. 96°;  $\alpha$ -naphthylamide, m.p. 241°], reduced ( $\text{Sn}\text{--HCl}\text{--AcOH}$ ) to the 4- $\text{NH}_2$ -derivative {*m*-nitrobenzylidene derivative, m.p. 182.5°; anilide, m.p. 142.5°, [by reduction of (I) with  $\text{Sn}\text{--HCl}$ ] (*m*-, m.p. 217.5°, and *p*-nitrobenzylidene derivative, m.p. 243°)}, the hydrochloride of which with  $\text{S}_2\text{Cl}_2$  in dry  $\text{C}_6\text{H}_6$  at 40—80° gives a thiazthionium salt ( $\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  replaced by Cl), converted by  $\text{NH}_2\text{Ph}$  into the thiazthionium chloride (II) which is a bordeaux-red basic dye. Nitration of  $\beta$ -naphthyloxyacetic acid (Spitzer, *loc. cit.*) affords mainly its 1- $\text{NO}_2$ -derivative, m.p. 191—192° [anilide (III), m.p. 169° (lit. m.p. 139°)], and an isomeric (?) 6- $\text{NO}_2$ -derivative, m.p. 157—185° [anilide (IV), m.p. 217°]. Reduction of (III) with  $\text{Sn}\text{--HCl}$  gives the lactam of 1-amino-2-naphthyloxyacetic acid; (IV) is reduced to (?) 6-amino-2-naphthyloxyacetic acid, m.p. 187—188°. 2:6- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{Na}$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}\text{--NaOH}$  afford the  $\text{Na}_2$  salt +  $2\text{H}_2\text{O}$  (converted by crystallisation from dil. HCl into the  $\text{Na}_1$  salt) of 6-sulpho-2-naphthyloxyacetic acid, converted by  $\text{HNO}_3$  (d 1.397) into its 1- $\text{NO}_2$ - (V) and (from the mother-liquor) (?) 4- $\text{NO}_2$ -derivative. Reduction of (V) with  $\text{Fe}\text{--}20\%$   $\text{AcOH}$  and subsequent neutralisation gives the  $\text{Na}$  salt of the lactam of 6-sulpho-1-amino-2-naphthyloxyacetic acid, hydrolysed by  $\text{NaOH}$  to the  $\text{Na}$  salt of the corresponding  $\text{NH}_2$ -acid. 2:3:6- $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{SO}_3\text{H}$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  give the 2:3-dioxyacetic acid (as its  $\text{Na}$  salt), but 1:8:3:6- $\text{C}_{10}\text{H}_4(\text{OH})_2(\text{SO}_3\text{H})_2$  affords only a mono-oxyacetic acid (as its  $\text{Na}$  salt), and 1:8:4- $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{SO}_3\text{H}$  gives the 1-oxyacetic acid. J. W. B.

**Preparation of resorcinol.** N. I. VOLINKIN (J. Appl. Chem. Russ., 1936, 9, 885—888).—A process for the prep. of resorcinol consists in sulphonating  $\text{C}_6\text{H}_6$  with oleum, fusing the  $\text{Na}$  salt of the  $\text{m}\text{--C}_6\text{H}_4(\text{SO}_3\text{H})_2$  with an equal wt. of  $\text{NaOH}$  at 300—320°, and recrystallising from  $\text{PhMe}$ . R. T.

**Raman spectra of isoeugenol and the safrole series.**—See this vol., 922.

**Polymeric phenols having a tetramethylene structure.** E. PUXEDDU (Rend. semin. fac. sci. Univ. Cagliari, 1933, 3, 64—66; Chem. Zentr., 1934, ii, 934).—Polemical against Haworth and Mavin (A., 1931, 954); it is suggested that disoeugenol is 2:6-dihydroxy-3:7-dimethoxy-9:10-diethyl-9:10-dihydroanthracene. H. N. R.

Structural isomerides and stereo-isomerides of methylcyclo-[1:2:2]-heptanols and -heptanones. II. G. KOMPPA and S. BECKMANN (Annalen, 1936, 523, 68—86; cf. A., 1935, 1123).—When boiled for some hr., cyclopentadiene (I) and CHMe:CH:CO<sub>2</sub>H (II) give much dicyclopentadiene (III) and about 30% of trans-3-exomethylcyclo-[1:2:2]-heptene-2-endocarboxylic acid (IV), b.p. 137—139°/18 mm., m.p. 95° (amide, m.p. 131—132°; anilide, m.p. 111—112°) (cf. A., 1929, 820), hydrogenated to trans-3-exomethylcyclo-[1:2:2]-heptene-2-endocarboxylic acid (A), m.p. 68—69° (chloride, b.p. 87—89°/14 mm.; amide, m.p. 140—141°; anilide, m.p. 144—145°). (I) or (III) with (II) at about 170° gives a mixture of (IV) and its cis-isomeride (called



the iso-acid), m.p. 62—63°, b.p. 133—134°/13 mm. (amide, m.p. 146° anilide, m.p. 129—130°), hydrogenated (Pd) to iso-3-methylcyclo-[1:2:2]-heptene-2-carboxylic acid, m.p. 40—41°, b.p. 125—126°/9 mm. (amide, m.p. 146—147°; chloride, b.p. 87—89°/16 mm.). Curtius degradation leads to trans-3-exomethylcyclo-[1:2:2]-heptyl-2-endoamine (hydrochloride; carbamide derivative, m.p. 200—201°) and the isoamine (hydrochloride, m.p. > 275°; carbamide derivative, m.p. 206—207°), respectively. The structure of these bases, though probable, is not certain, since each with HNO<sub>2</sub> gives a mixture of isoposantenol (7-methylcyclo-[1:2:2]-heptan-2-ol) (V), b.p. 89—90°/17 mm., m.p. 85—86° (H phthalate, m.p. 165—166°), apocamphenilol (3-methylcyclo-[1:2:2]-heptan-2-ol) (VI), b.p. 80—81°/12 mm., m.p. 21—22° (H phthalate, m.p. 131—132°), and aposantenol (VII) [not obtained pure; a stereoisomeride of (VI)], b.p. 83—84°/9 mm., m.p. about 50—55°, separable only by way of the H phthalates. With K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> (V) gives isoposantenone, b.p. 181—183°/767 mm. (semicarbazone, m.p. 199—200°), and with KMnO<sub>4</sub>-NaOH at 40—50° cis-isoposantenic acid (methylcyclopentane-2:5-dicarboxylic acid), m.p. 155° (anhydride, m.p. 174°; anilido-acid, m.p. 197—198°), rearranged by HCl at 170—210° to a mixture of a cis-isomeride (VIII), m.p. 154—155° (anhydride, m.p. 151—152°; anilido-acid, m.p. 167—168°), with a little of an impure acid, probably a trans-isomeride. (VI) gives similarly apocamphenilone (6-methylnorcamphor) (semicarbazone, m.p. 187—188°). (VII), as isolated, is shown by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-oxidation to contain >5% of (V) and 25—30% of (VI); crude (VII) with KMnO<sub>4</sub> gives (VIII), which is largely unchanged by HCl at 180°, yielding only a little trans-aposantenic acid, m.p. 116—117°. Et<sub>2</sub> methylcyclopenta-3:4-dione-2:5-dicarboxylate (from Et<sub>2</sub> β-methylglutarate and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), when hydrogenated (PtO<sub>2</sub>) and distilled with KHSO<sub>4</sub>, gives Et<sub>2</sub> methylcyclopentadiene-2:5-dicarboxylate, which by hydrogenation and hydrolysis affords (VIII). R. S. C.

Catalytic hydrogenation of β-nitro-α-methoxy-α-arylethanes. B. REICHERT (Arch. Pharm., 1936, 274, 369—372).—The nitromethoxystyrene and NaOMe-MeOH give β-nitro-α-methoxy-p-, m.p. 57—58° (lit. an oil), and -o-anisylethane, m.p. 54°, which are hydrogenated (PtO<sub>2</sub>) in dry EtOH in presence of

H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in 70% yield to β-methoxy-β-p-, b.p. 140°/12 mm. [hydrochloride, m.p. 186—187° (decomp.; lit. 165—166.5°)], and -o-anisylethylamine [hydrochloride, m.p. 197—198° (decomp.); oxalate]. β-Methoxy-β-3:4-dimethoxyphenylethylamine is obtained similarly in 80% yield. R. S. C.

Reducing action of halogeno-organomagnesium derivatives. Optically active triarylcannabinols. A. GARCÍA BANÚS and J. MONCHE (Anal. Fis. Quim., 1935, 33, 655—679).—By reaction of the appropriate Mg aryl halides with ketones the following new carbinols were obtained; these with AcCl give chloromethanes, which in C<sub>6</sub>H<sub>6</sub> with Hg yield in certain cases triarylmethyls: phenyl-p-tolyl-p-anisyl-carbinol, a resin [chloromethane, m.p. 99—100°; triarylmethyl, orange solution (peroxide, m.p. 140—143°)], phenyl-p-tolyl-α-naphthylmethyl Et ether, m.p. 131—132° [triarylmethyl, red solution (peroxide, m.p. 179—182°)], 2:3-diphenyl-1-α-naphthylinden-1-ol, m.p. 155—158° (Et ether, m.p. 158—160°; chloride, m.p. 163°), -1-p-anisylinden-1-ol, a resin (Et ether, m.p. 205°; chloride, m.p. 145°), 1:2:3-triphenylinden-1-ol Me ether, m.p. 153°. Phenyldiphenyl-1-α-naphthylmethyl chloride (Karagunis *et al.*, A., 1933, 1041) yields the isoamyl ether, m.p. 154—155°, and an active amyl ether, m.p. 106°, [α]<sub>D</sub><sup>20</sup> +13.25° in Et<sub>2</sub>O. Attempts to prepare phenyl-o-tolyl-p-anisyl- and -p-tolyl-carbinols resulted in resins or pinacones.

F. R. G.

Differences in behaviour of cis- and trans-cyclohexanediols during dehydration. M. TIFFE-NEAU and (MLLE.) B. TCHOUBAR (Compt. rend., 1936, 202, 1931—1934).—cis-1-Methylcyclohexane-3:4-diol with Al<sub>2</sub>O<sub>3</sub> at 270—290° affords mainly 3-methylcyclohexanone (which indicates that mainly the 4-OH is eliminated) and some 1-methyl-3-cyclopentylformaldehyde, which is the only product of dehydration of the trans-isomeride (cf. A., 1935, 340; 1934, 1098). cis-1-Ethylcyclohexane-1:2-diol similarly affords 90—95% of 2-ethylcyclohexanone (I) and 5—10% of ethylcyclopentylformaldehyde (II) whereas the trans-isomeride gives 80—85% of (I) and 15—20% of (II). The cis-isomerides suffer a vinyl dehydration and the trans- a hydrobenzoin type of change (cf. A., 1935, 616).

J. L. D.

cis-trans-Transformations of cyclic systems in the light of the solvate theory. A. A. NIKOLAEV (J. Gen. Chem. Russ., 1936, 6, 182—184).—In presence of high concn. of KOH cyclohexene iodohydrin affords a mixture of the trans- and cis-diols, whilst with low [KOH] the former is the sole product. The results are explained on the basis of solvation. R. T.

Sterol group. XXII. 3-Chloroallonorcholonic acid and its epimeride. T. BARR, I. M. HEILBRON, and F. S. SPRING. XXIII. Location of the ethenoid linkage of α-dihydrofucosterol and the identity of sitostanol, fucostanol, stigmastanol, and orestastanol. D. H. COFFEY, I. M. HEILBRON, and F. S. SPRING (J.C.S., 1936, 737—738, 738—741).—XXII. Since the OH of ergosterol is now known to be attached to C<sub>3</sub>, (cf. A., 1935, 210), the chloroallonorcholonic acid of Heilbron *et al.* (A., 1933, 1290) must be the 3-Cl-compound; with reference to the H attached to C<sub>3</sub>, it is suggested that the Cl is cis.



(*trans*.-?) 3-Chloroallocholanolic acid, m.p. 195—196°, is converted by  $\text{CH}_2\text{N}_2$  into *Me* (*trans*.-?) 3-chloroallocholanate, m.p. 134—135°, which, when treated with  $\text{MgPhBr}$  and the product oxidised by  $\text{CrO}_3$  in  $\text{AcOH}$ , affords 3-(*trans*.-?) chloroallonorcholanolic acid. The *Me* ester of this is identical with the product from chloroergostane.

**XXIII.**  $\alpha$ -Dihydrofucosterol (I) with  $\text{BzO}_2\text{H}$  affords  $\alpha$ -dihydrofucosterol oxide (II), m.p. 134°,  $[\alpha]_D^{20} -35.6^\circ$  in  $\text{CHCl}_3$  [acetate, m.p. 141°, from (II) or by the action of  $\text{BzO}_2\text{H}$  on the acetate of (I)]. (II) with  $\text{H}_2\text{SO}_4$ , or the acetate of (I) with  $\text{H}_2\text{O}_2$ , affords  $\alpha$ -fucostanetriol, m.p. 248—250°, converted by  $\text{CrO}_3$  in  $\text{AcOH}$  into  $\alpha$ -fucostanedionol, m.p. 256°. This with  $\text{HCl}$  in  $\text{CHCl}_3$  gives  $\alpha$ -fucostenedione, m.p. 166°, converted by  $\text{Zn-AcOH}$  into  $\alpha$ -fucostanediol (III), m.p. 192—194°, giving a pyridazine derivative, m.p. 200°, the formation of which proves the 3:6-positions of the CO groups in (III), whence (I) contains an ethylenic linking between  $\text{C}_{(5)}$  and  $\text{C}_{(6)}$ . The  $\text{Br}_2$ -derivative of (I), treated with  $\text{CrO}_3\text{-AcOH}$  and then with  $\text{Zn-AcOH}$ , affords  $\alpha$ -fucostenone (IV), m.p. 81—82° (*semicarbazone*, m.p. 250°); the substance, m.p. 158°, previously described as this is a mixture. (IV) shows the absorption spectrum of an  $\alpha\beta$ -unsaturated ketone, so that wandering of the  $\Delta^{5:6}$  ethylenic linking to the  $\Delta^{4:5}$  position must occur during oxidation of (I). Fucostanol (V) (3:5-dinitrobenzoate, m.p. 214—215°,  $[\alpha]_D^{20} +13.8^\circ$  in  $\text{C}_6\text{H}_6$ ; benzoate, m.p. 135—136°) is converted by oxidation into fucostanone (VI) and fucostanedicarboxylic acid, m.p. 227—229° (*Me* ester, m.p. 89—90°). Reduction of (VI) affords epifucostanol, m.p. 200°,  $[\alpha]_D^{20} +25.5^\circ$  in  $\text{CHCl}_3$  (acetate, m.p. 86—87°,  $[\alpha]_D^{20} +27.4^\circ$  in  $\text{CHCl}_3$ ). It is maintained that (V) and stigmastanol, and that (I) and  $\Delta^{5:6}$ -sitosterol, are identical pairs; comparative tables of m.p. and  $[\alpha]_D$  are given.

P. G. C.

#### Introduction of nitrogen into sterol molecules.

M. VANGHELOVICI and G. VASILIU (Bul. Soc. Chim. Romania, 1935, 17, 249—265).—3-Chloro-6-oximinocholestene, m.p. 178°, and  $\text{Na-EtOH}$  give 6-aminocholestane, m.p. 126° (*hydrochloride*, decomp. 270°; *Ac* derivative, m.p. 187°). 3-Bromositostene (prep. by  $\text{PBr}_3\text{-C}_6\text{H}_6$ ), m.p. 75°, and  $\text{HNO}_3\text{-NaNO}_2$  give a poor yield of the 6- $\text{NO}_2$ -derivative, m.p. 130°. 3-Bromocholestene (I) gives similarly the 6- $\text{NO}_2$ -derivative, m.p. 154°, reduced by  $\text{Zn dust-AcOH}$  to cholestan-6-one, m.p. 90° (oxime, m.p. 197°), probably identical with, but possibly a stereoisomeride of, Windaus' ketone, m.p. 98° (A., 1920, i, 434). The reactivity of the halogen in sterol derivatives is greatly influenced by other groups present. Thus, 3-chlorocholestane is stable to hot  $\text{Na-Hg}$ , 3-chlorocholestan-6-one loses its Cl to this reagent, whilst the Cl of the acid (II) is removed by hot aq.  $\text{NaOH}$ . (I), 3-chlorocholestene at 170°, or its dibromide with  $\text{NHPh-NH}_2$ , give *N-phenyl-N-3-cholesterylhydrazine*, m.p. 196° (*Ac* derivative, m.p. 138°; *picrate*, m.p. 182°), the *as*-structure of which is proved by formation of benzylidene, m.p. 150°, *salicylidene*, m.p. 137°, *cinnamylidene*, m.p. 156°, *p-hydroxybenzylidene*, m.p. 158°, *phenylmethylmethylen*, m.p. 159°, *propylidene*, m.p. 83°, and *p-nitrobenzylidene*, m.p. 165°, derivatives, a *hydrazone* with *Et acetoacetate*, m.p. 127°, and a *tetrazine*, m.p. 165°. *N-p-Tolyl-N-3-cholesterylhydrazine*, m.p. 163°, and *N-phenyl-N-3-sitosterylhydrazine*, m.p. 193° (*Ac*, m.p. 110°, *benzylidene*, m.p. 105°, and *phenylmethylmethylen*, m.p. 185°, derivatives; *tetrazine*, m.p. 132°), are similarly prepared. (I) and the appropriate base give 3-anilino-, m.p. 177°, *o-toluidino*-, m.p. 170°, and *o-anisidin*ositostene, m.p. 134°. Ergosterol and  $\text{PCl}_5\text{-C}_6\text{H}_6$  give a *cholestatriene*, m.p. 102° (*hydrochloride*, m.p. 106°), probably stereoisomeric with the known compound, m.p. 105°.

R. S. C.

**Antirachitic irradiation product of 7-dehydrocholesterol.** A. WINDAUS, F. SCHENCK, and F. VON WERDER (Z. physiol. Chem., 1936, 241, 100—103; cf. A., 1935, 1363).—The ultra-violet irradiation product of 7-dehydrocholesterol, vitamin- $D_3$  [3:5-dinitrobenzoate (I), m.p. 129°; *allophanate*, m.p. 173—174°], antirachitic val. 24,000 international units per mg., obtained from the crude material by chromatographic adsorption on  $\text{Al}_2\text{O}_3$ , occurs in the liver oil of the tunny.  $-D_3$  obtained on hydrolysis of (I) exhibits absorption max. at 265 m $\mu$  and differs from calciferol in having  $\text{-CH}_2\text{-CH}_2\text{Bu}^\beta$  instead of  $\text{-CH:CH-CHMePr}^\beta$  in the side-chain.

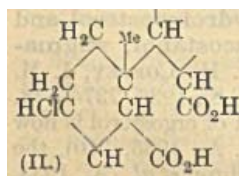
W. McC.

**7-Dehydrositosterol.** W. WUNDERLICH (Z. physiol. Chem., 1936, 241, 116—124).—Sitosteryl acetate with  $\text{CrO}_3$  in  $\text{AcOH}$  at 55—60° yields 7-ketositosteryl acetate, m.p. 176°,  $[\alpha]_D^{17} -9.4^\circ$  in  $\text{CHCl}_3$  (*semicarbazone*, m.p. 250—252° decomp.,  $[\alpha]_D -265^\circ$  in  $\text{CHCl}_3$ ), which with  $\text{Al(OPr}^\beta)_3$  in  $\text{Pr}^\beta\text{OH}$  and subsequent hydrolysis gives 7-hydroxysitosterol, m.p. 151—153° [*dibenzoate* (I), m.p. 179°,  $[\alpha]_D^{19} +96^\circ$  in  $\text{CHCl}_3$ ], and isomerides. (I) heated at 200°/1 mm. gives the benzoate, m.p. 149°,  $[\alpha]_D^{21} -5.4^\circ$  in  $\text{CHCl}_3$ , which on hydrolysis in  $\text{N}_2$  at  $>64^\circ$  yields 7-dehydrositosterol (II), m.p. 144—145°,  $[\alpha]_D^{21} -116^\circ$  in  $\text{CHCl}_3$  [acetate (III), m.p. 151—152°,  $[\alpha]_D^{21} -71^\circ$  in  $\text{CHCl}_3$ ]; compound with maleic anhydride, m.p. 182—183°. (II) has absorption spectrum very similar to that of ergosterol and is converted by ultra-violet light into an antirachitic substance. Visible light converts (II) in presence of eosin and absence of  $\text{O}_2$  into a sparingly sol. substance, m.p. 200—201° (decomp.),  $[\alpha]_D -165^\circ$  in  $\text{C}_6\text{H}_5\text{N}$  [*diacetate* (IV), m.p. 202—203°,  $[\alpha]_D^{20} -105^\circ$  in  $\text{CHCl}_3$ ]. (IV) is also obtained by the action of light on (III) in presence of eosin and absence of air.

W. McC.

**7-Dehydrostigmasterol.** O. LINSERT (Z. physiol. Chem., 1936, 241, 125—128).—Stigmasteryl acetate oxidised with  $\text{CrO}_3$  in  $\text{AcOH}$  at 50° for 9 hr. yields 7-ketostigmasteryl acetate, m.p. 183°, which when boiled for 5 hr. in  $\text{Pr}^\beta\text{OH}$  with  $\text{Al(OPr}^\beta)_3$  and subsequently hydrolysed gives 7-hydroxystigmasterol (I), m.p. 154° [*di-3:5-dinitrobenzoate*, m.p. 197° decomp.; *dibenzoate* (II), m.p. 156—158°]. (II) in a vac. at 195° gives the benzoate, m.p. 180°, which on hydrolysis yields 7-dehydrostigmasterol (III), m.p. 154°,  $[\alpha]_D^{20} -113.15^\circ$  in  $\text{C}_6\text{H}_6$  (acetate, m.p. 172°). (I), (II), and (III) give a blue colour with  $\text{CCl}_3\text{-CH(OH)}_2$ . (III) exhibits almost the same absorption spectrum as does ergosterol (IV) and its structure differs from that of (IV) in having  $\text{Et}$  at  $\text{C}_{(24)}$ .

W. McC.



m.p. 137°, *cinnamylidene*, m.p. 156°, *p-hydroxybenzylidene*, m.p. 158°, *phenylmethylmethylen*, m.p. 159°, *propylidene*, m.p. 83°, and *p-nitrobenzylidene*, m.p. 165°, derivatives, a *hydrazone* with *Et acetoacetate*, m.p. 127°, and a *tetrazine*, m.p. 165°. *N-p-Tolyl-N-3-cholesterylhydrazine*, m.p. 163°, and *N-phenyl-N-3-sitosterylhydrazine*, m.p. 193° (*Ac*, m.p. 110°, *benzylidene*, m.p. 105°, and *phenylmethylmethylen*, m.p. 185°, derivatives; *tetrazine*, m.p. 132°), are similarly prepared. (I) and the appropriate base give 3-anilino-, m.p. 177°, *o-toluidino*-, m.p. 170°, and *o-anisidin*ositostene, m.p. 134°. Ergosterol and  $\text{PCl}_5\text{-C}_6\text{H}_6$  give a *cholestatriene*, m.p. 102° (*hydrochloride*, m.p. 106°), probably stereoisomeric with the known compound, m.p. 105°.

**Synthesis of vitamin-A. II.** I. M. HEILBRON, W. E. JONES, A. LOWE, and H. R. WRIGHT (J.C.S., 1936, 561—563; cf. A., 1935, 978).—When  $\beta$ -keto- $\delta$ -hydroxy- $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\zeta$ -methyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octadiene (I) (p-tolylsemicarbazone, m.p. 168—169°; p-chlorobenzoylhydrazone, m.p. 204°) is heated at 160° with anhyd.  $\text{H}_2\text{C}_2\text{O}_4$ , it is dehydrated to  $\beta$ -keto- $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\zeta$ -methyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatriene (II), m.p. 138—144°. (II) with  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$  gave *Et*  $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatetraene- $\alpha$ -carboxylate, b.p. 150°/2 $\times$ 10<sup>-4</sup> mm., which could not be easily distilled even at 0.1 mm., and was hydrolysed in the cold to an acid which could not be obtained pure as it was partly converted into alkali-insol. material on attempted recrystallisation, but gave a Me ester, b.p. 135—140°/2 $\times$ 10<sup>-4</sup> mm. (I) with  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$  yielded *Et*  $\delta$ -hydroxy- $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatriene- $\alpha$ -carboxylate, b.p. 140—142°/4 mm., which was hydrolysed and converted into the *Ba* salt, which when distilled with  $(\text{HCO}_2)_2\text{Ba}$  at 2 $\times$ 10<sup>-4</sup> mm. gave  $\alpha$ -aldehydo- $\delta$ -hydroxy- $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatriene (phenylsemicarbazone, m.p. 181—182°) and not  $\alpha$ -aldehydo- $\theta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatetraene.  $\epsilon$ -(2:2:6-Trimethyl- $\Delta^6$ -cyclohexenyl)- $\gamma$ -methylpent- $\delta$ -en- $\alpha$ -yn-ol treated with  $\text{AcOH}$  in presence of 2:7- $\text{C}_{10}\text{H}_6(\text{SO}_3)_2\text{Hg}$  gave a semi-solid product, probably a mixture of the mono- and di-acetate. From the product of hydrolysis by cold alkali, a OH-ketone, b.p. 90—100°/2 mm. (phenylsemicarbazone, m.p. 174—178°), was obtained, probably  $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{COMe}$ , but possibly  $\text{R}\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$  ( $\text{R}=\text{CH}_2\langle\text{CH}_2\cdot\text{CMe}\rangle\text{C}\cdot$ ). The p-tolylsemicarbazone, m.p. 172—173°, and p-chlorobenzoylhydrazone, m.p. 202—203°, of  $\alpha$ -aldehydo- $\delta$ -(2:2:6-trimethyl- $\Delta^6$ -cyclohexenyl)- $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -butadiene have been prepared. W. O. K.

**Naturally occurring chicken provitamin-D.**—See this vol., 1033.

**Preparation of pentadeuterobenzoic acid.** H. ERLÉNMEYER, H. LOBECK, and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 793—794).— $\text{MgBr}\cdot\text{C}_6\text{D}_5$  (prep. from  $\text{C}_6\text{D}_6$  by  $\text{Br}\cdot\text{Fe}$  etc.) and  $\text{CO}_2$  give nearly pure pentadeuterobenzoic acid,  $\text{C}_6\text{D}_5\text{H}_0\cdot\text{CO}_2\text{H}$ , m.p. 120.9°. 1.21 times as sol. in  $\text{H}_2\text{O}$  at 18° as is  $\text{BzOH}$ .

R. S. C.

**Action of hydrogen peroxide on organic sulphur compounds.** J. J. HERRERA (Anal. Fis. Quim., 1935, 33, 877—886).—A review of the methods of replacing S by O. The reaction  $\text{CS} + 2\text{NaOH} + 4\text{H}_2\text{O}_2 = \text{CO} + \text{Na}_2\text{SO}_4 + 5\text{H}_2\text{O}$  (cf. Kitamura, J. Pharm. Soc. Japan, 1934, 54, 1) has been attempted with the following results:  $\text{CSPH}\cdot\text{NH}_2$  gives  $\text{NH}_2\text{Bz}$ ;  $\text{Me}\cdot\text{CS}\cdot\text{OH}$  gives  $\text{AcOH}$ ;  $\text{Bz}_2\text{S}$  and  $\text{Bz}_2\text{S}_2$  are unchanged;  $\text{CS}(\text{NH}_2)_2$  and  $\text{OEt}\cdot\text{CS}_2\cdot\text{K}$  yield unidentified S compounds. F. R. G.

**Benzoyl persulphide.** E. MONESS, W. A. LOTT, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 397—402).— $\text{Bz}_2\text{S}_2$  is prepared by treating KSH with  $\text{BzCl}$  to give  $\text{KSBz}$ , which is oxidised by I or, more economically, by  $\text{H}_2\text{O}_2$  after addition of

$\text{HCl}$ , the yields being respectively 95 and 91% calc. on  $\text{BzCl}$ . F. O. H.

**Synthesis of toluic acids.** N. S. KOZLOV, P. N. FEDOSEEV, and V. S. LAZAREV (J. Gen. Chem. Russ., 1936, 6, 485—486).—4-Methyl- or 4:4'-dimethylbenzophenone and  $\text{KOH}$  (200—270°; 55 min.) yield p-toluic acid and  $\text{C}_6\text{H}_5$  or  $\text{PhMe}$ , whilst 2:4-dimethylbenzophenone affords  $\text{BzOH}$  and 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$ . R. T.

**Oxidation of  $\alpha$ - and  $\beta$ -naphthyl methyl ketones.** L. F. FIESER, H. L. HOLMES, and M. S. NEWMAN (J. Amer. Chem. Soc., 1936, 58, 1055).— $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$  is conveniently prepared in 87% yield by oxidation of  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{COMe}$  (I) with aq.  $\text{KOCr}$  [from  $\text{Ca}(\text{OCl})_2$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{KOH}$ ] at 60—70°.  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{H}$  is most conveniently prepared from  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  and  $\text{CO}_2$ . Caille's method (A., 1911, i, 792) of prep. of  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{COMe}$  gives a product containing <30% of (I); separation is best effected through the picrates (cf. Pfau and Ofner, A., 1926, 837).  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{COMe}$  [picrate, m.p. 119—120° (corr.); oxime, m.p. 139.5—140.5° (corr.); semicarbazone, m.p. 228.5—229.5°] [from  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{CO}_2\text{Me}$  and  $\text{EtOAc}$  (method: Mosettig and van de Kamp, A., 1933, 1052)] has b.p. 151.5—152° (corr.)/9 $\pm$ 0.5 mm., 302° (corr.)/760 mm.

H. B.

**Constitution of bile acids. LIV. Unsaturated acids.** H. WIELAND, K. KRAUS, H. KELLER, and H. OTTAWA. **LV. Weak acids of ox bile.** H. WIELAND and G. HANKE (Z. physiol. Chem., 1936, 241, 47—67, 93—99; cf. A., 1933, 1161; 1934, 653).—**LIV.** Lithocholic acid (I) (probably  $\Delta^{2:3}$ -cholic acid), m.p. 156°,  $[\alpha]_D +16.3^\circ$  in  $\text{EtOH}$ , obtained from lithocholic acid by elimination of  $\text{H}_2\text{O}$ , yields with  $\text{BzO}_2\text{H}$  an oxide, m.p. 185°, and with  $\text{Br}$  in  $\text{AcOH}$  dibromides (probably *cis*- and *trans*-), m.p. (II) 171° and (III) 233°, respectively, together with a difficulty hydrolysable dibromide, m.p. 240°, which, on removal of  $\text{Br}_2$  with  $\text{Zn}$  and  $\text{AcOH}$ , yields an acid (probably  $\Delta^{3:4}$ -cholic acid), m.p. 160°,  $[\alpha]_D +18.7^\circ$ . (II) heated with 0.1N- $\text{KOH}$  at 135—140° for 5 hr. yields two hydroxy-cholic acids, m.p. (IV) 144—147° and (V) 188°, respectively, which are also obtained from (I) by oxidation with  $\text{SeO}_2$ , together with a dihydroxycholic acid (VI), m.p. 248°. With  $\text{PtO}_2\cdot\text{H}_2$  (IV) and (V) give cholic acid (VII) and (VI) gives *epi*-3-hydroxy-allocholic acid and (VII). When heated slowly to 230° (IV) gives, after subsequent distillation in a vac. at 270°,  $\Delta^{2:3:4:5}$ (?)-choladienic acid, m.p. 156°, and (V) gives an impure acid, m.p. about 145°. (II) with  $\text{KOH}$  in boiling  $\text{MeOH}$  gives methoxycholic acid, m.p. 187°, and with  $\text{KOH}$  in boiling  $\text{EtOH}$  ethoxycholic acid, m.p. 175°. The cholic acid (VIII),  $[\alpha]_D -38.6^\circ$  (probably a mixture of  $\Delta^{5:6}$ - and  $\Delta^{6:7}$ -cholic acid), obtained from 6-hydroxyallocholic acid by elimination of  $\text{H}_2\text{O}$  gives with  $\text{Br}$  in  $\text{AcOH}$ , together with unstable  $\text{Br}$ -compounds, a stable dibromide (IX), m.p. 227° (decomp.), which with  $\text{Zn}$  and  $\text{AcOH}$  yields an acid (X), m.p. 160°,  $[\alpha]_D -66.8^\circ$ . (IX) loses  $2\text{HBr}$  on boiling with  $\text{KOH}$  in  $\text{H}_2\text{O}\cdot\text{EtOH}$  for 6 hr. giving  $\Delta^{4:5:6:7}$ -choladienic acid (XI), m.p. 171—173° [*Me* ester (XII), m.p. 95—96°, and its dibromide, m.p. 178°]. (X) and (XI) with  $\text{PtO}_2\cdot\text{H}_2$  give (VII) and allocholic acid. (VIII) in  $\text{CHCl}_3$  shaken for 22 hr. with



SeO<sub>2</sub> in AcOH gives 7-hydroxycholenic acid, m.p. 217—218°. The cholenic acid, m.p. 148—151°, obtained from 7-hydroxycholenic acid by elimination of H<sub>2</sub>O, when shaken for 4 hr. with SeO<sub>2</sub> in CHCl<sub>3</sub>-Ac<sub>2</sub>O gives an acid, m.p. 160—162°. The choladienic acid (XIII) obtained from deoxycholic acid by elimination of H<sub>2</sub>O is a mixture of < 2 isomerides one of which has m.p. 134—136°, [α]<sub>D</sub> +36.5°. (XIII) gives with Br in AcOH two tetrabromides, m.p. (XIV) 236—237° (decomp.) and (XV) 183—184° (decomp.), respectively. Removal of Br<sub>4</sub> with Zn and AcOH from (XIV) and (XV) gives choladienic acids, m.p. (XVI) 135—138° and (XVII) 133—135° and [α]<sub>D</sub> +37.8° and +29.9°, respectively. Rebromination of (XVI) gives (XIV) and a substance, m.p. 180—184°, and of (XVII) gives (XV) and (XIV).

LV. The fraction of ox bile which contains the fatty and very weak acids yields sapocholic acid (XVIII), probably C<sub>29</sub>H<sub>46</sub>O<sub>3</sub>, m.p. 198—201° [K salt; Me ester (XIX), m.p. 146°; bromolactone (XX), m.p. 215—217°]. The alkali salts of (XVIII) are insol. in H<sub>2</sub>O. (XIX) is not hydrolysed on boiling for several hr. with KOH in MeOH. Zn and AcOH convert (XX) into (XVIII). (XVIII) is closely related to the sapogenins and is accompanied in the bile by an acid, m.p. > 250°.

W. McC.

**Preparation of γ-m-methoxyphenylbutyric acid.** C. K. CHUANG and Y. T. HUANG (Ber., 1936, 69, [B], 1505—1508).—Gradual addition of conc. H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> (d 1.4) to CH<sub>2</sub>Bz·CH<sub>2</sub>·CO<sub>2</sub>H in conc. H<sub>2</sub>SO<sub>4</sub> at >0° gives β-m-nitrobenzoylpropionic acid, m.p. 165—166°, reduced by FeSO<sub>4</sub>-NH<sub>3</sub> is β-m-aminobenzoylpropionic acid (I), m.p. 130—131° (Et ester, m.p. 66—67°). (I) is converted into β-m-hydroxybenzoylpropionic acid, m.p. 146—147°, transformed by NaOH and Me<sub>2</sub>SO<sub>4</sub> into β-m-methoxybenzoylpropionic acid, m.p. 110°, which is reduced by Zn-Hg and HCl to γ-m-methoxyphenylbutyric acid, m.p. 49—50°.

H. W.

**Phenolic esters of p-methoxycinnamic acid.** C. W. SONDERN (J. Amer. Pharm. Assoc., 1936, 25, 418—419).—Heating the acid and phenol in PhMe in presence of PCl<sub>3</sub> or P<sub>2</sub>O<sub>5</sub> affords the following esters of p-methoxycinnamic acid: *guaiacyl*, m.p. 102—103°, *α-naphthyl*, m.p. 102° (cf. Foote, A., 1928, 1374), *resorcinol diester*, m.p. 173—173.5° [monoester (?), m.p. 135—137° (decomp.)].

F. O. H.

**Synthesis of cis- and trans-dl-1-isopropylcyclopropane-1:2-dicarboxylic acids.** E. O. PHILLIPS, G. R. RAMAGE, and J. L. SIMONSEN (J.C.S., 1936, 828—829).—Et α-isopropylacrylate (A., 1905, i, 626) with Et diazoacetate at 75—80° (A., 1933, 1160) affords *Et* 1-isopropylcyclopropane-1:2-dicarboxylate, b.p. 130—135°/20 mm., hydrolysed (MeOH-KOH) to dl-trans- (I), m.p. 194—195° (p-phenylphenacyl ester, m.p. 175—176°), and dl-cis-1-isopropylcyclopropane-1:2-dicarboxylic acid (II), m.p. 117—118° (+1H<sub>2</sub>O, m.p. 97—98°, loses 1H<sub>2</sub>O at 100°; p-phenylphenacyl ester, m.p. 116—117°). (I) with Ac<sub>2</sub>O at 220° gives the anhydride of (II), b.p. 138—140°/20 mm., from which the monohydrate is obtained with H<sub>2</sub>O.

J. L. D.

**Chemiluminescence of phthalic acid derivatives.** A. I. PORTNOV (J. Gen. Chem. Russ., 1936,

6, 626—633).—The intensity of the luminescence obtained when H<sub>2</sub>O<sub>2</sub> is added to aq. NaOH solutions of derivatives of phthalhydrazide (I) increases in the order Cl<sub>1</sub>=Cl<sub>4</sub><Cl<sub>3</sub><(I)<Cl<sub>2</sub> (II) (all of type C<sub>6</sub>H<sub>3</sub>Cl<CO·NH<CO·NH<NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub><CO·NH<CO·NH and its Ac<sub>2</sub> derivative. The intensity rises with increasing concn. of (I) or its derivatives to a max., falling at higher concns. Addition of fluorescent substances intensifies luminescence only in those cases, such as (II), in which the products of the reaction are not themselves fluorescent.

R. T.

**Condensation of 3- and 4-nitrophthalic anhydride with phenol and anisole.** P. C. MITTER and P. N. DUTT (J. Indian Chem. Soc., 1936, 13, 228—235).—3-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O, AlCl<sub>3</sub>, and PhOH at 135° give 3-nitro-2-salicylbenzoic acid, m.p. 237—238° (Ac derivative, m.p. 158°; Me ester, m.p. 162°), reduced [Fe(OH)<sub>2</sub>] to the 3-NH<sub>2</sub>-acid, m.p. 217° (decomp.), the diazonium salt of which in boiling H<sub>2</sub>O gives the 3-OH-acid, m.p. 199—200° (Ac<sub>2</sub> derivative, m.p. 186°), converted by H<sub>3</sub>BO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-SO<sub>3</sub> into chrysazin, the formation of which proves the structure of its predecessors. With PhOMe and AlCl<sub>3</sub> at room temp. (I) gives much 3- (II), m.p. 207° (Me ester, m.p. 123°), and a little 6-nitro-2-p-anisoylbenzoic acid (III), m.p. 215°. The structure of (II) is proved by conversion into the 3-NH<sub>2</sub>-, m.p. 169—170°, and 3-OH-acid, m.p. 211—213°, and thence into 1:6-dihydroxyanthraquinone; that of (III) is probable, since the acid resists esterification; the 6-NH<sub>2</sub>-acid has m.p. 186°. 4-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O does not condense with PhOH, but with PhOMe and AlCl<sub>3</sub> at 20—25° gives 4-, m.p. 217—218° (Me ester, m.p. 178°), and 5-nitro-2-p-anisoylbenzoic acid, m.p. 219—220° (Me ester, m.p. 188°), converted into the 4-, m.p. 156°, and 5-NH<sub>2</sub>-acid, m.p. 160°, the 4-, m.p. 203°, and 5-OH-acid, m.p. 225°, and 2:6- and 2:7-dihydroxyanthraquinone, respectively.

R. S. C.

**Retene. VI. Retenediphenic [3-methyl-4'-isopropylidiphenic] acid and its derivatives.** D. E. ADELSON, T. HASSELSTROM, and M. T. BOBERT (J. Amer. Chem. Soc., 1936, 58, 871—872).—Oxidation (30% H<sub>2</sub>O<sub>2</sub>, AcOH) of retenequinone gives 65% of retenediphenic acid (I), m.p. 191—191.5° (all m.p. are corr.) (cf. Fogelberg, A., 1928, 290) [Me H, m.p. 126—126.5°, and Et H, m.p. 105—105.5°, esters; monoanilide, m.p. 251—252°, and monoamide, m.p. 201—202° (lit. 196—197°), all prepared from the anhydride, m.p. 112—112.5°], and a little of a hydroxymethylisopropylidiphenylcarboxylic acid lactone (II), m.p. 137—137.5°. (II) is methylated (Me<sub>2</sub>SO<sub>4</sub>, alkali) to the corresponding OMe-acid, m.p. 122—122.5°, which with cold conc. H<sub>2</sub>SO<sub>4</sub> affords a methoxymethylisopropylfluorenone, m.p. 126—126.5°. The bornyl and glyceryl esters of (I) resemble artificial resins.

H. B.

**Di-substituted derivatives of naphthalic acid.** K. DZIEWOŃSKI, T. MAJEWICZ, and L. SCHIMMER (Bull. Acad. Polonaise, 1936, A, 43—55; cf. A., 1929, 186).—The compound obtained by the action of fuming H<sub>2</sub>SO<sub>4</sub> (25% SO<sub>3</sub>) on naphthalic anhydride at 200—230° is 3:6-disulphonaphthalic anhydride, since it is

converted by  $\text{PCl}_5$  at  $300^\circ$  into 3:6-dichloronaphthalic anhydride (I), m.p.  $253^\circ$  [phenylhydrazone, m.p.  $232-233^\circ$ ; corresponding imide, m.p.  $327-328^\circ$ ; 3:6-dichloronaphthalfluorescein, m.p.  $326-328^\circ$  (decomp.)], transformed by  $\text{HgO}$  in  $\text{H}_2\text{O}$  at  $160-170^\circ$  into 3:6-dichloro-1-naphthoic acid, m.p.  $238-239^\circ$ , [ $\text{Ba} (+4\text{H}_2\text{O})$  salt;  $\text{Me}$  ester, m.p.  $112^\circ$ ], which is decarboxylated to 3:6- $\text{C}_{10}\text{H}_6\text{Cl}_2$ , also obtained directly from (I),  $\text{HgO}$ , and  $\text{H}_2\text{O}$  at  $200-210^\circ$ . 3:6-Dihydroxynaphthalic anhydride (II), m.p.  $330^\circ$ , from  $\text{Na}_4$  disulphonaphthalate and  $\text{KOH}$  at  $230-250^\circ$  [corresponding imide, m.p.  $395^\circ$  (decomp.)], is transformed by  $\text{Me}_2\text{SO}_4$  and  $\text{NaOH}$  into 3:6-dimethoxynaphthalic anhydride, m.p.  $280^\circ$ , decarboxylated to 3:6- $\text{C}_{10}\text{H}_6(\text{OMe})_2$ . 4-p'-Nitrobenzeneazo-3:6-dihydroxynaphthalic anhydride has m.p.  $330-332^\circ$  (decomp.). (II) and  $\text{NH}_3-\text{H}_2\text{O}$  at  $200-210^\circ$  give 3:6-diaminonaphthalimide (III), m.p.  $406^\circ$  (decomp.) [ $\text{Ac}_2$  derivative, m.p.  $>400^\circ$  (decomp.)], which when tetrarazotised and coupled with  $\beta\text{-C}_{10}\text{H}_7\text{-OH}$  yields 6:2'-hydroxynaphthalene-1'-azo-3-hydroxynaphthalimide, m.p.  $333-335^\circ$  (decomp.). (III) and boiling 60%  $\text{H}_2\text{SO}_4$  give 3:6-diaminonaphthalic anhydride, m.p.  $>450^\circ$ .

H. W.

**Condensation of ethyl  $\beta$ -methyladipate with ethyl oxalate.** A. S. BROWN (J. Gen. Chem. Russ., 1936, 6, 612-615).— $\text{Et}_2\beta$ -methyladipate,  $\text{Et}_2\text{C}_2\text{O}_4$ , and  $\text{Na}$  in  $\text{EtOH}-\text{Et}_2\text{O}$  yield, amongst other unidentified products,  $\text{Et}_2$  6-methyl-2:3-diketocyclohexane-1:4-dicarboxylate, b.p.  $206-207^\circ/15$  mm. (monoxime, m.p.  $124-125.5^\circ$ ).

R. T.

**Constituents of natural phenolic resins. V. Synthesis of dl-matairesinol dimethyl ether and dl-cubebinolide.** R. D. HAWORTH, W. KELLY, and T. RICHARDSON. VI. **Synthesis of compounds related to cubebinolide (hinokinin).** R. D. HAWORTH and W. KELLY (J.C.S., 1936, 725-730, 745-747).—V.  $\alpha$ -Acetyl- $\beta$ -(3:4-dimethoxybenzyl)-butyrolactone (I), m.p.  $69-70^\circ$ , is obtained from  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  and  $O$ -methyleugenol oxide; its constitution is proved by treatment of its  $\text{Na}$  compound with 3:4-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3\cdot\text{COCl}$  to give  $\alpha$ -(3:4-dimethoxybenzoyl)- $\beta$ -(3':4'-dimethoxybenzyl)butyrolactone, m.p.  $125-126^\circ$ , and thence ( $\text{MeOH}-\text{HCl}$ ) into 1-hydroxy-6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-3-hydroxymethyl-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid lactone, m.p.  $124-126^\circ$ , dehydrated by  $\text{KHSO}_4$  to the known 6:7-dimethoxy-1-(3':4'-dimethoxyphenyl)-3-hydroxymethyl-3:4-dihydronaphthalene-2-carboxylic acid lactone. The  $\text{Na}$  derivative of (I) with 3:4-( $\text{OMe}$ ) $_2\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Cl}$  affords  $\alpha$ -acetyl- $\alpha\beta$ -bis-(3:4-dimethoxybenzyl)butyrolactone, b.p.  $270-280^\circ/0.5$  mm., converted by  $\text{MeOH}-\text{Ba}(\text{OH})_2$  into  $\alpha\beta$ -bis-(3:4-dimethoxybenzyl)butyrolactone (dl-matairesinol  $\text{Me}_2$  ether) (II), m.p.  $106-107^\circ$ , in small yield. Better yields of (II) are obtained by the action of conc.  $\text{HCl}$  on the condensation product from  $\text{Me}$  3:4-dimethoxybenzyl- $\alpha$ -cyanoacetate, m.p.  $75-76^\circ$ , and  $O$ -methyleugenol oxide. dl-Dibromomatairesinol  $\text{Me}_2$  ether, from (II) in  $\text{AcOH}$  and  $\text{Br}$ , has m.p.  $109-110^\circ$ ; dl-dinitro-, m.p.  $179-180^\circ$ , and dl-tetranitro-matairesinol  $\text{Me}_2$  ether, m.p.  $185-186^\circ$ . The  $\text{Na}$ -compound of  $\text{Me}$  3:4-methylenedioxybenzyl- $\alpha$ -cyanoacetate, m.p.  $79-80^\circ$ , treated with safrole oxide, and the condens-

ation product boiled with conc.  $\text{HCl}$ , affords  $\alpha\beta$ -bis-(3:4-methylenedioxybenzyl)butyrolactone (dl-cubebinolide) (III), m.p.  $106-107^\circ$ . dl-Dibromo-, m.p.  $119-120^\circ$ , and dl-dinitro-cubebinolide, m.p.  $160-161^\circ$ , are described.  $\beta$ -(3:4-Dimethoxybenzoyl)- $\alpha$ -(3':4'-dimethoxybenzylidene)propionic acid  $\gamma$ -lactone with  $\text{H}_2\text{-PtO}_2$  affords  $\alpha$ -(3:4-dimethoxybenzyl)- $\gamma$ -(3':4'-dimethoxyphenyl)butyrolactone, m.p.  $126-127^\circ$ , converted by  $\text{MeOH}-\text{KOH}-\text{KMnO}_4$  into  $\beta$ -(3:4-dimethoxybenzoyl)- $\alpha$ -(3':4'-dimethoxybenzyl)propionic acid, m.p.  $107-108^\circ$ .  $\text{Na}$   $\beta$ -(3:4-dimethoxybenzoyl)propionate, 2-bromo-4:5-dimethoxybenzaldehyde, and  $(\text{AcO})_2\text{O}$  afford  $\beta$ -(3:4-dimethoxybenzoyl)- $\alpha$ -(2'-bromo-4':5'-dimethoxybenzylidene)propionic acid  $\gamma$ -lactone, m.p.  $202^\circ$  (free acid, m.p.  $225^\circ$ ;  $\text{Me}$  ester, m.p.  $140-141^\circ$ ). Ultra-violet spectrographic data for (II), (III), and  $l$ -matairesinol  $\text{Me}_2$  ether [same as for (II)] are given.

VI.  $\text{Na}$   $\beta$ -(3:4-methylenedioxybenzoyl)propionate, piperonaldehyde, and  $\text{Ac}_2\text{O}$  afford  $\beta$ -(3:4-methylenedioxybenzoyl)- $\alpha$ -(3':4'-methylenedioxybenzylidene)-propionic acid  $\gamma$ -lactone, m.p.  $236-237^\circ$  (free acid, m.p.  $193^\circ$ ). The latter with aq.  $\text{NaOH}$  and  $\text{CH}_2\text{O}$  affords  $\beta$ -(3:4-methylenedioxybenzoyl)- $\alpha$ -(3':4'-methylenedioxybenzylidene)- $\beta$ -methylene- $\gamma$ -propionic acid, m.p.  $184-185^\circ$ , converted into 6:7-methylenedioxy-1-(3':4'-methylenedioxyphenyl)-2-hydroxymethylnaphthalene-3-carboxylic acid lactone (IV), m.p.  $264^\circ$ . Oxidation of (IV) with  $\text{KMnO}_4$  affords 6:7-methylenedioxy-1-(3':4'-methylenedioxyphenyl)naphthalene-2:3-dicarboxylic acid (anhydride, m.p.  $244-246^\circ$ ;  $\text{Me}$  ester, m.p.  $214-215^\circ$ ), also obtained from 3:4-( $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{H}$  and  $(\text{AcO})_2\text{O}$ . Bis-(3:4-methylenedioxyphenyl)methylsuccinic acid, shrinks from  $130^\circ$ , m.p.  $140^\circ$ , prepared from  $\text{C}_6\text{H}_4\cdot\text{O}_2\text{CH}_2$  (prep. given) and  $\text{Et}$  hydroxymethylenesuccinate, could not be converted into the corresponding 4-ketotetrahydronaphthalene derivative. The  $\text{Na}$  derivative of  $\alpha$ -acetyl- $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone with 3:4-( $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\cdot\text{COCl}$ ) affords  $\alpha$ -(3:4-methylenedioxybenzoyl)- $\beta$ -(3:4-methylenedioxybenzyl)butyrolactone, m.p.  $136-137^\circ$ , which when treated with  $\text{MeOH}-\text{HCl}$  followed by  $\text{KHSO}_4$  at  $155^\circ$  gives 6:7-methylenedioxy-1-(3':4'-methylenedioxyphenyl)-3-hydroxymethyl-3:4-dihydronaphthalene-2-carboxylic acid lactone, m.p.  $228-229^\circ$ , hydrogenated ( $\text{Pd}$ -black) to 6:7-methylenedioxy-1-(3':4'-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (V), m.p.  $273-275^\circ$ . Neither  $l$ - nor  $dl$ -hinokinin could be converted into (IV) or (V) by  $\text{Pb}(\text{OAc})_2$ .

P. G. C.

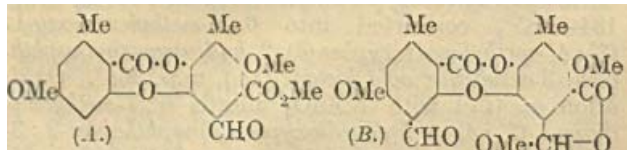
**Structure of abiestic acid. II. Attempted synthesis of 1:3-dimethylcyclohexane-1:2:3-tricarboxylic acid.** B. A. ARBUSOV and O. M. SCHAPCHINSKAJA (J. Gen. Chem. Russ., 1936, 6, 404-416).— $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  and  $\text{CNaMe}(\text{CO}_2\text{Et})_2$  in  $\text{EtOH}$  (at the b.p.) yield the  $\text{Et}_4$  ester of  $\alpha\epsilon$ -dimethylpentane- $\alpha\alpha\epsilon\epsilon$ -tetracarboxylic acid (I), together with by-products, amongst which  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{CO}_2\text{Et})_2$  is identified. (I) and aq.  $\text{EtOH}-\text{KOH}$  (5 hr. at the b.p.) afford  $\alpha\epsilon$ -dimethylpimelic acid, which, with red  $\text{P}$  and  $\text{Br}$  (2 hr. at  $100^\circ$ ), followed by  $\text{EtOH}$  (3.5 hr. at the b.p.), yields  $\text{Et}_2\alpha\epsilon$ -dibromo- $\alpha\epsilon$ -dimethylpimelate, b.p.  $182.5-184^\circ/2.4$



mm., and this is condensed with  $\text{CNa}_2(\text{CO}_2\text{Et})_2$  in EtOH (100°; 3 hr.) to give the  $\text{Et}_3$  ester of 1:3-dimethylcyclohexane-1:2:3-tetracarboxylic acid (II), b.p. 206—208°/2 mm., together with some  $\text{Et}_2$   $\alpha$ -dimethyl- $\Delta^{6,8}$ -pentadiene- $\alpha$ -dicarboxylate, b.p. 138—139°/2 mm., from which the acid  $\text{CH}_2(\text{CH}:\text{CMe}:\text{CO}_2\text{H})_2$ , m.p. 168—171°, is obtained by hydrolysis. The acid obtained by hydrolysis of (II) ( $\text{EtOH-KOH}$ ) yields a glassy mass,  $\text{C}_{11}\text{H}_{14}\text{O}_5$  ( $\text{Me}_3$  ester, b.p. 158—162°/0.7 mm.), when heated in vac. at 160—165°. The structure of the final product was not definitely established.

R. T.

**Lichen substances. LXVII. Stictic acid. III.** Y. ASAHINA, M. YANAGITA, and I. YOSIOKA (Ber., 1936, 69, [B], 1370—1375).—The isolation of stictic acid (I) and a trace of norstictic acid (II) from *Lobaria pulmonaria* (from Oregon) and of *l*-usnic acid, (I), and a little (II) from *L. oregana* (from Oregon) is described. Transformation of the monoanil of (I) into the dianil of (II) is effected by MeI or  $\text{NH}_2\text{Ph.HI}$ . Treatment of (I) with MeI and  $\text{Ag}_2\text{CO}_3$  (cf. Curd and Robertson, A., 1935, 1501) gives a Me ether Me ester, m.p. 176°, having structure A, since it yields a di-*p*-nitrophenylhydrazone, m.p. 245° (decomp.), and is



hydrogenated to hyposalazinolide  $\text{Me}_2$  ether, m.p. 283°; the isomeric Me ether Me ester, m.p. 243°, has structure B, since it gives a mono-*p*-nitrophenylhydrazone, m.p. 259°, and is hydrogenated to Me hypostictate Me ether (III), m.p. 230°, also obtained from hypostictic acid, MeI, and  $\text{Ag}_2\text{O}$ . Similar methylation of salazic acid leads to Me salazate Me ether, m.p. 246°, which loses Me (from OMe) when hydrogenated and gives (III). Stictinic acid di-*p*-nitrophenylhydrazone, decomp. 200° after darkening at 160°, is described.

H. W.

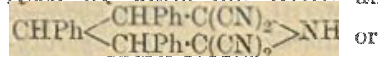
**Oil of *Primula auricula*, L.**—See this vol., 911.

**Synthesis of safranal.** R. KUHN and G. WENDT (Ber., 1936, 69, [B], 1549—1555).—Oxidation of  $\beta$ -cyclocitral [2:6:6-trimethyl- $\Delta^{1,2}$ -cyclohexene-1-aldehyde] [thiosemicarbazone, m.p. 202° (decomp.)] by  $\text{H}_2\text{SeO}_3$  in boiling EtOH- $\text{H}_2\text{O}$  gives rise to safranal [ $\beta$ -trimethyl- $\Delta^{6,7}$ -hexadien- $\alpha$ -aldehyde] (I). The yield is very small, and the desired product is isolated by fractional distillation followed by conversion into a mixture of semicarbazones which is separated by fractional sublimation in high vac. The oxime, m.p. 65°, thiosemicarbazone, m.p. 199—200°, and 2:4-dinitrophenylhydrazone, m.p. 186°, of (I) are described. The following substances are incidentally described: Me  $\alpha$ -cyclogeranyl dibromide, m.p. 71—72°;  $\alpha$ -cyclogeranyl acetate dibromide, m.p. 112°;  $\alpha$ -cyclocitralsemicarbazone dibromide, m.p. 148.5° (decomp.);  $\alpha$ -cyclocitral Et. acetal, b.p. 67—68°/1.3 mm. The prep. of homogeneous  $\alpha$ - (II) and  $\beta$ -cyclocitral is described. (II) is transformed by reduction with  $\text{Al}(\text{OPr}^i)_3$  in  $\text{Pr}^i\text{OH}$  into  $\alpha$ -cyclogeraniol.

H. W.

# System benzaldehyde-ammonia-malonic acid.

T. BOEHM and (FRL.) M. GROHNWALD (Arch. Pharm., 1936, 274, 329—342).— $\text{PhCHO}$ ,  $\text{CH}_2(\text{CO}_2\text{H})_2$  (I), and  $\text{NH}_3$ -EtOH at 0° ppt. immediately a mixture of hydrobenzamide (II) and  $\text{NH}_4$  H malonate, which in hot EtOH gives  $\text{NH}_4$  H benzylidenemalonate (III), m.p. 148° (cf. A., 1927, 137). (III) is best obtained from (I) and (II) alone in EtOH, and hydrofurfuramide and (I) similarly give a good yield of furfurylidene-malonic acid; reaction probably occurs by hydrolysis to  $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{NH}_2$  and condensation thereof with (I). Evaporation of (III) in 50% aq. EtOH to dryness during 5 hr. and treatment of the residue with hot HCl affords  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (IV) and  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (V); no (IV) is obtained by heating (III) directly with HCl (cf. loc. cit.) and it is probable that reaction occurs by decarboxylation of some (III) to (V) and hydrolysis of the remainder to (I) and  $\text{PhCHO}$ , followed in the more conc. solution by formation of (II) and thence of (IV). (II) and (I) in dry Et<sub>2</sub>O give an unstable 1:2 additive compound, decomp. about 70°, which in hot MeOH yields  $\alpha$ -( $\alpha'$ -benzylideneaminobenzylamino)benzylmalonic ("tribenzylidenedi-iminomalonic") acid,  $\text{CHPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})_2$ , m.p. 142°. With hot 5% HCl this yields  $\text{PhCHO}$  and the lactone (6-keto-2:4-diphenyltetrahydro-1:3-oxazine), m.p. 243° (hydrochloride, m.p. 253°; Ac derivative, m.p. 201°), of  $\beta$ - $\alpha$ -hydroxybenzylamino- $\beta$ -phenylpropionic acid and thence (IV). *p*-Methylhydrobenzamide (VI) (1 mol.) and (I) (2 mols.) in Et<sub>2</sub>O give  $\alpha$ -( $\alpha'$ -*p*-methylbenzylideneamino-*p*-methylbenzylamino)-*p*-methylbenzylmalonic acid, very unstable. (II) and  $\text{CH}_3(\text{CN})_2$  give  $\alpha$ -( $\alpha'$ -benzylideneaminobenzylamino)benzylmalondinitrile (VII),  $\text{CHPh}\cdot\text{N}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})_2$ , m.p. 142°, which is hydrolysed by cold KOH or 25% HCl or hot 5% HCl to  $\text{PhCHO}$  and  $\text{CHPh}\cdot\text{C}(\text{CN})_2$  (VIII). (VI) gives a similar dinitrile, m.p. 128°.  $\text{CH}_3(\text{CN})_2$  (2 mols.),  $\text{PhCHO}$  (3 mols.), and  $\text{NH}_3$ -EtOH give a compound,  $\text{C}_{27}\text{H}_{19}\text{N}_5$ , m.p. 192° (decomp.), also obtained in good yield from (VIII) and cold  $\text{NH}_3$ -EtOH or in poor yield by boiling (VII) in EtOH; it is stable to cold conc. HCl, but is hydrolysed by warm dil. KOH and is thus probably



$\text{CHPh} \begin{array}{c} \text{C}(\text{CN})_2\cdot\text{CHPh} \\ \text{C}(\text{CN})_2\cdot\text{CHPh} \end{array} \text{NH}$ .  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}:\text{CH}(\text{CN})_2$  and  $\text{NH}_3$ -MeOH give a similar  $(\text{CN})_4$ -compound, +MeOH or +0.5 dioxan, m.p. 162° (decomp.). (II) and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  in EtOH give the mononitrile-monoamide, +EtOH or  $\text{C}_6\text{H}_6$ , decomp. 158° [decomposed by cold, conc. HCl to  $\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ ], derived from (VII), and (VI) gives a similar compound, decomp. 155°.

R. S. C.

**Products of the transformation of 2:4:6-trinitro- and 2:4-dinitro-benzylideneaniline under the action of sodium carbonate in alcoholic solution.** S. SECAREANU and I. LUPAS (Bull. Soc. chim., 1936, [v], 3, 1161—1164).—2:4:6-Trinitrobenzaldehyde is converted by insolation in sunlight into 4:6-dinitro-2-nitrosobenzoic acid, which, with  $\text{NH}_2\text{Ph}$  in AcOH, gives a mixture of products none of which is similar to the substances obtained from

tri- or di-nitrobenzylideneaniline under the action of  $\text{Na}_2\text{CO}_3$  in EtOH; the indazolone structure of these compounds is thus indirectly confirmed.

H. W.

***o*-Chlorobenzaldehyde diacetate.** S. M. SCHERLEN (J. Gen. Chem. Russ., 1936, 6, 508—510).—The substance described by Erdmann and Schwechten (cf. A., 1891, 448) as *o*-chlorobenzaldehyde diacetate (I) is actually *o*-chlorocinnamic acid. (I), m.p. 53°, is obtained from *o*-chlorobenzaldehyde and  $\text{Ac}_2\text{O}$  in AcOH (170°; 5 hr.), and condenses with *o*-toluidine in presence of Cu (160—175°; 4 hr.) to yield  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , m.p. 74—75°. R. T.

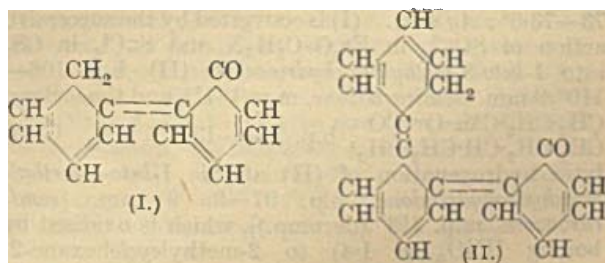
**Elimination of methyl from an *o*-methoxybenzaldehydeanil.** Y. ASAHINA and I. YOSIOKA (Ber., 1936, 69, [B], 1367—1369).—Removal of Me from an *o*-methoxybenzaldehydeanil by MeI or, more correctly, by  $\text{NH}_2\text{Ph}\cdot\text{HI}$  occurs readily only when OH or OAlk is also present in position 3 or 6. 2:3:4-Trimethoxybenzaldehydeanil, m.p. 75°, and  $\text{NH}_2\text{Ph}\cdot\text{HI}$  at 100° give 2-hydroxy-3:4-dimethoxybenzaldehydeanil, m.p. 153—154°, whence 2-hydroxy-3:4-dimethoxybenzaldehyde, m.p. 73°. Similarly the anil of cotarninemethine methiodide gives the substance,  $\text{C}_{13}\text{H}_{18}\text{O}_4\text{NI}$ , m.p. 271° (decomp.), and benzoyl-cotarnineanil affords benzoylnorcotarnine, isolated as the benzoate, m.p. 159°. Atranol Me<sub>2</sub> ether is converted by  $\text{NH}_2\text{Ph}$  into the anil, m.p. 102—103°, converted with some difficulty by  $\text{NH}_2\text{Ph}\cdot\text{HI}$  into atranol Me<sub>2</sub> ether. *o*-Methoxybenzaldehydeanil and 3-nitro-2-methoxybenzaldehydeanil, m.p. 60—61°, are scarcely affected by  $\text{NH}_2\text{Ph}\cdot\text{HI}$ . H. W.

**Complex chemical ring systems with para-linkages. I. Copper derivatives of bis-*p*-hydroxybenzylidene- and bis-vanillylidene-*o*-phenylenediamine.** Y. NAKATSUKA and H. IINUMA (Bull. Chem. Soc. Japan, 1936, 11, 358—362).—When  $\text{Cu}(\text{OAc})_2$  is warmed with *p*-OH- $\text{C}_6\text{H}_4\cdot\text{CHO}$  and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{H}_2\text{O}$ , *Cu* bis-*p*-hydroxybenzylidene-*o*-phenylenediamine (+2 $\text{H}_2\text{O}$ ; anhyd. from MeOH) is obtained, for which a formula is suggested. A compound could not be obtained using  $\text{NH}_3$ ,  $\text{NH}_2\text{Ph}$ , *m*- or *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  as base. Vanillin and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$  give a similar *Cu* bis-vanillylidene-*o*-phenylenediamine (+ $\frac{3}{2}\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}$ ), and a more complex compound, probably  $\text{C}_6\text{H}_4(\text{N})_2[\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{Cu}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2]_2\cdot 5\text{H}_2\text{O}$ . Copper divanillin,  $\text{Cu}[\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}]_2$ , and *Cu* diguaiacol are also described. J. T. A.

**Cannizzaro reaction. V. Derivatives of 3:5-dimethoxybenzaldehyde.** G. LOCK and G. NOTTES (Monatsh., 1936, 68, 51—67; cf. A., 1935, 1238).—3:5-Disulphobenzoic acid (from BzOH and 65% oleum at 240—250°) (as Ba salt) with NaOH+KOH at 280—310° gives 3:5-(OH)<sub>2</sub>- $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$  (I), m.p. 237—240° (decomp.) (lit. 220—240°). 3:5-(OMe)<sub>2</sub>- $\text{C}_6\text{H}_3\cdot\text{CHO}$  (II), prepared from 3:5-(OMe)<sub>2</sub>- $\text{C}_6\text{H}_3\cdot\text{COCl}$  by Mauthner's method (A., 1920, i, 743), is converted by warm 50% KOH into 3:5-(OMe)<sub>2</sub>- $\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$  and 3:5-(OMe)<sub>2</sub>- $\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{OH}$ . (II) and Br (1 mol.) in AcOH afford 85% of 2-bromo-3:5-dimethoxybenzaldehyde (III), m.p. 107° (phenylhydrazone, m.p. 108°), converted by 50% KOH into

2-bromo-3:5-dimethoxybenzyl alcohol, m.p. 96° (*p*-nitrobenzoate, m.p. 165°), and 2-bromo-3:5-dimethoxybenzoic acid, m.p. 202—203° (corr.) (Ag salt) [also obtained by oxidation ( $\text{KMnO}_4$ ) of (III)]. 4-Bromo-3:5-dimethoxybenzoic acid, m.p. 251° (corr.), is prepared by methylation ( $\text{Me}_2\text{SO}$ , 5% NaOH) of 3:5:4-(OH)<sub>2</sub>- $\text{C}_6\text{H}_2\cdot\text{Br}\cdot\text{CO}_2\text{H}$ . 2:6-Dibromo-3:5-dimethoxybenzaldehyde, m.p. 222—223° (corr.) (with darkening) [phenylhydrazone, m.p. 158° (corr.)], from (II) or (III) and Br in AcOH, is oxidised to the acid, m.p. 256° (corr.) (darkening) (Ag salt), and converted by 50% KOH into  $\text{HCO}_2\text{H}$  and 4:6:1:3- $\text{C}_6\text{H}_2\text{Br}_2(\text{OMe})_2$ . 2-Chloro-3:5-dimethoxybenzaldehyde (IV), m.p. 119.5° [semicarbazone, m.p. 218° (corr.)], and 50% KOH give 2-chloro-3:5-dimethoxybenzyl alcohol, m.p. 127°, and -benzoic acid (V), m.p. 181—182° (corr.). (V) is also prepared by oxidation of (IV) and by methylation of 2-chloro-3:5-dihydroxybenzoic acid, m.p. 249° (corr.) [from (I) and  $\text{SO}_2\text{Cl}_2$  in Et<sub>2</sub>O]. (II) or (IV) and  $\text{Cl}_2$  in AcOH afford 2:6-dichloro-3:5-dimethoxybenzaldehyde, m.p. 180—181° (corr.) [semicarbazone, m.p. 272° (decomp.)], which is oxidised to the acid, m.p. 209° (corr.), and converted by 50% KOH into  $\text{HCO}_2\text{H}$  and 4:6:1:3- $\text{C}_6\text{H}_2\text{Cl}_2(\text{OMe})_2$ . (III) [in  $\text{HNO}_3$  (d 1.4)] with  $\text{HNO}_3$  (d 1.5) gives 2-bromo-6-nitro-3:5-dimethoxybenzaldehyde, m.p. 213° (corr.) [phenylhydrazone, m.p. 153° (corr.)]; corresponding acid, m.p. 232° (corr.) (decomp.), which with 50% KOH affords  $\text{HCO}_2\text{H}$  and 4-bromo-6-nitroresorcinol Me<sub>2</sub> ether. (II) and  $\text{HNO}_3$  (d 1.5) at -5° give 2:6-dinitro-3:5-dimethoxybenzaldehyde, m.p. 228° (corr.) [phenylhydrazone, m.p. 211° (corr.) (decomp.)]; corresponding acid, m.p. 232—233° (corr.) (decomp.), readily converted by 50% KOH into  $\text{HCO}_2\text{H}$  and 4:6-dinitroresorcinol Me<sub>2</sub> ether. All the above substitution reactions with (II) result in the exclusive introduction of substituents *ortho* to CHO. H. B.

**Alicyclic compounds. II. Electrolytic oxidation of cyclohexanone.** F. PIRRONE (Gazzetta, 1936, 66, 244—253).—Electrolysis of cyclohexanone in  $\text{H}_2\text{SO}_4$  or MeOH, using  $\text{PbO}_2$  or Pt anodes, under varying conditions, gives a mixture of a ketone  $\text{C}_{18}\text{H}_{14}\text{O}$ , b.p. 253—257°/760 mm. (oxime, m.p. 145—146°), probably represented by (I); a ketone



$\text{C}_{18}\text{H}_{14}\text{O}$ , b.p. 268—270°/760 mm. (oxime, m.p. 152—154°), for which formula (II) is suggested, triphenylene, and maleic acid. E. W. W.

**Ethyl acetal of cyclohexanone, and its transformation into cyclohexenyl ether.** A. E. ARBU-SOV and B. M. MICHAÏLOVA (J. Gen. Chem. Russ., 1936, 6, 390—393).—cycloHexanone (I) and  $\text{CH}(\text{OEt})_2$  in EtOH afford the acetal (II) of (I). A 1:2:4 mixture of (II),  $\text{P}_2\text{O}_5$ , and  $\text{C}_5\text{H}_5\text{N}$  (100°; 5 hr.)



yields the *Et* ether, b.p. 56—56.5°/15 mm., of  $\Delta^1$ -cyclohexenol. R. T.

**Cyclic thioketones. I. Synthesis of non-polymerised thiocyclo-hexanone and -pentanone and their derivatives.** D. C. SEN (J. Indian Chem. Soc., 1936, 13, 268—272).—Passage of dry HCl and H<sub>2</sub>S into cyclohexanone in EtOH for 3 hr. gives the trimeride of thiocyclohexanone, m.p. 102°, but after 1—1.5 hr. monomeric thiocyclohexanone (I), b.p. 76°/15 mm. (*Pb* salt), is obtained. With NHPH.NH<sub>2</sub> and semicarbazide (I) affords cyclohexanone-phenylhydrazones (II) and -semicarbazones, respectively. When freshly distilled, it is pink, changing to orange, and then colourless; titration with I (which reacts with SH, but not with CS) in EtOH shows 38% of the thiol form immediately and 70% 1 hr. after distillation. The Na salt of (I) with MeI in Et<sub>2</sub>O gives methylthiol- $\Delta^1$ -cyclohexene, b.p. 55°/15 mm., unstable to Br and KMnO<sub>4</sub>, which with NHPH.NH<sub>2</sub> affords (II) and SHMe. (I), NaOAc, and hot Ac<sub>2</sub>O afford acetylthiol- $\Delta^1$ -cyclohexene, pink (stable), b.p. 85°/10 mm., unsaturated to Br and KMnO<sub>4</sub>, which with NHPH.NH<sub>2</sub> yields (II) and H<sub>2</sub>S. Thiocyclopentanone (III), b.p. 86—88°/10 mm., and acetylthiol- $\Delta^1$ -cyclopentene, b.p. 67°/8 mm., are similarly prepared and have similar properties. The mol. wts. in cold C<sub>6</sub>H<sub>6</sub> of the Ac derivatives are normal, but those of (I) and (III) are 50% too high, indicating partial association. R. S. C.

**General methods of synthesis of poly-alicyclic  $\alpha$ -ketones with angular methyl group.** C. K. CHUANG, Y. L. TIEN, and C. M. MA (Ber., 1936, 69, [B], 1494—1505).—Two general methods are illustrated. Et  $\beta$ -cyclohexan-2-one-1-propionate is hydrolysed by boiling conc. HCl to cyclohexanonepropionic acid, m.p. 66—67°, the Me ester, b.p. 140—141°/10 mm., of which is transformed by MgMeI into Me  $\beta$ -2-hydroxy-2-methylcyclohexylpropionate. This is converted by SOCl<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N—Et<sub>2</sub>O into Me  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylpropionate (I), b.p. 149—150°/10 mm., which does not dissolve in NaOH or Na<sub>2</sub>CO<sub>3</sub> and is hydrolysed by KOH—EtOH to  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylpropionic acid, b.p. 117—120°/0.6 mm. (dibromide, m.p. 137°; *p*-bromophenacyl ester, m.p. 73—73.5°; Ag salt). (I) is converted by the successive action of SOCl<sub>2</sub> in Et<sub>2</sub>O—C<sub>5</sub>H<sub>5</sub>N and SnCl<sub>4</sub> in CS<sub>2</sub> into 1-keto-8-methylhexahydroindene (II), b.p. 106—110°/9 mm. (semicarbazone, m.p. 187°), and the lactone, CH<sub>2</sub>·CH<sub>2</sub>·CMe·O·CO·CH<sub>2</sub>·CH<sub>2</sub>·CH·CH<sub>2</sub>·CH<sub>2</sub>, b.p. 135—137°/6 mm. Catalytic hydrogenation of (II) affords 1-keto-8-methylhexahydroindene, b.p. 97—98°/9 mm. [semicarbazone, m.p. 213° (decomp.)], which is oxidised by boiling HNO<sub>3</sub> (d 1.4) to 2-methylcyclohexane-2-carboxylic-1-acetic acid, m.p. 163—164°.

2-Methylcyclohexanone is converted by CH<sub>2</sub>Br·CO<sub>2</sub>Et into Et 2-methylcyclohexan-1-ol-2-acetate, b.p. 134—135°/18 mm., dehydrated by SOCl<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N to Et 2-methyl- $\Delta^1$ -cyclohexenylacetate, b.p. 110—111.5°/14 mm., reduced (Bouveault) to  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylethyl alcohol, b.p. 97—98.5°/8 mm. Unstable  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylethyl bromide and CHK(CO<sub>2</sub>Et)<sub>2</sub> afford Et  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylethylmalonate, b.p. 142—

145°/2 mm., whence  $\beta$ -2-methyl- $\Delta^1$ -cyclohexenylethylmalonic acid, m.p. 92—93°, and  $\gamma$ -2-methyl- $\Delta^1$ -cyclohexenylbutyric acid (III), b.p. 115—116°/0.5 mm. (*p*-bromophenacyl ester, m.p. 65—66°). (III) is converted through its chloride into 1-keto-9-methyloctahydronaphthalene (IV), b.p. 110—112°/9 mm. (semicarbazone, m.p. 226—227°; oxime, m.p. 99—100°). (IV) is reduced (Clemmensen) to the corresponding hydrocarbon, which does not react with Se at 320—350° or 350—400°, but passes at 430—450° into C<sub>10</sub>H<sub>8</sub>, thus establishing the position of Me. Hydrogenation (Pt sponge in abs. EtOH) of (IV) leads to 1-keto-9-methyldecahydronaphthalene (semicarbazone, m.p. 225—226°), oxidised by conc. HNO<sub>3</sub> to 1-methylcyclohexene-1-carboxylic-2- $\beta$ -propionic acid (Ag salt). H. W.

**Tertiary  $\alpha$ -keto-alcohols, and the influence of radicals (methyl and phenyl) entering into their composition.** A. M. CHALETZKI (J. Gen. Chem. Russ., 1936, 6, 1—14).—CHPhMe·CHO or  $\text{CPhMe} \cdot \text{CH} \cdot \text{O}$  and MgBu<sup>+</sup>Cl yield a mixture of C<sub>2</sub>Me<sub>6</sub>,  $\beta$ -phenyl-*n*-propyl alcohol, b.p. 113—114°/10 mm., and  $\beta$ -phenyl- $\alpha$ -tert.-butyl-*n*-propyl alcohol (I), b.p. 106—108°/10 mm., which is oxidised by aq. H<sub>2</sub>CrO<sub>4</sub> in presence of KHSO<sub>4</sub> to yield CPhMe (II) and Bu<sup>+</sup>CO<sub>2</sub>H (III); with more mild oxidation the products are a mixture of (I), (II), (III), and  $\alpha$ -phenylethyl Bu<sup>+</sup> ketone (IV), b.p. 103—104°/10 mm. A mixture of (I) and (IV) reacts with Br in H<sub>2</sub>O in presence of CaCO<sub>3</sub> to yield  $\alpha$ -bromo- $\alpha$ -phenylethyl Bu<sup>+</sup> ketone (V), b.p. 152—153°/10 mm., and  $\beta$ - $\gamma$ -dibromo- $\beta$ -phenyl-*dimethyl-n-pentane*, m.p. 167—168°, whilst with PBr<sub>3</sub> in light petroleum the products are  $\gamma$ -bromo- $\alpha$ -phenyl- $\delta$ -*dimethyl-n-pentane*, b.p. 122—124°/10 mm., and (V). (V) decomposes when heated at 100° with BaCO<sub>3</sub> to yield  $\alpha$ -hydroxy- $\alpha$ -phenylethyl Bu<sup>+</sup> ketone (VI) (semicarbazone, m.p. 196—197°). The cyanohydrin of (II) and MgBu<sup>+</sup>Cl at -10° afford C<sub>2</sub>Me<sub>6</sub>, (II), and (VI), the products of oxidation (KMnO<sub>4</sub>) of which are (II) and (III). (VI) is converted into  $\alpha$ -phenylvinyl Bu<sup>+</sup> ketone (VII), b.p. 88—89°/18 mm., when heated in EtOH with a few drops of H<sub>2</sub>SO<sub>4</sub>. (VII) and MgMeBr afford  $\gamma$ -hydroxy- $\beta$ -phenyl- $\gamma$ -*trimethyl- $\Delta^2$ -n-pentene*, b.p. 106—107°/18 mm., oxidised by KMnO<sub>4</sub> to give a mixture of HCO<sub>2</sub>H, BzOH, and COMeBu<sup>+</sup>. R. T.

**Direct synthesis of 2'-halogenomesobenzanthrones.** I. M. HEILBRON, R. N. HESLOP, and F. IRVING (J.C.S., 1936, 781—785).—*s*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> with AlCl<sub>3</sub> in dry CHCl<sub>3</sub> at 30° affords *s*-pentachloropropane, converted by the theoretical amount of EtOH—KOH into  $\alpha$  $\beta$  $\gamma$ -tetrachloro- $\Delta^2$ -propylene (I) (cf. A., 1914, i, 648), which with anthrone in conc. H<sub>2</sub>SO<sub>4</sub> at 50° gives 2'-chloromesobenzanthrone, identical with the product obtained by the interaction of Cu<sub>2</sub>Cl<sub>2</sub> and HCl with mesobenzanthrone-2'-diazonium sulphate. Similarly, 1:4- (cf. A., 1929, 1289) and 1:5-dichloroanthrone (cf. J.C.S., 1923, 123, 2549) afford 2':5-*S*, m.p. 180—181°, and 2':4-*S*-trichloromesobenzanthrone, m.p. 190—191°, respectively. 4-Chloroanthrone similarly yields 2':4-dichloro-, m.p. 203—204°, and 2':5-dichloromesobenzanthrone, m.p. 240°, oxidised (CrO<sub>3</sub>—AcOH) to

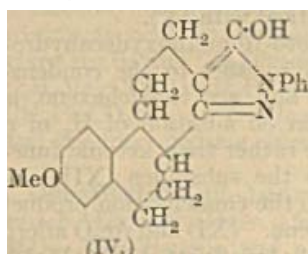
4- and 5-chloroanthraquinone-1-carboxylic acid, respectively. 2-Chloro-, 2':5-dichloro-, and 2':5:8-trichloro-*mesobenzanthrones* when fused with EtOH-KOH afford purple vat dyes, whereas the 2':4-Cl<sub>2</sub>- and 2':4:8-Cl<sub>2</sub>-compounds do not, probably because the Cl<sub>4</sub> renders the 2 position unreactive. *s*-C<sub>2</sub>H<sub>5</sub>Br<sub>2</sub> with CHCl<sub>3</sub> in presence of AlCl<sub>3</sub> gives  $\alpha\gamma$ -trichloro- $\alpha\beta$ -dibromopropane, converted by EtOH-KOH into a mixture of chlorobromopropylenes (II), hydrolysed by conc. H<sub>2</sub>SO<sub>4</sub> at 30–40° to bromomalondialdehyde (III), m.p. 139–140° (cf. A., 1914, i, 648). (II) gives no *mesobenzanthrone* with anthrone in conc. H<sub>2</sub>SO<sub>4</sub>, but with anthrone, conc. H<sub>2</sub>SO<sub>4</sub> at 60°, and SO<sub>2</sub>, (III) gives 1'-bromomesobenzanthrone, m.p. 174–175° (lit., 170°), identical with the product of bromination of *mesobenzanthrone*, which with boiling CH<sub>3</sub>Ph-CN containing Cu<sub>2</sub>(CN)<sub>2</sub> gives 1'-cyanomesobenzanthrone. 2'-Bromo-, m.p. 194–195° (converted by fusion with EtOH-KOH into a dibenzanthrone), and 2'-cyano-*mesobenzanthrone*, m.p. 285–286°, are obtained from the 2'-NH<sub>2</sub>-compound and are different from the 1'-compounds (above). The latter with boiling 50% H<sub>2</sub>SO<sub>4</sub> gives *mesobenzanthrone*-2'-carboxylic acid, m.p. 341–342° (lit., 347°) (*Et* ester, m.p. 172–173°). J. L. D.

**Reagents for isolation of carbonyl compounds from unsaponifiable material.** (MISS) M. ANCHEL and R. SCHOENHEIMER (J. Biol. Chem., 1936, 114, 539–546).—Cholestanone (I), cholestenone (II), and coprostanone (III) give with aminoxyacetic acid, *oxime O-carboxymethyl ethers*, m.p. 151–152°, 158–159° (decomp.), and 150–151° (decomp.), and with NH<sub>2</sub>·NH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H autoxidisable *p*-carboxyphenylhydrazones, decomp. > 200° [those of (I) and (III) are hydrolysed by CH<sub>2</sub>O; that of (II) is stable to CH<sub>2</sub>O, but is hydrolysed by AcCO<sub>2</sub>H]. (I) gives readily with hydrazinoacetic acid a *carboxymethylhydrazone*, sol. in Et<sub>2</sub>O and rapidly hydrolysed by alkali; the *carboxymethylhydrazone* of (II) is formed only slowly, is not readily extracted by Et<sub>2</sub>O, is stable to CH<sub>2</sub>O, but is hydrolysed by AcCO<sub>2</sub>H. NH<sub>2</sub>·NH·CO·CH<sub>2</sub>·NMe<sub>3</sub>Cl gives with (I) a compound, hydrolysed by H<sub>2</sub>O. The separation of (I), (II), and cholesterol in mineral oil by means of *p*-NH<sub>2</sub>·NH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H is described. Hydrazones of  $\alpha\beta$ -unsaturated ketones are generally more resistant to hydrolysis than are those of saturated ketones.

R. S. C.

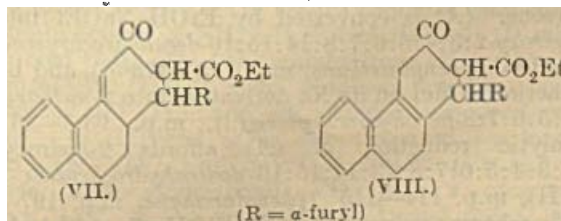
**Synthesis of substances related to the sterols.** IX. R. ROBINSON and J. WALKER. X. Condensation of furfurylidene-tetralone with ethyl acetoacetate, and analogous studies. D. A. PEAK, R. ROBINSON, and J. WALKER. XI. Constitution of the condensation products from acetylcyclopentene or acetylcyclohexene and methoxytetralone. D. M. CROWFOOT, W. S. RAPSON, and R. ROBINSON. XII. Some hydrochrysene derivatives. D. A. PEAK and R. ROBINSON. XIII. Hydrocyclopentanophenanthrene derivatives. J. R. HAWTHORNE and R. ROBINSON (J.C.S., 1936, 747–752, 752–757, 757–759, 759–763, 763–765).—IX. The Grignard reagent from  $\gamma$ -*m*-methoxyphenylpropyl chloride with CH<sub>2</sub>Cl·CH<sub>2</sub>·COCl gives, probably,  $\beta$ -chloroethyl  $\gamma$ -*m*-methoxyphenylpropyl ketone, b.p.

200–212°/0.27 mm.  $\gamma$ -*m*-Methoxyphenylbutyryl chloride and Et sodio- $\alpha$ -acetylglutarate afford, after intermediate treatment, *Me* 5-*keto*-8-*m*-methoxyphenyl-octoate, b.p. 180–187°/0.2 mm., converted by NaOEt into  $\beta$ -*m*-methoxyphenylethylcyclohexane-2:6-dione, m.p. 150°. Treatment by the known method affords 1-*keto*-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene, hydrogenated (Pd-SrCO<sub>3</sub>, or colloidal Pd) to 7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene-1-ol- $\alpha$  (I); from MeOH, (I) softens at 99–104° and clears at 105°; from EtOAc, it sinters at 106°, softens from 108°, and clears at 111° (*p*-nitrobenzoate, m.p. 125–126° after sintering at 120°). (I) is probably stereoisomeric with the substance described by Robinson and Schlittler (A., 1935, 1499). Beckmann's mixture converts it into 1-methoxy-1:2:3:4-tetrahydrophenanthrene [2:4-dinitrophenylhydrazone, m.p. 304° (decomp.)], but CrO<sub>3</sub>-AcOH affords 1-*keto*-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene (II), m.p. 109°, isolated by way of the semicarbazone, m.p. 225°, or Girard's reagent; the material so obtained is only partly cryst., the oily portion affording further crystals when treated with hot aq. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. X-Ray analysis indicates that (II) is the *trans*-form; 2:4-dinitrophenylhydrazone, sinters 205°, m.p. 209.5° (decomp.). (II) and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> afford *Et* 1-*keto*-7-methoxy-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate (III), b.p. 195–205°/0.35 mm. From NHPh·NH<sub>2</sub> and (III), 5-hydroxy-1-phenyl-3:4-(1'-ethoxy-3':4':9':10':11':12'-hexahydrophenanthreno-1':2')-pyrazole (IV) is obtained, sinters at approx. 230°, softens from 245°, m.p. 258–260° (decomp.). The K derivative of (III) and MeI afford *Et* 1-*keto*-7-methoxy-2-methyl-



1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate, b.p. 180–192°/0.13 mm.

X. Et  $\beta$ -formylpropionate (V) (from Et hydroxymethylenesuccinate), CH<sub>3</sub>Ac·CO<sub>2</sub>Et, and Ac<sub>2</sub>O afford *Et*  $\gamma$ -carbethoxypropylideneacetoacetate, b.p. 168–170°/10 mm.; a purer product is obtained using HCl in place of (AcO)<sub>2</sub>O. Neither this substance nor (V) could be condensed with 6-methoxytetralone. Furfuraldehyde and  $\alpha$ -tetralone (VI) afford 2-furfurylidene- $\alpha$ -tetralone, m.p. 75–76°, which condenses with CHNaAc·CO<sub>2</sub>Et to give two forms of *Et* 3-*keto*-1- $\alpha$ -furylhexahydrophenanthrene-2-carboxylate,  $\alpha$ -form (probably VII), m.p. 119–120°,  $\beta$ -form (probably VIII), m.p. 120–121°. (VII) is also obtained from *Et* furfurylideneacetoacetate and the Na derivative



of (VI). Hydrolysis of (VIII), or a modified prep. of (VII), affords 3-*keto*-1-furyl-1:2:3:4:9:10-hexahydro-



phenanthrene, m.p. 113—114°. Hydrogenation (Pd-SrCO<sub>3</sub> catalyst) of (VII) affords *Et* 3-keto-1-furyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate, m.p. 134.5—135.5°, converted by way of its K derivative and MeI into *Et* 3-keto-1-furyl-2-methyl-1:2:3:4:9:10:11:12-octahydrophenanthrene-2-carboxylate, m.p. 93—93.5°. 6-Methoxy-2- $\alpha$ -furfurylidene- $\alpha$ -tetralone, m.p. 104.5°, is obtained from 6-methoxy- $\alpha$ -tetralone (IX) and C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>; with CHNaAc.CO<sub>2</sub>Et it affords *Et* 3-keto-7-methoxy-1- $\alpha$ -furyl-1:2:3:4:9:10-hexahydrophenanthrene-2-carboxylate, m.p. 137—138°, and a second substance, m.p. 122°, probably formed by dehydrogenation during the reaction. Veratraldehyde and (IX) afford 6-methoxy-2-veratrylidene- $\alpha$ -tetralone, m.p. 111—112°; if the reaction is effected in EtOH a substance (X), m.p. 110—111°, of unknown structure is obtained, possibly containing OEt in place of OMe. Condensation of *m*-OEt.C<sub>6</sub>H<sub>4</sub>.CHO and CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>, followed by esterification, affords *Et* *m*-ethoxycinnamate, b.p. 158°/1 mm., hydrogenated (Pd-SrCO<sub>3</sub> catalyst) to *Et*  $\beta$ -*m*-ethoxyphenylpropionate, b.p. 148°. Na-EtOH reduction gives  $\gamma$ -*m*-ethoxyphenylpropyl alcohol, b.p. 130°/3 mm., converted by SOCl<sub>2</sub> into  $\gamma$ -*m*-ethoxyphenylpropyl chloride, b.p. 111°/1 mm. The corresponding  $\gamma$ -*m*-ethoxyphenylbutyronitrile, b.p. 127°/0.6 mm., is hydrolysed to  $\gamma$ -*m*-ethoxyphenylbutyric acid, m.p. 65—66° (amide, m.p. 84—85°), which with H<sub>2</sub>SO<sub>4</sub> affords 6-ethoxy- $\alpha$ -tetralone, m.p. 46—47°. The veratrylidene derivative, m.p. 119—120°, is not identical with (X).

XI. The structure, 2-keto-10-methoxydecahydrochrysene, ascribed (A., 1935, 1498) to the condensation product from (IX) and acetylcyclohexene, is confirmed by the formation on addition of H<sub>2</sub> of a substance (XI) of alcoholic rather than ketonic function; this also applies to the substance (XII) obtained by addition of H<sub>2</sub> to the condensation product of (IX) and acetylcyclopentene. (XI) and Ac<sub>2</sub>O afford 2-acetoxy-10-methoxy-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene, m.p. 155—156°, whilst 3-acetoxy-7-methoxy-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene, m.p. 102—103°, is obtained similarly from (XII). The X-ray crystal analyses of (XI), (XII), and the two OAc-derivatives confirm the ascribed structures.

XII. Condensation of the Na derivative of (VI) with acetylcyclohexene affords three isomeric 2-keto-decahydrochrysenes; (A), m.p. 200—200.5°, and (B), m.p. 152—153°, have identical absorption spectra, similar to that of benzylideneacetone, whilst (C), m.p. 115—115.5°, has an entirely different spectrum; it is suggested that (A) and (B) are stereoisomeric 2-keto-2:3:4:5:6:7:8:14:15:16-decahydrochrysenes, and that (C) is 2-keto-1:2:3:4:5:6:7:8:15:16-decahydrochrysene. (A) is converted by EtOH-NaOEt into 2-hydroxy-2:3:4:5:6:7:8:14:15:16-decahydrochrysene, m.p. 136° (phenylurethane, m.p. 173—173.5°), and by the action of MeI on its Na derivative into 2-methoxy-3:4:5:6:7:8-hexahydrochrysene (?), m.p. 95.5—96°. Catalytic reduction of (A) affords 2-hydroxy-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene- $\alpha$  (XIII), m.p. 114—115° (phenylurethane, m.p. 197—198°), whereas reduction by Na-EtOH affords 2-hydroxy-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene- $\beta$  (XIV), m.p. 134—135° (phenylurethane, m.p.

197—198°). (XIII) is converted into (XIV) by a hot solution of Na in *iso*-C<sub>5</sub>H<sub>11</sub>.OH, and with CrO<sub>3</sub>-AcOH both give 2-keto-1:2:3:4:5:6:7:8:13:14:15:16-dodecahydrochrysene, m.p. 145—146° [oxime, m.p. 220—221° (decomp.); semicarbazone (XV), m.p. 223—224°]; a benzylidene derivative could not be prepared, neither could the ketone be methylated. Clemmensen reduction of (A) affords a mixture of decahydrochrysenes, but NaOEt converts (XV) into a homogeneous decahydrochrysene, m.p. 93—94°. This substance and (A) both afford chrysene when heated with Se; a by-product of the second of these dehydrogenations is a substance, C<sub>18</sub>H<sub>12</sub>O, m.p. 210—220° (decomp.) after darkening at 205°.

XIII. Condensation of the Na derivative of (IX) with acetylcyclopentene affords a mixture of substances containing 3-keto-3:9:10:11-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 169—170° [oxime, m.p. 235.5° (decomp.)]. Catalytic reduction gives 3-hydroxy-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene (XVI), m.p. 106° (phenylurethane, m.p. 175°), oxidised (CrO<sub>3</sub>-AcOH) to 3-keto-3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene (XVII), m.p. 115—116.5°; the semicarbazone, m.p. 191—192°, is converted by NaOEt (sealed tube) into 3:9:10:11-tetrahydro-1:2-cyclopentanophenanthrene, b.p. 164—165°/3 mm. Reduction of (XVII) (Clemmensen) affords 3:4:9:10:11:12-hexahydro-1:2-cyclopentanophenanthrene, b.p. 201°/16 mm. (XVI) is converted by Se into 1:2-cyclopentanophenanthrene. 6-Ethoxy- $\alpha$ -tetralone and acetylcyclopentene condense by the usual method to give 3-keto-7-ethoxy-3:9:10:11-tetrahydro-1:2-cyclopentanophenanthrene, m.p. 154—156°.

Attempted synthesis of natural sterols. I. Possibility of ring closure of hydrogenated naphthylbutyric acids and a ready method of preparing 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene. G. HABERLAND (Ber., 1936, 69, [B], 1380—1386).—1-Keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (I) is converted by boiling AcOH-HBr (*d* 1.48) into 1-keto-6-hydroxy-1:2:3:4-tetrahydronaphthalene, m.p. 150°. (I) is transformed by Zn and CH<sub>2</sub>Br.CO<sub>2</sub>Et into the corresponding 1-hydroxy-1-acetic ester, dehydrated to a mixture of esters (II) which with Na and boiling MeOH gives *r*- $\beta$ -6-methoxy-1:2:3:4-tetrahydro-1-naphthylethanol (III), b.p. 162°/0.5 mm. (3:5-dinitrobenzoate, m.p. 108°), and *r*-6-methoxy-1:2:3:4-tetrahydro-1-naphthylacetic acid, m.p. 87° (whence *r*-6-hydroxy-1:2:3:4-tetrahydro-1-naphthylacetic acid, m.p. 137°). (III) is converted by PBr<sub>3</sub> in presence of CHCl<sub>3</sub>-NPhMe, into the corresponding bromide, which is condensed with CHNa(CO<sub>2</sub>Et)<sub>2</sub>, hydrolysed, and decarboxylated to  $\gamma$ -6-methoxy-1:2:3:4-tetrahydro-1-naphthylbutyric acid (IV), b.p. 170°/0.08 mm., m.p. 79°, accompanied by 1-keto-7-methoxy-1:2:3:4:9:10-hexahydrophenanthrene (2:4-dinitrophenylhydrazones, m.p. 257°). The following dehydrogenations are effected by S at about 200°: a mixture of 6-methoxy-1-methyl-3:4-dihydronaphthalene and 6-methoxytetrahydronaphthylidene-methane to 6-methoxy-1-methylnaphthalene, m.p. 48°; (II) to 6-methoxy-1-naphthylacetic acid, m.p. 155°; (IV) to  $\gamma$ -6-methoxy-1-naphthylbutyric acid (V), m.p.

151°. Treatment of (V) with 90%  $H_2SO_4$  affords 1-keto-7-methoxy-1:2:3:4-tetrahydrophenanthrene, m.p. 101° [2:4-dinitrophenylhydrazone, m.p. 300—310° (decomp.) according to the rate of heating; semicarbazone, m.p. 304—308° (decomp.) after softening at 293°]. Ring-closure of (IV) by  $SnCl_4$  or 40%  $H_2SO_4$  is described. H. W.

**Sex hormones.** XIV. Preparation of enolic derivatives of ketones of the cholesterol and androsterol series. L. RUZICKA and W. H. FISCHER. XV. *cis*-Testosterone and other 17-*cis*-derivatives of androstane and androstene. L. RUZICKA and H. KAGI (Helv. Chim. Acta, 1936, 19, 806—810, 842—849; cf. this vol., 606).—XIV. Cholestanone and  $AcCl$  at 100° (sealed tube) give 3-chlorocholestene, m.p. 81°. Cholestanone and  $BzCl$  (excess) at 100° (sealed tube) give 3-chlorocholestadiene, m.p. 61.5—62.5°, but at 160—170° (open flask) or in boiling  $PhMe$  or ligroin (b.p. 100—110°) give the benzoate, m.p. 117.5 (gives liquid crystals, stable to >153°), of the enolic form; with boiling  $Ac_2O$  it gives slowly the corresponding acetate, m.p. 78°. Androstene-3:17-dione and  $BzCl$  (3 mols.) in boiling ligroin (not without a solvent) give an enolic benzoate, m.p. 176—180° (decomp.; sintering from 168°).

XV. Crude 3-*trans*-acetoxy-17-benzoyloxy- $\Delta^5$ -androstene contains some 3-*trans*-acetoxy-17-*cis*-benzoyloxy- $\Delta^5$ -androstene, m.p. 133—134°, converted by cold  $NaOH$ - $MeOH$  into 17-*cis*-benzoyloxy- $\Delta^5$ -androstene-3-*trans*-ol (I), m.p. 150—151°, and by hot  $NaOH$ - $MeOH$  into  $\Delta^5$ -androstene-3-*trans*-17-*cis*-diol (II), m.p. 198—198.5° (diacetate, m.p. 169.5—170.5°), which with  $Br$ - $CrO_3$ - $AcOH$  gives *trans*-androstenedione and with  $H_2$ - $PtO_2$ - $AcOH$ - $EtOH$  gives androstane-3-*trans*-17-*cis*-diol, m.p. 213.5—214.5° (diacetate, m.p. 146—147.5°), oxidised by  $CrO_3$  to androstenedione. (I) and  $Br$ - $CrO_3$ - $AcOH$  give a benzoate, m.p. 136.5—138°, hydrolysed to  $\Delta^4$ -androstene-3-*trans*-ol-17-*cis*-ol (*cis*-testosterone) (III), m.p. 220—221°,  $[\alpha]^{20} + 71.5^\circ$  in  $EtOH$  [oxime, m.p. 220—225° (decomp. from 200°); semicarbazone, m.p. 221—222° (decomp.); acetate, m.p. 115.5—116.5°], oxidised by  $CrO_3$  (no protection by  $Br$  necessary) to  $\Delta^4$ -androstene-3:17-dione. The ethylenic linking in (III) is relatively unreactive. (II) and (III) have very little physiological action. The supposed 3-*trans*-17-*cis*-compounds of Ruzicka and Rosenberg (*loc. cit.*) have considerable physiological activity and are probably mixtures; one of them contained the 3-*cis*-17-*trans*-, another the 3-*trans*-17-*trans*-derivative. M.p. are corr. R. S. C.

**Migration reactions in polycyclic systems.** I. Fries rearrangement of 4-benzoyloxydiphenyl. D. H. HEY and E. R. B. JACKSON (J.C.S., 1936, 802—806).—4-Benzoyloxydiphenyl in  $C_2H_5Cl_4$  with  $AlCl_3$  at 140° affords 4-hydroxydiphenyl and 4-hydroxy-3-benzoyldiphenyl, m.p. 89° [*Bz* and *Ac* derivatives, m.p. 95—96° and 136—137°, respectively; *OMe*-derivative (I), m.p. 93° (2:4-dinitrophenylhydrazone, m.p. 218—219°)], but no alkali-sol. product (cf. A., 1932, 273). 4-Methoxydiphenyl with  $BzCl$  in  $CS_2$  containing  $AlCl_3$  at room temp. affords 4-methoxy-4'-benzoyldiphenyl (II), m.p. 166° (2:4-dinitrophenylhydrazone, m.p. 221°), and 4-methoxy-

3:4'-dibenzoyldiphenyl, m.p. 170° (2:4-dinitrophenylhydrazone, m.p. 221°). The Grignard derivative of 3-bromo-4-methoxydiphenyl (cf. A., 1930, 904) with  $PhCHO$  in boiling  $Et_2O$  affords a sec. alcohol (III) which with  $K_2Cr_2O_7$ - $H_2SO_4$  at 40—50° gives (I). 4-Hydroxy-3-aldehyddiphenyl (A., 1927, 145) with  $MeI$  in  $EtOH$ - $KOH$  gives 4-methoxydiphenyl-3-aldehyde, m.p. 79°, which with  $MgPhBr$  in dry  $Et_2O$  gives (III) and thence (I). 4-Benzoyldiphenyl with  $HNO_3$  ( $d$  1.46) at 0—5° affords 4-nitro-4'-benzoyldiphenyl (IV), m.p. 154—156°, reduced ( $SnCl_4$ - $HCl$ ) to the 4- $NH_2$ -compound, m.p. 143—144° (*Ac* derivative, m.p. 206—207°), the diazonium sulphate of which at 100° yields 4-hydroxy-4'-benzoyldiphenyl, methylated to (II).  $Ph_2$  with *p*- or *m*- $NO_2$ - $C_6H_4$ - $COCl$  in  $C_6H_6$  containing  $AlCl_3$  gives 4-*p*-, m.p. 165°, and 4-*m*-nitrobenzoyldiphenyl, m.p. 130°, different from (IV). Neither 4'-bromo- nor 4'-iodo-4-methoxydiphenyl reacts with  $Mg$ .

J. L. D.

**Action of ethyl hydrogen peroxide on  $\alpha$ -diketones. Mechanism.** R. P. BARNES and R. E. LEWIS (J. Amer. Chem. Soc., 1936, 58, 947—948).—Fission of  $\alpha$ -diketones by  $EtO_2H$  in aq.  $MeOH$ - $NaOH$  occurs thus (cf. Weitz and Scheffer, A., 1921, i, 868):  $COR \cdot COR + EtO_2H \rightarrow COR \cdot CR(OEt) \cdot O \cdot OH \rightarrow RCO_2Et + RCO_2H$ . Benzil thus gives  $BzOH$  and  $EtOBz$ : 4:4'-dimethoxybenzil affords anisic acid (I) and its *Et* ester (II); *p*-methoxybenzil yields (I), (II),  $BzOH$ , and  $EtOBz$  (owing to addition at either CO);  $COPh \cdot CO \cdot CH_2Ph$  gives  $BzOH$  and  $CH_2Ph \cdot CO_2H$ ; *s*- $C_6H_5Me_3CO \cdot CO \cdot CH_2Ph$  affords *s*- $C_6H_5Me_3CO_2H$  and  $CH_2Ph \cdot CO_2H$ . In the last two cases fission is slow and the intermediate esters undergo hydrolysis.

H. B.

**Constitution of benzoylformoin.** P. KARRER and F. LITWAN (Helv. Chim. Acta, 1936, 19, 829—831).—The dienolic and not the semi-acetal form of benzoylformoin (I) is responsible for the absorption of I, since 2-deoxy-*l*-ascorbic acid is inert to I. In aq.  $EtOH$  (I) absorbs 0.4 mol. of I at once, a further 0.2 mol. in 20 sec., and the remaining 0.4 mol. very slowly. In pure  $EtOH$  very little I is absorbed at once. Thus, equilibrium between the two forms varies with the solvent. R. S. C.

**Quinhydrones.** II. R. CIUSA, L. BRULL, and G. OTTOLINO (Gazzetta, 1936, 66, 209—215).—Prep. of mixed quinhydrones in the benzoquinone, benzoquinoneanil, and benzoquinonedianil series is attempted. Benzoquinone (I) and chloroquinol heated in  $EtOH$  or  $C_6H_6$  do not give either of the possible mixed quinhydrones. In absence of solvent, a product is obtained of lower Cl content than chloroquinhydrone. *p*- $NHPh \cdot C_6H_4 \cdot OH$  (II) and (I) mixed in cold  $C_6H_6$  give benzoquinhydrone (III). In light petroleum, (III) is again obtained, but also benzoquinoneanil (IV), and an additive compound, m.p. 104°, of (II) and (IV), also prepared by mixing (II) and (IV). *p*- $NHPh \cdot C_6H_4 \cdot NHPh$  (V) and (I) give benzoquinonedianil (VI), with a compound, m.p. 132°, of (V) and (VI). (VI) and quinol give, by the reverse reaction, (V) and (III). (II) and (VI) mixed in cold  $EtOH$  and treated with  $HBr$



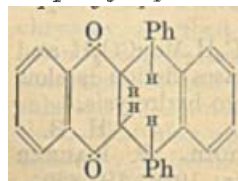
give the blue *meri*-quinonoid salt,  $C_{30}H_{16}ON_3Br$ , m.p. 168°, of type  $[NH:C_6H_4:NH_2 \cdot OH \cdot C_6H_4 \cdot NH_2]Br$ , while (V) and (VI) give the blue *meri*-quinonoid salt,  $C_{36}H_{32}N_4Br_2$ , m.p. 195°, of type  $[NH_2 \cdot C_6H_4 \cdot NH_2 \cdot NH_2 \cdot C_6H_4 \cdot NH_2]Br_2$ , also obtained when HBr is added to a hot mixture of (II) and (VI) in EtOH. E. W. W.

**Molecular forces between benzoquinone and cyclopentadiene.**—See this vol., 781.

**Potentiometric study of [sodium]  $\beta$ -naphthaquinonesulphonate. Semiquinone problem.** L. MICHAELIS (J. Amer. Chem. Soc., 1936, 58, 873—878).—Reduction (method: A., 1933, 97) of Na  $\beta$ -naphthaquinonesulphonate (I) at  $p_H$  9—12 gives a brown intermediate (II), which is a semiquinone radical. The max. amount of (II) which can exist in equilibrium with the other forms of (I) is about 50% (at  $p_H$  10—12.5); the concn. of (II) decreases with fall in  $p_H$  and is nil at  $< 7.5$ . H. B.

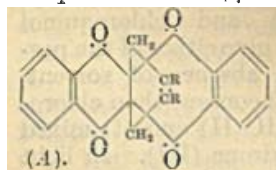
**Manufacture of alkylated and aralkylated polyaminoanthraquinones.**—See B., 1936, 537.

**Synthesis of rubrene.** C. F. H. ALLEN and L. GILMAN (J. Amer. Chem. Soc., 1936, 58, 937—940).—Naphthacene-5:12-quinone (I) and MgPhBr (6 equivs.) in  $Et_2O-Bu^a_2O$  give two stereoisomeric 6:11-diphenyltetrahydronaphthacene-5:12-quinones (II), m.p. 224—225° and 293—297°, both of which are oxidised (atm.  $O_2$  in EtOH-KOH) to 6:11-diphenylnaphthacene-5:12-quinone (III), m.p. 284°, KOH-fusion of which affords BzOH, 1:4- $C_{10}H_6Ph_2$ , and 1:4:2- $C_{10}H_5Ph_2 \cdot CO_2H$  (Ag salt). The production of (II) and (III) confirms the structure suggested by Fieser (A., 1935, 1509) for (I). (III) is converted by LiPh (not by MgPhBr) into 5:12-dihydroxy-



5:6:11:12-tetraphenyl-5:12-dihydronaphthacene [the dihydroxydihydrrubrene of Dufraisse and Badoche, A., 1931, 1052], m.p. 308—310°, reduced (Fe, AcOH) to 5:6:11:12-tetraphenylnaphthacene [rubrene] (cf. Dufraisse and Velluz, this vol., 462). The mechanism of the formation of rubrenes from, e.g.,  $CPh_2C \cdot CPh_2Cl$  is discussed. H. B.

**Addition of dienes to naphthacenediquinone.** L. F. FIESER and J. T. DUNN (J. Amer. Chem. Soc., 1936, 58, 1054—1055).—Naphthacene-5:6:11:12-diquinone and  $\beta\gamma$ -dimethylbutadiene in AcOH at 100° give 87% of the adduct (A, R=Me), m.p. 255—256°, which is cleaved by 25% MeOH-KOH in air to  $o$ - $C_6H_4(CO_2H)_2$  and 2:3-dimethylantraquinone. The adduct (A, R=H), m.p. 243—244°, from butadiene similarly affords anthraquinone. H. B.



***m*-Xylylacetic acid. Preparation from pinonic acid.** J. V. HARRISPE (Compt. rend., 1936, 202, 1591—1593; cf. A., 1909, i, 301).—Pinonic acid with Br in conc. HCl at 100° gives a Br-derivative which is converted into *m*-xylylacetic acid, isolated from its

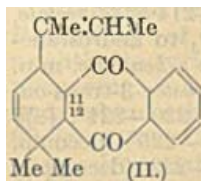
Me ester, b.p. 138°/20 mm. A mechanism for the reaction is suggested. J. L. D.

**Rotatory dispersion and circular dichroism of 2:2-dinitrocamphane in the ultra-violet.**—See this vol., 925.

**Isomerisation of oxides of terpenes. I. Isomerisation of  $\alpha$ -pinene oxide by Reformatski's reaction.** B. A. ARBUSOV (J. Gen. Chem. Russ., 1936, 6, 417—422).— $\alpha$ -Pinene oxide (I), Zn, and  $CH_2Br \cdot CO_2Et$  in  $C_6H_6$  (2 hr. at the b.p.) afford the substance  $\begin{matrix} CHMe \cdot CMe \\ | \\ CH-CH_2 \end{matrix} > CH \cdot CH(OH) \cdot CH_2 \cdot CO_2Et$  (II), b.p. 146—147°/4 mm., from which the corresponding acid, m.p. 74—75°, is obtained by hydrolysis (MeOH-NaOH). (I) and ZnBr, in  $C_6H_6$  (at the b.p.) afford campholenaldehyde, which yields (II) when treated with Zn and  $CH_2Br \cdot CO_2Et$ . R. T.

**Synthesis of camphor from pinene. II.** B. G. S. ACHARYA and T. S. WHEELER (J. Univ. Bombay, 1935, 4, Part II, 118—122; cf. A., 1935, 496).—Details are given for the prep. of camphor from pinene by way of the hydrochloride and camphene and thence (a) by direct oxidation or (b) through isobornyl acetate and isoborneol in over-all yields of 43 and 45%, respectively. R. S. C.

**Isomerisation of  $\alpha$ -pinene into the aliphatic terpene *alloocimene*. III. Conditions of formation and properties of the terpene. IV. Structure of the terpene.** B. A. ARBUSOV (J. Gen. Chem. Russ., 1936, 6, 206—216, 217—226).—III. *alloocimene* (I) is obtained by passing  $\alpha$ -pinene over reduced CuO (26.5% yield) or glass (24.6% yield), at 340—350°. (I) in EtOH and naphthaquinone (100°; 3 hr.) yield the substance (II), m.p. 122°, from which 2 H are eliminated (C atoms 11 and 12) by atm.  $O_2$  in presence of KOH, to afford a product, m.p. 120—120.5°. This is oxidised by  $HNO_3$  (200°; 5 hr.) to yield a substance, m.p. 331°, probably a naphthaquinonedicarboxylic acid. (I) in AcOH and  $H_2SO_4$  afford dipentene, a diterpene, b.p. 142—143°/4 mm., and polyterpenes (not isolated).



IV.  $CMc_2 \cdot CH \cdot CH_2Br$  and  $CHMe \cdot CMe \cdot CHO$  in  $Et_2O$  are added to Mg, when an alcohol,  $C_{10}H_{18}O$ , b.p. 82—83°, is obtained. This is dehydrated by  $KHSO_4$  at 180° to yield an unidentified terpene, b.p. 160.5°, not identical with the expected (I), and condensing with maleic anhydride to afford a product, m.p. 70—71°. (I) obtained from pinene is shown to be identical with natural (I), and with that obtained synthetically by the method of Fischer and Lowenberg (A., 1933, 592). R. T.

**Preparation and toxicity of bismuth salts of camphoric acid esters.** W. M. LAUTER and H. A. BRAUN (J. Amer. Pharm. Assoc., 1936, 25, 394—397).—Interaction of the appropriate Na alkyl camphorate (Edminson and Hilditch, J.C.S., 1910, 97, 223) with  $Bi(NO_3)_3$  in aq. glycerol affords *Bi tri(methyl camphorate)*, m.p. 60.5—62.5° [7.06% sol. in oil of sweet almonds (I); 10.07% in (I) containing 10% of camphor (II)], *Bi tri(ethyl camphorate)*, m.p.

54—57° [16.03% sol. in (I); 38.18% in (I) containing 10% of (II)], and *Bi tri-(n-butyl camphorate)*. The 50% min. lethal dose for intramuscular injection in rats is respectively 0.35, 0.25, and 0.15 g. of Bi per kg. body-wt.

F. O. H.

**$\alpha$ - and  $\beta$ -Camphylic acids.** J. R. LEWIS and J. L. SIMONSEN (J.C.S., 1936, 734—737).— $\alpha$ -Camphylic acid (I) has been shown to be 2 : 2 : 3-trimethyl- $\Delta^{1,4}$ -cyclopentadiene-1-carboxylic acid and the  $\beta$ -acid (II) is 2 : 3 : 3-trimethyl- $\Delta^{1,4}$ -cyclopentadiene-1-carboxylic acid (dehydroisauronic acid). (I) is reduced (Pd-H<sub>2</sub>) to dihydro- $\alpha$ -campholytic acid (*p-phenylphenacyl* ester, m.p. 93°), and is oxidised (KMnO<sub>4</sub>) to COMePr<sup>8</sup> (*phenylsemicarbazone*, m.p. 101—102°) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Me  $\alpha$ -camphylate with  $\alpha$ -naphthaquinone yields an additive product, m.p. 106°, showing the presence of a system of conjugated linkings. Titration of (II) with percamphoric acid shows 2 ethylenic linkings and hydrogenation (Pt-H<sub>2</sub>) gives dihydroisauronic acid (*p-phenylphenacyl* ester, m.p. 68—69°). Oxidation of (II) gives COMePr<sup>8</sup> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and condensation of the Me ester with  $\alpha$ -naphthaquinone yields an additive product, m.p. 135°. Oxidation (O<sub>3</sub>) of isobromodihydro- $\beta$ -camphylic acid gives an unstable Br-acid, which after treatment with NaOH is oxidised with NaOBr to *as-dimethylsuccinic acid*. The relationships of the acids are discussed.

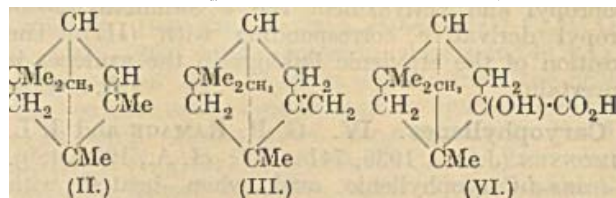
F. R. S.

**Synthesis of umbellularic acid; a synthetic proof of the presence of the cyclopropane bridge in the terpenes of the thujane series.** H. N. RYDON (J.C.S., 1936, 829—832).—Et isopropylfumarate and CH<sub>2</sub>N<sub>2</sub> give Et 1-isopropylcyclopropane-1 : 2-dicarboxylate, b.p. 121—122°/13 mm., hydrolysed (KOH) to a mixture of di-trans-, m.p. 197°, and di-cis-1-isopropylcyclopropane-1 : 2-dicarboxylic acid, m.p. 126—127° (+H<sub>2</sub>O, m.p. 98—99°). The trans-acid is resolved through *brucine* 1- (+6H<sub>2</sub>O), m.p. 149—151° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup><sub>401</sub> -98.8° in CHCl<sub>3</sub>, and *brucine* d-salts, [ $\alpha$ ]<sub>D</sub><sup>25</sup><sub>461</sub> -15.39° in CHCl<sub>3</sub>, into l-, m.p. 155°, [ $\alpha$ ]<sub>D</sub><sup>21</sup><sub>461</sub> -236.2° in COMe<sub>2</sub>, and d-trans-1-isopropylcyclopropane-1 : 2-dicarboxylic acid, m.p. 155°, [ $\alpha$ ]<sub>D</sub><sup>17</sup><sub>461</sub> +232.1° in COMe<sub>2</sub>. The cis-acid is resolved through *brucine* d-, m.p. 110—120° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup><sub>61</sub> +6.2° in COMe<sub>2</sub>, and *brucine* l-salts, [ $\alpha$ ]<sub>D</sub><sup>16</sup><sub>461</sub> -29.5° in COMe<sub>2</sub>, into d-, m.p. 119—120°, [ $\alpha$ ]<sub>D</sub><sup>10</sup> +86.9° in CHCl<sub>3</sub> (+H<sub>2</sub>O, m.p. 78—79°), and l-cis-1-isopropylcyclopropane-1 : 2-dicarboxylic acid, m.p. 119—120°, [ $\alpha$ ]<sub>D</sub> -88.8° in CHCl<sub>3</sub> [+H<sub>2</sub>O (I), m.p. 78—79°]. The monohydrate of umbellularic acid is identical with (I) and this confirms the structure assigned by Semmler.

F. R. S.

**Fenchene series. VI. Two homologous fenchenes. Racemisation of hydrocarbons of the pentocean system.** G. KOMPPA and G. A. NYMAN (Annalen, 1936, 523, 87—100; cf. A., 1934, 415).—dl-2-Methylisofenchol (I), b.p. 91°/15 mm., m.p. 50—51° (*phenylurethane*, m.p. 100—101°), when heated for 30 min. with KHSO<sub>4</sub> at 170° and then distilled at 230°, gives a mixture containing about equal parts (determined by ozonisation) of 1-methyl- $\gamma$ - (II), b.p. 154—156°,  $d_4^{20}$  0.8439,  $n_D^{20}$  1.45284 (*nitrosochloride*, m.p. 165°, readily formed), and  $\beta$ -fenchene (III), b.p. 163—164°,  $d_4^{20}$  0.8497,  $n_D^{20}$  1.46212 (*nitrosochloride*, m.p.

121—121.5°, not readily formed), separable with difficulty by fractionation (cf. A., 1929, 1076). The l-form (IV), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -10.2°, of (I) with KHSO<sub>4</sub> gives the same inactive mixture, probably owing to retropinacol inversion rearrangement of (IV). Analogies to this inversion are discussed. (I) is obtained from MgMeI and dl-isofenchone (V), b.p. 193—196° (semicarbazone, m.p. 225—226°), prepared in 80% yield from dl-isofenchol by HNO<sub>3</sub> (mixture of conc. and fuming) at < 25°. (IV) is obtained similarly from l-isofenchone, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -8.13° [semicarbazone, m.p. 230—231° (lit. 221—222°)]. The structure of (II) is proved by ozonisation to 4-acetyl-1 : 1 : 4-trimethylcyclopentane-2-aldehyde [*disemicarbazone*, m.p. 234.5—235° (decomp.)], the corresponding acid (dl-isofenchocamphoric acid), and a little (V) [derived from (III) present as impurity]. The structure of (III) is proved by ozonisation to (V) and oxidation by KMnO<sub>4</sub> to dl-1-methyl- $\beta$ -hydroxyfenchonic acid (VI), m.p. 119—120° (K salt) [with PbO<sub>2</sub> and 60% H<sub>2</sub>SO<sub>4</sub> gives (V)]. The mixture of (II) and (III) is slowly hydrated by AcOH-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O at 60—65° to the nearly homogeneous acetate, b.p. 97—100°/15 mm., of (I), and with



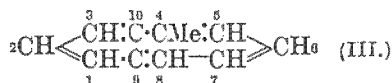
HCl-Et<sub>2</sub>O gives a hydrochloride, b.p. 95—96°/19 mm., which with CaO-H<sub>2</sub>O at 50—60° gives "1-methyl- $\beta$ -fenchene hydrate," an isomeride of (I), m.p. 30° (*phenylurethane*, m.p. 110—111°).

R. S. C.

**Volatile plant products. IV. Constitution of the azulenes.** A. S. PFAU and P. PLATTNER (Helv. Chim. Acta, 1936, 19, 858—879; cf. A., 1935, 1128).—Previously proposed formulae for azulenes are refuted. Eucazulene [from the sesquiterpenes of *Eucalyptus globulus* labill. (mostly aromadendrene)] and gurgunazulene (from an oil composed mostly of  $\alpha$ -gurgunene by Se or Ni) are identical with S-guajazulene (I), which is also obtained from geranium oil [Barbier and Bouveault's formula, C<sub>20</sub>H<sub>34</sub>O (A., 1895, i, 4), is incorrect], *Geranium macrorrhizum*, L., patchouli, and vetiver oils.  $\alpha$ -Gurgunene gives, however, also other products which are possibly azulenes. Pterates and styphnates are unsuitable for identification of azulenes, which is best effected by the C<sub>6</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>3</sub> or C<sub>6</sub>H<sub>2</sub>Me(NO<sub>2</sub>)<sub>3</sub> compounds, from which the hydrocarbons are recovered by heating with (NH<sub>4</sub>)<sub>2</sub>S-EtOH, followed by distillation in steam. The best conditions for preparing (S and Se) and purifying azulenes are detailed. The Br test in CHCl<sub>3</sub> or AcOH is best for determining whether a sesquiterpene hydrocarbon or alcohol will yield azulenes, but it is not sp. Guaiol and boiling HI-red P give 1 : 4 : 6-C<sub>10</sub>H<sub>5</sub>Me<sub>2</sub>Pr<sup>8</sup>; vetiver oil gives 1 : 5 : 7-C<sub>10</sub>H<sub>5</sub>Me<sub>2</sub>Pr<sup>8</sup>. C<sub>10</sub>H<sub>8</sub> derivatives are also obtained with SiO<sub>2</sub> gel at 300° in vac. The oxidation products from the sesquiterpenes give ketones with 1 C less in the ring, which yield phenols on catalytic dehydrogenation. Thus, these sesquiterpenes contain a 7-ring. 2 : 3-



Trimethylene- $\Delta^2$ -cycloheptanone (II) and MgMeI give 1-methyl-2:3-trimethylene- $\Delta^{1:6}$ -cycloheptadiene, b.p. 103—106°/10 mm., dehydrogenated by Ni at 335—375° to 3-methylcyclopentadieno-1':2':1:2-cycloheptatriene (called 4-methylazulene) (III) (5% yield), blue [picrate, black, m.p. 144°;  $C_6H_3(NO_2)_3$  compound, black, m.p. 177.5—178°]. MgEtBr and MgPhBr



give 1-ethyl-, b.p. 109—111°/10 mm., and 1-phenyl-2:3-trimethylene- $\Delta^{1:6}$ -cycloheptadiene, b.p. 160—190°/10 mm., and 4-ethyl-, blue (prep. by S at 175—210° or Ni at 340—400°) [picrate, m.p. 128.5°; impure styphnate, m.p. 123°;  $C_6H_3(NO_2)_3$  compound, m.p. 147.5°], and 4-phenylazulene, blue [picrate, m.p. 80—81°;  $C_6H_3(NO_2)_3$  compound, m.p. 86—87°; a pale green compound,  $C_{16}H_{22}$ , m.p. 210—211°, unstable to  $KMnO_4$ , is also formed]. Hydrogenation and reduction (Na-EtOH) of (II) gives an alcohol, which gives a cycloheptene, dehydrogenated by S or Ni to a blue mixture. (I) is the 1:4-dimethyl-7-isopropyl and vetivazulene the 4:8-dimethyl-2-isopropyl derivative corresponding with (III). The position of the ethylenic linkings in the azulenes is uncertain. R. S. C.

**Caryophyllenes.** IV. G. R. RAMAGE and J. L. SIMONSEN (J.C.S., 1936, 741—742; cf. A., 1935, 489).—*trans-d*-Caryophyllenic acid when heated with  $Ac_2O$  gives *caryophyllenic anhydride*, b.p. 157—158°/12 mm., which is hydrolysed to *cis-caryophyllenic acid*, m.p. 77—78°,  $[\alpha]_{5461}^{20} -7.4^\circ$  in  $CHCl_3$ . The *trans*-acid forms a *dianilide*, m.p. 282°, and *di-p*-phenylphenacyl ester, m.p. 121—122°, and the *cis*-acid yields a *dianilide*, m.p. 120°. The keto-acid,  $C_{11}H_{18}O_3$ , is oxidised (NaOBr) to homocaryophyllenic acid (*dianilide*, m.p. 179—180°) (cf. Ruzicka and Wind, A., 1931, 734). F. R. S.

**Derivative of sciadopitene and reduction of the two isomerides.**—See this vol., 1037.

**Saponin from *Primula elatior*.** H. RUTKOFF and P. MOHS (Ber., 1936, 69, [B], 1522—1527).—Treatment of *P. elatior* with dil.  $NH_3$  extracts non-cryst. *elatioric acid* (I), m.p. 220° (decomp.),  $[\alpha]_D^{20} -67.2^\circ$  in  $C_5H_5N$ ,  $-29.9^\circ$  in MeOH ( $NH_4$  salt, m.p. 220° (decomp.),  $[\alpha]_D^{20} -28.8^\circ$  in  $H_2O$ ; K salt, m.p. 251° (decomp.),  $[\alpha]_D^{20} -28.1^\circ$  in  $H_2O$ ), dehydrogenated by Se at 320—340° to 1:2:5:6- $C_{10}H_4Me_4$ , m.p. 116° (picrate, m.p. 156°). Cautious acidic hydrolysis of (I) gives *elatigenin* (II),  $C_{32}H_{52}O_3$ , m.p. 241°,  $[\alpha]_D^{20} +25.5^\circ$  in  $C_5H_5N$ , which contains 2 active H (*diacetate*, m.p. 213.5°,  $[\alpha]_D^{20} +28.7^\circ$  in  $CHCl_3$ ; *di-p*-nitrobenzoate, m.p. 245°,  $[\alpha]_D^{20} +40.4^\circ$  in  $CHCl_3$ ). Since cautious treatment with  $CrO_3$ -AcOH gives exclusively neutral products, a primary OH is not present. The third O atom is presumably in a ring, since the product does not react with ketonic reagents. Catalytic hydrogenation (Adams-Shriner or Willstätter) does not disclose the presence of an unsaturated linking, but such is probably present, since 1.5 O is absorbed from  $BzO_2H$ . The sugar component of the saponin is present as a uronic acid and, probably, a

disaccharide. Hydrolysis appears to occur thus:  $C_{50}H_{80}O_{19} + 2H_2O \rightarrow C_{32}H_{52}O_3 + C_6H_{10}O_7 + C_{12}H_{22}O_{11}$ .

**Lignin. X. Lignin from oat straw.** M. PHILLIPS and M. J. GOSS (J. Biol. Chem., 1936, 114, 557—565; cf. A., 1935, 214).—Lignins from oat straw closely resemble those from barley straw. 2% NaOH-EtOH extracts a *lignin*,  $C_{36}H_{32}O_7(OH)_4(OMe)_4$  (*tetraacetate*), which with  $Cl_2$  gives a *substance*,  $C_{40}H_{32}O_{15}Cl_6$ , of lower OMe content, with molten KOH gives protocatechuic acid, with hot 12% HCl gives  $CH_2O$ , with  $CH_2N_2$  affords an *ether*,  $C_{36}H_{34}O_9(OMe)_6$ , but with  $Me_2SO_4$ -40% NaOH by fission an *ether*,  $C_{36}H_{31}O_6(OMe)_9$ . Hot 4% aq. NaOH then removes a *lignin*,  $C_{36}H_{26}O_8(OH)_4(OMe)_4$  (*tetraacetate*), giving with  $CH_2N_2$  an *ether*,  $C_{36}H_{28}O_{10}(OMe)_6$ , and with HCl  $CH_2O$ . A third fraction, obtained by cold, fuming HCl, gives  $CH_2O$  with 12% hot HCl. R. S. C.

**Lignin.** S. A. WAKSMAN and T. C. CORDON (J. Amer. Chem. Soc., 1936, 58, 969—972).—The lignin (I) extracted by 80%  $H_2SO_4$  from wheat straw (II) at 2° (Ia, yield 27.07%) contains less OMe and C than those isolated at 8.5—9° (Ib, 21.38%) and 18—20° (Ic, 21.86%), owing to incomplete hydrolysis of the carbohydrates. Subsequent treatment of (Ia)—(Ic) with 80%  $H_2SO_4$  at room temp. gives approx. the same yield of "final lignins" (III) containing the same amount of OMe. Analogous differences are found with the (I) similarly isolated from (II) which has been pre-treated with 2% HCl at 100°; the final yields are somewhat smaller, probably because the pre-treatment destroys some hemicellulose (IV) [i.e., (III) contain this (IV)]. Less (I) is extracted from (II) by 5% NaOH at room temp. than at 100° [at which temp. some of the (I) is probably destroyed]. The sum of the (I) extracted by the cold alkali and that left in the residue is practically the same as the amount removed by 80%  $H_2SO_4$  alone. Hilpert's view (A., 1935, 344, 550) that (I) does not exist in plant materials has no foundation. H. B.

**Wood lignins.** E. E. HARRIS (J. Amer. Chem. Soc., 1936, 58, 894—896).—In accordance with previous findings (A., 1934, 653), the lignins isolated ( $H_2SO_4$  method) in 19—25.8% yield from (a) hardwoods (sugar maple, aspen, beech, basswood, white oak) contain 6 OMe, whilst those from (b) softwoods (yield 25.5—30%) (spruce, slash pine, Eastern hemlock) contain 5 OMe. Extraction with MeOH-HCl gives (a) 6—7% and (b) 4% of lignins which contain approx. 7.5 and 6.5 OMe, respectively; the residual lignins (subsequently extracted with  $H_2SO_4$ ) have about 5 and 4 OMe, respectively. All the lignins isolated are methylated ( $Me_2SO_4$ ) to methyl-lignin (32% OMe, i.e., 10 OMe); treatment with  $Cl_2$  in  $CCl_4$  results in the loss of 2 OMe and introduction of 8 Cl. H. B.

**Beech lignin.** E. WEDEKIND and O. MÜLLER (Ber., 1936, 69, [B], 1517—1521).—Beech lignin (I) has been prepared according to Freudenberg's method and in parallel experiments the wood is subjected between treatments with  $Cu(OH)_2-NH_3$  to the action of 1%  $H_2SO_4$ , 7%  $H_2C_2O_4$ , and 3% NaOH, respectively. The three products do not differ externally from one another or from (I) obtained by other methods.

The analytical composition is not influenced by treatment with 64%  $\text{H}_2\text{SO}_4$ . Acetylation of (I) gives a product with 20–21%  $\text{Ac}$  = 7.9–8.3% of  $\text{OH}$ . Treatment of (I) with  $\text{PhOH}$  and conc.  $\text{HCl}$  at 90–95° gives a phenol-lignin ( $\text{C}$  66.2,  $\text{H}$  5.7,  $\text{OMe}$  17.5%) which contains phenolic  $\text{OH}$  and is transformed by  $\text{NaOH-Me}_2\text{SO}_4$  into an alkali-insol. product with 31.1%  $\text{OMe}$ . There appears no reason therefore to doubt the existence of lignin, since humification processes are avoided as completely as possible. Hilpert's introduction of a hypothetical carbohydrate appears unnecessary. H. W.

**Separation of the ligninsulphonic acids precipitable with amines.** W. NIRPE (Ber., 1936, 69, [B], 1239–1245).—Treatment of a sulphite liquor with  $\text{NaCl}$  and of the filtrate with  $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2\text{-SO}_2\text{-NaCl}$  causes separation of a ligninsulphonate- $\alpha$ , (I) in which one of the firmly united  $\text{SO}_3\text{H}$  groups is satisfied with  $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$  and the remaining two with  $\text{Na}$ . Treatment of the compound with  $\text{NaCl-H}_2\text{O}$  followed by  $\text{EtOH}$  gives the  $\text{Na}_3$  salt (II). Addition of benzidine in dil.  $\text{HCl}$  to the filtrate from (I) ppts. ligninsulphonic acid- $\alpha_3$  as *tribenzidine* salt, converted into the  $\text{Na}_3$  compound (III). (I) and (III) contain one and two loosely combined  $\text{SO}_3\text{H}$  groups, respectively (per 100 $\text{Me}$ ), removal of which by dil. alkali is accompanied by great liability to autoxidation and by dil. acid to condensation. (II) and (III) give *nona-* and *deca-p-toluenesulphonyl* derivatives, respectively. The formulae of the  $\alpha_1$  salt (IV), (II), and (III) can therefore be resolved into  $\text{C}_{90}\text{H}_{82}\text{O}_{14}(\text{OH})_4(\text{OH})_4(\text{OMe})_{10}(\text{SO}_3\text{Na})_3$ ,  $\text{C}_{85}\text{H}_{71}\text{O}_9(\text{OH})_4(\text{OH})_4(\text{OMe})_{10}(\text{SO}_3\text{Na})_3$ , and  $\text{C}_{80}\text{H}_{62}\text{O}_7(\text{OH})_4(\text{OH})_4(\text{OH})_2(\text{OMe})_{10}(\text{SO}_3\text{Na})_4$ , respectively. In each compound 4  $\text{OH}$  are phenolic, 4 aliphatic, and the remainder acidic, the no. of the last-named coinciding with that of loosely-united  $\text{SO}_3\text{H}$ . Possibly the unstable union with  $\text{H}_2\text{SO}_3$  is due to the presence of  $\text{CO}$ , but such groups could not be detected with  $\text{NH}_2\text{OH}$  or  $\text{N}_2\text{H}_4$ . The analytical homogeneity of the salts is established together with their producibility from different liquors, but it is probable that they are mixtures of isomerides. (II) and (III) resemble (IV) in their fluorescence in ultra-violet light and in its change with increasing alkalinity attributed to phenoxide formation. H. W.

**Lignin.** XV. K. FREUDENBERG, A. JANSON, E. KNOPF, and A. HAAG (Ber., 1936, 69, [B], 1415–1425).—Pine lignin is transformed by  $\text{KOH}$  at 210° into alkali-sol., phenol-like, complex degradation products which are converted by methylation and oxidation into veratric acid (I) (10–14%), veratroyl-formic acid, isohemipinic acid (2–4%), and a more complex acid containing two  $\text{C}_6\text{H}_6$  nuclei (3%); the most urgent requirements of the constitution assigned previously are thereby fulfilled. Pine wood is treated successively with  $\text{EtOH-C}_6\text{H}_6$ , cold alkali, and  $\text{HCO}_2\text{H}$ , thereby giving polysaccharide *A* and *B* and component *C*; these together comprise unorganised lignin, and of them *C* is the most important. Repeated treatment of the residue with Schweitzer's reagent alternated with 1%  $\text{H}_2\text{SO}_4$  leaves "organised lignin." Similar treatment of beech wood gives a much higher proportion of *B* and *C* and an "organised lignin" which contains 21%  $\text{OMe}$  and yields proto-

catechuic and gallic acid when fused with  $\text{KOH}$ . Unorganised pine lignin very closely resembles polymeric coniferyl alcohol, for which, since it affords (I) when oxidised, side-chain polymerisation must now be considered. The production of >20% of aromatic acids from organised lignin strengthens the conception of its aromatic nature. The possible transformations of lignin during its isolation and the relationship between the aromatic constituents of wood are discussed. H. W.

**Lignin and related compounds.** XXII. Fractionation of methanol-lignin. J. COMPTON, (Miss) M. GREIG, and H. HIBBERT (Canad. J. Res., 1936, 14, B, 115–119; cf. this vol., 609).—Fractionation of methanol-lignin with  $\text{C}_6\text{H}_6$ -dioxan gives an insol. fraction,  $\text{C}_{42}\text{H}_{32}\text{O}_5(\text{OMe})_6(\text{OH})_4$  [identical with that previously described (A., 1935, 1373)], and a sol. fraction with  $\text{OMe}:\text{OH}=5:3$  (*triacetate*; *Me ether*,  $\text{OMe}=32.6\%$ , prepared by  $\text{Me}_2\text{SO}_4\text{-aq. NaOH-COMe}_2$ ) in the proportions 4:1 if the extraction is effected at 70–75°, but 2:1 if at 90–100°.

R. S. C.  
**Bitter principles of Colombo root.** III. *Palmarin*. F. WESSELY, K. SCHÖNOL, and W. ISEMANN (Monatsh., 1936, 68, 21–28).—*Palmarin* (I),  $\text{C}_{20}\text{H}_{22}\text{O}_7$ , m.p. 258–260° (slight decomp.) (sinters at 246°),  $[\alpha]_D^{25}$  about +12.5° in  $\text{C}_5\text{H}_5\text{N}$ , is isolable from the crude  $\text{Et}_2\text{O}$ -extract of the root through its sparing solubility in  $\text{COMe}_2$ . Methylation ( $\text{Me}_2\text{SO}_4$ , 10%  $\text{NaOH}$ ,  $\text{EtOH}$ ) of (I) gives the *Me ether* (II), m.p. 254° (slight decomp.) (sinters at 245°),  $[\alpha]_D^{25} +39.47^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . (I), which appears to be isomeric with chasmanthin (Feist *et al.*, A., 1908, i, 100; 1935, 864), contains a lactone ring and 2 double linkings; reduction ( $\text{H}_2$ ,  $\text{Pd-C}$ ,  $\text{AcOH}$ ) results in the absorption of 6  $\text{H}$  and gives *hydropalmaric acid*,  $\text{C}_{20}\text{H}_{28}\text{O}_7$ , m.p. 213–218°,  $[\alpha]_D^{25} +29.78^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , which is methylated (as above) to the *Me ether*, m.p. 262° (sinters at 257°),  $[\alpha]_D^{25} +57.62^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  [also obtained by reduction of (II)]. H. B.

**Tannin from the Indian gooseberry (*Phyllanthus emblica*).**—See this vol., 911.

**Grayanotoxins, active constituents of *Leucothoe grayana*.** II. S. MIYAJIMA and S. TAKEI (J. Agric. Chem. Soc. Japan, 1936, 12, 497–502; cf. A., 1934, 1359).—Grayanotoxin-I and -III in  $\text{C}_5\text{H}_5\text{N}$  yielded the same *Ac* derivative, m.p. 226°. Acetylation with  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  gave amorphous products which with alkali gave *anhydrograyanotoxin-III*,  $\text{C}_{20}\text{H}_{30}\text{O}_5$ , m.p. 220–224°, isomeric with grayanotoxin-II. Both contain a double linking. With  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  -II gave a *tetra-acetate*, m.p. 172°, and catalytic hydrogenation yielded *dihydro-tetra-acetyl-II*, m.p. 170°, which was obtained also by acetylation of dihydro-II in  $\text{C}_5\text{H}_5\text{N}$ . Spring leaves of *L. grayana* contain grayanotoxins-I, -II, and -III, whilst summer leaves contain only -II. J. N. A.

**Citrolimonin.** I. K. FEIST and L. S. OVERBERG (Ber., 1936, 69, [B], 1322–1323).—*Citrolimonin* (isolation from lemon pips described), m.p. 304°,  $[\alpha]$  about  $-135^\circ$  in  $\text{CH}_2\text{Cl}_2$ , is probably  $\text{C}_{28}\text{H}_{36}\text{O}_6$ . It does not contain active  $\text{H}$  and cannot be acetylated.  $\text{OMe}$  and  $\text{O}_2\text{CH}_2$  are absent. Two lactone groups are present. Catalytic hydrogenation gives *tetra-*



*hydrocitrolimonin* and more highly hydrogenated, acidic compounds. Distillation with Zn dust gives a mixture of hydrocarbons, one of which yields a picrate and (?) *o*-cresol. Fusion with KOH affords  $\text{COMe}_2$ , volatile oil, and a non-volatile acid. H. W.

**Vegetable cardiac poisons. X. Antiarin.** R. TSCHESCHE and W. HAUPT (Ber., 1936, 69, [B], 1377—1379).— $\alpha$ - (I) and  $\beta$ - (II) -antiarin give a positive Legal test, and hence are  $\alpha\beta$ -unsaturated lactones of the *Digitalis* type. Analyses and lactone titrations establish the composition  $\text{C}_{20}\text{H}_{42}\text{O}_{11}$ . When catalytically hydrogenated (II) absorbs 4 H, of which 2 are used in saturating the double linking of the lactone side-chain. Hydrolysis of (I) and (II) requires such energetic conditions that the genin cannot be isolated as such and the product is *dianhydroantiarigenin* (III),  $\text{C}_{23}\text{H}_{28}\text{O}_5$ , m.p. 200—205°,  $[\alpha]_D^{20} -160.2^\circ$  in MeOH, since it absorbs 8 H when hydrogenated, 2 of which are required by  $\text{C}=\text{O}$ . Although (III) does not give the typical aldehydic reactions (also not shown by strophanthidin) the presence of  $\cdot\text{CHO}$  rather than  $\cdot\text{CO}$  is considered probable, since the absorption spectrum shows absence of conjugation. (III) gives a *monobenzoate*, m.p. 249—250°; only one OH is therefore *sec*. H. W.

***l*-Pimaric acid.** R. G. R. BACON and L. RŮŽICKÁ (Chem. and Ind., 1936, 546).—Catalytic reduction of *l*-pimaric acid (I) yields firstly (in inert solvents) dihydro- and finally (in AcOH) mixed tetrahydro-*l*-pimaric acids from which an *acid*, m.p. 195—197°,  $[\alpha]_D +7^\circ$  (*Me* ester, m.p. 76—77°,  $[\alpha]_D +3^\circ$ ), is obtained. This, and the fact that with maleic anhydride a *compound*, m.p. 227°,  $[\alpha]_D -29^\circ$  (*Me* ester, m.p. 215°,  $[\alpha]_D -29^\circ$ ), identical with the analogous compound derived from abietic acid is formed, proves that (I) is tricyclic and contains a conjugated system.

F. N. W.

$\alpha$ - and  $\beta$ -Leprosol. XLVI. Phthiocerol.—See this vol., 1028.

**Drugs from Bolivia.**—See this vol., 1037.

**Catalytic hydrogenation of furan.** Tetrahydrofuran. I. I. SCHUJIKIN and E. M. TSCHILIKINA (J. Gen. Chem. Russ., 1936, 6, 279—282).—Furan is readily hydrogenated at 65—70° (Os-asbestos catalyst) to tetrahydrofuran (I); the reverse process does not take place at 300° (Pt catalyst). (I) is unchanged by heating at 110° with 30—60%  $\text{H}_2\text{SO}_4$ . R. T.

**Synthesis of furfuralazine.** S. A. TEBINOV (J. Gen. Chem. Russ., 1936, 6, 528—529).—Furfuraldehyde and  $\text{N}_2\text{H}_4\cdot\text{HCl}$  in  $\text{H}_2\text{O}$  at room temp. yield furfuralazine; the reaction does not proceed in non-aq. solvents. R. T.

**Hydrol character of furylphenylcarbinol.** R. PAUL (Compt. rend., 1936, 202, 1444—1446; cf. A., 1930, 923).—2-Furylphenylcarbinol (I) with aromatic amines in AcOH gives intensely coloured solutions; when distilled in  $\text{CO}_2$  or over  $\text{ThO}_2$  it gives furylphenylmethane (II) [also obtained when (I) is reduced with Na in EtOH] and with  $\text{PhNCO}$  at room temp. affords  $\text{CO}(\text{NHPh})_2$ . (I) with  $\text{Ni-H}_2$  affords tetrahydrofurylphenylcarbinol, b.p. 147—148°

10 mm., and no tetrahydrofurylphenylmethane, b.p. 112—113°/11 mm., which, however, is obtained when (II) is reduced, and with HBr in AcOH gives  $\alpha\delta$ -dibromo- $\epsilon$ -phenylpentane, b.p. 153—155°/4 mm. (decomp.). J. L. D.

**Theory of double linkings. VI. Condensation of "furanic" compounds.** V. N. TSCHELINCEV [with E. K. NIKITIN and M. A. ABRAMOVA] (Bull. Soc. chim., 1936, [v], 3, 1035—1047).—In alkaline or acid, but not in neutral solution, distyryl ketone (I) and MeCHO give styryl propylidene ketone and then dipropylidene ketone and PhCHO. Similarly, (I) and furfuraldehyde (II) afford difurfurylidene ketone (III) and PhCHO. Analogously (II) is formed from (III) and MeCHO. Reaction proceeds much more rapidly in alkaline than in acid solution. Displacement is characteristic of the group  $\cdot\text{CH}:\text{CH}:\text{CO}\cdot$ , which appears capable of hydrolysis, O becoming attached to C most distant from CO and H to that nearest CO. The reactions are particularly marked with compounds containing the group  $\text{CHPh}:$

or  $\begin{array}{c} \text{CH}:\text{CH} \\ \text{CH}=\text{O} \end{array} > \text{C}:\text{CH}:$ . The reactivity of fatty aldehydes shows that their double linkings have a peculiar character not possessed by the ordinary ethylenic linking. This peculiarity is shown also by pulegone, citral, mesityl oxide, and phorone, and seems general for compounds of this class, thus creating a resemblance to the oximes and hydrazones. The group  $\cdot\text{CH}:\text{CO}\cdot$  is designated "carbonyl-ethylenic" or "carbonylenic." H. W.

**Action of mixed organo-magnesium compounds on esters; furylidenemalononic, furylidene-cyanoacetic, and furylideneacetoacetic esters.** N. MAXIM and (MLE.) E. GEORGESCU (Bull. Soc. chim., 1936, [v], 3, 1114—1124).—Addition of the reagent occurs in the  $\alpha\delta$ -positions. Thus,  $\text{Et}_2$  furylidene-malonate and  $\text{MgBu}^n\text{Cl}$  give  $\text{Et}_2$   $\beta$ -2-furyl- $\delta$ -methyl-pentane- $\alpha\alpha$ -dicarboxylate, b.p. 153°/14 mm., hydrolysed and decarboxylated to  $\beta$ -2-furyl- $\alpha$ -methyl-*n*-hexoic acid, b.p. 153°/15 mm. (*amide*, m.p. 79°). Similarly,  $\text{Mg isoamyl bromide}$  yields  $\text{Et}_2$   $\beta$ -2-furyl- $\delta$ -methylhexane- $\alpha\alpha$ -dicarboxylate, b.p. 165°/12 mm., whence  $\beta$ -2-furyl- $\epsilon$ -methyl-*n*-heptoic acid, b.p. 156°/8 mm. (*amide*, m.p. 55°), and  $\text{MgPhBr}$  gives  $\text{Et}_2$   $\beta$ -2-furyl- $\beta$ -phenylethane- $\alpha\alpha$ -dicarboxylate, b.p. 203°/14 mm., whence  $\beta$ -2-furyl- $\beta$ -phenylethane- $\alpha\alpha$ -dicarboxylic acid, m.p. 151°, and  $\beta$ -2-furyl- $\beta$ -phenylpropionic acid, b.p. 186°/15 mm., m.p. 105°.  $\text{MgPr}^n\text{Br}$  and Et furylidene-cyanoacetate yield Et  $\alpha$ -cyano- $\beta$ -2-furylhexoate, b.p. 154°/8 mm., cautiously hydrolysed to  $\alpha$ -cyano- $\beta$ -2-furyl-*n*-hexoic acid, m.p. 140°, and drastically hydrolysed to the corresponding dicarboxylic acid, whence  $\beta$ -2-furyl-*n*-hexoic acid, b.p. 152°/15 mm. Et  $\alpha$ -cyano- $\beta$ -2-furyl- $\delta$ -methyl-*n*-hexoate has b.p. 171°/20 mm.  $\text{MgEtI}$  and Et furylideneacetoacetate afford Et  $\alpha$ -acetyl- $\beta$ -2-furyl-*n*-valerate, b.p. 152°/21 mm., hydrolysed to  $\beta$ -2-furyl-*n*-butyl Me ketone. Similarly Et  $\alpha$ -acetyl- $\beta$ -2-furyl-*n*-hexoate, b.p. 155°/15 mm., yields  $\beta$ -2-furylamyl Me ketone. Et  $\alpha$ -acetyl- $\beta$ -phenyl- $\beta$ -2-furylpropionate, b.p. 195°/14 mm., is hydrolysed to Me  $\beta$ -phenyl- $\beta$ -2-furylethyl ketone, b.p. 160°/14 mm. (semicarbazone, m.p. 142°). H. W.

**Condensation of benzoin and thymol. I. Preparation of 2-benzoylthymol** [2-hydroxy-6-methyl-3-isopropylbenzophenone] and constitution of desylthymol. O. DISCHENDORFER and A. VERDINO (Monatsh., 1936, 68, 10—20).—The "cymodiphenylfuran" obtained by Japp and Meldrum (J.C.S., 1899, 75, 1035) from benzoin, thymol, and 73%  $\text{H}_2\text{SO}_4$  is 1:2-diphenyl-3-methyl-6-isopropylcoumarone, m.p. 116—117° [5-Br-derivative (I), m.p. 152°], since it is oxidised ( $\text{CrO}_3$ , AcOH) to the benzoate, m.p. 104°, of 2-hydroxy-6-methyl-3-isopropylbenzophenone, m.p. 97° [5-Br-derivative, m.p. 128—129°, oxidised ( $\text{KMnO}_4$ ) to BzOH]. (I) is oxidised ( $\text{CrO}_3$ , AcOH) to the benzoate, m.p. 129.5°, of 4-bromo-2-hydroxy-6-methyl-3-isopropylbenzophenone, m.p. 91°. The desylthymol of Japp and Meldrum (*loc. cit.*) is 1:5:2:4-OH- $\text{C}_6\text{H}_2\text{MePr}^3\text{CHPhBz}$ ; its benzoate, m.p. 140° (sinters at 137°), is oxidised to the benzoate (not isolated) of 4-hydroxy-2-methyl-5-isopropylbenzophenone, m.p. 153°. H. B.

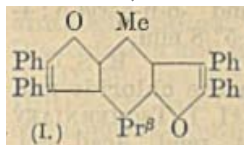
**Geometrical inversion of the acids derived from coumarins. II. Cis to trans.** T. R. SESHADRI and P. S. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 293—296; cf. A, 1935, 211).—*o*-Coumaric acid (I) and its 4-Me (II) and 5- $\text{NO}_2$ -derivative (III) result from the interaction of  $\text{HgO}$  in aq. NaOH [(I) and (II) at room temp.; (III) at 100°] and coumarin (IV) and its 7-Me and 6- $\text{NO}_2$ -derivatives, respectively. With cold aq. NaOH and  $\text{Hg}(\text{OAc})_2$ , or hot aq. NaOH and  $\text{HgO}$ , (IV) affords mercurated coumaric acids which yield pure (I) with  $\text{H}_2\text{S}$  in aq.  $\text{NH}_3$  solution. F. N. W.

**Condensation of deoxybenzoin with aromatic aldehydes and ketones. I. Condensation with salicylaldehyde.** D. W. HILL (J.C.S., 1936, 806—807).—Salicylaldehyde and deoxybenzoin with  $\text{C}_5\text{H}_{11}\text{N}$  condense to *salicylidenedeoxybenzoin*, m.p. 129°, which with  $\text{HCl}$ -AcOH, followed by  $\text{FeCl}_3$ , forms 3-phenylflavylium ferrichloride (I), and with AcOH or  $\text{Ac}_2\text{O}$  yields 2:3-diphenylbenzo-2-pyranol Et ether, also obtained from (I) and KOH. F. R. S.

**Reaction of anthocyanins with the sulphites.** A. KOZLOWSKI (Science, 1936, 83, 465).—Treatment of citric acid extracts of the anthocyanins of *Pelargonium zonale* and other plants with powdered  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_4$ , respectively, discharges the red colour, which is restored to its original intensity by the addition of tincture of I. Mg and HCl reduce flavonols giving a red pigment which is not decolorised by sulphites. Flavonols extracted from the yellow flowers of various plants give no red colour after treatment with  $\text{Na}_2\text{S}_2\text{O}_4$  or with Mg in presence of org. acids. Mg decolorised the above extracts of anthocyanins more or less irreversibly in absence of air. The results support the old hypothesis of the formation of anthocyanins by an oxidation of anthocyanogens. L. S. T.

**Condensation of benzoin and thymoquinol.** O. DISCHENDORFER and A. VERDINO (Monatsh., 1936, 68, 41—46; cf. this vol., 82).—Thymoquinol (1 mol.), benzoin (2 mols.), and 73%  $\text{H}_2\text{SO}_4$  at 150° give alkali-sol. resinous products (probably hydroxy-

coumarones) and about 8% of 2:3:5:6-di-4':5'-diphenyl-2':3'-furano-*cymene* (I), m.p. 261°, oxidised ( $\text{CrO}_3$ -AcOH in  $\text{C}_6\text{H}_6$ ) to the dibenzoate, m.p. 235°, of 3:6-dihydroxy-2:5-dibenzoyl-*p-cymene*, m.p. 205° (sinters from 190°) [diacetate, m.p. 141° (sinters at 134°)].



H. B.

**Action of sulphur on organic compounds. XII. Action of sulphur on coumarin.** L. SZFERL and A. CHMIELNICKA (Rocz. Chem., 1936, 16, 101—103).—Coumarin and S (220—230°; 48 hr.) yield a thiophen derivative,  $\text{C}_{18}\text{H}_8\text{O}_4\text{S}$ , m.p. 331—331.5°.

R. T.

**Catalytic transformations of heterocyclic compounds. IV. Catalytic dehydrogenation of tetrahydrothiophen (thiophan).** J. K. JURIEV and A. E. BORISSOV (Ber., 1936, 69, [B], 1395—1398).—Tetrahydrothiophen (I) (compound with  $\text{HgCl}_2$ , m.p. 124.5—125.5°) is dehydrogenated by Pt-C at 315°, 350°, or 400° with production of thiophen (V),  $\text{H}_2\text{S}$ , unsaturated hydrocarbons,  $\text{H}_2$ , and saturated hydrocarbons. Ni on  $\text{Al}_2\text{O}_3$  at 350° yields diene hydrocarbons, butene, saturated hydrocarbons, and  $\text{H}_2$ , whilst NiS on  $\text{Al}_2\text{O}_3$  gives similar products with  $\text{H}_2\text{S}$  and (II). Catalytic desulphurisation of petroleum fractions containing (I) appears impossible. H. W.

**Electrolytic reduction of pyrrole.**—See this vol. 943.

**Action of hydrazine on oximinotriphenylpyrrole. II.** T. AJELLO and S. GIANFERRARA (Gazzetta, 1936, 66, 228—235; cf. A., 1935, 763).—In absence of HCl,  $\text{N}_2\text{H}_4$  (I) reduces oximinotriphenylpyrrole (II) to the  $\text{NH}_2$ -compound (III). In presence of HCl, (I) and (II) yield a substance ( $\text{C}_{22}\text{H}_{18}\text{ON}_3$ ), (IV), m.p. 235—236° (dihydrochloride; sulphate; dipicrate, m.p. 218—220°;  $\text{Ac}_2$ , m.p. 181—182°, and  $\text{Bz}_2$ , m.p. 190°, derivatives), which is reduced to (III). In the prep. of (IV), by-products, m.p. 168°, 290°, and 176—178°, are also obtained. E. W. W.

**Action of the Grignard reagent on the amide group. IX. 6-Hydroxy-1-methyl-6-alkyl-2-piperidones and 1-methyl-6-alkyl-3:4-dihydro-2-pyridones.** R. LUKEŠ and J. GOROCHOLINSKIJ (Coll. Czech. Chem. Comm., 1936, 8, 223—235; cf. this vol., 82).—*N*-Methylglutarimide and  $\text{MgRX}$  give 6-hydroxy-1-methyl-6-alkyl-2-piperidones, which, when distilled at 12—15 mm., are more or less, or when distilled through a 25 cm. column, are completely, dehydrated to 1-methyl-6-alkyl-3:4-dihydro-2-pyridones. The lower members of both series are very sol. in or miscible with  $\text{H}_2\text{O}$ . The following are described. 6-Hydroxy-1:6-dimethyl-, m.p. 52—53°, -1-methyl-6-ethyl-, m.p. 69°, -6-propyl-, m.p. 70—71°, b.p. 175—177°/7 mm., -6-n-butyl-, m.p. 76—77°, b.p. 226°/6 mm., -6-n-amyl-, m.p. 83°, and -6-n-hexyl-2-piperidone, m.p. 88—89°, which with 5%  $\text{H}_2\text{SO}_4$  give  $\delta$ -keto-*n*-hexoic, + $\text{H}_2\text{O}$ , m.p. 38—39° (lit. 37°), -heptoic, m.p. 55° (lit. 50°), -octoic, -nonoic, m.p. 46° (lit. 40°), -decoic, m.p. 58° (*Ba* salt), and -undecoic acid, m.p. 62° (*Ba* salt). 1:6-Dimethyl-, b.p. 96—98°/9 mm., and + $\text{H}_2\text{O}$ , m.p. 52—53°, 1-methyl-6-ethyl-, b.p. 108.5—111°/11 mm., -6-n-propyl-, b.p.



116.5°/10 mm., -6-*n*-butyl, b.p. 134°/8 mm., -6-*n*-amyl-, b.p. 145.5°/9.5 mm., and -6-*n*-hexyl-3:4-dihydro-2-pyridone, b.p. 158—158.5°/8 mm.

R. S. C.

**Interaction of pyridine with the chloride and bromide of Blomstrand salt.** I. I. TSCHERNIAEV and A. M. RUBINSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 111—114).—The chloride of Blomstrand salt (I) dissolves in  $C_5H_5N$ , evaporation of the solution yielding the compound

$[Pt(NH_3)_2(NO_2)_2C_5H_5NCl]Cl$  which gives a cryst. oxalate, and with Reise's base forms the mol. compound  $[Pt(NH_3)_2(NO_2)_2Cl_2][Pt_2Cl_2(NH_3)_4]$ . The bromide of (I) gave similar results. Conductivity data are given.

H. J. E.

**Reactions of selenium oxychloride and selenium tetrachloride with pyridine.** B. EDGINGTON and J. B. FIRTH (J.S.C.I., 1936, 55, 192r).— $SeOCl_2$  (1 mol.) and  $C_5H_5N$  (2 mol.) give a compound,  $(C_5H_5N)_2SeOCl_2$ , whilst an equimol. mixture at 145° yields Se and a compound,  $(C_5H_5N)_2SeCl_4$ , which loses Cl on storing and with Br forms a compound,  $(C_5H_5N)_2SeCl_2Br_4$ .  $SeO_2$  (1 mol.) and  $C_5H_5N$  (2 mol.) afford a substance which is chiefly  $(C_5H_5N)_2SeO_2$ , and  $SeO_2$  with  $C_5H_5N$  and  $Cl_2$  give a compound,  $(C_5H_5N)_2SeO_2Cl_2$ .  $C_5H_5N$  and  $SeCl_4$  yield a compound,  $(C_5H_5N)_2SeCl_4$ , m.p. 73°.

F. R. S.

**Pyridine. XXI. Preparation of 3-aminopyridine from 3:5-diaminopyridine.** H. MATER-BODE (Ber., 1936, 69, [B], 1534—1537).—Gradual addition of Br to a mixture of  $C_5H_5N$ , HCl and  $HgCl_2$  at 212—215° affords 3-bromo- (I) and 3:5-dibromopyridine (II) in 55% and 27.5% yield, respectively. (I) is converted by 25%  $NH_3$  containing  $CuSO_4$  at 140° into 3-aminopyridine, whilst under similar treatment at 130° (II) gives 3:5-diaminopyridine, m.p. 110—111° (dicarbethoxy-derivative, m.p. 195—196°), in 56% yield. (I) is converted by NaOH,  $CuSO_4$ ,  $KNaC_4H_4O_6$ , and  $H_2O$  at 200° into 3-hydroxypyridine, m.p. 127°.

H. W.

**3-Aminopyridine. III. Iodination.** Z. RODEWALD and E. PŁAŻEK (Rocz. Chem., 1936, 16, 130—135).—3-Aminopyridine (I) and ICl in fuming HCl yield an additive compound, of variable composition, which, when boiled with  $H_2O$ , gives 2:6-di-iodo-3-aminopyridine (II), m.p. 153° (3-*N*-Ac derivative, m.p. 199—201°), also obtained when β-aminopicolinic acid is taken in place of (I). (II) in  $EtOH-H_2SO_4$  and  $NaNO_2$  afford 2:6-di-iodopyridine, m.p. 130—145°, together with some 2:6-di-iodo-3-ethoxypyridine, m.p. 96—98°. 3-Acetamidopyridine (III) and ICl in AcOH afford an additive compound, m.p. 163°, from which (III) or 3-aminopyridine (IV) is obtained by the action of acids or alkalis. The hydrochloride of (IV) and ICl at 200° yield dichloro-3-aminopyridine, m.p. 118°.

R. T.

**3-Aminopyridine derivatives substituted in position 5.** A. MARCINKOW and E. PŁAŻEK (Rocz. Chem., 1936, 16, 136—140).—3:5-Dibromopyridine (I) and  $NH_3$  in MeOH in presence of  $CuSO_4$  (135—140°; 20 hr.) yield 3-bromo-5-aminopyridine, m.p. 63—64°, from which 3-bromo-5-hydroxypyridine (II), m.p. 163—165°, is obtained by treating the diazo-derivative with boiling  $H_2O$ . (II) and aq.  $NH_3$  in

presence of  $CuSO_4$  (135—140°; 20 hr.) yield 3-amino-5-hydroxypyridine, m.p. 158—160°. (I) and aq.  $NH_2Me$  (200°; 20 hr.) afford 3-bromo-5-methylaminopyridine, m.p. 87—89° (picrate, m.p. 182—184°), which with aq.  $NH_3$  and  $CuSO_4$  (135—140°; 20 hr.) gives 3-amino-5-methylaminopyridine, b.p. 190—195°/10 mm. (picrate, m.p. 223—225°; 3:5-*N*-Ac<sub>2</sub> derivative, m.p. 162—163°). (I) and aq.  $NHMe_2$  (200°; 20 hr.) yield 3-bromo-5-dimethylaminopyridine, m.p. 175—177°, which affords 3-amino-5-dimethylaminopyridine, m.p. 133—135° (picrate, m.p. 214—216°; 3-*N*-Ac derivative, m.p. 194—195°), with aq.  $NH_3$  and  $CuSO_4$  (135—140°; 20 hr.).

R. T.

**Tryptophan metabolism.**—See this vol., 885.

**Preparation of substituted indoles by catalytic decomposition of phenylhydrazones.** A. E. ARBU-SOV, I. A. ZAITZEV, and A. I. RAZUMOV (J. Gen. Chem. Russ., 1936, 6, 289—291).—The phenylhydrazone of COEtPr<sup>a</sup>, b.p. 153°/12 mm., and CuCl at 200° yield 2:3-diethyl- and/or 3-methyl-2-propyl-indole, b.p. 167°/15 mm. (picrate, m.p. 144°). Similarly,  $NHPh:N:CMcBu$  affords 2-methyl-3-propylindole, b.p. 159—161°/11 mm. (picrate, m.p. 134°), and  $NHPh:N:CPhEt$ , m.p. 47°, gives 2-phenyl-3-methylindole, m.p. 112.5° (picrate, m.p. 139°).

R. T.

**Direct synthesis of chloro- and hydroxy-quinoline from nitrobenzene.** T. MAZONSKI and E. SUCHARDA (Rocz. Chem., 1936, 16, 146—150).— $PhNO_2$ , glycerol, and conc. HCl (160—170°; 8 hr.) yield chiefly 6-chloroquinoline, together with 6- and 8-hydroxy- and 6:8-dichloro-quinoline. The probable mechanism of the reaction is outlined.

R. T.

**Preparation of 8-hydroxyquinoline from 8-chloroquinoline.** N. N. VOROSCHCOV, jun., and S. P. MITZENGENDLER (J. Gen. Chem. Russ., 1936, 6, 63—67).—8-Hydroxyquinoline is obtained in 87% yield from 8-chloroquinoline (1 mol.) and 2.2% NaOH (4 mols.) (250°/40 atm.; 2 hr.).

R. T.

**Synthesis of lepidine and its derivatives by Knorr's method.** I. Synthesis of lepidine. G. MICHAÏLOV (J. Gen. Chem. Russ., 1936, 6, 511—515).—Acetoacetanilide and  $H_2SO_4$  at 90—95° yield 2-hydroxylepidine (95% yield), converted by heating with  $POCl_3$  into 2-chlorolepidine, from which a triple salt, m.p. 145—147°, of lepidine,  $SnCl_2$ , and HCl is obtained by heating at 70—80° for 10 hr. with Sn and conc. HCl. Lepidine is obtained by treating the salt with conc. aq. NaOH.

R. T.

**Colour reaction of isatin with pyridine and acetic anhydride.** W. BORSCHKE (Ber., 1936, 69, [B], 1376).—The hypotheses concerning the constitution of the coloured substance derived from isatin and  $Ac_2O$ ,  $C_5H_5N$ , tetrahydroisoquinoline, and NaOAc (Grassman *et al.*, this vol., 612) are weakened by the observation that the "oxindolemethinecarboxylic acid" is actually 2-hydroxyquinoline-4-carboxylic acid.

H. W.

**Behaviour of pyrroles towards *p*-quinones.** P. PRATESI (Gazzetta, 1936, 66, 215—223; cf. Zaucker, Diss., Munich, 1928).—2:4-Dimethylpyrrole (I) and benzoquinone (II) in EtOH give 2:5-bis-(2':4'-dimethyl-1'-pyrryl)benzoquinone; 2:3:4-trimethyl- (III) and 2:4-dimethyl-3-ethyl-pyrrole

(IV) react similarly with (II). (I) and toluquinone yield 5(or 6)-(2':4'-dimethyl-1'-pyrryl)-2-methylbenzoquinone. (I) and 2:5-dibromobenzoquinone yield 3:6-dibromo-2:5-bis-(2':4'-dimethyl-1'-pyrryl)quinol, m.p. 278° (*Ac*<sub>2</sub> derivative, m.p. 255°), which is oxidised to the corresponding benzoquinone. (I) and  $\alpha$ -naphthaquinone (V) form 2':4'-dimethyl-1'-pyrryl- $\alpha$ -naphthaquinone (reduced to leuco- and diacetyl-leuco-derivatives). (III) and (V) give 2':3':4'-trimethyl-1'-pyrryl- $\alpha$ -naphthaquinone (reduced as before). (IV) and (V) give 2':4'-dimethyl-3'-ethyl-1'-pyrryl- $\alpha$ -naphthaquinone (reduced as before). Opso-pyrrole reacts with (II) to form an unstable product, and with (V) to give a compound C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>N, but not with thymoquinone. 2:3:5-Trimethyl-4-ethylpyrrole gives unstable products with quinones, but the fact that it does react shows that in these products the pyrryl group is attached through N. 1-Methylpyrrole reacts with quinones only when dil. H<sub>2</sub>SO<sub>4</sub> is added, but 1-methyl-2:5-diethylpyrrole reacts spontaneously, the product with (V) being 3- $\alpha$ -naphthaquinonyl-1-methyl-2:5-diethylpyrrole, m.p. 184—185° (reduced to a leuco-compound). The reaction product of (VI) and (V) is similarly reducible. The tendency of pyrroles in general to condense with quinones increases with the basicity of the pyrroles.

E. W. W.

**Acridine. XIV. *ms*-Acridine derivatives. V. Acridine 5:10-peroxide.** K. LEHMSTEDT and H. KLEE (Ber., 1936, 69, [B], 1514—1516).—Treatment of acridine with BzO<sub>2</sub>H in C<sub>6</sub>H<sub>6</sub> yields acridine 5:10-peroxide (I), decomp. 178° in bath preheated to 175°. (I) is unstable in solution, becoming either isomerised to 10-hydroxvacridone (conc. H<sub>2</sub>SO<sub>4</sub>; NaOH-EtOH) or converted into acridone and resinous substances.

H. W.

**3-Bromo-7-nitroacridone.** M. POLACZEK (Rocz. Chem., 1936, 16, 76—80).—2-Chloro-5-nitrobenzoic acid is heated at 175—180° for 4 hr. with p-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>3</sub>, NaOAc, and CuO in PhNO<sub>2</sub>, to yield 5-nitro-2-p-bromoanilinobenzoic acid (I), m.p. 287—289° (chloride, m.p. 139—142°; amide, m.p. 245—247°; Et ester, m.p. 141—142°). (I) and POCl<sub>3</sub> (120°; 4 hr.) yield 3-bromo-7-nitroacridone, m.p. >370°, which with NPhMe<sub>2</sub> and POCl<sub>3</sub> (100°; 2 hr.) affords 3-bromo-7-nitro-5-p-dimethylanilinoacridine, m.p. 284—284.5°. 3-Bromo-5-p-dimethylanilinoacridine, m.p. 239—240° (decomp.), is prepared analogously from 3-bromoacridone.

R. T.

**Kinetics of formation of poly-membered rings.**—See this vol., 940.

**Decomposition of a binary molecular compound in a ternary system.** The systems: XI. Salicylic acid-salipyrine-thymol. XII. Salicylic acid-antipyrine-thymol. K. HRYNAKOWSKI and M. SZMYTÓWNA (Rocz. Chem., 1936, 16, 57—63).—The fusion curves indicate dissociation of salipyrine in presence of thymol, with formation of an unstable mol. compound of antipyrine with thymol (not isolable).

R. T.

**4-(or 5)-Guanidinoglyoxaline and 4-(or 5)-carbamidoglyoxaline from guanine.** G. HUNTER. Dissociation and ultra-violet absorption spectra. W. D. MCFARLANE (Biochem. J., 1936, 30, 1189—1201).—The base C<sub>4</sub>H<sub>7</sub>N<sub>5</sub> obtained by acid hydrolysis of guanine is 4-(or 5)-guanidinoglyoxaline (I) [dihydrochloride, m.p. 288° (decomp.); sulphate, m.p. 219°; dipicrate, m.p. 216—217°; carbonate]. Guanidine is obtained in 91 and 76% yield, respectively, on oxidation of (I) with Br and KMnO<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, HCO<sub>2</sub>H, and small amounts of glycine being produced at the same time. Hydrolysis in N<sub>2</sub> of (I) with aq. Ba(OH)<sub>2</sub> gives 4-(or 5)-carbamidoglyoxaline (II), m.p. 194—195° [hydrochloride, m.p. 210°; sulphate, m.p. 197° (and +2H<sub>2</sub>O); picrate, m.p. 210° (and +H<sub>2</sub>O)], NH<sub>3</sub>, and other products. (II) is hydrolysed by aq. Ba(OH)<sub>2</sub> with loss of NH<sub>3</sub> and is possibly an intermediate in the production of glycine. The titration curve of (I) (*pK*<sub>H</sub> 10.5) and the light absorption curves of (I) and glycine have been plotted.

W. McC.

**Aliphatic polyamines. I. J. VAN ALPHEN** (Rec. trav. chim., 1936, 55, 412—418).—Interaction of (CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O with (CH<sub>2</sub>Br)<sub>2</sub> in EtOH yields triethylenetetramine [ $\alpha\beta$ -bis(aminoethylamino)ethane] (A., 1891, 414) (I). This forms NN'N''N'''-tetra-(phenylcarbamyl), m.p. 237°, -tetra-(phenylthiocarbamyl), m.p. 206°, -tetra-(2:4-dinitrophenyl), m.p. 285°, and tetrapicryl, m.p. 165° (decomp.) (obtained by nitration of the last derivatives). With PhCHO, the product is 2-phenyl-1:3-bis- $\beta$ -benzylideneaminoethyltetrahydroglyoxaline, m.p. 86°, decomposed by HCl; with CS<sub>2</sub>,  $\alpha\beta$ -bis(tetrahydro-2-thio-1-glyoxalanyl)ethane, m.p. 165°. A by-product with (I), "tetraethylenetetramine," is identified as 1-(aminoethylaminoethyl)piperazine, b.p. 266—270°/31 mm., since it yields a B<sub>3</sub> derivative, m.p. 221° (decomp.) [dipicrate, m.p. 221° (decomp.)]; it also forms a tetrapicrate, m.p. 212°, oxalate, m.p. 239° (decomp.), and a tri(phenylthiocarbamyl) derivative, m.p. 132—140°, and, with PhCHO, a product reduced by Na-EtOH to 1-(benzylaminoethylaminoethyl)piperazine, m.p. (+H<sub>2</sub>O) 50° [picrate, m.p. 212° (decomp.)].

E. W. W.

**Derivatives of barbituric acid.** V. PRELOG and V. HAHN (Coll. Czech. Chem. Comm., 1936, 8, 219—222).—OEt·[CH<sub>2</sub>]<sub>2</sub>·O·[CH<sub>2</sub>]<sub>2</sub>·CH(CO<sub>2</sub>Et)<sub>2</sub>, NaOEt, and EtBr give Et<sub>2</sub> ethyl- $\alpha\beta'$ -ethoxyethoxyethylmalonate ( $\alpha\beta'$ -ethoxyethoxy-n-pentane- $\gamma\gamma'$ -dicarboxylate), b.p. 173—175.5°/10 mm. (Ba salt of corresponding acid), which by hydrolysis and decarboxylation gives  $\alpha\beta'$ -ethoxyethoxy-n-pentane- $\gamma$ -carboxylic acid, b.p. 180—181°/11 mm., or by condensation with carbamide 5-ethyl-5- $\beta\beta'$ -ethoxyethoxyethylbarbituric acid (I), m.p. 96.5—97°. Methylcarbamide or its Ac derivative gives similarly the 1-Me derivative, m.p. 45.5—46.5°, of (I), which in doses of 140 mg. per kg. (intraperitoneal injection into white mice) produces hyperexcitability instead of hypnosis. In doses of 1.1 g. per kg. (I) produces hypnosis followed by spasms.

R. S. C.

**Action of thiocarbamide on aryl alkyl ketones.** K. DZIEWOŃSKI, L. BERNAKIEWICZ, and L. GIZLER (Rocz. Chem., 1936, 16, 41—48).—COPhMe and CS(NH<sub>2</sub>)<sub>2</sub> (170°; 8 hr.) yield 2-thiol-4:6-diphenyl-



6-methyl-1 : 2 : 3 : 6-tetrahydropyrimidine, (I), m.p. 172—174° (acetate, m.p. 140°; Ag salt, m.p. 190—195°; 1 : 3-Bz<sub>2</sub> derivative, m.p. 152—153°). (I) and MeI in MeOH (100°; 4 hr.) yield *s*-C<sub>6</sub>H<sub>5</sub>Ph<sub>3</sub> in small amount, together with 6-methylthiol-4 : 6-diphenyl-3 : 6-dihydropyrimidine hydriodide, m.p. 89—90°, from which the free base (II), m.p. 82—84° (picrate, m.p. 165—167°), is prepared (aq. Na<sub>2</sub>CO<sub>3</sub>). (I) with EtOH and HCl (100°; 3 hr.) gives the hydrochloride, m.p. 206—208° (decomp.), of the 6-ethylthiol homologue of (II). (I) is converted into the corresponding 2-keto-derivative by heating with HgO in AcOH. *p*-Tolyl Me ketone and CS(NH<sub>2</sub>)<sub>2</sub> (170°; 10—15 hr.) afford 2-thiol-4 : 6-di-*p*-tolyl-6-methyl-1 : 2 : 3 : 6-tetrahydropyrimidine, m.p. 170—171° (Ag salt, m.p. 188—189°), which decomposes when heated under reduced pressure to yield, amongst other unidentified products, *s*-C<sub>6</sub>H<sub>5</sub>Ph<sub>3</sub>. R. T.

**New organic reagent for metals, particularly silver.** S. E. SHEPPARD and H. R. BRIGHAM (J. Amer. Chem. Soc., 1936, 58, 1046—1049).—CO<sub>2</sub>Et·CH<sub>2</sub>·NH·CS<sub>2</sub>·NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et (from NH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Et and EtOH·CS<sub>2</sub>) with CS<sub>2</sub> in boiling EtOH gives (probably) *Et* 5-keto-2-thionhexahydropyrimidine-4-carboxylate (I), m.p. 276—280° (Pb, steel-blue, and Ag, deep purple, salts), which forms coloured compounds with neutral solutions of Cd, NH<sub>4</sub>, Cu, Fe, Pb, Zn, and Ag (also in acid) salts; 10<sup>-7</sup> g. of Ag per c.c. can be detected in slightly acid solution [(I) is thus more selective for Ag than Feigl's reagent (A., 1928, 1108)]. (I) could not be prepared from CS(NH<sub>2</sub>)<sub>2</sub> and CH<sub>2</sub>Cl·CO·CHCl·CO<sub>2</sub>Et; CO(CH<sub>2</sub>Cl)<sub>2</sub> and CS(NH<sub>2</sub>)<sub>2</sub> give 5-keto-2-thionhexahydropyrimidine, m.p. 241° (decomp.). *Et* 2-thiohydantoin-3-acetate, m.p. 95.5—96.6°, is prepared for comparison with (I). H. B.

**Complex salts of 2 : 2'-dipyridyl.**—See this vol., 944.

**Experiments in the heterocyclic series.** E. C. WAGNER and J. K. SIMONS (J. Chem. Educ., 1936, 13, 265—272).—Directions are given for the prep. of 1 : 4-dioxan, hydantoin, 5 : 5-dimethylhydantoin, benzimidazole, 8-hydroxyquinoline, trimeric methylene-*p*-toluidine, acridone, furoic acid, and furan.

L. S. T.

**Hydrolysis of guanine.** G. HUNTER (Biochem. J., 1936, 30, 1183—1188; cf. this vol., 744).—Guanine is converted by strong acids (e.g., HCl at 158° for 90 min.) into xanthine, glycine (I), a base (II) C<sub>4</sub>H<sub>7</sub>N<sub>5</sub>, NH<sub>3</sub>, guanidine, and glycoevamine. (II) is probably an intermediate in the production of (I). (II) gives a blue colour with alkaline diazo-reagent.

W. McC.

**Constitution of the purine nucleosides. IV. Adenosine and related nucleotides and coenzymes.** J. M. GULLAND and E. R. HOLIDAY (J.C.S., 1936, 765—769).—Comparisons of ultra-violet absorption spectra of aq. solutions of adenosine (I), obtained from yeast-nucleic acid, and of inosine (II), prepared from the acid by deamination (HNO<sub>3</sub>), at different *p*<sub>H</sub> vals., have been made. The spectra of (I) closely resemble those of 9- but not those of 7-methyladenine, and the spectra of (II) resemble more closely those of 9- than those of 7-methyl-

hypoxanthine. This indicates that the ribose radicals of (I) and (II) are attached to position 9 of adenine. Conversion of muscle-adenylic acid by bone-phosphatase gives (I), and the spectra of adenylic acid are identical with those of 9-methyladenine; it must therefore be adenine-9-riboside-5-phosphoric acid.

F. R. S.

**Synthesis of lactoflavin-5-phosphoric acid.** R. KUHN, H. RUDY, and F. WEIGAND (Ber., 1936, 69, [B], 1543—1547).—Lactoflavin is converted by CPh<sub>3</sub>Cl in C<sub>5</sub>H<sub>5</sub>N at 70—80° into 5'-triphenylmethyl-lactoflavin, m.p. > 250° (block) when slowly heated, transformed by Ac<sub>2</sub>O in dry C<sub>5</sub>H<sub>5</sub>N into 5'-triphenylmethyl-lactoflavin 2' : 3' : 4'-triacetate, m.p. 223—224°, hydrolysed by boiling 80% AcOH to lactoflavin 2' : 3' : 4'-triacetate (I), m.p. 202—203°. Treatment of (I) with POCl<sub>3</sub> and C<sub>5</sub>H<sub>5</sub>N followed by hydrolysis leads to lactoflavin-5'-phosphoric acid, identical with the natural product in solubility of its Ca and Na salts, behaviour on adsorption, dependence of fluorescence on *p*<sub>H</sub>, oxidation-reduction potential, and physiological activity.

H. W.

**Dihydropyrophosphoride-*a* and pyrophosphoride-*b*.**—See this vol., 886.

**Redox potential of murexide.** R. KUHN and J. C. LYMAN (Ber., 1936, 69, [B], 1547—1549).—Murexide (I) is immediately decolorised by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and the colour is completely restored when the solution is shaken with air. (I) can be sharply titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and it is thus shown that most methods for the prep. of (I) give very impure products composed mainly of uramil. Piloty's method affords (I) in 97—98% purity, but the yield is only 2% of the allantoin taken. Potentiometric titration does not give sharp vals. if Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is used owing to further reduction of leucomurexide. In feebly acidic solution titration can be effected with TiCl<sub>3</sub>, whereby harmonising vals. are obtained with Au or Pt electrodes. The redox potential of (I) is +0.02±0.01 volt.

H. W.

**Polyazines. I. Structure of the dimethyl-aziethan of Curtius and Thun.** B. G. ZIMMERMAN and H. L. LOCHTE (J. Amer. Chem. Soc., 1936, 58, 948—949).—Polyazines (I) of the type NH<sub>2</sub>·N'·CMe·[CMe·N·N'·CMe]<sub>*n*</sub>·COMe are formed (i) from Ac<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in aq. Na<sub>2</sub>CO<sub>3</sub>, whereby (·CMe·N·NH<sub>2</sub>)<sub>2</sub> (II) is also produced, (ii) by treatment of COMe·CMe·N·NH<sub>2</sub> with dil. HCl or EtOH-picric acid, (iii) from (II) and Ac<sub>2</sub> in EtOH, and (iv) decomp. of COMe·CMe·N·NHAc by Diels' method (A., 1902, i, 205; A., 1915, i, 127). (I) with EtOH·N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O yields (II). The dimethylaziethan of Curtius and Thun (A., 1891, 1355) is a polyazine.

H. B.

**Spectrochemistry of nitrogenous organic compounds. Structure and absorption of benzoxazole, benzoxazolone, and phenmorpholones.** (MME.) RAMART-LUCAS and V. VANTU (Bull. Soc. chim., 1936, [v], 3, 1165—1173).—Benzoxazolone (I) and its *N*-Et derivative have almost identical absorption spectra in the region approaching the visible. The corresponding *O*-Et compound has a very similar graph which is somewhat displaced towards shorter  $\lambda$ . Each spectrum nearly resembles that of anisole. (I), therefore, exists in solution

mainly in the lactam form, but the evidence of the possible presence of the imino-alcohol variety is inconclusive. The spectra of phenmorpholine (II) and its derivatives are closely similar to that of ethoxy-methylene-*o*-anisidine which has the same chromophors. In solution, therefore, (II) exists mainly in the amide form but the graphs of the isomerides are so closely alike that it is impossible to decide whether the imino-alcohol variety is present in appreciable amount.

H. W.

**Dioximes.** CXI. Phenylloximinooacetoneitrile oxide. CXII. Phenylbenzoyloximinooacetoneitrile oxide. G. PONZIO. CXIII. E. DURIO and S. DUGONE. CXIV. G. LONGO and G. RANDONE (Gazzetta, 1936, 66, 127—134, 134—139, 139—145, 145—154).—CXI.  $\alpha$ -Phenylglyoxime peroxide (I) with aq.  $\text{Na}_2\text{CO}_3$  at  $0^\circ$  yields phenylloximinooacetoneitrile oxide (II),  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{CN}:\text{O}$ , m.p. 112—113°, which with boiling  $\text{AcOH}$  affords phenylhydroxyglyoxime, m.p. 187—188° (*Ni* salt), with  $\text{NH}_3$  or primary amines (e.g.,  $\text{NH}_2\text{Ph}$ ) amino- $\alpha$ -phenylglyoxime, m.p. 154—155°, or derivatives (e.g.,  $\alpha$ -anilinophenylglyoxime, m.p. 189—190°), with  $\text{Bz}_2\text{O}$  dibenzoylphenylhydroxyglyoxime, m.p. 155—156° (decomp.) (cf. A., 1926, 850), and with 50% aq.  $\text{EtOH}$  phenylbenzamidofurazan and phenylmetazonic acid (cf. A., 1926, 1159). With boiling  $\text{EtCO}_2\text{H}$  or aq.  $\text{NaOH}$ , (II) yields 5-hydroxy-3-phenyl-azoxime, m.p. 201—203°, with  $\text{HCl}$  phenylchloroglyoxime (A., 1923, i, 472), and with  $\text{NaOEt}$  reacts like (I) forming an acid  $\text{Na}$  salt of hydroxyphenylglyoxime whilst (I) or (II) with  $\text{Ac}_2\text{O}\cdot\text{NaOAc}$  affords the  $\text{Ac}_2$  derivative [ $\text{OAc}\cdot\text{N}:\text{CPh}\cdot\text{C}_2\text{O}_2\text{N}_2$ , m.p. 117—118°]. (II) with  $\text{MgMeI}$  yields a complex,  $\text{CPh}\cdot\text{N}\cdot\text{OMgI}\cdot\text{CMe}\cdot\text{N}\cdot\text{OMgI}$ , reacting with  $\text{HCl}$  to give  $\text{CNPh}$  and  $\alpha$ -phenylmethylglyoxime. The reactions of (I) indicate the structure  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}:\text{N}:\text{O}$ .

CXII.  $\text{OBz}\cdot\text{N}:\text{CPh}\cdot\text{CN}:\text{O}$  with  $\text{HCl}$  in  $\text{Et}_2\text{O}$  yields 2-benzoyl- $\alpha$ -phenylchloroglyoxime (A., 1931, 223) (corresponding *Br*-derivative, m.p. 172—173°) and with  $\text{Bz}_2\text{O}$  tribenzoylphenylhydroxyglyoxime, m.p. 163—165°. Phenylbromoglyoxime, m.p. 203—204° (decomp.), and phenylidoglyoxime (A., 1932, 1146) result from (II) and  $\text{HCl}$  or  $\text{HI}$ . The transformation of  $\beta$ -phenylfuroxan into (II) is analogous to that of  $\alpha$ -phenylfuroxan into phenyloximinocyanomethane; (I) has one of the *syn-anti* configurations of  $\text{NO}\cdot\text{CPh}\cdot\text{CH}\cdot\text{NO}$  and the peroxide of  $\beta$ -phenylglyoxime is 4-phenyl-1 : 2 : 3 : 6-dioxadiazine.

CXIII. Diaminoglyoxime with aq.  $\text{NH}_3$  at  $155^\circ$  does not yield 3 : 4-diaminofurazan but  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The action of  $\text{NH}_2\text{OH}$  on the thioamide or amide of 3-carboxy-5-phenyl-1 : 2 : 4-oxadiazole yields the amidoxime (III), m.p. 158°, the *O*-*Bz* derivative, m.p. 206°, of which with hot 20%  $\text{NaOH}$  affords 5 : 5'-diphenyl-3 : 3'-di-(1 : 2 : 4-oxadiazole), m.p. 247—248° (cf. Zinkeisen, A., 1890, 122). (III) with boiling 10%  $\text{NaOH}$  for a few min. gives 3-amino-4-benzamidofurazan (IV), m.p. 145—146° (*Ag*, m.p. 190—205°, and *Cu* derivative), which with excess of  $\text{BzCl}$  at  $100^\circ$  affords 3 : 4-di(benzamido)furan, m.p. 178°. (IV) with 10%  $\text{NaOH}$  and slight excess of  $\text{Br}$  or  $\text{KMnO}_4$  yields 3 : 3'-azo-4 : 4'-di(benzamido)furan, m.p. 262—265° (decomp.), reduced ( $\text{Zn}\cdot\text{AcOH}$ ) to the corresponding hydrazo-compound,

m.p. 224—225° (decomp.) [*phenylhydrazone*, m.p. 211—212° (decomp.)]; also prepared by direct action of  $\text{NHPh}\cdot\text{NH}_2$  (6 mol.) on the azo-compound (1 mol.) in  $\text{Et}_2\text{O}$ . (IV) with  $\text{NaNO}_2\cdot\text{AcOH}$  at  $0^\circ$  yields 3 : 3'-azoimino-4 : 4'-di(benzamido)furan, m.p. 162° (decomp.); coupling with  $\mu\text{-C}_{10}\text{H}_7\cdot\text{OH}$  affords (red) 3- $\beta$ -naphtholazo-4-benzamidofurazan, m.p. 223—224°.

CXIV.  $\text{NH}_2\text{Me}$  with (I) or (II) yields  $\alpha$ -methylamino-phenylglyoxime,  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{NMe})\cdot\text{NH}\cdot\text{OH}$ , m.p. 178° (decomp.) [ $\text{Ac}$ , m.p. 160° (decomp.),  $\text{Ac}_3$ , m.p. 117°, and  $\text{Bz}_2$  derivative, m.p. 170—171°]; the last two with  $\text{NaOH}$  yield 4-methylamino-3-phenylfuran, m.p. 62°, the isomeride  $\beta$ -methylaminophenylglyoxime,  $\text{OH}\cdot\text{N}:\text{CPh}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NHMe}$ , m.p. 159—160° [hydrochloride, m.p. 202° (decomp.)];  $\text{Bz}_2$  derivative, m.p. 155°, being afforded by heating the  $\alpha$ -form in  $\text{AcOH}\cdot\text{Ni}(\text{OAc})_2$  or treating phenylchloroglyoxime with  $\text{NH}_2\text{Me}$  and pptn. of the *Ni* salt, m.p. 256° (decomp.). Similarly prepared are  $\alpha$ -benzylaminophenylglyoxime, m.p. 174° (decomp.) [*Na* salt, m.p. 219—220° (decomp.)];  $\text{Ac}_3$ , m.p. 126—127°, and  $\text{Bz}_2$  derivative, m.p. 150°, the last two affording 4-benzylamino-3-phenylfuran, m.p. 98°, and  $\beta$ -benzylaminophenylglyoxime, m.p. 158—159° [hydrochloride, m.p. 191—192° (decomp.)]; *Ni* salt, m.p. 218° (decomp.);  $\text{Ac}_2$ , m.p. 122—123° (decomp.),  $\text{Ac}_3$ , m.p. 114° and  $\text{Bz}_2$  derivative, m.p. 162°. The above compounds illustrate structural differences in explanation of m.p. anomalies between  $\alpha$ - and  $\beta$ -series of dioximes.

F. O. H.

**Synthesis of benzthiazole and its  $\mu$ -alkyl-derivatives.** A. I. KIPRIANOV, Z. P. SITNIK, and N. E. GRIGORIEVA (J. Gen. Chem. Russ., 1936, 6, 232—235).— $\text{HCO}_2\text{H}$  in  $\text{C}_6\text{H}_6$  and (*o*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}$ ) $_2\text{Zn}$  (I) (5 hr. at the b.p.) yield benzthiazole (80% yield),  $\text{Ac}_2\text{O}$  in  $\text{C}_6\text{H}_6$  and (I) (3 hr. at the b.p.) yield 1-methyl- (73% yield),  $\text{EtCO}_2\text{H}$  and (I) (18 hr. at the b.p.) afford 1-ethyl-, m.p. 185—185.5° (72% yield),  $\text{PrCO}_2\text{H}$  and (I) (6 hr. at the b.p.) give 1-*n*-propyl-, m.p. 181° (90% yield), and *n*-valeric acid and (I) (20 hr. at the b.p.) yield 1-*n*-butyl-benzthiazole, m.p. 160° (30% yield).

R. T.

**Metachromism: metachromatic dyes and chromotropic substances.** L. LISON (Arch. Biol., 1935, 46, 599—668).—The ability of basic dyes such as methylene-blue to produce metachromatic coloration, i.e., to colour certain histological specimens in different tints from the normal, is associated with their chemical constitution, and depends on the presence of at least one  $\text{NH}$ . A substrate is not necessary for the metachromatic colour change, which can be produced in solution by pure substances called by the author chromotropes. The colour change is not due to liberation of the free colour-base chromotrope, but to a chemically and spectroscopically different coloured substance. Metachromatic dyes in  $\text{H}_2\text{O}$  exist in two forms, "normal" and "metachromatic," in reversible equilibrium; increase of concn. or  $p_{\text{H}}$  or lowering of temp. favours production of the "metachromatic" form, whilst dilution, heat, acidification, electrolytes,  $\text{EtOH}$ , and  $\text{COMe}_2$  shift equilibrium towards the "normal" side. Chromotropes shift the equilibrium towards the "metachromatic" side without forming any new substances. Metachromism is a true sp. reaction, characteristic of higher



alkylsulphuric acids and their salts; the chromotropic power  $\propto$  the mol. wt. R. N. C.

**Cyanine dyes. I. Thiocarbocyanines.** A. I. KIPRIANOV, Z. P. SITNIK, and E. D. SITSCH (J. Gen. Chem. Russ., 1936, 6, 42—49).—The 8-methyl, 5:5'-dimethyl, 5:5':8-trimethyl, 5:5'-diethoxy-, 5:5'-diethoxy-8-methyl, 8-methoxy-, 8-methoxy-5:5'-diethoxy-, 8-phenyl, 8-methoxy-5:5'-dimethyl, and 8-phenyl-5:5'-dimethyl derivatives of 2:2'-diethylthiocarbocyanine iodide have been prepared by boiling a mixture of the appropriate substituted benzthiazole ethiodide with Et ortho-formate, -acetate, or -benzoate, in  $C_5H_5N$ . The above substances are violet dyes, exerting a sensitising action on photographic emulsions.

R. T.

**Ephedrine synthesis. I. Propiophenone diethyl acetal and  $\alpha$ -ethoxy- $\alpha$ -phenyl- $\Delta^a$ -propylene.** E. L. BEALS and F. A. GILFILLAN (J. Amer. Pharm. Assoc., 1936, 25, 426—427).—COPhEt condensed with  $CH(OEt)_3$  in EtOH-HCl affords *propiophenone Et<sub>2</sub> acetal*, b.p. 108—110°/14 mm., 226—228°/760 mm. (slight decomp.), which with  $C_5N_5N$  and AcCl yields  $\alpha$ -ethoxy- $\alpha$ -phenyl- $\Delta^a$ -propylene, b.p. 105°/19 mm., 220—221° (corr.)/760 mm. (slight decomp.).

F. O. H.

**Alkaloids of jaborandi leaves. IX. Synthesis of *r*-isopilocarpine.** A. M. POLJAKOVA, V. A. PREOBRASHENSKI, and N. A. PREOBRASHENSKI (Ber., 1936, 69, [B], 1314—1316).—*r*-isopilopyl  $CHN_2$  ketone (I) is transformed by  $Ag_2O$  and abs. EtOH into *Et r*-homoisopilopate, b.p. 106—108°/0.3 mm., hydrolysed to *r*-homoisopilocic acid (II), b.p. 163°/1 mm., m.p. 74.2°, also obtained from (I) and  $Na_2S_2O_3$ - $Ag_2O$ - $H_2O$  or  $AgNO_3$ - $NH_3$ - $H_2O$ -EtOH followed by hydrolysis. (II) is transformed through its chloride and  $CHN_2$  ketone into *r*-homoisopilopyl  $CH_2Cl$  ketone, m.p. 47—47.5°, whence *r*-homoisopilopyl phthalimido-methyl ketone, m.p. 129—130°, and *r*-homoisopilopyl  $CH_2$ - $NH_2$  ketone hydrochloride, m.p. 148—149°. The amine and KCNS afford 2-thiol-4(5)-*r*-homoisopilopyl-quinoxaline, m.p. 207—208.5°, oxidised by  $FeCl_3$  to *r*-isopilocarpidine (nitrate, m.p. 114—114.5°), which with MeI affords *r*-isopilocarpine (nitrate, m.p. 134—135°).

H. W.

**Alkaloids of Senecio. II. Senecionine and squalidine.** G. BARGER and J. J. BLACKIE (J.C.S., 1936, 743—745).—Pure senecionine (I),  $C_{18}H_{25}O_5N$  (nitrate, m.p. 214°,  $[\alpha]_D$  -34.2° in  $H_2O$ ), isolated from *S. viscosus*, has m.p. 232°,  $[\alpha]_D$  -54.6° in  $CHCl_3$ . (I) is obtained pure from *S. vulgaris* in April and September, but in summer it is mixed with another alkaloid. From *S. squalidus*, (I) is isolated along with squalidine,  $C_{18}H_{25}O_5N$ , m.p. 169°,  $[\alpha]_D$  -26.9° in  $CHCl_3$ , hydrolysed to squalineic acid, m.p. 129°. (I) is hydrolysed to retronecine and senecic acid, m.p. 153°, an unsaturated lactonic acid, which is reduced ( $H_2$ -PtO<sub>2</sub>) to dihydrosenecic acid, m.p. 106°, and oxidised ( $HNO_3$ ) to a substance,  $C_6H_8O_4$ , m.p. 142°.

F. R. S.

**Ergotocine, ergometrine, ergostetrine, and ergobasine.**—See this vol., 1022.

**Synthesis and reactions of natural substances under physiological conditions. VI. Biogenesis of vasicine (peganine). Synthesis of deoxyvas-**

**icine under physiological conditions.** C. SCHOFF and F. OECHLER (Annalen, 1936, 523, 1—29; cf. A., 1935, 981).—Under "physiological" conditions  $o$ - $NH_2$ - $C_6H_4$ -CHO (I), primary bases, and  $CH_2O$  give 4-hydroxy-3-alkyltetrahydroquinazolines, which react as  $\psi$ -bases of 3-alkyl-1:2-dihydroquinazol-3-inium salts, which in turn readily give 4-hydroxy-3-alkyl-3:4-dihydroquinazolines. (I) and  $NH_2$ - $[CH_2]_3$ - $CH(OEt)_2$  (II) in a citrate buffer solution of  $p_H$  4.8—5.0 at 30° give in 4 days a solution probably containing 4-hydroxy-2:3-cyclopentanotetrahydroquinazoline, since addition of  $C_6H_5(NO_2)_3 \cdot OH$  gives a 75% yield of 2:3-cyclopentano-1:2-dihydroquinazol-3-inium picrate (III), m.p. 168—170°, and shaking with Pd-black in  $H_2$  for 5 hr. prior to addition of  $C_6H_5(NO_2)_3 \cdot OH$  gives by a shift of 2 H from (III) a 18% yield of deoxyvasicine [with much  $o$ - $NH_2$ - $C_6H_4$ - $CH_2 \cdot OH$ , which necessitates assumption of an equilibrium between (I), (II), and their condensation product]. (I) may be derived from tryptophan.  $NH_2$ - $[CH_2]_2$ - $CH(OH) \cdot CHO$  may be derived from  $\alpha$ -hydroxyornithine and would lead similarly to vasicine or, by the acetonedicarboxylate synthesis, to hydroxytryptophan. Other hypothetical syntheses are discussed. If (I) in  $H_2O$  is treated first with  $CH_2$ - $CH$ - $CH_2$ - $NH_2$ - $HCl$  (IV) and then with  $CH_2O$  (natural  $p_H$  4.8—5.2, const.) and kept for 3 days at room temp., it affords 71—74% of 3-allyl-1:2-dihydroquinazol-3-inium picrate (V), m.p. 139—140°; if after admixture the  $p_H$  is adjusted to 7 or 9, the yield is only 55 and 25%, respectively. If the  $CH_2O$  is added before the base, there is formed instead of (V) a 65% yield of  $NN'$ -methylenebis- $o$ -aminobenzaldehyde (VI), m.p. 160—161°, whence it follows that the initial condensation must be extremely rapid, and

that (I) and  $CH_2O$  condense to  $o$ - $C_6H_4$ - $\begin{matrix} CH(OH) \\ | \\ NH-CH_2 \end{matrix}$ - $O$ ,

which reacts with  $CH_2O$  but not (or only very slowly) with (IV). The possibility of photosynthesis by reactions which must take place in a given order is discussed with reference to this and other cases. The structure of (V) is proved by oxidation ( $CrO_3$ -AcOH; 60°) to 3-allyl-4-quinazolinone, also obtained from isatic anhydride,  $NH_2$ - $CH_2$ - $CH$ - $CH_2$ , and  $HCO_2H$ , and by oxidation of 3-allyl-3:4-dihydroquinazoline. If (I), (IV), and  $CH_2O$  are allowed to react for 1 day at  $p_H$  7.1, then treated with  $K_3Fe(CN)_6$  at 0°, and kept for 4 days at room temp., the (V) is oxidised to the quinazolinium base, which is isolated as the  $\psi$ -base, 4-hydroxy-3-allyl-3:4-dihydroquinazoline, m.p. 136—137° after sintering at 135° [picrate, +EtOH (0.5 mol. lost at 70°/vac.), m.p. 138—139°], also obtained from (V) and  $Pb(OAc)_4$  at 60—70°. (I) reacts with  $NH_2Me$ - $HCl$  more slowly than with (IV); thus under analogous conditions much (VI) is formed with  $CH_2O$ ; however, if 30 min. elapse before addition of the  $CH_2O$ , there is obtained at  $p_H$  4.6—5.0 an 80% yield of 3-methyl-1:2-dihydroquinazol-3-inium picrate, m.p. 185—186°, which with  $CrO_3$  affords 3-methyl-4-quinazolinone, m.p. 103—104° [picrate, m.p. 211—212°; also obtained from isatic anhydride (modified procedure) and from 3-methyl-3:4-dihydroquinazoline], and with  $Pb(OAc)_4$  gives 4-hydroxy-3-methyl-3:4-dihydroquinazoline, m.p. 164—165° (lit. 162—163°) [picrate, +EtOH (0.5 mol. lost at 80°/vac.), m.p.

145—146° (decomp.). *Formylanthranilmethylamide* has m.p. 110—112°. If the prep. of (III) is carried out at 25°, some tris-*o*-aminobenzaldehyde is obtained. No (III) is obtained at  $p_H$  4.5, 5.7, or 9 if (II) is previously hydrolysed with  $H_2C_2O_4$ , which makes it probable that the free aldehyde is too unstable to exist. (III) is oxidised by  $CrO_3$  to 2:3-cyclopentano-4-keto-3:4-dihydroquinazoline ( $\Delta^9$ -pegen-8-one) and by  $Pb(OAc)_4$  to 2:3-cyclopentanoquinazol-3-inium picrate, +EtOH (retained at 70°/vac.), m.p. 146—147°, whence NaOH yields 2:3-cyclopentano-4-hydroxy-3:4-dihydroquinazoline (8-hydroxy- $\Delta^9$ -pegene), m.p. 176—177° (decomp.). *Vasicine picrate* has m.p. 190—191° (decomp.). (I),  $NH_4Cl$ , and  $CH_2O$  give only (VI). R. S. C.

$\alpha$ - and  $\beta$ -Hydroxylaudanosines. I. Their preparation from papaverinol. F. E. KING, P. L'ECUYER, and F. L. PYMAN (J.C.S., 1936, 731—733).—*Papaverinol methochloride*, m.p. 205—206°, is reduced ( $Sn-HCl$ ) to  $\alpha$ -hydroxylaudanosine (I), m.p. 138°, laudanosine, and a hydrochloride (II), m.p. 235°, whilst catalytic reduction ( $H_2$ -PtO<sub>2</sub>) affords (I) [*hydrochloride*, m.p. about 135° (efferv.)]; *picrate*, m.p. 198° (decomp.), and  $\beta$ -hydroxylaudanosine, m.p. 108—109° [*hydrochloride*, m.p. 235°, identical with (II)]; *picrate*, m.p. 178—179°. No other products are formed, the total yield being theoretical.

F. R. S.

Harmine and harmaline series. I. N-Alkyl derivatives of harmine and harmaline. R. A. KONOVALOVA and A. P. OREKHOV (J. Gen. Chem. Russ., 1936, 6, 487—498).—2-*N*-Methylbenzylideneharmine (I), m.p. 192—193°, and EtI in PhMe-PhNO<sub>2</sub> yield the *ethiodide*, m.p. 230—231°, of (I), not attacked by boiling 10% aq. NaOH or 25% aq.  $NH_3$ . 2-*N*-Ethylbenzylideneharmine, m.p. 199—200°, and MeI, under analogous conditions, yield a *methiodide*, m.p. 251—252°. 2-*N*-Methylnorharmine and EtI afford an *ethiodide*, m.p. 280—281°, not identical with the *methiodide*, m.p. 262°, of 2-*N*-ethylnorharmine, m.p. 221—222°. 2-*N*-Ethylharmaline, m.p. 163—164° [from harmaline *ethiodide*, m.p. 232—233° (decomp.)], and MeI in MeOH yield a *methiodide*, m.p. 241—243°, identical with that obtained from 2-*N*-methylharmaline and EtI in EtOH. The results are in accordance with the views of Perkin and Robinson (J.C.S., 1919, 115, 2481; 1924, 126, 657) on the structure of harmine and harmaline. R. T.

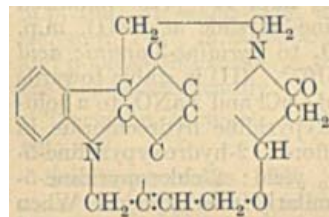
Chemical individuality of the alkaloids of ergot of rye. C. H. LIBERALLI (Rev. Quim. Farm., 1936, 1, 168—170).—A review. L. A. O'N.

Anhydromethylenecitrates of alkaloids. I. Salts of cinchona and nux vomica alkaloids. S. ANSELMi (Annali Chim. Appl., 1936, 26, 221—224).—Cinchonine, quinidine, strychnine, and brucine form salts 2 base, 1 acid with anhydromethylenecitric acid. Cinchonidine forms 1:1, quinine 2:1 and 1:1 salts. L. A. O'N.

Rhoeadine and rhoeagenine. E. SPATH, L. SCHMID, and H. STERNBERG (Monatsh., 1936, 68, 33—40).—Rhocadine (I),  $C_{20}H_{18}O_5 \cdot N \cdot OMe$ , m.p. 256—257.5° (vac.),  $[\alpha]_D^{25} +232^\circ$  in  $CHCl_3$  (*hydriodide*), is extracted (0.031% yield) from the dry flowers of

*Papaver rhoeas*, L., by aq. 2% AcOH. Successive treatment of (I) with warm 2*N*-HCl and aq. NaOH in absence (or presence) of air gives rhoeagenine (II),  $C_{19}H_{16}O_5 \cdot NMe$ , m.p. 236—238° (vac.),  $[\alpha]_D^{25} +168^\circ$  in AcOH (*hydriodide*), which is OMe-free. (I) and (II) contain 1 and 2 active H, respectively. (II) is oxidised (aq.  $KMnO_4$  in  $CO_2$  at room temp.) to 3:4-methylenedioxyphthalic acid and its methyl-imide; Zn-dust distillation affords isoquinoline. Reduction ( $Sn$ , 7% HCl, little MeOH) of (II) gives an oil, b.p. 230—240°/0.02 mm., which when distilled with Zn dust affords impure cryst. products, m.p. 136—143° and 172—179°. H. B.

Strychnine. VI. Alkali-fusion of strychnin-olone, strychninonic acid, and strychnine. M. KOTAKE (Proc. Imp. Acad., Tokyo, 1936, 12, 99; cf. this vol., 871).—



Fusion of strychnin-olone (I), strychninonic acid, or strychnine (II) for 10—15 min. with 3 parts of KOH gives  $\beta$ -3-indolyethylamine. (I) gives also a little

BzOH. (II) thus has not the formula proposed by Robinson or Leuchs, but contains the annexed grouping. R. S. C.

Constitution of chondodendrine. F. FALTIS, K. KADIERA, and F. DOBLHAMMER (Ber., 1936, 69, [B], 1269—1281).—*d*-Chondodendrine (I) has  $[\alpha]_D +262.8^\circ$  in  $CHCl_3$ . *d*-Chondodendrine  $Me_2$  ether,  $[\alpha]_D +335.0^\circ$  in  $C_5H_5N$ ,  $+314.5^\circ$  in  $CHCl_3$ , is converted by MeI in MeOH into *d*-O-methylchondodendrine *methiodide*,  $[\alpha]_{5461} +170^\circ$ ,  $[\alpha]_D +137^\circ$  in  $H_2O$  (corresponding *methochloride*,  $[\alpha]_{5461} +190^\circ$ ,  $[\alpha]_D +160^\circ$  in  $H_2O$ ). Methylation of (I) by  $Me_2SO_4$  and NaOH and treatment of the product with NaOH gives the following substances: optically inactive  $\alpha$ -*nordimethylchondodendrimethine*, m.p. 217—218° after softening at 214°;  $\beta$ -*nordimethyl-d-chondodendrimethine*, m.p. 154—155°,  $[\alpha]_D +136.3^\circ$  in  $CHCl_3$  (*methiodide*,  $[\alpha]_D +48^\circ$  in 50% MeOH);  $\alpha\alpha'$ -*dimethylchondodendrimethine* (II), m.p. 134—135°, also (+3 $H_2O$ ), m.p. (indef.) 80—93°, and (+1 $C_6H_6$ ), m.p. (indef.), 80—93°. Ozonisation of (II) followed by the conversion of the products into the *methiodides* and thence into the *methochlorides* and subsequent oxidation of the latter with  $KMnO_4$  yields 3:4-dimethoxy-2-*p*-carboxyphenoxy-6-vinylbenzoic acid (cf. A., 1934, 423) and 4-methoxy-3-6'-methoxy-4'-carboxyphenoxy-6-vinylbenzoic acid (III), m.p. 264—265° (decomp.). Decarboxylation of (III) by Cu powder in boiling quinoline and oxidation of the product with  $KMnO_4$  in  $COMe_2$  affords 3-methoxy-*p*-2'-methoxyphenoxybenzoic acid, m.p. 163.5° after softening at 160° (*Me ether*, m.p. 46° after softening at 40°), obtained synthetically from *Me vanillate* and *o*- $C_6H_4Br \cdot OMe$ . H. W.

N-Alkyl group of aconine (aconitine). W. A. JACOBS and R. C. ELDERFIELD (J. Amer. Chem. Soc., 1936 58 1059).—Fusion of aconine (hydrochloride) with KOH in  $H_2$  or  $Ba(OH)_2$  (cf. Ehrenberg and Purfürst A., 1892, 1254) gives  $NH_2Et$ , whilst treatment



with HI affords MeI (from OMe) and then EtI; the *N*-Et group is thus present. The production of oxonitine (I) from aconitine probably involves removal of this *N*-Et. A substance, m.p. 261°,  $[\alpha]^{20}_D$  -98° in CHCl<sub>3</sub>, is formed as a by-product during the prep. of (I). H. B.

**Pyridine. XX. Pyridine-3-arsinic acid and related compounds.** A. BINZ and O. VON SCHICKL (Ber., 1936, 69, [B], 1527—1534).—Addition of NaNO<sub>2</sub> in H<sub>2</sub>O to 3-aminopyridine, AsCl<sub>3</sub>, and CuCl in conc. HCl at 0° followed by treatment of the solution with KI and SO<sub>2</sub>, yields 3-pyridyldichloroarsine hydrochloride (+1H<sub>2</sub>O) (I), m.p. 217—230°, reduced by H<sub>3</sub>PO<sub>2</sub> in presence of KI and conc. HCl to 5:3'-arsenopyridine, from which it is regenerated by 3% H<sub>2</sub>O<sub>2</sub> in conc. HCl. (I) is transformed by NH<sub>3</sub>-H<sub>2</sub>O into 3-pyridylarsine oxide, m.p. 118—119° [oxidised by 30% H<sub>2</sub>O<sub>2</sub> to pyridine-3-arsinic acid (II), m.p. 156°], and by 30% H<sub>2</sub>O<sub>2</sub> to pyridine-3-arsinic acid hydrochloride, m.p. 195—197°. (II) is stable towards boiling H<sub>2</sub>O. Addition of CuCl and NaNO<sub>2</sub> to a solution of 5-amino-2-hydroxypyridine hydrochloride in conc. HCl at >10° affords 2-hydroxypyridine-5-arsinic acid (III) in 43% yield; 2-chloropyridine-5-arsinic acid is obtained similarly in 50% yield. When reduced to the arseno-compound and then treated with H<sub>2</sub>O<sub>2</sub> in conc. HCl, (III) yields 2-hydroxypyridyldichloroarsine hydrochloride (+0.5H<sub>2</sub>O), m.p. about 154° after softening at 92—110°. 3-Pyridyltetrachlorostibine hydrochloride, m.p. 240° (decomp.), is described. H. W.

**Configuration of heterocyclic compounds. IV. Optical resolution of 10-phenylphenoxarsine-2-carboxylic acid.** (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1936, 730—731).—10-Phenylphenoxarsine-10-oxide-2-carboxylic acid, m.p. 320°, prepared by oxidation (KMnO<sub>4</sub>) of 10-phenyl-2-methylphenoxarsine, is reduced (SO<sub>2</sub>; I) to dl-10-phenylphenoxarsine-2-carboxylic acid, m.p. 208—209°, which was resolved through the l- $\alpha$ -phenylethylamine d-, m.p. 208—209°,  $[\alpha]^{20}_{D_{91}} +184.3^\circ$  in MeOH, and l-10-phenylphenoxarsine-2-carboxylate, m.p. 199—200°,  $[\alpha]^{20}_{D_{91}} -191.2^\circ$  in MeOH, to give d-, m.p. 189—190°,  $[\alpha]^{20}_{D_{91}} +223.1^\circ$  in EtOH, and l-10-phenylphenoxarsine-2-carboxylic acid, m.p. 189—190°,  $[\alpha]^{20}_{D_{91}} -232.2^\circ$  in EtOH. The acid possesses high optical stability. F. R. S.

**Organic boron derivatives. I. Action of halogens and hydrogen peroxide on diarylboric acids.** N. N. MELNIKOV (J. Gen. Chem. Russ., 1936, 6, 636—639).—The reactions BR<sub>2</sub>·OH (I) + X<sub>2</sub> + H<sub>2</sub>O → BR(OH)<sub>2</sub> (II) + HX + RX; (II) + X<sub>2</sub> + H<sub>2</sub>O → RX + HX + H<sub>3</sub>BO<sub>3</sub>; (I) + H<sub>2</sub>O<sub>2</sub> → ROH + (II); (II) + H<sub>2</sub>O<sub>2</sub> → ROH + H<sub>3</sub>BO<sub>3</sub> (R = Ph, *p*-C<sub>6</sub>H<sub>4</sub>X, *p*-C<sub>6</sub>H<sub>4</sub>Me, *p*-OMe·C<sub>6</sub>H<sub>4</sub>·; X = Cl, Br) are shown to take place in H<sub>2</sub>O at room temp. R. T.

**Relative reactivities of organometallic compounds. IX. Cadmium.** H. GILMAN and J. F. NELSON (Rec. trav. chim., 1936, 55, 518—530).—CdCl<sub>2</sub> can be used in the Grignard reaction, for the prep. of organo-Cd compounds of type CdR<sub>2</sub> and CdRX from MgRX (X preferably = Br). Organo-Cd compounds are less reactive than organo-Zn, but more reactive than organo-Hg, compounds. Their colour

test with Michler's ketone is described. CdEt<sub>2</sub> (I) combines very slowly with PhCHO; in Bu<sub>2</sub>O with CPhMe at 50—60° CPh·CH·COPh is formed. Cd compounds prepared from MgRX, but not isolated, react readily with acyl chlorides to form ketones, in much better yields than from Zn compounds. The following are prepared by this means, using the appropriate chloride. From MgMeBr, CPhMe, *m*-C<sub>6</sub>H<sub>4</sub>Me·COMe, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·COMe; from MgEtBr, COMeEt, CPhEt, *n*-C<sub>17</sub>H<sub>35</sub>·COEt, and 2-furyl Et ketone; from MgPr<sup>*δ*</sup>Br, COPr<sup>*δ*</sup>·Pr<sup>*δ*</sup>; from MgBu<sup>*γ*</sup>Cl, COMeBu<sup>*γ*</sup>; from CH<sub>3</sub>Ph·MgCl, CH<sub>3</sub>Ph·COMe; from MgPhBr, CPhMe and CPh<sub>2</sub>; and from LiPh, CPhMe. (COCl)<sub>2</sub> and (I) react rapidly to form C<sub>2</sub>Et·Pr<sup>*δ*</sup>·OH; CO<sub>2</sub>Et·COCl and Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> both give OH·C<sub>2</sub>Et<sub>2</sub>·CO<sub>2</sub>Et. PhSO<sub>2</sub>Cl forms SO<sub>2</sub>Ph<sub>2</sub>, PhCl, and PhSO<sub>2</sub>H. E. W. W.

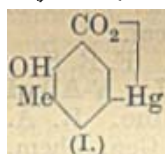
**Organic compounds of germanium. K. BURCHKIES** (Ber., 1936, 69, [B], 1313; cf. this vol., 871).—A lit. addendum. H. W.

**Mercury derivatives of o-cresotic acid.** A. LESPAGNOL and (Mlle.) D. BAR (Bull. Soc. chim., 1936, [v], 3, 1107—1114).—Na 2-hydroxy-*m*-toluate is converted by Hg(OAc)<sub>2</sub> at room temp. into the Hg<sup>II</sup> salt, which passes when heated into "basic Hg o-cresotate" (I), transformed by KCN into homogeneous K 2-hydroxy-5-cyanomercuritolate. Nitration of the latter or of (I) affords 5-nitro-2-hydroxy-*m*-toluic acid, m.p. 205°, reduced to 5-amino-2-hydroxy-*m*-toluic acid, m.p. 308°, which is decarboxylated to 1:3:4-OH·C<sub>6</sub>H<sub>2</sub>Me·NH<sub>2</sub> or diazotised and then decarboxylated to 1:2:5-C<sub>6</sub>H<sub>3</sub>Me(OH)<sub>2</sub>. H. W.

**Synthesis of organic tin compounds from diazo-compounds.** K. A. KOTSCHESCHKOV, A. N. NESMEJANOV, and V. A. KLIMOV (J. Gen. Chem. Russ., 1936, 6, 167—171).—Certain aryldiazonium stannichlorides react with Sn in boiling EtOAc, as follows: (R·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>Cl)<sub>2</sub>·SnCl<sub>4</sub> + Sn → (R·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnO + C<sub>6</sub>H<sub>6</sub> + (R·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> (R = *o*-Me, *p*-Cl, *p*-Br). When R = *o*-OMe, the product is (OMe·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>, m.p. 113°; when R = *o*-CO<sub>2</sub>Me the substance *o*-CO<sub>2</sub>Me·C<sub>6</sub>H<sub>4</sub>·SnCl<sub>3</sub>, m.p. 164°, is obtained. R. T.

**Arsenical azoproteins and ability of phenylalanine, tryptophan, proline, and hydroxyproline to couple with diazobenzenearsinic acid.** R. KAPPELLER-ADLER and G. BOXER (Biochem. Z., 1936, 285, 55—66).—Tables summarise the As and N contents of the coupling products of diazobenzenearsinic acid (I) with caseinogen, fibrin, zein, and gelatin. The N contents are close to those of the original proteins whilst the As contents of the azoproteins are, respectively, about 8, 4, 8, and 14.8%. Similar compounds are obtained with phenylalanine, tryptophan, proline, and hydroxyproline, the N and As contents of which corresponded closely with the requirements of the corresponding bis-(I) derivatives, indicating that coupling had occurred. P. W. C.

**Denaturation of proteins. XV. Formol titration of proteins in carbamide solution.** C. Y. CHOU and H. WU (Chinese J. Physiol., 1936, 10, 303—314).—The NH<sub>2</sub>-N content of glycine or cryst. oval-



bumin determined by  $\text{CH}_3\text{O}$  is the same whether the protein is dissolved in  $\text{H}_2\text{O}$  or in 40%  $\text{CO}(\text{NH}_2)_2$  solution, i.e., denaturation by  $\text{CO}(\text{NH}_2)_2$  does not affect the  $\text{NH}_2\text{-N}$ . This finding is used to determine the  $\text{NH}_2\text{-N}$  content of proteins insol. in  $\text{H}_2\text{O}$ , and sol. in  $\text{CO}(\text{NH}_2)_2$  solution. The  $\text{NH}_2\text{-N}$  of ovalbumin, cryst. pepsin, horse serum-albumin, edestin, and casein is 6.5, 11.9, 9.3, 9.0, 2.4, and 7.4 mg. per g., respectively.

F. A. A.

**Densities of protein crystals and hydration of proteins.** G. S. ADAIR and M. E. ADAIR (Proc. Roy. Soc., 1936, B, 120, 422—446).—The  $d$  of protein crystals as measured by a flotation method in aq. media depends on the composition and  $p_{\text{H}}$  of the medium, and is < that of the anhyd. protein, probably owing to greater hydration in the former. The  $d$  of heat-coagulated proteins is slightly > that of the crystals.

F. A. A.

**Acetylation of agar.** E. G. V. PERCIVAL and W. S. SIM (Nature, 1936, 137, 997—998).—Agar is readily (cf. this vol., 593) acetylated, with no apparent degradation, when suitably-prepared material is treated with  $\text{C}_5\text{H}_5\text{N}$  and  $\text{Ac}_2\text{O}$ . The  $\text{CHCl}_3$ -sol. acetates,  $[\alpha]_{\text{D}}^{25} -30^\circ$  approx., contain 36—43% Ac according to the time of acetylation. Evaporation of the  $\text{CHCl}_3$  solution of the acetate leaves a tough, colourless film.

L. S. T.

**Modifications of physico-chemical properties of protein solutions with age.**—See this vol., 1012.

**Raman effect in analytical chemistry.**—See this vol., 949.

**Addition of hydrogen peroxide in the determination of nitrogen in organic compounds.** C. F. POE and B. T. DEWEY (J. Amer. Pharm. Assoc., 1936, 25, 419—422).—Addition of 30%  $\text{H}_2\text{O}_2$  accelerates the oxidation of, and gives accurate results with, substances containing  $\text{-NH}_2$  but not  $\text{-NO}_2$  groups (Gunning-Kjeldahl method).

F. O. H.

**Colorimetric determination of peroxides in unsaturated compounds.** C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (Ind. Eng. Chem. [Anal.], 1936, 8, 198—199).—A method is described depending on the oxidation of  $\text{FeSO}_4$  in presence of  $\text{NH}_4\text{CNS}$ , using MeOH as solvent.

E. C. S.

**Determination of small concentrations. XII. Colorimetric determination of acetate.** R. V. TEIS and E. M. JOFINOVA-GOLDFEIN (J. Appl. Chem. Russ., 1936, 9, 957—964).—The blue colour developing when 5% aq.  $\text{La}(\text{NO}_3)_3$ , aq.  $\text{NH}_3$ , and I in EtOH are added to aq. acetates is not  $\propto$  the  $[\text{OAc}']$ . A more intense coloration is obtained by raising the  $[\text{La}''']$ , but the reaction does not become more sensitive, its limits of applicability remaining at 0.35—1.7 mg. of  $\text{OAc}'$ . The rate of colour development, and its intensity, fall with increasing  $[\text{NH}_3]$ , or in presence of neutral salts; at the same time tendency towards ppt. formation increases.

R. T.

**Utilisation of S-benzylthiuronium chloride for isolation and identification of organic acids.** J. J. DONLEAVY (J. Amer. Chem. Soc., 1936, 58, 1004—1005).—S-Benzylthiuronium chloride, two forms, m. p. 146—148° and 172—174° (all m.p. except

these are corr.) [from  $\text{CS}(\text{NH}_2)_2$  and  $\text{CH}_2\text{PhCl}$  in EtOH], and the appropriate Na or K salt in  $\text{H}_2\text{O}$  or aq. EtOH give S-benzylthiuronium formate, m.p. 146°, acetate, m.p. 134°, propionate, m.p. 148°, n-, m.p. 146°, and iso-, m.p. 143°, butyrate, isovalerate, m.p. 153°, laurate, m.p. 141°, myristate, m.p. 139°, palmitate, m.p. 141°, stearate, m.p. 143°, oxalate, m.p. 193°, succinate (+2 $\text{H}_2\text{O}$ ), m.p. 149°, H maleate, m.p. 163°, fumarate, m.p. 178°, crotonate, m.p. 162°, glycollate, m.p. 141°, lactate, m.p. 153°, diglycollate, m.p. 154°, benzoate, m.p. 166°, o-, m.p. 159°, m-, m.p. 163°, and p-, m.p. 182°, -nitrobenzoate, o-, m.p. 142°, m-, m.p. 149°, and p-, m.p. 166°, -aminobenzoate, o-, m.p. 140°, m-, m.p. 164°, and p-, m.p. 190°, -toluate, salicylate, m.p. 146°, m-chlorobenzoate, m.p. 155°, m-bromobenzoate, m.p. 168°, anisate, m.p. 177°, phthalate, m.p. 151°, cinnamate, m.p. 175°, mandelate, m.p. 166°, diphenylacetate, m.p. 145°, benzenesulphonate, m.p. 144°, m-nitrobenzenesulphonate, m.p. 140°, and p-toluenesulphonate, m.p. 178°. Some of the salts are hydrolysed readily.

H. B.

**Titration of weak acids and bases.**—See this vol., 949.

**Semicarbazides. IV. m-Tolylsemicarbazide** as a reagent for the identification of aldehydes and ketones. P. P. T. SAH, S. M. WANG, and C. H. KAO (J. Chinese Chem. Soc., 1936, 187—192).—m-Tolylsemicarbazide, m.p. 106—108°, condenses readily with aldehydes and ketones and the m-tolylsemicarbazones of the following substances may be used for identification: MeCHO, m.p. 104—105°; EtCHO, m.p. 88—89°; Pr<sup>n</sup>CHO, m.p. 76—78°; Bu<sup>n</sup>CHO, m.p. 81—82°; n-hex-, m.p. 112—113°; n-hept-, m.p. 119—121°; n-oct-, m.p. 115—117°; n-non-, m.p. 124—250°; n-dec-, m.p. 99—100°; benz-, m.p. 175—176°; m-nitrobenz-, m.p. 187—188°, and salicylaldehyde, m.p. 202—203°; furfuraldehyde, m.p. 142—143°; COMe<sub>2</sub>, m.p. 158—160°; COMeEt, m.p. 109—110°; Me hexyl ketone, m.p. 82—84°; COMe·CH<sub>2</sub>CHPh, m.p. 192—193°; CPhMe, m.p. 186—187°; p-methyl-, m.p. 200—201°; m-nitro-, m.p. 232—332°, and p-bromo-acetophenone, m.p. 206—207°; CPh<sub>2</sub>, m.p. 181—182°; lævulic acid, m.p. 186—187°; CH<sub>3</sub>Ac·CO<sub>2</sub>Et, m.p. 118—120°; Et, m.p. 97—98°, and CH<sub>2</sub>Ph, m.p. 112—113°, lævulate.

F. R. S.

**Use of 2:4-dinitrophenylhydrazine as a reagent for carbonyl compounds.** N. R. CAMPBELL (Analyst, 1936, 61, 391—395).—Tables of all recorded m.p. of 2:4-dinitrophenylhydrazones are given. Many are erroneous and many corrected m.p. have been determined. 2:4-Dinitrophenylhydrazones of the following are new: o-C<sub>6</sub>H<sub>4</sub>Cl·CHO, m.p. 206—207°; vanillin, m.p. 271° (decomp.); diacetone alcohol, m.p. 202—203°; dibenzylideneacetone, m.p. 180°; cinnamylideneacetone, m.p. 222—223°; dicinnamylideneacetone, m.p. 208°; CHAcBz·CO<sub>2</sub>Et, m.p. 223°; CH<sub>2</sub>Ac<sub>2</sub>, m.p. 209°; Ac<sub>2</sub>, charred > 300°; cinnamylideneacetophenone, m.p. 218—219° (decomp.); 2-C<sub>10</sub>H<sub>7</sub>·Ac, m.p. 262° (decomp.); piperitone, m.p. 119°; 2-C<sub>10</sub>H<sub>7</sub>·Bz, m.p. 257—258°; β-benzoyl-diphenyl, m.p. 214°; furoin, m.p. 216—217°; phenanthraquinone, m.p. 312—313° (decomp.), and chryssoquinone, m.p. 308—309° (decomp.). Recorded vari-



ations in the m.p. of acetaldehydedinitrophenylhydrazones are due to the presence of impurities and not to a metastable modification. Brady's method, using  $\text{Pr}^{\text{e}}\text{OH}$  instead of  $\text{EtOH}$ , was used for the prep.

E. H. S.

**Azides. VI. *p*-Brombenzazide as a reagent for the identification of primary and secondary amines.** P. P. T. SAH, C. H. KAO, and S. M. WANG (J. Chinese Chem. Soc., 1936, 4, 193—197).—*p*-Bromobenzazide, m.p.  $46^{\circ}$  (decomp.), prepared by diazotisation of the hydrazide, gives *p*-bromophenylcarbamides of the following amines and amides:  $\text{NH}_2\text{Ph}$ , m.p.  $230$ — $231^{\circ}$ ; *o*-, m.p.  $207$ — $208^{\circ}$ ; *m*-, m.p.  $215$ — $216^{\circ}$ , and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m.p.  $264$ — $266^{\circ}$ ; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ , m.p.  $218$ — $219^{\circ}$ ; *o*-, m.p.  $198$ — $199^{\circ}$ ; *m*-, m.p.  $223$ — $224^{\circ}$ , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ , m.p.  $282$ — $284^{\circ}$ ; *m*-nitro-*p*-toluidine, m.p.  $214$ — $216^{\circ}$ ;  $\alpha$ -, m.p.  $272$ — $274^{\circ}$ , and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ , m.p.  $223$ — $224^{\circ}$ ;  $\alpha$ - $\text{C}_{10}\text{H}_7\cdot\text{NHAc}$ , m.p.  $157$ — $158^{\circ}$ ;  $\text{NHPhAc}$ , m.p.  $141$ — $142^{\circ}$ ; *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHAc}$ , m.p.  $179$ — $180^{\circ}$ ; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NHAc}$ , m.p.  $163$ — $165^{\circ}$ ; *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , m.p.  $152$ — $153^{\circ}$ ; *o*-, m.p.  $114$ — $115^{\circ}$ , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$ , m.p.  $146$ — $147^{\circ}$ , and  $\text{NHPhMe}$ , m.p.  $123$ — $124^{\circ}$ .

F. R. S.

**Simplified copper reagent.** E. J. MUELLER (J. Pharm. Chim., 1936, [viii], 24, 18).—The reagent for sugars is made up of 100 c.c. of 29.9%  $\text{NaOH}$ , 1 g. of  $\text{CuSO}_4$ , and 10 c.c. of distilled  $\text{H}_2\text{O}$ .

H. D.

**Use of the ninhydrin reaction in the determination of amino-acids.** M. POLONOVSKI and F. MORENO-MARTÍN (Anal. Fís. Quím., 1935, 33, 574—587).—A more detailed account of work already published (A, 1935, 1044). In the method of Cherbuliez *et al.* (*ibid.*, 102) it is essential to work always with reagents of the same concn. Addition of  $\text{AcOH}$  to counteract increase in the  $p_{\text{H}}$  of the solution has been investigated and the method applied to the determination of  $\text{NH}_2$ -acids in milk.

F. R. G.

**Potentiometric determination of polypeptides and amino-acids. II. Formaldehyde titration.** E. W. BALSON and A. LAWSON (Biochem. J., 1936, 30, 1257—1263).—From measurements of the changes in the titration curves of  $\text{NH}_2$ -acids produced by the presence of  $\text{CH}_2\text{O}$  it is concluded that primary  $\text{NH}_2$ -acids and polypeptides react with up to three mols. of  $\text{CH}_2\text{O}$ , *sec.* with one only; *tert.* do not react.

H. D.

**Sullivan colorimetric test for guanidine.** C. E. BRAUN and F. M. REES (J. Biol. Chem., 1936, 114, 415—417).—*p*-Anilino-,  $\alpha$ -naphthyl-, *ar*-tetrahydro- $\alpha$ -naphthyl-, and *o*-tolyl-guanidine and *p*-tolylidiguanidine, but not 31 other guanidine derivatives, are indistinguishable from guanidine by the Sullivan colorimetric test.

R. S. C.

**Reaction of borneol.** O. CARLETTI (Boll. Chim. farm., 1936, 75, 299—303).—The Borisch reaction (development of a violet colour when commercial camphor and vanillin are mixed in  $\text{H}_2\text{SO}_4$  and diluted with  $\text{H}_2\text{O}$ ) is due to borneol (I), which gives the reaction as strongly as does menthol (II). The reaction may be used as a sensitive test for (I) and for isoborneol; also to distinguish (II) from menthone.

E. W. W.

**Approximate determination of furfuraldehyde in solutions.** E. K. NIKITIN (J. Appl. Chem. Russ., 1936, 9, 950—956).—The approx. concn.  $X$  of furfuraldehyde (I) is given by  $X/C=K$ , where  $C$  is the concn. of (I) in a standard solution (usually 0.2%), and  $K=1/\{1+(v-v_1)/(v_2-v_1)\}$  for solutions of pure (I), and  $2/\{1+2(v-v_1)/(v_2-v_1)\}$  for crude distillates, where  $v$  is the time elapsing before appearance of turbidity in a mixture of 2 ml. of neutral aq. (I) (approx. 0.2%), 2 ml. of 0.01% aq.  $\text{COMe}_2$ , and 2 ml. of 60%  $\text{KOH}$ , and  $v_1$  and  $v_2$  are respectively the times for 0.2 and 0.1% (I).

R. T.

**Micro-reaction of caffeine with iodine-potassium iodide.** C. VAN ZIJP (Pharm. Weekblad, 1936, 73, 767—768).—Exact details are given.

S. C.

**Determination of chlorophyll with the aid of the light of a Lange electrical colorimeter.** T. N. GODNEV and S. V. KALESEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 77—79).—Chlorophyll in solutions containing 0.25 mg. per litre can be determined Lange's colorimeter;  $\geq 30$  c.c. of solution are needed. Using a Schott red filter  $\text{COMe}_2$  extracts can be used directly.

P. G. C.

**Determination of total creatine.**—See this vol., 1038.

**Iodometric determination of cysteine.** T. T. CHEN (Chinese J. Physiol., 1936, 10, 315—326).—High concns. of  $\text{HCl}$  and  $\text{KI}$  inhibit the reaction between cysteine and  $\text{I}$ , whilst low ones favour oxidation of cysteine beyond the cystine stage. In the presence of 1%  $\text{KI}$  and 0.9*M*- $\text{HCl}$ , cysteine may be titrated to cystine by  $\text{KIO}_3$ ; in the indirect procedure, adding excess  $\text{KIO}_3$  to cysteine and titrating the  $\text{I}$ , the  $[\text{HCl}]$  should be 3*M*.

F. A. A.

**Application of 5 : 7-dibromo-8-hydroxyquinoline to the determination of small amounts of iron, titanium, and aluminium in mixtures.**—See this vol., 952.

**Reaction of ferric salts with pyrimidone in presence of complex cyanides of iron.**—See this vol., 947.

**Colorimetric determination of carnosine and histidine.** N. P. MESCHKOVA (Z. physiol. Chem., 1936, 240, 199—207).—In presence of histidine (I) carnosine (II) cannot be determined by Kapeller-Adler's method (A., 1934, 574). The method which employs Pauly's diazo-reagent (A., 1904, i, 1068) gives satisfactory results if the optimal amount of reagent is used and the aq.  $\text{Na}_2\text{CO}_3$  is added at once in the case of (II) and after 1—3 hr. in that of (I). Interference by glycine, asparagine, and uric acid is overcome by adding excess of the reagent. Urea does not interfere. Equimol. solutions of (I) and (II) produce equal intensity of colour with the reagent.

W. McC.

**Determination of average lethal dose in the biological assay of digitalis by the frog method.**—See this vol., 892.

**Microchemical identification of -cocaine.** R. CECCONI (Annali Chim. Appl., 1936, 26, 218—220).—

With  $\text{KMnO}_4$  in acid solution, *d*-cocaine gives characteristic hexagonal crystals, whereas *l*-cocaine forms rectangular plates, tropacocaine minute prisms, and eucaine an irregular or non-cryst. mass. Other derivatives become oxidised. L. A. O'N.

**Berberine as a microchemical reagent.** C. VAN ZIJP (Pharm. Weekblad, 1936, 73, 764—767).—Characteristic micro-cryst. ppts. are formed when, solutions containing berberine- $\text{H}_2\text{SO}_4$  (I) are treated with solutions containing Na-luminal, Na salicylate, or meconic acid. Uric acid, theocine, atophan, luminal, rutonal, dial, propional, salicylic acid, saccharin, and fumaric acid give ppts. immediately when solutions containing (I) are treated with  $\text{NH}_3$ , preferably by the hanging-drop method. Veronal and evipan give ppts. with  $\text{NH}_3$  slowly. Theobromine, cystine, tyrosine, leucine, cotoine,  $\text{CO}(\text{NH}_2)_2$ , aspirin,

anisic, cinnamic, and succinic acids give no definite ppt. S. C.

**Biuret reaction of proteins.** F. LIEBEN and H. JESSERER (Biochem. Z., 1936, 285, 36—46).—The colours obtained in the biuret reaction, carried out under standardised conditions, with varying protein concns. obey the Beer-Lambert rule, the colour strength and tone for all the investigated proteins, peptones, etc. being the same for the same wt. concns. and independent of the mol. size and the  $\text{NH}_2$ -acid content of the substrate. A method is described for separation of the red and blue components of the colour, which are shown to give different extinction coeffs. in the step photometer. Clupein Me ester hydrochloride gives the same colour strength and tone and the same Cu content as the same concn. of caseinogen. P. W. C.

## Biochemistry.

**Influence of high and low concentrations of carbonic acid on oxygen consumption of frogs.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 122, 325—327).—Low concns. (0.6—0.8%) of  $\text{CO}_2$  increase and high concns. (25%) decrease the  $\text{O}_2$  consumption of frogs. F. O. H.

**Variation of respiratory exchange of active dormice with temperature.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 122, 328—330).—Diminution of temp. from  $30^\circ$  to  $-10^\circ$  produces a steady increase in heat production from 1.2 to 4.5 g.-cal. per kg. per hr. (cf. A., 1935, 387).

F. O. H.

**Modification of the Haldane-Henderson apparatus for the analysis of respiratory gases.** N. CORDERO (Chinese J. Physiol., 1936, 10, 373—376).—A 3-way stopcock allows either the  $\text{CO}_2$  absorber, or the  $\text{O}_2$  absorber only, to be connected with the temp.-control tube, and eliminates frequent turning of the stopcock communicating with the gas burette.

F. A. A.

**Conductivity curves of ox red corpuscles in relation to the number of dispersed elements and  $p_{\text{H}}$ .** G. ACHARD (Compt. rend. Soc. Biol., 1936, 122, 571—574).

H. G. R.

**Degradation of adenosine triphosphate in cells.** V. A. ENGELHARDT and G. G. LIPSHITZ (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 104—105).—Degradation in nucleated avian (pigeon, fowl) erythrocytes (respiration inhibited by KCN) does not lead to liberation of free  $\text{H}_2\text{P}_2\text{O}_7$ .

W. McC.

**Phosphates and phosphate metabolism in red blood cells.** H. VON EULER and K. M. BRANDT (Z. physiol. Chem., 1936, 240, 215—231).—The state of combination of  $\text{PO}_4'''$  in erythrocytes varies greatly from species to species (sheep, ox, pigeon, rat, guinea-pig). Inorg. P is increased by  $\text{Mg}^{++}$  and decreased by NaF. Added muscle-adenylic acid and cozymase decrease the inorg. P and increase the amount of phosphoric esters hydrolysed in 3 hr. In rats on diets free from vitamin-D, inorg. P is decreased and

the content of readily-hydrolysed phosphoric esters is increased. W. McC.

**Effect of proteins on electrophoretic mobility and sedimentation velocity of red cells.** B. R. MONAGHAN and H. L. WHITE (J. Gen. Physiol., 1936, 19, 715—726).—The isoelectric point of red cells cannot be determined, but it is  $<$  that of any plasma-protein. With cells kept in acid solution, the surface is damaged so that they adsorb proteins from low concn. When bulk  $\eta$  is increased, the mobility of the cells is unchanged, indicating surface hydration, and the aggregating effect of certain proteins is said to be due to dehydration. H. G. R.

**Carbhaemoglobin.** F. J. W. ROUGHTON (Biochem. Z., 1936, 285, 150—152).—The method of Groscurth and Havemann (A., 1935, 1260) for determination of  $\text{CO}_2$  bound with haemoglobin as carbamyl derivative is not trustworthy, and the author's method is not invalidated by their observations. P. W. C.

**Carbhaemoglobin.** G. GROSCURTH and R. HAVE-MANN (Biochem. Z., 1936, 285, 153—155).—A reply to Roughton (preceding abstract). P. W. C.

**Effect of  $\text{CO}_2$  tension and temperature on the dissociation curves of the oxyhaemoglobin of blood.** S. SEVERIN, E. GEORGIEVSKI, and V. TUNIN (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 137—138).—Changes in temp. ( $28^\circ$ ,  $33^\circ$ ,  $38^\circ$ ) at const. pressure (38 mm. of Hg) and in pressure (20.4, 56 mm.) at const. temp. ( $37.5^\circ$ ) considerably alter the positions of the curves, but not their shapes. The degree of aggregation of the haemoglobin mols. increases as the  $\text{O}_2$  tension increases, but is unaffected by changes in temp. or  $\text{CO}_2$  tension. W. McC.

**Methaemoglobin formed post-mortally, spontaneously, and by chemicals, and that formed by drying.** E. BECHTOLD (Z. Fleisch- u. Milchhyg., 1935, 45, 227—230, 267—270, 287—291, 326—329; Chem. Zentr., 1935, ii, 2146).—The processes occurring are discussed in detail. H. N. R.

**Methaemoglobinising action *in vivo* of sodium nitrite.** A. RABBENO and S. RAPPEPORT-LEWEY



(Boll. Soc. ital. Biol. sperim., 1936, 11, 34—35).—With rabbits approx. 0.12 g. of  $\text{NaNO}_2$  per kg. body-wt. is lethal. Death occurs when 80% of the hæmoglobin (I) is converted into methæmoglobin. With cats, the amount of (I) converted  $\propto$  time; with rabbits the conversion starts slowly and is accelerated in the final phase. E. P.

**Detection and determination of bilirubin.** G. B. ARBUINOV (Klin. Med. U.S.S.R., 1934, 12, 111—115).—Hæmolytic bilirubin A gives no direct colour reaction and is not pptd. by EtOH. It can be determined by the Herzfeld or the van den Bergh method. Bilirubin B gives a good colour reaction and is pptd. by EtOH. It can be determined by the Herzfeld method in serum not treated with EtOH.

CH. ABS. (e)

**Isoionic point of serum-proteins. I. Method of determination and results.** G. SANDOR (Bull. Soc. Chim. biol., 1936, 18, 877—907; cf. A., 1935, 822).—Methods of determination are discussed and details of an approx. and of an exact method are given. For the globulins of horse serum the val. varies between  $p_H$  5.8 and 6.0, and for the cryst. albumin between 5.10 and 5.14, although in some cases the latter val. is raised to 5.4. H. G. R.

**Nephelometry of blood-proteins. I. Rapid determination of globulin. II. Sulphosalicylic acid reaction in determination of proteins.** K. PLOTNER (Biochem. Z., 1936, 286, 128—134, 135—139).—I. The globulin content of normal and pathological sera (and of other biological fluids) is determined, without separation from albumin, by half-saturating with aq.  $(\text{NH}_4)_2\text{SO}_4$  and measuring in a nephelometer the degree of turbidity produced.

II. The determination of protein in body-fluids by measuring the turbidity produced by sulphosalicylic acid is untrustworthy. W. McC.

**Albumin/globulin ratio of normal and pathological human sera.** A. ROCHE, M. DORIER, and L. SAMUEL (Compt. rend., 1936, 202, 1720—1722).—Fractional salting-out with  $(\text{NH}_4)_2\text{SO}_4$  indicates unchanged solubilities of serum-albumin and -globulin during cirrhosis, but modifications of their micellar character during hypertension. F. O. H.

**Influence of intravenously injected carbon suspensions on blood-proteins and albumin/globulin quotient.** A. LUMIERE, P. MEYER, and M. A. THIBAUDET (Compt. rend. Soc. Biol., 1936, 122, 308—310).—Injection of C suspensions into fasting rabbits decreases blood-proteins, but increases the albumin/globulin ratio. F. O. H.

**Influence of intravenously injected carbon suspensions on blood-sugar.** A. LUMIERE and P. MEYER (Compt. rend. Soc. Biol., 1936, 122, 311—313).—Injection of C suspensions into fasting rabbits produces a hyperglycæmia inhibited by ergotamine, but not by atropine, and therefore related to the adrenal-sympathetic system. F. O. H.

**Physiological variations of the blood-sugar level in rabbits and dogs.** S. G. GENESS and V. P. KOMISSARENKO (Biochem. Z., 1936, 285, 420—428).—Tables and curves summarise the blood-sugar vals. of large nos. of dogs and rabbits, including

the normal fasting levels, variation over periods of days and months, and variations on administering glucose. The normal fasting level for 1020 rabbits was 0.06—0.16% (mean 0.108%) and for 100 dogs 0.60—0.13% (mean 0.92%). The variations from day to day and over months are considerable, but are less for dogs than for rabbits. The mean increase in the vals. for 8 rabbits receiving glucose 128 times is 0.41—0.51%. P. W. C.

**Changes in blood-sugar content after ligation of arteries.** H. HUNGERLAND (Arch. exp. Path. Pharm., 1936, 181, 435—443).—Tying the carotid and femoral arteries in dogs caused a rise in blood-sugar; the max. occurred earlier after carotid ligation. Anomalous results were obtained by ligation under morphine-pernoctone narcosis. J. N. A.

**New experimental hyperlipæmia in rabbits. Genesis of venesection lipæmia.** T. HATAKEYAMA (Biochem. Z., 1936, 285, 11—28).—Hyperlipæmia can be brought about in rabbits merely by suction on the ear and without venesection. The suction lipæmia is seen first as an alimentary lipæmia and later as a persistent lipæmia, and can be obtained without decrease of either erythrocytes or serum-protein. Neither suction nor venesection lipæmia is obtained with animals in the fasting condition. The mechanism is discussed. P. W. C.

**Combined and free lipins in blood plasma.** L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 886—889).—Plasma-lipins are separated into 3 fractions, (a) not pptd. by saturation with  $(\text{NH}_4)_2\text{SO}_4$ , (b) pptd. by  $(\text{NH}_4)_2\text{SO}_4$  and directly extracted from the ppt. by  $\text{Et}_2\text{O}$ , and (c) pptd. by  $(\text{NH}_4)_2\text{SO}_4$  and not extracted by  $\text{Et}_2\text{O}$  but by boiling EtOH. Variations in (a), (b), and (c) with fasting and fat-containing and -free diets are tabulated. F. O. H.

**Dependence of the composition of the blood-plasma and -serum on the nature of the diet.** (A) E. G. SCHENCK. (B) E. ABDEHJALDEN (Z. physiol. Chem., 1936, 240, 232—236, 237—240; cf. A., 1935, 1261).—Polemical. W. McC.

**Determination of hippuric acid in blood.** H. MINIBECK and N. NEUMANN (Mikrochem., 1936, 20, 91—103).—The hippuric acid (I) is extracted from the albumin-free filtrate with  $\text{Et}_2\text{O}$  and titrated as  $\text{NH}_2\text{-N}$  in  $\text{COMe}_2$  with 0.025N-HCl in EtOH (indicator  $\alpha$ -naphthyl-red). Satisfactory results are obtained with 1—1.5  $\times 10^{-3}\%$  of (I) in blood. (I) does not occur in health, but develops in cases of heart, kidney, and liver complaints and in febrile pneumonia. J. W. S.

**Level of certain phenylamines ("tyramine equivalent") in hypertensive sera.** M. LOEPER and A. LESURE (Compt. rend. Soc. Biol., 1936, 122, 292—294).—The tyramine equiv. (determined colorimetrically with phosphomolybdic acid) is increased (average 4.6 mg. per litre) in sera of hypertensive patients. Normally there exists a vasotonic equilibrium between acetylcholine and adrenaline, and pathologically between tyramine and histamine, the ratio of the last two being characteristic. F. O. H.

**Determination of urea in blood-serum by the action of hypobromite and titration of excess of the reagent.** J. RENAUDIN (Bull. Soc. Chim. biol., 1936, 18, 908—910).—Levinson's method (A., 1935, 1525) gives good results with pure solutions of urea, but is less precise with serum.  
H. G. R.

**Determination of alcohol in blood and urine.** R. HEIDUSCHKA and G. STEULMANN (Pharm. Zentr., 1936, 77, 405—409).—A modification of Liebesny's method for 1 c.c. of blood or urine is described in which excess of 0.15N-K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is determined by liberation of I from KI and titration with 0.1N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  
P. G. M.

**Determination of alcohol in blood.** W. BRANDT (Chem.-Ztg., 1936, 60, 485—488).—Methods of determining blood-EtOH, the course of blood- and cerebrospinal fluid-EtOH following ingestion or injection of EtOH, and the bearing of the methods and results on jurisprudence are discussed.  
F. O. H.

**Blood-ammonia in eviscerated and anoxæmic dogs.** F. D'ARBELLA and A. BILLI (Boll. Soc. ital. Biol. sperim., 1935, 10, 958—959).—Removal of the intestines or deprivation of O<sub>2</sub> increases blood-NH<sub>3</sub> in dogs.  
F. O. H.

**Adsorption of blood-calcium.** L. BUTTURINI and V. BIANCHI (Boll. Soc. ital. Biol. sperim., 1935, 10, 941—942).—Data for the adsorption (in no case complete) of Ca from serum by Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, C, BaSO<sub>4</sub>, kaolin, talc, and powdered bone are tabulated and discussed.  
F. O. H.

**Adsorption of blood-calcium.** L. BUTTURINI and V. BIANCHI (Boll. Soc. ital. Biol. sperim., 1936, 11, 13—15).—Blood-serum is treated with Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, animal C, BaSO<sub>4</sub>, kaolin, talc, and powdered bones, and the Ca contents of the serum are measured before and after treatment.  
E. P.

**Calcium content of the blood of adenoids.** C. F. PORTA (Boll. Soc. ital. Biol. sperim., 1936, 11, 30).—The average Ca content was 9.5%, of which 63.3% was dialysable. Normal vals. were 12.7 and respectively.  
E. P.

**Effect of the irritation of vagus and sympathetic nerves on composition of blood.** E. ZAKRSHEVSKI (Platz. Utschen. Med., 1936, 124—131).—Stimulation of the vagus in cats decreases blood-Ca and increases -K, whilst stimulation of the sympathetic has the opposite effect. The blood-lipase and -diastase are not significantly altered.  
W. O. K.

**Nature, properties, and determination of iron in blood.** E. M. WALL and F. M. SHORLAND (J. New Zealand Inst. Chem., 1936, 1, 15—21).—Non-hæmoglobin Fe is determined by treating fresh whole blood with 4% aq. Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. After 15 min. an equal vol. of 20% CCl<sub>3</sub>·CO<sub>2</sub>H is added, and the solution is filtered. The filtrate is treated with 0.0012M-2:2'-dipyridyl in 5N-NH<sub>4</sub>OAc, and reduced with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Fe is determined colorimetrically.  
J. S. A.

**Influence of alkalosis on serum-magnesium.** R. WOLFF, M. RANGIER, and A. BOURQUARD (Compt.

rend. Soc. Biol., 1936, 122, 391—392).—Serum-Mg is increased by ingestion of NaHCO<sub>3</sub>.  
H. G. R.

**Magnesium in parturient women and in the new-born.** Z. KARAMAN, A. ALEXIU, and A. URSU (Compt. rend. Soc. Biol., 1936, 122, 705—707).—Blood-Mg is < normal after pregnancy, whilst that of the new-born child tends to be > normal.  
H. G. R.

**Blood-iodine level.** G. PFEIFFER, W. MÖBIUS, and K. POHL (Arch. exp. Path. Pharm., 1936, 181, 444—450).—A discussion on methods for determining I in org. substances.  
J. N. A.

**Absorption apparatus for micro-determination of volatile substances.** V. Micro-determination of bromide with application to blood and urine and observations on the normal human subject. E. J. CONWAY and J. C. FLOOD (Biochem. J., 1936, 30, 716—727).—For the micro-determination of Br' the Br' is oxidised by acid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to free Br, which is absorbed in KI and the liberated I, when Br is >8×10<sup>-5</sup> g., determined by titration with 0.05N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> or with smaller amounts colorimetrically after addition of starch. When the [Cl<sup>-</sup>] is ≥1% NaCl, the determination is independent of Cl<sup>-</sup>. I<sup>-</sup>, however, must be completely removed by a preliminary treatment, which can be made the basis of an I<sup>-</sup> determination. The method is applied to determination of Br in 1 ml. of blood or urine and, after administration of Br, in 0.2 ml. of finger-blood. [Br<sup>-</sup>] in normal blood was 227—572×10<sup>-6</sup> g. per 100 ml.; the mean vals. for blood and urine were 372 and 656×10<sup>-6</sup> g. per 100 ml., respectively, and the average urinary Br:Cl ratio (in milliequiv.) was 1:2150.  
P. W. C.

**Phosphatæmia induced by daily ingestion of disodium phosphate.** L. CORBIAU (Compt. rend. Soc. Biol., 1936, 122, 474—475).—Hyperphosphatæmia cannot be maintained by this means.  
H. G. R.

**Electrolyte balance and cellular and refractometric changes in blood during pneumothorax and after phrenectomy.** A. RISI (Z. Biol., 1936, 97, 173—179).—Hypotensive pneumothorax and unilateral phrenectomy produce a slight shifting of the anion-cation balance towards the basic side; a corrective mechanism is, however, evident. The protein balance and (consequently) *n* rise and, whilst erythrocytes vary only slightly, a marked leucocytosis occurs. Correlations between these and changes in the lung ventilation and capacity are discussed (cf. A., 1935, 385).  
F. O. H.

**Presence of hypertensive substances in dog's blood during permanent compression of the renal arteries.** E. DICKER (Compt. rend. Soc. Biol., 1936, 122, 476—477).  
H. G. R.

**Are the vasopressor substances found in the serum of nephritis also present in normal serum?** P. GOVAERTS and E. DICKER (Compt. rend. Soc. Biol., 1936, 122, 807—809).—Highly conc. EtOH extracts of normal sera had no hypertensive action on the chloralised dog.  
A. L.

**Hæmolytic power of extracts of various organs.** R. D. DE LA RIVIÈRE, N. KOSOVITCH,



and S. ISHII (Compt. rend. Soc. Biol., 1936, **122**, 555—558).—Hæmolysing extracts from stomach, pancreas, and duodenum are completely inactivated by EtOH and slightly inactivated by heating at 56° for 30 min.

H. G. R.

**Influence of alexin on the flocculating power of serum.** C. MOREL (Compt. rend. Soc. Biol., 1936, **122**, 254—256).—The protective action of serum towards hydrophobic sols is greatest at 37° and  $\propto$  the content of alexin.

F. O. H.

**Multiplicity of flocculation zones and gelation of serum.** I. KOPACZEWSKA and W. KOPACZEWSKI (Compt. rend., 1936, **202**, 1716—1718).—Addition of HCl (to 6*N*) and of NaOH (to 8*N*) to normal human serum produces 5 zones of flocculation interspaced by 5 zones of gelation.

F. O. H.

**Venom of *Lachesis (Bothrops)* snakes. III. Separation of coagulatory principle from bothropotoxin and other constituents.** D. VON KLOBU-SITZKY and P. KÖNIG (Arch. exp. Path. Pharm., 1936, **181**, 387—398; cf. this vol., 622).—Fractionation of the venom by  $(\text{NH}_4)_2\text{SO}_4$  pptn. of the globulin fraction by Pb acetate, electrodialysis, adsorption, etc. yields the blood-coagulating principle (the properties of which indicate it to be a coagulase) practically free from bothropotoxin.

F. O. H.

**Precipitation reaction [antisera]. Multiple zones.** G. L. TAYLOR and M. E. ADAIR (J. Hyg., 1935, **35**, 169—173).—An antiserum containing antibodies for two unrelated antigens, cryst. ovalbumin and cryst. horse serum-albumin, when titrated with mixtures of the antigens could produce a single or two zones of optimal particulation according to the concn. of the components of the antigenic mixture. A single zone does not necessarily indicate a single antigen-antibody mixture but multiple zones imply the presence of  $\geq$  one system.

CH. ABS. (p)

**Increase of globulin in diphtheria antitoxins, shown by the precipitation reaction.** G. L. TAYLOR (J. Hyg., 1935, **35**, 174—179).—By titration against horse serum the antisera fall into three classes according to the antibodies responsible for the main or earliest particulating zone, i.e., antibodies against globulin, albumin, or both. To determine the protein fraction in a horse serum it is necessary to use an antiserum containing a main-zone antibody acting with that protein only.

CH. ABS. (p)

**Concentrated anti-plague serum.** J. H. H. PIRIE and E. GRASSET (Brit. J. Exp. Path., 1935, **16**, 126—128).—The method of prep. is based on fractional pptn. by  $\text{Na}_2\text{SO}_4$ .

CH. ABS. (p)

**Antibodies with multiple affinities.** K. MEYER (Ann. Inst. Pasteur, 1936, **56**, 684—699).—The union of antibody with antigen is more stable (to heat at 60°) when it is effected through two affinities. This can be explained by the assumption of two different fixative groups, in the case of antibody *F* to *B. dysenteriae* (Shiga).

P. G. M.

**Antibodies compared with carbohydrates. III. Experiments with a carbohydrate preparation prepared by degradation of gum-arabic**

with respect to nitrogen, according to the method of Sevag, and with glycogen. P. UHLENHUTH and E. REMY (Z. Immunitats., 1935, **85**, 328—336).—The carbohydrate, the C, H, and O contents of which are approx. the same as those of gum-arabic, but the N content only half, produces antibodies only in isolated cases in rabbits, and is non-anaphylactogenic. Continued removal of N weakens the antigenic effect still more; glycogen is without effect. The antigenic effect of gum-arabic hence depends on the sp. protein.

R. N. C.

**Polysaccharide of the typhus bacillus. I. Toxic and immunising action. II. Attenuation by means of formaldehyde, benzaldehyde, and salicylaldehyde.** A. SPANEDDA (Boll. Soc. ital. Biol. sperim., 1936, **11**, 21—22, 22—24).—I. An agar culture of the bacillus was dialysed and the polysaccharide pptd. by means of  $\text{COMe}_2$  and dissolved in a little sterile  $\text{H}_2\text{O}$ . Injected into rabbits, this solution is toxic. It produces agglutinin (two types) and bacteriolysin and has a notable immunising action.

II. By treatment with aldehydes the toxic but not the immunising action is diminished. A solution containing 0.4% of PhCHO is the most efficient.

E. P.

**Analysis of the antigens of *Vibrio cholerae*.** R. T. SCHOLTENS (Ann. Inst. Pasteur, 1936, **56**, 710—716).—The antibody *B* and its antigen are concerned in the fixation of complement. Strains which have two antigens *A'* and *B'* absorb agglutinin *A* less readily than those which have only antigen *A'*.

P. G. M.

**Hæmatology of the fowl. (A) Normal chick and normal adult blood. (B) Hæmatology of chicks with pullorum infection: adult carriers of pullorum disease.** J. W. KELLY and R. S. DEARSTYNE (North Carolina Agric. Exp. Sta. Tech. Bull., 1935, No. 50, 69 pp.).

A. G. P.

**Bioelectric and oxidation-reduction potentials of the amphibian egg.** V. A. DOREMAN (Bull. Biol. Med. Exp. U.R.S.S., 1936, **1**, 135—136).—A p.d. of about 10 mv. exists between the poles of the unfertilised frog's egg (animal pole positive,  $p_H$  6.18; vegetative pole negative,  $p_H$  5.64). The bioelectric and redox potentials are distributed in different ways. Regular correlation exists between distribution of  $p_H$  and aerobic redox potentials.

W. McC.

**Composition of healthy and rachitic bone.** J. MAREK, O. WELLMANN, and L. URBANYI (Z. physiol. Chem., 1936, **240**, 208—214; cf. A., 1935, 1004).—In young pigs the composition of the various parts of the bones and the Ca : P and Ca : Mg ratios are altered by the disease. The results confirm the view that the mineral matter of bone consists chiefly of a mixture of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$ .

W. McC.

**Orientation of crystallites in tooth-enamel.** W. I. SCHMIDT (Naturwiss., 1936, **24**, 361; cf. Bale and Hodge, this vol., 623).—The orientation has been investigated by the polarisation-microscopical method. The val. of the data obtained by this method in confirming the results of X-ray analysis is discussed.

A. J. M.

**Crystal orientation in tooth-enamel.** H. MÖLLER and G. TROMEL (*Naturwiss.*, 1936, 24, 377—378).—Repetition of earlier work (A., 1933, 296) on the examination of tooth-enamel by X-ray analysis shows, in agreement with Bale and Hodge (this vol., 623), that no new type of crystal is present in the surface of the enamel. A. J. M.

**Bromine content of the pituitary.** G. MORUZZI and P. GUARESCHI (*Boll. Soc. ital. Biol. sperim.*, 1936, 11, 28—29).—The [Br] in the pituitary and in the blood is the same. The larger amounts of non-diffusible Br in the pituitary and the absence of inorg. Br suggest that the pituitary is not an accumulating but an elaborating organ for Br. The Br content of the human pituitary varies with age and sex. With oxen the amount in the middle-posterior is much > that in the anterior lobe. E. P.

**Biochemistry of bromine.** I. A. H. NEUFELD (*Canad. J. Res.*, 1936, 14, B, 160—194).—Methods of determining Br in plant and animal tissues are critically examined. A modified Francis-Harvey incineration (A., 1933, 1317) followed by oxidation according to Yates (A., 1934, 202) gives satisfactory results. The distribution of Br in marine and land animals and plants is examined. Marine algae always contain Br, but there is no apparent relation between their Br and I contents. Land plants contain much less Br. No relation can be found between the distribution of Br and I in mammalian tissues, and no functional significance can as yet be ascribed to Br. The Br content of mammalian blood and thyroid is > that of other tissues. E. A. H. R.

**Change in the solubility of sodium compounds during the autolysis of muscle tissue.** I. A. SMORODINCEV and J. N. LIASKOVSKAJA (*Bull. Soc. Chim. biol.*, 1936, 18, 741—746).—The ratio Na/Ca in the aq. extract of fresh cow muscle is 20—28; after 24—72 hr. autolysis, however, the val. falls to 10—13. A. L.

**Titanium content of mammals.** L. C. MAILLARD and J. ETTORI (*Compt. rend.*, 1936, 202, 1459—1461).—Many analyses (accuracy  $10^{-6}$  g.; cf. this vol., 652) show that Ti is distributed irregularly. J. L. D.

**Distribution of titanium in the tissues.** L. C. MAILLARD and J. ETTORI (*Compt. rend.*, 1936, 202, 1621—1622).—The Ti content of various tissues ranges from 1.5 (kidney) to  $11.0 \times 10^{-6}\%$  (spleen). J. L. D.

**X-Ray structure of animal and plant polysaccharides.** I. F. MAY and L. GRAF (*Z. Biol.*, 1936, 97, 167—172).—Animal polysaccharides, pretreated in various ways, give the same amorphous X-ray pattern whether they are glycogens or galactogens. Plant starches, however, have a cryst. structure, the patterns varying with differences in constitutional hexoses. O. H.

**Chemical constitution of the fat in human subcutaneous connective tissue.** VII. Reichert-Meissl value. G. STOLFI (*Boll. Soc. ital. Biol. sperim.*, 1936, 11, 12—13).—Vals. for the fat of adipose tissue in adults are < in infants. The change occurs in early childhood. In benign and malign

neoplasm and in cancerous cachexy the results of Wacker (A., 1912, ii, 1079) have been confirmed. E. P.

**Ratio of  $\alpha$ - and  $\beta$ -glycerophosphoric acids in human brain-lecithin.** C. ANTONIANI (*Arch. Sci. biol.*, 18, 420—425; *Chem. Zentr.*, 1935, ii, 1902).—The  $\beta$ -acid forms 66—80% of the total. H. N. R.

**Influence of vitamin-D and certain carcinogenic hydrocarbons on the hydrophilic coefficient of lipins.**—See this vol., 935.

**Variations in the nitrogen fractions and water content of rabbit muscle at different stages of growth.** I. Water, residual nitrogen, and pre-formed amino-nitrogen. II. Total and amino-nitrogen in hydrolysed muscle. E. ASMOLOV (*Bull. Biol. Med. Exp. U.R.S.S.*, 1936, 1, 119—120, 121—122).—I. As age increases the  $H_2O$  content of the muscle decreases, and the residual N and  $NH_3$ -N contents increase. The ratio residual N: $NH_3$ -N decreases from 52 to 34. Changes are possibly due to production of polypeptides and cyclic compounds.

II. As age increases total N and  $NH_3$ -N of the hydrolysates increase, whilst the ratios total N:residual N and  $NH_3$ -N:total N remain practically const. W. McC.

**[Constituents of] octopus muscle. Isolation of adenylypyrophosphoric acid and arginine-phosphoric acid and their behaviour.** K. LOHMANN (*Biochem. Z.*, 1936, 286, 28—44).—The isolation of argininephosphoric acid (I) and adenylypyrophosphoric acid (II) from octopus muscle is described. (II) is converted into adenylic acid (III) by the muscle when  $Mg^{++}$  is present and into adenosinediphosphoric acid (IV) when it is absent and (I) is enzymically hydrolysed only when (II) or (IV) is present. The muscle contains zymohexase, converts  $\beta$ - and  $\gamma$ -phosphoglyceric acid and phosphopyruvic acid (V) into  $AcCO_2H$  and  $H_3PO_4$  only if  $Mg^{++}$  and the (III) system are present, and converts  $AcCHO$  into lactic acid (VI) only if glutathione is present. Synthesis of (I) in the muscle from arginine and (V) gives poor yields probably because (VI) production is very small. Deamination of (III) occurs to a moderate extent only in the muscle. W. McC.

**Amino-acids of submaxillary mucoprotein.** C. OLDFELDT (*Z. physiol. Chem.*, 1936, 240, 261—264).—In submaxillary mucoprotein the N distribution is similar to those found in the most acidic proteins. W. McC.

**Biochemistry of the proteins of brain.** V. Alanine content of the proteins in vertebrates. M. K. KARJAGINA (*Bull. Biol. Med. Exp. U.R.S.S.*, 1936, 1, 117—118).—The alanine content varies from 5.05 to 6.7%, vals. being high in birds, frogs, and fish. W. McC.

**Arginine content of proteins of the brain in vertebrates.** A. M. BUDANOVA (*Bull. Biol. Med. Exp. U.R.S.S.*, 1936, 1, 115—116).—The arginine (I) content of the proteins varies from 7.4 (hen) to 10.5% (sheep). In the same animal there is no relation between age and (I) content of brain-proteins. W. McC.



**Determination of glucosamine in proteins.** I. NILSSON (Biochem. Z., 1936, 285, 386—389).—The method of Elson and Morgan (A., 1934, 175) for colorimetric determination of glucosamine (I) and chondrosamine in proteins is shown to be applicable with very slight modification to determination of (I) added to caseinogen and to blood-serum (man, pig, calf). P. W. C.

**Composition of snake venom and comparative action of the globulins and albumins.** F. R. MERCHANTE (Compt. rend. Soc. Biol., 1936, 122, 487—489).—The protein in the venom is chiefly albumin. Analytical data and physiological reactions of the various fractions are given. H. G. R.

**Mucoproteins.** C. OLDFELDT (Z. physiol. Chem., 1936, 240, 249—260; cf. Roche, this vol., 359).—Data of isoelectric points, acid- and base-binding capacities, and titration curves are given. Sub-maxillary mucoprotein has low acid- and high alkali-binding power. Preps. from umbilical cord, cornea, and vitreous humour are also described.

W. McC.

**Properties of a new vitellin from spiders.** M. PARAT and C. JACQUIERT (Compt. rend. Soc. Biol., 1936, 122, 626—629). H. G. R.

**Modifications of the physico-chemical properties of protein solutions with age.** W. DUCE (Boll. Soc. ital. Biol. sperim., 1935, 10, 977—978).—The keeping of aq. solutions of purified caseinogen and of serum- and ov-albumin at reactions near their isoelectric point is accompanied by variations in dynamic and static  $\gamma$  and in  $\kappa$ . F. O. H.

**Titration curve of feather-keratin.** J. B. SPEAKMAN and F. TOWNEND (Trans. Faraday Soc., 1936, 32, 897—902).—Purified seagulls' feather-keratin combines with acids through the basic side-chains of arginine, lysine, and histidine, which probably do not take part in the formation of lateral peptide linkings. The isoelectric range is  $p_{H}$  4.3—6.3, suggesting equivalence between the dicarboxylic acids and the basic  $NH_2$ -acids and amide-N. Determinations of amide-N and dicarboxylic acid content are in agreement. L. J. J.

**Double refraction of chitin.** E. S. CASTLE (J. Gen. Physiol., 1936, 19, 797—805).—Double refraction of crayfish hair is positive with respect to the axis and caused by the arrangement of chitin particles parallel to the axis. H. G. R.

**Adsorption of glucose by albumin.**—See this vol., 933.

**Relation between low-temperature research and colloid chemistry.**—See this vol., 934.

**Stability of lyophilic bio-colloids.**—See this vol., 935.

**Kinetics of muscle-haemoglobin.** G. A. MILLIKAN (Proc. Roy. Soc., 1936, B, 120, 366—388).—The rates of combination of horse heart muscle-haemoglobin with  $O_2$  and CO are several times as fast as the corresponding rates for blood-haemoglobin. The rate of dissociation of the oxygenated pigment is  $<$  that of the corresponding blood compound, but that of the CO complex is much faster. F. A. A.

**Cytochromes. II. Haematinic pigments of *Actinia*: actiniohaematin.** J. ROCHE (Bull. Soc. Chim. biol., 1936, 18, 825—840).—The actiniohaematin of MacMunn is a mixture of cytochrome-*b*, cytochrome-*a* (traces), and a protohaematin which is probably the "free intracellular haematin" of Keilin. Cytochrome-*b* is derived from the same porphyrin as -*c* but differs probably in the N complex, to which the prosthetic group is linked to form a parahematin, and also in the N base on a side-chain of the porphyrin nucleus. H. G. R.

**Constituents of visual purple and its relation to the visual cells.** M. L. VERRIER and R. PANNIER (Compt. rend., 1936, 202, 1614—1616).—Vitamin-A, xanthophyll, albumins, and pigment are extracted by Na tauro- or glyco-cholate. Extracts of the retinae of frogs exposed to light contain the same constituents, although they are yellow as compared with pale rose-coloured controls. J. L. D.

**Pigments of the retina. I. Bull frog.** G. WALD (J. Gen. Physiol., 1936, 19, 781—795).—The interrelations of visual purple, retinene, and vitamin-A (I) and the concn. and distribution of xanthophyll, (I), and flavin have been determined. H. G. R.

**Preparation of protein-free milk-serum in the cold.** W. LEITHE and E. MÜLLER (Z. Unters. Lebensm., 1936, 71, 319—322).—To remove traces of sol. protein, the  $CuSO_4$ - or  $Pb(OAc)_2$ -treated milk is shaken with kaolin and centrifuged.

E. C. S.

**Effect of ingested cottonseed meal on distribution of the constituent fatty acids of goat's milk.** R. W. RIEMENSCHNEIDER and N. R. ELLIS (J. Biol. Chem., 1936, 114, 441—447; cf. A., 1936, 501).—Inclusion of cottonseed meal in the diet of goats increased the proportions of hexoic, lauric, myristic, and stearic acids in the butter-fat at the expense of palmitic and oleic acids. H. D.

**Micro-determination of fats in human milk.** J. M. CLAVERA and F. MORENO MARTÍN (Anal. Fis. Quím., 1935, 33, 815—819).—0.5 or 1 c.c. of milk is treated with HCl and extracted with  $CHCl_3$ , or treated with NaOH and extracted with  $Et_2O$ . The vals. obtained are comparable with those given by macro-methods. F. R. G.

**Precursors in cows' blood of milk fat and other milk constituents.** W. R. GRAHAM, jun., T. S. G. JONES, and H. D. KAY (Proc. Roy. Soc., 1936, B, 120, 330—346).—The fat of cows' milk is derived mainly from the non-phospholipin fatty acids of blood, and, possibly, from fatty acids of cholesterol esters. The P compounds of milk are derived from the blood-inorg. P. Sugar is absorbed from the blood during its passage through the udder. A cow yielding 4 gals. of milk per day may have a blood circulation of about  $1\frac{1}{4}$  gals. per min. through the active mammary gland. F. A. A.

**Differential reactions of human and cow's milk.** M. POLONOVSKI and F. MORENO MARTÍN (Anal. Fis. Quím., 1935, 33, 457—462).—Umikoff's test for human milk is due to reaction between  $NH_3$  and lactose. Cow's milk does not give the coloration owing to its higher buffering power. F. R. G.

**Effect of udder irrigation and milking interval on milk secretion.** E. R. GARRISON and C. W. TURNER (Missouri Agric. Exp. Sta. Res. Bull., 1936, No. 234, 39 pp.).—Irrigation lowers the yield and lactose (I) content of milk and increases the  $p_H$ ,  $Cl'$ , fat, protein, catalase, and leucocyte contents. Fat secretion is inversely  $\propto$  milk yield and is practically independent of other milk constituents. Irrigation with aq.  $CaCl_2$  is more detrimental to milk secretion than is that with aq.  $NaCl$  of the same % concn. Aq. (I) is more injurious than  $H_2O$ . Irrigation with paraffin oil causes as much disturbance as with  $H_2O$  and recovery is slower. Introduction of  $O_2$  into the udder produces results similar to those of liquids. Suspended milking causes smaller changes. Disturbances are attributed to increased permeability of secretory cells to blood constituents caused by direct pressure. The osmotic balance between blood and milk is maintained under these conditions by increased synthesis of (I). A. G. P.

**Effect of thyroxine on milk secretion and on the blood- and milk-phosphatase of the lactating cow.** S. J. FOLLEY and P. WHITE (Proc. Roy. Soc., 1936, B, 120, 346—365).—Daily subcutaneous injections of thyroxine (approx. 0.02 mg. per kg.) into cows in declining lactation cause increases in milk secretion, and in fat and non-fatty solids of milk. An increase in serum-phosphatase and a sharp decline in milk-phosphatase also result. Milk-phosphatase is probably not derived directly from serum-phosphatase. F. A. A.

**Influence of insulin on the lymph-sugar of the silkworm (*Bombyx mori*).** K. WENIG and J. JOACHIM (Biochem. Z., 1936, 30, 98—100).—The total reduction of silkworm lymph amounts to  $106 \pm 5.3$  mg. per 100 ml. (in glucose equiv.) and that due to fermentable sugar (I) to  $22.5 \pm 5.5$  mg. per 100 ml. After injection of insulin (0.1 clinical unit) the (I) completely disappeared in 1 hr., but the total reduction remained unchanged, some non-fermentable reducing substance replacing (I). P. W. C.

**Coloration by mucicarmine and composition of mucin.** M. CHAMBON, P. CROIZAT, P. MALLET-GUY, and A. CHAMBON (Compt. rend. Soc. Biol., 1936, 122, 305—307).—The carminophilic properties of mucin increase with increase in prosthetic group content. The isoelectric point of submaxillary and gastric mucin is  $p_H$  2.4—2.7 and 4, respectively. Histological characteristics are described. F. O. H.

**Protein content of human parotid saliva.** R. G. BRAMKAMP (J. Biol. Chem., 1936, 114, 369—371).—Human parotid saliva, secreted at rates of 0.5 and 2.0 c.c. per min., contained 11 and 58 mg. of protein per 100 c.c., respectively. The protein was chiefly albumin. H. D.

**Excretion of agglutinogens [in the saliva].** G. BRUYNOGHE (Compt. rend. Soc. Biol., 1936, 122, 472—474). H. G. R.

**Composition of biliary mucus.** M. CHAMBON, P. MALLET-GUY, P. CROIZAT, and A. CHAMBON (Compt. rend. Soc. Biol., 1936, 122, 303—305).—Human biliary mucus contains mucin 0.02—0.05, mucoids

0.005—0.15, globulin+nucleoprotein 0.011—0.048, albumin 0.042—0.102, and pseudoglobulin up to 0.103%, the variations occurring according to the site of secretion. F. O. H.

**Biochemical properties of bile-pigments. VI. Insolubility of calcium, barium, and strontium salts of bilirubin and biliverdin. VII. Anticoagulating power *in vitro* of bilirubin, biliverdin, bile, and biliary salts.** A. CLEMENTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 899—900, 900—902; cf. A., 1934, 94).—VI. The loss of agglutinating activity of bilirubin (I) and biliverdin (II) on addition of  $Ca^{++}$ ,  $Ba^{++}$ , or  $Sr^{++}$  is related to the formation of insol. salts on addition of these ions to Na salts of (I) and (II) in aq.  $NaOH$  or  $NH_3$ .

VII. The rate of coagulation of blood *in vitro* is diminished by (I), (II), bile, or Na tauro- or glycocholate. The action is most marked with (I) and (II) and is inhibited by addition of  $Ca^{++}$ . F. O. H.

**Constitution of bile acids. LIV, LV.**—See this vol., 983.

**Detection and approximate determination of acetone in urine with *p*-nitrophenylhydrazine.** W. DEHIO (Z. anal. Chem., 1936, 104, 417—422).—Urine (2 c.c.) is warmed to  $53^\circ$  in a micro-beaker, covered with a glass bearing a drop of *p*-nitrophenylhydrazine in  $AcOH$ . In presence of  $> 0.005\%$  of  $COMe_2$ , a cryst. deposit is obtained within 10 min., the amount and rate of formation being approx.  $\propto [COMe_2]$ . J. S. A.

**Colour reaction for creatinine.** S. R. BENEDICT and J. A. BEHRE (J. Biol. Chem., 1936, 114, 515—532).—Creatinine (I) is determined in dil. urine by addition of 3 : 5-dinitrobenzoic acid in  $EtOH$  and of 6%  $NaOH$ , and colorimetric comparison with a standard. Creatine and glucose do not react and ketones only in concns.  $>$  those found usually in diabetics. The method gives rather lower vals. than the picrate method. With tungstomolybdic acid blood filtrates, the colour produced is different, and it is concluded that the chromogenic substance in blood is not (I). H. D.

**Presence of histidine in human urine.** R. KAPPELLER-ADLER (Biochem. Z., 1936, 285, 123—124).—The paper by Foldes (this vol., 362) is discussed. P. W. C.

**Bile-pigments. II. Test for bilirubin in urine : detection in normal urine.** H. N. NAUMANN (Biochem. J., 1936, 30, 762—764; cf. this vol., 625).—The pigments are adsorbed on talc, and this is treated with a drop of Fouché's reagent or 10%  $HNO_3$ , when the production of blue bilicyanin indicates the presence of bilirubin (I). Normal urine contains approx. 0.3 mg. of (I) per 100 c.c. The limits of detectability of pure (I) dissolved in dil.  $NaOH$ , dil.  $EtOH$ , and urine free from preformed (I) are 0.8, 0.6, and 0.9 p.p.m., respectively. J. N. A.

**Bile-pigments. III. Determination of urobilin and urobilinogen in urine and faeces.** H. N. NAUMANN (Biochem. J., 1936, 30, 1021—1025; cf. preceding abstract).—The optimal conditions for the colorimetric determination of urobilin and urobilinogen



in urine and faeces by the  $p$ -NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO method are determined and shown to depend chiefly on the mode of reduction of urobilin by Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>.

H. D.

**Reticulocyte-stimulating principle for the pigeon in normal human urine.** G. E. WAKERLIN and H. D. BRUNER (Arch. Int. Med., 1936, 57, 1032—1038).—Injection of normal urine before or after heating (100° for 2 hr.) in the absence of air produces an effect similar to that of the erythropoietic substance of liver.

E. D. Y.

**Amibiarsen in the treatment of chronic intestinal amebiasis.** R. N. CHOPRA, B. SEN, and G. SEN (Indian Med. Gaz., 1935, 70, 324—328).—Successful use of amibiarsen (As compound similar to carbosone Lilly; 4-carbamylphenylarsinic acid) is described.

CH. ABS. (p)

**Experimental anæmias and their suitability for the assay of anti-anæmic preparations. II. Collargol-saponin anæmia in rats.** P. GOTTELEBE and W. SKIBBE (Arch. exp. Path. Pharm., 1936, 181, 317—324).—Intravenous or subcutaneous injection of saponin (I) into rats produces a condition simulating pernicious anæmia for 10—15 days, during which time parenteral administration of active liver preps. produces typical increases in erythrocyte and reticulocyte counts. Injection of (I)+collargol produces a more prolonged anæmia suitable for both qual. and quant. tests. The origin of the anæmias is discussed.

F. O. H.

**Dissociation curves of blood-oxygen in anæmia and erythræmia.** N. KORJUEV and BELUSOV (Bull. Biol. Méd. Exp. U.R.S.S., 1936, 1, 139—140).—The positions of the curves are altered in opposite directions in these diseases. Compared with normal blood, anæmic blood appears to have a relatively better, erythræmic blood a relatively worse, respiratory function.

W. McC.

**Glutathione in blood and the organs in experimental anæmia.** G. L. BESOZZI and R. ZANINI (Arch. Sci. biol., 18, 497—505; Chem. Zentr., 1935, ii, 1904).—Glutathione (I) is decreased in the organs and whole blood, but increased in the erythrocytes, of rabbits made anæmic by NHPh·NH<sub>2</sub> or bleeding. All vals. become normal when the anæmia disappears. The increase in (I) in erythrocytes is probably a compensatory reaction of the organism against the loss of oxidative power.

R. N. C.

**Copper and iron in the blood of anæmic infants.** E. LESNÉ, P. ZIZINE, and S. B. BRISKAS (Compt. rend. Soc. Biol., 1936, 122, 532—534).—Fe is decreased and Cu increased.

H. G. R.

**Phthalein test of kidney function in anæmia.** E. M. CHAPMAN (New England J. Med., 1935, 213, 166—167).—Anæmia alone does not affect the excretion of phenolsulphonaphthalein by kidneys.

CH. ABS. (p)

**Dietary production and prevention of anæmia in larval amblystoma.** E. M. PATCH (Science, 1936, 83, 560—561).

L. S. T.

**Influence of cations on fermentation by tumour cells. VI. Calcium and magnesium. II.** A. LASNITZKI (Biochem. Z., 1936, 285, 101—114; cf.

this vol., 243).—K and Ca (1.8× and 3.6×10<sup>-3</sup> mol. of CaCl<sub>2</sub> per litre) acting directly on tumour cells (Jensen sarcoma and Flexner-Jobling carcinoma) increase fermentation (Ca both in presence and absence of K). When, however, K or Ca is added after the cells have undergone a fermentation period in K- or Ca-free Ringer's solution, then K still accelerates fermentation, whereas Ca is inactive. The action of Mg resembles that of Ca, but is smaller. The mechanism is discussed.

P. W. C.

**Chemical composition of the nucleic acid of malignant tissue.** G. KLEIN and J. BECK (Z. Krebsforsch., 1935, 42, 163—177; Chem. Zentr., 1935, ii, 2075).—The acid is identical with thymus-nucleic acid.

R. N. C.

**Demonstration of prolan in tumours.** M. BAUDLER (Arch. Gynakol., 1935, 159, 101—125; Chem. Zentr., 1935, ii, 2080).

R. N. C.

**Tumour tissue. II. Effect of protein on the swelling of normal and tumour cells of mice *in vitro*.** M. J. SHEAR (Amer. J. Cancer, 1935, 23, 771—783).—The swelling of normal and tumour cells in salt solutions is independent of the salt concn. Presence of protein in the salt solution retards and may inhibit swelling. Cells swollen in salt solution shrink when transferred to a protein solution.

CH. ABS. (p)

**Tumour metabolism in the presence of anti-carcinogenic substances.** I. BERENBLUM, L. P. KENDAL, and J. W. ORR (Biochem. J., 1936, 30, 709—715).—(CH<sub>2</sub>Cl·CH<sub>2</sub>)<sub>2</sub>S (mustard gas), (CH<sub>2</sub>Cl·CH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>, and cantharidin, which inhibit the induction *in vivo* of tar tumours, reduce the glycolysis of minced Jensen sarcoma tissue *in vitro* more than its respiration. (CH<sub>2</sub>Cl·CH<sub>2</sub>)SO, thiodiglycol and croton oil, which have no inhibiting effect on carcinogenesis, do not reduce glycolysis more than respiration. Ethylenebis-β-chloroethyl sulphide, which inhibits the induction of tumours, has no selective action on glycolysis.

P. W. C.

**Immunising characteristics of lipin extracts in cancer.** R. ZDRAZIL (Compt. rend. Soc. Biol., 1936, 122, 417—418).—The "liver-antigen" has an immunising action against Ehrlich's cancer.

H. G. R.

**Fixation of complement in cancer.** R. ZDRAZIL (Compt. rend. Soc. Biol., 1936, 122, 418—420).—The prep. of the "bile-antigen" and the flocculation reactions with cancerous serum are described.

H. G. R.

**Action of fibrin on cancerous serum.** J. KABELIK (Compt. rend. Soc. Biol., 1936, 122, 421—422).—The reaction of Fuchs is not sp. for cancer, but is observed to a smaller extent in syphilis and tuberculosis.

H. G. R.

**Carcinogenic effect of a virus on tarred skin.** P. ROUS and J. G. KIDD (Science, 1936, 83, 468—469).

L. S. T.

**Melanogen and melanin.** H. K. BARRENSCHEEN and H. PRINZ (Biochem. Z., 1936, 285, 130—149).—Et<sub>2</sub>O-sol. and -insol. melanogens were isolated from the urines of 4 cases of melanotic sarcoma without using heavy-metal salts. The Et<sub>2</sub>O-sol. compound

was N- and S-free, acidic, was methylated with  $\text{CH}_2\text{N}_2$ , and did not appear to be a pyrocatechol, but was possibly a quinol derivative. The  $\text{H}_2\text{O}$ -insol. melanogen was not quinonoid, did not contain a free CHO group, gave a N:C ratio of 1.428, and had a small S content (entirely as ethereal sulphate). Red and brown intermediate substances were obtained by acid treatment of the melanogens and a melanin obtained by tryptic digestion of tumour tissue was compared with the acid melanin of the urinary melanogen.

P. W. C.

**Total thyroidectomy in man.** M. T. SCHNITKER, L. H. VAN RAALTE, and E. C. CUTLER (Arch. Int. Med., 1936, 57, 837—886).—Thyroidectomy after cardiac disease causes a fall in the basal metabolic rate and a rise in serum-cholesterol. Serum-Ca, -P, -K, and -I are more variable. Serum-protein is lowered, but -I shows a temporary rise. Thyroidectomy has a beneficial effect in diabetes mellitus.

E. D. Y.

**Blood in cholera: urine analysis.** V. T. LOH and T. Y. TAL (Chinese Med. J., 1936, 50, 651—664).

H. D.

**Physiological significance of unsaturated fatty acids and the iodine-fixing power of the blood.** G. HOLLAND and K. HINSBERG (Z. ges. exp. Med., 1934, 94, 485—494; Chem. Zentr., 1935, ii, 2229).—

Unsaturated fatty acids (I) in the blood of normal men remain const. under different conditions. The I val. is increased in uncompensated circulation disease;  $\text{O}_2$  respiration is apparently without effect. In compensated circulation disease the I val. is < in uncompensated circulation disease, but > normal. It is also increased in liver disease. (I) fall in pernicious anemia. The I val. is increased again on administration of liver diet.

R. N. C.

**Daily variation in sugar content of blood and urine during treatment of diabetes mellitus.** F. L. ROGERS (Arch. Int. Med., 1936, 57, 1027—1031).—The blood-sugar and urinary sugar often rise in the early morning and fall in the afternoon.

E. D. Y.

**Effect of intravenous injections of sodium "ferriscorbon" on acetonuria in spontaneous diabetes of the dog.** F. ARLOING, A. MOREL, A. JOSSERAND, P. COLLET, and A. BADINAND (Compt. rend. Soc. Biol., 1936, 122, 575—577).—Acetonuria is considerably diminished without affecting the glycosuria (cf. A., 1935, 1526).

H. G. R.

**Infantile dehydration.** G. PAISSEAU, BOEGNER, and C. VAILLE (Bull. Soc. Chim. biol., 1936, 18, 645—648).—Infantile dehydration (diarrhoea) is accompanied by increases in blood-N, in the ratio erythrocyte-Cl'/plasma-Cl', and in the vol. of blood-corpuscles, and by a decrease in alkaline reserve.

A. L.

**Organic oxidation in fever. Oxido-reduction (dehydrogenation) and the oxidising enzymes in fibrous tissue-processes.** A. SPINELLI (Arch. ital. Biol., 89, 103—114; Chem. Zentr., 1935, ii, 2544—2545).—In fever the activity is increased.

H. N. R.

**Pressor substance in the blood in malignant hypertension.** R. S. AITKEN and C. WILSON

(Quart. J. Med., 1935, 4, 179—190).—No evidence of pressor activity was found.

CH. ABS. (p)

**Disadvantages of di-iodotyrosine in the treatment of hyperthyroidism.** W. H. BECKHUIS (Nederl. Tijds. Geneesk., 1935, 79, 3963—3971; Chem. Zentr., 1935, ii, 2537).

R. N. C.

**Blood-cholesterol in leprosy.** V. CHORINE and O. CROUGUE (Compt. rend. Soc. Biol., 1936, 122, 621—624).—Leprosy in rats is accompanied by slight hypocholesterolaemia.

H. G. R.

**Total glutathione of leprosy.** R. O. PRUD'HOME (Compt. rend. Soc. Biol., 1936, 122, 739—741).—The decrease in the amount of reduced glutathione (I) in the organs of rats infected with Stefansky's bacillus is not due to the oxidation of (I), since the total (I) is also < normal.

A. L.

**Lipins of leprous granuloma. I. Histochemistry. II. Chemistry.** I. CIACCIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 929—931, 931—933).—I. The distribution of lipins in tissue elements is described.

II. Data of the distribution of phospholipins, free and combined cholesterol, and total  $\text{COMe}_2$ -sol. and free fatty acids are tabulated.

F. O. H.

**Oxidation-reduction processes (glutathione) in diseases of the liver and endocrine glands.** S. S. KAMENETZKI (Platz. Utschen. Med., 1936, 236—249).—In various diseases, the ratio of reduced to oxidised glutathione in the blood deviates from its normal val.

W. O. K.

**Neutral fat content of the blood in liver disease.** J. J. VAN LEEUWEN (Nederl. Tijdschr. Geneesk., 1935, 79, 3983—3987; Chem. Zentr., 1935, ii, 2538).—Addition of carbohydrate to a fat diet increases liver-fat only when liver disease exists.

R. N. C.

**Significance of lower fatty acids normally present in serum in the Takata reaction.** W. GROS (Munch. med. Woch., 1935, 82, 1151—1152; Chem. Zentr., 1935, ii, 1924).—The influence is negligible.

H. N. R.

**Changes in proteins of blood-sera of monkeys infected with malarial plasmodia.** B. N. GHOSH and J. N. SINTON (Rec. Malaria Survey India, 1935, 5, 173—202).—Disturbance of the serum-protein equilibrium after acute parasitic attack is characterised by a decrease in total protein (I) and albumin (II) and an increase in globulin (III). In quiescent intervals between attacks (I) returns towards normal, but the (III)/(II) ratio is frequently abnormally large. Return to normal vals. is accelerated by quinine, atabrin, plasmoquin, or stovarsol.

CH. ABS. (p)

**Activity of melanin, distilled water, and various indicators in Henry's reaction.** F. TRENSZ (Compt. rend. Soc. Biol., 1936, 122, 666—668).—Only melanin and salts containing Fe (e.g., saccharate) are reactive. Indicators and dyes are practically inert, the flocculate formed in the presence of carmine having the characteristics of a "super-flocculation" in  $\text{H}_2\text{O}$  (cf. A., 1935, 1149).

H. G. R.

**Lipin composition of the guinea-pig placenta.** E. M. BOYD (Canad. J. Res., 1936, 14, B, 155—159).—



The lipin composition of the guinea-pig placenta varies with the duration of pregnancy. Between the 20th and 40th days phospholipin and cholesterol increase to a val. which is maintained until term. Neutral fat increases steadily throughout, but cholesterol esters remain unchanged. These changes indicate an alteration of placental lipin metabolism as pregnancy advances, and an increase in physiological activity as early as the 20th day. E. A. H. R.

**Cholesterol content of serum and its cholesterololytic power *in vitro* in skin disease.** H. HRUSZEK (Klin. Woch., 1935, 14, 779—781).—Sera show positive, neutral, or negative cholesterololytic vals. according to the amount of cholesterol (I) dissolved after addition of excess (I). The cholesterololytic val. has no diagnostic importance for skin disease or psoriasis, and does not affect the Wassermann reaction. R. N. C.

**Report of chemistry section.** B. C. ASTON (New Zealand Dept. Agric. Ann. Rept., 1933—1934, 54—58; cf. A., 1935, 1150).—On certain pastures lambs developed a bone disorder resembling rickets, the foreleg bones having low ash, Ca, and P contents and low (50% normal) ash/org. matter ratio. The solubility of limonite in dil. acids and its efficiency in preventing bush sickness were greatly decreased by heating at 500—600°. Air-dried friable limonite gave best results. CH. ABS. (p)

**Variations of serum-protein fractions during an attack of rinderpest.** M. H. FRENCH (Ann. Rept. Dept. Vet. Sci. Tanganyika Territory [1933], 1934, 42—48).—Changes in the % total N, total protein, total globulin, pseudoglobulin, euglobulin (I), and albumin occurring, prior to death of an infected ox, following inoculation, and following vaccination are recorded. The antibody is associated with the (I) fraction. Feeding on poor pasture caused changes in the protein-N fractions, but non-protein-N was unaffected by the plane of nutrition. CH. ABS. (p)

**Pathogenesis of silicotic tissue alterations.** II. Morphological investigation of the retention of quartz-dust in silicotic tissue. III. Nature of asbestosis particles. G. F. KOPPEHÖFER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 18—37, 38—62; Chem. Zentr., 1935, ii, 1746).—II. The quartz particles undergo partial change into colloidal  $\text{SiO}_2$ , which is the injurious factor.

III. The mechanism of gelatinisation of the asbestos particles is described and factors influencing the process are discussed. H. N. R.

**Non-tropical sprue.** A. M. SNELL (Arch. Int. Med., 1936, 57, 837—856).—Cases show symptoms of gastric anacidity, fatty stools, and lowered serum-Ca, -P, and -protein, sometimes with anæmia and tetany, but respond to liver therapy. E. D. Y.

**Effect of therapy on the behaviour of ether-soluble anti-thyroid protective substances of the blood in thyroid disease.** K. FELLINGER and A. SCHLESINGER (Klin. Woch., 1935, 15, 685—686).—The protective substances are depressed in hyper- and increased in hypo-thyrosis; therapy tends to restore them to normal. R. N. C.

**Experimental hyperglycæmia in rabbits with tubercle (Yersin type) infection.** E. S. PANAYOTOPoulos (Compt. rend. Soc. Biol., 1936, 122, 275—276).—The course of infection (3—4 weeks with fatal termination) is accompanied by an increased hyperglycæmia following ingestion of glucose. F. O. H.

**Tubercle allergy and blood-cholesterol.** V. SPOUJITCH and D. BORITCH (Compt. rend. Soc. Biol., 1936, 122, 340—342).—A definite relationship between allergic reaction and blood-cholesterol could not be established in tubercular patients. F. O. H.

**Biochemistry of pulmonary tuberculosis during aurotherapy.** I. V. BALANESCO, S. OERIU, and V. VARTIC (Bull. Soc. Chim. biol., 1936, 18, 687—702).—In pulmonary tuberculosis the analytical vals. for the blood constituents are closely related to the gravity of the disease. In severe cases there is an increase in sedimentation rate,  $\text{PO}_4'''$ , and creatinine, and a decrease in cholesterol,  $\text{Cl}'$ , total N, hæmoglobin,  $p_H$  val., and  $\text{NH}_2$ - and uric acids. After aurotherapy when the condition of the disease ameliorates, the above vals. approach normal. A. L.

**Sulphur and glutathione content of the blood and tissues in experimental uræmia.** A. A. CHRISTOMANOS (Z. ges. exp. Med., 1934, 94, 504—506; Chem. Zentr., 1935, ii, 2229).—Blood- and tissue-glutathione are decreased. Acid-sol. tissue-N is > residual N of the blood. Neutral S is increased. R. N. C.

**Automatic metabolism apparatus with continuous recording of oxygen consumption for small animals.** H. HÄUSLER (Arch. exp. Path. Pharm., 1936, 181, 345—366). F. O. H.

**Variations in impedance and chemical action during muscular contraction.** M. DUBUISSON (Compt. rend. Soc. Biol., 1936, 122, 817—820).—During contraction, the impedance of frog muscle to an electric current of frequency 2000 cycles per sec. shows two overlapping curves. As fatigue sets in, the first of these falls and the second rises, the latter being affected only by  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ . The two curves are related to the decomp. and synthesis of adenylypyrophosphoric acid and phosphagen, respectively. A. L.

**Effect of alimentary disequilibrium on respiratory quotient and basal metabolism of pigeons.** R. LECOQ and J. M. JOLY (Compt. rend., 1936, 202, 1709—1711).—With diets rich in glucose, galactose, or fructose and free from vitamin-B, the R.Q. (normally 0.75—0.82) is diminished and basal metabolism increased. Addition of yeast to the diet tends to inhibit the changes only with the glucose diets (cf. A., 1933, 433, 872; this vol., 368). F. O. H.

**Periodicity in the metabolism of the pancreas of the white mouse during recovery [from pilocarpine injection].** P. B. VAN WEEL (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 278—281).—Variations in R.Q. are repeated after 7 hr. The mechanism of the changes is discussed. A. G. P.

**Changes in reduction-oxidation potential of the cornea of eyes enucleated from cadavers.** Dependence on the length of time after enucle-

ation and conditions of preservation. P. M. KURISCHKIN (Platz. Utschen. Med., 1936, 24—34).—The corneas show a progressive fall in their  $E_h$  vals. during the first 6—8 days after death.

W. O. K.

Method for the study of tissue oxidations. V. R. POTTER and C. A. ELVEHJEM (J. Biol. Chem., 1936, 114, 495—504).—The method consists in the rapid homogenisation of the tissue in buffer solution by a motor-driven pestle and the measurement of the  $O_2$  uptake of the suspension at various dilutions. In rat's liver and brain and chick's liver and kidney,  $Q_{O_2}$  (with and without added substrate) decreases with increasing dilution.

H. D.

Role of erythrocytes in protein metabolism.

III. Distribution of amino-nitrogen between erythrocytes and plasma. I. B. ŚBARSKI. IV. Effect of amino-acids on the respiration of nuclear erythrocytes. S. BICHKOV (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 125—127, 123—124).—III. In dogs ingestion of meat results in increase in the  $NH_2-N$  content of the whole blood. The increase occurs in the erythrocytes which transport the  $NH_2$ -acids; plasma- $NH_2-N$  remains nearly const.

IV. The respiration of erythrocytes (pigeon) is decreased by addition of  $NH_2$ -acids (histidine > tryptophan > *d*-alanine > *d*-leucine). The extent to which these  $NH_2$ -acids are adsorbed at the surface of the erythrocytes varies in the same order.

W. McC.

Oxidation and catalysis in the muscles of warm-blooded animals. II. White and red muscles. A. CHARIKOVA and M. TIKHAJA (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 111—112).—In the pigeon respiration and oxidase content in breast muscle are > in leg muscle, whilst the reverse is the case in the hen. The difference in the function of the muscles affects the intensity but not the character of the oxidation.

W. McC.

Inhibition of formation of lactic acid in the cell by oxygen. I. A. HAHN and H. NIEMER (Z. Biol., 1936, 97, 195—200).—With 0.04M- $PO_4^{'''}$  extraction of muscle pulp, the inhibitory action of  $O_2$  on lactic acid formation occurs with muscle residue+extract, but not with either component alone or with heated extracts. Pptn. of proteins from the extract by  $COMe_2$  at 0° gives a filtrate which, after removal of  $COMe_2$  is active even after heating. The nature of this heat-stable constituent, which is not an  $O_2$  carrier in lactic acid dehydrogenation, is discussed.

F. O. H.

Effect of diet on the constitution of the organism. R. BERG (Med. Klinik, 1935, 31, 917—920, 947—950; Chem. Zentr., 1935, ii, 2229—2230).

R. N. C.

Composition and calorific value of diets consumed in two [Italian] maritime colonies. A. CARTENI and C. VACCA (Atti R. Accad. Lincei, 1936, [vi], 23, 216—217).—The protein, fat, and carbohydrate contents and calorific val. calc. by Rubner's and Benedict's methods are tabulated.

F. O. H.

Variations in urinary excretion of allantoin in rats on ketogenic and anti-ketogenic diets. G. BERGAMI, P. BAER, and E. BOERI (Atti R. Accad.

Lincei, 1936, [vi], 23, 198—199).—Diets rich in fats (ketogenic) and carbohydrates (anti-ketogenic) respectively decrease and increase excretion of allantoin; excretion of uric acid follows a parallel but less significant course.

F. O. H.

Growth-stimulating properties of grass juice. G. O. KOHLER, C. A. ELVEHJEM, and E. B. HART (Science, 1936, 83, 445).—Addition of fresh, clear, grass juice to a diet of mineralised milk produced on winter rations markedly increased growth in young rats.

L. S. T.

Experimental renal insufficiency produced by partial nephrectomy. IV. Creatine content of hypertensive hypertrophied rat heart after dried meat diet. A. CHANUTIN and S. LUDEWIG (Arch. Int. Med., 1936, 57, 887—892).—Ventricular creatine (I) is independent of dietary (I). (I) per unit wt. is const. (I) per unit surface area increases in hypertension due to increase in muscular tissue.

E. D. Y.

Distribution of the urinary constituents of nitrogen metabolism and its physiological significance. VIII. Fundamental principles for the study of nitrogen catabolism. E. F. TERROINE (Bull. Soc. Chim. biol., 1936, 18, 665—686).—A discussion.

A. L.

Metabolism of glycollic acid in progressive muscular dystrophy. A. T. MILHORAT and V. TOSCANI (J. Biol. Chem., 1936, 114, 461—466).—The possibility that glycollic acid (I) is a precursor of glycine (II) is investigated. Feeding (I) to patients with muscular dystrophy produced a much smaller increase in creatinuria than feeding (II).

H. D.

Decarboxylation of amino-acids by tissues. K. M. ROSANOV (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 109—110).—Sliced kidney (guinea-pig) shaken with histidine solutions produces a substance having a pharmacological action similar to that of histamine (I). No such effect is observed with liver and other organs, possibly because the (I) produced is then destroyed.

W. McC.

Role of carbohydrates in protein metabolism in the overheated organism. E. S. NOVAKOVSKAJA (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 128—129).—Alterations in the protein and other metabolism produced by overheating are counteracted by giving glucose, which has a sp. dynamic effect and causes restoration of normal conditions.

W. McC.

Phosphoaminolipins of the enteric mucosa and fat absorption. I, II. Qualitative and quantitative variations following administration of iodinated fat. C. ARTOM and G. PERETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 867—868, 869—871).—I. Following ingestion of iodinated fat (I) (11 g. per kg.) by rabbits, the fraction of the mucosa-lipins insol. in  $COMe_2+MgCl_2$  contains I, the content being max. after 14 hr. and attaining a const. level at 24—72 hr. This I occurs in the purified phosphoaminolipins (II).

II. Ingestion of (I) increases (II), carnitine, and  $COMe_2$ -insol. fatty acids in the mucosa. The data indicate that fat absorption produces increased lipin metabolism of the mucosa.

F. O. H.



**Intestinal absorption of oils of varying degree of unsaturation.** G. PERETTI and L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 871—873).—Variations occur in the rate of absorption in rats of different unsaturated fatty acids, but no parallelism appears to exist between rate of absorption and degree of unsaturation. F. O. H.

**Absorption of oleic acid in the form of mono- and di-olein.** G. PERETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 873—874).—When expressed as % of oleic acid entering the intestine (rat), oleic acid and mono- and di-olein are absorbed to an extent of 55, 88.4, and 82.7, respectively; thus the last two are absorbed approx. as rapidly as triolein. F. O. H.

**Total fatty acids of the liver after administration of fats of varying degree of unsaturation.** G. PERETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 875—876).—The increase in liver-fatty acids in rats varies considerably with, but is not related to, the degree of unsaturation of the oil ingested. F. O. H.

**Total fatty acids of the liver after administration of oleic acid and mono- and di-olein.** G. PERETTI and L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 876—877).—The increase in liver-fatty acids following ingestion of oleic acid by rats is > that after ingestion of mono- or di-olein and < that after ingestion of olive oil. F. O. H.

**Lipins of thoracic lymph during absorption of neutral fats.** C. ARTOM and G. PERETTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 877—880).—Following ingestion of horse fat (I) by dogs, the lymph-fat occurs totally as triglycerides, whilst the l val. is > that of (I). The lipin-P (but not specifically phosphatidolipin P) and cholesterol levels tend to increase. F. O. H.

**Effect of iodoacetic acid and of adrenalectomy on fat transport.** L. LASZT and F. VERZAR (Biochem. Z., 1936, 285, 356—367).—The development of fatty liver in rats after P poisoning and on fasting is inhibited by  $\text{CH}_2\text{I}-\text{CO}_2\text{H}$  poisoning and by adrenalectomy. It appears that for transport fat is converted into phosphatides, and that the process is under adrenal hormonal influence in the same way as is fat synthesis in the intestinal mucosa during absorption. P. W. C.

**Fat-sugar metabolism.** I. ABELIN (Z. ges. exp. Med., 1935, 96, 9—17; Chem. Zentr., 1935, ii, 2234).—Rats fed exclusively on fats have a greater glycogen-storing capacity than those fed normally, the liver- and muscle-glycogen being 40—60% > average; oils have a greater effect than semi-solid fats. H. N. R.

**Deuterium as indicator in the study of intermediary metabolism. VI. Synthesis and destruction of fatty acids in the organism.** R. SCHOENHEIMER and D. RITTENBERG (J. Biol. Chem., 1936, 114, 381—395; cf. this vol., 630).—Rats on a carbohydrate diet supplemented with  $\text{D}_2\text{O}$  showed an increased content of D-containing fatty acids reaching a max. in 6—8 days; the increase is shown to be due to synthesis of new acids. Rats fed on a D-containing diet and then transferred to a carbohydrate diet alone showed a destruction of the D-containing fatty acids

approx. as rapid as their synthesis. Azelaic acid isolated from the fat of rats on a D-containing diet contained the same ratio of D : H as the total fatty acids. Injection of 5%  $\text{D}_2\text{O}$  into a developing chick's egg failed to cause D to enter the fatty acid mols. of the embryo. H. D.

**Presence of lactic acid in investigation of the stomach contents, after Ewald and Boas, must be ascertained by a limit-reaction.** G. SANT (Pharm. Tijds. Nederl.-Indie, 1935, 12, 184—187; Chem. Zentr., 1935, ii, 2251).—A suitable reaction is described. H. N. R.

**Lungs and ketone metabolism.** A. I. ODINOV (Biochem. Z., 1936, 286, 101—109).—Pulped dogs' lung at 37—38° produces  $\text{CH}_3\text{Ac}-\text{CO}_2\text{H}$  (optimal at  $p_{\text{H}}$  5.6) and  $\beta$ -hydroxybutyric acid (I) (optimal at  $p_{\text{H}}$  7.0), probably as a result of autooxidation. Production of ketones in the pulp from added  $\text{Pr}^{\text{C}}\text{CO}_2\text{H}$  when the amount of preformed ketones is high is < when it is low. Intravenous administration of  $\text{Pr}^{\text{C}}\text{CO}_2\text{Na}$  usually increases the (I) content of the lungs, but the amount of (I) in the arterial blood is sometimes >, sometimes <, that in the right heart. The lungs probably produce and (especially when the ketone content of the body is high) retain ketones. W. McC.

**Ketogenesis in muscular tissue.** L. M. GOLBER (Platz. Utschen. Med., 1936, 286—299).—Intravenous injection of  $\text{PrCO}_2\text{Na}$  into starving rabbits increases ketonic substances (I) in the derived muscle pulp incubated for 24 hr. at 37°, but no such increase is found with normal rabbits even when the salt is added directly to the pulp. Injection of methylsuccinic acid (II) decreases the formation of (I) in the muscle-pulp, but direct addition of (II) has no significant effect. W. O. K.

**Calcium compounds in dentistry.** A. R. BLISS, jun. (Dental Cosmos, 1935, 77, 763—766).—Ca absorption by mice after administration by stomach tube was determined by the min. dose of  $\text{MgSO}_4$  required to produce narcosis. Rates of Ca absorption were in the (descending) order: Ca lactate, Ca gluconate,  $\text{CaCl}_2$ , Ca inositol hexaphosphate,  $\text{CaHPO}_4$ , Ca glycerophosphate. CH. ABS. (p)

**Phosphorus in the early development of the frog.** M. A. ZIELINSKI (Bull. Acad. Polonaise, 1935, B, 293—304).—Inorg. and labile P were determined in the frog's embryo during development. Inorg. P increased at the expense of the labile; the latter passed through a min. between the 60th and 80th hr. and then increased, the increase being associated with increased powers of muscular contraction. H. D.

**Influence of fasting on the rate of oxidation of ethyl alcohol in rats.** E. LE BRETON (Compt. rend. Soc. Biol., 1936, 122, 330—332).—In rats starved for 1.5—6 days, the rate of oxidation of intraperitoneally injected EtOH diminishes more rapidly than does the basal metabolism. F. O. H.

**Rate of oxidation of ethyl alcohol in homoiotherms during growth.** E. LE BRETON (Compt. rend. Soc. Biol., 1936, 122, 561—564).—In the rat (insensitive to the quantity) the val. decreases with

age, whilst in the cock (sensitive to quantity) little variation occurs.

H. G. R.

Percentage of oxidation due to ethyl alcohol in poikilotherms. E. LE BRETON (Compt. rend. Soc. Biol., 1936, 122, 564—565).—With tortoises and frogs the val. is approx. 90%, the other 10% being due to utilisation of protein.

H. G. R.

Intestinal absorption of castor oil. G. VALETTE and R. SALVANET (Bull. Soc. Chim. biol., 1936, 18, 911—917).—Approx. 68% of the oil administered is recovered in the faeces as fatty acid or as soap while 22% is absorbed. This low val. is not attributed to any anomalous action with the bile or the lipolytic enzymes of the intestines.

H. G. R.

Biochemical and physiological significance of the oxidation of ethyl alcohol in the organism. E. LE BRETON (Compt. rend. Soc. Biol., 1936, 122, 565—568).—A summary of results obtained since 1933.

H. G. R.

Metabolism of polycyclic compounds. III. Anthrhylmecapturic acid. E. BOYLAND and A. A. LEVI (Biochem. J., 1936, 30, 1225—1227; cf. this vol., 234).—Rats and rabbits fed on an anthracene-containing diet excreted 1-anthrhylmecapturic acid, m.p. 193—195°,  $[\alpha]_D^{20}$   $-6^\circ$  to  $-10^\circ$  in EtOH, which on alkaline hydrolysis gave  $\alpha\alpha$ -dianthrhyll disulphide, m.p. 191—193°. Traces of anthraquinone were probably also excreted.

H. D.

Metabolism of normal and tumour tissue. XVII. Action of some derivatives of phenazine, quinoline, and pyridine on the Pasteur reaction. F. DICKENS (Biochem. J., 1936, 30, 1233—1241).—The inhibition of the Pasteur mechanism in normal and tumour tissues by phenosafranine is not due merely to its negative oxidation-reduction potential or to its photosensitising properties, but may be imitated by a group of derivatives of  $C_5H_5N$ , acridine, and quinoline containing  $N^+$  and a conjugated chain terminating in a basic group. The sarcoma-producing styryl 430" of Browning increases the respiration and aerobic and anaerobic glycolysis of rat's liver.

H. D.

Elimination of certain polycyclic hydrocarbons from the animal body. J. G. CHALMERS and P. R. PEACOCK (Biochem. J., 1936, 30, 1242—1248; cf. A., 1934, 1127).—The tissues and excreta of animals fed with hydrocarbons were saponified and the unsaponifiable fraction was treated with digitonin; pigments were removed with fuller's earth and the fluorescence spectrum of the solution was examined. 1:2:5:6-Dibenzanthracene and 1:2-benzpyrene (I) injected intramuscularly into fowls did not appear in the excreta; with the chick embryo (I) was eliminated 90 hr. after injection, but did not appear in the gall-bladder. Injection of (I), methylcholanthrene, and anthracene into mice produced fluorescent substances in the bile after 1—2 hr.

H. D.

Photodynamic sensitisation. Biological action and therapeutic application. A. EIDINOW (Proc. Roy. Soc. Med., 1935, 28, 633—640).—Diseases associated with abnormal reactions of skin to light are due to exogenous photo-biochemical substances which sensitise the skin cells to light. Inborn errors of

metabolism and abnormal production of porphyrin pigments in the excreta cause skin disease.

CH. ABS. (p)

Fast electron beams and their significance in radiation therapeutics. R. GLOCKER (Strahlenther., 1935, 53, 417—423; Chem. Zentr., 1935, ii, 2396—2397).—A review. Tests on the penetration in biological materials are described.

H. J. E.

Destruction of the anterior pituitary by X-rays. I. Destruction of the anterior pituitary and magnesium, calcium, and phosphorus metabolism. L. CANNAVÒ and R. BENINATO (Endokrinol., 1935, 15, 389—404).—Serum-Mg in rabbits falls continuously after X-irradiation of the pituitary, Mg excretion in the urine and faeces decreasing simultaneously. Serum-Ca is unchanged, whilst serum-P oscillates slightly downwards; both Ca and P excretion are almost unaltered.

R. N. C.

Action of ultra-violet irradiation on surface tension of serum-albumin solutions. F. COSSU (Boll. Soc. ital. Biol. sperim., 1935, 10, 973—975).—Aq. serum-albumin at  $p_H$  1.4—8.6 has a min.  $\gamma$  at the isoelectric point; following irradiation,  $\gamma$  is max. at, with a second val. towards the acid side of, the isoelectric point.

F. O. H.

Effect of training on muscle-glycogen of pigeons, rabbits, and hens. V. O. ROZENHARDT (Platz. Utschen. Med., 1936, 280—285).—The increase in glycogen content due to repeated electrical stimulation for 20—28 days varies with different muscles.

W. O. K.

Ammonia production in the non-medullated nerve of the mollusc *Anodonta*. A. V. GOLUBTSOVA and J. L. KAHN (Bull. Biol. Méd. Exp. U.R.S.S., 1936, 1, 130—132).—Electrical stimulation of the nerve in presence of dil.  $H_2SO_4$  results in a 370% increase in  $NH_3$  production. The increased  $O_2$  consumption in the presence of acid is probably due entirely to  $NH_3$  production.

W. McC.

Mitogenetic radiation. H. BARTH (Biochem. Z., 1936, 285, 311—339).—This problem is critically reinvestigated in collaboration with the Gurwitsch school. The results ascribed to mitogenetic radiation are due to the short-wave portion of the radiation, and since in earlier work the sensitivity of the apparatus was not applicable to the range 220—180 m $\mu$ , the negative results do not exclude the possibility of detection of radiation in terms of light-electric properties. Results indicating that similar effects can be obtained by change of moisture and electrostatic field are peculiar to the apparatus used. A method is described which gives statistical results with various protein and inorg. reactions. Absorption spectra of 9 substrates were investigated and striking analogies obtained with published mitogenetic spectra.

P. W. C.

Electrostatic measurements on single motor end-plates and muscle fibres. II. Effect of curare poisoning and radium irradiation. F. BUCHTHAL and J. LINDHARD (Skand. Arch. Physiol., 1935, 72, 35—50; Chem. Zentr., 1935, ii, 2082).

R. N. C.

Does heavy water influence physiological processes? M. F. VON DUNGERN (Z. Biol., 1936,



97, 187—194).—Heavy  $H_2O$  (0.05—10%  $D_2O$ ) has no influence on hydrolysis by ptyalin, pepsin, or trypsin, blood-coagulation, action of thrombin, oxyhaemoglobin spectrum, movement of ciliated epithelial cells, surviving frog's heart, or fatigue and recovery of frog's gastrocnemius muscle. Certain effects ascribed to  $D_2O$  preps. are probably due to impurities.

F. O. H.

**Antagonism between iodine and fluorine in the organism.** W. MAY (Klin. Woch., 1935, 14, 790—792).

R. N. C.

**Diuretic action of organic mercury compounds.** H. U. SIMMERT (Klin. Woch., 1935, 14, 530—532; Chem. Zentr., 1935, ii, 2398).—The action of "novurit" is extra-renal in origin, consisting of an alteration in the tissue-NaCl.

H. N. R.

**Ketogenesis in liver poisoned with phosphorus.** S. LEITES and A. ODINOV (Biochem. Z., 1936, 286, 93—100; cf. this vol., 236).—Production of  $CH_3Ac \cdot CO_2H$  and  $\beta$ -hydroxybutyric acid in rabbits' liver pulp remains unaffected when they are moderately poisoned with P, but decreases if poisoning is severe. Ketogenesis following aseptic autolysis in poisoned liver is  $>$  in healthy liver. Addition of  $Pr^+CO_2Na$  usually has less ketogenic effect when added to poisoned liver pulp than when added to liver pulp from fasting rabbits. Intravenous administration of  $Pr^+CO_2Na$  neither increases the ketone content of the liver nor alters the extent of ketogenesis there, but sometimes increases the ketone content of the lungs.

W. McC.

**Regulation of tissue-nourishing blood-circulation by carbonic acid and cholates.** A. FLEISCH (Arch. int. Physiol., 1935, 40, 385—397; Chem. Zentr., 1935, ii, 1910—1911).—Perfusion of the small intestine with Ringer's solution containing  $H_2CO_3$  or bile acids causes vaso-dilatation.

H. N. R.

**Diet and thyroid function. II. Effect of acetonitrile and potassium iodide on the basal metabolism and histological picture of the thyroid.** F. BRUMAN and A. MILDWURF (Z. ges. exp. Med., 1935, 96, 223—232; Chem. Zentr., 1935, ii, 1738).—The thyroid shows no difference from the normal.

R. N. C.

**Effect of salicyl derivatives on isolated frog and turtle hearts.** R. L. JOHNSON (J. Pharm. Exp. Ther., 1936, 57, 193—197).—Aspirin solution kept for one day is toxic owing to hydrolysis. Other salicylates also reduce the amplitude of heart contractions.

E. D. Y.

**Effect of dinitrophenol on rate of alcohol metabolism.** H. W. NEWMAN and M. L. TAINTER (J. Pharm. Exp. Ther., 1936, 57, 67—73).—The increased loss of EtOH from the blood of dogs, produced by dinitrophenol, is due to the higher rate of respiration and consequent increased loss in the lungs, and not to increased oxidation.

W. O. K.

**Action of various nitro-compounds on metabolism and [body-]temperature.** C. HEYMAKS and H. CASIER (Arch. int. Pharmacodyn. Thér., 1935, 50, 20—64; Chem. Zentr., 1935, ii, 2234—2235).—The effects of many  $NO_2$ -compounds in stimulating metabolism and in raising the body-temp. and their

toxicities are described.  $C_6H_5$  and  $C_{10}H_7$  compounds have equal activities and  $(NO_2)_2$ -compounds are more effective than  $(NO)_1$ - or  $(NO_2)_3$ -, whilst  $(OH)_1$ -compounds are more effective than  $(OH)_2$ -. Etherification of a phenolic OH or introduction of an aliphatic or aromatic group increases the activity. The  $NO_2$  and OH must be in the same ring: introduction of  $SO_3H$ ,  $NH_2$ ,  $CO_2H$ , and further  $NO_2$  lessens the influence on metabolism, but increases the effect on body-temp.

H. N. R.

**Edema and glyoxaline compounds.** M. LOEDER, E. BIOY, M. PERRAULT, and A. VARAY (Presse méd., 1935, 43, 697—699; Chem. Zentr., 1935, ii, 2235).—The hydropigenous action of known tissue-extracts is parallel to their content of glyoxaline compounds. Many synthetic glyoxaline derivatives have a similar activity.

H. N. R.

**Toxicity and effect on blood-sugar of a number of amidine and guanidine derivatives.** W. A. BROOM (J. Pharm. Exp. Ther., 1936, 57, 81—97).—Of various guanidine and amidine compounds (cf. Easson and Pyman, A., 1932, 55), some produced in rabbits an initial hyperglycaemia (I) followed by hypoglycaemia, whilst others caused (I) only. The most active hypoglycaemic compounds were sebac-amidine and *n*-decane-1:10-diamidine, but neither was as active as synthalin. In a homologous series of diamidines  $(CH_2)_n[C(NH) \cdot NH_2]_2$  the toxicity and hypoglycaemic action both increase with *n*, reaching a max. at *n*—8 or 10. The activity of these compounds is chiefly due to their toxic effect on the liver, and not to an insulin-like action. None of the compounds is of clinical value.

W. O. K.

**Influence of bromocholine on gastric secretion.** J. MASEK (Compt. rend. Soc. Biol., 1936, 122, 430—433).—Injection of bromocholine into men increases the gastric acidity; the time to reach a max. is  $>$  that with histamine, but is not accompanied by any ill-effects.

H. G. R.

**Inhibition by fats of the gastric secretion caused by histamine.** B. FIERENS and P. P. DE NAYER (Compt. rend. Soc. Biol., 1936, 122, 805—807).—In dogs with a gastric fistula the secretion of gastric juice produced by histamine is much decreased when arachis oil is administered. This is not in agreement with the findings of Roberts (Quart. J. Med., 1930, 24, 133).

A. L.

**Influence of fatty acids on blood-glycolysis.** G. D'ALESSANDRO and S. PETRUCCI (Biochem. Z., 1936, 285, 72—75).—Addition of castor oil, oleic or more highly unsaturated acids, or of nonoic acid to washed blood corpuscles increases the glycolysing power considerably, the increase varying with the concn. of added acid and being different for the corpuscles of different individuals.

P. W. C.

**Phloridzin and urinary excretion of phosphorus.** A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, 122, 468—470).—The P threshold is raised and that of glucose lowered by injection of phloridzin into dogs.

H. G. R.

**Dependence of the action of adrenaline on physiological variables.** P. DE LA PEÑA (Biochem. Z., 1936, 286, 77—80).—In rabbits injection of

adrenaline (I) frequently leads to increase in the hæmoglobin concn. of the blood, the magnitude of the effect being dependent also on the temp. of the animals' surroundings and on the activity of the thyroid gland. When the temp. is low (4—6°) the increase in the blood-sugar concn. following (I) injection is < when the temp. is 19—20°. W. McC.

**Specific action of products of intermediate tissue disintegration.** J. A. LAZARIS (Platz. Utschen. Med., 1936, 220—230).—The claim of Mascherpa (A., 1935, 1276) that proteins from organs or tumours injected into an animal result in the preferential deposition of Co in the homologous tissue, is not confirmed. W. O. K.

**Effects of physiological agents on adult tissues *in vitro*.** H. S. SIMMS (Science, 1936, 83, 418—419).—The effects of various agents on the initial growth of adult tissue (mainly chicken aorta) *in vitro* are recorded. Papain and trypsin stimulate growth; the effect of the latter is due to proteolytic digestion of the tissue with apparent removal of an inhibitor. Embryo and spleen extracts have little effect, whilst pituitary growth-hormone is slightly stimulating. Blood-plasma contains a growth stimulant, the "A factor," which is also present in tissues, lymph, urine, and serum, and is essential for growth and for the cells in a resting condition. It is an acid of low mol. wt. and can be pptd. with Ca or Cu with subsequent recovery of activity. The physiological condition of adult tissue cells appears to involve a balance between hormone-like controlling agents, of which there are at least four factors, A, B, C, and D, present in plasma. The rôles of these factors are described. L. S. T.

**Effect of lecithin and cholesterol in combination with insulin on carbohydrate metabolism.** G. CAIZZONE (Biochim. Terap. sperim., 1933, 20, 339—343; Chem. Zentr., 1935, ii, 1907).—A mixture of insulin, lecithin, and cholesterol retained its activity for 1 year. Injection of very large doses may prevent the appearance of hypoglycæmic symptoms. A synergistic action between the components of the mixture is indicated. A. G. P.

**Effect of insulin on the hepatic and renal lipinosis of chloroform narcosis.** B. BARONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 933—936).—Insulin has a transient inhibitory effect on  $\text{CHCl}_3$ -lipinosis in guinea-pigs. F. O. H.

**Some anaesthetic circulatory and respiratory agents.** P. REGNIERS and G. DE VLEESCHOUWER (Arch. int. Pharmacodyn. Thér., 1935, 50, 65—93; Chem. Zentr., 1935, ii, 2237).—The effects of a no. of such agents on anaesthetised dogs are described. H. N. R.

**Anæsthetic power of hydrochloride and phenylpropionate of novocaine on the motor nerves of *Rana esculenta*.** J. RÉGNIER and A. QUEVAUVILLER (Compt. rend. Soc. Biol., 1936, 122, 251—254).—The phenylpropionate is 5—7 times as active as the hydrochloride (cf. this vol., 634). F. O. H.

**Vaso-depressor action of strychnine after ether, alcohol, barbital, and chloral.** H. GOLD and J. TRAVELL (Arch. int. Pharmacodyn. Thér.,

1935, 50, 1—14; Chem. Zentr., 1935, ii, 2235—2236).—Strychnine has a vaso-depressor action on animals under anæsthetic influence. H. N. R.

**Relative hypnotic effects of some aryl- and unsymmetrical alkylaryl-thiocarbamides.**—See this vol., 977.

**Assimilation of fructose during narcosis.** H. FUSS and G. SVEINDAL (Z. ges. exp. Med., 1934, 94, 436—441; Chem. Zentr., 1935, ii, 2236).—During  $\text{Et}_2\text{O}$  narcosis the blood-sugar of rabbits is only transiently affected. H. N. R.

**Extraction and detection of veronal and luminal.** J. H. KREPELKA and V. ŠVARC (Coll. Czech. Chem. Comm., 1936, 9, 191—206).—62% of veronal (I) and 65% of luminal (II) are recovered from flesh by Wasicky's method, 93.5 and 90%, respectively, from urine by Straub and Mihalovits' method. Other methods are less satisfactory. Zwicker's colour reaction is excellent for (I), but may be indistinct for (II). (I) and (II) are best purified by sublimation at 12 mm., for which an apparatus is described. R. S. C.

**Behaviour of blood-sugar in pigeons under the action of poisons of the central nervous system.** R. ALLERS and J. BRILL (Biochem. Z., 1936, 285, 6—10).—A table summarises the effect on the body-temp. and blood-sugar of pigeons of amytal (2 injections), morphia, urethane, chloral (all blood-sugar increasing), and paraldehyde (blood-sugar decreasing). Intramuscular injection of tetrahydro- $\beta$ -naphthylamine causes a fall in body-temp. together with an increase in blood-sugar, the latter effect being greater in the fasting condition. P. W. C.

**Speed of adsorption of medicaments in relation to the osmotic pressures of their solutions.** I. SIMON (Arch. int. Pharmacodyn. Thér., 1935, 50, 180—194; Chem. Zentr., 1935, ii, 1908).—Relations between the velocity of absorption and the osmotic pressure are discussed; no rules of practical significance can be deduced. H. N. R.

**Significance of complex formation and solubility changes for the action of medicines.** J. BUSSEMAKER (Arch. exp. Path. Pharm., 1936, 181, 503—511).—A new method for the detection of complexes in aq. solution is described. Caffeine forms complexes with Na salicylate and with novocaine hydrochloride, and veronal with pyrimidone and antipyrine. The importance of complex formation depends on change in solubility, and this is discussed for various medicinal combinations. J. N. A.

**Antipyretic action of a new antipyrine derivative.** C. L. YI and B. E. READ (Chinese J. Physiol., 1936, 10, 297—302).—1-Phenyl-2-methyl-4-ethylpyrazol-5-one has a much stronger antipyretic action on rabbits than has antipyrine (I): the min. lethal dose for mice is < that of (I). F. A. A.

**Active principles of senna leaves.** W. STRAUB and H. GEBHARDT (Arch. exp. Path. Pharm., 1936, 181, 329—407).—The cathartic principles in Tinivelly senna leaves (D.A.B. VI) (approx. 200 mouse-units per g.) include an anthranol glucoside (which on hydrolysis with acids yields an anthraquinone deriv-



ative, identical with aloe-emodin), a cryst. glucoside (containing 42% of emodin and difficultly hydrolysed by acids), and a glucoside readily hydrolysed even by plant acids in the leaf. F. O. H.

**Cumulative and toxic actions of cardiazol and coramine.** F. ZINNITZ and F. VON BERGMANN (Arch. exp. Path. Pharm., 1936, 181, 335—344).—Continuous administration of small doses (e.g., 5 mg. per kg.) of cardiazol (pentamethylenetetrazole) (I) or coramine (II) into rabbits maintains the blood pressure at 10—15 mm. Hg above normal; larger doses give higher vals. but are rapidly lethal. Individual variations in toxicity occur with (II) but not (I). Narcotics and analeptics are mutually antagonistic. Large doses of (II) are necessary to depress the blood-pressure of spinal cats, whilst (I) is ineffective and less toxic. (II), unlike (I), appears to have a peripheral action. F. O. H.

**Comparative action of cardiazol and coramine in animals.** L. LENDLE (Arch. exp. Path. Pharm., 1936, 181, 408—420).—The action on the respiratory vol. of morphinised rabbits indicates that coramine (I) has a wider range, whilst the dose-effect curve of cardiazol (II) is steeper. With pernocton and avertin narcosis, the effective range of (II) and, to a greater extent, of (I) is increased. With narcotised rats, threefold convulsive doses of (I) prolong narcosis and delay the convulsive and lethal effects. F. O. H.

**Fall in body-temperature in birds after administration of pyrogenic substances.** J. BRILL (Biochem. Z., 1936, 285, 1—5).—Intramuscular injection of tetrahydro- $\beta$ -naphthylamine into hens and pigeons results in a mean fall of body-temp. of 3—3.5° (max. 5.8°), rapid at first, reaching the max. val. in about 1.5 hr. and slowly disappearing. With large doses the temp. may remain subnormal for 2.5 days. The fall in temp. was not strictly  $\propto$  the dose. Cocaine and caffeine also lower the body-temp. P. W. C.

**Action of valerian and a method of assay.** M. KOCHMANN and H. KUNZ (Arch. exp. Path. Pharm., 1936, 181, 421—434).—In sufficiently large doses macerated valerian (I) causes paralysis of the dog's cerebrum; infusions produce paralysis of the mid-brain. Alcoholic and hot and cold H<sub>2</sub>O extracts have approx. the same action. The min. narcotic dose in the white mouse is close to the lethal dose. With rabbits the therapeutic val. of (I) can be determined by its antagonistic action towards the stimulating effect of caffeine. J. N. A.

**Experimental investigation of salvarsan allergy.** P. KALLOS and L. KALLÓS-DEFFNER (Klin. Woch., 1935, 14, 1074—1076; Chem. Zentr., 1935, ii, 1910).—Experiments with guinea-pigs are described. H. N. R.

**Observations on the pharmacological action of ergotamine by experiments on the Pagano-Hering reflex.** E. BECCARI (Arch. int. Pharmacodyn. Ther., 1935, 50, 195—210; Chem. Zentr., 1935, ii, 1908—1909).—Experiments on dogs are described. H. N. R.

**Derivatives of barbituric acid.**—See this vol., 999.

**Toxicity of organic salts of novocaine and morphine. Determination of mean lethal doses.** J. RÉGNIER, S. LAMBIN, and E. SZOLLOSZ (Compt. rend. Soc. Biol., 1936, 122, 759—762).—By subcutaneous injection the toxicities of novocaine phenylpropionate (I) and isobutyrate (II) are equal to, and that of the phenylacetate (III) is slightly >, that of novocaine hydrochloride (IV). (I) and (II) have 1/5—1/6, and (III) has 1/3, the toxicity of cocaine. Intravenously, the three salts have the same toxicity as (IV). Subcutaneously morphine benzoate, cinnamate, and citrate have the same toxicity as the hydrochloride (V), the toxicity of the phenylpropionate being <, and that of the salicylate >, that of (V). A. L.

**Action of cocaine on the respiratory function of the blood.** G. FELLONI (Arch. ital. Biol., 89, 69—75; Chem. Zentr., 1935, ii, 2229).—Absorption of O<sub>2</sub> is restrained. R. N. C.

**Bronchodilator action of sympathomimetic compounds after histamine-induced bronchial spasm.** W. M. CAMERON and M. L. TAINTER (J. Pharm. Exp. Ther., 1936, 57, 152—169).—The order of efficiency was: adrenaline, epinine, 3:4-dihydroxyephedrine > ethyl-norsuprarenin, arterenol, neo-synephrine, cobefrin, atropine > *l*-*m*-hydroxyephedrine, ephedrine, benzedrine, octin > (no activity) ephetonal, propadrin, *m*-hydroxynorephedrine, *p*-hydroxyephedrine. Amines with the pyrocatechol nucleus are the most effective. E. D. Y.

**Ergotocine, ergometrine, ergostetrine, and ergobasine.** K. K. CHEN, E. E. SWANSON, E. C. KLEIDERER, and G. H. A. CLOWES (J. Pharm. Exp. Ther., 1936, 57, 74—80).—Ergotocine, ergometrine, ergostetrine, and ergobasine in the form of maleates have identical effects on the isolated rabbit's uterus, the cock's comb, and the isolated rabbit's intestine. They also give approx. equal colours with *p*-dimethylaminobenzaldehyde, whilst the combustion figures agree closely (cf. Kharasch *et al.*, this vol., 489). W. O. K.

**Influence of pilocarpine on the metabolism of the [salivary] gland and of smooth muscle.** R. VLADESCO and G. NICHITA (Compt. rend., 1936, 202, 1533—1535).—Lactic acid of the blood passes into the saliva, where its content after injection of pilocarpine is > that after stimulation of the chorda tympani nerve, and is parallel to the blood level. The effect of pilocarpine is considered to be due partly to intermediate metabolism of the salivary gland and partly to that of smooth muscle. E. W. W.

**Pharmacology of *Duboisia Hopwoodii* (*d*-nornicotine).** C. S. HICKS, F. T. BRÜCKE, and E. F. HUEBER (Arch. int. Pharmacodyn. Ther., 1935, 57, 335—353).—*d*-Nornicotine present in *D. Hopwoodii* (cf. this vol., 125) is very similar pharmacologically to nicotine, but is 2.5 times as toxic to rats. W. O. K.

**Action of thyroid extracts in experimental lead-poisoning.** R. GARBINI (Arch. int. Pharmacodyn. Ther., 1935, 50, 211—215; Chem. Zentr., 1935, ii, 1911).—In rabbits, injection of thyroid extracts before Pb hastens death, whereas injection after Pb prolongs life. H. N. R.

**Selenium and duck sickness.** A. C. TWOMEY and S. J. TWOMEY (Science, 1936, 83, 470—471).—The poisoning produced in ducks by low concns. of  $\text{Na}_2\text{SeO}_3$  indicates that Se is a contributing factor in duck sickness. L. S. T.

**Chronic carbon monoxide poisoning.** H. BURESCH (Z. Hyg. Infekt., 1935, 117, 153—160; Chem. Zentr., 1935, ii, 1911).—Chronic CO poisoning may be, but is not necessarily, produced by repeated inhalation of small amounts of CO. H. N. R.

**Detoxication of cyanides.** G. AURISICCHIO and G. DE NITO (Boll. Soc. ital. Biol. sperim., 1935, 10, 946—948).—Polemical against Meneghetti (this vol., 377). F. O. H.

**Toxicity of sodium tetrathionate.** E. MENEGHETTI (Boll. Soc. ital. Biol. sperim., 1936, 11, 51—55).—Less than half the dose, stated by Aurisicchio (preceding abstract) to be harmless, is lethal. E. P.

**Urinary sulphate as a measure of exposure to benzene.** W. P. YANT, H. H. SCHRENK, and F. A. PATTY (J. Ind. Hyg., 1936, 18, 349—356).—Exposure of men to  $\text{C}_6\text{H}_6$  vapour decreased urinary  $\text{SO}_4$ . H. D.

**Comparative animal investigations on the action of toluene and xylene on blood.** W. E. ENGELHARDT (Arch. Hyg. Bakt., 1935, 114, 219—233; Chem. Zentr., 1935, ii, 2085).—PhMe and xylene are less injurious to blood than  $\text{C}_6\text{H}_6$ ; it is suggested that they should replace  $\text{C}_6\text{H}_6$  in practice. H. N. R.

**Poisonous vapours of some hydrocarbons and alcohols.** II. C. W. RAADSVELD (Chem. Weekblad, 1936, 33, 288—291).—A review with particular reference to the effects of poisoning by  $\text{C}_6\text{H}_6$  and the lower aliphatic alcohols. S. C.

**Physico-chemical properties of organic poisons and the products derived from them in the animal organism.** N. V. LAZAREV and T. V. STARYZYNA (Bull. Soc. Chim. biol., 1936, 18, 723—740).—A study of the b.p., m.p., *d*, solubility,  $\gamma$ , and  $\epsilon$  of org. poisons and the products of their transformation in the animal organism shows that such products are generally of greater polarity. A. L.

**Activation and inhibition of apodehydrogenases.** H. VON EULER (Biochem. Z., 1936, 286, 72—76).—The activities of the dehydrogenases (lactic, fumaric, malic, succinic acid, EtOH) vary greatly according to the substrate (muscle and brain of pigeon, guinea-pig, rat, rabbit) apparently because of the varying amounts of activators and inhibitors in the substrates, the co-enzyme content of the substrates having an important effect. Activation and inhibition also result from addition of  $\text{NH}_2$ -acids, purines, adrenaline, acetylcholine, glutathione, and other substances. W. McC.

**Optical detection of hydrogenation and dehydrogenation of pyridine in the fermentation co-enzyme.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1936, 286, 81—82).—The partly hydrogenated (but not the non-hydrogenated) co-enzyme (I) is fluorescent in Hg light (360  $\text{m}\mu$ ). Reduction of (I) by carbohydrate occurs only if sp. colloids are present.  $\text{Na}_2\text{S}_2\text{O}_4$  reduces in absence of colloids. W. McC.

**Laccase of Japanese lac.** II. Reactivity of laccase towards polyhydric phenols and diamines. K. SUMINOKURA (Bull. Chem. Soc. Japan, 1936, 11, 299—309; cf. A., 1930, 1474).—48 substances are examined for aerial oxidation in the presence of laccase from Japanese lac. The order of reactivity is  $p\text{-(NH}_2)_2 > o\text{-(OH)}_2 > o\text{-(NH}_2)_2$ -compounds > compounds with 1 OH and 1 OMe. *m*-Compounds,  $p\text{-C}_6\text{H}_4(\text{OEt})_2$ , various substituted phenols, safrole, aliphatic diamines, alizarin, protocatechuic acid, and dihydroxyphenylalanine are not oxidised; dihydrourosinol only with difficulty. Exceptions are *o*- and *m*- (but not *p*-) cresol, which are slowly oxidised. R. S. C.

**Mechanism of enzyme action.** Decomposition of monoethyl hydrogen peroxide by catalase and of an intermediate enzyme-substrate compound. K. G. STERN (J. Biol. Chem., 1936, 114, 473—494).—The decomp. of  $\text{EtO}_2\text{H}$  (I) by horse liver-catalase, with the formation of  $\text{MeCHO}$ , is unimol. at  $0^\circ$ , the reaction velocity increasing rapidly with rise of temp. The activity- $p_{\text{H}}$  curve has a sharp max. at  $p_{\text{H}}$  10. The catalyst is thermolabile and inhibited by KCN. The ultra-violet absorption spectrum of the reaction mixture indicates the formation of an enzyme-substrate complex with bands at 570 and 534  $\text{m}\mu$  with a reaction rate > that of the decomp. of (I), a low temp. coeff., and no  $p_{\text{H}}$  optimum. H. D.

**Action of aromatic sulphonic acids on carbonylase.** F. AXMACHER and H. LUDWIG (Biochem. Z., 1936, 286, 1—6; cf. this vol., 375; Labes *et al.*, A., 1935, 120).—Amongst aromatic sulphonic acids there is no simple relation between toxicity to carbonylase, mol. wt. (158—1438), and no. of  $\text{SO}_3\text{H}$  groups (1—6). The increase in the toxicity of germanin with increasing concn. is due to adsorption. W. McC.

**Two types of plant-diestase.** G. L. TELLER (J. Biol. Chem., 1936, 114, 425—430).—The existence of two types of diastase, differing in their optimal  $p_{\text{H}}$  and temp., is shown in a no. of plants. One predominates in the flour of sound mature wheat and the other in the bran of germinating cereals. H. D.

**Ascorbic acid and diastase.** P. HOLTZ (Arch. Exp. Path. Pharm., 1936, 181, 514—524).—Merck's diastase (I) but not Merck's pancreatin (II) has a peroxidase activity (reaction with  $\text{H}_2\text{O}_2$  and guaiacum tincture) which is considerably reduced by ascorbic acid (III). (III) also reduces the diastatic activity of (I), but has very little action on that of (II). Cysteine has no effect on either activity of (I). Blood-, saliva-, and pancreas-(I) have their activities diminished by (III). J. N. A.

**Intracellular regulation of enzyme reactions with particular reference to the action of amylase.** S. J. VON PRZYLECKI (Ergebn. Enzymforsch., 1935, 4, 111—146).—Theoretical. R. N. C.

**Characteristics of animal amylases in relation to enzyme source.** W. R. THOMPSON and I. FRIEDMAN (J. Gen. Physiol., 1936, 19, 807—828).—Specificity of the amylases is dependent on species rather than on organ source. The activities of pigs pancreatin, depancreatized dog's serum, and human saliva appear to be due to single chemical substances, that of



saliva being reversibly dissociable. Human and pig's amylases have a common amylolytic radical.

H. G. R.

**Effect of temperature and hydrogen-ion concentration on the  $\alpha$ -amylase of cow's milk.** A. SCHLOEMER (Z. Unters. Lebensm., 1936, 71, 311—318).—The amylase of milk is an  $\alpha$ -amylase (Kuhn, A., 1925, i, 636). The optimum temp. for its activity is approx. 37°, but the optimum and max. temp. for activity and stability vary with the concn. of enzyme, salt, and [H<sup>+</sup>]. The optimum  $p_H$  is 6.3—6.7, but this  $\propto$  the nature of the activators and buffer salts present. Neither dilution nor cold storage affects activity.

E. C. S.

**Activity of amylase solutions in presence of organic salts.** M. E. ALESSANDRINI (Annali Chim. Appl., 1936, 26, 156—162).—The activity of H<sub>2</sub>O-glycerol solutions of malt or fungus amylase is not destroyed by Na lactate (I), citrate (II), or formate (III). If well prepared, the solutions retain their activity indefinitely. In aq. solution the activity is retained longer in the presence of the salts, especially (II) and (III).

L. A. O'N.

**Increase of the amount of active amylase in ungerminated cereals by hydrogen sulphide and papain.** T. CHRZĄSZCZ and J. JANICKI (Biochem. Z., 1936, 285, 47—54).—The amount of active amylase (I) in extracts of ungerminated barley can be increased by H<sub>2</sub>S to an even greater extent than by papain, the effect being reversed by replacing H<sub>2</sub>S by N<sub>2</sub>. The effect is not due to the freeing by H<sub>2</sub>S of (I) bound to protein, but is more probably due to a mobilisation or setting free of activators present in the cereals.

P. W. C.

**Amylase of rye during development and ripening.** T. CHRZĄSZCZ and J. JANICKI (Biochem. Z., 1936, 286, 13—19).—The saccharifying fraction of the amylase suffers partial inactivation as ripening proceeds, whilst the starch-liquefying and dextrin-producing fractions suffer almost complete inactivation because they are progressively adsorbed by sisto-substances which increase in amount as ripening advances. If the stage of development is not too far advanced addition of peptone (as cleuto-substance) counteracts the inactivation. The partial loss of saccharifying power is probably chiefly due to oxidation of the activators which stimulate this power. The views of Purr (A., 1934, 934) and Nordh *et al.* (A., 1932, 303) are contradicted in part.

W. McC.

**Taka-amylase. XI—XIII.** T. KITANO (J. Soc. Chem. Ind. Japan, 1936, 39, 163—165b; cf. this vol., 519).—The adsorption of amylase and maltase from taka-diaxase solutions by Pb and Ca phosphates, ortho-(AlOH)<sub>3</sub>- $\gamma$ , and poly-Al(OH)<sub>3</sub>-A has been determined at various [H<sup>+</sup>]. CaC<sub>2</sub>O<sub>4</sub> does not adsorb the enzymes.

P. G. C.

**Semi-micro-method for iodometric determination of maltose in studies of amylase action.** M. L. CALDWELL, S. E. DOEBBELING, and S. H. MANIAN (Ind. Eng. Chem. [Anal.], 1936, 8, 181—183).—The procedure combines the recommendations of Caldwell *etc.* (cf. this vol., 519) with the micro-method of Linderstrom-Lang and Holter (cf. A., 1933, 864).

E. C. S.

**Specificity of glucosidases.** E. HOFMANN (Biochem. Z., 1936, 285, 429—447).—Tables summarise results of the action of glucosidases of horse kidney, liver, and intestinal mucosa on a variety of  $\beta$ -glucosides and  $\beta$ -galactosides. Differences in  $p_H$  optima, velocity of reaction, *etc.* are so great as to oppose the view that there is only a small no. of sp. glucosidases.

P. W. C.

**Formation of milk sugar. *In-vitro* synthesis of lactose by active mammary gland preparations.** A. P. WEINBACH (J. Gen. Physiol., 1936, 19, 829—841).—Mammary glands of lactating rats, dried in vac. while frozen, yield a non-fermentable reducing substance on incubation with glucose alone or with pig's serum + glucose, galactose, or lactose.

H. G. R.

**Existence of a lipase in fatty tissue.** G. QUAGLIARIELLO and G. SCOZ (Arch. Sci. biol., 1932, 17, 513—529; Chem. Zentr., 1935, ii, 1733).—The lipase (I) content of subcutaneous fatty tissue in dogs is approx. the same as that of the stomach. The (I) is almost equally active towards lower and higher triglycerides, is activated by bile salts, CaCl<sub>2</sub>, quinine (II) (high concns.), and ovalbumin, and inhibited by NaCl, (II) (low concns.), and atoxyl. The glycerol extract of the tissue also contains an enzyme which hydrolyses atoxyl, liberating H<sub>3</sub>AsO<sub>3</sub>.

A. G. P.

**Influence of ketonic substances on serum-lipase.** J. BENEDICT and G. MAYER (Biochem. Z., 1936, 285, 299—305).—Serum-lipase (guinea-pig, man) is not inhibited by COMe<sub>2</sub> *in vitro* in concns. up to 0.35% but is inhibited, especially with guinea-pig lipase, by  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hydroxybutyric acids (most by the  $\gamma$ - and least by the  $\beta$ -acid), inhibition being complete with 0.13—0.16% of acid.

P. W. C.

**Structure and properties of esterases. II. Relationship of ascorbic acid and liver-esterase.** W. VON PANTSCHENKO-JUREWICZ and H. KRAUT (Biochem. Z., 1936, 285, 407—419).—Preps. of liver esterase (I) possess the strong reducing properties characteristic of ascorbic acid (II). The (I) "pheron" or carrier (A., 1935, 251) acquires (I)-activity on adding (II). The blood- and liver-(I) contents of living animals increase on administration of (II). The reaction is not a simple one, however, since the amount of (II) required to reactivate the carrier far exceeds that detectable in (I) preps.

P. W. C.

**Formation of intermediate products during pancreatic digestion of neutral fats.** C. ARTOM and L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 883—884).—Partial hydrolysis (triglyceride hydrolysis, 6—55%) of olive oil by aq. extracts of dog's pancreas yields a product the Ac and sap. vals. of which indicate the presence of mono- and/or di-olein.

F. O. H.

**Products of synthetic action of pancreatic lipase on oleic acid and glycerol.** C. ARTOM and L. REALE (Boll. Soc. ital. Biol. sperim., 1935, 10, 884—886).—Dog's pancreas preps. with oleic acid and glycerol at 38° for 3—10 days produce mainly di- with some mono-olein when the synthesis is 50—55% complete and tri-+di-olein when 55—65% complete.

F. O. H.

**Castor-bean lipase. IX. Enzymic oil synthesis and its activating substance.** E. TAKAMURA (J. Agric. Chem. Soc. Japan, 1936, 12, 401—405).—A substance (not dihydroxystearic acid) exists which activates lipase but, after air oxidation, retards fat synthesis, due to the changed oxidation-reduction potential. P. G. M.

**Action of adrenaline and insulin on proteolytic enzymes of blood.** FERRANTI and MICHELI (Boll. Soc. ital. Biol. sperim., 1935, 10, 956—957).—Injection of insulin (15 units) and adrenaline (1 mg.) into men respectively decreases and increases the blood-proteases. F. O. H.

**Proteolytic enzymes of human embryos at different stages of development.** E. BLUM, A. I. JARMOSCHKEVITSCH, and A. I. JAKOVTSCHUK (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 113—114).—The liver, kidney, intestine, and pancreas of the embryos contain dipeptidase from the 2nd month onwards. The intestine and pancreas, from the 5th—6th month, contain protease (I) and carboxypolypeptidase (II). Catheptic (I) [but not catheptic (II)] occurs in liver and kidney from the 3rd month onwards. W. McC.

**Isolation of crystalline pepsinogen from swine gastric mucosæ and its autocatalytic conversion into pepsin.** R. M. HERRIOTT and J. H. NORTHROP (Science, 1936, 83, 469—470).—Details of the isolation of pepsinogen (I) as a colourless protein crystallising in needles from 0.4-saturated  $(\text{NH}_4)_2\text{SO}_4$  at  $p_H$  5.2—5.6 are given. (I) is converted into pepsin at  $p_H$  4.6 by an autocatalytic reaction similar to the conversion of trypsinogen into trypsin; the change probably involves rupture of a peptide linking. L. S. T.

**Ascorbic acid as activator of hepatic cathepsin in presence of ionised or complex-forming metals.** A. BADINAND (Compt. rend., 1936, 202, 1714—1716).—The activation [which does not occur with dehydroascorbic acid (I)] of cathepsin by ascorbic acid (II) is enhanced by  $\text{Ca}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ , or  $\text{Zn}^{++}$ , but not by  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Pb}^{++}$ , or  $\text{Ti}^{+++}$ , whilst  $\text{Cu}^{++}$  has an inhibitory effect. Complexes containing  $\text{Fe}$ ,  $\text{Zn}$ ,  $\text{Pb}$ ,  $\text{Ti}$ ,  $\text{Ca}$ ,  $\text{Ba}$ ,  $\text{Mg}$ , or  $\text{Cu}$  with (I) or (II) are also active. F. O. H.

**Changes in the activity of the dipeptidases in the regenerating tissues of amphibians.** V. N. ORECHOVITSCH (Biochem. Z., 1936, 286, 91—92; cf. A., 1935, 779).—In the regenerating tails of tadpoles and axolotl, dipeptidase activity on the 2nd day after amputation is 2—2.5 times as great as in ordinary tissue and reaches its max. when regeneration is complete. Subsequently the activity decreases. W. McC.

**Effect of deuterium oxide on action of enzymes.** D. I. MACHT and H. F. BRYAN (J. Amer. Chem. Soc., 1936, 58, 729—731).—Methylene-blue is decolorised more rapidly by suspensions of muscle (I) (rat) and brain in saline containing  $\text{D}_2\text{O}$  (1 in 100—5000) than in aq. saline; a similar acceleration is found for aq.  $\text{D}_2\text{O}$  (1 in 500—2000) extracts of *Lupinus albus* seeds (II) compared with aq. extracts.  $\text{H}_2\text{O}_2$  is decomposed more rapidly by catalase from (I) and

(II) in presence of  $\text{D}_2\text{O}$  (1 in 100). In some cases the more conc. solutions of  $\text{D}_2\text{O}$  cause an initial retardation which is followed by a more marked acceleration. H. B.

**Action of heavy water on fumarase and phosphatase systems.** PEREIRA-FORJAZ and K. P. JACOBSON (Bull. Soc. Chim. biol., 1936, 18, 926—931).—The enzymes are not inhibited by  $\text{D}_2\text{O}$  and it is probable that its action *in vivo* is due to changes in membrane diffusion. H. G. R.

**Fermentation co-enzyme.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1936, 285, 156—158).—The mixture of phosphoric esters obtained from horse red corpuscles (this vol., 377) contains both  $\text{H}_2$ -transporting co-enzyme (I) and fermentation co-enzyme (II). A method for the separation of (I) and (II) is described. (II) contains 13% N, 8% P [(I) contains 13% P], and on hydrolysis gives adenine and nicotinamide. P. W. C.

(A) **Cozymase.** H. VON EULER, H. ALBERS, and F. SCHLENK. (B) **Pyridine as the active group of dehydrogenating enzymes.** O. WARBURG and W. CHRISTIAN (Biochem. Z., 1936, 286, 140—141, 142).—Polemical and claims to priority. W. McC.

**Glycolysis and phosphate metabolism in cell-free extracts of mammalian brain.** H. VON EULER, G. GÜNTHER, and R. VESTIN (Z. physiol. Chem., 1936, 240, 265—278).—Glycolysis in the extracts (calf, rabbit, rat) requires the presence of  $\text{PO}_4'''$ , although not in the amounts required for glycolysis in muscle. In presence of  $\text{NaF}$ ,  $\text{AcCO}_2\text{H}$  and hexose diphosphate interact in the extracts to produce lactic acid and phosphoglyceric acid as in muscle extracts. The process is activated by cozymase, heat-inactivated cozymase, adenylic acid, and adenosinetriphosphoric acid, but not by glutathione and cysteine. The best substrates for glycolysis by the extracts are glucose and fructose; the extent of degradation of glycogen is smaller and varies considerably. W. McC.

**Salivary phosphatase.** K. V. GIRI (Biochem. Z., 1936, 285, 306—310).—Saliva of adults and children contains a phosphatase, probably identical with urinary phosphatase, which hydrolyses Na glycerophosphate ( $p_H$  optimum 4—5) and more readily Na hexose diphosphate ( $p_H$  optimum 7), which can be dialysed without serious loss of activity and is not activated by  $\text{Mg}^{++}$  at  $p_H$  5. P. W. C.

**Yeast phosphatases.** W. SCHUCHARDT (Biochem. Z., 1936, 285, 448—456).—By selective inactivation by treatment with dil. acid or alkali (this vol., 521) yeast is shown to contain two isodynamic phosphatases, of which that with acid is able to hydrolyse all the investigated phosphoric esters ( $\alpha$ - and  $\beta$ -glycerophosphoric acids, hexose mono- and diphosphate, phosphopyruvic acid, and 3-phosphoglyceric acid), whilst that with alkali using brewery yeast shows considerable relative specificity which, however, is absent using pure cultures of yeast, especially when grown on wort-agar. P. W. C.

**Pyrophosphate of yeast cells. I. Behaviour of the pyrophosphate towards enzymes.** M. M. LEVITOV (Bull. Biol. Méd. Exp. U.R.S.S., 1936, 1,



106—108; cf. this vol., 522).—Adenosine triphosphate comprises < 10% of the total pyrophosphate of yeast. W. McC.

**Balance sheet of sugar fermentation by yeasts.** R. GUILLEMET (Bull. Soc. Chim. biol., 1936, 18, 941—958).—EtOH and CO<sub>2</sub> formed and unutilised sugar were determined during fermentation of glucose, fructose, sucrose, and maltose (I) by various yeasts. With (I), especially in a very dil. medium, the ratio of EtOH formed to reducing sugar utilised sometimes exceeds the theoretical yield of 51%, owing to auto-fermentation. The production of EtOH without CO<sub>2</sub> was also observed in fermentation of (I), particularly with small quantities of yeast. H. G. R.

**Nitrogen assimilation of yeast. VI. Assimilation of formol-titratable nitrogen compounds from beer-wort.** N. NIELSEN and A. LUND (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 13, 239—246).—There is a greater decrease in formol-titratable N (I) than in total N in wort during fermentation, as the former is much more readily assimilated by yeast. If the medium is so diluted that the whole of the assimilable N is taken up, only about 50—70% of (I) is assimilated. Autolysis causes small amounts of (I) to be liberated. E. A. H. R.

**Role of oximinopyruvic and acrylic acids in the synthesis of alanine by yeasts during alcoholic fermentation.** C. FROMAGEOT and P. DESNUELLE (Bull. Soc. Chim. biol., 1936, 18, 820—824).—Neither of these acids is an intermediate in the synthesis of alanine from AcCO<sub>2</sub>H. H. G. R.

**Effect of complex organo-metallic derivatives of vitamin-C on the fermenting power of brewer's yeast.** F. ARLOING, A. MOREL, A. JOSSEAND, L. THÉVENOT, and J. M. PERRET (Compt. rend. Soc. Biol., 1936, 122, 577—579).—Complexes containing Cu have a definite inhibiting action, whilst the accelerating action of other complexes occurs only if the metal is in the complex state (cf. this vol., 626). H. G. R.

**Effect of arsenates on fermentation.** O. MEYERHOF and W. KIESSLING (Naturwiss., 1936, 24, 361—362).—AsO<sub>4</sub><sup>'''</sup> increases the rate of fermentation of phosphopyruvic acid (I) up to the same val. as that of sugar. Fermentation and dephosphorylation of (I) occur only in the presence of a co-enzyme. Mg and the adenyllic acid system have co-enzymic activity, but cozymase is more active. The action of AsO<sub>4</sub><sup>'''</sup> is attributed to an accelerated decomp. of a cozymase pyrophosphate (II). M/500-AsO<sub>4</sub><sup>'''</sup> decomposes sufficient (II) in yeast maceration juice to account for the max. fermentation rate observed in the presence of AsO<sub>4</sub><sup>'''</sup>. (II) is obtained from cozymase by esterification with (I) and may be isolated as the Ba salt. Dephosphorylation of (I) is very rapid and is followed by decarboxylation of AcCO<sub>2</sub>H. The rate of decomp. of (II) determines the rate of fermentation of (I). This is a max. when (a) the PO<sub>4</sub><sup>'''</sup> formed can esterify sugars present, and (b) in the presence of M 500-AsO<sub>4</sub><sup>'''</sup> if sugars are absent. E. A. H. R.

**Incorporation of deuterium into growing organisms. IV.** F. SALZER and K. F. BONHOEFFER (Z. physikal. Chem., 1936, 176, 202—208; cf. this

vol., 639).—Yeast has been grown in culture solutions of sucrose (I) in heavy H<sub>2</sub>O. D was assimilated in a form which could not be washed out and the ratio of the D content of the H of the dry substance of the yeast to that of the H of the H<sub>2</sub>O was approx. 0.42. The D contents of the H of the mixture of amino-acids, the glycogen (II), and the cell-wall hemicelluloses (III) isolated from the yeast were approx. 11, 3, and 15%, respectively. It is inferred that (II) is elaborated from the original (I) in a more direct way than is (III). Only (III) has a D content approx. the same as that of the total dry substance of the yeast. R. C.

**Conjugated action of follicular hormone and mineral catalysts on growth of yeast.** G. BERTRAND and A. P. WEBER (Compt. rend., 1936, 202, 1629—1632).—The increased growth of two species of *Rhodotorula* due to follicular hormone is further enhanced by addition of a mixture of traces of B, I, Cu, Mn, Tl, and Zn; of these catalysts Zn has an outstanding effect. F. O. H.

**Action of follicular hormone on growth of micro-organisms.** A. LUND (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 12, 231—238).—The growth of *Aspergillus niger* and *Saccharomyces cerevisiae* is unaffected by both commercial progynon and pure follicular hormone. E. A. H. R.

**Relation of accessory substances to heavy metals, including molybdenum, in the nutrition of *Aspergillus niger*.** R. A. STEINBERG (J. Agric. Res., 1936, 52, 439—448).—Accessory growth substances are not required by *A. niger*. Decreased growth following the use, in media, of sugar purified by EtOH (to remove bios and co-enzyme R) is due to removal of Mo and Zn in the process. Beneficial effects of yeast, malt extract, etc., usually ascribed to accessory substances, may also be due to heavy metals thus introduced into media. A. G. P.

**Influence of hydrogen acceptors on the fermentation of fucose by *Aspergillus oryzae*.** T. TADOKORO (Bull. Chem. Soc. Japan, 1936, 11, 239—247).—Fermentation of fucose by *A. oryzae* gives kojic, glycollic (I), and lactic (II) acids, a little H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, a keto-acid (? glycuronic acid), m.p. 155—158°, possibly citric and tartaric acid, and glyceraldehyde. In presence of Me-blue maleic acid is obtained in place of (I) and (II). R. S. C.

**Production of acids from sugar by *Aspergillus niger*. VI. Factors affecting accumulation of citric acid.** K. BERNHAUER and A. IGLAUER (Biochem. Z., 1936, 286, 45—59; cf. A., 1932, 1168).—Best yields of the acid are obtained when the sugar concn. is 17.5—20% (yield 70%) and when the experimental details given are closely followed. Suitable strains of *A. niger* propagated as described must be used. W. McD.

**Conversion of acetic into citric acid by moulds.** T. CHRZĄSZCZ and M. ZAKOMORNY (Biochem. Z., 1936, 285, 340—347).—Strains of *A. niger* grow on Ca(OAc)<sub>2</sub> and convert it chiefly into citric acid (I) or into (I) —H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (II), addition of small amounts of sugar having a favourable effect on the reaction. Mycelia feebly growing due to unfavourable media and old

mycelia gave little (I) but considerable yields of (II). The view that (I) arises from mycelial substances is incorrect. The formation of aconitic acid as an intermediate was not detected. P. W. C.

**Significance of malic acid in the conversion of acetic to citric acid by moulds.** T. CHRZASZCZ and M. ZAKOMORNY (Biochem. Z., 1936, 285, 348—355).—Addition of *l*-malic acid (I) (Na salt) to a medium containing 4% of  $\text{Ca}(\text{OAc})_2$  (II) led, with strains of *A. niger*, to increased formation of citric acid (III), the effect being almost as great as that on addition of small amounts of sugar (cf. preceding abstract). Free AcOH or (I) is toxic. Addition of 0.5% (I) (Na salt)+0.5% sugar had a better effect on the production of (III) than that of 2% sugar, the amount of (III) formed increasing to 50% of the (II) used. The conversion of sugar into (III) thus requires the simultaneous presence of  $\text{AcOH} + (\text{I})$ . P. W. C.

**Biochemistry of filamentous fungi. IV. Mycelial constituents of *Oospora sulphureo-ochracea*.** I. H. NISHIKAWA (Bull. Agric. Chem. Soc. Japan, 1936, 12, 47—50).—This mould was grown on koji wort of 8° Balling at 20°; 1.2 g. of dried mycelium is obtained per 100 c.c. of medium. Extraction of the powdered mycelium with  $\text{Et}_2\text{O}$  yields three cryst. compounds,  $\text{C}_{17}\text{H}_{16}\text{O}_8$ , needles, m.p. 214° (from EtOH), giving a violet colour with  $\text{FeCl}_3$ -EtOH;  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , pale yellow needles, m.p. 257° (decomp.), from AcOH, sol. in NaOH but insol. in  $\text{NaHCO}_3$ , giving a green colour with  $\text{FeCl}_3$ -EtOH;  $\text{C}_{17}\text{H}_{16}\text{O}_8$ , rhombs, m.p. 200° (with effervescence), from EtOH, giving no colour with  $\text{FeCl}_3$ . A fourth compound, (?)  $\text{C}_{18}\text{H}_{18}\text{O}_8$ , m.p. 190°, is sometimes obtained. P. G. M.

**Content of vitamin- $B_1$  in wheat-germ extracts.** W. H. SCHOPFER and A. JUNG (Compt. rend. Soc. Biol., 1936, 122, 249—251).—The effect of wheat-germ extracts on the growth of *Phycomyces* is partly due to presence of vitamin- $B_1$ . F. O. H.

**Production of vitamins by *Aspergillus oryzae*.** A. SCHEUNERT and M. SCHIEBLICH (Biochem. Z., 1936, 286, 66—71).—*A. oryzae* grown on a mixture free from vitamins produces vitamin- (6 international units from 1 g.) and about twice as much  $-B_2$  as occurs in dry yeast, but no  $-A$ . W. McC.

**Production by moulds and bacteria of substances similar to vitamin-C.** K. BERNHAUER, B. GORLICH, and E. KOCHER (Biochem. Z., 1936, 286, 60—65).—*Aspergillus niger* produces a reducing substance (I) similar to ascorbic acid from sucrose (II), glycerol, sorbitol, and inositol and, in poorer yield, from glucose, mannose, galactose, fructose, sorbose, and lactose. The amount of (I) produced from (II) increases as the (II) concn. increases, the max. yield being attained in 15—25 days. The optimal  $p_H$  for the process is 2.8—3.0. Production of (I) is stimulated by the presence of free acid (citric) and the yield increases as the acid concn. is increased. W. McC.

**Action of *p*-aminophenylsulphamide on moulds.** E. FOURNEAU, J. TREFOUEL, (MME.) J. TRÉFOUEL, F. NITTI, and D. BOVET (Compt. rend. Soc. Biol., 1936, 122, 652—654).—An inhibition of growth

occurs which, in a series of derivatives, runs parallel to the anti-streptococcal activity. H. G. R.

**Invasiveness of skin infections caused by pathogenic fungi and subsurface mycelium.** J. W. WILLIAMS (Science, 1936, 83, 396—397).—The ability of various fungi to invade various solid media with hydrolysed hair or skin as the source of N has been studied and the changes produced are recorded. L. S. T.

**Symbiosis and digestion of cellulose in termites and in mammals.** U. PIERANTONI (Boll. Soc. ital. Biol. sperim., 1935, 10, 944—946).—Utilisation of cellulose due to symbiotic protozoa in the intestines of animals is discussed with special reference to symbiosis of flagellates and termites. F. O. H.

**Blood-iron in experimental *Trypanosoma annamense* infection in rabbits.** L. LAUNOY and H. LAGODSKY (Compt. rend. Soc. Biol., 1936, 122, 633—636).—A diminution in the red cells,  $d$ , and respiratory capacity of the blood was observed. H. G. R.

**Surface electric charge of micro-organisms.** N. CHOUCROUN (Compt. rend., 1936, 202, 1711—1714).—Characteristic variations in the electrophoretic potential of bacteria are discussed. F. O. H.

**Fermentation of dibasic  $C_4$ -acids by *Aerobacter aerogenes*.** H. A. BARKER (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 674—683).—The fermentation of *d*-tartaric (I), *d*-malic, *l*-malic (II), fumaric (III), maleic, and succinic (IV) acids by *A. aerogenes* was investigated. Only (I), (II), and (III) were decomposed. The fermentation appears to proceed by an initial oxidation-reduction between 2 mols. of the substrate, thus accounting for the formation of (IV) in the process. In the decomp. which follows there is no direct splitting of a  $C_4$  mol. into 2  $C_2$  mols.;  $\text{AcCO}_2\text{H}$  is first formed, and this undergoes further decomp. into  $\text{HCO}_2\text{H}$  and AcOH or  $\text{CO}_2$  and MeCHO. Further degradation of  $\text{HCO}_2\text{H}$  may account for the small amounts of  $\text{H}_2$  formed; the presence of EtOH may be due to MeCHO acting as a H-acceptor for the dehydrogenation of (III). E. A. H. R.

**Influence of various sources of carbon on the nitrogen metabolism of *B. perfringens*.** D. GRINEV, D. GORFUNKEL, E. CHAPIRO, and J. GURVITSCH (Bull. Inst. Metchnikoff, 1936, 1, 65—68).—Carbohydrates, alcohols, and salts of org. acids exercise different effects on the N metabolism of *B. perfringens*. W. O. K.

**Hydrogen donators for pneumococcus.** D. BACH (Compt. rend. Soc. Biol., 1936, 122, 558—560).— $\text{AcCO}_2\text{Na}$  added to the culture preserves the activity of glucose-dehydrogenase. H. G. R.

**Nitrogenous nutrition of propionic bacteria.** I. II. Utilisation of ammonia nitrogen. C. FROMAGEOT and P. LAROUX (Bull. Soc. Chim. biol., 1935, 18, 797—811, 812—819).—I. Growth of propionic bacteria in a broth containing decorticated, crushed maize is appreciable only in presence of  $\text{NH}_4$  salts of org. or weak mineral acids.



II. Maize contains a substance enabling propionic bacteria to utilise  $\text{NH}_4\text{-N}$  as a sole source of N.

H. G. R.

**Dehydrogenation in presence of nitrate.** E. AUBEL and F. EGAMI (Compt. rend. Soc. Biol., 1936, 122, 248—249).—The action of various poisons indicates that bacterial dehydrogenation (optimum  $p_{\text{H}}$  9—9.5) of lactic acid in presence of methylene-blue differs from that when  $\text{KNO}_3$  is the  $\text{H}_2$  acceptor; no differentiation is apparent with *l*-alanine as substrate and O and  $\text{KNO}_3$  as  $\text{H}_2$  acceptors. F. O. H.

**Dehydrogenation of lactic acid by staphylococci.** M. G. SEVAG and N. NEUENSCHWANDER-LEMMER (Biochem. Z., 1936, 286, 7—12).—*S. aureus* and *S. albus* convert lactic acid (I) to the extent of 92 and 85% into  $\text{AcCO}_2\text{H}$ , no  $\text{MeCHO}$ ,  $\text{AcOH}$ , or succinic acid being produced. The organisms do not attack  $\text{AcCO}_2\text{H}$  and  $\text{AcOH}$ . With (I), glucose, and glycerol as substrate they consume  $\text{O}_2$  and liberate  $\text{CO}_2$ . W. McC.

**Formation of cadaverine from lysine.** A. I. VIRTANEN and T. LAINE (Suomen Kem., 1936, 9, B, 17—18).—Conversion of lysine (I) into cadaverine (II) by *B. coli* and *B. fluorescens liquefaciens* occurs when (I) is added to media or is acted on by washed bacterial suspensions. (I) is probably excreted from leguminous root nodules and the occurrence of (II) in soil is thus possible. A. G. P.

**Bacterioxanthophyll, the yellow pigment of *Sarcina lutea*.** T. NAKAMURA (Bull. Chem. Soc., Japan, 1936, 11, 176—179).—Evaporation of a  $\text{MeOH}$  extract of *S. lutea* gives a residue, from which a little  $\text{MeOH}$  dissolves the pigment preferentially. Dilution with  $\text{H}_2\text{O}$  (2.3 parts) and extraction with  $\text{Et}_2\text{O}$  gives a crude pigment, shown by colour reactions, solubility, oxidation by  $\text{H}_2\text{O}_2$ , reduction by  $\text{Mg-HCl}$ , absorption spectrum (max. at 490, 460, and 433  $\text{m}\mu$  in  $\text{CS}_2$ ), and saponification to be an ester of xanthophyll type. The pigment is adsorbed on  $\text{Al}_2\text{O}_3$  etc., but is difficult to elute; it gave traces of crystals. R. S. C.

**Lipins of tubercle bacilli. XLV. Isolation of  $\alpha$ - and  $\beta$ -leprosol.** J. A. CROWDER, F. H. STODOLA, and R. J. ANDERSON. XLVI. Phthiocerol, an alcohol from the wax of the human tubercle bacillus. F. H. STODOLA and R. J. ANDERSON (J. Biol. Chem., 1936, 114, 431—439, 467—472; cf. this vol., 899).—XLV. The viscous, unsaponifiable matter from the  $\text{COMe}_2$ -sol. fat from *B. leprae*, when treated with ligroin, gives a mixture, resolved by way of the acetates (prep. by  $\text{C}_5\text{H}_5\text{N-Ac}_2\text{O}$ ) into  $\alpha$ - (I), m.p. 100—101° [acetate, m.p. 69—70°; *Br*-derivative, m.p. 66—67° (resolidifies at 59°, remelts at 73—74°)], and  $\beta$ -leprosol (II),  $\text{OH}\cdot\text{C}_{25}\text{H}_{42}\cdot\text{OMe}$ , m.p. 84—85° (acetate, m.p. 47—48°, resolidifies at 45°, remelts at 51—52°; *Br*-derivative, m.p. 42°, remelts at 45—46°; 3:5-dinitrobenzoate, m.p. 86—87°; urethane, an oil). With HI (I) and (II) give compounds (III),  $\text{C}_{25}\text{H}_{42}(\text{OH})_2$ , m.p. 113—114° and 104—105°, respectively, the latter giving a diacetate, m.p. 48°. (I) and (II) are indifferent to  $\text{CH}_2\text{N}_2$ , but with  $\text{Me}_2\text{SO}_4\text{-KOH}$  in aq.  $\text{EtOH}$  give *Me ethers* (called leprosol *Me*, ethers),  $\text{C}_{25}\text{H}_{42}(\text{OMe})_2$ , m.p. 78—79° (remelts at 80—81°) and 70°, respectively, which are not obtained from (III).

(I) and (II) give no sterol colour reactions, but give a ppt. with digitonin, and are feebly acidic; (I), (II), and (III) give  $\text{FeCl}_3$  and phosphomolybdate reactions. They probably contain a  $\text{C}_6\text{H}_6$  ring carrying the OH and OMe.

XLVI. Hydrolysis of the wax, m.p. 55—56°,  $[\alpha]_D^{25} +0.55^\circ$  in  $\text{CHCl}_3$ , from human tubercle bacilli gives no *d*-eicosan- $\beta$ -ol or *d*-decan- $\beta$ -ol, but affords phthiocerol,  $\text{C}_{34-35}\text{H}_{67-69}(\text{OH})_2\cdot\text{OMe}$ , m.p. 73—74°,  $[\alpha]_D^{25} -4.8^\circ$  in  $\text{CHCl}_3$  (diacetate, m.p. 37—38°; HI gives a hydrocarbon,  $\text{C}_{34}\text{H}_{70}$ , m.p. 58.5—59.5°, stable to Br and giving no colour in the Liebermann-Burchard reaction, probably identical with phytoglycol (A., 1934, 699). R. S. C.

**Phosphorus-containing lipins from human tubercle bacillus.** K. BLOCH (Biochem. Z., 1936, 285, 372—385).—Anderson's A3 phosphatide does not contain an org. N base, the N content being due to impurities, and cannot be any known aminophosphatide or sphingomyelin. By warming with  $\text{COMe}_2$  an unsaponifiable substance AII, m.p. 37°, separates which contains neither P nor N, does not give sterol reactions, and appears to be a wax alcohol. Treatment with dil.  $\text{HCl}$  removes org. bound Mg, and two phosphatides can then be separated: AI, P 3.55%, insol. in  $\text{COMe}_2$ , almost N-free, high m.p. and non-hygroscopic; B, P 2.44%, N < 0.1%, yellow oil, sol. in warm  $\text{COMe}_2$ . Substances AI and B probably are similar in structure excepting that in B the unsaturated and saturated liquid fatty acids predominate. The carbohydrate content of A3 is not chemically bound to the phosphatide. P. W. C.

**Medium for production of a highly active tetanus toxin.** M. GLUSMANN, M. TCHERVIKOV, and G. STAROBINETZ (Bull. Inst. Metchnikoff, 1936, 1, 51—52).—The medium is prepared from a peptone produced by autoclaving meat protein with dil.  $\text{HCl}$  under 2 atm. pressure. W. O. K.

(A) Nitrogen metabolism of *B. tetanus*. (B) Comparisons of strains of different toxicity. D. GRINEV, D. GORFUNKEL, E. CHAPIRO, and J. GURVITSCH (Bull. Inst. Metchnikoff, 1936, 1, 47—48, 49—50).—(A) When *B. tetanus* (I) is grown on peptone media, the changes in various N fractions depend on the type of peptone employed.

(B) The N metabolism of various strains of (I) is the more intense the greater is the activity of the toxins which they produce. W. O. K.

**Chemistry of the somatic antigen of dysentery bacillus.** L. MESROBEANU and G. CALALB (Compt. rend. Soc. Biol., 1936, 122, 496—497).—The fatty acid and sugar contents of various strains are tabulated.

H. G. R.

**Toxicity and specificity of the somatic antigen of dysentery bacillus.** G. CALALB and L. MESROBEANU (Compt. rend. Soc. Biol., 1936, 122, 497—499).—The antigens of the smooth forms have practically the same toxicity. Pptn. reactions with anti-sera at various dilutions are described. H. G. R.

**Staining of bacterial flagella.** S. LEVENSON (Ann. Inst. Pasteur, 1936, 56, 634—643).—Casares-Gil's method is improved by substituting Ag-impreg-

nation by means of aq.  $\text{NH}_3\text{-AgNO}_3$  for treatment with methylene-blue or other basic dye, after mordanting.

P. G. M.

**Luciferin-oxy-luciferin.**—See this vol., 938.

**Inactivation of bacteriophage by ascorbic acid.** I. LOMINSKI (Compt. rend. Soc. Biol., 1932, 122, 766—768).—Ascorbic acid in very low concn. inactivates bacteriophage, the bacteria themselves being less sensitive. Cysteine hydrochloride and pyrogallol have a similar action.

A. L.

**Spontaneous reappearance of lytic activity of bacteriophage inactivated by heat.** I. LOMINSKI (Compt. rend. Soc. Biol., 1936, 122, 769—771).—Bacteriophage heated for 60—90 min. at 60° loses its activity, but reactivation takes place on keeping. The fixation of the bacteriophage by the bacteria is unaffected by the treatment.

A. L.

**Adaptation of bacteriophage to heat.** J. JADIN (Compt. rend. Soc. Biol., 1936, 122, 470—471).—By heating at successively increasing temp. for short periods, the resistance to heat is increased.

H. G. R.

**Ultrafilterability and probable dimensions of bacteriophages.** C. LEVADITI, M. PAIC, J. VOET, and D. KRASSNOFF (Compt. rend. Soc. Biol., 1936, 122, 354—358).—The diameters of various bacteriophages have been determined by ultrafiltration methods.

H. G. R.

**New group of filterable organisms.** P. P. LAIDLAW and W. J. ELFORD (Proc. Roy. Soc., 1936, B, 120, 292—303).—Three strains of a new group of saprophytic organisms have been isolated from sewage; these may be cultivated on artificial media. Each strain shows a marked variation in size, but the organisms are retained by filters of average pore diameter 0.25  $\mu$ . The small forms, which are of about the same size as vaccinia virus, yield cultures containing the large form.

F. A. A.

**Purification of ultra-virus.** V. DEUTSCH (Compt. rend. Soc. Biol., 1936, 122, 529—532).—Vaccinia virus cannot be eluted by Sato and Kodama's method. Ideal purification is not obtained by adsorption and elution, since protein passes into solution with the virus during elution.

H. G. R.

**Antiseptic and bactericidal power of diacetyl.** M. LEVY-BRUHL and Y. CADO (Compt. rend. Soc. Biol., 1936, 122, 373—374).—0.04% is bactericidal for certain pathogenic species.

H. G. R.

**Triethanolamine. [Action on bacteria.]** A. BERTHELOT, G. AMOUREUX, and F. VAN DEINSE (Bull. Soc. Chim. biol., 1936, 18, 652—655).—Technical  $\text{N}(\text{CH}_2\text{-CH}_2\text{-OH})_3$  (I) was without toxic action on a no. of bacteria at 7.3—7.8. In certain cases cultures were obtained when (I) was the only source of C and N.

A. L.

**Natto, or fermented soya bean.** I. Effect of the dipicolinic acid produced. S. UDO (J. Agric. Chem. Soc. Japan, 1936, 12, 386—394).—Accumulation of dipicolinic (pyridine-2:2'-dicarboxylic) acid (I) to a concn. of 1.2—1.5% completely suppresses the growth of *Bacillus natto*, which is also partly inhibited by the viscous substance produced around the soya-

bean grains. The growth of *B. subtilis* and of *Penicillium glaucum* is also inhibited by (I).

P. G. M.

**Chemotherapy of streptococcal infections by derivatives of p-aminophenylsulphonamide.** E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, F. NITTI, and D. BOVET (Compt. rend. Soc. Biol., 1936, 122, 258—259; cf. this vol., 232).—Orientation, replacement, or substitution of the  $\cdot\text{NH}_2$ , substitution of the  $\cdot\text{SO}_2\cdot\text{NH}_2$ , or introduction of a third group generally produces diminished anti-streptococcal activity. Diazotisation and coupling produces active derivatives.

F. O. H.

**Chemotherapeutic efficacy of arsenic compounds of sulphur-rich protein fission products.** W. A. COLLIER and M. KRAUSE (Z. Hyg. Infekt., 1935, 117, 190—195; Chem. Zentr., 1935, ii, 2083).—Condensation products of hydroxy-, amino-, and hydroxylamino-phenylarsine oxides with S-rich keratin fission products of high mol. wt. have been tested. The chemotherapeutic index (mice and rabbits) for the best prep. is 1:120 for trypanosomes and 1:20 for spirochaetes of relapsing fever.

H. N. R.

**Chemotherapeutic action on *Spirillum minus* in mice by certain anil- and styryl-quinoline compounds free from metals or metalloids.** C. H. BROWNING and R. GULBRANSEN (J. Pharm. Exp. Ther., 1936, 57, 56—66).—2-(p-Dimethylaminoanil)-6-acetamidoquinoline methochloride and methosulphate have a marked therapeutic action on *S. minus* infections of mice. Certain related compounds are also active, but to a smaller extent. No obvious relationship was detected between the degree of activity and chemical constitution.

W. O. K.

**Adrenaline binding by different protein substances, lipins, and ground muscular tissue.** J. T. BALABA (Platz. Utschen. Med., 1936, 231—235).—Certain proteins (e.g., caseinogen but not gelatin), peptone, and muscular tissue bind considerable quantities of adrenaline, the effect being increased by lactic acid.

W. O. K.

**Adrenaline secretion in hypophysectomised dogs.** L. KÉPINOV (Compt. rend. Soc. Biol., 1936, 122, 351—354).—After injection of large doses of insulin, the secretion of adrenaline is increased as the blood-sugar falls, the max. coinciding with the appearance of hypoglycæmic convulsions.

H. G. R.

**Adrenaline and the metabolic activity of the warm-blooded heart.** B. WEICKER (Arch. exp. Path. Pharm., 1936, 181, 525—540).—Lactic acid (I) and P fractions were determined in the muscles of the surviving cat's heart after coronary perfusion with adrenaline (II). Under aerobic conditions, therapeutic doses of (II) caused a slight increase of (I) and small changes in the sol. P. Toxic doses of (II) with the unfatigued heart caused cleavage of phosphagen, adenylyl pyrophosphate, and hexose esters with production of  $\text{PO}_4^{''}$ , but performance of work quickly caused resynthesis. There was a similar result under anaerobic conditions, and renewal of the  $\text{O}_2$  supply caused a resynthesis of cleavage products. With hearts poisoned with HCN, (II) increased (I) nearly 500%. The action of strophanthin is very similar to



that of (II), and the differences in degree of their action are discussed. J. N. A.

**Potassium: a basal factor in the syndrome of cortico-adrenal insufficiency.** R. L. ZWEMER and R. TRUSZKOWSKI (*Science*, 1936, **83**, 558—560).—An important function of the adrenal cortex is the regulation of K metabolism and known symptoms of cortico-adrenal insufficiency may be due to a disturbance of cortico-adrenal-K relationships. The beneficial effect of cortin in certain other pathological conditions suggests that the same mechanism is involved. L. S. T.

**Antagonistic action of adrenal cortex hormone towards the fat- and carbohydrate-metabolism hormones of the anterior pituitary gland.** K. J. ANSELMINO, F. HOFFMANN, and E. RHODEN (*Arch. exp. Path. Pharm.*, 1936, **181**, 325—327).—Simultaneous administration of adrenal cortex hormone inhibits the ketogenic (indicated by fall in blood-COMe<sub>2</sub>) and liver-glycogenolytic actions of anterior pituitary fat- and carbohydrate-metabolism hormones (either as crude or purified preps.), respectively. F. O. H.

**Action of the fat metabolism hormone of the anterior pituitary on the saturated and unsaturated fatty acids of the liver.** K. J. ANSELMINO, G. EFFKEMANN, and F. HOFFMANN (*Z. ges. exp. Med.*, 1935, **96**, 209—220; *Chem. Zentr.*, 1935, ii, 1736).—Serum of individuals who have eaten a fat meal, injected into pigeons or rats, causes a rise of unsaturated fatty acids in the liver, which reach a max. in 6 hr. Total fat falls when the initial val. is low, and rises when it is high. Pituitary extracts that contain the fat-metabolism hormone (I) exert the same effects. The active material of the serum is similar to (I) in its ultrafilterability, thermostability, solubility, and response to acids and alkalis; the two are probably identical. R. N. C.

**Liver enlargement following administration of anterior pituitary and organ extracts.** G. EFFKEMANN and L. HEROLD (*Z. ges. exp. Med.*, 1935, **96**, 195—208; *Chem. Zentr.*, 1935, ii, 1736). R. N. C.

**Anterior pituitary hormone and the male genital apparatus: problem of puberty.** G. PIGHINI (*Biochim. Terap. sperim.*, **20**, 161—183; *Chem. Zentr.*, 1935, ii, 1903). R. N. C.

**Action of anterior pituitary sex hormones on different endocrine glands (pancreas, adrenals, pituitary, thyroid) after ligation of the deferentiae.** G. LUCARELLI (*Biochim. Terap. sperim.*, **20**, 10—13; *Chem. Zentr.*, 1935, ii, 1903). R. N. C.

**Thyrotropic hormone of the pituitary gland and iodine metabolism.** B. F. STIMMEL, D. R. McCULLAGH, and V. PICHA (*J. Pharm. Exp. Ther.*, 1936, **57**, 49—55).—Administration of the thyrotropic pituitary hormone (I) to chicks and guinea-pigs lowers the I content of the thyroid. A method for the assay of (I) based on this observation is suggested. (I) is partly inactivated by heating at 100° for 15 min. W. O. K.

**Amount of thyroid-stimulating hormone in the anterior lobe of the pituitary of the thyroid-**

**ectomised rabbit.** G. CHEN and H. B. VAN DYKE (*Chinese J. Physiol.*, 1936, **10**, 285—296).—Thyroidectomy in young female rabbits results, in three months, in an increase in the thyrotropic hormone (I) content of the anterior lobe of the pituitary. No increase in (I) in male rabbits is observed, although hypertrophy of the pituitary is greater. No sexual difference occurs in the total (I) content in normal rabbits. The H<sub>2</sub>O content of hypertrophied is > that of normal pituitary. F. A. A.

**Method for obtaining a preparation of the melanophore hormone of the pituitary gland.** R. L. STEHLE (*J. Pharm. Exp. Ther.*, 1936, **57**, 1—5).—From by-products obtained in the isolation of the pressor and oxytocic principles of the posterior lobe of the pituitary (cf. this vol., 643) a brown hygroscopic powder has been prepared 25 times as potent in its melanophore-dilating action as the standard pituitary powder and having only slight pressor and oxytocic activity. It contains N 14.6, tyrosine 2.9, and cystine 1—2%, and its action is increased by previous treatment with 0.1N-NaOH at 100° (cf. Jores, *Z. ges. exp. Med.*, 1933, **87**, 266). W. O. K.

**Ovarian hormones and carbohydrate metabolism.** E. DE AMILIBIA, M. M. MENDIZABAL, and J. BOTELLA-LLUSIA (*Klin. Woch.*, 1935, **14**, 900—901).—Follicular hormone (I) raises and corpus luteum hormone (II) lowers blood-sugar in young female rabbits after 24 hr.; the effects are abolished by thyroidectomy. Liver-glycogen in rats is lowered by (I) and raised by (II). R. N. C.

**The oestrogenic and gonadotropic hormones in epithelioma of the neck of the uterus.** R. IMBERT, M. MOSINGER, and H. BONToux (*Compt. rend. Soc. Biol.*, 1936, **122**, 692—694).—Hyperfolliculinæmia occurs with ovarian tumours and epitheliomata and is also caused by X-ray or Ra treatment. In cases of epithelioma, an inverse proportionality between prolan-A and folliculin is observed and, despite an increase in prolan-B, no dependence on the oestrogenic hormone was observed. H. G. R.

**Ovarian hormonal antagonism caused by the two crystalline hormones.** R. COURRIER (*Compt. rend. Soc. Biol.*, 1936, **122**, 661—664).—The activity of 1.5 mg. of progesterin is neutralised by approx. 0.04 mg. of dihydrofolliculin. H. G. R.

**Hormones of urine of pregnancy and cholesterolæmia.** L. CIOGLIA (*Boll. Soc. ital. Biol. sperim.*, 1935, **10**, 890—892).—Injection of urine from women during the first 4 months of pregnancy produces hypercholesterolemia in rabbits; during the last 4 months the urine is normally inactive, but after Et<sub>2</sub>O extraction (which tends to increase the activity of the early urine) it is active owing to removal of follicular hormone which, in large doses, produces hypocholesterolemia (cf. A., 1935, 667, 1174). F. O. H.

**Influence of oestrogens on the prostate gland.** S. ZUCKERMAN (*Nature*, 1936, **137**, 1032). L. S. T.

**Synthetic oestrogenic agents without the phenanthrene nucleus.** E. C. DODDS and W. LAWSON (*Nature*, 1936, **137**, 996).—Oestrogenic activities for various org. compounds are tabulated. The phen-

anthrene condensed ring structure is not necessary for this activity, and *p*-(OH)<sub>2</sub>-derivatives of Ph<sub>2</sub> and CH<sub>3</sub>Ph<sub>2</sub> are the only ones so far found to be active.

L. S. T.

Mechanism of the action of sexual (follicular) hormone. III. State of the pituitary. P. HAUPTSTEIN (Klin. Woch., 1935, 14, 1103—1107).

R. N. C.

Products of ultra-violet irradiation of follicular hormone. M. LAPORTA and C. VACCA (Atti R. Accad. Lincei, 1936, [vi], 23, 212—215).—The irradiated hormone retains its oestrogenic activity (the produced oestrus persists for a period > that due to the normal hormone), but completely loses its anti-masculine character and hypercalcaemic action; [ $\alpha$ ] and m.p. are decreased.

F. O. H.

Follicle-stimulating hormone in the urine of vegetative-stigmatised young men with generative disturbance. H. GOLDHAMMER and P. LOEWY (Klin. Woch., 1935, 14, 704—705).

R. N. C.

Action of the male hormone on the sexual characteristics of the crested triton: test for the hormone. A. BEAUNE and R. FALK (Compt. rend. Soc. Biol., 1936, 122, 721—723).—The development of sexual characteristics in the male crested triton (*T. cristatus*), castrated by withdrawal of food, may be used as a test for the male hormone. A. L.

Anti-masculinising action of the male hormone. C. CHAMPY (Compt. rend. Soc. Biol., 1936, 122, 631—632).—Given in large doses (10—12 times the dose of folliculin required to show the same effect) testosterone acetate exhibits an anti-masculinising action in the castrated silver pheasant, which is an ideal species to demonstrate this characteristic.

H. G. R.

Masculinising action on the guinea-pig of water-soluble extracts of ox adrenal. D. HODLER (Compt. rend. Soc. Biol., 1936, 122, 512—514).—Alkaline H<sub>2</sub>O-sol. extracts of adrenal cortex have a masculinising action on females and castrated males.

H. G. R.

Sexual periodicity and the causes which determine it. F. H. A. MARSHALL (Nature, 1936, 137, 1056—1057).

L. S. T.

Sex hormones. XIV, XV.—See this vol., 991.

Intensity of action of insulin in healthy and diseased men. F. MEYTHALER and G. SCHROFF (Klin. Woch., 1935, 14, 893—894).—The disturbance of carbohydrate metabolism by insulin is overcome in 1½ hr. in healthy men. With a disturbed liver function the intensity of action is increased, whilst with pituitary and adrenal disturbances it shows characteristic changes.

R. N. C.

Interpretation of the hypoglycaemia (recovery) curve obtained after injection of insulin in the dog. E. AUBERTIN and R. CASTAGNOU (Compt. rend. Soc. Biol., 1936, 122, 826—829).—The shapes of different types of curves obtained are discussed.

A. L.

Hypoglycaemic action of insulin in partial pancreatectomy in dogs. E. AUBERTIN, A. LACOSTE, R. CASTAGNOU, and R. SARIC (Compt. rend. Soc. Biol., 1936, 122, 830—834).—In partial pan-

createctomy in dogs, the extent of the hypoglycaemic action of injected insulin  $\propto$  the functional val. of the remaining pancreas.

A. L.

Influence of different histolysates administered parenterally and orally on the effect of insulin. V. P. KOMSARENKO (Platz. Utschen. Med., 1936, 56—72).—The action of insulin (I) administered parenterally on the blood-sugar of normal or diabetic dogs is increased when certain tissue lysates are given simultaneously. (I) administered orally with tissue lysates is able to reduce the blood-sugar level, but the order of efficiency of the lysates is not the same as with parenteral administration.

W. O. K.

Anti-hormones and pineal gland. P. ENGEL (Klin. Woch., 1935, 14, 970—971).

R. N. C.

Constituents of blood after injection of thymus extract. C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1936, 122, 710—712).—A diminution in K and inorg. P occurs.

H. G. R.

Biological effects of thymectomy in successive generations of rats. N. H. EINHORN and L. G. ROWNTREE (Science, 1936, 83, 443—445).—Retardation in the rate of growth and a slight delay in the rate of development result.

L. S. T.

Antagonistic effect of the thyroid hormone on the corpus luteum and of the follicular hormone on the pseudo-pregnant uterus. E. ENGELHART (Klin. Woch., 1935, 14, 1068—1070).

R. N. C.

Relation between thyroid and central nervous system. H. VOSS (Klin. Woch., 1935, 14, 881—884).

R. N. C.

Crystallisation of sodium chloride in the serum of guinea-pigs and rabbits during experimental hyperthyroidism and hyperpituitarism. V. BERGAUER (Compt. rend. Soc., Biol., 1936, 122, 426—427).—Crystallisation occurs *in vivo*.

H. G. R.

Thyroid and vitamin-C reserves. E. NESTOR (Compt. rend. Soc. Biol., 1936, 122, 427—430).—The ascorbic acid content of the tissues is reduced by thyroid medication and increased by thyroidectomy.

H. G. R.

Influence of thyroxine on the passage of galactose [into the blood and urine]. N. FRIESINGER and M. NAVILLE (Compt. rend. Soc. Biol., 1936, 122, 637—638).—Administration of thyroxine diminishes galactosuria, whilst prolonged dosage increases it.

H. G. R.

Specificity of the substance inhibiting the hypertensive action of vasopressin in serum of pregnancy. J. A. SCHOCKAERT and J. LAMBILLON (Compt. rend. Soc. Biol., 1936, 122, 481—484).

H. G. R.

Absorption of villikinin by the intestines. E. DE KOKAS and G. DE LUDANY (Compt. rend. Soc. Biol., 1936, 122, 413—416).—Villikinin is active orally, is not inactivated by erepsin, and is absorbed in the duodenum.

H. G. R.

Echinenone as a provitamin-A. E. LEDERER and T. MOORE (Nature, 1936, 137, 996).—Echinenone (A 1935, 1145) can function as a provitamin-A.

L. S. T.



**Distribution of vitamin-A between light petrol and aqueous methyl alcohol.** A. E. GILLAM and B. J. SENIOR (Biochem. J., 1936, 30, 1249—1252).—Vitamin-A distributes itself equally between 90% aq. MeOH and light petroleum (I), whilst with 70% MeOH the concn. is 8 times that in (I). The presence of carotene and temp. variation between 10° and 30° were without influence, whilst cholesterol increased the amount in the (I) phase. H. D.

**Mechanism of elimination of vitamin-A.** A. SANTOS RUIZ (Anal. Fis. Quím., 1935, 33, 820—828).—The observations of Davies and Moore (A., 1935, 261) have been confirmed. The excess vitamin-A is eliminated mainly in the urine as a degradation product giving a considerable increase in I val. F. R. G.

**Synthesis of vitamin-A.** II.—See this vol., 983.

**Ash-manna as a source of vitamins and a cause of alimentary disturbances.** R. LECOQ (Bull. Soc. bot. France, 1934, 81, 782—792).—Manna in large quantities causes disturbances similar to polyneuritis in birds, in spite of the addition of large quantities of vitamin-B. In smaller quantities it does not cause disturbances, and the carbohydrates are utilised by the organism. It contains -B and -D, but neither -A nor -C. It can be used in infantile therapy. R. N. C.

**Vitamin-B<sub>1</sub> content and feeding value of some important [East] Indian foodstuffs. Is katjang idjoe the most suitable means of combating mild cases of beri-beri?** W. F. DONATH and J. P. SPRUYT (Geneesk. Tijds. Nederl.-Indie, 1936, 76, 642—695).—22 native foodstuffs (seeds and beans) were examined for H<sub>2</sub>O, protein, fat, carbohydrate, pentosan, crude fibre, ash, SiO<sub>2</sub>, CaO, MgO, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, and vitamin-B<sub>1</sub> contents. Several, especially "katjang tanah" (*Arachis hypogaea*, L.), contain more -B<sub>1</sub> than does "katjang idjoe" (*Phaseolus radiatus*) (which is unpalatable, and deficient in fat), and are more suitable for combating beri-beri. The -B<sub>1</sub> content should be determined in the finally prepared food and not in the raw material. S. C.

**Growth effect of the residue remaining after alcoholic extraction of yeast.** M. R. RYMER and R. C. LEWIS (J. Biol. Chem., 1936, 114, 361—367).—The growth-promoting effect on rats of yeast residue after alcoholic extraction (A., 1931, 271) may be largely replaced by vitamins-B<sub>1</sub> and -B<sub>2</sub>, so that the postulation of a third factor in yeast is considered unjustifiable. H. D.

**Liver as a source of vitamin-B<sub>12</sub>.** E. R. BECKER and N. F. MOREHOUSE (Science, 1936, 83, 530—531). L. S. T.

**Vitamin-C metabolism in the foetus. I. Resorption of ascorbic acid from the placenta. II. Storage of vitamin-C in the adrenals.** W. NEUWEILER (Klin. Woch., 1935, 14, 1040—1041; Chem. Zentr., 1935, ii, 1907).—The foetus probably obtains vitamin-C from the placenta and stores it in the adrenals. A. G. P.

**Resistance of capillaries in experimental C-avitaminosis of animals and men. Use of the phenomenon of the fall in resistance of capillaries for rapid determination of vitamin-C**

**activity of foods.** I. I. MATUSIS (Platz. Utschen. Med., 1936, 139—154).—The resistance to negative pressure of the capillaries of guinea-pigs on a scorbutic diet rapidly decreases within 2—3 days. Administration of vitamin-C results in the capillaries returning to their normal condition. In man the fall in resistance is slower, becoming evident in 8—10 days, and -C effects only a relatively slow cure. W. O. K.

**Renal and hepatic elimination of ascorbic acid.** M. LOEPER, E. CHABROL, J. COTTET, and A. LESURE (Compt. rend. Soc. Biol., 1936, 122, 404—406).—Increased elimination in the bile and, to a greater extent, in the urine follows intravenous injections of ascorbic acid. H. G. R.

**Ascorbic acid in the liver during hepatitis.** M. LOEPER, J. COTTET, and A. LESURE (Compt. rend. Soc. Biol., 1936, 122, 388—390).—In cases of cirrhosis the ascorbic acid (I) content of the liver is low. Guinea-pigs with acute P hepatitis have increased (I) in the liver. H. G. R.

**Relation between the antiscorbutic activity and mode of administration of ascorbic acid.** H. C. HOU (Chinese J. Physiol., 1936, 10, 213—220).—The min. protective dose of ascorbic acid (I) given orally to guinea-pigs is twice that given subcutaneously. Rectal administration is ineffective. Subminimal protective doses given twice daily are not more effective than four times the dose given once every two days. The (I) content of different organs varies little with degree of protection, except that with the higher doses there is an increased content in the adrenals. F. A. A.

**Behaviour of d-araboascorbic acid and vitamin-C towards ferrous salts.** K. MAURER and B. SCHIEDT (Biochem. Z., 1936, 285, 67—71).—The blue complex substance (I) formed when ascorbic acid (II) or iso-(II) is neutralised and Fe<sup>II</sup> salt added in presence of air can be isolated by addition of excess of EtOH. COMe<sub>2</sub>, or dioxan. An aq. solution of (I) slowly on keeping, more quickly on adding H<sub>2</sub>O<sub>2</sub>, deposits 0.4—0.5 mol. of FeC<sub>2</sub>O<sub>4</sub>. P. W. C.

**Glutathione and ascorbic acid.** H. BORSOOK and C. E. P. JEFFREYS (Science, 1936, 83, 397—398).—The antiscorbutic potency of a solution of oxidised ascorbic acid (I) is equal to the quantity of oxidised (I) which can be converted into the reduced form by H<sub>2</sub>S in acid solution. At  $p_H < 5.5$  and 37° the reversibly oxidised form undergoes an irreversible change, losing its antiscorbutic potency and its reducibility by H<sub>2</sub>S. The change proceeds as quickly in a vac. as in air and is rapid at  $p_H 7.4$ . The reversibly oxidised form is protected from this change *in vivo* by reduction. Glutathione (II) (0.1—0.2%) rapidly effects the reduction. Previous failures to observe this action of (II) are ascribed to the use of insufficient (II) and too low a  $p_H$ . L. S. T.

**Effect of light on the oxidation-reduction potential of ascorbic acid.** E. MARTINI (Biochim. Terap. sperim., 20, 505—517; Chem. Zentr., 1935, ii, 1907).—In PO<sub>4</sub>'''-buffer solutions, the redox potential of ascorbic acid (I) is lowered by exposure to light. Fluorescent substances [methylene-blue (II), eosin] intensify this effect. Glucose in the presence of (II)

behaves similarly. Rapid decolorisation of (II) by milk in light is probably due to (I). A. G. P.

**Occurrence of vitamin-C in cerebrospinal fluid and aqueous humour.** M. TATSUMI, Y. NAGAO, K. OKAMURA, and J. GAMO (Klin. Woch., 1935, 14, 1007).—Ascorbic acid increases the vitamin-C content of the aq. humour of a dog, but not that of the cerebrospinal fluid of a dog or a scorbutic child.

R. N. C.

**Ascorbic acid content of animals in C-avitaminosis.** A. GIROUD, A. S. RUIZ, C. P. LEBLOND, and A. R. RATSIMAMANGA (Bull. Soc. Chim. biol., 1936, 18, 750—756).—The amount of ascorbic acid in the livers and kidneys of guinea-pigs deprived of dietary vitamin-C decreases progressively for about 10 days, when a steady val. is reached. A. L.

**Isolation of crystalline vitamin-C from lombok (*Capsicum annuum*, L.).** J. P. SPRUYT and A. G. VAN VEEN (Geneesk. Tijds. Nederl.-Indie, 1936, 76, 1065—1071).—Cryst. ascorbic acid (0.1 g.) was isolated from 500 g. of lombok by a slight modification of the Banga-Gyorgyi Pb(OAc)<sub>2</sub> method. S. C.

**Chemical composition and vitamin-C content of liang-hsu (*Dioscorea cirrosa*, Lour.?).** D. Y. LIU and C. S. YANG (Chinese J. Physiol., 1936, 10, 355—358).—This tuber contains about 11% of total solids, mainly sugar and starch, and is a good source of vitamin-C (92 mg. ascorbic acid per kg.). F. A. A.

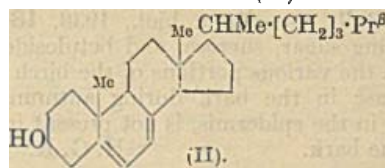
**Combined ascorbic acid in foodstuffs.** B. C. GUHA and J. C. PAL (Nature, 1936, 137, 946).—Extracts of cabbage and of the bel (*Aegle marmelos*), but not mangoes, with EtOH or Et<sub>2</sub>O give much greater vitamin-C vals. on heating. This increase is ascribed to the liberation of combined -C in the foodstuff and not to inactivation of -C oxidase by heat (cf. A., 1935, 1176). L. S. T.

**Ultra-violet spectra of tissue extracts and their ascorbic acid content.** J. A. DE LOUREIRO (Bull. Soc. Chim. biol., 1936, 18, 757—768).—A spectrographic examination of the extract of brain-tissue after deproteinisation with COMe<sub>2</sub> followed by pptn. with phosphotungstic acid and Hg(OAc)<sub>2</sub> at *p*<sub>H</sub> 5.6 shows that the reducing power of the extract determined by the Tillmans' method is due mainly to ascorbic acid. A. L.

**Changes in the ascorbic acid and glutathione contents of stored and sprouting potatoes.** L. B. PETT (Biochem. J., 1936, 30, 1228—1232).—The ascorbic acid (I) and glutathione (II) contents of potatoes is at a max. at maturity; the decrease which occurs on storage increases with rise of temp. Forced sprouting at any stage of the decline resulted in a rapid rise in the (I) and (II) contents followed by a rapid fall. H. D.

**Naturally occurring chicken provitamin-D.** A. G. BOER, E. H. REERINK, A. VAN WIJK, and J. VAN NIEKERK (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 622—632).—Pure provitamin-D acetate (I), m.p. 129—130°,  $[\alpha]_D^{20}$  -85.3°, was obtained from a crude cholesteryl acetate containing 4.5% of provitamin-D (II) by fractional adsorption and elution followed by recrystallisation from MeOH. Hydrolysis of (I) by EtOH-KOH gives (II), m.p. 150°,

$[\alpha]_D$  -127° (3:5-dinitrobenzoate, m.p. 205—206° (decomp.)). (II) undergoes the same photochemical change on irradiation as ergosterol. The activity for chickens of irradiated (II) is the same as that of cod-



The suggested structure for (II) is supported by its taking up only 1 mol. of H<sub>2</sub> on hydrogenation, as one of the con-

jugated double linkings is difficult to hydrogenate. Ozonisation confirms the absence of a double linking in the side-chain. Differences between the m.p. and biological activity of (II) and the prep. of Windaus *et al.* (A., 1935, 1363) are due to impurities in the earlier prep. The identity of 7-dehydrocholesterol with (II) is established. E. A. H. R.

**Absorption spectra of sterols from natural sources with particular reference to ergosterol and other vitamin-D precursors.** A. E. GILLAM and I. M. HEILBRON (Biochem. J., 1936, 30, 1253—1256).—Sterols from *Arenicola marina*, sea anemones, and oysters have absorption bands identical with those of ergosterol. *A. marina* sterols, like dehydroergosterol, have max. also at 346, 328, and 316 mμ.

H. D.

**Antirachitic effectiveness of vitamin-D from various sources.** R. W. HAMAN and H. STEENBOCK (J. Biol. Chem., 1936, 114, 505—514).—Heated and irradiated purified cholesterol (I) has absorption bands in the ultra-violet and vitamin-D activity similar to those of irradiated crude (I). The antirachitic activity of some fish oils was not increased by irradiation. The solvent in which ergosterol or (I) was dissolved during irradiation had no influence on the resultant -D activity. H. D.

**Antirachitic irradiation product of 7-dihydrocholesterol.**—See this vol., 982.

**7-Dehydrositosterol and 7-dehydrostigma-sterol.**—See this vol., 982.

**Mutual reactions between plant extracts and heteroplasmic graft components, and their immunological and genetic significance.** D. KOSTOV (Bull. Acad. Sci. U.R.S.S., 1935, 1177—1216).—Polemical, against Chester and Silberschmidt (cf. A., 1934, 1273). R. T.

**Phytoserology.** E. G. DANKERT (Anal. Asoc. Quim. Argentina, 1935, 23, 153—161).—Preliminary experiments on Mez' blood-serum method for diagnosing the relationships of plants are described. Attention is directed to the necessity for studying the protein content of the vegetable extracts and the *p*<sub>H</sub> and lipin content of the solutions. F. R. G.

**Assimilation methods of various types of *Chlorella*.** H. GAFFRON and K. WOHL (Naturwiss., 1936, 24, 412).—Calculation of the quantum efficiency for the assimilation process of *Chlorella* from the data due to Emerson gives a val. only 1/12 that of Warburg *et al.* This discrepancy, originally attributed to an error in measurement of light intensity, is now ascribed to the fact that Warburg used *C. pyrenoidosa*, whereas



Emerson used *C. vulgaris*, the two varieties having very different assimilation capacities. A. J. M.

**Variations in the composition of the birch (*Betula alba*, L.) during the year.** A. Sosa and C. Sosa-Bourdoul (Bull. Soc. Chim. biol., 1936, 18, 918—925).—Reducing sugar, sucrose, and betuloside were determined in the various portions of the birch; all show an increase in the bark during autumn. Betulin, very conc. in the epidermis, is not present in other portions of the bark. H. G. R.

**Cultivation of an alga in concentrated heavy water.** H. MEYER (Naturwiss., 1936, 24, 346).—*Chlorella vulgaris* grew on a medium containing  $\text{MgSO}_4$  0.001,  $\text{K}_3\text{PO}_4$  0.001,  $\text{KNO}_3$  0.07, and  $\text{FeCl}_3$  0.0001% in heavy  $\text{H}_2\text{O}$  (> 96%  $\text{D}_2\text{O}$ ) as well as in a control medium with  $\text{H}_2\text{O}$  in place of  $\text{D}_2\text{O}$ . W. O. K.

**Light, temperature, and the reproduction of plants.** V. H. BLACKMAN (Nature, 1936, 137, 931—934, 971—973).—A lecture. L. S. T.

**Rubber content of golden-rod (*Solidago*) leaves affected by light.** J. T. PRESLEY (Science, 1936, 83, 436).—Exposure to light reduces the rubber content of these leaves after harvesting. L. S. T.

**Chemotropism of plant roots. I. Chemotropic stimulation by mineral salts.** B. NIKLEWSKI and J. DUDA. II. Stimulation by colloids. B. NIKLEWSKI, H. BRODOWSKA, M. DYDO, and M. KAHL (Biochem. Z., 1936, 286, 110—119, 120—127).—I. The chemotropic effect of substances contained in an agar block placed on one side of the root tip of *Sinapis alba* seedlings was always positive (curvature towards the block) in healthy seedlings. Negative curvature was due to pathological causes. The most powerful effects were produced by  $\text{PO}_4'''$ ,  $\text{K}'$ ,  $\text{Hg}''$ ,  $\text{Al}'''$ ,  $\text{Fe}'''$ ,  $\text{UO}_2''$ , eosin, and Me-violet. Substances which restricted growth had more powerful action than those which did not. No reversal of direction of curvature resulted from altering the concn. of the substance.

II. Chemotropic effects are produced by colloidal solutions of Au, Ag,  $\text{Fe}(\text{OH})_3$ , Cu,  $\text{As}_2\text{S}_3$ , resins, gums, and humus pptd. from extracts of farmyard manure with HCl, but not by those of proteins, starch,  $\text{NH}_3$ -acids, or by suspension of quartz. The effects appear to depend on the particle size of the colloids.

W. McC.

**Photosynthetic unit'' in the assimilation process of green plants.** J. WEISS (Nature, 1936, 137, 997; cf. Kohn, this vol., 907).—It is assumed that for every chlorophyll mol. on the surface of the lipid phase reducing  $\text{CO}_2$  there are approx. 500 mols. in the interior which provide the surface mol. with the necessary 4 quanta of energy. L. S. T.

**Effect of potassium on carbon assimilation in plants.** G. RÖHDE (Z. Pflanz. Dung., 1936, 44, A, 1—24).—A review. A. G. P.

**Carbon dioxide storage. IX. Germination of lettuce seeds at high temperatures in light and in darkness.** N. C. THORNTON (Contr. Boyce Thompson Inst., 1936, 8, 25—40; cf. A., 1935, 1177).—Germination of lettuce was effected at 20—26° in an atm. containing 5—10% of  $\text{CO}_2$  and 20% of  $\text{O}_2$

within 17 hr. either in light or darkness. At 35°, 40—80% of  $\text{CO}_2$  and a period of 65 hr. were necessary. Seeds made dormant by moist storage at 35° in the absence of  $\text{CO}_2$  germinated at this temp. during and after exposure to the higher  $[\text{CO}_2]$ . Seedlings produced by these treatments subsequently grow well in air. A. G. P.

**Induced changes in respiration rates and time relations in the changes in internal factors.** L. P. MILLER, J. D. GUTHRIE, and F. E. DENNY (Contr. Boyce Thompson Inst., 1936, 8, 41—61).—Treatment of potato tubers with the vapour of chemicals which increase their  $\text{CO}_2$  output produced an increase in sugar content and in catalase (I) and peroxidase (II) activity, but not until the peak of respiratory activity had passed. EtOH decreased the  $\text{CO}_2$  output and (II) activity, but increased (I). Enhanced capacity to reduce methylene-blue resulting from treatment with  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$  (III) or Bu halides began after the rise in respiration rate. The citric acid (IV) content of treated tubers declined and the  $p_H$  increased simultaneously with the increase in respiration. Additional  $\text{CO}_2$  produced was probably derived, to a large extent, from (IV). (III) increased the glutathione (V) and decreased the  $\text{SO}_4''$  content of tubers at a period later than the action on respiration. Bu halides lowered the (V) content. A. G. P.

**Chemical allometry in plant growth.** P. MEUNIER (Bull. Soc. Chim. biol., 1936, 18, 636—644).—The equation  $y = bx^a$ , where  $y$  is the total wt. of one constituent,  $x$  the total wt. of the organism, and  $b$  and  $a$  consts. for a particular constituent, previously applied to animal growth also applies to plant growth. A. L.

**Growth-accelerating and -inhibiting action of fluorescein on plants.**—See B., 1936, 612.

**Action of adrenaline and extracts of adrenal cortex on the growth of *Hyacinthus orientalis*.** L. DESOLE (Boll. Soc. ital. Biol. sperim., 1935, 10, 980—981).—A growth-promoting action was observed. F. O. H.

**Modifications in the root (especially root-tip) of *Hyacinthus orientalis* grown in solutions of adrenaline and adrenal cortex extracts.** L. DESOLE (Boll. Soc. ital. Biol. sperim., 1935, 10, 982—983).—The roots partly darken in colour, those tissues affected giving a positive Viale reaction for adrenaline. F. O. H.

**Follicular hormone and the time of blooming of chrysanthemums.** I. STORMER (Biochem. Z., 1936, 285, 29—35).—The development of buds and blooms and the plant length of the chrysanthemum "Majestic" were unaffected by commercial progynon or by the pure hormone or its Na salt. P. W. C.

**Esters as plant hormones.** P. W. ZIMMERMAN, A. E. HITCHCOCK, and F. WILCOXON (Contr. Boyce Thompson Inst., 1936, 8, 105—112; cf. A., 1935, 1548).—Plant responses, characteristic of growth-substances, were induced by Me and Et naphthylacetate, Me, Et,  $\text{Bu}^a$ , and  $\text{Bu}^b$  phenylacetate, Me  $\beta$ -indolylacetate (I), and Me  $\beta$ -indolylpropionate. (I) was more effective than hetero-auxin. Me esters of indole compounds were more, and those of the

$C_{10}H_7$  and Ph compounds less, active in inducing bending responses than were the corresponding free acids. The activity of corresponding esters was in the order  $Me > Et > Bu$ . Plants absorbed the esters through the roots (from soil) and transported them to aerial organs. A. G. P.

**Effect of growth substances on the rooting response of cuttings.** A. E. HITCHCOCK and P. W. ZIMMERMAN (Contr. Boyce Thompson Inst., 1936, 8, 63—79).—Treatment of various cuttings with indolyl-acetic, -propionic, and -butyric or naphthylacetic acid induced earlier rooting and an increased no. of roots which emerged over a greater stem area than in untreated controls. Aq. solutions of the growth substances were 100—500 times as effective, in many cases, as lanoline preps. of similar concn. Effects of the duration of treatment with various concns. were examined. Substances stimulating rooting also retarded the growth of non-dormant buds. A. G. P.

(A) Influence of  $Cl^-$  and  $SO_4^{--}$  on growth of white ramie (*Boehmeria nivea*) rhizomes. (B) Effect of external factors on the activity of the rhizosphere. A. A. ISAKOVA (Bull. Acad. Sci. U.R.S.S., 1935, 1143—1146, 1147—1162).—(A) Concns.  $> 0.17M$ -NaCl or  $0.15M$ - $Na_2SO_4$  separately, or  $0.085M$ -NaCl and  $0.075M$ - $Na_2SO_4$  together, are lethal to the rhizomes.

(B) Addition of NaCl and  $Na_2SO_4$  to cultures of soil micro-organisms promotes or inhibits decomp. of peptone, glycine, glucose (I), sucrose (II), cellulose, NaOBz, or  $Na_2C_2O_4$ , according to the type of organisms present, and to the concn. of the salts. In the rhizosphere,  $Cl^-$  intensifies ammonification and the decomp. of (II), but inhibits decomp. of (I) and of org. acids; the opposite effects are produced by  $SO_4^{--}$ . R. T.

**Phytochemical problems.** T. WEEVERS (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 757—761).—The phytochemical characteristic of a species, genus, or family of plants is due to a combination of several chemical compounds. Similar compounds occurring in unrelated families always originate by way of simple reactions from products of metabolism of general occurrence. This is discussed in reference to cineole in Labiatae, Myrtaceae, and Zingiberaceae, alkaloids in Papaveraceae, Fumaroidaceae, and Papaveroidae, heart aglucones, nicotinic acid, and trigonelline. It is suggested that a co-enzyme, probably identical with that of Warburg, is present in all higher plants. P. G. C.

**Dissolved carbon dioxide and the ripening of tomatoes.**—See B., 1936, 617.

**Occurrence in pears of metabolic gases other than carbon dioxide.** E. HANSEN and H. HARTMAN (Oregon Agric. Exp. Sta. Bull., 1935, No. 342, 10 pp.).—Emanations (probably  $C_2H_4$ ) from ripe pears at room temp. and from unripe pears in cold storage caused epinasty in tomato plants, retarded germination of certain seeds, and accelerated the ripening of newly picked fruit. After cold-storage for a short period fruit did not respond to the emanations. A. G. P.

**Gravity-position of tomato stems and their production of the emanation causing leaf epinasty.** F. E. DENNY (Contr. Boyce Thompson Inst., 1936, 8, 99—104; cf. A., 1935, 1179, 1548).—Emanations from tomato plants causing epinasty in potato leaves similar to that caused by  $C_2H_4$ , are more effective when tomato stems are horizontal than when vertical. A. G. P.

**Spectrum analysis of some woods from Spain and Fernando Po.** S. PINA DE RUBIES and L. LEMMEL (Anal. Fis. Quim., 1935, 33, 492—499).—A more detailed account of work already published (A., 1935, 1289). F. R. G.

(A) Microcrystalline structure of thorns. S. PIENKOWSKI and Z. KULESZANKA. (B) X-Ray examination of resin in wood. S. PIENKOWSKI and L. JURKIEWICZ (Acta phys. polon., 1934, 3, 393—400, 435—446; Chem. Zentr., 1935, ii, 1733—1734).—Structures are examined by X-ray methods. A. G. P.

**Tables for the calculation of the osmotic value of expressed plant juices, sugar solutions, and some salt solutions.** H. WALTER (Ber. deut. bot. Ges., 1936, 54, 328—339).—A compilation of f.p. depression and osmotic data for glucose, sucrose, NaCl,  $Na_2SO_4$ , and  $MgSO_4$ , for use in calculating the composition of plant saps etc. F. A. A.

[Constituents of] *Polygonum hydropiper*. C. MASINO (Boll. Chim. farm., 1936, 75, 242—248).—The air-dried root contains 0.42—0.64% of Fe. Traces of anthraquinone glucosides occur in the roots, but not leaves or stems. The whole plant (40 kg.) yields an essential oil (9 g.), tannin, and, on hydrolysis, a keto-hexose. F. O. H.

**Composition and uses of the fruit of the giant cactus (*Carnegiea gigantea*) and its products.** R. A. GREENE (J. Chem. Educ., 1936, 13, 309—312). L. S. T.

**Determination of calcium, magnesium, potassium, and sodium in plants by extraction with hydrochloric acid.** F. TERLIKOWSKI and S. SOZANSKI (Rocz. Nauk. roln. leśn., 1935, 34, 143—148; Chem. Zentr., 1935, ii, 2095).— $< 10$  g. of the finely-divided material are shaken for 1 hr. with 500 c.c. of  $N$ -HCl; the filtrate is analysed by standard methods. H. N. R.

**Ratio of iron soluble in cold water to total iron in the leaves of healthy and injured plants.** A. HELLER (Kl. Mitt. Ver. Wasser-, Boden-, Lufthvg., 1935, 11, 43—47; Chem. Zentr., 1935, ii, 2834).—The determination of the two forms of Fe in the leaves does not constitute a test for smoke injury, and the time required does not make it practicable in leaf analysis. R. N. C.

**Distribution of manganese and iron in Quebec pines.** P. RIOU, G. DELORME, and HORMISDAS (Compt. rend., 1936, 202, 1811—1812).—The ash, Fe, and Mn contents of *P. strobus*, *P. resinosa*, and *P. banksiana* are determined. Higher vals. for Fe are accompanied by lower vals. for Mn. J. L. D.

**Rarer elements in the ash of *Polyporus fomentarius* and its host trees.** B. NEMEC (Ber. deut. bot. Ges., 1936, 54, 276—278).—The ash of



*P. fomentarius* contains relatively more Cu, Zn, Al, and Mn, and less Ti, Si, Fe, Ca, and Mg than does that of beechwood (*Fagus silvatica* and *Carpinus betulus*). Au, Cr, and V are also present in traces. F. A. A.

Phosphorus content of citrus.—See B., 1936, 612.

Biological role of hydroxylamine. II. Reaction for hydroxylamine. III. Hydroxylamine in the leaves of higher plants. M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Bull. Soc. Chim. biol., 1936, 18, 841–867, 868–876).—II. Blom's reaction (A., 1928, 674) is modified to increase the specificity and the reaction with related substances is studied.

III.  $\text{NH}_2\text{OH}$  is obtained by autolysis of green leaves, but is also present in the fresh leaves, whence it is obtained by hydrolysis from both volatile and non-volatile constituents. H. G. R.

Relations between the natural system of plants and their chemical structure. P. KLASON (Svensk Pappers-Tidn., 1935, 38, 450–454; Chem. Zentr., 1935, ii, 2835).—The higher N content of marine algæ is the result of their marine life. North Sea algæ contain about 27% of lignin, which, unlike that of higher plants, contains an alcohol complex. R. N. C.

Carbohydrates of the fruits of *Rosa rugosa*. E. VOTOČEK and L. SGARZI (Coll. Czech. Chem. Comm., 1936, 8, 185–190).—The fruits of *R. rugosa*, preserved in EtOH, yield to hot EtOH a syrup,  $[\alpha]_D +27.8^\circ$ , which contains fructose and glucose. Dried fruits yield a little sucrose. They contain a hygroscopic, amorphous "gum," sol. in  $\text{H}_2\text{O}$ , insol. in EtOH, which gives mannose and the reactions of pentoses when hydrolysed. Hydrolysis of the EtOH-insol. portions with 5%  $\text{H}_2\text{SO}_4$  yields galactose; the product gives pentose reactions and with  $\text{HNO}_3$  yields mucic acid. The residual insol. material yields glucose when heated first with 80% and then with 6%  $\text{H}_2\text{SO}_4$ . R. S. C.

Reserve polysaccharides of plants and their significance in the animal economy. I. *d*-Galacto-*d*-mannan of lucerne (*Medicago*, L.). F. MAX and A. S. SCHULZ (Z. Biol., 1936, 97, 201–217).—The occurrence of galactans in animal and plant tissues is discussed. Extracts (aq. KOH) of lucerne seeds are pptd. by EtOH and the ppt. is redissolved in  $\text{H}_2\text{O}$  and successively pptd. from KOH, HCl, and aq. solution by EtOH to yield 8.6% of a polysaccharide mixture (bound galactose, 36.7%). Purification by digestion with human saliva followed by pptn. with alkaline Cu reagent, regeneration of the Cu compound by HCl, and pptn. by EtOH affords a *d*-galacto-*d*-mannan,  $[\alpha]_D^{20} +93.74^\circ$  in  $\text{H}_2\text{O}$ , hydrolysed by acids to galactose and mannose (1:1). F. O. H.

Acidic character of cellulose. Oxidation processes in membranes. M. LUDTKE (Biochem. Z., 1936, 285, 78–97).—Crude cellulosic material always has a higher acid val. than the cellular material obtained from it, the acidic cuticular substances not being removable by treatment with neutral extraction agents, e.g.,  $\text{C}_6\text{H}_6$ -EtOH. Both unripe material and material attacked by moulds and bacteria show higher acid vals. than ripe and healthy material. During the

bleaching of cotton-wool by dil.  $\text{Cl}_2$ - $\text{H}_2\text{O}$  and aq.  $\text{NH}_3$ , the acid val. decreased during the first 6 days from 15 to 2 and then slowly increased in the following 22 days to 6. The rapid initial fall corresponds with the oxidative removal of cuticular substance. Crit. examination indicates that the residual acidity is due to contaminating substances and their degradation products and is not a natural property of cellulose nor the result of oxidation of the terminal groups of the cellulose chains to  $\text{CO}_2\text{H}$ . P. W. C.

Composition of the plant cell wall. R. S. HILPERT [with W. ROSSÉE and R. WAGNER] (Ber., 1936, 69, [B], 1509–1514).—The C content of the cell walls of seedlings is considerably > that of cellulose (I) and treatment with NaOH or  $\text{NaHSO}_3$  leaves a residue with the approx. composition of a (I) anhydride. The hypothesis that (I) is the sole primary product between the fibres of which new substances, including lignin, are subsequently deposited must therefore be abandoned. The C content of stems in the initial stages is < that of seedlings, but increases during growth. During the whole growth the % of lignin increases. The % OMe increases almost regularly, and it appears that the carbohydrates are partly methylated, particularly those which give insol. products with acids. The primary seedling has a low OMe no., but elimination of  $\text{H}_2\text{O}$  has already proceeded considerably. During the formation of the stem a new skeleton substance appears which in course of ripening loses  $\text{H}_2\text{O}$  and becomes methylated. The max. of both processes is reached in the ripe plant. During ripening small amounts of non-carbohydrate material appear to be produced. H. W.

Lignin from oat straw.—See this vol., 994.

Colorimetric and mol. wt. determination of digitalis glucosides. W. NEUMANN (Z. physiol. Chem., 1936, 240, 241–248).—The method is similar to that of Hauschild (A., 1935, 1531). Solutions must be maintained at 18–22° and readings made after 10 and 20 min. W. McC.

Glucoside from blueberry leaf. N. K. EDGARS (J. Amer. Pharm. Assoc., 1936, 25, 288–291).—Acid-MeOH extracts of dried leaves (approx. constitution determined) of *Vaccinium corymbosum* freed from wax, resin, and chlorophyll yield 2% of a galloylmethoxy-glucose, *neomyrtillin*,  $\text{C}_{24}\text{H}_{36}\text{O}_{16}$ , m.p.  $57^\circ$ ,  $[\alpha]_D -0.7^\circ$  (0.1% aq. solution), which diminishes alimentary hyperglycaemia in piqued rabbits. F. O. H.

Japanese sago plant. III. Enzyme chemistry of a constituent containing formaldehyde. I. K. NISHIDA and A. YAMADA (J. Agric. Chem. Soc. Japan, 1935, 11, 357–364).—The distillate from seeds crushed in  $\text{H}_2\text{O}$  contained  $\text{CH}_2\text{O}$ . None was obtained from fresh seed boiled with  $\text{H}_2\text{O}$  for 30 hr. The  $\text{H}_2\text{O}$  extract of crushed seed yielded with AcOH and subsequently EtOH a ppt. having the action of emulsin which liberated  $\text{CH}_2\text{O}$  when added to the boiled seed.  $\text{CH}_2\text{O}$  probably occurs as a glucoside in the seed. The enzyme action was optimum at  $p_H$  3.3 and 42–45°. CH. ABS. (p)

Flavone compounds of *Polygonum hydropiper*, L. H. P. KRYNSKA (Wiadom. farm., 1935, 62, 215–216; Chem. Zentr., 1935, ii, 2696).—Extraction of the

powdered drug with  $\text{COMe}_2$  affords 0.11% of a cryst. substance, apparently rhamnazin. H. N. R.

**New hesperidin.**—See this vol., 970.

**Nucleic acid of ergot of rye.** II. M. GATTY-KOSTYAL and J. TESARZ (Bull. Acad. Polonaise, 1936, B, 1—32; cf. A., 1934, 709).—Hydrolysis of the nucleic acid (I) from ergot gave 10 atoms of purine-N to 4 of P; the purines were pptd. with  $\text{Ag}+\text{aq. NH}_3$  and the ppt. was decomposed with  $\text{H}_2\text{S}$ . After concn., guanine (II) was pptd. quantitatively with 1% aq.  $\text{NH}_3$  or  $\text{AcOH}$  and adenine (III) from the filtrate with dil.  $\text{H}_2\text{SO}_4$  and  $\text{CuSO}_4+\text{NaHSO}_3$ . (I) contained (II) and (III) in equimol. proportions and a pentose. Uracil and cytosine were isolated from (I) after hydrolysis at 150—160°. The data indicate a structure similar to that of yeast-nucleic acid. H. D.

**Synthesis of djenkolic acid.**—See this vol., 973.

**Constitution of the azulenes.**—See this vol., 993.

**Volatile oil from western yarrow.** R. L. McMURRAY (J. Amer. Pharm. Assoc., 1936, 25, 304—306).—The oil from the flowers of *Achillea millefolium lanulosa*, Piper,  $d_{25}^{20}$  0.8995,  $[\alpha]_{25}^{20}$  —8.98°,  $n_{25}^{20}$  1.4657, acid val. 1.82, sap. val. 26.75, ester val. 24.93, differs from the oil from eastern yarrow (*A. millefolium*, L.).

F. O. H.

**Crystalline diterpene, sciadopitene, from the oil of leaves and twigs of *Sciadopitys verticillata*, S. and Z. II. Derivative of sciadopitene and the reduction of the two isomerides.** K. NISHIDA and H. UOTA (J. Agric. Chem. Soc. Japan, 1936, 12, 308—312; cf. this vol., 207).—isoSciadopitene prepared by heating the diterpene with dil.  $\text{H}_2\text{SO}_4$  has m.p. 108—109°,  $[\alpha]_{\text{D}}^{20}$  +22.13° in  $\text{CHCl}_3$ , and forms a monohydrochloride, m.p. 106—108°,  $[\alpha]_{\text{D}}^{20}$  +3.96° in  $\text{CHCl}_3$ .

Catalytic reduction (Pt-black in  $\text{COMe}_2$ ) of the diterpene or of the isomeride yields dihydrosciadopitene, m.p. 71—72°,  $[\alpha]_{\text{D}}^{20}$  +22.8° in  $\text{CHCl}_3$ .

A. G. P.

**Isolation from cottonseed oil of an alcohol resembling  $\alpha$ -tocopherol from wheat-germ oil.**—See this vol., 963.

**Occurrence of quebrachitol in stems of *Haplophyton cinicidum*.** E. P. CLARK (J. Amer. Chem. Soc., 1936, 58, 1009—1010).—Quebrachitol (I), m.p. 192—193° (corr.) (lit. 186—187°),  $[\alpha]_{\text{D}}^{20}$  —81.2° in  $\text{H}_2\text{O}$ , is isolated in about 0.7% yield. (I) is demethylated by  $\text{HI}$  ( $d$  1.7) to *l*-inositol, m.p. 242—243° (sinters at 195°) (lit. 238°),  $[\alpha]_{\text{D}}^{20}$  —64.7° in  $\text{H}_2\text{O}$  [hexabenzoate, m.p. 247° (lit. 252°)]. Crystallographic data are given. H. B.

**Solubility of tannins of chestnut wood.** M. QUENDIAC (Compt. rend., 1936, 202, 1697—1700).—Pre-treatment of chestnut wood with  $\text{COMe}_2$  increases the amount of tannin extractable by  $\text{EtOH}$ . The bearing of extraction data on the nature of the tannins is discussed. F. O. H.

**Grayanotoxins, active constituents of *Leucothoe grayana*.**—See this vol., 995.

**Carotenoids and their physiological importance.** L. ZECHMEISTER (Chem.-Ztg., 1936, 60, 505—508).—A review.

**Petroleum-soluble fluorescent constituents of leaves.** H. H. STRAIN (Nature, 1936, 137, 946—947).—Two fluorescent substances have been isolated from the leaves of many plants, and from etiolated maize and barley seedlings, by chromatographic adsorption (light petroleum-MgO). By their fluorescence and activation these materials may affect many processes such as photosynthesis, pigment formation, etc. L. S. T.

**Determination of chlorophyll.**—See this vol., 1006.

**Purification and fluorescence spectrum of chlorophyll-*b*.**—See this vol., 923.

**Physostigmine-like drug.** F. W. FREISE (Pharm. Zentr., 1936, 77, 378—379).—Characteristics of the seeds [alkaloids (identical with physostigmine), 1.58—2.85% (mainly in testa); oil, 6—9%] of certain species of *Dioclea* (resembling *Physostigma venenosum* and found in S. America) are described. F. O. H.

***Atropa betica*.** E. GÓMEZ MÚGICA (Anal. Fis. Quim., 1936, 34, 100—102).—*A. betica* contains 0.58% of hyoscyamine and 0.18% of atropine. F. R. G.

**Drugs from Bolivia.** L. KOON (Arch. Pharm., 1936, 274, 343—369).—Steam-distillation of the rhizomes and roots of *Dorstenia brasiliensis* gives a neutral substance,  $\text{C}_{34}\text{H}_{18}\text{O}_{10}$ , m.p. 151°, present partly as ester; ligroin extracts the same ester, and hydrolysis of the extract gives also a volatile, pungent substance and an acid,  $\text{C}_{37}\text{H}_{23}\text{O}_{10}$ , m.p. 139°. Further general chemical characteristics of this and other plants are given. R. S. C.

**Pharmacognosy of peyotl. II. Microscopy and chemistry.** E. BECCARI (Arch. Farm. speriment., 1936, 61, 161—185).—The characteristics of preps. of the dried testa of *Echinocactus Williamsi*, Lem. (mezcal buttons; cf. Kauder, A., 1899, i, 650), and of common adulterants are described. Analytical data for contents of ash, waxes, resins, and  $\text{CHCl}_3$ - and  $\text{EtOH}$ -sol. fractions and for total alkaloids and their distribution are given. F. O. H.

**Proteins of wheat bran.** I. S. JAITSCHNIKOV and T. V. SCHVEDOVA (J. Gen. Chem. Russ., 1936, 6, 584—587).—The content of  $\text{H}_2\text{O}$ -, aq.  $\text{NaCl}$ -, and aq.  $\text{NaOH}$ -sol. proteins is determined. R. T.

(A) "Proto-acid" of the field nut. V. A. DALMATOV. (B) "Proto-acid" of fibrin. S. S. PEROV. (C) Identity of racemisation curves of some "proto-acids." I. LEONTEV and K. MARKOVA. (D) "Proto-acid" of soya bean. S. S. PEROV, P. DJATSCHENKO, and K. SCHELPAKOVA. (E) "Proto-acid" of lupin. S. S. PEROV, P. DJATSCHENKO, and K. SOVETINOVA. (F) "Proto-acid" of ovalbumin. S. S. PEROV. (G) Transformation of globulin into "proto-acid." P. DJATSCHENKO (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1933, No. 4, 50—53; No. 5, 39—54; 1935, No. 7, 17—25, 39—51, 52—54, 55—61, 67—75).—(A) The proto-acid (I) extracted with  $\text{NaOH}$  from the fat-free nut has the same acidity, N content, electrical conductivity,  $\eta$ , surface tension, and  $n$  (in 1% solution) as casein (II).

(B) Blood contains a (I) similar to (II). Differ-



ences in blood-proteins are ascribed to complexes consisting of (I) combined as a salt or ester with other compounds.

(c) Every protein dissolved in dil. alkali exhibits a definite rate of racemisation. The (I) of egg-white, fibrin, (II), soya beans, and peas shows the same racemisation curve.

(d) The (I) of soya bean (prep. described) has the same composition and physical consts. as (II), including coagulation by rennin.

(e) The (I) is physically identical with (II), which it can replace in the manufacture of glue and plastics.

(f) Prep. of the (I) is described. It is indistinguishable from (II).

(g) Conversion of glycinin (from soya bean) into (I) is described. The (I) is identical with (II).

CH. ABS. (p)

**Casein** ("caseinic acid"). S. S. PEROV (Trud. Belkovo Lab. Sborn., 1931, 82 pp.).—The separation, purification, and titration of casein are examined and the cryst. product is prepared. Milk contains only a single protein, lactalbumin, lactoprotein, etc. being merely physical modifications of casein.

CH. ABS. (p)

**Vegetable "proto-acid."** S. S. PEROV and M. LISITZUIN (Trud. Belkovo Lab. Sborn., 1932, 69 pp.).—The prep. and properties of proto-acid from beans, oats, peas, and wheat are described. All yield the same acid, which is similar to "caseinic acid" (see preceding abstract).

CH. ABS. (p)

**Structure of protein phases in plant substrata.** S. S. PEROV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1932, No. 3, 32—50).—The classification of proteins into globulins, albumins, etc. is criticised. Globulin from peas is an impure proto-acid.

CH. ABS. (p)

**Physicochemical and immunological properties of the protein from seeds of *Phaseolus aureus*,** R. I. LEONTEV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1933, No. 5, 62—67).—The purified proto-acid has the same physical consts. as has casein and produces no anaphylactic shock in guinea-pigs. Geographical, meteorological, and soil conditions prevailing during the growth of a plant have no effect on the chemical and physiological structure of the protein in the seed. CH. ABS. (p)

**Preparation of pure proto-acid from peas on a semi-plant scale.** V. A. DALMATOV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1935, No. 7, 76—94).—Yields of 17% of proto-acid and 42% of starch are obtained from ground peas. CH. ABS. (p)

**Interferometer for biological work.** R. JONNARD (Compt. rend. Soc. Biol., 1936, 122, 396—398). H. G. R.

**Electron microscopic photographs of chitin objects.**—See this vol., 955.

**Micro-electrode for determining  $p_H$ .** V. A. DORFMAN (Bull. Biol. Med. Exp. U.R.S.S., 1936, 1, 133—134).—Apparatus is described. Determinations are made in  $H_2$  and an agar block containing 0.1N-KCl is used instead of a solution. Strictly anaerobic determinations cannot be made. W. McC.

**Resistance for determination of redox potentials in biological fluids.** M. E. FREEMAN (Science, 1936, 83, 562). L. S. T.

**Potentiometric adaptation of the Shaffer-Hartmann sugar method.** L. F. NEY and E. S. WEST (J. Biol. Chem., 1936, 114, 547—550).—The sugar solution, Fe or Zn blood filtrate, or  $Fe_2(SO_4)_3$ -Lloyd's reagent urine filtrate is heated with Shaffer-Somogyi reagent (A., 1933, 699), a  $K_3Fe(CN)_6$ -citrate solution is added, and the potential against a blank, similarly treated, is determined. H. D.

**Use of ceric salts in the micro-determination of glucose.**—See this vol., 968.

**Micro-determination of mol. wt. in exaltone.**—See this vol., 956.

**Micro-method for accurate determination of  $D_2O$  in water.**—See this vol., 949.

**Determination of total base in blood and other biological fluids by the electro dialysis method of Adair and Keys.** A. KEYS [with W. V. CONSOLEZIO] (J. Biol. Chem., 1936, 114, 449—459).—The application of the method (A., 1935, 52) to biological fluids is described. An average error of 1% with samples of 0.2 ml. was obtained. H. D.

**Determination of total creatine.** C. CIACCIO and I. CIACCIO (Boll. Soc. ital. Biol. sperim., 1935, 10, 927—928).—The tissue is deproteinised by means of  $CCl_3CO_2H$ , the extract is conc. in presence of HCl, neutralised, pptd. by  $ZnSO_4-NaOH$ , and creatine in the resulting filtrate is determined by  $NaOH$ -picric acid reagent. F. O. H.

**Photo-electric micro-determination of copper.** B. EISLER, K. G. ROSDAHL, and H. THEORELL (Biochem. Z., 1936, 285, 76—77).—The method permits the determination of  $0.5 \times 10^{-6}$  g. of Cu in biological material in presence of Fe. P. W. C.

**Determination of chlorides in biological fluids by use of adsorption indicators.** Use of diphenylamine-blue for volumetric micro-determination of chlorides in urine and blood-filtrates. A. SAIFER and M. KORNBLUM (J. Biol. Chem., 1936, 114, 551—555).— $Cl^-$  is determined by acidification, addition of octyl alcohol, and titration with  $AgNO_3$  with  $NHPh_2$ -blue as indicator. H. D.

**Micro-determination of fluorine in plant and animal matter.** A. MAYRHOFER and A. WASITSKY [with W. KORN] (Mikrochem., 1936, 20, 29—48).—The material is mixed with glass powder and  $H_2SO_4$ , the F being distilled off as  $SiF_4$  and absorbed in NaOH. The Si is determined colorimetrically with  $NH_4$  molybdate, quinol, and a mixture of  $Na_2CO_3$  and  $Na_2SO_3$ , comparison being made with a synthetic solution (aq.  $CuSO_4$  with  $NH_3$  and traces of picric acid) standardised against aq.  $Na_2SiO_3$ . Natural products are ashed and the F in the sol. portion of the ash is pptd. with  $La(OAc)_3$  and ignited gently, this product being combined with the insol. ash for the determination. J. W. S.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

SEPTEMBER, 1936.

### General, Physical, and Inorganic Chemistry.

**Atomic hydrogen and the disappearance of hydrogen in discharge tubes.** R. DELAPLACE (Compt. rend., 1936, 202, 1986—1987).—If traces of  $\text{H}_2\text{O}$  vapour and Hg are excluded from the discharge, no fall in pressure occurs and no CO and  $\text{CH}_4$  are formed. In absence of  $\text{H}_2\text{O}$  vapour the formation of at. H is restricted. Heating the glass liberates traces of  $\text{CO}_2$ , CO, and  $\text{H}_2$ . H. J. E.

**Intensities in the principal series of lithium.** S. WEINTROUB (Proc. Physical Soc., 1936, 48, 535—548).—The effect of using orthogonal wave functions in the calculation of the optical terms and oscillator strengths ( $f$  nos.) of the first three lines of the principal series of Li has been investigated. Good agreement with observed vals. is obtained for the optical terms; the agreement for the  $f$  nos. is not so good, but is better than that obtained using non-orthogonal wave functions. W. R. A.

**Spectra Be III and Be IV.** H. A. ROBINSON (Physical Rev., 1936 [ii], 50, 99).—New determinations of the  $\lambda\lambda$  of the  $1s^21S_0-1s.np^1P_1$  series of Be III and the  $1s^2S-np^2P$  series of Be IV are recorded. A. J. M.

**Absorption coefficients of the 4774, 5770, and 6290 A. oxygen bands.** L. HERMAN and (MME.) R. HERMAN-MONTAGNE (Compt. rend., 1936, 202, 2064—2066).—Data are recorded. The absorption  $\propto$  the square of the pressure (4—12 kg. per sq. cm.). H. J. E.

**Influence of carbon monoxide, adsorbed by a platinum electrode, on the current-potential relations of the electrical discharge in oxygen.** V. SIHVONEN (Z. Elektrochem., 1936, 42, 538—544).—In streaming  $\text{O}_2$  at low pressure CO is produced at a C anode and is oxidised to  $\text{CO}_2$  by  $\text{O}_2$  adsorbed by a Pt cathode. When C is the cathode,  $\text{CO}$  is strongly adsorbed by the Pt anode and prevents emission of ions until removed by the streaming  $\text{O}_2$ , when the current momentarily passes. E. S. H.

**Stark effect in neon.** N. RYDE (Z. Physik, 1936, 100, 771—773).—Polemical, against Steubing and Kindler (this vol., 653). A. B. D. C.

[Stark effect in neon.] W. STEUBING and H. KINDLER (Z. Physik, 1936, 100, 773).—A reply to Ryde (see above). A. B. D. C.

**Transparency of sodium and potassium films in the Schumann region.** W. H. WATSON and D. G. HURST (Nature, 1936, 138, 124).—A Na film on fluorite is an ideal filter to remove all visible and ultra-violet light of  $\lambda > 2100$  A., and to pass the entire Schumann region. The results for Na and K

do not support the existing theory of the optical properties of metals. L. S. T.

**Isotope shift in the resonance line of magnesium.** D. A. JACKSON and H. KUHN (Proc. Roy. Soc., 1936, A, 154, 679—683).—The singlet resonance line 2852 A. of Mg is shown by the at. beam method to possess two components at a separation of 0.033  $\text{cm}^{-1}$ , the component of longer  $\lambda$  being much stronger than the other. The splitting of the line is ascribed to an isotope shift, the stronger line being due to the abundant isotope 24 and one of the other two, and the weaker line to the third isotope. L. L. B.

**Band spectrum of sulphur.** A. CHRISTY (Physical Rev., 1935, [ii], 47, 251).—A reply to criticism (this vol., 397). L. S. T.

**Optical L spectra of chlorine, Cl VIII, Cl IX, Cl X, and Cl XI.** B. EDLÉN (Z. Physik, 1936, 100, 726—733). A. B. D. C.

**Nuclear spin and magnetic moment of potassium (41).** J. H. MANLEY (Physical Rev., 1936, [ii], 49, 921—924; cf. Fox, this vol., 1).—The spin of the  $^{41}\text{K}$  nucleus and the hyperfine structure separation of the  $^2S_1$  normal state were measured by the method of zero moments, the high resolution for separating the two isotopes being obtained by passing a beam of neutral K atoms through a weak inhomogeneous magnetic field 153 cm. long. The spin was  $3/2$ , and the hyperfine structure separation and magnetic moments  $0.554 \pm 0.2\%$  of those of  $^{39}\text{K}$ , the vals. of which give for  $^{41}\text{K}$  0.22 nuclear Bohr magneton and  $0.00853 \pm 0.0001 \text{ cm}^{-1}$  for magnetic moment and separation, respectively. The abundance ratio  $^{39}\text{K}/^{41}\text{K}$  is  $13.4 \pm 0.5$ . N. M. B.

**Narrow continuous band of potassium in the extreme red.** T. OKUDA (Nature, 1936, 138, 168).—A broadening of the resonance lines in the extreme red absorption spectrum of K vapour in  $\text{H}_2$ , and the appearance, at higher temp., of a narrow, continuous band at approx. 7220 A. has been observed. L. S. T.

**Use of the reflexion echelon for interferometric wave-length comparisons extending into the Schumann region.** D. L. MACADAM (Physical Rev., 1936, [ii], 50, 185).—Measurements of eight  $\lambda\lambda < 2100$  A. for Cu II agree to  $< 0.004$  A. with calc. vals. Difficulties of the method are discussed. N. M. B.

**Emission spectrum of diatomic arsenic.** G. M. ALMY and G. D. KINZER (Physical Rev., 1935, [ii], 47, 199).—The mol. spectrum of As in emission



consists of an extensive group of bands between 2250 and 3750 Å. and a weak group near 4200 Å.

L. S. T.

**Structure of bromine III.** K. R. RAO (Nature, 1936, 138, 168).—An extension of previous work (A., 1935, 423).

L. S. T.

**Hyperfine structure of the cadmium resonance line.** A. G. SHENSTONE (Physical Rev., 1935, [ii], 47, 317).

L. S. T.

**Fluorescence spectra of antimony vapour excited by cadmium, zinc, and magnesium sparks.** R. SIKSNA (Acta phys. polon., 1933, 2, 253—265; Chem. Zentr., 1935, ii, 3062).—Data for the line and band fluorescence are given.

H. J. E.

**Fluctuation bands of the vapour of diatomic tellurium.** M. DESIRANT and A. MINNE (Bull. Acad. roy. Belg., 1936, [v], 22, 646—658).—A series of wide and symmetrical bands showing fluctuations in intensity have been observed in the spectrum of the vapour of  $\text{Te}_2$ . The bands are composed of numerous fine bands degraded towards the red. Two systems may be recognised, one extending from the last bands of the principal system to 6000 Å., the other from 6000 Å. into the red. The heat of dissociation for the normal state of  $\text{Te}_2$  is calc. to be 2.3 volts.

A. J. M.

**First spark spectrum of caesium as excited by electron impact.** R. R. SULLIVAN (Physical Rev., 1936, [ii], 49, 912—916).—An apparatus for the study of the controlled excitation of spectra of volatile metals is described. Certain aspects of the optical excitation functions for several Cs II lines are given. Onset potentials are compared with those predicted by existing energy level schemes, and possible transitions are suggested for the unclassified lines  $\lambda\lambda$  4264.7 and 4763.6.

N. M. B.

**Resonance radiation of mercury 2536.7 Å. line, avoiding Doppler broadening.** S. YEN (Helv. phys. Acta, 1935, 8, 225—246; Chem. Zentr., 1935, ii, 2782).—The Doppler broadening is avoided by exciting the resonance line in a beam of Hg at. rays. Zeeman resolution of the line is observable with very low magnetic fields, revealing a new magnetic effect.

J. S. A.

**Paschen-Back effect of hyperfine structure. III. Separation of  $^{199}\text{Hg}$ .** J. B. GREEN (Physical Rev., 1936, [ii], 50, 126—128; cf. A., 1935, 137).—The magnetic components due to  $^{199}\text{Hg}$  have been separated. The lines studied were  $\lambda\lambda$  3125, 5461, 4358, and 4047. An almost complete Paschen-Back effect is observed, each ordinary Zeeman component being accompanied by two satellites due to the nuclear spin  $i = \frac{1}{2}$ . Results agree closely with theory.

N. M. B.

**Afterglow in electrically excited mercury vapour.** K. NARKIEWICZ-JODKO (Acta phys. polon., 1933, 2, 311—333; Chem. Zentr., 1935, ii, 3064).—Measurements at  $100\text{—}300^\circ/2.6\text{—}87\text{ mm.}$  are recorded. The mm. pressure for the afterglow was 2 mm. The effective diameter of excited Hg was  $6 \times 10^{-8}\text{ cm.}$ , assuming a life of  $10^{-7}\text{ sec.}$

H. J. E.

**Distribution of atomic nuclear spins.** S. TOLANSKY (Nature, 1936, 137, 1071; A., 1935, 676).—Diagrams showing the distribution of nuclear spins in atoms of odd at. wt. are given. The preponderance of spin of val.  $\frac{1}{2}$  in the case of nuclei with an odd nuclear neutron indicates that neutron spin and orbital moments tend to oppose each other.

L. S. T.

**Electrical discharge between rotating copper electrodes.** A. KOTECKI (Acta phys. polon., 1934, 3, 105—114; Chem. Zentr., 1935, ii, 3209).—The voltage drop across a 10-mm. arc in air at atm. pressure does not vary with the speed of rotation of the electrodes (Cu or Al).

H. J. E.

**Second sheath near the [oxide-coated] cathode of an arc discharge [in rare gases].** N. WARMOLTZ (Nature, 1936, 138, 36).

L. S. T.

**Ultra-violet stellar spectra with aluminium-coated reflectors. IV. Spectrum of  $\alpha$  Boötis.** R. W. SHAW (Astrophys. J., 1936, 83, 225—237).—Lines between 3150 and 3950 Å. are tabulated. Al, Cr, Cu, Fe, Ni, Na, Ti, and V, and the NH mol. spectrum have been identified.

L. S. T.

**Effect of oxygen on the auroral afterglow.** J. KAPLAN (Nature, 1936, 138, 35).

L. S. T.

**Absorption-line intensities in B-type stars.** E. G. WILLIAMS (Astrophys. J., 1936, 83, 279—304).

L. S. T.

**Connexion between emission intensity and violet displacement of the absorption lines in the spectrum of P. Cygni.** T. ARAKI and M. KURIHARA (Proc. Imp. Acad. Tokyo, 1936, 12, 125—127).

A. J. M.

**X-Ray wave-length scales.** A. E. RUARK (Physical Rev., 1935, [ii], 47, 316; cf. A., 1934, 333).—When  $4.806 \pm 0.003 \times 10^{-10}\text{ e.s.u.}$  is used for  $e$  and  $1.7579 \times 10^7\text{ e.m.u./g.}$  for  $e/m$ , the discrepancy between measured photo-electron energies and those calc. from X-ray  $\lambda\lambda$  is explained.

L. S. T.

**Absorption of X-rays of wave-length 50 to 150 Å. by elements of low atomic number.** T. R. CUYKENDALL (Physical Rev., 1936, [ii], 50, 105—109).—Mass absorption coeffs. accurate to 2% were determined for C, Na, Al, S, K, Ni, and Cu for the range 50—209 Å. Vals. of the electronic scattering coeff. by the Klein-Nishina formula are in good agreement with experiment for C in the range 40—100 X. The photo-electric absorption in Cu is  $\propto \lambda^2$ .

N. M. B.

**Absorption of ultra-short X-rays by elements of high atomic number.** M. T. JONES (Physical Rev., 1936, [ii], 50, 110—114; cf. preceding abstract).—Mass absorption coeffs. accurate to 0.8% were measured for Pb, Ta, Sn, Ag, Mo, and Nb for the range 30—185 Å. Photo-electric absorption is calc. and discussed in relation to at. no. and the Klein-Nishina formula.

N. M. B.

**Structure of the extremely soft X-ray absorption of solids.** H. M. O'BRYAN (Physical Rev., 1936, [ii], 49, 944).—The absorption of Li and Mg on celluloid and of Li and Na halides in the range 170—500 Å. shows, for Li, an additional band at 196 and a faint edge at 225 Å.; LiCl gives very sharp bands

at 204 and 192 Å., the other Li halides give similar bands, but the Na halides only one prominent band at 372 Å. Mg halides show a band near 235 Å. Mg gives a stronger edge at 237 than at 250 Å. The bands for the halides are due to the alkali ion of the crystal. There must be two sets of lattice levels. Results are in poor agreement with calculations.

N. M. B.

**Shape of the Compton lines.** A. SOMMERFELD (Physical Rev., 1936, [ii], 50, 38—40).—The continuous Compton band observed for bound electrons must have a definite limit on the short-wave side. Beyond this limit, and up to the unmodified Rayleigh line, there should be a no. of discrete lines, which may be termed Raman lines. There is no discontinuity in the intensity. The experimental conditions for observing these lines are discussed and it is suggested that lines observed by Ray in the spectrum of X-rays which have passed through thin films (A., 1930, 833) might thus be explained.

A. J. M.

**Correlation between scattering and recoil in the Compton effect.** J. C. JACOBSEN (Nature, 1936, 138, 25).—Experiments with  $\gamma$ -rays from Ra-Th confirm the usual theory of the Compton effect (cf. this vol., 265).

L. S. T.

**Relative and absolute values of atomic levels.** A. E. SANDSTROM (Phil. Mag., 1936, [vii], 22, 171—180).—A discussion of data obtained from X-ray absorption spectra and from the magnetic deflection of secondary electrons.

H. J. E.

**Natural width of the  $K\alpha$  lines.** H. MARGENAU (Physical Rev., 1935, [ii], 47, 89—90).

L. S. T.

**K Radiation of boron.** J. SERPE (Compt. rend., 1936, 202, 1979—1981).—The K radiation of powdered B is a single continuous band. The effect of temp. on its structure is discussed.

H. J. E.

**K Radiation of crystallised boron.** A. HAUTOT (Compt. rend., 1936, 202, 2138—2140).—The increase of conductivity and the variation in the K radiation bands with rise of temp. for cryst. B prepared by reducing  $\text{BCl}_3$  with  $\text{H}_2$  in a condensed high-frequency spark are explained on the supposition that the valency electrons are held in the crystal lattice at low temp. ( $600^\circ$ ), and are liberated at high temp. ( $1530^\circ$ ).

C. R. H.

**$K\alpha$  Satellite lines.** L. G. PARRATT (Physical Rev., 1936, [ii], 50, 1—15).—The  $K\alpha_{3,4}$  group of X-ray satellite lines has been recorded for the elements from S (at. no. 16) to Ge (32). For elements of at. no. between 16 and 28 there are five components of the satellite lines, and for those between 29 and 32 there are four. The widths, indices of asymmetry, and overlapping factors of the  $K\alpha_{1,2}$  lines were also determined. The effect of chemical linking, determined by using targets of various Ca compounds, was negligible.

A. J. M.

**$L\alpha$  Satellites for the elements 72, 73, 75, 83, 90, and 92.** (MLLE.) Y. CAUCHOIS (Compt. rend., 1936, 202, 2068—2069; cf. this vol., 3).—Data are summarised and discussed.

H. J. E.

**Formation of a potassium film on silver.** J. J. BRADY (Physical Rev., 1935, [ii], 47, 197).—The

photo-electric properties of K films deposited on a freshly evaporated Ag surface have been investigated with special reference to the saturation of the photo-current.

L. S. T.

**Use of the image potential for the surface photo-electric effect.** R. D. MYERS (Physical Rev., 1936, [ii], 49, 938—939).—The calc. surface photo-electric effect, taking account of the image force between electron and metal, shows an increased no. of slow electrons and a somewhat steeper max. of the effect as a function of the illuminating frequency.

N. M. B.

**Photo-electric effect of the deuteron.** G. BREIT and E. U. CONDON (Physical Rev., 1936, [ii], 49, 904—911).—Theoretical cross-sections for the dissociation of the deuteron by absorption of  $\gamma$ -rays (the Chadwick-Goldhaber effect) are calc., and curves of cross-section as a function of energy for various assumed widths are given and discussed.

N. M. B.

**Thermionic emission from platinum in bromine and chlorine vapour.** S. KALANDYK (Acta phys. polon., 1934, 3, 165—178; Chem. Zentr., 1935, ii, 3209—3210).—The negative emission from Pt is increased by the presence of Br and occurs at a relatively low temp. ( $160^\circ$  for 0.235 mm. Br pressure). The effect increases with the Br pressure. It is attributed to a chemical reaction. The + emission is unchanged. At very high temp. the normal emission from Pt is observed. Similar results were obtained for Cl<sub>2</sub> and I.

H. J. E.

**Ionisation of gases by collisions of their own accelerated atoms.** R. N. VARNEY (Physical Rev., 1936, [ii], 50, 159—161).—Neutral atom beams of rare gases of energies 20—400 volts were produced by accelerating ionised atoms and then neutralising the charges. The min. energies needed by these neutral atoms to ionise gas atoms by collision were determined. Ne, Ar, Kr, and Xe ionised their own gases at energies about three times the actual ionisation potentials.

N. M. B.

**Total ionisation of nitrogen by electron collisions.** (MISS) G. A. ANSLOW and (MISS) M. DE B. WATSON (Physical Rev., 1936, [ii], 50, 162—169).—The total ionisation by beams of electrons of homogeneous velocity and energies  $> 1500$  volts increases rapidly up to 75 volts, then less rapidly but linearly to 375 volts, for which there is a break in the ionisation curve, indicating the onset of K electron ionisation; the ionisation again increases rapidly near 750 volts and less rapidly but linearly after 1200 volts. The mean effective ranges and electron energies nearly obey the relation  $R_0 = 0.07 + 1.88 \times 10^{-6} V^2$  cm. at 1 mm. pressure. The average total ionisation per cm. of absorbing gas layer shows a max. above 100 volts in the primary ionisation region and a second max. at 750 volts, twice the ionisation potential of the K electrons of N, these characteristics being similar to those for air.

N. M. B.

**Secondary electron emission from a hot nickel target due to bombardment by hydrogen ions.** (MISS) M. HEALEA and E. L. CHAFFEE (Physical Rev., 1936 [ii], 49, 925—930).—Consistent vals. were



obtained after keeping the target hot for 6 weeks. The no. of electrons emitted from the target per positive ion varied from 0.046 at 303 e.v. to 0.223 at 1539 e.v. ion energy. N. M. B.

(A) Inelastic scattering of electrons from solids. E. RUDBERG. (B) Theory of inelastic scattering of electrons from solids. E. RUDBERG and J. C. SLATER (Physical Rev., 1936, [ii], 50, 138—150, 150—158).—(A) The energy distribution of electrons scattered inelastically from Cu, Ag, and Au surfaces deposited in vac. was investigated for the energy range 50—400 volts. For certain vals. of the energy loss suffered by the scattered electron the curves show max. characteristic of the material and independent of the primary voltage. Each metal has two max. below 10 volts, and these appear to correspond roughly with regions of high optical absorption. The penetration depth of the scattered electron, estimated from energy distribution measurements on films of Ca, CaO, Ba, and BaO of known thickness deposited on Ag, shows that inelastic scattering is determined by the first few at. layers near the surface. The Ca and Ba deposits show a high rate of oxidation, even at  $< 10^{-7}$  mm. pressure. The distribution curves for the oxides differ entirely from those for the metal.

(B) Mathematical. A detailed calculation is given for Cu. The distribution curve and its two max. are in good agreement with experiment. N. M. B.

Anomalies in the charging of gas molecules by slow ions. F. WOLF (Naturwiss., 1936, 24, 447—448).—An earlier method (this vol., 539) has been improved, and the form of the charge transference cross-section against ionic velocity studied for  $H_2^+ \rightarrow N_2$ ,  $H^+ \rightarrow A$ , and  $H^+ \rightarrow H_2$  for low ionic velocities. There is a more or less definite secondary max. or min. in the curves at low velocities.

A. J. M.

Production of radiation and ionisation from helium atoms by potassium positive ions. (Miss) A. C. DAVIES (Proc. Roy. Soc., 1936, A, 155, 123—141).—The excitation and ionisation of neutral He atoms by a beam of  $K^+$  ions of controlled energy has been investigated. The beginning of measurable ionisation plus radiation effects occurs at about 450 volts. The no. of electrons produced per K ion per cm. of path at a 1 mm. pressure by 750-volt ions is estimated as  $8.7 \times 10^{-3}$ , and by 3000-volt ions as  $2.3 \times 10^{-1}$ . Possible causes of the discrepancies in results of previous investigators are discussed.

L. L. B.

Preparation and investigation of a new alkali ion source. J. KOCH (Z. Physik, 1936, 100, 669—684).—An alkali chloride mixed with degassed W powder is a very pure source of Cs, Rb, and K ions.

A. B. D. C.

Incidence of positive caesium ions on a degassed tungsten surface. J. KOCH (Z. Physik, 1936, 100, 685—701).—Cs ions incident on a W surface are largely reflected, and the saturation Cs layer is  $< 0.1$  monat.

A. B. D. C.

New process of negative ion formation. F. L. ARNOT (Nature, 1936, 138, 162).—The majority of negative ions formed by the passage of a stream

of electrons through Hg vapour,  $H_2$ ,  $N_2$ ,  $O_2$ , and  $CO_2$  do not arise by the attachment of an electron to an atom. They are formed from positive ions which extract two electrons from any negatively charged electrode, including the filament, to which they are driven. Occasionally the positive ion is dissociated by its collision with the surface and the negative ion then formed is one of the products of dissociation; e.g., the negative ions detected in  $CO_2$  are  $CO_2^-$ ,  $CO^-$ ,  $O_2^-$ ,  $O^-$ , and  $C^-$ . In  $O_2$ , both  $O_2^-$  and  $O^-$  are found, but Hg vapour,  $H_2$ , and  $N_2$  give only the at. negative ion. The probability of conversion of positive into negative ions on a Ni surface in each gas increases as the energy of the positive ion is increased, and data for the conversion of a 180-volt positive ion are recorded. L. S. T.

Fundamental at. wts. Ratio of silver nitrate to silver chloride. O. HONIGSCHMID and R. SCHLEE (Angew. Chem., 1936, 49, 464—466).—The mean of eight determinations yields a val. of 1.185241 for the ratio  $AgNO_3 : AgCl$ . Combining with the vals. 1.57479 and 4.042592 for the ratios  $AgNO_3 : Ag$  and  $AgCl : Cl$ , respectively, the at. wts. of Ag, Cl, and N are 107.8812, 35.4562, and 14.0088, respectively.

J. W. S.

Calculation of at. wts. from nuclear reaction energies. H. A. WILSON (Proc. Roy. Soc., 1936, A, 154, 560—563; cf. A., 1935, 1443).—It is shown that at. wts. with  $^{16}O = 16$  can be calc. from nuclear reaction energies without making use of at. wts. determined by other methods. Vals. obtained for 18 light elements in this way are in agreement with those of Bethe and of Oliphant, Kempton, and Rutherford from mass spectrograph results (cf. A., 1935, 910).

L. L. B.

Masses of  $^9Be$ ,  $^{10}Be$ , and  $^{11}B$  as determined from transmutation data. H. R. CRANE and C. C. LAURITSEN (Physical Rev., 1935, [ii], 47, 420).—Vals. deduced are  $^9Be$  8.0059,  $^{11}B$  11.0095 or 11.0093,  $^{10}Be$  9.0125 (approx.  $2 \alpha$ -particles + 1 neutron).

L. S. T.

Differences in the isotopic composition of atmospheric and aqueous oxygen and the electrolytic separation factor of oxygen isotopes. N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 414—418).—The  $d$  of light  $H_2O$  prepared by combination of  $D_2$ -free  $H_2$  and atm.  $O_2$  indicates that atm.  $O_2$  is 0.0007% heavier than  $O_2$  from  $H_2O$ , and that the electrolytic separation factor for  $O_2$  isotopes is  $1.01 \pm 0.01$ .

C. R. H.

Influence of density differences between atmospheric and aqueous oxygen on data for oxygen and hydrogen isotopes. N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 419—424).—Contemporary vals. for the ratio  $D : H$  and for the electrolytic separation factor for O isotopes are compared and discussed.

C. R. H.

Isotopes in induced radioactivity. T. R. WILKINS and L. S. SHNIDMAN (Physical Rev., 1935, [ii], 47, 251).—The final stable products of nuclear transformations resulting from  $\alpha$ -ray bombardment, viz.,  $^{30}Si$ ,  $^{13}C$ ,  $^{27}Al$ , etc., are all isotopes of rarest occurrence according to mass spectrum data. In

transformations from neutron bombardment the resulting stable atoms such as  $^{16}\text{O}$ ,  $^{24}\text{Mg}$ ,  $^{32}\text{S}$ , etc. are the most frequently occurring isotopes. Transformations occurring in nature thus appear to be more frequently of the neutron type. L. S. T.

**Isotopic constitution of iron and nickel.** A. J. DEMPSTER (Physical Rev., 1936, [ii], 50, 98).—The mass spectrum of Fe obtained by sparking between pure electrolytic Fe electrodes indicates the existence of isotopes of Fe of mass 54, 56, 57, and 58, the last being the weakest. The mass spectrum of Ni obtained by fractionating  $\text{Ni}(\text{CO})_4$  showed the presence of isotopes of mass 58, 60, 61, 62, and 64. A. J. M.

**Mass spectrograph analysis of bromine.** J. P. BLEWETT (Physical Rev., 1936, 49, 900—903).—Attempts to observe a third isotope to explain the three periods of artificial radioactivity induced by slow neutrons show that an isotope 77 or 83 cannot be present to more than 1 in 3000. The abundance ratio  $81/79$  was  $0.975 \pm 0.025$ , giving the at. wt. of Br  $79.92 \pm 0.02$  on Aston's scale or  $79.90 \pm 0.02$  on the at. wt. scale. The processes of formation of positive and negative Br ions by slow electrons were studied, giving heat of dissociation of  $\text{Br}_2$   $1.9 \pm 0.5$  volts, and electron affinity of Br  $3.8 \pm 0.2$  volts. N. M. B.

**Isotopic constitution of barium and cerium.** A. J. DEMPSTER (Physical Rev., 1936, [ii], 49, 947; cf. Blewett, this vol., 772).—Mass spectra photographs of Ba ions formed in a high-frequency spark between Ba electrodes show very faint isotopes at 130 and 132; Ce gives similar results at 136 and 138. On a neutron-proton plot of the isotopes  $^{130}\text{Ba}$  and  $^{136}\text{Ce}$  fall on the straight line indicating the lower mass limit for nuclear stability. N. M. B.

**Isotopic constitution of strontium and tellurium.** A. J. DEMPSTER (Physical Rev., 1936, [ii], 50, 186).— $^{84}\text{Sr}$  is confirmed (cf. Blewett, this vol., 772). Mass spectra of the charged atoms from a spark between Te and Pd electrodes show a new faint  $^{120}\text{Te}$ , but no trace of  $^{127}\text{Te}$  indicated by Bainbridge (cf. A., 1933, 1099). N. M. B.

**Mass equivalent of the energy in radioactive transformations.** A. J. DEMPSTER (Nature, 1936, 138, 201).—A spark between electrodes of Pb and Pd or Pt-Rh forms doubly-charged Pb ions which give close doublets in the mass spectrograph with the singly-charged Rh and Pd ions at 102, 103, and 104. The at. masses deduced for the Pb isotopes are  $206.00 \pm 0.01$  and  $208.00 \pm 0.01$ . These vals. agree with those obtained for U-Pb and Th-Pb from the radioactive transformations of U and Th, provided that an allowance is made for the mass equivs. of the energy emitted in these processes. L. S. T.

**Isotopic constitution of lead from hyperfine structure.** J. L. ROSE and R. K. STRANATHAN (Physical Rev., 1936, [ii], 49, 916—920; cf. A., 1935, 270).—The % relative abundances of the Pb isotopes, determined from intensity measurements of the hyperfine structure components of the spark line  $\lambda = 2203$ , were 51.5, 26.3, 21.4, and 0.8 for isotopes 208, 206, 207, and 204, respectively. For integral

masses of the isotopes the mean mass no. is  $207.22_8$ , giving 207.20 on the at. wt. scale, assuming a packing factor of +1. N. M. B.

**Atomic masses of uranium and thorium.** A. J. DEMPSTER (Nature, 1936, 138, 120).—Doublets obtained in the mass spectrograph with  $\text{Th}^{++}$  and  $^{116}\text{Sn}$ , and  $\text{U}^{++}$  and  $^{119}\text{Sn}$  give 232.070 and 238.088 ( $\text{O} = 16.000$ ) for the at. masses of Th and U, respectively. Doubly-charged ions of  $^{235}\text{U}$ , mass 235.084  $\pm 0.01$ , also appeared. Reduced to the chemical scale, the at. wts. become 232.024 for Th and 238.028 for the mean of the two U isotopes, compared with the accepted vals. of 232.12 and 238.14, respectively. Electrodes prepared from heated  $\text{UO}_2(\text{NO}_3)_2$  and Na uranyl acetate also gave  $^{235}\text{U}$ , which is regarded as isomeric with the short-lived isotope formed by neutron bombardment of U (this vol., 773). These isotopes have the same mass and charge, but differ in nuclear properties. L. S. T.

**Mechanism of isotopic exchange reactions.** E. OGAWA (Bull. Chem. Soc. Japan, 1936, 11, 425—427).—Theoretical. Polarisation of atoms probably plays the most important part, an element being richer in the heavier isotope when it is in the more positively polarised state. C. R. H.

**Arrangement of chemical elements in teaching.** E. WIBERG (Angew. Chem., 1936, 49, 480—481).—A new layout of the periodic table is described, in which the sub-groups and transition elements are introduced between the Ti and Ge sections of group II. J. W. S.

**Anchoring of radium emanation on nuclei.** G. ALIVERTI and G. ROSA (Atti R. Accad. Sci. Torino, 1934—1935, 70, I, 266—271; Chem. Zentr., 1935, ii, 2847).—The binding of Rn on nuclei in measurements of atm. radioactivity is improbable; the effect is probably due to Th-Em. J. S. A.

**Disintegration constant of thorium and branching ratio of thorium-C.** A. F. KOVARIK and N. I. ADAMS, jun. (Physical Rev., 1936, [ii], 50, 99).—By means of a mechanical counter to determine the rate of emission of  $\alpha$ -particles from  $\text{ThO}_2$  and its products, the  $\text{ThO}_2$  being covered with celluloid to prevent escape of Th-Em, the val. of the disintegration const.  $\lambda$  was found to be  $5.17 \times 10^{-11}$  years $^{-1}$ , the half val. period being  $1.34 \times 10^{10}$  years. The branching ratio of Th-C is 0.660. A. J. M.

**Materialisation of the energy of  $\beta$ -rays from radium-C.** A. M. DA SILVA (Compt. rend., 1936, 202, 2070—2072).—Data are recorded for the no. of positrons observed in a Wilson chamber with varying thicknesses of Pb surrounding the source. The effects due to the source and to  $\gamma$ - and  $\beta$ -rays are separated. Preliminary experiments with Al screens are described. H. J. E.

**$\gamma$ -Radiation from Po + Be.** G. BERNARDINI and L. EMO (Ric. sci. Prog. tec., 1935, II, 6, 17—23; Chem. Zentr., 1935, ii, 2924).—The max. energy of secondary electrons from Po+Be, measured by absorption in Al, is  $3.5 \times 10^6$  e.v. corresponding with  $\gamma$ -rays of  $3.7 \times 10^6$  e.v. J. S. A.



**Photon theory and Compton effect.** W. BOTHE and H. M. LEIBNITZ (Physical Rev., 1936, [ii], 50, 187).—Investigations showed that the Compton effect for Ra-C  $\gamma$ -rays is in agreement with the photon theory, and Shankland's anomalous results (cf. this vol., 265) are not supported but were probably due to inhomogeneity of the  $\gamma$ -rays. N. M. B.

**Experimental proof of the diffraction of neutrons.** H. VON HALBAN and P. PREISWERK (Compt. rend., 1936, 203, 73—75).—Data for the angular distribution of neutrons after diffraction through Fe powder at 90° and 300° abs. show that at lower temp. the intensity diminishes and increases for small and large deviations, respectively. C. R. H.

**Quantum energy of  $\gamma$ -rays excited by slow neutrons.** S. KIKUCHI, K. HUSIMI, and H. AOKI (Nature, 1936, 137, 992—993).—The absorption curves of the secondary electrons due to  $\gamma$ -rays emitted from 24 elements under bombardment by slow neutrons are discussed. L. S. T.

**Neutron.** H. A. SHADDUCK (J. Chem. Educ., 1936, 13, 303—308).—A summary of recent work. L. S. T.

**Neutrality of the neutron.** P. B. MOON (Proc. Physical Soc., 1936, 48, 658).—From the lack of influence of an electric field on neutrons of thermal velocities it is shown that the neutron has no electric charge as great as  $10^{-7}$  of the electronic charge. W. R. A.

**Experiments with neutrons having thermal energies.** J. R. TILLMAN (Proc. Physical Soc., 1936, 48, 642—647).—Different views regarding the influence of temp. on the properties of neutrons are discussed. W. R. A.

**Slowing down of neutrons by thin layers of paraffin.** S. NISHIKAWA, S. NAKAGAWA, and I. SUMOTO (Proc. Imp. Acad. Tokyo, 1936, 12, 128—130).—An analysis of neutron groups was made by passing neutrons through layers of paraffin of various thicknesses and measuring the  $\beta$ -activity induced by the neutrons in Ag and I. Cd filters were also used. A. J. M.

**Passage of neutrons through paraffin wax.** P. B. MOON (Proc. Physical Soc., 1936, 48, 648—657).—The velocity distribution of neutrons passing through paraffin wax is investigated on the assumption that the collisions made before thermal velocity has been reached are elastic collisions with protons. The no. of neutrons crossing unit area is investigated and the ratio of the flux of thermal neutrons in the interior to that at the surface is calc. W. R. A.

**Diffusion and absorption of neutrons in paraffin spheres.** D. M. YOST and R. G. DICKINSON (Physical Rev., 1936, [ii], 50, 128—132).—Measurements were made of the activities imparted to Ag and In detectors in paraffin spheres of various sizes with a Ra-Be source of neutrons at the centre. Results are in fair agreement with theory for distances from the source  $> 8$  cm. The mean free path of the neutrons in paraffin is 0.53 cm., and the ratio of the sp. absorption rate const. to the diffusion const. 0.026 cm.<sup>-2</sup> N. M. B.

**Cross-section measurements with slow neutrons of different velocities.** P. PREISWERK and H. VON HALBAN, jun. (Nature, 1936, 138, 163).—A correction (this vol., 772). L. S. T.

**Photo-neutrons.** D. P. MITCHELL, F. RASETTI, G. A. FINK, and G. B. PEGRAM (Physical Rev., 1936, [ii], 50, 189).—The slowing by H<sub>2</sub>O of neutrons obtained from the photo-disintegration of Be by Rn  $\gamma$ -rays was investigated, and the growth in no. was compared with that of neutrons from a Rn-Be source. The mean free paths of the Rn  $\gamma$ -Be photo-neutrons and Rn  $\alpha$ -Be neutrons were approx. 5 and 9 cm., respectively. The relative no. of photo-neutrons and  $\alpha$ -particle neutrons was 0.2 : 1. Similar experiments were made with the Rn bulb in the centre of a 200-c.c. sphere of pure D<sub>2</sub>O; the photo-neutrons were much slower, and their no. was 2% of the no. of neutrons from Rn-Be. N. M. B.

**Action of neutrons on heavy water.** W. F. LIBBY, E. A. LONG, and W. M. LATIMER (Physical Rev., 1935, [ii], 47, 424—425).—Interposition of D<sub>2</sub>O between target and source (Rn+Be) results in a large decrease in induced radioactivity. L. S. T.

**Scattering of slow neutrons. II.** A. C. G. MITCHELL, E. J. MURPHY, and M. D. WHITAKER (Physical Rev., 1936, [ii], 50, 133—137; cf. A., 1935, 1441; this vol., 541).—Scattering curves are given for neutrons from Fe, Ni, Ag, Cu, and C with various detectors, and the scattering cross-sections for a number of elements are tabulated. Differences in the curves for the Fermi groups are most marked when the scatterer is itself a good absorber of one of the groups. The temp. effect on the neutrons which activate In has been investigated. N. M. B.

**Possibility of selective phenomena for fast neutrons.** G. GAMOW (Physical Rev., 1936, [ii], 49, 946).—In nuclear transformations due to collisions with fast neutrons, resonance phenomena in the region of semi-light nuclei are predicted, with an indication of fast neutron energy for which resonance disintegration should be observed. The reactions discussed are:  ${}^{27}_{13}\text{Al} + {}^4_2\text{He} \rightarrow {}^{30}_{15}\text{P} \rightarrow {}^{30}_{15}\text{Si} + {}^1_1\text{H}$ ;  ${}^{24}_{12}\text{Mg} + {}^4_2\text{He} \rightarrow {}^{28}_{14}\text{Si} \rightarrow {}^{28}_{13}\text{Al} + {}^1_1\text{H}$ ; and  ${}^{28}_{14}\text{Si} + {}^1_0\text{n} \rightarrow {}^{29}_{14}\text{Si} \rightarrow {}^{28}_{13}\text{Al} + {}^1_1\text{H}$ . N. M. B.

**Capture, stability, and radioactive emission of neutrons.** J. R. DUNNING, G. B. PEGRAM, and G. A. FINK (Physical Rev., 1935, [ii], 47, 325).—The no. of neutrons detected in an ionisation chamber 25 cm. distant when a Rn+Be source is placed in the centre of solid spheres of diameters up to 25.7 cm. have been measured for H<sub>2</sub>O, C (coal), Al, sand, Cu and Pb shot. The probability of capture indicated is  $> 25\%$  per collision and may be  $< 10\%$  for most cases. The disappearance of neutrons is apparently  $>$  that required by capture in the production of artificial radioactive atoms, by transfer of momentum on impact and by loss of energy in excitation, without supposing the neutron itself to be disintegrated by nuclear impact. L. S. T.

**Mass spectrographic determination of the mass difference  ${}^{14}\text{N} + {}^1\text{H} - {}^{15}\text{N}$  and the nitrogen disintegration reactions.** E. B. JORDAN and K. T.

BAINBRIDGE (Physical Rev., 1936, [ii], 50, 98).—The isotopic ion  $^{15}\text{N}^+$  was matched in intensity with the mol. ion  $(^{14}\text{N}^1\text{H})^+$ . The doublet separations gave the mass difference  $^{14}\text{N}^1\text{H} - ^{15}\text{N} = 0.01074 \pm 0.0002$  mass units. The use of this val. together with the previously determined mass difference for  $^3\text{H} - ^2\text{D}$ , gives  $8.57 \pm 0.2$  m.e.v. for the energy release in the N deuteron disintegration  $^{14}\text{N} + ^2\text{D} \rightarrow ^{15}\text{N} + ^1\text{H}$ . The mass differences in the production of radio-O and in other N disintegration reactions are also calc.

A. J. M.

Proton emission resulting from  $\alpha$ -ray bombardment of boron and phosphorus. R. F. PATON (Physical Rev., 1935, [ii], 47, 197).—When bombarded with  $\alpha$ -particles from Th-C' the protons emitted from B consist of  $\approx$  four groups with characteristic velocities and energies, the vals. for three of which agree with those obtained using Po  $\alpha$ -particles. With P, new proton groups are emitted.

L. S. T.

Selection rules for the  $\beta$ -disintegration. G. GAMOW and E. TELLER (Physical Rev., 1936, [ii], 49, 895—989).—The rules are stated on the basis of Fermi's neutrino theory.

N. M. B.

Decomposition of beryllium under influence of  $\gamma$ -rays. G. BERNARDINI and M. MANDÒ (Ric. sci. Prog. tec., 1935, 6, II, 38—41; Chem. Zentr., 1935, ii, 2627).—If a Be isotope  $^9\text{Be}$  + a neutron are formed by the  $\gamma$ -ray disintegration of  $^9\text{Be}$ , the isotope must either be stable, or else emit  $\alpha$ -rays of range  $\approx 2.5$  mm.

J. S. A.

Fermi proton effect. A. VON GROSSE and M. S. AGRUSS (Physical Rev., 1935, [ii], 47, 91).—Filling a Ag cup with  $\text{H}_2\text{O}$  increases the activity produced in the Ag by irradiation with neutrons from Be+Rn. Surrounding the cup with  $\text{H}_2\text{O}$  increases the activity still further.  $n\text{-C}_5\text{H}_{12}$  has a similar effect, but not  $\text{CCl}_4$  or  $\text{CS}_2$ . The addition of 5% of  $\text{UO}_2(\text{NO}_3)_2$  or  $\text{H}_3\text{BO}_3$  to the  $\text{H}_2\text{O}$  reduces the effect. The protons of the  $\text{H}_2\text{O}$  absorb the energy of the neutrons by elastic collisions, and the neutrons are then more easily captured with the production of stable or radioactive isotopes.

L. S. T.

$\gamma$ -Ray neutrons and the Fermi proton effect. A. VON GROSSE and M. S. AGRUSS (Physical Rev., 1935, [ii], 47, 93).—Neutrons emitted by  $\gamma$ -rays from Be show the Fermi proton effect. Irradiation of I by Be+ $\gamma$ -rays from Ra gives a product with a half-period of 24 min. Surrounding the source with  $\text{H}_2\text{O}$  increases the induced radioactivity five-fold (cf. preceding abstract).

L. S. T.

Disintegration of beryllium by photons and its possible bearing on the mass of  $^9\text{Be}$ . L. N. RIDENOUR, K. SHINOHARA, and D. M. YOST (Physical Rev., 1935, [ii], 47, 318).—Bombardment of Be with X-rays at 50 cycle a.c. at 0.9 m.e.v. gives results which indicate that the mass of  $^9\text{Be}$  is too high. A val. of 9.0114 is calc.

L. S. T.

Evidence from efficiency curves for the nature of the disintegration process for boron. J. H. WILLIAMS and W. H. WELLS (Physical Rev., 1936, [i], 50, 186—187).—Efficiency curves for the production of  $\alpha$ -particles by bombarding a  $\text{B}_2\text{O}_3$  thick target

with protons of 120—240 kv. are given and discussed. The suggested reaction  $^1\text{H} + ^{11}\text{B} \rightarrow ^9\text{Be} + ^4\text{He}$  is probably a case of resonance disintegration. N. M. B.

Ranges of particles emitted in the disintegration of boron and lithium by slow neutrons. J. ROTBLAT (Nature, 1936, 138, 202).—The ranges of particles emitted during disintegration of  $^{10}\text{B}$  and  $^6\text{Li}$  by slow neutrons from a Po-Be source, using a B- or Li-coated ionisation chamber, have been determined, and the energies calc. An additional release of energy from B, possibly related to  $\gamma$ -rays, is indicated. The cross-section of the B nucleus for capture of a slow neutron is 8 times that of the Li nucleus.

L. S. T.

Absorption and scattering of neutrons. W. F. LIBBY and W. M. LATIMER (Physical Rev., 1935, [ii], 47, 193).—Interposition of  $\text{H}_2\text{O}$  between a Ag target and the neutron source (Be+Rn) markedly increases the activation induced.  $\text{H}_3\text{BO}_3$  decreases the activation of Ag and Cu, as do KCl, NaCl,  $\text{CCl}_4$ , and  $\text{BiONO}_3$  with Cu. Absorption with NaF, NaI, BeO, and CuO is negligible, and  $\text{NH}_4\text{NO}_3$  and S produce small increases in activation.

L. S. T.

Bifurcation in the transmutation of aluminium by the action of fast neutrons. P. DE LA CIERVA (Anal. Fis. Quim., 1936, 34, 541—548).—The no. of atoms of Al transformed into  $^{27}\text{Mg}$  to every atom transformed into  $^{24}\text{Na}$ , on bombardment with neutrons from different sources, is as follows: Be+Rn source, 2:1; Be+Ra, 3:2; Be+Ra, with Pb between Al and neutrons, 3:23; Be+Ra, with paraffin interposed, 3:09 (also forms  $^{28}\text{Al}$ ); Li+Rn, no  $^{27}\text{Mg}$  or  $^{24}\text{Na}$ , but  $^{28}\text{Al}$ ; Mg+Rn, only  $^{27}\text{Mg}$ .

L. A. O'N.

Artificial radioelements. M. E. NAHMIAS and R. J. WALEN (Compt. rend., 1936, 203, 71—73).—Evidence has been obtained for the formation of  $^{20}\text{F}$ ,  $^{19}\text{O}$ , and  $^{16}\text{N}$  from F, and  $^{20}\text{F}$  and  $^{23}\text{Ne}$  from Na, as a result of neutron bombardment. With periods of the order of 1 sec. the results are inconclusive, but the activation of Be is confirmed,  $^9\text{Li}$  probably being formed.

C. R. H.

Disruption of atoms by neutrons. E. MATZNER (Sitzungsber. Akad. Wiss. Wien, 1934, 143, 579—590; Chem. Zentr., 1935, ii, 2628).—The yields obtained by the neutron disintegration of C, Al, S, Fe, Co, Ni, Cu, Zn, Ga, Mo, Ag, Cd, Sn, Pt, and Pb have been measured by scintillation and Wilson chamber methods.

J. S. A.

Disruptibility of light elements investigated with the double-tube electrometer. J. SCHINTLMEISTER and G. STETTER (Sitzungsber. Akad. Wiss. Wien, 1934, 143, 597—617; Chem. Zentr., 1935, ii, 2629).—The disintegration yield of the light elements up to Cl shows an exponential fall from a max. in the case of N, on which is superposed a periodic function giving a uniformly higher yield from "odd" elements than from "even." J. S. A.

Radioactive isotope of iron. E. B. ANDERSEN (Nature, 1936, 138, 76—77).—Active Fe, probably  $^{56}\text{Fe}$ , decaying with a period of approx. 72 hr. has been isolated from Co irradiated by neutrons.

L. S. T.



**Artificial activation of thorium by neutrons.** E. RONA and E. NEUNINGER (Naturwiss., 1936, **24**, 491).—By bombardment of pure ThCl<sub>4</sub> with slow and rapid neutrons, products were obtained with half-life periods of 25 min. (isotope of Th), 3.5 hr. (isotope of Ac), and 42 hr. (isotope of Ac). The most probable scheme of disintegration is  $^{232}_{90}\text{Th} + ^1_0\text{n} = ^{229}_{88}\text{Ra} + ^4_2\alpha$ ;  $^{229}_{88}\text{Ra} \xrightarrow{\beta} ^{229}_{89}\text{Ac} \xrightarrow{\beta} ^{229}_{90}\text{Th} \xrightarrow{\alpha} ^{225}_{86}\text{Ra} \xrightarrow{\beta} ^{225}_{87}\text{Ac}$ . A. J. M.

**Energy of cosmic rays. I. Electro-magnet and cloud chamber.** P. M. S. BLACKETT. **II. Curvature measurements and the energy spectrum.** P. M. S. BLACKETT and R. B. BRODE (Proc. Roy. Soc., 1936, **A**, 154, 564–573, 573–587).—I. Details are given of a large cloud chamber in a strong magnetic field, for measuring high-energy cosmic ray tracks.

**II.** The sources of error are considered, and a preliminary determination of the energy spectrum of 188 vertical cosmic rays is made. L. L. B.

**Frequency of secondary phenomena of the radiation penetrating lead.** A. DRIGO (Ric. sci. Prog. tec., 1935, **I**, 6, 529–534; Chem. Zentr., 1935, **ii**, 2925).—Measurements of the dependence of the no. of particles on the thickness of the absorbing screens do not support Rossi's views (A., 1935, 804). J. S. A.

**Origin of the hardening of cosmic rays in passing through matter.** W. F. G. SWANN (Physical Rev., 1935, [ii], 47, 250). L. S. T.

**Production of cosmic-ray showers.** W. H. PICKERING (Physical Rev., 1935, [ii], 47, 423). L. S. T.

**Bursts of cosmic radiation.** A. R. HOGG (Nature, 1936, **138**, 77–78). L. S. T.

**Critique of daily course of cosmic radiation.** A. WAGNER (Sitzungsber. Akad. Wiss. Wien, 1934, **143**, 533–561; Chem. Zentr., 1935, **ii**, 2629–2630).—Data recorded previously are analysed. J. S. A.

**Electrostatic deflexion of cosmic radiation.** W. E. DANFORTH and W. F. G. SWANN (Physical Rev., 1935, [ii], 47, 421). L. S. T.

**Influence of earth's magnetic field on penetrating radiation in geographical latitude of Florence.** G. BERNARDINI and D. BOCCIARELLI (Ric. sci. Prog. tec., 1935, **6**, II, 36–37; Chem. Zentr., 1935, **ii**, 2630). J. S. A.

**Form of nuclear levels [of rhodium].** P. PREISWERK and H. VON HALBAN, jun. (Nature, 1936, **138**, 163). L. S. T.

**Self-consistent field, with exchange, for beryllium. II. The (2s)(2p)<sup>3</sup>P and <sup>1</sup>P excited states.** D. R. HARTREE and W. HARTREE (Proc. Roy. Soc. 1936, **A**, 154, 588–607; cf. A., 1935, 912).—Fock's equations for the self-consistent field, including exchange terms, have been obtained and solved numerically for the (2s)(2p)<sup>3</sup>P and <sup>1</sup>P terms of neutral Be. The calc. energy vals. are in agreement with observation. L. L. B.

**Present state of the neutrino hypothesis.** G. BECK (Physical Rev., 1935, [ii], 47, 202).—A discussion. The hypothesis does not remove difficulties arising from experimental evidence. L. S. T.

**Mass and energy.** K. WAGNER (Physikal. Z., 1936, **37**, 522–523).—It is not necessary to regard the relationship between mass and energy as a relativistic conception. It follows from Maxwell's work on the pressure of light. A. J. M.

**Nuclear structure and isotope systems.** T. I. EFREMENKO (Ukrain. Chem. J., 1936, **11**, 103–118).—Theoretical. R. T.

**Nomenclature of elementary corpuscles.** P. GRUNER (Helv. phys. Acta, 1935, **8**, 326–327; Chem. Zentr., 1935, **ii**, 2923).—For the electrical particles (electrons) the names positon, negaton, and nulliton (uncharged) are proposed. Material particles (materions) are termed neutrons, protons, deutons, tritons, etc., with neproton as a negative particle of mass 1. J. S. A.

**Extended Thomas-Fermi method for atomic nuclei.** F. S. WANG (Z. Physik, 1936, **100**, 734–741). A. B. D. C.

**Nuclear radius.** A. K. SOLOMON (Physical Rev., 1935, [ii], 47, 249).—For both light and heavy nuclei, the nuclear radius  $\propto$  the cube root of the at. wt. of the product nucleus. The slopes of the lines for heavy and light elements are parallel. When the nuclear radius is plotted against at. no. a random distribution of radioactive nuclei is obtained. L. S. T.

**Value of the electronic charge.** R. T. BURGE and E. McMILLAN (Physical Rev., 1935, [ii], 47, 320; cf. this vol., 133, 404).—A discussion and recalculation of Schopper's val. (A., 1935, 279). L. S. T.

**Conservation laws in quantum theory.** N. BOHR (Nature, 1936, **138**, 25–26).—Doubts concerning the validity of conservation of energy and momentum in at. phenomena are now largely removed. The root of the still unsolved difficulties of quantum electrodynamics lies in the atomistic nature of electricity. L. S. T.

**Atomic collisions and radiation from meteors.** E. ÖRIK (Acta Univ. Tartuensis, 1934, **26**, A, No. 2, 37 pp.; Chem. Zentr., 1935, **ii**, 2798).—Theoretical. J. S. A.

**Absorption spectra of iodine solutions. II. Influence of iodide.** A. V. PANFILOV and R. V. TEIS (J. Gen. Chem. Russ., 1936, **6**, 588–605).—Progressive dilution of I in KI solutions with aq. KI leads to a shift in the position of the absorption bands and to diminution in intensity of coloration; these changes are reversed by further addition of aq. KI. Similar effects are obtained in presence of starch. Beer's law is followed more closely when the solution is diluted with H<sub>2</sub>O than with aq. KI. The effects are ascribed to the existence of a series of equilibria between I, KI, KI<sub>3</sub>, and H<sub>2</sub>O. R. T.

**Induced pre-dissociation and energy exchange in nitric oxide.** E. KONDRATEEVA and V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1935, **3**, 1–10).—

The ratio of intensities of the  $\beta$ - and  $\gamma$ -bands in the emission spectrum of NO alone and when mixed with A has been determined. In the spectrum of pure NO the  $\gamma$ -bands are much more intense than the  $\beta$ -bands, but in that of the mixture they are of approx. equal intensity. The phenomena can be explained on the hypothesis of induced pre-dissociation in the  $^2\Sigma$  state. The probability of the transfer of a quantum of vibrational energy of an excited NO mol. into kinetic energy on collision with an A atom is calc. to be approx. 1. A. J. M.

**Band spectra of boron and aluminium halides.** E. MIESCHER (Helv. phys. Acta, 1935, 8, 279—308; Chem. Zentr., 1935, ii, 2633).—Emission spectra from  $\text{BCl}_3$  vapour between 2600 and 2900 Å. and from  $\text{BBr}_3$  vapour between 2850 and 3100 Å. are analysed and referred to  $^1\Pi \rightarrow ^1\Sigma$  transitions. Similar  $^3\Pi \rightarrow ^1\Sigma$  bands excited in  $\text{AlBr}_3$  and  $\text{AlI}_3$  are described. Dissociation energies are calc. J. S. A.

**Ultra-violet band systems of SiCl.** W. JEVONS (Proc. Physical Soc., 1936, 48, 563—573).—The emission spectrum of SiCl, produced from  $\text{SiCl}_4$  vapour, has three systems of doublet bands degraded towards the further ultra-violet. The bands are discussed and compared with the data of Datta. W. R. A.

**Absorption spectrum of tellurium dichloride vapour.** J. LARIONOV (Acta Physicochim. U.R.S.S., 1935, 3, 11—22).—The absorption spectrum of  $\text{TeCl}_2$  has been investigated in the visible and ultra-violet. The bands in the visible may be classified into three sequences, the spectrum being made up of broad diffuse bands without heads with a superimposed continuous absorption. There is a further continuous absorption in the ultra-violet. The first continuous absorption in the visible may be due to  $\text{TeCl}_2 + h\nu \rightarrow \text{TeCl} + \text{Cl}$ ;  $\text{TeCl}_2 + h\nu \rightarrow \text{TeCl} + \text{Cl}'$ ; or  $\text{TeCl}_2 + h\nu \rightarrow \text{Te} + \text{Cl}_2$ . The corresponding heats of dissociation for these processes are 54, 56, and 51 kg.-cal., respectively. A. J. M.

**Emission spectrum of bismuth fluoride.** H. G. HOWELL (Proc. Roy. Soc., 1936, A, 155, 141—150).—An emission spectrum attributed to BiF has been excited by means of a high-frequency discharge in the vapour of  $\text{BiF}_3$ . The bands lie in the region 4150—5100 Å. and are degraded to the red. A vibrational analysis has been made. The vibrational consts. are nearly equal to those of  $\text{PbF}$ . L. L. B.

**Change in the absorption spectrum of cobalt chloride in aqueous hydrochloric acid solution with change of temperature.** O. R. HOWELL and A. JACKSON (Proc. Roy. Soc., 1936, A, 155, 33—41).—The absorption spectra of several aq. solutions containing a fixed amount of  $\text{CoCl}_2$  and varying amounts of HCl have been measured at a series of temp. The extinction coeffs. at the max. of the two principal bands, 695 m $\mu$  and 666 m $\mu$ , have been plotted against temp. For a given [HCl], the extent of the transformation from red to blue over a wide range of temp. is small compared with the total change observed on increasing [HCl] at const. temp. The results are explained in terms of the theory previously advanced (A., 1934, 7). L. L. B.

**New absorption band in potassium bromide crystals.** E. REXER (Physikal. Z., 1936, 37, 523).—Electron migration in a KBr crystal may produce absorption bands which do not give rise to photochemical processes. A KBr crystal, heated for some time in air, gives an absorption band due to electron migration with a max. at 302 m $\mu$ . Absorption in this band does not give rise to photochemical colouring, but to the emission of fluorescence with a max. at 453 m $\mu$ . A. J. M.

**Band spectrum of FeH.** A. HEIMER (Naturwiss., 1936, 24, 491—492).—The strongest band in the spectrum of FeH is the 0—0 band at 4288 Å. It is degraded towards the red, and consists of single P and R branches. It arises from a  $^1\Sigma \rightarrow ^1\Sigma$  transition. A. J. M.

**The 2530 Å. band of NH.** R. W. LUNT, R. W. B. PEARSE, and E. C. W. SMITH (Proc. Roy. Soc., 1936, A, 155, 173—182).—The 2530 band of NH has been excited by a hollow-cathode discharge in streaming  $\text{NH}_3$  with sufficient intensity to photograph under high dispersion. The band corresponds with a  $^1\Pi$  transition, and the  $^1\Pi$  state is the same as that already known as the initial state concerned in the emission of the 3240 and 4502 bands. The rotational consts. for the six electronic states now known for NH are tabulated. L. L. B.

**Absorption of light by some gases in the far ultra-violet.** G. RATHENAU (Physica, 1936, 3, 727—728).— $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{C}_6\text{H}_6$  show continuous absorption in the region 150—270 Å. O. D. S.

**Band spectrum of  $\text{OH}^+$ .** M. KOVNER (Physical Rev., 1936, [ii], 50, 188; cf. Loomis, this vol., 267).—Term differences and multiplet splitting consts. are evaluated. N. M. B.

**Band spectrum of arsenic oxide ( $\text{AsO}$ ) and lead oxide ( $\text{PbO}$ ).** F. MORGAN and E. N. SHAWHAN (Physical Rev., 1935, [ii], 47, 192—199).—The band spectrum of  $\text{AsO}$  has been studied in emission and absorption and that of  $\text{PbO}$  in absorption. L. S. T.

**Absorption spectra and photodissociation of some inorganic molecules.** M. JAN-KHAN and R. SAMUEL (Proc. Physical Soc., 1936, 48, 626—641).—The regions of absorption in  $\text{PCl}_3$ ,  $\text{PBr}_3$ ,  $\text{PCl}_5$ ,  $\text{PBr}_5$ ,  $\text{POCl}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{SbOCl}$ , and  $\text{BiCl}_3$  are correlated with certain photodissociation processes. A comparison with the mean bond energies calc. from thermochemical data allows certain conclusions to be reached as to the structure of these mols. W. R. A.

**Absorbing and reflecting powers of sulphuric acid solutions in the far infra-red.** C. H. CARTWRIGHT (J. Chem. Physics, 1936, 4, 413—417).—Measurements are recorded with 2—37.4N- $\text{H}_2\text{SO}_4$  for  $\lambda$  52—152  $\mu$  monochromatic. A broad absorption band at approx. 60  $\mu$ , similar to the 60  $\mu$  band of  $\text{H}_2\text{O}$ , was observed in dil. and conc.  $\text{H}_2\text{SO}_4$ . This appears to be of interat. origin. The reflecting and absorbing powers of aq.  $\text{H}_2\text{SO}_4$  are those of  $\text{H}_2\text{O}$  or  $\text{H}_2\text{SO}_4$ . It is suggested that with < 5% of  $\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_4^{--}$  and  $\text{OH}_4^{--}$  ions may be formed.



On further dilution  $H^+$  and  $H_3SO_4^+$  are formed. In dil. solutions  $H^+$  and  $SO_4^{2-}$  are present. H. J. E.

**Far ultra-violet absorption spectrum of methyl iodide.** W. C. PRICE (Physical Rev., 1935, [ii], 47, 419).—Analysis of this spectrum at low pressures in the region 2000—1200 Å. gives two ionisations potentials, viz., 9.489 and 10.113 volts ( $\pm 0.003$  volt).

L. S. T.

**Absorption spectrum of alkyl iodides in extreme quartz ultra-violet. I. Experimental.** G. MILAZZO (Z. physikal. Chem., 1936, B, 33, 109—119).—The v.p. and absorption spectra of the saturated vapours of  $PrI$ ,  $BuI$ ,  $Pr^iI$ , and  $Bu^iI$  have been measured at various temp. as far as 1960 Å.

R. C.

**Electronic state of radicals in polyatomic molecules.** V. HENRI (Compt. rend., 1936, 203, 67—69).—The CN group in cyanides and thiocyanates is in the normal inactive state  $X(^2\Sigma)$  and in halogen derivatives and carbylamines it is in the active state  $B(^2\Sigma)$ . In nitriles it appears to be in a higher state than those known, the frequency being approx.  $2250\text{ cm}^{-1}$ . The groups  $C\equiv C$ ,  $N\equiv N$ , and  $NO$  are, respectively, in the states  $A(^3\Pi)$ ,  $C(^3\Pi)$ , and  $X(^2\Pi)$ .

C. R. H.

**Tetramethylethylene and the influence of the double linking.** J. ERRERA, P. MOLLET, and (MILE.) M. L. SHERRILL (Compt. rend., 1936, 203, 66).—The positions of the spectral absorption bands for  $C_2Me_4$  are discussed in relation to the band positions of saturated and ethylenic hydrocarbons (cf. this vol., 1049).

C. R. H.

**Ultra-violet absorption of some aromatic hydrocarbons. IV. Constitution of hexahydropyrene.** M. PESTEMER and F. MANCHEN (Monatsh., 1936, 68, 92—100).—The absorption spectrum of hexahydropyrene (I) (2500—4500 Å.) resembles those of  $C_{10}H_8$  and its alkyl derivatives. It is concluded that (I) contains an intact  $C_{10}H_8$  ring system and that hydrogenation occurs symmetrically in the two remaining rings in the mol. The partly hydrogenated products obtained by the action of nascent H have absorption spectra corresponding with mixtures of (I) and pyrene.

H. J. E.

**Variations in the ultra-violet spectrum of phenol as a function of  $p_H$ .** M. GEX (Compt. rend., 1936, 202, 2145—2147).—The ultra-violet absorption of PhOH solutions of varying  $p_H$  indicates that on passing from PhOH to phenoxide an intermediate modification of PhOH exists between  $p_H$  7 and 9.

C. R. H.

**Ultra-violet absorption by liquids.** L. A. GINSEL (Physica, 1936, 3, 578—584).—Preliminary. Qual. diagrams of the ultra-violet absorption bands of *o*- and *m*- $C_6H_4Cl\cdot OH$  and  $PhNO_2$  are given.

O. D. S.

**Absorption spectra of hydroxyanthraquinones in different solvents.** K. LAUER and M. HORIO (J. pr. Chem., 1936, [ii], 145, 273—280).—Absorption spectra of 1- (I) and 2-hydroxy- and 1:8-, 1:3-, 1:6-, 2:3-, 2:6-, and 2:7-dihydroxy-anthraquinone in  $C_6H_6$ , cyclohexane, EtOH, conc.  $H_2SO_4$ , and aq. NaOH are detailed. The OH gives a band with max. about 4000 Å., shifted for all compounds except (I)

by  $H_2SO_4$  and NaOH to about 5000 Å. or higher  $\lambda$ ; with (I) only NaOH causes this shift. The absorption max. of 1- and 2-aminoanthraquinone move to higher  $\lambda$  with increasing  $\epsilon$  of the solvent, in contradiction to Scheibe's rule. R. S. C.

**Behaviour of the absorption band of uranine solution under high pressure.** W. J. LYONS (Physical Rev., 1935, [ii], 47, 198).—For pressures up to 915 kg. per sq. cm., the absorption band max. of a dil. sq. solution of uranine did not show the expected shift to regions of longer  $\lambda$ .

L. S. T.

**Substitution and absorption-band displacement. VII. Anthracene and naphthalene derivatives.** H. CONRAD-BILLROTH (Z. physikal. Chem., 1936, B, 33, 133—144; cf. A., 1935, 913).—The application of the rule previously described (A., 1933, 445) to the above compounds is examined. The absorption bands consist of two groups, the position of which in the unsubstituted mols. is characterised by a zero point common to both ring systems and by two "ring-fusion influence vectors" which in substitution are included in the geometrical addition. These lie in the plane of the mol. and in the axis of symmetry. The direction of the substituent "influence vectors" is towards the centre of the ring system, not the centre of single rings. With these modifications the rule is valid. R. C.

**Spectroscopic studies of the simpler porphyrins. I. Absorption spectra of porphin, *ms*-methyl-, -ethyl-, -propyl-, and -phenylporphin.** V. M. ALBERS and H. V. KNORR (J. Chem. Physics, 1936, 4, 422—425).—Curves for the mol. absorption coeffs. of  $Et_2O$  solutions for 3700—7000 Å. are recorded. There is a very strong band at 3900 Å. in porphin, at 4130 Å. in all the aliphatic-substituted mesoporphins (I), and at 4140 Å. in *ms*-phenylporphin. For (I) the absorption coeff. for this band decreases as the length of the C chain increases. Beer's law holds. H. J. E.

**Fluorescence of the porphyrins. III.** A. STERN and M. DEŽELIĆ (Z. physikal. Chem., 1936, 347—357).—The fluorescence spectrum of solutions of octaethylporphin (I) varies little with the solvent, the band max. being shifted towards the blue compared with those of solid (I). The spectrum of adsorbed (I) has its max. in approx. the same position as that of a HCl solution, indicating that adsorption involves primarily the N atoms of the pyrrolenine nuclei, and these in a similar way to salt formation. Hen- and duck-egg shells give similar spectra, showing the same porphyrin, ooporphyrin (II), to be present in each. The (II) is present in the shell in mol. solid solution, not in the adsorbed state, for the spectra resemble that of protoporphyrin in neutral solution.

R. C.

**Absorption spectrum of bilirubin.** J. HENRY-CORNET and L. A. M. HENRY (Bull. Acad. roy. Belg., 1936, [v], 22, 553—559).—There is a max. in the absorption spectrum of bilirubin between 2300 and 3800 Å., made up of a no. of max. and min. The absorption spectrum is characteristic and may be used to identify the substance. Deter-

mination of the extinction const. may be used to measure the concn. of bilirubin in serum.

A. J. M.

**Conditions for excitation of fluorescence of proteins.** F. VLÈS (Compt. rend., 1936, 202, 2184—2186).—The fluorescence of certain proteins and  $\text{NH}_2$ -acids when subjected to ultra-violet light is described.

C. R. H.

**Influence of van der Waals forces on energy states of molecules on basis of luminescence of solidified gases.** L. VEGARD (Avh. norsk. Vid.-Akad. Oslo, 1935, No. 2, 14 pp.; Chem. Zentr., 1935, ii, 2783; cf. A., 1935, 147).—The fluorescence bands of solid  $\text{N}_2$ -inert gas mixtures are broadened towards longer  $\lambda$  by van der Waals forces. Electronic terms are affected to a greater extent than vibrational terms.

J. S. A.

**Photographic infra-red absorption spectrum of gaseous ammonia.** S. H. CHAO (Physical Rev., 1936, [ii], 50, 27—37).—The absorption bands of  $\text{NH}_3$  at 10,000, 7920, and 6470 Å. have been re-investigated using apparatus with greater dispersion and resolving power. Some difficulty was experienced in analysing the bands, the complexity of structure being probably due to the fact that the bands are made up of several parallel-type and perpendicular-type bands. The effect of pressure on the width of the lines is considerable, but in mixtures of  $\text{NH}_3$  and air, increase of air pressure produced only slight broadening. The broadening with increase of pressure may be due to the intermol. Stark effect connected with the dipole moments of the mols.

A. J. M.

**Near infra-red spectrum of  $\text{MgO}$ .** R. B. BARNES and R. R. BRATTAIN (Physical Rev., 1935, [ii], 47, 416).

L. S. T.

**Infra-red spectrum of heavy acid solutions.** D. WILLIAMS and E. K. PLYLER (J. Chem. Physics, 1936, 4, 460).— $\text{D}_2\text{O}$  solutions of  $\text{DCl}$ ,  $\text{D}_2\text{SO}_4$ , and  $\text{D}_3\text{PO}_4$  have absorption bands at 5.7 and 3.4  $\mu$ .

H. J. E.

**Infra-red spectra and organic chemistry.** R. B. BARNES (Rev. Sci. Instr., 1936, [ii], 7, 265—271).—A general survey of applications to deuterio-chemistry, polymerisation, isomerism, tautomerism, detection of H linkings, qual. analysis, and determination of particle size.

N. M. B.

**Effect of association on the infra-red absorption spectrum of acetic acid.** R. H. GILLETTE and F. DANIELS (J. Amer. Chem. Soc., 1936, 58, 1139—1142).—The infra-red absorption spectrum has been obtained at 25° and 172°, corresponding with single and associated mols., respectively. Three of the fundamental frequencies are the same in both mols., and two are shifted. Modes of vibration of the two mols. are suggested. The association of carboxylic acids to dimers probably occurs through the formation of H linkings leading to ring structure, which gives rise to different absorption frequencies.

E. S. H.

**Effect of substitution on the infra-red absorption spectrum of acetic acid.** R. H. GILLETTE (J. Amer. Chem. Soc., 1936, 58, 1143—1144).—Uniform shifts in the infra-red absorption spectra of  $\text{AcOH}$

and mono-, di-, and tri-chloro-, mono-bromo- and -iodo-, di-, and tri-methyl-, and diethyl-acetic acid have been determined.

E. S. H.

**[Absorption] spectra in the near infra-red. Methane and its chloro- and nitro-derivatives.** C. CORIN (J. Chim. phys., 1936, 33, 448—475).—Absorption bands between 0.8 and 2.7  $\mu$  are listed for  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^n\text{OH}$ , allyl alcohol, glycerol,  $\text{EtCHO}$ ,  $\text{C}_6\text{H}_5\text{CHO}$ ,  $\text{COMe}_2$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ ,  $\text{AcCO}_2\text{H}$ ,  $\text{NEt}_3$ ,  $\text{NH}_2\text{Et}$ ,  $\text{NH}_2\text{Et}$ , nitrosodipropylamine, and  $\text{EtONO}$ . Liquid  $\text{CH}_4$  has a band at 2.0  $\mu$  not present in the vapour. The absorption of the Cl-derivatives of  $\text{CH}_4$  diminishes as the no. of C-H linkings decreases.  $\text{CCl}_3\text{NO}_2$  has 7 bands at 1.40—2.59  $\mu$  at  $\lambda$  identical with those of  $\text{C(NO}_2)_4$ . Frequencies are allocated to the CH, NO, C-NO<sub>2</sub>, and NO<sub>2</sub> groupings.

J. G. A. G.

**Photometric and spectrophotometric studies. XI. Absorption spectra of hydrocarbons and halogen derivatives in the near infra-red.** E. TRABERT and K. SCHAUM (Z. wiss. Phot., 1936, 35, 153—170).—The absorption spectra in the near infra-red of the following compounds are recorded: the normal paraffins,  $\text{C}_n\text{H}_{2n+2}$  ( $n=5-9$ ),  $\text{EtBr}$ ,  $\text{EtI}$ ,  $\text{Pr}^n\text{Cl}$ ,  $\text{Pr}^n\text{Cl}$ ,  $\text{Pr}^n\text{Br}$ ,  $\text{Pr}^n\text{Br}$ ,  $\text{Bu}^n\text{Cl}$ ,  $\text{Bu}^n\text{Br}$ ,  $\text{Bu}^n\text{Cl}$ ,  $\text{Bu}^n\text{Br}$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_{10}\text{H}_8$ , phenanthrene, Ph.,  $\text{CH}_2\text{Ph}_2$ ,  $\text{CHPh}_3$ , cyclo-hexane and -hexene, tetra- and deca-hydronaphthalene, PhMe, *m*-xylene, 1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ .

A. J. M.

**Infra-red absorption of liquid hydrocarbons. Influence of the double linking.** J. ERRERA, P. MOLLET, and (MLLE.) M. L. SHERRILL (Compt. rend., 1936, 202, 2141—2142).—Variations in infra-red absorption of saturated and unsaturated aliphatic hydrocarbons are described.

C. R. H.

**Infra-red absorption of rubber and related hydrocarbons.** D. WILLIAMS (J. Chem. Physics, 1936, 4, 460).—Very thin films of styrene, isoprene, and cymene all show intense absorption bands at 3.4, 6.2, and 7.0  $\mu$  and weaker bands between 7  $\mu$  and 9  $\mu$ . Pure gum rubber gave a band at 5.8  $\mu$  and in a low-S vulcanised rubber the corresponding absorption was at 6.0  $\mu$ . At all other  $\lambda$  from 2.5 to 9.0  $\mu$  the absorption spectrum of rubber resembles that of isoprene. Polymerised butadiene gave strong bands at 5.5 and 6.0  $\mu$  and less intense bands beyond 7  $\mu$ . Rubber hydrochloride gave a very intense band at 8.4  $\mu$ , which was not characteristic of the other hydrocarbons studied.

H. J. E.

**Evidence from Raman effect for a slight asymmetry of the carbon atom.** R. T. DUFFORD (Physical Rev., 1935, [ii], 47, 199).—The Raman spectra of many simple C compounds afford evidence of two slightly different strengths of linking. Similar but less extensive evidence exists for O and N.

L. S. T.

**Raman spectra of  $\text{N}_3^-$ ,  $\text{NCS}^-$ , and  $\text{CO}_2$ .** A. LANGSETH and J. R. NIELSEN (Physical Rev., 1935, [ii], 47, 198).—A further study (cf. A., 1935, 145) and application to the constitution of  $\text{N}_3^-$  and  $\text{CNS}^-$ . New measurements of the depolarisations and relative intensities of the principal Raman bands of  $\text{CO}_2$  have been made.

L. S. T.



**Raman effect of water vapour.** D. BENDER (Physical Rev., 1935, [ii], 47, 252).—H<sub>2</sub>O vapour at 135° excited by Hg 2536 Å. gives only one Raman band 3654.5 cm.<sup>-1</sup> and extending approx. 5 cm.<sup>-1</sup> on both sides of its centre. There is no indication that the line is double (cf. A., 1934, 1155). No pure rotation band was found. L. S. T.

**Raman spectra. III. Deuterium-substituted acetic acids.** W. R. ANGUS, A. H. LECKIE, and C. L. WILSON (Proc. Roy. Soc., 1936, A, 155, 183—194).—The Raman spectra of Ac<sub>2</sub>O, AcOH, AcOD, and CD<sub>3</sub>·CO<sub>2</sub>D have been studied. Ac<sub>2</sub>O exhibits some lines not found in the spectra of the acetic acids. The lines of the acids are divisible into three categories: those unmodified on D substitution, those showing a progressive modification as the D content is increased, and those modified in CD<sub>3</sub>·CO<sub>2</sub>D only. This classification leads to the assignment of the most prominent frequencies. That corresponding with the symmetrical C-D vibration is 2111 cm.<sup>-1</sup>, and with the CD<sub>2</sub> group 1100 cm.<sup>-1</sup> L. L. B.

**Raman spectra of the deuteromethanes.** G. E. MACWOOD and H. C. UREY (J. Chem. Physics, 1936, 4, 402—406).—MeD, CH<sub>2</sub>D<sub>2</sub>, CHD<sub>3</sub>, and CD<sub>4</sub> were prepared by the interaction of MeI, CH<sub>2</sub>I<sub>2</sub>, and CHBr<sub>3</sub> with D<sub>2</sub>O with a Al-Hg couple and by interaction of CO<sub>2</sub> and D<sub>2</sub> with a supported Ni catalyst at 310°, respectively. The first three substances were studied at a pressure of 2 atm., and the last-named at 5 atm. 20 lines were measured and analysed. Rotational structure of CD<sub>4</sub> was observed. H. J. E.

**Raman spectrum of cyclopropane.** R. ANANTHAKRISHNAN (Nature, 1936, 138, 123).—Data for the liquid and vapour are compared and discussed; those for the liquid include new frequencies at 736, 1503, 2852, and 2952 cm.<sup>-1</sup> L. S. T.

**Raman spectra of some substituted epoxy-cyclohexanes.** E. CANALS, M. MOUSSERON, L. SOUCHE, and P. PEYROT (Compt. rend., 1936, 202, 2084—2086).—Data are recorded for epoxycyclohexane and various alkyl and aryl derivatives. They are compared with corresponding vals. for cyclohexane. H. J. E.

**Raman spectrum of some substituted epoxy-cyclopentanes.** E. CANALS, M. MOUSSERON, L. SOUCHE, and P. PEYROT (Compt. rend., 1936, 202, 1989—1992).—Data for a series of derivatives are recorded and discussed. H. J. E.

**Raman spectrum of indole.** G. B. BONINO and R. MANZONI-ANSIDEI (Ric. sci. Prog. tecn., 1935, 6, I, 579—580; Chem. Zentr., 1935, ii, 3082).—The spectrum contains the lines of a C-disubstituted pyrrole and of an o-disubstituted C<sub>6</sub>H<sub>6</sub>, confirming the chemical formulation as a pyrrole ring fused to a C<sub>6</sub>H<sub>6</sub> ring. H. N. R.

**Raman spectrum of divinyl sulphide.** G. B. BONINO, R. MANZONI-ANSIDEI, and D. DINELLI (Ric. sci. Prog. tecn., 1935, 6, I, 505—506; Chem. Zentr., 1935, ii, 3081—3082).—The spectrum is compared with those of thiophen and diallyl sulphide. Conjugation of the S with the C:C linking shifts the C:C line from 1630—1650 cm.<sup>-1</sup> to 1580—1590 cm.<sup>-1</sup> The absence of such a line in thiophen points to the

absence of C:C linkings. A similar shift in compounds containing a C:C conjugated with a C<sub>6</sub>H<sub>6</sub> ring cannot be taken as evidence for the validity of the Kekule structure. H. N. R.

**Raman spectrum of pyrrole and its derivatives.** G. B. BONINO (Gazzetta, 1936, 66, 316—336).—Theoretical; a recent paper by Stern and Thalmayer (this vol., 546) is discussed and criticised. E. W. W.

**Electrical resistance of cadmium films.** E. TOWNES and D. ROLLER (Physical Rev., 1935, [ii], 47, 197).—Cd films deposited on a glass plate cooled by liquid air or solid CO<sub>2</sub> in a mol. beam apparatus become conducting at a thickness of 2—7 × 10<sup>-7</sup> cm. and have a crit. thickness of 6—8 × 10<sup>-7</sup> cm., at which the resistivity is approx. 15 times that of the bulk metal. The bearing of these results on photo-electric phenomena in metal films and on theories of film structure is discussed. L. S. T.

**Electrical properties of anodically oxidised aluminium.** J. W. HOLST (Tids. Kjem., 1936, 16, 73—76; cf. this vol., 565).—The dry Al<sub>2</sub>O<sub>3</sub> layer has low electrical conductivity, only slightly unidirectional, probably due to presence of Al(OH)<sub>3</sub>. It is concluded that the rectifying properties of the oxidised Al electrode cannot be due to a pure electron flow through the oxide layer. M. H. M. A.

**Crystal photo-effect and rectifying action in the bulk of the crystal.** G. GROETZINGER and J. LICHTSCHNEIN (Nature, 1936, 138, 163—164).—Illumination of a cuprite crystal in contact with two electrodes through which an a.c. is passing produces an additional direct voltage. Curves showing the variation of this voltage with the a.c. and its relation to the crystal photo-electric effect are given. The additional current is probably connected with events occurring in the interior of the crystal (bulk rectification). L. S. T.

**Contact potential differences between single crystal surfaces of different orientations.** I. H. KURZKE and J. RORTGARDT (Z. Physik, 1936, 100, 718—725).—The contact p.d. between the (111) and the (111) planes of a single Bi crystal is +0.36 volt. A. B. D. C.

**Influence of atmospheric gases on the electrical conductivity of cuprous oxide.** L. DUBAR (Compt. rend., 1936, 203, 46—48).—The influence of dry O<sub>2</sub>, dry N<sub>2</sub> (O<sub>2</sub>-free), and H<sub>2</sub>O vapour on the surface κ of Cu<sub>2</sub>O, which has been heated in vac., has been studied. N<sub>2</sub> and H<sub>2</sub>O vapour have little effect, but O<sub>2</sub> increases κ. Subsequent treatment with N<sub>2</sub> or H<sub>2</sub>O reduces κ to its original val. C. R. H.

**Recent investigations of semi-conductors.** A. SCHULZE (Chem.-Ztg., 1936, 60, 545—547).—A review of literature concerning Si, C, Ti, Zr, Hf, Th, B, As, and Te. T. G. P.

**Theory of non-independent flow of electricity in gases.** H. MACHE (Elektrotech. u. Maschinenbau, 1935, 53, 253—258, 269—273; Chem. Zentr., 1935, ii, 2784).—Theoretical. An approx. theory is developed and applied to the calculation of the discharge characteristics of condensers with nonhomogeneous ionisation. J. S. A.

**Dielectric losses in a high-frequency alternating field and molecular dimensions.** J. HENRION (Compt. rend., 1936, 203, 52—54).—Data for high-frequency dielectric losses for polar mols. in a non-polar solvent, at  $\lambda$  7 m., have been applied to the calculation of mol. dimensions, using the formula  $t = 4\pi\eta^3/kT$  ( $t$ =time of relaxation in sec.,  $k$ =Boltzmann const.,  $\eta$ =viscosity,  $T$ =abs. temp.,  $r$ =radius of mol. supposed spherical). For non-spherical mols.  $r^3$  can be replaced by the product of 3 radii along 3 orthogonal axes, one of which is in the same direction as the electric moment, and passing through the centre of gravity of the mol. C. R. H.

**Absorption of various alcohols at high frequencies.** R. ZOUCKERMANN and R. FREYMAN (Compt. rend., 1936, 202, 2079—2081).—No narrow bands were observed in the absorption by 7 primary alcohols of waves of 3—12 m. length. In a homologous series with a fixed  $\lambda$ , the conductivity increases rapidly at first, and tends to a const. val. for mols. with  $> 5$  C. H. J. E.

**Dipole ortho-effect.** L. TIGANIK (Keem. Teated, 1935, 2, 88—106; Chem. Zentr., 1935, ii, 2936).—On the view that the ortho-effect is due to electron displacements, not to deflexion of valency angles, a theory is developed on classical electrostatic lines, and applied to  $C_6H_6$  and its substitution products. Vals. for dipole moments so calc. agree with experimental vals. It is considered, however, that in  $C_6H_6$ , the H atoms are displaced from the plane of the ring. J. S. A.

**Electric dipole moments of nitrophenols.** H. O. JENKINS (J.C.S., 1936, 1049).—The dipole moment of  $o$ -NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH in C<sub>6</sub>H<sub>6</sub> solution at 25° has been redetermined and its relatively low val. confirmed. The moments of substituted phenols are discussed briefly. D. C. J.

**Index of refraction of water and paraffin at high frequencies.** L. S. SKAGGS and R. T. DUFFORD (Physical Rev., 1935, [ii], 47, 201—202).—Measurements at  $\lambda\lambda$  of approx. 10 cm. agree with classical electromagnetic theory. L. S. T.

**Effect of pressure on the refractive index of carbon disulphide.** F. E. POINDEXTER (Physical Rev., 1935, [ii], 47, 202).—Vals. of  $n$  for CS<sub>2</sub> for each of the Hg lines 5790, 5460, and 4360 Å. are recorded for pressures from 1 to 1880 kg. per sq. cm. Dispersion increases over the whole range of pressure, the increase being more rapid at lower pressures. L. S. T.

**Influence of dilution on the molecular refractivities of complex cyanides and cobaltammines.** A. K. BHATTACHARYA (J. Indian Chem. Soc., 1936, 13, 284—293).—The  $R_L$  of complex cyanides at 21° and of cobaltammines at 30° were measured at concns. up to 0.1 mol. For the more stable cyanides  $R_L$  decreases with dilution, but for the less stable cyanides and for most of the cobaltammines  $R_L$  increases with dilution. This latter effect is ascribed to the decomposition of the complex ions into simpler ions. C. R. H.

**Utilisation of molecular refraction for determining constitution and configuration of sugars.**—See this vol., 1094.

**Refractivity of  $\alpha$ -chloronitriles.** J. VANDEWIJER (Bull. Soc. chim. Belg., 1936, 45, 251—269).—The prep.,  $d$ , and  $n$  for the  $H_a$ ,  $H_\beta$ ,  $H_\gamma$ , and  $D$  lines at 15° and 30° of the first 10 members of the homologous series commencing CH<sub>2</sub>Cl·CN are recorded. The  $n$  of the series is minimal at C<sub>3</sub> and a periodicity persists to C<sub>7</sub>. From the mol. refractivities at 20°, the sp. refractivity of Cl less that of H is  $H_a$  5.059,  $D$  5.083,  $H_\beta$  5.155,  $H_\gamma$  5.201, from which data for H (A., 1934, 132) give the sp. refractivities of Cl  $H_a$  6.086 and  $D$  6.120. J. G. A. G.

**Liquids of high refractive index.** B. W. ANDERSON and C. J. PAYNE (Nature, 1936, 138, 168).—A correction (cf. A., 1934, 163) and an acknowledgment of priority. L. S. T.

**Optical polarisation ellipsoids of the hydrogen halide gases.** C. H. D. CLARK (Nature, 1936, 138, 126).—These ellipsoids constitute similar solid figures. The four H halides have equal optical anisotropies and the optical polarisability perpendicular to the internuclear axis of symmetry is approx. 75% of that along this axis. This latter val. is equal to the polarisability of the halogen ion X<sup>-</sup>. L. S. T.

**Optical rotation of tartaric acid in presence of titanium ion.** M. SCHENK (Helv. Chim. Acta, 1936, 19, 639—645).—The val. of  $[\alpha]$  of Ti<sup>IV</sup> tartrate depends on [H<sup>+</sup>], and shows max. in both acid and alkaline solutions separated by a sharp min. Aq. tartaric acid in presence of Ti<sup>IV</sup> oxalate (contrary to the sulphate) shows mutarotation during neutralisation with KOH, due to slow hydrolysis of the tartrate. T. G. P.

**Rotatory power of methyl tartrate.**—See this vol., 1093.

**Analysis of rotatory dispersions of configurationally related halides.** P. A. LEVENE, A. ROTHEN, and R. E. MARKER (J. Chem. Physics, 1936, 4, 442—449).—Rotatory dispersion curves of halides of the type CHMeR·[CH<sub>2</sub>] <sub>$n$</sub> ·X (X=halogen, R=alkyl) have been analysed in the visible and ultra-violet regions. Changes due to variations of X and R and the val. of  $n$  (1—4) are discussed. H. J. E.

**Variation with temperature of the magnetic birefringence of nitric oxide and oxygen under pressure.** H. BIZETTE and B. TSAI (Compt. rend., 1936, 202, 2143—2145).—Previous work (this vol., 140) has been extended to temp. —80° to 20°. C. R. H.

**Old and new chemistry of radicals.** P. H. HERMANS (Chem. Weekblad, 1936, 33, 442—450).—A lecture. S. C.

**Valency and molecular structure.** J. DEVRIES (J. Chem. Educ., 1936, 13, 320—324). L. S. T.

**Nature of the hydrogen bond. I. Association in carboxylic acids.** R. H. GILLETTE and A. SHERMAN (J. Amer. Chem. Soc., 1936, 10, 1135—1139).—Theoretical. The wave function should include polar and homopolar terms. The H linking consists of at least the states X·H·X<sup>-</sup>, X·HX, and XH·X. E. S. H.

**Chemical linking.** A. E. VAN ARKEL (Chem. Weekblad, 1936, 33, 454—457).—A lecture dealing



principally with the quantum mechanics of simple mols. S. C.

Relations between functions of cohesion forces of liquids and their chemical function at the b.p. under constant pressure. G. DUCH (Compt. rend., 1936, 202, 1977—1979).—Theoretical.

H. J. E.

Dissociation energy of diatomic sulphur, selenium, and tellurium vapours. P. GOLDFINGER, W. JEUNEHOMME, and B. ROSEN (Nature, 1936, 138, 205—206).—Vals. deduced from spectroscopic and thermochemical data are discussed.

L. S. T.

Relation between internuclear distance and group number for diatomic hydrides. H. C. CORBEN (Phil. Mag., 1936, [vii], 22, 144—145).—The equilibrium internuclear distance for the ground state ( $r_e$ ) is related to the no. of electrons outside closed shells ( $n$ ) by the expression  $r_e n - a + bn - c(n-1)^3$ , where  $a$  and  $c$  are consts. and  $b$  depends on the mol. period. The following vals. of  $r_e$  are predicted: SH 1.362, SeH 1.90, TiH 1.81, VH 1.72, CrH 1.64, MnH 1.55 Å.

H. J. E.

Distribution of energies of electrons. J. S. E. TOWNSEND (Phil. Mag., 1936, [vii], 22, 145—171).

H. J. E.

Nuclear separation of the  $S_8$  molecule by electron diffraction. L. R. MAXWELL, V. M. MOSLEY, and S. B. HENDRICKS (Physical Rev., 1936, [ii], 50, 41—45).—The nuclear separation of the  $S_8$  mol. from  $S_8$  vapour at 800° was  $1.92 \pm 0.03$  Å. The electron diffraction pattern of the vapour changes considerably at temp.  $< 800^\circ$  owing to the formation of  $S_{2+n}$  mols. The S—S—S angle in the higher mol. forms is about  $100^\circ$ , and the S—S distance between neighbouring atoms, 2.1 Å. These vals. are in agreement with those found by Warren *et al.* (A., 1935, 285) for the symmetrical puckered  $S_8$  ring in the rhombic form.

A. J. M.

Atomic forces of solid states, I, II. W. WEN-PO (Phil. Mag., 1936, [vii], 22, 49—68).—Theoretical. A method of calculating at. radii and thermal expansion is described.

H. J. E.

Ground state vibrational frequencies. H. G. HOWELL (Nature, 1936, 138, 36).—The arithmetic mean of the vibrational frequencies of two mols.  $A_2$  and  $B_2$  belonging to the same periodic group approx. equals the frequency of the mol. AB. PN and AsN do not conform to this rule.

L. S. T.

Determination of van der Waals forces. H. S. W. MASSEY and R. A. BUCKINGHAM (Nature, 1936, 138, 77).—Vals. of the van der Waals energy const.  $C$  calc. from data (A., 1935, 1295) on the collision of rare gas with alkali atoms agree with those derived from the polarisabilities of the atoms, suggesting that the free path method serves for the determination of these forces.

L. S. T.

Van der Waals potential and the lattice energy of a  $n\text{-CH}_3$  chain molecule in a paraffin crystal. A. MULLER (Proc. Roy. Soc., 1936, A, 154, 624—639).—The van der Waals potential of a  $\text{CH}_3$  group in a paraffin crystal is calc. by applying London's theory (A., 1930, 525). The mol. must be subdivided for the

purpose of calculation, but it is found that for different modes of subdivision the final val. of the potential is the same.

L. L. B.

Molecular energy of alkali halides. E. J. W. VERWEY and J. H. DE BOER (Rec. trav. chim., 1936, 55, 431—443).—More correct vals. of the lattice and mol. energies (cf. A., 1932, 564) have been calc., which give the following vals. of the electron affinity:  $F'$  92.2,  $Cl'$  83.0,  $Br'$  77.2, and  $I'$  69.9 kg.-cal. Mol. energy vals. for the alkali halide vapours are calc. for different mol. models, and the effect of the polarisation forces is also considered. The mols. of the alkali halides are perfect ionic mols.

O. J. W.

Energy and structure of the molecules of the alkaline-earth oxides. J. H. DE BOER and E. J. W. VERWEY (Rec. trav. chim., 1936, 55, 443—450; cf. preceding abstract).—The lattice energies of  $\text{BeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$  have been calc. The calc. val. of the electron affinity of O ( $\text{O} \rightarrow \text{O}'$ ) is  $-173$  kg.-cal. The vals. of the mol. energy calc. for these mols. are considerably  $<$  those derived from the lattice and sublimation energies. It is probable that the vapours of these oxides, which have ionic lattices in the solid state, consist mainly of homopolar mols.

O. J. W.

Physical chemistry of homologous series. E. M. BRUINS (Rec. trav. chim., 1936, 55, 419—420).—Formulae are derived for the electrostatic potential in a homologous series surrounding a single charge and a dipole.

O. J. W.

Determination of linking moments in polyatomic molecules. R. MECKE (Z. physikal. Chem., 1936, B, 33, 156—162).—Theoretical. The previously described method (this vol., 268) of calculating for characteristic valency vibrations, where the energy is largely localised in a linking, the linking moment,  $u$ , from the intensities of the overtones has been simplified. By plotting the transition moments derived from the total absorption of the individual bands against  $v$  and extrapolating to  $v=0$   $\mu$  is obtained. An examination of the conditions for this extrapolation indicates that it would be possible to derive abs. partial dipole moments from suitable absorption measurements.

R. C.

Characteristic periods of vibrations of ionised gases in a magnetic field. T. V. IONESCU (Compt. rend., 1936, 203, 57—59).—Mathematical.

C. R. H.

Electron affinity of free radicals. X. Potentiometric method for determining  $\Delta F$  for the addition of sodium to an organic compound. H. E. BENT and N. B. KEEVIL (J. Amer. Chem. Soc., 1936, 58, 1228—1233; A., 1935, 1188).—Apparatus and procedure are described. Didiphenylenediphenylethane has an abnormally high electron affinity, which is related to the strength of phenylfluorene as an acid.

E. S. H.

Collisions of the second kind and electron affinity. L. GOLDSTEIN (Compt. rend., 1936, 202, 2057—2059; cf. this vol., 656).—Negative ions cannot be produced directly in pure  $\text{O}_2$ ,  $\text{SF}_6$ , or  $\text{CF}_4$ . In presence of 1% of A, Kr, or Xe, metastable atoms of the rare gas are produced by electronic collisions,

and these dissociate  $O_2$ ,  $SF_6$ , or  $CF_4$  by collisions of the second kind. The resulting electronegative atoms can form negative ions.

H. J. E.

**Functional space in quantum mechanics.** L. CHADENSON (Compt. rend., 1936, 202, 1974—1977).

H. J. E.

Some lattice sums involved in the calculation of elastic constants. M. GOEPFERT-MAYER and A. MAY (Physical Rev., 1936, [ii], 50, 99).—The method of calculation of the electrostatic part of the consts.  $C_{11}$  and  $C_{12}$  for crystals of the CsCl type is given.

A. J. M.

**Rotation of dipole molecules in solid bodies.** J. FRENKEL (Acta Physicochim. U.R.S.S., 1935, 3, 23—36).—Fowler's theory of the rotation of mols. in solids (A., 1935, 683) is compared with the Pauli method of determining the orientation of mols. in a polar gas on application of an external field. The theory is extended to the case where the orienting field acting on any given mol. of the crystal depends on the neighbouring mols. and has not a const. val. An expression is obtained for the transition temp. of a solid, this expression being similar to that for the Curie temp. of a ferromagnetic solid.

A. J. M.

**Surface tension of mercury in presence of gases.** I. Dry air. M. KERNAGHAN (Physical Rev., 1935, [ii], 47, 202; cf. A., 1931, 788).— $\gamma$  falls rapidly from 464 dynes per cm. in a vac. until an apparently crit. pressure of 7 mm. of dry air is reached. At higher pressures  $\gamma$  remains approx. const.

L. S. T.

(A) Increments of parachor of polymethylenic rings. (B) Multiple linkings in molecules of carbon compounds, and the structural constants of molecular refraction. V. S. GUTIRIA (J. Gen. Chem. Russ., 1936, 6, 340—349, 455—459).—(A) Experimental vals. of increments in parachors of homologous series of cyclic polymethylenic hydrocarbons differ considerably from those calc. from Mumford and Phillips' formulæ (A., 1929, 1219), or from other formulæ derived by Gutiria.

(B) The structural consts. of mol. refraction,  $MR$ , of  $C-C$ ,  $C=C$ , and  $C\equiv C$  compounds are derived from  $K - am \sin \alpha + b$ , where  $m$  represents the no. of linkings between C atoms,  $\alpha$  is the angle subtended by the lines of valency, and  $a$  and  $b$  are consts., depending on the  $\lambda$  of the light used. The vals. calc. for  $MR$  are in satisfactory agreement with those calc. by the usual formula, and with experiment, for a no. of hydrocarbons.

R. T.

**Temperature function of X-ray reflexion in the neighbourhood of the m.p. of a crystal.** R. B. JACOBS and A. GOETZ (Physical Rev., 1935, [ii], 47, 94—95).—Deviations from the Debye-Waller function near the m.p. of Bi crystals are described.

L. S. T.

**Effect of temperature on the reflexion of X-rays by crystals.** III. High temperatures. Allotropic crystals. C. ZENER and S. BILINSKY (Physical Rev. 1936, [ii], 50, 101—104; cf. this vol., 273).—The former discrepancy at high temp. disappears when account is taken of the variation of the characteristic temp. with temp. A relationship is found

between the temp. factors for two allotropic forms of the same element.

N. M. B.

**Absolute atomic factors of sulphur and lead.** P. DE LA CIERVA and J. PALACIOS (Anal. Fis. Quím., 1935, 33, 34—38).—The intensity of the (220) reflexion of PbS has been compared with that of the (200) reflexion of NaCl, whence from the data of James *et al.* (A., 1928, 225) the val. of the  $F$  factor for PbS is 63.15 for  $\sin \theta/2 = 0.238$ , which, combined with the authors' curves (A, 1935, 908) for Pb and S, gives the abs. curves of the  $F$  factors.

F. R. G.

**New and unexplained effects in Laue X-ray reflexion in calcite.** J. W. M. DUMOND and V. L. BOLLMAN (Physical Rev., 1936, [ii], 50, 97).—Incomplete blackening was observed where complete blackening of the plate would be expected in the Laue X-ray reflexion through thin cleaved plates of calcite. It was found that emergent beams which should be parallel were slightly convergent. Along the lengths of paired spectral lines there were marked fluctuations of intensity not due to interference.

A. J. M.

**Mathematical modulus derived from X-ray data for evaluation of residual distortion in crystals.** G. L. CLARK and M. M. BECKWITH (Physical Rev., 1935, [ii], 47, 200; cf. A., 1935, 1193).

L. S. T.

**Scattering of X-rays by gases.** E. O. WOLLAN (Physical Rev., 1935, [ii], 47, 201).

L. S. T.

**Diffuse scattering of X-rays by crystals.** G. E. M. JAUNCEY (Physical Rev., 1935, [ii], 47, 201).

L. S. T.

**Recrystallisation and crystal growth in aluminium.** A. VON ZEERLEDER (Schweiz. Arch. angew. Wiss. Tech., 1935, 1, 148—151; Chem. Zentr., 1935, ii, 2873).—Crystal growth in deformed Al at 550° is discussed.

J. S. A.

**Crystallisation of supercooled dielectric liquids in an electric field.** R. SWINNE (Wiss. Veroff. Siemens-Werken, 1936, 15, 124—128).—Polar substances ( $PhNO_2$ , fenchone, and  $PhCN$ ) were crystallised from the supercooled liquids with and without the application of an electric field (up to 5 kv. per cm.). Without a field, crystals did not usually appear between the electrodes, but when the field was applied crystallisation between them was more marked than elsewhere. With non-polar substances ( $C_6H_6$ ) the field caused no difference in the crystallisation.

A. J. M.

**Structure of radicals in crystals.** W. H. ZACHARIASEN (Physical Rev., 1935, [ii], 47, 201).

L. S. T.

**Nature of viscid fluid threads.** (Sir) J. LARMOR (Nature, 1936, 138, 74).

L. S. T.

**Orientation of molecules on the surface of solids and liquids.** F. KOROSI (Tech. Kurir, 1936, 7, No. 7, 2—4).—A review.

E. P.

**Crystal structure of carbon.** U. HOFMANN and D. WILM [with E. CSALAN] (Z. Elektrochem., 1936, 42, 504—522).—X-Ray determinations for coarsely-cryst. graphite give  $a$  4.252,  $c$  6.69 Å. As the crystal size diminishes, lattice distortion appears, reaching a max. in active C. There is a continuous



gradation of structure from graphite to active C; distortion is already detectable in Ceylon and Acheson graphite. Crystal growth begins at 1400°. The alteration of the structure by oxidation has been studied. E. S. H.

**Composition and crystal structure of trigonal chromium and manganese carbides.** A. WESTGREN (Jernkont. Ann., 1935, 118, 231—240).—The cell dimensions are: Cr carbide,  $a$  13.98,  $c$  4.523 Å.; Mn carbide  $a$  13.87,  $c$  4.53 Å. On rotation photographs of the latter about the axis (001) the only prism reflexions ( $hko$ ) visible are those with  $h$  and  $k$  even. The no. of atoms in the unit cell must be a multiple of 4. The formula  $Mn_7C_3$  (80 atoms per unit cell) is supported. CH. ABS. (c)

**Structure of potassium tetroxide.** V. KASSATOKHIN and V. KOTOV (J. Chem. Physics, 1936, 4, 458).— $KO_2$  forms a tetragonal face-centred lattice of the  $CaC_2$  type ( $a$  5.70,  $c$  6.72 Å.; 4 mols. in unit cell; space-group  $D_{4h}^{17}-F4/mmm$ ). The distance between adjacent O nuclei is  $1.28 \pm 0.07$  Å. The formula  $KO_2$  is supported. H. J. E.

**Fourier analysis of X-ray patterns of vitreous  $SiO_2$  and  $B_2O_3$ .** B. E. WARREN, H. KRUTTER, and O. MORNINGSTAR (J. Amer. Ceram. Soc., 1936, 19, 202—206).—Analysis of the patterns obtained in vac. with monochromatic Mo and Cu radiations showed that  $SiO_2$  is a tetrahedral Si—O network and that  $B_2O_3$  is a triangular co-ordination of B atoms surrounded by shared O atoms. The results agree with the Zachariasen prediction of the structure of oxide glasses. The glass-forming tendency of these two oxides is due to the complex irregular aggregate structures which require much rearrangement during cooling to assume a symmetrical (cryst.) structure and to the flexibility (i.e., stability) of the linking between an O and two cations. J. A. S.

**Crystal structure and colloid-chemical properties of vanadium pentoxide.** J. A. A. KETELAAR (Natuurwetensch. Tijds., 1936, 18, 80).—A brief discussion (cf. this vol., 274). D. R. D.

**Cation arrangement in a few oxides with crystal structures of the spinel type.** E. J. W. VERWEY and J. H. DE BOER (Rec. trav. chim., 1936, 55, 531—540).—The electrical conductivity of  $Fe_3O_4$ , with a cubic spinel lattice, is  $10^8$  times that of  $Mn_3O_4$  and  $Co_3O_4$  with a closely related tetragonal lattice. This difference is to be explained by differences in the valency state of the cations, and in the arrangement of the cations among the lattice points of the spinel unit cell. The high conductivity of  $Fe_3O_4$  may be explained on the conception that the oxide is  $FeO.Fe_2O_3$ . The crystal contains equal amounts of  $Fe^{++}$  and  $Fe^{+++}$  in the equiv. lattice points. The low conductivity of  $Co_3O_4$  together with considerations of energy, and study of X-ray structure, leads to the conclusion that it is made up of  $Co^{++}$  and  $Co^{+++}$ .  $Mn_3O_4$  has a structure similar to  $Co_3O_4$ , but the cell is distorted tetragonally. Both  $Mn_3O_4$  and  $Co_3O_4$  are true spinels. The X-ray diagram of  $\gamma\text{-Fe}_2O_3$ , having crystal structure closely related to spinel, shows that there are a no. of vacant cationic positions. The  $Mn_2O_3.H_2O$  obtained by Dubois (A., 1935, 181,

946) may be regarded as  $\gamma\text{-Mn}_2O_3$ . It has a face-centred tetragonal cell, similar to the  $\gamma\text{-Fe}_2O_3$  cell, but distorted. A. J. M.

**Structure of metal hydroxides with the emanating power 1.00.** O. ERBACHER (Z. physikal. Chem., 1936, B, 33, 47—53).— $Fe(OH)_3$  preps. of this type (cf. A., 1926, 332) give an amorphous X-ray diagram. Their radioactive emanating power shows them to have an exceptionally open internal structure. R. C.

**Morphology of pigments. III. X-Ray study of litharge.** E. G. IVANTSHEVA (J. Gen. Chem. Russ., 1936, 6, 621—625).— $PbO$  prepared by the Barton process crystallises in the rhombic system, whilst oven  $PbO$  consists of tetragonal crystals.  $Pb_2O_3$  gives a characteristic X-ray spectrum, indicating that it is not a mixture of  $PbO$  and  $PbO_2$ . R. T.

**Structure of silver azide.** M. BASSIÈRE (Bull. Soc. franç. Min., 1935, 58, 333—340; cf. this vol., 16). L. S. T.

**Monohydrated sulphates of the magnesium series.** F. HAMMEL (Compt. rend., 1936, 202, 2147—2149).—The dimensions of the unit cells of monohydrated Mg, Mn, Fe, Co, Ni, Cu, and Zn sulphates have been calc. (cf. this vol., 413). C. R. H.

**Calcium sulphate hemihydrate and the anhydrites. I. Crystallography.** W. A. CASPARI (Proc. Roy. Soc., 1936, A, 155, 41—48).—The prep., properties, and morphology of single crystals of  $CaSO_4.0.5H_2O$  (I) are described. X-Ray analysis gives the probable space-group as  $D_{2d}^{13}$  or  $D_{2d}^{14}$ , 3 mols. per unit cell,  $d$  2.60. The arrangement of ions in the lattice is discussed. The suggested structure leaves channels between  $Ca^{++}$  and  $SO_4^{--}$  ions, along which  $H_2O$  mols. can circulate. Dehydration of (I) under conditions short of conversion into anhydrite (II) causes slight mechanical changes in the crystal, but leaves the lattice unaltered. From the fact that the dihydrate and (I) yield the same substance under these conditions, it is concluded that there is only one crystal species intermediate between (II) and dihydrate. Sol. (I) has crystals belonging to the trigonal system,  $a$  6.82,  $c$  6.24 Å.,  $d$  2.70. L. L. B.

**Crystalline form and optical properties of calcium iodate.** J. MÉLON (Bull. Soc. franç. Min., 1935, 58, 343—349).— $Ca(IO_3)_2.6H_2O$  is not truly dimorphous. Crystals obtained in presence of  $HNO_3$  and of  $CaCrO_4$  show only facial differences.  $n_D$  1.686,  $n$  1.644, and  $n_p$  1.604. L. S. T.

**Crystallography of caesium molybdotellurates.** J. D. H. DONNAY and J. MÉLON (Amer. Min., 1936, 21, 299—311).—Cs molybdotellurate crystallises in two types, (i) equant, biaxial positive, and (ii) tabular, biaxial negative, both being triclinic and apparently holohedral. (i) has  $a:b:c=0.9498:1:0.6059$ ,  $\alpha$   $96^\circ 41'$ ,  $\beta$   $102^\circ 1'$ ,  $\gamma$   $101^\circ 31'$ ,  $n_a$  1.709,  $n_\beta$  1.716,  $n_\gamma$  1.797. (ii) has  $a:b:c=0.9365:1:0.7989$ ,  $\alpha$   $93^\circ 45'$ ,  $\beta$   $94^\circ 8'$ ,  $\gamma$   $88^\circ 21'$ ,  $n_a$  1.669,  $n_\beta$  1.734,  $n_\gamma$  1.738. L. S. T.

**Crystal structure of metaldehyde.** L. PAULING and D. C. CARPENTER (J. Amer. Chem. Soc., 1936, 58,

1274—1278).—X-Ray data indicate a body-centred unit, having  $a_0$  10.40,  $c_0$  4.11 Å., containing two mols. of  $(\text{MeCHO})_4$ . The space-group is  $C_4^2-I_4$ ; parameter vals. have been determined. The mol. consists of an 8-membered  $-\text{O}-\text{C}-\text{O}-\text{C}-$  ring with H and Me attached to each C. The interat. distances and linking angles are the same as in  $(\text{MeCHO})_3$ .

E. S. H.

**Crystallographic study of tartaric acid derivatives.** J. WYART and Y. KI-HENG (Compt. rend., 1936, 203, 95—97).—The vals. of  $a$ ,  $b$ , and  $c$ , respectively for the following compounds are: tartramide, 10.0, 12.2, 4.90; tartramic acid 12.30, 7.96, 6.00; Me tartrate, 18.50, 10.00, 8.45; K borotartrate, 4.88, 18.00, 7.65 Å.

C. R. H.

**Diffraction of X-rays by the higher polyethylene glycols and by polymerised ethylene oxides.** W. H. BARNES and S. ROSS (J. Amer. Chem. Soc., 1936, 58, 1129—1131).—The X-ray diagrams show no essential difference between the higher polyethylene glycols and polymerised ethylene oxides.

E. S. H.

**Change of lattice of fibroin when completely dried in a vacuum.** V. MATSUNAGA (Naturwiss., 1936, 24, 446—447).—The lattice const. of ordinary fibroin (containing some  $\text{H}_2\text{O}$ ) is the same as that of the substance which has taken up as much  $\text{H}_2\text{O}$  as possible, and  $>$  that of completely dried fibroin.

A. J. M.

**X-Ray analysis of keratins.**—See this vol., 1138.

**Crystal orientation in tooth-enamel.**—See this vol., 1010, 1011.

**Formation and crystallisation of vitreous media.** W. T. RICHARDS (J. Chem. Physics, 1936, 4, 449—457).—A discussion. It is shown to be unnecessary to postulate a vitreous state of aggregation, since all the properties of glasses appear to be those of undercooled liquids of high  $\eta$ .

H. J. E.

**Electron-optical reproduction with electrons liberated photo-electrically.** H. MAHL and J. POHL (Z. tech. Phys., 1935, 16, 219—221; Chem. Zentr., 1935, ii, 2626; cf. A., 1935, 139).

J. S. A.

**Kikuchi lines from etched copper crystal.** W. COCHRANE (Nature, 1936, 138, 202—203).—An etched single crystal of Cu, protected from distortion, gives Kikuchi lines, in addition to the cross-grating pattern of spots, by diffraction of a fast electron beam. These lines form a criterion of perfection of the crystal lattice.

L. S. T.

**Oxide layer on a polished copper surface.** S. DOBINSKI (Nature, 1936, 138, 31).—The electron diffraction pattern usually attributed to polished Cu is due to  $\text{Cu}_2\text{O}$ . Polishing in absence of air gives haloes of different size corresponding with spacings of 1.91 and 1.16 Å.

L. S. T.

**Anomalous values of lattice spacings obtained by electron diffraction.** E. PICKUP (Nature, 1936, 137, 1072).—Attention is directed to discrepancies in lattice spacings calc. from electron diffraction patterns. These anomalies may invalidate the results of electron-wave methods for measuring at. consts.

L. S. T.

3 z

**Analytic method of interpretation of electron diffraction photographs of gases.** S. H. BAUER (J. Chem. Physics, 1936, 4, 406—412).—A simplified method of calculating interat. distances and valency angles is described. Published data for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{COCl}_2$  are recalcd. and modified. New measurements on  $\text{C}_3\text{H}_8$  are recorded.

H. J. E.

**Electron-diffraction study of paraldehyde.** D. C. CARPENTER and L. O. BROCKWAY (J. Amer. Chem. Soc., 1936, 58, 1270—1273).— $(\text{MeCHO})_3$  consists of a staggered, 6-membered ring of alternate C and O atoms, having a C—O distance of  $1.43 \pm 0.02$  Å. The linking angles are tetrahedral and the Me groups are placed symmetrically about the mol. in nearly the same plane as the ring, with the possibility that only one Me may be above the plane of the ring. The C of the Me groups are attached to the C of the ring by linkings having a length of  $1.54 \pm 0.02$  Å.

E. S. H.

**Study of the nature of liquids by means of X-ray diffraction.** G. W. STEWART (Physical Rev., 1935, [ii], 47, 201).

L. S. T.

**Theory of the piezo-resistive effect.** J. W. COOKSON (Physical Rev., 1935, [ii], 47, 194—195).—The change in electrical resistance which a homogeneous body undergoes when subjected to mechanical stress is discussed for a Bi crystal.

L. S. T.

**Dependence of dielectric properties of Seignette salt crystals on mechanical factors.** R. DAVID (Helv. phys. Acta, 1935, 8, 431—484; Chem. Zentr., 1935, ii, 3207—3208).—The effect of pressure on the hysteresis and polarisation phenomena was studied.

H. J. E.

**Magnetic properties of manganese heated in nitrogen.** L. F. BATES, R. E. GIBBS, and D. V. REDDI-PANTULU (Proc. Physical Soc., 1936, 48, 665—671).—The combination of amorphous Mn with  $\text{N}_2$  has been studied between  $300^\circ$  and  $1000^\circ$ . Ferromagnetic compounds are formed at temp. much  $<$  previously reported. The magnetic hysteresis phenomena, the ferromagnetic Curie points, and an X-ray study of the compounds are described. The ferromagnetism can be associated with the  $\gamma$ -phase of Mn with a slightly enlarged lattice const.; the function of the  $\text{N}_2$  is not understood.

W. R. A.

**Ferromagnetism of nickel. II. Temperature effects.** J. C. SLATER (Physical Rev., 1936, [ii], 49, 931—937; cf. this vol., 671).—With the help of Fermi statistics and the model previously proposed, the free energy is calc. as a function of temp. and magnetic moment. The val. of the latter for which the free energy is a min. decreases with rise of temp. to zero at the Curie point, and, with the free energy val. at the min., as a function of temp., agrees with experiment. At abs. zero not all the spins are parallel, and this effect probably becomes more pronounced on approaching Fe in the ferromagnetic series, explaining the fact that alloys of Fe and Co show the highest saturation moments, the moment decreasing in Fe and in its alloys with lighter elements.

N. M. B.

**Magnetisation of nickel under compressive stresses and the production of magnetic dis-**



continuities. C. W. HEAPS (Physical Rev., 1936, [ii], 50, 176—179).—Hysteresis curves for stresses up to the elastic limit have been obtained. The existence of contiguous compressed and stretched regions appears necessary for the production of large Barkhausen discontinuities. N. M. B.

Behaviour of some solidified gases in polarised light. E. POHLAND (Angew. Chem., 1936, 49, 482—483).—Optical examination in polarised light between crossed nicols shows that solid HCN, NO, and SO<sub>2</sub> are double refracting, and that SbH<sub>3</sub> is dimorphous, the cubic form being the stable one. J. W. S.

Cryolite. Index of refraction, birefringence, and crystalline forms. G. CESARO and J. MELON (Bull. Acad. roy. Belg., 1936, [v], 22, 362—372).—*n* for cryolite is 1.343 at 6620 Å. and 1.319 at 4770 Å. The vals. obtained at other  $\lambda$  agree with those calc. from the Cauchy formula. The birefringence for various faces, and the angles between the faces, are calc. A. J. M.

Allotropy of very pure calcium. A. SCHULZE (Z. Metallk., 1936, 28, 55—57).—The ordinary face-centred cubic ( $\alpha$ ) form of Ca is converted into a body-centred ( $\beta$ ) form at 300° and into a close-packed hexagonal ( $\gamma$ ) form at 450°. The  $\beta$ - $\gamma$  change is accompanied by a heat evolution of 5.3 g.-cal per g. These results have been established by thermal, dilatometric, X-ray, and electrical resistance methods. A. R. P.

Highly polymerised compounds. CXLI. Osmotic mol. wt. determinations with polymer-homologous series of substances of high mol. wt. G. V. SCHULZ (Z. physikal. Chem., 1936, 176, 317—337).—Mol. wts. of cellulose nitrates, polyethylene oxides, and polystyrenes have been deduced from osmotic pressure measurements by means of the equation previously suggested (this vol., 146). Mol. wts. up to 10<sup>6</sup> may be determined by this method. A convenient osmometer is described. R. C.

$\alpha$ - $\beta$  Transition with mechanically treated and with untreated zirconium. J. H. DE BOER, P. CLAUSING, and J. D. FAST (Rec. trav. chim., 1936, 55, 450—458).—Measurements of the electrical resistance of Zr rods, which had been subjected to varying preliminary treatment, show that the indefinite character of the  $\alpha$ - $\beta$  transition is not due to the transition itself, but to the heating of the rods in air during the mechanical working. The  $\alpha$ - $\beta$  transition temp. is 865±10° (cf. A., 1932, 219). O. J. W.

Influence of oxygen and nitrogen on the  $\alpha$ - $\beta$  transition of zirconium. J. H. DE BOER and J. D. FAST (Rec. trav. chim., 1936, 55, 459—467; cf. preceding abstract).—Zr can take up homogeneously < 10 at.-% of O and of N, and in presence of these gases the  $\alpha$ - $\beta$  transition is no longer sharp, but extends over a temp. range. With 10 at.-% O the transition commences below 910° and extends to >1550°. In this temp. range the  $\beta$ -phase is in equilibrium with an  $\alpha$ -phase which is richer in O. The resistance curves are scarcely influenced by the addition of Al. O. J. W.

High-temperature properties of niobium. A. L. REIMANN and C. K. GRANT (Phil. Mag., 1936, [vii], 22, 34—38).—Measurements of the sp. resistance, total thermal radiation, electron emission, and rate of evaporation at 1800—2400° abs. are recorded. The m.p. was 2770° abs. H. J. E.

Electrical resistivity of bismuth single crystals. A. B. FOCKE and J. R. HILL (Physical Rev., 1936, [ii], 50, 179—184).—Measurements in the temp. range —185° to 100° on Bi crystals containing Pb, Sn, Sb, or Te showed, in general, that falling temp. results in greater effectiveness of the impurity except when the impurity concn. allows phase separation at low temp. Less than 0.03% of all impurities cause a sharp increase in the resistance. The effect of larger amounts depends on the nature of the impurity; Pb and Sn increase the resistance; Te lowers it below the val. for pure Bi; Sb causes the initial rise to fall off and then to be slowly re-established; >0.03% Sn and >0.2% Pb result in a negative temp. coeff. for resistance parallel to the principal axis. N. M. B.

Electrical resistance of bismuth alloys. N. THOMPSON (Proc. Roy. Soc., 1936, A, 155, 111—123).—The electrical resistance of single crystals of Bi containing traces of Pb, Sn, Ge, Se, Te, and other elements has been measured from 14° to 400° abs. Pb, Sn, and Ge dissolves in the Bi lattice, giving an alloy with a high negative temp. coeff. of resistance parallel to the principal axis of the crystal, and a similar, but smaller, effect perpendicular to the axis. Se and Te dissolve in Bi, but there is no negative temp. coeff.; the addition of the first trace of the impurity lowers the sp. resistance, both parallel and perpendicular to the axis, except at low temp. The results are discussed in the light of Jones' theory of Bi (A., 1935, 153). L. L. B.

Time effects in superconductors. K. MENDELSSOHN and R. B. PONTIUS (Nature, 1936, 138, 29—30). L. S. T.

Carrier electrons in superconduction. R. FORRER (Compt. rend., 1936, 202, 2059—2061).—The electrons which are responsible for superconduction are the *s* electrons of incomplete shells. H. J. E.

Electrostatic behaviour of superconductors. H. LONDON (Proc. Roy. Soc., 1936, A, 155, 102—110; cf. A., 1935, 689).—It follows from measurements of the capacity of a superconducting condenser that no electrostatic fields exist in a pure superconductor, and that in all stationary cases the surface of a superconductor is equipotential. L. L. B.

Conductivity of *p*-axoxyanisole. M. JEZEWSKI and M. MIESOWICZ (Acta phys. polon., 1934, 3, 279—283; Chem. Zentr., 1935, ii, 5052).—Conductivity data are recorded at 121° for d.c. and a.c., and with longitudinal and transverse magnetic fields of 4000 gauss. H. J. E.

Magnetic measurements in chemistry. J. S. ANDERSON (Chem. and Ind., 1936, 555—559).—The application of magnetic susceptibility measurements to chemical problems is reviewed. J. S. A.

**Collective electron specific heat and spin paramagnetism in metals.** E. C. STONER (Proc. Roy. Soc., 1936, A, 154, 656—678).—General expressions are obtained which show how the sp. heat and spin paramagnetism, and their temp. variation, depend on the band form. Only the low temp. range is considered. A method of determining the effect of interchange interaction is developed. Positive interchange interaction does not necessarily result in ferromagnetism, even at the lowest temp. The magnetic properties of the elements of the first two columns of the periodic table and of the transition elements and rare earths are considered on the basis of the theoretical treatment. L. L. B.

**Magnetic properties of the plasma of gas discharges.** M. STEENBECK (Wiss. Veroff. Siemens-Werken, 1936, 15, 1—17).—The plasma of a gas discharge may be treated as a metal with freely moving, non-degenerate electron gas. The diamagnetic susceptibility and magnetic moment induced in the plasma are determined. The susceptibility is > that of any other diamagnetic substance. A. J. M.

**Preparation of lithium alum.** J. F. SPENCER and G. T. ODDIE (Nature, 1936, 138, 169).—Concn. and cooling in an ice-NaCl freezing mixture of an aq. solution of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (1:1) yields isotropic crystals, a combination of cube and octahedron, of Li alum. At room temp. the crystals decompose; at  $200^\circ$ , all  $\text{H}_2\text{O}$  is lost and a bulky, friable mass remains. The mass susceptibility is  $-0.541 \times 10^{-6}$ . L. S. T.

**Magne-crystalline action. IV. Magnetic behaviour of paramagnetic ions in the S-state in crystals.** K. S. KRISHNAN and S. BANERJEE (Phil Trans., 1936, A, 235, 343—366; cf. A., 1935, 924).—Special technique for the measurement of feeble anisotropies, and data for 10 paramagnetic single crystals of  $\text{Mn}^{++}$  and  $\text{Fe}^{+++}$  salts, 13 isomorphous diamagnetic crystals obtained by replacing Mn by Mg or Zn, and Fe by Al, and abs. susceptibilities of the 10 first-mentioned are given. Causes discussed contributing to the anisotropy are: diamagnetism of the crystal, mutual influence of the magnetic moments and their non-cubic arrangement in the crystal lattice, and the Stark splitting of the  $^6\text{S}$  levels under the influence of the cryst. electric fields. A method for calculating the magnitude of the Stark separation from the anisotropy and the "characteristic temp." is described. The part played by Stark splitting in various low-temp. phenomena is reviewed; the entropy-temp. and sp. heat-temp. curves of the crystals around  $0.1^\circ$  abs. can be predicted from magnetic measurements at room temp. Data for some mixed crystals are given. N. M. B.

**Optical method for the measurement of paramagnetic susceptibilities. Application to the ethyl sulphates of the rare earths in the direction of the optic axis.** J. BECQUEREL (Physica, 1936, 3, 705—723; cf. Van Vleck and Hebb, A., 1934, 944).—Vals. of the magnetic susceptibilities of the hydrated Et sulphates of Pr, Nd, Ds, and Er parallel to the optic axis are deduced from measurements of the magnetic rotatory power at temp.

between  $1.45^\circ$  abs. and room temp. Those for Ds are in agreement with direct measurements and all are compatible with the theory of paramagnetism.

O. D. S.

**Magnetic properties of some compounds of the rare elements.** S. VELAYOS (Anal. Fis. Quim., 1935, 33, 5—33; cf. A., 1934, 586).— $\chi$  for  $\text{Er}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Gd}_2(\text{SO}_4)_3$ ,  $\text{Pr}_2\text{O}_3$ , and  $\text{Nd}_2\text{O}_3$  has been measured over the range  $80$ — $720^\circ$  abs., whence the magneton nos. are 52.0, 46.8, 38.97, 39.1, 17.5, and 16.4.  $\text{Pr}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  do not obey the Weiss-Curie law but obey the modification proposed by Cabrera *et al.* (A., 1925, ii, 755),  $(\chi + k)(T + \Delta) = C$ . The magneton nos. of  $\text{Pr}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  agree more closely with the theoretical vals. of Hund than those of Van Vleck and Frank. F. R. G.

**Critical examination of Pascal's value for the magnetic susceptibility of the  $\text{CH}_3$  group.** S. S. BHATNAGAR and N. G. MITRA (J. Indian Chem. Soc., 1936, 13, 329—334).—Recalculation of Pascal's val. for  $\chi$  of the  $\text{CH}_3$  group, using modern vals. for at. wts. and correcting for the new val. for  $\text{H}_2\text{O}$ , gives, as an average of 50 vals.,  $-11.68 \times 10^{-6}$  (cf. Pascal's val.  $-12.35 \times 10^{-6}$ ). C. R. H.

**Search for a photomagnetic effect.** R. M. EMBERSON and R. T. DUFFORD (Physical Rev., 1935, [ii], 47, 202).—Measurements of the magnetic susceptibilities of >60 substances, including Grignard solutions giving the photovoltaic effect, failed to reveal a change in susceptibility due to illumination. L. S. T.

**Dispersion of sound in oxygen.** L. S. SINNESS and W. E. ROSEVEARE (J. Chem. Physics, 1936, 4, 427—431).—The velocity of a 1000-cycle sound wave in  $\text{O}_2$  of various degrees of humidity at  $26.5^\circ$  was measured. The velocity was a min. for  $p_{\text{H}_2\text{O}} = 1$ —3 mm. The change in velocity due to dispersion was 0.16%. The  $\text{H}_2\text{O}$  mols. are effective in bringing the heat capacity of the first vibrational state of  $\text{O}_2$  into equilibrium with the sound wave. H. J. E.

**Acoustic experiments for the investigation of molecular collisions.** H. O. KNESER (Sitzungsber. Ges. Naturwiss. Marburg, 1935, 69, 189—194; Chem. Zentr., 1935, ii, 3213).—The absorption of sound waves by air or  $\text{O}_2$  is small for high or low frequencies, and is a max. for moderate frequencies. Addition of 1% of  $\text{H}_2$  at EtOH increases the absorption considerably.  $\text{N}_2$ , CO, or He does not change it. H. J. E.

**Molecular absorption of sound in gases.** H. O. KNESER (Z. tech. Phys., 1935, 16, 213—219; Chem. Zentr., 1935, ii, 3213; cf. preceding abstract).—Measurements with air,  $\text{O}_2$ , and  $\text{CO}_2$  agree with the theory of mol. absorption. Foreign gases increase the absorption coeff. H. J. E.

**Direct calorimetric determination of  $C_p$  of the hydrogen isotope in the solid and liquid state.** E. BARTHOLOME and A. EUCKEN (Z. Elektrochem., 1936, 42, 547—551).—Apparatus and technique are described and results reported for solid  $\text{H}_2$  (11.20—17.75° abs.), solid  $\text{D}_2$  (11.60—21.23° abs.), liquid  $\text{H}_2$  (15.33—23.13° abs.), and liquid  $\text{D}_2$  (19.62—23.49° abs.). The determinations of  $C_p$



are discussed. Vals. of  $\theta$  are 105 for  $H_2$  and 97 for  $D_2$ . E. S. H.

**Specific heat, entropy, and dissociation of technical gases and vapours.** E. JUSTI and H. LUDER (Forsch. Ingenieur. Ausg., 1935, 6, A, 209—216; Chem. Zentr., 1935, ii, 2789—2790).—Data given previously (A., 1935, 289) are supplemented by data for  $H_2$ ,  $D_2$ ,  $N_2$ ,  $O_2$ , HD, OH, CO, NO,  $H_2O$ ,  $D_2O$ ,  $CO_2$ ,  $SO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_2$ , and air. The variations of  $C_p$  and  $C_p$  with pressure are discussed, and data are given for the dissociation of  $H_2$ ,  $N_2$ ,  $O_2$ , NO,  $H_2O$ ,  $CO_2$ ,  $N_2O$ ,  $SO_2$ ,  $C_2H_6$ , and for the water-gas reactions. J. S. A.

**Mean specific heats of gases, for use in fuel technical calculations.** W. GUMZ (Feuerungstechn., 1935, 23, 85—86; Chem. Zentr., 1935, ii, 2789).—Mean sp. heats between  $0^\circ$  and  $3500^\circ$  are given for  $CO_2$ ,  $SO_2$ ,  $H_2O$ ,  $N_2$ ,  $O_2$ , A, CO,  $CH_4$ ,  $H_2$ , and air. J. S. A.

**Entropy of water and the third law of thermodynamics.** Heat capacity of ice from  $15^\circ$  to  $273^\circ$  abs. W. F. GIAUQUE and J. W. STOUT (J. Amer. Chem. Soc., 1936, 58, 1144—1150).—The discrepancy between the spectroscopic val. of the entropy and the  $\int_0^T C_p/dT$  for  $H_2O$  has been evaluated as 0.82 g.-cal./degree/mol. Heat capacity data for ice are recorded. No difference in thermal properties was observed whether the ice was cooled slowly or rapidly to low temp. or kept for a long time at low temp. E. S. H.

**Specific heat of nickel.** E. C. STONER (Phil. Mag., 1936, [vii], 22, 81—106).—An analysis of the sp. heat of Ni is made in terms of the lattice vibration term, the dilatation term, and the electronic and magnetic sp. heats. H. J. E.

**Electronic specific heat in palladium.** G. L. PICKARD (Nature, 1936, 138, 123).—Determinations of the sp. heat of Pd between  $2.5^\circ$  and  $22^\circ$  abs. give  $C = 0.0000224T^3 + 0.0031T$  g.-cal. per degree for the at. heat. The first term represents the component due to the lattice vibrations, and the second the sp. heat of the free electrons or positive holes (unfilled quantum states). As predicted by Mott, the val. of the electronic sp. heat is  $>$  that for normal metals and is even  $>$  that of Ni. L. S. T.

**Exact determination of specific heats at high temperatures. VIII. Additive law for the atomic heats of metals in their binary compounds.** F. M. JAEGER and T. J. POPPEMA (Rec. trav. chim., 1936, 55, 492—517; cf. A., 1934, 354).—Further measurements of  $C_p$  for Sb and Pd and for the binary compounds  $MgZn_2$ ,  $PtSb_2$ ,  $PdSb$ ,  $PdSb_2$ ,  $PdSb$ ,  $PdCu$ , and  $PdCu_3$  are recorded. The observed mol. heat differs in general from that calc. from the component at. heats, and the differences increase with the temp. Some X-ray data for  $\beta$ - $Pd_3Sb$  are given. O. J. W.

**Specific heats of solid substances at high temperatures. XI. Specific heats, electrical resistance, and thermo-electric behaviour of titanium in their dependence on temperature.** F. M. JAEGER, E. ROSENBOHM, and R. FONTEYNE (Rec. trav. chim., 1936, 55, 615—654).—Ti exists in

an  $\alpha$ -form with hexagonal symmetry, stable below  $\sim 905^\circ$ , and a body-centred cubic  $\beta$ -form stable above  $880$ — $905^\circ$ . Measurements of the heat given out in cooling, the resistance,  $R$ , at  $250$ — $940^\circ$ , and the thermo-e.m.f.,  $E$ , at  $50$ — $1020^\circ$  show that transition occurs very slowly. The true at. heat,  $C_p$ , rises from 6.507 at  $200^\circ$  to 8.901 at  $817^\circ$ . From  $817^\circ$  onwards it rises very rapidly, then drops abruptly to 7.525, which is the val. for the  $\beta$ -form and does not vary with temp. Apparently  $817$ — $905^\circ$  is a transition interval. A series of "minor transition points" have also been observed. At these, peculiar hysteresis effects occur on cooling; some, at least, of these points are partly due to the presence of traces of O and N and the production within the metal of oxide films and their partial reduction by the excess of Ti at various temp. These gases also affect the transition  $\beta$ -Ti. The modification of the Saladin-Le Chatelier method for the precise measurement of the variation of  $E$  and  $R$  with temp. in a high vac. is described. R. C.

**Isotherms of methane between  $0^\circ$  and  $150^\circ$  for densities up to 225 Amagat. Calculated specific heat, energy, and entropy in the same region.** A. MICHELS and G. W. NEDERBRAGT (Physica, 1936, 3, 569—577; cf. this vol., 20).—Isotherms of  $CH_4$  have been determined at  $25^\circ$  intervals between  $0^\circ$  and  $150^\circ$  and are represented by an empirical formula. Calc. vals. of the sp. heat, internal and free energies, and entropy are tabulated. O. D. S.

**Specific heat of formic acid and its aqueous solutions.** A. A. GLAGOLEVA and S. I. TSCHERBOV (J. Gen. Chem. Russ., 1936, 6, 685—690).—Sp. heat data are recorded for the range  $25$ — $80^\circ$ . R. T.

**Amorphous and crystalline forms of rubber hydrocarbon.** G. S. PARKS (J. Chem. Physics, 1936, 4, 459).—It is suggested that the cryst. rubber hydrocarbon described by Bekkedahl and Matheson (this vol. 417) was in reality a mixture of cryst. material with approx. 70% of amorphous material. The heat of fusion of the pure cryst. material was recalcd. as 17.4 g.-cal. per g., which is of the same order of magnitude as the val. for other hydrocarbons of m.p.  $> 200^\circ$  abs. H. J. E.

**M.p. and b.p. in series of homopolar substances.** J. F. DURAND (Bull. Soc. chim., 1936, [v], 3, 1382—1388).—When the b.p. (abs. temp.) of A, Kr, and Xe are plotted as abscissæ and those of the corresponding substances  $PCl_3$ ,  $AsBr_3$ , and  $SbI_3$  as ordinates, the three points lie on a straight line. The same holds for  $SiCl_4$ ,  $GeBr_4$ , and  $SnI_4$ . Similarly, when the b.p. of He, Ne, A, Kr, and Xe are plotted against those of  $H_2$ ,  $F_2$ ,  $Cl_2$ , Br, and I, the five points lie on a straight line, but when the m.p. are plotted only the vals. for  $Cl_2$ , Br, and I are in alignment. By extrapolation, the halogen at. no. 85 should have b.p. about  $684^\circ$  and m.p. about  $572^\circ$  abs. E. S. H.

**Determination of physico-chemical constants.** M. WOJCIECHOWSKI and E. R. SMITH (Nature, 1936, 138, 30).—The difference between the b.p. and condensation temp. enables the consts. for the pure substance or azeotropic mixture to be calc. The

b.p. of *iso*-C<sub>5</sub>H<sub>11</sub>·OH and *d*<sup>25</sup> for Pr<sup>o</sup>OAc thus obtained are 131·806° and 0·88299(3) g. per c.c., respectively.

L. S. T.

**Vapour pressure of barium.** J. A. M. VAN LIEMPT (Rec. trav. chim., 1936, 55, 468—470; cf. A., 1935, 1454).—The following expression for the v.p. is obtained:  $\log p = -9727/T + 7·83$  (*p* in mm.), and the following data for Ba are calc.: heat of evaporation 44,450 g.-cal. per g.-atom, b.p. 1696°, Trouton's const. 22·6.

O. J. W.

**Vapour pressure of deuterium water from 20° to 230°.** F. T. MILES and A. W. C. MENZIES (J. Amer. Chem. Soc., 1936, 58, 1067—1069).—V.p. are recorded for D<sub>2</sub>O and the differences of latent heat of vaporisation for D<sub>2</sub>O and H<sub>2</sub>O calc. The v.p. of D<sub>2</sub>O and H<sub>2</sub>O are identical at about 224°.

E. S. H.

**Vapour pressure, b.p., and heat of vaporisation of HDO and H<sub>2</sub>O<sup>18</sup>.** E. H. RIESENFELD and T. L. CHANG (Z. physikal. Chem., 1936, B, 33, 127—132).—The v.p. of HDO at 100° and of H<sub>2</sub>O<sup>18</sup> at 65—100° have been calc. from the increased concn. of these in the residue after partial distillation of H<sub>2</sub>O (cf. A., 1935, 1064). The empirical equations  $p_{\text{D}_2\text{O}}/p_{\text{H}_2\text{O}} = 1·35e^{-259/RT}$  and  $p_{\text{H}_2\text{O}^{18}}/p_{\text{H}_2\text{O}} = 1·013e^{-13/RT}$  have been obtained. The b.p. of HDO and H<sub>2</sub>O<sup>18</sup> are calc. to be 100·7° and 100·1°, and the mol. heats of vaporisation  $\lambda_{\text{H}_2\text{O}} + 130$  and  $\lambda_{\text{H}_2\text{O}} + 13$  g.-cal., respectively.

R. C.

**Vapour pressure and heat of vaporisation of heavy water.** E. H. RIESENFELD and T. L. CHANG (Z. physikal. Chem., 1936, B, 33, 120—126).—The excess of the v.p. of H<sub>2</sub>O over that of D<sub>2</sub>O has been measured at 20—230°. With rising temp. it passes through a max., 82·6 mm., at 170°, and is zero at 225° and negative above. The excess of the heat of vaporisation of D<sub>2</sub>O over that of H<sub>2</sub>O falls with rising temp., but is always positive.

R. C.

**Vapour pressure of ethyl alcohol and toluene as a criterion of purity.** F. SCHOUTEDEN and J. DEVEUX (Natuurwetensch. Tijds., 1936, 18, 242—247).—The v.p.-temp. curve of the liquid is determined in a closed space (e.g., in a glass-spring manometer) under such conditions that (1) the vol. of the vapour phase is negligible, (2) the vol. of the liquid phase is negligible compared with that of the vapour. For a pure substance, the two curves are coincident. Curves are recorded for pure EtOH and PhMe. A method of calculating the heat of mixing from v.p. data is obtained thermodynamically.

D. R. D.

(A) Isotherms of nitrogen between 200 and 300 atm. and 0° and 150°. (B) Calculation of thermodynamic properties of nitrogen up to 3000 atm. between 0° and 150°. A. MICHELS, H. WOUTERS, and J. DE BOER (Physica, 1936, 3, 585—589, 597—604; cf., A., 1934, 355, 837).—(A) Earlier measurements are extended to higher densities (up to 578 Amagat). The results are not accurately represented by either of the empirical formulae tried.

(B) From the isotherm data the change in internal energy, sp. heat, entropy, and free energy on compression have been calc.

O. D. S.

**Determination of coefficient of equilibrium for condensed (gas) systems.** S. M. LEVINSON (Chimstr., 1935, 7, 262—264).—Coeffs. for CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, and C<sub>5</sub>H<sub>10</sub> have been derived for the range -90° to 30° and 0 to 50 atm. CH. Abs. (e)

**Thermodynamical researches.** N. A. DE KOLOSOVSKI (Acta Univ. Asiae Med., 1934, [vi], 1, No. 7, 3—91).—A thermodynamical treatment of the properties of liquids and vapours.

E. S. H.

**Volume energy of real gases (He, Ne, H<sub>2</sub>).** V. JACYNA (Acta phys. polon., 1934, 3, 15—32; Chem. Zentr., 1935, ii, 3212).—Data are recorded, and deviations from the ideal gas laws are discussed.

H. J. E.

**Röntgenographic measurements of expansion of crystalline masses.** W. BUSSEM [with M. BLUTH and G. GROCHTMANN] (Ber. deut. keram. Ges., 1935, 16, 381—392; Chem. Zentr., 1935, ii, 2848).—X-Ray measurements of lattice parameters are given for MgO, cristobalite, corundum, sillimanite, and SiC from -182° to 1400°.

J. S. A.

**Heat conduction by rarefied gases. I. Thermal accommodation coefficient of helium, hydrogen, neon, and nitrogen on glass at 0°.** W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 716; cf. A., 1911, ii, 253; 1933, 1).—The accommodation coeffs. of He (0·336), H<sub>2</sub> (0·283), Ne (0·670), and N<sub>2</sub> (0·855) on glass at 0° have been measured by Schleiermacher's method.

J. L. D.

**Heat conductivity of tungsten and cooling effects of leads on filaments at low temperatures.** I. LANGMUIR and J. B. TAYLOR (Physical Rev., 1936, [ii], 50, 68—87).—The theory of the effect of the temp. of the leads to a W wire in an evacuated vessel on the temp. distribution and resistance is given, and general equations are given for W filaments up to 600° abs. It is shown that the heat conductivity,  $\lambda$ , may be calc. from determinations of temp. or resistance resulting from the passage of a current through the filament. For low temp. (<600° abs.) it is more convenient to use the resistance.  $\lambda$  at 273° abs. is 1·66 watts per cm. per degree and decreases with rising temp. according to  $\log \lambda = 0·951 - 80·30 \log T$ .

A. J. M.

**Heat losses from a tungsten wire in helium.** W. C. MICHELS and G. WHITE (Physical Rev., 1935, [ii], 47, 197).—The accommodation coeff. found is 0·092, which becomes 0·069 when corr. for thermal etching produced in cleaning the wire.

L. S. T.

(A) Conduction of heat by some metals at low temperatures. H. BREMMER and W. J. DE HAAS. (B) Determination of the heat-resistance of mercury at the temperatures obtainable with liquid helium. W. J. DE HAAS and H. BREMMER. (C) Heat conductivity of superconductive alloys. H. BREMMER and W. J. DE HAAS (Physica, 1936, 3, 672—686, 687—691, 692—704).—(A) The heat-resistance ( $R_h$ ) of Pb has been measured between 2·5° and 77° abs. and of Cu and W between 14° and 22° abs. Below the threshold of superconductivity of Pb  $R_h$  has different vals.,  $W_n$  and  $W_s$ , in the presence or absence of a magnetic field of strength sufficient to



destroy the superconductivity.  $W_n < W_s$ . Both pass through min. vals. at about  $5^\circ$  and  $8^\circ$  abs., respectively. The "ideal resistance,"  $R_i$ , of Pb also passes through a min.  $R_i$  of Cu is still decreasing at  $14.5^\circ$  abs.  $R_i$  of W appears to tend to a min. at low temp.

(n) Relative vals. of  $R_h$  of Hg between  $2.5^\circ$  and  $4^\circ$  abs. are given.  $W_s$  and  $W_n$  both show a min. val. at about  $3.5^\circ$  abs.

(c)  $R_h$  has been measured for alloys of the following compositions: Pb 56, Sn 44 wt.-%,  $15-70^\circ$  abs.: Bi 50, Pb 25, Sn 25 wt.-%, eutectic mixture,  $2.6-276^\circ$  abs.: In-Pb alloys containing 8.6, 50, and 99 wt.-% Pb,  $2.5-278^\circ$  abs. In all cases  $R_h$  increases rapidly at low temps. but more slowly than is predicted by theory. O. D. S.

**Viscosity of halogen compounds of the elements of group V of the periodic system.** (MLLE.) A. I. LICHATSCHEVA and G. P. LUTSCHINSKI (J. Chim. phys., 1936, 33, 488-491).—The variations with temp. of the viscosities of  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{PBr}_3$ ,  $\text{AsBr}_3$ , and  $\text{SbBr}_3$  follow Batschinski's formula (cf. A., 1935, 438). The limiting vals.,  $\omega$ , of the chlorides are  $>$  those of the bromides, and the  $\omega$  of the group V elements decrease with increase of at. wt.

J. G. A. G.

**Viscosity of air and the electronic charge.** G. KELLSTROM (Physical Rev., 1936, [ii], 50, 190; cf. A., 1935, 1455).—Improved apparatus gave the result  $\eta_{20^\circ} = (18201 \pm 27) \times 10^{-8}$  or  $\eta_{23^\circ} = (18349 \pm 27) \times 10^{-8}$ ; this, with Millikan's data, gives  $e = (4.818 \pm 0.011) \times 10^{-10}$  e.s.u. N. M. B.

**Measurements of the viscosity of water and water vapour up to the critical region.** K. SIGWART (Forsch. Geb. Ingenieurw., 1936, 7, 125-140).—A flow method for the determination of  $\eta$  of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  vapour at high pressure and temp. is described. The  $\eta$  of  $\text{H}_2\text{O}$  depends on its  $d$ , that of the vapour on both its  $d$  and temp. The slope of the isotherms of  $\eta$  against pressure for  $\text{H}_2\text{O}$  vapour remains practically const. up to the saturation pressure, where an increase occurs. Below  $275^\circ$  the increase in  $\eta$  is small, amounting to only 5% for a pressure increase of 100 atm. The  $\eta$  of  $\text{H}_2\text{O}$  at the crit. point was found to be  $3.85 \times 10^{-6}$  kg. sec. per sq. m.

R. B. C.

**Relationship between the constitution and viscosity characteristics of hydrocarbons.** W. R. WIGGINS (J. Inst. Petroleum Tech., 1936, 22, 305-327).—The viscosity ( $\eta$ ) of hydrocarbons in relation to their constitution is considered in the light of published data. It is shown that the fractional  $\eta$ -temp. coeff.  $(1/\eta)(\Delta\eta/\Delta t)$  has a linear relationship with  $\log \tau$ , i.e.,  $(\Delta\eta/\Delta t)(1/\eta \log \eta) = \text{const.}$  This function is approx. const. for the same hydrocarbon, varying from 0.03 to 0.04 for aliphatic hydrocarbons and those of simple cyclic structure, whilst branched and polycyclic hydrocarbons give higher vals. The corresponding expression in kinematic units is regarded as a simple index for classifying viscous hydrocarbons. C. C.

**Density of mixtures of some molten electrolytes.** V. P. MASCHOVETZ and Z. F. LUNDINA (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev,

1935, 191-212).—The  $d$  of  $\text{MgCl}_2$ ,  $\text{NaCl}$ , and  $\text{KCl}$  falls linearly with rise of temp. from  $100^\circ$  to  $1000^\circ$ . The  $d$ -composition curves of the systems  $\text{MgCl}_2$ - $\text{NaCl}$  and  $\text{KCl}$ ,  $\text{KCl}$ - $\text{BaCl}_2$ , and  $\text{MgCl}_2$ - $\text{KCl}$ - $\text{NaCl}$  have been determined. R. T.

**Fused salts.** V. A. IZBEKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 142-152).—A lecture. R. T.

**Viscosity of butyric acid-water mixtures.** C. R. BURY and J. GRINDLEY (J.C.S., 1936, 1003-1004).—The  $\eta$ -composition curves at  $-3^\circ$  to  $35^\circ$  afford no evidence for micelle formation, although anomalous in the crit. solution region is apparent at  $-3^\circ$ . The max. at approx. 70% acid are not accepted as evidence for compound formation.

C. R. H.

**Dielectric constant of dioxan-water mixtures between  $0^\circ$  and  $80^\circ$ .** G. ÅKERLOF and O. A. SHORT (J. Amer. Chem. Soc., 1936, 58, 1241-1243).—Data have been obtained for  $\lambda = 150$  m., using a resonance method. E. S. H.

**Solid solutions of methane and krypton.** M. VON STACKELBERG, F. QUATRAM, and H. J. ANTWEILER (Z. Elektrochem., 1936, 42, 552-557).—Thermal analysis and v.-p. determinations show that  $\text{CH}_4$  and Kr form an unbroken series of solid solutions. The f.p. and b.p. of all mixtures lie between those of the components. E. S. H.

**Aggregative states. II. Connexion between composition and properties in eutectics of binary systems of type I.** E. I. ACHUMOV (J. Gen. Chem. Russ., 1936, 6, 559-575; cf. this vol., 21).—Mathematical. R. T.

**Piezometric researches. III. Effect of high pressures on the melting curve of binary mixtures.** L. DEFFET (Bull. Soc. chim. Belg., 1936, 45, 213-250; cf. A., 1935, 688).—Data are recorded for the binary mixtures  $\text{C}_6\text{H}_6$ - $\text{C}_{10}\text{H}_8$  and  $\text{C}_6\text{H}_6$ -urethane over a wide range of composition. The composition of the  $\text{C}_6\text{H}_6$ - $\text{C}_{10}\text{H}_8$  eutectic varies only slightly with pressure, and, in general, with increase of pressure, the eutectic is enriched with respect to that component which has the smaller val. of  $\delta$  (*loc. cit.*). The influence of pressure on the solubility of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  has also been examined. J. G. A. G.

**Two eutectic cycles with diphenyl.** A. M. VASILIEV (J. Gen. Chem. Russ., 1936, 6, 555-558).—The eutectics in the systems  $\text{Ph}_2$ - $\text{COPh}$ ,  $\text{Ph}_2$ - $\text{NHPh}$ ,  $\text{NHPh}_2$ - $\text{COPh}$ , and  $(\text{CH}_2\text{Ph})_2$ - $\text{Ph}_2$ - $\text{C}_{10}\text{H}_8$ , as determined by Lee and Warner (A., 1933, 228; 1935, 448), agree closely in composition with the requirements of Flavitzki's formula (A., 1906, ii, 152). R. T.

**Chemical composition and optical properties of solutions. II. Optical properties of solutions in the quaternary system  $\text{NH}_4\text{Cl}$ - $\text{NaCl}$ - $\text{KCl}$ - $\text{H}_2\text{O}$  at  $15^\circ$ .** E. I. ACHUMOV and M. P. GOLOVKOV (J. Gen. Chem. Russ., 1936, 6, 542-548; cf. this vol., 22).— $n$ -composition diagrams are recorded.

R. T.

**System nickel-zinc.** W. HEIKE, J. SCHRAMM, and O. VAUPEL (Metallwirts., 1936, 15, 655-662).—Alloys containing 22-29 and 45-52% Ni have been

re-examined by thermal methods. From the results and a detailed consideration of other work, a revised diagram is presented. C. E. H.

**Copper-tin alloys.** C. HAASE and F. PAVLEK (Z. Metallk., 1936, 28, 73—80).—The accepted solid solubility of Sn in Cu is 14% at temp. up to 400°, this val. being obtained with annealed alloys, prolonged ageing of which at  $\geq 400^\circ$  fails to decompose the solid solution. If, however, such alloys are cold-rolled after annealing and then aged at 300°, pptn. of a Sn-rich phase occurs. From sp. resistance and hardness measurements and from micrographic and X-ray analysis of cold-worked alloys after various methods of ageing, it is shown that the true solid solubility of Sn in Cu is 13.5% at 400°, 10.9% at 350°, 5.5% at 300°, 2.8% at 250°, and about 1.2% at 200°. The pptd. phase is  $\text{Cu}_3\text{Sn}$  at  $< 370^\circ$  and  $\text{Cu}_3\text{Sn}_\delta$  ( $\delta$ ) at  $> 370^\circ$ .  $\text{Cu}_3\text{Sn}$  pptd. at 300° is hexagonal,  $a$  2.7523 Å,  $c/a$  1.5697. The min. amount of cold-work required to produce pptn. is the lower the higher is the degree of supersaturation, and the rate of pptn. is the greater and the period of induction the shorter the higher is the degree of reduction above the min. The rate of pptn. is retarded by crystal recovery and recrystallisation phenomena above 300°. Pptn. is a continuous single-phase process which produces little hardening, but a characteristic change in the micro-structure. A. R. P.

**Reflecting power of the binary mixed crystal series copper-nickel.** P. BERGMANN and W. GUERTLER (Z. tech. Phys., 1935, 16, 235—236; Chem. Zentr., 1935, ii, 2634).—The selective reflective power of Cu in texturally homogenised Cu-Ni alloys disappears completely with  $> 25\%$  Ni. J. S. A.

**X-Ray investigation of the transformations in aluminium-silver alloys.** W. HOEFMANN and K. E. VOLK (Metallwirts., 1936, 15, 699—701).—The work of Ageev and Shoyket (A., 1933, 1110) is confirmed. The  $\beta$ -phase has a body-centred cubic structure, and at 700°,  $a=3.24$  Å. C. E. H.

**Transformations in eutectoidal copper-aluminium alloys.** V. GRIDNEV and G. KURDJUMOV (Tech. Phys. U.S.S.R., 1936, 3, 135—141).—The transformations in the  $\beta$ -phase of Cu alloys with (a) 12% Al and (b) 12% Al and 2% Ni have been studied by thermal and dilatometric analysis. The change from the disordered  $\beta$  lattice to the ordered  $\beta_1$  lattice is accompanied by a small decrease in vol., whereas the martensitic-like transformation  $\beta_1 \rightarrow \beta'$  shows a slight increase in vol. On rapid heating of quenched specimens the  $\beta'$ -phase is converted directly into  $\beta$ ; to convert  $\beta'$  into  $\beta_1$  the quenched alloy must be tempered at 400°, but at 430° the  $\beta_1$ -phase breaks down into eutectoidal  $\alpha + \gamma$ . When  $\beta_1$  is reheated at 190° it is reconverted into  $\beta'$ , which then passes back to  $\beta_1$  at 225° without internal diffusion, and hence the diffusion-less lattice change of the metastable  $\beta$ - into  $\beta'$  is reversible after tempering. A. R. P.

**Magnetic investigations of the [precipitation-] hardening of beryllium-nickel alloys.** W. GERLACH (Z. Metallk., 1936, 28, 80—83).—During pptn.-hardening of quenched 2% Be-Ni alloy the  $d$ , magnet-

isation, remanence, coercivity, and magnetic transformation point all increase parallel with the hardness; the magnetic hardness produced by pptn. increases with the degree of supersaturation of the original solid solution. These results are explained thus: during pptn. treatment the Be atoms leave the solid solution lattice, which then contracts and being richer in Ni acquires a higher magnetic transformation point. The pptn. temp. is insufficiently high to allow diffusion to fill the lattice gaps by Ni atoms, and hence magnetic hardness is increased. The Ni-Be compound which is pptd. during ageing stabilises the incomplete Ni lattice and renders the increased magnetic hardness relatively insensitive to changes of temp. A. R. P.

**X-Ray analysis of the homogenous phase in the system Mg-Ni.** F. BACHMETEV (Acta Physico-chim. U.R.S.S., 1935, 3, 531).—A correction. The no. of mols. in the unit cell of the compound  $\text{MgNi}_2$  is 8 and not 16 as previously stated (cf. this vol., 152). O. D. S.

**System manganese-carbon and the carburising of manganese alloys.** R. SCHENCK, N. G. SCHMAHL, and O. RUETZ (Z. Elektrochem., 1936, 42, 569).—Cementation of Mn in  $\text{CH}_4$  at 700—900° has been studied.  $\text{Mn}_3\text{C}$  dissolves 0.5% of C at 800—900°. Higher carbides were not found. In cementing Mn-Fe alloys,  $\text{Mn}_3\text{C}$  stabilises an equiv. amount of  $\text{Fe}_3\text{C}$ ; above 900° excess of C is taken into solution. Cementation of Mn is reduced by adding Cu. E. S. H.

**Constitution and structure of alloys.** A. PORTEVIN (Bull. Soc. chim., 1936, [v], 3, 1189—1237).—A lecture.

**X-Ray investigations on the ternary system nickel-copper-zinc.** J. SCHRAMM and O. VAUPEL (Metallwirts., 1936, 15, 723—726).—Previous thermal and micrographic work by Schramm (Diss., Freiberg, 1934) is extended to the examination of the phases which occur at room temp. C. E. H.

**Alloys of iron, manganese, and carbon. XV. Ternary diagram and general summary.** F. M. WALTERS, jun., and C. WELLS (Trans. Amer. Soc. Met., 1936, 24, 359—374).—Previous work is summarised. W. P. R.

**X-Ray investigation of the iron-chromium-silicon phase diagram.** A. G. H. ANDERSEN and E. R. JETTE (Trans. Amer. Soc. Met., 1936, 24, 375—419).—The Fe-rich portion of the ternary diagram Fe-Cr-Si has been studied by X-ray methods. The parametric surface of Fe-rich solid solutions has been developed with considerable accuracy, and the range for which the  $\alpha$ -Fe phase is homogeneous at 600°, 800°, and 1000° has been determined. The boundary consists of three sections characterised by (a) the  $(\text{Fe,Cr})_3\text{Si}_2$  phase, (b) the  $\text{Cr}_3\text{Si}$  phase, and (c) the solid solution phase which dissolves up to 10% Si. This phase is formed by pptn. from the binary and ternary  $\alpha$ -solid solutions. W. P. R.

**Transformation in 18:8 [chromium-nickel] austenitic steel. I. Magnetic investigation of the  $\gamma \rightarrow \alpha$  transformation.** G. AKIMOV and L. PEVSNER. II. Investigation of the transformation by thermoelectric method. G. AKIMOV and



N. TOMASHOV. III. Thermal expansion of cold-worked 18:8 steels. IV. The  $\gamma \rightarrow \alpha$  transformation in 18:8 austenitic steel deformed by twisting at different temperatures. G. AKIMOV and J. FRIEDMANN. V. Thermal analysis of deformed and hardened stainless steel. G. AKIMOV and N. TOMASHOV (Tech. Phys. U.S.S.R., 1936, 3, 142—148, 149—154, 155—157, 158—164, 165—175).—I. When austenitic 18:8 stainless steel is cold-rolled, transformation of  $\gamma$  into  $\alpha$  starts along the grain boundaries and slip planes and reaches 45% after a reduction of 80% in thickness. On subsequent heating of the cold-worked metal the amount of  $\alpha$  begins to increase at 250° and the rate of transformation increases with the degree of reduction, a definite relation between  $\alpha$  and  $\gamma$  being established for a definite temp. and a definite degree of reduction. At 445° reconversion of  $\alpha$  into  $\gamma$  begins irrespective of the degree of reduction, but above 475° there is a definite equilibrium between the  $\alpha$  and  $\gamma$  for each temp., and this varies with degree of reduction up to about 600°, above which it again becomes independent of degree of reduction, since at this temp.  $\alpha$  has practically disappeared.

II. Measurements of the e.m.f. between deformed and undeformed 18:8 steel show a sudden change at 485—700° due to the  $\alpha \rightarrow \gamma$  transformation. Increase in degree of reduction from 48 to 71% lowers the temp. at which carbide pptn. occurs from 730° to 705°. The thermoelectric power-temp. curve for deformed steel resembles closely the magnetic saturation-temp. curve above 450°.

III. Dilatometric curves for cold-worked 18:8 steel show that a contraction occurs at 500° due to the  $\alpha \rightarrow \gamma$  change which is not affected by degree of reduction and an inflexion at 650° probably due to carbide pptn.

IV. The degree of work-hardening of 18:8 steel produced by twisting varies only slightly between 20° and 470°; as the deformation temp. is raised to 150° the magnetic saturation decreases sharply and at higher temp. approaches zero asymptotically, indicating that transformation of  $\gamma$  into magnetic  $\alpha$  practically ceases at 150°. Twisting at room temp. produces a more fine-grained structure, but tends to rupture the grains, whereas twisting at 450—470° produces no deformation of the microstructure and no refinement of the grain structure.

V. Thermal analysis of cold-worked 18:8 steel shows a heat effect due to removal of elastic stress starting at 490° and reaching a max. at 540°, a second effect due to carbide pptn. starting at 650° and reaching a max. at 695°, and a third effect due to the beginning of recrystallisation at 800°. On reheating the steel after quenching from 1200° heat effects occur at 435° and 540° due to stress removal and at 700° due to carbide pptn. A. R. P.

Low-temperature diffusion of solid aluminium into iron. L. G. HALL (Physical Rev., 1935, [ii], 47, 418—419).—A review of data relating to the diffusion of Al into Fe. L. S. T.

Diffusion in solid metals and its relation to other properties. W. SEITH and E. A. PERETTI (Z. Elektrochem., 1936, 42, 570—579).—The diffusion

velocities of Cu, Cd, In, Sn, and Sb in Ag at 650—895° have been determined by spectrum analysis. The results confirm those reported for diffusion in Pb (A., 1935, 158). E. S. H.

Diffusion of gases through metals. III. Degassing of nickel and diffusion of carbon monoxide through nickel. C. J. SMITHELLS and C. E. RANSLEY (Proc. Roy. Soc., 1936, A, 155, 195—212).—The gas evolved by heating commercial Ni in a vac. or in  $H_2$  is mainly CO. The measured rate of diffusion of CO through Ni is too small to account for the rate at which gas is evolved in the degassing process; it is therefore suggested that the CO is generated from C and  $O_2$  contained in the Ni. Measurements have also been made of the diffusion of C and  $O_2$  through Ni. The rate of diffusion of  $O_2$  is much < that of C, but it would seem that the rate of diffusion of C is the controlling factor in the rate at which CO is evolved. L. L. B.

Diffusion of sucrose in highly concentrated solutions. A. MERTENS (Bull. Ass. anc. Étud. Louvain, 1935, 35, 107—110; Chem. Zentr., 1935, ii, 3311).—The diffusion coeff. is tabulated from 18.5° to 160°. H. N. R.

Vaporisation of boric acid in the cold with the vapours of the lower homologues of primary alcohols. M. ARQUET (Bull. Soc. chim., 1936, [v], 3, 1422—1424).— $H_3BO_3$  vaporises rapidly from solutions in MeOH at room temp.; in EtOH solutions the loss of  $H_3BO_3$  is less. When coal gas, containing the vapour of MeOH, EtOH, or  $Pr^iOH$ , is passed over cryst.  $H_3BO_3$ , the latter is volatilised, the gas burning subsequently with a green flame. E. S. H.

Volatility and dehydration of boric acid. M. VON STACKELBERG and F. QUATRAM (Z. Elektrochem., 1936, 42, 551).—The influence of temp. (110—170°) and  $H_2O$ -v.p. (100—760 mm.) on the volatilisation of  $H_3BO_3$  in  $H_2O$  vapour has been determined.  $H_3BO_3$  vaporises as such and has a definite "solubility" in  $H_2O$  vapour, which is independent of the pressure. The main influence of  $H_2O$  is to prevent dehydration to  $HBO_2$ , which is non-volatile. E. S. H.

Solubility of slightly soluble electrolytes. M. HAÏSSINSKI (Acta Physicochim. U.R.S.S., 1935, 3, 517—528).—Methods used in the measurement of the solubilities of the hydroxides and sulphates of the heavy metals are criticised. The results of different methods are so discordant that the measured vals. cannot be regarded as characteristic consts. O. D. S.

Solubility of alkaline-earth fluorides in acids. I. TANANAEV and S. TSCHRELASCHVILI (J. Gen. Chem. Russ., 1936, 6, 606—611).—The solubility of  $CaF_2$ ,  $SrF_2$ , and  $MgF_2$  is given by  $S = [L[H^+]^2/4K^2 + 1]^{1/3} - M/1000$ , where  $S$  is g. of fluoride of mol. wt.  $M$  in 1 ml. of solution,  $L$  is the solubility product, and  $K$  the dissociation coeff. of HF. The formula does not apply to  $BaF_2$ . Formulae for deriving the vals. of  $L$  and  $K$  at different  $p_H$  are given. R. T.

Solubility of precipitates in acids. A. K. BABKO (Bull. Sci. Univ. Kiev, 1935, 1, 155—161).—Expressions are derived, whereby the solubility of

sparingly sol. salts ( $\text{BaC}_2\text{O}_4$ ,  $\text{CaC}_2\text{O}_4$ ) in presence of excess of cation or precipitant may be calc. Experimental results agree with theory in presence of excess of  $\text{H}_2\text{C}_2\text{O}_4$ , but not of  $\text{Ba}^{++}$  or  $\text{Ca}^{++}$ . R. T.

[Solubility of] nitrates of group II metals in liquid ammonia. M. A. PORTNOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 93—104).—The solubility of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in liquid  $\text{NH}_3$  increases between  $-70^\circ$  and  $70^\circ$  and shows a break at  $-46^\circ$ , corresponding with the transition to  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{NH}_3$ ; at  $25^\circ$  the solid phase is  $\text{Ca}(\text{NO}_3)_2 \cdot 6 \cdot 5\text{NH}_3$ . Solubility data are also recorded for  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$ ; the solubilities are in the order  $\text{Ca} > \text{Sr} > \text{Ba}$  at  $-50^\circ$ , and in the inverse order at  $50^\circ$ . Sr and Ba nitrates do not combine with  $\text{NH}_3$  at  $0^\circ$ ; they combine with 2.5 and  $4\text{NH}_3$ , respectively, at  $-12^\circ$ , and with  $8\text{NH}_3$  at  $-25^\circ$ . Curves connecting solubility with conductivity are recorded. R. T.

Solubility of organic compounds in water. A. E. VAN ARKEL and S. E. VLES (Rec. trav. chim., 1936, 55, 407—411).—Data are recorded for 9 chloroethanes and for  $s\text{-C}_2\text{H}_4\text{Br}_2$  in  $\text{H}_2\text{O}$  at  $0$ — $50^\circ$ . The results are discussed in reference to the dipole moments of the solutes and the formula (cf. A., 1934, 1064) expressing the relation between the heat of mixing and the cohesion energies of the two components. O. J. W.

Salting out. Influence of ammonium salts on solubility of nicotine. B. V. J. CUVELIER (Z. anal. Chem., 1936, 105, 325—328).— $(\text{NH}_4)_2\text{SO}_4$  has the largest salting out effect. J. S. A.

Equilibria in salt systems with deuterium water. F. T. MILES, R. W. SHEARMAN, and A. W. C. MENZIES (Nature, 1936, 138, 121).—When referred to the same no. of mols. of solvent the solubility of KCl in  $\text{D}_2\text{O}$  is  $<$  that in  $\text{H}_2\text{O}$  by approx. 7% at  $30^\circ$ , 3.6% at  $100^\circ$ , and 1.5% at  $180^\circ$ . At  $10^\circ$ ,  $\text{CuSO}_4 \cdot 5\text{D}_2\text{O}$  is approx. 12% less sol. in  $\text{D}_2\text{O}$  than is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ , and approx. 1.2% at  $96^\circ$ , where both salts are transformed into the triquo-forms. The relations between the solubility curves for  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{D}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{SrCl}_2 \cdot 2\text{D}_2\text{O}$  are also described. L. S. T.

Connexion between separate and reciprocal solubility of components in systems involving double decomposition. E. I. ACHUMOV (J. Gen. Chem. Russ., 1936, 6, 691—696).—Theoretical. R. T.

Dissolution of elements in molten  $\text{AlCl}_3$ -NaCl. V. A. PLOTNIKOV and N. S. FORTUNATOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 123—128).—The solubility of Hg, P, Mn, W, Mo, Cu, Si, and S in molten 1:1  $\text{AlCl}_3$ -NaCl has been measured at  $150$ — $370^\circ$ . Except in the case of S, chemical reaction does not take place between the solutes and the solvent. R. T.

Formation and growth of a new phase in relation to the influence of vectorial properties of a substance, and of external factors. IV. Influence of solvent and of admixtures on the form of the crystals separating. V. Influence of an electric field on the linear velocity of

crystallisation in supercooled liquids. S. S. URAZOVSKI and J. S. ROZUM (Ukrain. Chem. J., 1936, 11, 127—135, 136—142).—IV. The size and shape of crystals separating from supersaturated solutions of NaCl in  $\text{H}_2\text{O}$  or EtOH,  $\text{CdI}_2$  in  $\text{H}_2\text{O}$ , MeOH, EtOH, PrOH, BuOH,  $\text{Et}_2\text{O}$ ,  $\text{COMe}_2$ ,  $\text{CHCl}_3$ , or PhMe, and of  $\text{CO}(\text{NH}_2)_2$  in  $\text{H}_2\text{O}$ , EtOH, PrOH, BuOH,  $\text{Et}_2\text{O}$ , MeCHO,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ , PhEt, or  $\text{PhNO}_2$  vary according to the nature of the solvent, and of other substances ( $\text{PhOH}$  and  $\text{Bu}^n\text{CO}_2\text{H}$ ) present. The phenomena are interpreted on the basis of selective adsorption on different crystal edges.

V. The rate of crystallisation of salol, but not of  $\text{COPh}_2$ , is reduced in an electric field; the effect is ascribed to differences in the relative proportions of the different polymorphs of salol present. R. T.

Partition coefficient of iodine between water and carbon tetrachloride. G. HERRERO (Anal. Fis. Quim., 1936, 34, 549—552).—The partition coeff. increases from 75.07 to 84.7 as the [I] in the  $\text{CCl}_4$  layer increases from 1.27 to 15.45 g. per litre. L. A. O'N.

Distribution of nicotine between water and organic solvents. N. A. DE KOLOSOVSKI and F. S. KULIKOV (Acta Univ. Asiae Med., 1935, [vi], 1, No. 8, 1—28).—Distribution coeffs. for nicotine between  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_6$ , xylene, decalin, light petroleum,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{C}_2\text{H}_4\text{Br}_2$ , PhBr,  $\text{PhNO}_2$ ,  $\text{Et}_2\text{O}$ , isoamyl ether, iso- $\text{C}_5\text{H}_{11}\text{OH}$ ,  $\text{CH}_2\text{PhOH}$ , *m*-cresol, cyclohexanone, and  $\text{CS}_2$ , respectively, and between glycerol and  $\text{CS}_2$  at  $25^\circ$ , have been determined. The results are discussed. E. S. H.

Adsorption of argon and nitrogen from the lowest to the highest pressures by active carbon. A. VON ANTROPOFF [with F. STEINBERG, F. KALTHOF, L. SCHMITZ, and R. SCHAELEN] (Z. Elektrochem., 1936, 42, 544—547).—Adsorption has been determined from  $-160^\circ$  to  $200^\circ$  and from 0.005 to 200 atm. Adsorption increases linearly with increasing pressure at low pressures; at higher pressures and low temp. a max. is reached, whereas at still higher pressures adsorption decreases and eventually almost reaches zero. The apparent contradiction to Langmuir's equation is discussed. E. S. H.

Adsorption of radium emanation at low temperatures. L. WERTENSTEIN (Acta phys. polon., 1934, 3, 469—484; Chem. Zentr., 1935, ii, 3058—3059).—The life period of the absorbed material and the dependence of the adsorption equilibrium on the temp. have been determined. H. J. E.

Influence of platinum on the adsorption characteristics of charcoal in solutions of electrolytes. S. LEVINA, A. FRUMKIN, and A. LUNEV (Acta. Physicochim. U.R.S.S., 1935, 3, 397—412).—The effects which result from platinising can be reproduced by the mechanical mixing of Pt with the charcoal. It is suggested that the action of the Pt is purely electrochemical; the potential of the Pt, acting as a H<sub>2</sub> electrode, is communicated to the charcoal and determines its adsorption capacity. O. D. S.

Measurements of adsorption at the air-water interface by the microtome method. J. W. MCBAIN and R. C. SWAIN (Proc. Roy. Soc., 1936,



A., 154, 608—623).—The microtome method (A., 1932, 331) is shown to give reproducible quant. measurements of the abs. amount of adsorption in the air-H<sub>2</sub>O interface for all types of solutions. The results for positive adsorption of PhOH and of CH<sub>2</sub>Ph·CH<sub>2</sub>·CO<sub>2</sub>H, and for negative adsorption of NaCl agree closely with the predictions of the Gibbs theorem. L. L. B.

**Adsorbent properties of barium sulphate.** I. M. KOLTHOFF (Bull. Soc. chim. Belg., 1936, 45, 270—278).—The data and conclusions of de Brouckere (cf. this vol., 423) are disputed. J. G. A. G.

**Adsorbent properties of barium sulphate.** (MLLE.) L. DE BROUCKERE (Bull. Soc. chim. Belg., 1936, 45, 279—285).—A reply to Kolthoff (cf. preceding abstract). J. G. A. G.

**Adsorption of organic substances at crystal surfaces.** IV. Adsorption of sodium oleate and nonoate by cinnabar. N. A. HELD and I. A. CHAINSKI (Kolloid-Z., 1936, 76, 26—33; cf. A., 1935, 1069).—Potentiometric titrations show that a bimol. layer of the soap is adsorbed at the surface of cinnabar. E. S. H.

**Adsorption of dyes on glass.** J. LENOIR (Document. sci., 1935, 4, 193—199; Chem. Zentr., 1935, ii, 2933).—With very dil. solutions, the amount of dye adsorbed rises steeply with increasing concn., reaching a const. max. val. at fairly low dye concn. With Me-violet a bimol. adsorbed layer is formed. J. S. A.

**Sorption of vapours by gels of hydrates of the oxides of aluminium, iron, and titanium.** I, II. E. V. ALEXEEVSKI and G. M. BELOTZERKOVSKI (J. Gen. Chem. Russ., 1936, 6, 370—381, 382—389).—I. Max. sorptive capacity for CCl<sub>3</sub>·NO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> vapours is obtained by drying Fe(OH)<sub>3</sub> gel at 100—200°, Al(OH)<sub>3</sub> gel at 120—240°, and TiO<sub>2</sub> gel at 200°.

II. The sorptive power of Al(OH)<sub>3</sub> gel for C<sub>6</sub>H<sub>6</sub> vapour is > that of Fe(OH)<sub>3</sub> gel, and for H<sub>2</sub>O vapour is > that of CaCl<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, and SiO<sub>2</sub> gel. Adsorption of H<sub>2</sub>O proceeds according to the Langmuir equation. R. T.

**Periodic phenomena in diffusion and adsorption.** II. Experiments without membranes. H. WAELSCH and S. KITTEL (Kolloid-Z., 1936, 76, 19—26; cf. this vol., 284).—The concn. of aq. NaCl or CaCl<sub>2</sub> undergoes periodic changes with time after addition of BaSO<sub>4</sub>. This behaviour is traced to periodic adsorption of the electrolyte by the ppt. The periodic effect is destroyed by addition of NaNO<sub>3</sub>, NaOH, or H<sub>2</sub>S, but not by HCl or H<sub>2</sub>SO<sub>4</sub>; it depends also on the method of prep. of BaSO<sub>4</sub>, and on the relation of the amount of adsorbent to the electrolyte concn. E. S. H.

**Constitution of the surface of active carbon.** E. O. K. VERSTRAETE (Natuurwetensch. Tijds., 1936, 18, 107—113).—Diamond sols are negatively charged and do not become positive even after long activation in CO<sub>2</sub> at 1050°. The results are in accordance with Kruyt's theory of electron shift for positive C. S. C.

**Surface oxide films.** E. J. W. VERWEY and J. H. DE BOER (Rec. trav. chim., 1936, 55, 675—687).

—Theoretical. In the oxides formed by adsorption of O on alkaline-earth metals the surface oxide mols. are at. rather than ionic, yet the linking is sufficiently polar to produce a double layer, with the negative coating outside. There is an activation energy, *E*, because the O<sub>2</sub> mol. must be dissociated and the reacting atoms brought into an excited state. For C this is > for metals owing to the O atoms each being bound by two C atoms and C—C distance in the graphite lattice being small. The positive charge of outgassed C in contact with air and H<sub>2</sub>O is attributable to its adsorbing O and behaving as an O electrode. A negative ζ-potential combined with a positive Nernst (air) potential on C and on noble metals can be explained by the presence of a surface oxide layer with a large positive potential drop (cf. A., 1935, 1069). R. C.

**Thermomechanics of the surface film.** I. General; pure substances. II. Adsorption formula. III. Mixed phases. J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1936, [v], 22, 373—389, 390—401, 402—411).—Theoretical. A. J. M.

**Surface development of active zinc oxide.** G. GRAUE and R. KOPPEN (Z. anorg. Chem., 1936, 228, 49—56).—Changes in the surface of ZnO with various thermal treatments have been followed by the Hahn emanation method (A., 1935, 32). The emanation evolved increases rapidly after heating to 300°, decreases with pretreatment at 350—1000°, and rises somewhat after the specimen has been heated to >1000°. This agrees with the observed optimum catalytic activity of ZnO after heating to 300°. The adsorption of indigotin from C<sub>6</sub>H<sub>6</sub> solution is also a max. for ZnO previously heated at 300°. X-Ray photographs are given for specimens of ZnO after various heat-treatments. The adsorption of emanation by ZnO is diminished by long heating. It is a max. after heating at 300°. H. J. E.

**Stability of a surface of contact between two phases.** Concept of epiphases in mutual equilibrium. New enunciation of the phase rule. L. GAY (J. Chim. phys., 1936, 33, 476—487).—Theoretical. When a surface of contact between two phases becomes unstable, two or more epiphases in mutual equilibrium appear, and the variance, *V*, of the system of *n* components, *φ* phases, *φ'* epiphases, and *s* surfaces of contact is *V* = *n* - *φ* - *φ'* + *s* + 2. The theory is of general application to singular points in interfacial tension curves (cf. A., 1926, 348; 1932, 1200; 1935, 1071). J. G. A. G.

**Relations between the adhesion of particles of microscopic size and the activity coefficients of the electrolytes.** A. VON BUZAGH (Kolloid-Z., 1936, 76, 2—9).—The adhesion of quartz particles of 14.2 μ diameter to a wall of polished quartz has been determined in solutions of different electrolytes by the tilting-plate method. With neutral salts containing uni- and bi-valent cations the adhesion decreases with increasing activity coeff.; solutions of ter-, quadri-, and sexa-valent cations reverse the charge on the quartz particles, and the curve connecting adhesion with activity coeff. shows a max. and a

min. With salts of multivalent cations the relations are complicated by the effects of hydrolysis.

E. S. H.

**Permeability of membranes. I. Theory of ionic permeability. II. Experiments with artificial selective membranes.** K. H. MEYER and J. F. SIEVERS (Helv. Chim. Acta, 1936, 19, 649—664, 665—677).—I. A quant. theory of the ionic selectivity of membranes is given, in which the membrane is regarded as a network of chains carrying laterally fixed ionised groups. The permeability depends on (a) the concn. of the fixed ions, (b) the mesh of the network, (c) the external concn. of the electrolyte, and (d) the solubility of the ions in the membrane.

II. Methods are described for preparing neutral, acidic, basic, and amphoteric membranes, which have been studied. The results are interpreted in the light of the authors' theory. The selectivity of biological membranes and their powers of absorbing certain dyes have been correlated.

T. G. P.

**Cryoscopic constants.** J. F. DURAND and L. WAI-HSUN (Bull. Soc. chim., 1936, [v], 3, 1389—1391).—The relation  $K' = 0.0015MT'$ , where  $K'$  is the cryoscopic const.,  $M$  the mol. wt., and  $T'$  the abs. m.p., is deduced theoretically and confirmed experimentally for several org. substances. Exceptions are traced to association or other anomalies.

E. S. H.

**Nature of some dilute and concentrated non-electrolytes.** B. H. VAN RUYVEN (Rec. trav. chim., 1936, 55, 471—491).—F.p., b.p., and osmotic pressure data for aq. solutions of MeOH, sucrose, glucose, mannitol,  $\alpha$ -methylglucoside, and dulcitol are discussed. In many cases the depression of the f.p. ( $\Delta_f$ ) and the elevation of the b.p. ( $\Delta_b$ ) are given, even for conc. solutions, by  $\Delta_f = 1.85N_w$  and  $\Delta_b = 0.52N_w$ , where  $N_w$  = g.-mols. solute per 1000 g. H<sub>2</sub>O. The osmotic pressure is given by  $P = 22.41N_w \times T/273$ . Deviations from these equations are due mainly either to formation of complexes of solute mols. or to hydration of the solute mols.

O. J. W.

**Non-aqueous solutions.** I. A. KABLUKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 13—28).—A lecture.

R. T.

**Non-aqueous solutions. I. Ternary systems.** V. A. PLOTNIKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 29—45).—A review.

R. T.

**Specific heat of non-electrolytes in solution, and the effect of the dielectric constant of the solvent on the vibrational state of their molecules.** K. BENNEWITZ and L. KRATZ (Physikal. Z., 1936, 37, 496—511).—Results obtained by Heydweiller's method for CsCl and LiCl agree with those obtained by other methods. The sp. heats of aq. solutions of CO(NH<sub>2</sub>)<sub>2</sub>, glycerol, quinol, dioxan, glucose, lactose, sucrose, and solutions of some of these substances in other solvents of known dielectric const. have been determined. The solute usually has a larger mol. heat in solution than in the pure state. In explanation it is assumed that the dielectric const. of the solvent affects the directional forces of the oscillators in the solute mols. Calculation

of the mol. heat from the lowering of frequency due to the dielectric effect and the existence of dispersion gives satisfactory results for glucose and sucrose. This lowering of frequency could be demonstrated by an examination of the Raman lines of the solutions, which should show a displacement.

A. J. M.

**Dielectric constants of extremely dilute solutions.** F. E. HOECKER (J. Chem. Physics, 1936, 4, 431—434; cf. A., 1935, 1318).—Measurements by the heterodyne beat method are recorded for C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub> solutions of EtOH at mol. fraction vals. from 0.01 to 0.00007. Effects of association are absent in this concn. range. Derived vals. of the mol. polarisation of EtOH at 24.5° agree with measurements made on EtOH vapour. The electric moments of EtOH in C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub> solution are  $1.700 \pm 0.006 \times 10^{-18}$  and  $1.674 \pm 0.005 \times 10^{-18}$ , respectively. Vals. of  $d$  for dil. solutions of EtOH in C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, and CS<sub>2</sub> are recorded.

H. J. E.

**Dipole moments of molecules in solution.** S. H. BAUER (J. Chem. Physics, 1936, 4, 458—459).—Fluctuation for polar mols. dissolved in a non-polar solvent is discussed.

H. J. E.

(A) **Optical rotation of alkaline solutions of sucrose.** (B)  $p_H$  of solutions of calcium hydroxide in water and aqueous sucrose. K. SMOLEŃSKI (Rocz. Chem., 1936, 16, 270—280, 281—287).—(A) [with W. KOZŁOWSKI]. The fall in  $[\alpha]_M$  with increasing  $p_H$  is due to formation of uni- and bi-valent anions of sucrose, of  $[\alpha]_M$  20.6° and 18.4°; the vals. found agree with the view that sucrose is a dibasic acid, with  $k_1 = 3 \times 10^{-13}$  and  $k_2 = 3 \times 10^{-14}$ .

(B) [with S. POREJKO]. The  $p_H$  vals. found are in conformity with the above view.

R. T.

**Behaviour of methyl-red in alcohol-water solution.** F. REIMERS (Z. anorg. Chem., 1936, 228, 33—43).—The absorption curves of Me-red in acid, alkali, and buffered EtOH-H<sub>2</sub>O solutions (20—85% EtOH) have been measured spectrophotometrically. Absorption coeffs. for the isoelectric form (I) and indicator exponents for Me-red in 20—85% EtOH solution are calc. The change of indicator exponent with [EtOH] suggests that (I) is an uncharged mol.

H. J. E.

**Refraction of solutions of electrolytes, and ionic association.** A. I. BRODSKI, N. S. FILIPPOVA, and G. M. SCHERSCHEVER (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 72—79).—Refraction data for 0—0.12N-KCl and -NaCl support the theory of complete ionisation.

R. T.

**Nature of electrolytes in non-aqueous solutions.** M. I. USANOVITSCH (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 46—49).—Conductivity is associated with compound formation.

**Solvation in non-aqueous solutions.** V. S. FINKELSCHTEIN (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 50—53; cf. preceding abstract).—Usanovitsch's results are compatible with solvation rather than with compound formation.

R. T.

**Optical behaviour of dissolved ions and its significance for the structure of solutions of**



electrolytes. III. Optical absorption of sodium eosinate. G. KORTUM (Z. physikal. Chem., 1936, B, 33, 1—22; cf. this vol., 425).—The extinction coeffs.,  $\epsilon$ , for the various absorption bands rise rapidly with the concn.,  $c$ , except when this is very small, when they remain const. This effect is apparently connected with the decrease in fluorescence with rise in  $c$ . The effect of foreign salts on  $\epsilon$  indicates that the above variation of  $\epsilon$  is due, not to deformation of the eosin anions (I) in the Coulomb field of the ionic atm. nor to ionic association of (I) with cations, but to association of (I) with each other under the influence of van der Waals forces. This association is detectable at concns. as low as  $3 \times 10^{-6} M$ . R. C.

Dielectric constants of amphoteric electrolytes. G. HALBEDEL (Z. physikal. Chem., 1936, B, 33, 83—108).—Dielectric consts.,  $\epsilon$ , have been measured at 20—50° by a resonance method with a frequency of  $\sim 10^8$  hertz. For aq. solutions of antipyrine,  $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ , theobromine, caffeine, 7-methylpurine, and pyocyanine  $\epsilon$  is  $>$  for pure  $\text{H}_2\text{O}$ ; the possibility of a zwitterion structure for the first two substances thus seems improbable. For solutions of  $\text{NH}_2$ -acids and betaines in  $\text{H}_2\text{O}$  and  $\text{EtOH}$   $\epsilon$  is  $>$  that of the solvent by an amount  $\Delta\epsilon$  which increases linearly with the concn. up to a crit. concn.,  $c$ , at which mutual interaction of the mols. becomes effective;  $c$  depends on the length and dipole moment of the zwitterion.  $\Delta\epsilon$  per mol. of solute is approx.  $\propto$  the no. of members in the chain between the positive and negative charge. The technique of measuring  $\epsilon$  is discussed. R. C.

Complex aquo-phosphate ions with several [solvent molecule] shells. H. BRINTZINGER and C. RATANARAT (Z. anorg. Chem., 1936, 228, 61—64; cf. A., 1935, 824).—Determinations of the ionic wt. of  $\text{PO}_4'''$  by the dialysis method are recorded for  $p_{\text{H}}$  2.0—14.2, using  $\text{S}_2\text{O}_3''$  as the reference ion. Vals. corresponding with  $[\text{H}_2\text{PO}_4(\text{H}_2\text{O})_4]'$  at  $p_{\text{H}}$  2 and  $[\text{PO}_4(\text{H}_2\text{O})_{18}]'''$  at  $p_{\text{H}}$  14.2 have been obtained. The constitution of these ions is discussed. H. J. E.

Methods of dialysis. IV. Independence of ionic weight determination on the  $p_{\text{H}}$  of the solution to be dialysed. H. BRINTZINGER, C. RATANARAT, and W. ECKARDT (Z. anorg. Chem., 1936, 228, 77—82; cf. A., 1935, 579).—It is shown by measurements on various ions (e.g.,  $[\text{Fe}(\text{CN})_6]'''$ ,  $[\text{Co}(\text{NH}_3)_4\text{SO}_4]'$ ) that the ionic wt. is independent of the reference ion used and is the same whether the medium is alkaline, neutral, or acid. H. J. E.

Formation of aerosols. I. Technique. Sulphuric acid clouds. N. FUCHS and N. OSCHMAN (Acta Physicochim. U.R.S.S., 1935, 3, 61—78).—A method for preparing aerosols with reproducible particle concn. and particle size consists in rapidly mixing two air streams containing substances which will react to give the desired aerosol, followed by rapid expansion. In this way coagulation is almost entirely avoided. The production of  $\text{H}_2\text{SO}_4$  clouds by mixing air streams containing  $\text{SO}_3$  and  $\text{H}_2\text{O}$  is described. The radius of the particles was 1.2— $1.5 \times 10^{-6}$  cm. A. J. M.

Preparation of colloidal gold, and its detection in very small quantities. D. C. DALMAS and E. C. STATHIS (Praktika, 1935, 10, 106—110; Chem. Zentr., 1935, ii, 2644).— $\text{AuCl}$  is reduced by alcoholic phenolphthalein at 35—40° to a violet Au sol. The reaction may be used for the detection of Au.

J. S. A.

Synthesis of hydrosols of sparingly soluble metal salts by electrolysis. III. Copper arsenate and arsenite hydrosols. B. G. SAPROMETOV and S. P. KAMSOLOVO (Kolloid-Z., 1936, 76, 46—54; cf. A., 1934, 1305).—The prep. of negatively-charged  $\text{Cu}_3(\text{AsO}_4)_2$  and  $\text{Cu}_3(\text{AsO}_3)_2$  sols by electrolysis of  $\text{Na}_3\text{AsO}_4$  or  $\text{Na}_3\text{AsO}_3$  with a Cu anode and Pt cathode under fixed conditions of c.d., concn., and temp. is described. Positively-charged sols of  $\text{Cu}_3(\text{AsO}_4)_2$  have been prepared from  $\text{Zn}_3(\text{AsO}_4)_2$  and very dil. solutions of Cu salts. The  $\zeta$ -potential and the resistance to coagulation by KCl have been determined. Tests on the use of these sols as insecticides have been carried out.

E. S. H.

$\text{TiO}_2$  hydrosols. R. WINTGEN and K. LINS (Angew. Chem., 1936, 49, 489—492).—Dialysis of 1—3%  $\text{TiCl}_4$  solution yields sols more conc. than those prepared by Graham's method and of finer particle size than the method of grinding and suspending. Relatively clear sols are also obtained by pptg.  $\text{TiO}_2$  from aq.  $\text{TiCl}_4$  with  $\text{NH}_3$  and peptising the ppt. with  $\text{NaOH}$ . The sp. conductivities of the sols prepared in different ways have been measured and the average no. of  $\text{TiO}_2$ ,  $\text{Cl}'$ , and  $\text{H}_2\text{O}$  mols. per micelle are calc.

J. W. S.

Nature of cellulose ester solutions. S. GLÜCKMANN (Kolloid-Z., 1936, 76, 84—95).—Benzylcellulose has been fractionated by adding excess of  $\text{EtOH}$  to solutions in  $\text{C}_6\text{H}_6\text{-EtOH}$ . The viscosity and solubility of the fractions have been determined, and little difference in composition and properties is observed. The crit. amounts of excess of  $\text{C}_6\text{H}_6$  or  $\text{EtOH}$  required to coagulate the solutions at different temp. and the influence of variation in the proportions of  $\text{C}_6\text{H}_6$  and  $\text{EtOH}$  on the viscosity and vol. of the solution have been determined. The results are discussed in relation to adsorption and solvation phenomena.

E. S. H.

Viscosity of suspensions and solutions. VII. Viscosity of sphere suspensions. R. SIMHA (Kolloid-Z., 1936, 76, 16—19; cf. this vol., 679).—Mathematical.

E. S. H.

Pressure viscosimetry of kaolin suspensions. G. FUCHS (Acta Physicochim. U.R.S.S., 1935, 3, 137—146).—A new form of capillary viscosimeter is described. The relation between the viscosity,  $\eta$ , of suspensions of kaolin and structure formation has been examined.  $\eta$  at first increases with time and then decreases. This is attributed to aggregation, which may be supposed to occur in two stages. The primary aggregates cease to be formed after a time, and then a looser secondary aggregation occurs, accounting for the decrease in  $\eta$ . The greater is the initial degree of dispersion the more intensive is the structure formation. Dilution causes the destruction of the suspension. Addition of dehydrating agents

(EtOH) encourages structure formation and produces an increase in  $\eta$ . A. J. M.

**Refraction of light by colloidal solutions. I. Arsenic and antimony trisulphide sols.** A. S. MENON (Kolloid-Z., 1936, 76, 9—15).—Light refracted by freshly-prepared  $\text{As}_2\text{S}_3$  sols is almost completely plane-polarised. The degree of polarisation for long  $\lambda$  is  $>$  for short  $\lambda$ . Rayleigh's law has been confirmed for sols of particle size between 23 and 108 m $\mu$ . After keeping the sol for about 14 days, the refracted light contains about 10% of unpolarised light.  $\text{Sb}_2\text{S}_3$  sols show a weak, unpolarised component in the refracted light. E. S. H.

**Viscosimetric investigations of structure formation in ferric hydroxide sols. III. Destruction of ferric hydroxide sols on dilution.** G. FUCHS and Z. KAMSOLOVA (Acta Physicochim. U.R.S.S., 1935, 3, 127—136).—The destruction of young and aged conc.  $\text{Fe}(\text{OH})_3$  sols and gels on dilution has been studied. The effect of adding  $\text{FeCl}_3$  was also examined. The viscosity data indicate the existence of structures of different ages and solidity in the sol particles, which may be termed primary and secondary structures. The mechanism of destruction consists in the breakdown of secondary structures and displacement of the adsorption equilibrium with dilution. A. J. M.

**Effect of dilution of ferric hydroxide sols.** K. JABECZYNSKI and B. SAWONIAK (Rocz. Chem., 1936, 16, 301—305).—The velocity of coagulation of  $\text{Fe}(\text{OH})_3$  sols is given by  $k \times 10^{-3} = 63.3c^{1.5}$ , where  $c$  is the concn. of  $\text{Fe}(\text{OH})_3$ . The charge and dimensions of the particles are not affected by dilution. R. T.

**Electrochemistry of platinum sols. I. Preparation of the sols.** N. BACH and N. BALASCHOVA (Acta Physicochim. U.R.S.S., 1935, 3, 79—96).—Pt sols have been prepared by the arc method with  $\text{O}_2$ ,  $\text{H}_2$ , and air, respectively, above the  $\text{H}_2\text{O}$  in which dispersion takes place. The  $\text{O}_2$ -Pt sol is brown, and the conductivity of the sol is  $>$  that of the  $\text{H}_2\text{O}$  in which it is dispersed. The  $\text{H}_2$ -Pt sol is moderately stable and is grey. The conductivity of a  $\text{H}_2$ -Pt sol decreases when saturated with  $\text{O}_2$ ; that of an  $\text{O}_2$ -Pt sol increases when saturated with  $\text{H}_2$ . The conductivity of an air-Pt sol is about 15 times that of the  $\text{H}_2\text{O}$  in which it is dispersed, indicating the formation of foreign electrolytes, and not only  $\text{H}_2\text{Pt}(\text{OH})_6$ . When  $\text{H}_2\text{SO}_4$  was added to the  $\text{H}_2$ -Pt sol, which was then saturated with  $\text{O}_2$ , conductivity measurements show that the adsorption is essentially similar to that at platinised Pt electrodes, each particle of sol acting as a small gas electrode. Cataphoresis experiments show that the particles of the  $\text{H}_2$ -Pt sol are negatively charged, the cataphoretic velocity being 3—4  $\mu$  per sec. per volt per cm. A. J. M.

**Electrochemical properties of highly purified silica sols.** A. I. BAIBAEV and V. A. KARGIN (Acta Physicochim. U.R.S.S., 1935, 3, 97—118).— $\text{SiO}_2$  sols obtained by hydrolysis of  $\text{SiCl}_4$  cannot be prepared in the pure state by electrodialysis through a carefully purified parchment-paper membrane. The acidic properties of "pure"  $\text{SiO}_2$  sols are due to acid (usually  $\text{HCl}$ ) in the intermicellar liquid of the sol.  $\text{SiO}_2$

sols obtained by oxidation of  $\text{SiH}_4$  by  $\text{O}_3$  in aq. solution possess no acidic properties, and only a very small quantity of compensating ions in the outer shell of the double layer. The stability of such pure  $\text{SiO}_2$  sols is maintained solely by the lyophilic properties of  $\text{H}_2\text{SiO}_3$ , but  $\text{HCl}$  exerts a stabilising action. The cataphoretic velocity and the  $\zeta$ -potential are small, and are dependent to a high degree on the purity of the sol. A. J. M.

**Effect of supersonic waves on the viscosity of colloids.** O. KIMURA (J. Chem. Soc. Japan, 1935, 56, 842—851).—The viscosities of gum acacia and gelatin sols and of aq. Na stearate are diminished by the action of supersonic waves. This is attributed to a change in the micellar structure or in the degree of hydration. CH. ABS. (e)

**Electric double layer and the stability of lyophobic colloids.** E. J. W. VERWEY (Chem. Rev., 1935, 16, 363—415).—A review. CH. ABS. (e)

**Coagulation of sols of mercuric sulphide in alcohol.** K. VOLKOV and J. GLASMAN (Bull. Sci. Univ. Kiev, 1935, 1, 85—94).—The particles have a negative charge, the magnitude of which is characteristic of lyophobic colloids. The sol is irreversibly coagulated by  $\text{AgNO}_3$  or  $\text{CuCl}_2$ , probably due to formation of a surface layer of insol., undissociated mols. Progressive addition of  $\text{AlCl}_3$  or  $\text{FeCl}_3$  causes coagulation, followed by peptisation, which is ascribed to the adsorption of solvated mols.; the optimum coagulative concns. of undissociated salts ( $\text{HgCl}_2$ ,  $\text{HgI}_2$ ) cannot, however, be explained in this manner. R. T.

**Electrolytic coagulation of Prussian-blue sols.** E. L. LEDERER (Kolloid-Z., 1936, 76, 54—60).—The coagulation of Prussian-blue sols by a wide range of electrolytes, including uni-, bi-, and ter-valent ions, is in accordance with Ostwald's rule. The sols also conform to the requirements of Burton's rule. E. S. H.

**Dynamics of colloidal sols.** H. R. KRUYT (Natuurwetensch. Tijds., 1936, 18, 87—88).—A brief review. D. R. D.

**Dielectric constant of lyophilic colloids.** J. T. G. OVERBEEK (Natuurwetensch. Tijds., 1936, 18, 113—117).— $\epsilon$  has been determined (with  $\nu = 3.5 \times 10^8$ ) for starch, agar, arabinates, gelatin, and ovalbumin sols and gels. It is practically unchanged by gelation, alterations in  $p_H$ , or the addition of luteo- $\text{CoCl}_2$ . It falls slightly on coacervation and shows an unexplained slight increase over the calc. val. at higher temp. (43°). S. C.

**Effect of electrolytes on negatively charged silver iodide sols considered in conjunction with micro-cataphoresis [experiments].** F. BOSCH and H. HAEMERS (Natuurwetensch. Tijds., 1936, 18, 90—103).—Flocculation and cataphoresis experiments with  $\text{HNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Th}(\text{NO}_3)_4$ , and mixtures of these electrolytes are described. The results do not show whether discharge by  $\text{Th}(\text{NO}_3)_4$  is due to  $\text{Th}^{IV}$  or  $\text{Th}(\text{OH})_4$ . S. C.

**Velocity of cataphoresis and electrical conductivity of colloids.** A. J. RUTGERS and J. T. G.



OVERBEEK (Natuurwetensch. Tijds., 1936, 18, 88—89).—The differences in the charge on colloid particles as measured by cataphoresis and conductivity measurements are explained by assuming that the particle consists of a central nucleus with a charge  $(n+n')e$ , surrounded by a firmly attached  $H_2O$  layer (Smoluchowski), charge  $-n'e$ , in which the ions move freely with regard to the  $H_2O$ , and a diffuse layer, charge  $-ne$ . S. C.

**Sensitisation and protective action of starch on negative sols.** M. DE SMET (Natuurwetensch. Tijds., 1936, 18, 118—122).—In order to explain the clarification of coal-washing liquors by adding starch (I), NaOH, and  $Ca(OH)_2$ , the action of (I) and electrolytes on negative C and AgI sols has been studied. Small amounts ( $<10^{-4}\%$ ) of a hydrophilic colloid make a negatively charged hydrophobic colloid much more sensitive to electrolytes, but larger amounts have a stabilising effect. This adequately explains the action of (I) and  $Ca(OH)_2$ , but the action of NaOH is still obscure. No theoretical explanation of the phenomena is forthcoming. S. C.

**Composition and ionic exchange of ferric silicates and phosphates.** A. J. PUGH and M. S. DU TOIT (Soil Sci., 1936, 41, 417—431).—The composition and exchange reactions have been examined in relation to  $p_H$ . The colloidal condition of these complexes is attained by a continuous process of polymerisation with formation of covalent compounds, until the unit forms a micelle of colloidal dimensions. The dissociation of the complex forms the basis of exchange reactions, the mechanism of which is discussed. A. G. P.

**Chemical activity of silicic acid.** V. N. KRESTINSKAJA and O. S. MOLTSCHANOVA (Kolloid-Z., 1936, 76, 60—72).—When  $CuSO_4$  is added to sols of  $SiO_2$  or  $Na_2SiO_3$  solutions, Cu and Na are exchanged in equiv. amounts; with  $SiO_2$  sols the action of  $CuSO_4$  depends on the  $Na^+$  content of the sol. Potentiometric titration curves of  $SiO_2$  sols and  $Na_2SiO_3$  solutions with  $H_2SO_4$  are discussed. E. S. H.

**Gels of aluminium bromide with nitromethane.** J. P. MESHENNI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 85—87).— $MeNO_2$  and  $AlBr_3$  yield a gel, which gradually liquefies when exposed to the air, and decomposes to yield an emulsion of  $MeNO_2$  when immersed in  $H_2O$ . R. T.

**Gelatinised emulsions. II. Influence of electrolytes on the emulsifying power of alkali soaps.** L. KREMNEV and T. PAPKOVA-KVITZEL (Acta Physicochim. U.R.S.S., 1935, 3, 451—464; cf. this vol., 158).—The emulsifying power of alkali soaps is increased by the addition of small concns. of electrolytes. This is ascribed to the influence of the latter on the hydrolysis of the soaps, and is not observed on the addition of glucose. High concns. of electrolytes cause a marked decrease in emulsifying power, which is correlated with the degree of hydration of the added ions. Addition of glucose causes a decrease in emulsifying power. O. D. S.

**Emeraldin sols. II. Mechanism of stabilising effect of gelatin in the production of sols.** V. PTSHELIN (Kolloid-Z., 1936, 76, 72—81; cf. A., 1935, 580).—A min. amount of gelatin is required for the stabilisation of emeraldin sols, the amount depending on the conditions of prep. of the sol. When an incompletely protected sol is coagulated, all the gelatin is found in the ppt. The mechanism of stabilisation and protection is discussed. E. S. H.

**Influence of hydrogen-ion concentration on gelatin.** R. REIGER and S. BACH (Kolloid-Z., 1936, 76, 82—83).—The time of gelation of gelatin is uninfluenced by  $[H^+]$  between  $p_H$  4.05 and 7.8. E. S. H.

**Thixotropic gelation. I. Mechanism of thixotropic gelation.** J. L. RUSSELL and E. K. RIDEAL. II. Coagulation of clay suspensions. J. L. RUSSELL (Proc. Roy. Soc., 1936, A, 154, 540—549, 550—560).—I. Small amounts of  $Al_2O_3$  added to  $SiO_2$  suspensions produce thixotropic gels. Gelation is caused by as little as 1 part of  $Al_2O_3$  to 4000 parts of relatively coarse quartz particles. The increase in vol. of the gel  $\propto$  the wt. of  $Al_2O_3$  added with larger wts. of  $Al_2O_3$ . The results support the theory that thixotropic gelation is due to the oriented coagulation of the colloid.

II. Moderately conc. clay suspensions show three types of coagulation, depending on the electrolyte concn.; at low concn. there is a partial flocculation of a lyophobic nature, at medium concn. a thixotropic gelation, and at high concn. a complete flocculation of a hydrophilic nature. The properties of the suspensions show that the clay consists partly of a highly disperse gel-forming material, and partly of a coarser material with no capacity for gelation. The apparent viscosity of the thixotropic clay gels varies inversely as the cube of the applied stress. The gels show a well-defined breaking point when stretched beyond a certain limit, and no permanent rigidity at low stresses. L. L. B.

**Mechanism of the movement of ions of chlorine and hydrogen in the presence of gelatin.** S. A. SCHTSCHUKAREV and V. M. VDOVENKO (J. Phys. Chem. U.S.S.R., 1934, 5, 512—520).—Vals. for the sp. conductivity, relative  $\eta$ , and transport nos. of  $H^+$  and  $Cl^-$  for 0.1N-HCl in 0—10% gelatin at 40° are recorded. The mobility of  $Cl^-$  passes through a max. with increasing gelatin concn., whereas that of  $H^+$  falls continuously. A loose linking between  $H^+$  and gelatin is assumed, which reduces the effective  $[H^+]$ . The gelatin also increases  $\eta$  and so decreases the mobility of both  $Cl^-$  and  $H^+$ . CH. ABS. (e)

**Electrokinetic phenomena. XII. Electroosmotic and electrophoretic mobilities of protein surfaces in dilute salt solutions.** L. S. MOYER and H. A. ABRAMSON (J. Gen. Physiol., 1936, 19, 727—738).—The ratio of the two mobilities of protein-coated surfaces (quartz, Pyrex, or paraffin coated with gelatin) is approx. 1.0. H. G. R.

**Effect of denaturation on the colloidal behaviour of ovalbumin.** P. KOETS and J. SCHOOF (Natuurwetensch. Tijds., 1936, 18, 103—106).—Observations on the coacervation and flocculation

of normal and denatured ovalbumin (I) on the addition of Na arabinatesols, as well as measurements of electrocataphoresis, show that during the denaturing process (heating to 100°) no change takes place in the density of the charge on (I) but that the sol changes in character from hydrophilic to hydrophobic.

S. C.

**Thermodynamic equations at the absolute zero.** V. A. PLOTNIKOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 37—44).—Theoretical. R. T.

**Inner thermodynamics. II.** V. NJEGOVAN (Acta phys. polon., 1934, 3, 213—214; Chem. Zentr., 1935, ii, 2930).—Theoretical. J. S. A.

**Thermodynamics of intermediate reactions.** H. SCHMID (Z. Elektrochem., 1936, 42, 579).—Theoretical. E. S. H.

**Inversion of the ammonia equilibrium.** E. N. EREMIN and N. I. KOBOSEV (Acta Physicochim. U.R.S.S., 1935, 3, 151—160).—The inversion of the  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  equilibrium at high temp. noted by Maxted is connected with the thermal dissociation of  $H_2$ . The inversion temp. corresponds with that at which the dissociation of  $H_2$  becomes marked. At. H combines readily with  $N_2$  at 1000—1500° abs. The problem is treated quantitatively and the results agree well with experiment. A. J. M.

**Nomogram for the formation of ammonia in the equilibrium reaction  $2NH_3 \rightleftharpoons 3H_2 + N_2$ .** P. MONTAGNE (Bull. Soc. chim., 1936, [v], 3, 1424—1427). E. S. H.

**Limiting high-temperature rotational partition function of non-rigid molecules. IV.** Ethylene, propylene,  $\Delta^a$ -butene, *cis*- and *trans*- $\Delta^2$ -butene, isobutene, trimethylethylene, tetramethylethylene, and butadiene. V. Equilibrium constants for reactions of paraffins, olefines, and hydrogen. L. S. KASSEL (J. Chem. Physics, 1936, 4, 435—441; cf. this vol., 673).—IV. Data are calc. and compared with experimental vals.

V. Equilibrium consts. for the dehydrogenation of  $C_2H_6$ ,  $C_3H_8$ , and *n*- and *iso*- $C_4H_{10}$  are calc. on the basis of vibrational frequency data, and compared with experimental vals. The discrepancies are discussed. Equilibrium consts. for the reactions  $2C_2H_4 \rightleftharpoons C_4H_8$ ,  $CH_4 + C_2H_4 \rightleftharpoons C_3H_8$ ,  $CH_4 + C_3H_8 \rightleftharpoons C_4H_{10}$ , and  $C_2H_6 + C_2H_4 \rightleftharpoons C_4H_{10}$  are also calc. H. J. E.

**Dissociation relations of the water HOD.** I. H. ERLÉNMEYER and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 677—680).—From previous data  $[H^+]$  and  $[D^+]$  in pure HOD are calc. to be  $0.564$  and  $0.111 \times 10^{-7}$ , respectively. T. G. P.

**Extremely weak acids.** W. K. McEWEN (J. Amer. Chem. Soc., 1936, 58, 1124—1129).—The acidity of 30 compounds (arylated hydrocarbons, alcohols, enols, amines) is determined by three different methods: (i) colorimetric; essentially that of Conant and Wheland (A., 1932, 572); (ii) spectroscopic; the compound is titrated with  $CNaPh_3$  in an inert atm. using aetioporphyrin I as indicator; (iii) polarimetric; the compound is treated with Na *l*-menthoxide and the position of equilibrium determined. The  $pK$  vals. are tabulated. *tert*.-Butyl-fluorene, m.p. 61°,

is obtained by reduction (red P, HI, AcOH) of the -fluorenol. H. B.

**Relation between the dissociation constants of substituted aliphatic acids and the distance between the dissociating and the substituted groups.** J. P. GREENSTEIN (J. Amer. Chem. Soc., 1936, 58, 1314—1316).—An inverse linear relation exists between  $pK$  and  $l^2$  (the square of the distance, in A., from the centre of the dipole group to the carboxyl centre on the assumption of an extended chain), when  $l^2$  is substituted for  $d$  in MacInnes' equation (A., 1928, 1326). For  $\alpha\beta$  substitution  $l^2$  is about twice, and for a  $\gamma$  substitution about three times, that for an  $\alpha$  substitution. E. S. H.

**Dissociation constants of ascorbic acid and its iodine oxidation product.** G. CARPÉNI (Compt. rend., 1936, 203, 75—78).—Dissociation consts. of ascorbic acid obtained electrometrically are  $2 \times 10^{-5}$  and  $6.3 \times 10^{-13}$  at 1°, and  $6.76 \times 10^{-5}$  and  $2.75 \times 10^{-12}$  at 20°. If the oxidation product, oxyascorbic acid, is titrated rapidly with NaOH, without waiting for equilibrium to be attained, the const. obtained is  $2.4 \times 10^{-9}$  at 20°, but a return titration with HCl gives a new curve indicating two consts.,  $8.9 \times 10^{-4}$  and  $1.6 \times 10^{-5}$ . Slow titration with NaOH indicates three consts.,  $6 \times 10^{-4}$ ,  $1.2 \times 10^{-8}$ , and  $5.1 \times 10^{-11}$ , whilst the return titration indicates  $1.8 \times 10^{-3}$ ,  $7.1 \times 10^{-5}$ , and  $3.2 \times 10^{-9}$ . C. R. H.

**Activity coefficients of ions.** (MLLE.) M. QUINTIN (J. Chim. phys., 1936, 33, 433—447).—Full details are given of work previously reported (this vol., 289). From e.m.f. data for  $CuSO_4$ , the calc. radii (Debye  $a$ ) of  $Cu^{+}$  and  $SO_4^{--}$  are  $3.5 \pm 0.2$  and  $1.3$  A., respectively. J. G. A. G.

**Thermodynamics of liquid-vapour equilibrium in system nitrogen-oxygen.** I. R. KRITSCHESVSKI and N. S. TOROTSCHESCHNIKOV (Z. physikal. Chem., 1936, 176, 338—346).—The fugacity,  $f$ , of  $N_2$  has been calc. at 100—125° abs. and 2.5—32 atm. from  $p$ - $v$ - $T$  and from thermal data; the two methods yield concordant results. For  $N_2$  in the vapour in equilibrium with a liquid  $N_2$ - $O_2$  mixture  $f$  is equal to the product of the mol. fraction of  $N_2$  in the liquid and the fugacity of pure  $N_2$  under a pressure equal to the total v.p. of the mixture.  $f$  for the  $O_2$  must obey a similar law. R. C.

**Vapour pressure measurements of the system calcium chloride-water.** A. LANNUNG (Z. anorg. Chem., 1936, 228, 1—18).—Measurements made with a hot-wire manometer (cf. A., 1934, 1170) at 0—50° are recorded. The dihydrate exists in two forms. Basset's observations on the tetrahydrate are confirmed (cf. A., 1933, 352). Heats of linking of the separate  $H_2O$  mols. in the hydrates are calc. H. J. E.

**Vapour pressures of saturated aqueous solutions. Mono- and di-ammonium hydrogen phosphates.** E. J. ROEHL (J. Amer. Chem. Soc., 1936, 58, 1291—1292).—For  $NH_4H_2PO_4$  at 19—90° the results are given by  $\log P = -2240/T + 8.862$ , and for  $(NH_4)_2HPO_4$  at 19—55° by  $\log P = -2240/T + 8.807$  with mean deviations of 0.8% and 0.4%, respectively. These and previous data



for other saturated aq. solutions show a linear relation between  $\log P$  and  $1/T$ , which when plotted gives lines parallel to that for  $H_2O$ . E. S. H.

**Heavy water of crystallisation.** J. R. PARTINGTON and K. STRATTON (*Nature*, 1936, **137**, 1075—1076).—The dissociation pressure of  $CuSO_4 \cdot 5D_2O$  is 6.655 mm. at  $25^\circ$  and 9.285 mm. at  $30^\circ$ . If the reaction is  $CuSO_4 \cdot 5D_2O \rightleftharpoons CuSO_4 \cdot 3D_2O + 2D_2O$ , this gives 4437 g.-cal. for the heat of combination of  $2D_2O_{liq.}$ , the corresponding val. for  $2H_2O$  being 5560 g.-cal. L. S. T.

**System albite-fayalite.** N. L. BOWEN and J. F. SCHAIRER (*Proc. Nat. Acad. Sci.*, 1936, **22**, 345—350).—F.p. and m.p. are recorded for the entire range of mixtures. The eutectic, m.p.  $1050^\circ \pm 5^\circ$ , contains 84% of albite (I), and the liquidus of (I) is a straight line. J. G. A. G.

**Representation of ternary systems.** E. SCHEIL (*Arch. Eisenhüttenw.*, 1935—6, **9**, 571—573).—To assist in understanding ternary diagrams it is recommended that the interrelationships of the 3- and 4-phase equilibria be summarised in a tabular form; examples of these are given for numerous Fe systems. A. R. P.

**Ternary systems  $KI-K_2SO_4-H_2O$  and  $NaI-Na_2SO_4-H_2O$ .** J. E. RICCI (*J. Amer. Chem. Soc.*, 1936, **58**, 1077—1079).—Equilibrium data are given for  $KI-K_2SO_4-H_2O$  at  $25^\circ$  and for  $NaI-Na_2SO_4-H_2O$  at  $15^\circ$ ,  $25^\circ$ , and  $45^\circ$ . No double salts or solid solutions are formed. E. S. H.

**Phase-rule study of the calcium arsenates.** G. W. PEARCE and L. B. NORTON (*J. Amer. Chem. Soc.*, 1936, **58**, 1104—1108).—Study of the system  $CaO-As_2O_5-H_2O$  at  $90^\circ$  shows the existence of  $CaHAsO_4$ ,  $Ca_5H_2(AsO_4)_4$ ,  $Ca_3(AsO_4)_2$ , and  $3Ca_3(AsO_4)_2 \cdot Ca(OH)_2$ . E. S. H.

**Equilibria in the system  $Li_2O-SiO_2-CO_2$ .** C. KROGER and E. FINGAS (*Festschr. Tech. Hochschule Breslau*, 1935, 296—306; *Chem. Zentr.*, 1935, ii, 2793; cf. A., 1933, 916).—The equilibrium state resulting from the action of  $SiO_2$  on  $Li_2CO_3$  has been studied. J. S. A.

**Equilibrium diagrams of salts for salt baths.** V. **System  $BaCl_2-CaCl_2-KCl$ .** T. SATO and T. AMANO (*Kinz-no-Kenk.*, 1934, **11**, 549—560; cf. A., 1935, 303).—In the system  $CaCl_2-KCl$  the compound  $CaCl_2 \cdot KCl$  (m.p.  $760^\circ$ ) is formed. This forms eutectics with  $KCl$  and  $CaCl_2$  at  $655^\circ$  (25 mol.-%  $KCl$ ) and  $615^\circ$  (76 mol.-%  $KCl$ ), respectively. The ternary eutectics are at  $543^\circ$ ,  $553^\circ$ , and  $552^\circ$  ( $BaCl_2$  23, 26, 21,  $CaCl_2$  58, 18, 17,  $KCl$  19, 56, 62 mol.-%, respectively). CH. ABS. (e)

**Systems zirconium oxalate-alkali oxalates-water.** (MLLE.) J. BOULANGER (*Compt. rend.*, 1936, **203**, 87—90).—The following solid phases were obtained:  $3Na_2X \cdot 2ZrOX \cdot H_2X \cdot 8H_2O$ ;  $2Na_2X \cdot ZrOX \cdot H_2X \cdot 2H_2O$ ;  $2(NH_4)_2X \cdot ZrOX \cdot H_2X \cdot 2H_2O$ ;  $2Li_2X \cdot ZrOX \cdot H_2X \cdot 7H_2O$  ( $X = C_2O_4$ ). C. R. H.

**Equilibrium in the reaction of hydrogen with ferrous oxide in liquid iron at  $1600^\circ$ .** M. G. FONTANA and J. CHIPMAN (*Trans. Amer. Soc. Metals*, 1936, **24**, 313—332).—An error in previous work is shown to be due to concn. gradients in the gas

caused by temp. gradients. The present work shows that the equilibrium const.  $K$  is 4.75 and is independent of  $[O]$ , and the activity of  $FeO$  dissolved in liquid  $Fe$   $\propto$  its wt.-%. The free energy of formation of  $FeO$  in 1% solution is  $-34,740$  g.-cal. at  $1600^\circ$ . The val. of  $K$  for the  $C + FeO \rightleftharpoons Fe + CO$  reaction is calc. to be 0.006, in good agreement with the experimental val. 0.010 previously obtained. W. P. R.

**Equilibrium between iron and nickel and their silicates saturated with silicic acid.** P. BARDENHEUER and E. BRAUNS (*Mitt. Kaiser-Wilh.-Inst. Eisenforsch.*, 1935, **17**, 127—132; *Chem. Zentr.*, 1935, ii, 2872).—Equilibrium data at  $1600^\circ$  are recorded. H. J. E.

**Equilibrium between niobium pentoxide, sodium carbonate, and carbon dioxide.** P. SUE (*Compt. rend.*, 1936, **203**, 90—92).—The reactions  $Nb_2O_5 + Na_2CO_3$  and  $NaNbO_3 + Na_2CO_3$  have been studied by measuring the equilibrium pressure of  $CO_2$  liberated. The heats of reaction are, respectively, 25 and 91.5 kg.-cal. C. R. H.

**Systems  $CaO-Al_2O_3-CaCl_2-H_2O$  and  $CaO-SiO_2-CaCl_2-H_2O$ .** R. NACKEN and R. MOSEBACH (*Z. anorg. Chem.*, 1936, **228**, 19—27; cf. B., 1935, 1096).—Aq.  $CaCl_2$  reacts fairly rapidly with  $3CaO \cdot Al_2O_3$  at  $30^\circ$ , forming the compound  $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ . Solubility data are given. This reaction controls the influence of  $CaCl_2$  on the setting of Portland cement. No corresponding compound is formed from  $3CaO \cdot SiO_2$  and aq.  $CaCl_2$ . The  $CaCl_2$  retards the reaction between  $3CaO \cdot SiO_2$  and  $H_2O$ . H. J. E.

**Thermal equilibrium in ternary systems.** XIII. **Tetramorphism of ammonium nitrate in the ternary system with carbamide and resorcinol.** K. HRYNAKOWSKI and M. SZMYTÓWNA (*Rocz. Chem.*, 1936, **16**, 181—186).—The fusion diagram has been constructed. The transition points for the various polymorphs of  $NH_4NO_3$  are the same as for the pure salt. R. T.

**Free energy of dissociation of hydrogen.** E. N. EREMIN (*Acta Physicochim. U.R.S.S.*, 1935, **3**, 147—150).—The spectroscopic val. for the heat capacity of  $H_2$  and the experimental vals. of the heat of dissociation are used in deriving an equation for the free energy of dissociation of  $H_2$ . The equilibrium consts. of the dissociation calc. from the equation for different temp. are in good agreement with the vals. obtained by Giaque. A. J. M.

**Determination of heats of dissolution [of silicates] in acids of various concentration.** H. E. SCHWIETE and A. PRANSCHKE (*Zement*, 1935, **24**, 593—598; *Chem. Zentr.*, 1935, ii, 2931).—With a large excess of acid, the heat of dissolution changes only by an amount which corresponds with the heat of dilution of the acid. The heat of hydration of  $CaO$  is determined as 15 kg.-cal. per mol. J. S. A.

**Molecular conductivity of strong electrolytes in concentrated solutions.** S. KANEKO (*J. Chem. Soc. Japan*, 1935, **56**, 793—795).—A formula is derived for the mol. conductivity of binary salts of equal ionic valency. For  $KCl$  it is valid up to 1*N*.

CH. ABS. (e)

**Electric conductivity and viscosity of salts dissolved in solutions of carbohydrates and glycerol.** J. DĚDEK and J. DYKÝJ (Coll. Czech. Chem. Comm., 1936, 8, 261—287).—The data refer to aq. solutions at 20—50° containing 0—88 g. of sucrose, glucose, and glycerol per 100 c.c. of solution and 0.001—1.0*N* concns. of electrolyte. The relation  $1/\Lambda_v\eta = ax + b$ , where  $\Lambda_v$  is the equiv. conductivity at dilution  $v$  and  $\eta$  is the viscosity of the aq. non-electrolyte ( $x$  g. per 100 c.c. of solution) and  $a$  and  $b$  are const., applies, in general, when  $x$  is  $>30$ , and, in some cases when  $x$  is  $>0$ . With Cl' as anion,  $a$  and  $b$  increase for the cations in the order  $H^+ < K^+ < Na^+ < Li^+$ . With const. [KCl], the order of the vals. of  $a$  and  $b$  is glycerol < glucose < sucrose, but with rise of temp.,  $a$  decreases (becomes less negative) and  $b$  increases.  $a$  and  $b$  decrease as  $v$  increases. The relation of these results to the rules of Walden and Johnston is discussed. J. G. A. G.

**Influence of pressure on conductivity of solutions.** P. Z. FISCHER (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 303—307).—A review.

R. T.

**Effect of non-electrolytes on the conductivity of electrolyte solutions.** V. A. PLOTNIKOV, P. Z. FISCHER, and V. P. BARABANOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 211—226).—The sp. conductivity of 0.33—3.83*N*-KCl, 0.5—2.5*N*-KNO<sub>3</sub>, and 0.3—4.94*N*-AgNO<sub>3</sub> in presence of CO(NH<sub>2</sub>)<sub>2</sub> (19 and 35%), mannitol (3—9%), or sucrose (5—50%) shows no obvious connexion with the viscosity; the formation of dissociable non-electrolyte-electrolyte complexes is postulated.

R. T.

**Influence of non-electrolytes on conductivity of aqueous electrolytes.** K. VOLKOV and A. ALMAZOV (Bull. Sci. Univ. Kiev, 1935, 1, 191—205).—The conductivity ( $\kappa$ ) and  $\eta$  of aq. KCl-dextrin (I) or sol. starch (II) do not run parallel. With const. concn. of (I) or (II), the % diminution in  $\kappa$  rises to a max. at 0.03—0.5*N*-KCl, thereafter steadily falling with further rise in [KCl], whilst when the relative concns. of (I) and KCl are maintained const. but the total concn. is progressively increased,  $\kappa$  rises asymptotically to a const. val. It is inferred that aq. (I) and (II) have a discontinuous structure, and that the effects are not due to dehydration of ions by the added colloids.

R. T.

**Electrochemistry of ternary systems in solvents of low dielectric constant.** E. J. GORENBEIN (Bull. Sci. Univ. Kiev, 1935, 1, 101—129).—Sp. conductivity in the systems AlBr<sub>3</sub>-MBr-solvent (M=Li, K, Rb, Cu, Ag; solvent=C<sub>6</sub>H<sub>6</sub>, PhMe, C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, EtBr) rises with increase in the dielectric const. of the solvent. In systems containing Li, K, or Rb, Al is deposited at the cathode during electrolysis.

R. T.

(A) Compounds of aluminium bromide with lithium, copper, and silver bromide. (B) Electrochemical study of the systems AlBr<sub>3</sub>-SbBr<sub>3</sub> in toluene, (C) AlBr<sub>3</sub>-BiBr<sub>3</sub> in benzene, (D) aluminium bromide-silver and copper halides-organic solvents (ethyl bromide, ethylene dibromide, benzene). V. A. PLOTNIKOV (Mem. Inst. Chem.

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Ukrain. Acad. Sci., 1935, 2, 3—9, 227—233, 235—244; 1936, 3, 89—109).—(A) [with E. J. GORENBEIN]. Conductivity in the systems AlBr<sub>3</sub>-EtBr-LiBr, -CuBr, and -AgBr is ascribed to the compounds LiBr, AlBr<sub>3</sub>, m.p. 192°, CuBr, AlBr<sub>3</sub>, m.p. 241°, and 2AgBr, 3AlBr<sub>3</sub>, m.p. 180—185°. Stability of the compounds towards H<sub>2</sub>O falls in the order given.

(B) [with V. A. KIKETZ and P. A. RADOMSKI]. Max. sp. conductivity  $\kappa$  is found for mixtures in which Sb : Al = 1 : 2, suggesting the compound SbBr<sub>3</sub>, 2AlBr<sub>3</sub>. The decomp. potential (18°) is 0.9 volt, Sb being deposited at the cathode.

(C) [with V. A. KIKETZ and L. A. KOROL]. The  $\kappa$ -composition curve has a max. corresponding with the compound 2BiBr<sub>3</sub>, 2AlBr<sub>3</sub>. Electrolysis with a Bi anode leads to deposition of Bi in accordance with Faraday's law (decomp. potential 0.9 volt).

(D) [with E. J. GORENBEIN]. The value of  $\kappa$  rises in the systems AlBr<sub>3</sub>-MX-EtBr, -C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, or -C<sub>6</sub>H<sub>6</sub> (M=Cu, Ag; X=Cl, Br, I) with increasing [MX]; no obvious connexion exists between dipole moment of solvent and  $\kappa$ . Cu or Ag is deposited in theoretical yield at the cathode. Decomp. potentials are recorded.

R. T.

**Measurement of conductivity of fused salts, and conductivity in the system NaCl-CaCl<sub>2</sub>.** V. BARZAKOVSKI (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 153—158).—Apparatus for determining the conductivity ( $\kappa$ ) of fused salts is described. The  $\kappa$ -composition curves at 700—1000° have a min., and the temp. coeff. of  $\kappa$ -composition curves a max., at 70—80 mol.-% of CaCl<sub>2</sub>;  $\kappa$  rises with increasing temp.

R. T.

**Electrolysis of sodium chloride in liquid ammonia.** II. E. I. ACHUMOV and N. A. GONTCHAROV (J. Gen. Chem. Russ., 1936, 6, 534—541; cf. A., 1935, 1080).—Sp. conductivities are recorded for solutions of NaCl, NH<sub>4</sub>Cl, and NaCl+NH<sub>4</sub>Cl in liquid NH<sub>3</sub>, at -34° to 34°; for saturated solutions of NaCl max.  $\kappa$  is at -8.4°. Curves connecting decomp. potential with temp. are given for solutions of NaCl in NH<sub>3</sub> and H<sub>2</sub>O.

R. T.

(A) Diffusion of potassium ferrocyanide, ferricyanide, and dichromate, and of sodium, magnesium, potassium, and calcium chloride, and the mobility of the ions of these salts. (B) Diffusion coefficient of potassium perrhenate. S. PLEŚNIEWICZ (Rocz. Chem., 1936, 16, 223—240, 241—244).—(A) The diffusion coeffs.  $D$  in 0.1*N* solutions at 20° are: K<sub>4</sub>Fe(CN)<sub>6</sub> 0.845, K<sub>3</sub>Fe(CN)<sub>6</sub> 0.917, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 1.043, NaCl 1.166±0.007, MgCl<sub>2</sub> 0.832±0.003, KCl 1.449, CaCl<sub>2</sub> 0.896±0.008.  $D$  cannot be calc. from Nernst's equation  $D=RT/F^2[(1/v_k)+(1/v_a)] \cdot u_k u_a / (u_k + u_a)$ , since  $u$  applies to infinite dilution. The conception of mean transport nos.  $v$ , applying to a given concn. gradient, is introduced,  $v_a$  being equal to  $kv_k$ , and  $1/D = (F^2/RT)n_k n_a / (n_k + n_a) \cdot (1/v_k + 1/v_a)$ , where  $n_a$  and  $n_k$  are the valencies and  $v_a$  and  $v_k$  the mean transport nos. of the anion and cation, respectively, and  $k$  and  $F$  are const.

(B) The  $D$  of KReO<sub>4</sub> (0.01*N*) at 20° is 1.233, and the  $v$  of ReO<sub>4</sub>' at 18° is 44.07.

R. T.

**Structure of molecules in solution.** C. DUVAL (Document. sci., 1935, 4, 145—148; Chem. Zentr.,



1935, ii, 3051).—From observations on electrophoresis and analyses of the contents of the anode and cathode compartments the following structural formulæ are suggested: kainite  $[\text{MgSO}_4\text{Cl}(\text{H}_2\text{O})_3]\text{K}$ ;  $(\text{CrO}_3\text{SO}_4)_2\text{H}_2$ ;  $(\text{SO}_3\text{SO}_4)_2\text{H}_2$ ;  $(\text{CrO}_3\text{CrO}_4)_2\text{H}_2$ ;  $[\text{Co}(\text{CO}_3)_3]\text{Co}$ ;  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]\text{H}$ ;  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]_2\text{Co}$ ;  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Li}$ .  
H. J. E.

**Solid electrolytes.** P. FISCHER (Bull. Sci. Univ. Kiev, 1935, 1, 131—140).—A review. R. T.

**Nomogram for the relation between quinhydrone potential and  $p_{\text{H}}$  at various temperatures.** G. KNAYSI (Food Res., 1936, 1, 297—299).  
E. C. S.

**Poisoning of platinum in hydrogen electrodes.** H. JABECZYNSKA-JEDRZEJEWSKA (Rocz. Chem., 1936, 16, 306—312).—Pt electrodes are poisoned by 0.00025N- $\text{H}_2\text{S}$ , the potential tending to a const. min. val. of 160 mv., irrespective of the  $[\text{H}_2\text{S}]$ . The effect increases with increasing  $p_{\text{H}}$ . Reactivation is possible by the successive action of nascent O and H.  
R. T.

**Potentials at the interface of two liquid phases.** III. K. KARCEWSKI (Rocz. Chem., 1936, 16, 254—258; cf. this vol., 928).—The potential at the interface  $\text{Bu}^n\text{OH}$ -aq. K salt becomes more positive with increasing  $[\text{K}_2\text{SO}_4]$ , and less positive in the case of KCl, KBr, KI, KCNS,  $\text{K}_2\text{CO}_3$ ,  $\text{HCO}_2\text{K}$ ,  $\text{KNO}_3$ ,  $\text{KClO}_3$ , and  $\text{KClO}_4$ .  
R. T.

**Influence of composition of solutions on the electrocapillary curve of mercury.** W. KEMULA and E. BEER (Rocz. Chem., 1936, 16, 259—269).—The electrocapillary curves obtained by the static and dynamic methods coincide in the case of conc. but not dil. solutions. Irregularities in the curves obtained by the dynamic method are ascribed to the influence of the  $\zeta$ -potential. The results for KCl,  $\text{BaCl}_2$ , and  $\text{LaCl}_3$  are in agreement with Stern's theory (Z. Elektrochem., 1924, 30, 508).  
R. T.

**Polarographic studies with the dropping mercury cathode.** LIX. Anomalous curves of certain potassium chloride solutions. A. R. WEIR (Coll. Czech. Chem. Comm., 1936, 8, 239—245).—The current-voltage curves for the electrolysis of aq. KCl saturated with  $\text{Hg}_2\text{Cl}_2$  are similar to those for NaCl except in solutions containing 45.6—59.5 g. of KCl per 1000 g. of  $\text{H}_2\text{O}$  which give variable curves of anomalous contour. These results are parallel with v.p. anomalies (cf. this vol., 678). J. G. A. G.

**Anode polarisation of metallic electrodes. I. Polycrystalline and liquid electrodes.** W. TRZEBIATOWSKI and M. SARNOWSKI (Rocz. Chem., 1936, 16, 187—198).—The polarisation of Cu anodes ( $0^\circ$ ,  $25^\circ$ , and  $50^\circ$ ) in aq.  $\text{CuSO}_4$ - $\text{H}_2\text{SO}_4$  varies with the crystal structure of the metal.  
R. T.

**Decomposition potentials of fused salts.** V. M. GUSKOV (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 159—173).—E.m.f. measurements relating to the cell  $\text{Mg}|\text{molten MgCl}_2|\text{Cl}$  (C anode; molten NaCl-KCl- $\text{MgCl}_2$  electrolyte) at 665—793° afford no evidence of the existence of complex anions of the type  $\text{MgCl}_3^-$ . The temp. coeff. of the e.m.f. is  $0.7 \times 10^{-3}$ . The results suggest that cryolite dissociates as follows:  $\text{Na}_3\text{AlF}_6 \rightleftharpoons 3\text{Na}^+ + \text{Al}^{+++} + 6\text{F}^-$ ,

the reaction at the C anode being  $2\text{Al}_2\text{O}_3 + 3\text{C} + 6\text{F}_2 \rightarrow 4\text{AlF}_3 + 3\text{CO}_2$ ;  $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ .  
R. T.

**Decomposition potential of aluminium chloride amines.** V. A. PLOTNIKOV and M. S. FORTUNATOV (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 251—256).— $\text{N}_2$  is evolved, in accordance with Faraday's law, at a Pt anode from a molten mixture of  $\text{AlCl}_3$  amines. The decomp. potentials vary with temp. and c.d.  
R. T.

**Electrolysis of non-aqueous solutions.** V. S. FINKELSCHTEIN (Coll. Trans. 1st U.S.S.R. Conf. Non-aq. Solutions, Kiev, 1935, 54—71).—Previous explanations of deviations from Faraday's law are not satisfactory. In the system  $\text{AsCl}_3$ - $\text{Et}_2\text{O}$  the val. of the decomp. potential is affected only by addition of solvents the dipole moment of which is  $>$  that of  $\text{Et}_2\text{O}$ . Electrolysis in liquid  $\text{NH}_3$  and deposition of Al from non-aq. solvents are discussed.  
R. T.

**Strong oxidising agents in nitric acid solution.**

I. Oxidation potential of cerous-ceric salts.  
II. Oxidation potential of thalious-thallic salts. A. A. NOYES and C. S. GARNER (J. Amer. Chem. Soc., 1936, 58, 1265—1268, 1268—1270).—I. E.m.f. of cells of the type  $\text{Pt}-\text{N}_2$  (1 atm.)  $|\text{HClO}_4(c'), \text{HNO}_3(c) + \text{Ce}^{\text{IV}}(c_2) + \text{Ce}^{\text{III}}(c_1)|\text{Pt}$  at  $25^\circ$  and  $0^\circ$  are recorded.  $E_0$  varies little with considerable change in the  $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$  ratio, acid concn., or ionic strength. It follows that nitrate complexes are formed only slightly, if at all, and that a hydrolytic reaction, such as  $\text{Ce}^{\text{IV}} + \text{H}_2\text{O} = \text{CeOH}^{+++} + \text{H}^+$ , does not occur appreciably. The  $\text{Ce}^{\text{III}}$ - $\text{Ce}^{\text{IV}}$  oxidation potential in  $\text{HNO}_3$  is  $1.609 \pm 0.0007$  volts at  $25^\circ$  and 1.601 volts at  $0^\circ$ .

II. E.m.f. measurements of cells of the type  $\text{Pt}-\text{H}_2$  (1 atm.)  $|\text{HClO}_4(c'), \text{HNO}_3(c) + \text{Tl}^{\text{III}}(c_2) + \text{Tl}^{\text{I}}(c_1)|\text{Pt}$  show that the formal oxidation potential of  $\text{Tl}^{\text{III}}-\text{Tl}^{\text{I}}$  is  $1.2303 \pm 0.0007$  volts at  $25^\circ$  and  $1.193 \pm 0.001$  volts at  $0^\circ$  in  $\text{HNO}_3$ . These vals. remain const. when  $\text{Tl}^{\text{I}}/\text{Tl}^{\text{III}}$  is varied 100-fold and over a wide range of  $[\text{HNO}_3]$ , showing that hydrolysis of  $\text{Tl}(\text{NO}_3)_3$  or formation of nitrate complexes does not occur appreciably.  
E. S. H.

**Extension of Arrhenius' conception of a chemical reaction.** J. A. CHRISTIANSEN (Z. physikal. Chem., 1936, B, 33, 145—155; cf. A., 1935, 707).—Assuming an open sequence of reactions with many or an infinite no. of steps in series with each other, the above concept leads for a unimol. reaction to an expression similar to Nernst's reaction velocity = (chemical force)/(chemical resistance). The force is equal to the difference in activity between the initial and final states of the system and the resistance to an integral which varies with temp.  
R. C.

**Kinetics of gas reactions: an attempt to connect thermal decomposition and oxidation processes.** M. W. TRAVERS (Nature, 1936, 138, 26—27).—The similarity in the curves representing the rate of thermal decomp. and that of oxidation of  $\text{CH}_2\text{O}$  and  $\text{MeCHO}$  can be accounted for by the formation of short-lived intermediates.  
L. S. T.

**Period of induction in the inflammation of gas mixtures.** A. E. MALINOVSKI (Acta Physicochim. U.R.S.S., 1935, 3, 509—516).—Induction periods of chain reactions ( $\alpha$ ) when the no. of active centres

generated in unit time is const. throughout the reaction, and (b) when no active centres are generated after the commencement of the reaction, are calc.

O. D. S.

**Kinetics of simultaneous polymerisation and ring formation.** M. STOLL (Trans. Faraday Soc., 1936, 32, 1031—1033).—A criticism of the work of Salomon (cf. this vol., 296).

O. J. W.

**Forjaz's effect.** L. ROSENKEVITSCH (Acta Physicochim. U.R.S.S., 1935, 3, 161—162).—The accelerating effect of a powerful alternating field on the reaction between EtOH and AcOH noted by Forjaz (A., 1934, 40) is attributed to the heating effect of the field.

A. J. M.

**Oxidation of hypophosphorous acid by iodine in aqueous sulphuric acid.** J. KAMECKI (Rocz. Chem., 1936, 16, 199—206).—The velocity of oxidation of  $\text{H}_3\text{PO}_2$  to  $\text{H}_3\text{PO}_3$  by (I) rises with increasing  $[\text{H}_2\text{SO}_4]$  to 1.0*N*, thereafter remaining const. Oxidation of  $\text{H}_3\text{PO}_3$  proceeds slowly.  $\text{H}_3\text{PO}_2$  is determined in presence of  $\text{H}_3\text{PO}_3$  by determining the latter in one sample, by the method of Wolf and Jung (A., 1932, 135), adding  $\text{H}_2\text{SO}_4$  to 1—2*N* and a small excess of I to another sample, and titrating excess of I after 2.5 hr. at 20° (in the dark).

R. T.

**Kinetics of the tervalent vanadium-iodine reaction.** J. B. RAMSEY and M. J. HELDMAN (J. Amer. Chem. Soc., 1936, 58, 1153—1157).—At 24–95° the reaction in  $\text{HClO}_4$  at const. ionic strength, is  $\propto [\text{I}_2']$  and  $[\text{V}^{III}]$ , and inversely  $\propto [\text{H}']$  and  $[\text{I}']$ . The rate-determining step is probably bimol., between I mols. and  $\text{VOH}^{II}$ . The salt effect has been determined and an explanation for its large negative magnitude is advanced.

E. S. H.

**Kinetics of the nitrite-iodine reaction.** G. G. DURRANT, R. O. GRIFFITH, and A. McKEOWN (Trans. Faraday Soc., 1936, 32, 999—1013).—The kinetics of the reaction between  $\text{NaNO}_2$  (and  $\text{KNO}_2$ ) and I have been investigated in phosphate buffers at 40°, 50°, and 60°. The reaction rate is given by an equation, which can be explained by a mechanism involving  $\text{NO}_2$  and I atoms as intermediaries. This mechanism is supported by results of experiments in which nitrite and oxalate react simultaneously with I.

O. J. W.

**Speed of decomposition of chromic acid in hot aqueous solutions of sulphur trioxide, and relation between this reaction and oxidising power.** H. C. S. SNETHLAGE (Rec. trav. chim., 1936, 55, 712—722).—The rate of decomp., yielding  $\text{O}_2$ , has been determined in aq.  $\text{H}_2\text{SO}_4$  at 133° and in  $\text{SO}_3$ – $\text{H}_2\text{SO}_4$  mixtures at 100°. There occur simultaneously (1) a pseudo-unimol. reaction of the  $\text{CrO}_3$  with  $\text{SO}_3$  or  $\text{H}_2\text{S}_2\text{O}_7$ , giving  $\text{Cr}_2\text{O}_3$ , and (2) a bimol. reaction, possibly  $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \text{O}_2$ . As the  $\text{H}_2\text{SO}_4$  concn., *c*, rises above 60% the velocity passes through a max. (81%), then a min. (96–98%), and finally rises rapidly; below 60% there is no measurable decomp. The velocity coeff. of (1),  $k_1$ , rises slowly with *c* up to ~99%, then much more rapidly, corresponding with the appearance in the solvent of  $\text{H}_2\text{S}_2\text{O}_7$ . With (2) the velocity coeff.,  $k_2$ , rises with *c* up to 81%, then falls up to 99%. The relation of

$k_1$  and  $k_2$  to *c*, however, varies somewhat with  $[\text{CrO}_3]$ . These results explain the data obtained (A., 1935, 1140) for the oxidation of org. substances with  $\text{CrO}_3$ – $\text{H}_2\text{SO}_4$  mixtures; the oxidising power of the latter is probably governed by (2).

R. C.

**Rate of reaction of sodium sulphite with oxygen dissolved in water.** R. M. HITCHENS and R. W. TOWNE (Amer. Soc. Test. Mat., Preprint, June, 1936, 8 pp.).—The reaction proceeds with great rapidity and is complete in <1 min. at temp. approaching 100°, regardless of the type of  $\text{H}_2\text{O}$ , if a slight excess of  $\text{Na}_2\text{SO}_3$  is employed. A 20% excess of  $\text{Na}_2\text{SO}_3$  doubles the reaction rate and a 100% excess almost quadruples it.

R. B. C.

**Kinetics of hydrolysis of esters in alkaline media.** V. A. GOLTZSCHMIDT, N. K. VOROBJEV, and I. V. POTANOV (J. Gen. Chem. Russ., 1936, 6, 757—763).—The velocity coeffs.  $k$  of hydrolysis by aq. NaOH of a no. of esters,  $\text{R}\cdot\text{CO}_2\text{R}'$ , at 10°, 20°, and 30° fall with increase in the no. of C atoms in R and R'; for a given R,  $k_{\text{Et}}/k_{\text{Me}} = 0.57$ ,  $k_{\text{Pr}}/k_{\text{Et}} = 0.84$ , and  $k_{\text{Bu}}/k_{\text{Pr}} = 0.93$ , but for a given R',  $k_{\text{Et}}/k_{\text{Me}} = 0.84$ , and  $k_{\text{Pr}}/k_{\text{Et}} = 0.62$ . It is concluded that the activity coeff. and the energy of activation both fall with increase in mol. wt. of the ester.

R. T.

**Rates of esterification of alcohols in formic and acetic acids and of formic acid in *tert*-butyl alcohol.** A. KAILAN and S. ROSENBLATT (Monatsh., 1936, 68, 109—170).—The rate of esterification of menthol, borneol, cyclohexanol,  $\alpha$ -chloropropan- $\beta$ -ol, ethylene chloro-, bromo-, and iodo-hydrin,  $\beta\gamma$ -dichloro-,  $\beta\gamma$ -dibromo-,  $\beta\gamma$ -di-iodo-, and  $\beta$ -chloro-*n*-propyl alcohol was studied at 15° and 25° in AcOH and  $\text{HCO}_2\text{H}$ , with and without addition of HCl, and with varied initial  $[\text{H}_2\text{O}]$ . The rate in AcOH containing HCl was increased on increasing the  $[\text{H}_2\text{O}]$ . In absence of HCl, or in  $\text{HCO}_2\text{H}$ , it was reduced. The increase in rate due to HCl was  $\propto$  its concn. The rate of esterification decreases as the no. of halogen atoms in the mol. is increased. Replacement of one six-membered by two five-membered rings increases the rate.

H. J. E.

**Effect of pressure up to 12,000 kg. per sq. cm. on reactions in solution.** E. G. WILLIAMS, M. W. PERRIN, and R. O. GIBSON (Proc. Roy. Soc., 1936, A, 154, 684—703).—Velocity coeffs. have been measured, by means of the apparatus previously described (A., 1935, 1082), for the following reactions: the interaction of NaOEt and EtI in EtOH solution, between 15° and 30° at 5000, 8500, and 12,000 kg. per sq. cm.; the hydrolysis of  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$  by aq. NaOH, between 40° and 80° at 1, 3000, 7600, and 12,000 kg. per sq. cm.; the esterification of  $\text{Ac}_2\text{O}$  by EtOH in EtOH solutions, between 15° and 40° at 1, 1000, 2000, and 3000 kg. per sq. cm., and in PhMe,  $\text{COMe}_2$ ,  $\text{C}_6\text{H}_{14}$ , and amyl ether solutions, at various temp. at 1 and 3000 kg. per sq. cm.; the decomp. of phenylbenzylmethylallylammonium bromide (I) in  $\text{CHCl}_3$  between 25° and 45° at 1 and 3000 kg. per sq. cm. In each case the temp. coeffs. of the reactions were measured, in an attempt to show whether the change in the velocity coeff. is due to a change in the const. *A* or *E* in the Arrhenius equation.



The reactions fall into three classes. (1) "Normal" reactions, where pressure has a small accelerating effect which falls at high pressures, the increase in velocity being of the order of 5 times at 12,000 kg. per sq. cm. The acceleration is due chiefly to a decrease in the activation energy. (2) "Slow" reactions, where pressure has a greater accelerating influence which increases with rise of pressure, the increase in velocity being of the order of 10 times at 5000 kg. per sq. cm., and 45 times at 8500 kg. per sq. cm. The consts.  $A$  and  $E$  of the Arrhenius equation both increase with rise of pressure. (3) Unimol. decomp. The decomp. of (I) in  $\text{CHCl}_3$  solution is retarded 1.5 times at 3000 kg. per sq. cm. The pressure effect on the  $\text{EtOH}$  and  $\text{Ac}_2\text{O}$  reaction varies with change of solvent, but it is always of the same order of magnitude.

L. L. B.

**Kinetic study of the hydrolysis and alcoholysis of phenyl acetate.** W. A. WATERS (J.C.S., 1936, 1014—1023).—The rates of decomp. of  $\text{PhOAc}$  by  $\text{EtOH-H}_2\text{O}$  mixtures containing  $\text{HCl}$  have been investigated. The reactions  $\text{PhOAc} + \text{EtOH} \rightarrow \text{EtOAc} + \text{PhOH}$  (1) and  $\text{PhOAc} + \text{H}_2\text{O} \rightarrow \text{AcOH} + \text{PhOH}$  (2) proceed simultaneously at comparable rates. The formation of  $\text{PhOH}$  followed a unimol. course in all experiments and was irreversible, no other aromatic product being formed. This supports the view that carboxylic esters undergo acid hydrolysis and alcoholysis by fission of an alkoxy-group. The crit. increment of activation for both  $\text{PhOH}$  and  $\text{AcOH}$  liberation is approx. the same, suggesting that the activated complexes in both (1) and (2) are the same, not involving  $\text{EtOH}$  or  $\text{H}_2\text{O}$ . Ester hydrolysis in acid solution may be a unimol. reaction occurring between activated ester-proton complexes and normal solvent mols.

D. C. J.

**Determination of parameters  $k$  and  $n$  in the differential equation  $dx/dt = k(a-x)^n t^{p-1}$ . Chemical applications.** J. M. GONZALEZ BARREDO (Anal. Fis. Quím., 1935, 33, 844—853).—Mathematical. The hydrolysis of  $\text{EtOAc}$  is discussed as an example.

**Graphical methods in kinetics.** J. L. G. CAAMAÑO (Anal. Fis. Quím., 1936, 34, 327—330).—Attention is directed to errors in the work of Gonzalez Barredo (preceding abstract).

F. R. G.

**Kinetics of bimolecular associations in solution and in the gaseous state. Mechanism of additions to double linkings. IV.** A. WASSERMANN (J. C. S., 1936, 1028—1034; cf. this vol., 685).—The kinetics of the addition of cyclopentadiene to acraldehyde, benzoquinone,  $\alpha$ -naphthaquinone, cyclopentadiene-benzoquinone, and cyclopentadiene are measured in  $\text{C}_6\text{H}_6$  solution, and compared with the kinetics of corresponding syntheses in the gas phase (*ibid.*, 297). The factor in the Arrhenius equation independent of temp. is much  $<$  the collision frequency in the gas phase, and it is suggested that this is due to the complicated structure of the reactants. The conclusion is reached that the collision frequency in solution is approx. the same as that in the gas phase both for "normal" and "slow" bimol. reactions.

D. C. J.

**Reaction of iodoacetate and of iodoacetamide with various thiol groups, with urease, and with yeast preparations.** C. V. SMYTHE (J. Biol. Chem., 1936, 114, 601—612).—The rates of reaction of  $\text{CH}_2\text{I}\cdot\text{CO}_2^-$  (I) and  $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$  (II) with a no. of substances containing  $\cdot\text{SH}$  were in the order: thioglucose  $>$  thiosalicylic acid  $>$  cysteine  $>$  glutathione  $>$  thioglycol; in all cases the rate with (II) was  $>$  that with (I). Urease was very resistant to inhibition by (I) but quite susceptible to that by (II);  $\text{NH}_2\text{Ac}$  and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  were ineffective. It is concluded that inactivation of urease by (II) requires that only 0.25—0.5 of the  $\cdot\text{SH}$  be destroyed. The inhibition of fermentation of yeast extracts by (I) is more rapid than that by (II).

H. D.

**Ionisation of amines in alcohol: a possible slow reaction.** A. G. OGSTON (J.C.S., 1936, 1023—1025).—A quant. investigation of the slow increase in electrical conductivity found when solutions of  $\text{NH}_3$  in  $\text{MeOH}$  and  $\text{EtOH}$  are diluted is made (cf. A., 1934, 1071). Similar behaviour is found using  $\text{NHEt}_2$ ,  $\text{NH}_2\text{Bu}^t$ ,  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ , and piperidine. A rapid change, accounting for 0.66 of the total, occurs in the first 2 min. and then the reaction becomes slow and of the first order. The effect is ascribed to a slow ionic reaction.

D. C. J.

**Rate of absorption of water by magnesium sulphate.** A. S. MIKULINSKI and R. N. RUBINSTEIN (Z. anorg. Chem., 1936, 228, 89—91).—The rate of absorption of  $\text{H}_2\text{O}$  by  $\text{MgSO}_4\cdot\text{H}_2\text{O}$  (I) and  $\text{MgSO}_4\cdot 2\text{H}_2\text{O}$  (II) in atm. of 100, 70, and 50% R.H. at  $18^\circ$  was measured. The initial rate is smaller for (I) than for (II).

H. J. E.

**Derivation of general formula for velocity of crystallisation of sucrose from experimental data.** A. KIROV (Sovet. Sach., 1933, No. 9, 30—33).—The crystallisation const. and velocity are calc. from the formula  $\Delta p = K\Delta C/\eta$  ( $C$ =concn.;  $\eta$ =viscosity).

CH. ABS. (e)

**Rate of dissolution of alkali borate glasses.** R. L. MÜLLER and C. V. WEINSTEIN (Acta Physicochim. U.R.S.S., 1935, 3, 465—502; cf. A., 1932, 447).—The rates of dissolution of glasses of formula  $\text{B}_2\text{O}_3 + \text{M}_2\text{O}$ , where M is Li, Na, K, Rb, or Cs, have been investigated for a series of compositions between  $\text{B}_4\text{O}_6$  and  $\text{M}_2\text{B}_4\text{O}_7$ . For glasses where the molar fraction,  $q$ , of  $\text{M}_2\text{B}_4\text{O}_7$  is  $> 0.1$  the rate is determined by diffusion and convection. When  $q$  is  $< 0.5$  the rate is independent of the rate of stirring of the liquid and has a temp. coeff. of 7—8% per  $1^\circ$ . It is deduced that the rate of dissolution is here determined by a chemical reaction at the solid-liquid interface which begins to be important in the range  $0.1 < q < 0.5$ . The formerly observed correlation between the molar conductivity and the rate of dissolution is fortuitous.

O. D. S.

**Catalytic oxidation effect of complex metallic compounds. XI. Catalytic oxidation in heavy water.** K. YAMASAKI (Bull. Chem. Soc. Japan, 1936, 11, 431—433).—The rate of oxidation of pyrogallol, alone or catalysed by complex Co salts, is greater in  $\text{H}_2\text{O}$  than in  $\text{D}_2\text{O}$ .

C. R. H.

**Kinetics of the oxidation of solutions of sulphurous acid.** S. S. VASSILIEV, L. I. KASCHTANOV, and T. L. KASTORSKAIA (Acta Physicochim. U.R.S.S., 1935, 3, 413—434).—The oxidation of aq.  $\text{SO}_2$  by air has been studied with and without the addition of 0.01% of  $\text{MnSO}_4$  as catalyst. For low  $[\text{SO}_2]$  the rate  $\propto [\text{SO}_2]$ , the catalysed being 7—8 times as fast as the uncatalysed reaction. For high  $[\text{SO}_2]$  the rate becomes equal to the rate of dissolution of  $\text{O}_2$ .

O. D. S.

**Acid catalysis in liquid ammonia. Kinetics of the ammonolysis of santonin in liquid ammonia in the presence of ammonium salts.** A. I. SCHATTENSTEIN (Acta Physicochim. U.R.S.S., 1935, 3, 37—52).—The kinetics of the ammonolysis of santonin were investigated polarimetrically. The catalytic effect of  $\text{NH}_2$ -acids [santonamide,  $\text{CO}(\text{NH}_2)_2$ ] and of several  $\text{NH}_4$  salts was examined. The velocity coeffs. for 0.1*N* solutions of catalysts are in the order:  $\text{NH}_4\text{Cl} > \text{NH}_4\text{Br} > \text{NH}_4\text{NO}_3 > \text{NH}_4\text{I} > \text{NH}_4\text{ClO}_4$ . The parallelism observed between conductivity and thermodynamic activity and catalytic activity in the case of aq. solutions does not hold when the solvent is liquid  $\text{NH}_3$ . If to the solution of the acid ( $\text{NH}_4$  salt) a neutral (Na) salt with the same anion is added, there is a definite increase in the reaction velocity. The proportionality between velocity coeff. and concn. of catalyst is the better the weaker electrolyte is the catalyst. The mechanism of the catalysis is discussed.

A. J. M.

**Acid-base catalysis of the mutarotation of glucose in protium oxide-deuterium oxide mixtures.** W. H. HAMILL and V. K. LA MER (J. Chem. Physics, 1936, 4, 395—401).—The velocity of the  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$ -catalysed reaction  $\propto$  the fraction of heavy glucose and depends only indirectly on the  $[\text{D}_2\text{O}]$  in the water. The velocity of the acid ion catalysis varies linearly with  $[\text{D}_2\text{O}]$ . The rate of  $\text{OAc}'$  catalysis varies linearly with the fraction of  $\text{D}_2\text{O}$  or of  $\text{AcOD}$ . The decrease in the rate of the  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$ -catalysed reaction with increasing  $[\text{D}_2\text{O}]$  arises from a decrease in the entropy of activation and not from an increase in the activation energy.

H. J. E.

**Inhibition of chemical reactions. VI. Influence of ether and nitrobenzene on the absorption of ethylene by sulphuric acid.** K. C. BAILEY and W. E. CALCUTT (Sci. Proc. Roy. Dublin Soc., 1936, 21, 309—315).— $\text{Et}_2\text{O}$  and  $\text{PhNO}_2$  inhibit the rate of absorption of  $\text{C}_2\text{H}_4$  (cf. A., 1932, 1085) in conc.  $\text{H}_2\text{SO}_4$ . Every  $\text{Et}_2\text{O}$  mol. in the surface appears to inhibit equally 4—5 adjacent  $\text{H}_2\text{SO}_4$  mols. from absorbing the gas. A similar explanation is impossible for  $\text{PhNO}_2$ . When the absorbing surface is constantly renewed the inhibiting effect of  $\text{Et}_2\text{O}$  or  $\text{PhNO}_2$  is  $<$  in a static system, indicating that the inhibitor acts at the gas-liquid interface rather than in the bulk of the liquid.

J. L. D.

**Ozone as oxidising catalyst. XI. Ozonisation of aliphatic aldehydes in different solvents and in the gaseous state.** E. BRINER and A. LARDON (Helv. Chim. Acta, 1936, 19, 850—857; cf. this vol., 570).—Ozonisation of  $\text{CH}_2\text{O}$ ,  $\text{MeCHO}$ ,  $\text{EtCHO}$ , and  $\text{PrCHO}$  in the gas phase and in solution in  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ , or  $\text{C}_6\text{H}_{14}$  has been studied. T. G. P.

**Release of protons and deuterons from organic molecules in general basic catalysis, exemplified by bromination of nitromethane.** O. RETZ (Z. physikal. Chem., 1936, 176, 363—387).—The rates of bromination,  $k$ , of  $\text{MeNO}_2$  and  $\text{CD}_3\text{NO}_2$  both in pure  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  and in presence of acetate and chloroacetate buffers have been measured at 25° and 35°.  $k$  falls with increasing D content of the  $\text{NO}_2$ -compound, linearly at first, but with increasing slowness at the higher D contents. The ratio of  $k$  for  $\text{MeNO}_2$  to that for  $\text{CD}_3\text{NO}_2$  under the same conditions is 4—7, which is therefore also the ratio of the rate of protolysis to that of deuterolysis, since these are the processes which determine the rate of bromination as a whole. There is, however, no detectable difference between the energies of activation. Substitution of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  as solvent depresses  $k$  by ~20%. The ratio of the strength of  $\text{H}_2\text{O}$  as a base to that of  $\text{D}_2\text{O}$  is ~1.6. At 83° the distribution ratio of D between  $\text{H}_2\text{O}$  and  $\text{MeNO}_2$  is ~0.8. The prep. of  $\text{CD}_3\text{NO}_2$  is described.

R. C.

**Thermal decomposition of sodium sulphate in presence of silica and kaolin.** J. A. FIALKOV and S. D. SCHARGORODSKI (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 269—283).—Decomp. of  $\text{Na}_2\text{SO}_4$ - $\text{SiO}_2$  mixtures commences at 1100°, the velocity of the reaction increasing with rise of temp. and with the degree of dispersion of the  $\text{SiO}_2$ . It is catalysed by  $\text{CeO}_2$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ , but not appreciably by  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . At 1200° the greatest decomp. velocity is attained by heating with kaolin, and the least with river sand, kieselguhr and  $\text{SiO}_2$  gel being intermediate. Decomp. is greatly accelerated by raising the kaolin content of the mixtures. The products are  $\text{SO}_2$  (evolved chiefly during the first hr. of heating) and Na silicates, aluminates, and aluminosilicates. The mass is readily converted by dil.  $\text{H}_2\text{SO}_4$  into  $\text{SiO}_2$  gel and  $\text{Al}_2(\text{SO}_4)_3$ .

R. T.

**Catalytic oxidation of sodium sulphite in presence of cupriferous charcoal.** K. VOLKOV and D. STRASHESKO (Bull. Sci. Univ. Kiev, 1935, 1, 95—99).—The velocity of oxidation of  $\text{SO}_3''$  in presence of C-Cu increases with the  $[\text{Cu}'']$  of the solution;  $\text{SO}_3'''$  or  $\text{SO}_4''$  are not adsorbed by the C, and the reaction takes place exclusively in the aq. phase.

R. T.

**Effect of catalysts and ant catalysts on the kinetics and mechanism of oxidation of sulphur dioxide by ozone.** L. I. KASCHTANOV and V. P. RISHOV (J. Gen. Chem. Russ., 1936, 6, 732—747).—The stoichiometric coeff.  $a$  (no. of mols. of  $\text{SO}_2$  oxidised per mol. of  $\text{O}_3$ ) rises with increasing  $[\text{SO}_2]$  and diminishing  $[\text{O}_3]$  to a max. of 18; the val. of  $a$  is unaffected by varying the rate of flow of the gas mixture, by presence of  $\text{PhOH}$ , alone or with  $\text{MnSO}_4$ , or by presence of benzoquinone, and remains const. at 0—60°. The velocity of reaction increases with rising temp., and falls with increasing  $[\text{H}_2\text{SO}_4]$  in the absorbent solution. The reaction is catalysed by  $\text{MnSO}_4$ .  $\text{O}_3$  oxidises  $\text{PhOH}$  to benzoquinone, and Mn to  $\text{MnO}_4^-$ , but  $\text{MnO}_4^-$  production is inhibited by  $\text{PhOH}$ . The application of the above findings to desulphurisation of flue gas, with recovery of  $\text{H}_2\text{SO}_4$ , is discussed.



**Influence of crystalline addenda on the velocity of evolution of gas from carbonates.** II. B. SREBROW (*Kolloid-Z.*, 1936, 76, 149—153; cf. A., 1935, 942).—The rate of thermal decomp. of  $\text{ZnCO}_3$  at  $254^\circ$  and of  $\text{NiCO}_3$  at  $330^\circ$  is increased by adding small amounts of  $\text{ZnO}$ ,  $\text{MnO}_2$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{PbO}$ , or  $\text{WO}_3$ . E. S. H.

**Mechanism of catalytic oxidation of carbon monoxide on manganese dioxide.** III. Existence of a critical lower pressure limit in the heterogenous oxidation. F. CHARACHORIN, S. ELOVITZ, and S. ROGINSKI (*Acta Physicochim. U.R.S.S.*, 1935, 3, 503—508; cf. A., 1935, 942).—Results to be published (IV, V) are discussed. Comparison of rates of CO absorption and oxidation at  $17^\circ$  indicates that for  $p_{\text{CO}} < 0.525$  mm. reaction takes place according to  $\text{CO} + \text{MnO}_2 = \text{CO}_2 + \text{MnO}$ . Above 0.525 mm. reaction is mainly CO (adsorbed) +  $\text{O}_2$  (adsorbed)  $\rightarrow \text{CO}_2$ . The possibility of chain reactions is considered. O. D. S.

**Speed of dissociation of carbon monoxide in presence of iron and its oxides.** F. MEUNIER (*Rev. Mét.*, 1936, 33, 258—264).—The degree of dissociation of CO in the presence of Fe has been measured at temp. from  $460^\circ$  to  $850^\circ$ . At all temp. the rate of dissociation is very rapid at first but quickly falls. Thus at  $525^\circ$  the rate in the first sec. is about 12 times the rate after 75 sec. The results are discussed in relation to the reactions occurring in the different zones of the blast furnace. W. P. R.

**Catalytic oxidation of carbon.**—See B., 1936, 675.

**Catalytic oxidation of carbon.** H. M. CASSEL (*J. Amer. Chem. Soc.*, 1936, 58, 1309—1310).—C, deposited on a glass surface from a gas flame, is more readily oxidised by  $\text{O}_2$  at  $600^\circ$  when the glass surface is roughened than when it is smooth. The reaction is probably facilitated wherever two adjacent crystals touch each other or project into the gaseous phase. The catalytic effect of NaCl on the combustion of C is discussed in this light. E. S. H.

**Catalytic properties of charcoal.** I. "Peroxidase" activity. C. SCHWOB (*J. Amer. Chem. Soc.*, 1936, 58, 1115—1117).—The peroxidase activity of C in the indophenol reaction has been determined at room temp. and  $p_{\text{H}}$  4.5. A hydrosol of C shows peroxidase activity in the formation of indophenol; no catalase activity has been observed. The C sol affects the e.m.f. of the cell  $\text{Pt}|\text{H}_2\text{O}_2, \text{KCl} (0.1N)|\text{Hg}_2\text{Cl}_2, \text{Hg}$  in the same way as does potato peroxidase. E. S. H.

**Reduction of carbon dioxide to methane.**—See B., 1936, 676.

**Catalytic investigation of alloys.** II. Decomposition of formic acid vapour on copper-silver alloys. G. RIENACKER and W. DIETZ (*Z. anorg. Chem.*, 1936, 228, 65—76; cf. this vol., 941).—The decomp. of  $\text{HCO}_2\text{H}$  on Ag-Cu catalysts (3, 59, 84, 92, 97% Ag) was measured by a flow method at  $180$ — $235^\circ$ . The activation energies for pure Cu and Ag were 21.6 and 18.8 kg.-cal., respectively. With 3% Ag (i.e., with excess of Cu component

embedded in eutectic) the val. was 17.3 kg.-cal. With 59% Ag it was 27.7 kg.-cal. The effect of composition on the activity of the catalyst is discussed.

H. J. E.

**Catalyst poisoning from the point of view of the specificity of active centres.** I. Relative durations of sojourn of ethyl alcohol and acetaldehyde molecules on copper. II. Effect of temperature on relative durations of sojourn of ethyl alcohol and acetaldehyde, and true activation energy of ethyl alcohol dehydrogenation on copper. A. BORK and A. A. BALANDIN (*Z. physikal. Chem.*, 1936, B, 33, 54—72, 73—82).—I. The dehydrogenation of EtOH to MeCHO has been studied at  $258^\circ$  by a streaming method, and the effect of MeCHO examined. The rate is given by  $dm/dt = k(M-m)/N$ , where  $M$  and  $N$  are the no. of EtOH mols. and total no. of mols. of all kinds, respectively, passing over the catalyst in unit time and  $m$  is the no. of EtOH mols. decomposed in unit time, and  $k$  contains no adsorption magnitudes. The above durations of sojourn are equal, and that of H.

II. This equality persists down to  $200^\circ$ . The true energy of activation is 12,800 g.-cal. per mol., and even near equilibrium is uninfluenced by the back reaction. The logarithmic relation between the consts. of Arrhenius' equation holds (cf. this vol., 435). The heats of adsorption of EtOH and MeCHO on the catalyst are equal. R. C.

**Vapour-phase catalytic oxidation of toluene.**—See B., 1936, 682.

**Mechanism of decomposition of methyl alcohol.** E. KUSS (*Angew. Chem.*, 1936, 49, 483—486).—The decomp. of MeOH at surfaces of fused  $\text{SiO}_2$ , Ag wool, Pt gauze, Al, Cu, Fe, CaO, and compressed charcoal can be interpreted on the basis of the reactions (a)  $\text{MeOH} \rightleftharpoons \text{CH}_3\text{O} + \text{H}_2$ , (b)  $2\text{MeOH} \rightleftharpoons \text{Me}_2\text{O} + \text{H}_2\text{O}$ , (c)  $\text{Me}_2\text{O} \rightleftharpoons \text{CH}_3 + \text{CH}_3\text{O}$ , (d)  $\text{Me}_2\text{O} \rightleftharpoons \text{CO} + \text{C} + 3\text{H}_2$ , (e)  $\text{CH}_3\text{O} \rightleftharpoons \text{CO} + \text{H}_2$ , (f)  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ . Ag and Al are the best sp. catalysts for reactions (a) and (b), respectively. Fe is initially a good catalyst for (a), but deteriorates rapidly owing to deposition of C produced by reactions (e) and (f). J. W. S.

**Electrolytic oxidation of sodium chloride to sodium chlorate.** L. DELAVENNA and J. MAILLARD (*Compt. rend.*, 1936, 202, 1663—1664).—The yield of  $\text{NaClO}_3$  in the electrolytic oxidation of NaCl has been improved by preventing the escape of  $\text{Cl}_2$  by rapid circulation of the electrolyte under pressure, employing a high anodic c.d., and cooling the liquid. With a c.d. at the anode of 20 amp. per sq. dm., in saturated NaCl at  $0^\circ$ , under a pressure of 400 cm.  $\text{H}_2\text{O}$ , the efficiency is 95% and  $\text{NaClO}_3$  of 99.5% purity separates. M. S. B.

**Electrolysis of aluminosilicates.** M. S. FORTUNATOV (*Mem. Inst. Chem. Ukrain. Acad. Sci.*, 1935, 2, 257—259).—Electrolysis of molten 1:2:12  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--NaHCO}_3$  leads to deposition of Si at the cathode. Al is not deposited before most of the Si has been eliminated. R. T.

**Electrolytic separation of polonium and radium-D.** G. B. PEGRAM and J. R. DUNNING (*Physical Rev.*, 1935, [ii], 47, 325).—Po and Ra-D

can be completely separated from solutions and from each other by the use of the Fink-Rohrman rapidly-spinning disc cathode. L. S. T.

**Effect of ultrasonic radiation on electro-deposits.** W. T. YOUNG and H. KERSTEN (J. Chem. Physics, 1936, 4, 426—427).—Sound waves with a frequency of about 1700 kc. produce ripples in electro-deposited Fe, Co, Cd, Zn, brass, or black Ni. It is suggested that stationary waves are set up in the solution and that the metal ions are relatively more conc. in layers separated by half  $\lambda$ . For Fe and Zn the best effect was obtained in conc. solutions.

H. J. E.

**Standardisation of photochemical methods for the measurement of solar ultra-violet radiation.** H. S. MAYERSON (Amer. J. Hyg., 1935, 22, 106—136).—Methods of controlling errors in the bleaching of a COMe<sub>2</sub>-methylene-blue mixture by light are given. The blackening of ZnS is satisfactory if the change in reflexion factor is measured. The H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>-UO<sub>2</sub>SO<sub>4</sub> method is best. CH. ABS. (e)

**Reactions induced by the photoactivation of the water molecule.** I. H. FRICKE and E. J. HART (J. Chem. Physics, 1936, 4, 418—422).—Unbuffered gas-free solutions of MeOH in H<sub>2</sub>O are decomposed to H<sub>2</sub> and CH<sub>2</sub>O (about 10—20% of the H<sub>2</sub> formed) on irradiation with  $\lambda$  1850—2000 Å. H<sub>2</sub>O alone is unchanged, but it absorbs these  $\lambda$  and serves to sensitise the decomp. of MeOH. H. J. E.

**Catalytic decomposition of hydrogen peroxide in a bromine-bromide solution. Effect of light on the steady-state rate.** R. LIVINGSTON and E. A. SCHOELD (J. Amer. Chem. Soc., 1936, 58, 1244—1246).—The rate is increased by light, but may be represented by  $V=k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$  for either the dark or light reaction. The increase in the abs. rate is explained by the increase in the steady-state [HBr]. The calc. average quantum yield for the reaction is < 1. E. S. H.

**Influence of wave-length of light on the development of the latent image.** (Mlle.) A. TOURNAIRE and E. VASSY (Compt. rend., 1936, 202, 1984—1986).—Measurements are recorded showing the effect of the time of development of the latent image on the density after development (for  $\lambda$  3520—2320 Å.). The development of the latent image depends on the  $\lambda$  of the light used. H. J. E.

**Photographic photometry in the extreme ultra-violet.** (MME.) R. HERMAN-MONTAGNE, L. HERMAN, and R. RICARD (Compt. rend., 1936, 202, 1668—1670).—When Na salicylate is used for sensitising Lumière plates (blue label) for use in the ultra-violet, the contrast factor for const. illumination is practically const. (to within 6%) not for the range 3000—1250 Å. only, but also up to 700 Å. These plates have been compared with those prepared by destroying the gelatin support of ordinary plates with dil. H<sub>2</sub>SO<sub>4</sub>. The latter are less sensitive than the former to strong but much more sensitive to feeble illumination, and are, therefore, more satisfactory for the detection of rays or bands of low intensity.

M. S. B.

**Photolysis of formaldehyde, acetaldehyde, and acetone at high temperatures.** E. I. AKEROYD and R. G. W. NORRISH (J.C.S., 1936, 890—894).—The results of previous workers are confirmed (cf. Leermakers, A., 1934, 976). MeCHO and CH<sub>2</sub>O exhibit chain reactions; COMe<sub>2</sub> does not. From vals. of the temp. coeffs. obtained from velocity readings between room temp. and 400° heats of activation of 9.8 kg.-cal. for MeCHO and 16.0 kg.-cal. for CH<sub>2</sub>O were obtained. A slight simplification of Leermakers' mechanism is proposed, and the propagation of the chains by Me radical carriers is confirmed.

D. C. J.

**Photochemical oxidation of formaldehyde and acetaldehyde.** J. E. CARRUTHERS and R. G. W. NORRISH (J.C.S., 1936, 1036—1042).—The oxidation of CH<sub>2</sub>O and MeCHO proceeds by short-length chains, that of CH<sub>2</sub>O being through HCO<sub>2</sub>H and of MeCHO through Ac<sub>2</sub>O<sub>2</sub> (cf. A., 1930, 434). No peroxide or peracid is formed in the case of CH<sub>2</sub>O. Quantum efficiencies for CH<sub>2</sub>O+O<sub>2</sub> and 2CH<sub>2</sub>O+O<sub>2</sub> give vals. of 12.6 and 9.0 mols. per quantum absorbed, respectively. For the MeCHO oxidation, determined in a closed system and by a flowing method, vals. of the order of 20 mols. per quantum absorbed are obtained.

D. C. J.

**Mechanism of the photo-decomposition of acetone.** R. SPENCE and W. WILD (Nature, 1936, 138, 206; cf. this vol., 437).—At room temp. the photo-decomp. of COMe<sub>2</sub> yields 1.5 vols. of C<sub>2</sub>H<sub>6</sub> to 1 of CO, and Ac<sub>2</sub> is also formed. At 60°, approx. equal amounts of CO and C<sub>2</sub>H<sub>6</sub> are formed together with some CH<sub>4</sub>. The primary photochemical process appears to be COMe<sub>2</sub>+ $h\nu$ →Me+MeCO (cf. A., 1934, 1184).

L. S. T.

**Photochemical peroxide formation.**—See this vol., 1091.

**Photochemical decomposition of vitamin-A.**—See this vol., 1159.

**Photo-reduction of fluorescent substances by ferrous ions.** J. WEISS (Nature, 1936, 138, 80—81).—A reply to criticism (this vol., 907). L. S. T.

**Effect of supersonic vibrations on chemical reactions.** S. SOKOLOV (Tech. Phys. U.S.S.R., 1936, 3, 176—182).—Exposure to supersonic vibrations tends to coagulate colloidal solutions which are on the point of coagulation, i.e., those in which the size of the particles is relatively great. On the other hand in some cases in which the colloid is almost completely pptd. exposure to supersonic vibrations results in re-dispersion of the colloid. Numerous examples of both cases are cited. Supersonic vibrations produce inversion in slightly acid solutions of sucrose but not in neutral solutions.

A. R. P.

**Sonic activation in chemical systems: oxidations at audible frequencies.** E. W. FLOSDORF, L. A. CHAMBERS, and W. M. MALISOFF (J. Amer. Chem. Soc., 1936, 58, 1069—1076).—A quant. investigation of the oxidation of H<sub>2</sub>O<sub>2</sub>, aq. NaCl, and aq. Na<sub>2</sub>SO<sub>3</sub> at audible frequencies shows that the reactions are brought about by the production of activated O in association with cavitation. A compound of Na 3-aminophthalhydrazide and



sonically-produced  $\text{H}_2\text{O}_2$  can be energised to produce chemiluminescence in absence of the usual secondary oxidants. E. S. H.

**Theoretical interpretation of radiochemical reactions via molecular clusters.** R. LIVINGSTON (Bull. Soc. chim. Belg., 1936, 45, 334—352; cf. A., 1934, 497).—A discussion of the various possible types of reaction occurring by  $\alpha$ -ray activation, based on the theories of Lind and of Mund (A., 1931, 1139). A theoretical expression is developed for the ionic yield in the special case where the chemical reaction occurs inside the "clusters" which, when applied to the system  $\text{Br}_2\text{--H}_2\text{--HBr}$ , gives results in fair agreement with the experiments of Lind and Livingston (this vol., 688), and when applied to the polymerisation of  $\text{C}_2\text{H}_2$  gives an expression very similar to that developed by Mund (A., 1931, 604).

R. C. M.

**Production of light water and determination of deuterium concentration in normal water.** N. MORITA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 403—413).— $\text{H}_2$  and  $\text{O}_2$  obtained respectively by fractional and complete electrolysis of  $\text{H}_2\text{O}$  were combined to form light  $\text{H}_2\text{O}$ . In this way variations in  $d$  due to the electrolytic separation of O isotopes were eliminated. By comparing  $d$  with the val. for ordinary  $\text{H}_2\text{O}$  the ratio D : H in the latter is 1 : < 5600.

C. R. H.

**Sodium xanthate.** L. FILIPCZYK and M. KULESZA (Rocz. Chem., 1936, 16, 245—253).—Pure Na xanthate (I) is prepared by adding excess of  $\text{CS}_2$  to NaOEt in EtOH, and, after 30 min. at  $0^\circ$ , adding 5 vols. of  $\text{Et}_2\text{O}$ , collecting the ppt. of  $\text{NaCS}_2(\text{OEt})_2\cdot\text{H}_2\text{O}$ , and dehydrating in vac. at  $35^\circ$ . When (I) is dissolved in ordinary distilled  $\text{H}_2\text{O}$  an emulsion forms, and the titre of the solution (I in KI) falls rapidly, whilst with twice-distilled,  $\text{CO}_2$ -free  $\text{H}_2\text{O}$  the clear solution obtained remains unchanged for 3—10 hr. R. T.

**Cuprous thiocyanate. Formation of coloured cuprous thiocyanate precipitates.** D. KRÜGER, W. BÜSSEM, and E. TSCHIRCH (Ber., 1936, 69, [B], 1601—1610).—Pure white  $\text{CuCNS}$ , obtained by slow, spontaneous decomp. of very dil. solutions of  $\text{Cu}(\text{CNS})_2$ , has an X-ray diagram with very few lines and appears to have a cryst. form of high symmetry, probably hexagonal or trigonal. Black  $\text{Cu}(\text{CNS})_2$  gives a diagram with many lines and appears of lower symmetry.  $\text{CuCNS}$  obtained by addition of  $\text{Na}_2\text{S}_2\text{O}_3$  to solutions of  $\text{Cu}(\text{CNS})_2\text{--H}_2\text{SO}_4$  appears rhombic and yields a diagram rich in lines; its formation cannot be attributed to  $\text{Na}_2\text{S}_2\text{O}_3$  or  $\text{Na}_2\text{S}_4\text{O}_6$  embedded in the lattice. Addition of small amounts of KI to neutral or acid solutions of  $\text{Cu}(\text{CNS})_2$  accelerates the separation of  $\text{CuCNS}$  and leads to the formation of ppts. ranging in colour from sandy to intensely violet. The possibility that the colour is due to adsorbed I is rendered improbable by the shade of the ppts. and excluded by the observation that violet deposits are obtained from solutions of  $\text{CuSO}_4\text{--KCNS--KI}$  of such small concn. that free I is not present. X-Ray examination of the violet material shows the presence of both modifications of  $\text{CuCNS}$  described above and a no. of new lines, including a very characteristic double line, not identical with those of  $\text{CuI}$

or  $\text{Cu}(\text{CNS})_2$  and ascribed to a third modification of  $\text{CuCNS}$ . H. W.

**Order of affinity of metals for copper, iron, cobalt, and nickel.** A. S. RUSSELL (Nature, 1936, 138, 161).—Certain metals show a definite order with respect to their power of combining with Cu, Fe, Co, and Ni. For combination with Cu, the order is Al, Sn, Zn, Cd, Hg, and Pb. If Cu be competed for by two of these metals the one earlier in the series combines to the exclusion of the other. When added to a compound of Cu and one of these metals, a metal earlier in the series displaces the combined metal completely. Ternary and even quaternary compounds may temporarily be formed, but ultimately the metal lower in the series is set free. With a metal later in the series no reaction occurs. With Fe the most stable compounds are  $\text{AlFe}_3$ ,  $\text{SnFe}_2$ ,  $\text{ZnFe}_7$ , and  $\text{HgFe}_4$  and the order is Al, Sn, Zn, Hg, Cd, and Pb. Neither Sn nor Zn can displace Al from  $\text{AlFe}_3$ , which is most easily prepared by adding Al to a Sn-Fe or Zn-Fe compound in Hg. With Co the most stable compounds are  $\text{AlCo}$ ,  $\text{SnCo}_2$ ,  $\text{ZnCo}$ , and  $\text{HgCo}$ , and with Ni,  $\text{AlNi}$ ,  $\text{Sn}_4\text{Ni}_5$ ,  $\text{ZnNi}$ , and  $\text{HgNi}$ . With Co and Ni, the order is the same as for Fe. L. S. T.

**Cuprotartrates.**—See this vol., 1093.

**Complex compounds of dicarboxylic acid hydrazides.** K. A. JENSEN and B. BAK (Z. anorg. Chem., 1936, 228, 83—88).—The blue cryst. compounds  $[\text{Cu}\{\text{X}(\text{NH}\cdot\text{NH}_2)\}_2]\text{SO}_4$  ( $\text{X}=\text{CHO}$ , Ac, or Bz) were prepared by interaction of aq.  $\text{CuSO}_4$  with the corresponding hydrazide and pptn. with EtOH. Hydrazides of the dicarboxylic acids yielded a series of cryst. compounds of the general formula  $[\text{Cu}\{(\text{NH}_2\cdot\text{NH})\text{C}(\text{O})_2(\text{CH}_2)_n\}_2]\text{SO}_4$  ( $n=2\text{--}8$ ). Hydrazides of  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{CH}_2(\text{CO}_2\text{H})_2$  gave compounds of variable composition containing > 1 atom of Cu to 1 mol. of hydrazide. H. J. E.

**Reactions in the solid state. II. Investigation of the formation of copper ferrite by the Hahn emanation method.** R. JAGITSCH and A. MASCHIN (Monatsh., 1936, 68, 101—108; cf. A., 1935, 1333).—Addition of  $\text{CuO}$  to active  $\text{Fe}_2\text{O}_3$  lowers the temp. at which the escape of emanation is a min. from approx.  $950^\circ$  to  $850^\circ$ .  $\text{CuO}$  has no effect up to  $650^\circ$ .  $\text{Fe}_2\text{O}_3$  decreases the escape of emanation from active  $\text{CuO}$  at  $> 600^\circ$ . Changes in activity with time at  $660\text{--}800^\circ$  were measured. The rate of formation of crvst. ferrite increases rapidly above  $700^\circ$ . H. J. E.

**Dehydration of brucite.** J. GARRIDO (Compt. rend., 1936, 203, 94—95).—The dehydration of brucite at temp. between  $500^\circ$  and  $1100^\circ$  has been studied in relation to the crystal form of the  $\text{MgO}$  formed.

C. R. H.

**Mechanism of dehydration of calcium sulphate hemihydrate.** H. B. WEISER, W. O. MILLIGAN, and W. C. EKHOLM (J. Amer. Chem. Soc., 1936, 58, 1261—1265).—Isobaric dehydration gives a definite step, indicating that  $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$  is a true hydrate. X-Ray examination shows that the hemihydrate and its dehydration product do not possess identical structures. E. S. H.

**Preparation of anhydrous calcium sulphate.** S. D. WILSON and L. TING-HSI (J. Chem. Eng. China, 1936, 3, 131).—Anhyd.  $\text{CaSO}_4$  for use as a laboratory desiccating agent is prepared from gypsum by heating at  $160^\circ$ , hydrating to give a slab of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , breaking this up, screening, and heating the sized fragments separately at  $240$ – $260^\circ$  for 2 hr. C. I.

**Formation of crystalline calcium silicate hydrate.** W. KOHLER (Tonind.-Ztg., 1935, 59, 739–740, 754–756; Chem. Zentr., 1935, ii, 3215).—Wollastonite was unchanged by heating for 14 days with 4 times its quantity of  $\text{H}_2\text{O}$  at  $100^\circ$ ,  $150^\circ$ ,  $212^\circ$ , and  $290^\circ$ .  $2\text{CaO} \cdot \text{SiO}_2$  when treated with  $\text{H}_2\text{O}$  at  $212^\circ$  and  $290^\circ$  formed  $2 \cdot 2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , which commenced to lose  $\text{H}_2\text{O}$  at  $>300^\circ$ . Hydrothermal treatment of  $3\text{CaO} \cdot \text{SiO}_2$  gave  $\text{Ca}(\text{OH})_2$  and doubly refractive needles of  $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$ , which may also be prepared hydrothermally from a mixture of ground quartz and  $\text{CaO}$ . H. J. E.

**Synthesis of hydrated monocalcium silicates under pressure.** (MLLE.) J. FORET (Compt. rend., 1936, 203, 80–83).— $\text{CaO}$  and  $\text{SiO}_2$ , 1 : 1, heated under pressure in presence of  $\text{H}_2\text{O}$  at temp. between  $100^\circ$  and  $200^\circ$ , yield  $\text{Ca}_1$  silicate of two different structures according as the temp. is  $<$  or  $> 140^\circ$ . C. R. H.

**Action of calcium carbide on methyl alcohol.**—See this vol., 1091.

**Crystallisation of zinc borate.** R. PARIS and P. MONDAIN-MONVAL (Compt. rend., 1936, 202, 2075–2077).—Crystallisation of  $3\text{ZnO} \cdot 2\text{B}_2\text{O}_3$  commences at  $500^\circ$ . The rate increases to a max. at  $820^\circ$  and then decreases up to the m.p. ( $980^\circ$ ). H. J. E.

**Argento-mercuric compound.** P. SPACU (Compt. rend., 1936, 202, 1987–1989).—The compound  $\text{Hg}(\text{CN})_2 \cdot \text{AgNO}_3 \cdot 2\text{H}_2\text{O}$  has a characteristic X-ray spectrum, and is therefore not a mixture of  $\text{Hg}(\text{CN})_2$  and  $\text{AgNO}_3$ . H. J. E.

**Antagonisms and alliances, experimentally demonstrated in effervescent and silent corrosion of aluminium, zinc, iron, tin, and lead in dilute acids, are of electrical nature.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1301–1303).—The electrical nature of corrosion is discussed. E. S. H.

**Theory agrees with experimental results concerning intrinsic and extrinsic impurities in metals immersed in dilute acids.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1303–1306).—The role of impurities in the dissolution of metals in acids is discussed. E. S. H.

**Alumina.** T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1936, 39, 203–204B).—Heating samples of  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  obtained from different sources produced  $\gamma\text{-Al}_2\text{O}_3$  at the same temp. but on subsequent further heating the change  $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$  took place at different temp. with the different samples. On heating  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Al}(\text{OAc})_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{AlCl}_3$ ,  $\gamma\text{-Al}_2\text{O}_3$  was first formed in all cases. T. W. P.

**Preparation of synthetic zeolites.** J. K. DELIMARSKI (Bull. Sci. Univ. Kiev, 1935, 1, 175–189).—Synthetic zeolite (I), in common with kaolin, under-

goes exothermic transformation at  $900$ – $1000^\circ$ . (I) is a salt of "permuteic acid" (II), sols of which may be obtained by treating (I) with dil.  $\text{HCl}$ . Gels of (II) yield (I) when treated with 4–5*N*- $\text{NaOH}$ ; such gels as do not exhibit the exothermic transformation at  $900^\circ$  will not yield active (I). R. T.

**[Reaction of tin with dilute acids.]** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1290–1294).—Thin Sn foil, impure, but without external heterogeneity, dissolves in dil.  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  with effervescence, but with thicker foil there is no effervescence. In the latter case, dissolution takes place through the reaction  $\text{Sn} + 2\text{HCl} + \text{O} \rightarrow \text{SnCl}_2 + \text{H}_2\text{O}$ . E. S. H.

**By their antagonisms and alliances, corrosion reactions tend towards a maximum or a minimum.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1306–1309).—Observations on the corrosion of tinplate in dil.  $\text{HCl}$  are discussed. E. S. H.

**Conditions for the preparation of oxide hydrates from ethylates and for the detection of hydrates from the  $p$ - $x$  curves.** P. A. THIESSEN and R. KOPPEN (Z. anorg. Chem., 1936, 228, 57–60; cf. A., 1931, 323).—A reply to criticisms by Weiser and Milligan (A., 1935, 433; this vol., 287). The formation of stable oxide hydrates of Sn, Si, Al, and Cr is reaffirmed. H. J. E.

**[Reaction of lead with dilute acids.]** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1294–1297).—Observations on the conditions under which effervescence occurs are reported. E. S. H.

**Hexametaphosphoric acid.** (MME.) R. SALIH (Bull. Soc. chim., 1936, [v], 3, 1391–1396).— $\text{H}_6(\text{PO}_3)_6$  has been prepared by decomp.  $\text{Pb}_3(\text{PO}_3)_6$  with  $\text{H}_2\text{S}$ . The aq. solution gives white gelatinous ppts. with  $\text{Ag}^+$  or  $\text{Pb}^{++}$ . Conductometric titration curves with  $\text{NaOH}$  show that all the H atoms are replaceable, the first four more easily than the remaining two. E. S. H.

**Preparation of hypophosphoric acid from  $\text{PCl}_3$ .** J. H. KOLITOWSKA (Rocz. Chem., 1936, 16, 313–317).— $\text{PCl}_3$  is hydrolysed at  $0^\circ$  in an acetate buffer at  $p_{\text{H}}$  5.7, and 0.1*N*-I is added;  $\text{H}_4\text{P}_2\text{O}_6$  is obtained in 10% yield. The probable reaction is  $\text{O} \cdot \text{PH}(\text{OH})_2 + \text{I}_2 \rightarrow 2\text{HI} + [\text{PO}(\text{OH})_2]_2$ . R. T.

**Isotopic separation of oxygen, chlorine, bromine, and nitrogen by chemical methods.** E. OGAWA (Bull. Chem. Soc. Japan, 1936, 11, 428–430).—Experiments which support the author's theories are described (cf. this vol., 1043). C. R. H.

**Hydrolysis of sulphur by water below  $100^\circ$ .** E. CHERBULIEZ and R. WEIBEL (Helv. Chim. Acta, 1936, 19, 796–801).—Hydrolysis proceeds by the reaction  $4\text{S} + 3\text{H}_2\text{O} = 2\text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_3$ . T. G. P.

**Reactions of selenium oxychloride and selenium tetrachloride with pyridine.**—See this vol., 998.

**Polymetatelluric acid esters.**—See this vol., 1097.

**Hexaiodotellurates of aromatic amines and heterocyclic bases.** T. KARANTASSIS and L. CAPAPOS (Compt. rend., 1936, 203, 83–84).—The hexaiodotellurates of  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7 \cdot \text{NH}_2$ ,  $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ,



benzidine, dianisidine, piperidine, and cinchonine have been prepared. The general formula is  $I_6Te(HB)_2$  or  $I_6TeH_2B$  according to whether  $B$  (base) is uni- or bi-valent. They are cryst., anhyd., and hydrolysed by  $H_2O$ . C. R. H.

**Preparation of Bjerrum's green hydrate of chromic chloride.** M. G. DE CELIS (Anal. Fis. Quim., 1936, 34, 553—556).—A modified method of prep. consists in slowly adding a solution of Recoura's chlorosulphate, cooled to  $0^\circ$ , to  $Et_2O$  saturated with  $HCl$ , at  $0^\circ$ , at the same time passing in a current of gaseous  $HCl$ . The yield of  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$  is  $>80\%$ . L. A. O'N.

**Extraction of uranium-X by ferric hydroxide precipitation.** M. BACHELET (Compt. rend., 1936, 203, 69—71).—Aq.  $UO_2(NO_3)_2$  (200 g. per litre) is treated, in presence of  $Fe^{III}$  salt, with sufficient aq.  $NH_3$  to give  $p_H$  3.55, at which  $p_H$  little U is pptd. The  $Fe(OH)_3$  ppt., containing U-X and some U, is collected, washed, and, after dissolving in  $HCl$ , is added to a solution of  $(NH_4)_2CO_3$  and  $(NH_4)_2S$ . U-X and U dissolve as double carbonates and, after concn.,  $HCl$  is added, and the solution boiled and filtered from S, which is inactive. Pptn. with aq.  $NH_3$  followed by ignition of the ppt. yields  $U_3O_8$  85—95% active. C. R. H.

**Isotope exchange between hydrogen bromide and bromine.** B. TOPLEY and J. WEISS (J.C.S., 1936, 912).—Br containing the radioactive isotope is added to approx. equiv. amounts of dry  $HBr$  in  $CCl_4$  solution, and the free Br immediately removed by Hg. The  $HgBr$  and the  $HBr$  in the filtrate are converted into  $AgCl$  and the sp. activities of the two  $AgBr$  samples are found to be equal. This complete interchange occurs at room temp. in  $<2$  min. Possible mechanisms of the interchange are discussed. D. C. J.

**Steel, partly tinned and polished, does not effervesce with dilute acids.** P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1297—1301). E. S. H.

**Ferric hydroxides, and ferrous and silver ferrites.** A. KRAUSE (Rocz. Chem., 1936, 16, 318—322).—Polemical, against Rodt (cf. A., 1934, 1320). R. T.

**Preparation and composition of wustite phases.** E. E. WOOD and J. B. FERGUSON (J. Washington Acad. Sci., 1936, 26, 289—293).—Attempts to obtain  $FeO$  by heating  $Fe(OH)_2$  prepared in an atm. of  $N_2$  gave a product containing 80.4%  $FeO$ . The product always contained some  $Fe^{III}$ , the amount being the greater the higher was the temp. of dehydration. A wustite is probably a primary product. The action of heat on  $FeC_2O_4$  in vac. does not give pure  $FeO$ .  $Fe$  and  $Fe_3O_4$  produced by the thermal decomp. of wustite recombine at higher temp. An attempt to make  $FeO$  by the complete combination of  $Fe$  and  $Fe_3O_4$  was unsuccessful. The limits of the wustite field were determined. A. J. M.

**Metal carbonyls. Metal carbonyl hydrides.** W. HIEBER [with K. KRAMER and H. SCHULTEN] (Angew. Chem., 1936, 49, 463—464; cf. A., 1932, 485; 1933, 685).— $Co(CO)_4$  (3 mols.) reacts with bases yielding *Co carbonyl hydride*  $Co(CO)_4H$  (2 mols.) and

$Co(CO)_3$  (1 mol.) with strong bases or  $Co(OH)_2$  (1 mol.) with weak bases. The compound has m.p.  $-22^\circ$  and decomposes above  $-18^\circ$  yielding  $Co(CO)_4$  and  $H_2$ . With complex *o*-phenanthroline-Ni and -Co ions it yields the compounds  $[Co(CO)_4]_2[Ni(C_{12}H_8N_2)_3]$  and  $[Co(CO)_4]_2[Co(C_{12}H_8N_2)_3]$ . With conc. solutions containing  $[Ni(NH_3)_6]^{2+}$  it yields the compound  $[Co(CO)_4]_2[Ni(NH_3)_6]$ . Action of conc. aq.  $NH_3$  on  $Co(CO)_4$  yields the compound  $[Co(CO)_4]_2[Co(NH_3)_6]$ . The series relationships of the Fe, Co, and Ni carbonyls and carbonyl hydrides and their structures are discussed. J. W. S.

**Action of ammonium chloride on oxides.** E. MONTIGNIE (Bull. Soc. chim., 1936, [v], 3, 1388—1389).—Aq.  $NH_4Cl$  partly dissolves hydroxides of Mg, Sn, Cd, Zn, Mn, or Fe. With hydroxides of Ni, Co, Cu, and Hg the products are  $NiCl_2 \cdot 8NiO \cdot 13H_2O$ ,  $CoCl_2 \cdot 3CoO \cdot 3H_2O$ ,  $CuCl_2 \cdot 3CuO \cdot xH_2O$ , and  $2HgCl_2 \cdot HgO$ , respectively.  $Ag_2O$  is converted into  $AgCl$ . E. S. H.

**Basic salts. XIV. Constitution of solid basic salts of bivalent metals. II. Basic nickel halides with simple laminated lattices.** W. FEITKNECHT and A. COLLET (Helv. Chim. Acta, 1936, 19, 831—841; cf. this vol., 669).—The hydrolysis of aq.  $NiCl_2$  above  $100^\circ$  yields  $NiCl_2 \cdot 3Ni(OH)_2$  or  $NiCl_2 \cdot Ni(OH)_2$  according to the concn. An ill-defined basic bromide, of ideal formula  $NiBr_2 \cdot 3Ni(OH)_2$ , has but a narrow homogeneity range. The lattices of these compounds have been studied by means of X-rays. T. G. P.

**Recent advances in microanalysis.** (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1936, 45, 189—212).—The trustworthiness of methods for determining the elements is tested (see also this vol., 1132). J. G. A. G.

**Analytically useful efficiency of chemical reactions.** A. SCHLEICHER (Z. anal. Chem., 1936, 105, 385—392).—The analytical efficiency of a reaction is made up of two factors, a capacity and an intensity factor; both factors can be derived from the abs. quantity in g. and the logarithm of the enrichment ( $\alpha$ ), where  $\alpha$  is the product of the relation between the initial and final concn. of the reactants, and the relation of the reaction consts. A. R. P.

**Foaming analysis.** W. O. OSTWALD and A. SIEHR (Kolloid-Z., 1936, 76, 33—46).—Foaming analysis is the production of a foam in a solution by agitation with a gas followed by continuous separation of the foam, thus giving a "spumate" and a residue. Apparatus and technique for foaming analysis are described. Examples of the recovery of dissolved substances from aq. solutions are given, and the technical applications of the process discussed. E. S. H.

**Determination of acidity in heavy water mixtures.** V. K. LA MER and S. KORMAN (Science, 1936, 83, 624—626).—D substitution exerts an influence  $>$  expected on the chemical properties of acid-base catalysis and acid dissociation consts. The quinhydrone electrode is satisfactory for measurements in the second case, and data are given for  $H_2O$ , quinol,  $AcOH$ , salicylic acid, etc. The effect of D

substitution appears to be sp., but, in general, is more pronounced for weaker acids. The potential of the quinhydrone electrode in HCl and DCl solutions is 0.0345 volt more positive in D<sub>2</sub>O than in H<sub>2</sub>O, owing to unsymmetrical distribution of D in  $QH_2 + 2DCl \rightleftharpoons QD_2 + 2HCl$ . Other exchange equilibrium consts. are tabulated.

L. S. T.

**New fluorescent indicators (naphthionic acid and Schaeffer's salt).** M. DÉRIBÉRE (Ann. Chim. Anal., 1936, [iii], 18, 173; cf. this vol., 810).—The fluorescence of Schaeffer's salt changes from zero below  $p_H$  5.0, through bluish-violet and greenish-blue to bright blue above  $p_H$  11. That of naphthionic acid changes from zero below  $p_H$  3 to bright blue between  $p_H$  6.5 and 9, thence to yellow-green between  $p_H$  10 and 12.

E. C. S.

**Indicators.** I. M. KOLTHOFF (Ind. Eng. Chem. [Anal.], 1936, 8, 237—239).—Future developments are discussed.

E. S. H.

**Preparation of diphenylamine indicator solution.** H. M. STATE (Ind. Eng. Chem. [Anal.], 1936, 8, 259).—Dissolution in H<sub>2</sub>SO<sub>4</sub> is facilitated by first melting the amine and then adding H<sub>2</sub>SO<sub>4</sub> to the liquid.

E. S. H.

**Determination of chlorides.**—See this vol., 1038.

**Determination of active chlorine in bleach liquors.**—See B., 1936, 692.

**Vanadium sulphate as a reducing agent.** II. **Determination of chlorates, nitrates, and persulphates.** P. C. BANERJEE (J. Indian Chem. Soc., 1936, 13, 301—304).—Chlorates and nitrates are reduced to chlorides and NH<sub>3</sub>, respectively, by VSO<sub>4</sub> in boiling dil. H<sub>2</sub>SO<sub>4</sub> and in a current of CO<sub>2</sub>. The reduction of persulphates takes place at room temp. in the presence of Fe<sup>III</sup> salt. In each case the excess of VSO<sub>4</sub> is titrated with KMnO<sub>4</sub> solution.

C. R. H.

**Application of Andrews' iodine monochloride method to the iodine bromide process.** R. LANG (Z. anal. Chem., 1936, 106, 12—23).—ICl solution treated with saturated aq. KBr in presence of CCl<sub>4</sub> first liberates I, which on further addition of KBr disappears again. This is attributed to the suppression of the [I'] through the action of excess of Br', causing recombination of I and Br (produced by initial decomp. of IBr) re-forming IBr. Presence of KBr (1.3 mol. per litre) also prevents hydrolysis of IBr to yield HBr, I, and HIO<sub>3</sub>, whereas KCl does not. To apply the IBr process to the determination of I or of I' by KIO<sub>3</sub>, the sample, containing >0.16 g. of I, is treated with 22 g. of KBr and 5 c.c. of conc. HCl and diluted to 100 c.c., 5 c.c. of CCl<sub>4</sub> being added. It is titrated with KIO<sub>3</sub> with vigorous agitation until the CCl<sub>4</sub> is decolorised. The method can also be used for titration of Sb<sup>III</sup> etc. in presence of [HCl] too great for the ICl method. For titration of reducing agents, e.g., CH<sub>2</sub>O, 10 c.c. of 0.05M-CH<sub>2</sub>O are treated with 5 c.c. of aq. ICl and 20 c.c. of 2.5N-NaOH in which 15 g. of KBr are dissolved. After 5—10 min., a further 22 g. of KBr are added and 10 c.c. of conc. HCl. The solution is diluted to 200 c.c. and titrated with KIO<sub>3</sub> in presence of CCl<sub>4</sub>. Other oxidising agents [KIO<sub>4</sub>, KMnO<sub>4</sub>, KBrO<sub>3</sub>, KClO<sub>3</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>, chloramine-T, Br,

and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>] can be used in place of KIO<sub>3</sub> in the titration of I' by this method.

J. W. S.

**Nephelometric determination of fluorine [in minerals].** R. E. STEVENS (Ind. Eng. Chem. [Anal.], 1936, 8, 248—252).—Decomp. of the mineral is effected by the Berzelius method and the resulting solution of F' and NaCl is treated with gelatin, EtOH, and CaCl<sub>2</sub>. CaF<sub>2</sub> is formed as a protected colloid and may be determined nephelometrically. The accuracy is about 1% of F. AsO<sub>4</sub><sup>'''</sup>, SO<sub>4</sub><sup>''</sup>, and PO<sub>4</sub><sup>'''</sup> interfere and should be removed.

E. S. H.

**Fluorescence method for the determination of low concentrations of ozone.** M. KONSTANTINOVA-SCHLESINGER (Acta. Physicochim. U.R.S.S., 1935, 3, 435—450).—Small quantities of O<sub>3</sub> are determined by passing the gas through an alcoholic solution of dihydroacridine. The acridine formed by oxidation is determined by photometric measurement of the intensity of its fluorescence.

O. D. S.

**Volumetric determination of selenocyanate.** G. SPACU and C. G. MACAROVICI (Z. anal. Chem., 1936, 105, 408—410).—KCNS<sub>2</sub> can be titrated in 20% aq. KNO<sub>3</sub> (to prevent hydrolysis) with 0.1N-AgNO<sub>3</sub>, using diphenylcarbazone as indicator.

**Potentiometric titration of selenocyanate.** R. RIPAN-TILICI (Z. anal. Chem., 1936, 105, 410—412).—The solution is titrated with Hg(ClO<sub>4</sub>)<sub>2</sub> using an amalgamated Pt wire as indicator electrode.

A. R. P.

**Determination of arsenic in analytical reagents.** C. BUSQUETS (Anal. Fis. Quím., 1936, 34, 557—579).—An apparatus for the rapid determination of small quantities (<0.0001 mg.) of As, by a modified Gutzeit method, is described. Limits of As permissible in the common reagents are tabulated.

L. A. O'N.

**Volumetric determination of antimony, arsenic, and iodide in the presence of bromide by L. W. Andrews' method.** A. MUTSCHIN (Z. anal. Chem., 1936, 106, 1—11).—The acidity in the titration of Sb<sup>III</sup> by Andrews' method (with KIO<sub>3</sub> in presence of CCl<sub>4</sub> or CHCl<sub>3</sub>) is preferably 20 c.c. of conc. HCl ( $d$  1.19) per 100 c.c. of final solution. It should be <15 c.c., but can be increased to 30 c.c. when large quantities of Sb are to be titrated; too high acidity retards the reaction. For the titration of HSbO<sub>2</sub> with KIO<sub>3</sub> in presence of ICl, the [HCl] should be 30—40 c.c. per 100 c.c. of final solution. Too little leads to hydrolysis of the ICl. Moderate addition of KBr or H<sub>2</sub>SO<sub>4</sub>, or dilution, does not affect the results. Potentiometric titration must be carried out in H<sub>2</sub>SO<sub>4</sub> solution, the potential change for 0.025 c.c. of 0.025M-KIO<sub>3</sub> being 0.2—0.3 volt. The optimum [HCl] for the titration of As<sup>III</sup> with KIO<sub>3</sub> in presence or absence of ICl is 30—40 c.c. per 100 c.c. of final solution. I' can be titrated with KIO<sub>3</sub> by Andrews' method in presence of any quantities of Cl' or Br'.

J. W. S.

**Micro-determination of silicon.** F. DE EDS and C. W. EDDY (J. Biol. Chem., 1936, 114, 667—672).—Si is determined by addition of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> and reducing the resultant yellow complex to a blue one with *p*-hydroxyphenylglycine; the colour de-



veloped is compared with a standard in a photo-electric colorimeter. H. D.

**Microchemical test for silicon.** L. W. STAPLES (Amer. Min., 1936, 21, 379—383).—1 mg. of the mineral is heated with 2 mg. of fluorite and 2 drops of conc.  $\text{H}_2\text{SO}_4$  in a Pt or Pb spoon at  $>75^\circ$  for 10 min. The  $\text{SiF}_4$  evolved is retained by 1 drop of dil.  $\text{HNO}_3$  (1:7) placed on the underside of a celluloid slide covering the spoon, which is embedded in a charcoal block. A small particle of NaCl is added to the solution of  $\text{H}_2\text{SiF}_6$  and the  $\text{Na}_2\text{SiF}_6$  is identified under the microscope. Ge but not Zr, Ti, or Sn minerals give the test.  $\text{BF}_3$  is not volatilised at the temp. used. The test is preferable to the metaphosphate bead, the Rb silicomolybdate, and the benzidine tests. L. S. T.

**Determination of carbon monoxide in air.**—See B., 1936, 693.

**Aqueous alcoholic uranyl magnesium reagent.** A. KRASSILCHIK (Compt. rend., 1936, 203, 78—80).—Errors arising from the micro-determination of Na by means of Blanchetiere's reagent are discussed and an improved technique is described. C. R. H.

**Determination of silver by means of potassium ferricyanide.** M. I. PERIE and M. M. LOBUNETZ (Bull. Sci. Univ. Kiev, 1935, 1, 141—145).—Excess of standard  $\text{K}_3\text{Fe}(\text{CN})_6$  and 2—3 g. of  $\text{KNO}_3$  are added to the solution at  $80$ — $90^\circ$ , the solution is filtered (ppt. washed with 2%  $\text{KNO}_3$ ), 1—2 g. of  $\text{ZnSO}_4$  and 10 c.c. of 10% KI are added to the filtrate, and the I liberated is titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$ . The results are 0.3% low; if, instead of filtering, the ppt. of  $\text{Ag}_3\text{Fe}(\text{CN})_6$  is allowed to settle and a sample of the supernatant fluid is taken, the error is +0.6%. R. T.

**Reaction adaptable to the volumetric determination of silver chloride.** G. A. D. HASLEWOOD (J.C.S., 1936, 1049).—Glacial AcOH added to a solution of AgCl in  $\text{Na}_2\text{S}_2\text{O}_3$  gives a cryst. ppt. corresponding with  $\text{Na}_5\text{Ag}_3(\text{S}_2\text{O}_3)_4 \cdot 2\text{H}_2\text{O}$ . The mother-liquor contains approx. 0.3 mg. per 100 c.c. calc. as AgCl. The ppt. from a known wt. of AgCl gives good results on dissolution in 0.01N-I and back titration with 0.005N- $\text{Na}_2\text{S}_2\text{O}_3$ . D. C. J.

**Rapid detection of silver halide in presence of silver cyanide.** R. E. D. CLARK (J.C.S., 1936, 1050).—On addition of  $\text{HNO}_3$ ,  $\text{AgNO}_3$ , and 5%  $\text{HgNO}_3$  solutions to a solution suspected of containing halide and  $\text{CN}'$ , the black coloration obtained if  $\text{CN}'$  is present dissolves in excess of  $\text{HgNO}_3$ , leaving a permanent white ppt. if halides are present. D. C. J.

**Gravimetric determination of barium by weighing as anhydrous oxalate.** G. DÍAZ VILLAMIL (Anal. Fís. Quím., 1936, 34, 580—586; cf. A., 1924, ii, 783).—Ba may be determined by pptn. as oxalate, drying in a current of air at  $250^\circ$  for 1 hr., and weighing as  $\text{BaC}_2\text{O}_4$ . This is definite and stable below  $300^\circ$ , and is little hygroscopic. It is not necessary to add EtOH before pptn. The accuracy is  $\pm 0.2\%$ . L. A. O'N.

**Determination of radioactivity.** A. R. OLSON, W. F. LIBBY, F. A. LONG, and R. S. HALFORD (J. Amer. Chem. Soc., 1936, 58, 1313—1314).—Modi-

fied procedure is described. The radioactive material is dissolved and the solution introduced into a counter. E. S. H.

**Sensitive reagents for the detection and determination of magnesium.** F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 184—186).—A 0.1% EtOH solution of *pp'*-dinitrodiazaminobenzene when added to aq.  $\text{Mg}(\text{OH})_2$  gives a heliotrope colour, whilst *p*-nitrobenzenediazoamino-4-nitronaphthalene gives a sky-blue.  $0.1 \times 10^{-6}$  g. of Mg per ml. may be detected with this reagent. *p*-Nitrobenzenediazoaminoazobenzene gives a cornflower-blue and 4-nitronaphthalene-4'-aminoazobenzene a cerise-blue. No hydroxide other than  $\text{Mg}(\text{OH})_2$  gives a colour with the latter. R. S.

**Polarisation effects in the spectral analysis of zinc and tin.** R. BRECKPOT (Natuurwetensch. Tijds., 1936, 18, 173—180).—Several elements (particularly In, Tl, Pb, Mg) show increased intensity when placed in the anode of an arc. Similar effects are observed, but to a smaller degree, with Sn. In these cases intensification is not due, as with Cu, to fractional volatilisation of the impurities. With Sn, As gives more intense lines in the cathode. Similar effects are obtained with either metals or oxides, and they are connected with the differences in ionisation potential of the impurities and the base metals. S. C.

**Spectrographic investigation in analysis.** J. VAN CALKER (Z. anal. Chem., 1936, 105, 396—406).—The spectrum is excited by an arc of 30,000 volts at 0.02 amp. operated from a Röntgen inductor supplied with 15—20 amp. at 100 volts at the primary. The substance is placed in a small cavity in the lower electrode consisting of a Cu, Fe, or Ag wire 8 mm. thick. The technique adopted is illustrated by the qual. analysis of bauxite, by the detection of Pb in a Swedish bituminous coal shale, by the analysis of a mineral  $\text{H}_2\text{O}$ , and by the detection and determination of minute amounts of Hg. A. R. P.

**Determination of cuprous oxide, cupric oxide, and copper in mixtures.** Microscopical method. S. ZERFOSS and M. L. WILLARD (Ind. Eng. Chem. [Anal.], 1936, 8, 303).—A statistical method is based on a microscopical count of the various particles, identified by the action of dil. HCl. E. S. H.

**Potentiometric determination of cerous salts with ferrocyanide.** I. A. ATANASIU (Z. anal. Chem., 1936, 105, 422—423).—Polemical against Spacu (this vol., 443). A. R. P.

**Colorimetric determination of iron as  $\text{Fe}(\text{CNS})_3$ .** M. BERTIAUX (Document. sci., 1935, 4, 49—52; Chem. Zentr., 1935, ii, 3135).—The effect of the concn. of the  $\text{NH}_4\text{CNS}$  solution on the intensity of the red colour has been studied. H. J. E.

**Detection of ferricyanide ions in insoluble ferricyanides.** L. KÜHLBERG (Z. anal. Chem., 1936, 106, 30—32).—When HCl-sol. ferricyanides (e.g., of Cd and Zn) or ferricyanides of metals with readily oxidisable hydroxides (Mn and Ce) are treated with a 1% solution of leuco-malachite-green in 50% HCl (I) and the solution diluted, a green colour is produced.  $\text{Hg}_3[\text{Fe}(\text{CN})_6]_2$  and  $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$  are detected by

decomp. with 1%  $\text{NiSO}_4$  and addition of excess of  $\text{NaOH}$ , when the  $\text{Ni}(\text{OH})_3$  pptd. yields a green colour on addition of (I).  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$  and  $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$  can be treated directly with  $\text{NaOH}$ , the  $\text{Ni}(\text{OH})_3$  and  $\text{Co}(\text{OH})_3$  oxidising the reagent.  $\text{Fe}(\text{CN})_6^{4-}$  in Turnbull's blue can be detected by treatment with 1% aq.  $\text{Ti}_2\text{SO}_4$  and then with excess of  $\text{NaOH}$ . The ppt.  $[\text{Ti}(\text{OH})_3, \text{Fe}(\text{OH})_3 \text{ and } \text{Fe}(\text{OH})_2]$  is collected and treated with an  $\text{AcOH}$  solution of benzidine, when the appearance of a blue colour indicates presence of  $\text{Fe}(\text{CN})_6^{4-}$ . This method can also be used to detect the presence of  $\text{Fe}(\text{CN})_6^{3-}$  in  $\text{Fe}(\text{CN})_6^{4-}$ .

J. W. S.

**Potentiometric determination of tungsten.** A. K. BABKO (Bull. Sci. Univ. Kiev, 1935, 1, 147—153).—The W is reduced to  $\text{W}^{\text{V}}$  by  $\text{Hg-Bi}$  in conc.  $\text{HCl}$ , and the  $\text{W}^{\text{V}}$  is determined by electro-titration to  $\text{W}^{\text{VI}}$  by means of  $\text{K}_2\text{Cr}_2\text{O}_7$ . Reduction to  $\text{W}^{\text{IV}}$  involves the use of large amounts of Zn, and is not recommended.  $\text{W}^{\text{III}}$ , obtained as  $[\text{W}_2\text{Cl}_9]^{3-}$  by reduction with  $\text{Hg-Pb}$  at  $50^\circ$ , has a high potential, and its transition to  $\text{W}^{\text{V}}$  is not distinct.  $\text{Hg-Pb}$  in the cold gives W as a complex,  $[\text{WCl}_5]^{2-}$ , having a lower potential than  $[\text{W}_2\text{Cl}_9]^{3-}$ , but considerable time is required for complete reduction. The method proposed consists in reduction with  $\text{Hg-Pb}$  to appearance of a red coloration (due to  $\text{W}^{\text{III}}$ ), and oxidation to a potential of +0.1 volt ( $\text{W}^{\text{V}}$ ), followed by further oxidation to  $\text{W}^{\text{VI}}$  (+0.35 volt).

R. T.

**Separation of tungsten from tin by 8-hydroxyquinoline in presence of sodium oxalate.** A. JÍLEK and A. RYŠANEK (Coll. Czech. Chem. Comm., 1936, 8, 246—260; cf. A., 1933, 584).—The quantities of W found in W-Sn mixtures by the method previously given are high since the W ppt. retains some stannic acid. The wt. of ppt. obtained from 40—100 mg. of W and 5—200 mg. of Sn in a medium of aq.  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{NaOAc}$ , 2%  $\text{AcOH}$ , and the reagent corresponds with the W, since the co-pptd. Sn compensates for the W left in solution. Double pptn. effects quant. separation. The solution is treated with 50 c.c. of 10%  $\text{H}_2\text{C}_2\text{O}_4$ , neutralised with  $\text{NaOH}$ , diluted to 200—250 c.c., and 2 c.c. of reagent (2 g. of 8-hydroxyquinoline in 5 c.c. of  $\text{Ac}_2\text{O}$ ) are added to the solution at  $60-80^\circ$ . After 1 hr. the ppt. is removed, washed first with aq.  $\text{Na}_2\text{C}_2\text{O}_4$  at  $70^\circ$ , then with reagent, and finally with  $\text{H}_2\text{O}$ , boiled with conc.  $\text{H}_2\text{SO}_4$ , cooled, and reheated after addition of  $\text{H}_2\text{O}_2$ . Excess of  $\text{NaOH}$  is added, and repptn. is effected with  $\text{H}_2\text{C}_2\text{O}_4$  etc. as above. The ppt. is ignited in presence of  $\text{H}_2\text{C}_2\text{O}_4$ .

J. G. A. G.

**Colour reactions of ter- and quadri-valent titanium.** M. SCHENK (Helv. Chim. Acta, 1936, 19, 625—639).—Aq.  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$  sulphates react to give a brownish-violet complex containing  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$  in the ratio 4:3.  $\text{Ti}^{\text{III}}$  sulphate gives an intense blue compound with conc. aq. alkali thiocyanates, but the reaction is unsuitable for quant. analysis. The reaction between  $\text{Ti}^{\text{IV}}$  solutions and  $\text{H}_2\text{O}_2$  has been investigated.

T. G. P.

**Separation of bismuth from lead and copper.** E. A. OSTROUMOV (Z. anal. Chem., 1936, 106, 36—45).—Bi and Pb can be separated by Moser and Maxymovicz'  $\text{Br}^--\text{BrO}_3^-$  hydrolysis method (A., 1926, 264),

by Feigl and Ordell's pyrogallol method, or by Pinkus and Dernies' cupferron method (A., 1928, 1109). The method of Benkert and Smith (A., 1897, ii, 435) leads to irregular results. Bi can be separated from Cu by Moser and Maxymovicz' method and also by a modification of the cyanide method. In each case the first method is preferred. The pyrogallol method cannot be used in presence of a large excess of Cu.

J. W. S.

**Specific reaction for bismuth by production of the monoxide.** N. A. TANANAEV (Z. anal. Chem., 1936, 105, 419—422).—The reagent,  $\text{K}_4\text{Mn}(\text{CN})_6$  (I), is prepared by adding aq. 10%  $\text{MnSO}_4$  to a 0.5—0.33-saturated KCN solution until the ppt. first formed only just redissolves. On adding a Bi solution in 1:10  $\text{HCl}$  to (I) a black ring of  $\text{BiO}$  forms at the interface. To detect Bi in Cu the metal is dissolved in  $\text{HNO}_3$ ,  $\text{FeCl}_3$  added followed by aq.  $\text{NH}_3$ , and the well-washed ppt. dissolved in 1:10  $\text{HCl}$  for the test. Ag and Hg do not interfere.

A. R. P.

**Analytical chemistry of tantalum, niobium, and their mineral associates.** XXXI. Determination of tungsten in earth-acid minerals. W. R. SCHOELLER and E. F. WATERHOUSE (Analyst, 1936, 61, 449—455; cf. this vol., 696).—The W is pptd. with the earth acids by tartaric hydrolysis at fairly high concn. (cf. A., 1934, 983) and then determined by pptn. with a slightly ammoniacal aq. Mg salt (A., 1935, 1217). High  $\text{WO}_3$  contents lead to negative errors of 0.0003—0.002 g., and it is recommended that for such cases a correction, deduced by experiment on a synthetic mixture, be applied.

J. W. S.

**Thermoregulator of the ordinary type, regulating the heating current without a relay.** K. KALINOWSKI (Rocz. Chem., 1936, 16, 288—289).

R. T.

**Apparatus for the maintenance of a graded series of constant temperatures.** S. O. MAST (Science, 1936, 84, 69—70).

L. S. T.

**Precision m.-p. apparatus.** E. B. HERSHBERG (Ind. Eng. Chem. [Anal.], 1936, 8, 312—313).—A mechanically-stirred, electrically-heated, cyclic liquid bath for use with capillary-tube specimens is described.

E. S. H.

**Micro-determination of b.p. of liquids at different pressures.** E. E. HAYS, F. W. HART, and R. G. GUSTAVSON (Ind. Eng. Chem. [Anal.], 1936, 8, 286).—The apparatus can be used for determining b.p. at pressures between 10 and 900 mm.

E. S. H.

**Adiabatic calorimeter.** W. WEINRICH and H. GASTARI (Ind. Eng. Chem. [Anal.], 1936, 8, 307—310).—Apparatus in which the rate of  $\text{O}_2$  absorption and rate of temp. change due to the heat of reaction of finely-divided substances with  $\text{O}_2$  are measured is described. Adiabatic conditions are maintained by a differential thermopile and a photo-electric relay; the  $\text{O}_2$  pressure is controlled automatically by an electronic relay and an electrolysis cell. Experiments with bituminous coal at 1 atm. and 50 initial temp. show that  $\text{O}_2$  absorption and rise of temp. are nearly linear functions of time.



Balanced circuit for resistance thermometers, combustible gas indicators, etc. M. G. JACOBSON (Physical Rev., 1935, [ii], 47, 336). L. S. T.

Simon desorption method between temperatures of 90° and 40° abs. A. VAN ITTERBEEK and W. VEREYCHEN (Physica, 1936, 3, 666—671).—Apparatus is described by means of which temp. of 67—45° abs. are obtained. O. D. S.

Spectral transmission of developed photographic emulsions. M. ROULLEAU (Compt. rend., 1936, 202, 2066—2067).—Data for the transmission of various types of plate for  $\lambda$  8650—3650 Å. are discussed. The type of developer used has a small influence. H. J. E.

Physical methods in chemical laboratories. XXXII. New method of quantitative emission spectrum analysis, applicable also as a micro-method. G. SCHEIBE and A. RIVAS (Angew. Chem., 1936, 49, 443—446).—The material is dissolved and about 0.01 c.c. of the solution placed on each electrode of a C arc. The initial spectrum is photographed over a period of 30 sec., the arc current being maintained const. The relative intensities of certain lines of each element are measured. The method is particularly applicable to the determination of traces of one metal in another and is illustrated by data for Mg in Al and Al and Cr in Fe. J. W. S.

Identification of crystalline materials. Classification and use of X-ray diffraction patterns. J. D. HANAWALT and H. W. RINN (Ind. Eng. Chem. [Anal.], 1936, 8, 244—247).—The identification of X-ray patterns by comparison with a collection of standard patterns is discussed. E. S. H.

Improved grating microspectrograph and its use in chemical microscopy. E. E. JELLEY (J. Roy. Microscop. Soc., 1936, [iii], 56, 101—112).—An improved grating instrument, allowing visual observation of orthoscopic and conoscopic interference effects and their spectra, is described. Spectra may be photographed without disturbing the adjustments of the crystal and polarising microscope. The dispersion is such that the distance between centres of adjacent perforations of the film corresponds with 50 m $\mu$ , the perforations providing an accurate  $\lambda$  scale. A Wollaston prism on a sliding mount provides for the study of pleochroism. A technique for studying and recording the dichroism and trichroism of minute crystals is described. N. M. B.

Arc support for routine spectroanalysis. R. BRECKPOT (Bull. Soc. chim. Belg., 1936, 45, 375—378).—An improved form of Gramont's support is described. The electrode holders are detachable, thus permitting the removal of oxide dust which would otherwise cause contamination. Fumes should be drawn into a glass dust chamber above the arc. R. C. M.

Polarisation effects in the Hilger E1 quartz spectrograph. J. W. ELLIS and J. KAPLAN (Physical Rev., 1935, [ii], 47, 255).—Serious limitations encountered when the light is partly or wholly polarised are described. L. S. T.

Technique of polarimetric determination in condensed gases. A. I. SCHATTENSTEIN (Acta

Physicochim. U.R.S.S., 1935, 3, 53—60).—The method of determining the rotation of the plane of polarisation of optically active substances dissolved in condensed gases is described. The results of determinations of the sp. rotation of sucrose in liquid NH<sub>3</sub>, and of santonamide in the presence of salts in liquid NH<sub>3</sub>, are recorded. A. J. M.

Magneto-optic method of chemical analysis. III. Location of minima and quantitative analysis. S. S. COOPER and T. R. BALL (J. Chem. Educ., 1936, 13, 326—328; cf. this vol., 949).—Procedure is detailed using salicylic acid as an example. L. S. T.

Photography of minima in magneto-optic apparatus. G. HUGHES and R. GOSLIN (Physical Rev., 1935, [ii], 47, 317).—The reality and reproducibility of the min. have been photographically demonstrated. L. S. T.

Automatic ionisation spectrometer. W. A. WOOSTER and A. J. P. MARTIN (Proc. Roy. Soc., 1936, A, 155, 150—172).—An apparatus in which a crystal, having been once set, is moved automatically through a pre-arranged series of reflecting positions has been designed. The crystal and ionisation chamber are moved together slowly through the reflecting ranges while the ionisation current is automatically recorded, and rapidly in between. L. L. B.

Physical methods in chemical laboratories. XXXI. Determination of dielectric loss as a physico-chemical method of investigation. L. ROHDE, P. WULFF, and H. SCHWINDT (Angew. Chem., 1936, 49, 437—443).—The method of measurement of dielectric loss factor is described and its application to the testing of commercial oils etc. discussed. Presence of OH groups produces especially high losses. In presence of CO<sub>2</sub>H groups, the loss factor increases with rising temp. to a max. and then decreases, this being attributed to the dissociation of double mols. J. W. S.

Mass spectrograph. W. B. PIETENPOL (Physical Rev., 1935, [ii], 47, 331—332).—A new type well suited to bracketing methods of determining isotopic wts. is described. L. S. T.

Construction and use of Geiger-Muller counters. G. L. LOCHER (Physical Rev., 1935, [ii], 47, 326).—Technique of construction, criteria, and tests are described. L. S. T.

High-speed Geiger-counter circuit. H. V. NEHER and W. W. HARPER (Physical Rev., 1936, [ii], 49, 940—943).—An improved circuit is described. N. M. B.

New ion source for mass spectroscopy. A. J. DEMPSTER (Physical Rev., 1935, [ii], 47, 331; cf. A., 1935, 677). L. S. T.

Measurement of small rapidly changing gas volumes. H. LORENZ (Z. Physik, 1936, 100, 761—769).—Vols. of 0.1 c.c. changing within 0.1 sec. can be measured to 0.01 c.c. A. B. D. C.

Burette with automatic zero adjustment. J. BITSKEI and B. BITSKEI (Z. anal. Chem., 1936, 105, 406—408).—The burette has a conical upper end which protrudes just inside a pear-shaped bulb having

its lower end inclined downwards and joined to a thick-walled vertical tube passing to the bottom of the stock-bottle holding the standard solution. The bottle is provided with a side-tube and rubber bulb for forcing the liquid into the burette. A. R. P.

**The micro-balance.** G. GORBACH (*Mikrochem.*, 1936, 20, 254—336).—A comprehensive review.

**Pressure regulator for a partial vacuum.** E. CHERBULIEZ (*Helv. Chim. Acta*, 1936, 19, 794—795). T. G. P.

**Experimental methods for the kinetic study of the oxidation of metals.** G. VALENSI (*Bull. Soc. chim.*, 1936, [v], 3, 1405—1422).—Apparatus and technique, with the corresponding methods of calculation of results, are described. E. S. H.

**Jena glass apparatus for the chemical laboratory.** P. H. PRAUSNITZ and H. SCHÄFER (*Oesterr. Chem.-Ztg.*, 1936, 39, 114—116).—New and modified apparatus is described. E. S. H.

**Apparatus for determination of the adsorption of small quantities of gas by solutions.** H. E. BENT, W. F. GRESHAM, and N. B. KEEVIL (*J. Amer. Chem. Soc.*, 1936, 58, 1307—1309).—Apparatus and procedure are described. E. S. H.

**Electrodialyser.** F. E. BARTELL (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 247).—Apparatus is described. E. S. H.

**Micro-vaporimetric determination of mol. wt.** J. B. NIEDERL, O. R. TRAUTZ, and A. A. PLENTL (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 252—255).—Modified apparatus for v.d. determinations of substances of b.p.  $> 320^\circ$  is described. E. S. H.

**Measuring the thickness of thin, flowing, liquid films.** H. H. BECK and K. G. WECKEL (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 258—259).—The shift in the reflected beam, when an incident beam of light is directed on to the surface at  $45^\circ$ , gives a measure of changes in thickness of films covering the surface. E. S. H.

**Making extremely thin films.** J. D. HOWE and E. M. PURCELL (*Physical Rev.*, 1935, [ii], 47, 329; cf. this vol., 183). L. S. T.

**Concentric cylinder viscosimeters.** L. SQUIRES and R. L. DOCKENDORFF (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 295—297).—By applying the relation between friction factor and Reynolds no.,  $\eta$  of liquids can be determined in a concentric-cylinder viscosimeter even when the liquids are so fluid that their motion during the determination is turbulent. E. S. H.

**Modification of the suspended-level viscosimeter.** E. H. PAYNE and C. C. MILLER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 300—302). E. S. H.

**Dynamic surface tension from liquid bells.** E. BUCHWALD and H. KÖNIG (*Ann. Physik*, 1936, [v], 26, 659—672).—In a method for the determination of the dynamic surface tension  $\alpha_{dyn}$ , a stream of liquid impinges on a plate forming a liquid bell. A surface tension equation based on the theory of Boussinesq holds over a wide range of conditions if the thickness of the bell is  $>$  a certain val.  $\alpha_{dyn}$  is  $5-8\% > \alpha_{stat.}$  for  $H_2O$ ,  $EtOH$ ,  $AcOH$ , and  $EtOAc$ ,

and 16.4% greater in the case of  $CCl_4$ , owing to diminished mol. orientation, whilst the  $\alpha_{dyn}$  and of  $C_6H_6$  are equal. R. S.

**Preparation of flattened copper tubing coils.** E. P. BARRETT and W. L. BARRETT (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 311).—Procedure for flattening, coiling, and joining Cu tubes is described. E. S. H.

**Laboratory stirrer.** E. B. HERSHBERG (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 313).—Agitation of solid-liquid mixtures is facilitated by attaching corrosion-resistant alloy wire to a glass stirrer. E. S. H.

**Organic combustion apparatus for highly volatile and inflammable liquids.** J. H. BRUUN and W. B. M. FAULCONER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 315—316). E. S. H.

**Apparatus for [quantitative] semi-micro-hydrogenations.** L. ZECHMEISTER and L. VON CHOLNOKY (*Chem.-Ztg.*, 1936, 60, 655—656).—A simple volumetric method, of accuracy 1—3%, for use at room temp. and in presence of a catalyst is described. R. C. M.

**Illumination of menisci.** J. ZELENY (*Rev. Sci. Instr.*, 1936, [ii], 7, 289; cf. Collins and Blaisdell, *ibid.*, 213).—A simple and efficient method, using white paper ruled at  $45^\circ$  with black lines, is described. N. M. B.

**Technique for making sound ingots for density determinations.** P. G. WALDO and W. P. DAVEY (*Physical Rev.*, 1935, [ii], 47, 338). L. S. T.

**High-speed oil-diffusion pump.** H. W. EDWARDS (*Physical Rev.*, 1935, [ii], 47, 259; cf. A., 1935, 840). L. S. T.

**Centrifugal filtration tube.** D. F. HOUSTON and C. P. SAYLOR (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 302).—The centrifuge tube is provided with a filtration crucible, perforated support, and receiver for the filtrate. E. S. H.

**Filter trains.** P. BRUERE (*J. Pharm. Chim.*, 1936, [viii], 24, 49—58).—Filters for the ventilators of rooms used for collective gas protection are described and their control is discussed. F. N. W.

**Ultrafiltration and concentration by ultrafiltration by a centrifuge method.** R. BRINKMAN and J. VAN STEINFORN (*Biochem. J.*, 1936, 30, 1523—1525).—By coating porcelain cylinders with water-glass, ultrafilters are obtained which are not clogged by the disperse phase, and will withstand prolonged use. 2 c.c. of filtrate can be obtained in 10 min. J. N. A.

**Micro- and macro-Kjeldahl steam-distillation apparatus.** J. M. FIFE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 316).—Modified apparatus is described. E. S. H.

**Glass head for laboratory water still.** P. F. SHARP and E. B. STRUBLE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 316). E. S. H.

**Moisture tube.** H. B. ALEXANDER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 314).—The apparatus is based on the principle of distillation with a  $H_2O$ -immiscible solvent. E. S. H.



**Overhead heater for rapid evaporation, drying, and charring.** L. F. NIMS and M. K. HORWITT (Ind. Eng. Chem. [Anal.], 1936, 8, 275).—Heating is by radiation from an electrical heating element, placed above the containers. E. S. H.

**Battery-type stand assembly for distilling equipment.** R. L. MOBLEY (Ind. Eng. Chem. [Anal.], 1936, 8, 281). E. S. H.

**Lecture experiment in combustion chemistry.** K. CLUSIUS and H. GUTSCHMIDT (Angew. Chem., 1936, 49, 446—447).—The temp. of an electric oven is raised slowly while a current of air is drawn through it and a drop of hydrocarbon periodically dropped in. The temp. when the drop first ignites spontaneously is noted. The temp. is then allowed to fall and the temp. noted when drops cease to ignite. Addition of 1%  $\text{Fe}(\text{CO})_5$  or 1.5%  $\text{EtNO}_2$  raises or lowers the ignition temp., respectively, and illustrates the effects of knocks and antiknocks. J. W. S.

**Distribution of gas in liquids.** P. H. PRAUSNITZ (Kolloid-Z., 1936, 76, 227).—A lecture experi-

ment, illustrating the influence of surface tension on bubble size, is described. E. S. H.

**Conception of elements in chemistry. II. Ancient Greek philosophy.** V. A. PLOTNIKOV, I. L. KATZNELSON, and O. V. BERNSCHEIN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 3—36).—Philosophical. R. T.

**Ruska's researches on the alchemy of Al-Razi.** R. WINDERLICH (J. Chem. Educ., 1936, 13, 313—315). L. S. T.

**Beraut's theory of calcination (1747).** D. MCKIE (Ann. Sci., 1936, 1, 269—293).—Historical. E. S. H.

**Precursors of rhenium and masurium.** J. G. F. DRUCE (Chem. and Ind., 1936, 577—578).—Several of the unsubstantiated claims for the discovery of new elements during the last century possibly corresponded with Ma and two, perhaps, to Re, whilst others may have been Hf. R. C. M.

## Geochemistry.

**Content of heavy water (deuterium oxide) in medicinal mineral waters.** K. HANSEN, E. RUSTUNG and J. HVEDING (Klin. Woch., 1935, 14, 684—685; Chem. Zentr., 1935, ii, 2921).—No deviation from the normal isotope ratio was detected in many medicinal waters. J. S. A.

**Geochemical significance of the hydrolysis of sulphur by water.** E. CHERBULIEZ and A. HERZENSTEIN (Helv. Chim. Acta, 1936, 19, 801—806; cf. this vol., 1079).—The origin of the S compounds and especially the significance of the ratio  $\text{H}_2\text{S} : \text{S}_2\text{O}_3^{2-}$  in natural waters are discussed. T. G. P.

**Alkali waters of the London chalk layers.** J. LEPERSONNE (Bull. Soc. géol. Belg., 1934—1935, 58, 38—63; Chem. Zentr., 1935, ii, 3080).—Normal hard  $\text{H}_2\text{O}$  and strongly alkaline fresh  $\text{H}_2\text{O}$  are found. The latter comes from a base exchange in the glauconite-bearing sands, and contains  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ , and  $\text{NaI}$ . H. J. E.

**Mineral waters of Arequipa, Peru.** E. POZZI-ESCOR (Bull. Soc. chim., 1936, [v], 3, 1382).—Free  $\text{Cl}_2$  and  $\text{NaIO}_3$  have been detected. E. S. H.

**Colorimetric determination of the  $p_{\text{H}}$  of some Peruvian waters.** L. PRÓ Y CASTILLO (Bol. Soc. Quim. Peru, 1936, 2, 7—8).—The  $p_{\text{H}}$  vals. of natural waters (at the temp. of the source), and drinking waters have been determined. L. A. O'N.

**Radioactivity of some natural springs in the Kabylie de Collo (Constantine, Algeria).** M. ROUBAULT (Compt. rend., 1936, 203, 100—101).—Eight springs occurring in eocene schists and in granite masses were examined, those from the latter sources having the greatest activity. C. R. H.

**Alkali metals in natural waters.** R. BOSSUET (Compt. rend., 1936, 203, 63—65).—Natural waters of Corsica, Algeria, Tunis, and Madagascar are

divided into two groups according to the presence or absence of Cs. C. R. H.

**"Brown" snowfall in New Hampshire and Vermont.** W. O. ROBINSON (Science, 1936, 83, 596).—Dust of colloidal dimensions from the fall of brown snow at Wells River, Vermont, contained  $\text{SiO}_2$  48.9,  $\text{Al}_2\text{O}_3$  20.4,  $\text{Fe}_2\text{O}_3$  6.1,  $\text{CaO}$  5.4,  $\text{MgO}$  3.2, loss on ignition 16.0%. L. S. T.

**Sulphur in cyrtolite and its indication of galena.** O. B. MUENCH (Amer. Min., 1936, 21, 374—378).—The S determinations recorded throw no light on the low val. for the at. wt. of Pb obtained for Bedford cyrtolite (A., 1935, 558). Both samples of Bedford cyrtolite contained the same % S. L. S. T.

**Mineralogy and origin of the Taconic limonites.** D. H. NEWLAND (Econ. Geol., 1936, 31, 133—155).—Siderite is probably the parent source of much of the limonite of the Taconic belt of eastern New York and western New England. The deposits are consistently manganiferous (1—2%) and the high  $\text{SiO}_2$  content (10—20%) is due partly to admixed detrital quartz and feldspar and partly to amorphous  $\text{SiO}_2$  in the groundmass. Appreciable amounts of carbonaceous matter are frequently present and pyrite and Zn are const. minor constituents. L. S. T.

**Mineralised spherulitic limestone in the Cheltenham [St. Louis] fireclay.** V. T. ALLEN (Amer. Min., 1936, 21, 369—373).—The limestone described contains quartz, calcite, pyrite, ankerite, and sphalerite, probably deposited in this order. The spherulites have  $\text{CaCO}_3$  75.57,  $\text{MgCO}_3$  1.64,  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  1.12,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{BaO}$  none, insol. 18.88% [R. F. ROLUFS]. The origin of the spherulites is discussed. L. S. T.

**Nepheline contrasts.** N. L. BOWEN and R. B. ELLESTAD (Amer. Min., 1936, 21, 363—368).—

Chemical analyses of nepheline from a Na-rich phonolite, typical of the E. African Rift, and from a K-rich melilite-leucite nephelinite, typical of the Central African Rift, show that the two nephelines are Na- and K-rich, respectively, emphasising, contrary to the view of Morozewicz (A., 1929, 45), the variability of the composition of nepheline and its control by the parent magma. L. S. T.

**Metamorphic differentiation at contacts between serpentinite and siliceous country rocks.** A. H. PHILLIPS and H. H. HESS (Amer. Min., 1936, 21, 333—362).—The changes in mineralogical composition, supported by chemical analyses, which have resulted from the permeation of hydrothermal solutions along contacts between serpentinite and siliceous country rock are described for several localities. An explanation of the origin of the mineral zones is given and the general process of metamorphic differentiation involved is discussed. L. S. T.

**Ejected blocks of the Laacher See district.** G. KALB and P. M. HOPMANN (Tsch. Min. Petr. Mitt., 1936, 48, 1—26; cf. A., 1935, 60; 1936, 307).—Further examples are given of the formation of sanidinites of various kinds from cryst. schists. L. J. S.

**Rare stylolites.** P. B. STOCKDALE (Amer. J. Sci., 1936, [v], 32, 129—133).—In all observed cases the origin is consistent with the solution theory. L. J. S.

**Variation of the lead-uranium-thorium ratio in a single crystal of uraninite.** C. M. ALTER and E. M. KIPP (Amer. J. Sci., 1936, [v], 32, 120—128; cf. this vol., 135).—Successive layers of a single crystal from Wilberforce, Ontario, were dissolved in  $\text{HNO}_3$  and the following determinations made on the outer (I), intermediate (II), and central (III) sections. (I) was brown, and U had already been leached from it, but (II) and (III) were black and pure, and from these the age is now given as  $760 \times 10^7$  years. (I) Pb 9.739, U 37.848, Th 8.360%; Pb/(U+0.36Th) 0.2383; (II) 11.927, 58.475, 14.093%; 0.1877; (III) 11.865, 60.699, 8.051%; 0.1866. L. J. S.

**Tectonics of the Nemours region.** M. GAUTIER (Compt. rend., 1936, 202, 2092—2094). H. J. E.

**Tin occurrence in marble at Arandis, S.W. Africa.** P. RAMDOHR (Neues Jahrb. Min., 1935, A, 70, 1—48; Chem. Zentr., 1935, ii, 3080).—The minerals are described. H. J. E.

**Thermal analysis of the hydrated iron ores of Krivoi Rog.** V. A. IZBEKOV and K. J. SKARTSCHENKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 31—44).—The presence and approx. content of hydrated ores can be determined from the heating curves of the ore, under standard conditions. R. T.

**Zircon discoloured by sunlight (hyacinthine).** K. CHUDOKA (Deut. Goldschmiede-Ztg., 1935, 38, 303—304; Chem. Zentr., 1935, ii, 3219).—Zircons from Laacher Lake and Mongka lost their rose colour after 1 min. irradiation in direct sunlight and became grey. A brownish-red colour was restored by exposure to  $\text{RaBr}_2$ , or (more slowly) on keeping in the dark. The latter effect is due to radioactive substances in the mineral. H. J. E.

**Rare earth content of European and Japanese argillite.** E. MINAMI (Nachr. Ges. Wiss. Göttingen, 1935, IV, 1, 155—170; Chem. Zentr., 1935, ii, 3218).—The average rare earth contents of European and Japanese palaeozoic argillites were 0.0243 and 0.0225%, respectively. That of Japanese mesozoic argillite was 0.0173%. H. J. E.

**Origin of the segmental coloration of amethyst and smoky quartz.** C. FRONDEL (Amer. Museum Nov., 1935, No. 758, 15 pp.).—Examples are described. The phenomenon is attributed to the variation, with respect to crystallographic forms, of the rates of absorption of pigment during growth. CH. ABS. (e)

**Primary banding in basic plutonic rocks.** R. R. COATS (J. Geol., 1936, 44, 407—419).—The nature and suggested modes of origin of the mineralogically dissimilar bands often observed in basic plutonic rocks are reviewed. A mechanism, supported by experiments with labradorite and pyroxene, involving simultaneous crystallisation and differential settling of two or more minerals in a lighter magma, is suggested for the production of some of these bands. L. S. T.

**Granitic sequence in the Southern Complex of Upper Michigan.** R. M. DICKEY (J. Geol., 1936, 44, 317—340).—Granites representing three distinct periods of pre-Cambrian intrusion are described. L. S. T.

**Helium content of beryls.** H. J. WALKER (Physical Rev., 1935, [ii], 47, 969).—A discussion. The He content of beryls may be due to the disintegration of non-radioactive Be isotopes. L. S. T.

**Sun-burning [of basaltic rocks].** W. HOPPE (Z. deut. geol. Ges., 1935, 87, 452—473; Chem. Zentr., 1935, ii, 3220).—The phenomenon is found in basic but not in acid basalts. It differs from normal weathering in that it originates in the glassy material, in which hydrolysis and subsequent hydration occur. A grey layer is formed. It may be produced artificially by boiling for 40 hr. with  $\text{H}_2\text{O}$ , followed by prolonged treatment with  $\text{CO}_2$ . H. J. E.

**Sun-burning [of basaltic rocks].** H. STUTZEL (Z. deut. geol. Ges., 1935, 87, 473—480; Chem. Zentr., 1935, ii, 3220; cf. preceding abstract).—The characteristic appearance of the rock is described. H. J. E.

**Immiscible silicate melts, approximating in their composition to that of natural rocks.** D. P. GRIGORIEV (Zentr. Min., 1935, A, 242—254; Chem. Zentr., 1935, ii, 3219).—Melts of complex silicate tend to separate into two layers. A melt of alum (10), quartz (30),  $\text{MgCO}_3$  (30),  $\text{CaF}_2$  (5), and  $\text{B}_2\text{O}_3$  (2 pts.) forms on slowly cooling an upper dark glassy layer containing tridymite, a lower layer of Mg mica, and an intermediate layer. H. J. E.

**Baryte deposits of Virginia.** R. E. EDMUNDSON (Amer. Inst. Min. Met. Eng., 1936, Tech. Publ., 725, 17 pp.).—Baryte in Virginia occurs in fissure veins, replacement deposits, breccia zones, and residual deposits, in limestones and igneous rocks. The average content of BaO in the limestones is 0.06% and in a pegmatite 0.12%. The mineral could not have



been derived by leaching from these country-rocks. It was no doubt deposited by magmatic waters.

L. J. S.

**Ore-body zoning.** L. B. RILEY (Econ. Geol., 1936, 31, 170—184).—A method for examining ore-body zoning, *i.e.*, spacial variation of minerals and elements around and within an ore, is described. Examination of an incompletely oxidised Ag-Pb ore body at Sierra Mojada, Coahuila, Mexico, is used to illustrate the method, optical and micro-chemical tests being employed to detect the ions and minerals present.

L. S. T.

**Gold-bismuth occurrence in British Columbia.** H. V. WARREN (Econ. Geol., 1936, 31, 205—211).—Galenobismutite (I) (Bi 51.00, Pb 30.50, Fe 1.50, S 16.40, total 99.40%) and cosalite (II) (Pb 41.20, Bi 39.35, Cu 3.60, S 16.40, total 100.55%) accompany the pyrite (III) which occurs massive or cryst. to the extent of 10—25% in the quartz veins of the Cariboo Gold Quartz Mine. Free Au is associated with (I) and (II), which proves the hypogene nature of the ore bodies. A telluride has also been found with (I). The paragenesis is probably (III) and quartz, followed by (III); galena and sphalerite; ankerite (?); (II), (I), and Au. L. S. T.

**Minor intrusions of Glen Shee, Perthshire.** W. O. WILLIAMSON (Geol. Mag., 1936, 73, 145—157).—Additional data are given (*cf.* this vol., 185).

L. S. T.

**Xenolithic pegmatite in the Dalbeattie "granite."** M. MACGREGOR (Geol. Mag., 1936, 73, 171—185).—A pegmatite containing numerous xenoliths of more basic rock found in this "granite" is described. Interaction of the xenoliths and the pegmatite, and the origin of the xenolithic pegmatite, are discussed.

L. S. T.

**Heavy accessories of certain pre-Cambrian intrusives of the Canadian Shield.** E. L. BRUCE and W. JEWITT (Geol. Mag., 1936, 73, 193—213).—All the granites from the different localities examined contain zircon, apatite, and titanite, and some contain rutile. The crystal habits of these heavy accessories vary widely.

L. S. T.

**Hierro and Gomera Islands (Canary Archipelago).** E. JÉRÉMINE (Bull. Soc. franç. Min., 1935, 58, 350—362).—Trachytes, basalts, limburgites, tephrites, and basaltic tuffs composing Hierro Island are described, and an analysis of ankaratrite from Ajate, near Valverde, is given. Trachytes, phonolites, trahitites, andesites, and basalts from Gomera are also described.

L. S. T.

**Tin deposits of Llallagua, Bolivia.** E. AHLFELD (Econ. Geol., 1936, 31, 219—221).—A discussion of previous conclusions (A., 1935, 601).

L. S. T.

**Xenoliths in the Organ batholith, New Mexico.** K. C. DUNHAM and M. A. PEACOCK (Amer. Min., 1936, 21, 312—320).—The geology and mineralogy of large xenoliths near South Canyon and metamorphic effects are described. Green diopside [F. A. GONYER] ( $\text{SiO}_2$  53.10,  $\text{TiO}_2$  0.17,  $\text{Al}_2\text{O}_3$  2.55,  $\text{Fe}_2\text{O}_3$  none,  $\text{Cr}_2\text{O}_3$  none,  $\text{FeO}$  0.97,  $\text{MnO}$  0.08,  $\text{MgO}$  17.25,  $\text{CaO}$  25.80,  $\text{H}_2\text{O}$  0.04, total 99.96%) is associated with the uvarovite.

L. S. T.

**Peculiar type of zoning in feldspar.** J. M. TREFETHEN (Amer. Min., 1936, 21, 327—329).

L. S. T.

**Hydrothermal leaching in the Virginia mining district, New Mexico.** S. G. LASKY (Econ. Geol., 1936, 31, 156—169).—The tourmaline-Cu deposits of this district lie along veins that have been plugged and reopened repeatedly during the process of mineral deposition. Between the second and third stages of deposition the solutions removed calcite, sericite, and chlorite from interstitial and included fragments of altered wall rock in the veins, producing first- and second-stage minerals, chiefly specularite, quartz, and chalcopryite, on which minerals of later stages were deposited. A mechanism is suggested to account for their presence at places previously traversed by alkaline or neutral solutions.

L. S. T.

**Hydrothermal experiments with lead and zinc minerals.** O. H. KRISTOFFERSON (Econ. Geol., 1936, 31, 185—204).—The extent to which  $\text{PbCl}_2$  and  $\text{ZnCl}_2$  can be transported in the vapour phase in presence of  $\text{H}_2\text{O}$  and  $\text{HCl}$  vapour at temp.  $>500^\circ$  has been determined. Below  $290^\circ$ , sphalerites ( $\text{ZnS}$ ) from various localities were unaffected by steam + 20%  $\text{HCl}$ . Above  $290^\circ$ , the Zn volatilises as  $\text{ZnCl}_2$ , and curves showing decomp. and volatilisation from  $300^\circ$  to  $500^\circ$  are given. Steam alone had no effect. Galena from Yellowstone, Wisconsin, is tarnished by steam above  $300^\circ$  owing to oxide formation. With steam and  $\text{HCl}$  in a dynamic system, volatilisation commences at  $300^\circ$ , and at  $400^\circ$   $\text{PbCl}_2$  accumulates in the system; at  $475^\circ$ , loss by volatilisation practically equals the amount of  $\text{PbCl}_2$  formed, and above  $475^\circ$  the amount volatilised increases rapidly. The bearing of these results on the deposition of minerals is discussed.

L. S. T.

**Ice as an agent of rock weathering.** O. R. GRAWE (J. Geol., 1936, 44, 173—182).

L. S. T.

**South Hill lamprophyre, Jersey.** H. G. SMITH (Geol. Mag., 1936, 73, 87—91).—The mineral composition of the intrusion is described.

L. S. T.

**Reverse and oscillatory zoning in plagioclase feldspars.** E. S. HILLS (Geol. Mag., 1936, 73, 49—56).—A discussion of Phemister's theory (A., 1934, 862), and other possible causes of reverse zoning.

L. S. T.

**Pyroxmangite, new locality: identity of sobralite and pyroxmangite.** E. P. HENDERSON and J. J. GLASS (Amer. Min., 1936, 21, 273—294).—Pyroxmangite (I) from Idaho has  $\text{SiO}_2$  45.47,  $\text{MnO}$  27.06,  $\text{FeO}$  20.91,  $\text{CaO}$  2.62,  $\text{MgO}$  2.14,  $\text{Fe}_2\text{O}_3$  1.50,  $\text{H}_2\text{O}$  0.32, total 100.02% [E. P. HENDERSON] and  $\alpha$  1.737,  $\beta$  1.740,  $\gamma$  1.754 ( $\pm 0.001$ ). Physical, optical, chemical, and X-ray properties agree with those of the mineral from the original locality at Iva, S. Carolina. Sobralite from Sweden is identical with (I). Comparison of (I) and rhodonite shows differences in optical properties, and X-ray patterns indicate a structural difference which justifies the retention of both mineral species.

L. S. T.

**Amygdaloidal dykes.** R. S. MOEHLMAN (Amer. Min., 1936, 21, 329—331).

L. S. T.

**Notation of polymorphic modifications.** A. K. BOLDYREV (Tsch. Min. Petr. Mitt., 1936, 47, 517—

522)—Four different notations are noted; that which gives  $\alpha$ ,  $\beta$ ,  $\gamma$  in the chronological order of discovery of each modification is recommended. For example,  $\alpha$ -quartz (low quartz, quartz<sub>-575</sub>,  $\beta$ -quartz of Boeke) and  $\beta$ -quartz (high quartz, quartz<sub>+575</sub>,  $\alpha$ -quartz of Boeke). Boeke's notation, according to the order of lower temp. stability, is not practicable when there are several modifications, as with ice and S. L. J. S.

**Chemical composition of the titanomagnetites.** G. JOURAVSKY (Compt. rend., 1936, 202, 1689—1691).—The chemical composition and physical properties of titanomagnetites (I) are not in agreement with the assumption that they are solid solutions of magnetite and ilmenite in a state of false equilibrium through rapid cooling.  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  are both present in considerable amount and may both play an important part in the formation of (I).

M. S. B.

**Uranotile.** V. BILLIET (Natuurwetensch. Tijds., 1936, 18, 79).—X-Ray investigation confirms the formula  $\text{CaO}, 2\text{UO}_3, 2\text{SiO}_2, 6\text{H}_2\text{O}$ . Uranotile forms rhombic crystals isomorphous with sklodowskite (A., 1924, ii, 868).

D. R. D.

**New cobalt minerals.** L. DE LEENHEER (Natuurwetensch. Tijds., 1936, 18, 77—78).—Three Co minerals found in Katanga (Belgian Congo) are described, viz., black ore,  $2\text{Mn}_2\text{O}_3, 3\text{Co}_2\text{O}_3, 5\text{CuO}, 15\text{H}_2\text{O}$  or  $(\text{Mn}, \text{Co})_2\text{O}_3, \text{CuO}, 3\text{H}_2\text{O}$ ; boodtite,  $5\text{Co}_2\text{O}_3, \text{CuO}, \text{Fe}_2\text{O}_3, 11\text{H}_2\text{O}$  or  $2[\text{Co}_2\text{O}_3(\text{CuO}, \text{Fe}_2\text{O}_3)], 3\text{H}_2\text{O}$ ; and a mineral  $3(\text{Mn}_2\text{O}_3, \text{MnO}_2), \text{Co}_2\text{O}_3, 3\text{CuO}, 8\text{H}_2\text{O}$ . Mindigi spherocobaltite is a mixture containing 57% of rhombohedral mixed crystals of  $\text{CoCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{FeCO}_3$ , and small proportions of malachite, quartz, hematite, mindigit, chalcopryrite, bornite, linnæite, phyllite, cyanite, and tourmaline.

D. R. D.

**Dissolution, transportation, and precipitation of manganese.** W. S. SAVAGE (Econ. Geol., 1936, 31, 278—297).—Primary Mn in rocks is dissolved mainly by the action of percolating carbonated waters. Peat solution is the next most effective solvent. Distilled  $\text{H}_2\text{O}$  is a poor solvent, but has a solvent action on the Mn in diabase > that on the Mn in syenite. Oxygenated  $\text{H}_2\text{O}$  has the least solvent action, but is more effective on diabase than on syenite. Mn is transported chiefly as  $\text{Mn}(\text{HCO}_3)_2$  in  $\text{H}_2\text{CO}_3$ -acid waters, and when these become neutral or slightly alkaline some unstable  $\text{Mn}(\text{OH})_2$  will be formed and remain in solution. Further transportation can take place with  $\text{Mn}(\text{HCO}_3)_2$  and  $\text{Mn}(\text{OH})_2$  in unstable equilibrium until conditions which result in pptn. are encountered. The presence of org. matter in the  $\text{H}_2\text{O}$  does not appear to affect the transportation of Mn under these conditions. Conditions which effect pptn. such as aeration, the alkaline reaction of certain bacteria, and passage over a limestone bed are discussed.

L. S. T.

**Genesis of the Tri-state zinc and lead ores.** J. RIDGE (Econ. Geol., 1936, 31, 298—313).—The jasperoid is composed of small xenomorphic crystals of quartz, the dark colour being due to org. matter. The paragenesis of the minerals is discussed.

L. S. T.

**Structure and primary mineralisation of the zinc mine at Balmat, New York.** J. S. BROWN (Econ. Geol., 1936, 31, 233—258).—The geology of the district, the nature of the deposit and its constituent minerals are described. The origin of the Zn ores from solutions derived from underlying igneous masses, probably a pre-Cambrian granite, is discussed. A chemical and a mineralogical analysis of the ore are recorded.

L. S. T.

**Elasticity of rock melts.** M. P. VOLAROVITSCHEV and A. A. LEONTEVA (Z. anorg. Chem., 1936, 228, 28—32).—Measurements at 870—1120° on two basalts and one diabase are recorded. The temp. of initial crystallisation was 1060—1150°.

H. J. E.

**Economic application of the insoluble residue method.** H. S. McQUEEN (Amer. Inst. Min. Met. Eng., 1936, Tech. Publ. 724, 12 pp.).—The residues obtained by treatment of limestone and dolomites or other sedimentary rocks containing  $\text{MgCO}_3$  and  $\text{CaCO}_3$  with dil. HCl permit correlations to be made between widely separated regions and different geological provinces. The successful economic application of the method in the drilling of  $\text{H}_2\text{O}$ , oil, and gas wells, in the study of ore deposits, and in the sp. investigation of limestones, is described.

L. S. T.

**Luminescence investigations with fluorites and other minerals.** H. HABERLANDT (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, 143, 591—596; Chem. Zentr., 1935, ii, 3066; cf. A., 1935, 915).—The yellowish-white photo-fluorescence of certain fluorites is due to bituminous impurities. Lines of the rare earths and of U were observed for other specimens.

H. J. E.

**Synthetic emerald.** JAEGER and ESPIG (Deut. Goldschmiede-Ztg., 1935, 38, 347—349; Chem. Zentr., 1935, ii, 2992).—Synthetic emeralds identical in physical properties, crystal structure, zoned structure, etc. with the natural stone have been prepared and are now produced industrially.

J. S. A.

**Tin in Rumania.** G. CRUGLICOV (Miniera, 1935, 10, No. 5—6, 5—8; No. 7—8; 5—9; Chem. Zentr., 1935, ii, 2936).—Deposits in the mountains of southern Roumania are considered to be of economic val.

J. S. A.

**Formation of carbon dendrites.** K. D. LUKE, W. M. MADGIN, and H. L. RILEY (Nature, 1936, 138, 161—162).—The formation of C dendrites by the cathodic reduction of colloidal solutions of graphitic oxide is described.

L. S. T.

**Crystals of pyrites in ironstone concretions in coal formations.** A. SCHÖP (Natuurwetensch. Tijds., 1936, 18, 167—172).—Ironstone (sphaeroidite) consists of ankerite or some carbonate of similar composition and not of pure siderite. The reason for the occurrence therein of  $\text{FeS}_2$  is discussed.

D. R. D.

**Alteration of coal seams by intrusion of igneous dykes.**—See B., 1936, 674.

**Rate of fall of meteoric material on the earth.** C. C. WYLLIE (Physical Rev., 1935, [ii], 47, 192).—The annual amount of meteoric material estimated is 10 g. per sq. mile.

L. S. T.



## Organic Chemistry.

**Variation of physical constants in homologous series. I. Hydrocarbons.** V. G. ARANDA (Anal. Fis. Quim., 1936, **34**, 513—524).—The mol. vol. at 20° of hydrocarbons is given by  $V = aM + b$ , where  $a$  is 1.155, the quotient of the increment for each  $\text{CH}_2$  and its mol. wt. ( $M$ ), and  $b$  is for paraffins 30.3; olefines 25.8; diolefines 21.3; cyclopentanes 16.7; cyclohexanes 14.8; cycloheptanes 9.7; cyclohexenes 6.4; cyclohexadienes 4.4; aromatic hydrocarbons —0.8. Hence  $d$  is  $1/(1.155 + b/M)$ , where  $b$  has the above vals.;  $d$  is thus a hyperbolic function of  $M$  and when  $M$  is high,  $d$  for all the series approaches the val. 0.8658.  $n^{20}$  has similarly a common formula  $(1.815M + a)^{1/2}/(0.825M + c)^{1/2}$ , where, for the paraffins,  $a$  is 33.382,  $c$  28.759; olefines,  $a$  29.268,  $c$  24.066; cyclohexanes,  $a$  and  $c$ , 14.800; cyclohexenes,  $a$  6.786,  $c$  6.207; aromatic hydrocarbons,  $a$  0.358,  $c$  —1.379.  $d$  is thus a hyperbolic function of  $M$  tending to the val. 1.4832 for high vals. of  $M$ . The surface tension similarly may be represented  $(2.7857 + d)^4/(1.155M + b)$  and the parachor,  $2.7857M - d$ , where  $b$  has the vals. given above and  $d$  is for paraffins 28.6; olefines 23.2; diolefines 17.8; cyclohexanes 6.1; cyclohexenes 0.7; cyclohexadienes —4.7; aromatic hydrocarbons —10.1.

F. R. G.

**Decomposition of gaseous paraffins induced by ethylene oxide.** L. S. ECHOLS, jun., and R. N. PEASE (J. Amer. Chem. Soc., 1936, **58**, 1317; cf. Heckert and Mack, A., 1929, 1243).— $\text{C}_3\text{H}_8$  and  $n$ - and  $iso$ - $\text{C}_4\text{H}_{10}$ , but not  $\text{C}_2\text{H}_6$ , are "cracked" in presence of decomposing  $(\text{CH}_2)_2\text{O}$  at 425°. The relative amount of olefine produced increases with the size of the paraffin and the amount initially present. Fletcher's results (this vol., 570) on the accelerated decomp. of  $\text{MeCHO}$  by  $(\text{CH}_2)_2\text{O}$  are confirmed.

H. B.

**Action of nitrosyl chloride on  $n$ -hexane in presence of light.** S. MITCHELL and S. C. CARSON (J.C.S., 1936, 1005—1006).— $\text{NOCl}$  and  $n$ - $\text{C}_6\text{H}_{14}$  in bright sunlight form a brown oil, which on steam-distillation gives  $\text{COMeBu}^a$  and  $\text{COEtPr}^a$ . By excluding red light, a blue solution which probably contains  $\beta\beta$ - and  $\gamma\gamma$ -chloronitrosohexanes is obtained. The blue liquid undergoes two changes with red light; in the absence of  $\text{O}_2$ , oxime hydrochlorides are formed, and in its presence, photo-oxidation takes place.

F. R. S.

**Heptadecane. Action of selenium on stearic acid.** S. H. BERTRAM (Chem. Weekblad, 1936, **33**, 457—459).— $\text{C}_{17}\text{H}_{36}$  is formed in approx. 50% yield by heating stearic acid with Se at 310—325°. The remainder is dehydrogenated to  $\text{C}_{17}\text{H}_{34}$ . There is no evidence of formation of oleic or elaidic acid.

S. C.

**Olefine formation.** S. C. J. OLIVIER (Rec. trav. chim., 1936, **55**, 567—568).—Contrary to Taylor (A., 1935, 1465)  $\text{CHMeBr}$ , and  $\text{KOH}$ -aq.  $\text{EtOH}$  give mainly  $\text{C}_6\text{H}_8\text{Br}$  and a little  $\text{C}_6\text{H}_8$ , but no  $\text{MeCHO}$ .

R. S. C.

**Inhibition of chemical reactions. VI. Influence of ether and nitrobenzene on the absorption of ethylene by sulphuric acid.**—See this vol., 1075.

**Significance of organo-compounds of alkali metals in synthesis.** K. ZIEGLER (Angew. Chem., 1936, **49**, 455—460, 499—502).—A review.

E. W. W.

**Effect of oxygen on reaction between bromine and butadiene.** G. B. HEISIG and H. M. DAVIS (J. Amer. Chem. Soc., 1936, **58**, 1095—1097).—Addition (method: A., 1935, 827) of  $\text{Br}$  (1 mol.) to butadiene (1 mol.) occurs much more rapidly with  $\ll 2$  mm. of  $\text{O}_2$ , the total pressure being atm. Reaction is fast even in presence of  $\text{O}_2$  (2 and 375 mm.). These and previous results (*loc. cit.*) suggest a chain mechanism with short chains initiated at the surface.

H. B.

**Unimolecular elimination and the significance of the electrical conduction, racemisation, and halogen replacement of organic halides in solution.** E. D. HUGHES, C. K. INGOLD, and A. D. SCOTT (Nature, 1936, **138**, 120—121).— $\text{Bu}^n\text{Cl}$  absorbs  $\text{Br}$  quantitatively in  $\text{SO}_2$  to yield isobutylene dibromide and  $\text{HCl}$ , suggesting a somewhat rapid equilibrium  $\text{Bu}^n\text{Cl} + \text{CMe}_2\text{CH}_2 + \text{HCl}$ . Pure  $\text{CHPhMeCl}$  in pure  $\text{SO}_2$  does not give a conducting solution, but addition of  $\text{Br}$  produces a quant. yield of  $\text{CHPhBr} + \text{CH}_2\text{Br}$ . When conditions of purity are such that conduction takes place,  $\text{CHPh}:\text{CH}_2$  and  $\text{HCl}$  are present. These results and others on racemisation, and unimol. replacement of halogen in  $\text{SO}_2$ , are grouped under a general mechanism in which ionisation of the halide determines the rate, and the instability of an alkyl cation containing a potential proton is responsible for the production of olefine.

L. S. T.

**Heavy chloroform,  $\text{CDCl}_3$ .** R. TRUCHET (Compt. rend., 1936, **202**, 1997—1998).—Addition of  $\text{D}_2\text{O}$  to a suspension of  $\text{CaO}$  in  $\text{CCl}_3\text{CHO}$  affords mainly trichlorodeuteromethane, b.p. 61.3—61.5°, as shown by its Raman spectrum which includes three pairs of lines, three polarisable and three non-polarisable. The increment in mol. refraction due to  $\text{D}$  is 1.11.

J. L. D.

**$s$ -Tetrachlorodideuteroethane.** F. W. BREUER (J. Amer. Chem. Soc., 1936, **58**, 1289—1290).— $\text{C}_2\text{D}_2$  and  $\text{Cl}_2$  in presence of light and a carrier (prepared by action of  $\text{Cl}_2$  on a mixture of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Sb}$ , and sand on asbestos) give  $s$ -tetrachlorodideuteroethane (I), b.p.  $145.7 \pm 0.05/737$  mm. The v.p. of (I) at 20—80° is 6—9% < that of  $s$ - $\text{C}_2\text{H}_2\text{Cl}_4$ .

H. B.

**Bromination of nitromethane.**—See this vol., 1075.

**Decomposition of methyl alcohol.**—See this vol., 1076.

**Synthesis under pressure of aliphatic compounds.** (SIR) G. T. MORGAN (Bull. Soc. chim. Belg., 1936, **45**, 287—312).—A review. At 400°/200 atm. using  $\text{CoSO}_4$  with some  $\text{CuO}$  and  $\text{MnO}$  as catalyst,  $\text{CO}_2$  and  $\text{H}_2$  give a mixture containing  $\text{MeOH}$  (17%),  $\text{EtOH}$  (22%), higher alcohols, chiefly normal (11%), and  $\text{CH}_4$  (47%). From  $\text{EtOH}$  and  $\text{CO}_2$  at 370°/150 atm.  $\text{Bu}^n\text{OH}$  (19.5%), hexyl (4.6%), octyl (1.2%), and higher alcohols (1%) are obtained. Using  $\text{H}_3\text{PO}_4$  and  $\text{Cu}_3(\text{PO}_4)_2$  as catalyst at 330—340°, from  $\text{MeOH}$ ,

the largest yield of AcOH is 44.9% with 9.5% Me<sub>2</sub>O. EtCO<sub>2</sub>H and higher acids may be obtained similarly in small yield from the corresponding alcohol, the active substance being the olefine derived by dehydration from the alcohol.

F. R. S.

#### Action of calcium carbide on methyl alcohol.

A. CONTARDI and B. CIOCCA (R. Ist. lombardo Sci. Lett., Rend., [ii], 1935, 68, 126—128; Chem. Zentr., 1935, ii, 3085).—Ca(OMe)<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> are formed vigorously at room temp.; hence CaC<sub>2</sub> cannot be used, in the presence of MeOH, for determination of H<sub>2</sub>O.

H. N. R.

**Electrolysis of organic substances in non-aqueous media.** II. G. GIACOMELLO (Gazzetta, 1936, 66, 350—357; cf. A., 1935, 1349).—Electrolysis of NaOMe in MeOH containing CO<sub>2</sub> yields at the cathode H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and some CO, and Na<sub>2</sub>CO<sub>3</sub>; that of NaOMe and HCO<sub>2</sub>Me in MeOH gives H<sub>2</sub> and much more CO, with some CO<sub>2</sub> and CH<sub>4</sub>. Conductivity of NaOMe—HCO<sub>2</sub>Me mixtures suggests the formation of compounds, HCO<sub>2</sub>Me, NaOMe and HCO<sub>2</sub>Me, (NaOMe)<sub>2</sub>, probably enolic complex ions. Electrolysis of a mixture of NaOMe and CO(OEt)<sub>2</sub> yields H<sub>2</sub>, CO<sub>2</sub>, hydrocarbons, and CO, with resins at the anode. ClCO<sub>2</sub>Et also yields H<sub>2</sub> and CO<sub>2</sub>. When NaOMe in MeOH containing CO<sub>2</sub> is electrolysed in a cell with porous compartments, both Na<sup>+</sup> and CO<sub>2</sub> increase at the cathode. This is ascribed to the formation of MeO·CO<sub>2</sub>Na, dissociating into [CO<sub>2</sub>Na]<sup>+</sup> and OMe<sup>−</sup>, the former yielding CO<sub>2</sub> and Na, and thus CO<sub>2</sub>, H<sub>2</sub>, and NaOMe.

E. W. W.

**Nitro-chromic reaction and its application to the determination of small quantities of alcohol.** D. A. WEBB (Sci. Proc. Roy. Dublin Soc., 1936, 21, 281—284).—Modifications of Agulhon's reaction (cf. A., 1911, ii, 1140) described enable the [EtOH] to be determined to ±2%. The method is applied to small quantities of biological fluids.

J. L. D.

**Synthesis of monohydric unsaturated alcohols with systems of double linkings.** P. PELKIS (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 45—60).—CMe<sub>2</sub>:CH·COMe (I), CH<sub>2</sub>:CH·CH<sub>2</sub>Br, and Mg in Et<sub>2</sub>O afford βδ-dimethyl-Δ<sup>βδ</sup>-heptadien-8-ol, b.p. 58°/2 mm. (yield 75%). When CHPh:CH·COMe is taken in place of (I) the product is α-phenyl-γ-methyl-Δ<sup>αα</sup>-hexadien-γ-ol, b.p. 122—123°/2 mm. (31% yield), whilst with CHPh:CH·COPh αγ-diphenyl-Δ<sup>αα</sup>-hexadien-γ-ol, b.p. 170—170.5°/2 mm., is obtained, in 18.7% yield.

R. T.

**New constituents in the unsaponifiable matter of sperm blubber oil.** S. UENO and R. KOYAMA (Bull. Chem. Soc. Japan, 1936, 11, 394—403).—Laborious fractionation of the unsaponifiable matter of the oil has yielded the following substances; heptanol (4-iododiphenyl-4'-urethane, m.p. 150°); octan-α-ol, b.p. 95—97°/17 mm. (further identified as its phenyl- and α-naphthyl-urethane); alcohol C<sub>9</sub>H<sub>20</sub>O, b.p. 102—105°/15 mm., oxidised to an acid (amide, C<sub>9</sub>H<sub>19</sub>ON, m.p. 97°); decan-α-ol (phenylurethane, m.p. 72.5°; α-naphthylurethane, m.p. 66°); dodecanol (α-naphthylurethane, m.p. 74°; two isomeric phenylurethanes, m.p. 71° and 69.5°, respectively), as a mixture of two isomerides named "catadontidaeyl"

and "isocatadontidaeyl alcohol"; "agorophyl alcohol," C<sub>8</sub>H<sub>16</sub>O, b.p. 94—95°/15 mm.; "macrocephaly alcohol," C<sub>10</sub>H<sub>20</sub>O, b.p. 100—102°/15 mm.; alcohol, C<sub>11</sub>H<sub>22</sub>O, b.p. 140—141°/17 mm., converted by ozonolysis into *n*-nonoic acid and (probably) H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and therefore Δ<sup>β</sup>-undecen-α-ol; "odontocetyl alcohol," C<sub>12</sub>H<sub>24</sub>O, b.p. 156—158°/17 mm.; ethers, C<sub>18</sub>H<sub>34</sub>O, b.p. 120°/17 mm. converted by hydrogenation (Pt-black) at 100 atm. into C<sub>18</sub>H<sub>38</sub>O, b.p. 223—224°/75 mm., and reduced by HI to decan-α-ol among other substances, thus indicating the constitution C<sub>10</sub>H<sub>21</sub>·O·C<sub>8</sub>H<sub>17</sub>.

A. T.

**Hydroxylation of the double linking.** N. A. MILAS and S. SUSSMAN (J. Amer. Chem. Soc., 1936, 58, 1302—1304).—CHR:CHR' with Bu'OH-anhyd. H<sub>2</sub>O<sub>2</sub> (prep. described) in presence of a little OsO<sub>4</sub> gives (mainly) OH·CHR·CHR'·OH. The following are prepared: OH·CMe<sub>2</sub>·CH<sub>2</sub>·OH; OH·CMe<sub>2</sub>·CHMe·OH; glycerol (from allyl alcohol); OH·CHPh·CH(OH)·CO<sub>2</sub>H; OH·CHMe·CH(OH)·CO<sub>2</sub>H; *dl*- and *meso*-tartaric acids (from fumaric and maleic acid, respectively).

H. B.

**Photochemical peroxide formation.** III. **Oxidation of glycerol by molecular oxygen in ultra-violet light.** Photochemical production of perglycerol. R. CANTIENI (Ber., 1936, 69, [B], 1796—1798).—In analogy with the behaviour of primary alcohols, glycerol (I) is assumed to yield perglycerol (II), OH·CH<sub>2</sub>·CH(OH)·CH<sub>2</sub>·O<sub>2</sub>H and the photo-oxidation of (I) to follow the course: OH·CH(CH<sub>2</sub>·OH)<sub>2</sub> + 7(II) → 3H<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O + 7OH·CH(CH<sub>2</sub>·OH)<sub>2</sub>. The rate of formation of (II) diminishes when the concn. of (I) is >10%. At the commencement of the reaction approx. equal amounts of (II) are produced in equal intervals of time, but the change tends towards an equilibrium.

H. W.

**Properties of the two modifications of glyceryl trinitrate.** J. HACKEL (Rocz. Chem., 1936, 16, 213—222).—The formation of the stable modification of glyceryl trinitrate, m.p. 13°, is favoured by presence of C<sub>6</sub>H<sub>5</sub>(NO<sub>2</sub>)<sub>3</sub> or kieselguhr, whilst cellulose nitrate and Et and Ph carbamate favour crystallisation of the unstable form, m.p. 1.9°; many other substances are without effect. The stable form is more sensitive to shock than the unstable one, but the explosive power and velocity of detonation are the same for both forms.

R. T.

**Explosions arising from ethers.** E. C. WILLIAMS (Chem. and Ind., 1936, 580—581).—All ethers studied form peroxides on storage, but the rate of formation is variable. Danger occurs whenever an ether is dry-distilled, and with practically all ethers explosions have been experienced. Peroxides are determined by adding acidified KI—EtOH and titrating the I liberated; they may be destroyed by adding FeSO<sub>4</sub>, NaHSO<sub>3</sub>, acidified KI, or Na<sub>2</sub>SO<sub>3</sub>. The ether may also be distilled with steam. Oxidation inhibitors such as NHPh<sub>2</sub>, α- and β-C<sub>10</sub>H<sub>7</sub>·OH, and quinol retard development of peroxides.

F. R. S.

**Relative mobilities of normal alkyl radicals in their chlorothioformates.** P. CARRÉ and L. PEIGNÉ (Compt. rend., 1936, 202, 2159—2161; cf. A.,



1935, 1105).—The temp. of decomp. of  $\text{ClCOSR}$  into  $\text{RCl}$  and  $\text{COS}$  in presence of quinoline ( $\text{R} = n\text{-alkyl}$ ,  $\text{C}_1\text{—C}_{11}$ ) shows an alternation effect with the no. of C in the radical. The results are compared with those of  $\text{ClCO}_2\text{R} \rightarrow \text{RCl} + \text{CO}_2$  and discussed in terms of the mobility of the radicals.

F. N. W.

**Synthesis and hydrolysis of phosphoric esters derived by methylation of  $\beta$ -hydroxyethyl dihydrogen phosphate.** O. BAILLY and J. GAUMÉ (Bull. Soc. chim., 1936, 3, [v], 1396—1405).— $\text{Na}_2\beta$ -hydroxyethyl phosphate (I) with an equimol. amount of  $\text{Me}_2\text{SO}_4$  gives  $\text{Me}\beta$ -hydroxyethyl H phosphate, isolated as *Ca* salt, which with dil.  $\text{Na}_2\text{CO}_3$  at  $100^\circ$  is converted quantitatively into (I) (cf. A., 1926, 1225; 1935, 471). (I) with aq.  $\text{AgNO}_3$  affords  $\text{Ag}_2\beta$ -hydroxyethyl phosphate, which with  $\text{MeI—Ag}_2\text{O}$  affords  $\text{Me}_2\beta$ -methoxyethyl phosphate, b.p.  $112\text{—}113^\circ/9$  mm., hydrolysed rapidly by cold *N-NaOH* to *Na Me*  $\beta$ -methoxyethyl phosphate, which when heated loses 50% of its P to give  $\text{NaPO}_3$ , but is stable in boiling *N-NaOH* (cf. A., 1926, 384).  $\text{OMe}[\text{CH}_2]_2\text{OH}$  with  $\text{P}_2\text{O}_5$  in anhyd.  $\text{Et}_2\text{O}$  affords  $\beta$ -methoxyethyl H phosphate (*Ca*, *Sr*, and *Ba* salts). J. L. D.

**Boric esters of polyalcohols.** A. DUPIRE (Compt. rend., 1936, 202, 2086—2087; cf. A., 1932, 937).—Almost quant. yields of the borates of  $(\text{CH}_2\text{OH})_2$ , glycerol, propane- $\alpha\beta$ -diol,  $\alpha$ -chloropropane- $\beta\gamma$ -diol, and butane- $\alpha\gamma$ -diol were prepared from the alcohol and acid in presence of  $\text{PhMe}$ . H. J. E.

**Boric acid derivatives of tetrasubstituted glycerol.** P. PASTUREAU and (Mlle.) M. VEILER (Compt. rend., 1936, 202, 1683—1685; cf. A., 1925, i, 500).— $\gamma$ -Chloro- $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol (cf. A., 1934, 753) with  $\text{H}_3\text{BO}_3$  in  $\text{H}_2\text{O}$  gives a *H borate*, m.p.  $132^\circ$ . *H borates* (m.p. in parentheses) of the following are prepared:  $\beta\delta$ -dimethylpentane- $\beta\gamma\delta$ -triol ( $118^\circ$ ),  $\beta\gamma\delta$ -trimethylpentane- $\beta\delta$ -diol ( $72^\circ$ ),  $\delta$ -chloro- $\gamma\epsilon$ -dimethylhexane- $\gamma\epsilon$ -diol ( $58^\circ$ ), and  $\delta$ -chloro- $\epsilon$ -methyl- $\gamma$ -ethylhexane- $\gamma\epsilon$ -diol ( $55^\circ$ ). Aryl-substituted glycerols do not give similar derivatives. J. L. D.

**$\alpha$ -Halogenated thioethers.** H. BOHME (Ber., 1936, 69, [B], 1610—1615).— $\text{CH}_2\text{Cl Et sulphide}$  (I), b.p.  $128\text{—}131^\circ/760$  mm., is obtained in 60% yield by passing  $\text{HCl}$  into a suspension of polyoxymethylene in  $\text{EtSH}$  at room temp. It is hydrolysed by  $\text{H}_2\text{O}$  to  $\text{CH}_2\text{O}$ ,  $\text{EtSH}$ , and  $\text{HCl}$ , which react with formation of  $\text{CH}_2(\text{SEt})_2$ , b.p.  $184^\circ/763$  mm. [also obtained from (I) and  $\text{NaSEt}$  in  $\text{EtOH}$ ], and oxidised by  $\text{H}_2\text{O}_2$  in  $\text{AcOH}$  to the sulphone, m.p.  $104^\circ$ . (I) and  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$  at  $-15^\circ$  give  $\text{CH}_2\text{Cl Et sulphone}$ , b.p.  $128^\circ/14$  mm., m.p.  $33^\circ$ .  $\text{OEt-CH}_2\text{ Et sulphide}$ , b.p.  $134\text{—}136^\circ/735$  mm., is derived from (I) and  $\text{NaOEt}$  in  $\text{EtOH}$  or from  $\text{CH}_2\text{Cl-OEt}$  and  $\text{NaSEt}$ .  $\text{OEt-CH}_2\text{ Et sulphone}$  has b.p.  $122^\circ/13$  mm.  $\text{CH}_2\text{Ph Et sulphide}$ , b.p.  $222\text{—}223^\circ/750$  mm., obtained from (I) and  $\text{MgPhBr}$  is oxidised to the sulphoxide, m.p.  $49^\circ$ , and sulphone, m.p.  $84^\circ$ .  $\text{Ethylthiolacetoneitrile}$ , b.p.  $72\text{—}73^\circ/13$  mm., from (I) and  $\text{Hg}(\text{CN})_2$ , is hydrolysed by fuming  $\text{HCl}$  to ethylthiolacetic acid, b.p.  $118^\circ/11$  mm. H. W.

**Bromomethanetrisulphonates.** H. J. BACKER and P. TERPSTRA (Rec. trav. chim., 1936, 55, 602—605).—Crystallographic and solubility data are given

for the  $\text{Li}_3$  ( $+9\text{H}_2\text{O}$ ),  $\text{Na}_3$  ( $+3\text{H}_2\text{O}$ ),  $\text{Rb}_3$  (I) ( $+ \text{H}_2\text{O}$ ),  $\text{Cs}_3$  ( $+ \text{H}_2\text{O}$ ),  $\text{Ba}_{1.5}$  ( $+9\text{H}_2\text{O}$ ), and *tristrychnine* ( $+3\text{H}_2\text{O}$ ) salts. X-Ray analysis of (I) is reported.

R. S. C.

**Structure of the isomeride of isoprenesulphone.** H. J. BACKER, J. STRATING, and A. J. ZUTHOFF (Rec. trav. chim., 1936, 55, 761—764).— $\text{COEt-CH}_2\text{Cl}$ , b.p.  $114^\circ$  [obtained with  $\text{COMe-CHMeCl}$  (I), b.p.  $133\text{—}135^\circ$ , from  $\text{COMeEt}$  and  $\text{Cl}_2$ ], with  $(\text{NH}_4)_2\text{SO}_3$  at  $70^\circ$  gives *n-butan- $\beta$ -one- $\alpha$ -sulphonic acid* (*Ba* and *K* salt, hygroscopic). (I) gives similarly *n-butan- $\beta$ -one- $\gamma$ -sulphonic acid* [*Ba* ( $+ \text{H}_2\text{O}$ ) and *K* salts].  $\text{OH-CH}_2\text{-SO}_3\text{K}$  and  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  give a product, hydrolysed by  $\text{H}_2\text{SO}_4$  to *n-butan- $\gamma$ -one- $\alpha$ -sulphonic acid* (II) (*Ba* and *K* salts). Crystallographic data of the *Ba* salts are given. (II) is identical with the acid given by  $\text{O}_3$  from the isomeride (ultra-violet illumination) of isoprenesulphone (A., 1935, 1105), the structure of which is thus proved to be *3-methyl-4:5-dihydrothiophen 1:1-dioxide*.

R. S. C.

**Syntheses using tautomeric sodium organic compounds.** G. V. TSCHELINCEV (J. Gen. Chem. Russ., 1936, 6, 650—657).—Theoretical. R. T.

**Reaction of iodoacetate and of iodoacetamide with thiol groups, with urease, and with yeast preparations.**—See this vol., 1074.

**Kinetics of hydrolysis of esters in alkaline media.**—See this vol., 1073.

**Action of liquid ammonia on acetone compounds of  $\alpha$ -hydroxy-acids.** H. ŌEDA (Bull. Chem. Soc. Japan, 1936, 11, 385—389).—*dl*-Lact-, *l*-leuc-, *dl*-mandel-, and *l*- $\alpha$ -hydroxy- $\beta$ -phenylpropionamide were synthesised by treating the respective  $\text{CMe}_2$  compounds with liquid  $\text{NH}_3$ , best at  $-33^\circ$ .

A. T.

**Keto-enol tautomerism of ethyl acetoacetate.** M. BEYAERT (Natuurwetensch. Tijds., 1936, 18, 209—228).—The methods employed for determining the % of enol in keto-enol tautomerides in general and  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  in particular are reviewed. Equilibrium between the two forms of this ester is established only very slowly in the vapour phase, and attempts to determine the composition of the vapour at equilibrium were unsuccessful. The dielectric const. and  $n$  at various temp. of the pure keto-form and mixtures of this with the enolic form (up to 90% enolic) have been determined and follow the additive mixture law.

D. R. D.

**Condensation of acetaldehyde with ethyl  $\alpha$ -methylacetoacetate.** T. WENDLING (Bull. Soc. chim., 1936, [v], 3, 790—798).— $\text{CHMeAc-CO}_2\text{Et}$  (I),  $\text{MeCHO}$  (II),  $\text{K}_2\text{CO}_3$ , and  $\text{H}_2\text{O}$  at  $5^\circ$  give *Et  $\alpha$ -methyl- $\alpha$ -( $\alpha'$ -hydroxyethyl)acetoacetate*, b.p.  $87\text{—}88^\circ/1.2$  mm., which with  $\text{AcCl}$  gives the *acetate*, b.p.  $108\text{—}111^\circ/1.1$  mm., and regenerates (I) and (II), slowly when kept and more rapidly at higher temp. It is decomposed by  $\text{Ac}_2\text{O}$  into (I) and (II), a trace of  $\text{Et}_2$  ethyldenedi- $\alpha$ -methylacetoacetate being also formed. Attempts to prepare its pyrazolone failed, only that of (I) being isolated.

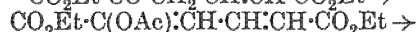
H. G. M.

**Preparation of hydroxy-acids [dihydroxystearic acid].** A. W. RALSTON and S. T. BAUER (Oil and Soap, 1936, 13, 170—171; cf. B., 1931, 199).

—A prep., m.p. 114–116°, consisting apparently essentially of the same dihydroxystearic acid, m.p. 124–127°, as is obtained by oxidising oleic acid (I) with alkaline  $\text{KMnO}_4$ , has been obtained by oxidising (I) in a solution containing  $\text{NaOH}$  (4%) and  $\text{Ni}(\text{NO}_3)_2$  (0.5%) and a few crystals of  $\text{MnCl}_2$  through which  $\text{Cl}_2$  was bubbled. The intermediate formation of  $\text{Ni}_2\text{O}_7$  is postulated. E. L.

**Sodium xanthate.**—See this vol., 1078.

**Preparation of polyenes.** Synthesis of hexatriene- $\alpha\zeta$ -dicarboxylic acid and octatetraene- $\alpha\theta$ -dicarboxylic acid. R. KUHN and C. GRUNDMANN (Ber., 1936, 69, [B], 1757–1765).—The synthesis follows the lines:  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \rightarrow$



$\text{CO}_2\text{H}\cdot[\text{CH}\cdot\text{CH}]_2\cdot\text{CO}_2\text{H}$ . Thus  $\text{Et}_2\alpha$ -acetoxymuconate is converted by  $\text{Al-Hg}$  in  $\text{Et}_2\text{O-H}_2\text{O}$  into  $\text{Et}_2\alpha$ -acetoxy- $\alpha\delta$ -dihydromuconate, b.p. 144–146°/2 mm., hydrolysed by  $\text{KOH-MeOH}$  to  $\text{Me}_2$  trans-trans-muconate, m.p. 56°, and by  $\text{KOH-H}_2\text{O}$  to trans-trans-muonic acid, m.p. 298° (Berl.; decomp.). Similarly  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ ,  $\text{KOEt}$ , and  $\text{Et}_2\text{C}_2\text{O}_4$  afford the *K* salt,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{OK})\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ , converted by successive treatment with  $\text{Ac}_2\text{O}$ ,  $\text{Al-Hg}$ , and hydrolysis into trans-trans- $\beta$ -methylmuconic acid, m.p. 232° (decomp.).  $\text{Et}_2\alpha$ -acetoxy- $\Delta^{\gamma\epsilon}$ -hexatriene- $\alpha\zeta$ -dicarboxylate is converted into  $\text{Et}_2\alpha$ -acetoxy- $\Delta^{\beta\delta}$ -hexadiene- $\alpha\zeta$ -dicarboxylate (I), b.p. 158–160°/1 mm., hydrolysed by  $\text{KOH-MeOH-H}_2\text{O}$  to  $\Delta^{\gamma\epsilon}$ -hexatriene- $\alpha\zeta$ -dicarboxylic acid (II), m.p. 316–318° (decomp.) when placed in bath at 250° and quickly heated, gradual decomp. > 280° when slowly heated [ $\text{Me}_2$  ester, m.p. 172°, from (II) through the acid chloride or with  $\text{CH}_3\text{N}_2$ , but best obtained from (I) and  $\text{KOH-MeOH}$ ;  $\text{Et}_2$  ester, m.p. 90°]. (II) and  $\text{Br}$  in diffuse daylight afford  $\alpha\beta\gamma\delta\epsilon\zeta$ -hexabromosuberlic acid, gradual decomp. > 200°. (III) is hydrogenated ( $\text{PtO}_2$  in 0.1*N*- $\text{NaOH}$ ) to suberic acid, m.p. 141–142°. (II) is reduced by  $\text{Na-Hg}$  to  $\Delta^{\beta\delta}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid, m.p. 190°, the constitution of which is established by its condensation with  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  in presence of  $\text{Pb}$  oxide and  $\text{Ac}_2\text{O}$  to  $\alpha\mu$ -diphenyl- $\Delta^{\gamma\epsilon\eta\theta}$ -dodecahexaene, m.p. 263°; it is isomerised by boiling 20%  $\text{KOH}$  to  $\Delta^{\gamma\epsilon}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid, m.p. 225–227°.  $\text{Et}$   $\gamma$ -methylsorbatate,  $\text{Et}_2\text{C}_2\text{O}_4$ , and  $\text{KOEt}$  afford *Et* ethoxalyl- $\gamma$ -methylsorbatate, m.p. 103.5°, transformed by successive treatment with  $\text{Ac}_2\text{O}$ ,  $\text{Al-Hg}$ , and  $\text{KOH-H}_2\text{O}$  into  $\gamma$ -methyl- $\Delta^{\gamma\epsilon}$ -hexatriene- $\alpha\zeta$ -dicarboxylic acid, m.p. 296° (decomp.).  $\text{Et}_2\text{C}_2\text{O}_4$  and  $\text{Me}$  octatriene-carboxylate in presence of  $\text{KOEt}$  give *Et* ethoxalyl-octatrienecarboxylate, m.p. 119–120°; condensation occurs better in presence of  $\text{KOPr}^{\delta}$ . The mixture of esters is converted by  $\text{Ac}_2\text{O}$  followed by  $\text{Al-Hg}$  and  $\text{KOH-MeOH}$  into  $\text{Me}_2$   $\Delta^{\gamma\epsilon\eta\theta}$ -octatetraene- $\alpha\theta$ -dicarboxylate, m.p. 212°, hydrolysed by 5%  $\text{KOH}$  to  $\Delta^{\gamma\epsilon\eta\theta}$ -octatetraene- $\alpha\theta$ -dicarboxylic acid, m.p. 309° (decomp.), which is reduced by  $\text{Na-Hg}$  to octatriene- $\alpha\theta$ -dicarboxylic acid, m.p. 195° (decomp.). H. W.

**Acyclic keto-acids.** N. A. PREOBRASHENSKI, M. N. SCHTSCHUKINA, and A. F. VOMPE (Ber.,

1936, 69, [B], 1618–1620).— $\text{Et}_2$  ethylsuccinate,  $\text{Et}_2\text{C}_2\text{O}_4$ , and  $\text{NaOEt}$  in  $\text{Et}_2\text{O}$  at room temp. yield *Et*<sub>2</sub> ethoxalylethylsuccinate (yield 80–90%), which passes when distilled under diminished pressure into  $\text{CO}$  and  $\text{Et}_3$  butanetricarboxylate. It is hydrolysed by boiling conc.  $\text{HCl}$  to  $\gamma$ -keto- $\alpha$ -ethylglutaric acid [semicarbazone, m.p. 177–178° (decomp.); 1-phenyl-5-ethylpyridazin-6-one, m.p. 159–160° (decomp.)], the *Et* ester, b.p. 148.5°/15 mm., 269°/741.5 mm. (semicarbazone, m.p. 130.5–131°), of which condenses with  $\text{HCO}_2\text{Et}$  to *Et*<sub>2</sub>  $\gamma$ -keto- $\beta$ -aldehydo- $\alpha$ -ethylglutarate; this could not be distilled without decomp. and gives a phenylhydrazine and semicarbazone which are difficult to purify. H. W.

**Rotatory power of methyl tartrate: influence of solvent, temperature, and neutral salts.** Y. K. HENG (Bull. Soc. chim., 1936, [v], 3, 1004–1019).—In aq. solution  $\alpha$  is reduced by the addition of neutral salts. The effect depends on the cation, showing a periodicity which corresponds with the periodic table. Salts of  $\text{Fe}^{\text{III}}$  and  $\text{Th}$  increase  $\alpha$ . The influence of temp. varies according to the solvent. E. S. H.

**Cuprotartrates.** Y. K. HENG (Bull. Soc. chim., 1936, [v], 3, 993–1004).—The reactions of  $\text{NaOH}$  +  $\text{Cu}(\text{OH})_2$  with tartaric acid, tartramide, and Me tartrate have been investigated by following the change in optical rotation. The curves obtained show the existence of the salts  $2\text{C}_4\text{H}_4\text{O}_6\text{NH}_2\cdot\text{CuO}$ ,  $[\text{CuO}\cdot\text{C}_4\text{H}_4\text{O}_6\text{NH}_2]_2\text{Na}_2$ ,  $[2\text{C}_4\text{H}_4\text{O}_6(\text{NH}_2)_2\cdot\text{CuO}]_2\text{Na}_2$ , and  $[\text{C}_4\text{H}_4\text{O}_6\text{Me}_2\cdot\text{CuO}]\text{Na}$ . E. S. H.

**Preparation and constitution of alginic acid.** V. C. BARRY and T. DILLON (Sci. Proc. Roy. Dublin Soc., 1936, 21, 285–287; cf. A., 1932, 931; 1935, 550).—Extraction of the fronds of *Laminaria digitata* with aq.  $\text{NH}_3$  (details given) affords alginic acid,  $\text{C}_6\text{H}_{10}\text{O}_7$  (equiv. wt. 192;  $[\alpha]_D^{20}$  –133.4° in  $\text{H}_2\text{O}$ , for the Na salt, which supports the view that the polymerising unit is the uronic acid). J. L. D.

**Derivatives of alginic acid. I. Acetylation of alginic acid.** V. C. BARRY, T. DILLON, and P. O'MUINEACHAIN (Sci. Proc. Roy. Dublin Soc., 1936, 21, 289–296).—Alginic acid (I) (cf. preceding abstract) affords a trace of  $\text{Ac}_1$  (?) with  $\text{NaOAc}$  and boiling  $\text{Ac}_2\text{O}$  and a  $\text{Ac}_3$  derivative with  $\text{Ac}_2\text{O}$  containing  $\text{ZnCl}_2$  at 80°. (I) with boiling  $\text{Ac}_2\text{O}$  containing a little I affords  $\text{Ac}_3$  and  $\text{Ac}_2$  derivatives and with  $\text{HI}$  in  $\text{Ac}_2\text{O}$  affords, in good yield,  $\text{Ac}_2$  derivatives,  $[\alpha]_D^{20}$  –93.1°, –113.9°, and –136.8° (Na salt) in  $\text{H}_2\text{O}$ , respectively, which are probably derivatives of degradation products of (I) of different degrees of polymerisation. The results support the view that the entire uronic acid is the polymerising unit. J. L. D.

**Glycuronic acid.** A. LEULIER (J. Pharm. Chim., 1936, [viii], 24, 64–76, 122–131).—A review.

**n-Butyl esters of thio-acids.** E. MULLER and A. FREYTAG (J. pr. Chem., 1936, [ii], 145, 318–320).— $\text{NaBu}\cdot\text{SO}_4$  (modified prep.), aq.  $\text{KOH}$ , and  $\text{CS}_2$  give  $\text{Bu}^n\text{SH}$ , which with  $\text{Pb}(\text{OAc})_2\cdot\text{EtOH}$  affords the stable *Pb* salt. With the appropriate acid chloride in  $\text{Et}_2\text{O}$  this gives >80% yields of *S-Bu*<sup>n</sup> thio-propionate, b.p. 64.5°/15 mm., -butyrate, b.p. 80.1°/12



mm., and -isovalerate, b.p. 86.5°/12 mm., only slowly attacked by oxidising agents. R. S. C.

$\alpha\beta$ -,  $\alpha\gamma$ -,  $\beta\gamma$ -Disulphobutyric acids. H. J. BACKER and N. BENNINGA (Rec. trav. chim., 1936, 55, 605—614).— $\text{SO}_3\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and oleum at 90° give mainly  $\alpha\beta$ -disulphocrotonic acid, hydrogenated (Pt-black) in dil. AcOH to  $\alpha\beta$ -disulphobutyric acid ( $\text{Ba}_{1-}$ ,  $+2\text{H}_2\text{O}$ , and  $\text{Ti}_3$  salts), the tristrychnine salt,  $+9\text{H}_2\text{O}$ , of which, when recrystallised, yields the d-acid (I),  $[\text{M}]_D^{+16}$  in  $\text{H}_2\text{O}$  ( $\text{Na}_3$  salt,  $[\text{M}]_D^{-6}$  in  $\text{H}_2\text{O}$ ). The non-resolvable acid (A., 1935, 1107) is thus proved to be the  $\beta\beta$ -disulpho-acid.  $\text{Br}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{NH}_4$  and  $(\text{NH}_4)_2\text{SO}_3$  at 135° give  $\gamma$ -sulphobutyric acid,  $+0.5\text{H}_2\text{O}$ , m.p. 93—93.5° (distrychnine,  $+2.5\text{H}_2\text{O}$  (non-resolvable),  $\text{Ba}$ ,  $+5\text{H}_2\text{O}$ , and  $\text{Ag}_2$  salts;  $\text{Me}_2$  ester, b.p. 150—153°), which with oleum at 85—95° gives  $\alpha\gamma$ -disulphobutyric acid ( $\text{Ba}_{1-}$  salt,  $+8\text{H}_2\text{O}$ ), the tristrychnine salt,  $+8\text{H}_2\text{O}$ , of which leads to the active acid (II),  $[\text{M}]_D^{+7.2}$  ( $\text{Ba}_{1-}$  salt,  $[\text{M}]_D^{+9.1}$ ).  $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{NH}_4$  and  $(\text{NH}_4)_2\text{SO}_3$  at 50° give  $\gamma$ -sulphocrotonic acid (III) ( $+0.5\text{H}_2\text{O}$ ), m.p. 94—96° after sintering at about 87°, hygroscopic ( $\text{Ba}$ ,  $+3\text{H}_2\text{O}$ ,  $\text{Na}_2$ , hygroscopic,  $\text{Ag}_2$ , and diguinine,  $+1.5\text{H}_2\text{O}$ , salts; dichloride, b.p. 118—121°/2 mm.;  $\text{Me}_2$  ester, b.p. 140—142°/2 mm.; monoamide, hygroscopic solid), which with  $(\text{NH}_4)_2\text{SO}_3$  at 80° gives  $\beta\gamma$ -disulphobutyric acid,  $+2\text{H}_2\text{O}$ , m.p. 95°, hygroscopic [ $\text{Ba}_{1-}$ ,  $+5\text{H}_2\text{O}$ , and  $\text{Ti}_3$  salts; also obtained from  $\text{CHCl}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4$  and  $(\text{NH}_4)_2\text{SO}_3$  at 65°, the tristrychnine salt,  $+5\text{H}_2\text{O}$ , decomposes about 245°, of which leads to the d-acid (IV),  $[\text{M}]_{D_{460}}^{+59}$  in  $\text{H}_2\text{O}$  ( $\text{Ba}_{1-}$  salt,  $[\text{M}]_{D_{460}}^{+59}$  in  $\text{H}_2\text{O}$ ). (I) and (II), having an  $\alpha$ - $\text{SO}_3\text{H}$ , racemise in hot alkali, but (IV) does not. The addition of  $\text{KHSO}_3$  to (III) at 80° in 0.1M and 0.5M solution has  $k$  0.64 and 1.24, respectively, compared with 187 for  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  in 0.1M and 0.063 for  $\text{SO}_3\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  in M solution. R. S. C.

Formation of carbonyl compounds by the explosive decomposition of nitric esters. G. DENIGES (Compt. rend., 1936, 202, 1998—2000).—Me, Et, Pr<sup>a</sup>, Pr<sup>b</sup>, Bu<sup>a</sup>, Bu<sup>b</sup>, CH<sub>3</sub>Ph, and  $\alpha$ -phenylethyl nitrate decompose when heated to give CH<sub>2</sub>O, MeCHO, EtCHO, COMe<sub>2</sub>, PrCHO, COMeEt, PhCHO, and CPhMe, respectively. The rate of reaction is much decreased in CO<sub>2</sub>. Aldehydes corresponding with the higher esters undergo secondary decomposition. J. L. D.

Isomerisation of hydroxyaldehydes. VI. S. N. DANILOV and A. M. GACHOKIDZE (J. Gen. Chem. Russ., 1936, 6, 704—719).— $\beta$ -Bromoglucose tetra-acetate in 50% AcOH and Zn at 15—25° yield glucal triacetate, the Br-, Br<sub>1</sub>-, Cl<sub>2</sub>-, or Cl<sub>1</sub>-derivatives of which with aq. Pb(OH)<sub>2</sub> yield orthosaccharic acid (I) (phenylhydrazide, m.p. 176°; Ac<sub>4</sub> derivative, m.p. 110°, and its phenylhydrazide, m.p. 143°). (I) and MeI-Ag<sub>2</sub>O yield the Me ester, m.p. 81.5°, of tetramethylorthosaccharic acid (II), m.p. 92—94° (phenylhydrazide, m.p. 113°), obtained by hydrolysing the ester with aq. Ba(OH)<sub>2</sub>. Glucal and MeI-Ag<sub>2</sub>O yield 3:4:6-trimethylglucal, which is chlorinated in CHCl<sub>3</sub> to 1:2-dichloro-3:4:6-trimethylglucal, an oil, converted by shaking with Ag<sub>2</sub>CO<sub>3</sub> into the 2-Cl-derivative, an oil, and this yields trimethylortho-

saccharic acid (III) when warmed with aq. Pb(OH)<sub>2</sub>. (III), MeI, and Ag<sub>2</sub>O afford (II). R. T.

Photo-decomposition of acetone.—See this vol., 1077.

Preparation of  $\beta$ -chloroethyl and  $\beta$ -vinyl ketones. J. DÉCOMBE (Compt. rend., 1936, 202, 1685—1687; cf. A., 1907, i, 241, 418; 1908, i, 390, 398).—COMe<sub>2</sub>, COMeEt, and COEt<sub>2</sub> with CH<sub>2</sub>O in presence of K<sub>2</sub>CO<sub>3</sub> (cf. A., 1933, 1144) afford  $\alpha$ -hydroxybutan- $\gamma$ -one (I),  $\beta$ -hydroxymethylbutan- $\gamma$ -one (II), and  $\beta$ -hydroxymethylpentan- $\gamma$ -one (III), b.p. 97—98°/20 mm. (phenylhydrazone, m.p. 103°), respectively. (I), (II), and (III) in conc. HCl containing some AlCl<sub>3</sub> at 0° afford  $\alpha$ -chloro-,  $\beta$ -chloromethylbutan- $\gamma$ -one, b.p. 60—62°/16 mm., and  $\beta$ -chloromethylpentan- $\gamma$ -one, b.p. 65—66°/14 mm., respectively, which are unstable in air, and by distilling in presence of a little (I) give  $\Delta^a$ -buten- $\gamma$ -one,  $\beta$ -methyl- $\Delta^a$ -buten- $\gamma$ -one, b.p. 29—31°/60 mm. (oxime, m.p. 43°), and  $\beta$ -methyl- $\Delta^a$ -penten- $\gamma$ -one, b.p. 119—120° (semicarbazone, m.p. 158°), respectively. J. L. D.

Utilisation of molecular refraction for determining constitution and configuration of sugars. I. C. N. RIEBER (Z. physikal. Chem., 1936, 176, 358—362).—The mol. refraction of a methyloside is  $>$  that of the corresponding sugar by  $7.50 \pm 0.02$  ( $\Delta R_o$ ) or  $4.61 \pm 0.02$  ( $\Delta R_L$ ). R. C.

Reduction and oxidation by ultra-violet irradiated sugar. P. HOLTZ (Arch. exp. Path. Pharm., 1936, 182, 141—159).—Irradiation (especially in presence of O<sub>2</sub>) of glucose, fructose, arabinose, glycerol, sorbitol, and glucosamine produces reducing substances, the resulting solutions (in common with those of ascorbic acid, reductone, and sugar heated with alkali) having absorption max. between 265 and 290 m $\mu$ ; probably readily-enolised  $\cdot\text{CO}\cdot$  is formed. The products accelerate the autoxidation of cysteine and adrenaline. The bearing of the data on biological reducing systems and the possibility of a similar formation from irradiation of the skin are discussed. F. O. H.

Action of X-rays on glucose. P. HOLTZ and J. P. BECKER (Arch. exp. Path. Pharm., 1936, 182, 160—163).—X-Irradiation of glucose (I) in PO<sub>4</sub>''' buffer at  $\mu$  7.6 yields solutions which reduce methylene-blue and have an absorption max. at 275—290 m $\mu$ , i.e., similar to that of ultra-violet-irradiated (I) or of (I) heated in alkaline solution (cf. preceding abstract). F. O. H.

Action of dilute alkalis on glucose. I. R. NODZU and R. GOTO (Bull. Chem. Soc. Japan, 1936, 11, 381—385).—The distillate of a dil. Na<sub>2</sub>CO<sub>3</sub> solution of glucose is shown to contain acetol and a little Ac, but no COMe-CHO. Results are confirmed by spectroscopic evidence. A. T.

Acid-base catalysis of mutarotation of glucose.—See this vol., 1075.

Syntheses with 5:6-anhydroisopropylidene-glucose. III. 6-Glucosylpiperidine. H. OHLE, E. EULER, and W. MALERCZYK (Ber., 1936, 69, [B], 1636—1639).—5:6-Anhydroisopropylideneglucose (I) gives mainly monoglucosylamine when treated with a large excess of amine in the cold. In EtOH much

by-product, apparently formed by polymerisation of (I), results when the reactants are used in equimol. amount, but the proportion recedes with increasing amount and increasing concn. of amine. The following are described: *isopropylidene-6-d-glucosyl-methylamine*, b.p. 200—210° (bath)/0.15 mm., and *-dimethylamine*, m.p. 85°,  $[\alpha]_D^{25} + 8.7^\circ$  in  $\text{CHCl}_3$ , *-ethylamine*, b.p. 190—200° (bath)/0.15—0.2 mm., m.p. 86°,  $[\alpha]_D^{25} - 8.5^\circ$  in  $\text{CHCl}_3$ , and *-diethylamine*, b.p. 120—125° (bath)/0.05 mm.,  $[\alpha]_D^{25} + 10.5^\circ$  in  $\text{CHCl}_3$ , *-benzylamine*, b.p. 275° (bath)/0.05 mm., m.p. 109.5°,  $[\alpha]_D^{25} - 2.6^\circ$  in  $\text{CHCl}_3$ , and *-dibenzylamine*, m.p. 133°,  $[\alpha]_D^{25} + 1.5^\circ$  in  $\text{CHCl}_3$ , *isopropylidene-6-d-glucosylpiperidine* (II), m.p. 115°,  $[\alpha]_D^{25} + 2.8^\circ$  in  $\text{CHCl}_3$  [*flavianate*,  $\text{C}_{14}\text{H}_{25}\text{O}_5\text{N}$ ,  $\text{C}_{10}\text{H}_6\text{O}_8\text{N}_2\text{S}$ ,  $0.5\text{H}_2\text{O}$ , m.p. 115—117° (decomp.), *diacetate*], does not condense with  $\text{COMe}_2$  in presence of anhyd.  $\text{CuSO}_4$  or conc.  $\text{H}_2\text{SO}_4$ . *isodisopropylidene-6-p-toluenesulphonate* and *piperidine* at 100° afford *isodisopropylidene-6-d-glucosylpiperidine*, b.p. 155°/0.2 mm.,  $[\alpha]_D^{25} + 32.37^\circ$  in  $\text{CHCl}_3$  [*monoflavianate*, m.p. 75° (decomp.)], hydrolysed by  $0.05N\text{-H}_2\text{SO}_4$  at 50° to (II), thus establishing the position of the piperidine residue at 6. Hydrolysis of (II) by  $N\text{-H}_2\text{SO}_4$  at 20° gives  *$\beta$ -6-d-glucosylpiperidine*, m.p. 150—151° (decomp.),  $[\alpha]_D^{25} + 47.3^\circ$  in  $\text{H}_2\text{O}$  (equilibrium val.), which could not be condensed with  $\text{COMe}_2$  in presence of anhyd.  $\text{CuSO}_4$ . It gives a *phenylosazone*, m.p. 131°, and is acetylated predominatingly to the  *$\beta$ -tetra-acetate*, m.p. 134°,  $[\alpha]_D^{25} + 13.4^\circ$  in  $\text{CHCl}_3$ . H. W.

**Molecular transformation of  $\lambda$ -glucosides.** R. KUHN and A. DANSI (Ber., 1936, 69, [B], 1745—1754; cf. Amadori, A., 1926, 60; 1929, 429; 1931, 1039, 1149).—The “labile” compound, m.p. 114—115°,  $[\alpha]_D^{25} - 92.5^\circ$  to  $-35.5^\circ$  in EtOH, obtained from glucose and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  in boiling EtOH, is  *$\beta$ -p-toluidino-d-glucopyranoside* (I), since it is converted by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into the tetra-acetate, m.p. 143—146°,  $[\alpha]_D^{25} - 57.5^\circ$  in  $\text{MeOAc}$ , identical with that derived from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  and acetobromoglucose or *d*-glucose 2 : 3 : 4 : 6-tetra-acetate. It is transformed by  $\text{Me}_2\text{SO}_4$  into 2 : 3 : 4 : 6-tetramethyl-*p*-toluidinoglucose, m.p. 147°,  $[\alpha]_D^{25} + 163^\circ$  in MeOH, identical with the product from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  and 2 : 3 : 4 : 6-tetramethylglucose. The “stable” isomeride (II), m.p. 150—152°,  $[\alpha]_D^{25} - 40^\circ$  in  $\text{H}_2\text{O}$ , cannot be methylated similarly, since it is unstable towards alkali. Treatment with  $\text{Ag}_2\text{O}$  and MeI gives *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$  as sole cryst. product. With  $\text{BzCl}$  it affords a *tetrabenzoate*, m.p. 119—120°, instead of the pentabenzoate required by Amadori’s formulation of it as a Schiff’s base. Catalytic hydrogenation ( $\text{PtO}_2$  in EtOH) readily gives the  $\text{H}_2$ -derivative  $\text{C}_{13}\text{H}_{21}\text{O}_5\text{N}$ , m.p. 195°,  $[\alpha]_D^{25} + 26^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ,  $+25^\circ$  in  $N\text{-HCl}$ , not identical with *N*-*p*-tolylglucosamine. Attempts to prepare an undoubted Schiff’s base from *al*-glucose 2 : 3 : 4 : 5 : 6-penta-acetate and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  gave only gummy products. Oxidation of (II) with  $\text{CrO}_3$  affords about twice as much  $\text{AcOH}$  as is obtained from (I) or *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ , showing that isomerisation is accompanied by the production of a fresh Me which must be in the sugar residue, since (II) gives *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  when hydrolysed. In view of the possibility that (II) is the *p*-toluidide

of a sugar carboxylic acid the following compounds have been prepared, none of which is identical with (II): *saccharin-p-toluidine*, m.p. 178—178.5°; *deoxy-glucono-p-toluidide*, m.p. 176°,  $[\alpha]_D^{25} + 10^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ; *d-glucono-p-toluidide*, m.p. 179°,  $[\alpha]_D^{25} + 15.9^\circ$ ; *p-toluidino-2-deoxyglucose*, m.p. 192° (decomp.),  $[\alpha]_D^{25} - 67.5^\circ$  to  $+10.0^\circ$  in 48 hr. in  $\text{EtOH-H}_2\text{O}$  (1 : 1) or  $[\alpha]_D^{25} + 42.5^\circ$  after addition of 2 drops of conc.  $\text{HCl}$ . The great reactivity of the *N*-glucosides is illustrated by the conversion of (I) by 4-nitro-5-amino-*o*-xylene into 4-nitro-5-amino-*o*-xylyl-*d*-glucoside, m.p. 213° (decomp.),  $[\alpha]_D^{25} + 54.6^\circ$  in  $\text{EtOH-H}_2\text{O}$  (4 : 1),  $0.0^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . H. W.

**Glycosides of madder.** R. HILL and D. RICHTER (Nature, 1936, 138, 38).—The glycoside obtained from various species of *Galium* and *Rubia* is the primveroside of purpurincarboxylic acid. The glycoside of alizarin has been cryst. from the products of enzymic hydrolysis and identified as primverose, and a primveroside of rubiadin has been obtained from the roots of *G. verum*. L. S. T.

**Saponins of the cyclopentanohydrophenanthrene group.** V. Tigonin. R. TSCHESCHE (Ber., 1936, 69, [B], 1665—1668).—Treatment of the mother-liquors obtained after the isolation of lanadigin from the leaves of *Digitalis lanata* with cholesterol affords *cholesterol tigonide*,  $\text{C}_{56}\text{H}_{92}\text{O}_{27}\cdot\text{C}_{27}\text{H}_{46}\text{O}$  ( $+4\text{H}_2\text{O}$  and  $+5\text{H}_2\text{O}$ ), gradual decomp.  $>200^\circ$ , transformed by  $\text{C}_5\text{H}_5\text{N}$  into *tigonin* (I),  $\text{C}_{58}\text{H}_{92}\text{O}_{27}$  (also  $+1\text{H}_2\text{O}$ ), m.p. 260° after softening at  $220^\circ$ . (I) is hydrolysed by  $\text{H}_2\text{SO}_4$  to galactose, glucose, and xylose (2 : 2 : 1-mol.). Since tigonin has only 1 OH at  $\text{C}_3$  the sugar mols. must be united thereto, probably as a chain. (I) is less suitable than digitonin as a pptg. agent for sterols. H. W.

**Saponins and sapogenins. IV. Isolation of amolonin and determination of hydrolysis products.** P. C. JURIS and C. R. NOLLER (J. Amer. Chem. Soc., 1936, 58, 1251—1255).—Details are given for the isolation of *amolonin* (I),  $\text{C}_{63}\text{H}_{87}\text{O}_{14}(\text{OH})_{17}$ ,  $[\alpha]_D^{25} - 75.5^\circ$  in  $\text{C}_5\text{H}_5\text{N}$  ( $\text{Ac}_{17}$  derivative,  $[\alpha]_D^{25} - 33.53^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ), from the bulbs of *Chlorogalum pomeridianum*, Kunth. (I) is hydrolysed (50% aq. MeOH containing 5%  $\text{H}_2\text{SO}_4$ ) to tigonin,  $\text{C}_{27}\text{H}_{43}\text{O}_2(\text{OH})$  (1 mol.), *d*-glucose (3 mols.), *d*-galactose (1 mol.), and *l*-rhamnose (2 mols.). Chlorogenin is  $\text{C}_{27}\text{H}_{42}\text{O}_2(\text{OH})_2$  (cf. A., 1935, 673). H. B.

**Mannans. III. Constitution of salep-mannan. Other carbohydrates of *Tubera salep*.** F. KLAGES and R. NIEMANN (Annalen, 1936, 523, 224—234; cf. A., 1934, 1093).—*T. salep* contains  $\text{H}_2\text{O}$  12, ash 1.5, and insol. matter 3%.  $\text{H}_2\text{O}$  removes 30% of salep-mannan (I) and 13% of a dextrin, composed of varying amounts of glucose and mannose. 5%  $\text{NaOH}$  then removes 31% of starch, and finally  $\text{CuSO}_4\text{-NH}_3$  removes 2% of cellulose. (I) is proved by methylation and hydrolysis to consist of mannose units joined in the 1 : 4 positions. The max. mol. wt. (yield of tetramethylglucose) is 12,000, the min. (f.p. depression of  $\text{C}_6\text{H}_6$ ) 5600. (I) closely resembles mannan-A and -B from ivory nut in solubility, rate of hydrolysis,  $[\alpha]$ , and  $[\alpha]$  of derivatives. The viscosity of mannans is unusually low. Probably



the mols. are joined together (e.g., bridged by  $\text{CH}_2\text{O}$ ) to give the rigid natural structures. R. S. C.

**Fructose anhydrides. XVII. Constitution of sinistrin.** H. H. SCHLUBACH and W. LOOP (Annalen, 1936, 523, 130—143).—Expression of the bulbs of *Scilla maritima* and purification of the extract with basic  $\text{Pb}(\text{OAc})_2$  and  $\text{H}_2\text{S}$  followed by pptn. of the carbohydrates with  $\text{EtOH}$  yields sinistrin (I),  $[\alpha]_D^{20}$   $-44.5^\circ$  in  $\text{H}_2\text{O}$ , the homogeneity of which is established by its identity in  $[\alpha]$ , half period of acid hydrolysis, and mol. size in  $\text{H}_2\text{O}$  with a specimen obtained by hydrolysis (Zemplén) of the optically homogeneous triacetate (II),  $[\alpha]_D^{20}$   $-23.5^\circ$ . (I) is a white hygroscopic powder which rapidly becomes a syrup when exposed to air. It contains 0.11% of ash. It does not reduce Fehling's solution. It decomposes at about  $215^\circ$  after softening at  $170^\circ$ , but degradation is obvious after some hr. at  $60^\circ$ . Acid hydrolysis effects 94.4% fission according to reducing power and 88.5% fission according to  $[\alpha]$ . The maximal aldose val. (Auerbach-Bodlander) is 1.8%. Since reversion and simultaneous formation of furfuraldehyde derivatives inhibit the complete hydrolysis of polyfructosans and a similar small aldose val. is observed with other fructosans, it is concluded that (I) is formed exclusively of fructose units. The formation of an optically inactive reducing sugar could not be confirmed. (II) is readily methylated in  $\text{COMe}_2$  according to Haworth to non-cryst. methylsinistrin,  $[\alpha]_D^{20}$   $-57.0^\circ$  in  $\text{CHCl}_3$ , which retains solvent very obstinately. It is hydrolysed by successive treatments with  $\text{H}_2\text{C}_2\text{O}_4$ - $\text{EtOH}$  and 0.25%  $\text{HCl}$  and the product is treated with  $\text{MeOH}$ - $\text{HCl}$  and benzoylated, whereby the following are isolated: pentamethylfructose, b.p.  $66^\circ/0.01$  mm.,  $[\alpha]_D^{20}$   $+62.0^\circ$ , hydrolysed to 1:3:4:6-tetramethylfructose, b.p.  $74^\circ/0.01$  mm.; trimethylmethylfructoside benzoate, b.p.  $130^\circ/0.01$  mm., converted into a trimethylmethylfructoside, b.p.  $77^\circ/0.01$  mm., and thence into a trimethylfructose, b.p.  $90^\circ/0.01$  mm.,  $[\alpha]_D^{20}$   $+19.2^\circ$  to  $+13.7^\circ$  in  $\text{CHCl}_3$ ,  $+5.8^\circ$  to  $0^\circ$  in  $\text{H}_2\text{O}$ , which gives the osazone of 3:4:6-trimethylfructose in small amount, but is probably a mixture of isomerides; dimethylmethylfructoside dibenzoate giving a dimethylmethylfructoside, b.p.  $92^\circ/0.01$  mm., and thence a dimethylfructose, b.p.  $132^\circ/0.01$  mm.,  $[\alpha]_D^{20}$   $-6.8^\circ$  in  $\text{CHCl}_3$ ,  $[\alpha]_D^{20}$   $-45.2^\circ$  to  $-54.6^\circ$  in  $\text{H}_2\text{O}$ ,  $-19.3^\circ$  to  $-23.7^\circ$  in abs.  $\text{MeOH}$ , which yields a monomethylfructosazone, m.p.  $202^\circ$ . The ratio of di:tri:tetra-methylfructose appears to be 1:3:1. H. W.

**Enzymic degradation of starch.** J. BLOM, A. BAK, and B. BRAAE (Z. physiol. Chem., 1936, 241, 273—287).—The limit of hydrolysis of starch (I) by  $\alpha$ -amylase (II) is at 47%; there are checks at 33% and 40%. The limit for purest  $\beta$ -amylase (III) [(II) destroyed by  $\text{AcOH}$  at  $0^\circ$  and  $p_H$  3.6] is  $53.1 \pm 0.5\%$ , this val. being independent of the concn. of (III) and of the presence of maltose, and the limit for (II)+(III) is  $80.1 \pm 0.4\%$ . Very high concns. of malt amylase (free from maltase but containing complement) convert (I) quantitatively into disaccharides and amylase from *Aspergillus oryzae* converts (I) quantitatively into monosaccharides. The capability to give the "starch-iodide" reaction

is destroyed partly by (III) and wholly by (II). These results and the properties of the dextrans produced at the different stages of hydrolysis indicate that the disaccharide residues in (I) are united by four different types of linking which exhibit unequal resistance to attack. The (I) mol. is probably made up of 30n monosaccharide or 15n disaccharide residues.

W. McC.

**Nature of cellulose.** E. HEUSER (Amer. Dye-stuff Rep., 1936, 25, 55—60, 80—83, 116—120, 135—137, 315—318, 338—339).—A review.

A. J. H.

**Cellulose as a highly polymerised compound.** K. FREUDENBERG (Ber., 1936, 69, [B], 1627—1631).—A historical account of the conception of cellulose as a highly polymerised compound. H. W.

**Action of metallic sodium on cellulose.** P. SCHORIGIN and N. N. MAKAROVA-SEMLJANSKAJA (Ber., 1936, 69, [B], 1713—1721).—Examination of the action of Na in liquid  $\text{NH}_3$  on cellulose shows that all its 3 OH groups participate in the change. There is no marked difference in the reactivity of the individual OH groups and the product is stable to Na. The individual Na atoms are united with different firmness, as shown by the marked partial alcoholysis of the  $\text{Na}_3$  derivatives; probably this is due mainly to the heterogeneous structure of cellulose. Only about one third of the ONa groups are active towards  $\text{MeI}$ , and the methylcellulose produced is a mixture of products in which the no. and position of the Me vary. During attempts to establish the presence of free OH at 6 it is shown that re-etherification does not occur during the action of  $\text{CPh}_3\text{Cl}$  on methylcellulose. The interaction of  $\text{Na}_3$  cellulose and  $\text{CS}_2$  is very sluggish and the products have a very low sap. val. The alkoxy-structure of "soda cellulose" is confirmed, since its reactions are similar in principle to those of  $\text{Na}_3$  cellulose. H. W.

**Selenium-substituted amino-acids. I. Synthesis of  $\alpha\alpha'$ -diamino- $\beta\beta'$ -diselenodipropionic acid (selenocystine).** A. FREDGA (Svensk Kem. Tidskr., 1936, 48, 160—165).—Interaction of  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{Me}\cdot\text{HCl}$  with  $\text{K}_2\text{Se}_2$  in alkaline medium at room temp. and subsequent evaporation gives  $\alpha\alpha'$ -diamino- $\beta\beta'$ -diselenodipropionic acid (I), two forms, rectangular plates, m.p. about  $215^\circ$  (decomp.) after becoming grey at about  $180^\circ$ , and rhombic plates (*r*- and *meso*-isomerides) (*Cu* salt). (I) is transformed by Hg in acid solution followed by  $\text{Na}_2\text{S}$  and  $\text{CH}_2\text{PhCl}$  in alkaline solution into benzylselenol-cysteine,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NSe}\cdot\text{H}_2\text{O}$ , m.p. about  $185^\circ$  (decomp.) after softening at  $150^\circ$ . H. W.

**New type of hypnotic amide. Diethylacet- $\beta$ -ketopropylamide.** W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 310).— $\text{CHET}_2\cdot\text{COCl}$  with  $\text{C}_5\text{H}_5\text{N}$  (in  $\text{C}_6\text{H}_6$ ) yields the mol. compound, which with aminoacetone hydrochloride affords the above amide, m.p.  $96$ — $97^\circ$ , having no pronounced hypnotic activity. F. O. H.

**Action of magnesium ethyl bromide on butyryl-ethylanilide.** M. MONTAGNE and Y. ISAMBERT (Compt. rend., 1936, 203, 331—333).—The action of  $\text{MgEtBr}$  on butyryl-ethylanilide (I) in boiling  $\text{Et}_2\text{O}$

or PhMe gives considerable amounts of  $C_2H_5$ ,  $CEt_2Pr^a \cdot OH$ , and  $\beta$ -hydroxy- $\alpha$ - $\beta$ -diethylhexethylamylide (II), b.p. 155—157°/3 mm. (II) passes when distilled under atm. pressure or boiled with NaOH-EtOH into  $COEtPr^a$  and (I) and is hydrolysed by boiling 48% HBr to  $NHPhEt$  and neutral products, including  $\delta$ -ethyl- $\Delta^8$ -heptene, b.p. 138—145°/760 mm. (*di*-bromide, b.p. 95—100°/20 mm.), and a lactone  $CP^a \begin{cases} \text{CHET} \cdot CO \\ \text{CHMe} \cdot O \end{cases}$  or  $CHET \begin{cases} \text{CHET} \cdot CHET \\ O \cdot CO \end{cases}$ , b. 132°/18, mm. The formation of ketone or *tert.* amine as from  $HCO \cdot NPhEt$  or  $HCO \cdot NEt_2$  is scarcely observed.

H. W.

**Transformation of carbamide into ammonium carbonate.** E. TOPORESCU (Compt. rend., 1936, 202, 2075).—2% aq.  $CO(NH_2)_2$ , placed in the inner cell of a parchment dialyser, with 6% aq. NaCl in the outer compartment, was partly converted into  $(NH_4)_2CO_3$  in 24 hr. at 40°.

H. J. E.

**Oxidation products of thiocarbamide.** The dioxide as derivative of sulphoxylic acid. J. BOESEKEN (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 717—721).— $CS(NH_2)_2$  in 50% EtOH with slightly more than the calc. amount of an acid and  $\frac{1}{2}$  mol. of  $H_2O_2$  affords salts of dithioformamidine (I).  $CS(NH_2)_2$  in neutral solution with  $H_2O_2$  or  $AcO_2H$  affords thiocarbamide dioxide (II) and not, as suggested by Barnett (J.C.S., 1910, 97, 63), formamidinesulphinic acid. It is neutral to litmus and to Congo-red, and is a strong reducing agent, pptg. many metals from solutions. Dil. NaOH reacts to form  $Na_2S_2O_3$ , and  $Ba(OH)_2$  affords  $BaSO_4$  and  $CO(NH_2)_2$ . With  $AcO_2H$ , (II) affords formamidinesulphonic acid (III), also obtainable from  $CS(NH_2)_2$  and 3 mols. of  $AcO_2H$ , whereas  $AcO_2H$  in presence of  $NaNO_3$  and  $AcOH$  converts  $CS(NH_2)_2$  into the nitrate of (I). (III) does not react with cold, acid  $KMnO_4$  solution, but  $Ba(OH)_2$  affords  $BaSO_3$  and  $CN \cdot NH_2$ . No experimental details are given.

P. G. C.

(A) Hydrazides, (B) azides, of unsaturated fatty acids. (c) Hydrazides and azides of naphthenic acids. A. OSKERKO (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 69—77, 79—92, 293—302).—(A) The hydrazides of oleic acid (I), m.p. 95—96° (hydrochloride, m.p. 110—112°), erucic acid (II), m.p. 77—78° (hydrochloride, m.p. 120—121°), and undecenoic acid (III), m.p. 84—85° (hydrochloride, m.p. 128—130°), are obtained by boiling the Me esters of the appropriate acids with  $N_2H_4 \cdot H_2O$ .

(B) The azides of (I), (II), and (III), prepared from the above hydrochlorides and aq.  $NaNO_2$ , or from the acid chlorides and  $NaN_3$  in  $COMe_2$ , are oils, readily decomp. at room temp. to yield carbimides; when boiled with EtOH they yield respectively the urethane of (I), m.p. 42—43°, of (II), m.p. 47—48°, and of (III), m.p. 53—54°.

(c) The hydrazide, m.p. 28—29° (hydrochloride, m.p. 157—159°), and azide (IV), an oil, of decahydronaphthoic acid (V) have been prepared by the above methods. (IV) decomposes at room temp. to yield the carbimide, b.p. 194—196°/7 mm., of (V), the urethane, b.p. 84—86°/3 mm., of which is obtained by boiling with EtOH. Gaseous or aq.  $NH_3$  converts (IV) into the amide of (V).

R. T.

**Complex compounds of dicarboxylic acid hydrazides.**—See this vol., 1078.

**Reaction of semicarbazones with alcohols.** E. W. McCLELLAND and C. E. SALKELD (J.C.S., 1936, 1050).—*iso*- $C_5H_{11} \cdot OH$  and the aldehyde or ketone semicarbazone react with elimination of  $NH_3$  to give *isoamyl benzylidene*-, m.p. 103°,  $\alpha$ -phenylethylidene-, m.p. 74°, *o*-hydroxybenzylidene-, m.p. 140°, *piperonylidene*-, m.p. 83°, and *o*-nitrobenzylidene-hydrazine-carboxylate, m.p. 95°.

F. R. S.

**Organo-arsenic compounds. III.** H. N. DAS-GUPTA (J. Indian Chem. Soc., 1936, 13, 305—308).— $AsMeCl_2$  and  $C_2H_2$  give methyl- $\beta$ -dichlorovinylarsine and methyl- $\beta$ -chlorovinylchloroarsine, b.p. 110—115°, which with  $H_2O_2$  affords methyl- $\beta$ -chlorovinylarsinic acid, m.p. 149—150°, with  $MgPhBr$  yields phenyl-methyl- $\beta$ -chlorovinylarsine, and with the appropriate reagents forms methyl- $\beta$ -chlorovinylarsenious sulphide, cyanide, and oxide.

F. R. S.

**Resolution of  $\alpha$ -arsino-carboxylic acids.** H. J. BACKER and C. H. K. MULDER (Rec. trav. chim., 1936, 55, 594—601).—*d*- $\alpha$ -Arsino-propionic, -butyric, -valeric, -hexoic, -heptioic, -octoic, -nonoic, and -phenyl-acetic acids (I), m.p. 134°, 127°, 116—117°, 96°, 82—83°, 114°, and 115°,  $[M]_D +41^\circ$ ,  $+25.7^\circ$ ,  $+19.3^\circ$ ,  $+6.1^\circ$ ,  $+21.9^\circ$ ,  $+3^\circ$ ,  $+3.4^\circ$ , and  $+3.1^\circ$  in  $H_2O$ , respectively, are obtained from the *dl*-acids by way of the diquinine salts,  $+6$ ,  $5$ ,  $4$ ,  $3$ ,  $2$ ,  $5.5$ ,  $5$ , and  $6H_2O$ , respectively. The *Ba H* salts have  $[M]_D -8.5^\circ$ ,  $-10.5^\circ$ ,  $-15.7^\circ$ ,  $-8.2^\circ$ ,  $-19.4^\circ$ ,  $-5^\circ$ ,  $-7.5^\circ$ , and  $+4.2^\circ$  in  $H_2O$ , respectively, there being an inversion in all except the last case; addition of a third equiv. of *Ba* has little effect. The *Ba* salts, except that of (I), do not racemise. The free acids racemise slowly [(I) fast], slightly faster in presence of HCl.

R. S. C.

**Polymetatelluric acid esters.** M. PATRY (Compt. rend., 1936, 202, 2088—2090).— $MeOH$ ,  $EtOH$ , and  $Pr^aOH$  dissolve hydrated  $TeO_3$  in the cold.  $Bu^aOH$  and  $C_5H_{11} \cdot OH$  dissolve it on heating. By refluxing and evaporating a residue is obtained from which the normal esters  $(TeO_4R_2)_n$  can be extracted with  $Et_2O$  (except in the case of  $MeOH$ ). *sec.* and *tert.* saturated alcohols do not react with polymetatelluric acid, but glycerol and  $CH_2Ph \cdot OH$  readily yield esters. The properties of polymetatelluric esters (I) are reviewed. Orthotelluric acid dissolves slowly when heated with  $MeOH$ ,  $EtOH$ ,  $PrOH$ ,  $BuOH$ , and  $C_5H_{11} \cdot OH$ . Evaporation of the solution yields (I). A solution of  $CH_2N_3$  in  $Et_2O$  with hydrated  $TeO_3$  yields the normal ester,  $TeMe_2O$ , on evaporation.

H. J. E.

**Formation of organo-magnesium halides and their behaviour towards halogen acids, their ammonium and amine salts, and towards aniline.** J. HOUBEN, J. BOEDLER, and W. FISCHER (Ber., 1936, 69, [B], 1766—1788).—The use of *Mg* powder in the prep. of Grignard reagents is not generally advisable, since when preserved it readily absorbs  $H_2O$  and is partly converted into  $MgO$  and  $Mg(OH)_2$ , whereby ultimately the Würtz-Fittig synthesis is facilitated; if used, it should be freshly filed from a *Mg* block, but does not then exceed



Mg turnings in activity, particularly if the latter are freshly triturated in a warm mortar. In the complete absence of air and moisture (presence of Na) in the alkyl halide series  $C_1$  to  $C_{16}$  the mean yields of  $MgAlkHal$  are 97.6%, 89.6%, and 85.8%, respectively, in the cases of chloride, bromide, and iodide. The min. yield of 79.7% is observed in the case of Mg cetyl iodide. Grignard's observation that the Würtz-Fittig synthesis predominates when  $C$  is  $>6$  is therefore erroneous under these conditions. Contrary to Hess *et al.* (A., 1921, i, 777),  $MgEtI$  is completely decomposed by  $HBr$ , although, under some conditions, only partly by  $HI$ ; if excess of the latter is used, complete decomp. of  $MgEtI$  and all other Grignard reagents, whether "individual" or in  $Et_2O$ , is achieved. A ready prep. of  $HBr$  or  $HI$  from  $Br$  or  $I$  and boiling tetrahydronaphthalene is described. Only  $MgEtI$  (and possibly  $MgMeI$ ) is smoothly decomposed by  $NH_4Cl$ ,  $NH_4Br$ , and  $NH_4I$ , whereas  $NH_4F$  is without action.  $NH_4Cl$  and  $NH_4Br$  are inactive towards  $MgEtCl$  and  $MgEtBr$ , whereas both are decomposed by  $NH_4I$ . Possibly the difference is due to the differing solubility of the  $NH_4$  salts in the Grignard solutions and depends somewhat on their state of division.  $NH_2Me.HCl$  is only slightly more active than  $NH_4Cl$ .  $NEt_3.HCl$  is more active, whereas  $NEt_3I$  is completely ineffective even in presence of  $FeCl_3$ .  $NH_2Ph.HCl$  is as vigorous as  $NH_2Ph$  in its action on  $MgEtCl$ . With mixtures of Grignard reagents a difficultly explicable inactivation is observed. The apparent inertia of a mixture of  $NHPh.MgI$  and  $MgMeI$  towards  $CO_2$  in a closed vessel (Houben, A., 1905, i, 873) is caused by the liberation of an equal vol. of  $CH_4$  thus:  $NHPh.MgI + MgMeI + CO_2 = MgMeI + NHPh.CO_2.MgI = MgI.NPh.CO_2.MgI + CH_4$ .

H. W.

**Complex compounds of the olefines with metallic salts. II. Homologues of Zeise's salt.** J. S. ANDERSON (J.C.S., 1936, 1042—1049).—The formation of compounds of  $PtCl_2$  with olefines has been shown to be effected by the reactions (a) displacement of  $Cl'$  from  $PtCl_2$  anion and (b) displacement of one olefine from such complexes by another olefine. By this reaction, compounds analogous to ethylene Pt chloride (I) may be obtained and evidence is advanced that bis-olefine compounds may exist. Reaction (b) affords conclusive evidence that the attachment of the olefines is truly co-ordinative, and not by principal valencies. The co-ordinating ability decreases in the order  $C_6H_4 > CHPh.CH_3 > indene > cyclohexene > CPh.CH_2$  and  $CPhMe.CH_3$ , and this is discussed in relation to steric and polar influences on the double linking. With  $K_2PtCl_4$ , styrene gives  $K$  styrenetrichloroplatinite, which with tetramminoplatinous chloride forms tetramminoplatinous styrenetrichloroplatinite, whilst indene yields  $K$  indenetrichloroplatinite, converted by  $[CoCl_2.en_2]Cl$  into 1:6-dichlorobisethylenediaminocobaltic indenetrichloroplatinite. cycloHexene with  $EtOH-H_2PtCl_4$  gives a complex, which with  $[CoCl_2.en_2]Cl$  yields 1:6-dichlorobisethylenediaminocobaltic cyclohexenetrichloroplatinite. Styrene with Zeise's salt gives  $K$  styrenetrichloroplatinite, and with (I) forms distyreneplatinous chloride.  $\Delta^B$ -Amylene with (I) yields

amyleneplatinous chloride. Anilinium carbonyltrichloroplatinite does not react with styrene.

F. R. S.

**Contact transformation of cis- and trans-dimethylcyclohexane.** E. I. MARGOLIS (Ber., 1936, 69, [B], 1710—1713).—With *o*-, *m*-, and *p*-dimethylcyclohexane passage over Os-asbestos at 50—70° does not cause isomerisation of the *trans*- into the *cis*-form.

H. W.

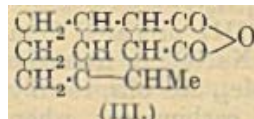
**Addition and additive products of halogens to benzene derivatives. VII. Addition of chlorine to penta- and hexa-chlorobenzene.** T. VAN DER LINDEN (Rec. trav. chim., 1936, 55, 569—576; cf. this vol., 975).— $C_6HCl_5$  and liquid  $Cl_2$  in light give (5 months) mainly mixed crystals (I), m.p. 90—92°, of 1:2:3:3:4:4:5:5:6:6-nonachloro- $\Delta^1$ -cyclohexene (91.5%) and an isomeride thereof (8.5%) with a little  $C_6Cl_6$  [probably produced by loss of  $Cl$  from (I), less probably by direct substitution]. The nature of (I) is determined by quant. reaction with  $Zn-EtOH$  to  $C_6HCl_5$  and with  $NaOH-MeOH$  to much  $C_6Cl_6$  and a little octachloro- $\Delta^{2:5}$ -cyclohexadiene (II).  $C_6Cl_6$  and an excess of liquid  $Cl_2$  in light give (3 months) dodecachlorocyclohexane (III), sublimes from 250°, m.p. about 285° (decomp. with liberation of  $Cl_2$ ; sealed tube), not volatile in steam, almost odourless, and stable to fuming  $HNO_3$ .  $C_6Cl_6$  and  $3Cl_2$  give very slowly (III) and decachlorocyclohexene (IV), m.p. about 92°. (III) and (IV) react only slowly with  $NaOH-EtOH$ . The substance, m.p. 66—68°, of Smith *et al.* (A., 1934, 40) is not (III); it may be a stereoisomeride (chair-boat forms), but this is improbable. Addition of  $Cl_2$  probably occurs first at  $CH:CCl$  and then mainly at the ends of the conjugated system of ethylenic linkings thus produced. cycloHexadienes with conjugated linkings are too unstable to exist. The preferential formation of certain isomerides by addition of  $Cl_2$  to  $C_6H_6$  and its derivatives probably depends on energy relations. (II) is the only  $Cl$ -derivative in this series to lose  $HCl$  to  $Zn-EtOH$ .

R. S. C.

**Isomerisation of cyclic hydrocarbons with isolated systems of double linkings.** J. M. SLOBODIN (J. Gen. Chem. Russ., 1936, 6, 129—136).—1-Vinyl- $\Delta^3$ -cyclohexene when heated at 200—235° in presence of floridin is converted into 1-vinyl- $\Delta^2$ -cyclohexene (I), b.p. 130—137°, yielding 1- $\alpha$ -hydroxyethyl-1:2:3-trihydroxycyclohexane (II), m.p. 48°, on oxidation with  $KMnO_4$  at 0°. (II) yields  $\alpha$ -ketoadipic acid with  $K_2Cr_2O_7$  and  $H_2SO_4$  in  $H_2O$  (at the b.p.). (I) with maleic anhydride at 100° affords (III). *d*-Limonene at 210—235° in presence of floridin yields chiefly islimonene.

R. T.

**Phenylcyclopentylmethane and cyclohexylcyclopentylmethane and their behaviour during catalytic hydrogenation.** J. I. DENISSENKO (Ber., 1936, 69, [B], 1668—1670).—cycloPentanone and  $CH_2Ph.MgCl$  yield 1-benzylcyclopentan-1-ol, b.p. 129—130°/11 mm., dehydrated by anhyd.  $H_2C_2O_4$  to phenyl- $\Delta^1$ -cyclopentenylmethane, b.p. 120—122°/10 mm., catalytically hydrogenated (Pt-black in  $EtOH$ )



to *phenylcyclopentylmethane* (I), b.p. 234—236°/750 mm. When passed with  $H_2$  over Pt-C at 190—200°, (I) gives *cyclopentylcyclohexylmethane* (II), b.p. 224—226°/750 mm. Passage of (I) or (II) over Pt-C at 300—310° is accompanied by fission of the *cyclopentyl* groups and gives mainly *n*-hexylbenzene. H. W.

**Terpenoid ring systems. II. Polyionone.** H. VOGEL and M. STOHL (Ber., 1936, 69, [B], 1573—1575; cf. A., 1933, 1055).—Polyionone (improved prep.) is probably  $CRMe:CH:C(CH:CHR):CH:COR$  ( $R=CH:CH-C \begin{smallmatrix} CMe_2 \cdot CH_2 \\ CMe \cdot CH_2 \end{smallmatrix} > CH_2$ ). It is readily

autoxidised and must be preserved under  $N_2$  in the dark. When its solution in  $Et_2O$  is placed over 25% HCl a bluish-violet zone is formed and after agitation the acid layer becomes dark violet, whilst the ethereal solution becomes lighter in colour. H. W.

**Formation of carbon chains during the catalytic hydrogenation of alkyl halides.** M. BUSCH and W. WEBER [with C. DARBOVEN, W. RENNER, H. J. HAHN, G. MATHAUER, F. STRATZ, K. ZITZMANN, and H. ENGELHARDT] (J. pr. Chem., 1936, [iii], 146, 1—55).—Under conditions similar to those adopted with Pd, Pt causes little elimination of Br from PhBr. Os, Ru, and Rh are similarly unsuitable. Kelber's Ni in presence of KOH— $EtOH-H_2$  is inactive; with  $N_2H_4$  as source of H, however, the change is very rapid, and only with PhCl is Pd superior to Ni. The formation of  $Ph_2$  is never observed. Diaryl production is not therefore due to intermediate radical formation, but is a sp. action of Pd. Since  $Ph_2$  is produced only in min. amount from PhBr and Pd— $CaCO_3$  in  $H_2O$  in presence of  $H_2$  or  $N_2H_4$ , a sp. action of MeOH (EtOH) is indicated, and when PhBr is heated in KOH—MeOH containing Pd— $CaCO_3$   $Ph_2$  is obtained in 15—20% yield which is not influenced by presence of  $H_2$  or  $N_2H_4$ . H is derived therefore from MeOH, and, accordingly,  $CH_2O$  is detected in the solution. The initial reaction is therefore  $PdH_2 + PhBr \rightarrow HBr + PdPhH$ . In presence of active H in sufficient concn. the following step is  $PdPhH + 2H \rightarrow PdH_2 + C_6H_6$ , whereas in its absence reaction is  $PdPhH + PhBr \rightarrow PdPh_2 + HBr$  and  $PdPh_2 + H_2 \rightarrow PdH_2 + Ph_2$ . The favourable influence of  $N_2H_4$  on the yield of diaryl depends on its power of reaction with  $CH_2O$  to form  $(CH_2)_2N_2$  which is ultimately reduced to  $NH_2Me$ , whereby the concn. of active H is diminished. As expected, an optimal concn. of  $N_2H_4$  is observed. The hydrogenation of PhBr under widely varied conditions is described. With compounds  $C_6H_4XY$  ( $X=Cl$  or  $Br$ ;  $Y=NH_2$ ,  $NMe_2$ ,  $Me$ ,  $CO_2H$ ,  $OMe$ , or  $OH$ ), Cl is less readily eliminated than Br, and Cl-compounds are therefore less suitable for the production of diaryls. Little difference in the degree of diaryl formation is observed between *m*- and *p*-derivatives, whereas *o*-compounds are more difficult to hydrogenate and nuclear union is seldom observed. Loss of halogen increases with increasing concn. of  $N_2H_4$ , but greater production of diaryl is not general. *p*- $C_6H_4Br \cdot COMe$  in presence of  $N_2H_4$  affords the azine and hydrazone of CPhMe and *pp'*-diacetophenonedihydrazone, decomp. 195—200°, which passes when preserved into the diazine,

$OMe < \begin{smallmatrix} C_6H_4 \cdot C_6H_4 \\ N \quad N \end{smallmatrix} > CMe$  or  $\begin{smallmatrix} N \cdot CMe \cdot C_6H_4 \cdot C_6H_4 \cdot CMe \cdot N \\ N \cdot CMe \cdot C_6H_4 \cdot C_6H_4 \cdot CMe \cdot N \end{smallmatrix}$  decomp. > 350°. 3-Bromopyridine affords  $C_5H_5N$  and 3:3'-dipyridyl. *p*- $C_6H_4Br_2$  affords  $Ph_2$ , *p*- $C_6H_4Ph_2$ , and (*p*- $C_6H_4Ph$ ) $_2$ , isolated by extraction of the catalyst with suitable solvents, and *p*-quinquiphenyl, m.p. 395°, *p*-sexiphenyl, m.p. 475°, and *p*-septiphenyl, m.p. 545°, obtained by fractional sublimation under diminished pressure from the catalyst. Hydrogenation of *m*- $C_6H_4Br_2$  in presence of KOH—MeOH— $H_2O$ —Pd— $N_2H_4$  at 140° yields *m*-noniphenyl  $C_{54}H_{38}$ , m.p. 166° after softening at 163°, *m*-deciphenyl, m.p. 184° after softening at 180°, *m*-undeciphenyl, m.p. 202° after softening at 195°, *m*-duodeciphenyl, m.p. 223° after softening at 214°, *trideciphenyl*, m.p. 245° after softening at 239° ( $NO_2$ -derivative, (?)  $(NO_2)_3C_6H_2 \cdot [C_6H_3 \cdot NO_2]_{11} \cdot C_6H_2(NO_2)_3$ , m.p. 185° (decomp.); *Cl*-derivative,  $C_{78}H_{41}Cl_{13}$ , m.p. 156° after softening at 152°), whereas in boiling solution *m*-quinquiphenyl, m.p. 112°, with products composed of 11—14 nuclei and containing Br results. When *m*- $C_6H_4I_2$  is used the product is greatly contaminated with coloured materials. *o*- $C_6H_4Br_2$  gives  $C_6H_6$ , some  $Ph_2$ , and very little more complex material. 3:5- $C_6H_3MeBr_2$  yields 3:3'-ditolyl, *m*-tritolyl,  $C_6H_3Me(C_6H_4Me)_2$ , m.p. 65°, and a little more complex product. With phenols little chain formation is observed, whereas 2:4- $C_6H_3Br_2 \cdot OMe$  gives PhOMe with considerable amounts of *pp'*- and some *oo'*-dianisole. 1:8- $C_{10}H_6Br_2$  affords  $C_{10}H_8$ , di- and tetra-hydronaphthalene, with indications of the presence of perylene, but analogous experiments with 1:8- $C_{10}H_6I_2$  are unsatisfactory. 1:6-Dibromo-2-naphthol gives  $\beta$ - $C_{10}H_7 \cdot OH$  and 2:2'-dihydroxy-1:1'-dinaphthyl. 3:5-Dibromopyridine yields diprydil (30%), *terpyridyl* (18%), m.p. 249—251°, (?) *quaterpyridyl* (5%), m.p. 290° (*hydrochloride*; *perchlorate*), and (?) *quinquipyridyl* (2%), m.p. 330°. *s*- $C_6H_3Br_3$  yields highly complex products, m.p. 241° after softening at 235°, m.p. 259—261°, and m.p. 280—285°, respectively, probably containing 30, 16, and 22  $C_6H_6$  nuclei, respectively. *pp'*-Dibromodiphenylmethane affords 4:4'-dibenzylidiphenyl, m.p. 114—115°, *terdiphenylmethane*, m.p. 179—180° after softening at 175°, *quaterdiphenylmethane*, m.p. 239—240°, and (?) *quinquidiphenylmethane*, m.p. 280°. 2:2'-Dibromodiphenylmethane yields  $CH_2Ph$ , and fluorene (14% yield). 2:2'-Dibromo-5:5'-diaminodiphenylmethane gives 5:5'-diaminodiphenylmethane and diaminofluorene, m.p. 164° (yield 3.5%). Dihydrophenanthrene (yield about 30%) and  $(CH_2Ph)_2$  are obtained from 2:2'-di-iododibenzyl. Under the usual conditions  $CH_2PhCl$  and  $CH_2PhBr$  afford PhMe and  $(\cdot CH_2Ph)_2$ , but in very conc. solution  $CH_2PhCl$  affords  $CH_2Ph \cdot OEt$  and  $N(CH_2Ph)_2 \cdot NH_2$ .  $CHPhCl_2$  gives  $(\cdot CHPhCl)_2$  further hydrogenated to stilbene.  $CPhCl_3$  gives a mixture of  $\alpha$ - and  $\beta$ -( $CPhCl_2$ ) which also appears to be derived from  $(\cdot CPhCl)_2$ . Drastic reduction of  $(\cdot CPhCl)_2$  affords  $(\cdot CH_2Ph)_2$ , also obtained from stilbene. *o*- $C_6H_4Cl \cdot CH_2Cl$  gives *o*- $C_6H_4Cl \cdot CH_2 \cdot OMe$ , whereas *p*- $C_6H_4Cl \cdot CH_2Cl$  affords *p*- $C_6H_4Cl \cdot CH_2 \cdot OEt$  and  $(\cdot CH_2Ph)_2$ .  $(\cdot CHPh)_2$  and  $CHPh \cdot OMe$  result from  $CH_2PhBr$ . Phenylcyclohexylmethyl chloride gives  $\alpha\beta$ -diphenyl- $\alpha\beta$ -dicyclohexylethane, m.p. 198—200°.  $CHPhBr \cdot CO_2Et$  yields  $(\cdot CHPh \cdot CO_2H)_2$ , but



$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  gives  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .  $\text{CHPh}\cdot\text{CHBr}$  affords diphenylbutadiene (and polymerides) which could not be hydrogenated further. H. W.

**Nuclear-substituted derivatives of isopropylbenzene.** W. QVIST and A. SALO (*Acta Acad. Aboensis Math. Phys.*, 1934, 8, No. 4, 30 pp.; *Chem. Zentr.*, 1934, ii, 594—595).—The  $\text{Pr}^i$  group in  $\text{PhPr}^i$  is more readily replaced by Cl than in *p*-cymene. Passage of  $\text{Cl}_2$  into  $\text{PhPr}^i$ , in  $\text{CCl}_4$  at  $0^\circ$  in presence of I in daylight, affords mainly 2:4:5-trichlorocumene (I), b.p.  $240\text{--}245^\circ$ , which with  $\text{HNO}_3$  gives 2:4:5-trichloro-1:3-dinitrobenzene, m.p.  $102\text{--}5\text{--}103\text{--}5^\circ$ ; this with  $\text{EtOH}\cdot\text{NH}_3$  yields 6-chloro-2:4-dinitro-m-phenylenediamine, m.p.  $249\text{--}249\text{--}5^\circ$ , and, with  $\text{NH}_4\text{Ph}$ , 6-chloro-2:4-dinitro-1:3-dianilinobenzene, m.p.  $188^\circ$ . (I) is accompanied by *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ ; 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$ , m.p.  $139\text{--}5\text{--}140\text{--}5^\circ$ , yielding the 3- $\text{NO}_2$ , m.p.  $99\text{--}100^\circ$ , and 3:3-( $\text{NO}_2$ ) $_2$ , m.p.  $232\text{--}233^\circ$ , compounds, with  $\text{HNO}_3$ ; 1:3:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$  and  $\text{C}_6\text{HCl}_5$ . Passage of  $\text{Cl}_2$  into  $\text{PhPr}^i$  containing I and Fe at  $0^\circ$  in the dark affords *p*-chlorocumene (II), b.p.  $190\text{--}200^\circ$ , 3:4-dichlorocumene (III), b.p.  $120\text{--}125^\circ/9\text{ mm.}$ , (I), b.p.  $125\text{--}130^\circ/9\text{ mm.}$ , 2:4:5:6-tetrachlorocumene (IV), m.p.  $41\text{--}41\text{--}5^\circ$ , and 2:3:4:5:6-pentachlorocumene (V), m.p.  $81\text{--}82^\circ$ . (II) is oxidised to *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$  and (III) to 2:4:5- $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{CO}_2\text{H}$ , m.p.  $164\text{--}165^\circ$ . (IV) with  $\text{HNO}_3$  yields 2:4:5:6-tetrachloro-1:3-dinitrobenzene, m.p.  $153\text{--}154^\circ$ , yielding 6-chloro-2:4-dinitro-1:3:5-trianilinobenzene, m.p.  $179\text{--}180^\circ$ , with  $\text{NH}_2\text{Ph}$ . (V) with  $\text{HNO}_3$  yields  $\text{C}_6\text{Cl}_5\cdot\text{NO}_2$ , m.p.  $144\text{--}145^\circ$ , reduced to  $\text{C}_6\text{Cl}_5\cdot\text{NH}_2$ , m.p.  $232\text{--}233^\circ$ .

CH. ABS. (r)

**Condensation of aryl methyl ketones.** K. BERNHAUER, P. MÜLLER, and F. NEISER (*J. pr. Chem.*, 1936, [ii], 145, 301—308).—Condensation of ketones,  $\text{COArMe}$ , by  $\text{KHSO}_4$  and a little  $\text{H}_2\text{SO}_4$  to triarylbenzenes is favoured by the presence of negative and hindered by that of positive substituents in the Ar.  $\text{COPhEt}$ ,  $\text{COPhPr}^a$ ,  $\text{COPhPr}^b$ ,  $\alpha$ - and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{COMe}$ , and  $\text{COPh}\cdot\text{CH}_2\text{Ph}$  (I) do not thus condense, presumably owing to steric hindrance. Yields are as stated, reaction being effected at  $80\text{--}85^\circ$  unless otherwise stated: *s*- $\text{C}_6\text{H}_3\text{Me}_3$  (37%); also obtained by I at  $195^\circ$  or in poor yield by  $\text{HgI}_2$  at  $240\text{--}250^\circ$ ; *s*-tri-*p*-tolyl-, m.p.  $170^\circ$  (14%), *p*-chlorophenyl-, m.p.  $238^\circ$  (46%); also obtained by I at  $170^\circ$ , *m*-nitrophenyl-, m.p.  $298\text{--}299^\circ$  (68%), *p*-diphenyl-, (51% at  $125^\circ$ ), m.p.  $230\text{--}231^\circ$ , and *p*-nitro-*p*-diphenyl-benzene, m.p.  $345\text{--}346^\circ$  (32% at  $160^\circ$ ). *p*-Nitrophenyl-4-acetophenone, m.p.  $151^\circ$ , b.p.  $256\text{--}265^\circ/10\text{ mm.}$ , is obtained in 11% yield from *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{Ph}$ ,  $\text{AcCl}$ , and  $\text{AlCl}_3$  in  $\text{PhNO}_2$  at  $80^\circ$ . (I) with I at  $330\text{--}340^\circ$  gives an 18% yield of *s*-tetraphenylfuran, m.p.  $168\text{--}5\text{--}169^\circ$  [identified by oxidation by  $\text{HNO}_3\text{--AcOH}$  to  $(\text{CPhBz})_4$ ], probably by dehydrogenation of the intermediate  $\text{CH}_2\text{Ph}\cdot\text{CPh}\cdot\text{CHPhBz}$ .

R. S. C.

**Dipole moments of certain polynitro-compounds.**—See this vol., 924.

**Chlorination of *p*-chlorotoluene.** H. WAHL (*Compt. rend.*, 1936, 202, 2161—2163).—Direct chlorination of *p*- $\text{C}_6\text{H}_4\text{MeCl}$  ( $20\text{--}40^\circ$ ; Fe catalyst) yields 1:2:4- (58%) and 1:3:4- $\text{C}_6\text{H}_3\text{MeCl}_2$  (42%).

At  $100^\circ$  without catalyst, side-chain substitution occurs except in presence of  $\text{PbCl}_2$ , when normal nuclear substitution results. F. N. W.

**Plano-radiate compounds. IV. Hexa(-chloro- and -iodo-methyl)benzene.** H. J. BACKER (*Rec. trav. chim.*, 1936, 55, 591—594; cf. this vol., 715).— $\text{C}_6(\text{CH}_2\cdot\text{OH})_6$  (I) gives mixtures with  $\text{HCl}\text{--H}_2\text{SO}_4$  and  $\text{SOCl}_2$ .  $\text{Cl}_2$  and  $\text{C}_6\text{Me}_6$  in boiling  $\text{C}_2\text{HCl}_5$  give hexa(chloromethyl)benzene, m.p.  $287\text{--}5^\circ$  (crystallographic data given), converted by hot  $\text{KOAc}\text{--Ac}_2\text{O}$  into  $\text{C}_6(\text{CH}_2\cdot\text{OAc})_6$  (I) and HI saturated at  $0^\circ$  give hexa(iodomethyl)benzene, decomp. from  $200^\circ$ . Hexa(alkylthiomethyl)benzenes,  $\text{C}_6(\text{CH}_2\cdot\text{SR})_6$ , give mixtures with  $\text{HgCl}_2$ ; however, when R is Me, Et, or Bu<sup>a</sup>, a tetra-, m.p.  $100\text{--}102^\circ$ , octa-, m.p.  $98\text{--}99^\circ$ , and tetra-iodide, m.p.  $84\text{--}5^\circ$ , respectively, are obtained. R. S. C.

**Nitroschlorides of the benzene series.** R. PERROT (*Compt. rend.*, 1936, 203, 329—331).—When  $\text{NOCl}$  is added to the unsaturated aromatic compound dissolved in  $\text{CCl}_4$  or  $\text{CHCl}_3$  at a low temp. nitroschlorides of the following compounds are obtained, frequently better characterised by converting them by piperidine in  $\text{C}_6\text{H}_6$  into the corresponding nitrol-piperidines, the m.p. of which are recorded in parentheses:  $\text{CHPh}\cdot\text{CH}_2$ , m.p.  $102\text{--}5^\circ$  ( $136^\circ$ ); *p*-tolylethylene, m.p.  $101^\circ$  ( $163\text{--}5^\circ$ );  $\text{CHPh}\cdot\text{CHMe}$ , m.p.  $129\text{--}5^\circ$  ( $115^\circ$ );  $\text{CH}_2\cdot\text{CHPhMe}$ , m.p.  $89^\circ$  ( $122^\circ$ );  $\text{CHPh}\cdot\text{CHBr}$ , m.p.  $99\text{--}100^\circ$  ( $162\text{--}163^\circ$ ); anethole, m.p.  $126^\circ$  (about  $90^\circ$ );  $\text{CPh}\cdot\text{CH}_2$ , m.p.  $95^\circ$  ( $131^\circ$ );  $\text{CHPh}\cdot\text{CMc}_2$ , m.p.  $121\text{--}5^\circ$  ( $163^\circ$ );  $\text{CHPh}\cdot\text{CHPh}$ , m.p.  $138^\circ$  ( $155^\circ$ ); cyclohexene, m.p.  $150^\circ$  ( $119^\circ$ ); 1:4-dihydronaphthalene, m.p.  $143\text{--}144^\circ$  ( $146^\circ$ ); indene, blackens at about  $150^\circ$  ( $157^\circ$ );  $\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$ , m.p.  $116^\circ$  (about  $60^\circ$ ). The mol. wt. of the compounds of each series determined cryoscopically in  $\text{C}_6\text{H}_6$  or dioxan is 1.3—1.8 times as great as that expected. H. W.

**Resolution of an allene hydrocarbon into optical antipodes by asymmetric catalysis.** P. MAITLAND and W. H. MILLS (*J.C.S.*, 1936, 987—998).— $\beta$ -Hydroxy- $\beta$ -phenyl- $\beta$ -1-naphthylpropionophenone, m.p.  $167\text{--}169^\circ$ , obtained from  $\text{Mg}$ , 1- $\text{C}_{10}\text{H}_7\cdot\text{Br}$ , and  $\text{CH}_2\text{Bz}_2$ , is converted (HCl) into *Ph*  $\beta$ -phenyl- $\beta$ -1-naphthylvinyl ketone, m.p.  $107\text{--}108^\circ$ , which with 1- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  yields  $\alpha$ -diphenyl- $\alpha$ -di-1-naphthylallyl alcohol (I), m.p.  $187\text{--}189^\circ$ . The ketone may also be prepared by dehydration (HCl) of  $\alpha$ -bromo- $\beta$ -phenyl- $\beta$ -1-naphthylpropionophenone, m.p.  $196\text{--}198^\circ$ , obtained from 1- $\text{C}_{10}\text{H}_7\cdot\text{MgBr}$  and  $\text{CHPh}\cdot\text{CHBz}$ . Dehydration of (I) with  $\text{Ac}_2\text{O}$  or *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  affords *r*- $\alpha$ -diphenyl- $\alpha$ -di-1-naphthylallene (II), m.p.  $242\text{--}244^\circ$ . With *d*-camphor- $\beta$ -sulphonic acid, (I) is dehydrated to a mixture of (II) and the *d*-allene, m.p.  $158\text{--}159^\circ$ ,  $[\alpha]_{\text{D}}^{25} +43^\circ$  in  $\text{C}_6\text{H}_6$ , and with the *l*-acid, the *l*-allene, m.p.  $158\text{--}159^\circ$ ,  $[\alpha]_{\text{D}}^{25} -43^\circ$  in  $\text{C}_6\text{H}_6$ , is obtained. The optically active allenes show great configurative stability and it is difficult to racemise them by heating. The configuration of (II) is confirmed by conversion with either  $\text{AcOH}$  and  $\text{HCl}$  or I into 1:3-diphenyl-1-naphthyl-4:5-benzindine, m.p.  $233\text{--}234^\circ$ , the optically active forms of (II) giving an inactive product. Oxidation ( $\text{KMnO}_4$ ) of (II) gives  $\text{COPh}\cdot\text{C}_{10}\text{H}_7\cdot 1$  and reduction

(HI-P) affords  $\alpha\gamma$ -diphenyl- $\alpha\gamma$ -di-1-naphthyl- $\Delta^a$ -propene, m.p. 167—169°, which is obtained when the reaction product of  $\beta$ -phenyl- $\beta$ -1-naphthylpropionophenone and  $1\text{-C}_{10}\text{H}_7\text{MgBr}$  is dehydrated with  $\text{Ac}_2\text{O}$ . The mechanism of the asymmetric catalysis is discussed. F. R. S.

**Diphenylindenes. III. Hydrogenation of diphenylindenes and diphenylindone and other reactions of this group.** A GARCÍA BANUS and E. DE SALAS (Anal. Fis. Quim., 1935, 33, 53—71).—Reduction of both 1:2- and 2:3-diphenylindene (I) (cf. A., 1929, 688) by P and HI or Na and amyl alcohol gives two forms of diphenylhydrindene (cf. Bergmann *et al.*, A., 1930, 1030), whilst catalytic H (PtO<sub>2</sub>) yields solely the isomeride, m.p. 124—125°. Contrary to de Fazi (A., 1931, 731), the existence of two forms of (I) is considered not to be due to stereoisomerism. Reduction of 2:3-diphenylindone (II) with Zn and AcOH or H<sub>2</sub>, and Pt or PtO<sub>2</sub> with HCl gives *cis*-2:3-diphenylhydrindone (III), m.p. 157—158°, and 1-hydroxy-2:3-diphenylindene (IV), two forms, m.p. 84—85° and 134—135°, both of which give the same Ac derivative (cf. Thiele *et al.*, A., 1912, i, 866), whilst Fe and AcOH or H<sub>2</sub> and Pt on BaSO<sub>4</sub> or PtO<sub>2</sub> yields *trans*-2:3-diphenylhydrindone (V), m.p. 100—101° (cf. Schenk *et al.*, A., 1928, 1035). (III) is converted into (V) by distillation at 22 mm., whilst they both give the same phenylhydrazone, m.p. 137—139°, and a sparingly sol. polymeride, m.p. 200—201° (decomp.), which by distillation under reduced pressure yields (V), which is also formed from  $\text{CHPh}\cdot\text{CHPh}\cdot\text{COCl}$  with  $\text{AlCl}_3$  in  $\text{CS}_2$ . (III) is assigned the *cis*-structure on the basis of its greater reactivity than (V) and its formation by hydrogenation in acid. (III), (IV), and (V) with PbO<sub>2</sub> all yield (II). 1-Amino-2:3-diphenylindene hydrochloride (improved prep.) (A., 1929, 688) with  $\text{HgCl}_2$  and NaOH in EtOH gives 1-imino-2:3-diphenylindene, m.p. 141—142°. Similarly 9-aminofluorene yields 9-iminofluorene, m.p. 123—124°, which with dil. HCl gives fluorenone. F. R. G.

**Naphthalene homologues of coal tar.** O. KRUBER and W. SCHADE [in part with W. MORNEWEG] (Ber., 1936, 69, [B], 1722—1729).—A neutral fraction, b.p. 258—260°, is converted by conc.  $\text{H}_2\text{SO}_4$  at 45° into 1:7-dimethylnaphthalene-4-sulphonic acid [Na salt (I); corresponding sulphonamide, m.p. 204—205°], transformed by superheated steam in presence of 70%  $\text{H}_2\text{SO}_4$  into 1:7-dimethylnaphthalene (II), b.p. 261—262°/760 mm. (picrate, m.p. 121°). (I) is transformed by molten KOH into 1:7-dimethyl-4-naphthol, m.p. 102°, which with  $\text{PhN}_2\text{Cl}$  gives the dye  $\text{C}_{18}\text{H}_{16}\text{ON}_2$ , m.p. 137°. (II) is oxidised by  $\text{CrO}_3$  in 50% AcOH to 1:7-dimethyl-5:8-naphthaquinone, m.p. 135—136°, and 3-methyl-o-phthalic acid, m.p. 157°. Treatment of (II) with dil.  $\text{HNO}_3$  followed by  $\text{K}_3\text{Fe}(\text{CN})_6$  gives 1:7- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ , m.p. 308° (decomp.) after softening (*Me*<sub>2</sub> ester, m.p. 89°), which is obtained synthetically by converting 2:8- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$  into 2:8- $\text{CN}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$  and thence into 2:8-dicyanonaphthalene, m.p. 152—154°, which is hydrolysed with 40% KOH-EtOH. The isolation of 2- $\text{C}_{10}\text{H}_7\text{Et}$  from a suitable coal-tar fraction is described. H. W.

**Nitration of 2-ethylnaphthalene. Synthesis of 2-ethyl-8-naphthol.** G. LEVY (Compt. rend., 1936, 203, 337—339).—Nitration of 2- $\text{C}_{10}\text{H}_7\text{Et}$  affords 2:1- $\text{C}_{10}\text{H}_6\text{Et}\cdot\text{NO}_2$  and an oil which is reduced by Fe and AcOH to a mixture of amines from which 2:8- $\text{C}_{10}\text{H}_6\text{Et}\cdot\text{NH}_2$  [hydrochloride; Ac derivative (I), m.p. 148.5—149° (corr.)] is separated. (I) is converted by 1%  $\text{H}_2\text{SO}_4$  at 200° into 2-ethyl-8-naphthol (II) m.p. 51° (picrate, m.p. 145°), synthesised as follows.  $(\text{CH}_2\cdot\text{CO})_2\text{O}$ , PhEt, and  $\text{AlCl}_3$  in benzene afford  $\beta$ -p-ethylbenzoylpropionic acid, m.p. 102—103°, reduced (Clemmensen) to  $\gamma$ -p-ethylphenylbutyric acid, m.p. 70°, the chloride, b.p. 143—145°/18 mm., of which is cyclised by  $\text{AlCl}_3$  to 8-keto-2-ethyl-5:6:7:8-tetrahydronaphthalene, b.p. 152—154°/18 mm. [semicarbazone, m.p. 197° (corr.)], dehydrogenated by Se to (II). H. W.

**1- and 2-Mononitroanthracene.** M. BATTEGAY and P. BÖHLER (Compt. rend., 1936, 203, 333—335).—Treatment of 2-anthracenyldiazonium borofluoride (I) in 80%  $\text{H}_2\text{SO}_4$  with conc.  $\text{HNO}_3$  at 10—15° and of the solution with EtOH at 70° affords  $\text{N}_2$ , MeCHO, a violet-black insol. substance, and 1-nitroanthracene, m.p. 146°, identified by reduction to 1-aminoanthracene and oxidation to 1-nitroanthraquinone. (I) is transformed by  $\text{NaNO}_2$  in presence of  $\text{CuSO}_3\cdot\text{Cu}_2\text{SO}_4$  into anthracene and 2-nitroanthracene, m.p. 172°, identified by conversion into 2-aminoanthracene and 2-nitroanthraquinone. H. W.

**Extremely weak acids.**—See this vol., 1069.

**Dissociable organic oxides. 9-Phenylanthracene and its derivatives.** C. DUFRASSE, L. VELLUZ, and (MME.) L. VELLUZ (Compt. rend., 1936, 203, 327—329).—9-Phenylanthracene (I), 10-bromo- (II) and 10-iodo- (III), m.p. 132°, -9-phenylanthracene, 9-phenylanthracene-10-carboxylic acid (IV), m.p. 264°, and its *Me* ester (V), m.p. 162° (obtainable only by use of  $\text{CH}_2\text{N}_2$ ), are photo-oxidisable, but the process is complicated by the evolution of halogen from (II) and (III) and is irregular in the case of (IV). (I) gives an oxide,  $\text{C}_{20}\text{H}_{14}\text{O}_2$ , in poor yield by reason of its extreme sensitiveness to light, and its thermal decomp. occurs vigorously at about 155° with appreciable liberation of  $\text{O}_2$ . (V) affords a normally dissociable oxide,  $\text{C}_{22}\text{H}_{16}\text{O}_4$ . The presence of *meso*-H is invariably an obstacle to the dissociability of the photo-oxides of anthracene. H. W.

**Hydrophenanthrenes and related ring systems from dieneinenes.** P. S. PINKNEY, G. A. NESTY, R. H. WILEY, and C. S. MARVEL (J. Amer. Chem. Soc. 1936, 58, 972—976; cf. A., 1933, 591, 1270).—1-Acetylenylcyclohexanol (I), b.p. 83—84°/25 mm., m.p. 31—32° (*Hg* derivative, m.p. 175.5—176.5°), obtained in 81% yield from cyclohexanone (II) (in Et<sub>2</sub>O-*tert*-amyl alcoholic K *tert*-amylaldehyde) and Et<sub>2</sub>O- $\text{C}_2\text{H}_2$  at -15° followed by aq.  $\text{NH}_4\text{Cl}$ , is converted by successive treatment with  $\text{MgEtBr}$  and cyclopentanone or (II) into  $\alpha$ -1-hydroxycyclopentyl- $\beta$ -1-hydroxycyclohexylacetylene (III), m.p. 93—94°, or  $\alpha\beta$ -di-1-hydroxycyclohexylacetylene (IV) [also obtained by Dupont's method (A., 1914; i, 134)], respectively. (IV) is dehydrated (40%  $\text{H}_2\text{SO}_4$ ) to  $\alpha\beta$ -di- $\Delta^1$ -cyclohexenylacetylene, b.p. 126—128°/3 mm., which is



reduced [ $\text{H}_2$  (1500—2000 lb.), Raney Ni, methylcyclohexane,  $250^\circ$ ] to *s*-dicyclohexylethane, b.p.  $93-94^\circ/2$  mm., and is converted by AcOH-conc.  $\text{H}_2\text{SO}_4$  or, better, 85%  $\text{HCO}_2\text{H}$  into 9-keto- $\Delta^{11}$ -dodecahydrophenanthrene (V), b.p.  $130-132^\circ/2$  mm. (2:4-dinitrophenylhydrazones, m.p.  $227-228^\circ$ ), and a little of an isomeric ketone, m.p.  $93-94^\circ$  (2:4-dinitrophenylhydrazone, m.p.  $186-187^\circ$ ) [not identical with the 9-keto- $\Delta^{10}$ -dodecahydrophenanthrene, m.p.  $88-90^\circ$  (2:4-dinitrophenylhydrazone, m.p.  $226-227^\circ$ ), of Rapson and Robinson (A., 1935, 1498)]. (IV) and AcOH-conc.  $\text{H}_2\text{SO}_4$  give a smaller yield of (V) and a little dodecahydrobenzil (? 2:4-dinitrophenylhydrazone, m.p.  $120-121^\circ$ ), whilst (IV) and 85%  $\text{HCO}_2\text{H}$  afford (V) and 3-keto-2:5-dichloropentamethylene-tetrahydrofuran (2:4-dinitrophenylhydrazone, m.p.  $162-162.5^\circ$ ) (Dupont, loc. cit.). Clemmensen reduction of (V) gives  $\Delta^{11}$ -dodecahydrophenanthrene, b.p.  $81-82^\circ/1.5$  mm. (cf. Schmidt and Mezger, A., 1907, i, 1022), which is reduced further (Ni; as above) to tetradecahydrophenanthrene, b.p.  $86-89^\circ/2$  mm. (also obtained by similar repeated reduction of phenanthrene); this could not be dehydrogenated (Se at  $300-320^\circ$ ).

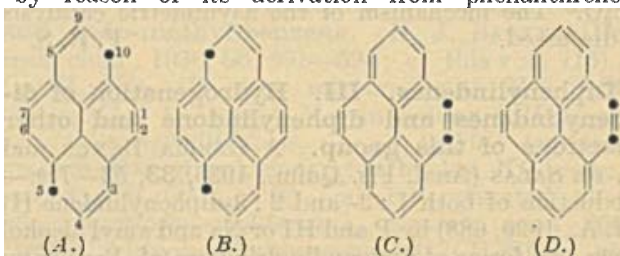
(III) is similarly dehydrated to  $\alpha$ - $\Delta^1$ -cyclopentenyl- $\beta$ - $\Delta^1$ -cyclohexenylacetylene, b.p.  $103-104^\circ/2.5$  mm., reduced (Ni) to  $\alpha$ -cyclopentyl- $\beta$ -cyclohexylethane, b.p.  $74-76^\circ/2$  mm., and cyclised (as above) to 4-keto-1:2-trimethylene-3:4:5:6:7:8:9:10-octahydronaphthalene, b.p.  $114-116^\circ/2.5$  mm. (2:4-dinitrophenylhydrazone, m.p.  $221-222^\circ$ ) (ozonolysis product, adipic acid), which is reduced (Clemmensen) to the 1:2-trimethylenecyclooctahydro-, b.p.  $74-76^\circ/3$  mm., and thence (Ni) to the 1:2-trimethylenedecaahydro-naphthalene, b.p.  $71-72^\circ/2.5$  mm. H. B.

**cis- and trans-as-Octahydrophenanthrene.** J. VAN DE KAMP and E. MOSETTIG (J. Amer. Chem. Soc., 1936, 58, 1062—1063).—Repeated fractionation of *as*-octahydrophenanthrene (from 1- $\beta$ -phenylethylcyclohexanol and  $\text{P}_2\text{O}_5$ ) gives 70% of *cis*- (I), b.p.  $142.6-142.8^\circ/9.2$  mm., and 20% of *trans*- (II), b.p.  $135.5-135.7^\circ/10.5-10.8$  mm., forms. (I) gives an Ac derivative, an oil (semicarbazone, m.p.  $211-213^\circ$ ), oxidised to an octahydrophenanthrenecarboxylic acid, m.p.  $230-232^\circ$ ; the corresponding derivatives from (II) have m.p.  $94-94.5^\circ$ ,  $230-231.5^\circ$ , and  $226-228^\circ$ , respectively. H. B.

**Spiran by-product in the phenanthrene synthesis.** M. T. BOGERT (Science, 1936, 84, 44-45; cf. A., 1933, 601).—Evidence that the lower-b.p. fraction obtained from the crude *as*-octahydrophenanthrene by van de Kamp and Mosettig (preceding abstract) is a spiran and not a phenanthrene derivative is summarised. L. S. T.

**Aromatic hydrocarbons. XXI. Structure of pyrene according to the anellation process.** E. CLAR (Ber., 1936, 69, [B], 1671—1685).—Chemical evidence permits the following fine structures for pyrene. The absorption spectrum of it and its derivatives indicates *A* (*symm-pyr*-condition) and not *B*; it reacts at positions 3 and 8 and, with  $K=6$ , is the first representative of the *symm-pyr*-condition of which there is no sign in  $\text{Ph}_2$  or phenanthrene. The state *B* can be forced by anellation in the

3:4:9:10-position. The absorption spectra of pyrenes invariably give evidence of the *o*-condition represented by *C* or *D*, of which the former is preferred by reason of its derivation from phenanthrene.



In addition, in certain derivatives a further *o*-condition is evidenced apparently related to the unsymmetrical structure of the mol. Greater complexity of the mol. has no spectroscopically novel effect. Pyrene,  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ , and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  yield 3-*o*-toluoylpyrene, m.p.  $139-140.5^\circ$  or m.p.  $107^\circ$  and m.p.  $137^\circ$  after re-solidification, whence 2':3'-naphtha-3:4-pyrene (I), m.p.  $265-266^\circ$ , and a substance,  $\text{C}_{24}\text{H}_{14}$ , m.p. (indef.)  $220-260^\circ$  (very unstable picrate, m.p.  $205^\circ$ ). 3-Pyrenoyl-*o*-benzoic acid, m.p.  $220-222^\circ$ , passes at  $>300^\circ$  into 3:4-phthaloylpyrene, m.p.  $250-251^\circ$ . (I) and maleic anhydride in boiling xylene afford 2':3'-naphtha-3:4-pyrene-endo-1':4'- $\alpha\beta$ -succinic anhydride, decomp.  $298-300^\circ$ , or m.p.  $272-273^\circ$  and decomp.  $298-300^\circ$  after re-solidification.  $\text{CPh}_2\text{Cl}_2$ , pyrene, and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  yield 1'-phenylindeno-2':3':3:4-pyrene, m.p.  $279-280^\circ$ . 3:5:8-Tribromopyrene has m.p.  $259-260^\circ$ . H. W.

**Perylene and its derivatives. XLVIII.** The perylene tribromide of K. Brass and E. Clar. A. ZINKE and A. PONGRATZ (Ber., 1936, 69, [B], 1591—1593).—Repetition of the work of Brass and Clar (A., 1932, 57) shows that it is impossible to obtain a stable product of const. composition by the addition of Br to perylene (I) in  $\text{C}_6\text{H}_6$ ; the intermediate substance is very unstable and the Br content varies with conditions of prep. and age. (I) exposed in a thin layer to Br vapour rapidly absorbs 4 Br but evolution of HBr commences immediately. Recrystallisation of the product from boiling PhMe or  $\text{PhNO}_2$  leads to 3:9-dibromoperylene. The intermediate substance is therefore  $\text{C}_{20}\text{H}_{12}\text{Br}_4$  and, probably, a normal tetrabromide. H. W.

**Preparation of rubrene.** W. KOBLITZ and H. WITTMAYER (Ber., 1936, 69, [B], 1806).—Triphenylpropargyl alcohol is gradually treated with  $\text{SOCl}_2$  containing a little  $\text{AlCl}_3$  at  $0^\circ$ ; the solution is washed with  $\text{H}_2\text{O}$  and aq.  $\text{NaHCO}_3$  and the  $\text{C}_6\text{H}_6$  solution is evaporated to dryness. The residue is heated at  $120^\circ/\text{vac.}$ , thereby giving rubrene in 40% yield. H. W.

**Attempted partial synthesis of ergostane.** E. FERNHOLZ (Ber., 1936, 69, [B], 1792—1795).—Norcholy! Me ketone, m.p.  $112^\circ$  [semicarbazone, m.p.  $235^\circ$  (decomp.)], obtained by heating a mixture of Ba cholanate (I) and  $\text{Ba}(\text{OAc})_2$  at  $400^\circ$ , is converted by treatment with  $\text{MgPr}^6\text{Br}$  followed by boiling AcOH into  $\Delta^{24}\psi$ -ergostene,  $\text{C}_{29}\text{H}_{51}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}_2$ , m.p.  $103^\circ$ , hydrogenated (Pt-sponge in  $\text{Et}_2\text{O}$ ) to  $\psi$ -ergostane, m.p.

64°,  $[\alpha]_D^{25} +25.3^\circ$  in  $\text{CHCl}_3$ . (I) and  $(\text{EtCO}_2)_2\text{Ba}$  at 370°/vac. afford very small amounts of norcholy Et ketone [*semicarbazone*, m.p. 215° (decomp.)]. Ba allocholanate yields norallocholy Me ketone, m.p. 113° [*semicarbazone*, m.p. 218° (decomp.)], whence two hydrocarbons,  $\text{C}_{28}\text{H}_{48}$ , m.p. 128°,  $[\alpha]_D^{25} +19.4^\circ$  in  $\text{CHCl}_3$ , and m.p. 54—56°,  $[\alpha]_D^{25} +21.6^\circ$  in  $\text{CHCl}_3$ , each of which is hydrogenated to ergostane, m.p. 81—82°,  $[\alpha]_D^{25} +22.9^\circ$ , probably containing an isomeride in small amount. H. W.

**Preparation of aniline from benzene and ammonia in a high-frequency high-tension field.** V. K. RAZUMOV (Men. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 261—268).—The reactions  $\text{C}_6\text{H}_6 + \text{NH}_3 + \text{O} \rightarrow \text{NH}_2\text{Ph} + \text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_6 + \text{NH}_2\text{Ph} + \text{O} \rightarrow \text{NHPh}_2 + \text{H}_2\text{O}$ ;  $\text{C}_6\text{H}_6 + \text{O} \rightarrow \text{PhOH}$  take place when the gas mixture is passed through a high-frequency high-tension electromagnetic field. R. T.

**Alkylation of aniline in presence of mixed catalysts.** III. Mono-methyl- and -ethyl-aniline. N. I. SCHUJIN, A. N. BITKOVA, and A. F. ERMILINA (J. Gen. Chem. Russ., 1936, 6, 774—779).—The velocity of alkylation of  $\text{NH}_2\text{Ph}$  by EtOH or MeOH in presence of  $\text{Al}_2\text{O}_3$  is > with  $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$ , but the product in the latter case is free from dialkyl derivatives.  $\text{NHPhMe}$  is obtained in 45% yield in presence of 1:1  $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$  at 350°, and  $\text{NHPhEt}$  in 59% yield at 350° ( $\text{Al}_2\text{O}_3$  30—40,  $\text{Fe}_2\text{O}_3$  60—70%). The latter reaction is more rapid than the former, but loss of alcohol due to side reactions is greater. R. T.

**Hexaiodotellurates of aromatic amines etc.**—See this vol., 1079.

**Addition of chlorocarbamide to doubly-bound carbon.** I. RIBAS, E. TAPIA, and A. CAÑO (Anal. Fis. Quim., 1936, 34, 501—506).—*cyclo*Hexene with  $\text{NH}_2\text{CO}\cdot\text{NHCl}$  (I) gives, in addition to the chlorohydrin (cf. Detoeuf, A., 1922, i, 236), 2-chlorocyclohexylcarbamide, m.p. 185°, which with aq. KOH yields 2-amino-4:5-cyclohexano-oxazoline (cf. Birkenbach *et al.*, A., 1931, 832). (I) with  $\text{CHPh}\cdot\text{CHMe}$  gives probably  $\beta$ -chloro- $\beta$ -phenylisopropylcarbamide, m.p. 135°, and a liquid, b.p. 110—113°, probably a mixture of  $\text{CHPhCl}\cdot\text{CHMeCl}$  with the chlorohydrin. F. R. G.

**Phenylurethane anaesthetics.** II. E. S. COOK and T. H. RIDER (J. Amer. Chem. Soc., 1936, 58, 1079—1081; cf. A., 1930, 1031).— $\gamma$ -Dimethylamino-, m.p. 131—132.5° (all m.p. are corr.),  $\gamma$ -diethylamino-, m.p. 140.5—142.5°,  $\gamma$ -di-n-propylamino-, m.p. 159.5—160.5°,  $\gamma$ -di-n-butylamino-, m.p. 123—124°,  $\gamma$ -( $\beta$ -phenylethylmethylamino)-, m.p. 192.5—193.5°, and  $\gamma$ -piperidino-, m.p. 169—169.5°, -propyl, and  $\beta$ -diethylamino-, m.p. 137.5—138.5°, and  $\beta$ -piperidino-, m.p. 88—89.5°, - $\alpha$ -methyl ethyl phenylcarbamate hydrochlorides are prepared from the appropriate amino-alcohol and  $\text{PhNCO}$  in  $\text{Et}_2\text{O}$  followed by HCl.  $\text{NHPh}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NET}_2\cdot\text{HCl}$  has m.p. 142.5—143.5° (lit. 138—139°). Pharmacological data are given; the  $\text{NHPh}\cdot\text{CO}_2$  group appears to be more active than  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2$  in causing anaesthesia of mucous surfaces.  $\gamma$ -( $\beta$ -Phenylethylmethylamino)propyl alcohol, b.p. 155—157°/12 mm., is prepared from  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NHMe}$  and  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ . H. B.

**Molecular rearrangement of sulphenanilides.** III. M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 1091—1094; cf. A., 1935, 1120, 1359; this vol., 200).—2:4- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SOCl}$  and  $\text{NH}_2\text{Ar}$  in  $\text{Et}_2\text{O}$  give 4-chloro-2-nitrobenzenesulphen-anilide (I), m.p. 102°, and -o-toluidide (II), m.p. 127°, whilst  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SOCl}$  and  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$  afford o- (III), m.p. 130°, and p- (IV), m.p. 99—101°, -nitrobenzenesulphen-o-chloroanilide. (I) heated alone at 150—160° or, better, in an excess of  $\text{NH}_2\text{Ph}$  at 180—190° rearranges to 4-chloro-2-nitro-4'-aminodiphenyl sulphide, m.p. 127—129°; similarly, (II) in  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  gives 4-chloro-2-nitro-4'-amino-3'-methyldiphenyl sulphide, m.p. 113—115°, whilst (IV) in  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$  affords 3'-chloro-4-nitro-4'-aminodiphenyl sulphide, m.p. 127—129°.  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{R}$  ( $\text{R}=\text{H}$ , o-Cl, o- and p-Me) heated with  $\text{C}_6\text{H}_5\text{R}'\cdot\text{NH}_2$  ( $\text{R}'=\text{H}$ , o- and p-Me) give the aminodiphenyl sulphides derived from  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{R}'$ ; such displacement does not occur when  $\text{R}'$  is o-Cl. Thus, (III) heated in o- and p- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  affords 2-nitro-4'-amino-3', m.p. 101—103°, and 2-nitro-2'-amino-5', m.p. 105—107°, -methyldiphenyl sulphide, respectively. All  $\text{ArS}\cdot\text{NHAr}'$  are decomposed by acids to  $\text{Ar}_2\text{S}_2$  and  $\text{NH}_2\text{Ar}'$ . H. B.

**Preparation of naphthidine.** S. COHEN and R. E. OESPER (Ind. Eng. Chem. [Anal.], 1936, 8, 306—307).— $\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2\cdot\text{HCl}$  is diazotised and converted with  $\text{Na}_2\text{SO}_3$  into azonaphthalene (yield quant.), which is then reduced in EtOH at the boil with  $\text{SnCl}_2$  and HCl. The solution is rapidly cooled, and more HCl added to ppt. naphthidine hydrochloride. The crude base obtained on basification is recryst. from  $\text{EtOH}\text{--}\text{C}_5\text{H}_5\text{N}$ . The yield is 33.5%, m.p. 198—199°. S. C.

**Derivatives of (A) NN-2:4-di- [and] (B) NN-2:4:6-tri-nitrophenylmethylhydrazine.** J. J. BLANKSMA and (Miss) M. L. WACKERS (Rec. trav. chim., 1936, 55, 655—660, 661—668).— $\text{NHMe}\cdot\text{NH}_2$  and 2:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$  (I) or 2:4:6- $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_3$  in warm EtOH give NN-2:4-di-, m.p. 144° (Ac derivative), and NN-2:4:6-tri-nitrophenylmethylhydrazine, m.p. 171° (Ac derivative, m.p. 222°) [structure proved by condensation with aldehydes and expected because (I) condenses much faster with  $\text{NH}_2\text{Me}$  than with  $\text{NH}_3$ ]. Aldehydes are readily characterised by these hydrazines; reaction is rapid in hot EtOH containing a little  $\text{H}_2\text{SO}_4$  and the m.p. are conveniently lower than those of the non-methylated compounds. The following are described: 2:4-di- and 2:4:6-tri-nitrophenylmethylhydrazones and 2:4:6-trinitrophenylhydrazones, respectively, of  $\text{PhCHO}$ , m.p. 206°, 214°, 270°, o-, m.p. 176°, 164°, 246°, m-, m.p. 195°, 159°, 252°, and p- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ , m.p. 199°, 211°, 255°, o- (II), m.p. 183°, 224°, 265° (lit. 215°), m-, m.p. 239°, 216°, 251°, and p- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , m.p. 246°, 233°, 250°, o-, m.p. 191°, 220°, 275°, and p- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (III), m.p. 225°, 224°, 284°, p- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , m.p. 185°, 180°, 252°, 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHO}$ , m.p. 212°, 236°, 260°, 4:3- $\text{OH}\cdot\text{C}_6\text{H}_4(\text{OMe})\cdot\text{CHO}$  (IV), m.p. 178°, 200°, 276°, furfuraldehyde, m.p. 190°, 204°, 246° (lit. 230°), hydroxymethyl- (V), m.p. 100°, 196°,



216°, and 5-methyl-furfuraldehyde, m.p. 171°, 182°, 218°, MeCHO, m.p. 118°, 152°, —; 2:4-dinitrophenylhydrazones of *o*-, m.p. 209°, *m*-, m.p. 256°, and *p*-C<sub>6</sub>H<sub>4</sub>Cl·CHO, m.p. 270°, (II), m.p. 252°, (III), +H<sub>2</sub>O, m.p. 260°, (IV), m.p. 270°, and (V), m.p. 184°.

R. S. C.

***p*-tert.-Butylphenol**, a substance with the odour of Russian leather. G. SANDULESCU and S. SABETAY (Riechstoffind., 1935, 10, 84; Chem. Zentr., 1935, ii, 3021).—Butylphenol, m.p. 93–94°, b.p. 233–234°/762 mm., 127.5–128.5°/20 mm., and its Et, b.p. 110–111°/13 mm., *Pr*<sup>a</sup>, b.p. 122–123°/13 mm., *Pr*<sup>β</sup>, b.p. 113–114°/13 mm., *Bu*<sup>a</sup>, b.p. 136–137°/13 mm., and *Bu*<sup>β</sup>, b.p. 126–128°/13 mm., ethers are described. H. N. R.

**Sulphonation of 2-ethylnaphthalene.** Synthesis of 6-ethyl-β-naphthol. G. LEVY (Compt. rend., 1936, 202, 1679–1680; cf. A., 1932, 734, 842; 1933, 1287).—2-C<sub>10</sub>H<sub>7</sub>Et with conc. H<sub>2</sub>SO<sub>4</sub> at 95° affords 2:6-C<sub>10</sub>H<sub>6</sub>Et·SO<sub>3</sub>H, the Na salt of which after fusion with alkali gives 6-ethyl-β-naphthol (I), m.p. 97–98° (*picrate*, m.p. 106–107°). *p*-Methoxybenzyl chloride with CHNa(CO<sub>2</sub>Et)<sub>2</sub> affords Et<sub>2</sub> *p*-methoxybenzylethylmalonate, b.p. 161°/2 mm.; the corresponding acid, m.p. 131.5–132.5°, is decarboxylated to α-*p*-methoxybenzylbutyric acid, b.p. 195°/13 mm., the amyl ester, b.p. 188°/13 mm., of which is reduced by Bouveault's method to β-*p*-methoxybenzyl-*n*-butyl alcohol (II), b.p. 165°/13 mm. (II) with SOCl<sub>2</sub> and some NPhMe<sub>2</sub> affords the chloride, b.p. 160°/13 mm., which cannot be converted directly into β-*p*-methoxybenzylvaleronitrile (III), b.p. 172–175°/13 mm., but only through the *I*-compound, b.p. 165°/13 mm. (III) with boiling MeOH–KOH affords β-*p*-methoxybenzylvaleric acid, b.p. 205°/13 mm., the chloride, b.p. 175°/13 mm., of which with AlCl<sub>3</sub> in hexane is cyclised to 6-methoxy-4-keto-2-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 180°/13 mm. (*semicarbazone*, m.p. 171–172°), which is reduced (Clemmensen) to 6-methoxy-2-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 148–153°/13 mm. Dehydrogenation followed by demethylation yields 6-methoxy-2-ethylnaphthalene, m.p. 57–59°, and (I), respectively. J. L. D.

**Dyes from resorcinol, sulphuric acid, and alcohols.** E. BERTONASCO (G. Farm. Chim. Sci. affini, 1935, 84, 58–64; Chem. Zentr., 1935, ii, 3096).—MeOH, EtOH, PrOH, Bu<sup>β</sup>OH, and glycerol all give dyes on warming with resorcinol and conc. H<sub>2</sub>SO<sub>4</sub>. The products may be esters of resorcinol-disulphonic acid. H. N. R.

**Exchange between dihydroxybenzenes and heavy water.** F. K. MUNZBERG (Z. physikal. Chem., 1936, B, 33, 39–46).—In the exchange of H for D between resorcinol (I) and D<sub>2</sub>O in which it is dissolved the H of OH groups are exchanged immeasurably rapidly, two H of the nucleus in the *o*-position to OH are exchanged at a measurable rate by way of an enol-keto transformation (cf. following abstract), and the other two nuclear H are replaced directly and very slowly. Orcinol (II) behaves similarly. In quinol (III) H of both OH are rapidly exchanged, but all the nuclear H are exchanged very slowly and at the same rate;

apparently there is no kinetically effective enol-keto change. It is inferred that in the ring of (I) and (II) the C–C linkings are alternately double and single and do not exchange positions periodically, whilst in the ring of (III) there are at most two double linkings. R. C.

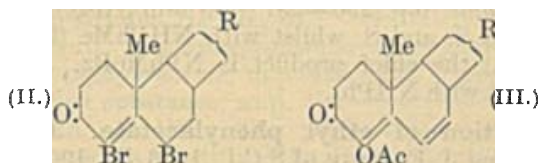
**Exchange between trihydroxybenzenes and heavy water.** F. K. MUNZBERG (Z. physikal. Chem., 1936, B, 33, 23–38).—In the exchange of H for D between pyrogallol (I) and D<sub>2</sub>O in which it is dissolved the H of OH groups are exchanged immeasurably rapidly, and the nuclear H more slowly, but each at a different rate. Experiments with Na gallate (II) show that in (I) the two nuclear H in the *o*-position to OH are exchanged more rapidly than the isolated nuclear H. All the H of phloroglucinol are quickly exchanged. Since in C<sub>6</sub>H<sub>6</sub> the H is not readily exchanged for D (A., 1934, 1080), it is inferred that H attached to C is readily exchanged if keto-enol tautomerism is possible. Hence the above compounds must contain double linkings, as, e.g., in the Kekulé formula. It appears that in the ring in (I) and (II) two different kinds of C–C linking alternate with each other and exchange positions on the average once in 1.4 × 10<sup>6</sup> sec. at 50°. R. C.

**Lichen substances. LXVIII. Preparation of higher homologues of orcinol.** Y. ASAHINA [with M. MIYASAKA and T. SEKIZAWA] (Ber., 1936, 69, [B], 1643–1646).—Et α-3:4:5-trimethoxybenzoylpropionate is converted by 5% KOH–EtOH at 60° into 3:4:5-trimethoxypropionophenone, m.p. 33°, reduced by Na and EtOH to 3:5-dimethoxypropylbenzene, b.p. 147°/29 mm., converted by boiling HI (*d* 1.7) into divarin, b.p. 169°/8 mm. (monohydrate, m.p. 51°; Br<sub>3</sub>-derivative, m.p. 99°). Similarly Et α-3:4:5-trimethoxybenzoylvalerate yields 3:4:5-trimethoxyvalerophenone, converted successively into olivetol Me<sub>2</sub> ether and olivetol (Br<sub>3</sub>-derivative, m.p. 87°). Et α-3:4:5-trimethoxybenzoyl-*n*-heptanoate, m.p. 39°, is transformed into 3:4:5-trimethoxyphenyl-*n*-hexyl ketone, b.p. 175–176°/4 mm., m.p. 29° (*semicarbazone*, m.p. 112°), whence sphaerophorol Me<sub>2</sub> ether, b.p. 150°/5 mm., and sphaerophorol, b.p. 175–176°/5 mm. (monohydrate, m.p. 57°; Br<sub>3</sub>-derivative, m.p. 75°). H. W.

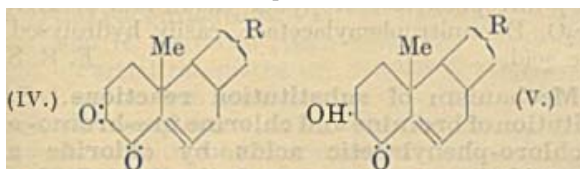
**Catalytic hydrogenation of some epoxides.** P. WEILL and F. KAYSER (Bull. Soc. chim., 1936, [v], 3, 841–844).—Catalytic reduction (Ni) of triphenylethylene oxide in EtOH at 35–40° yields solely αββ-triphenylethyl alcohol. Similarly α-anisyl-ββ-diphenyl- and α-tolyl-β-phenyl-ethylene oxides give solely α-anisyl-ββ-diphenyl- and α-tolyl-β-phenyl-ethyl alcohol. H. G. M.

**Transformations of brominated derivatives of cholesterol.** II. H. H. INHOFFEN (Ber., 1936, 69, [B], 1702–1710).—A modified prep. of the tri-bromoketone (I) from cholesterol is given (cf. this vol., 854). Treatment of (I) with KOAc in C<sub>6</sub>H<sub>6</sub>–EtOH affords the dibromide (II), m.p. 162–163° (decomp.), the constitution of which is supported by its absorption spectrum. When boiled with EtOH containing a little HBr it gives the enol ether of cholesterol-3:6-dione. Further treatment of (I) with

KOAc in EtOH gives the *enol acetate* (III), m.p. 158—159° after softening, also obtained directly from



(I). Hydrolysis of (III) by HCl-EtOH leads to the *o-diketone* (IV or V), m.p. 160—161°, which reduces

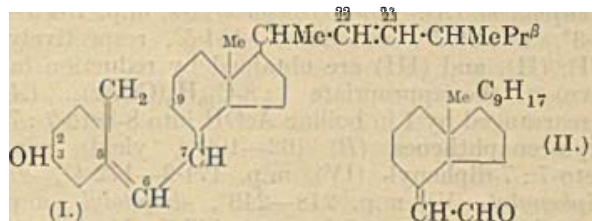


$\text{NH}_3\text{-Ag}_2\text{O}$  and gives a red-brown colour with  $\text{FeCl}_3$ ; its absorption spectrum indicates the presence of three conjugated double linkings. It yields a *di-oxime*, decomp. about 180° after softening, and a *quinoxaline* derivative,  $\text{C}_{33}\text{H}_{46}\text{N}_2$ , m.p. 175° (decomp.), which is unchanged by boiling  $\text{Ac}_2\text{O}$ . In support of structure (V) it reacts with  $\text{Ac}_2\text{O}$  without regenerating (III) and contains 1 OH (Zerevitinov). H. W.

**alloCholesterol and epiallocholesterol.** R. SCHOENHEIMER and E. A. EVANS, jun. (J. Biol. Chem., 1936, **114**, 567—582).—Cholestenone and hot  $\text{Al}(\text{OPr}^i)_3\text{-Pr}^i\text{OH}$  give a 1 : 1 mol. compound, m.p. 141°,  $[\alpha]_D^{21} + 84.1^\circ$  in  $\text{C}_6\text{H}_6$ , separable by digitonin (I) into *allocholesterol* (II), m.p. 132°,  $[\alpha]_D^{23} + 43.7^\circ$  in  $\text{C}_6\text{H}_6$  [pptd. by (I); *acetate*, m.p. 85°], and *epiallocholesterol* (III), m.p. 84°,  $[\alpha]_D^{24} + 120.8^\circ$  in  $\text{C}_6\text{H}_6$  [not pptd. by (I); *acetate*, m.p. 82.5°]. Hydrogenation ( $\text{PtO}_2$ ) of (II) in amyl ether gives *epicoprosterol* (IV), that of (III) gives (IV) and *epidihydrocholesterol*. (II) or (III) with hot 0.033*N*-HCl-EtOH gives  $\Delta^{2:4}$ -cholestadiene (V), m.p. 79°,  $[\alpha]_D^{23} - 112.5^\circ$  in  $\text{C}_6\text{H}_6$  (absorption max. at 229, 235, and 240  $\text{m}\mu$ ). The substance hitherto known as (II) is a 2 : 3 mixture of (II) and cholesterol (VI), since (a) its behaviour is paralleled by that of a synthetic mixture and (b) with HCl it gives about 40% of (V) with unchanged (VI), the latter being hitherto considered as the product of the reaction. Thirty-one examples show that the Rosenheim test is given only by those sterols having conjugated ethylenic linkings or capable of giving this system [e.g., containing  $\text{CH}:\text{CH}:\text{C}(\text{OH}):\text{CH}$ ] under the conditions of the test, but that compounds with  $\text{CO}:\text{C}:\text{C}:\text{C}$  do not give it. The hydrocarbon,  $\text{C}_{26}\text{H}_{42}$ , of Windaus *et al.* (A., 1915, i, 677) gives the test. The usual *cis-trans* nomenclature (referring to the H on  $\text{C}_{(5)}$ ) of sterols may be misleading and offers difficulty with  $\Delta^4$ - and  $\Delta^5$ -compounds. It is proposed to name compounds according to the relation of the Me on  $\text{C}_{(10)}$  to, first, the OH on  $\text{C}_{(3)}$  and, second, the H on  $\text{C}_{(5)}$ . Thus, dihydro-, epidihydro-, allo-, and epiallo-cholesterol are *cis-trans*, *trans-trans*, *cis*, and *trans*, respectively, coprosterol and epicoprosterol are *cis-cis* and *trans-cis*, cholesterol and epicholesterol are *cis* and *trans*, respectively. Only those compounds with a *cis*-configuration of OH-Me (first title) are pptd. by (I), and relationships are always clear.

R. S. C.

**Sterol group. XXIV. Constitution of calciferol.** I. M. HEILBRON, R. N. JONES, K. M. SAMANT, and F. S. SPRING. **XXV. Reactions of the isomeric ethers of cholesterol.** J. H. BEYNON, I. M. HEILBRON, and F. S. SPRING (J.C.S., 1936, 905—907, 907—910; cf. this vol., 981).—XXIV. Calciferol is (I), because (a) with  $\text{CrO}_3\text{-AcOH}$  or  $\text{KMnO}_4$ , best at room temp., it gives an *aldehyde* (II),  $\text{C}_{21}\text{H}_{34}\text{O}$ ,



an oil, the *semicarbazone*, m.p. 242°, of which has an absorption spectrum very similar to that of citral-semicarbazone (proof of the 7 : 8 ethylenic linking) and (b) with  $\text{O}_3$  gives  $\text{CH}_2\text{O}$  (proof of the presence of  $\text{CH}_2$ ) and a *keto-acid* (III),  $\text{C}_{13}\text{H}_{12}\text{O}_3$  (*semicarbazone*, m.p. 219°) (proof of the

22 : 23 and 7 : 8 ethylenic linkings).

**XXV. Cholesteryl *p*-toluenesulphonate (IV) and KOAc in hot EtOH give *cis-cholesteryl Et ether* (V), m.p. 47°,  $[\alpha]_D^{20} + 49.78^\circ$  in  $\text{CHCl}_3$ , and in  $\text{CH}_2\text{Ph-OH}$  at 100° some *trans*- and much *cis-cholesteryl benzyl ether* (VI), b.p. 170°/0.001 mm.,  $[\alpha]_D^{20} + 15.77^\circ$  in  $\text{CHCl}_3$ . (V), (VI), and the *cis*-Me ether with halogen acids in AcOH give the cholesteryl halide and with  $\text{Br-AcOH-Et}_2\text{O}$  give 3 : 5 : 6-tribromocholestan. *Cholesteryl iodide*, thus prepared, has m.p. 106.5—107°,  $[\alpha]_D^{20} - 11.94^\circ$ . The *trans*-ethers do not eliminate the alkoxy-group thus; with Br there are formed the *dibromides*, m.p. 107°, 80°, and 107°,  $[\alpha]_D^{20} - 52.95^\circ$ ,  $-50.75^\circ$ , and  $-50.2^\circ$  in  $\text{CHCl}_3$ , of *trans-cholesteryl* Me, Et, and  $\text{CH}_2\text{Ph}$  ether, respectively. Thus, the *cis*-ethers may have a  $\Delta^4$ -ethylenic linking, but this is unlikely as they do not give the colour with  $\text{SbCl}_5$  given by *allocholesterol* and its Me ether and  $\psi$ -cholesterene. (IV) with aq. KOH or aq. KOAc gives cholesterol and dicholesteryl ether (VII), with KOAc-AcOH gives *trans-cholesteryl acetate*, with  $\text{Ag}_2\text{O-H}_2\text{O}$  or dil.  $\text{H}_2\text{SO}_4$  gives (VII), and with  $\text{H}_2\text{SO}_4\text{-EtOH}$  *trans-cholesteryl Et ether*. The *cis-trans* nomenclature requires confirmation. R. S. C.**

**Derivative of vitamin-D and several sterols.** M. SUMI (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 635—640).—The following have been prepared : *calciferyl*, m.p. 132°,  $[\alpha]_D^{20} + 149.97^\circ$ , *cholesteryl*, m.p. 168°,  $[\alpha]_D^{20} 0^\circ$ , *sitosteryl*, m.p. 190°,  $[\alpha]_D^{20} + 2.5^\circ$ , and *ergosteryl  $\beta$ -naphthoate*, m.p. 175°, and the *anthraquinone-2-carboxylates* of the last three, m.p. 170° (or >250°),  $[\alpha]_D^{20} 0^\circ$ , m.p. 189° (or 253°),  $[\alpha]_D^{20} - 1.3^\circ$ , and m.p. 195° (or 200°), respectively. W. O. K.

**Pinacol-pinacolin rearrangement. VIII. Rearrangement of 7 : 8-dihydroxy-7 : 8-diarylace-naphthenes.** W. E. BACHMANN and E. J. H. CHU (J. Amer. Chem. Soc., 1936, **58**, 1118—1121).—The following are prepared from acenaphthenequinone and  $\text{MgArBr}$  in  $\text{Et}_2\text{O-C}_6\text{H}_6$  : 7 : 8-dihydroxy-7 : 8-



diphenyl-, m.p. 154.3—155.3° [a stereoisomeride, m.p. 173.5—175.6° (lit. 171—173°), is obtained from 1 : 8-C<sub>10</sub>H<sub>6</sub>Bz<sub>2</sub> and 1% Na-Hg in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> followed by dil. AcOH], -di-p-diphenyl-, m.p. 220°, -di-p-tolyl- (I), m.p. 182—182.5°, -di-m-tolyl-, m.p. 152.3—153.3°, -dianisyl-, m.p. 168—169°, -diphenetyl-, m.p. 144.5—145.5°, -di-p-chlorophenyl- (II), m.p. 222—223°, and -di-p-fluorophenyl- (III), m.p. 220—221°, -acenaphthene (A). Diastereoisomerides, m.p. 154.3—155.3°, 78—79.5°, and 153.5—154.5°, respectively, of (I), (II), and (III) are obtained by reduction (as above) of the appropriate 1 : 8-C<sub>10</sub>H<sub>6</sub>(COAr)<sub>2</sub>. (A) are rearranged by I in boiling AcOH into 8-keto-7 : 7-diarylaacenaphthenes (B) (62—100% yield), viz., 8-keto-7 : 7-diphenyl- (IV), m.p. 171.3—172.4°, -di-p-diphenyl- (V), m.p. 248—249°, -di-p-tolyl-, m.p. 128.5—129.5°, -di-m-tolyl-, m.p. 147.5—148.5°, -dianisyl-, m.p. 151.5—152.5°, -diphenetyl-, m.p. 122.8—123°, -di-p-chlorophenyl-, m.p. 145.5°, and -di-p-fluorophenyl-acenaphthene, m.p. 127.5—128.5°, respectively. (IV) is synthesised from  $\alpha$ -C<sub>10</sub>H<sub>7</sub>-CPh<sub>2</sub>-COCl and SnCl<sub>4</sub> in CS<sub>2</sub>; the chloride of di-p-diphenyl- $\alpha$ -naphthylacetic acid, m.p. 216—217° (from the CAr<sub>2</sub>Cl and 45% Na-Hg in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> followed by CO<sub>2</sub>), similarly gives (V). Fusion of (B) with KOH (at usually 250°) affords 8-benzhydryl-, m.p. 226°, 8-di-p-diphenylmethyl-, m.p. 247—248°, 8-di-p-, m.p. 159.3—160.3°, and -m-, m.p. 189.5—190.5°, -tolylmethyl-, 8-dianisylmethyl-, m.p. 173.5—174.5°, 8-diphenetylmethyl-, m.p. 170—171°, 8-di-p-chlorophenylmethyl-, m.p. 225—226°, and 8-di-p-fluorophenylmethyl-, m.p. 221—222°, -1-naphthoic acid, whilst oxidation (CrO<sub>3</sub>, AcOH) of (A) gives 1 : 8-C<sub>10</sub>H<sub>6</sub>Bz<sub>2</sub> and 1 : 8-di-p-phenylbenzoyl-, m.p. 219—220°, 1 : 8-di-p-, m.p. 181.5—182.5°, and -m-, m.p. 157.3—158.3°, -toluoyl-, 1 : 8-dianisoyl-, m.p. 215—216°, 1 : 8-diethoxybenzoyl-, m.p. 197—197.5°, 1 : 8-di-p-chlorobenzoyl-, m.p. 188°, and 1 : 8-di-p-fluorobenzoyl-, m.p. 166.5—167.5°, -naphthalene. The appropriate (A) with dry HCl in cold CHCl<sub>3</sub> afford the dichlorides, converted by NaI in COMe<sub>2</sub> into 7 : 8-diphenyl-, m.p. 161.3°, 7 : 8-di-p-diphenyl-, m.p. 189.5—190.5°, 7 : 8-di-p-tolyl-, m.p. 137.2—137.7°, 7 : 8-di-p-chlorophenyl-, m.p. 204.5—205.5° (obtained using AcOH-HI), and 7 : 8-di-p-fluorophenyl-, m.p. 153.5—154.5°, -acenaphthylene. H. B.

**Conversion of carboxylic acids into their homologues.** F. ARNDT and B. EISTERT (Ber., 1936, 69, [B], 1805).—Mainly a reply to Preobrashenski *et al.* (A., 1935, 872; this vol., 1002) concerning the transitions, R·CO<sub>2</sub>H  $\rightarrow$  R·COCl  $\rightarrow$  R·CO·CHN<sub>2</sub>  $\rightarrow$  CH<sub>2</sub>R·CO<sub>2</sub>H. The yields of esters from diazoketones (I) are considerably improved if Ag<sub>2</sub>O is added in successive small quantities to the mixtures of (I) and alcohols. Ag<sub>2</sub>O acts as alkali and source of colloidal Ag which is the actual catalyst. H. W.

**Synthesis of dibenzoyl disulphide.** R. S. SHELTON and T. H. RIDER (J. Amer. Chem. Soc., 1936, 58, 1282—1284).—Bz<sub>2</sub>S<sub>2</sub>, m.p. (tube) 129—130° (decomp.), (bar) 132°, is prepared by oxidation (H<sub>2</sub>O<sub>2</sub>) of BzSH (from BzCl and 35% aq. NaHS in O<sub>2</sub>). H. B.

**Action of secondary amines on dibenzoyl disulphide.** L. SZPERL and M. WASILEWSKA

(Rocz. Chem., 1936, 16, 207—212).—(Ph·CO·S)<sub>2</sub> (I) and NHPr<sup>a</sup><sub>2</sub> in C<sub>6</sub>H<sub>6</sub> at room temp. yield *benzdi-n-propylamide*, b.p. 290—291°/746 mm., together with BzSH, H<sub>2</sub>S, and S, whilst with NPhMe (27 hr. at the b.p.) the chief product is NPhMeBz. (I) does not react with NPhPh<sub>2</sub>. R. T.

**Nitration of ethyl phenylacetate.** J. F. J. DIPPY and J. E. PAGE (J.S.C.I., 1936, 55, 190—192).—Nitration of CH<sub>2</sub>Ph·CO<sub>2</sub>Et with (a) HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> gives 2 : 4-dinitrophenylacetic acid, (b) HNO<sub>3</sub>-AcOH, Et *p*-nitrophenylacetate (poor yield), and (c) HNO<sub>3</sub>-Ac<sub>2</sub>O, Et *o*-nitrophenylacetate, easily hydrolysed to the acid. F. R. S.

**Mechanism of substitution reactions. Substitution of bromine and chlorine in  $\alpha$ -bromo- and  $\alpha$ -chloro-phenylacetic acids by chloride and bromide ions in aqueous solution.** M. J. YOUNG and A. R. OLSON (J. Amer. Chem. Soc., 1936, 58, 1157—1162).—The heats of activation and collision factors for these reactions are determined at 15—50° and compared with those for the halogenosuccinate system (A., 1934, 847; this vol., 569). In accordance with theory, the reaction *l*-CHBrPh·CO<sub>2</sub>H + Cl<sup>-</sup>  $\rightarrow$  *d*-CHClPh·CO<sub>2</sub>H + Br<sup>-</sup> is accompanied by complete inversion in configuration. H. B.

**Configuration of aminophenylacetic acid.** H. REIHLEN and L. KNOPFLE (Annalen, 1936, 523, 199—210).—Me d(-)- $\alpha$ -aminophenylacetate (hydrochloride, m.p. 202°, [ $\alpha$ ]<sub>D</sub> -121° in H<sub>2</sub>O; Ac, m.p. 114—117°, [M]<sub>5893</sub> -363° in MeOH, and Bz derivative, m.p. 101.5°, [M]<sub>5893</sub> -270° in MeOH; [M] are given also for 3 other  $\lambda$  and 6 solvents) readily affords d(-)- $\alpha$ -aminophenylacetamide, decomp. > 150°, [M]<sub>5893</sub> -188° in H<sub>2</sub>O (Ac, m.p. 175°, [ $\alpha$ ]<sub>D</sub> -242° in CHCl<sub>3</sub>, and Bz derivative, m.p. 217.5°, [ $\alpha$ ]<sub>D</sub> -119° in CHCl<sub>3</sub>), stable to dehydrating agents. Hydrogenation (Pt-C) of d(-)- $\alpha$ -NH<sub>2</sub>·CHl h·CO<sub>2</sub>H (I) in 2N-HCl at 70° gives d(-)- $\alpha$ -aminocyclohexylacetic acid (II) {Me [hydrochloride, m.p. 186° (decomp.); Ac, m.p. 118°, [M]<sub>D</sub> -53° in CHCl<sub>3</sub>, and Bz derivative, m.p. 130°, [M]<sub>D</sub> -105° in CHCl<sub>3</sub>] and Et ester (hydrochloride, m.p. 167°; Ac, m.p. 93°, [M]<sub>D</sub> -116° in CHCl<sub>3</sub>, and Bz derivative, m.p. 125°, [M]<sub>D</sub> -117° in CHCl<sub>3</sub>)}. Comparison of [M] in 4 solvents of the Ac, m.p. 61.5°, [M]<sub>D</sub> +112° in CHCl<sub>3</sub>, and Bz derivative, m.p. 110.5°, [M]<sub>D</sub> +115° in CHCl<sub>3</sub>, of the Me ester and the Bz derivative, m.p. 77.5—78°, [M]<sub>D</sub> +137° in CHCl<sub>3</sub>, of the Et ester of *l*(+)-valine (III) and of the effects of acid and alkali on [ $\alpha$ ] for (III) with the corresponding [M] and changes in the (II) series proves the configurations of (I) and (II) stated above. *dl*-(I) is hydrogenated only after purification by way of the nitrate. R. S. C.

**Condensation of (A) dihydroxydiethylamine with potassium cyanide, formaldehyde, and benzaldehyde, (B)  $\beta$ -hydroxypropylamine with potassium cyanide, benzaldehyde, and cyclohexanone.** V. F. LIUBOMUDROV (Ukrain. Chem. J., 1936, 11, 119—122, 123—126).—(A) NH(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>2</sub>·HCl, aq. KCN, and aq. CH<sub>2</sub>O (12 hr. at room temp.) afford CN·CH<sub>2</sub>·N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>2</sub>, hydrolysed by aq. HCl to yield di-( $\beta$ -hydroxyethyl)-aminoacetic acid. *Di*-( $\beta$ -hydroxyethyl)aminophenyl-

acetic acid, m.p. 143—144°, is prepared analogously, using PhCHO in place of CH<sub>2</sub>O.

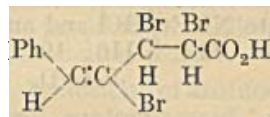
(b) OH·CHMe·CH<sub>2</sub>·NH<sub>2</sub>·HCl, PhCHO, and aq. KCN afford  $\beta$ -hydroxypropylaminophenylacetonitrile, m.p. 90° (hydrochloride, m.p. 121—122°), yielding an unidentified substance, m.p. 199—200°, when hydrolysed with aq. HCl. The product obtained when cyclohexanone is substituted for PhCHO in the reaction is 1-cyano-1- $\beta$ -hydroxypropylaminocyclohexane, m.p. 49—50° (hydrochloride, m.p. 115°). R. T.

**Partial racemisation.** I. H. LETTRE, H. BARNBECK, and H. STAUNAU (Ber., 1936, 69, [B], 1594—1598).—Partial racemates are defined as compounds related to the true racemates or pseudoracemates in which the components differ either sterically or by different substitution. Investigation of the system OH·CHPh·CO<sub>2</sub>H—hexahydromandelic acid shows that *r*-mandelic acid (I) is a true racemate. *r*-Hexahydromandelic acid (II) is also racemic. l(+)-Mandelic acid and d(−)-hexahydromandelic acid give a partial racemate the m.p. of which is > that of either component. (I) and (II) give an unbroken series of mixed crystals. Where partial racemism occurs [(I)–(II); malic acid (III)–tartaric acid (IV)] the corresponding racemic compounds are isomorphous, and where this is not the case [(I)–(III); (I)–(IV)] the racemic compounds are not isomorphous. Further examples are quoted from the lit. and the relationship may be general. H. W.

**$\beta$ -Arylacrylic compounds.** Y. DE SCHUTTENBACH (Ann. Chim., 1936, [xi], 6, 53—96).—Comparison of the rates of hydrolysis of CHPh:CPh·CO<sub>2</sub>Me (I), *p*-OMe·C<sub>6</sub>H<sub>4</sub>:CH:CPh·CO<sub>2</sub>Me (II), and CH<sub>2</sub>O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>:CH:CPh·CO<sub>2</sub>Me (III) and of esterification of the corresponding acids shows that the appreciable retarding action of the double linking is accentuated when  $\beta$ -Ph is replaced by  $\beta$ -CH<sub>2</sub>O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub> and further enhanced by  $\beta$ -*p*-C<sub>6</sub>H<sub>4</sub>:OMe. The absorption in the ultra-violet is displaced towards the visible during passage from (I) to (II) and thence to (III). *Me*  $\alpha$ -phenyl- $\beta$ -*p*-anisylacrylate, b.p. 250°/25 mm., m.p. 90—91°, and *Me*  $\alpha$ -phenyl- $\beta$ -piperonylacrylate, m.p. 106—107°, are obtained by condensation of CH<sub>2</sub>Ph·CO<sub>2</sub>Me with Na powder and the appropriate aldehyde. CPhMe:CH·CO<sub>2</sub>Me is transformed by MgMeI into the alcohol, CPhMe:CH·CMe<sub>2</sub>·OH, dehydrated to  $\beta$ -phenyl- $\gamma$ -methyl- $\Delta^{\beta}$ -butene, b.p. 107—108°/18 mm., which is oxidised to CPhMe by CrO<sub>3</sub> in AcOH. CPhMe:CH·CO<sub>2</sub>Me and MgPhBr give CPh<sub>2</sub>Me·CH<sub>2</sub>·COPh. Addition of CHPh:CPh·CN to CH<sub>2</sub>Ph·MgCl in boiling Et<sub>2</sub>O gives  $\alpha\beta\gamma$ -triphenylbutyronitrile, m.p. 192°; under apparently identical conditions a second experiment gave the impure diastereoisomeride, m.p. 129—131°, hydrolysed to acids, C<sub>22</sub>H<sub>19</sub>O<sub>2</sub>, m.p. 138° and m.p. 152—153°, respectively. H. W.

$\alpha\beta\gamma$ -Tribromocinnamylacetic [tribromo- $\delta$ -phenyl- $\Delta^{\gamma}$ -pentoic] acid. H. LOHAUS and W. GUSSMANN (Annalen, 1936, 523, 294—299).— $\alpha\beta\gamma$ -Tribromo- $\delta$ -phenyl- $\Delta^{\gamma}$ -pentoic acid (I), m.p. 157°, obtained from  $\alpha\beta$ -trans- $\gamma\delta$ -cis- $\gamma$ -cis-bromo- $\delta$ -phenylpentadienoic acid (II) and Br·CHCl<sub>3</sub>, gives (II) with NaI·COMe<sub>2</sub> or Zn dust in dry Et<sub>2</sub>O, and with KMnO<sub>4</sub>·COMe<sub>2</sub> gives an isomeride, +2H<sub>2</sub>O, m.p. 163°, and

mesodibromotartaric acid, whence it follows that (I) has the annexed formula. (I) gives a 2:1 pyridinium compound, C<sub>27</sub>H<sub>23</sub>O<sub>4</sub>NBr<sub>6</sub>, decomp. 142°, stable to hot AcOH, converted into its components by hot alcoholic



alkali or conc. HCl. The mother-liquor from the prep. of (I) yields the 1:1 pyridinium compound, m.p. 85°, of a dibromophenyl- $\Delta^{\gamma}$ -pentoic acid. The Me ester of (II) with Br·CHCl<sub>3</sub> gives the *Me* ester, m.p. 59—60°, of (I) [also obtained from (I) by CH<sub>2</sub>N<sub>2</sub>], and a *Me* dibromo- $\delta$ -phenyl- $\Delta^{\gamma}$ -pentoate (III), m.p. 117°, isolated in this reaction as 1:1 pyridinium compound (IV), m.p. 151° (decomp.), or by the action of C<sub>5</sub>H<sub>5</sub>N·Et<sub>2</sub>O on the tetrabromide of (II). (IV) and O<sub>3</sub> in H<sub>2</sub>O give CHO·CO<sub>2</sub>Me, but no PhCHO, wherefore it is probable that one Br in (III) is in the Ph nucleus. R. S. C.

**5:6:7:8-Tetrahydro- $\alpha$ -naphthylamine-4-carboxylic acid, and certain of its derivatives.** S. I. SERGIEVSKAJA and V. V. NESVADBA (J. Gen. Chem. Russ., 1936, 6, 633—666).—4-Nitro-5:6:7:8-tetrahydro-1-naphthylamine is diazotised, and the product is treated with CuCN to yield the corresponding 1-nitrile (I), m.p. 121°, reduced by SnCl<sub>2</sub> in HCl at room temp. to 4-cyano-5:6:7:8-tetrahydro-1-naphthylamine, m.p. 114° (*Ac* derivative, m.p. 203°). (I) and HCl (140°:10 hr.) yield 1-nitro-5:6:7:8-tetrahydronaphthalene-4-carboxylic acid, m.p. 161—162°, the *Et* ester, m.p. 37°, of which is reduced by H<sub>2</sub> (Pt-black) to the *Et* ester, m.p. 90° (*Ac* derivative, m.p. 165—166°), of 5:6:7:8-tetrahydro- $\alpha$ -naphthylamine-4-carboxylic acid, from which the free acid, m.p. 188° (decomp.), is obtained by boiling with EtOH·KOH. R. T.

**New type of vanadyl salicylate.** P. BRAUMAN (Compt. rend., 1936, 202, 1992—1994).—Addition of Li<sub>2</sub>CO<sub>3</sub> to a mixture of 50% aq. VOCl<sub>3</sub> and excess of OH·C<sub>6</sub>H<sub>4</sub>:CO<sub>2</sub>Et in MeOH gives a mixture of a blue product [of type R'O(VO)O·C<sub>6</sub>H<sub>4</sub>:CO<sub>2</sub>R] and a green product, which cannot be separated. With Bu or isoamyl *p*-hydroxybenzoate only the green compounds are formed, of composition V<sub>2</sub>C<sub>15</sub>H<sub>28</sub>O<sub>10</sub> and V<sub>2</sub>C<sub>16</sub>H<sub>30</sub>O<sub>10</sub>, respectively. With the Ph ester the green product is V<sub>2</sub>C<sub>12</sub>H<sub>22</sub>O<sub>10</sub>, and is a derivative of OH·C<sub>6</sub>H<sub>4</sub>:CO<sub>2</sub>Me. The green compounds probably contain MeOH of crystallisation. The composition OMe(VO)O(VO)O·C<sub>6</sub>H<sub>4</sub>:CO<sub>2</sub>R, 3MeOH is suggested. H. J. E.

**Action of mixed organo-magnesium compounds on aromatic *N*-diethylamides with phenolic groups.** P. COUTURIER (Compt. rend., 1936, 202, 1994—1996; cf. A., 1926, 837; 1927, 458).—Diethylamides (m.p. in parentheses), prepared by interaction of the acid chloride and NHET<sub>2</sub>, of the following acids are described: *o*- (104°), *m*- (84°), and *p*-hydroxybenzoic (121°), protocatechuic [(149—151°) *Ac*<sub>2</sub> derivative (72°)], gallic [(137°) *Ac*<sub>2</sub> derivative (113°)], and anisic acid (42°). Salicyldiethylamide with MgEtBr in boiling Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, or Bu<sub>2</sub>O affords *o*-hydroxypropiophenone, m.p. 20—22°. The *m*- and *p*-analogues react less easily. The other amides do not react. *p*-OMe·C<sub>6</sub>H<sub>4</sub>:CO·NET<sub>2</sub> reacts more



readily with  $\text{MgEtBr}$  than the phenol to give  $p\text{-OMe-C}_6\text{H}_4\text{-COEt}$  and a *tert.* base, the hydrochloride of which decomposes at  $90^\circ$  into  $\text{NH}_4\text{Et}_2\text{HCl}$  and an unsaturated hydrocarbon (cf. A., 1905, i, 116; 1926, 942; 1910, i, 728).  
J. L. D.

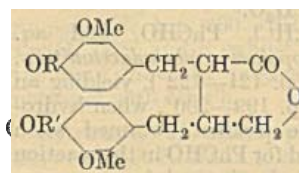
**Oxidation of phenols with peracetic acid.** C. GRUNDMANN [with H. TRISCHMANN] (Ber., 1936, 69, [B], 1755—1757).—*o*-Hydroxycinnamic acid is oxidised by  $\text{AcO}_2\text{H}$  in the dark to *cis-cis*-muconic acid in very small amount; in presence of light a more or less complete isomerisation to the *trans-trans*-acid takes place. 2:2'-Dihydroxydiphenyl gives 2'-hydroxy-2-phenyl-*p*-benzoquinone, m.p.  $193^\circ$  (Berl; corr.; decomp.), and  $\alpha$ -*o*-hydroxyphenylmuconolactone,  $\text{O} < \text{CO} > \text{C}_6\text{H}_4 > \text{C}:\text{CH}:\text{CH}:\text{CH}:\text{CO}_2\text{H}$ , m.p.  $194\text{--}195^\circ$  (Berl; corr.).  
H. W.

**Action of light on  $\beta$ -bromobenzylidenepyruvic acid.** M. REIMER (J. Amer. Chem. Soc., 1936, 58, 1108—1111).—Exposure of a saturated  $\text{C}_6\text{H}_6$ -solution of  $\text{CHPh}:\text{CBr}:\text{CO}:\text{CO}_2\text{H}$  (I) (A., 1924, i, 642) in a quartz tube and  $\text{N}_2$  atm. to bright sunlight gives about 80% of a dimeride (II) (+2MeOH), m.p.  $201^\circ$  (decomp.) [ $\text{Me}_2$  ester ( $\text{CH}_2\text{N}_2$ ), m.p.  $212^\circ$  and then slow decomp.]; a yellow intermediate is formed in diffused light (not in dark); this changes rapidly in sunlight into (II). In presence of dry  $\text{O}_2$ , (II) and  $\beta\beta$  (or  $\beta\gamma$ )-dibromo- $\gamma$  (or  $\beta$ )-hydroxy- $\alpha$ -keto- $\gamma$ -phenylbutyric acid (+ $\text{H}_2\text{O}$ ), m.p.  $107^\circ$  (opaque; clear at  $109^\circ$ ) [also obtained from (I) and Br (vapour) in  $\text{H}_2\text{O}$ ], are produced. In moist  $\text{C}_6\text{H}_6$ , some  $\beta\beta\gamma$ -trihydroxy- $\alpha$ -keto- $\gamma$ -phenylbutyric acid (III), m.p.  $134^\circ$  (decomp.), is formed. Finely-divided (I) is converted by prolonged exposure into a dimeride, m.p.  $280^\circ$  (decomp.) ( $\text{Me}_2$  ester, m.p.  $233\text{--}234^\circ$ ). (III), which is cleaved by alkaline  $\text{H}_2\text{O}$ , to mandelic acid and  $\text{H}_2\text{C}_2\text{O}_4$  and is oxidised by  $\text{Pb}(\text{OAc})_4$  to  $\text{PhCHO}$ , is also formed from (I) and  $\text{KMnO}_4$  in aq.  $\text{COMe}$ , + little  $\text{H}_2\text{SO}_4$  at  $-3^\circ$  to  $0^\circ$ .  
H. B.

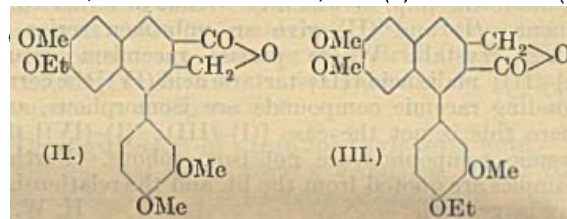
**Hydrogen esters of tetrachlorophthalic acid.** V. TETERIN and S. ZONIS (J. Gen. Chem. Russ., 1936, 6, 658—662).—*Mono*-esters of the following alcohols are obtained by boiling with  $\text{C}_6\text{H}_5\text{Cl}_4(\text{CO}_2\text{H})_2$  (I) in  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{-CHCl}_2$ , or  $\text{C}_6\text{H}_5\text{-Et}_2\text{O}$  (2—10 hr.):  $\text{MeOH}$ , m.p.  $142^\circ$ ; *n*-, m.p.  $105\text{--}106^\circ$ , *iso*-, m.p.  $97\text{--}98^\circ$ , and *sec*-. $\text{BuOH}$ , m.p.  $121\text{--}122^\circ$ ; *iso*-. $\text{C}_5\text{H}_{11}\text{-OH}$ , m.p.  $112\text{--}113^\circ$ ;  $\beta$ -naphthylethyl alcohol, m.p.  $179\text{--}180^\circ$ ; *p*-nitrobenzyl alcohol, m.p.  $179\text{--}180^\circ$ ; cyclohexanol, m.p.  $150\text{--}151^\circ$ ; menthol, m.p.  $99\text{--}100^\circ$ ; benzhydrol, m.p.  $149\text{--}150^\circ$ ;  $\beta$ -naphthylmethyl-, m.p.  $155\text{--}155.5^\circ$ , and -ethylcarbinol, m.p.  $159.6\text{--}161^\circ$ . Esters were not obtained under the above conditions with  $\text{OH-CH}_2\text{-CH}_2\text{Cl}$ ,  $\text{OH-CHCl-CHCl-CH}_2\text{Cl}$ ,  $\text{PhOH}$ , and certain *tert.* alcohols. The esters of alcohols of low b.p. decompose when heated to yield the anhydride of (I) and the alcohol, whilst esters of *sec.* alcohols afford (I) and unsaturated hydrocarbons.  
R. T.

**Constituents of natural phenolic resins. VII. Arctigenin.** R. D. HAWORTH and W. KELLY (J.C.S., 1936, 998—1003; cf. this vol., 985).—*l*-Arctigenin is A ( $\text{R}=\text{H}$ ,  $\text{R}'=\text{Me}$ ), (a) because its

*Et* ether (I) ( $\text{A}$ ,  $\text{R}=\text{Et}$ ,  $\text{R}'=\text{Me}$ ; obtained by hot  $\text{Et}_2\text{SO}_4\text{-KOH-EtOH}$ ), an oil [ $\text{Br}_2$ -, m.p.  $128\text{--}129^\circ$ , and ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $166\text{--}167^\circ$ ], has an absorption spectrum identical with that of the *dl*-ether, which is synthesised, whereas the isomeric ether ( $\text{A}$ ;  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ ; also synthesised) has an absorption spectrum which, although similar, has a lower intensity of absorption at the max.,  $2800 \text{ \AA}$ , and (b) because (I) with  $\text{Pb}(\text{OAc})_4\text{-AcOH}$  at  $80^\circ$  gives the lactones (II), m.p.  $223\text{--}224^\circ$ , of 6-methoxy-7-ethoxy-1-3':4'-dimethoxyphenyl-2-hydroxymethylnaphthalene-3-carboxylic acid, and (III), m.p.  $247\text{--}248^\circ$ , of 6:7-dimethoxy-1-3'-methoxy-4'-ethoxyphenyl-3-hydroxymethylenenaphthalene-2-carboxylic acid, which are both synthesised. The lactones, also synthesised, expected from the alternative formula ( $\text{A}$ ;  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ ) for (I) differ from (II)



(I) differ from (II) and (III). 3:4- $\text{OMe-C}_6\text{H}_3(\text{OEt})\text{-CHO}$  (IV) and hot  $\text{KMnO}_4\text{-aq. NaHCO}_3$  give 3-methoxy-4-ethoxybenzoic acid, m.p.  $195^\circ$ , the chloride (V), b.p.  $158\text{--}160^\circ/0.2 \text{ mm.}$ , m.p.  $73^\circ$ , of which with  $\text{NaOEt}$  and  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  gives a product, converted by  $\text{NH}_4\text{Cl-aq. NH}_3$  into *Et* 3-methoxy-4-ethoxybenzoylacetate, m.p.  $79\text{--}78^\circ$ . With  $\text{NaOEt}$  and  $\text{CH}_2\text{Br-CO}_2\text{Et}$  this yields  $\beta$ -3-methoxy-4-ethoxybenzoylpropionic acid (VI), m.p.  $136\text{--}137^\circ$ . *O*-Ethyleugenol and  $\text{I-HgO-Et}_2\text{O-H}_2\text{O}$  give the oxide (VII), b.p.  $137\text{--}138^\circ/0.2 \text{ mm.}$ , m.p.  $37\text{--}38^\circ$ . (IV),  $\text{CN-CH}_2\text{-CO}_2\text{Na}$ , and aq.  $\text{NaOH}$  give  $\alpha$ -cyano- $\beta$ -3-methoxy-4-ethoxyphenylacrylic acid, m.p.  $212\text{--}213^\circ$ , reduced (2%  $\text{Na-Hg-CO}_2$ ;  $0^\circ$ ) to  $\alpha$ -cyano- $\beta$ -3-methoxy-4-ethoxyphenylpropionic acid, m.p.  $152\text{--}153^\circ$  [ $\text{Me}$  ester (VIII), m.p.  $61\text{--}62^\circ$ ]. The Na derivative of (VIII) with *O*-methyl-eugenol oxide in  $\text{EtOH}$  gives  $\beta$ -3:4-dimethoxybenzyl- $\alpha$ -3-methoxy-4-ethoxybenzylbutyrolactone [=dl-(I)], m.p.  $105\text{--}106^\circ$  [ $\text{Br}_2$ -, m.p.  $88\text{--}89^\circ$ , and ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $159^\circ$ ]. 3:4-( $\text{OMe})_2\text{C}_6\text{H}_3\text{-CH}_2\text{-CNa}(\text{CN})\text{-CO}_2\text{Me}$  and (VII) in  $\text{EtOH}$  give  $\alpha$ -3:4-dimethoxybenzyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone ( $\text{A}$ ;  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ ), m.p.  $95\text{--}96^\circ$  [ $\text{Br}_2$ -, m.p.  $99\text{--}100^\circ$ , and ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $172\text{--}173^\circ$ ]. (VII) and  $\text{CHNaAc-CO}_2\text{Et}$  in  $\text{EtOH}$  at room temp. afford  $\alpha$ -acetyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone, m.p.  $87\text{--}88^\circ$ , the Na derivative of which with 3:4-( $\text{OMe})_2\text{C}_6\text{H}_3\text{-COCl}$  in  $\text{C}_6\text{H}_6$  yields  $\alpha$ -3:4-dimethoxybenzoyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone, m.p.  $129\text{--}130^\circ$ , converted by warming with  $\text{HCl-MeOH}$  and subsequent dehydration with  $\text{KHSO}_4$  at  $180^\circ$  into the lactone, m.p.  $189\text{--}190^\circ$ , of 6-methoxy-7-ethoxy-1-3':4'-dimethoxyphenyl-3-hydroxymethyl-3:4-dihydronaphthalene-2-carboxylic acid, which is oxidised by  $\text{Pb}(\text{OAc})_4$  to the lactone, m.p.  $243\text{--}244^\circ$ , of 6-methoxy-7-ethoxy-1-3':4'-dimethoxyphenyl-3-hydroxy-



and (III). 3:4- $\text{OMe-C}_6\text{H}_3(\text{OEt})\text{-CHO}$  (IV) and hot  $\text{KMnO}_4\text{-aq. NaHCO}_3$  give 3-methoxy-4-ethoxybenzoic acid, m.p.  $195^\circ$ , the chloride (V), b.p.  $158\text{--}160^\circ/0.2 \text{ mm.}$ , m.p.  $73^\circ$ , of which with  $\text{NaOEt}$  and  $\text{CH}_2\text{Ac-CO}_2\text{Et}$  gives a product, converted by  $\text{NH}_4\text{Cl-aq. NH}_3$  into *Et* 3-methoxy-4-ethoxybenzoylacetate, m.p.  $79\text{--}78^\circ$ . With  $\text{NaOEt}$  and  $\text{CH}_2\text{Br-CO}_2\text{Et}$  this yields  $\beta$ -3-methoxy-4-ethoxybenzoylpropionic acid (VI), m.p.  $136\text{--}137^\circ$ . *O*-Ethyleugenol and  $\text{I-HgO-Et}_2\text{O-H}_2\text{O}$  give the oxide (VII), b.p.  $137\text{--}138^\circ/0.2 \text{ mm.}$ , m.p.  $37\text{--}38^\circ$ . (IV),  $\text{CN-CH}_2\text{-CO}_2\text{Na}$ , and aq.  $\text{NaOH}$  give  $\alpha$ -cyano- $\beta$ -3-methoxy-4-ethoxyphenylacrylic acid, m.p.  $212\text{--}213^\circ$ , reduced (2%  $\text{Na-Hg-CO}_2$ ;  $0^\circ$ ) to  $\alpha$ -cyano- $\beta$ -3-methoxy-4-ethoxyphenylpropionic acid, m.p.  $152\text{--}153^\circ$  [ $\text{Me}$  ester (VIII), m.p.  $61\text{--}62^\circ$ ]. The Na derivative of (VIII) with *O*-methyl-eugenol oxide in  $\text{EtOH}$  gives  $\beta$ -3:4-dimethoxybenzyl- $\alpha$ -3-methoxy-4-ethoxybenzylbutyrolactone [=dl-(I)], m.p.  $105\text{--}106^\circ$  [ $\text{Br}_2$ -, m.p.  $88\text{--}89^\circ$ , and ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $159^\circ$ ]. 3:4-( $\text{OMe})_2\text{C}_6\text{H}_3\text{-CH}_2\text{-CNa}(\text{CN})\text{-CO}_2\text{Me}$  and (VII) in  $\text{EtOH}$  give  $\alpha$ -3:4-dimethoxybenzyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone ( $\text{A}$ ;  $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ ), m.p.  $95\text{--}96^\circ$  [ $\text{Br}_2$ -, m.p.  $99\text{--}100^\circ$ , and ( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p.  $172\text{--}173^\circ$ ]. (VII) and  $\text{CHNaAc-CO}_2\text{Et}$  in  $\text{EtOH}$  at room temp. afford  $\alpha$ -acetyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone, m.p.  $87\text{--}88^\circ$ , the Na derivative of which with 3:4-( $\text{OMe})_2\text{C}_6\text{H}_3\text{-COCl}$  in  $\text{C}_6\text{H}_6$  yields  $\alpha$ -3:4-dimethoxybenzoyl- $\beta$ -3-methoxy-4-ethoxybenzylbutyrolactone, m.p.  $129\text{--}130^\circ$ , converted by warming with  $\text{HCl-MeOH}$  and subsequent dehydration with  $\text{KHSO}_4$  at  $180^\circ$  into the lactone, m.p.  $189\text{--}190^\circ$ , of 6-methoxy-7-ethoxy-1-3':4'-dimethoxyphenyl-3-hydroxymethyl-3:4-dihydronaphthalene-2-carboxylic acid, which is oxidised by  $\text{Pb}(\text{OAc})_4$  to the lactone, m.p.  $243\text{--}244^\circ$ , of 6-methoxy-7-ethoxy-1-3':4'-dimethoxyphenyl-3-hydroxy-

*methyl-naphthalene-2-carboxylic acid*.  $\alpha$ -Acetyl- $\beta$ -3:4-dimethoxybenzylbutyrolactone and (V) lead similarly to  $\alpha$ -3-methoxy-4-ethoxybenzoyl- $\beta$ -3:4-dimethoxybenzylbutyrolactone, m.p. 123—124°, the lactone, m.p. 192—193°, of 6:7-dimethoxy-1-3'-methoxy-4'-ethoxyphenyl-3-hydroxymethyl:4-dihydronaphthalene-2-carboxylic acid, and (III). 3:4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·CH<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>Na (IV), and Ac<sub>2</sub>O at 100° give the  $\gamma$ -lactone, m.p. 180°, converted by hot NaOMe into  $\beta$ -3:4-dimethoxybenzoyl- $\alpha$ -3-methoxy-4-ethoxybenzylidenepropionic acid, m.p. 188—189°; when the  $\beta$ -methylene-derivative (prep. by CH<sub>2</sub>O and aq. NaOH at room temp.), m.p. 180°, thereof is kept with HCl-AcOH and the product is heated first with dil. NaOH and then with dil. acid, (II) is obtained. (VI), veratraldehyde, and Ac<sub>2</sub>O lead similarly to  $\beta$ -3-methoxy-4-ethoxybenzoyl- $\alpha$ -3:4-dimethoxybenzylidenepropionic acid (IX), m.p. 189—190°, by way of the  $\gamma$ -lactone, m.p. 162—163°, and thence to the  $\beta$ -methylene-derivative, m.p. 176—177°, of (IX), and the lactone, m.p. 214—215°, of 6:7-dimethoxy-1-3'-methoxy-4'-ethoxyphenyl-2-hydroxy-methyl-naphthalene-3-carboxylic acid. R. S. C.

**Bile acids. XLIX. Oxidation product of bilianic acid. Effect of carbamide on oxidations with nitric acid.** M. SCHENCK (Z. physiol. Chem., 1936, 242, 81—88; cf. this vol., 605).—Oxidation of bilianic acid (I) at room temp. with HNO<sub>3</sub> gives the tetrabasic acid (II), C<sub>21</sub>H<sub>35</sub>O<sub>10</sub>N, decomp. 175—180°. There is no action if CO(NH<sub>2</sub>)<sub>2</sub> is added. Hot HNO<sub>3</sub> oxidises (I), but only small yields of biloidanic acid are obtained. CO(NH<sub>2</sub>)<sub>2</sub> does not interfere with the action of cold HNO<sub>3</sub> on the hydroxamic acid C<sub>21</sub>H<sub>36</sub>O<sub>8</sub>N<sub>2</sub>, but it prevents the oxidation of the lactam of bilianic acid oxime. W. McC.

**Aldehydes and hydroxyaldehydes of the polymethylenic series. I. Transformations of hexahydrobenzaldehyde.** E. D. VENUS-DANILOVA (J. Gen. Chem. Russ., 1936, 6, 697—703).—Hexahydrobenzaldehyde (I) and HgBr<sub>2</sub> in C<sub>5</sub>H<sub>5</sub>N (140—144°; 4 hr.) yield cyclopentyl Me ketone, higher yields of which are obtained from (I), H<sub>2</sub>SO<sub>4</sub>, and HgSO<sub>4</sub> in aq. EtOH. R. T.

**Transformations between stereoisomeric ald-oximes.** W. THIELACKER and L. H. CHOU (Annalen, 1936, 523, 143—153).— $\beta$ -2:6-Dichloro-3-nitrobenzaldehyde is quantitatively converted by cold, dil. NaOH into HCl and 6-chloro-3-nitrosalicylonitrile, whereas the  $\alpha$ -isomeride (II) is completely unchanged. The proportion of (I) in a mixture of the oximes can therefore be determined by titration (Volhard). It is thus shown that the same equilibrium mixture is formed from (I) or (II) under the action of very conc. HCl. When the method is applied to the equilibration of (I) and (II) in org. media it is found that the end-point of the titration is greatly obscured by the solvent, and the results are not very accurate. In EtOH, COMe, and EtOAc (I) tends to an equilibrium greatly displaced towards (II); (II) is isomerised much more slowly, and accidental catalytic influences are strongly in evidence. Attempts to follow the isomerisation of (I) and (II) in Et, *d*-tartrate by alteration of  $[\alpha]$  are hampered by the great dependence of this val. on time, but experiments with  $\alpha$ - and  $\beta$ -anisaldoxime in the same solvent show

that an equilibrium and not a complete isomerisation occurs (position of equilibrium deduced from m.p. of products). Similarly, an equilibrium ensues in the molten oximes. H. W.

**Reactions of aminoethyl alcohol with aldehydes and malonic acid.** A. I. KIPRIANOV and T. S. KUSNER (J. Gen. Chem. Russ., 1936, 6, 641—644).—NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH (I), CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, and PhCHO in EtOH at the b.p. yield cinnamic acid; in the cold the product, m.p. 135—136° (decomp.), is CHPh·C(CO<sub>2</sub>H)<sub>2</sub>·NH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH (II). An analogous product, m.p. 137° (decomp.), is obtained when furfuraldehyde is taken in place of PhCHO, whilst salicylaldehyde gives the salt, m.p. 196—197°, of (I) and coumarin-3-carboxylic acid, and piperonaldehyde yields an unstable product, converted into piperonylideneacrylic acid during recrystallisation. (II) yields cinnamic acid when heated at the m.p., and CHPh·C(CO<sub>2</sub>H)<sub>2</sub> when treated with aq. acids. R. T.

**Conversion of ald-oximes into carboxylic acids by hot alkali. Elimination of water from ald-oximes.** E. JORDAN and C. R. HAUSER (J. Amer. Chem. Soc., 1936, 58, 1304—1305).—Some aromatic  $\beta$ -ald-oximes (I) are converted (slowly) into a mixture of the  $\alpha$ -oxime (II) and the corresponding acid by 2*N*-NaOH at 97—100°; (II) undergoes slower conversion into the acid. (I) thus eliminates H<sub>2</sub>O [to give ArCN which is then hydrolysed] more readily than (II). Benzaldoxime and *m*-nitro-, *p*-methoxy-, and 3:4-methylenedioxy-benzald-oximes are used. In agreement with Brady and Goldstein (A., 1927, 973),  $\alpha$ - and  $\beta$ -furfurald-oximes similarly undergo interconversion; furoic acid is produced in greater amount from the  $\beta$ . H. B.

**Synthesis of a pyrogallolaldehyde [methyl ether].** F. MAUTHNER (J. pr. Chem., 1936, [ii], 145, 313—317).—CPh<sub>2</sub>Cl<sub>2</sub> (prep. in excellent yield by PCl<sub>5</sub> at 160—170°), b.p. 167°/14 mm., and Me gallate in C<sub>6</sub>H<sub>6</sub> give Me 3-hydroxy-4:5-diphenyl-methylenedioxybenzoate, which with MeI-NaOMe yields Me 4:5-diphenylmethylenedioxy-3-methoxybenzoate, hydrolysed by fuming HCl to gallic acid 3-Me ether, m.p. 220—222°, which at 250—270° gives pure pyrogallol 1-Me ether, b.p. 136—137°/13 mm., m.p. 37—40°. With Zn(CN)<sub>2</sub> (modified prep.) and HCl in Et<sub>2</sub>O this affords 3:4-dihydroxy-2-methoxybenzaldehyde (less probably the 2:3-dihydroxy-4-methoxy-compound), m.p. 118—119° [green FeCl<sub>3</sub> colour; *p*-nitrophenylhydrazone, m.p. 249—250° (decomp.)], which with MeI-K<sub>2</sub>CO<sub>3</sub>-COMe<sub>2</sub> yields 2:3:4-(OMe)<sub>3</sub>C<sub>6</sub>H<sub>4</sub>·CHO (*p*-nitrophenylhydrazone, m.p. 198—199°). R. S. C.

**Reaction of  $\alpha\beta$ -dibromo- $\beta$ -phenylethyl methyl ketone with azides.** V. A. KUZMIN and S. G. FRIDMAN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1935, 2, 55—67).—CHPhBr·CHBr·COMe does not react with NaN<sub>3</sub> in Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, or ligroin, at the b.p., or with AgN<sub>3</sub> in Et<sub>2</sub>O: in boiling EtOH or COMe<sub>2</sub> a monoazide, C<sub>10</sub>H<sub>9</sub>ON<sub>3</sub>, m.p. 78—79° [semi-carbazone, m.p. 167° (decomp.)], is obtained. H. I.

**Ketones of the formula CHRPh·CO·R'. P.** JULIEN (Bull. Soc. chim., 1936, 3, [v], 1347—1353;



cf. A., 1930, 213).—MgPr<sup>2</sup>Br with CHPrPh·CN in PhMe or xylene at 80–100° affords  $\alpha$ -phenyl-*n*-butyl Pr<sup>2</sup> ketone, b.p. 134–135°/17 mm. (semicarbazone, m.p. 152°). The following are prepared similarly:  $\alpha$ -phenyl- $\beta$ -methyl-*n*-propyl Et ketone, b.p. 130–145°/23 mm. (semicarbazone, m.p. 181°);  $\alpha$ -phenyl-*n*-amyl Pr<sup>2</sup>, b.p. 142–145°/15 mm. (semicarbazone, m.p. 107°), and Bu<sup>2</sup> ketone, b.p. 280–282° (semicarbazone, m.p. 116°);  $\alpha$ -phenyl- $\gamma$ -methyl-*n*-butyl Me, b.p. 138–145°/22 mm. (semicarbazone, m.p. 118°), Et, b.p. 132–140°/14 mm. (semicarbazone, m.p. 127–128°), Pr<sup>2</sup>, b.p. 139–144°/19 mm. (semicarbazone, m.p. 156°), and Bu<sup>2</sup> ketone, b.p. 153–160°/20 mm. (semicarbazone, m.p. 109°). MgPrBr with  $\alpha$ -phenyl- $\beta$ -methylbutyramide in Et<sub>2</sub>O affords  $\alpha$ -phenyl- $\beta$ -methyl-*n*-propyl Pr ketone, b.p. 135–137°/23 mm. (semicarbazone, m.p. 162°). J. L. D.

**Preparation of dibenzyl and benzyl methyl ketones.** C. D. HURD and C. L. THOMAS (J. Amer. Chem. Soc., 1936, 58, 1240; cf. A., 1933, 821).—CH<sub>2</sub>Ph·CO<sub>2</sub>H heated with Ac<sub>2</sub>O–KOAc followed by slow distillation gives 41% of CO(CH<sub>2</sub>Ph)<sub>2</sub> (I) and 16% of COMe·CH<sub>2</sub>Ph (II). (I) and (II) arise by pyrolysis of (CH<sub>2</sub>Ph·CO)<sub>2</sub>O and CH<sub>2</sub>Ph·CO<sub>2</sub>Ac, respectively. H. B.

**Condensation of *o*-nitrobenzaldehyde with *m*-nitroacetophenone.** Photochemical behaviour of the resulting *o*-nitro-derivatives. I. TANASESCU and E. TANASESCU (Bull. Soc. chim., 1936, [v], 3, 865–870).—*o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·COMe, and NaOEt–EtOH–Et<sub>2</sub>O yield 2 : 3'-dinitrochalcone (I), m.p. 163° (lit. 161°), and *m*-nitrophenyl  $\beta$ -hydroxy- $\beta$ -*o*-nitrophenylethyl ketone (II), m.p. 124° (Bz derivative, m.p. 142°), converted quantitatively by EtOH–alkalis into indigotin. (I) is not formed when the Et<sub>2</sub>O in the foregoing mixture is replaced by EtOH. (I) when boiled with NaOH–EtOH and then treated with HCl gives indigotin. Reduction of (I) and (II) with Zn–AcOH gives unidentified products, m.p. 159° and m.p. 178°, respectively. (II) when irradiated loses 1 mol. of H<sub>2</sub>O, giving a substance, m.p. about 300°, with acidic properties. H. G. M.

**Anthracene structure of dissociable organic oxides.** Properties of anthracene photo-oxide. C. DUFRAISSE and M. GÉRARD (Compt. rend., 1936, 202, 1859–1861).—Anthracene photo-oxide (I) (A., 1935, 1488) is shown to have the bond-structure of anthracene. It can be titrated with KI, which reduces it to anthranol or oxanthrol, but isomerisation and subsequent aerial oxidation to other products also occur. (I) resembles oxanthrone in state of oxidation and in giving with HCl and HBr 10-chloro- (II) and -bromo-anthrone, respectively. (II) melts on a block at 165° with loss of HCl and resolidification owing to immediate passage into 10-chloro-10 : 10'-dihydro-10 : 10'-dianthrone, m.p. 235°. The m.p., 225°, previously assigned to (II), is due to this transformation, which occurs appreciably even at 100°. 10-Halogenoanthrones are best identified by transformation into 10-methoxvanthrone, m.p. 103–104°. R. S. C.

**Synthesis of mixed benzoin.** II. R. T. ARNOLD and R. C. FUSON (J. Amer. Chem. Soc.,

1936, 58, 1295–1296; cf. A., 1935, 1499).—Condensation of arylglyoxals, COAr·CHO (Ar = *p*-C<sub>6</sub>H<sub>4</sub>Cl, b.p. 123–125°/17 mm., m.p. 40–42°; *p*-C<sub>6</sub>H<sub>4</sub>Br, b.p. 115°/7 mm., m.p. 51–52°), prepared by a slight modification of Riley and Gray's method (this vol., 471), with Ar'H by means of AlCl<sub>3</sub> (or, occasionally ZnCl<sub>2</sub>) in absence or (usually) presence of CS<sub>2</sub> gives benzoin, COAr·CHAr'·OH (I) (35–90% yields), oxidised (method: Corson and McAllister, A., 1929, 1301) to COAr·COAr'. The following (I) are described: benzoin; benzoyl-anisyl-, -naphthyl-, m.p. 128°, -chlorophenyl-, -bromophenyl-, m.p. 125–126°, -tolyl-, and -mesityl-carbinols; mesitoyl-mesityl-, m.p. 59–60°, and -phenyl-carbinols; *p*-bromobenzoylphenyl-carbinol, m.p. 108–109°; *p*-C<sub>6</sub>H<sub>4</sub>Cl·CO·CHPh·OH; C<sub>6</sub>H<sub>4</sub>Me·CO·CHPh·OH. Ph C<sub>10</sub>H<sub>7</sub> diketone, m.p. 87°, is new. H. B.

**Preparation of  $\alpha$ -mono-oximes of aryl aliphatic diketones.** C. PHILIPP (Annalen, 1936, 523, 285–289).—COMe·CH<sub>2</sub>N·OH and acid diazonium solutions, best in presence of CuSO<sub>4</sub>, give good yields of the  $\alpha$ -oximes, OH·N(CMe)·COR, in which R is Ph, *p*-C<sub>6</sub>H<sub>4</sub>Me, *p*-C<sub>6</sub>H<sub>4</sub>Cl, *p*-OMe·C<sub>6</sub>H<sub>4</sub>, *p*-OEt·C<sub>6</sub>H<sub>4</sub>, and  $\beta$ -C<sub>10</sub>H<sub>7</sub>. The  $\alpha$ -oximes of *p*-chlorophenyl and  $\beta$ -C<sub>10</sub>H<sub>7</sub> Me diketone melt at 174° and 152°, respectively. R. S. C.

**Preparation and properties of *o*-bromophenyl benzyl diketone.** Methylation of  $\alpha$ -diketones. R. P. BARNES and N. F. PAYTON (J. Amer. Chem. Soc., 1936, 58, 1300–1302).—*o*-C<sub>6</sub>H<sub>4</sub>Br·COMe and PhCHO in aq. EtOH–NaOH at 15–20° give *o*-bromophenyl styryl ketone (I), b.p. 183–185°/2 mm. [dibromide, m.p. 86°, converted by 10% KI in COMe<sub>2</sub> into (I)], oxidised (30% H<sub>2</sub>O<sub>2</sub>, aq. EtOH–NaOH) to *o*-bromophenyl benzyl diketone (II), b.p. 155°/2 mm. [quin-oxaline, m.p. 110°, from *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>], which is 100% enolic in the solid state, m.p. 107° (III) [obtained by acidification of the red upper layer from (II) and aq. EtOH–NaOH]. (II) is cleaved by alkaline H<sub>2</sub>O<sub>2</sub> in MeOH to CH<sub>2</sub>Ph·CO<sub>2</sub>H and *o*-C<sub>6</sub>H<sub>4</sub>Br·CO<sub>2</sub>H. Methylation (Me<sub>2</sub>SO<sub>4</sub>, aq. KOH) of (III) gives *o*-bromophenyl  $\alpha$ -methoxystyryl ketone, b.p. 280–285°/2 mm. The amount of *O*-Me ether formed during methylation of an  $\alpha$ -diketone is considered to be  $\propto$  the acidity of the enol; COR·C(CHR)·OH can be regarded as a glyoxylic acid with :O replaced by :CHR.  $\beta$ -Diketones cannot give such derivatives. *o*-C<sub>6</sub>H<sub>4</sub>Br·CO·CO<sub>2</sub>H has  $k^{25}$  8.6  $\times 10^{-2}$ . H. B.

**Formation of cholestane-3 : 6-dione from cholestenone dibromide and from  $\Delta^4$ - and  $\Delta^5$ -cholestenone.** Y. URUSHIBARA and T. ANDO (Bull. Chem. Soc. Japan, 1936, 11, 434–436).—Cholestane-3 : 6-dione is formed by treatment of  $\Delta^4$ - or  $\Delta^5$ -cholestenone with an equiv. amount of Br in abs. EtOH. Cholesterol is regenerated from its dibromide in good yield by heating the latter in abs. EtOH. A. T.

**Testosterone.**—See this vol., 1156.

**Displacement of the anisoyl group in the nitration of dimethoxybenzophenones.** C. W. POHL-MANN (Rev. trav. chim., 1936, 55, 737–752).—Tetranitration of *oo'*- (I) or *pp'*-dimethoxybenzophenone (II) or of their NO<sub>2</sub>-derivatives is accompanied

by much replacement of the aroyl group by  $\text{NO}_2$ , forming dinitro-anisoles and -anisic acids. This does not occur with the *m*-OMe-compounds, since the aroyl is never *m*- to a  $\text{NO}_2$ . 10 g. of (II) with abs.  $\text{HNO}_3$  at  $-15^\circ$  (method A) give the 3:3':5:5'-( $\text{NO}_2$ )<sub>4</sub>-derivative (III) 6.5, dimorphous, m.p.  $182^\circ$  and  $197^\circ$ ; 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OMe}$  (IV) 5.6, and 4:3:5-OMe- $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{CO}_2\text{H}$  (V) 1.75 g., and with  $\text{HNO}_3$ - $\text{Ac}_2\text{O}$  at  $0^\circ$  (method B) 5 g. give (III) 0.3, (IV) 0.6, the 3:3'-( $\text{NO}_2$ )<sub>2</sub>-derivative (VI) of (II) 3.9, and 3:4- $\text{NO}_2\text{-C}_6\text{H}_3(\text{OMe})\text{-CO}_2\text{H}$  (VII) 0.55 g. (VI) (2 g.) gives (III) 1.1, (IV) 0.65, and (V) 0.74 g. 2 g. of 3-nitro-4:4'-dimethoxybenzophenone [from PhOMe, 3:4- $\text{NO}_2\text{-C}_6\text{H}_3(\text{OMe})\text{-COCl}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$ , not from *o*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-OMe}$  and  $\text{OMe-C}_6\text{H}_4\text{-COCl}$ ], m.p.  $143^\circ$ , gives by (A) (III) 0.95, (IV) 0.59, and 4:3:5-OH- $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{CO}_2\text{H}$  0.69 g., or by (B) (III) 1.28, (IV) 0.13, and (VII) 0.13 g. (I) and Br-AcOH yield much 3:3'-dibromo- (VIII), m.p.  $182^\circ$ , and a little 3-bromo-4:4'-dimethoxybenzophenone (IX), m.p.  $89^\circ$  (also obtained from 4:3-OMe- $\text{C}_6\text{H}_3\text{Br-COCl}$  and PhOMe). (VIII) with  $\text{HNO}_3\text{-H}_2\text{SO}_4$  gives only 2:4:6-( $\text{NO}_2$ )<sub>3</sub>- $\text{C}_6\text{H}_2\text{Br-OMe}$  (X) and by (A) 3:3'-dibromo-5:5'-dinitro-4:4'-dimethoxybenzophenone, m.p.  $177^\circ$ , and traces of (X) and 4:3:5-OMe- $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CO}_2\text{H}$  (XI). (IX) (2 g.) gives by (A) 3-bromo-3':5:5'-trinitro-4:4'-dimethoxybenzophenone (XII), m.p.  $175^\circ$  (1.24 g.), (XI) (0.83 g.), and (IV) (0.68 g.), or by (B) (1.5 g.) 3-bromo-3'-nitro-4:4'-dimethoxybenzophenone (XIII) (also obtained from the 3- $\text{NO}_2$ -derivative and Br-AcOH), m.p.  $166^\circ$  (1.35 g.), 4:3-OMe- $\text{C}_6\text{H}_3\text{Br-CO}_2\text{H}$  (0.19 g.), and (IV) (0.17 g.). 1.4 g. of (XIII) gives by (A) (XII) 1.1, (XI) 0.29, and (IV) 0.18 g. (I) (3.5 g.) gives by (B) 5:5'-dinitro-2:2'-dimethoxybenzophenone (XV), m.p.  $188^\circ$  (2.44 g.; gives 2:7-dinitroxanthone with 75%  $\text{H}_2\text{SO}_4$  at  $150^\circ$ ), 2:5-OMe- $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{CO}_2\text{H}$  (1.11 g.; prep. from 5:2- $\text{NO}_2\text{-C}_6\text{H}_3\text{Cl-CO}_2\text{H}$  and MeOH), and *o*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-OMe}$  (0.9 g.), and by (A) (2 g.) 3:3':5:5'-tetranitro-2:2'-dimethoxybenzophenone (XVI), m.p.  $175^\circ$  (1.76 g.), (IV) (0.4 g.), 2:3:5-OMe- $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{CO}_2\text{H}$  (XVII) (0.64 g.), and 2:4:6- $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{-OH}$  (a trace). 0.6 g. of (XV) gives by (A) (XVI) 0.33, (IV) 0.14, and (XVII) 0.24 g. 3:3'-Dimethoxybenzophenone gives by (A) only the 4:4':6:6'-( $\text{NO}_2$ )<sub>4</sub>-derivative, m.p.  $231^\circ$ , converted by  $\text{HNO}_3\text{-H}_2\text{SO}_4$  at  $100^\circ$  into the 2:4:4':6:6'-( $\text{NO}_2$ )<sub>5</sub>-derivative, m.p.  $209^\circ$ , and a trace of a substance, m.p.  $143^\circ$ . (XVI) with the appropriate base in EtOH at  $100^\circ$  gives 1:3:7:9-tetranitro-acridone, m.p.  $337^\circ$  (block), and its 10-Me, m.p.  $318^\circ$  (block), -Et, m.p.  $282^\circ$  (block), -Pr<sup>a</sup>, m.p.  $273^\circ$  (block), -Bu<sup>a</sup>, m.p.  $260^\circ$  (block), -n-amyl, m.p.  $195^\circ$ , -n-hexyl, m.p.  $174^\circ$ , and -n-heptyl, m.p.  $167^\circ$ , derivatives. R. S. C.

**Paprika dye. IX. Partial degradation of capsanthin.** L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1936, 523, 101—108).—Oxidation of capsanthin diacetate (I) with  $\text{CrO}_3$  (= 2 O) gives unrecognised by-products, unchanged material, and capsanthinone diacetate, (II), m.p.  $123\text{--}124^\circ$  (corr.; block). Capsanthinone therefore contains 2 OH and 3 CO. Since it exactly resembles capsorubin in absorption spectrum it contains 2 CO in unbroken

conjugation with 9 C:C linkings and an isolated CO and hence is  $\text{COMe-CH}_2\text{-CH(OH)-CH}_2\text{-CMe}_2\text{-CO-[CH:CH-CMe:CH]}_2\text{-[CH:CH-CH:CMe]}_2\text{-CH:CH-CO-CMe}_2\text{-CH}_2\text{-CHPr}^a\text{-OH}$ . The presence of 2 CO in the  $\alpha\epsilon$  position is shown by the conversion of (II) by 10% KOH-MeOH at room temp. into anhydrocapsanthione,  $\text{C}_{40}\text{H}_{56}\text{O}_4$ , the spectrum of which is explained by the conjugation of the "isolated" CO with a newly-formed C:C. More drastic oxidation of (I) with  $\text{CrO}_3$  leads to capsanthylal, m.p.  $127^\circ$  (corr.) [oxime, m.p.  $184^\circ$  (corr.)], which is shown spectroscopically to contain an unbroken sequence of 11 conjugated linkings and hence to be  $\text{CHO-[CMe:CH-CH:CH]}_2\text{-[CH:CMe-CH:CH]}_2\text{-CO-CMe}_2\text{-CH}_2\text{-CHPr}^a\text{-OH}$ , capsyl aldehyde [oxime, m.p.  $172^\circ$  (corr.)], the absorption spectrum of which is identical with that of  $\beta$ -carotene aldehyde and which is therefore  $\text{CHO-CH:CH-CMe:CH-CH:CH-CH:CMe}_2\text{-CH:CH-CO-CMe}_2\text{-CH}_2\text{-CHPr}^a\text{-OH}$ , and  $\beta$ -hydroxycarotene aldehyde [oxime, m.p.  $189^\circ$  (corr.)] which is  $\text{COMe-CH}_2\text{-CH(OH)-CH}_2\text{-CMe}_2\text{-CO-[CH:CH-CMe:CH]}_2\text{-CH:CH-CH:CMe-CH:CH-CHO}$ .

The structure  $\text{OH-CH-CH-CH}_2\text{-CMe}_2\text{-CH}_2\text{-C-[CH:CH-CMe:CH]}_2\text{-[CH:CH-CH:CMe]}_2\text{-CH:CH-CO-CMe}_2\text{-CH}_2\text{-CHPr}^a\text{-OH}$  may therefore be ascribed to capsanthin (III) in which the cyclic system, the OH, 18 C atoms, and position of CO are assured. Treatment of (III) with KOH-EtOH-MeOH-H<sub>2</sub>O at  $70\text{--}80^\circ$  in absence of air is a practicable method for its degradation; a crvst. substance, m.p.  $112^\circ$  (corr.), has been isolated. H. W.

**Reaction between toluoquinone and cinnamaldehyde under the influence of light.** A. ANGELI (Atti R. Accad. Sci. Torino, Cl. Sci. fis., 1934—5, 70, I, 326—330; Chem. Zentr., 1935, ii, 2945).—Cinnamic acid, 2-methylquinol, and (probably) 4-hydroxy-3-methylphenyl cinnamate, m.p.  $163^\circ$ , are formed. H. N. R.

**Condensation of aldehydes with 2-hydroxy-1:4-naphthaquinone. Synthesis of hydrolapachol.** S. C. HOOKER (J. Amer. Chem. Soc., 1936, 58, 1163—1167; cf. J.C.S., 1896, 69, 1356).—The following 3-hydroxy-2- $\Delta^a$ -alkenyl-1:4-naphthaquinones (A) are obtained from 2-hydroxy-1:4-naphthaquinone and RCHO in AcOH-conc. HCl at  $75\text{--}80^\circ$ : propenyl (I), m.p.  $135.2\text{--}135.7^\circ$  (accompanied by a little of a compound, m.p.  $160\text{--}160.5^\circ$ ), butenyl (II), m.p.  $107.5^\circ$  (acetate, m.p.  $83.5\text{--}84^\circ$ ), pentenyl, m.p.  $98\text{--}98.5^\circ$ , heptenyl, m.p.  $86.5^\circ$ , styryl, m.p.  $166.5\text{--}167.5^\circ$  (acetate, m.p.  $138.7\text{--}139.2^\circ$ , red and orange-yellow forms), and  $\gamma$ -phenylpropenyl (III), m.p.  $140.5\text{--}141.5^\circ$  (decomp.). (A) could not be prepared from MeCHO and Pr<sup>a</sup>CHO. (I) heated in EtOH decomposes to a compound, m.p.  $197\text{--}198^\circ$  (decomp.); an EtOH-solution of (II) slowly deposits a substance, m.p.  $207\text{--}208^\circ$  (decomp.), whilst (III) undergoes autoxidation in  $\text{C}_6\text{H}_6$  to a compound,  $\text{C}_{19}\text{H}_{14}\text{O}_4$ , m.p.  $227\text{--}228^\circ$  (decomp.). Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) of (A) and, in some cases, the isomeric  $\Delta^b$ -alkenyl derivatives (Fieser, A., 1927, 155, 462) followed by atm. oxidation, gives the 3-hydroxy-2-alkyl-1:4-naphthaquinones: the Pr<sup>a</sup>, m.p.  $100.5\text{--}101.5^\circ$ , Bu<sup>a</sup>, m.p.  $101\text{--}101.5^\circ$ , n-amyl, m.p.  $104\text{--}104.3^\circ$ , n-heptyl, m.p.  $82.7\text{--}83.3^\circ$ ,  $\beta$ -



*phenylethyl*, m.p. 171.5—172.5°, and *γ-phenylpropyl*, m.p. 131.7—132.2°, derivatives are described. 3-Hydroxy-2-*γ*-methyl- $\Delta^2$ -butenyl-1:4-naphthaquinone (*isolapachol*) (cf. *loc. cit.*) is similarly reduced to the 2-*isoamyl* derivative (*hydrolapachol*), m.p. 93.5—94.5° (lit. 87—89°), identical with the reduction product of *lapachol*. H. B.

**Oxidation of 2-hydroxy-1:4-naphthaquinone derivatives with alkaline potassium permanganate.** [I. Mechanism.] S. C. HOOKER. II. Compounds with unsaturated side-chains. S. C. HOOKER and A. STEYERMARK (*J. Amer. Chem. Soc.*, 1936, 58, 1174—1179, 1179—1181).—I (cf. Fieser *et al.*, below). Oxidation of  $\text{o-C}_6\text{H}_4\text{C}(\text{CO-C-CH}_2\text{R})(\text{CO-C-OH})$  (I) (R=H, Me—hexyl, Ph,  $\text{CH}_2\text{Ph}$ , and  $\text{-CH}_2\text{-CH}_2\text{Ph}$ ) with  $\text{KMnO}_4$  ( $\Rightarrow 2\text{O}$ ) in aq. NaOH in absence or presence of air gives  $\text{o-C}_6\text{H}_4\text{C}(\text{CO-C-OH})(\text{CO-CR})$  (II) in (usually) 70—96% yield. Reaction probably occurs thus: (I)  $\rightarrow \text{o-CO}_2\text{H-CO-C}_6\text{H}_4\text{-CO-CH}_2\text{R} \rightarrow \text{CO}_2 + \text{o-C}_6\text{H}_4\text{C}(\text{CO-CO})(\text{CO-CHP})$  (II). The same reaction also occurs when R is unsaturated. 3-Hydroxy-2-ethyl-, m.p. 138.2—138.7°, and -2-*n*-hexyl-, m.p. 98—98.5°, -1:4-naphthaquinones are new. 2-Hydroxy-1:4-naphthaquinone and its saturated derivatives give a dark blue colour with conc.  $\text{H}_2\text{SO}_4$  and  $\text{C}_6\text{H}_6$  containing thiophen.

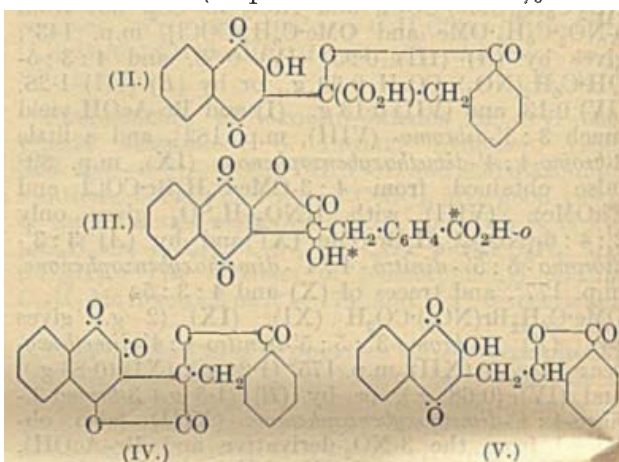
II. 3-Hydroxy-2-allyl-, -2-*γ*-methylallyl-, and -2-cinnamyl-1:4-naphthaquinones are similarly oxidised (usually in more dil. NaOH) to 3-hydroxy-2-vinyl-, m.p. 121.5—123.5°, -2- $\Delta^2$ -propenyl-, and -2-styryl-1:4-naphthaquinone, respectively.

H. B.

**Action of light on 2-hydroxy-1:4-naphthaquinone.** S. C. HOOKER (*J. Amer. Chem. Soc.*, 1936, 58, 1212—1216).—Exposure of dil. aq. solutions of 2-hydroxy-1:4-naphthaquinone (improved prep.) at 70° to light from a "Uviarc" lamp gives *isonaphthazarin* and (mainly) 3:3'-*dihydroxy*-2:2'-*dinaphthyl*-1:4:1':4'-*diquinone* (I), m.p. about 270—275° (decomp.) (sublimes from 250°), converted

the prep. (method: Thiele and Winter, A., 1900, i, 504) of 1:2:4- $\text{C}_{10}\text{H}_5(\text{OAc})_3$ . H. B.

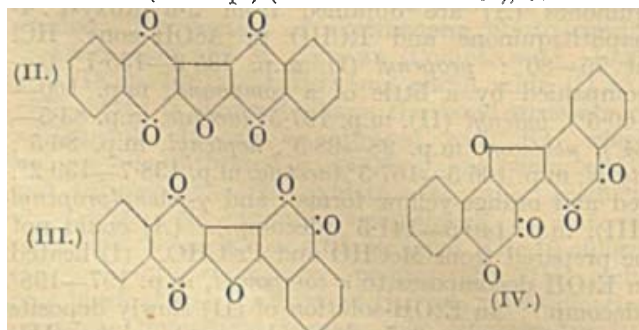
**Wichelhaus' "di- $\beta$ -naphthaquinone oxide."** S. C. HOOKER and L. F. FIESER (*J. Amer. Chem. Soc.*, 1936, 58, 1216—1223).—1:2-Naphthaquinone is oxidised by aq.  $\text{FeCl}_3$  at 65—70° (bath) to 1:1'-*dinaphthyl*-3:4:3':4'-*diquinone* and (mainly) 3-hydroxy-2:2'-*dinaphthyl*-1:4:3':4'-*diquinone* (I), m.p. 253—254° (decomp.) (darkens about 240°) (*acetate*, m.p. 205—205.5°). (I) is the "di- $\beta$ -naphthaquinone oxide" of Wichelhaus (A., 1898, i, 33). Distillation of (I) with Zn dust gives 2:2'-*dinaphthyl*, whilst oxidation (evaporation of solution in 6% NaOH



at room temp. in air) affords the *lactonic acid* (II), m.p. 203—205° (decomp.) (softens about 201°) [ $\text{Me}_2$  derivative ( $\text{CH}_2\text{N}_2$ ), m.p. 225—226° (softens about 220°)], which is converted by boiling AcOH into the *lactonic acid* (III), m.p. 264° (decomp.; after loss of  $\text{H}_2\text{O}$ ) [ $\text{Me}_2$  ester, m.p. 249—250° (previous softening)], also formed from (I) and 30%  $\text{H}_2\text{O}_2$  in AcOH. (III) heated in xylene affords the corresponding *dilactone*, m.p. 264°, by loss of  $\text{H}_2\text{O}$  between \*\*. (II) is dehydrated by conc.  $\text{H}_2\text{SO}_4$  at room temp. to the *dilactone* (IV), m.p. 248—249.5°, hydrolysed (1% NaOH) to (III). (II) heated with EtOH gives (III) and the *lactone* (V), m.p. 177.5—178° [better obtained from (II) and Cu powder in  $\text{C}_5\text{H}_5\text{N}$ ] [ $\text{Me}_1$  derivative ( $\text{CH}_2\text{N}_2$ ), m.p. 165—166°], converted by cold conc.  $\text{H}_2\text{SO}_4$  into an *anhydro*-derivative,  $\text{C}_{19}\text{H}_{10}\text{O}_4$ , decomp. about 220—225°.

1:2'-*Dinaphthyl*, m.p. 72—73° [*dipicrate*, m.p. 127—127.5° (corr.)] (cf. Smith, J.C.S., 1879, 35, 227) is obtained by dehydrogenation (S at 230—250°) of the distilled product, b.p. 217—219°/3 mm., from  $\beta\text{-C}_{10}\text{H}_7\text{-MgBr}$  and 1-keto-1:2:3:4-tetrahydronaphthalene. H. B.

**Mechanism of the Hooker oxidation.** L. F. FIESER, J. L. HARTWELL, and A. M. SELIGMAN (*J. Amer. Chem. Soc.*, 1936, 58, 1223—1228).—The following results confirm Hooker's view (see above) that oxidation of 2-hydroxy-3-alkyl- (or aralkyl)-1:4-naphthaquinones involves fission of the quinone ring and subsequent ring closure in a different manner, so that the 2- and 3-substituents exchange positions. 6-Bromo-1:2:4-triacetoxynaphthalene, m.p. 162° (from 6-bromo-1:2-naphtha-



by AcOH—dil.  $\text{H}_2\text{SO}_4$  into the *anhydride* (II), m.p. 349—350° (Berl block), and a little of the *anhydride* (III), m.p. 317—318° (decomp.) (block) [*quinoxaline*, m.p. 329—330° (block)]. (I) and conc.  $\text{H}_2\text{SO}_4$  at room temp. give (III) and a little of the *anhydride* (IV), decomp. 335—345° (*diquinoxaline*, m.p. 409—410°), whilst (I) and  $\text{Ac}_2\text{O}$ — $\text{NaOAc}$  or  $\text{-H}_2\text{SO}_4$  afford (IV) only. Tetra-acetoxynaphthyl is a by-product in

quinone and  $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ , is hydrolysed ( $\text{EtOH}-\text{KOH}$ ) and oxidised (air) to 6-bromo-2-hydroxy-1:4-naphthaquinone (I), m.p. 204–205°, which with  $\text{CH}_2\text{Ph}\cdot\text{CHO}$  in  $\text{AcOH}-\text{conc. HCl}$  at 80° gives 6-bromo-2-hydroxy-3-styryl-1:4-naphthaquinone, m.p. 243–244° (corresponding quinol triacetate, m.p. 197–198°), reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) to 6-bromo-2-hydroxy-3- $\beta$ -phenylethyl-1:4-naphthaquinone (II), m.p. 180–181° (quinol triacetate, m.p. 188–189°). (I) and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHO}$  similarly afford 6-bromo-2-hydroxy-3- $\gamma$ -phenyl- $\Delta^4$ -propenyl-1:4-naphthaquinone, m.p. 177–178°; the quinol triacetate, m.p. 170–171°, from this is reduced (Adams) to 6-bromo-1:2:4-triacetoxy-3- $\gamma$ -phenylpropylnaphthalene, m.p. 170–172°, which is hydrolysed ( $\text{EtOH}-\text{KOH}$  in air) to 6-bromo-2-hydroxy-3- $\gamma$ -phenylpropyl-1:4-naphthaquinone (III), m.p. 170–171°. The Ag salt of (I) with  $\text{CH}_2\text{PhBr}$  in  $\text{Et}_2\text{O}$  gives 6-bromo-4-benzoyloxy-1:2-naphthaquinone, m.p. 227–228°, 6-bromo-2-hydroxy-3-benzyl-1:4-naphthaquinone (IV), m.p. 192° (quinol triacetate, m.p. 202–203°), and 6-bromo-2-benzoyloxy-1:4-naphthaquinone, m.p. 201–202°. Oxidation (1%  $\text{KMnO}_4$ ) of (III) (in 1%  $\text{NaOH}+\text{C}_6\text{H}_6$ ) at 0° affords 6-bromo-3-hydroxy-2- $\beta$ -phenylethyl-1:4-naphthaquinone, m.p. 173–175° [which differs from (II)], further oxidised to (IV). Similar oxidation of (II) gives 6-bromo-3-hydroxy-2-benzyl-1:4-naphthaquinone, m.p. 158–159° (quinol triacetate, m.p. 196–197°), which differs from (IV). 3-Hydroxy-2-isobutyl-1:4-naphthaquinone (acetate, m.p. 53.5–54°) is similarly oxidised to the 2-isopropyl-derivative, m.p. 92–93°, and thence (by way of  $o\text{-CO}_2\text{H}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COPr}^t$ ) to  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$  and  $\text{Pr}^t\text{CO}_2\text{H}$ . 3-Hydroxy-2:6-dimethyl-1:4-naphthaquinone is oxidised in a more strongly alkaline medium to 2-hydroxy-6-methyl-1:4-naphthaquinone, m.p. 199° (decomp.) [*Me ether* (V), m.p. 167–167.5°; quinol triacetate, m.p. 157–158°]. Reduction ( $\text{Na}_2\text{S}_2\text{O}_4$ ) of the dye from diazotised  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  and 6:2- $\text{C}_{10}\text{H}_7\text{Me}\cdot\text{OH}$  (VI) affords 1:6:2- $\text{NH}_2\cdot\text{C}_{10}\text{H}_7\text{Me}\cdot\text{OH}$ , which is oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7$ , dil.  $\text{H}_2\text{SO}_4$ ) to 6-methyl-1:2-naphthaquinone, m.p. 126°. Successive treatment of this with  $\text{NaHSO}_3$ , boiling dil.  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ -dil.  $\text{H}_2\text{SO}_4$ , and  $\text{KCl}$  gives *K* 6-methyl-1:2-naphthaquinone-4-sulphonate ( $+\text{H}_2\text{O}$ ), converted by  $\text{MeOH}-\text{conc. H}_2\text{SO}_4$  into (V).  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ , (VI), and  $\text{AlCl}_3$  at 200° yield 1:8-phthaloyl-6-methyl- $\beta$ -naphthol (1-hydroxy-5-methylpleiadenedione), m.p. 194–194.5°, rearranged by 2:1 (vol.)  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  at 170° into 2'-hydroxy-4-methyl-1:2-benzanthraquinone, m.p. 256–258° (decomp.) (acetate, m.p. 218–219°). H. B.

**Chrysene.** III. K. FUNKE and J. RISTIC (J. pr. Chem., 1936, [ii], 145, 309–312; cf. this vol., 472).—8-Benzoylchrysene-1:2-quinone gives a *phenazine* derivative, m.p. 207°, proving the structure of the quinone. 2-Acetylchrysene and  $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$  give chrysene-1:2-quinone-8-carboxylic acid, m.p. 297° (phenazine derivative, m.p. >330°). 2:8-Dibromochrysene with  $\text{CrO}_3\text{-AcOH}$  gives a small amount of a Br-free substance, m.p. 323–324°, but with  $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$  affords 8-bromochrysene-1:2-quinone, m.p. 249–250° (phenazine derivative, m.p. 252°), which proves the orientation. 1- or 2-Sub-

stituted chrysene derivatives afford by oxidation 8- or 7-substituted 1:2-quinones, and derivatives substituted in the 1 or 2 and 7 or 8 positions give similar quinones if one substituent is readily removed. 2:8-Dicyanochrysene is stable to oxidising agents and affords no quinone.

R. S. C.

**Anthanthrone and its derivatives.** VII. Halogenation, nitration, and sulphonation of anthanthrone. A. CORBELLINI and M. ATTI (Chim. e l'Ind., 1936, 18, 295–298).—Anthanthrone (I) is chlorinated by  $\text{SO}_2\text{Cl}_2$  in  $\text{PhNO}_2$ , and is brominated (cf. G.P. 458,598) to the Cl- and Br-derivatives,  $\text{C}_{22}\text{H}_8\text{O}_2\text{X}_2$ . Iodination (G.P. 495,367) yields an impure I-derivative, containing <1 atom of I per mol. of (I). Nitration (G.P. 492,446) yields nitro- and dinitro-, decomp. 360°, -anthanthrone, from which the  $\text{NH}_2$ - and  $(\text{NH}_2)_2$ -compounds are prepared. Sulphonation (oleum) gives anthanthrone-sulphonic acid, from which the -sulphonyl chloride, m.p. 306.5–307.5°, is prepared, with disulphonyl compounds.

E. W. W.

**Woolly aphis and white pine chermes.**—See this vol., 1137.

**Pinic acid.** M. GRANDPERRIN (Ann. Chim., 1936, [xi], 6, 5–52).—Evidence is adduced in favour of the view that pinic acid obtained by the oxidation of pinonic acid in alkaline solution has the *trans*-configuration. *d*- $\alpha$ -Pinene,  $[\alpha]_D +42^\circ$ , is oxidised by  $\text{KMnO}_4$  in  $\text{H}_2\text{O}$  containing  $(\text{NH}_4)_2\text{SO}_4$  at 0° to pinonic acid (I),  $[\alpha]_D +95^\circ$ ; oxidation by  $\text{KMnO}_4$  in  $\text{COMe}_2$  appears more suited to the formation of neutral products. Oxidation of (I) by Br in alkaline solution gives  $\text{CBr}_4$ ,  $\text{CHBr}_3$ , and an acid which only becomes partly cryst. after long keeping (oxidation with  $\text{H}_2\text{O}_2$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{AcOH}$  gives less satisfactory results whereas treatment with  $\text{HNO}_3$  appears to give terebic acid). Crystallisation of the crude acid without distillation, which involves risk of racemisation, leads to pinic acid (II), m.p. 78–79°,  $[\alpha]_D +10.6^\circ$  in  $\text{Et}_2\text{O}$ ,  $-1.9^\circ$  in  $\text{CHCl}_3$ ,  $+5.1^\circ$  in  $\text{COMe}_2$ ,  $-4^\circ$  in  $\text{H}_2\text{O}$ . (II) is transformed by  $\text{SOCl}_2$  into the dichloride (III), b.p. 141–142°/15 mm.,  $[\alpha]_D -41.5^\circ$ , whence *Et*<sub>2</sub> pinate (IV), b.p. 148–149°/15 mm.,  $[\alpha]_D +3.36^\circ$  (also obtained from *Ag*<sub>2</sub> pinate and *EtI*), *Pr*<sup>*t*</sup> pinate (V), b.p. 161°/20 mm.,  $[\alpha] +1.36^\circ$ , and *Bu*<sup>*t*</sup> pinate, b.p. 181°/22 mm.,  $[\alpha] -0.48^\circ$ . (III) is converted by  $\text{NH}_3\text{-EtOH}$  into *pindiamide*, m.p. 190°, by  $\text{NH}_2\text{Ph}$  into the *dianilide*, m.p. 208°, by the requisite amount of  $\text{EtOH}$  followed by  $\text{NH}_2\text{Ph}$  into the *ester anilide*, m.p. 92° (with a non-identified product, m.p. 248°), and by *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  into the *di-p-anisidine*, m.p. 202°. (IV) and (V) are converted by  $\text{MgEtBr}$  into the corresponding *di-tert.*-glycols which could not be isolated free from their products of dehydration. Attempts to prepare pinic anhydride from (II) and  $\text{AcCl}$ , from (III) and  $\text{Na}_2\text{O}$ , or from (III) and  $\text{Ag}_2\text{O}$  were unsuccessful. Similarly the imide, anil, or anisidil could not be obtained. A ketonic ester is not formed by the action of  $\text{NaNH}_2$  on (IV). Dehydration of the crude *di-tert.*-glycol by  $\text{H}_2\text{SO}_4$ -pumice or  $2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$  and purification of the product with  $\text{H}_3\text{BO}_3$  leads to the hydrocarbon,  $\text{CET}_2\text{:C} \begin{smallmatrix} \text{CMe}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CH:CH.CET}_2$ , b.p.



148—149°/22 mm. Isomerisation of (II) under the action of  $\text{Ac}_2\text{O}$  is not observed. H. W.

**Preparation and properties of pinonic acid.** M. DELÉPINE (Bull. Soc. chim., 1936, 3, [v], 1369—1382).—Optically active pinonic acid (I) (prep. described) in KOH or when heated shows a rapidly decreasing  $\alpha$  owing to a *cis-trans* unimol. change; in aq.  $\text{NH}_3$  the change is 1/600 times as fast. The change is not one of racemisation but of mutarotation (much lit. cited). The action of alkali affords the pure *trans*-acid,  $[\alpha]_D +95^\circ$  in  $\text{CHCl}_3$ , and an oil which is a *trans-cis* mixture with a lower  $[\alpha]_D$  increased by treatment with alkali. The semicarbazone (II),  $[\alpha]_D +90^\circ$ , of (I) gives an Ac derivative which when pptd. from alkaline solution yields (II); the mother-liquors contain a semicarbazone,  $[\alpha]_D -88^\circ$ , which when hydrolysed affords a *trans*-acid with  $[\alpha]_D -77^\circ$ . The *cis*- and *trans-d*-acids give oximes, m.p. 128° and 191°, respectively, whilst the *l*-acids give oximes, m.p. 191° and 128°, respectively. J. L. D.

**Preparation of monoalkyl and aryl derivatives of  $\beta$ -campholide and of the corresponding  $\delta$ -hydroxy-acids.** J. VÈNE (Compt. rend., 1936, 202, 1681—1683).—Me camphoceanaldehyde  $\text{CHO}(\beta)\cdot\text{C}_6\text{H}_{14}\cdot\text{CO}_2\text{Me}(\alpha)$  (cf. A., 1917, i, 560; 1932, 1037) with  $\text{MgRX}$  affords  $\beta$ -substituted campholides (I). The following are prepared:  $\beta$ -methyl-, m.p. 178°, -ethyl-, m.p. 78°, -propyl-, impure, -butyl-, b.p. 179—181°/16 mm., -phenyl-, m.p. 212°, and -benzylcampholide, m.p. 102°. In attempting to prepare the higher aliphatic homologues, (I) tends to be converted into  $\beta$ -campholide. (I) with  $\text{NaOH-EtOH}$  at 100° give OH-acids (II) of which the following are prepared: 2 : 2 : 3-trimethyl-3- $\alpha$ -hydroxyethyl-, m.p. 135°, -3- $\alpha$ -hydroxypropyl-, m.p. 73° (+x $\text{H}_2\text{O}$ , m.p. 86°), -3- $\alpha$ -hydroxybenzyl-, m.p. 166°, -3-( $\alpha$ -hydroxy- $\beta$ -phenylethyl)-cyclopentane-1-carboxylic acid, m.p. 154°. (II) with  $\text{Ac}_2\text{O}$  or when heated give (I). J. L. D.

**Action of selenium dioxide on camphene and pinene.** W. ZACHAREWICZ (Rocz. Chem., 1936, 16, 290—300).—Pinene and  $\text{SeO}_2$  in EtOH at 60° yield myrtenol (I) and myrtenal [identified wrongly as verbenol and verbenone by Schenk *et al.* (A., 1932, 1253) and Dupont *et al.* (A., 1933, 1166)], formed by decomp. of dimyrtanyl selenide (II), m.p. 64—65°. (II) and Br in  $\text{CHCl}_3$  at 0° yield myrtenyl iodide, identified by conversion into (I). Camphene and  $\text{SeO}_2$  yield camphenilone and isoborneol in small amount, but the chief product is di-3-camphenyl selenide, b.p. 220—225°/8 mm., m.p. 93—94°, from which camphene is regenerated by Walbaum's reaction. R. T.

(A) **Products of oxidation of hydrazones of camphorquinone and 4-methylcamphorquinone.** (B) **Nitrogenous derivatives of 4-methylcamphor.** L. BRIUSOVA (J. Gen. Chem. Russ., 1936, 6, 667—673, 674—680).—(A)  $\beta$ -pericycloCamphanone (I) is regenerated from its hydrazone, m.p. 76.5—77.5°, by heating at 50—70° with HgO in EtOH; when the reaction is performed in a  $\text{CO}_2$  atm. in presence of I the 2 : 2- $I_2$ -derivative, m.p. 160—162°, of (I) is also produced. The dihydrazone (impure), m.p. 101—104° (hydrochloride, m.p. 177—180°), of 4-methylcamphorquinone (II) yields 4-methylecylene when

oxidised with HgO, and the dihydrazone, m.p. 196—198°, of camphorquinone gives tricycylene with HgO.

(B) The reactions of 4-methylcamphor (III) are on the whole analogous to those of camphor. 3-Amino-4-methylcamphor, m.p. 164—167° (Ac derivative, m.p. 127—128°, + $\text{H}_2\text{O}$ , m.p. 84—86°; carbonate, m.p. 152—155°; hydrochloride), is prepared by reducing 3-oximino-4-methylcamphor ( $\text{Zn-AcOH}$ ), whilst oxidation with  $\text{KMnO}_4$  in  $\text{COMe}_2$  yields 3-nitro-4-methylcamphor, m.p. 152—153°. The oxime of (III) and  $\text{HNO}_2$  afford the nitroimine, m.p. 52—53.5°, which with  $\text{NH}_3$  at 50° yields the imine, m.p. 64—67°. The nitroimine, m.p. 57.4—58.4°, of (II), obtained analogously, yields (II) when treated with EtOH-KOH, and the dioxime, m.p. 181—182°, of (II) with  $\text{NH}_2\text{OH}$  (100°; 30 min.). R. T.

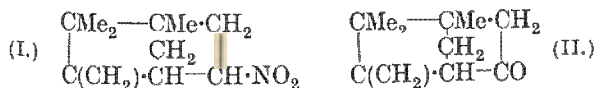
**Preparation of optically active *trans*--hydroxycamphor from optically active  $\alpha$ -*trans*-dihalogenocamphor.**—See B., 1936, 687.

**Optical superposition.** H. RUPE, F. HENKE, and F. BÜRKI (Helv. Chim. Acta, 1936, 19, 698—734).—[With H. HIRSCHMANN]. All except the first two pages of the paper by Rupe, Bürki, and Werdenberg (A., 1929, 529) are incorrect.

$[M]^{20}$  are determined for esters of *l*-, *d*-, and *dl*-hydroxymethylenecamphor (I) and -camphenylcarbinol (II) with *l*-, *d*-, and *dl*-bornylenecarboxylic (III) and -camphanecarboxylic acid (IV).  $[M]$  of the esters is not the sum of  $[M]$  of the free alcohols and acids. When both alcohols and acids are saturated,  $[M]$  of the esters is the sum of  $[M]$  of the alkyl and acyl radicals, but, when either is unsaturated or, more, so, if both are unsaturated, "polar" effects nullify this equality, so that the simple law of optical superposition no longer holds. Hydrogenation of the unsaturated esters gives only one stereoisomeride in each case; esters with different types of unsaturation give different stereoisomerides of the saturated esters owing to the formation of new asymmetric C.  $[M]$  of these forms conforms to the above-mentioned law when the contribution of each asymmetric centre is taken into account. It is shown how these contributions can be calc. from the  $[M]$  of the esters isolated. (I) is best obtained by the use of Na, since  $\text{NH}_2\text{Na}$  gives also much hydroxymethylenecamphorimide. The *dl*-form of (II) has b.p. 142°/11 mm. (benzoate, m.p. 73°); the *l*-form is also prepared. Esters of (I) are obtained by treating the dry Na salt (prep. by NaOMe) in  $\text{C}_6\text{H}_6$  with the chlorides, b.p. 110—111°/11 mm. and 107—108°/11 mm., of (III) and (IV), respectively. In most cases (I) gives only one ester (assumed to be the stable *trans*-form) under the conditions used; the *cis*-forms are the more readily reduced and have the higher m.p.; this leads to configurations in agreement with the calc. vals. of  $[M]$ . Esters of (II) are prepared by the acid chloride in  $\text{C}_5\text{H}_5\text{N}$  (1.5 parts). Hydrogenation of esters of (I) is effected by Pd- $\text{H}_2$  in EtOH at 1 or 60—80 atm., as Ni leads to much hydrolysis to camphor with or without further reduction to methylcamphor; esters of (II) are smoothly reduced by  $\text{H}_2$ -Ni. The following esters are prepared, indicated by their components, e.g., *d*-hydroxymethylenecamphor *d*-bornylenecarboxylate as *d*-(I)-*d*-(III), the angles

recorded being  $[\alpha]_D^{20}$  in  $C_6H_6$ . *d*-(I)-*d*-(III) (A), m.p. 119.5°, +215.54°; *d*-(I)-*dl*-(III), m.p. 131.5°, +104.31°; *l*-(I)-*d*-(III), trans-, m.p. 113.5°, -34.11°, and *cis*-form, m.p. 143.5°, -61.66°; *dl*-(I)-*d*-(III), m.p. 110.5°, +91.23°; *d*-(I)-*d*-(IV), trans-, m.p. 147.5°, +164.62°, and *cis*-form, m.p. 163.5°, +143.86°; *d*-(I)-*dl*-(IV), m.p. 155.5°, +100.5°; *l*-(I)-*d*-(IV), trans-, m.p. 147°, -36.6°, and *cis*-form, m.p. 164°, -45.11°; *dl*-(I)-*d*-(IV), m.p. 150.5°, +76.69°; *d*-(II)-*d*-(III), m.p. 110°, +88.93°; *d*-(II)-*dl*-(III), m.p. 114°, +28.63°; *l*-(II)-*d*-(III), m.p. 114°, +46.19°; *l*-(II)-*dl*-(III), m.p. 114°, -25.96°; *l*-(II)-*l*-(III), m.p. 110°, -90.08°; *dl*-(II)-*d*-(III), m.p. 110°, +72.15°; *dl*-(II)-*l*-(III), m.p. 112°, -70.93°; *d*-(II)-*d*-(IV) (B), m.p. 157.5°, +55.94°; *d*-(II)-*dl*-(IV), m.p. 158°, +25.84°; *l*-(II)-*d*-(IV), m.p. 160°, +3.64°; *dl*-(II)-*d*-(IV), m.p. 152°, +28.42°; *dl*-(II)-*l*-(IV), m.p. 158°, -31.22°. Esters, (III)-(IV), were obtained by hydrogenation as follows: from (A), m.p. 179°, +103.61°; from *trans*-, m.p. 182°, -68.38°, and *cis*-*l*-(I)-*d*-(III), m.p. 179.5°, -51.92°; from *dl*-(I)-*d*-(III), m.p. 180°, +30.55°; from *trans*-, m.p. 165°, +67.61°, and *cis*-*d*-(I)-*d*-(IV), m.p. 167°, +106.14°; from *trans*-, m.p. 142°, -30.34°, and *cis*-*l*-(I)-*d*-(IV), m.p. 168°, -39.04°; from *dl*-(I)-*d*-(IV), m.p. 161°, +43.07°; (C) from *d*-(II)-*d*-(III), m.p. 163.5°, +54.39°; from *d*-(II)-*dl*-(III), m.p. 167°, +24.28°; from *l*-(II)-*d*-(III), m.p. 164°, +16.78°; from *l*-(II)-*dl*-(III), m.p. 166.5°, -21.37°; from *l*-(II)-*l*-(III), m.p. 163.5°, -56.39°; from *dl*-(II)-*d*-(III), m.p. 172°, +38.37°; and from *dl*-(II)-*l*-(III), m.p. 162.5°, -37.39°. Mutarotation of *l*-(I) is much faster than that of *d*-(I), increasing in speed with time in both cases; no explanation can be offered. In spite of the difference in m.p. (B), obtained by direct esterification, is identical with (C), obtained by reduction, since both have the same  $[\alpha]$  and both, when hydrolysed, give the same (IV), m.p. 91°,  $[\alpha] +74^\circ$ . Hydrolysis of *d*-(II)-*dl*-(IV) gives *dl*-(IV), showing that no resolution takes place during esterification. Hydrolysis of the ester obtained by reduction of (A) gives a form of (IV), m.p. 91°,  $[\alpha] +54.66^\circ$ .  $\alpha$  is determined for the esters for six  $\lambda$ ; esters of (II), but remarkably not those of (I), show anomalous dispersion, particularly if  $\log [\alpha]\lambda^2$  is plotted against  $v^2$ . R. S. C.

**sec.- $\alpha$ -Nitro-4-methylcamphene and 4-methyl- $\alpha$ -camphenone.** S. S. NAMETKIN and A. S. ZABRODINA (Ber., 1936, 69, [B], 1789—1791).—4-Methylcyclohexene is converted by  $HNO_3$  (*d* 1.075) into  $\alpha$ -nitro-4-methylcamphene (I), b.p. 127—129°/16 mm., m.p.



40—40.5°, whence the  $\psi$ -nitrol, m.p. 91—92° (decomp.). (I) is transformed by cautious oxidation with  $KMnO_4$  in alkaline solution into 4-methyl- $\alpha$ -camphenone (II), m.p. 129—130° [semicarbazone, m.p. 211—212° (decomp.)], also obtained in small yield by Sn and fuming HCl. H. W.

**exo-2-o-Carboxybenzoylcamphane and endo-cyclophthaloylcamphane.** R. BOUSSET (Bull. Soc. chim., 1936, [v], 3, 871—875).—The acid, m.p. 154° (this vol., 206), may be separated by repeated crystall-

isation and by hydrolysis (cold) of its Me ester into two geometrical isomerides. The one, *exo*-2-o-carboxybenzoylcamphane, has m.p. 182° (corr.),  $[\alpha]_D^{20} +89.20^\circ$ , and the other, not yet obtained pure, readily cyclises in presence of alkalis to *endocyclophthaloylcamphane*, m.p. 216° (cf. *ibid.*, 475).

H. G. M.

**Use of 2:4-dinitrophenylhydrazine.** O. FERNANDEZ and M. CASTILLO (Anal. Fis. Quím., 1935, 33, 81—89).—A quant. study of the formation of the dinitrophenylhydrazones (I) of the following camphor derivatives:  $\alpha$ -carboxylic acid, m.p. 173°,  $\beta$ -sulphonic acid, yellow form, m.p. 215°,  $[\alpha]_D^{20} -130^\circ$  in dil. EtOH, red form, m.p. 193—195°,  $[\alpha]_D^{20} 0^\circ$ ,  $\alpha$ -cyano-, m.p. 225°,  $\alpha$ -hydroxy-, yellow form, m.p. 225°,  $[\alpha]_D^{20} +252^\circ$  in dil. EtOH, red form, m.p. 225°,  $[\alpha]_D^{20} +265^\circ$  in EtOH,  $\alpha$ -acetoxy-, m.p. 183°,  $\alpha$ -methoxy-, m.p. 171°,  $\alpha$ -acetamido-, m.p. 226.5°.  $\alpha$ -Acetamidocamphor, m.p. 121°, was obtained from the free base. Br,  $NO_2$ ,  $SO_3H$ , and  $NH_2$  in the  $\alpha$ -position prevent formation of (I). The difference between the red and yellow forms is discussed. F. R. G.

**Mechanism of diene synthesis.** E. R. LITTMANN (J. Amer. Chem. Soc., 1936, 58, 1316—1317).—Reaction between  $\alpha$ -phellandrene (I) and maleic anhydride (II) is more nearly unimol. in dil. (0.25*M*) than in conc. (*M*) solution in  $COMe_2$ . A reaction other than the formation of a coloured intermediate (cf. Diels and Alder, A., 1928, 1018) is involved (or side reactions occur). (I) and (II) react violently at 55—65° (no solvent) to give a non-volatile 3:4- or 4:5-polymeride of the type  $C_4H_2O_3(C_{10}H_6-C_4H_2O_3)_n C_4H_2O_3$ . H. B.

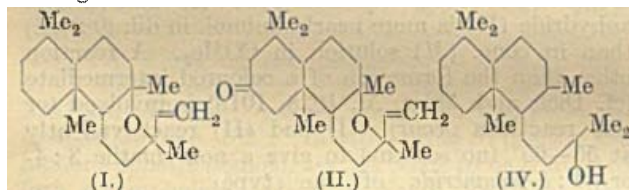
**Pyronenes.** G. DUPONT and R. DULOU (Compt. rend., 1936, 202, 1861—1863).—Conjugation of the ethylenic linkings of the pyronenes (A., 1935, 1127) is shown by the following reactions. The figures in parentheses are the frequencies of the lines of the Raman spectra.  $\alpha$ -(I) (nitrosochloride, m.p. 103°) and  $\beta$ -pyronene (II) show predominantly a line with frequency 1595 in the Raman spectra. Reduction of (I) by Na-EtOH gives a mixture of two hydrocarbons (1671, due to an intra-annular ethylenic linking attached to a *tert*-C). Hydrogenation of (I) in presence of Raney Ni leads to absorption of 2 H and disappearance of the characteristic line (1595), and formation of a mixture of three hydrocarbons (1673, 1658, and 1647, respectively). Absorption of 2 H in presence of Pt gives from (I) a  $H_2$ -derivative (630, 666, 841, 998, 1264, 1377, and 1674), also obtained with carvomenthene (1673) from (II) similarly or by  $H_2$ -Ni or Na-EtOH. *dl*-(II) (from *dl*-pinene) with  $CH_2 \cdot CH \cdot CHO$  at 110° gives an adduct,  $C_{12}H_{19} \cdot CHO$ , b.p. 123°/15 mm. (semicarbazone, m.p. 209—210°), and with maleic anhydride in boiling  $C_6H_6$  a product, hydrolysed to an acid,  $C_{12}H_{18}(CO_2H)_2$ , m.p. 154°. *dl*-(I) gives similarly an aldehyde (1116, 1184, 1270, 1627) and an acid, m.p. 195°.

R. S. C.

**Chemistry of the genus *Dacrydium*.** I. Resin of *D. Colensoi*. II. Diterpene alcohol from *D. biforme* wood. J. R. HOSKING and C. W. BRANDT (New Zealand J. Sci. Tech., 1936, 17, 750—755, 755—758).—I. The resin from *D. Colensoi*



gives 90% of neutral substances, which may be separated into manoyl oxide (I),  $C_{20}H_{34}O$ , m.p.  $29^\circ$ , a diterpene oxide, ketomanoyl oxide (II),  $C_{20}H_{32}O_2$ , m.p.  $76^\circ$ , a ketonic diterpene oxide, and a diterpene oxide (III),  $C_{20}H_{32}O_4$ , m.p.  $208^\circ$  (3 OH). (I) absorbs the equiv. of 1  $H_2$ , shows stability of O, is dehydrogenated (Se) to 1:5:6- $C_{10}H_5Me_3$  and 1:7:8-trimethylphenanthrene, and with  $HCO_2H$  gives isomanoene,  $C_{20}H_{32}$ , containing 2 double linkings. With HCl, (I) yields a stable trihydrochloride,  $C_{20}H_{35}Cl_3$ , from which the Cl could not be removed, and dihydromanoyl oxide similarly forms a dihydrochloride,  $C_{20}H_{36}Cl_2$ , dechlorinated to a dicyclic hydrocarbon,  $C_{20}H_{34}$ . The ozonide of (I) affords  $CH_2O$  and  $HCO_2H$  and oxidation ( $KMnO_4$ ) of (I) leads to a monocarboxylic acid,  $C_{19}H_{32}O_3$ , in which the oxide ring has remained intact. (I) is probably represented as shown. (II) is tricyclic; one O is ketonic and the other oxidic, and it differs only from (I) in the presence of CO which is adjacent to a  $CH_2$ . Dehydrogenation (Se) of the hydrocarbon obtained by treating (II) with HCl followed by  $NH_3Ph$ , gives some 1:3:5:6- $C_{10}H_4Me_4$ . (III) contains 3 OH, one oxide ring, 3 carbocyclic rings, and one ethylenic linking.



II. One of the fractions from the neutral oil from *D. biforme* is manool,  $C_{20}H_{34}O$ , m.p.  $56^\circ$ , which forms a trihydrochloride, m.p.  $119^\circ$ , identical with that from (I). It is a dicyclic diterpene alcohol, with 2 double linkings and a C skeleton identical with that of (I). Tetrahydromanool (IV) is converted into a monohydrochloride, which loses HCl to give tetrahydromanoene,  $C_{20}H_{36}$ . The hydrocarbon on ozonolysis gives a mixture of a ketone,  $C_{18}H_{32}O$  (semicarbazone, m.p.  $202^\circ$ ), and a monobasic acid,  $C_{16}H_{28}O_2$ , m.p.  $129^\circ$ . F. R. S.

**Behaviour of the apparent lignin during degradation of rye straw by hydrogen sulphite.** R. S. HILPERT and A. BOLLING (Ber., 1936, 69, [B], 1598—1601).—Treatment of rye straw with  $Ca(HSO_3)_2$  followed by NaOH or NaOCl shows the lignin to consist of 4 four chemically different components. About 67% of the lignin is dissolved by  $Ca(HSO_3)_2$  whilst the remaining 33% is unattacked. One half of the residue is stable towards NaOCl and 33% is insol. in NaOH. If the residue from treatment with NaOH is subjected to treatment with NaOCl a pure white cellulose with 4% of lignin is obtained. The results cannot be harmonised with the hypothesis that lignin is a chemically defined component but are readily explained if it is regarded as a reaction product of sensitive substances, presumably carbohydrates. H. W.

**Highly polymerised compounds.** CXLII. Lignin. H. STAUDINGER and E. DREHER (Ber., 1936, 69, [B], 1729—1737).—Determinations of the

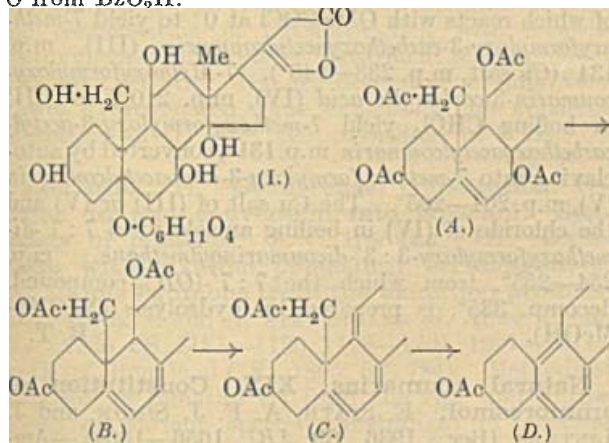
sp. viscosity of phenol-, acetylphenol-, *o*-cresol-, and *o*-acetylcresol-lignin in  $COMe_2$ , of beech-lignin in  $COMe_2$  and  $HCO_2H$ , and of Na ligninsulphonate in  $HCO_2H$  show that lignin has a relatively low mol. wt. These and other properties prove that its structural principle differs from that of cellulose and similar highly polymerised compounds and that it is not formed of long chains. Conc.  $HCO_2H$  at  $100^\circ$  dissolves about 50% of the lignin of pine without addition of mineral acid; the product is a mixture of aromatic substances rich in OMe. Gradual addition of  $H_2O$  to its solution in dioxan ppts. fractions differing little in OMe content and having mol. wt. about 1000 in freezing dioxan. Their solutions in dioxan or  $HCO_2H$  are of low viscosity. The treatment of pine wood with  $HCO_2H$  produces also considerable amounts of sugar-like substances sol. in  $H_2O$  from the polysaccharides present. Cellulose is also attacked to some extent, but the products formed are exempt from OMe. Insol. lignin has not the same structural principle as cellulose. H. W.

**Resin.** IV. Sublimed *l*-abietic acid. D. LIPKIN and W. A. LA LANDE, jun. (J. Amer. Chem. Soc., 1936, 58, 1310—1311).—Sublimation (method essentially that of B., 1934, 726) of *l*-abietic acid (I) gives an acid (II), m.p.  $150^\circ$ ,  $[\alpha]_D^{25} -35.1^\circ$  in EtOH (cf. Steele, A., 1922, i, 739), which is unaffected by light and air in the solid state. In xylene, however, (I) and (II) absorb  $O_2$  at the same rate (method: Dupont and Levy, A., 1930, 86). H. B.

**Biochemistry of micro-organisms.** LI. Metabolic products of *Aspergillus terreus*, Thom. II. Two new chlorine-containing mould metabolic products, geodin and erdin. H. RAISTRICK and G. SMITH (Biochem. J., 1936, 30, 1315—1322; cf. A., 1935, 662).—When a strain of *A. terreus*, Thom, was grown on a glucose-Czapek-Dox solution containing KCl as the sole source of Cl, the amount of Cl in solution diminished approx. at the same rate as the glucose. Final acidification with  $H_2SO_4$  gave a heavy ppt. containing 50% of the Cl originally present, from which were isolated: *geodin*,  $C_{17}H_{12}O_7Cl_2$ , m.p.  $235^\circ$ ,  $[\alpha]_D^{20} +179^\circ$ ,  $[\alpha]_D^{30} +149^\circ$  (both in  $CHCl_3$ ), dibasic ( $Na_2$  salt,  $[\alpha]_{541}^{30} +72.4^\circ$ ), containing 2 OMe; giving with  $CH_3N_2$  a compound,  $C_{16}H_{10}O_4N_2Cl_2(OMe)_3$ , m.p.  $151^\circ$ ,  $[\alpha]_{541}^{23} -58^\circ$  in  $C_6H_6$ : a  $H_2$ -derivative, m.p.  $229^\circ$ , optically inactive; and *erdin*,  $C_{16}H_{10}O_4Cl_2 + 0.5EtOH$ , m.p.  $211^\circ$  (decomp.), optically inactive, dibasic, containing 1 OMe, giving with  $CH_3N_2$  a compound,  $C_{16}H_7O_4N_2Cl_2(OMe)_3$ , m.p.  $154^\circ$ , not identical with the corresponding isomeric compound from geodin ( $H_2$ -derivative,  $C_{16}H_{12}O_7Cl_2 + 0.5H_2O$ , m.p.  $240^\circ$ , giving on heating a cryst. sublimate). Substitution of KBr or KI for KCl in the medium did not affect growth but did not result in the isolation of brominated or iodinated metabolic products. P. W. C.

**Ouabain.** L. F. FIESER and M. S. NEWMAN (J. Biol. Chem., 1936, 114, 705—710).—Ouabain is probably (I). The positions of the OH are determined by the course of acetolysis of hepta-acetyl-deoxydihydro-ouabain and isouabain, indicated in the partial formulæ (A)—(D). Loss of the *tert*-

$O\cdot C_6H_{11}O_4$  gives the grouping  $C\cdot C\cdot C\cdot OAc$ ; the next two ethylenic linkings arise by the tendency to form conjugated linkings coercing the activated  $OAc$ . Expulsion of  $CH_2\cdot OAc$  (as  $CH_2O$  and  $Ac_2O$ ) is caused by the tendency to form an aromatic ring. The aromatic nature of ring  $B$  is not precluded by its slow hydrogenation and is confirmed by the similarity of the absorption spectra of the trianhydrolactone (II) from *isouabain*, dihydrotrianhydrostrophanthidin, and *neogosterol*. (II) slowly absorbs 1—1.8  $O$  from  $BzO\cdot H$ .



R. S. C.

#### Crystalline substances from the adrenal gland.

H. L. MASON, C. S. MYERS, and E. C. KENDALL (J. Biol. Chem., 1936, 114, 613—631).—Repeated partition of the crude extract of minced adrenal glands between  $H_2O$  and  $C_6H_6$  gives fractions, (I) more sol. in  $C_6H_6$ , (II) more sol. in  $H_2O$ , and (III) equally sol. in  $H_2O$  and  $C_6H_6$ , which are all mixtures. (I) yields substances (A),  $C_{26}H_{36}O_5$ , m.p. 177—179.5°,  $[\alpha]_{D}^{25} +347^\circ$  in  $C_6H_6$ , and (B),  $C_{24}H_{34(36)}O_5$ , m.p. 135—139°. With  $K_2Cr_2O_7$ , (A) gives the unsaturated acid-1,  $C_{20}H_{26}O_4$ , decomp. 245—260°,  $[\alpha]_{D}^{25} +290^\circ$  in 30% EtOH (contains 1 active H and 2 CO); crude (I) gives either this acid or the saturated acid-2,  $C_{20}H_{28}O_4$ , decomp. 240—260°,  $[\alpha]_{D}^{25} +267^\circ$  in 30% EtOH. (B) may be the precursor of acid-2. Acids-1 and -2 resist  $CrO_3$ , but are oxidised by alkaline  $Ag_2O$ . (I) gives sub-fractions, (a), (b), and (c). (a) yields a substance (C), m.p. 220—227°,  $[\alpha]_{D}^{25} +110^\circ$  in EtOH,  $+56^\circ$  in  $C_6H_6$ , probably impure  $C_{21}H_{34}O_5$  (contains 3 OH and 1 CO), which with alkaline  $Ag_2O$  gives 45% of a saturated acid-3,  $C_{21}H_{34}O_6$ , decomp. 240—242°, oxidised by  $K_2Cr_2O_7$  to a ketone-1,  $C_{20}H_{30}O_3$ , m.p. 159—160° after sintering at 156°. Oxidation of (b) with  $Ag_2O$  gives an unattacked mixture, m.p. 142—145° (decomp.), 10—20% of acid-3, and a mixture of acids; of the last-mentioned mixture part readily gives a lactone, stable to  $CrO_3$ , and the remainder is oxidised by  $CrO_3$  to ketone-2,  $C_{19}H_{28}O_3$ , m.p. 159—161° (semicarbazone, cryst.). (a) and (b) give acids with hot dil. NaOH; when the mixture (c) is thus treated, it gives a polyhydric alcohol, substance (D),  $C_{20}H_{36}O_5$ , m.p. 214—216° (usually softens at 170°),  $[\alpha]_{D}^{25} +29^\circ$  in  $COMe_2$ , very hygroscopic, which with HCl-EtOH gives an unsaturated substance,  $C_{20}H_{34}O_5$ ,  $+0.5H_2O$ , m.p. 150—155°, and with hot  $H_2SO_4$ -EtOH a substance,  $C_{20}H_{34(36)}O_5$ ,  $+0.5H_2O$ , m.p. 172—

178°. With  $CrO_3$ , (D) gives ketone-3,  $C_{18}H_{24}O_3$ , m.p. 160—161.5°,  $[\alpha]_{D}^{25} +229^\circ$  in  $C_6H_6$  [contains 1 OH and 1 CO; oxime, m.p. 205—232° (decomp.)]. (III) yields some (D) and substance (E),  $C_{21}H_{30}O_5$ , m.p. 201—208° (decomp.),  $[\alpha]_{D}^{25} +269^\circ$  in  $C_6H_6$  [absorption max. at 2370 Å.; 2:4-dinitrophenylhydrazones, m.p. 255—256° (decomp.)]. Unsaturation is detected by  $C(NO_2)_4$ , OH and CO by  $MgMeI$ . (C) is probably  $C_{19}H_{30}O(OH)_2 > C(OH)\cdot CHO$ , giving on oxidation  $C_{19}H_{30}O(OH)_2 > C(OH)\cdot CO_2H$  (acid-3) and then  $C_{19}H_{30}O(OH)_2CO$  (ketone-1). R. S. C.

Lactone group of the cardiac aglucones and the Grignard reagent. W. A. JACOBS and R. C. ELDERFIELD (J. Biol. Chem., 1936, 114, 597—599).—As expected from the presence of an active H in the  $\Delta^{\beta\gamma}$ -lactone group, the dianhydrolactone (I) from strophanthidin with  $MgMeI$  gives 1  $CH_4$ , digitoxigenin 3 and its acetate 2, but the  $H_4$ -derivative of (I) gives only 0.57 and the two anhydrodigitoxigenins only 1.4 mol. In general expectation is realised, but the exceptions in the lit. require explanation. R. S. C.

Action of mixed organo-magnesium compounds on the esters and N-disubstituted amides of  $\alpha$ -phenyl- $\beta$ -2-furylacrylic acid. N. MAXIM and N. STANCOVICI (Bull. Soc. chim., 1936, 3, [v], 1319—1328; cf. A., 1934, 1360).— $MgEtBr$  with  $\alpha$ -phenyl- $\beta$ -2-furylacryldiphenylamide (cf. A., 1935, 757) in boiling  $Et_2O$  affords  $\alpha$ -phenyl- $\beta$ -2-furylvalerdiphenylamide, b.p. 262°/11 mm., hydrolysed to  $\alpha$ -phenyl- $\beta$ -2-furylvaleric acid (I) (cf. A., 1935, 756). The following are prepared similarly: diphenylamide, b.p. 261°/10 mm., and diethylamide, b.p. 232°/14 mm., of  $\alpha\beta$ -diphenyl- $\beta$ -2-furylpropionic acid (II); diethylamide, b.p. 223°/12 mm., of (I); methylanilides, b.p. 244°/12 mm. and 262°/13 mm., of (I) and (II), respectively. Similarly from the appropriate esters of  $\alpha$ -phenyl- $\beta$ -2-furylacrylic acid (III) with  $MgEtBr$  are obtained exclusively the Et, Pr, b.p. 170°/8 mm., Bu, b.p. 179°/10 mm., and amyl ester, b.p. 192°/7 mm., of (I). With  $MgPhBr$ , the appropriate esters of (III) afford the Et, b.p. 210°/8 mm., Pr, b.p. 226°/9 mm., Bu, b.p. 230°/9 mm., and amyl ester, b.p. 236°/9 mm., of (II), together with  $\alpha\beta$ -triphenyl- $\gamma$ -2-furyl- $\Delta^{\beta}$ -propen- $\alpha$ -ol, m.p. 174°. J. L. D.

Action of mixed organo-magnesium compounds on  $\alpha$ -phenyl- $\beta$ -2-furylacrylonitrile. II. N. MAXIM and G. ALDEA (Bull. Soc. chim., 1936, 3, [v], 1329—1334; cf. A., 1935, 756).— $\alpha$ -Phenyl- $\beta$ -2-furylacrylic acid with  $MgMeI$  in boiling  $Et_2O$  affords  $\alpha$ -phenyl- $\beta$ -2-furylbutyronitrile, b.p. 167°/10 mm. (acid, b.p. 208°/18 mm.; acid chloride, b.p. 165°/12 mm.; amide, b.p. 221°/15 mm.; Et ester, b.p. 428°/15 mm.). The following are prepared similarly:  $\alpha\gamma$ -diphenyl- $\beta$ -2-furylbutyronitrile, b.p. 241°/18 mm. (acid, m.p. 118°; acid chloride, b.p. 184°/17 mm.; amide, m.p. 165°; Et ester, b.p. 230°/17 mm.);  $\alpha$ -phenyl- $\beta$ -2-furyl- $\epsilon$ -methylheptonitrile, b.p. 187°/13 mm. (acid, b.p. 215°/12 mm.; acid chloride, b.p. 187°/10 mm.; amide, m.p. 130°; Et ester, b.p. 192°/20 mm.); and  $\alpha$ -phenyl- $\beta$ -p-tolyl- $\beta$ -2-furylpropionitrile, b.p. 219°/20 mm. (acid, m.p. 163°). J. L. D.

Condensation of benzoin and thymol. II. Constitution of nitration products of 2:3-



**diphenyl-4-methyl-7-isopropylcoumarone.** O. DISCHENDORFER and A. VERDINO (Monatsh., 1936, 68, 81—91).—2:3-Diphenyl-4-methyl-7-isopropylcoumarone (I) with  $\text{HNO}_3$  in AcOH gives a substance which is the 6- $\text{NO}_2$ -derivative (II), m.p. 151°, since it is oxidised ( $\text{CrO}_3$ ) to 4-nitro-6-benzoyloxy-2-methyl-5-isopropylbenzophenone, m.p. 110°, which is hydrolysed to the 6-OH-compound [5-nitro-2-benzoylthymol], m.p. 130—131°, in which the  $\text{NO}_2$  is shown to be in the thymol nucleus by  $\text{KMnO}_4$  oxidation to BzOH. 3-Nitro-6-hydroxy-2-methyl-5-isopropylbenzophenone [4-nitro-2-benzoylthymol] (III), m.p. 124—125°, is prepared by nitration of 2-benzoylthymol (which with  $\text{KMnO}_4$  also gives BzOH), and this structure for (II) thereby excluded. With  $\text{NHPh}\cdot\text{NH}_2$  or  $\text{Na}_2\text{S}_2\text{O}_4$ , (II) yields the 6- $\text{NH}_2$ -derivative of (I), m.p. 146°, of which the  $\Delta\epsilon$  derivative, m.p. 231°, is nitrated to 5-nitro-6-acetamido-2:3-diphenyl-4-methyl-7-isopropylcoumarone, m.p. 281°. A second nitration product of (I) is 5-nitro-2:3-dihydroxy-2:3-diphenyl-4-methyl-7-isopropylcoumarone, m.p. 160°, which is oxidised ( $\text{CrO}_3$ ) to 3-nitro-6-benzoyloxy-2-methyl-5-isopropylcoumarone [4-nitro-2-benzoylthymol benzoate], m.p. 145°, which on hydrolysis yields (III). A third nitration product of (I) is also obtained, but not identified. E. W. W.

**Synthesis of 3-hydroxy-2-ketocoumaran and p-hydroxymandelic acid.** K. LADENBURG, K. FOLKERS, and R. T. MAJOR (J. Amer. Chem. Soc., 1936, 58, 1292—1294).— $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in 10% aq.  $\text{NaHSO}_3$  with aq.  $\text{NaCN} + \text{Et}_2\text{O}$  gives the unstable  $o$ -hydroxymandelonitrile, not distillable, converted by  $\text{Et}_2\text{O}\cdot\text{HCl}$  into the imino-ether hydrochloride, which is hydrolysed to 3-hydroxy-2-ketocoumaran (I), m.p. 107—108°. (I) is partly hydrolysed in aq. solution to  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$  (Ca salt).  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  is similarly converted into  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , m.p. 99—102° (lit. 98°), and thence into  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , m.p. 109.5—110.5° (lit. 105—108°) (Et ester, m.p. 128.5—129°). Introduction of  $o$ - or  $p$ -OH into  $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$  does not increase the bactericidal activity towards *S. aureus* and *E. typhi*. H. B.

**isoFlavone series.** P. C. MITTER and S. S. MAITRA (J. Indian Chem. Soc., 1936, 13, 236—259).—The azlactone, m.p. 168°, from  $\beta$ -resorcyraldehyde  $\text{Me}_2$  ether with boiling 10% NaOH gives 2:4-dimethoxyphenylpyruvic acid, hygroscopic, m.p. 156°, the oxime, m.p. 145° (decomp.), of which with  $\text{Ac}_2\text{O}$  at 100° gives 2:4-dimethoxyphenylacetone, m.p. 76°. This affords (Hoesch) 2:4:6-trihydroxy-2':4'-dimethoxyphenylacetophenone (I), m.p. 175°, the  $\text{Ac}$  derivative, m.p. 204—205°, of which with hot 1% KOH-EtOH yields 5:7-dihydroxy-2':4'-dimethoxy-2-methylisoflavone, m.p. 213—214° (does not fluoresce in aq. alkali; pink colour with  $\text{H}_2\text{SO}_4$ , violet  $\rightarrow$  brown with  $\text{FeCl}_3$ ). The  $(\text{CH}_2\text{Ph})_2$  derivative, m.p. 135°, of (I) does not condense with  $\text{HCO}_2\text{Et}$  and "mol." Na. R. S. C.

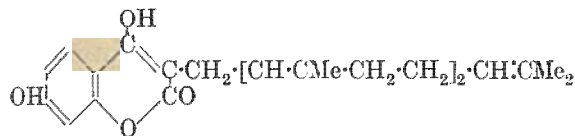
**Synthesis of (A) di(coumarino-3-carboxyl)-methane (B) 7:7'-dihydroxydi(coumarino-3-carboxyl)methane.** M. TRENNKERNOWNA (Rocz. Chem., 1936, 16, 6—11, 12—18).—(A) The chloride of coumarin-3-carboxylic acid (I) and  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$

(II) in boiling  $\text{CHCl}_3$  yield Et coumarinyl-3-carboxylacetate, m.p. 125—126°, converted into 3-acetoacetyl coumarin, m.p. 143—144°, the Cu salt, m.p. 280°, of which condenses with (I) (in boiling anisole; 3 hr.) to yield di(coumarino-3-carboxyl)methane, also prepared in the same way from (I) and Et (coumarinyl-3-carboxyl)acetate, or from Et di(coumarinyl-3-carboxyl)acetate (in boiling anisole; 20 min.).

(B) 2:4-(OH) $_2$  $\cdot\text{C}_6\text{H}_3\cdot\text{CHO}$  and  $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , in presence of piperidine, afford 7-hydroxy-3-carbethoxyacetyl coumarin, m.p. 146—148°, an aq. NaOH solution of which reacts with  $\text{OMe}\cdot\text{COCl}$  at 0° to yield 7-methoxyformyloxy-3-carbethoxyacetyl coumarin (III), m.p. 134° (Cu salt, m.p. 238—240°). 7-Methoxyformyloxy coumarin-3-carboxylic acid (IV), m.p. 210°, and (II) in boiling  $\text{CHCl}_3$  yield 7-methoxyformyloxy-3-acetyl carbethoxyacetyl coumarin, m.p. 131°, converted by autoclaving into 7-methoxyformyloxy-3-acetoacetyl coumarin (V), m.p. 204—205°. The Cu salt of (III) or (V) and the chloride of (IV) in boiling anisole yield 7:7'-dimethoxyformyloxy-3:3'-dicoumarinoylmethane, m.p. 254—255°, from which the 7:7'-(OH) $_2$ -compound, decomp. 335°, is prepared by hydrolysis ( $\text{NaOMe}\cdot\text{MeOH}$ ). R. T.

**Natural coumarins. XIX. Constitution of ammosesinol.** E. SPATH, A. F. J. SIMON, and J. LINTNER (Ber., 1936, 69, [B], 1656—1664).—Ammosiacum resin is shaken with  $\text{Et}_2\text{O}$  and the filtered solution is extracted with 5%  $\text{Na}_2\text{CO}_3$ . The extract is acidified with HCl, immediately extracted with  $\text{Et}_2\text{O}$ , and the residue left after removal of the solvent is converted by  $\text{Ac}_2\text{O}$  at 100° into diacetylammossesinol (I), b.p. 210—225° (bath)/0.02 mm., m.p. 101—102°. (I) is converted by cautious treatment with 2N- $\text{Na}_2\text{CO}_3$  in MeOH into acetylammossesinol (III), m.p. 128—129°, and by KOH-MeOH at 60° into ammosesinol (III), m.p. 107—108° (vac.). Analyses of (I), (II), and (III) confirm the formula  $\text{C}_{21}\text{H}_{30}\text{O}_4$  for (III). Treatment of (III) with  $\text{CH}_3\text{N}_2$  in MeOH- $\text{Et}_2\text{O}$  gives methylammossesinol (IV), b.p. 220—235° (bath)/0.005 mm., difficultly sol. in cold, readily in hot, dil. aq. alkali indicating that 2 O of (III) are present in a lactone group. Styphnic and  $\beta$ -resorcylic acid are formed by the degradation of (I). Oxidation of (IV) with  $\text{KMnO}_4$  yields 2-hydroxy-4-methoxy- and 2:4-dimethoxybenzoic acid. Repetition of Caspari's work shows that the oxidation of (I) leads to 2-hydroxy-4-acetoxybenzoic acid [whence the 2:4-(OMe) $_2$ -acid] and not  $\gamma$ -resorcylic acid, the residue of which is therefore not a component of (III). Catalytic hydrogenation (Pd-C in AcOH) of (I) affords diacetylhexahydroammossesinol, b.p. 210—220° (bath)/0.02 mm., m.p. 62—64°, oxidised by  $\text{KMnO}_4$  in alkaline solution to 80u-trimethyltetradecic acid (V), b.p. 135—145°/0.03 mm. [ $p$ -xenylamide, m.p. 98—99° (vac.)]. The constitution of (V) is established by its formation by the oxidation of  $\beta$ 5x-trimethylpentadecan- $\xi$ -one (VI) by Br in NaOH and by its conversion into (VI) by treatment with  $\text{SOCl}_2$  followed by Zn-Cu, MeI, and EtOAc in  $\text{C}_6\text{H}_6$ . (III) therefore contains a single carbocyclic 6-membered ring. Further insight into the structure of the side-chain is afforded by the ozonolysis of (I) to  $\beta$ -methyl- $\Delta^8$ -hepten- $\xi$ -one, indicating the presence

of isoprene units. Distillation of (III) at 200—230°/0.3 mm. affords resacetophenone and 7-hydroxy-3-methylbenzotetronic acid (VII), m.p. 304—305°. (III)



is therefore A. (VII) is obtained synthetically by the condensation of  $\text{CHMe}(\text{CO}_2\text{Et})_2$  with 2:4-diacetoxybenzoyl chloride and treatment of the product with 50%  $\text{H}_2\text{SO}_4$ . Its  $\text{Ac}_2$  derivative is only very slowly hydrogenated, thus explaining the apparent saturation of (I) after the absorption of 3  $\text{H}_2$ .

H. W.

**Lomatol. II. Occurrence, constitution, relation to and conversion into lapachol. Synthesis of lapachol.** S. C. HOOKER. **III. Oxidation with alkaline potassium permanganate. IV. Violet quinone from the oxidation product.** S. C. HOOKER and A. STEYERMARK (J. Amer. Chem. Soc., 1936, 58, 1181—1190, 1198—1201, 1207—1211). —II (cf. Rennie, J.C.S., 1895, 67, 784). Methods of isolation of lomatol (I) from the ripe and unripe fruits of various species (Australian) of *Lomatia* are given; (I) is absent from seeds of several species from Chile. (I) is now shown to be 3-hydroxy-2- $\beta$ -hydroxy- $\gamma$ -methyl- $\Delta^8$ -butenyl-1:4-naphthaquinone. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) of (I) affords either (mainly) hydroxylomatol (the 2- $\beta$ -hydroxy- $\gamma$ -methylbutyl derivative), m.p. 101—102° [converted by conc.  $\text{H}_2\text{SO}_4$  into (VI) (below)], or hydroxylapachol (the 2-isoamyl derivative), m.p. 93.5—94°, probably owing to variations in the catalyst. *iso*Lomatol (II) (the 2- $\beta$ -hydroxy- $\gamma$ -methyl- $\Delta^7$ -butenyl derivative) and hydroxylapachol (J.C.S., 1896, 69, 1355) are both similarly reduced to 3-hydroxy-2- $\beta$ -hydroxy-isoamyl-1:4-naphthaquinone (=hydroxylomatol- $\beta$ -hydroxyhydroxylapachol) (III), m.p. 120.5—121.5°; (I) and (II) are not, therefore, stereoisomerides (cf. *loc. cit.*). (I) is converted by cold aq.  $\text{H}_2\text{SO}_4$  into dehydro-*iso*- $\beta$ -lapachone (5:6-benzo-1-isopropenylcoumaran-3:4-quinone) (IV), m.p. 116—116.5° [quinoxaline, m.p. 157.5—158°, from  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ ], hydrolysed (1% NaOH) to (II). (II) and dil.  $\text{H}_2\text{SO}_4$  also give (IV); conc.  $\text{H}_2\text{SO}_4$  affords hydroxy- $\beta$ -lapachone (3-hydroxy-2:2-dimethyl-3:4-dihydro- $\alpha\beta$ -naphthopyran-5:6-quinone), m.p. 203—205°. (IV) is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH-AcOH) to *iso*- $\beta$ -lapachone (the 1- $\text{Pr}^{\beta}$  derivative) (V), m.p. 124.5—125.5°, which could not be prepared by reduction of the corresponding coumarone (*loc. cit.*). (V) is hydrolysed (1% NaOH) to (III), which is converted by conc.  $\text{H}_2\text{SO}_4$  into  $\beta$ -lapachone (VI). The above work also constitutes a synthesis of lapachol.

**III.** Lomatol is oxidised (1%  $\text{KMnO}_4$ , 1% NaOH) to 3-hydroxy-2- $\gamma$ -hydroxy- $\beta$ -methyl- $\Delta^8$ -propenyl-1:4-naphthaquinone (VII) and a little 1-methyl-4:5-benzocoumarone-3:6-quinone, m.p. 246—247° (largely unaffected by dil. alkali). (VII) heated alone or with dil. HCl passes into the red 3-methyl- $\beta\beta$ -naphthopyran-5:10-quinone (VIII), m.p. 196.5—197.5°, reduced (Adams) to the 3:4- $\text{H}_2$ -derivative (IX),

m.p. 170.5—171°, which is hydrolysed (1% NaOH) to 3-hydroxy-2- $\gamma$ -hydroxyisobutyl-1:4-naphthaquinone (X), m.p. 147.5—148.5°, also obtained with the 2-Bu $^{\beta}$  derivative by reduction of (VII). (X) and conc.  $\text{H}_2\text{SO}_4$  give 3-methyl-3:4-dihydro- $\alpha\beta$ -naphthopyran-5:6-quinone (XI), m.p. 148—148.5° (quinoxaline, m.p. 163—163.5°), hydrolysed (boiling alkali) to (X) and converted by conc. HCl at 55—65° into (IX).

**IV.** Hydrolysis (1% NaOH) of (VIII) gives an unstable OH-compound which passes readily into the violet 3-methyl- $\alpha\beta$ -naphthopyran-5:6-quinone (XII), m.p. 156—158° (decomp.) (quinoxaline, m.p. 163—163.5°); a little of a compound, m.p. 239—240° (decomp.), is also isolated. (XII) is converted into (VIII) by boiling EtOH,  $\text{H}_2\text{O}$ , or very dil. HCl; hydrolysis (conc.  $\text{H}_2\text{SO}_4$  or, better, 0.25% NaOH in air) affords 3-hydroxy-2- $\beta$ -formyl- $\Delta^8$ -propenyl-1:4-naphthaquinone, m.p. 229—230° (decomp.) [*Me*, 160—161°, *Et*, m.p. 184.5—185.5° ( $\text{H}_2$ -derivative, m.p. 185—186°), and *Bu* $^{\alpha}$ , m.p. 121.5—122°, *semiacetals*, formed by the action of AlkOH, which may be 2-alkoxy-3-methyl- $\beta\beta$ -naphthopyran-5:10-quinones], which is converted by aq.  $\text{NH}_3$  into a compound, m.p. 136—137°, and by boiling AcOH into an anhydride,  $\text{C}_{28}\text{H}_{18}\text{O}_7$ , m.p. 243—244° (decomp.). (XII) is reduced (Adams) to (XI). H. B.

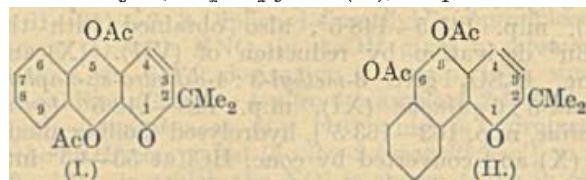
#### Constitution of lapachol and its derivatives.

**IV. Oxidation with potassium permanganate. V. Structure of Paterno's "isolapachone."** S. C. HOOKER (J. Amer. Chem. Soc., 1936, 58, 1168—1173, 1190—1197). —IV. Oxidation (1%  $\text{KMnO}_4$ ) of lapachol (3-hydroxy-2- $\gamma$ -methyl- $\Delta^8$ -butenyl-1:4-naphthaquinone) in 1% NaOH at about 0° gives 3-hydroxy-2- $\beta$ -methyl- $\Delta^8$ -propenyl-1:4-naphthaquinone (I), m.p. 119—120° [acetate, m.p. 85.5—86°; compound,  $\text{C}_{20}\text{H}_{16}\text{ON}_2$ , m.p. 226—227° (decomp.), with  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ ], which is further oxidised to 2-hydroxy-1:4-naphthaquinone and is reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) to 3-hydroxy-2-isobutyl-1:4-naphthaquinone (II), m.p. 132.5—133.5°. Similar oxidation of hydroxylapachol affords (II), whilst hydroxyhydroxylapachol (J.C.S., 1892, 61, 611; 1896, 69, 1356) yields 3-hydroxy-2- $\beta$ -hydroxyisobutyl-1:4-naphthaquinone (III), m.p. 121—122°. 3-Hydroxy-2-sec-butyl-1:4-naphthaquinone, m.p. 92.5—93°, is obtained by reduction of the 2- $\alpha$ -methylallyl derivative (Fieser, A., 1927, 462). (I) and (III) are converted by short treatment with cold conc.  $\text{H}_2\text{SO}_4$  into 5:6-benzo-1:1-dimethylcoumaran-3:4-quinone, m.p. 187—188° [quinoxaline, m.p. 154—155°, from  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ ], which is hydrolysed (1% NaOH) to (III), is converted by aq. HCl at 50—65° into 3-hydroxy-2- $\beta$ -chloroisobutyl-1:4-naphthaquinone, m.p. 147—148° (decomp.), and is isomerised by HBr (*d* 1.49) at 65—69° to 4:5-benzo-1:1-dimethylcoumaran-3:6-quinone, m.p. 183—184° [also obtained from (III) and boiling dil. HCl or  $\text{H}_2\text{SO}_4$ ], also hydrolysed (1% NaOH) to (III). Lapachol and 3-hydroxy-2-*n*-amyl-1:4-naphthaquinone with  $\text{PbO}_2$  in AcOH give peroxides, m.p. 154—155° and 117—118°, respectively.

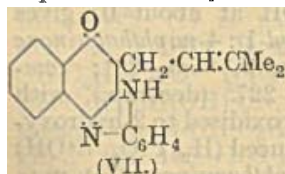
**V.** Acetylation ( $\text{Ac}_2\text{O}$ -NaOAc) of lapachol affords 5:10-diacetoxy-2:2-dimethyl- $\beta\beta$ -naphthopyran (I), m.p. 131—132° [identical with the Ac $_2$  derivative described



by Paterno (A., 1883, 210)], and 5:6-diacetoxy-2:2-dimethyl- $\alpha$ - $\beta$ -naphthpyran (II), m.p. 128—129°,



which give different colours with conc.  $\text{H}_2\text{SO}_4$ . Successive reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{EtOH}$ ) [whereby the 3:4- $\text{H}_2$ -derivatives, m.p. 169.8—170° and 162—162.6°, respectively (cf. Monti, A., 1915, i, 824), are produced] and hydrolysis ( $\text{AcOH}$ — $\text{H}_2\text{SO}_4$  in air) of (I) and (II) gives  $\alpha$ -lapachone (2:2-dimethyl-3:4-dihydro- $\beta$ - $\beta$ -naphthpyran-5:10-quinone) (III) and  $\beta$ -lapachone (2:2-dimethyl-3:4-dihydro- $\alpha$ - $\beta$ -naphthpyran-5:6-quinone) (IV), respectively. Hydrolysis ( $\text{AcOH}$ —dil.  $\text{H}_2\text{SO}_4$ , aq.  $\text{NaOH}$ , or  $\text{EtOH}$ — $\text{KOH}$  in air) of both (I) and (II) affords *dehydrolapachone* (most probably 2:2-dimethyl- $\beta$ - $\beta$ -naphthpyran-5:10-quinone) (V), m.p. 142.5—143°, reduced (Adams) to (III) and converted by  $\text{Zn}$ — $\text{Ac}_2\text{O}$  into (I). Paterno's *isolapachone* (*loc. cit.*) is (V). Reductive acetylation of "isopropylfuran-1:2- and -1:4-naphthaquinones" (J.C.S., 1896, 69, 1353), which are isomeric with (V), gives the corresponding *quinol diacetates*, m.p. 135.5—136.5° and 167—168°, respectively. The above formulation of (V) as a 1:4-quinone is uncertain in view of the following results.  $o$ - $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , and (V) in  $\text{AcOH}$  yield *dehydrolapazine* (VI), m.p. 156.5—157°, which is formulated as the quinoxaline from 2:2-dimethyl- $\alpha$ - $\beta$ -naphthpyran-5:6-quinone; lapachol similarly furnishes *lapaurhodone* (VII), m.p.

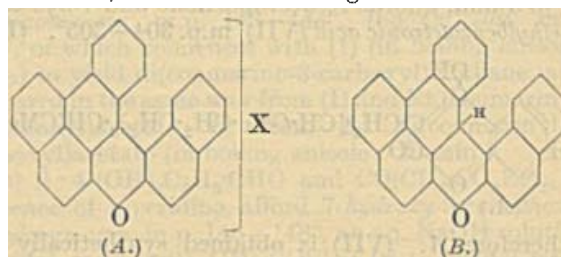


161.5—162.5°, which is oxidised (air in aq.  $\text{NaOH}$  +  $\text{Et}_2\text{O}$ ) to (VI). Reduction (Adams) of (VI) gives *lapazine*, two forms, m.p. 130.5—131.5° and 121.5—122.5°, also obtained from (VII) and cold conc.  $\text{H}_2\text{SO}_4$  and from (IV) and  $o$ - $\text{C}_6\text{H}_4(\text{NH}_2)_2$ . Methyl-lapaurhodone [from lapachol and  $o$ -tolylenediamine (VIII)] is oxidised [as (VII)] to *methyldehydrolapazine*, two forms, m.p. 149—151.5° and 169.5—171.5°, also formed from (V) and (VIII). Bromo- $\beta$ -lapachone [the 3-Br-derivative of (IV)] (J.C.S., 1892, 61, 611) is hydrolysed by 1%  $\text{NaOH}$  at room temp. to dihydroxyhydrolapachol (IX) (*loc. cit.*) and a little (V); 5%  $\text{NaOH}$  affords (IX) and 3-hydroxy-2- $\beta$ -methyl- $\Delta^5$ -propenyl-1:4-naphthaquinone, m.p. 119—120° [also obtained from (V) and 10%  $\text{NaOH}$  alone or in presence of  $\text{Zn}$  dust (with subsequent atm. oxidation)]. Acetylation ( $\text{Ac}_2\text{O}$ — $\text{NaOAc}$ ) of 3-hydroxy-2-allyl-1:4-naphthaquinone gives a *diacetate*,  $\text{C}_{17}\text{H}_{14}\text{O}_5$ , m.p. 178.5—179.5°, in addition to that [new m.p. 223.5—224.5° (decomp.)] described by Fieser (A., 1927, 155).

H. B.

**Pyrenium compounds. XXV. Dehydrenium dyes;** new class of carbenium salts. W. DILTHEY and F. QUINT [in part with R. KNIPP] (Ber., 1936, 69, [B], 1575—1591).—Treatment of *ms*-phenyldibenzoxanthanol with  $\text{AlCl}_3$  at 175—200° affords *dehydro-ms-phenyldibenzoxanthenium*

*chloride* (I) (A;  $\text{X}=\text{Cl}$ ) (corresponding *picrate* and *perchlorate*). The one-sided ring-closure is established



by analysis of the salts and by the similarity of the reaction with the corresponding *o*-tolyl compounds (see below). With carbinols the change is effected with certainty by  $\text{AlCl}_3$ , but with the salts irradiation or treatment with  $\text{ZnCl}_2$  is requisite. Thus *ms*-phenyldibenzoxanthenium perchlorate and  $\text{ZnCl}_2$  at 400—500° yield (I), whence the corresponding *bromide* ( $\text{X}=\text{Br}+0.5\text{HBr}$ ) and *iodide*,  $\text{C}_{27}\text{H}_{16}\text{O}_2$ . Reduction of (I) by  $\text{Zn}$  dust in boiling  $\text{AcOH}$  affords *dehydro-ms-phenyldibenzoxanthane* (B), m.p. 250—252° (decomp.), immediately re-oxidised to A by  $\text{PbO}_2$  in  $\text{AcOH}$ . *ms*-*o*-Chlorophenyldibenzoxanthanol and  $\text{AlCl}_3$  eliminate  $\text{HCl}$  with production of (I). *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$  and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$  in  $\text{AcOH}$ —12*N*- $\text{HCl}$  at 100° afford *ms-p-tolyldibenzoxanthane*, m.p. 228—229°, oxidised by  $\text{PbO}_2$  in  $\text{AcOH}$  to *ms-p-tolyldibenzoxanthanol*, m.p. 265—266° (decomp.) after softening at 255°. Treatment of this with  $\text{AlCl}_3$  at 200° or exposure of its *perchlorate*, m.p. 286—287°, in  $\text{AcOH}$  to sunlight leads to *dehydro-ms-p-tolyldibenzoxanthenium chloride* (corresponding *picrate*), reduced to *dehydro-ms-p-tolyldibenzoxanthane*, m.p. 229—230° (decomp.) after softening.  $o$ - $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ , ( $\beta$ - $\text{C}_{10}\text{H}_7$ ) $_2\text{O}$ , and  $\text{AlCl}_3$  at 120—150° give *ms-o-tolyldibenzoxanthanol*, decomp. 245—246° after softening, transformed by  $\text{AlCl}_3$  into *dehydro-ms-o-tolyldibenzoxanthenium chloride*, which could not be reduced to a cryst. xanthane. *Dehydro-ms-o-tolyldibenzoxanthenium perchlorate* is obtained by irradiation of *ms-o-tolyldibenzoxanthenium perchlorate*, m.p. 293—294° (decomp.) after softening. Irradiation of *ms-o-chlorophenyldibenzoxanthenium perchlorate* is accompanied by loss of  $\text{HCl}$ . Dehydrogenation of *ms-o-chlorophenyldibenzoxanthane* cannot be effected with  $\text{AlCl}_3$  and only with difficulty by irradiation in  $\text{AcOH}$  in presence of  $\text{O}_2$  which can be replaced by methylene-blue or *p*-benzoquinone. *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{COCl}$ , ( $\beta$ - $\text{C}_{10}\text{H}_7$ ) $_2\text{O}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  yield *p-chlorophenyldibenzoxanthanol* (III), m.p. 275—276° (decomp.) after softening (*perchlorate*, m.p. 291°); it is transformed by  $\text{AlCl}_3$  into (I). *Dehydro-ms-p-chlorophenyldibenzoxanthenium perchlorate* is obtained slowly by exposure to sunlight and  $\text{O}_2$  of a solution of *ms-p-chlorophenyldibenzoxanthenium perchlorate* in boiling  $\text{AcOH}$  whereas the corresponding *picrate* is obtained similarly from (III) and picric acid in the same solvent.  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{OH}$  and  $\beta$ - $\text{C}_{10}\text{H}_7\cdot\text{CHO}$  in  $\text{HBr}$ — $\text{AcOH}$  give *ms-l'-naphthyldibenzoxanthane*, m.p. 245° and, after re-solidification, m.p. 253—254.5°, oxidised by  $\text{PbO}_2$  in boiling  $\text{AcOH}$  to *ms-l'-naphthyldibenzoxanthanol*, decomp. 280—281° when placed in bath preheated to 270°. *l'-Naphthyldibenzoxanthenium perchlorate*, m.p. 325° (decomp.) after softening at 315°, is dehydrogenated in sunlight by

O, in boiling AcOH to *dehydro-ms-1'-naphthylidibenzo-xanthenium perchlorate*.

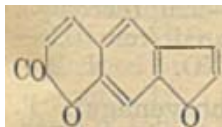
H. W.

**Biochemistry of micro-organisms.** L. RAVENELIN (1:4:8-trihydroxy-3-methylxanthone), a new metabolic product of *Helminthosporium Ravenelii*, Curtis, and of *H. Turcicum*, Passerini. H. RAISTRICK, R. ROBINSON, and D. E. WHITE (Biochem. J., 1936, 30, 1303—1314).—The yellow pigment, *ravenelin* (I),  $C_{14}H_{10}O_5$ , m.p. 267—268° (corr.), a metabolism product of the plant pathogens *H. Ravenelii*, Curtis, and *H. Turcicum*, Passerini, is optically inactive, has pseudo-acidic characters, contains 1 side-chain Me as shown by the Roth-Kuhn micro-method, gives an O-triacetate, m.p. 204—205° (corr.), O-tribenzoate, m.p. 255° (corr.), O-trianisoyl derivative, m.p. 216—218° (corr.), a  $Br_3$ -derivative, resorcinol by KOH fusion, a  $Me_2$  ether, m.p. 285—287° (corr.), and a  $Me_3$  ether (II), m.p. 178—179°. (II) was inert to alkalis and  $Ac_2O$ , was basic, and gave a ferrichloride,  $C_{17}H_{17}O_5FeCl_4$ , m.p. 174—175° (corr.), with  $HNO_3$  gave a nitrodimethylravenelin, m.p. 224—226°, with  $MgPhBr$  gave the Et ether of phenyltrimethoxyxanthanol, m.p. 166°, and with  $NaNH_2$  gave an oil identical with synthetic 2:5:3'-trimethoxy-3-methylidiphenyl ether since both gave the same  $Br_4$ -derivative, m.p. 152°. The above facts limit the structure to 1:4:8-(or 1:4:6)-trihydroxy-3-methylxanthone. The synthesis of 1:4:6-trimethoxy-3-methylxanthone, m.p. 157°, is described and as this is not identical with (II), (I) must be 1:4:8-trihydroxy-3-methylxanthone. The following compounds were synthesised in the preps. above: 4-bromo-2:5-dimethoxytoluene, m.p. 90—91° (corr.); 2:5:3'-trimethoxy-4-methylidiphenyl ether, b.p. 192—195°/2.5 mm., m.p. 72—74° (corr.) ( $Br_3$ -derivative, m.p. 130°); 2:5:3'-trimethoxy-3-methylidiphenyl ether, b.p. 165—166°/0.5 mm. [ $Br_3$ -derivative, m.p. 133° (corr.)]; 4:5:3'-trimethoxy-2-methylidiphenyl ether, b.p. 160—162°/0.2 mm., m.p. 68—69° (corr.) ( $Br_4$ -derivative, m.p. 115°). The optimum cultural conditions for the production of (I) by *H. Ravenelii* were determined and the relationship of (I) to the polyhydroxyanthraquinones also produced by *Helminthosporia* is discussed. Only two other naturally occurring hydroxyxanthenes—euxanthone and gentsin—have been previously isolated.

P. W. C.

**Colouring matter of the flowers of *Lantana camara*, Linn.**—See this vol., 1166.

**Components of leaves of *Ficus carica*.** K. OKAHARA (Bull. Chem. Soc. Japan, 1936, 11, 389—394).—The aq. extract of the leaves yields crystals of *ficusin* (I),  $C_{11}H_8O_3$ , m.p. 161—162°, which is sol. in warm alkali and contains a lactone ring, the third O being inert. Catalytic reduction affords tetrahydroficusin,  $C_{11}H_{10}O_3$ , m.p. 154°, methylation methylficusinic acid,  $OMe \cdot C_{10}H_6 \cdot CO_2H$ , m.p. 161—162°, and nitration in AcOH nitroficusin,  $C_{11}H_8O_3 \cdot NO_2$ , m.p. 254°. Oxidation of (I) with  $H_2O_2$  in alkaline solution yields furan-2:3-dicarboxylic acid and alkali fusion 4:6-dimethoxyisophthalic acid. (I) is therefore as shown. The  $COMe_2$  extract of the leaves contained bergapten which with  $Me_2SO_4$



and alkali gave methylbergaptenic acid,  $C_{14}H_{12}O_6$ , m.p. 138.

A. T.

**Arsenic and iodine compounds of the pyridine series.** A. BINZ and H. MATER-BODE (Angew. Chem., 1936, 49, 486—489; cf. A., 1935, 1156).—Details are given of the prep. of the As compounds described previously. 3-Iodo-2-hydroxypyridine and 3-iodo-2-pyridone-*N*-acetic acid have been prepared by diazotisation of 3-amino-2- and -4-hydroxypyridine, respectively. 5-Bromo-3-amino-4-hydroxypyridine has been prepared by reduction of 5-bromo-3-nitro-4-hydroxypyridine. Action of I in KI on 3-hydroxypyridine in the cold yields 2-iodo-3-hydroxypyridine, and warm yields (? 2:5-)di-iodo-3-hydroxypyridine. The stability of I-compounds of  $C_5H_5N$ , as examined by heating under pressure with  $H_2O$  at 170°, decomp. with  $HNO_3$ , and pptg. with  $AgNO_3$ , is that of the  $C_6H_6$  series, thus explaining why Selectan compounds can pass into the organism by intravenous application without eliminating I, and so can be used as harmless X-ray contrast media.

J. W. S.

**Reduction products of nicotinamide methiodide.** P. KARRER, G. SCHWARZENBACH, F. BENZ, and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 811—828).—Nicotinamide [from Et nicotinate (I) and  $NH_3 \cdot MeOH$  at 150°], m.p. 151° (methochloride, m.p. about 240°), gives a methiodide, m.p. 204°, which with  $Na_2S_2O_4$  yields a yellow, oily 1-methyldihydronicotinamide (II), which resembles Warburg's co-enzyme in that it is a very powerful reducing agent [cold  $AgNO_3$  instantaneously, methylene-blue, indigotin-di-, -tri-, and -tetra-sulphonate; can be titrated potentiometrically with  $K_3Fe(CN)_6$ ], gives a very high negative potential to Pt, and has an absorption band at 360 mμ, changed to 295—300 mμ by acid (which also causes much loss of reducing power). On these accounts and because it has no blue fluorescence (II) is a 1:2- or 1:6- $H_2$ -derivative. Acidification gives a colourless, cryst. isomeride, decomp. about 236° (darkening from 200°), which has an intense blue fluorescence, reduces  $AgNO_3$  only when heated, is stable to  $K_3Fe(CN)_6$ , and is thus the 1:4- $H_2$ -compound. 1-Methyl-2- or -6-butyl-1:2- or -1:6-dihydronicotine and *NN'*-dibenzyltetrahydrodipyridyl, but no 1:4- $H_2$ -compounds, can be titrated with  $K_3Fe(CN)_6$ . Nicotinmethylamide [from (I)], m.p. 102°, ω-ethoxynicotinimide dihydrochloride (III) (from nicotinonitrile and  $HCl \cdot EtOH$ ), m.p. about 233°, nicotinmethylamidine dihydrochloride [from (III) and  $NH_2Me$ ], m.p. about 240°, nicotinamide methoxymethochloride, and pyridine glucosidobromide do not give similar  $H_2$ -compounds.

R. S. C.

**Synthesis of *dl*-proline from pyrrole.** F. K. SIGNAIGO and H. ADKINS (J. Amer. Chem. Soc., 1936, 58, 1122—1124).—Alternate addition (in portions) of 1 mol. each of  $ClCO_2Et$  and  $MgEtBr$  to pyrrole +  $MgEtBr$  (1:1) followed by a further mol. of  $ClCO_2Et$  gives Et pyrrole-1- (26.4) and -2-carboxylate (1.5), and -1:2-dicarboxylate (65%). The last is reduced (method: this vol., 861) to Et pyrrolidine-1:2-dicarboxylate, hydrolysed (conc.  $HCl$ ) to *dl*-proline (over-all yield 57%).

H. B.

**Pyrrole series. I. Preparation of *N*-methylpyrroles.** A. H. CORWIN and W. M. QUATTLE-



BAUM, jun. II. Mechanism of aldehyde synthesis of pyrromethenes. A. H. CORWIN and J. S. ANDREWS (J. Amer. Chem. Soc., 1936, 58, 1081—1085, 1086—1090).—I. The question of *N*-isomerism (i.e., position of NH groups in porphin nucleus) is discussed briefly (cf. Fischer and Loy, A., 1923, i, 718; Conant and Bailey, A., 1933, 403). Et 2:4-dimethylpyrrole-3:5-dicarboxylate (I) (improved prep.) with Na in PhMe followed by  $\text{Me}_2\text{SO}_4$  gives the 1:2:4-*Me*<sub>3</sub> ester (II), m.p. 113—114°, converted by  $\text{SO}_2\text{Cl}_2$  in AcOH at 60° into Et 2-formyl-1:4-dimethylpyrrole-3:5-dicarboxylate, m.p. 94°, also prepared by methylation ( $\text{Me}_2\text{SO}_4$ , MeOH-KOH) of (VI) (below). (II) is hydrolysed (conc.  $\text{H}_2\text{SO}_4$  at <30°) to the 5-Et 3-*H* ester, decomp. 192°, decarboxylated in glycerol to Et 1:2:4-trimethylpyrrole-5-carboxylate, m.p. 47°, the 3-*Ac* derivative (III), m.p. 62°, of which, best prepared by methylation [as for (I)] of the 3-acetyl-2:4-dimethyl derivative, is reduced (method: Fischer *et al.*, A., 1929, 1463) to 1:2:4-trimethyl-3-ethylpyrrole (IV), b.p. 93°/23 mm. (IV) and 40%  $\text{CH}_2\text{O}$  in 95% EtOH give (provided mineral acid is absent) 1:3:5:1':3':5'-hexamethyl-4:4'-diethyl-2:2'-dipyrrylmethane (V), m.p. 106°, which could not be oxidised to a methene. (IV) and (V) are both oxidised (aq.  $\text{CrO}_3$ , 20%  $\text{H}_2\text{SO}_4$ ) to the *N*-Me derivative, b.p. 215—220°, of methylethylmaleimide. Reduction [ $\text{H}_2$  (2500 lb.), Raney Ni, EtOH, 150°] of (III) affords Et 1:2:4-trimethyl-3-ethylpyrrole-5-carboxylate, b.p. 124°/2 mm., also obtained by methylation ( $\text{Me}_2\text{SO}_4$ , *tert*-amyl alcoholic Na *tert*-amyloxide) of the 2:4-*Me*<sub>2</sub> ester. Et 2-formyl-4-methylpyrrole-3:5-dicarboxylate (VI) and Et 2:4-dimethylpyrrole-3-carboxylate with dry HCl in Et<sub>2</sub>O (other methods unsuccessful) give 3:5:4'-tricarboethoxy-4:3':5'-trimethylpyrromethene hydrochloride, sinters >120°, decomposed by boiling EtOH to (VI) and unidentified material. Hydrolysis (EtOH-KOH) of (II) yields the 3-Et 5-*H* ester, decarboxylated to Et 1:2:4-trimethylpyrrole-3-carboxylate, m.p. 62°, which with 40%  $\text{CH}_2\text{O}$  and EtOH-HCl affords 4:4'-dicarboethoxy-1:3:5:1':3':5'-hexamethyl-2:2'-dipyrrylmethane, m.p. 151—152°, which could not be oxidised (Br) to the methene. Attempts to prepare 1-methyl- and 1:1-dimethyl-pyrromethenes from some of the above *N*-Me derivatives were unsuccessful. 4:4'-Dicarboethoxy-3:5:3':5'-tetramethylpyrromethene (VII) could not be methylated [as for (I)]; decomp. occurs.

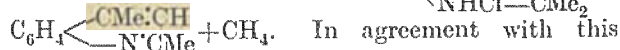
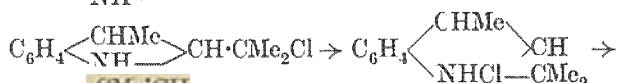
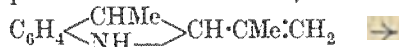
II. The (anomalous) production of (VII) from Et 2:4-dimethylpyrrole-3-carboxylate (VIII) and Et 2-formyl-4-methyl-3-ethylpyrrole-5-carboxylate (Fischer and Ernst, A., 1926, 621) is best explained by the intermediate formation (and subsequent fission) of a tripyrrylmethane (4). It is now shown that (4) can be intermediates in the Piloty synthesis of pyrromethenes. 4:4':4''-Tricarboethoxy-3:5:3':5':3''-5''-hexamethyltri-2-pyrrylmethane, new m.p. 220—225° (decomp.) (sinters at 195°) (prep. Fischer and Heyse, A., 1925, i, 76), with Et 5-formyl-2:4-dimethylpyrrole-3-carboxylate (IX) (improved prep.) in aq. MeOH-HBr give the hydrobromide of 4:4'-dicarboethoxy-3:5:3':5'-tetramethylpyrromethene (X) [best identified by reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , EtOH) to the methane, m.p. 230°], also obtained similarly from (IX) and (VIII). Et 5-

formyl-1:2:4-trimethylpyrrole-3-carboxylate (XI), m.p. 97° [from (IX) and  $\text{Na}_2\text{O}$  in  $\text{C}_6\text{H}_6$  followed by  $\text{Me}_2\text{SO}_4$ ], with (VIII) (2 mols.) and dry HCl in  $\text{C}_6\text{H}_{14}$  affords (X) (as hydrochloride) and Et 1:2:4-trimethylpyrrole-3-carboxylate (XII); with equimol. quantities, (X), (XI), and (XII) are isolated. 4:4':4''-Tricarboethoxy-1:3:5:3':5':3''-5''-heptamethyltri-2-pyrrylmethane, m.p. 177° (prep. *as loc. cit.*), is also cleaved by aq. MeOH-HBr to (X). Short treatment of (IX) and (XII) with aq. MeOH-HBr gives 4:4':4''-tricarboethoxy-1:3:5:1':3':5':3''-5''-octamethyltri-2-pyrrylmethane, m.p. 147—148° [also prepared from (IX), (XII), and  $\text{KHSO}_4$  at >150°], which is then cleaved to (X). (X) is also formed (cf. Fischer and Zerweck, A., 1922, i, 758; 1923, i, 364) from (IX) and aq. MeOH-HBr, but in presence of (XII) reaction occurs at a lower temp. and gives a better yield. Cryst. compounds could not be obtained from (XI) and (XII). H. B.

Oxindole-amines from isatin. W. R. CONN and H. G. LINDWALL (J. Amer. Chem. Soc., 1936, 58, 1236—1239; cf. A., 1935, 501).—Isatin and  $\text{MeNO}_2$  in EtOH-NHET<sub>2</sub> give 3-hydroxy-3-nitromethyl-oxindole (I), m.p. 135—140° (decomp. to original components); EtNO<sub>2</sub> similarly affords 3-hydroxy-3-*α*-nitroethyl-oxindole, m.p. 145—150° (red at 140°). 5-Bromo-3-hydroxy-1-ethyl-, m.p. 123—125° (decomp.), and 3-hydroxy-1-methyl-, m.p. 98—99° (decomp.), and -1-ethyl-, m.p. 84—85° (decomp.), -3-nitromethyl-oxindoles are obtained from the appropriate *N*-alkylisatin. These NO<sub>2</sub>-compounds gradually decompose into the original components when heated in neutral solvents; decomp. is retarded by a little AcOH and accelerated by inorg. or org. bases. Benzoylformanilide,  $\text{MeNO}_2$ , and EtOH-NHET<sub>2</sub> afford *α*-hydroxy-*α*-nitromethylphenylacetanilide, m.p. 143—144° (decomp.), reduced (Sn, conc. HCl) to a compound, m.p. 208—210°. Reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , AcOH) of (I) gives 3-hydroxy-3-aminomethyl-oxindole (II) [hydrochloride, m.p. 195—197° (decomp.); picrate, m.p. 165—166° (decomp.); *N*-Bz derivative, m.p. 177°], which with MeI in EtOH+Ba(OH)<sub>2</sub> affords 3-hydroxy-1-methyl-3-oxindolyltrimethylammonium iodide, m.p. 227° (decomp.). Reduction of (I) with mossy Sn and conc. HCl also gives (II), but in one case some 3-hydroxy-3-hydroxylaminomethyl-oxindole (hydrochloride, m.p. 194°; picrate, m.p. 174°) was also produced. 5-Bromo-3-hydroxy-1-ethyl-3-aminomethyl-oxindole (III) [hydrochloride, m.p. 192—194° (decomp.); picrate, m.p. 182—183°; ON-Bz<sub>2</sub> derivative, m.p. 204°] and 3-hydroxy-1-ethyl-3-aminomethyl-oxindole (IV) [hydrochloride, m.p. 180—182° (decomp.); picrate, m.p. 168—169°; ON-Bz<sub>2</sub> derivative, m.p. 191° (decomp.); *N*-CO<sub>2</sub>Et derivative, m.p. 166°] are also obtained by reduction with Sn and HCl. 3-Hydroxy-, m.p. 208—209° (decomp.), 3-hydroxy-1-ethyl-, m.p. 216—217° (decomp.), and 5-bromo-3-hydroxy-1-ethyl-, m.p. 218—220° (decomp.), -3-carbamidomethyl-oxindole are prepared from (II)—(IV) (as hydrochlorides) and aq. KCNO. H. B.

Supposed "acetoneanil" of Knoevenagel. P. KALNIN [with W. GRINSTEIN] (Annalen, 1936, 523, 118—129).—Oxidation of "acetoneanil" (I) with  $\text{KMnO}_4$  gives AcOH in large amount and a substance

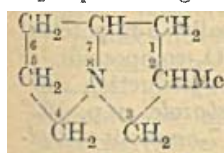
$C_{38}H_{39}O_3N_3$ , m.p. (indef.) 142—190°. The observations are not in harmony with Reddelien's formulation of (I), which appears to be 3-methyl-2-isopropenylindoline (II), passing into 2:4-dimethylquinoline (III) not by simple elimination of  $CH_4$  but by a complex mol. transformation,



hypothesis, a yellow intermediate product has been isolated which has the same composition as (II) and passes into (III) when treated with dry HCl. A mode of passage of  $\text{CMe}_2\text{NPh}$  into (II) is given. The methiodide, m.p. 251—252°, of (III) is converted by  $\text{MgMeI}$  in  $\text{Et}_2\text{O}$  into 1:2:2:4-tetramethyl-1:2-dihydroquinoline, m.p. 157—158° (corr.), the odour of which resembles that of (I) and which yields a picrate, m.p. 147°, identical with that of (I). Since (I) is not a dihydroquinoline derivative, a mol. rearrangement must occur either during the methylation of (I) or during the formation of the picrate.

H. W.

**Syntheses of a new heterocyclic type formed from two condensed pyrrolidine rings.** G. MENSCHIKOV (Ber., 1936, 69, [B], 1802—1804).—2-isoButylpyrrolidine is treated with Br in 5% NaOH at -5° and the oily bromoamine is treated with conc.  $\text{H}_2\text{SO}_4$  thus giving 2-methylpyrrolizidine (I), b.p.



162—163°/atm. pressure (picrate, m.p. 182—184°), which does not decolorise  $\text{KMnO}_4$  in 10%  $\text{H}_2\text{SO}_4$  and is inert towards  $\text{HNO}_3$ . The corresponding methiodide, m.p. 225—226°, passes when treated with  $\text{Ag}_2\text{O}$

and then heated into de- $\Delta$ -methyl-2-methylpyrrolizidine, b.p. 164—166°/atm. pressure, hydrogenated ( $\text{PtO}_2$  in 1% HCl) to dihydrode- $\Delta$ -methyl-2-methylpyrrolizidine (II), b.p. 165—167°/atm. pressure (picrate, m.p. 174—175°), which does not reduce acid  $\text{KMnO}_4$ . Since (II) is not identical with 1-methyl-2-isobutylpyrrolidine it is probably 1:4-dimethyl-2-n-propylpyrrolidine. Since (II) is not identical with the corresponding degradation product of heliotridane, the latter is certainly not (I).

H. W.

**Benzoylation of quinoline oxide.** M. HENZE (Ber., 1936, 69, [B], 1566—1568).—Quinoline oxide forms a picrate,  $(C_9H_7ON)_2 \cdot C_6H_5O_7N_3$ , m.p. 158°, which passes into the normal picrate, m.p. 143°, when treated with excess of picric acid. The corresponding hydrochloride is converted by  $\text{BzCl}$  and NaOH into 2-hydroxyquinoline [picrate, m.p. 132°; hydrochloride (+1H $_2$ O), m.p. 192° (decomp.)]. Addition of  $\text{BzCl}$  to 2-methylquinoline oxide hydrochloride and excess of KCN in  $\text{H}_2\text{O}$  affords 2-cyanoquinoline, m.p. 93°, transformed by cold, conc. HCl into the corresponding amide, m.p. 123°, and by the boiling reagent into the acid, m.p. 156° [ $\text{Cu}$  (+2H $_2$ O) salt].

H. W.

**Derivatives of 8-hydroxyquinoline.** E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc.,

1936, 25, 501—504).—2-Amino-p-propylphenol, m.p. 140—142° (from 2-nitro-p-propylphenol, b.p. 110°/4 mm.), by the Skraup reaction affords 8-hydroxy-5-propylquinoline, m.p. 52—52.5° (explosive; characterized by the 7-Cl-derivative [hydrochloride, m.p. 242° (decomp.)]). 5-Chloro-8-hydroxyquinoline in  $\text{PhNO}_2$  with  $\text{Me}_2\text{SO}_4$  affords a mixture of the methochloride and -sulphate. 8-Dimethylaminoethoxyquinoline dihydrochloride is prepared from 8-hydroxyquinoline (Na salt) and  $\text{NEt}_2 \cdot C_2H_4Br$ , HBr in EtOH whilst 5-amino-8-hydroxyquinoline refluxed with  $\text{NEt}_2 \cdot C_2H_4Cl$  in  $C_6H_6$  gives 5-( $\beta$ -diethylaminoethoxyamino)-8-hydroxyquinoline dihydrochloride. The Skraup reaction with Me 3-amino-4-ethoxybenzoate affords 8-ethoxyquinoline-5-carboxylic acid [diethylaminoethyl ester (impure), m.p. 86°]. 5-Chloro- and 5-nitro-8-hydroxyquinoline with  $\text{Hg}(\text{OAc})_2$  in aq. EtOH afford the corresponding anhydro-mercuric derivatives. None of the above compounds possesses significant trypanocidal or anaesthetic activity.

F. O. H.

**Optically active silver-hydroxyquinoline complexes.** F. HEIN and H. REGLER (Ber., 1936, 69, [B], 1692—1702; cf. A., 1935, 868).—Treatment of 8-hydroxyquinoline with  $\text{AgNO}_3$  in EtOH or  $C_5H_5N$  gives Ag di-8-hydroxyquinoline nitrate,  $[\text{Ag}(C_9H_6N \cdot OH)_2]NO_3$ , converted by  $NH_3$  into the corresponding base,  $OAg \cdot C_9H_6N \cdot OH \cdot C_9H_6N$ , and by  $C_5H_5N$  into the compound,  $[\text{Ag}(C_9H_6N \cdot OH)_2]C_5H_5N$ . The base is transformed by the requisite acid into the trichloroacetate, d-mandelate, and d-camphorsulphonate. Fractional treatment of it with  $\alpha$ -bromo-d-camphor- $\pi$ -sulphonic acid gives salts with extreme vals. of  $[\alpha]_D^{25} +37.4 \pm 0.5^\circ$  and  $+47.8 \pm 0.5^\circ$ , thus establishing the existence of salts of differing optical activity and probably of the tetrahedral configuration of the complex. Attempts to obtain an optically active base from the salt fractions were unsuccessful.

H. W.

**5:7-Di-iodo-8-hydroxyquinoline.** V. PAPESCH and R. R. BURTNER (J. Amer. Chem. Soc., 1936, 58, 1314).—8-Hydroxyquinoline in 15% HCl added slowly to ICl in 15% HCl at room temp. gives 83.5—92.5% of nearly pure 5:7-I $_2$ -derivative.

H. B.

**Preparation of 8-aminoquinoline from 8-chloroquinoline.** N. N. VOROSHOV, jun., and S. P. MITZENGENDLER (J. Gen. Chem. Russ., 1936, 6, 681—684).—8-Chloroquinoline (I) and aq.  $NH_3$  (20 mols.) in presence of  $\text{CuCl}$  (200°/49—55 atm.; 2.5 hr.) give 8-aminoquinoline in 69.3% yield. (I) undergoes partial decomp. to quinoline hydrochloride during distillation.

R. T.

**Organic nitrogen bases from pyrolysis of cotton-seed meal.** I. PARKER, C. L. GUTZEIT, A. C. BRATTON, and J. R. BAILEY (J. Amer. Chem. Soc., 1936, 58, 1097—1104).—The bases formed by pyrolysis of the meal consist of light petroleum-sol. (A) and -insol. (B) substances. The higher fractions of (B) have abnormally high N contents and tend to decompose to tars. The following are isolated from the lower fractions of (A):  $C_5H_5N$ ; 2-, 3-, and 4-methyl-, 3-ethyl-, 2:4-, 2:6-, and 3:5- [picrate, m.p. 242—243.5° (lit. 228—230° and 244°)]-dimethyl-, and 2:4:6-trimethyl-pyridine; quinoline; iso-



quinoline; 2- and 4-methyl- and 2:3:8-trimethyl-quinoline; a base, b.p. 283°/750 mm. [picrate, m.p. 261—263° (decomp.) (darkens at 259°); hydrochloride mercurichloride, m.p. 173—174° (sinters at 150°)], which is probably a dihydroquinazoline.

H. B.

**Quinoline derivatives.** IV. K. S. NARANG, J. N. RAY, and T. D. SACHDEVA (J. Indian Chem. Soc., 1936, 13, 260—263).—The azlactone from veratraldehyde with hot 3% KOH gives  $\alpha$ -benzamido-3:4-dimethoxycinnamic acid, m.p. 208°, reduced by 2.5% Na-Hg to  $\alpha$ -benzamido- $\beta$ -3:4-dimethoxyphenylpropionic acid, m.p. 158°, which with HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-AcOH at 50° affords the 6-NO<sub>2</sub>-acid, m.p. 208°; by reduction [Fe(OH)<sub>2</sub>] and spontaneous ring-closure this yields 3-benzamido-2-keto-6:7-dimethoxy-1:2:3:4-tetrahydroquinoline, m.p. 225°. Piperonal leads similarly to  $\alpha$ -benzamido-3:4-methylenedioxy-cinnamic acid, m.p. 224°,  $\alpha$ -benzamido- $\beta$ -3:4-methylenedioxypropionic acid (I), m.p. 122°, its 6-NO<sub>2</sub>-derivative (II), m.p. 210°, and 3-benzamido-2-keto-6:7-methylenedioxy-1:2:3:4-tetrahydroquinoline, m.p. 254°. Hydrolysis of (I) gives 3:4-methylenedioxyphenylalanine dihydrochloride, +H<sub>2</sub>O, m.p. 278—280°. Reduction [Fe(OH)<sub>2</sub>] of the anilide, m.p. 205°, of 6-nitro-3:4-methylenedioxy-cinnamic acid (III) does not give an amide, but affords by hydrolysis 6:7-methylenedioxy-2-quinolone, m.p. 205°, also obtained by direct reduction of (III). Similarly, reduction of (II) or of N- $\beta$ -6-nitro-3:4-methylenedioxyphenylpropionylantranilic acid [from the acid chloride of (II) and NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H in C<sub>5</sub>H<sub>5</sub>N], m.p. 208°, affords 2-keto-3:4-methylenedioxy-1:2:3:4-tetrahydroquinoline, m.p. 232°.

R. S. C.

**Quaternary derivatives of heterocyclic compounds.**—See B., 1936, 716.

**3:4:6-Triaminoquinolines.**—See B., 1936, 716.

**Synthesis of derivatives of 3-methylisoquinoline.** V. BRUCKNER and A. KRAMLI (J. pr. Chem., 1936, [ii], 145, 291—300).—The large-scale prep. of isosafrole  $\psi$ -nitrosite (78% yield) and thence of  $\beta$ -nitro- $\alpha$ -3:4-methylenedioxyphenyl-*n*-propyl acetate (68%) is described.  $\beta$ -Acetamido- $\alpha$ -3:4-methylenedioxyphenyl-*n*-propyl alcohol, prepared therefrom by reduction, is hydrolysed by hot 10% H<sub>2</sub>SO<sub>4</sub> and the base converted without isolation into other acylamino-derivatives. With POCl<sub>3</sub> in PhMe or xylene at 110—120° these give isoquinoline derivatives, the aralkoyl more readily than the aroyl compounds. The following are described:  $\beta$ -Phenylacetyl-, m.p. 136—138°, -homopiperonyl-, m.p. 152—153°, -homoveratroyl-, m.p. 139°, -benzoyl-, m.p. 135°, and piperonyl- $\alpha$ -3:4-methylenedioxyphenyl-*n*-propyl alcohol, m.p. 159°. 6:7-Methylenedioxy-1-benzyl-, m.p. 119° [hydrochloride, m.p. 264° (decomp.)], -piperonyl-, -veratryl-, m.p. 133° (lit. 125°) [hydrochloride, m.p. 219° (lit. 225°)], -phenyl-, and -3':4'-methylenedioxyphenyl-3-methylisoquinoline (I). (I) is accompanied by a substance, C<sub>18</sub>H<sub>15</sub>O<sub>5</sub>N, m.p. 107—108°.

R. S. C.

**Homoneurine series.** I. Bromo-derivatives of isoquinolinehomoneurine. C. CANDEA, E. MACOVSKI, and J. KUHN (Bull. Soc. chim., 1936, [v],

3, 1309—1318).—Allylisoquinolinium bromide (I) with 2 Br in MeOH affords  $\beta\gamma$ -dibromopropylisoquinolinium bromide (II), m.p. 190—192° [corresponding iodide, m.p. 145—146° (decomp.)], but with excess of Br affords a Br<sub>2</sub>-derivative, m.p. 86—87°, with 3 ionisable Br, which is reconverted into (II) by boiling EtOH. Allylisoquinolinium iodide (III) with Br in MeOH gives allylisoquinolinium dibromiodide (IV), m.p. 75—77°, stable in boiling EtOH. (I), (III), and (IV) with picric acid afford allylisoquinolinium picrate, m.p. 163—164°, and the  $\beta\gamma$ -Br<sub>2</sub>-derivatives yield  $\beta\gamma$ -dibromopropylisoquinolinium picrate, m.p. 153—154°.

J. L. D.

**Synthesis of isoquinoline derivatives.** W. KRABBE (Ber., 1936, 69, [B], 1569—1572).—OH·CPh<sub>2</sub>·CH<sub>2</sub>·NHBz is converted by MgPhBr in Et<sub>2</sub>O and finally at 200—205° into benz- $\beta\beta$ -diphenylvinylamide, m.p. 132—134°, converted by P<sub>2</sub>O<sub>5</sub> in boiling PhMe into 1:4-diphenylisoquinoline (I), m.p. 132—5° (picrate, m.p. 152°). Similarly benz- $\beta\beta$ -diphenylethylamide affords 1:4-diphenyl-3:4-dihydroisoquinoline, m.p. 122°, dehydrogenated (Pd-sponge at 230—240°) to (I).

H. W.

**Structural problems in the indole group.** 5- and 7-Nitrotetrahydrocarbazoles. S. G. P. PLANT (J.C.S., 1936, 899—902).—Reduction (Sn-HCl; 15 hr.) of 8-chloro-5-nitrotetrahydrocarbazole yields  $\alpha$ -amino-tetra-, m.p. 183° (Ac derivative, m.p. 198°), and -hexa-hydrocarbazole (Ac<sub>2</sub> derivative, m.p. 264°; Bz derivative, m.p. 245°). Elimination of NH<sub>3</sub> from cyclohexanone-*m*-nitrophenylhydrazone [aq. H<sub>2</sub>SO<sub>4</sub> (1:9)] affords principally 5-nitrotetrahydrocarbazole and not the 7-NO<sub>2</sub>-compound (I) (cf. Borsche *et al.*, A., 1908, 367). Reduction (Sn-HCl) of 7-nitro-9-methyltetrahydrocarbazole, m.p. 162° [from MeSO<sub>4</sub> and (I)], affords 7-amino-9-methylhexahydrocarbazole, m.p. 87—89° (Ac<sub>2</sub> derivative, m.p. 106°), identical with that obtained by electrolytic reduction of the 7-NO<sub>2</sub>-compound. Chlorination of the Bz<sub>2</sub> derivative, m.p. 199°, of 7-aminohexahydrocarbazole yields 6-chloro-7-benzamido-9-benzoylhexahydrocarbazole, m.p. 182°.

F. N. W.

**Manufacture of condensation products containing sulphur and organic sulphur compounds.**—See B., 1936, 686.

**Preparation of dihydroacridines by the Grignard reaction.** W. L. SEMON and D. CRAIG (J. Amer. Chem. Soc., 1936, 58, 1278—1282).—It is now shown (cf. A., 1935, 482) that *o*-NHPh·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>Me (I) and MgMeI give *o*-NHPh·C<sub>6</sub>H<sub>4</sub>·Bu<sup>+</sup> and 5:5-dimethyl-5:10-dihydroacridine (II), m.p. 125—126° [Ac, m.p. 153—154°, Bz, m.p. 294—297°, and N-Ph, m.p. 123°, derivatives; 1:1 compounds, m.p. 135—136° and 124°, with acridine and 5-methylacridine (III), respectively]; (II) is probably formed by dehydration of the intermediate *o*-NHPh·C<sub>6</sub>H<sub>4</sub>·CMe<sub>2</sub>·OH. (II) is also obtained from (III) or acridone (IV) and MgMeI in Bu<sup>+</sup>O. (II) heated with NaNH<sub>2</sub> gives the N-Na derivative (V), which with MeI in PhMe affords 5:5:10-trimethyl-5:10-dihydroacridine, m.p. 100—102°; the compound described by Stevens *et al.* (A., 1931, 1404) is a mixture of this and 5:10-dimethyl-5:10-dihydro-

acridine (VI), m.p. 140—141°. (V) heated further with (II) gives (III), which is also formed from (II) (0.3 mol.),  $\text{NHPh}$ , (0.45 mol.), and  $\text{HCl}$  (0.15 mol.) at 250°. Acridine methiodide and  $\text{MgMeI}$  yield (VI) and 10:10'-dimethyl-5:10:5':10'-tetrahydro-5:5'-diacridyl, m.p. about 280° (decomp.), which when heated to 350° decomposes to acridine and 10-methyl-5:10-dihydroacridine, m.p. 91—93°. (I) and  $\text{MgEtI}$  afford (probably) *o*-anilinophenyldiethylcarbinol, b.p. 175°/2 mm., dehydrated (conc.  $\text{H}_2\text{SO}_4$ ) to 5:5'-diethyl-5:10-dihydroacridine, m.p. 90—91° [also obtained from (IV) and  $\text{MgEtBr}$  in  $\text{Bu}^n\text{O}$ ], and (probably) an *o*-pentenyldiphenylamine, b.p. 150—155°/2 mm. 5:5-Di-*n*-butyl-5:10-dihydroacridine, m.p. 87—88°, is prepared from (IV) and  $\text{MgBu}^n\text{Br}$ . H. B.

**Phenanthrene series. X. Naphthquinolines.** E. MOSETTIG and J. W. KRUEGER (J. Amer. Chem. Soc., 1936, 58, 1311—1312).—3-Aminophenanthrene (*N*-Me, m.p. 69—70° (all m.p. are corr.) [hydrochloride, m.p. 190—200° (decomp.)], and *NN*-Me<sub>2</sub> derivative, m.p. 75—76° [hydrochloride, m.p. 210—213° (decomp.)], formed by methylation ( $\text{Me}_2\text{SO}_4$ , aq.  $\text{KOH}$ ) and separated by Hinsberg's method, glycerol,  $\text{H}_3\text{BO}_3$ ,  $\text{PhNO}_2$ ,  $\text{FeSO}_4$ , and conc.  $\text{H}_2\text{SO}_4$  give a naphthquinoline, m.p. 106—107° (hydrochloride, m.p. 239—243°), reduced ( $\text{H}_2$ , Cu chromite,  $\text{EtOH}$ , 135°) to a  $\text{H}_4$ -derivative, m.p. 72—74° (hydrochloride, m.p. 255—260°), which is further reduced ( $\text{H}_2$ ,  $\text{PtO}_2$ ,  $\text{AcOH}$ ) to an  $\text{H}_8$ -derivative, m.p. 111—112° (hydrochloride, m.p. 305—307°). 3- $\alpha$ -Aminoethylphenanthrene (hydrochloride, m.p. 265—266°) is prepared by reduction (2.5%  $\text{Na-Hg}$ ,  $\text{EtOH-AcOH}$ ) of 3-acetylphenanthrene oxime (the 2-isomeride has m.p. 196—198°). 2- $\alpha$ -Chloro- $\gamma$ -dimethylaminopropyl- [hydrochloride, m.p. 248—252° (decomp.)] (from the  $\alpha$ -OH-derivative and  $\text{PCl}_5$  in  $\text{CHCl}_3$ ) is reduced ( $\text{H}_2$ ,  $\text{Pd-CaCO}_3$ ,  $\text{EtOH}$ ) to 2- $\gamma$ -dimethylaminopropylphenanthrene (hydrochloride, m.p. 222—227°). H. B.

**Condensation of esters of unsaturated acids with carbamide.** III. Z. JERZMANOWSKA-SIENKIEWICZOWA (Rocz. Chem., 1936, 16, 172—180).— $\text{Et}_4$  ethylenetetracarboxylate,  $\text{CO}(\text{NH}_2)_2$ , and  $\text{NaOEt}$  in  $\text{EtOH}$ , at the b.p., yield  $\text{Et}_3$  hydantoinoethanetricarboxylate, m.p. 132—133°, which condenses with a further mol. of  $\text{CO}(\text{NH}_2)_2$ , and eliminates  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , to yield spirohydantoin. R. T.

**Preparation of pyridinium iodides.**—See B., 1936, 687.

**Synthesis of 1-phenyl-2-methyl-4-ethyl-5-pyrazolone.** Y. F. CHI and M. C. H. YANG (J. Amer. Chem. Soc., 1936, 58, 1152—1153).—formylbutyrate (I), b.p. 37—38°/2 mm. (semicarbazone, m.p. 108—108.5°), obtained by acidification ( $\text{AcOH}$ ) of the Na salt (A., 1935, 358), and the appropriate  $\text{NHAr-NH}_2$  give 1-phenyl- (II), m.p. 99—99.5°, 1-p-nitrophenyl-, m.p. 212—214° (slight decomp.), and 1-p-bromophenyl-, m.p. 170—171°, 4-ethyl-5-pyrazolone. (II) is methylated ( $\text{MeOH-MeI}$  at 100—110°) to the 2-Me derivative, m.p. 121—121.5°. (I) and aq.  $\text{NH}_4\text{OH}$  afford 4-ethyl-5-isooxazolone, b.p. 113—114°/2 mm. H. B.

**Sodium 1-phenyl-2:3-dimethylpyrazolonyl-4-aminomethylene sulfoxylate and dimethylpyrazolonyldiphenyl.** 4:4'-Di-(1-phenyl-3-methyl)pyrazolonyl.—See B., 1936, 762.

**Glyoxaline series.** R. WEIDENHAGEN and R. HERRMANN [with H. WEGNER, and (FRL.) D. WISCHNEVSKY, E. SEURIG, and G. RADNIK] (Z. Wirts. Zuckerind., 1935, 85, 762—778).—4-Nitro-5-methylglyoxaline and  $\text{SnCl}_2$  give a 67% yield of 4-amino-5-methylglyoxaline [not isolated free; dihydrochloride, m.p. 186° (decomp.); picrate, m.p. 193°;  $\text{CHPh}$ , m.p. 216°, *Ac*, m.p. 216°, *Bz*, m.p. 262°, *Bz*<sub>2</sub>, m.p. 176°, and phenylcarbamide derivative, m.p. 283°]. 4-Nitroglyoxaline gives similarly a 20% yield of  $\text{NH}_2$ -derivative. Glyoxalines are obtained, usually in good yield, from ammoniacal  $\text{CuO}$  (1 mol.) and  $\alpha$ -OH-aldehydes or  $\alpha$ -acetoxyaldehydes, which are readily oxidised to  $\alpha\beta$ -diketones; some  $\alpha$ -chloroketones, e.g.,  $\text{CH}_2\text{Cl-COMe}$ , are sufficiently reactive to give glyoxalines in one step; others can be used by preliminary hydrolysis without isolation of the OH-ketone. Thus are obtained glyoxaline and the following derivatives: 4-Ph; 4-phenyl-2-methyl, m.p. 161—162° (lit. 158—159°); 4-phenyl-2-ethyl, m.p. 133°, and 2-isopropyl, m.p. 180°; 2:4-Ph<sub>2</sub>, m.p. 193° (hydrochloride, + $\text{H}_2\text{O}$ , m.p. 273°); 4-*o*-OH- $\text{C}_6\text{H}_4$ , m.p. 181°, 4-4'-hydroxy-*m*-tolyl, m.p. 136—137°, 4-*p*-anisyl, m.p. 136—137°, 4-*p*-NHAc- $\text{C}_6\text{H}_4$ , m.p. 250—251°, 4-*p*-NH<sub>2</sub>- $\text{C}_6\text{H}_4$ , +0.5 $\text{H}_2\text{O}$  and + $\text{H}_2\text{O}$ , m.p. 97°, 4-*p*-CO<sub>2</sub>H- $\text{C}_6\text{H}_4$ , m.p. 308° (hydrochloride, + $\text{H}_2\text{O}$ , m.p. 338°), 4-Me, 2:4-Me<sub>2</sub> (from acetoxy- or chloro-acetone), and 4-OH-CH<sub>3</sub> [from  $\text{CO}(\text{CH}_2\cdot\text{OH})$ ], m.p. 93—94°, derivatives.  $\omega$ -Chloro-*o*-hydroxyacetophenone and hot  $\text{H}_2\text{O}$  give much coumaranone and 20% of  $\omega\omega$ -dihydroxyacetophenone, m.p. 65°.  $\omega$ -Chloro-2-hydroxy-5-methylacetophenone gives similarly 40% of  $\omega\omega$ -dihydroxy-5-methylacetophenone, m.p. 76—77°. R. S. C.

**Thiobarbiturates.** II. E. MILLER, J. C. MUNCH, F. S. CROSSLEY, and W. H. HARTUNG (J. Amer. Chem. Soc., 1936, 58, 1090—1091).—The following 5:5-dialkyl-2-thiobarbituric acids are prepared from  $\text{CS}(\text{NH}_2)_2$  and  $\text{CAlkAlk}'(\text{CO}_2\text{Et})_2$  in  $\text{EtOH-NaOEt}$ : 5-ethyl-5-*n*-propyl-, m.p. 174.5°, and 5-isobutyl-, m.p. 170.5°; 5-*n*-propyl-5-isopropyl-, m.p. 168.5°, 5-allyl-, m.p. 138°, 5-*n*-, -iso-, and -sec-butyl, m.p. 135.5°, 132°, and 165°, respectively, and 5-*n*-hexyl-, m.p. 114.4°; 5-isopropyl-5-allyl-, m.p. 176.5°, 5-isobutyl-, m.p. 115—117°, and 5-*n*-amyl-, m.p. 98.5°; 5-*n*-amyl-, m.p. 112.5°, and 5-*n*-, m.p. 120—121°, and -iso-, m.p. 147°, -butyl-5-allyl-. H. B.

**$\text{N-Arylbarbituric acids}$ .** J. S. BUCK (J. Amer. Chem. Soc., 1936, 58, 1284—1286).—The following are prepared from  $\text{NH}_2\cdot\text{CO-NHAr}$  and  $\text{CEt}_2(\text{CO}_2\text{Et})_2$  or  $\text{CEtBu}^n(\text{CO}_2\text{Et})_2$  in  $\text{EtOH-NaOEt}$ : 1-phenyl-, m.p. 178°, 1-*p*-tolyl-, m.p. 155.5° (lit. 152—153°), 1-*o*-, m.p. 182°, and -*m*-, m.p. 133°, -tolyl-, 1-*o*-, m.p. 176.5°, and -*m*-, m.p. 115—116°, -anisyl-, 1-*p*-anisyl-, m.p. 129° (lit. 126—127°), 1-*o*-, m.p. 159°, and -*m*-, m.p. 114°, -phenetyl-, 1-*p*-phenetyl-, m.p. 160° (lit. 152—153°), and 1- $\alpha$ -, m.p. 207°, and m.p. 146°, -naphthyl-5:5-diethylbarbituric acids; 1-phenyl-, b.p. 203°/0.5 mm., m.p. about 70°, 1-*o*-, m.p. 135°, -*m*-, b.p. 212°/0.6 mm., m.p. about 89°, and -*p*-, m.p.



142°, -tolyl-, 1-o-, m.p. 139.5°, -m-, m.p. 102.5°, and -p-, m.p. 124°, -anisyl-, 1-o-, m.p. 131°, -m-, b.p. 216°/0.5 mm., m.p. 84–85°, and -p-, m.p. 100°, -phenetyl-, and 1- $\alpha$ -, m.p. 182°, and - $\beta$ -, m.p. 126°, -naphthyl- $\alpha$ -ethyl-5-n-butylbarbituric acids. H. B.

**Condensations of cyanoacetic esters with carbamide by magnesium methoxide.** H. LUND (Ber., 1936, 69, [B], 1621–1627).—Mg(OMe)<sub>2</sub> is a less powerful catalyst than NaOMe for the condensation of cyanoacetic esters with CO(NH<sub>2</sub>)<sub>2</sub> to cyanoacetylcarbamides and thence to 4-imidobarbituric acids. Reaction usually ceases at the conclusion of the first phase and is accompanied by the formation of much by-product. CN·CH<sub>2</sub>·CO<sub>2</sub>Et, Mg(OMe)<sub>2</sub>, and CO(NH<sub>2</sub>)<sub>2</sub> afford CN·CH<sub>2</sub>·CO·NH·CO·NH<sub>2</sub> in moderate yield when reaction is curtailed and 4-imidobarbituric acid when the change is prolonged. CN·CHPr<sup>o</sup>·CO<sub>2</sub>Et gives 4-imidoisopropylbarbituric acid, whence isopropylbarbituric acid, m.p. 216°. The prep. of 4-imidoethylbarbituric acid is described. Et cyclohexenylcyanoacetate (I) appears to be transformed by Mg(OMe)<sub>2</sub> or NaOEt in Et cyclohexylidenecyanoacetate, m.p. 274–275° (decomp.). Et benzylidenecyanoacetate gives benzylidenecyanoacetylcarbamide, m.p. 220° (decomp.), but no benzylidenobarbituric acid, which is obtained in 75% yield from CHPh·CH(CO<sub>2</sub>Et)<sub>2</sub>. 4-Imidodiallylbarbituric acid, decomp. 280–284°, whence diallylbarbituric acid, is derived from (CHMe·CH<sub>2</sub>)<sub>2</sub>C(CN)·CO<sub>2</sub>Et, whereas (CH<sub>2</sub>Ph)<sub>2</sub>C(CN)·CO<sub>2</sub>Et yields dibenzylcyanoacetylcarbamide, m.p. 188°. Et cyclohexenylethylcyanoacetate (II), b.p. 150–151°/15 mm., gives under varied conditions 4-imidocyclohexenylethylbarbituric acid, decomp. about 265°, cyclohexenylethylcyanoacetylcarbamide, m.p. 161°, and acetamide, m.p. 103°. (I) and guanidine afford cyclohexylidenecyanoacetylguanidine, whilst (II) yields cyclohexenylethylcyanoacetylguanidine, m.p. 256–258° (decomp.). H. W.

**4-N-Piperazylbenzenesulphonic acid.** V. PRELOG (Coll. Czech. Chem. Comm., 1936, 8, 288–290).—Sulphonation of N-phenylpiperazine gives 1-phenylpiperazine-p-sulphonic acid (Na salt; hydrochloride; Bz derivative). F. R. S.

**Reactions of aryl alkyl ketones with thiocarbamide.** K. DZIEWONSKI, K. BERNAKIEWICZ, and L. GIZLER (Bull. Acad. Polonaise, 1935, A, 564–571).—CS(NH<sub>2</sub>)<sub>2</sub> and CPhMe at 170° give 4 : 6-diphenyl-6-methyl-1 : 2 : 3 : 6-tetrahydro-2-thiopyrimidine (I), m.p. 172–174° (acetate, m.p. 140°; Ag salt, m.p. 190–195°; Bz<sub>2</sub> derivative, m.p. 152–153°). (I) is transformed by MeI–MeOH at 100° into 2-methylthiol-4 : 6-diphenyl-6-methyl-5 : 6-dihydropyrimidine, m.p. 82–84° (hydriodide, m.p. 88–90°; picrate, m.p. 165–167°), and by EtOH–conc. HCl into 2-ethylthiol-4 : 6-diphenyl-6-methyl-3 : 6-dihydropyrimidine hydrochloride, m.p. 206–208° (decomp.). (I) and HgO in boiling AcOH afford 2-keto-4 : 6-diphenyl-6-methyl-1 : 2 : 3 : 6-tetrahydropyrimidine, m.p. 179–181°. Similarly CS(NH<sub>2</sub>)<sub>2</sub> and COMe·C<sub>6</sub>H<sub>4</sub>Me-p give 4 : 6-di-p-tolyl-6-methyl-1 : 2 : 3 : 6-tetrahydropyrimidine, m.p. 170–171° (Ag salt, m.p. 193–194°; acetate, m.p. 129–130°; methiodide, m.p. 188–189°), transformed by BzCl and Na<sub>2</sub>CO<sub>3</sub> in boiling Et<sub>2</sub>O into 2-benzoylthiol-4 : 6-

di-p-tolyl-6-methyl-5 : 6-dihydropyrimidine, m.p. 152–153°. H. W.

**Pyrimidines. CLIII. Structure of vitamin-B<sub>1</sub>.** T. B. JOHNSON and A. LITZINGER (Science, 1936, 84, 25–26).—Thyminyllamine, OH·C<NH·CO>N=CH>C·CH<sub>2</sub>·NH<sub>2</sub>, has been synthesised. On heating, it gives uracil, CH<sub>2</sub>O, and NH<sub>3</sub>.

L. S. T.

**Pyrimidines. Synthesis of 4-methyl-5-n-butylcytosine.** Y. F. CHU (J. Amer. Chem. Soc., 1936, 58, 1150–1151).—CHAcBu<sup>o</sup>·CO<sub>2</sub>Et and CS(NH<sub>2</sub>)<sub>2</sub> in EtOH–NaOEt give 6-hydroxy-4-methyl-5-n-butyl-2-thiopyrimidine (I), m.p. 197–198°, which with EtBr, MeI, and CH<sub>2</sub>Cl·CO<sub>2</sub>Et in EtOH–NaOEt affords 6-hydroxy-2-ethylthiol- (II), m.p. 92–93°, -2-methylthiol-, m.p. 158–159°, and -2-carbethoxymethylthiol-, m.p. 110–111° (and thence -2-carboxymethylthiol-, m.p. 117–118°), -4-methyl-5-n-butylpyrimidine, respectively. (II) is hydrolysed (conc. HBr) to 4-methyl-5-n-butyluracil, m.p. 245°, also obtained from (I) and aq. CH<sub>2</sub>Cl·CO<sub>2</sub>H. 6-Chloro-2-ethylthiol-4-methyl-5-n-butylpyrimidine, b.p. 160°/2 mm. [from (II) and POCl<sub>3</sub> at 110–120°], with EtOH–NH<sub>3</sub> at 170–180° gives the 6-NH<sub>2</sub>-derivative, m.p. 104–105°, hydrolysed (48% HBr) to 4-methyl-5-n-butylcytosine (+0.75H<sub>2</sub>O), m.p. 299–300° (decomp.) [hydrobromide, m.p. 222° (decomp.); hydrochloride, m.p. 235°]. H. B.

**Quinazolines. IV.** S. S. BEDI and K. S. NARANG (J. Indian Chem. Soc., 1936, 13, 252–254).—Veratraldehyde is quantitatively nitrated at 5–10°. 6-Nitropiperonal and KMnO<sub>4</sub> at 40–60° give 6-nitropiperonylic acid, m.p. 175°, the amide, m.p. 191–193°, of which is reduced (SnCl<sub>2</sub>) to the NH<sub>2</sub>-amide, m.p. 172–174°; the Ac derivative, m.p. 212°, thereof in 1% NaOH at 40–50° gives 6 : 7-methylenedioxy-2-methyl-4-quinazoline, m.p. 346°. 6- $\beta$ -Carboxypropionyl-, m.p. 219°, and 6-butyrylaminopiperonylamide, m.p. 271°, and 6 : 7-methylenedioxy-2- $\beta$ -carboxyethyl-, m.p. 184°, and -2-n-propyl-4-quinazoline, m.p. 280°, are similarly prepared.

R. S. C.

**Heteropolar compounds. I. Complex halogenomeric salts of 4-hydroxy-2-thion-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline.** C. V. GHEORGHIU and (MLLE.) L. MANOLESCU (Bull. Soc. chim., 1936, [v], 3, 1353–1368; cf. A., 1934, 1011; 1935, 630, 1253).—2-Thion-4-ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline (I) with HgCl<sub>2</sub> in EtOH affords a yellow compound, m.p. 119–121°, and the Hg<sup>II</sup> chloride, m.p. 121–126°, of (I), an internal salt, which with hot xylene or with HCl in Ac<sub>2</sub>O (through the intermediate red carbonium compound) affords the HgCl<sub>2</sub> internal salt of 2-thion-1 : 4-anhydro-3-phenyl-2 : 3-dihydroquinazoline (II), m.p. 290–292°. Similarly, (I) with HgBr<sub>2</sub> affords a compound, m.p. 138–144° (decomp.), and a colourless Hg<sup>II</sup> bromide, m.p. 116–121°, which when heated with xylene or EtOBz affords the Hg<sup>II</sup> bromide (III) of (II), m.p. 276°, which with cold Ac<sub>2</sub>O containing HCl affords mercurybis-(2-thiol-4-hydroxy-3-phenyl-3 : 4-dihydroquinazoline) dihydrochloride (red), m.p. 230–232°. With HgI<sub>2</sub>, (I) affords a similar series

of compounds, m.p. 126—128°, 137—138° (decomp.) (IV) (converted into the former in hot EtOH), and 252—253°, respectively, which with HCl in Ac<sub>2</sub>O affords a red carbonium chloride, m.p. 106—108°. (II) in cold Ac<sub>2</sub>O with HClO<sub>4</sub> affords a carbonium perchlorate, m.p. 252—257°, whilst with warm Ac<sub>2</sub>O, mercurylbis-(2-thiol-3-phenyl-2 : 3-dihydroquinazoline) diperchlorate, m.p. 279—282°, is formed, identical with the perchlorate of (II). The Hg<sup>II</sup> bromide of (II) similarly affords, in the cold, the perchlorate, m.p. 190—191°, of 2-thiol-4-hydroxy-3-phenyl-3 : 4-dihydroquinazoline mercuric dibromide, converted when warmed with Ac<sub>2</sub>O into the perchlorate, m.p. 233°, of (III), which with COMe<sub>2</sub> affords (III). (IV) in the cold similarly yields a carbonium perchlorate, m.p. 207—208° (decomp.), which when heated gives the monoperchlorate, m.p. 219—221° (decomp.), of the bimol. form. The results are discussed in the light of recent work. J. L. D.

**Action of phenols on quinoxalinic and acridinic anhydrides.** P. PIUTTI [in part with G. B. MARINI] (Gazzetta, 1936, 66, 270—276).—Quinoxaline-2 : 3-dicarboxylic anhydride (I), when heated with PhOH or hydroxyphenols at 170°, gives Ph, m.p. 104°, and o-, m.p. 167°, m-, m.p. 175°, and p-hydroxyphenyl quinoxaline-2-carboxylate, m.p. 184°. At 110°, the reaction stops at the stage of Ph, m.p. 157°, and o-, m.p. 162°, m-, m.p. 202°, and p-hydroxyphenyl quinoxaline-3-carboxylate-2-carboxylic acid, m.p. 168°, all of which on further heating give the monocarboxylic esters. As a by-product, quinoxaline-2-carboxylic acid, m.p. 215° [also obtained by heating (I) alone], is formed. With N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O or NHPh·NH<sub>2</sub>, the monocarboxylic esters give quinoxaline-2-carbohydrazide, m.p. 204°, or -phenylhydrazide, m.p. 186°; PhOBz similarly gives NHBz·NH<sub>2</sub>. In none of these reactions was a phthalein obtained. Acridinic anhydride with phenols similarly gives no phthalein, but only decomp. products. E. W. W.

**Action of selenium dioxide on β-diketones.** P. PIUTTI (Gazzetta, 1936, 66, 276—277).—CH<sub>3</sub>(COMe)<sub>2</sub> and SeO<sub>2</sub> in EtOH give triketopentane, which with o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> yields 3-acetyl-2-methyl quinoxaline, m.p. 87—88°. COMe·CH<sub>2</sub>·COPh gives a product which is not Ph Me triketone. E. W. W.

**Conversion of ortho- into para- and of para- into ortho-quinone derivatives.** IV. Synthesis of furan derivatives of α- and β-naphthaquinones. S. C. HOOKER and A. STEYERMARK (J. Amer. Chem. Soc., 1936, 58, 1202—1207; cf. J.C.S., 1894, 65, 17).—3-Hydroxy-2-α-dibromoethyl-, -2-α-dibromo-n-propyl-, m.p. 156—157° (decomp.), -2-α-dibromo-n-butyl-, m.p. 133—134°, and -2-α-dibromo-β-phenylethyl- (I), m.p. 172·5—173·5° (decomp.), -1 : 4-naphthaquinones, prepared from the 2-Δ<sup>2</sup>-alkenyl derivatives and Br in CHCl<sub>3</sub>, are converted by EtOH (usually boiling) into 5 : 6-benzcoumarone-3 : 4-quinone, m.p. 209·5—210° (quinoxaline, m.p. 195—196°), and its 1-Me, m.p. 164—164·5° (quinoxaline, m.p. 209·5—210·5°), 1-Et, m.p. 143·5—144° (quinoxaline, m.p. 159—160°), and 1-Ph (II), m.p. 219·5—220·5° (quinoxaline, m.p. 237—238°), derivatives, respectively. (I) is accompanied by a little 2-bromo-1-phenyl-5 : 6-benzcoumaran-3 : 4-quinone, m.p. 218—

219° (quinoxaline, m.p. 237—238°), whilst small amounts of (III) (below) and a hydroxyphenylbenzcoumarone-3 : 4-quinone, m.p. about 275° (decomp.), are formed with (II). 1-Methyl-, m.p. 246—247°, 1-ethyl-, m.p. 145—145·5°, and 1-phenyl- (III), 2 forms, both m.p. 246·5—247·5°, -4 : 5-benzcoumarone-3 : 6-quinone are obtained when the isomeric 3 : 4-quinones (above) are treated with cold conc. H<sub>2</sub>SO<sub>4</sub>. Both series are cleaved by boiling 1% NaOH; 3-hydroxy-2-acetonyl-, m.p. 176·5—177·5° (IV), -2-propionylmethyl-, m.p. 165—165·5°, and -2-phenacyl-, m.p. 182·5—183·5°, -1 : 4-naphthaquinone are thus obtained. These are converted by conc. H<sub>2</sub>SO<sub>4</sub> into the above 3 : 4- and then into the 3 : 6-quinones. (IV) is reduced (Adams) to 3-hydroxy-2-β-hydroxypropyl-1 : 4-naphthaquinone, m.p. 115·5—116·5° (cf. Fieser, A., 1927, 155). H. B.

**Micro-hydrogenation by hyposulphite.** E. HAAS (Biochem. Z., 1936, 285, 368—371).—A method is described, using methylene-blue, indigotindisulphonic acid, and Me-orange as test substances, which indicates the extent of reduction by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> from pressure changes when the substance is mixed with a NaHCO<sub>3</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> solution in equilibrium with a CO<sub>2</sub>-A atm. P. W. C.

**Synthesis of sulphur derivatives of 1 : 2 : 4-triazole.** I. MATZUREVITSCH (Bull. Sci. Univ. Kiev, 1935, 1, 9—83).—NH<sub>2</sub>Ph and thiosemicarbazide (I) or (NH<sub>2</sub>·CS·NH<sub>2</sub>)<sub>2</sub> (II) at 180° afford 3 : 5-dianilino-4-thiol-1 : 2-diazole and 3-amino-5-thiol-4-phenyl-1 : 2 : 4-triazole (III) (dibenzyl derivative, m.p. 189—190°). NH<sub>2</sub>Ph and (NHPh·CS·NH<sub>2</sub>)<sub>2</sub> (at the b.p.) yield 3-anilino-5-thiol-4-phenyl-1 : 2 : 4-triazole (IV). NH<sub>2</sub>Ph and (o-C<sub>6</sub>H<sub>4</sub>Me·NH·CS·NH<sub>2</sub>)<sub>2</sub>, m.p. 168—170° (decomp.) [from (I) and o-C<sub>6</sub>H<sub>4</sub>Me·NCS], give (III) and (IV). o-Toluidine (V) and (I) or (II) afford 3-amino-5-thiol-4-o-tolyl-1 : 2 : 4-triazole, +H<sub>2</sub>O, m.p. 228—229° (Ag salt; platinichloride; 3-N·Ac, m.p. 190—191°, and 3-N·5-S-dibenzyl derivative, an oil), together with 3-amino-5-thiol-1 : 2-dihydro-1 : 2 : 4-triazole, its polymeride, not melting at 370°, and a no. of unidentified products; the corresponding 4-m-tolyl-, +H<sub>2</sub>O, m.p. 259—260° (Ac derivative, m.p. 188—189°), and 4-p-tolyl compound, +H<sub>2</sub>O, m.p. 271—272° (dibenzyl derivative, m.p. 237—238°), are obtained similarly. (V) and NH<sub>2</sub>·CS·NH·NH·CS·NHPh yield 3-o-toluidino-5-thiol-1 : 2 : 4-triazole, +H<sub>2</sub>O, m.p. 219—222° (Ac derivative, m.p. 184—185°); the corresponding 3-m-, +H<sub>2</sub>O, m.p. 247—248·5° (decomp.), 3-p-toluidino-, m.p. 263—264° (decomp.) (Ac derivative, m.p. 191—192°), and 3-xylylidino-compound, +H<sub>2</sub>O, m.p. 203—204°, were prepared analogously. NH<sub>2</sub>·CH<sub>2</sub>Ph and (I) (1·5 hr. at the b.p.) yield dibenzylthiocarbamide and an unidentified substance, m.p. 161—162°. The triazoles described give characteristic colorations with HNO<sub>2</sub> or with aq. K<sub>3</sub>Fe(CN)<sub>6</sub>. R. T.

**Relations between reduction-oxidation potential and chemical constitution of flavins.** R. KUHN and P. BOULANGER (Ber., 1936, 69, [B], 1557—1566).—Lumiflavin is slightly more negative than lactoflavin (I) in the complete region, p<sub>H</sub> 0·4—12·8. At p<sub>H</sub> 7·0, (I) has E<sub>0</sub> 0·185 volt. Investigation of 9-methyl-, 3 : 9-dimethyl-, 9-phenyl-, and 3-phenyl-



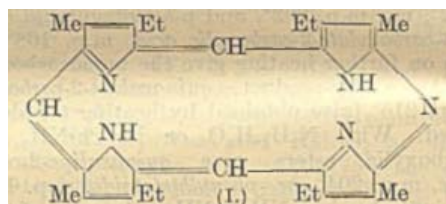
9-methylflavin and of 6:7-dimethyl- and 3:6:7-trimethyl-9-*d*-glucoflavin shows that methylation in position 3 has no appreciable influence. Me situated in the  $C_6H_6$  nucleus has a marked effect. Displacement of Me from position 7 to 8 causes an increase of 0.113 volt in potential. Me groups at 6 and 7 occasion the most negative potentials observed among synthetic flavins. The influence of the pentitol chain is very slight. Replacement of 9-1'-ribityl by hydroxyethyl, dihydroxypropyl, 1-1'-arabityl, *d*-1'-xylityl, or *d*-1'-sorbityl causes very slight positive increase in potential. An influence of the constitution and configuration of pentitol and hexitol chains could not be observed but differences are caused by the introduction of quite dissimilar groups, e.g., Ph,  $\cdot CH_2 \cdot CO_2H$ ,  $\cdot CH_2Ph$ , and cyclohexyl. Esterification of the vitamins with  $H_3PO_4$  has as little effect on the redox potential as on the absorption spectrum. The yellow enzyme is 0.12 volt more positive than its pigment component. The sp. protein substance is therefore united not only to the phosphoric residue but also to the flavin nucleus. The probability that NH at 3 is concerned in the union is strengthened by the observations that the enzyme, in contrast with (1) and lactoflavinphosphoric acid, does not exhibit fluorescence and that 3-methyl-lactoflavin, in contrast with (I), does not promote the growth of rats on a vitamin- $B_2$ -free diet.

H. W.

**Porphyryns. XXXVI. Vinyl- and amino-porphyrins.** H. FISCHER, E. HAARER, and F. STADLER (Z. physiol. Chem., 1936, 241, 201—219; cf. A., 1935, 362; this vol., 87).—The  $Me_2$  ester of mesoporphyrin-IX in MeOH with  $NH_2OH$  at 135° for 12 hr. gives the *dihydrazide* (I), m.p. >300° (*Cu* salt; compound with 2PhCHO, m.p. 275°), which with  $HNO_2$  at 0° yields the corresponding *diazide* (II). (II) with MeOH gives the corresponding *diurethane* (III), m.p. 252° (*Cu* salt, m.p. 270°), which with 10% HCl at 130—140° gives the *dihydrochloride*, m.p. >300°, of the corresponding diamine *dihydrochloride* [tetra-acetate (IV), m.p. 276°; *Cu* salt of (IV), m.p. 260°; compound (V) with  $Me_2SO_4$ , m.p. >300°]. (V) boiled for 3 hr. with 10% KOH in MeOH gives *isopropatoetioporphyrin* (VI), m.p. >300° [*Cu* salt, m.p. >300°; *Fe* salt (VII), m.p. >300°]. (VII) with  $Na+C_5H_{11}OH$  in  $H_2$  gives the corresponding *chlorin*. (VI) reacts successively with  $2CHN_2 \cdot CO_2Et$  and  $CH_2N_2$  to give a substance, m.p. 265°, with HI in AcOH to give *etioporphyrin-III*, m.p. >300°, and with HBr in AcOH to give a Br-compound which yields *hematoporphyrin* on alkaline hydrolysis and a  $(OMe)_2$ -derivative, decomp. about 180°, with MeOH. The *Fe* salt of tetramethyl-hematoporphyrin with HI in AcOH and subsequent esterification with  $CH_2N_2$  gives a *porphyrin*, m.p. 240° (*oxime*, m.p. 261°). (III) with 10% HCl gives the *hydrochloride* (VIII) of the corresponding amine. (VIII) after methylation with  $Me_2SO_4$  yields (VI) on boiling with 10% KOH in MeOH. (I) in dil.  $H_2SO_4$  oxidised with  $KMnO_4$  and esterified with  $CH_2N_2$  gives the ester (IX) of mesorhodin and (IX) on boiling with AcOH and esterifying with  $CH_2N_2$  gives the ester, m.p. 252°, of mesoverdin. The *Me* ester of rhodoporphyrin-XV with  $NH_2OH$  gives the

*monohydrazide* (X), m.p. 285°, and the  $Me_2$  ester gives the *dihydrazide*, m.p. >360°, and (X). Similarly the  $Me_8$  ester of uroporphyrin yields the *octahydrazide*, m.p. >360°, and the  $Me_8$  ester of isouroporphyrin-I yields the *octahydrazide*. The hydrazide of pyrroporphyrin-XV with PhCHO gives a compound, m.p. 290°. Phaeophorbide and phaeophytin heated with 30% KOH in MeOH at 180° for 6 hr. give a *K* salt which with  $Me_2SO_4$  yields the *Me* ester of pyrroporphyrin. The  $Me_4$  ester of coproporphyrin-I with  $NH_2OH$  gives the acid hydrazide, which with  $HNO_2$  yields the acid azide (XI). (XI) boiled with 50% AcOH gives the *hexahydrochloride* (XII) of the corresponding amine [octa-acetate (XIII), m.p. 287°; *Cu* salt of (XIII), m.p. 278°]. (XII) with  $Me_2SO_4$  and KOH in MeOH gives 1:3:5:7-tetramethyl-2:4:6:8-tetraynylporphyrin (XIV), m.p. >360° (*Cu* salt, m.p. >360°), with elimination of  $NMe_3$ . (XIV) in AcOH with Pd+H, gives *etioporphyrin-I*. W. McC.

**Imidoporphyrins. II. Synthesis of mono-imidoæti- and monoimido-copro-porphyrin.** H. FISCHER and W. FRIEDRICH (Annalen, 1936, 523, 154—164).—5:5'-Dibromo-4:4'-dimethyl-3:3'-diethylpyrromethene hydrobromide is converted by NaOH in  $H_2O-C_5H_5N$  at 130—140° into *mono-imidoætioporphyrin* (I), m.p. >300° (*Cu* salt), and a



(?) *di-imidoætioporphyrin*. Similarly 5:5'-dibromo-4:4'-dimethylpyrromethene-3:3'-dipropionic acid hydrobromide affords monoimido-copro-porphyrin, transformed by  $CH_2N_2$  into the  $Me_4$  ester, which sinters from 240°. Under like conditions 5-bromo-4:3':5'-trimethyl-3-ethylpyrromethene-4'-propionic acid hydrobromide passes into mesoporphyrin and *monoimido-mesoporphyrin*, and 5:5'-dibromo-3:3':4:4'-tetramethylpyrrometheno hydrobromide into *monoimido-octamethylporphyrin*. H. W.

**Chlorophyll. LXVIII. Ketophylloporphyrins and their transition into deoxophyllerythrin derivatives.** H. FISCHER, K. MÜLLER, and O. LESCHHORN (Annalen, 1936, 523, 164—198).—The *Fe* salt of phylloporphyrin *Me* ester (I) is converted by  $SnBr_4$  in  $(C_2H_5Cl)_2O$  into formylphylloporphyrin *Me* ester (II), m.p. 236° (*Fe*, m.p. 245°, and *Cu*, m.p. 208°, salts), the *oxime*, m.p. 257°, of which is transformed by boiling  $Ac_2O$  containing KOAc into 6-cyanophylloporphyrin *Me* ester, m.p. 255° (*Cu* salt, m.p. 256—257°), which could not be hydrolysed satisfactorily. (II) and anhyd. HCN in  $C_5H_5N$  containing  $K_2CO_3$  give 6-formylphylloporphyrin-cyanohydrin *Me* ester, m.p. 236°. Condensation of (II) with  $CH_2(CO_2H)_2$  in  $C_5H_5N$  containing piperidine under mild conditions gives the tricarboxylic acid (*Me* ester, m.p. 255°), whereas under more drastic circumstances deoxophyllerythrin-9-acetic acid (*Me* ester, m.p. 233°) is obtained. (II)

and MeOH—conc. HCl at 60° afford 9-methoxydeoxyphyllerythrin Me ester (III), m.p. 222—223°. Boiling  $C_5H_5N$  containing  $Na_2CO_3$  converts (II) into 9-hydroxydeoxyphyllerythrin Me ester (IV), m.p. 276° (Cu salt, m.p. 228°; Bz derivative, m.p. 253°; acetate, m.p. 234°). Treatment of (IV) with boiling  $CHCl_3$ —MeOH containing I affords 9:10-dimethoxydeoxyphyllerythrin ester, m.p. 220°, and 10-methoxyphyllerythrin ester, m.p. 268° (oxime). (III) and  $CH_3Ph \cdot OH$  containing I at 100° yield benzoyloxydeoxyphyllerythrin ester, m.p. 228°. HI (d 1.96) in AcOH at 65—70° converts (III) or (IV) into deoxyphyllerythrin, m.p. 276—277°. (I),  $Bz_2O$ , and  $SnBr_4$  at 70° yield 6-benzoylphyllerythrin Me ester (V), m.p. 303° (Cu, m.p. 258°, and Fe, m.p. 262°, salts). 9-Hydroxy-9-phenyldeoxyphyllerythrin Me ester, m.p. 278°, from (V) and boiling KOH—MeOH, is converted by HI (d 1.96) in AcOH at room temp. into 9-phenyldeoxyphyllerythrin Me ester, m.p. 258°. (II) and  $CH_3(CN)_2$  in  $C_5H_5N$  containing piperidine at 100° afford 9-dicyanomethyldeoxyphyllerythrin Me ester, m.p. 222°. The Fe salt of (II) is reduced by Na and boiling  $iso-C_4H_9 \cdot OH$  to deoxyphyllerythrin.

[With O. LESCHORN.] Chlorophyllin  $l_4$  Me<sub>2</sub> ester is converted by NaOEt in boiling  $C_5H_5N$ —xylene and treatment of the product with  $CH_3N_2$  into phylloerythrin. 3-Carbethoxy-5-formyl-4-methylpyrrole-2-propionic acid and hæmopyrrole in AcOH at 0° yield 4-carbethoxy-4':5':3-trimethyl-3'-ethylpyrromethene-5-propionic acid (VI), m.p. 61° [Me ester (VII), m.p. 165° (decomp.); hydrobromide, m.p. 204° (decomp.)]. Bromination of (VI) and (VII) gives products, m.p. 202° (decomp.) and m.p. 112°, respectively, but the action is accompanied by partial decarboxylation. Hæmopyrrolealdehyde, 3-carbethoxy-4-methylpyrrole-2-propionic acid, and HBr afford 4:5:4':5'-tetramethyl-3:3'-diethylpyrromethene hydrobromide, m.p. 218°. H. W.

**Derivatives of blood-pigments.** A. HANSIK (Z. physiol. Chem., 1936, 241, 156—167; cf. A., 1930, 1304; 1931, 745; Langenbeck, A., 1932, 412, 757).—Amorphous and cryst. hæmatin (I) with cold 80%  $HCO_2H$  gives formyl- and with AcOH acetyl-hæmin whilst the anhydride (II) and the half anhydride (III) do not react. Probably (II) and (III) are produced by loss of the OH attached to Fe. (I), (II), and (III) differ in solubility in  $C_5H_5N$  and 5% aq.  $NaHCO_3$ . The properties of (I) and the prep. of (III), glyoxaline-, histidine-, and pyridine-hæmatin, and the following derivatives of hæmin: glyoxaline-chloro- and -formyl-, pyridine-, pyridine-formyl-, -acetyl-, and -chloro-, and the K salt of protoporphyrin are described. W. McC.

**Fluorescence of the chlorophyll series.** Reversible reduction of chlorophyll-a and -b. V. M. ALBERS, H. V. KNORR, and P. ROTHMUND (Physical Rev., 1935, [ii], 47, 198; cf. A., 1935, 12).—Chlorophyll-a and -b were reduced in  $C_5H_5N$  under an atm. of  $N_2$  or  $CO_2$ , and reoxidised in air. The reduced chlorophyll (I) showed no characteristic absorption in the visible region. The absorption spectra of the original and reoxidised (I) were identical in the visible region. The fluorescence spectra of the reduced, re-oxidised, and original (I) were all

different, and fluorescence was more intense in the original (I). The fluorescence spectra for the reduced and reoxidised (I)-a and -b are different according as  $CO_2$  or  $N_2$  is used. L. S. T.

**Spectroscopic studies of simpler porphyrins.**—See this vol., 1048.

**Fluorescence of the porphyrins.**—See this vol., 1048.

**Compounds of pyrrole with furfuraldehyde.**

**I. Furfurylidene-pyrroles.** P. PRUTTI (Gazzetta, 1936, 66, 265—270).—2:4-Dimethyl-3-ethylpyrrole (I) with furfuraldehyde, AcOH, and a trace of HBr gives the 5-furfurylidene derivative (II), m.p. 185°, of (I). With a larger proportion of HBr, the hydrobromide, m.p. 83—84°, of (II) is formed, and is converted into the picrate, decomp. 154°, and the perchlorate, m.p. 217° (decomp.). 3-Acetyl-5-furfurylidene-2:4-dimethylpyrrole perchlorate, 2-furfurylidene-tetrahydrokatole picrate [both of which decompose without melting (up to 280°)], and 5-furfurylidene-2:4-dimethylpyrrole hydrobromide, m.p. <250°, are prepared similarly. E. W. W.

**isoOxazole group.** Action of nitric acid on unsaturated compounds. XIII—XV. Products of the reaction of nitric acid with citraconic acid. A. QUILICO and R. FUSCO (Gazzetta, 1936, 66, 278—286, 287—293, 293—299).—XIII. Eulite (I) (cf. this vol., 617), of which the prep. is modified, when dissolved in MeOH—NaOMe and treated with  $HgCl_2$  gives a mercurichloride,  $C_6H_5O_8N_4Cl_2Hg_2$ . The base A,  $C_6H_9O_2N_3$ , m.p. 136—137°, obtained by  $SnCl_2$  reduction of (I) (loc. cit.) is identified as 3-methyl-5-( $\beta$ -amino- $\alpha$ -oximinoethyl)isooxazole (II) (Ac derivative, m.p. 152°), which on prolonged boiling with HCl yields  $NH_4OH$  and 5-glycyl-3-methylisooxazole hydrochloride (III) [p-nitrophenylhydrazone, m.p. 215—216° (decomp.)]. The last is converted by NaOH into a yellow base, 2:5-(3':3'-dimethyl-5':5''-diisooxazolyl)dihydropyrazine (IV), m.p. 173—174° (Ac derivative, m.p. 220°). The second base, B,  $C_6H_{11}ON_3$  (loc. cit.), from (I) is identified as 3-methyl-5-( $\alpha\beta$ -diaminoethyl)isooxazole (Ac. derivative, m.p. 184°). A third base, C,  $C_6H_9O_2N_3$ , m.p. 165—166° (Ac derivative, m.p. 239°), is also isolated, and with  $HNO_3$  gives a diazo-acid,  $C_6H_5O_3N_3$ . It is concluded that (I) is 3-methyl-5-( $\alpha\beta$ -trinitroethyl)isooxazole.

XIV, XV. Thermal decomp. of (I) mixed with powdered glass gives, with  $N_2O_3$ , HCN, AcOH, MeCN, and  $MeNO_2$ , 5-nitroacetyl-3-methylisooxazole (V), m.p. 37°, b.p. 132—133°/25 mm. [phenylhydrazone, m.p. 111° (decomp.); p-nitrophenylhydrazone, m.p. 165° (decomp.); semicarbazone, m.p. 197—198° (decomp.)]. The oxime, m.p. 98° [Bz derivative, m.p. 185—190° (decomp.)], of (V) is reduced ( $SnCl_2$ ) to (II) (above); (V) is similarly reduced to (III). (V) condenses with aldehydes in presence of  $NH_2Me$ , thus giving 5- $\alpha$ -nitro-cinnamoyl-, m.p. 120° [p-nitrophenylhydrazone, m.p. 225° (decomp.)], and -p-methoxycinnamoyl-3-methylisooxazole, m.p. 130° (decomp.) [p-nitrophenylhydrazone, m.p. 227° (decomp.)]. Diphenyldihydropyrazine forms an Ac derivative, m.p. 190°. E. W. W.



**Preparation of morpholine.** L. MEDARD (Bull. Soc. chim., 1936, [v], 3, 1338—1343; cf. A., 1897, i, 314; 1898, i, 601).— $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$  with 0.55 part of conc.  $\text{H}_2\text{SO}_4$  at 175—180° affords morpholine, isolated as the hydrochloride, in nearly theoretical yield. The free base is difficult to obtain anhyd. J. L. D.

**Amides and urethanes derived from morpholine.** L. MEDARD (Bull. Soc. chim., 1936, [v], 3, 1343—1347).— $\text{HCO}_2\text{H}$  with aq. morpholine (I) affords *N*-formylmorpholine, b.p. 234°/760 mm. The following are also prepared: *N*-acetyl-, b.p. 242.2—242.6°/759 mm., *N*-propionyl-, b.p. 249°/760 mm., *N*-butyryl-, m.p. 27°, and *N*-hexoyl-morpholine, b.p. 293°/760 mm. (I) with  $\text{ClCO}_2\text{Me}$  in aq.  $\text{Na}_2\text{CO}_3$  affords morpholine methylcarbamate, b.p. 212.3—212.8°/759 mm. Et (A., 1898, i, 601), *Pr*, b.p. 238°/760 mm., and morpholine butylcarbamate, b.p. 252—252.3°/760 mm., are also prepared.

J. L. D.

**N-Hydroxyaryl-substituted morpholines.**—See B., 1936, 716.

**3 : 4 : 5 : 6-Tetrahalogeno-2-amino-1-hydroxybenzenes.**—See B., 1936, 685.

**Synthesis of thiazologlyoxaline and thiazolopurine derivatives.** E. OCHIAI (Ber., 1936, 69, [B], 1650—1655).—Treatment of Et 2-thiol-4-methylglyoxaline-5-carboxylate with  $\text{CH}_2\text{ClAc}$  in EtOH in presence or absence of  $\text{NaOEt}$  affords Et 2-acetonylthiol-4-methylglyoxaline-5-carboxylate, m.p. 108—109° (hydrochloride, decomp. 171°; semicarbazone, decomp. 140°), which is converted by boiling  $\text{POCl}_3$  into Et 4'-methyl-2' : 3'-thiazolo-2 : 1-4-methylglyoxaline-5-carboxylate,  $\text{C}(\text{CO}_2\text{Et})\text{N}(\text{CMe})\text{C}(\text{CMe})\text{N}(\text{C})\text{S} \rightarrow \text{CR}$  m.p. 146—147°,

and by boiling  $\text{Ac}_2\text{O}$  containing anhyd.  $\text{NaOAc}$  into Et 5'-acetyl-4'-methyl-2' : 3'-thiazolo-2 : 1-4-methylglyoxaline-5-carboxylate, m.p. 205° (p-nitrophenylhydrazone; oxime, decomp. 256°). 8-Chlorotheophylline and  $\text{NaHS}$  in  $\text{H}_2\text{O}$  at 150—155° give 8-thioltheophylline, decomp. 320—321°, transformed by  $\text{NaOEt}$  and  $\text{CH}_2\text{ClAc}$  into 8-acetonylthioltheophylline (I), m.p. 204—205° (oxime, decomp. 244° after blackening at about 230°), which is converted by  $\text{POCl}_3$  into 4'-methyl-2' : 3'-thiazolo-8 : 7-theophylline, m.p. 263°. The attachment of  $\text{CH}_2\text{Ac}$  to S in (I) is established by the observation that 8-thioltheophylline is converted by EtBr in boiling EtOH into 8-ethylthioltheophylline, m.p. 249°, which is not desulphurised by  $\text{NaNO}_2$  and requires treatment with 20%  $\text{NaOH}$  to cause loss of EtSH. Et 2-ethylthiol-4-methylglyoxaline-5-carboxylate, m.p. 144—145°, is described. H. W.

**Anthraquinone derivatives. Anthrazazole-anthraquinonecarboxylimides.**—See B., 1936, 686.

**Structure of vitamin-B<sub>1</sub>.**—See this vol., 1159.

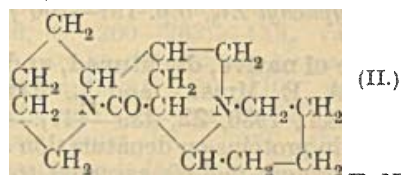
**Structure of cyanine dyes, and their optical and photographic properties II. Thiocyanines with sulphur-containing substituents.** A. I. KIPRIANOV, Z. P. SITNIKOV, and E. D. SITSCH (J. Gen. Chem. Russ., 1936, 6, 576—583).—*p*-Methylthiolacetanilide and  $\text{P}_2\text{S}_5$  at 115° yield *p*-methylthiolthioacetanilide, m.p. 114—115°, from which the expected benzthiazole derivative was not obtained

by oxidation with  $\text{K}_3\text{Fe}(\text{CN})_6$ . 1-Methylbenzthiazole and  $\text{HNO}_3\text{--H}_2\text{SO}_4$  afford 5-nitro-1-methylbenzthiazole, m.p. 164—165°, reduced by  $\text{SnCl}_2$  in  $\text{HCl}$  to the 5-NH<sub>2</sub>-compound, m.p. 122°, which is diazotised and treated at 70° with aq.  $\text{K}_2\text{CS}_3$ , the xanthate obtained is boiled with EtOH-KOH, and the product is treated with  $\text{Me}_2\text{SO}_4$ , to yield 5-methylthiol-1-methylbenzthiazole, the ethiodide, m.p. 215°, of which yields 5 : 5'-dimethylthiol-2 : 2'-diethylthiocarbocyanine iodide (I) with Et orthoformate and  $\text{C}_6\text{H}_5\text{N}$  (1.5 hr. at the b.p.), and the 8-Me derivative of (I) when treated with Et orthoacetate and  $\text{C}_6\text{H}_5\text{N}$  (1.5 hr. at the b.p.).  $\text{NaSMe}$  in EtOH yields methylthiolpyruvonnitrile,  $\text{SMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CN}$  (II), b.p. 74.5°/20 mm., with  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CN}$ , and Et ethylthiolpyruvate, b.p. 174—176°, with  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ . (II) and EtOH-HCl yield β-methylthioethyliminoether hydrochloride,  $\text{SMe}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{HCl}$ , readily decomp. in EtOH to afford Et methylthiolorthoacetate,  $\text{SMe}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})_2$ , b.p. 78—80°/30 mm., which condenses with 1-methylbenzthiazole ethiodide (III) in  $\text{C}_6\text{H}_5\text{N}$  or EtOH to yield 2 : 2'-diethyl-8-methylthiolmethylcarbothiocyanine iodide. The corresponding 8-SEt derivative is prepared from (III) and β-ethylthioethyliminoether,  $\text{SEt}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , b.p. 103—104° (prepared as above from ethylthiolpyruvonnitrile, b.p. 104—105°). Introduction of S-containing groups into carbothiocyanine dyes does not affect their sensitising and stabilising properties. R. T.

**Alkaloids of Heliotropium lasiocarpum. VI. Synthesis of pyrrolidine derivatives.** G. MENSCHIKOV and J. SCHDANOVITSCH (Ber., 1936, 69, [B], 1799—1802).—Addition of  $\text{Pr}^n\text{CN}$  to a solution of Mg and  $\text{OMe}[\text{CH}_2]_3\text{I}$  in  $\text{Et}_2\text{O}$  gives γ-methoxy-β-methylheptan-δ-one, b.p. 198—199°/1 atm., the oxime, b.p. 124—125°/12 mm., of which is reduced by Na and  $\text{Bu}^n\text{OH}$  to δ-amino-γ-methoxy-β-methylheptane (I), b.p. 200.5—201°/1 atm. (I) is converted by 50% HBr at 150—155° into 2-isobutylpyrrolidine, b.p. 163—164°/1 atm., which with  $\text{CH}_2\text{O}$  and  $\text{HCO}_2\text{H}$  affords 1-methyl-2-isobutylpyrrolidine (I), b.p. 163.5—165°/1 atm. (picrate, m.p. 138—139°; platini-chloride, m.p. 138—140°). 1-Methyl-2-*n*-butylpyrrolidine (II) is obtained similarly from  $\text{Pr}^n\text{CN}$ . Neither (I) nor (II) is identical with *dl*-dihydrode-N-methylheliotridane. H. W.

**Lupin alkaloids. X. Synthesis of *dl*-oxy-sparteine.** G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1936, 1025—1028; cf. A., 1933, 841).—Attempted Claisen condensation of 2 mols. of Me pyridyl-2-acetate under varying conditions yields complexes, m.p. 177° and 295°, only. Et piperidyl-2-acetate (I),  $\text{ClCO}_2\text{Et}$ , and  $\text{Na}_2\text{CO}_3$  (18 hr.; room temp.) afford Et 1-carbethoxypiperidyl-2-acetate, b.p. 148—150°/9 mm., converted into the acid, m.p. 65°, by refluxing with  $\text{C}_6\text{H}_6\text{--NaOEt}$  (6 hr.) followed by conc.  $\text{HCl}$  (12 hr.; 100°). (I) with  $\text{CH}(\text{OEt})_2$  and  $\text{Ac}_2\text{O}$  (2 hr.; reflux) yields 1-carbethoxy-4-keto-3-(2'-pyridyl)pyridocoline, b.p. 250—255°/1 mm., m.p. 126° (picrate, m.p. 216°), reduced ( $\text{Pt--AcOH--H}_2$  at 100 lb. per sq. in.) to impure 1-carbethoxy-4-keto-3-(2'-piperidyl)octahydropyridocoline, b.p. 200—210°/1 mm.; this on Bouveault reduction forms the corresponding 1-carbinol, which with  $\text{PBr}_3$  gives

1-bromomethyl-4-keto-3-(2'-piperidyl)octahydropyridocoline, converted by heating with  $K_2CO_3$  (18 hr.;  $100^\circ$ ) into *dl*-oxysparteine (II) [methiodide, m.p. 203—204°; hydriodide, m.p. 275° (decomp. 345°)], identical with that obtained by oxidation [ $NaOH \cdot K_3Fe(CN)_6$ ] of *dl*-sparteine (A., 1928, 1030). The structure of (II) is hence as shown.



F. N. W.

Lupin. XI. Alkaloids of *Lupinus barbariger*, S. Wats. J. F. COTCH (J. Amer. Chem. Soc., 1936, 58, 1296—1299).—Sparteine [dihydrobromide (+ $H_2O$ ), m.p. 197°; methiodide, m.p. 239—240°; zincchloride, m.p. 316—317°], *dilupine* (I), provisionally  $C_{16}H_{26}O_2N_2$ , an oil,  $[\alpha]_D^{20} + 65.59^\circ$  in  $H_2O$  (hydrobromide, m.p. 233—234°), *trilupine* (II),  $C_{15}H_{23}O_3N_2 \cdot 2H_2O$ , m.p. (anhyd.) 252°,  $[\alpha]_D^{20} + 63.76^\circ$  in  $H_2O$  [platnichloride (+ $4H_2O$ ), m.p. 224° (decomp.); aurichloride (+ $4H_2O$ ), m.p. 188—189° (decomp.)], and basic and much resinous material are isolated (method: A., 1935, 97) from the dry plant. (I) and MeI give a methiodide,  $C_{16}H_{26}ON_2 \cdot MeI$ , m.p. 253°, suggesting that (I) is a *C*-methyl-lupanine *N*-oxide. (II) is probably *d*-lupanine 1:9-dioxide (for nomenclature, see this vol., 741). Thus, (II) heated with acids affords the salts of *d*-lupanine (III) [dihydrochloride (+ $H_2O$ ), m.p. 163—164°; aurichloride, m.p. 206°], whilst (III) is oxidised ( $CaO_2 \cdot H_2O$ ) to (II). (II) and MeI give (probably) the 9-methiodide, m.p. 127°, of *d*-lupanine 1-oxide.

H. B.

Cocaine syntheses from hyoscyamine. I. Preparation of tropinonecarboxylic esters. N. A. PREOBRAZHENSKI, M. N. SCHTSCHUKINA, and R. A. LAPINA (Ber., 1936, 69, [B], 1615—1618).—Tropinone and  $Et_2CO_3$  condense readily in the presence of molten Na to Et tropinonecarboxylate (+ $2H_2O$ ), m.p. 64—65° (corresponding picrate, m.p. 151°). With  $Me_2CO_3$  the production of Me tropinonecarboxylate (+ $2.5H_2O$ ), m.p. 96—98° (corresponding picrate, m.p. 163—164°), is better achieved with the more readily fusible K. Both condensations are preferably performed in an inert solvent of suitable, high b.p., e.g., xylene.

H. W.

Amine oxides of alkaloids. X. Action of hydrogen peroxide on hydrastinine and hydrohydrastinine. XI. *NN'*-Dioxide of *NN'*-dimethylpiperazine. XII. *N*-Oxide of sparteine. MAX and MICHEL POLOXOVSKI (Bull. Soc. chim., 1936, [v], 3, 885—888, 888—891, 891—898).—X. Hydrastinine (I) with  $COMe_2 \cdot H_2O_2$  gives dehydrohydrastinine and hydrastinine anhydride, whilst hydrohydrastinine (II) yields its *N*-oxide (hydrochloride, m.p. 199—200°; hydrobromide, m.p. 174—175°), converted by  $SO_2$  into a *N*-sulphonic ester, (I), and (II). The formation of (I) is interpreted by means of a mol. transposition.

XI. Dimethylpiperazine with  $H_2O_2 \cdot COMe_2$  gives its *NN*-dioxide, m.p. 269° from  $CHCl_3$  and m.p. 239° from EtOH (dihydrochloride, m.p. 208—209°), from which the base is regenerated by  $SO_2$  and by Zn-HCl.

It is acid to litmus and slightly alkaline to Me-orange, and may be determined by silicotungstic acid.

XII. Dioxysparteine (III) (A., 1887, 1056; 1897, 231), obtained from sparteine and  $H_2O_2 \cdot COMe_2$ , and previously considered to be an *NN*-dioxide (cf. A., 1919, i, 414), is shown to be sparteine *N*-monoxide hydrate, m.p. 129° [hydrobromide, m.p. 138°; hydriodide (IV), m.p. 147°; dihydrochloride, m.p. 153°; dihydrobromide, m.p. 155°; dinitrate, m.p. 97—98°; dipicrate, m.p. 150°], which with KI gives (IV). The alleged methiodide of (III) (cf. *loc. cit.*) is shown to be (IV). The above di-salts lose some acid at 100° [cf. the alleged product,  $C_{15}H_{26}O_2N_2 \cdot 1.5HBr \cdot H_2O$  (*loc. cit.*)].

H. G. M.

Alkaloids of Chinese *Corydalis* tubers. (*Corydalis ambigua*, "Yen-Hu-So"). M. HUANG (Ber., 1936, 69, [B], 1737—1745).—The drug is moistened with  $Al_2(SO_4)_3$  solution and extracted with  $C_6H_6$ , thus yielding corydaline, m.p. 134—135°, and unidentified bases and considerable amounts of a volatile oil containing small amounts of crystals, m.p. 84—86°, which are not identical with cedrol and are possibly dimyristyl alcohol. Renewed extraction of the residue with  $C_6H_6$  after saturation of it with  $NH_3$  gives protopine, corybulbine, *r*-tetrahydropalmatine (identical with the corydalis *B* of Chou), *r*-tetrahydrocoptisine (corydalis *E*), and *l*-tetrahydrocoptisine (corydalis *D*). Extraction of the residue with EtOH yields coptisine and mesocorydaline.

H. W.

New alkaloids of ergot: ergosine and ergosinine. S. SMITH and G. M. TITMUS (Nature, 1936, 137, 1075).—By treatment with acids  $C_{30}H_{35}O_5N_5$  (this vol., 351) ("ergosinine") is converted into an isomeride, ergosine, decomp. 228°,  $[\alpha]_D^{20} -194^\circ$  in  $CHCl_3$ .

L. S. T.

Alkaloids of *Fritillaria roylei*. I. Isolation of peimine. Y. F. CHI, Y. S. KAO, and K. J. CHANG (J. Amer. Chem. Soc., 1936, 58, 1306—1307).—Details are given for the isolation of peimine (I),  $C_{26}H_{43}O_3N$  (not  $C_{19}H_{30}O_2N$ ; cf. Chou and Chen, A., 1932, 1178), m.p. 224° [hydrochloride, m.p. 295° (decomp.); hydrobromide, m.p. 293.5—294°; *H* sulphate, m.p. 278—280°; platnichloride, m.p. 233—235° (decomp.); aurichloride, m.p. 164—165°], from the corms. Verticin (*loc. cit.*) is probably (I).

H. B.

New derivatives of *p*-arsanilic acid. VII. *p*-Arsonoazelanilic and *p*-arsonozebacanilic acids and related compounds. G. T. MORGAN and E. WALTON (J.C.S., 1936, 902—905; cf. A., 1935, 768).—With  $SOCl_2$  Me H azelate yields its acid chloride, b.p. 150—155°/15 mm., which with Na *p*-arsanilate yields Me *p*-arsonoazelanilate (I) (*Na* salt). The Et compound (II) was similarly obtained through the acid chloride; b.p. 156—160°/20 mm. (I) and (II) are hydrolysed to the corresponding acid, which with  $SO_2 \cdot HCl$  affords crude *p*-dichloroarsinoazelanilic acid, hydrolysed to *p*-oxyarsinoazelanilic acid. The following amides, *p*-AsO $\cdot H_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot [CH_2]_7 \cdot COR$ , were prepared from (I) and the corresponding amine: R=NH, [*Na* salt (+ $H_2O$ )], NHMe (*Na* salt), NH $Et$  [*Na* salt (+ $3H_2O$ )]. Azelayl dichloride and Na *p*-arsanilate afford azelanilide-*pp'*-diarsonic acid (*Na*<sub>2</sub>



salt). With  $\text{SOCl}_2$  Me H sebacate (modified prep.) yields its acid chloride (III), b.p.  $177^\circ/23$  mm., which with Na *p*-arsanilate forms Me *p*-arsonosebacanilate (Na salt). The Et compound (Na salt) was similarly prepared. These esters are hydrolysed to the acid [Na salt (+ $\text{H}_2\text{O}$ )], which affords *p*-dichloroarsinosebacanilic acid, m.p.  $130-135^\circ$ , hydrolysed to *p*-oxyarsinosebacanilic acid. The following amides,  $\text{AsO}_3\text{H}_2\cdot\text{C}_8\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_8\cdot\text{COR}$ , are described:  $\text{R}=\text{NH}_2$  [Na salt (+ $\text{H}_2\text{O}$ )],  $\text{NHMe}$  [Na salt (+ $\text{H}_2\text{O}$ )],  $\text{NMe}_2$  (Na salt). (III) with  $\text{NH}_2\text{Ph}$  gives Me sebacanilate, m.p.  $67-68^\circ$  (free acid, m.p.  $121-122^\circ$ ). The corresponding acid chloride with *p*-arsanilic acid (at  $150^\circ$ ) forms sebacanilide-*p*-arsonic acid (Na salt). Sebacyl dichloride with Na-*p*-arsanilate and  $\text{Na}_2\text{CO}_3$  affords sebacanilide-*pp'*-diarsonic acid (Na salt). The Na salts of these compounds have a higher toxicity than those of the earlier series (A., 1931, 636; 1933, 290) but there is no increase in curative action.

F. N. W.

Organic compounds of mercury. XIII. Preparation of a new type of asymmetric organic mercury compounds as proof of the structure of alkanol- and  $\beta$ -alkyloxyalkyl-mercuri-salts. A. N. NESMEJANOV and R. C. FRIEDLINA (Ber., 1936, 69, [B], 1631-1635).—Confirmation of Hofmann's formulation of alkanol- and  $\beta$ -alkyloxyalkyl-mercuri-salts is found in their reaction with Sn aryl halides thus:  $2\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgX} + \text{SnAr}_2\text{X}_2 + 4\text{NaOH} = 2\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgAr} + \text{H}_2\text{SnO}_3 + 4\text{NaX} + \text{H}_2\text{O}$ . Thus Sn *p*-ditolyl dichloride and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}$  in boiling EtOH containing KOH afford Hg *p*-tolyl  $\beta$ -hydroxyethyl, m.p.  $52.5-53.5^\circ$ , quantitatively converted by 15% HCl into  $\text{C}_6\text{H}_5$  and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{HgCl}$ . cycloHexene (I) and  $\text{Hg}(\text{OAc})_2$  in  $\text{H}_2\text{O}$  give *o*-hydroxyacetomercuricyclohexane, m.p.  $112.5-113^\circ$ , transformed by  $\text{SnPh}_2\text{Cl}_2$  into Hg Ph *o*-hydroxycyclohexyl, m.p.  $101-102^\circ$ . (I) and  $\text{Hg}(\text{OAc})_2$  in EtOH yield *o*-ethoxyacetomercuricyclohexane, m.p.  $79^\circ$  after softening at  $76^\circ$ , whence Hg Ph *o*-ethoxycyclohexyl. Chloromercurimethyldihydrobenzofuran and  $\text{SnPh}_2\text{Cl}_2$  yield 1-phenylmercurimethyl-1:2-dihydrobenzofuran, m.p.  $60-61^\circ$ .  $\text{PhNCO}$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}$  in boiling  $\text{C}_6\text{H}_6$  afford bromomercuriethyl phenylcarbamate, m.p.  $124-126^\circ$ .

H. W.

Mercury derivatives of azo-dyes. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 499-501).—*p*-Aminophenylmercuriacetate, diazotised and coupled with *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  in dil. NaOH affords 4-hydroxymercuri-2'-amino-4'-hydroxyazobenzene; similarly *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  yields 4-hydroxymercuri-3'-nitro-4'-hydroxyazobenzene. These substances are too insol. for therapeutic use.

F. O. H.

Reactions of hexaethyldistannane and diethylstannane with organic mercury compounds as a method of preparing organic compounds of tin with substituents in the benzene nucleus. K. A. KOZESCHKOV, A. N. NESMEJANOV, and V. P. PUSIREVA (Ber., 1936, 69, [B], 1639-1642).—Reactions are described which proceed according to the schemes:  $\text{Sn}_2\text{R}_6 + \text{HgAr}_2 = 2\text{SnR}_3\text{Ar} + \text{Hg}$ ;  $\text{Sn}_2\text{R}_6 + \text{HgArCl} = \text{SnR}_3\text{Ar} + \text{Hg} + \text{SnR}_3\text{Cl}$  (where  $\text{Ar} = \text{Ph}$ ,  $\text{OH}\cdot\text{C}_6\text{H}_4$ , or  $\text{NMe}_2\cdot\text{C}_6\text{H}_4$  and  $\text{R} = \text{Et}$ ) and

$\text{Sn}_2\text{R}_6 + \text{HgCl}_2 = 2\text{SnR}_3\text{Cl} + \text{Hg}$  or  $\text{SnR}_2 + \text{HgCl}_2 = \text{SnR}_2\text{Cl}_2 + \text{Hg}$ . The compounds,  $\text{SnR}_3\text{Ar}$ , are heavy, colourless liquids which first lose Ar under the action of Br or  $\text{Hg}^{++}$  solutions. They reduce  $\text{AgNO}_3\text{-EtOH}$  or  $\text{PtCl}_4$ . The following are new: Sn *p*-dimethylaminophenyl  $\text{Et}_3$ , b.p.  $172-173^\circ/3$  mm. (complex compound with  $\text{AuCl}_3$ ); substance  $\text{SnEt}_3\text{Br}\cdot 2\text{NH}_3$ ; Sn *p*-hydroxyphenyl  $\text{Et}_3$ , b.p.  $197-200^\circ/3$  mm.

H. W.

Structure of native, denatured, and coagulated proteins. A. E. MIRSKEY and L. PAULING (Proc. Nat. Acad. Sci., 1936, 22, 439-447).—The changes which occur in proteins on denaturation are reviewed. The native protein mol. is assumed to consist of a polypeptide chain, folded into a uniquely defined configuration in which it is held by H-linkings between the peptide N and O atoms, and between the free  $\text{NH}_2$  and  $\text{CO}_2\text{H}$  of the diamino- and dicarboxyl amino-acid residues. The denatured protein mol. is characterised by the absence of a uniquely defined configuration, and thus lacks sp. properties. This view is supported by the difference of entropy between native and denatured proteins, and the heat change and activation energy of denaturation. Reagents causing denaturation [*e.g.*,  $\text{EtOH}$ ,  $\text{CO}(\text{NH}_2)_2$ ] are substances which affect H-linking formation. The action of ultra-violet light on the native protein mol. is to cause a break in the mol. so that it can be denatured at a lower temp. after illumination than before. Dehydration consists primarily in the coagulation of the protein mols. without loss of their special configurations.

A. J. M.

Glucoproteins. II. Polysaccharides of vitreous humour and of umbilical cord.—See this vol., 1138.

Apparatus for the microhydrogenation of organic compounds. H. JACKSON and R. N. JONES (J.C.S., 1936, 895-899).—An improvement of the apparatus of Smith (A., 1932, 619), the method of shaking being modified, the means of introducing the substance improved, and complete compensation for temp. changes made.

F. R. S.

Application of Andrews' iodine monochloride method to the iodine bromide process.—See this vol., 1081.

Recent advances in micro-analysis. II. Functional analysis. (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1936, 45, 313-333; cf. this vol., 1080).—A review of methods for determining various org. groups.

R. C. M.

Determination of hydroxyl groups in organic compounds. M. FREED and A. M. WYNNE (Ind. Eng. Chem. [Anal.], 1936, 8, 278-279).—The substance is heated to the b.p. with 2 c.c. of 20%  $\text{C}_5\text{H}_5\text{N-Ac}_2\text{O}$  reagent, cooled, boiled with  $\text{H}_2\text{O}$  for 5 min., and the AcOH titrated with NaOH (cresolphthalein), if necessary after adding EtOH to facilitate dissolution. Accurate results are obtained with most substances except sugar alcohols (2-5% low) and *tert*-alcohols (no reaction).

S. C.

Micro-determination of acetyl groups. A. ELEK and R. A. HARTE (Ind. Eng. Chem. [Anal.], 1936, 8, 267-269).—4-10 mg. of substance are hydrolysed with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ , the resultant solution is

evaporated to dryness in vac., and AcOH and SO<sub>2</sub> determined in the distillate iodometrically. A suitable apparatus is described. The method is relatively simple and accurate. S. C.

**Determination of the concentration of vaporised carbon tetrachloride.** J. C. OLSEN, H. F. SMYTH, G. E. FERGUSON, and L. SCHEFLAU (Ind. Eng. Chem. [Anal.], 1936, 8, 260—263).—CCl<sub>4</sub> vapour in air (>10 p.p.m.) can be determined by passing the gas through a SiO<sub>2</sub> tube at 1000—1100° and absorbing the HCl produced in H<sub>2</sub>O or NaOH. The R.H. of the air stream must be <70% otherwise Cl<sub>2</sub> is formed. Absorption is facilitated by using a sintered glass disc and by adding EtOH (5%) or 1% of a 0.1% saponin solution to the absorbent. S. C.

**Determination of volatile fatty acids by the partition method.** O. L. OSBURN, H. G. WOOD, and C. H. WERKMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 270—275).—The method described previously (A., 1933, 933) has been applied to fermentation liquors containing AcOH, EtCO<sub>2</sub>H, and PrCO<sub>2</sub>H. Mixtures of two acids may be analysed by using one partition coeff. between H<sub>2</sub>O and Et<sub>2</sub>O; mixtures of three acids require two coeffs. Nomographic methods are used. HCO<sub>2</sub>H is determined separately.

S. C.

**Reagent [mercuric chloride+sodium ethoxide] for determination of structure [of organic compounds].** R. CONNOR and J. H. VAN CAMPEN (J. Amer. Chem. Soc., 1936, 58, 1131—1134).—Treatment of CHR'R''COR and CHRY.CO<sub>2</sub>R' (Y=labilising group; R=H, Alk, or Ar) dissolved in EtOH-NaOEt with EtOH-HgCl<sub>2</sub> gives a colourless (or nearly so) ppt. (+ test). The test is limited to neutral compounds containing C, H, and O only. The behaviour of >200 compounds is investigated.

H. B.

**Acidity determination in non-aqueous solutions.** O. TOMIČEK and J. FELDMANN (Časopis českoslov. Lek., 1935, 15, 127—137; Chem. Zentr., 1935, ii, 2980).—Potentiometric titrations of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, BzOH, and salicylic acid in a wide range of solvents are described. A Te electrode (prep. described in detail) is useful in such titrations.

H. N. R.

**Differentiation between aldehydes and ketones.** E. GRAF (Anal. Fis. Quim., 1936, 34, 91—94).—Ketoximes and aldioximes with nascent Cl (freshly prepared solution of KMnO<sub>4</sub> in dil. HCl) give respectively a bluish-green coloration due to chloro-nitroso-compounds, and chloro-oximino-compounds which give a red colour with FeCl<sub>3</sub>. The reaction is not given by certain aromatic aldehydes.

F. R. G.

**Scheme for investigation of compounds containing the carbonyl group.** E. GRAF (Anal. Fis. Quim., 1936, 34, 95—99).—The reaction between compounds containing ·CO· and NH<sub>2</sub>OH.HCl is made the basis of a scheme for the recognition of acid chlorides, anhydrides, ketones, aldehydes, amides,

esters, lactones, and org. acids (cf. Feigl, A., 1934, 790, and preceding abstract). F. R. G.

**Analytical uses of Nessler's reagent. Determination of monosaccharides and disaccharides. Determination of furfuraldehyde.** II. M. GOSWAMI and B. C. DAS-PURKAYSTHA (J. Indian Chem. Soc., 1936, 13, 315—322).—Arabinose (2), glucose (4), fructose (5), sucrose (9), lactose (5), and maltose (5) may be determined by adding K<sub>2</sub>HgI<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, and dissolving the ppt. of Hg in excess of I, which is then determined volumetrically; for furfuraldehyde (2), Na<sub>2</sub>CO<sub>3</sub> is replaced by NaOH. The figures in parenthesis indicate the no. of O atoms utilised by 2 mols. of the sugar for oxidation. The method may be used for blood-sugar. F. R. S.

**Oxidation of amino-acids. Determination of the keto-acids and [detection of the] hydrogen peroxide produced.** F. BERNHEIM, L. C. BERNHEIM, and A. G. GILLASPIE (J. Biol. Chem., 1936, 114, 657—663).—When *dl*-alanine, *l*-valine, *d*-serine, *d*-leucine, *l*-isoleucine, *d*-phenylalanine, *dl*-methionine, *dl*- or *l*-proline, or *d*-histidine is oxidised by purified kidney enzymes, 54—98% of keto-acids are formed [as detected by H sulphite compounds or 2:4-dinitrophenylhydrazones (I), which do not give identical results]. H<sub>2</sub>O<sub>2</sub> is also formed, being detected by formation of methemoglobin. (I) are determined by reaction with I (2 I consumed) and back-titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

R. S. C.

**Precision combustion of natural products.** L. F. FIESER and R. P. JACOBSEN (J. Amer. Chem. Soc., 1936, 58, 943—947).—Baxter and Hale's method (this vol., 540) is adapted for use of about 1 g. of material. The following are analysed (the results agree with the theoretical vals. within about 0.02% for C and 0.01% for H): BzOH; C<sub>6</sub>H<sub>5</sub>Ph<sub>3</sub>; dihydro-cholesterol; dehydrodeoxycholic acid; chlorogenin, whence C<sub>27</sub>H<sub>44</sub>O<sub>4</sub> (cf. Liang and Noller, A., 1935, 673); sarsasapogenin, whence C<sub>27</sub>H<sub>44</sub>O<sub>3</sub> (cf. Simpson and Jacobs, *ibid.*, 864, 1248); fichtelite, whence C<sub>19</sub>H<sub>34</sub> (cf. Ruzicka and Waldmann, *ibid.*, 741).

**Determination of 5-methylfurfural[dehyde].** H. A. IDDLIS and K. S. FRENCH (Ind. Eng. Chem. [anal.], 1936, 8, 283—285).—5-Methylfurfuraldehyde is quantitatively pptd. with either 2:4-dinitrophenylhydrazine or thiobarbituric acid. It may also be determined by pptn. with phloroglucinol if a factor is introduced for the solubility of the ppt. Absorption of Br is erratic (varies from 2 to 5 mols.) and the volumetric KBrO<sub>3</sub>-KBr method is not therefore satisfactory.

S. C.

**Salting-out and salting-in microchemical reactions.** B. V. J. CUVELIER (Natuurwetensch. Tijds., 1936, 18, 73—74).—ZnHg(SCN)<sub>4</sub> is best prepared from Zn(NO<sub>3</sub>)<sub>2</sub> and NaHg(SCN)<sub>3</sub>. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is the best salt for salting-out nicotine. Antipyrine can be salted-out from H<sub>2</sub>O solution with Na<sub>2</sub>SO<sub>4</sub> or NaCl either in crystals, or in oily droplets.

S. C.



## Biochemistry.

Gaseous exchange in the human lung. I. Oxygen content and tension in arterial and venous blood. II. Equilibrium between oxygen tensions in alveoli and blood. K. MATTHES. III. Circulation and respiration during bodily work. K. MATTHES and W. HAUSS. IV. Gaseous exchange in the lungs during bodily work. K. MATTHES, M. BÖHME, and K. TIETZE (Arch. exp. Path. Pharm., 1936, **181**, 630—639, 640—654, 655—665, 666—673; cf. this vol., 91).—I. The degree of  $O_2$  saturation of a few drops of blood (from the capillaries) is determined photometrically, using a modified form of Kramer's apparatus (A., 1935, 371). Changes in the amount of light transmitted through the ear (after injection of histamine) registered by means of a photo-electric cell are a logarithmic function of the degree of arterial  $O_2$  saturation. When other vals. for arterial and venous blood are determined and calc. all the essential factors determining gaseous exchange in the lungs are known. The resting and (moderate) working vals. for degree of  $O_2$  saturation and tension of venous blood are 66 and 52% and 35 and 29 mm. of Hg respectively.

II. The difference between the  $O_2$  tensions in alveoli and blood when the inspired air has reduced  $[O_2]$  is  $<$  the val. calc. on the basis of the theory of incomplete equilibrium. This may be due to increase in the no. of all the alveolar capillaries.

III. The increased diffusion const. of gaseous exchange in the lungs during moderate exercise is explained similarly.

IV. Little reduction in the difference between the  $O_2$  tensions in alveoli and blood is caused by inspiring air of reduced  $O_2$  content when bodily work is performed and the rule of incomplete equilibrium holds apparently because the increase in the no. of alveolar capillaries reaches its limit as a result of the work alone. W. McC.

Effect of the composition of inspired air on the circulation through the brain. L. IRVING and M. S. WELCH (Quart. J. Exp. Physiol., 1935, **25**, 121—129).—Inhalation of 10%  $CO_2$  in  $O_2$  increased the blood-flow in the brain but decreased that in the hind leg. Alveolar  $O_2$  deficiency did not cause these changes. The  $CO_2$  pressure changed more rapidly in brain than in the leg. CH. ABS. (p)

Reflex regulation of respiration from the carotid sinus. G. STELLA (Quart. J. Exp. Physiol., 1935, **25**, 145—153).—Effects were more marked during respiration in air than in an atm. containing  $CO_2$  (3—5%) and air. CH. ABS. (p)

Breath odours from alliaceous substance. Cause and remedy. H. W. HAGGARD and L. A. GREENBERG (J. Amer. Med. Assoc., 1935, **104**, 2160—2163).—Odour comes entirely from particles of garlic or onions retained in the mouth. Expired air showed 0.0028—0.0035 mg. of diallyl sulphide per litre. Rinsing with 3%  $NH_4Cl$  destroyed all odour. CH. ABS. (p)

Oxygen dissociation curve of hæmoglobin in dilute solution. R. HILL and H. P. WOLFEKAMP

(Proc. Roy. Soc., 1936, **B**, **120**, 484—495).—Dil. suspensions of human blood corpuscles and whole blood show similar  $O_2$ -dissociation curves, but dil. solutions of human hæmoglobin have a three-fold increased affinity for  $O_2$ . The blood of other animals shows similar effects, to varying extents. F. A. A.

Gaseous nitrogen content of the blood. G. LEINER (Z. klin. Med., 1935, **128**, 560—567; Chem. Zentr., 1935, ii, 2837).—The mean normal  $N_2$  content is 1.2 vol.-%. It is increased in severe emphysema, bronchitis, and hypoxæmia. R. N. C.

Formation of hæmatoidin *in vitro* from mammalian erythrocytes. J. S. F. NIVEN (J. Path. Bact., 1935, **41**, 183—197).—Cryst. hæmatoidin was formed within macrophages from added erythrocytes in cultures of mammalian tissues. In some cases a diffuse yellow pigment, giving a diffuse Fe reaction, preceded the appearance of formed pigment. CH. ABS. (p)

Local formation of blood-pigments. R. MUIR and J. S. F. NIVEN (J. Path. Bact., 1935, **41**, 183—197).—In mice and rats formation of granular and cryst. pigment from subcutaneously injected erythrocytes is intracellular. Phagocytosis of erythrocytes is followed by production of diffuse and granular forms of hæmosiderin. Hæmatoidin (I) is formed subsequently (cf. preceding abstract). Similar effects are produced by injection of hæmoglobin. (I) is not produced in rabbits by this treatment. CH. ABS. (p)

Delicate test for blood-pigments. C. B. JENSEN and W. M. URBAIN (Food Res., 1936, **1**, 275—276).—The pigment is converted into nitrosohæmoglobin or nitrosohæmochromogen and then, by treatment with  $H_2O_2$ , into a green compound. E. C. S.

Derivatives of blood-pigments.—See this vol., 1129.

Ultra-violet spectrum of normal and leucæmic blood. I. MAGAT and M. MAGAT (Compt. rend., 1936, **202**, 2181—2184).—The ultra-violet absorption curve of the blood of leucæmic fowls lies slightly above that of the normal fowl between 200 and 450 m $\mu$ , especially between 240 and 290 m $\mu$ . Absorption bands at 411, 343, 280, and 240 m $\mu$  found by Suhrmann and Kollath (A., 1927, 688) are confirmed: a further max. occurs at 289.5 m $\mu$  (possibly due to material accompanying cancerous growths). F. N. W.

Absorption spectra of some modified snake venoms. H. F. HOLDEN (Austral. J. Exp. Biol., 1936, **14**, 121—130).—The hæmolysins were fairly resistant to dil. acid at 60° and very little change in the absorption spectra was observed, even when most of the hæmolysin was inactivated. In alkaline solution, inactivation was rapid and the absorption bands were rapidly obliterated. With  $CH_3O$  the hæmolysins were inactivated but changes in the spectra were irregular. H. G. R.

Blood-sugar of the bee (*Apis mellifica*). R. BEUTLER (Naturwiss., 1936, **24**, 486—491).—The blood-sugar of bees varies from 0 to 4% (and in a few

cases up to 7%; average 2%), is partly fermentable, and, together with the high serum-P, is probably related to muscular activity of flight. F. O. H.

**Glycerol content of the organism.** E. TRABUCHI (Boll. Soc. ital. Biol. sperim., 1932, 7, 916—921).—The glycerol (I) content of the blood of rabbits after injection  $\propto$  the amount of (I) injected, and is related to the amount fixed in the organs; the last two are independent of one another. The amount of (I) recoverable from the blood 5 min. after injection often reaches double the amount calc. on the basis of a uniform distribution throughout the organism. The concn. curve of (I) does not fall below this val. but stabilises itself. Injection of insulin immediately following (I) causes a fall of blood-(I). R. N. C.

**Protein and urea in the blood of rabbits infected with *Trypanosoma annamense*.** H. LAUNOY and H. LAGODSKY (Compt. rend. Soc. Biol., 1936, 122, 1055—1058).—During the first 15 days the albumin:globulin ratio decreased, there being an increase in globulin and a decrease in albumin. Total and urea-N do not vary, but hypercholesterolemia occurs. H. G. R.

**Blood [changes in anaemia and other diseases].** R. ISAACS, C. C. STURGIS, F. H. BETHELL, and S. M. GOLDHAMER (Arch. Int. Med., 1936, 57, 1186—1246).—A review of recent literature. E. D. Y.

**Extracting morphine from organ tissues, especially blood.** F. SUZUKI (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 50—51).—The sample is incubated with papain, digested with 0.2 vol. of EtOH, and repeatedly shaken with  $\text{CHCl}_3$ . Morphine in the  $\text{CHCl}_3$  extract is adsorbed on fuller's earth, re-extracted with  $\text{CHCl}_3$ , and titrated by Gordin's method with alizarin-red. CH. ABS. (p)

**Two mechanisms for the formation of hexose diphosphate from glucose in intact human erythrocytes.** Z. DISCHE (Naturwiss., 1936, 24, 462).—Phosphorylation of glucose in erythrocytes takes place by the transference of  $\text{PO}_4'''$  from adenosinetriphosphoric acid. In erythrocytes kept at 0° for some time, a second method involving intermediate formation of adenosinediphosphoric acid occurs. The latter process only is prevented by 0.004N- $\text{CH}_2\text{I}-\text{CO}_2\text{H}$ . A. L.

**Transfer of inorganic phosphorus across the red blood-cell membrane.** L. HALPERN (J. Biol. Chem., 1936, 114, 747—770).—In 29 out of 33 analyses of inorg. P in red blood cells and in serum, more inorg. P was present per unit of  $\text{H}_2\text{O}$  in serum than in cells, the differences ranging from 0.42 to 9.81 mg. per 100 c.c. of  $\text{H}_2\text{O}$ . At 3° there was no diffusion of inorg. P across the cells, and at 23° the process was very slow, but at 37.5° there was a large increase in diffusion, possibly related to the metabolism of glucose in the cell rather than to the temp. When carbohydrate metabolism *in vivo* was accelerated by injection of glucose and insulin, the concn. of inorg. P in cells and serum decreased. Addition of glucose and NaF *in vitro* at incubator temp. caused inorg. P to enter the cell during glycolysis, but this diffused out again when glycolysis was complete even though the concn.

in the serum was already > that in the cells. The simple laws of diffusion cannot explain the transfer of inorg. P, which seems to depend mainly on the metabolic processes in the cell. J. N. A.

**Oligolytic concentrations of saline with respect to the erythrocytes of the blood of various animal species.** S. MATUZAKI (Keijo J. Med., 1936, 7, 113—155).—Haemolysis curves and oligolytic concns. were determined. The curves are sp. for each species, but there is a similarity between those of related species. J. N. A.

**Somatic phenomenon of the weaning of children with respect to the water content of the blood.** T. RYÖ (Keijo J. Med., 1936, 7, 1—19).—Methods for determining  $\text{H}_2\text{O}$  content are discussed, and that of Kuroda (A., 1933, 1094) is recommended. The amount of  $\text{H}_2\text{O}$  decreases with age, but there is a sharp rise in  $\text{H}_2\text{O}$  content in boys from 250 to 400 days, and in girls from 400 to 500 days old, and then a decrease, corresponding with the period of weaning. In animals the  $\text{H}_2\text{O}$  content is high at birth, then falls to a lower level, and then rises at weaning and falls again, whilst with children the  $\text{H}_2\text{O}$  content is rather less at birth, and there is not the preliminary fall before weaning. J. N. A.

**Content of bromine in blood.** G. MORUZZI and P. GUARESCHI (Arch. Ist. Biochim. Ital., 1936, 8, 229—248).—Br' is determined in presence of I' and high [Cl'] by a modified Palmer-Clarke method (A., 1933, 312) with an error of approx.  $2 \times 10^{-5}$  g. Blood-Br of man and various animals is  $35 \pm 25 \times 10^{-5}\%$ . Approx. 40—80% of serum-Br is diffusible, whilst the distribution of Br between serum and corpuscles is uniform relative to their  $\text{H}_2\text{O}$  content. F. O. H.

**Blood-forming action of copper.** G. DOLFINI and S. CASUCCIO (Rass. Clin. Terap., 1933, 32, 291—318; Chem. Zentr., 1935, ii, 2837). R. N. C.

**Blood-iodine in clinical practice.** E. P. McCULLAGH and D. R. McCULLAGH (Arch. Int. Med., 1936, 57, 1061—1066). E. D. Y.

**Influence of diuretics on the alkali reserve of blood.** G. GOTTSEGEN (Wien. klin. Woch., 1935, 48, 1116—1118; Chem. Zentr., 1935, ii, 2840).—In general, the alkali reserve is increased by diuretics. H. N. R.

**Effect of bleeding on distribution of ions between erythrocytes and plasma in health and in hypertony and nephritis.** I. F. SCHMITT and W. BASSE (Arch. exp. Path. Pharm., 1936, 181, 584—597).—Removal of 500 c.c. of venous blood causes reduction (followed, in healthy persons, by a rise above the initial val.) in the  $\text{CO}_2$ -binding capacity of the blood in healthy and diseased persons. [Cl'], [Na'], and [K'] fall in the erythrocytes and rise in the plasma, but the increase in the plasma is only partly at the expense of the erythrocytes. [Ca'] rises in the plasma and erythrocytes. The effects in disease are < in health. W. McC.

**Porphyrin in the serum of foetuses and newborn children.** R. FIKENTSCHER (Klin. Woch., 1935, 14, 569—571).—The sera contain an  $\text{Et}_2\text{O}$ -sol. porphyrin spectroscopically different from proto-



porphyrin, and resembling most closely coproporphyrin. It is not present in the maternal serum.

R. N. C.

#### Blood-serum-lipins in cancer and other cases.

**I. Mean mol. wt. of the free and combined acids.** H. H. BARBER. **II. Ultra-violet absorption measurements.** L. A. WOODWARD (Biochem. J., 1936, 30, 1463—1467, 1467—1471).—I. No variation was observed in the sap. val. of the serum-lipins of normal and cancerous blood.

**II.** The shape of the absorption curve of an extract from blood-serum cannot be used as a diagnostic test for cancer.

H. G. R.

**Alexic properties of protein-C.** M. DOLADILHE and M. MICHEL (Compt. rend., 1936, 202, 1950—1952; cf. this vol., 875).—The capacity for hæmolysis possessed by alexic guinea-pig or human serum is enhanced or diminished as the concn. of protein-C derived from a foreign or homologous serum is increased. The effect is complementary when C is derived from fresh serum, but if C is heated for 15 min. at 57°, it is without effect on the hæmolysis. Serum deprived of its globulins (cf. this vol., 495) has no hæmolytic power until fresh C is added and is the greater the more C is present.

J. L. D.

**Modifications in the protein fractions of serum during periods of rest and crisis in anaphylaxis.** AUBRY, THIODET, and RIBERE (Compt. rend. Soc. Biol., 1936, 122, 947—950).—In a crisis the equilibrium is normal or low and is increased during periods of rest.

H. G. R.

**Hæmolysis and cholesterologeneses.** V. DE LAVERGNE and P. KISSEL (Ann. Inst. Pasteur, 1936, 57, 56—78).—The hypercholesterolaemia produced by inoculation with hæmolytic bacteria can be simulated by the use of saponin and solanine, if the surrounding medium is not sufficiently acid to ppt. the cholesterol.

P. G. M.

**Mechanism of hæmolysis from the point of view of active mass in heterogeneous systems.** H. NAKAMURA and K. KURODA (Keijo J. Med., 1936, 7, 20—97).—The active mass in the hæmolytic system can be distinguished from that in the ordinary heterogeneous system, for in the erythrocyte the system is not only heterogeneous, but is restricted by the cell wall. The "mechanical active mass," the kinetic active mass given to erythrocytes by mechanical agitation, is an important factor in hæmolysis. With const. temp., proportion of erythrocytes, and "mechanical active mass," the degree of hæmolysis is high in dil. saline; increase of [NaCl] causes a sudden fall to a min. val., and then, as the concn. increases, it slowly rises again. The concn. for min. hæmolysis differs markedly from the isotonic concn. and is 1—2% NaCl for ox, and 3% for hen, erythrocytes. It is called the "oligolytic concn.," and is sp. for each animal species. If the "mechanical active mass" be taken into account, hæmolysis occurs in isotonic saline, as well as in more conc. solutions. Washing erythrocytes with isotonic saline affects cell resistance. High and low temp. accelerate hæmolysis, but a medium temp. is almost without effect, and that temp. which causes

a min. hæmolysis is called the "oligolytic temp." Hæmolysis instantly reaches a max. when erythrocytes are placed in hypo-oligolytic saline, whilst action is very slow in iso- or hyper-oligolytic solutions. The  $\eta$  of the system retards hæmolysis because it diminishes the mechanical active mass. Hæmolysis increases with an increase of erythrocytes up to a certain val., but it decreases with high concns. of erythrocytes.

J. N. A.

**Classical theory of blood coagulation and its modern development.** E. WOHLISCH (Naturwiss., 1936, 24, 513—517).—A review.

**Clotting of blood and milk. I. Physical and chemical influences.** M. F. VON DUNGERN and G. NELZ (Z. Biol., 1936, 97, 277—296).—The clotting times of (human) blood ( $t_1$ ) and (cow's) milk ( $t_0$ ) are logarithmically related to the temp. Removal of CO<sub>2</sub> in a vac. lowers  $t_1$  to 3.5 min. at 25°, but does not affect  $t_2$ , whilst saturation with CO<sub>2</sub> raises  $t_1$  to 6 min. but diminishes  $t_2$ ; air, O<sub>2</sub>, N<sub>2</sub>O, and coal gas have no effect on either  $t_1$  or  $t_2$ . The vals. of  $t_1$  and  $t_2$  vary considerably according to the nature of the interface, those with glass and quartz (which are more easily wetted) being < those with paraffin wax etc.

P. G. M.

**Anti-complex of fibrin.** S. S. PEROV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1934, No. 6, 3—22).—Blood-fibrin consists of the proto-acid (this vol., 1037), combined with another protein, the "anticomplex." Isolation of the latter is described. In 1% solution, unlike the complex (fibrinic acid), it has very low  $\eta$ .

CH. ABS. (p)

**Tests for innocuity and antigenic potency of staphylococcus toxoid.** C. E. DOLMAN and J. S. KITCHING (J. Path. Bact., 1935, 41, 137—162).—Standardisation and formalinisation of toxins are examined.

CH. ABS. (p)

**Haptens and inhibition of the hæmolytic power of certain immuno-sera.** R. D. DE LA RIVIERE, N. KOSSOVITCH, and S. ISHII (Compt. rend. Soc. Biol., 1936, 122, 1045—1048).—Inoculation with hapten results in formation of the corresponding antibody only if protein is injected at the same time.

H. G. R.

**Nature of the tubercular antibody. Existence of protein-fat antibodies.** K. MEYER (Compt. rend. Soc. Biol., 1936, 122, 1037—1038).—In certain anti-tubercular sera, antibodies which react equally well with the protein- or fat-antigen of *B. tuberculosis* are present.

H. G. R.

**Size of antibodies.** J. BISCOE, F. HERÖIK, and R. W. G. WYCKOFF (Science, 1936, 83, 602—603).—The sedimentation consts. of several conc. antibody preps. are of the same order of magnitude as those of the globulins of normal sera. Antibody properties are not necessarily associated with exceptionally large mol. size.

L. S. T.

**Purification of antibodies in type I antipneumococcus serum; nature of the type-specific precipitin reaction.** B. F. CHOW and W. F. GOEBEL (J. Exp. Med., 1935, 62, 179—202).—Fractionation of the antibody protein by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

and dialysis yields a relatively inert euglobin and an active pseudoglobulin. The immune globulin contains 14.85% N; the antibody protein has approx. 2.75% of lipin and a prosthetic carbohydrate grouping. The distribution of basic  $\text{NH}_2$ -acids in globulins of normal and immune horse serum is similar except for a slight difference in lysine content. Replacement of one H in the primary  $\text{NH}_2$  by Ac largely decreases the capacity of the immune protein to ppt. the type-sp. polysaccharide. The specificity of the antibody protein is lost on treatment with  $\text{CH}_2\text{O}$ . Esterification shows the  $\text{CO}_2\text{H}$  to be of primary importance in rendering the type I polysaccharide serologically reactive; replacement of the  $\text{NH}_2$  or OH has a less pronounced effect. CH. ABS. (p)

**Ultracentrifugal and electrophoretic studies on antibodies.** M. HEIDELBERGER, K. O. PEDERSEN, and A. TISELIUS (Nature, 1936, 138, 165).—A horse-serum prep. of type I pneumococcus anti-carbohydrate showed almost homogeneous sedimentation with the const.  $S_{20}=17.2 \times 10^{-13}$ . The electrophoresis was homogeneous with an isoelectric point at  $p_H$  4.8. With horse antibodies the antibody function is connected with a heavy, and otherwise minor, component. With rabbit sera homogeneous sedimentation was obtained with no appreciable difference between the consts. of the globulin fractions of normal serum and immune serum, or of normal globulin and immune globulin containing up to 50% of anti-ovalbumin, or antibody to type III pneumococcus polysaccharide containing 90% of precipitin. The rabbit appears to produce antibody from the principal globulin component. L. S. T.

**Auto-antibody production for bone-marrow.** V. BURKE, C. F. BRADLEY and N. P. SULLIVAN (Res. Stud. State Coll. Washington, 1935, 3, 1—11).—Complement-binding iso- and auto-antibodies develop in rabbits following injection of rabbit bone-marrow antigen. Changes in the blood picture resemble anaemia and are less marked after subsequent injections. Anti-bone-marrow serum is non-haemolytic. Auto-agglutinins active at room temp. occur in some rabbits after bone-marrow injections. A. G. P.

**Hydrogen-ion concentration of Hortegea cells.** S. TAKEUCHI (Z. Klin. Path. Hamatol. [Japan], 1933, 2, 341).—Vals. obtained were very close to those of reticulo-endothelial cells and differed from those of oligodendroglia and astrocytes. CH. ABS. (p)

**Iodometric determination of small amounts of morphine in viscera.** S. IKESHIMA (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 51—52).—With 0.005N-I morphine (I) gives a const. ppt. [1 mol. of (I) with 2.55 atoms of I]. By this means 1 mg. of (I) is determined with an accuracy of 90%. CH. ABS. (p)

**Nitroprusside reaction as a test for reduced glutathione.** N. S. R. MALOEUF (Nature, 1936, 138, 75—76).—This test is sp. for reduced glutathione in normal living tissues when aq.  $\text{NH}_3$  is used as the alkali and no heat is applied. L. S. T.

**Microscopy of powdered, desiccated endocrine glands.** P. A. MATTIS (Amer. J. Pharm., 1936,

108, 276—302).—Methods for the identification of characteristic histological elements in powdered ovary, corpus luteum, thyroid, and pituitary preps. are described. F. O. H.

**Unsaponifiable matter of chrysalis oil.** J. OZAKI and B. KASAI (J. Agric. Chem. Soc. Japan, 1936, 12, 425—456).—Chrysalis oil from *Bombyx mori* contains 2.93% of unsaponifiable matter which consists of 18.07% of hydrocarbons ( $\text{C}_{23}\text{H}_{46}$ ,  $\text{C}_{24}\text{H}_{50}$ ,  $\text{C}_{26}\text{H}_{54}$ , and  $\text{C}_{28}\text{H}_{58}$ ) and 81.93% of sterols (cholesterol and sitosterol). J. N. A.

**Chemistry of insects. II. Woolly aphis and white pine chermes.** B. K. BLOUNT (J.C.S., 1936, 1034—1036).—The woolly aphis, *Eriosoma lanigerum*, Hausmann, gives a wax and a cryst. orange pigment, *lanigerin* (I),  $\text{C}_{17}\text{H}_{14}\text{O}_5$ , with 3 active H. (I) is probably a substituted polyhydroxy-anthraquinone. The white pine chermes, *Adelges (Pineus) strobi*, Börner, affords in addition to a wax, m.p. 106.1—106.4°, a dark purple-brown pigment, *strobilin* (II),  $\text{C}_{30}\text{H}_{24}\text{O}_8$ , with 3 active H. (II) gives the colour reactions of a substituted 2-hydroxy-phenanthraquinone. J. H. B.

**Coccids produced in Japan. IX. Carbohydrates and waxy substances of *Icerya purchasi*, Mask.** M. KONO and R. MARUYAMA (J. Agric. Chem. Soc. Japan, 1933, 11, 647—658).—The insect contained lignin 10.7, cellulose 0.7, pentosan 0.9, and mannan 1.9%. *l*-Arabinose was present in aq. extracts.  $\text{C}_6\text{H}_6$  extracts yield a wax ( $d_{15}^{20}$  0.914, m.p. 78°, sap. val. 157.5) of which ceryl alcohol, cerotic and palmitic acids and a resin acid,  $\text{C}_{10}\text{H}_{16}\text{O}_4$ , were the principal constituents, together with 31% of unsaponifiable matter. CH. ABS. (p)

**Growth and water content of the bones of newly born pups and kittens.** C. M. BURNS and N. HENDERSON (Biochem. J., 1936, 30, 1202—1206).—The  $\text{H}_2\text{O}$  content of very young bone, which depends mainly on the size and  $\text{H}_2\text{O}$  content of the epiphysis and marrow cavity, increases in the long bones shortly after birth chiefly because of increase in the  $\text{H}_2\text{O}$  content of the diaphysis. The  $\text{H}_2\text{O}$  contents of the femora, humeri, and tibiae exhibit no consistent differences. W. McC.

**Mineral constituents of bone. II. Effect of age on mineral constituents of bones from kittens and pups.** C. M. BURNS and N. HENDERSON (Biochem. J., 1936, 30, 1207—1214; cf. A., 1935, 1396).—The salt content of the diaphysis (especially cancellous tissue) decreases immediately after birth. Later, the Ca content of the cortex increases slowly whilst that of the cancellous tissue remains low in the kitten and increases slowly in the pup. In temporary tissues (e.g., calcified cartilage) the ratio  $\text{CO}_3^{2-}/\text{Ca}$  is low but it increases in tissues which are more slowly destroyed. In the bones of the adult dog and cat the ratio approaches that in dahlite. W. McC.

**apoCholic and dehydroapocholic acid.** D. ADLERSBERG and B. LUSTIG (Arch. exp. Path. Pharm., 1936, 181, 610—616).—Compared with apocholic acid, dehydroapocholic acid has less reducing effect on the surface tension of  $\text{H}_2\text{O}$ , less haemolytic action,



and lower toxicity but it has greater stimulating effect on bile secretion. Hence dehydrogenation of bile acids leads to reduction of toxicity and increased stimulating effect on bile secretion. W. McC.

**Nucleic acids of the pancreas. II. *allo*-Nucleic acid.** H. STEUDEL (Z. physiol. Chem., 1936, 241, 84—92; cf. A., 1935, 646).—*allo*Nucleic acid (I), the chief nucleic acid of the nucleoprotein (II) of the pancreas, contains guanylic (III) and adenylic acid in the ratio 4 : 1, cytosylic and possibly uracylic acid. (III) is eliminated from (II) by alkaline hydrolysis, which also removes one half of (III) from (I) more easily than the other. Partly purified (I) (P : N ratio of Cu salt 1 : 1.9) is obtained from (II) by treatment with Ba(OAc)<sub>2</sub> followed by pptn. with Cu(OAc)<sub>2</sub>. W. McC.

**Crystalline substances from the adrenal gland.**—See this vol., 1117.

**X-Ray analyses of keratins.** A. GEROUD and G. CHAMPETIER (Bull. Soc. Chim. biol., 1936, 18, 656—664).—The mucous body of malpighi (the epidermis giving rise to keratins) and several schizokeratins and sclerokeratins give the same X-ray diagram, indicating that they all possess the  $\alpha$ -keratin structure. The longitudinal unit spacing of the polypeptide skeleton is therefore unchanged during the process of keratin formation. A. L.

**Constituents of unsaponifiable matter of sperm blubber oil.**—See this vol., 1091.

**Absorption spectrum of bilirubin.**—See this vol., 1048.

**Absorption spectra of cerebrospinal fluid.** M. PAIC (Compt. rend. Soc. Biol., 1936, 122, 1029—1031).—The course of the absorption curve and the optical density of the max. (280 m $\mu$ )  $\propto$  the protein content. No difference was observed between serologically positive or negative fluids. H. G. R.

**Histospectrography of the corneal ring of Kayser and Fleischer.** A. POLICARD, P. BONNET, and G. BONAMOUR (Compt. rend. Soc. Biol., 1936, 122, 1120—1122).—Traces of Cu in the region of the ring only were found; Ag, Fe, and Zn were absent. H. G. R.

**Action of alkaline persulphate on amino-acids.** K. LANG (Z. physiol. Chem., 1936, 241, 68—70).—NH<sub>3</sub>, frequently in almost theoretical yield, is eliminated from NH<sub>2</sub>-acids by boiling with alkaline aq. K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. With aliphatic (NH<sub>2</sub>)<sub>1</sub>-acids CO<sub>2</sub> is also eliminated and the corresponding aldehydes are produced in yields which are poor but increase as the mol. wt. of the acid increases. With monoamino-dicarboxylic acids, serine, and cystine extensive decomp. accompanies NH<sub>3</sub> liberation. With diamino-monocarboxylic acids and arginine >1 but <2 mols. of NH<sub>3</sub> are liberated and with phenylalanine, tyrosine, and tryptophan the NH<sub>3</sub> yields are < theoretical. Proline loses CO<sub>2</sub> and yields an unstable pyrroline (*reineckate*, m.p. 195—210°). Alkaline K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> also attacks urea, creatine, and creatinine, with liberation of < the theoretical amount of NH<sub>3</sub>. W. McC.

**Effect of denaturation on colloidal behaviour of ovalbumin.**—See this vol., 1068.

**Spreading properties of azoproteins in the dermis.** A. CLAUDE (J. Exp. Med., 1935, 62, 229—244).—The spreading property of azoproteins when introduced intradermally is not specifically influenced by the aromatic component or the type of protein but is derived from the presence of the azo-group. It is controlled by the no. of diazo-groups in the protein mol. and  $\propto$  the concn. of the solution. Azo-compounds of low mol. wt. have no significant effect on skin permeability. CH. ABS. (p)

**Mechanism of coagulation of proteins by tannic acid.** S. S. PEROV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1935, No. 7, 26—38).—Tannic acid (I) ppts. protein, not by chemical combination with it but by increasing the [H<sup>+</sup>] to approach the isoelectric point. (I) may be adsorbed by pptd. protein. CH. ABS. (p)

**Glucoproteins. II. Polysaccharides of vitreous humour and of umbilical cord.** K. MEYER and J. W. PALMER [with E. M. SMYTH] (J. Biol. Chem., 1936, 114, 689—703; cf. A., 1935, 232).—Hyaluronic acid (I), from vitreous humour, is obtained substantially free from N-contaminants by means of Zn(OH)<sub>2</sub>; hydrolysis gives 1 mol. each of glucosamine and (?) glycuronic acid. Aq. extraction of umbilical cord gives a substance similar to (I) (probably derived from Wharton's jelly), and alkaline extraction of the residue gives a sulphuric ester (probably derived from the connective tissue) which yields chondrosamine. The viscosity of polyuronic acids depends on their source and treatment. Artificial mucoids are obtained from polyuronic acids and proteins. R. S. C.

**Nitrogen and phosphorus compounds of the muscles of thyroidectomised animals.** E. KRATINOVA (Ukrain. Biochem. J., 1932, 5, 58—70).—In the muscles of thyroidectomised rabbits and dogs, the H<sub>2</sub>O content was definitely and the creatine content but slightly increased, the creatinephosphoric acid was markedly decreased, whilst the residual N underwent no regular change. W. O. K.

**Oxygen dissociation curves of muscle-haemoglobin.** R. HILL (Proc. Roy. Soc., 1936, B, 120, 472—483).—Dissociation curves, determined spectroscopically, of heart muscle-haemoglobin (I) of ox, sheep, dog, and goose differ from those of blood-(I) in being hyperbolic and depending little on  $p_{H_2}$ , as recently found for horse heart muscle-(I) (Millikan, this vol., 1012). Muscle-(I) has a much higher O<sub>2</sub> affinity than blood-(I). The physiological function of muscle-(I) is discussed. F. A. A.

**Creatine derivatives. I. Presence of creatinine in muscular tissue. II. Supposed creatine of the residue of nervous and muscular tissues extracted with acids.** I. CIACCIO (Boll. Soc. ital. Biol. sperim., 1934, 9, 227—229, 229—231).—I. Extracts of frog muscle give a positive Jaffe reaction, which, however, is not sp. for creatinine.

II. The residue always gives a positive Jaffe reaction, the substance responsible, determined as creatine (I), representing approx. 1/3 of the amount of (I) extracted by CCl<sub>3</sub>·CO<sub>2</sub>H. It probably originates from the hydrolysis of acid-insol. protein-like material;

the amount is increased by heating for 2 hr. It is not adsorbed on kaolin, and is therefore not (I).

R. N. C.

**Cholesterol content of muscle.** W. R. BLOOR (J. Biol. Chem., 1936, 114, 639—648; cf. A., 1935, 109).—The cholesterol (I) contents of the different types of muscle were sharply differentiated and in the order: unstriped > cardiac > striped; it is suggested that a high phospholipin content, as in striped muscle, is associated with muscular activity and a high (I) content, as in unstriped muscle, with a more extensive nerve supply.

H. D.

**Rapid production of cholesterol from brain.** I. REMESOV and N. LEVASCHIOVA (Z. physiol. Chem., 1936, 241, 81—83).—Pure cholesterol (I) in 83% yield is obtained in 24 hr. by grinding 1 kg. of pulped brain in portions for 3—4 hr. with 4.5 vols. of liquid air, shaking the moist powder thus obtained twice with 2.5-litre portions of cold anhyd.  $\text{COMe}_2$ , filtering, evaporating the solvent under reduced pressure, and crystallising the residue from  $\text{EtOH-Et}_2\text{O}$ . A further amount of crude (I) is obtained by extracting the dried residue from the  $\text{COMe}_2$  treatment with hot  $\text{COMe}_2$ .

W. McC.

**Milk sera for refractometric studies.** R. TURNAU (Oesterr. Chem.-Ztg., 1936, 39, 121—124).—The refractive properties of two  $\text{CCl}_4$  sera of milk containing milk 50 c.c.,  $\text{CCl}_4$  5 c.c., and 20%  $\text{AcOH}$  1 c.c., one being prepared from heated (20 min. at  $100^\circ$ ) and subsequently cooled milk, are described. The heated milk serum shows the same  $n$  as Cu, Pb, and Ca acetate sera.

W. L. D.

**Determination of urine in milk.** L. BURUIANA (Lait, 1936, 16, 698—705).—Normal cow's urine [0.26% creatinine (I) content] contains 120 times as much (I) as does milk. The serum obtained by  $\text{CaO-Cu}$  pptn. of the milk-proteins uniformly contains 35% of the (I) of the milk. (I) in the serum is determined photometrically by the picrate method, which detects 1% of urine.

W. L. D.

**Differential reactions of human and cows' milk.** II. M. POLONOVSKI and F. MORENO MARTÍN (Anal. Fis. Quím., 1935, 33, 887—904; cf. A., 1935, 1267).—Three new methods are proposed to determine the amount of cows' milk or  $\text{H}_2\text{O}$  added to human milk. (a) 1 c.c. of milk is neutralised (phenolphthalein with 0.01N-NaOH, and the "buffer index" (c.c. of 0.01N- $\text{H}_2\text{SO}_4$  required for neutralisation in presence of Me-orange) is determined. This index varies with composition, from 2.5 for cows' to 10 for human milk. (b) 0.1 g. of the butter is saponified and distilled. The "volatile acid index" (c.c. of 0.01N-NaOH required to neutralise the acids using phenolphthalein)  $\propto$  the composition, from 0.3 for human to 6.5 for cows' milk. This method cannot give accurate vals. with separated milks. (c) Total carbohydrates, determined by the dichromate method of Polonovski *et al.* (A., 1931, 251),  $\propto$  the composition from 5 g. for cows' to 8 g. per litre for human milk.

F. R. G.

**Nitrogenous constituents of milk and their separate determination in human milk.** F. MORENO MARTÍN (Anal. Fis. Quím., 1935, 33, 905—

930).—In 2 c.c. of human milk total N is determined by the micro-Kjeldahl method, casein by pptn. with  $\text{NaOAc}$  and  $\text{AcOH}$  at  $p_H$  4.2, and albumin by pptn. with tannic acid.

F. R. G.

**Heat-coagulation of caseinogen. II. Rate of phosphorus cleavage.** G. R. HOWAT and N. C. WRIGHT (Biochem. J., 1936, 30, 1413—1415; cf. A., 1934, 1119).—When aq. solutions of Ca caseinogenate were heated at  $90$ — $115^\circ$  for 1—45 hr. the degree of coagulation varied directly with the liberation of acid-sol. P;  $Q_{10}$  was approx. 3.

H. D.

**Agglutinins in human milk.** S. AMAGASA (Z. Klin. Path. Hamatol. [Japan], 1932, 1, 99).—Colostrum, ripe milk, and final milk each contains one of the corresponding blood-group agglutinins. Colostrum and final milk have higher agglutination titres than has blood serum, and frequently show a non-sp. group agglutination.

CH. ABS. (p)

**Disturbing colorations in the lactic acid limit reaction for the stomach content.** G. SANT (Pharm. Tijds. Nederl.-Indie, 1935, 12, 223; Chem. Zentr., 1935, ii, 2854).—Addition of 3%  $\text{H}_2\text{O}$ , prevents disturbing side-colorations.

H. N. R.

**Effect of Schiff's zwieback on secretion of gastric glands.** S. D. FRUMIN (Problems of Nutrition [Russia], 1933, 2, No. 3, 56—60).—Administration of zwieback to dogs is followed by a type of gastric secretion intermediate between those produced by a meat and a bread diet. The amount and acidity of the secretion are greater when the dry product is used. Continuous feeding lowers the secretory function in 6 days.

CH. ABS. (p)

**Influence of soya beans on gastric secretion.** A. R. STRIGANOVA (Problems of Nutrition [Russia], 1933, 2, No. 4, 33—44).—The effect of soya-bean diet on gastric secretion is intermediate in character between those of bread and of meat diets. Soya-bean protein may serve, to some extent, as a substitute for meat protein.

CH. ABS. (p)

**Effect of hydrolysates of casein and those from the intestine on the secretion of gastric glands.** P. N. KURDJUMOV (Problems of Nutrition [Russia], 1933, 2, No. 5, 61—68).—Addition of the hydrolysate to a bread and  $\text{H}_2\text{O}$  diet for dogs increased gastric secretion. The latter was lowered by additions of milk and not appreciably affected by additions of meat.

CH. ABS. (p)

**Reactions of the contents of the jejunum and experimental production of peptic ulcer.** P. P. T. WU (Arch. Surg., 1935, 30, 557—562).

CH. ABS. (p)

**Determination of the hydrogen-ion concentration of the intestinal juice of the larvae of clothes- and wax-moths by means of the glass electrode.** F. DUSERVA (Z. physiol. Chem., 1936, 241, 168—176).—The  $p_H$  of a few drops of the juice (also of alkaline liquids in absence of  $\text{CO}_2$  and suspensions) is determined with a special type of glass electrode. The average  $p_H$  of juice from clothes- and wax-moths are 9.9 and 8.4, respectively. The val. is probably not affected by the quality of the food consumed.

W McC



**Origin of choline in semen.** E. KAHANE and J. LÉVY (Compt. rend., 1936, 202, 2186—2188).—The existence of free choline in semen is due to the action of an enzyme on a precursor. F. N. W.

**Urinary ammonia.** S. MIKAËLOFF (Bull. Soc. chim., 1936, [v], 3, 1048—1052).—The results of standard methods of determination are compared. The advantages of Sahli's method are discussed.

E. S. H.

**Determination of meconic acid in urine of opium addicts.** I. S. To and K. Yo (Japan. J. Med. Sci., IV, No. 1; Proc. Japan. Pharm. Soc., 1933, 6—9).—The sample is made alkaline with NaOH, treated with  $\text{CaCl}_2$ , filtered after 1 hr., and the ppt. dissolved in AcOH. A few drops of dil. HCl are added together with  $\text{FeCl}_3$ . The intensity of the red colour is measured. Samples showing colour with HCl but no  $\text{FeCl}_3$  are discarded. Tests on opium addicts are recorded. Positive reactions are obtained in most cases. Non-addicts all showed negative tests. Administration of meconic acid to man and animals caused a positive test in urine for 1—3 days.

CH. ABS. (p)

**Determination of morphine in urine of opium and of morphine addicts: practical application of the reaction.** S. To and A. RIN (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharm. Soc., 1933, 11—15).—The acidified (HCl) urine is conc., filtered, made alkaline with aq.  $\text{NH}_3$ , and extracted with  $\text{CHCl}_3$ . After evaporation of the  $\text{CHCl}_3$  the residue is dissolved in aq.  $\text{NH}_3$  and morphine (I) is extracted with  $\text{H}_2\text{SO}_4$ . After further treatment with aq.  $\text{NH}_3$ , (I) is extracted by  $\text{CHCl}_3$  and determined by customary methods. (I) is eliminated in urine of opium and (I) addicts. Applied in conjunction with the meconic acid test (preceding abstract) the test serves to distinguish the two classes of addicts. CH. ABS. (p)

**Acetoacetic acid in urine.** Constitution of the coloured compounds formed in the reaction of acetoacetic acid and its ester with sodium nitroprusside in presence of ammonia (with or without ammonium sulphate) and certain amines. F. E. RAURICH SAS (Anal. Fís. Quím., 1935, 33, 247—278).—The use of Lange's test for  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$  and  $\text{COMe}$ , in urine (cf. Fischer, A., 1934, 546) has been shown to be valueless by Bohrisch (Pharm. Zentr., 1907, 48, 181 *et seq.*). The test proposed by the author (A., 1935, 513) produces the complex  $\text{Na}_2[\text{Fe}''(\text{CN})_4(\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{NH}_2)_2]\cdot 2\text{H}_2\text{O}$ , or, with  $\text{NH}_2\text{Me}$  instead of  $\text{NH}_3$ ,  $\text{Na}_2[\text{Fe}''(\text{CN})_4(\text{NHMe}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\cdot)\text{NH}_2\text{Me}]\cdot 2\text{H}_2\text{O}$ .

F. R. G.

**Determination and excretion of flavins in normal human urine.** A. EMMERIE (Nature, 1936, 138, 164).—Flavins are determined colorimetrically in urine after addition of PbS, elution with  $\text{H}_2\text{O}$ ,  $\text{C}_5\text{H}_5\text{N}$ -AcOH, and oxidation with  $\text{KMnO}_4$  in AcOH solution. Normal male urine gives a daily output of  $819\text{--}1250 \times 10^{-6}$  g., and the hourly excretion varies between  $30 \times 10^{-6}$  and  $50 \times 10^{-6}$  g. After consumption of cooked ox liver an increased excretion of flavins occurs.

L. S. T.

**Uro- and copro-porphyrin-I in acute porphyrinuria.** H. FISCHER and H. LIBOWITZKY

(Z. physiol. Chem., 1936, 241, 220—222).—Uroporphyrin-I (I) and the ester of uroporphyrin-III have been isolated from the urine of acute porphyrinuria. Uroporphyrin ester has m.p.  $311^\circ$  (corr.). In chronic porphyrinuria, (I) is probably the chief porphyrin produced. The Cu reaction indicates that urobilin frequently occurs in urine and faeces. W. McC.

**Determination of fat in faeces.** P. MULLER (Nederl. Tijds. Geneesk., 1935, 79, 3960—3962; Chem. Zentr., 1935, ii, 2712).—Extraction with acid  $\text{COMe}_2$  is followed by evaporation and extraction of the residue with light petroleum. H. N. R.

**Acetonæmia in goats.** A. T. GILYARD and R. T. GILYARD (Cornell Veter., 1935, 25, 201—202).—The  $\text{COMe}_2$  content of a goat in late twin pregnancy in a state of paresis was lowered by injection of glucose.

CH. ABS. (p)

**Mineral exchange between plasma and erythrocytes in Addison's disease.** F. SCHMITT and W. BASSE (Arch. exp. Path. Pharm., 1936, 181, 581—583).—In a case  $[\text{Cl}']$  was low in the plasma and  $[\text{Cl}']$ ,  $[\text{Na}']$ , and  $[\text{Ca}']$  low and  $[\text{K}']$  high in the erythrocytes. Administration of cortin, NaCl, and  $\text{NaHCO}_3$  had favourable results and partly restored normal vals. for the ionic contents.

W. McC.

**Chemical changes in the blood in Addison's disease and their alteration in response to treatment.** E. N. ALLOTT (Lancet, 1936, 230, 1406—1411).—Cases of Addison's disease show low Na and Cl in the serum with high K and urea. Cortical extract appears to reduce K and urea to normal with little effect on Na and Cl. L. S. T.

**Role of sodium in adrenal insufficiency.** R. F. LOEB, D. W. ATCHLEY, and J. STAHL (J. Amer. Med. Assoc., 1935, 104, 2149—2154).—The decreased blood-Na observed in adrenal insufficiency results from increased excretion. Salt therapy mitigates symptoms of Addison's disease until destruction of adrenals is complete.

CH. ABS. (p)

**Release of a histamine-like substance from lungs of guinea-pigs during anaphylactic shock.** I. DE B. DALY, S. PEAT, and H. SCHILD (Quart. J. Exp. Physiol., 1935, 25, 33—59).—The reported increase in intestine-contracting substance in lungs of sensitised guinea-pigs and decrease after anaphylactic shock (Watanabe, 1932) is not confirmed. A histamine-like substance appears in the perfusate of isolated lungs during shock. CH. ABS. (p)

**Soil, iron, and copper and iron in the prevention and treatment of anaemia in suckling pigs.** H. C. H. KERNKAMP (J. Amer. Vet. Med. Assoc., 1935, 40, 37—58).—Development of anaemia was prevented by ingestion of powdered loamy soil in appropriate amounts. Use of Fe instead of soil was not effective, and addition of Cu to Fe had no additional beneficial effect.

CH. ABS. (p)

**Determination of the biologically potent element (cobalt) in limonite.** E. J. UNDERWOOD and J. F. FILMER (Austral. Vet. J., 1935, 11, 84—92).—The active element is Co, deficiency of which in foods causes enzootic marasmus. CH. ABS. (p)

Castle's intrinsic factor in pernicious anaemia. C. C. UNGLEY and R. MOFFETT (Lancet, 1936, 230, 1232—1235). L. S. T.

Spontaneous appearance of beri-beri symptoms in the mandarin duck (*Aix galericulata*, L.) kept in captivity. K. LI-PIN (Compt. rend. Soc. Biol., 1935, 119, 1114—1115). R. N. C.

Renal changes in biliary stasis and decompression in cats. H. L. STEWART, A. CANTAROW, and D. R. MORGAN (Arch. Path., 1935, 19, 807—818).—Changes in the distribution of stainable lipins are examined. CH. ABS. (p)

Nitrogen and sulphur metabolism in Bright's disease. G. B. GRABFIELD and B. PRESCOTT (Arch. Int. Med., 1936, 57, 1081—1084).—The N:S ratio of urinary protein in nephrosis is 30:1, in glomerular nephritis and other syndromes 20:1, and normally 250:1. E. D. Y.

Histological changes in the enamel and dentine of the rat incisor in acute and chronic experimental fluorosis. I. SCHOUR and M. C. SMITH (Arizona Agric. Exp. Sta. Tech. Bull., 1934, No. 52, 69—91).—F probably exerts a direct local action on the enamel-forming cells. Changes observed in enamel and dentine are not produced primarily by changes in blood-Ca and -P or by disturbances of the parathyroid. A. G. P.

Distribution of ions between plasma and erythrocytes. (A) In normal and hypochloræmic diabetics. (B) In nephritis. (C) In intestinal diseases. F. SCHMITT (Arch. exp. Path. Pharm., 1936, 181, 563—569, 570—574, 575—580).—(A) Sharp separation of erythrocytes from plasma is attained by using a special type of centrifuge tube. In the erythrocytes of hypochloræmic diabetics [Cl'] is very high and [Na'] (frequently), H<sub>2</sub>O, and cations are low. In the plasma [Na'] is low and [K'] and [Ca''] are high.

(B) In the erythrocytes of nephritis (hypochloræmic) [Cl'] is high and [Na'] normal. In the plasma [Na'] is low. When hyperchloræmia occurs [Na'] is normal in the plasma but [Cl'] and (frequently) [Na'] are high in the erythrocytes. In eclamptic uræmia the concn. of all electrolytes in the erythrocytes is high and plasma-Na is normal. Acidosis occurs in all cases.

(c) In stenosis of the pylorus there is genuine hypochloræmia. In carcinoma of the stomach and in cases of operable tumours there are no changes in the distribution of the ions. In cases of inoperable tumours [Cl'] in the erythrocytes is low (lower limit 92 mg. per 100 c.c.). W. McC.

Citric acid in blood and urine. O. OESTBERG (Z. ges. exp. Med., 1934, 94, 442—452; Chem. Zentr., 1935, ii, 3256).—Citric acid (I) is > normal in the blood in decompensation of the heart and diabetes mellitus, and less in inflammatory diseases, particularly pleurisy; the changes are associated with metabolic disturbances. (I) excretion can be altered by administration of acid or alkali without affecting blood-(I), with which it is unrelated. R. N. C.

Sodium chloride in diphtheria. A. MACLEAN (Lancet, 1936, 231, 129—131).—Administration of NaCl has a beneficial effect. There is probably a deficiency of Na and Cl in the blood-serum in the acute stage of diphtheria. L. S. T.

Muscular dystrophies. Presence of simple guanidine derivatives in the urine. M. X. SULLIVAN, W. C. HESS, and F. IRREVERRE (J. Biol. Chem., 1936, 114, 633—637).—From the urine of 70% of the cases of muscular dystrophy studied, guanidine (I) was isolated after treatment with AgNO<sub>3</sub> and Ba(OH)<sub>2</sub>. Aq. solutions of gluco-cyamidine and -cyamidine, but not of creatine, creatinine, or arginine, yield (I) by this treatment. Normal individuals do not excrete (I). H. D.

Prevention of nutritional encephalomalacia in chicks by vegetable oils and their fractions. M. GOETTSCH and A. M. PAPPENHEIMER [with A. HART] (J. Biol. Chem., 1936, 114, 673—687).—The protective factor against nutritional encephalomalacia of chicks in certain edible oils is EtOH-sol., stable to heat, ultra-violet irradiation, and aeration, and is present in the unsaponifiable fraction. H. D.

Lipin exchange in the post-encephalitic syndrome. L. BARGI (Minerva med., 1935, II, 71—78).—An average increase of 42% in neutral fats, 30% in free cholesterol, and 14% in phosphatides in blood is recorded. CH. ABS. (p)

Influence of  $p_H$  and of the alkaline reserve on the production and regression of experimental exophthalmia. J. LÉVY, L. JUSTIN-BESANÇON, and D. KOHLER (Compt. rend. Soc. Biol., 1936, 122, 1058—1060).—Exophthalmia in ephedrinised dogs is diminished by acidosis and its regression augmented, whereas alkalosis has a contrary effect. H. G. R.

Gout. Changes in symptoms and purine metabolism produced by high-fat diets in four gouty patients. L. M. LOCKIE and R. S. HUBBARD (J. Amer. Med. Assoc., 1935, 104, 2072—2075).—High-fat diet increased blood-uric acid, the effect persisting after changing to a high-carbohydrate, low-fat diet. CH. ABS. (p)

Paroxysmal hæmoglobinurias. L. J. WITTS (Lancet, 1936, 231, 115—120).—A lecture. L. S. T.

Hyperglycæmia in fasted rabbits following injury in the pituitary region. D. J. DAWSON and A. MILNE (Quart. J. Exp. Physiol., 1935, 25, 69—76). CH. ABS. (p)

Iodine metabolism in goitre. L. SCHEFFER and L. VON MEGAY (Klin. Woch., 1935, 14, 1360—1362).—I is retained, excretion falling to about half the normal val. Blood-I oscillates considerably. R. N. C.

Metabolism of inorganic salts and water in hepatic disturbances. I, II. H. SHIGEMI (Japan. J. Gastroenterol., 1935, 7, 12—18, 19—22).—I. In various hepatic infections, blood-K and -Ca tended to decrease, -Na to increase, and -Mg to remain unchanged. Hepatic injury in rabbits induced by CHCl<sub>3</sub>, CCl<sub>4</sub>, P, hepatotoxin, or ligation of the bile duct produced variable results.



II. Following liver injury by  $\text{CCl}_4$  or ligation of the bile duct, the Ca, Mg, K, and Na contents of the heart, liver, spleen, and kidney of rabbits tended to decrease, the change being most marked in the liver.

CH. ABS. (p)

**Spontaneous ketonuria from a ketogenic diet in hepatic patients.** L. CANNAVO and I. CAPIZZI (Diagnostica tec. lab. [Napoli], 1935, 6, 197—211).—Changes in ketonuria after feeding stearic acid are used in the diagnosis of parenchymal hepatic deficiency.  $\beta$ -Hydroxybutyric acid is the principal urinary product. The resulting increase in total org. acids in urine is not  $\propto$  the increase in "keto-acids."

CH. ABS. (p)

**Evidence for placental origin of the excessive prolan of late pregnancy toxæmia and eclampsia.** G. V. S. SMITH and O. W. SMITH (Surg. Gynecol. Obstet., 1935, 61, 175—183).—Sera of toxæmic and eclamptic patients have the same action on hypophysectomised rats as do sera of normal women. Placentas from such patients contain excessive prolan (I) and low levels of œstrin. Excessive (I) originates in the placenta and probably causes toxæmia and eclampsia.

CH. ABS. (p)

**Physiology of pregnancy in rats. Mechanism of parturition. Effect on female rats of antenatal administration of œstrin to the mother.** A. M. HAIN (Quart. J. Exp. Physiol., 1935, 25, 131—143).—Injection of œstrin (I) frequently prolonged the gestation period and modified the corpus urethræ of surviving female foetuses. Synergism between (I) and oxytocin observed in mice does not exist in rats. Administration to pregnant rats of placenta, pituitary, uterus, and blood of parturient rats did not cause abortion.

CH. ABS. (p)

**Protection of mice against streptococcal and other infections by *p*-aminobenzenesulphonamide and related substances.** G. A. H. BUTTLE, W. H. GRAY, and D. STEPHENSON (Lancet, 1936, 230, 1286—1290).— $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$  (I) protects mice against infection by streptococci of different serological types, but not by staphylococci or pneumococci. There is some protection against meningococcal infection. Streptococcidal action disappears when the no. of  $\text{SO}_2\text{NH}_2$  groups attached to the  $\text{C}_6$  is increased to 3.  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHPh}$  is as active as (I), but the acid itself has a smaller protective action. Azo-compounds derived from (I) and phenolic cinchona alkaloids are inferior to prontosil.

L. S. T.

**Chemical nature of tetany.** D. E. BABCOCK (J. Chem. Educ., 1936, 13, 317—319).—A discussion.

L. S. T.

**Pathophysiology of fat metabolism in thyroid diseases.** S. LETES, E. SORKIN, and A. AGALETZKAJA (Z. klin. Med., 1935, 128, 407—416; Chem. Zentr., 1935, ii, 2836—2837).—Blood-fat is not affected in hyperthyroidism by feeding with butter, but is increased in hypothyroidism, being restored to normal by thyroxine or thyroidin. Blood-ketones are increased in both cases.

R. N. C.

**Action of 3:5-di-iodotyrosine in the treatment of hyperthyroidism.** E. DELCOURT-BERNARD (Rev.

Belge Sci. méd., 1934, 6, 1—28; Chem. Zentr., 1935, ii, 3255).—The action is similar to that of Lugol's solution.

R. N. C.

**Selective absorption of ascorbic acid by tumour tissue from the guinea-pig.** E. BOYLAND (Biochem. J., 1936, 30, 1221—1224).—The indophenol-reducing material [probably mainly ascorbic acid (I)] of guinea-pig sarcoma (Dael and Biltris) is greatly reduced in amount when the animal is kept on a scorbutic diet; injected (I) is then selectively absorbed by the tumour and by those tissues which normally contain (I). The (I) content of the tumour is about the same as that of liver.

W. McC.

**Relation between tumour-lipins and length of life of persons suffering from tumours.** R. BIERICH and A. LANG (Fette u. Seifen, 1936, 43, 105—106).—The higher is the cholesterol content of a tumour the shorter is the expectation of life of the patient after removal of the tumour by operation. Active cancer cells may contain 0.9—5% of cholesterol.

F. C. B. M.

**Indophenol-reducing substance in Jensen rat sarcoma.** A. E. KELLIE and S. S. ZILVA (Biochem. J., 1936, 30, 1216—1220).—Spectrographic and biological examination of sarcoma extracts indicate that almost all the indophenol-reducing material which it contains is *l*-ascorbic acid.

W. McC.

**Factors from normal tissues influencing the growth of transplanted cancer.** D. A. MACFADYEN and E. STURM (Science, 1936, 84, 67—68).—A tumour-inhibiting action of the  $\text{H}_2\text{O}$  extract of the  $\text{Et}_2\text{O}$ -insol. fraction of the rabbit, mouse, and cow mammary gland, and a tumour-stimulating property of the  $\text{Et}_2\text{O}$ -sol. fraction of the same tissues, have been established. There appears to be a partial neutralisation of the two forces in the aq. extract of the unfractionated mammary tissue. Further support is thus given to the view that active normal tissues contain two factors, one inhibiting and the other augmenting the multiplication of cells.

L. S. T.

**Thioglycerol: a more stable thiol compound for use in healing wounds.** L. E. SUTTON (J. Amer. Med. Assoc., 1935, 104, 2168—2171).—Rapid healing follows use of  $\text{C}_3\text{H}_5(\text{OH})_2\cdot\text{SH}$  in glycerol or tragacanth (1 in 5000).

CH. ABS. (p)

**Silver manganite (simanite) in wound treatment.** A. SCHWEITZER (Med. Klinik, 1935, 31, 1175—1176; Chem. Zentr., 1935, ii, 2974).

R. N. C.

**Growth in relation to nutrition.** H. VON HOESSLIN (Z. Biol., 1936, 97, 229—243).—Four male dogs of the same litter were given diets in which (a) carbohydrate, (b) protein, (c) fat and starch, and (d) fat alone predominated. The first grew less quickly than the second but ultimately attained an equal size. The third, which received a diet containing only 10.45% of protein, still attained a size equal to that of the others although hair-growth was deficient. The rate of growth depended on the relative availability of the calorific val. of the diet.

P. G. M.

**Influence of intermittent supply on growth of albino rats.** R. SASAKI and N. ANDO (J. Agric.

Chem. Soc. Japan, 1935, **11**, 316—320).—Rats receiving intermittent supplies of protein required a longer time to attain standard growth. The wt. of organs was unaffected. CH. ABS. (p)

**Chimpanzee metabolism.** F. G. BENEDICT and J. M. BRUHN (Proc. Nat. Acad. Sci., 1936, **22**, 394—397).—Data for fasting R.Q. and basal heat production are recorded. A. G. P.

**Biochemistry of hibernation.** D. FERDMAN and O. FAINSCHMIDT (Ukrain. Biochem. J., 1932, **5**, 20—57).—During the hibernation of *Citellus gutatus*, the creatinephosphoric acid, adenosine pyrophosphate, hexose monophosphate, the total acid-sol. P, and the total P of the voluntary muscle decrease, but the inorg. P rises. Similar results are obtained for the heart-muscle and blood. The reducing substances of the blood decrease. W. O. K.

**Changes in the physicochemical constants of hen-egg plasma on incubation.** S. S. PEROV and K. DOLINOV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1932, No. 3, 3—20).—Data for  $\kappa$  and  $\eta$  are given. CH. ABS. (p)

**Infection of *Treponema pallidum* on metabolism of rabbit testis.** R. M. KRAFT, C. S. ROBINSON, and S. HARRIS (Amer. J. Syphilis Neurol., 1935, **19**, 354—363).—The rate of metabolism was decreased without change in type. CH. ABS. (p)

**Humidity and insect metabolism.** K. MELLANBY (Nature, 1936, **138**, 124—125).—The rate of metabolism and respiration of many insects are controlled by temp. and unaffected by changes in humidity. L. S. T.

**Destruction of oak by the death-watch beetle.** A. G. NORMAN (Biochem. J., 1936, **30**, 1135—1137).—Analyses of the frass in oak timber attacked by the larvæ of the beetle (*Xestobium rufovillosum*) indicate that the carbohydrate and especially the cellulose is predominantly utilised as food (cf. A., 1930, 262). W. O. K.

**Metabolism of cartilage.** E. G. L. BYWATERS (Nature, 1936, **138**, 30—31).—The metabolism of cartilage is anaerobic. Lactic acid is formed from glucose at a rate of approx. 0.2 cu. mm. of CO<sub>2</sub> (from H carbonate solution) per mg. dry wt. per hr. In presence of methylene-blue an immediate, large increase in O<sub>2</sub> uptake occurs. L. S. T.

**Metabolism of cartilage.** F. DICKENS and H. WEIL-MALHERBE (Nature, 1936, **138**, 125—126; cf. preceding abstract).—As with medulla of kidney (this vol., 629), the same association of anaerobic type of metabolism and poor O<sub>2</sub> supply has been found for the rib cartilage of the rat. For medulla of kidney, cartilage, and tumours the ratios of respiration, aerobic and anaerobic glycolysis are similarly related. L. S. T.

**Protein, fat, and carbohydrate metabolism in the white rat. II. Effect of fasting.** R. WETZEL, H. WOLLSCHITT, H. RUSKA, and T. OESTREICHER (Arch. exp. Path. Pharm., 1936, **181**, 703—738; cf. A., 1935, 1152).—The effect of fasting for various periods on the fat, protein, and carbo-

hydrate contents of the organs of adult males and on the wt. of the organs, the I val. of the fats, and the tissue respiration has been determined. W. McC.

**Effect of feeding (A) white mice, (B) young foxes, with the proto-acid of peas.** I. LEONTEV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 1, 93—94; 1935, No. 7, 95—100).—(A) White mice thrive equally well when the proto-acid (I) is substituted for casein in the diet.

(B) Young foxes thrive on a diet in which (I) is the sole protein constituent. CH. ABS. (p)

**Effect of parenteral injection of amino-acids and related substances on creatine formation and storage in the rat.** H. H. BEARD and T. S. BOGGESS (J. Biol. Chem., 1936, **114**, 771—782).—100 mg. of creatine (I), glycocyamine, arginine (II), histidine (III), glycine (IV), alanine, serine, and valine for 1 day gave 6—32% increases in muscle-(I). At the end of 2 days the increase for the first four varied from 16 to 40%, but that due to (IV) had disappeared. 200-mg. doses of (II) and (III) for 1 or 2 days gave an increase of 30—40% in muscle (I), whilst 200 mg. of (IV) caused <10% increase. Injection of 100 mg. of (II) with 100 mg. of (IV) for 2 days gave a 41% increase, which was due to (II) alone. 200 mg. of (II) for 1 day caused a 43% and 22% increase, respectively, in stomach- and liver-(I), whilst 100 mg. of (III) increased stomach-(I) by 19%. Formation of (I) from its precursors occurs chiefly in the muscles and its origin and storage are discussed. J. N. A.

**Compounds of serum-proteins with polysaccharides.** J. JANICKI and K. KASPRZYK (Biochem. J., 1936, **30**, 1526—1531).—H<sub>3</sub>PO<sub>4</sub>-free amylose combines with proteins. Euglobulin is the only serum-globulin which combines with non-ionised polysaccharides; pseudoglobulin has practically no binding power, whilst albumins combine to only a small extent. Albumin coagulated by boiling or by change of p<sub>H</sub> does not bind amylose. Fats do not affect combination between serum-euglobulins and amylose. J. N. A.

**Biological behaviour of clover- and potato-proteins in metabolism.** A. BICKEL, R. SANDER, and J. SCHILLING (Munch. med. Woch., 1935, **82**, 1482—1485; Chem. Zentr., 1935, ii, 2693).—Data for changes in the N balance, based on tests with rats, are discussed. The biological behaviour of these proteins is different from that of animal proteins. H. J. E.

**Loss of protein from working heart muscle.** K. LISSAK and J. HOYOS (Arch. exp. Path. Pharm., 1936, **181**, 607—609; cf. *ibid.*, 233).—Ringer's solution takes up from beating hearts protein (I) which, in low concn. (1 : 10<sup>3</sup>—10<sup>5</sup>), inhibits the action of Na oleate on the frog's heart. The amount of (I) given up to the solution is increased by electrical stimulation of the vagosympathic nerve. W. McC.

**Role of carnosine in muscle activity. Influence of training on the content of the muscle in chromogenic substance.** P. NORMARK and E. SAVRON (Ukrain. Biochem. J., 1932, **5**, 17—19).—The chromogenic material in the biceps femoris of



the rabbit determined in protein-free extracts by the method of Hanke and Koessler is increased after training by electrical stimulation. W. O. K.

**Renal function tests. Modern methods of investigation. III. Phenolsulphonaphthalein and other dyes.** M. FIORENTINO, E. MACCHIA, and N. SANGUIGNO (Diagnostic tec. lab. [Napoli], 1935, 6, 89—115).—A review. Of various dyes considered, phenolsulphonaphthalein is best.

CH. ABS. (p)

**Uric acid-excreting function of the liver in renal disturbances. I—III.** S. MATSUMOTO (Japan. J. Gastroenterol., 1935, 7, 1—6, 7—8, 9—11).—I. Injection of uric acid (I) into the bloodstream of rabbits after extirpation of one or both kidneys or ligation of renal vessels or ureters caused an increased output of (I) in bile, as compared with injection into normal rabbits.

II. In kidney disturbance caused by injection of U nitrate, cantharidin, or *Trimeresurus riukuuanus*, elimination of (I) in bile is increased.

III. Extirpation of the kidneys accelerates the (I)-excreting function of the liver. CH. ABS. (p)

**Disturbance and regulation of cholesterol metabolism. I. Effect of liver extract on the disturbed cholesterol metabolism. II. Thyroid and cholesterol metabolism.** A. O. SCHALLY (Z. klin. Med., 1935, 128, 365—375, 376—385; Chem. Zentr., 1935, ii, 2690).—I. Liver extracts restore increased or diminished serum-cholesterol (I) to normal.

II. (I) is reduced in hyperthyroidism, the fall  $\propto$  the extent of the disease; it is increased by therapy, particularly strumectomy. (I) is also depressed in other diseases of the thyroid, which has an inhibiting effect on (I) metabolism.

R. N. C.

**Chemistry of fatigue.** A. PALLADIN, L. PALLADINA, and E. PERSOVA (Ukrain. Biochem. J., 1932, 5, 7—16).—The lactic acid content of the biceps femoris of rabbits is increased after electrical stimulation for 5 min., but with trained muscle a decrease occurs.

W. O. K.

**Metabolism of organic salts.** G. SURANYI (Nourissn, 1934, Nov., 7 pp. [Sep.]).—The role of glutathione and cysteine in intermediate metabolism is examined.

CH. ABS. (p)

**Metabolism of sulphur. Determination of cystine in normal urine.** G. MEDES (Biochem. J., 1936, 30, 1293—1297).—The method for the determination of cystine (I) (this vol., 881) is applied to urine and compared with other methods. Glutathione, ergothioneine, and uric acid do not interfere. About 70% of the total S·S in urine consists of (I).

H. D.

**Recent researches on fat metabolism.** P. E. VERKADE (Bull. Soc. Chim. biol., 1936, 18, 989—1013).—A lecture.

**Distribution of fats introduced into the organism.** G. PERETTI, L. REALE, and L. CIOGLIA (Arch. Ital. Biol., 90, 59—70; Chem. Zentr., 1935, ii, 2693).—Fats administered intravenously or orally cause a rise in the fatty acid (I) content of the blood,

followed by a const. period and a fall. The (I) in the liver increases steadily (44 hr.) and then falls.

H. J. E.

**Glycogen and carbohydrate content of the fatty tissue of rats given unbalanced diets after fasting.** R. WETZEL and T. HEID (Arch. exp. Path. Pharm., 1936, 181, 689—702).—The effects of feeding unbalanced (all carbohydrate, protein-rich, fat-rich) diets on the contents of glycogen and reducing substances in the fatty tissues of rats after fasting have been examined.

W. McC.

**Correlation between rates of intestinal absorption of some simple sugars.** H. G. K. WESTENBRINK and A. MIDDELBEEK (Arch. Neerland. Physiol., 1936, 21, 283—293).—The rate and course of intestinal absorption of galactose (I) in rats approximates to that of glucose (II) but not to that of xylose; for each sugar variations occur with different rats. The absorptions of dietary constituents are generally independent of each other but with substances such as (I), (II), and fructose some degree of inter-relationship is evident.

F. O. H.

**Relative velocities of the absorption of different sugars from the intestine of rat and pigeon.** H. G. K. WESTENBRINK (Nature, 1936, 138, 203—204).—The ratios of the absorption velocities of *d*-galactose, *d*-glucose, *d*-fructose, *d*-mannose, *l*-xylose, and *l*-arabinose are fundamentally the same for rats and pigeons fed on the same diet.

L. S. T.

**Carbohydrate metabolism of the mammary gland *in vitro*.** C. ANTONIANI and A. S. CLERICI (Atti R. Accad. Lincei, 1936, [vi], 23, 73—76; cf. A., 1932, 1059; 1933, 83).—Finely-divided mammary gland (lactating cow) transforms phosphoglyceric acid into  $\text{AcCO}_2\text{H}$  with liberation of inorg. P (cf. A., 1934, 1261). Non-lactating (virginal) gland merely hydrolyses the ester.

E. W. W.

**Lactacidogen and lactic acid in the surviving pigeon brain.** H. GORODISSKI and S. EPELBAUM (Ukrain. Biochem. J., 1932, 5, 87—100).—During 2 hr. in isotonic NaCl solution, the lactacidogen (I) content of surviving pigeon brain decreases. The addition of starch or glucose is without effect. Lack of  $\text{O}_2$  accelerates and electrical stimulation retards the disappearance of (I).

W. O. K.

**Carbohydrate catabolism in cerebral cortex.** K. C. DIXON (Biochem. J., 1936, 30, 1479—1482).—The rates of anaerobic and aerobic carbohydrate catabolism have been calc. from the rates of respiration and glycolysis. The former is the greater, and the Pasteur effect is in operation in slices of cerebral cortex acting on glucose *in vitro*. Addition of KCl raises the aerobic val. to the anaerobic.

H. G. R.

**Effect of rise in temperature on the carbohydrate catabolism of cerebral cortex.** K. C. DIXON (Biochem. J., 1936, 30, 1483—1488).—The rates of respiration and of aerobic glycolysis at 42° are slightly > those at 37°, but are considerably increased at 45°. An abrupt rise in anaerobic glycolysis is observed above 42° but there is a rapid fall at 45°. The Meyerhof quotient being normal, there is no sp. inhibition in the Pasteur effect with

temp., and the rates of carbohydrate catabolism at various temp. do not follow Arrhenius' law.

H. G. R.

**Ossification by means of tissue culture.** R. SASAKI (Z. Klin. Path. Hamatol. [Japan], 1933, 2, 1246).—In tissue cultures of the surfaces of frontal bones of chick embryos, oxidase (I) and Fe appeared simultaneously in the tissue, followed by Ca deposition in 1–2 days. A close relationship between (I), Fe, and Ca is established.

CH. ABS. (p)

**Cortico-adrenal insufficiency and potassium metabolism.** I. Determination of potassium in small amounts of blood and tissues. II. Blood-potassium of normal and adrenalectomised cats. III. Potassium content of skeletal and cardiac muscle in cortico-adrenal insufficiency. R. TRUSZKOWSKI and R. L. ZWEMER (Biochem. J., 1936, 30, 1345–1353).—Methods for determination of K in 0.2 ml. of blood and in small amounts of muscle are described. Normal vals. (19 cats) were: plasma 19.3, serum 20.2, and whole blood 21.4 mg. of K per 100 ml. The vals. for blood-K in 18 bilaterally adrenalectomised cats varied within wide limits (11 to 46 mg. per 100 ml.) for different animals at different times after the operation. The most consistent effect was a rapid rise in blood-K to a max. val. on the 3rd or 4th day. An average of 0.415% wet wt. or 1.9% dry wt. was found for skeletal muscle of animals in the terminal stage of adrenal insufficiency and of 275 and 1277 mg. per 100 g., respectively, for myocardium. The vals. for wet wt. are < and for dry wt. > for normal cats. The syndrome of cortico-adrenal insufficiency is intimately associated with a disturbance of K metabolism.

P. W. C.

**Role of non-electrolytes in imbibition.** D. KOHLER (Compt. rend. Soc. Biol., 1936, 122, 1050–1052).—Imbibition of desiccated *Laminaria flexicaulis* is decreased by non-electrolytes in the early stages, but later is increased.

H. G. R.

**Influence of reaction of the external medium on the survival and the  $p_H$  of the hæmolymph of oysters.** A. JULLIEN and J. G. RICHARD (Compt. rend. Soc. Biol., 1936, 122, 1106–1108).—The optimum  $p_H$  for the Portuguese oyster is 7.5, but it will survive for some time at a  $p_H$  between 4.5 and 9.2. The  $p_H$  of the internal medium (6.1–8.3) is 0.3–0.4 < that of the external medium.

H. G. R.

(A) Relation between natural tolerance to heroin and the partition coefficient of the drug for the central nervous system. (B) Changes in partition coefficient in heroin habituation. (C) Changes in partition coefficient of morphine by heroin habituation. (D) Changes in partition coefficient of heroin by morphine habituation. (E) Change in partition coefficient of morphine by cocaine habituation. M. WATANABE (Japan. J. Med. Sci., IV, 7, No. 2–3; Proc. Japan. Pharmacol. Soc., 1933, 32–34, 34–35, 36, 36–37, 37–38).

CH. ABS. (p)

**Action of nymphalin on the heart and blood-vessels.** M. RYSZKOWSKA (Wiad. farm., 1935, 62, 249–251, 263–266; Chem. Zentr., 1935, ii, 2695).—

Nymphalin, a glucoside from *Nymphaea alba* and *Nuphar luteum*, has cardiac activity but does not cause constriction of the blood-vessels in therapeutic doses.

H. N. R.

**Contradictory actions of caffeine, coramine, and metrazole.** A. H. MALONEY (Quart. J. Exp. Physiol., 1935, 25, 155–166).—The depressant action of barbital was accentuated by caffeine, coramine (I), or metrazole (II) under certain conditions. Transitory reverse effects occurred with certain dosages of (II) and (I).

CH. ABS. (p)

(A) Resting metabolism of the frog ventricle.

(B) Influence of depressants on rate of asphyxiation of frog ventricle. A. J. CLARK (Quart. J. Exp. Physiol., 1935, 25, 167–180).—(A) Examination of ventricles poisoned with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  indicates that phosphagen is utilised by the resting as well as by the contracting ventricle.

(B) Data for resting and contracting ventricles at different temp. are given. Acetylcholine reduces the metabolism of arrested ventricles by 50%.

CH. ABS. (p)

**Observations on perfused lungs of guinea-pigs.**

A. S. DALE and B. NARAYANA (Quart. J. Exp. Physiol., 1935, 25, 85–97).—Effects of acetylcholine (I), atropine (II), and eserine (III) on broncho- and vaso-constriction are examined. The action of (I) was counteracted by (II) but not by (III).

CH. ABS. (p)

**Barbiturates. XV. Excretion of barbital in normal and nephritic subjects.** W. P. ARGY, C. R. LINEGAR, and J. M. DILLE (J. Pharm. Exp. Ther., 1936, 57, 258–263).—In men, kidney disease (arteriosclerosis or nephritis) causes a marked reduction in the urinary output of barbital administered orally.

A. L.

**Diuretic action of the digitalis group.** I. MATSUYAMA (Japan. J. Med. Sci., IV, 7, No. 2–3; Proc. Japan. Pharmacol. Soc., 1933, 166–167).—Effects of digalen, diagfolin, pangital, digitoxin, scillaren, and strophanthin are compared in different animals.

CH. ABS. (p)

**Mechanism of uric acid excretion of cinchophen.** H. OKA (Japan. J. Med. Sci., IV, 7, No. 2–3; Proc. Japan. Pharmacol. Soc., 1933, 170–171).—Cinchophen lowers the excretion threshold in the kidney, thereby decreasing the uric acid concn. in blood.

CH. ABS. (p)

**Influence of *o*-, *m*-, and *p*-hydroxybenzoic acid on the gaseous metabolism of the kidney in relation to urine formation.** K. TAMURA and G. KIHARA (Japan. J. Med. Sci., IV, 7, No. 2–3; Proc. Japan. Pharmacol. Soc., 1933, 171–175).—The *m*-acid is more, and the *p*-acid less, irritant than salicylic acid. The theobromine Na salts of *p*- and *m*-acids are not less diuretic but more irritant than the corresponding *o*-acid salt.

CH. ABS. (p)

**Phenylurethane anaesthetics. II.**—See this vol., 1103.

**Intensity of action of anaesthetics as a function of their emulsified state or solution in the blood.** N. LAZAREV (Compt. rend. Soc. Biol., 1936, 122, 891–893).—With increasing partition coeff. (oil–



H<sub>2</sub>O), the hæmoglobin-fixation and anæsthetic activity increase. H. G. R.

**Local anæsthetic actions of certain pyrazoline and quinoline compounds.** H. K. SINHA (J. Pharm. Exp. Ther., 1936, 57, 199—220).—Using 1-phenyl-5-(4'-methoxy-3'-ethoxyphenyl)-3-(β-N-piperidinoethyl)pyrazoline hydrochloride (I), di-(quinolyl-8'-methyl)-1:4-piperazine tetrahydrobromide (II), and 8-(diethylaminoethylethylaminomethyl)quinoline trihydrobromide (III), a comparison of the three methods of determining anæsthetic activity, viz., (a) the rate of paralysis of the frog's sciatic nerve, (b) the rabbit's cornea, and (c) the human wheal methods, indicates that the simplest method is to determine the concn. of the drug which produces anæsthesia for a standard time and this method is applied to methods (b) and (c). With method (a) results are variable. (I) and (II) may be of val. for clinical application to mucosæ and for infiltration anæsthesia, whilst (III) is equal to novocaine for nerve-trunk anæsthesia. A. L.

**Sensitivity of various animals towards anæsthetics.** A. BRUSILOVSKA (Compt. rend. Soc. Biol., 1936, 122, 983—995).—The concns. in the blood of various anæsthetics lethal to frogs and mice are given. H. G. R.

**Galvano-narcosis as a means of investigating the action of hypnotics and narcotics on the frog.** P. ADLER and C. HRADECKY (Arch. exp. Path. Pharm., 1936, 181, 541—552).—The min. current required to produce narcosis is reduced following administration of hypnotics and narcotics but is restored to the initial val. as the effect of these passes off, the strength of current required being (within limits) inversely ∝ the depth of narcosis produced by the substances. 17—36% reduction of the min. effective dose corresponds with 50% reduction in the current strength. W. McC.

**Chemical transmission of the nervous influx at the level of the central synapses.** G. BENETATO and N. MUNTEANU (Compt. rend. Soc. Biol., 1936, 122, 1128—1132).—A substance similar to acetylcholine is formed in the venous blood of the bulb during stimulation of the vagus. H. G. R.

**Role of acetylcholine in transmission of nervous stimulation in striated muscle.** L. LAPIOQUE (Compt. rend. Soc. Biol., 1936, 122, 990—993).—It is suggested that acetylcholine is formed not between the nerve and the muscle but in the muscle itself and serves to generalise the stimulations. H. G. R.

**Gel formation in hen egg plasma.** K. DOLINOV (Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ., 1931, No. 2, 21—27).—Na salicylate (5—35% solution) gelatinises white plasma and in concns. >4.9% gelatinises yolk plasma. CH. ABS. (p)

**Action of ethylene on cell processes.** F. F. NORD (Austral. J. Exp. Biol., 1936, 14, 131—133).—Polemic (cf. A., 1935, 1165). H. G. R.

**Effect of pyocyanine on the animalisation of the sea-urchin caused by calcium-free seawater and sodium thiocyanate.** J. RUNNSTROM and D. THORNBLOM (Naturwiss., 1936, 24, 447).—

Eggs of the sea-urchin were treated with a mixture of 90 parts of Ca-free sea-H<sub>2</sub>O and 10 parts of 0.54M-NaCNS, and with this mixture together with 2.15 × 10<sup>-4</sup>% of pyocyanine (I). They were then fertilised and hatched. After 12 hr. treatment with the solution containing (I), 80% of the eggs were animalised, whereas in a solution without (I) only 10% were animalised. The curves expressing animalisation against time of treatment are S-shaped and agree with the formula of Rahn (this vol., 506). (I) accelerates the respiration of the unfertilised egg. A. J. M.

**Food allergy.** H. STEVENS (Oil and Soap, 1936, 13, 162—165).—Clinical evidence concerning the allergic effects attributed to ingested cottonseed products is often incomplete, and the conclusions are therefore invalidated. E. L.

**Effect of the epithelial cell and colloid substance on the thyroid gland, and of alcoholic hydrochloric acid extracts of the thyroid and of residues from such extracts on tissue respiration.** K. MUNE (Folia Endocrinol. Japon., 1933, 9, 27—28).—The O<sub>2</sub> consumption of living extirpated tissues of rats was increased by treatment with aq. extract of epithelial cell substance or EtOH-HCl extract of thyroid gland, but was decreased by aq. or EtOH-HCl extract of the colloid substance. CH. ABS. (p)

**Tyramine: its moderating effect on basal metabolism.** P. JACCHIA (Boll. Soc. ital. Biol. sperim., 1934, 9, 276—279).—Tyramine administered orally to patients with normal basal metabolism causes a fall, a steady min. being reached in 3 hr. R. N. C.

**Existence in blood and urine of substances promoting liver function.** I. N. MIZUTA and T. MATSUURA (Japan. J. Gastroenterol., 1935, 7, 23—35).—After extirpation of kidneys or in drug-induced nephritis rabbit's blood contains a substance promoting pigment excretion in the liver; it is sol. in H<sub>2</sub>O and Et<sub>2</sub>O, fairly stable in neutral and slightly acid media, but rapidly destroyed by alkalis. It also occurs in blood in cases of kidney malfunction. CH. ABS. (p)

**Influence of cations and carbohydrate on the formation of inorganic phosphoric acid during the autolysis of brain extracts.** H. GORODISSKI and S. EPSCHTEIN (Ukrain. Biochem. J., 1932, 5, 101—112).—In autolysing extracts of pigeon's and cat's brains, "summarisches" H<sub>3</sub>PO<sub>4</sub> (I) (inorg. H<sub>3</sub>PO<sub>4</sub>+creatinephosphoric acid) is formed, but at a constantly diminishing rate. K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Ca<sup>++</sup> retard but Mg<sup>++</sup> accelerates production of (I). Addition of glucose, galactose, glycogen, dextrin, and starch to the autolysing extract of cat's brain retards the reaction but maltose first retards and then accelerates it. W. O. K.

**Influence of oral administration of saponin with adrenaline, ephedrine, and insulin on blood-sugar and -inorganic phosphorus contents.** T. ICHJO (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 54—56).—Saponin tended to increase the action of the three substances. CH. ABS. (p)

**3-Diethylaminomethyl- and 3-piperidomethylbenzodioxan do not enhance the hypoglycæmic**

action of insulin in the dog. E. ZUNZ, J. PERLA, and F. JOURDAN (*Arch. int. Pharmacodyn.*, 1935, 49, 470—474).  
R. N. C.

Site of action of barium, strychnine, and veratrine in the striated muscle of the toad. G. RUSSO (*Arch. ital. Biol.*, 1934, 91, 60—74; *Chem. Zentr.*, 1935, ii, 3126).  
R. N. C.

Effect of adrenalone, ephedrine, and adrenaline on rabbit blood-sugar. K. AKIMOTO (*Japan. J. Med. Sci.*, IV, 7, No. 1; *Proc. Japan. Pharmacol. Soc.*, 1933, 34—35).—Max. changes occur 30 min. after administration. Threshold doses for oral, rectal, and subcutaneous administration are compared.  
CH. ABS. (p)

Biological identification of proteins. I, III—V, VII. I. LEONTEV. VIII. I. LEONTEV and Z. GRAFSKAJA, IX, X, XII. I. LEONTEV (*Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ.*, 1931, No. 1, 61—65; No. 2, 69—71; 1932, No. 3, 51—55, 56—58; 1933, No. 3, 55—60; No. 4, 62—65, 60—61; No. 5, 61; 1935, No. 7, 65—66).—I. The proto-acid of peas produces no anaphylactic shock in rabbits. III, IV. Injection of protein into cold-blooded animals produced no shock.

V. Neither "fibrin acid" nor ovalbumin produced shock in guinea-pigs.

VII. Proteins of seed of watermelons, muskmelons, and pumpkins, tested biologically, were identical.

VIII. Proto-acid extracted from sunflower seed by NaOH produces no shock. That extracted by 10% aq. NaCl causes typical shock.

IX. Proto-acid from field nut, unlike the protein obtained by Osborne's method, causes no shock.

X. Proto-acid from yellow acacia (15% N) has the same immunological effect on guinea-pigs as does that of peas, beans, etc. and differs from the protein (Osborne's method) in producing no shock.

XII. The Me ester hydrochloride of glycine (I) contained no lysine or tryptophan. Both (I) and the Me derivative produced shock. Guinea-pigs sensitised to (I) suffered shock when re-injected with methylglycine and vice versa.  
CH. ABS. (p)

Parenteral injection of proto-acid ("caseinic acid"). M. N. TSCHUKITSHEVA-FEDOROVA, V. A. DALMATOV, and I. P. TSCHUKITSHEV (*Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ.*, 1931, No. 1, 68—74).—Effects of injected protein are due to the degree of dispersion of the protein and not to the fact that it is foreign to the organism. Rabbits tolerate large injections of proto-acid without pathological changes and retain the substance.  
CH. ABS. (p)

Action of extremely minute amounts of protein ("caseinic acid") on blood pressure. I. P. TSCHUKITSHEV and B. JORDANSKI (*Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ.*, 1932, No. 3, 21—22).—Increased blood pressure observed persists for a longer period than that produced by adrenaline.  
CH. ABS. (p)

Artificial protein plasma. M. N. TSCHUKITSHEVA and I. P. TSCHUKITSHEV (*Trud. Lab. Izuch. Belka Belkovogo Obmen. Organ.*, 1933, No. 5, 35—38).—Injection of casein (I) into rabbits and dogs

produced no ill-effects. (I) cannot be regarded as foreign to the organism (cf. Perov, this vol., 1038).

CH. ABS. (p)

Histochemical study of gold depots in cells. R. COHEN (*Compt. rend. Soc. Biol.*, 1936, 122, 1123—1124).  
H. G. R.

Role of the reticulo-endothelial system in the chemotherapeutic action of arsenobenzene derivatives. I, II. M. ZOLOG and O. COMSIA (*Compt. rend. Soc. Biol.*, 1936, 122, 1135—1137, 1138—1140).—I. Blockage or destruction of the reticulo-endothelial system increases the quantity of therapeutic agent available and the apparent activity is increased.

II. Blockage or destruction of the system prior to infection is without action on the course of the latter. Blockage before infection and 3 days before treatment has a favourable effect, whilst destruction slightly reduces the parasitocidal effect.  
H. G. R.

Action of arsenobenzene derivatives on experimental trypanosomiasis. M. ZOLOG and O. COMSIA (*Compt. rend. Soc. Biol.*, 1936, 122, 1132—1134).—The active principle is dialysable and cannot be a toxalbumin. It is not necessary for the therapeutic substance to be reduced in the organism for it to acquire therapeutic properties.  
H. G. R.

Composition of food poor in heavy metals and its influence on rats. J. A. F. KOK [with C. WAAL] (*Arch. Neerland. Physiol.*, 1936, 21, 247—265).—The prep. of a synthetic diet containing only traces of Cu and Fe is described. Rats on such a diet have a low haemoglobin val., which is increased to normal levels by addition of Fe alone to the diet; growth is approx. normal but fatty degeneration of liver and kidney occurs.  
F. O. H.

High-potassium diet and the survival of adrenalectomised rats. R. A. CLEGHORN and G. A. McVICAR (*Nature*, 1936, 138, 124).—These rats lived longer when the diet (Purina Dog Chow) containing cereals, meat, molasses, and vitamins was supplemented by bread. The low K content of the bread may have favoured survival.  
L. S. T.

Effect of weaning on the excretion of calcium in the urine of lactating rats. L. I. PUGSLEY (*Biochem. J.*, 1936, 30, 1271—1273).—The urinary Ca of lactating rats increases on weaning; the greatest effect is obtained by weaning 15 days after parturition. Removal of the mammary glands after 10 days' lactation causes no increased excretion of Ca over the pre-parturition rate.  
H. D.

Action of magnesium dithiosalicylate on the experimental elimination of cystine. J. DELPHAUT and S. FLEURENT (*Compt. rend. Soc. Biol.*, 1936, 122, 957—958).—Excretion of cystine in the urine increases.  
H. G. R.

Action of intravenous and intramuscular injections of callicrein in man. E. K. FREY, E. WERLE, and E. SACKERS (*Z. ges. exp. Med.*, 1935, 96, 404—413; *Chem. Zentr.*, 1935, ii, 3256).  
R. N. C.

Effect of intravenously-given callicrein on cerebrospinal fluid pressure. T. REEKE and E. WERLE (*Z. ges. exp. Med.*, 1935, 96, 398—403; *Chem. Zentr.*, 1935, ii, 3256).  
R. N. C.



**Callicrein in the saliva and its intervention during the chemical transmission of the nervous influx.** G. UNGAR and J. L. PARROT (Compt. rend. Soc. Biol., 1936, **122**, 1052—1055).—Callicrein is the hypotensive substance in saliva and it may be the cause of vasodilation following stimulation of the lingual nerve. H. G. R.

**Pharmacology of aromatic selenium compounds.** S. KONDO (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 132—135).—Effects of  $\text{OH}^-$ ,  $(\text{OH})_2$ , and carboxy-derivatives of  $\text{Ph}_2\text{Se}$  and  $\text{Ph}_3\text{Se}_2$  are recorded. CH. ABS. (p)

**Pharmacological action [of drugs] in hypervitaminosis-B.** A. ALLEGRI (Boll. Soc. ital. Biol. sperim., 1934, **9**, 236—240). R. N. C.

**Oestrogenic activity of certain phenanthrene and hydrophenanthrene derivatives.** G. PINCUS and N. T. WERTHESSEN (Science, 1936, **84**, 45—46).—The activities in mice of the derivatives prepared by Fieser *et al* (this vol., 203) are recorded. The effect of constitution on activity is discussed. L. S. T.

**Pharmacology of methylglyoxal.** I. G. ARAKI (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 44—47).—Lethal dosages are determined. In alkalosis the val. was  $>$  that in acidosis.  $\text{AcCHO}$  rapidly disappears from blood, producing a marked decrease in alkali reserve.  $\text{HCO}_2\text{H}$  is among the decomp. products. CH. ABS. (p)

**Convulsants of the picrotoxin group.** H. KUSUMOTO (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 89—90).—Physiological data for coriamyrtin, tutin, picrotoxin, and picrotoxinine are given. CH. ABS. (p)

**Pharmacological action of tannic acid. VI. Minimum lethal dose by intravenous injection.** U. SAMMARTINO (Arch. Farm. sperim., 1936, **61**, 156—159).—The min. lethal dose in rabbits is 0.16 g. per kg. E. P.

**Variations in blood-cholesterol and -sugar after slow, continuous, mesenteric injection of chlorinated arsenical water containing sodium hydrogen carbonate.** E. CHABROL, J. COTTET, and J. SALLET (Compt. rend. Soc. Biol., 1936, **122**, 905—907).—A decrease in cholesterol and sugar occurs. H. G. R.

**Pharmacology of sodium furfuralacrylate. I. Effect on the frog heart.** M. NODA (Aichi Igak. Zasshi, 1933, **40**, 1503).—The depressive effect of Na furfuralacrylate (I) on the heart action was unaffected by previous administration of Gynergen, but was reinforced by adrenaline. The weakened contractions were not improved by  $\text{BaCl}_2$ . (I) affects the heart muscle directly. CH. ABS. (p)

**Anhidrotic action of agaric acid.** K. HATTORI (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 157—160).—Agaric acid acts on the parenchyma of sweat glands. CH. ABS. (p)

**Influence of phosphorus poisoning on the synthesis of menthologlycuronic acid. II.** B. NAZARJANZ (Ukrain. Biochem. J., 1932, **5**, 129—

132; cf. A., 1935, 1533).—The impaired ability of rabbits poisoned with P and injected with menthol to synthesise menthologlycuronic acid is accompanied by pathological changes in the liver, involving fatty degeneration. Lesions of the kidney do not effect the synthesis of conjugated glycuronic acids.

W. O. K.

**Action of sulphur in experimental carbon monoxide poisoning.** K. VOIT and H. H. SCHMIDT (Munch. med. Woch., 1935, **82**, 1393—1395; Chem. Zentr., 1935, ii, 2842).—Injection of S prevents the erythrocytosis and hyperglycaemia arising from CO poisoning. H. N. R.

**Bismuth poisoning.** H. C. LUETH, D. C. SUTTON, C. J. McMULLEN, and C. W. MUEHLBERGER (Arch. Int. Med., 1936, **57**, 1115—1124).—A case report of a permanent blue discoloration of the skin as in argyria after prolonged treatment with Bi subnitrate (4 g. per day). E. D. Y.

**Influence of chronic thallium poisoning on the function of the female sex organs of rats.** T. ARASHIMA (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 135—136).—In rats treated with  $\text{TlCl}$  solutions, sex functions are affected only in association with nutritive changes. CH. ABS. (p)

**Effect of injection of potassium cyanide on hydrogen-ion concentration of blood plasma especially in relation to certain hormones. I. Effect of potassium on plasma- $p_{\text{H}}$ . II. Relation to thyroid. III. Relation to insulin.** N. NAKATSUGAWA (Folia Endocrinol. Japon., 1934, **9**, 99—100).—I. Injection of 0.2—0.8 c.c. of 0.5% aq. KCN produced an initial increase in  $p_{\text{H}}$ , followed by a decline to  $<$  normal vals.

II. Fluctuations in  $p_{\text{H}}$  following injection are intensified by feeding small doses of thyroid gland. Large doses accelerated the second (declining) phase.

III. Injection of insulin, alone or with glucose, decreased the variations due to injection of KCN. CH. ABS. (p)

**Fluorides in Foochow waters and dental defects.** T. H. WANG (J. Chinese Chem. Soc., 1936, **4**, 172—177).—The occurrence of mottled dental enamel is related to the high F content of drinking  $\text{H}_2\text{O}$ . R. S.

**Effect of age on sensitivity to metabolic poisons.** H. YAMAGATA (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 142—150).—The  $\text{O}_2$  intake of liver, kidney, and muscle tissues was decreased by  $\text{As}_2\text{O}_3$  and increased by thyroxine to approx. the same extent in young and old rabbits in each case. CH. ABS. (p)

**Effect of age on sensitivity to blood poisons.** T. ISOBE (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 150—154).—Resistance of young rats to CO, HCN,  $\text{H}_2\text{S}$ ,  $\text{NHPh}\cdot\text{NH}_2$ , and  $\text{NH}_2\text{Ph}$  was  $>$  that of adults. Splenectomy did not influence susceptibility. CH. ABS. (p)

**Mechanism of iodoacetate poisoning of muscle.** A. GHAFFAR (Quart. J. Exp. Physiol., 1935, **25**, 61—67).—The effect of  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Na}$  (0.001N) on the glycolytic activity and lactic acid production of frog

muscle is examined in relation to I liberation, time, and temp. CH. ABS. (*p*)

**Toxicity of some cations to *Saprolegnia*.** F. MOREAU and (MME.) F. MOREAU (Compt. rend., 1936, 202, 2175—2177).—The inhibitory effect of the following cations (as 0.3—1.0% aq. chlorides) on the growth of *Achyla colorata* gives the series:  $\text{Li} > \text{Na} > \text{K}$ ;  $\text{Ba} > \text{Sr} > \text{Ca}$ ;  $\text{Mg} > \text{Ca}$ . F. N. W.

**Pathological effects of poisons used for rodents.** J. G. WRIGHT (Vet. Rec., 1936, 16, 599—602).—A review of the pharmacological actions of HCN,  $\text{As}_2\text{O}_3$ , P,  $\text{BaCO}_3$ , red squill (I), and strychnine. Of these,  $\text{BaCO}_3$  and (I) are the most suitable for poisoning rodents, but from a humane point of view a combination of one of these poisons with an appropriate narcotic is recommended. J. N. A.

**Toxicity of flavins.** R. KUHN and P. BOULANGER (Z. physiol. Chem., 1936, 241, 233—238).—The following isoxalloxazines are toxic to mice (rats on vitamin- $B_2$ -free diet were also used) in the doses given (mg. per kg.): 9-Me- 125 (60 with rats and irradiated mice), 9-Ph- (I) 17, 9- $\text{CH}_2\text{Ph}$ - 50, 9-cyclohexyl- 50, 9-hydroxyethyl- 280, 9-dihydroxypropyl- 200, 6 : 8 : 9-Me $_3$ - 300—310, 9-OAc- 130: the following are less toxic: 6 : 9-Me $_2$ - 350, 6 : 7 : 9-Me $_3$ - 330, 9-acetyl-6 : 7-dimethyl- 775, and lactollavin 340. Hence Me in the 6 : 7-positions reduces the toxicity. (I) loses its toxicity when heated with dil. aq. NaOH, being converted into a ketocarboxylic acid with loss of urea. The toxic doses of alloxazine and its 6 : 7-Me $_2$  derivative are 305 and 250, respectively. In some cases the toxicity is increased by irradiation of the animals. W. McC.

**Pharmacological and toxicological properties of vinyl ether.** H. MOLITOR (J. Pharm. Exp. Ther., 1936, 57, 274—288).—For a 3-hr. anaesthesia, the toxicity of vinyl ether (I) to mice is 0.19 c.c. per litre of air. The corresponding vals. for  $\text{Et}_2\text{O}$  and  $\text{CHCl}_3$  are 0.18 and 0.026 c.c., respectively. Decomp. of (I) is accompanied by loss in anaesthetic power, although there is no decomp. when it is circulated through the body. In low concn.,  $\text{Et}_2\text{O}$  has a quicker action; (I), however, acts more rapidly at high concn., and recovery is always more rapid. A. L.

**Value of sodium formaldehydesulphoxylate in mercury poisoning.** W. E. ROBERTSON and V. L. TUCK (J. Chemother., 1935, 12, 226—231).

CH. ABS. (*p*)

**Unsuccessful attempts to treat and prevent cyanide poisoning by dinitrophenol.** R. HAZARD and P. HAUTEVILLE (J. Pharm. Chim., 1936, [viii], 24, 5—8). H. D.

**Biological action of metals irradiated by the quartz lamp.** III. I. M. GOLDBERG and V. G. BOUDYLINE. IV. I. M. GOLDBERG (Acta med. scand., 1935, 85, 136—146, 147—153).—III. Solutions of Cu salts irradiated with ultra-violet light stimulate haematopoiesis in normal rabbits. Irradiated Cu and Fe salt solutions administered parenterally accelerate regeneration of blood after experimental hemorrhagic anaemia.

IV. Irradiated Cu and Fe solutions depress the

local anaphylactic reactions but apparently do not affect the course of anaphylaxis. R. N. C.

**Effects of  $\beta$ -rays from radium on the agent of the Rous sarcoma, on bacteriophage, on tetanus toxin, and on certain bacteria, antibodies, and enzymes.** S. L. BAKER (Brit. J. Exp. Path., 1934, 16, 148—155).—The relative susceptibility to destruction by  $\beta$ -rays is examined. The agent of Rous sarcoma is not of an enzymic character.

CH. ABS. (*p*)

**Effect of ultra-violet light irradiation on carbohydrate metabolism. I. Changes of blood-sugar and blood-diastase after total irradiation from the noonday sun.** A. MARCHIONINI and C. HOVELBORN (Klin. Woch., 1935, 14, 1387—1392).—The fasting blood-sugar val. in man is sometimes depressed and blood-diastase raised by total ultra-violet irradiation, suggesting a relation between skin-function and insulin output. R. N. C.

**Reduction and oxidation by ultra-violet irradiated sugar.**—See this vol., 1094.

**Heliotropism of cholesterol.** A. H. ROFFO (Strahlenther., 1935, 53, 317—325; Chem. Zentr., 1935, ii, 2828).—The appearance of tumours as a result of irradiation with light of  $\lambda$  180—340 m $\mu$  is preceded by local increase of blood-cholesterol.

R. N. C.

**Biological assay of hydrastine, berberine, and their mixtures by the isolated intestine.** F. MERCIER (Compt. rend. Soc. Biol., 1936, 122, 965—968). H. G. R.

**Biological assay of liquid extracts of *Hydrastis*.** F. MERCIER and L. VIGNOLI (Compt. rend. Soc. Biol., 1936, 122, 968—970). H. G. R.

**Recent advances in enzyme chemistry.** E. WALDSCHMIDT-LEITZ (Chem. and Ind., 1936, 620—626).—A lecture.

**Borders of physics and biology.** C. E. GUYE (Arch. Sci. phys. nat., 1936, [v], 18, 154—171).—Probability considerations are discussed in relation to mol. theories of life. Thermal agitation alone is insufficient to account for the appearance of high degrees of asymmetry in mols. of high mol. wt.

F. A. A.

**Reversible enzymic oxidation of *d*-gluco-ascorbic acid.** S. S. ZILVA (Biochem. J., 1936, 30, 1215; cf. A., 1934, 707).—The enzyme from apples which dehydrogenates *l*-ascorbic acid also reversibly dehydrogenates *d*-glucoascorbic acid at  $p_H$  4.4 and room temp. W. McC.

**Lactic dehydrogenase of animal tissues.** D. E. GREEN and J. BROSTEAUX (Biochem. J., 1936, 30, 1489—1508).—With enzyme-co-enzyme-lactate-carrier systems, the product of oxidation,  $\text{AcCO}_2\text{H}$ , inhibits almost completely the oxidation of lactate, but in presence of KCN or  $\text{NH}_2\text{OH}$  the oxidation proceeds linearly for a long time. The enzyme is very sensitive to  $p_H$ , and is associated with the enzymes oxidising malate, fumarate, and  $\beta$ -hydroxy-propionate and -butyrate. It catalyses the oxidation of *l*-lactate, whilst *d*-lactate, lactamide, and isoserine are not oxidised. It can be determined in the tissues of pigeons, rabbits, and rats, and  $\text{H}_2\text{O}$ -clear solutions can



be prepared with  $Q_{10}$  of 400—500. Very small amounts of lactate are not oxidised with an appreciable velocity, and there is no crit. concn. of co-enzyme below which the rate of oxidation of lactate falls sharply. The co-enzyme is reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  or by the enzyme system, and when reduced is unstable in acid, but not in alkaline solution. The co-enzyme is a sp. carrier between lactic acid and the O carrier, and cannot be replaced by the co-enzyme of hexose monophosphate dehydrogenase. Flavin, adrenaline, and, to a slight extent, yellow pigment can act as carriers, but ascorbic acid, cytochrome, and glutathione are inactive. A new classification of dehydrogenase systems is given. J. N. A.

**Components of dehydrogenase systems. XII. Mechanism of dehydrogenation of alcohol and of triose phosphates. Mechanism of oxidation-reduction.** H. VON EULER, E. ADLER, and H. HELLSTROM (Z. physiol. Chem., 1936, 241, 239—272; cf. this vol., 519).—EtOH in presence of its sp. apodehydrogenase reversibly converts cozymase (I) into dihydrocozymase (II), an equiv. amount of EtOH being converted into MeCHO. (II) exhibits an absorption max. at 340 m $\mu$ , is stable in alkaline and slightly acid media (rapidly destroyed at  $p_{\text{H}}$  3) and to heat at  $p_{\text{H}}$  7.6, and is re-oxidised by flavin enzyme. The point of equilibrium in the reaction  $(\text{I}) \rightleftharpoons (\text{II})$  favours formation of (I) and  $K$  increases as  $p_{\text{H}}$  decreases. Reversible reduction of (I) with  $\text{Na}_2\text{S}_2\text{O}_4$  at  $p_{\text{H}} > 8$  and with Zn in 0.1N-NaOH at 0° yields a yellow product exhibiting absorption max. at 360 m $\mu$ . This product reduces methylene-blue and  $\text{AgNO}_3$ , is not inactivated by acid, but loses its colour on neutralising, and is rapidly inactivated by heat. Dihydroxyacetonephosphoric acid is dehydrogenated by a dehydrogenase from yeast with (I) acting as sp. co-enzyme. Since the H donor in the oxidation-reduction process of alcoholic fermentation is probably a triosephosphoric acid it follows that (I) acts as a H carrier, transferring H to MeCHO. W. McC.

**Dehydrogenase systems in seeds of various plants.** T. THUNBERG (Lunds. Univ. Arsskr., 1934, II, 30, No. 13, 44 pp.).—The enzyme occurs in widely varying amounts in certain seeds.

CH. ABS. (p)

**Allantoinase in insects.** M. L. ROCCO (Compt. rend., 1936, 202, 1947—1948).—Aq. extracts of many winged insects when incubated at 39—40° contain allantoin acid enzymically derived from allantoin.

J. L. D.

**Reduction of biliverdin to bilirubin in tissues.** R. LEMBERG and R. WYNDHAM (Biochem. J., 1936, 30, 1147—1170).—Biliverdin (I) is reduced anaerobically by guinea-pig's tissues (liver, kidney, spleen, brain, lung, muscle, blood, and heart, but not skin) and aerobically by the liver, spleen, kidney, and brain. The liver of man, horse, cat, rat, mouse, fowl, pigeon, *Echidna*, and (less powerfully) frog also reduce (I). Dehydrogenase systems and ascorbic acid in guinea-pig's liver reduce (I). Aldehydes (II), lactate, EtOH, citrate, formate, and (less effectively) succinate act as H donors in presence of liver enzymes. Glucose (III) dehydrogenase also reduces (I) slightly

but most of the activity of (III) is due to glycolysis. (II) are activated by proteins and by an aldehyde dehydrogenase (probably not xanthine oxidase), and the other substrates by their sp. dehydrogenases. With MeCHO activated by protein the system is stable to heat and acts much more rapidly on (I) than on methylene-blue. (I) and mesobiliverdin are reduced in a few min. to the corresponding rubins by Zn in aq.  $\text{NH}_3$  in absence of  $\text{O}_2$ .

W. McC.

**Enzymic degradation of starch.**—See this vol., 1096.

**Amylase during the growth and ripening of grains.** T. CHRZĄSZCZ and J. JANICKI (Biochem. J., 1936, 30, 1298—1302).—All three amylolytic functions (liquefying, dextrinising, and saccharifying) appear in the forming grain of barley, wheat, and oats immediately after flowering. The subsequent decrease in activity is antagonised by peptone or dil. NaCl solutions. H. D.

**Amylosynthase. XXV. Zymogen of yeast amylosynthase. XXVI. Zymogen of higher plant amylosynthase. Distribution in higher plants which accumulate starch. XXVII. Amylosynthase of higher plants which accumulate starch. XXVIII. Reaction velocity of amylosynthase.** T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1935, 11, 370—373; cf. A., 1935, 1162).—XXV. Yeast extract, after treatment with papain and filtration, contained amylosynthase (I). The latter was originally present as zymogen (II). Aq.  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , KCl, and NaCl extract (II) but not (I).

XXVI. (I) was extracted from higher plants by means of papain. It occurs in many seeds (notably rice) and in tubers of potato and *Sagittaria sagittifolia*.

XXVII. (I) occurs mainly in the endosperm of rice. The embryo contains amylase (III). Samples from glutinous rice differed from yeast-(I) in being sol. in glycerol but not in  $\text{COMe}_2$  and inactivated by  $\text{H}_2\text{S}$ ,  $\text{HgCl}_2$ , and  $\text{Pb}(\text{OAc})_2$ .

XXVIII. (I) from rice showed optimum activity at 35—46° and  $p_{\text{H}}$  6.0—6.4 according to the substrate used. (I)-(III) mixtures showed antagonistic actions.

CH. ABS. (p)

(A) **Mechanism of production of a specific bacterial enzyme which decomposes the capsular polysaccharide of type III pneumococcus.** R. DUBOS. (B) **Use of graded collodion membranes for the concentration of the enzyme.** R. DUBOS and J. H. BAUER (J. Exp. Med., 1935, 62, 259—269, 271—279).—(A) The micro-organism effecting decomp. of the polysaccharide produces the enzyme when grown on the sp. substrate, but not when grown on a casein hydrolysate medium. The yield of enzyme is dependent on the concn. of polysaccharide present and on the no. of cells used as inoculum. The enzyme is not produced in the absence of cellular multiplication.

(B) The enzyme is associated with a protein, the separation of which by membrane filtration is described.

CH. ABS. (p)

**Effect of hæmolytic substances on blood-catalase.** A. LEVI (Arch. Farm. sperim., 1936, 61,

121—142).—The contents of red corpuscles, haemoglobin (I), and catalase (II) in blood (rabbit) are diminished by intravenous injection of  $\text{KClO}_3$  or  $\text{Na}_2\text{TeO}_3$ . Solanine and the venom of *Vipera aspis* decrease erythrocytes and, to a greater extent, (I) and (II). The level of (II) is related to the content of erythrocytes and pigments derived from (I).

E. P.

**Role of cozymase in phosphorylation in yeast systems.** Å. LENNERSTRAND (Naturwiss., 1936, 24, 462—463).—The cessation of  $\text{O}_2$  uptake after a time in the system apozymase+glucose+hexose diphosphate (I)+cozymase (II)+pyrocyanine (III)+phosphate buffer ( $p_{\text{H}}$  6.2), its renewal on the addition of (II) or (I)+(II), and the fact that no inactivation of (II) takes place in the absence of F' and (III) are explained by the view that (II) is present in a higher and a lower and less stable phosphorylated condition. During fermentation the higher phosphorylated substance is formed from the lower with the  $\text{PO}_4'''$  set free from phosphorylated  $\text{C}_3$  compounds. In presence of F', however, the additional  $\text{PO}_4'''$  can only come from (I), and this reaction, being slower than the preceding one, leads to inactivation of (II). A. L.

**Cozymase. X. Phosphatase and cozymase.** K. MYRBACK and B. ÖRTENBLAD. **XI. Reducing group of cozymase.** K. MYRBACK (Z. physiol. Chem., 1936, 241, 148—155, 223—232; cf. A., 1935, 1278).—X. The inactivating effect of ordinary kidney- and bone-phosphatase (I) on cozymase (II) is not due to (I) itself but to an accompanying enzyme. The purity of (II) cannot be satisfactorily determined with apozymase (III) because of alterations in (III) on keeping.

XI. In its behaviour towards  $\text{HOI}$ , Hagedorn and Jensen's reagent, and  $\text{Mg}+\text{H}_2\text{SO}_4$ , (II) closely resembles ouabain and the lactone of angelic acid (cf. Thiele *et al.*, A., 1902, i, 155). W. McC.

**Composition of cozymase.** H. VON EULER and F. SCHLENK (Svensk Kem. Tidskr., 1936, 48, 135—137).—The empirical formula of highly purified cozymase is  $\text{C}_{21}\text{H}_{27}\text{O}_{14}\text{N}_7\text{P}_2$ , in agreement with its being made up of 1 mol. each of adenine and nicotinamide and 2 mols. of pentose phosphate. Its chemical properties can be interpreted in terms of this structure.

E. A. H. R.

**Inhibition of the action of Schardinger's enzyme by co-enzymes containing adenine.** B. ANDERSSON (Z. physiol. Chem., 1936, 241, 11—16; cf. A., 1935, 1414).—Adenine and substances of which it is a constituent [adenosine > adenylic acid (I) > adenosinediphosphoric acid (II) and adenylyl pyrophosphate, cozymase (III), and Warburg's co-enzyme] restrict in varying degrees the action of the enzyme. The effect produced by (I) and (II) is not altered following treatment with dil. aq.  $\text{NaOH}$  but that of (III) is greatly increased, the increase not being due to liberation of (I) or of  $\text{H}_4\text{P}_2\text{O}_7$ .  $\text{Na}_4\text{P}_2\text{O}_7$  has no inhibitory effect and nicotinamide only a slight effect.  $\text{NaOH}$  probably causes rearrangement of the (III) mol. and since no acid  $\text{OH}$  is thus liberated a formula for (III) similar to that of Barrenscheen is to be preferred to that of Lohmann. W. McC.

4 F

**Intermediate metabolism and oxidation processes. I. Co-enzyme and intermediate carbohydrate metabolism.** A. UTEVSKI (Ukrain. Biochem. J., 1932, 5, 71—86).—In presence of washed muscle tissue, glycogen, glucose, fructose, and glycerol do not yield  $\text{MeCHO}$  (I) but pyruvate (II) is decarboxylated. The addition of boiled muscle juice (III) restores the power to produce (I) and also to oxidise (II). The conversion of fumaric into malic acid is effected by washed muscle tissue, but the further metabolism of malic acid proceeds normally only when (III) is added. Probably a co-enzyme essential in intermediate metabolism is present in (III). W. O. K.

**Action of dyes on enzymes. Nature of the union between yeast invertase and sucrose.** J. H. QUASTEL and E. D. YATES (Enzymologia, 1936, 1, 60—80).—The reversible inactivation of invertase by acid (I) and basic dyes (II) has been interpreted quantitatively in terms of the mass action law. Variation of dye, sucrose, and  $[\text{H}^+]$  indicates a reaction between (I) ion and (II) ion and positive and negative ions of the enzyme, respectively. Glucose competes mainly with (II), fructose with (I), and sucrose with both (I) and (II). Reduced dyes are usually less toxic. E. D. Y.

**Swedish top yeast: carboxylase.** K. WULFERT (Tids. Kjemi, 1936, 16, 77—79, 82—86).—To obtain high carboxylase (I) activity, the yeast to be dried must be very fresh. Extracts of the dried yeast give vals. for Neuberg's const. <1, in agreement with theory. The effects on the (I) activity of dried yeast of warming, addition of sugars, autolysis, plasmolysis, and poisoning with  $\text{PhMe}$  or  $\text{CHCl}_3$  have been studied.

M. H. M. A.

**$\beta$ -Glucosidase from *Sorghum saccharatum*.** C. ANTONIANI (R. Ist. lombardo Sci. Lett. Rend., 1935, 68, 355—362; Chem. Zentr., 1935, ii, 2683—2684).—The enzyme from ungerminated seed shows optimum activity at  $p_{\text{H}}$  4.6 and, unlike the  $\beta$ -glucosidase from bitter almonds and malt, decomposes cellobiose and salicin at approx. the same rates. Hydrolysis of salicin is inhibited by glucose but not by galactose. The enzyme does not decompose lactose and contains no  $\beta$ -galactosidase. A. G. P.

**Synthetic action of  $\beta$ -glucosidase on glucose.** I. VINTILESCO, C. N. IONESCO, and A. KIZYK (Bul. Soc. Chim. Romania, 1935, 17, 283—292).—The amount of  $\alpha$ -glucose in the  $\alpha$ - $\beta$  equilibrium mixture is increased by increasing the concn. or by adding  $\text{COMe}_2$ . Changes in  $[\alpha]$  of glucose (I) treated with emulsin in  $\text{H}_2\text{O}$  and aq.  $\text{COMe}_2$  and the further change on destruction of the (I) by yeast show that the synthesis of gentiobiose from 2 mols. of  $\beta$ - and of cellobiose from 1 mol. of  $\beta$ - and 1 mol. of  $\alpha$ -glucose follow the law of mass action. Increase in the amount of  $\alpha$ -form favours the formation of cellobiose, in accordance with expectation.

R. S. C.

**Biochemical synthesis of  $\beta$ -glucosides derived from alcohols immiscible with water.** I. VINTILESCO, C. N. IONESCO, and M. SOLOMON (Bul. Soc. Chim. Romania, 1935, 17, 267—281).—A solution containing  $n\text{-C}_6\text{H}_{13}\cdot\text{OH}$  (30),  $\text{H}_2\text{O}$  (19.2),  $\text{COMe}_2$  (51.9), and glucose (1.5%) with emulsin (I) (0.5 g. per



100 c.c.) gives  $\beta$ -n-hexylglucoside, m.p. 87—89°,  $[\alpha]_D^{20}$  —33.28° in H<sub>2</sub>O, hydrolysed by (I) or dil. acid. The above proportions are shown to be the optimum by a study of the solubility relations of the quaternary system.

R. S. C.

**Serum-lipase during naphthalene ocular lesions in rabbits and its probable role in the pathogenesis of senile cataract.** D. MICHAEL and I. PACURARIU (Compt. rend. Soc. Biol., 1936, **122**, 1125—1128).—Serum-lipase is lowered during C<sub>10</sub>H<sub>8</sub> intoxication with the appearance of ocular symptoms, reaching a min. when the opacity becomes total. The val. then slowly (4—5 months) returns to normal.

H. G. R.

**Deaminating enzyme of flesh-fly larvae.** A. W. A. BROWN and L. FARBER (Biochem. J., 1936, **30**, 1107—1118).—The deaminase activity of extracts of the larvae of *Lucilia sericata* and *Calliphora erythrocephala* is max. at  $p_H$  7.6, is greater under anaerobic than under aerobic conditions, and increases linearly with temp over the range 10—37.5°. The extracts do not deaminate NH<sub>2</sub>-acids or di- or tri-peptides but attack the higher hydrolytic products of protein; they possess proteinase, poly- and di-peptidase, uricase, and slight deaminase activities.

W. O. K.

**Proteolytic enzymes. IX. Inactivation of papain with iodine.** M. BERGMANN and L. ZERVAS. **X. Enzymes of papain and their activation.** M. BERGMANN and W. F. ROSS (J. Biol. Chem., 1936, **114**, 711—715, 717—726).—IX. HCN does not affect the specificity of papain towards benzoylisoglutamine (I), but it increases the amount of active enzyme, and thus accelerates the cleavage of (I). Inactivation of papain with I extends not only to cleavage of gelatin and acylated peptides, but also to free peptides. Reactivity can be regenerated by HCN, but it is always < that of the original papain. The loss of activity is more pronounced in the case of substrates with a small cleavage rate.

**X. Hydrolysis of (I) by HCN—papain is completely suppressed by small amounts of NHPh·NH<sub>2</sub> (II), but (II) has no effect on the hydrolysis of peptone from albumin. HCN-activated papain consists of two distinct enzymes, papain peptidases I and II. Peptidase I is inhibited by (II) and very probably contains a CHO group, whilst peptidase II is unaffected by (II) and is reversibly inactivated by I. Peptidase I is the first proteolytic enzyme of known specificity which requires neither terminal NH<sub>2</sub> nor CO<sub>2</sub>H, and is thus an endopeptidase, in distinction to an exopeptidase which requires a terminal peptide linking. It is influenced by the nature of the NH<sub>2</sub>-acid forming or lying near the ·CO·NH<sub>2</sub> group which is hydrolysed. It is suggested that in natural papain there is an equilibrium between the peptidases I and II and a compound of these.**

J. N. A.

**Enzymic histochemistry. XXI. Proteolytic enzymes of the larvae of clothes- and wax-moths.** F. DUSPIVA (Z. physiol. Chem., 1936, **241**, 177—200; cf. this vol., 244, 759).—Larvae of *Galleria mellonella* cannot digest keratin (I). In the intestinal juice the proteinase (II), which is the most active enzyme present, exhibits optimal action [on caseinogen (III)] at  $p_H$  9.6. In *Tineola biselliella* the val. is 9.3 and the

amount of (III) digested  $\propto$  the amount of (II). In both species the optimal  $p_H$  for the aminopoly-peptidase action (on alanyl-glycylglycine) is 8.1 and those for the dipeptidase action (on alanylglycine) are 7.5 (*Tineola*) and approx. 7.8 (*Galleria*). The peptidases are equally sensitive to the action of ·SH compounds [e.g., thioglycolic acid (IV)], but whereas (II) of *Tineola* is unaffected by low concns. of (IV), the action of (II) of *Galleria* is restricted. The ability of insects to utilise (I) is due entirely to the existence of a negative oxidation-reduction potential in their intestinal juice.

W. McC.

**Proteases of acid proteolytes.** M. E. C. GORINI and L. GORINI (R. Ist. lombardo Sci. Lett. Rend., 1935, **68**, 115—125; Chem. Zentr., 1935, ii, 2964).—Enzymic activity in filtered solutions increases with the age of the culture from which it is obtained. Best results were obtained with 24-hr. cultures. Citrate additions have a favourable effect. Activity is max. at  $p_H$  7.0 and ceases at 4.3.

A. G. P.

**Digestive enzymes in marine invertebrates. II. Proteolytic enzymes in the starfish, *Diosasterias nipon*, Doderlein.** E. SAWANO (Sci. Rep. Tokyo Bunrika Daigaku, 1936, **2**, B, 179—199; cf. this vol., 521).—Extracts of the stomach of *D. nipon* hydrolyse glycylglycine (I) but not gelatin; those of the pyloric caecum hydrolyse proteins, peptones, and (I) and contain (as does the rectal gland) a cathepsin-like enzyme and a trypsin-like carboxy-polypeptidase accelerated by cystine and inhibited by cysteine. Optimum  $p_H$  vals. are given for various substrates.

F. O. H.

**Location of the anti-enzyme in egg-white.** J. S. HUGHES, H. M. SCOTT, and J. ANTILYES (Ind. Eng. Chem. [Anal.], 1936, **8**, 310—311).—The anti-proteolytic enzyme in new-laid eggs is chiefly located in the inner thin white.

S. C.

**Alcohol and peptic digestion.** E. TRABUCCHI (Arch. Farm. speriment., 1936, **61**, 186—208).—The inhibition by EtOH of *in-vitro* proteolysis by pepsin is due not merely to inactivation of the enzyme but to modifications of the physico-chemical properties of the substrate, e.g., diminution of dissociation and of enzyme-substrate adsorption, increase in  $\eta$ , and, particularly, inhibition of preliminary swelling (due to dehydration by EtOH) of substrate necessary for subsequent hydrolysis.

F. O. H.

**Inactivation of crystalline pepsin.** J. STEINHARDT (Nature, 1936, **138**, 74—75).—At  $p_H$  vals. > 6.45, cryst. pepsin inactivates unimolecularly at a rate  $\propto 1/[H^+]^5$ . Equilibria governing the concn. of an unstable species of pepsin ion, formed by dissociation of five acidic groups, probably determine the rate. Between ionic strengths of 0.012 and 0.10, the velocity at const.  $p_H$  increases by > 30 times. On agitation, a heterogeneous reaction, independent of  $p_H$  and ionic strength over wide limits, obscures the results.

L. S. T.

**Phosphatase distribution in higher plants.** V. IGNATIEFF and H. WASTENEYS (Biochem. J., 1936, **30**, 1171—1182).—The phosphatase contents of various parts of bean, potato, radish, and wheat plants

at different stages of development have been determined. W. McC.

**Phosphatase of potato and sugar-beet.** E. PFANKUCH (Z. physiol. Chem., 1936, 241, 34—46; cf. A., 1935, 1181).—The phosphatase (I) content of the press-juice from potatoes is that of any other vegetable material. (I) is non-sp. but hydrolyses substrates at different rates (Na inositol hexaphosphate : Na hexose diphosphate : Na  $\alpha$ -glycerophosphate : Na phosphoglycerate : Na  $\beta$ -glycerophosphate as 23 : 52 : 61 : 66 : 100). The action of (I) (optimal at  $p_H$  5.8—5.9) is easily inhibited by  $PO_4^{4-}$  and very easily by NaF, which acts more powerfully with high substrate concn. Inhibition is also caused by org. and inorg. anions and cations,  $Cu^{++}$  being especially powerful. The effect of  $Cu^{++}$  is counteracted by  $CN'$  and glutathione (II) and partly counteracted by ascorbic acid (III) although (II) and (III) alone have no effect on (I).  $Mg^{++}$  does not activate (I).

W. McC.

**Serum-phosphatase in the domestic fowl.** R. H. COMMON (J. Agric. Sci., 1936, 26, 492—508).—The serum-phosphatase (I) of laying hens was > that of cocks and pullets. Vals. for hens altered very little during periods of suspended egg-production. In chicks, (I) increased rapidly until 10—12 days after hatching, and subsequently fell sharply to a lower level at 3 weeks. Thereafter vals. for male birds declined steadily until maturity, those for females being of a similar order until increasing again at the onset of laying. Variations for laying birds were not decreased in range by administration of Radiostol (3000 international units of vitamin-D per ml.). In pullets the increase in (I) vals. on a low-Ca ration was  $\gg$  when  $CaCO_3$  supplements were fed.

A. G. P.

**Brain phosphatase.** K. V. GIRI and N. C. DATTA (Biochem. J., 1936, 30, 1089—1096).—The phosphatase activity of aq. extracts of  $COMe_2$ -treated brain tissue is max. at  $p_H$  5.0 and 9.4—9.6, indicating that two distinct phosphatases are present. Their ratio is approx. const. for brains of animals of the same species. Both hydrolyse hexose diphosphate more rapidly than  $\beta$ -glycerophosphate. Purification of the enzymes may be effected by isoelectric pptn. of the inert material at  $p_H$  4.8, dialysis, ultrafiltration through Cellophane membranes, and  $COMe_2$  pptn.  $Mg^{++}$  activates the enzyme in alkaline but not in acid solution, the activation being enhanced when preps. are purified by dialysis. The rate of hydrolysis by either phosphatase is initially linear irrespective of the purity of the enzyme and presence or absence of  $Mg$ , but depends on the concn. of substrate.

W. O. K.

**Enzymes in cancer. II. Glycerophosphatases of human erythrocytes.** J. W. SCHOONOVER (Biochem. J., 1936, 30, 1097—1106).—Hæmolysates of normal and cancerous erythrocytes hydrolyse  $\alpha$  and  $\beta$ -glycerophosphate optimally at  $p_H$  5.6, the rate being about 6 times as great for  $\alpha$  as for  $\beta$ . Hydrolysis is more rapid in presence of  $Mg^{++}$ , but the effect with  $\beta$  is relatively > that with  $\alpha$  and less evident with cancerous than with normal erythrocytes. The  $\beta$ -glycerophosphatase activity of

erythrocytes is relatively const. in normal but often increased in cancerous individuals. The  $\alpha$ -glycerophosphatase activity is less const. in normals and is not significantly increased in cases of cancer.

W. O. K.

**Effects of activators, inhibitors, and destructive agents on urease.** T. BERSIN and H. KOSTER (Z. ges. Naturwiss., 1935, 1, 230—242; Chem. Zentr., 1935, ii, 2965).—Active urease (I) is a  $\cdot SH$  compound. Glutathione and  $K_2S_2O_8$  at  $p_H$  7.16 increase the activity of soya-bean preps. The latter are hydrogenated by succino-dehydrogenase. In plants the dehydrogenase regulates the activity of (I). Effects of various As and Se compounds and of  $CH_2I \cdot CO_2'$  are examined. Ascorbic acid alone has no effect on (I), but in presence of Fe is injurious.

A. G. P.

**Reaction of iodoacetate and of iodoacetamide with various thiol groups, with urease, and with yeast preparations.**—See this vol., 1074.

**Diastase determination in blood. II.** F. BALTZER (Klin. Woch., 1935, 14, 1395—1397; Chem. Zentr., 1935, ii, 2854; cf. this vol., 747).

H. N. R.

**Yeast grown in cyanide. II.** L. B. PETT (Biochem. J., 1936, 30, 1438—1445; cf. A., 1935, 1165).—Yeast cultured in the presence of  $CN'$  differed from top and bottom yeast in its respiration and fermentation properties, having a high flavin (I) content, exhibiting no Pasteur reaction or  $CN'$  inhibition. Prolonged sub-culturing in  $CN'$  media gave a yeast with no (I) but containing a blue fluorescing pigment.

H. D.

**Comparative effects of the elements on the growth of *Aspergillus niger* (stimulation and toxicity).** K. PIIRSCHLE (Planta, 1935, 24, 649—710).—The toxicity of  $Fe^{III}$ ,  $Ce^{IV}$ , and  $Hg^{II}$  salts is > that of the corresponding  $Fe^{II}$ ,  $Ce^{III}$ , and  $Hg^I$  salts, respectively. The very toxic action of  $Fe(CN)_6^{4-}$  and  $Fe(CN)_6^{3-}$  is not due to the formation of  $CN'$ .  $Ni^{II}$  exhibits greater toxicity and stimulative effects than  $Co^{II}$ . Metals of the Pt group show progressively varying effects according to their position in vertical or horizontal series. The indispensability of Mn is questioned, although its stimulative action is very marked. In general elements in anionic forms are usually more toxic than in cationic forms (exception, uranyl salts more toxic than uranates). The following relative toxicities are established:  $S_2O_4^{2-} > S^{2-} > SO_3^{2-} = S_2O_8^{2-} > SO_4^{2-}$ ;  $TeO_3^{2-} > TeO_4^{2-}$ ;  $SeO_3^{2-} > SeO_4^{2-}$ ;  $AsO_3^{3-} > AsO_4^{3-}$ ;  $SeO_4^{2-} > TeO_4^{2-} > SO_4^{2-}$ ;  $SeO_3^{2-} > TeO_3^{2-} > SO_3^{2-}$ ;  $CrO_4^{2-} > MoO_4^{2-} > SO_4^{2-}$ ;  $AsO_4^{3-} > SbO_4^{3-} > PO_4^{3-}$ . Stimulative effects are in the relative order  $Zn > Cd > Hg$ ;  $Ge > Sn > Pb$ ;  $Al > Y > La$ ;  $Si > Ti$ ;  $P > As$ ;  $P > V$ ;  $S > Se$ ;  $S > Cr$ .

A. G. P.

**Effect of zinc on the metabolism of *Aspergillus niger*.** G. M. VASSILIEV (Arch. Mikrobiol., 1935, 6, 250—275).—Zn affects the growth of *A. niger* and also its metabolism. In the latter respect Zn acts principally on the course of formation and consumption of intermediate products of sugar metabolism and of gluconic (I) and citric (II) acids. With strains producing (I), or (I) and (II), Zn decreases the production of the acids, but with (II)-producing



strains, acid accumulation is favoured. Zn affects metabolism not by direct action on the protoplasm, but indirectly as a result of its influence on vegetative growth. It does not modify the respiration of the mould. A. G. P.

**Acids and alcohols as nutrients for *Monascus*.** K. SATO and I. NAITO (J. Agric. Chem. Soc. Japan, 1935, 11, 473—479).—*M. anka* assimilated citric, fumaric, gluconic, lactic, malic, and succinic acids, but not AcOH,  $\text{H}_2\text{C}_2\text{O}_4$ , kojic or tartaric acids. Suitable acids and alcohols were as effective as glucose as C sources. CH. ABS. (p)

**Fermentation of arabinose and fucose by *Aspergillus oryzae*.** II. T. TADOKORO (J. Agric. Chem. Soc. Japan, 1935, 11, 365—369; cf. this vol., 639).—Arabinose yielded  $\text{CO}_2$ ,  $\text{HCO}_2\text{H}$  (I), citric and glycollic (II) acids with smaller amounts of  $\text{H}_2\text{C}_2\text{O}_4$  and kojic acid and glyceraldehyde. From fucose, (I), (II), and lactic acid were produced.  $\text{MeCHO}$ ,  $\text{COMe}_2$ , EtOH, and AcOH were not obtained from either sugar. CH. ABS. (p)

**Formation of *d*-fructose from mannitol by means of *Penicillia*.** A. ANGELETTI (Annali Chim. Appl., 1936, 26, 234—236).—*d*-Fructose is produced from mannitol by the action of *P. crustaceum* (L.), Fries, and *P. luteum purpurogenum* after 20 days' fermentation. L. A. O'N.

***Rhizopus*.** I. Production of *d*-lactic acid. G. E. WARD, L. B. LOCKWOOD, O. E. MAY, and H. T. HERRICK (J. Amer. Chem. Soc., 1936, 58, 1286—1288).—*R. oryzae*, *arrhizus*, and *tritici* produced 19—62% of lactic acid (I) on a medium containing glucose, nutrient salts, and  $\text{CaCO}_3$ . Some strains produced little (I). In absence of  $\text{CaCO}_3$  and with urea as N-source, *R. nigricans* (1 strain) and *chinensis* formed appreciable quantities of EtOH. H. B.

**Assimilation of nitrites by fungi.** Ia, II. K. SAKAGUCHI and Y. WANG (Bull. Agric. Chem. Soc. Japan, 1936, 12, 59—62, 63—69; cf. A., 1934, 1405).—Ia. Using  $\text{NaNO}_2$  in place of  $\text{NaNO}_3$  in the Czapek medium, the classification of black *Aspergilli* has been studied. They can be divided into three groups.

II. *A. oryzae*, *A. aureus*, and *A. batatae* (but not *A. oryzae*, Takahashi) convert  $\text{NaNO}_2$  into  $\text{NaNO}_3$ , but neither is produced from  $\text{NH}_4\text{Cl}$  by *A. oryzae*.  $\text{NaNO}_2$  is assimilated selectively by all three species in presence of  $\text{NaNO}_3$ , which is attacked only after complete utilisation of  $\text{NaNO}_2$ .  $\text{NaNO}_3$  and  $\text{NH}_4\text{Cl}$  are used up nearly at the same rate, and  $\text{NaNO}_2$  is regarded as an intermediate in the resorption of  $\text{NaNO}_3$  by moulds. A method for the determination of  $\text{NO}_2^-$  in presence of  $\text{NO}_3^-$  is described. J. N. A.

**Chemistry of growth substance B.** N. NIELSEN and V. HARTELUS (Nature, 1936, 138, 203).—The growth substance previously described (A., 1933, 638) is produced when sucrose is inverted by means of org. or inorg. acids. Glycollic (I) + pyruvic acid (II) together act as growth substances for *Aspergillus niger*, but alone have little or no effect. Glyoxylic acid (III) alone, and (III) or ascorbic acid added to (I) + (II), have a similar effect. Oxidation with

$\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$  destroys the growth substances which act on yeast, but not those which act on moulds. L. S. T.

**Metabolic products of *Aspergillus terreus*.** Thom. Geodin and erdin.—See this vol., 1116.

**Ravelenin, a metabolic product of *Helminthosporium Ravenelii*, Curtis, and of *H. Turcicum*, Passerini.**—See this vol., 1121.

**Reactions of *Helvella*.** II. G. REIF (Z. Unters. Lebensm., 1936, 71, 435—442; cf. A., 1935, 1181).—The substance present in *H. esculenta* which reduces  $\text{SeO}_3$  to Se is removed from aq. alkaline solution by distillation or by extraction with  $\text{Et}_2\text{O}$  or  $\text{CHCl}_3$ . The distillate gives a violet colour with a phosphotungstic-phosphomolybdic acid reagent, and, in acid solution, with fuchsin- $\text{SO}_2$  reagent. With the exception of that from *H. crispa*, no other fungus distillate gives these reactions. The  $\text{SeO}_3$ - $\text{H}_2\text{SO}_4$  reagent may be used to differentiate aldoses and ketoses. E. C. S.

**"Tryptone" medium for detection of flat-sour spores.** O. B. WILLIAMS (Food Res., 1936, 1, 217—221).—Plate counts with a casein digest medium give better results than with other solid media or dilution methods with liquid media. Low-resistant spores are destroyed by 5 min. boiling, but resistant forms are not destroyed by 30 min. boiling. E. C. S.

**Growth-promoting activity of certain sterols on *Trichomonas columbae*.** R. CAILLEAU (Compt. rend. Soc. Biol., 1936, 122, 1027—1028).—The activity of cholesterol, modified in either the cyclic portion or the side-chain, is described. H. G. R.

**Effect of emetine on *Endamoeba histolytica* in culture.** J. H. ST. JOHN (Amer. J. Hyg., 1933, 18, 414—432).—Lethal dosages are examined in relation to lethal time. CH. ABS. (p)

**Chemotherapy of experimental trichiniasis.** D. N. GREENWOOD (J. Chemother., 1935, 12, 232—234).—Tartar emetic, acetarsone, emetine, parathormone, Ca gluconate, and viosterol were without parasitocidal action and did not increase calcification of the cyst wall or of trichinellae. CH. ABS. (p)

**Function of protohæmin in protozoa and parametotropic bacteria.** A. LWOFF (Compt. rend. Soc. Biol., 1936, 122, 1041—1042).—In presence of cytochrome-c, only 2/3 of the protohæmin is transformed into hæmin-c. H. G. R.

**Acetic bacteria produced in Formosa.** VI. S. TANAKA (J. Agric. Chem. Soc. Japan, 1935, 11, 435—455).—Organisms from fruit, sake, etc. are examined. CH. ABS. (p)

**Relation between iron and oxidase reaction. *Bacillus* occurring in mussels at the bottom of a mussel-hill of the later stone age.** R. KATSUNUMA (Z. Klin. Path. Hamatol. Japan, 1933, 2, 1).—Bacteria which could be cultivated repeatedly on an Fe-free medium are described. A slow decline occurs in oxidase activity of successive generations. CH. ABS. (p)

**Bacteriological and biochemical relationships in the *pyocyaneus-fluorescens* group.** I. Chro-

mogenic function in relation to classifications. G. E. TURFITT (Biochem. J., 1936, 30, 1323—1328).—Media are elaborated on which the *pyocyaneus-fluorescens* group of bacteria exhibit a marked constancy in pigment production, and evidence is obtained for the classification of these organisms into a single genus on the basis of their chromogenic function.

P. W. C.

Pigments of purple bacteria. I. Spirilloxanthin, a component of the pigment complex of *Spirillum rubrum*. C. B. VAN NIEL and J. H. C. SMITH (Arch. Mikrobiol., 1935, 6, 219—229).—The isolation of spirilloxanthin,  $C_{48}H_{66}O_3$ , is described. It is a purple pigment, highly unsaturated (15 double linkings), contains  $\geq$  one OH, and no free  $\cdot CO_2H$ . Other carotenoid pigments are also present in the organism.

A. G. P.

Nodule bacteria. IX. Electrical properties of the accessory substance. A. ITANO and A. MATSUURA (J. Agric. Chem. Soc. Japan, 1936, 12, 457—466; cf. this vol., 899).—Extracts of bean nodules in hot and cold  $H_2O$ , and  $EtOH$ +hot  $H_2O$ , were dialysed and compared with a yeast extract. The accessory substance was found mainly in the cathode chamber. The yeast extract was inert towards electrodialysis. There was no relation between the accessory substance and N content.

J. N. A.

Anaerobic bacteria. VI. Nature and systematic position of a new chromogenic *Clostridium*. E. MCCOY and L. S. MCCLUNG. VII. Serological relations of *Cl. acetobutylicum*, *Cl. felsineum*, and *Cl. roseum*. L. S. MCCLUNG and E. MCCOY (Arch. Mikrobiol., 1935, 6, 231—238, 239—249; cf. B., 1935, 476).—VI. The pigmentation, biochemical, and agglutination activities are recorded.

VII. Antigenic differences and relationships are examined.

A. G. P.

Effect of concentration of sorbitol on production of sorbose by the action of *Acetobacter suboxydans*. E. I. FULMER, J. W. DUNNING, J. F. GUYMON, and L. A. UNDERKOFER (J. Amer. Chem. Soc., 1936, 58, 1012—1013).—The rate of production and the final yield of sorbose (I) from sorbitol (II) and *A. suboxydans* (which is much superior to *A. xylinum*) increase with rise in the surface-vol. ratio. For a given ratio the yield of (I) is a linear function of  $\log t$  up to 80%. With concns. of (II)  $<40\%$ , rate of production is decreased by increased concn. of (II), but the final yield is little affected. Little or no action occurs with concns.  $>40\%$ .

H. B.

Paracolon group of bacteria. B. R. SANDIFORD (J. Path. Bact., 1935, 41, 77—78).—The organisms are coliform, but ferment lactose either atypically or not at all. They produce indole. Fermentation of rhamnose follows a course different from that commonly found in bacterial fermentations. Gases other than  $H_2$  and  $CO_2$  are probably produced.

CH. ABS. (p)

Growth of bacteria in media containing previously-heated ovalbumin as the source of nitrogen. E. POZERSKI (Compt. rend. Soc. Biol., 1936, 122, 909—911).—*B. coli* cannot utilise oval-

bumin (deprived of peptone and coagulated at various temp.) as a sole source of N.

H. G. R.

Hydrogen donators for *Proteus vulgaris*. D. BACH (Compt. rend. Soc. Biol., 1936, 122, 1065—1067).—Alcohols, saturated aldehydes, and some org. acids (including  $NH_2$ - and unsaturated acids), but not unsaturated aldehydes, act as donators.

H. G. R.

Development of the dehydrogenases of *Proteus vulgaris*. D. BACH (Compt. rend. Soc. Biol., 1936, 122, 1068—1070).—The dehydrogenase activity decreases with the age of the culture; this is independent of the media, but in some cases this decrease is retarded.

H. G. R.

Independence of the production of proteases and of the development of the cell of *B. prodigiosum*. W. MOYCHO (Compt. rend., 1936, 202, 2007—2009; cf., A., 1928, 1402; this vol., 245).—Cultures in buffered 1% peptone media grow best at  $p_H$  7.5. The proteolytic capacity increases with increasing acidity, allowance being made for diminished reproductive capacity, and is nil in feebly alkaline media. As  $[PO_4^{''}]$  decreases from  $N/8$  to  $N/15$ , proteolysis increases but growth diminishes.

J. L. D.

Streptococci producing a substance inhibiting growth of lactic streptococci. G. A. COX and H. R. WHITEHEAD (New Zealand J. Agric., 1936, 52, 38—43).—The irregular occurrence in milk of streptococci, originating in dung, fodder, or the udder, which produce a substance inhibiting the growth of lactic streptococci is described.

W. L. D.

Growth and metabolism of cells of *Streptococcus lactis* in sterilised milk (logarithmic phase). T. MATUSZEWSKI (Polish Agric. Forest. Ann., 1935, 34, 403—455).—Lactic acid production per cell per hr. is determined for *S. lactis* and *S. cremoris*.

CH. ABS. (p)

Nutritive medium for the preparation of tuberculin. D. A. ZUVERKALOV and A. K. SARKISOV (Ann. Inst. Pasteur, 1936, 57, 111—119).—After suitable hydrolysis a medium can be prepared from potato which will give a heavy growth of tubercle bacilli over a long period. The high buffering power maintains an optimal  $p_H$  for several months. The tuberculin prepared from potato broth produces no reaction in healthy animals, whilst the broth alone gives no reaction even in tuberculous animals and when concn. tenfold.

P. G. M.

Influence of hæmoglobin on the virulence of tubercle bacilli. H. PORGES (Wien. med. Woch., 1935, 85, 1023—1024).—Hæmoglobin was without effect.

A. G. P.

Spontaneous protein flocculation in old, acidified cultures of human *B. tuberculosis* in Sauton's medium and its acceleration by heat. F. VAN DEINSE (Compt. rend. Soc. Biol., 1936, 122, 1019—1020).—The pptn. occurs after 40 days at a  $p_H$   $\geq 6.6$ . The ppt. firmly adsorbs tuberculin and may be redissolved in dil. alkali. It is also irregularly observed in bovine but never in avian cultures.

H. G. R.

Action of poppy-seed oil, with and without added cholesterol, on staphylococcus toxin.



J. SCHWARTZ (Compt. rend. Soc. Biol., 1936, **122**, 1006—1009).—The neutralising action of the oil is not observed when the former contains 3% of added cholesterol.

H. G. R.

**Bactericidal action of ethylapoquinine and ethylhydrocupreine on type strains of pneumococci. I. *In vitro*.** S. MATSUDA (Japan. J. Med. Sci., IV; Proc., 1933, **7**, 45—47).—Ethylapoquinine hydrochloride (I) inhibits types I, II, and III pneumococci in concns. of 1 in 2 million; optoquin (II) requires 1 in 512,000. As a bactericide (I) is 2—8 times as potent as (II). Type III pneumococcus was much more susceptible than type I or II.

CH. ABS. (p)

**Changes produced in spirochaetes of relapsing fever by action of pharmacological reagents. III. Effect of pyridine and its alkyl derivatives.** K. HOSHINA (Luea, Bull. Soc. Jap. Syphiligraph. Kyoto, **7**, 129—136).—The toxicity of 2-methyl-, 2:6- and 2:4-dimethyl-, and 1:4:6-trimethylpyridine increased with increasing length of the side-chain. Low concns. of the first three named caused an increase in mobility, the effect decreasing in the order given.

CH. ABS. (p)

**Inhibitory power of the neutral sulphate of 8-hydroxyquinoline ("sunoxol") on tubercle bacilli in different media, particularly in homogeneous cultures.** P. COURMONT, A. MOREL, L. PERROT, and F. DENARD (Compt. rend. Soc. Biol., 1936, **122**, 1110—1113).—The sulphate is a powerful antiseptic for the bacillus.

H. G. R.

**Inhibitory power of two derivatives of 8-hydroxy-6-methylquinoline on pathogenic bacteria.** A. MOREL, A. ROCHAIX, L. PERROT, and M. Moutou (Compt. rend. Soc. Biol., 1936, **122**, 1113—1114).—The hydrochloride is a powerful antiseptic, comparable with "sunoxol" (cf. preceding abstract), the action being only slightly affected by methylation of the Ph nucleus whereas it is markedly decreased by sulphonation.

H. G. R.

**Inhibitory power of derivatives of 8-hydroxyquinoline on pathogenic bacteria.** A. MOREL, A. ROCHAIX, L. PERROT, and A. PEGON (Compt. rend. Soc. Biol., 1936, **122**, 1115—1116).—The salicylate and sulphosalicylate are only slightly less antiseptic than "sunoxol" (I) (cf. preceding abstract) but are less caustic. The bacterial val. is decreased by sulphonation, but not to the same extent as with (I).

H. G. R.

**Action of ultra-violet light on bacteria.** G. DREYER and M. L. CAMPBELL-RENTON (Proc. Roy. Soc., 1936, B, **120**, 447—472).—The lethal effect of ultra-violet radiation on the 26 species and strains of bacteria tested is greatest for  $\lambda$  2655, and  $2536 > 2804 > 2482 > 2700$ . The bactericidal effect is not  $\propto$  the relative energies of these  $\lambda$ . The shape of the growth-exposure curve varies for different bacteria and between the strains of some bacteria, including some which are serologically alike. Sensitisation by erythrosin markedly increases the sensitivity to long  $\lambda$ ; the effect with shorter  $\lambda$  varies widely. Gram-positive organisms show a much greater sensitivity to long  $\lambda$  than do Gram-negative. The curves

of sensitivity to various dilutions of disinfectants differ from each other and from the corresponding ultra-violet sensitivity curves. In the greater dilutions growth stimulation is observed.

F. A. A.

**Cholesterol and the lytic power of bacteriophage.** B. S. LEVIN and I. LOMINSKI (Compt. rend. Soc. Biol., 1936, **122**, 1063—1065).—The conc. bacteriophage is inhibited by large amounts of cholesterol (I), but when diluted is inhibited by a high and enhanced by a low concn. of (I).

H. G. R.

**Inactivation of crystalline tobacco-mosaic virus protein.** W. M. STANLEY (Science, 1936, **83**, 626—627).—Treatment of the active cryst. protein (A., 1935, 1181) with  $H_2O_2$ ,  $CH_3O$ ,  $HNO_2$ , or ultra-violet light produces inactive native proteins which, although slightly altered, retain certain chemical and serological properties characteristic of the virus protein. The inactive proteins do not produce the mosaic disease, or a protein of high mol. wt. on inoculation into Turkish tobacco plants, or local lesions in *Nicotiana glutinosa*, L.

L. S. T.

**Protective action of rabbit serum for vaccinia virus at high temperatures.** E. W. GOODPASTURE and G. J. BUDDINGH (Science, 1936, **84**, 66—67).—Normal inactivated rabbit serum maintains the viability of vaccinia virus at 37° for longer times than do 50% glycerol, gum acacia, 3% mucin in saline, and sterile egg yolk.

L. S. T.

**New oestrogenic substance from ovaries.** R. H. ANDREW and F. FENGER (Science, 1936, **84**, 18—19).—Crystals, m.p. 95.1° (uncorr.), mol. wt. 320, of a substance (I), probably  $C_{20}H_{41}O_2N$ , which differs chemically and physiologically from urinary oestrogenic substances have been isolated from ovaries. 0.00001 mg. of (I) produces oestrus in rats after 96 hr.

L. S. T.

**Effect of ovarian extracts on oxygen consumption of the uterus.** M. A. KHAYYAL and C. M. SCOTT (Quart. J. Exp. Physiol., 1935, **25**, 77—83).—Fresh follicular fluid from cows contains a substance (not oestrin or luteal hormone) which increases the rate of  $O_2$  consumption of the isolated uterus of mice. The substance also occurs in human serum and is probably released from the ovary by the action of anterior pituitary hormones. Thyroxine also increases the  $O_2$  consumption.

CH. ABS. (p)

**Production *in vitro* of oestrogenic substances from organs.** P. RONDONI, V. CARMINATI, and A. CORBELLINI (Z. physiol. Chem., 1936, **241**, 71—80).—Pulped horse liver containing 5% of added cholesterol yields oestrogenic material after being left for 5—6 weeks at 38—53°.

W. McC.

**Influence of oestrin injections on the balance between the prehypophyseal gonadotropic hormones of the rat.** A. LIPSCHÜTZ (Quart. J. Exp. Physiol., 1935, **25**, 109—120).—The action of oestrin is probably due to a change in the balance between the oestrogenic and luteinising hormones, the proportion of the latter being lowered. Spermatogenesis is usually disturbed.

CH. ABS. (p)

**Testosterone, the crystalline male hormone from ox testes.** K. DAVID (Acta Brev. neerl.

Physiol., 1935, 5, 85—86; Chem. Zentr., 1935, ii, 3254; cf. A., 1933, 1933).—Testosterone forms an *acetate*, m.p. 140—141°, and an *oxime*, m.p. 221—222.5°. It is not acidic, and is saturated. The ultra-violet absorption spectrum is similar to that of cholestenone. Mild oxidation produces a diketone, m.p. 171—173°, with practically the same absorption spectrum, and probably identical with androstenedione.

R. N. C.

Characteristics of the testes hormone. K. MATSUZAKI (Japan. J. Med. Sci., IV, 7, No. 2—3; Proc. Japan. Pharmacol. Soc., 1933, 140—142).—Injection of lipin fractions into normal and castrated male rats during 10 days caused hypertrophy of sex organs.

CH. ABS. (p)

Action of the male sex hormone preparation androstin in female hypertension. H. MAYR-HOFER (Wien. med. Woch., 1935, 85, 1038).

R. N. C.

Assay of *trans*-dehydroandrosterone and its effects on male and female gonadectomised rats. V. KORENCHESKY and M. DENNISON (Biochem. J., 1936, 30, 1514—1522).—*trans*-Dehydroandrosterone (I) is a very weak sex hormone (rat unit approx.  $940 \times 10^{-6}$  g.). (I) shows some of the typical properties of the female hormones, and its restorative effect on the atrophied sexual organs of male and female gonadectomised rats is definite, but (except in the case of the preputial glands) small. The co-operative effect when injected with œstrone is only slight for males and doubtful for females. The ratio of the % increase in wt. of the prostate to that of seminal vesicles after injection of (I) is similar to that of gonadotropic hormone, but different from that observed during normal development.

J. N. A.

Biological determination of the male hormone in carp. A. BEAUNE (Bull. Sci. pharmacol., 1935, 42, 193—199; Chem. Zentr., 1935, ii, 2835).

R. N. C.

Treatment of inefficiency phenomena with male hormone. E. BRAUN (Deut. med. Woch., 1935, 61, 1482).

R. N. C.

Protective action of progesterone on the genital organs of male mice. H. BURROWS (Nature, 1936, 138, 164).—Progesterone protects the genital organs of non-castrated mice from the injurious effects of excessive dosage with œstrone.

L. S. T.

Sexual hormones and related substances.

IX. Substance having powerful action on the vesicular glands of the castrated male mouse. W. DIRSCHERL, J. KRAUS, and H. E. VOSS (Z. physiol. Chem., 1936, 241, 1—10; cf. this vol., 472).—Cryst. follicular hormone from mares' urine (and also probably stallions' but not men's urine) contains a substance (I) which on treatment with  $\text{PtO}_2 + \text{H}_2$  gives a hormone (II) having a powerful stimulating action on the vesicular glands of the castrated male mouse. The purest samples of (II) contained 1 mouse unit in 0.02 mg. and had no effect on the capon's comb. (II) (1 unit in 0.1—0.2 mg.) was also obtained without hydrogenation from wool fat and quassia bark. Other sex hormones also [e.g., equilin, equilenin, testosterone (III)] probably contain (I) and/or (II). The conversion of (I) into (II) possibly involves con-

version of  $\text{:CO}$  into  $\text{:CH}\cdot\text{OH}$  and when this change is made in (III) the effect on the glands is increased tenfold.

W. McC.

Action of follicular hormone on the thyroid of castrated women. M. BENAZZI (Boll. Soc. ital. Biol. sperim., 1932, 7, 472—476).

R. N. C.

Behaviour of calcium and potassium in the blood-serum of castrated bitches following treatment with follicular hormone. L. MANZI (Boll. Soc. ital. Biol. sperim., 1932, 7, 642—646).—Castration increases serum-K slightly without affecting Ca. Follicular hormone causes a rise of Ca, K remaining steady.

R. N. C.

Primary hypercholesterolaemia in rabbits after administration of the luteinising hormone (prolan-B). G. TEILUM (Compt. rend. Soc. Biol., 1936, 122, 981—984).—A few min. after injection, blood-cholesterol is increased by approx. 50%, returning to normal after approx. 1 hr.

H. G. R.

Relation between excretion of chloride and that of water after injection of pituitrin. K. UNNA and L. WALTERSKIRCHEN (Arch. exp. Path. Pharm., 1936, 181, 681—688; cf. Dittmar, A., 1933, 1075).—In fasting dogs with fistulae of the bladder subcutaneous and (at much lower concn.) intravenous injection of small doses of pituitrin (I) increases the urinary excretion of  $\text{Cl}'$  without appreciably increasing the vol. of urine. The min. effective doses of (I) are the same as the min. doses required to inhibit diuresis in dogs receiving much  $\text{H}_2\text{O}$  and the excretion of  $\text{Cl}'$  increases as the dose increases. Doses  $\gg$  the min. effective increase the vol. of urine, the increase depending chiefly on the  $\text{Cl}'$  excretion; small doses also increase the vol. in dogs on a diet rich in  $\text{NaCl}$ .

W. McC.

Effect of extracts of anterior lobe of the pituitary on blood-sugar after elimination of the adrenals. K. J. ANSELMINO and F. HOFFMANN (Arch. exp. Path. Pharm., 1936, 181, 674—680; cf. A., 1935, 1544).—In dogs with adrenals extirpated (or ligated) subcutaneous injection of extracts containing the pancreatropic hormone (I) produces great decrease in the blood-sugar. In the intact dog the increase is very slight because the increased secretion of insulin caused by (I) is followed by increased adrenaline output. After destruction of (I) by heat the action of the substance in the extracts which increases the blood-sugar is unaffected by removal or ligation of the adrenals.

W. McC.

Effect of the fat-metabolism hormone of the anterior pituitary on ketone excretion by rats under experimental conditions. C. SIEVERT (Z. ges. exp. Med., 1935, 96, 429—441; Chem. Zentr., 1935, ii, 3255).—Spontaneous ketonuria under the conditions of Butts, Cuttler and Deuel, Burn, or Ging is caused by fasting or administration of a pure fat diet. The fat-metabolism hormone increases ketonuria on the fat diet, but not in fasting. The hormone in the blood after overcharging with fat corresponds with the pituitary hormone in its properties.

R. N. C.

Pituitary hormones in cerebrospinal fluid. V. COLOMBI and V. PORTA (Boll. Soc. ital. Biol. sperim., 1932, 7, 1103—1105).—The cerebrospinal



fluid of normal men and pregnant women contains no gonadotropic hormones, but exerts a slight oxytocic effect on the isolated uterus of the guinea-pig, even if the animal has been hypophysectomised. The fluid causes a slight increase of blood-pressure in dogs.

R. N. C.

Secretion of an antidiuretic pituitary hormone in response to the need for renal water conservation. A. GILMAN and L. S. GOODMAN (Science, 1936, 84, 24—25).—The posterior pituitary of rats and dogs secretes an antidiuretic hormone which acts on the kidney, escaping ultimately into the urine, in which it is relatively stable. The need for H<sub>2</sub>O conservation by the body is the stimulus for secretion.

L. S. T.

Biological effects of homologous thymus implants in successive generations of rats. N. H. ENHORN and L. G. ROWNTREE (Science, 1936, 84, 23—24).—Frequent implants in albino rats accelerate the rate of growth and development of the young, similarly to daily injections of thymus extract.

L. S. T.

Effect of various hormones on the blood picture, especially on nuclear displacement according to Arneth. I. Thyroid gland. II. Effect of insulin in the correlation between thyroid and insulin. S. MORMOTO (Folia Endocrinol. Japon., 1934, 9, 105—106).—I. After feeding thyroid and in Basedow's disease the blood picture shows a "left shift," and after thyroidectomy a right shift. Thyroid hormone probably stimulates leucopoiesis in bone-marrow.

II. Injection of insulin into rabbits causes a right shift followed by a left shift in the blood picture. Leucocyte changes involved are arrested by feeding thyroid. In thyroidectomised animals leucocyte changes are slow.

CH. ABS. (p)

Effect of the blood-serum of rabbits, in which the thyroid function has been experimentally disturbed, on tissue respiration. K. MUNE (Folia Endocrinol. Japon., 1934, 9, 102—103).—The O<sub>2</sub> consumption of rat muscle is > normal when suspended in serum of hyperthyroidised rabbits, and < normal when in serum of thyroidectomised rabbits.

CH. ABS. (p)

Association and dissociation reactions of thyroglobulin. H. P. LUNDGREN (Nature, 1936, 138, 122).—Previous work (A., 1935, 1522) has been confirmed. Conditions which favour dissociation are low concn. of thyroglobulin (I), low salt concn., high temp.,  $\epsilon$ , and  $p_H$ . Under appropriate conditions, (I) dissociates or associates at slow, measurable rates into components of lower or higher mol. wt. having well-defined sedimentation boundaries. These rates are too slow under the conditions existing in the living cell for these factors alone to account for the mechanism of (I) economy in the body.

L. S. T.

Relations between parathyroid hormone and vitamin-D. M. COPPO and P. FRUGONI (Boll. Soc. ital. Biol. sperim., 1934, 9, 148—151).—Growth of rats is diminished by excess and prevented by absence of vitamin-D; parathormone (I) causes loss of wt. in both cases. The ash content of the body is diminished, but its Ca and P contents are increased and the Ca/P

ratio is diminished in all cases, the increase and diminution being less if (I) is given. -D and (I) do not appear to exhibit antagonism in thyro-parathyroidectomised animals.

R. N. C.

Effect of parathyroid hormone on serum-calcium and calcium excretion of normal and adrenalectomised rats. L. I. PUGSLEY and J. B. COLLIP (Biochem. J., 1936, 30, 1274—1279).—A possible relationship between the adrenal and parathyroid glands is investigated. Adrenalectomised rats show a greater increase in serum- and urinary Ca following injection of parathyroid hormone (I) than do normal rats. With adequate Ca-containing diets, continued injection of (I) produces decreasing responses until the serum- and urinary Ca remain normal.

H. D.

Explanation of adrenaline action. W. J. R. CAMP and J. A. HIGGINS (Science, 1936, 83, 622).—Most of the changes effected by adrenaline are actually produced by K.

L. S. T.

Effect of adrenal capsule on the regulation of blood-sugar. I. Effect of adrenalectomy. II. Effect of removal of the cortex and of the medulla of adrenal capsules. K. YAGI (Folia Endocrinol. Japon., 1934, 9, 113—114, 114—115).—I. In adrenalectomised rabbits a single administration of sugar causes an increase in blood-sugar (I) > that produced in normal animals. The return to normal level is also accelerated. The Staub effect after two administrations of sugar was more marked in treated rabbits.

II. After cauterisation of the cortex of both adrenal capsules the Starke effect was decreased, the increase in (I) was greater, the duration of hyperglycæmia was longer, and the ability to assimilate carbohydrates < that of normal animals. Cauterisation of the medulla produced opposite effects.

CH. ABS. (p)

Effect of age and method of administration on adrenaline action. M. HASEGAWA (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharm. Soc., 1933, 14—15).

CH. ABS. (p)

Adrenaline in the adrenal glands of dogs under low atmospheric pressures. L. BINET and J. LANXADE (Compt. rend. Soc. Biol., 1936, 122, 1011—1012).—The val. is doubled in 1 hr. at pressures equiv. to an altitude of 10,000 m.

H. G. R.

Biological assay of the adrenal cortical hormone by the survival of young [adrenalectomised] rats. P. SCHULTZER (Compt. rend. Soc. Biol., 1936, 122, 978—981; cf. A., 1935, 1421).

H. G. R.

Action of thyroid hormone on cells grown *in vitro*. J. VERNE and D. ODIETTE (Compt. rend. Soc. Biol., 1936, 122, 988—990).—Plasma after injections of thyroxine at first augments and, after repeated injections, retards the growth of *in-vitro* cultures of fibroblasts of chick embryo.

H. G. R.

Isolation of a hypoglycæmic principle in the jejunal mucosa. F. RATHERY, A. CHOAY, and P. DE TRAVERSE (Compt. rend., 1936, 202, 1949—1950).—An aq. EtOH extract of the jejunal mucosa of the ox contains a substance, 10—20 mg. of which lowers the blood-sugar of a rabbit and may produce convulsions.

J. L. D.

**Standardisation of insulin.** J. ŠTEFL (Arch. exp. Path. Pharm., 1936, 181, 617—624).—The method is based on determination of the amount of the material containing insulin required to produce hypoglycaemic convulsions in rabbits. Abs. specificity is attained by taking account only of convulsions which are arrested by injection of glucose. The average experimental error is  $\pm 20\%$ . W. McC.

**Changes in the glutathione content of the blood after insulin treatment.** L. LIACI (Biochim. Terap. sperim., 1933, 20, 329—332; Chem. Zentr., 1935, ii, 2837).—Blood-glutathione is increased.

R. N. C.

**Action of insulin in pregnancy.** E. SAPEGNO (Boll. Soc. ital. Biol. sperim., 1932, 7, 690—691).—The action of insulin in pregnant rabbits is the same as in normal animals, but the effect of the hypoglycaemia on body-temp. is more marked.

R. N. C.

**Insulin and experimental beri-beri in the pigeon.** A. BAGLIONI and V. CONSOLE (Boll. Soc. ital. Biol. sperim., 1934, 9, 153—155).—Insulin (I) lowers the beri-beri quotient in vitamin-B-deficient pigeons to an extent  $\propto$  the quantity of (I) injected, and retards the appearance of the beri-beri symptoms. The effect is not due to anti-beri-beri action of (I), which appears to antagonise -B.

R. N. C.

**Absorption spectra as an aid to vitamin research.** H. RUDY (Naturwiss., 1936, 24, 499—505).—A review.

**Photochemical decomposition of vitamin-A in alcoholic solution. I. Primary reactions.** A. CHEVALIER and P. DUBOULOZ (Bull. Soc. Chim. biol., 1936, 18, 703—722).—Vitamin-A in slightly acid EtOH solution is decomposed by light of  $\lambda$  3650 Å. giving two substances in const. proportion characterised by their absorption spectra and solubility, the quantum yield being  $1/28$ . From the kinetics of the decomp. a method for the determination of -A in blood is proposed. Irradiation of -A in alkaline EtOH solution does not cause the same decomp. A. L.

**Primary, secondary, and non-specific effects of experimental A-avitaminosis in rats.** T. H. DE RUYTER and O. ROSENTHAL (Z. Vitaminforsch., 1936, 5, 169—185).—Primary effects include atrophy and metaplasia of epithelial tissue and atrophy of the lymphatic system, secondary are cessation of growth, loss of appetite, and susceptibility and lowered resistance to infection, whilst indirectly secondary are anaemia and changes in fat metabolism.

F. O. H.

**Action of vitamin-containing ointments on the healing of wounds.** H. J. LAUBER and H. ROCHOLL (Klin. Woch., 1935, 14, 1143—1146).—Vitamin-A added to cholesterol ointments accelerates the healing effect in small and medium doses, but slightly restrains it in large doses.

R. N. C.

**Determination of vitamin-A.** J. F. WARD and T. M. HAINES (Nature, 1936, 138, 128; cf. this vol. 646).

L. S. T.

**Structure of vitamin-B<sub>1</sub>.** R. R. WILLIAMS (J. Amer. Chem. Soc., 1936, 58, 1063—1064).—Cleavage of vitamin-B<sub>1</sub> (I) with liquid NH<sub>3</sub> gives a base,

C<sub>8</sub>H<sub>10</sub>N<sub>3</sub>, the absorption of which resembles that of a 6-amino-5-alkylpyrimidine. The aminosulphonic acid (A., 1935, 1035) and Na in liquid NH<sub>3</sub> afford a little 6-amino-2:5-dimethylpyrimidine. The hydroxy-sulphonic acid (*loc. cit.*) is 6-hydroxy-2-methyl-5-sulphomethylpyrimidine. The compound, C<sub>7</sub>H<sub>11</sub>O<sub>5</sub>N<sub>3</sub>, of Windaus *et al.* (A., 1934, 1415) is probably 6-hydroxy-5-ethoxymethylpyrimidine nitrate. The following structure is now assigned (*cf.* A., 1935, 504) to (I).

H. B.

**Role of adenylic acid in vitamin-B<sub>1</sub> deficiency.** T. W. BIRCH and L. W. MAPSON (Nature, 1936, 138, 27—28).—Adenosine, or adenylic acid (I) from muscle or yeast, increases the bradycardia present in rats deficient in vitamin-B<sub>1</sub>. The -B<sub>1</sub>-deficient animals are unable to render these compounds innocuous at the same rate as does the normal animal. The deaminase activity of -B<sub>1</sub>-deficient cardiac tissue is 20% < that of similar tissues on full diet. This failure of the deaminase mechanism may result in increased accumulation of (I) in the tissue, which is the cause of bradycardia. Other effects, *e.g.*, increased lactic acid and decreased O<sub>2</sub> consumption, obtained with -B<sub>1</sub>-deficient tissue may be due to the inhibition by (I) of oxidative mechanisms which are responsible for the removal of these metabolites.

L. S. T.

**Determination of reduced ascorbic acid in blood-serum and plasma.** F. H. L. TAYLOR, D. CHASE, and J. M. FAULKNER (Biochem. J., 1936, 30, 1119—1125).—Reduced ascorbic acid (I) is determined in 2 c.c. of serum or plasma by pptg. the proteins with tungstic acid and titrating the filtrate with 2:6-dichlorophenol-indophenol. For accuracy it is necessary to dissolve and reppt. the proteins several times. In 33 normal human sera, (I) varied from 0.83 to 2.43 (average 1.61), whilst in 10 scorbutics, the max. val. was 0.55 mg. per 100 c.c. W. O. K.

**Determination of ascorbic acid.** A. EMMERIE and M. VAN EEKELEN (Z. physiol. Chem., 1936, 241, 134).—Wachholder *et al.* (this vol., 766) have overlooked the procedure of the authors (*ibid.*, 255).

W. McC.

**Determination of vitamin-C by Bezssonoff's method.** N. BEZSSONOFF and E. STOERR (Z. Vitaminforsch., 1936, 5, 193—221).—The technique of the use of monomethylphosphotungstic acid in determining vitamin-C in urine, blood, cerebrospinal fluid, milk, adrenal gland, liver, and vegetable tissues is described (*cf.* A., 1935, 670).

F. O. H.

**Vitamin-C content of the ocular fluids and tissues with particular reference to the aqueous humour and the crystalline lens.** G. BIETTI and A. CARTENI (Boll. Soc. ital. Biol. sperim., 1934, 9, 283—286).—Analytical vals. are given for the aq. humour and cryst. lens of the ox, sheep, rabbit, and dog. Ascorbic acid is present in other ocular tissues. The content depends on age and the nutritional state.

R. N. C.

**Variations in the ascorbic acid content of the ovaries, particularly in the corpus luteum.** A.



GIROUD, I. CESA, R. RATSIMAMANGA, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1936, **122**, 899—901).—Ascorbic acid in the corpus luteum increases during the period of formation and decreases during degeneration. H. G. R.

**Alleged formation of vitamin-C from mannose by liver-pulp.** R. AMMON and G. GRAVE (Z. Vitaminforsch., 1936, **5**, 185—192).—The claim of Guha and Ghosh (A., 1935, 131) that vitamin-C is formed from mannose added to rat's liver-pulp at 38° could not be confirmed. Addition of cysteine produces an increase in reducing power of the tissue, but this is probably due to the experimental method.

F. O. H.

**Relations between ascorbic acid and glutathione.** F. G. HOPKINS and E. J. MORGAN (Biochem. J., 1936, **30**, 1446—1462).—The velocity of oxidation of ascorbic acid (I) by hexoxidase (II)  $\propto$  concn. of (II), varies with  $p_H$ , and is const. with time. Glutathione (III) alone is unaffected by (II) but inhibits the oxidation of (I) by (II), being oxidised itself at the same rate as (I) when alone; when (III) is almost completely oxidised the oxidation of (I) begins. 0.002*M*-KCN inhibits the oxidation. The rate of oxidation of (I) is 1/5 that of reduction of the oxidised (I) anaerobically induced by adding (III) when the oxidation is complete. When a dialysed prep. of (II) is used the rate of reduction diminishes rapidly with time. At  $p_H$  7.4 (I) is rapidly autoxidised in the presence of Cu, and (III) much more slowly; when both (I) and (III) are in solution together (I) is wholly protected from oxidation although the oxidation of (III) is unchanged. At  $p_H$  6.0 neither constituent of the mixture is oxidised. Suspensions of liver-tissue from well-fed rabbits show an initial reduction of (III) followed by oxidation whilst the concn. of (I) remains approx. const. With liver from animals starved for 48 hr. oxidation of both (III) and (I) occurs immediately and rapidly; addition of a large excess of (III) inhibits the oxidation of (I).

H. D.

**Ascorbic acid and glutathione contents of immunised animals.** H. I. JUSATZ, T. BERSIN, and H. KOSTER (Klin. Woch., 1935, **14**, 1419—1420).—Blood-glutathione (I) in rabbits is depressed by immunisation with horse serum. Both (I) and ascorbic acid (II) are lowered in the adrenals of immunised animals fed on a diet poor in vitamin-C. (I) and (II) are utilised in antibody formation during immunisation.

R. N. C.

**Destruction of ascorbic acid in water.** H. C. HOV (J. Chinese Chem. Soc., 1936, **4**, 224—234).—Ordinary distilled H<sub>2</sub>O and Shanghai tap-H<sub>2</sub>O have a marked destructive effect on ascorbic acid (I). This effect is considerably reduced when the solutions are sterilised, and hence is at least partly due to certain micro-organisms, the addition of which increases the destructive effect of a sterilised solution. Certain other organisms have a stabilising effect. Aq. (I) is only slightly decomposed when heated rapidly to the b.p.

F. R. S.

**Reduction of iron by tissue extracts and by ascorbic acid, with a note on the stabilisation of ascorbic acid solutions.** W. D. McFARLANE

(Biochem. J., 1936, **30**, 1472—1478).—Reduction of tissue-Fe *in vivo* by ascorbic acid (I) involves some form of Fe-protein complex. Catalytic oxidation of (I) by Cu is inhibited by Na diethyldithiocarbamate (II), cystine, cysteine, and glutathione, and the aerobic oxidation in orange juice by 2:2'-dipyridyl (III) and (II) together; this is not affected by (II) alone and may be increased by (III).

H. G. R.

**Reversible oxidation of ascorbic acid demonstrated by assays with guinea pigs.** N. BEZSSONOFF and M. WOLOSZYN (Compt. rend. Soc. Biol., 1936, **122**, 944—946).—Biological tests confirm the modification of the properties of vitamin-C in biological media as compared with those in pure solution (cf. this vol., 255).

H. G. R.

**Oxidation of vitamin-C.** N. BEZSSONOFF and M. WOLOSZYN (Compt. rend. Soc. Biol., 1936, **122**, 941—944).—It is suggested that a hypothetical "di-ascorbic ether" is an intermediate in the oxidation of ascorbic to dehydroascorbic acid.

H. G. R.

**Effect of light on production and distribution of ascorbic acid in germinated soya-beans.** W. Y. LEE and B. E. READ (J. Chinese Chem. Soc., 1936, **4**, 208—218).—Soya beans germinated at 25° in the dark form ascorbic acid (I) in increasing amount up to the 9th—11th day when approx. 0.4 mg. per seedling is present largely in the reversibly oxidised form. Sunlight increases production of (I), and the possible correlation of these results with the development of the plant and the formation of chlorophyll is discussed.

F. R. S.

**Formation and distribution of vitamin-C in the germinating pea, *Pisum sativum*, L.** W. Y. LEE (J. Chinese Chem. Soc., 1936, **4**, 219—223).—Peas sprouted in the dark for 13 days have a max. content (0.040%) of ascorbic acid on the 8th day. The vitamin is apparently formed in the cotyledons, which have a relatively high content by the 6th day.

F. R. S.

**Role of vitamin-C in animals resistant to scurvy: effects of insulin and adrenaline.** K. M. DAOUD and M. A. S. EL AYYADI (Biochem. J., 1936, **30**, 1280—1292).—The rate of urinary excretion of vitamin-C by rats is decreased by a scorbutic diet or injection of adrenaline (I), and increased by 24 hr. starvation. The -C content of the adrenals is not affected by a scorbutic diet, 24 hr. starvation, or injection of insulin (II) or (I), whilst that of the liver is increased by injection of (II) in rats on a scorbutic diet but not by (I). The quantity of -C in the bodies of rats influences the glycogenolytic response to (I).

H. D.

**Vitamin-C requirements of the guinea-pig.** S. S. ZILVA (Biochem. J., 1936, **30**, 1419—1429).—The relationship of the intake of ascorbic acid (I) to the content in the tissues, the susceptibility to scurvy, and the urinary excretion of (I) is investigated. With scorbutic guinea-pigs (I) appeared in the tissues after injection of 5—8 mg. per day and reached a limiting concn. when 20 mg. per day were injected; increasing the dose caused excretion of (I) in the urine. The time taken for a guinea-pig to die on a scorbutic

diet was independent of the amount of (I) previously ingested. H. D.

**Allergy and vitamin-C.** A. HOCHWALD (Zentr. inn. Med., 1935, 56, 769—771; Chem. Zentr., 1935, ii, 2692).—Vitamin-C and glutathione inhibit anaphylactic but not histamine shock. R. N. C.

**Behaviour of vitamin-C in Addison's disease.** S. SRWE (Klin. Woch., 1935, 14, 1311—1313).—Vitamin storage is not increased by excessive dosage, the excess being excreted immediately in the urine. R. N. C.

**Capillary resistance. IV. Effect of vitamin-C therapy on lowered capillary resistance in patients with gastric achylia.** P. SCHULTZER and O. GRUS (Acta med. scand., 1935, 85, 563—573).—Normal resistance is re-established in certain cases. R. N. C.

**Cataract and ascorbic acid in the guinea-pig eye.** S. W. JOHNSON (Biochem. J., 1936, 30, 1430—1437).—The ascorbic acid (I) content of the aqueous humour and lens, determined both by titration and spectrographically, became zero after 9 days on a scorbutic diet; the rate of disappearance and reappearance after injection ran parallel with that in other tissues. No cataract appeared in animals devoid of (I). H. D.

**Vitamin-D in child health.** F. O. TONNEY (Amer. J. Publ. Health, 1936, 26, 665—671).—A review.

**Formation of a sulphate salt of the anti-rachitic vitamin.** A. E. SOBEL, G. GOLDSTEIN, and B. KRAMER (J. Amer. Chem. Soc., 1936, 58, 1056—1057).—Calciferol (I) and  $C_5H_5N,SO_3$  in  $C_5H_5N-C_6H_6$  give  $C_5H_5N$  calciferyl sulphate which, unlike the ergosteryl and cholesteryl salts (A., 1935, 903), is hydrolysed by aq. KOH to (I). Approx. 60% of the vitamin-D (II) present in cod-liver oil concentrates is separable by successive treatment with  $C_5H_5N,SO_3$  and aq. KOH in presence of light petroleum [which dissolves (II)]. H. B.

**Energy equivalents of vitamin-D units.** R. W. HAMAN and H. STEENBOCK (Ind. Eng. Chem. [Anal.], 1936, 8, 291—293).—Measurements of the energy absorbed when ergosterol is converted into vitamin-D shows that an international unit requires 900 ergs and a Steenbock unit 3000 ergs. Biological tests for potency give a similar ratio. S. C.

**Mode of action of vitamin-D. I. Phosphorus compounds in muscles, liver, and kidneys as influenced by different levels of vitamin-D and phosphorus in the diet.** R. NICOLAYSEN (Biochem. J., 1936, 30, 1329—1337).—In rachitic rats, the vals. for inorg. P+phosphagen of muscle and for inorg. P of liver and kidneys are < for rats on the same diet, but with addition of therapeutic amounts of vitamin-D. A similar reduction was obtained in lipin-P and protein-P in liver and kidneys of rachitic rats but not in muscle. No definite change was observed in readily or difficultly hydrolysable esters in muscles or liver or the difficultly hydrolysable esters of kidney. When P was added to the rachitic diet and the Ca content reduced, the animals remained normal and gave the same results as on the rachitic

diet+D. Addition of -D to this P-rich diet, although giving better calcified bones, did not influence the amounts of P compounds in muscle, liver, and kidney. Massive doses of -D administered for short periods to rachitic rats increased inorg. P to the normal level in muscle, liver, and kidneys and for 2 weeks resulted only in an increase of inorg. P in the kidneys up to double the normal val. P. W. C.

**Isomerides of cholesterol and experimental rickets. II. Pharmacological action of iso-cholesterol.** U. SAMMARTINO (Arch. Farm. sperim., 1936, 61, 88—96).—The failure of normal and irradiated isocholesterol to replace totally vitamin-D in the cure of rats on a rachitogenic diet is similar to that of allo- or  $\beta$ -cholesterol (cf. A., 1933, 1088). F. O. H.

**Cereals and rickets. VII. Role of inorganic phosphorus in calcification on cereal diets.** J. T. LOWE and H. STEENBOCK (Biochem. J., 1936, 30, 1126—1134).—Autolysed, germinated, immature, and HCl-treated maize are less rachitogenic than is mature maize due to the higher content of inorg. P. The inorg. P content of variously treated samples of maize varied directly with their antirachitic action and inversely with their phytin (I) content. (I) fed to rats was a poorly available source of P as compared with inorg. P or Na glycerophosphate (cf. A., 1934, 682). As acid-treated maize produced slightly better calcification than could be accounted for by its inorg. P content, it is possible that other factors still undiscovered play a part in rickets. W. O. K.

**Antirachitic action of the irradiated unsaponifiable fraction of lanoline.** M. DE CARO (Boll. Soc. ital. Biol. sperim., 1932, 7, 1097—1099; Chem. Zentr., 1935, ii, 2839).—Experiments with rats point to a definite antirachitic activity. H. N. R.

**Effect of cod- and tunny-liver oils and of irradiated ergosterol and cholesterol preparations on avian rickets.** M. J. L. DOLS (Z. Vitaminforsch., 1936, 5, 161—169).—Equiv. amounts (as measured in rat-units) of the oils or irradiated cholesterol preps. are effective in healing avian rickets, whilst 10 times this dosage of irradiated ergosterol is insufficient. Calciferol is therefore not identical with the vitamin-D in fish-liver oils, whilst the provitamin-D of impure cholesterol is not ergosterol. F. O. H.

**Antirachitic vitamin from tunny-liver oil.** H. BROCKMANN (Z. physiol. Chem., 1936, 241, 104—115).—The oil on treatment with light petroleum and MeOH followed by chromatographic adsorption on  $Al_2O_3$  using a red indicator, production of a crude 3:5-dinitrobenzoate, and repetition of the adsorption yields vitamin- $D_3$ ,  $[\alpha]_D^{25} +100^\circ$  in  $CHCl_3$ , identical with the irradiation product of 7-dehydrocholesterol.  $-D_3$  combines with maleic anhydride. W. McC.

**Antirachitic substance from tunny-liver oil.** G. A. D. HASLEWOOD and J. C. DRUMMOND (Chem. and Ind., 1936, 598—599).—Tunny-liver oil, containing no vitamin-A and 80,000 international units (I.U.) per g. of -D, gave an inactive fraction, selective absorption at 2760 A., and a strongly adsorbed fraction with antirachitic activity of  $1.5 \times 10^6$  I.U.



A specimen of oil, containing -A, 90,000 I.U. and -D, 30,000 I.U., has been converted into a mixture of allophanates, the most insol. portion having m.p. 185—195°, hydrolysed to a fraction of activity  $10\text{--}20 \times 10^6$  I.U. The substance obtained by Brockmann (preceding abstract) is probably not identical with that now described. F. R. S.

**Antirachitic activity for chicken and rat of vitamin-D from various sources.** A. BLACK and H. L. SASSAMAN (Amer. J. Pharm., 1936, 108, 237—243).—Blue fin, yellow fin, and striped tuna-liver oils contain a vitamin half as active for chicken as for rat. Oils from swordfish, halibut, mackerel, cod, and irradiated cholesterol show no difference, whilst irradiated phytosterol and unsaponifiable matter from lucerne simulate irradiated ergosterol. E. D. Y.

**Determination of vitamin-D.** H. BROCKMANN and Y. H. CHEN (Z. physiol. Chem., 1936, 244, 129—133).—Vitamin-D<sub>2</sub> and -D<sub>3</sub> are colorimetrically determined even in presence of a 5—6-fold excess of -A by means of the orange colour reaction with SbCl<sub>3</sub> in CHCl<sub>3</sub>. Vegetable oils and other sterols (except tachysterol) and sterol derivatives do not interfere unless present in very large excess. EtOH must be absent. W. McC.

**Constituents of rice embryo. II. Vitamin-E.** R. H. KIMM (J. Agric. Chem. Soc. Japan, 1935, 11, 514—523).—The unsaponifiable matter, after removal of sterols, yields on distillation an oil containing vitamin-E and a hydrocarbon, C<sub>15</sub>H<sub>16</sub>, devoid of -E activity. CH. ABS. (p)

**Vitamin-P. Flavanols as vitamins.** S. RUSZNYAK and A. SZENT-GYORGYI (Nature, 1936, 138, 27).—Vitamin-P, closely allied to -C, cures pathological fragility and permeability of the capillary walls to plasma protein. It occurs in Hungarian red pepper and lemon juice, and appears to be flavone or flavonol glucoside. L. S. T.

**Respiration of mango leaves (*Mangifera indica*).** N. K. CHATTERJI (Proc. Nat. Acad. Sci. India, 1936, 6, 149—160).—The CO<sub>2</sub>/O<sub>2</sub> relationship of young (red), mature (green), and old (yellow) leaves is examined. The O<sub>2</sub> intake exceeds the CO<sub>2</sub> output in red and green but not in yellow leaves. The apparently excessive O<sub>2</sub> intake is partly utilised during the conversion of sugars into org. acids in the leaves. In yellow leaves the low O<sub>2</sub> intake is attributed to actual liberation of O<sub>2</sub> resulting from the production of fats from sugars. A. G. P.

**Anaerobiosis in higher plants.** K. PAECH (Planta, 1935, 24, 529—551).—After short anaerobiosis and prior to the onset of irreversible injury, changes occur in the  $\eta$  and permeability of the protoplast similar to those characteristic of narcosis. There is no evidence that the changes result from the formation of an anaerobic product in the system. The EtOH/CO<sub>2</sub> ratio in the products of anaerobic metabolism is much nearer to theoretical val. than is usually supposed. Instances of an apparently large excess of CO, produced are attributed to faulty analysis. Cases of smaller excess may be due to further oxidation of a portion of the EtOH by H-

acceptors present in the cell. Anaerobic metabolism is similar to alcoholic fermentation. A. G. P.

**Effects of soil drought on photosynthesis and respiration in plants.** A. A. ZAITZEVA (Bull. Acad. Sci. U.R.S.S. [Sci. math. nat.], 1935, 19—39).—Respiration of wheat plants was reduced during wilting and remained below normal 40—48 hr. after watering. Increased photosynthesis was observed 20—40 hr. after watering. CH. ABS. (p)

**Tropical fruits. I. Development, ripening, and senescence with special reference to respiration.** C. W. WARDLAW and E. R. LEONARD. **II. Internal gas concentrations in fruit.** C. W. WARDLAW (Ann. Bot., 1936, 50, 621—653, 655—676).—I. Changes in the [O<sub>2</sub>] and [CO<sub>2</sub>] in the interior of large hollow fruits (e.g., papaw) are examined. An increase in [CO<sub>2</sub>] appears prior to the onset of the climacteric and continues steadily thereafter, without any sp. change corresponding with the peak vals. seen in "external" respiration. The post-climacteric decline in external respiration corresponds with a decrease in internal [O<sub>2</sub>] which continues until anaerobic conditions are reached. The onset of ripening is associated with a peak val. for [O<sub>2</sub>]. The later, senescent, stage probably results from failure of O<sub>2</sub> to gain access to fleshy tissue.

II. Changes in internal gas concn. resulting from modification of the external atm. are examined. The rate of respiration as determined by evolution of CO<sub>2</sub> from the external surface is not necessarily a reflexion of cellular respiration and is influenced by the CO, present in the flesh. High initial rates on removal of fruit from air to N<sub>2</sub> are due to adjustment between internal and external [CO<sub>2</sub>]. Subsequent metabolism proceeds at < normal rates. A. G. P.

**Assimilation and respiration of tropical trees of West Java.** O. STOCKER (Planta, 1935, 24, 402—445).—Effects of temp. and light intensity are examined. The quotient, max. assimilation/respiration indicates that dry matter production and H<sub>2</sub>O exchange in plants in all climates fall within certain limits. Variations among species in the same habitat are > the average variation from habitat to habitat. A. G. P.

**Do cut leaves give physiologically correct assimilation values?** P. BAUER (Planta, 1935, 24, 446—453).—Assimilation in cut leaves examined for short periods ( $\approx$  1 hr.) is the same as that in intact leaves. A. G. P.

**Transport in the cotton plant. V. Oxygen supply and the activation of diffusion.** T. G. MASON and E. PHILLIS (Ann. Bot., 1936, 50, 455—499; cf. this vol., 531).—Coating leaf petioles with wax caused an increase and subsequent decline in the carbohydrate (I) content of the lamina and increased the (I) and P in the petiole. Exclusion of O<sub>2</sub> from stems may restrict transport through them but the restriction of growth is much more marked. When the O<sub>2</sub> supply through lenticels is cut off some O<sub>2</sub> may be obtained from the transpiration current. Coating defoliated stems checked the movement of (I) and N to similar extents and that of P, K, and Mg to a smaller degree. Activation of diffusion probably

depends on a special organisation in the cytoplasm, maintained by metabolic energy, which lowers the resistance to solute movement sufficiently to permit diffusion in the sieve tube at rates comparable with those in a gas. A. G. P.

**Effect of potassium on the nitrogen economy of etiolated and green seedlings.** H. JAENICHEN (Angew. Bot., 1935, 17, 374—445).—The growth and succulence of rape, wheat, and maize seedlings increases with the K supply to a max. beyond which larger applications of K have the reverse effects. In amounts  $\gt$  optimum K increases the intake and storage of  $H_2O$ , and the influence of K on the nutrient intake and N distribution of the plants is largely attributable to the improved  $H_2O$  status of the tissues. Differences in the interpretation of analytical data expressed as % of fresh wt. and as total per leaf or plant are emphasised. A. G. P.

**Radio-physiological importance of potassium in chlorophyll-containing and -free cells.** J. STOKLASA (Strahlenther., 1935, 53, 276—295; Chem. Zentr., 1935, ii, 2833—2834).— $\beta$ - and  $\gamma$ -Rays emitted by K accelerate germination, and increase dry matter yield, by their action on the photosynthetic process. Photosynthetic assimilation of  $CO_2$  occurs only in the presence of K and for this purpose Mg cannot replace K. A. G. P.

**Seasonal variations in *Chondrus crispus*.** M. R. BUTLER (Biochem. J., 1936, 30, 1338—1344).—The ash, N, and carbohydrate contents of a series of monthly collections of this marine alga from the same locality are compared with the corresponding contents of the polysaccharide complex (I) extracted therefrom by the method already described (A., 1934, 1047). Similar variations occur in the ash contents of both the whole plant and of (I). The N present in (I) depends directly on the N content of the plants. The carbohydrate content (%) is low until March or April, then increases, and a high level extends from May to October. Carbohydrate and  $SO_4^{--}$  determinations show that an acid type of ester predominates from January to May, the normal type from May to October, whilst from October to January there appears to be a gradual return to the acid type of salt. P. W. C.

**Supply of iron to cultivated plants.** P. EHRENBURG (Z. Pflanz. Düng., 1936, 45, A, 1—95).—The causes of Fe chlorosis, and soil conditions influencing the availability of Fe, are reviewed. An extensive bibliography is given. A. G. P.

**Effect of aluminium ions on plant growth.** K. SCHARRE and W. SCHROPP (Z. Pflanz. Düng., 1936, 45, A, 83—95).—Toxicity tests with various [Al] in sand and  $H_2O$  cultures are recorded. The sensitivity of various crops was in the descending order, barley, wheat, rye, oats, maize, i.e., almost the same order as the susceptibility to  $H^+$ . In some instances small [Al $^{+++}$ ] increased the yield of oats and maize. Al caused root injury in all cases. A. G. P.

**Dependence of the [plant] "condition indicators" on salt nutrition.** Wheat. W. H. FUCHS (Planta, 1935, 24, 725—741; cf. A., 1935, 904).—The influence of  $Na^+$ ,  $K^+$ ,  $Mg^{++}$ ,  $Ca^{++}$ ,  $Cl^-$ ,  $SO_4^{--}$ , and  $NO_3^-$  in nutrient media on the osmotic pressure, conductivity,

and sugar level of the expressed sap of wheat seedlings is examined. A. G. P.

**Nutrient supply and water requirements in cereals and pasture plants.** A. H. K. PETRIE (J. Austral. Inst. Agric. Sci., 1935, 1, 77—78).—Increased N supply has no effect on the transpiration rate per unit wt. of leaf but increases the ratio of leaf to whole plant throughout most of the growing period. Reduction in transpiration ratio following increased N supply is effected by the action of N on growth. Increasing P supply lowers the transpiration per unit wt. of leaf and the leaf: total wt. ratio. The resulting decrease in respiration per unit wt. of plant is  $>$  the increase produced by the growth effect of P. CH. ABS. (p)

**Hydrogen-ion concentration and titratable acidity at different stages of fruit ripening.** N. L. PAL (Proc. Nat. Acad. Sci. India, 1936, 6, 131—135).—Data for *Lycopersicum esculentum*, *Psidium guajava*, *Citrus medica*, and *C. aurantium* at different stages of maturity are given. The [H $^+$ ] increased over the greater part of the period but declined in the final stages. The titratable acidity increased steadily throughout except in the case of *Lycopersicum*. No direct relationship was apparent between the two sets of vals. A. G. P.

**Plant growth-substances. XIX. Effect of unknown factors on the response of *Avena sativa*.** F. KÖGL, A. J. HAAGEN-SMIT, and C. J. VAN HULSEN (Z. physiol. Chem., 1936, 241, 17—33; cf. this vol., 122).—The great variations in the sensitivity of plants to auxins are not due to changes in atm. pressure, intensity of cosmic rays, electrical state of the atm., or p.d. in the plant. The unknown factors which cause the variations appear to be responsible for parallel variations in the respiration and movement of the protoplasm, whilst the nature of the illumination (red or orange light) has a definite effect. W. McC.

**Electrotropism in pollen tubes.** H. D. WULF (Planta, 1935, 24, 602—608).—Growth of pollen tubes through the tissue of the style is probably related to the movement of growth-substance in the tube under the influence of the potential gradient in the style. A. G. P.

**Plant tissue cultures from a hormone viewpoint.** J. BONNER (Proc. Nat. Acad. Sci., 1936, 22, 426—430).—Means of purification of plant hormone-containing materials and of examining their potency in bean tissue cultures are described. A. G. P.

**Endosperm growth-substance and the growth-substance of the coleoptile tip.** R. POHL (Planta, 1935, 24, 523—526).—The growth of the oat coleoptile in light and in darkness is controlled by the growth-substance (I) in the endosperm. The tip does not produce (I) but activates the reserve from the endosperm. The shorter growth of the coleoptile in light may be due to the lower activity of (I), or to smaller ability of the cells to react to (I) in daylight than in darkness. The ability of cells to stretch is not lessened in light, since they respond equally in light and darkness to (I) from urine or to  $\beta$ -indolylacetic acid paste. A. G. P.



**Influence of  $\beta$ -indolylacetic acid on leaf movement and the formation of adventitious roots in *Coleus*.** O. FISHNICH (Planta, 1935, 24, 552—583).—Application of  $\beta$ -indolylacetic acid to stems induces root initiation only from treated areas. With leaf stems and midribs response is slower and roots appear on the underside of the leaf at a distance from the point of application and later on the stem at a distance of 2—3 nodes. A. G. P.

**Light-growth response and auxin curvatures of *Avena*.** J. VAN OVERBEEK (Proc. Nat. Acad. Sci., 1936, 22, 421—425).—The rate of curvature of decapitated coleoptiles treated unilaterally with auxin-A shows a similar response to continuous exposure to light as does the growth rate of the intact seedling on illumination (base growth response). The initial light-growth response of the *Avena* coleoptile (decrease in growth rate) is comparable to the response of the *Raphanus* hypocotl. A. G. P.

**Plant growth effects of heteroauxin applied to soil and plants.** W. F. LOEWING and L. C. BAUGNESS (Science, 1936, 84, 46—47).—Addition of a dil. solution of  $\beta$ -indolylacetic acid (I) to the soil produces a transitory acceleration of growth in stock seedlings. Symptoms due to accelerated growth also appear when localised areas of the plants are treated with (I). L. S. T.

**Vitamins and growth factors in plants. Solubility of growth factors. The factor in urine.** W. H. SCHOPFER (Arch. Mikrobiol., 1935, 6, 290—308).—Small amounts of a growth-substance affecting *Phycomyces* are obtained from wheat germ by extraction with  $\text{CHCl}_3$  and from rice polishings with  $\text{C}_6\text{H}_6$ . The solubility of the active materials and of the growth factor from urine is compared and the possible identity of these factors with vitamin-B<sub>1</sub> is discussed. A. G. P.

**Presence of free sugar in green algae and its relation to photosynthesis.** I. *Codium latum*, Suringar. II. *Cladophora Wrightiana*, Harvey. S. ENDO (Sci. Rep. Tokyo Bunrika Daigaku, 1936, 2, B, 223—231, 291—295).—I. Glucose (I), non-reducing polysaccharide (II) of low mol. wt., and starch (III) are present. The variations in their levels from day to day and with difference in intensity of light indicate that (I) is the first product of photosynthesis of carbohydrate.

II. Fructose (the first product of photosynthesis) and (II), but not (III), are present. F. O. H.

**Plant nutrition. V. Carbohydrate metabolism in relation to nutrient deficiency and to age in barley leaves.** F. G. GREGORY and E. C. D. BAPTISTE (Ann. Bot., 1936, 50, 579—619; cf. this vol., 908).—In sand-cultured barley N deficiency increased the total sugar (I) content but had no consistent effect on the reducing sugars (II) of fully emerged leaves. P deficiency increased (II) but had a much smaller effect on (I). K deficiency decreased both (II) and, to a greater extent, (I). In early leaves little difference in sugar contents appeared before external symptoms of deficiency. Consistent differences in (I) level occurred only after tillering. During senescence the (I) of the earliest

leaves declined with advancing age. In later leaves the reverse change occurred at varying stages of growth. In K-deficient plants the decline in (I) with increasing age was general. The ratio sucrose/(II) was high in N-, low in K-, and intermediate in P-deficient plants. High vals. for (II) in P deficiency are related to the high ratio of amide-/NH<sub>2</sub>-N, both vals. increasing rapidly at the emergence of the fourth leaf. Changes in (I) level are discussed in relation to C assimilation, translocation, protein synthesis, respiration, and meristematic activity. A. G. P.

**Fixation and transfer of nitrogen in the soya bean with special reference to the mechanism of transfer of fixed nitrogen from bacillus to host.** G. BOND (Ann. Bot., 1936, 50, 559—578).—A large proportion (probably 80—90%) of the N fixed by nodule bacteria diffuses into the host cytoplasm and is translocated to other parts of the plant. Storage of N by the organisms is small. Fixation of N is regarded as a form of respiratory activity rather than a stage in the synthesis of bacterial protein. The decline in N-fixing activity with advancing growth of the plant may result from diminished supply of carbohydrate to the bacteria or to the accumulation of inactive organisms. A. G. P.

**Fat oxidation system in *Lupinus albus*.** F. N. CRAIG (J. Biol. Chem., 1936, 114, 727—746).—Pulverised seeds of *L. albus*, when shaken with H<sub>2</sub>O, consume O<sub>2</sub> and form CO<sub>2</sub> with a CO<sub>2</sub>/O<sub>2</sub> ratio  $\approx 0.3$ . There is a small anaerobic production of CO<sub>2</sub>. The optimum  $p_{\text{H}}$  is approx. 7 in PO<sub>4</sub>''' buffer, but no O<sub>2</sub> is used up below 4 in HCl-citrate or above 12 in NaOH-glycine buffers. Acid is produced in very small quantity during the reaction, which is due to a mixture of enzymes on the oil or fatty acid in the seed. O<sub>2</sub> consumption is inhibited by CO, urethane, and under certain conditions by KCN, but is increased by PO<sub>4</sub>''' and sometimes by KCN. Vals. of  $\mu$  in the Arrhenius equation are 11,700 between 5° and 35° when the system is saturated with oil, and 15,200 above 30°, and 3500 below 20° in absence of added oil. J. N. A.

**Mechanism of symbiotic nitrogen fixation. I. Influence of nitrogen pressure.** P. W. WILSON (J. Amer. Chem. Soc., 1936, 58, 1256—1261).—The fixation of N<sub>2</sub> by red clover (*Trifolium pratense*) in absence or presence of A and He is independent of  $p_{\text{N}_2}$ ,  $>0.1$ — $0.2$  but decreases rapidly when  $<0.1$  atm. This function of  $p_{\text{N}_2}$  is characteristic of the N-fixing process; it is not observed in plants supplied with combined N. H. B.

**Phaeophytin formation in leaf organs after temperature effects.** M. ROSEN and M. STERN (Kl. Mitt. Ver. Wasser-, Boden-, Lufthyg., 1935, 11, 47—56; Chem. Zentr., 1935, ii, 2835).—Phaeophytin (I) cannot be detected spectroscopically in heated or frozen leaves, moist and dry heat and chilling showing the same effect, but depending on the reaction of the sap. Withered and dried leaves contain no (I). R. N. C.

**Platinum-gold difference in relation to the potential of indifferent electrodes in tissue pulp of potato tubers.** H. WARTENBERG (Planta, 1935, 24, 711—724).—In certain cases the initial stage of

biological oxidation processes, viz., the transference of the oxidative power from  $O_2$  to a reversible carrier, can be followed potentiometrically by utilising the difference in  $O_2$  sensitivity of Pt and Au electrodes. The method is applied to the examination of tyrosinase activity in potato tuber by means of the  $O_2$  consumption during melanin formation. A. G. P.

**Delayed killing of maize seedlings with X-rays.** G. N. COLLINS and L. R. MAXWELL (Science, 1936, 83, 375—376).—Irradiation of dried seeds with X-ray dosages within a certain range resulted in the death of all plants in the seedling stage without impairment of germination. Higher doses completely inhibited germination. A cytological explanation of these results is discussed. L. S. T.

**Variations of the nitrogen content of the lily-of-the-valley during forcing.** R. QUETEL (Compt. rend., 1936, 202, 2096—2098).—The changes in N content during forcing with  $Et_2O$  are similar to those of the lilac (A., 1933, 758). H. D.

**Effect of acetaldehyde on the structure of the plant cell.** M. MASCRÉ (Compt. rend., 1936, 202, 2094—2096).—The modifications of the tissues of lupins, peas, and of *Allium* by exposure to acetaldehyde vapour are described. H. D.

**Isoelectric point of plant protoplasm.** G. YAMAHARA (Sci. Rep. Tokyo Bunrika Daigaku, 1936, 2, B, 209—221).—The isoelectric points (determined by cataphoresis and/or dye-fixation) of spermatia, zoospores, various parts of pollen mother cells, and of single algae have vals. between *n.* 3.0 and 4.5. F. O. H.

**Chemical composition and structure of the plant plasma.** H. KAHO (Keem. Teated, 1934, 2, 17—26; Chem. Zentr., 1935, ii, 2968).—A review. The role of lipins as dispersive agents in the plasma is emphasised. A. G. P.

**Concentration of solutes in [plant] sap and tissue and the determination of bound water.** T. G. MASON and E. PHILLIS (Ann. Bot., 1936, 50, 437—454).—Comparison of the sugar and  $Cl^-$  contents of expressed sap, of the press-residue and of whole leaves of cotton indicates the presence of bound  $H_2O$  in the tissue. The amount of sap-sol. K (and probably that of other constituents) cannot be determined by aq. extraction of oven-dried material. Approx. 25% of the total K in leaves is not dissolved in the sap. There is no evidence of absorption of sucrose or  $Cl^-$  by tissue. The concn. of these constituents in intact plants is best determined in sap expressed from frozen material. A. G. P.

**Content and alkalinity of the ash of beetroot.** H. COLIN and M. SIMON (Compt. rend., 1936, 202, 2171—2173).—The ash content of the root, stem, and leaves of dried edible and sugar beet is approx. const. (11.0—14.0%) even when grown in soil containing varying amounts of N fertiliser. The acid val. of the ash varies, that of the edible beet being the higher. F. N. W.

**Presence of maltose in the storage organs of *Lathyrus silvestris*.** A. MEUNIER (J. Pharm. Chim., 1936, [viii], 24, 9—17; cf. A., 1933, 990).—Maltose is isolated from the roots of *L. silvestris* by

pptn. with  $Ba(OH)_2$ . The content in the roots falls to a min. in December. H. D.

**Determination of small quantities of fermentable sugars [in plant materials] by carbon dioxide production.** W. O. JAMES and A. L. JAMES (New Phytol., 1936, 35, 1—10).—Determination of sugars by loss of reducing power after fermentation with yeast gave erroneous results in the case of barley embryos when the material was aerated to prevent formation of  $EtOH$ . Reducing substances (probably  $CH_3CO_2H$ ) were formed during the fermentation. Better results are obtained by measurement of  $CO_2$  evolved [ $Ba(OH)_2$  method] during fermentation with a starved yeast culture in the presence of HCN and in an atm. of  $N_2$ . A separate determination is made of  $CO_2$  evolved during autofermentation of yeast. Disaccharides are preferably hydrolysed and determined as hexose. A. G. P.

**Soya-bean proteins. II. Preparation of glycinin.** R. J. HARTMAN and L. T. CHENG (J. Chinese Chem. Soc., 1936, 4, 152—156).—Improvements in Osborne and Campbell's method (A., 1898, ii, 626) are suggested. F. R. S.

**Tryptophan and chlorophyll in the leaves of seedlings of barley mutants.** N. LOFGREN (Z. physiol. Chem., 1936, 241, 142—147).—Tryptophan (I) is determined by heating the dried material with 20% aq. NaOH at  $150^\circ$  for 2.5 hr., adding  $H_2SO_4$ , pptg. with  $HgSO_4$ , dissolving the ppt. in HCl, and reprecip. with the reagent of Folin *et al.* (A., 1927, 892) followed by photometric measurement. In the leaves of chlorophyll-defective barley mutants there is no relation between gramine (A., 1935, 1040) and (I) contents but the (I) levels are low compared with those of normal barley plants. The chlorophyll contents of various mutants appear to bear a simple relation to each other. W. McC.

**Amino-acids of plants. I. Tryptophan content of leguminous plants at different stages of growth.** A. I. VIRTANEN and T. LAINE (Biochem. J., 1936, 30, 1509—1513).—A method for determining the tryptophan (I) content of plants is described. With peas and clover, the content of (I) (as % of total N) is a max. at an early stage of growth before blooming, the level in the plants being double that in the seeds; the val. then falls rapidly until it is only slightly > that in the seeds. With peas there is a definite fall in the abs. amount of (I), but during the early stages of growth there is a remarkable rise, which possibly plays an important part in the metabolism of the young plant. The carotene and (I) contents of clover reach a max. simultaneously. J. N. A.

**Non-protein-nitrogen of pulses. II. Partitioning of the nitrogen and determination of the essential amino-acids.** K. BHAGVAT and M. SREENIVASAYA (Biochem. J., 1936, 30, 1416—1418; cf. A., 1935, 672, 1936, 913).—A discrepancy between the Van Slyke and enzyme methods of arginine (I) determination in the seeds of *Phaseolus mungo* and *Cicer arietinum* indicates the presence of a new base other than (I). H. D.



**Histochemical localisation of hordenine in barley plantules.** R. REILHES (Compt. rend. Soc. Biol., 1936, 122, 852—854).—The alkaloid is localised, together with lipid substances, in the young vacuoles of the meristematic cells.  
H. G. R.

***Strophanthus dichotomus*, D.C.** A. H. MILLARD (Pharm. J., 1936, 137, 147—148).—The seeds yield a powerful cardiac poison on extraction with 70% EtOH. Extracts are distinguished from those of other varieties of *Strophanthus* by the colour reactions with  $H_2SO_4$ , resorcinol-HCl, and PhOH-HCl.  
F. O. H.

**Alkaloid in *Vallesia dichotoma*.** V. CÁRCAMO (Bol. Soc. Quim. Peru, 1936, 2, 25—26).—A preliminary account of an alkaloid or alkaloids present in the "cuncuna," a plant indigenous to Peru.  
L. A. O'N.

**Alkaloids of *Fritillaria roulei*.**—See this vol., 1131.

**Alkaloids of *Lupinus barbiuer*.**—See this vol., 1131.

**Chemical composition of carob seed.** G. IGLESIAS (Anal. Fis. Quim., 1935, 33, 114—118).—The albumin of seeds of *Ceratonia siliqua* (cf. B., 1935, 779) from Majorca contains 77% of mannose and 23% of galactose (cf. Bourquelot *et al.*, A., 1899, i, 968). The embryo contains 6.51% of protein. The phytin, isolated by Boutwell's method (A., 1917, i, 374), contains 42.3%  $P_2O_5$  and is free from inorg. phosphates.  
F. R. G.

***Cuscuta reflexa*, Roxb. III. Constituents of the seed-oil.** R. R. AGARWAL and S. DUTT (J. Indian Chem. Soc., 1936, 13, 264—267; cf. A., 1935, 1550).—The seeds contain 0.05% of cuscutalin, a flavone, and an oil, which yields linolenic (9.92), linoleic (17.26), oleic (25.58), stearic (27.2), and palmitic acid (11.5%), and 1.8% of unsaponifiable matter, including a *phytosterol*, m.p. 134—135°,  $[\alpha]_D^{20}$  —30.9° in  $CHCl_3$  (acetate, m.p. 124—125°).  
R. S. C.

**Latex of *Brosimum galactodendron*.** J. GÓMEZ (Anal. Fis. Quim., 1935, 33, 360—363).—The latex contains 3.48% of rubber, a cryst. wax, m.p. 64—65°, and  $\alpha$ -amyrin.  
F. R. G.

**Preparation and constitution of alginic acid.**—See this vol., 1093.

**Glycosides of madder.**—See this vol., 1095.

**Almonin and its hydrolysis products.**—See this vol., 1095.

**Colouring matter of the flowers of *Lantana camara*, Linn.** J. B. LAL (Proc. Nat. Acad. Sci. India, 1936, 6, 128—130).—The flowers contain an anthocyanin and carotene. The former, isolated from the AcOH extract of flowers, yields reddish-purple *camerin hydrochloride*, m.p. 195° (sintering 180°).  
A. G. P.

**Odorous substance containing sulphur from "shoyu."** S. AKABORI and T. KANEKO (Proc. Imp. Acad. Tokyo, 1936, 12, 131).—The volatile part of "shoyu" contains OPr $\cdot$ SM $\cdot$ , isolated as the compound,  $C_4H_{10}OS, 2.5HgCl_2$ , m.p. 128—128.5°.  
J. N. A.

**Resin of *Dacrydium Colensii*.** Diterpene alcohol from *D. biforme* wood.—See this vol., 1115.

**Hu-man-chiang.** T. OKANISHI (Japan. J. Med. Sci., IV, 7, No. 1; Proc. Japan. Pharmacol. Soc., 1933, 62—63).—The toxic components of *Gelsemium elegans* are substantially the same as those recorded for *G. sempervirens*.  
CH. ABS. (p)

**Components of leaves of *Ficus carica*.**—See this vol., 1121.

**Organic nitrogen bases from pyrolysis of cotton-seed meal.**—See this vol., 1123.

**Determination of alcohol.**—See this vol., 1091.

**Determination of pentoses as furfuraldehyde in citrus fruits.** W. B. SINCLAIR and E. T. BARTHOLOMEW (Amer. J. Bot., 1935, 22, 829—842).—The bromate method gives practically theoretical results for furfuraldehyde (I) but the conversion of *d*-xylose and *l*-arabinose into (I) by the customary acid distillation method is incomplete. In the examination of citrus fruits the (I) distillate contains substances which interfere with the  $BrO_3^-$ , but not with the phloroglucinol. method of analysis. Pre-extraction with 95% EtOH and  $Et_2O$  removes the interfering materials. Data for the peel of Valencia and navel oranges and of lemons are given.  
A. G. P.

**Identification of lactose, alone or associated with glucose, in urine.** F. MORENO MARTIN and A. SEBASTIAN (Anal. Fis. Quim., 1935, 33, 931—936).—Umikoff's reaction (warming with aq.  $NH_3$  and NaOH) is proposed for the detection of lactose (I). 0.5 part per 1000 can be detected in 3 c.c. of urine whether glucose (II) is present or not. (I) is removed by warming with animal charcoal until no positive Umikoff reaction is given, (II) (or other sugars) in the filtrate being determined with Fehling's solution.  
F. R. G.

**Direct micro-titration method for blood-sugar.** B. F. MILLER and D. D. VAN SLYKE (J. Biol. Chem., 1936, 114, 583—595).—Sugar is determined in the Fujita-Iwatake blood filtrate (A., 1932, 75), after removal of Cd with  $BaCO_3$ , by addition of a large excess of  $Fe(CN)_6^{4-}$  (I) and direct titration of the reduced (I) with  $Ce(SO_4)_2$  with setopaline-C as indicator. The vals. obtained agree well with the fermentable sugar vals.  
H. D.

**Determination of saccharides.**—See this vol., 1133.

**Enzymic histochemistry. Micro-determination of alkalis in tissue.** K. LINDERSTRÖM-LANG (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, 111—122).—The tissue is ashed with a mixture of  $Ba(OH)_2$ ,  $BaCO_3$ , and  $BaCl_2$ ; the ash is extracted with  $H_2O$  and the extract, which contains NaCl, KCl,  $BaCl_2$ , and traces of  $CaCl_2$  and  $MgCl_2$ , is treated with  $(NH_4)_2CO_3$  and aq.  $NH_3$  to remove Ba, Ca, and Mg. On evaporating the filtrate to dryness and igniting the residue only KCl and NaCl remain and are determined by electrometric titration of  $Cl^-$  (A., 1931, 1455). The method, applied to material containing  $<4 \times 10^{-4}$  m.-equiv., is accurate to within  $10^{-6}$  m.-equiv.  
W. O. K.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

OCTOBER, 1936.

### General, Physical, and Inorganic Chemistry.

Energy and velocity as parameters for excitation by collision. W. HANLE and R. JUNKELMANN (Physikal. Z., 1936, 37, 593—594).—Excitation of He by collision with H and D, respectively, provides a simple method of deciding which parameter, energy or velocity, determines the intensity of excitation. The excitation function of He was determined for H and D collisions, and plotted against energy and velocity, respectively. The excitation is not a simple function of either. The excitation function of the H<sub>γ</sub> and D<sub>γ</sub> lines was also determined for He collisions. D was more strongly excited than H.

A. J. M.

Stark effect in the hydrogen isotopes. J. S. FOSTER and A. H. SNELL (Physical Rev., 1935, [ii], 47, 338).

L. S. T.

Interpretation of anomalous Stark intensities. J. S. FOSTER (Physical Rev., 1935, [ii], 47, 329—330).

L. S. T.

Predissociation and autoionisation in term series of the hydrogen (H<sub>2</sub>) spectrum. H. BEUTLER and H. O. JÜNGER (Z. Physik, 1936, 101, 285—303).—A predissociation and an autoionisation limit in the triplet system are 6048 cm.<sup>-1</sup> apart.

A. B. D. C.

Light excitation in helium by collision with potassium ions. W. MAURER (Z. Physik, 1936, 101, 323—334).—An alkali ion source that maintains a current of 0.1 m.amp. for 60 hr. under an acceleration of 1000 volts was used to study light excitation in He from 750 to 12,000 volts.

A. B. D. C.

Fine structure and hyperfine structure of doubly-ionised beryllium. S. S. BALLARD, O. E. ANDERSON, and H. E. WHITE (Physical Rev., 1935, [ii], 47, 256).—Lines arising from the transition 1s2s, <sup>3</sup>S<sub>1</sub>—1s2p, <sup>3</sup>P<sub>0,1,2</sub> are observed at 3720 Å.; the hyperfine structure is narrow.

L. S. T.

Lyman series absorbed by oxygen bands. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 213—221).—A marked weakening of certain lines of the Lyman series of H was due to the presence of a small amount of O<sub>2</sub>, which has strong absorption bands in the neighbourhood of the Lyman lines L<sub>3,5,8,13</sub> (cf. Price, this vol. 1) L<sub>3</sub> may disappear entirely or undergo selective weakening

I B

Relative intensity of the neon lines 744 and 736 Å. against their higher members. T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 207—212; cf. this vol., 537).—Contrary to the results for pure Ne, if He containing a trace of Ne is used, λλ 744 and 736 are of only moder-

ate intensity, but the higher members are considerably more enhanced. The change in electron temp. for the mixed gases is suggested as an explanation.

N. M. B.

Stark effect of alkali metal atoms. T. Y. WU (Chinese J. Physics, 1936, 2, 15—21).—Theoretical.

O. D. S.

Electric moment of the <sup>1</sup>Σ<sub>+</sub> to O<sup>+</sup> transition in the continuum of Cl<sub>2</sub>. G. E. GIBSON and O. K. RICE (Physical Rev., 1936, [ii], 50, 380; cf. A., 1933, 991).—A correction.

N. M. B.

Spectrum of trebly ionised argon, A IV. T. L. DE BRUIN (Physica, 1936, 3, 809—814).—Term tables for A IV are given. 50 A IV lines are identified.

O. D. S.

Absorption spectrum of potassium. N. T. ZÉ and W. W. PO (Compt. rend., 1936, 203, 429—431).—Using a long column of K vapour at 500—800° a no. of new lines have been observed and are classified empirically into series.

J. W. S.

Spectrum of ionised calcium excited by shock waves. H. MURAOUR and A. MICHEL-LÉVY (Compt. rend., 1936, 203, 316—319).—The differences between the spectrum of ionised Ca in A and He excited by shock waves from the detonation of pentaerythritol tetranitrate and that obtained by burning a mixture of CaC<sub>2</sub>O<sub>4</sub> and "hexogen" are discussed (cf. this vol., 655).

C. R. H.

Nuclear spin separation of some cobalt terms. E. RASMUSSEN (Z. Physik, 1936, 102, 229—242).—The hyperfine structure of 25 lines of the Co I spectrum has been examined, and the separation factors are calc. for 22 of them. The nuclear spin, *I*, is 7/2.

A. J. M.

Continuous absorption spectrum of bromine. A. P. ACTON, R. G. AICKIN, and N. S. BAYLISS (J. Chem. Physics, 1936, 4, 474—479).—The variations with temp. of the absorption coeffs. of the continuous absorption spectrum of Br vapour between λλ 3274 and 5717 have been determined in the range 20—632°. The continuum probably consists of two overlapping continua; the stronger with its max. at λ4150 is assigned to the transition and the weaker with its max. at λ4950 is assigned to <sup>3</sup>Π<sub>0+u</sub>←<sup>1</sup>Σ<sub>g</sub><sup>+</sup>. Alternative interpretations are discussed.

J. G. A. G.

Displacement of the higher members of the principal series of rubidium by inert gases. N. T. ZÉ and C. S. YI (Compt. rend., 1936, 203, 242—243).—The principal series of Rb has been studied in presence of He (≳ 1.75 atm.), Ne (≳ 13.59 atm.), and



A ( $\approx 7.12$  atm.). He and Ne cause displacement towards shorter  $\lambda$  and A displacement towards longer  $\lambda$ . With He the displacement is a max. for the  $5S-12P$  line, whilst that with A and Ne increases continuously as higher members of the series are reached. The results accord with Fermi's theory (A., 1935, 136). J. W. S.

**Nuclear spins and magnetic moments of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ .** S. MILLMAN and M. FOX (Physical Rev., 1936, [ii], 50, 220—225).—The at. beam method of "zero moments" was applied to measure the nuclear spins and hyperfine structure separations,  $\Delta\nu$ , of the  $^2S_{1/2}$  states of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ . Respective vals are: spins,  $5/2$  and  $3/2$ ;  $\Delta\nu$   $0.1018$  and  $0.229 \pm 1\%$   $\text{cm}^{-1}$ ; calc. magnetic moments,  $1.44$  and  $2.92$  nuclear magnetons. The ratio of magnetic moments  $\mu_{87}/\mu_{85}$  is  $2.026 \pm 0.2\%$ . The val. of  $\Delta\nu$ , measured for Cs, was  $0.307 \text{ cm}^{-1}$  (cf. Granath, this vol., 2).

N. M. B.

**Red line of cadmium as a standard of wavelength.** C. U. JACKSON (Proc. Roy. Soc., 1936, A, 155, 407—419).—The Michelson Cd lamp under standard conditions gives a  $\lambda$  of Cd  $6438.4696$  reproducible to within  $0.0001 \text{ \AA}$ . The presence of a small pressure of air in the tube is advantageous. The new Osram Cd lamp or the Schuler lamp may also be used as a source of Cd. L. L. B.

**Discharge in tellurium vapour.** R. ROMPE (Z. Physik, 1936, 101, 214—233). A. B. D. C.

**Third spectrum of xenon.** C. J. HUMPHREYS (J. Res. Nat. Bur. Stand., 1936, 16, 639—648).—The third spectrum of Xe, due to  $\text{Xe}^{++}$ , has been studied in the region  $2200-8900 \text{ \AA}$ . The lowest states are  $^3P$ ,  $^1D$ , and  $^1S$ , with an electron configuration  $5s^25p^4$ ; the excited states are  $^4S$ ,  $^2D$ , and  $^2P$ , and are formed by the addition of an  $ns$ ,  $np$ , or  $nd$  electron to the  $5s^25p^3$  configuration. The ionisation potential is  $32.0$  volts. R. S. B.

**Spectrum of trebly ionised cerium.** R. J. LANG (Canad. J. Res., 1936, 14, A, 127—130; cf. A., 1935, 1183).—The following terms have been located:  $6S$ ,  $7S$ ,  $8S$ ,  $6P$ ,  $5D$ ,  $6D$ ,  $7D$ ,  $4F$ ,  $5F$ ,  $5G$ , and  $6G$ . 30 lines are classified. The three  $S$  terms follow a Ritz formula, and give  $296,197 \text{ cm}^{-1}$  for the abs. val. of the deepest term,  $4F_{5/2}$ . The ionisation potential of Ce IV from this term is  $36.5$  volts. A. J. M.

**Intensity distribution and total radiation of the super-high-pressure mercury discharge.** W. ELENBAAS (Physica, 1936, 3, 859—871).—The intensity distribution and total radiation of Hg discharges at pressures from  $20$  to  $200$  atm. have been measured between  $0.4$  and  $3\mu$ . O. D. S.

**Emission and absorption spectrum of mercury vapour at very high pressures (up to  $300$  atm.).** W. DE GROOT (Ingenieur [s'Gravenhage], 1935, 50, No. 24, E, 92—94; Chem. Zentr., 1935, ii, 3484).—The discharge through Hg vapour in a narrow tube shows diffuse lines, mostly displaced towards the red, an intense continuum between  $2300$  and  $12,000 \text{ \AA}$ , and a region of absorption at  $2637 \text{ \AA}$ , the breadth of which is a function of the pressure. J. S. A.

**Intensity variations of mercury molecular spectra and the origin of the bands at  $2482 \text{ \AA}$ .** T. C. CHOW and K. J. CHAO (Chinese J. Physics, 1936, 2, 22—37).—The variations with current, pressure, and addition of  $\text{N}_2$  of the  $2482$  band of Hg and of the  $3300$  and  $2345 \text{ \AA}$  bands in a high-pressure discharge tube are compared, and found to be dissimilar. It is concluded that the  $2482$  band is due to a mercury mol. ion dissociating to  $\text{Hg}'(^3P_1)$  and  $\text{Hg}^+$ . O. D. S.

**Isotope effect of ionised mercury hydride ( $\text{Hg}^+\text{H}/\text{Hg}^+\text{D}$ ).** T. HORI and J. HURUTTI (Z. Physik, 1936, 101, 279—284).—Analysis of  $\text{Hg}^+\text{H}$  and  $\text{Hg}^+\text{D}$  band spectra gives isotope effects that are accurately accounted for by mass differences alone. A. B. D. C.

**Hyperfine structure separations of some terms in the thallium II spectrum.** S. SMITH and J. CONVEY (Canad. J. Res., 1936, 14, A, 139—151).—The hyperfine structure separations of 25 terms of the Tl II spectrum have been determined. Considerable isotope displacements were found in 5 terms arising from the  $5d^26s^26p$  configuration and in the  $6p^2\ ^3P$ , and  $6p^2\ ^1D_2$  terms, all of which are configurations containing completed  $6s$  systems. The summation rules were applied to the separation factors of the  $6snd$  and  $6snf$  configurations. The greatest discrepancy occurs for the  $6s7d$  configuration, and is due to perturbation. The ratio of magnetic to mechanical moment of the nucleus,  $g(I)$ , is calc. from the separation factors. A. J. M.

**Zeeman effect of thallium I  $\lambda 5351 \text{ \AA}$ .** J. OKUBO and S. SATO (Sci. Rep. Tohoku, 1935, 25, 141—155).—The vals. obtained for the separation and intensity of the various  $s$  and  $p$  components of the green Tl line at  $5351 \text{ \AA}$ . are in close agreement with those calc. from Goudsmit and Bacher's expression. A. R. P.

**Hyperfine structure of lead III.** A. M. CROOKER (Canad. J. Res., 1936, 14, A, 115—126).—Hyperfine structures at  $\lambda 2117-5858$  in the spectrum of Pb III excited by an electrodeless discharge lead to an  $I$ -val. of  $1/2$  and a  $g(I)$  factor of  $1.2$  for  $^{207}\text{Pb}$ , confirming published results. The isotope displacements between  $^{208}\text{Pb}$  and  $^{207}\text{Pb}$  are  $0.5 \text{ cm}^{-1}$  for each  $6s$  electron (cf. A., 1933, 2). There was no definite evidence of  $^{204}\text{Pb}$ . J. G. A. G.

**Phenomenon of photo-luminescence in the upper atmosphere; excitation by sunlight of the  $6300 \text{ \AA}$ . line of oxygen.** J. CABANNES and H. GARRIGUE (Compt. rend., 1936, 203, 484—487).—The variations of intensity of the  $6300 \text{ \AA}$ . line in the night spectrum with altitude have been deduced. On one date, a max. intensity was reached at  $110 \text{ km}$ . approx. It was possible to obtain vals. up to  $1000 \text{ km}$ . on a favourable occasion. D. C. J.

**Relative luminosity in the extreme red.** C. F. GOODEVE (Proc. Roy. Soc., 1936, A, 155, 664—683).—The relative luminosity in the extreme red has been measured by the threshold method up to  $900 \text{ m}\mu$ . At this  $\lambda$  the relative luminosity is  $1.66 \times 10^{-8}$  of that at  $556 \text{ m}\mu$ . When working above  $820 \text{ m}\mu$ , it is necessary to use a double monochromator and an infra-red filter to ensure that the light seen is not

scattered light. Some of the photo-chemical conclusions to be reached from the experiments are discussed.  
L. L. B.

**Spark potential of pre-ionised glow discharges.** C. DEIMEL (Physikal. Z., 1936, 37, 610—623).—The effect of pre-ionisation (produced by a discharge behind the cathode) on the spark potential, cathode drop, and characteristics of the glow discharge in Ne, He, A, and H<sub>2</sub> was examined in the pressure range 0.5—15 mm. The normal cathode drop was considerably diminished by the pre-ionisation.  
A. J. M.

**Inert gas-mercury vapour lamps. II.** K. SIEBERTZ (Z. Physik, 1936, 101, 255—259).—The origin of spectroscopic effects previously observed (cf. A., 1934, 1280) has been investigated by Langmuir's probe method.  
A. B. D. C.

**Tungsten spark as light source for Schumann region.** R. SERVANT (Rev. Opt. théor. inst., 1935, 14, 293—294; Chem. Zentr., 1935, ii, 3548).—A condensed W spark, running in N<sub>2</sub>, may be used down to 1250 Å. where a continuum is not required.  
J. S. A.

**Relative intensities of the X-ray non-diagram lines in the K-series.** M. SAWADA (Japan. J. Physics, 1936, 11, 1—8).—The ratio of intensities of the non-diagram Al K $\alpha$  lines was measured, for the excitation range 4—16 kv., by the photographic photometric method. Results indicate that the origin of K $\alpha_3$  and K $\alpha_4$  differs from that of K $\alpha_5$  and K $\alpha_6$  lines. With Kennard's view as to origin (cf. A., 1935, 138) relative probabilities of single and double, and of single and triple, ionisation are estimated.  
N. M. B.

**Fine structure of the X-ray K absorption spectrum of nickel.** T. HAYESI (Sci. Rep. Tohoku, 1935, 25, 1—10).—The principal absorption region is divided into two parts, the absorption intensity on the long-wave side being about half that on the short-wave side. The fine structures of the K absorption spectrum of the 50:50 Ni-Cu alloy is similar to that of pure Ni.  
A. R. P.

(A) **Fine structure in the K X-ray absorption edge of gallium.** W. W. MURCH. (B) **Theoretical investigation.** R. SMOLUCHOWSKI (Physical Rev., 1936, [ii], 50, 197—201, 201—203).—(A) Investigation from the main K absorption edge towards shorter  $\lambda\lambda$  for about 250 volts for Ga foil at room temp. shows no fine structure; at  $-67^\circ$  and  $-140^\circ$  progressive extended fine structure appears with fall of temp. The  $\lambda$  of the main K absorption edge is 1192.5 Å.

(B) The fine structure of the Ga X-ray absorption edge is calc. by Kronig's theory. A method previously reported (cf. A., 1935, 812) for calculating the fine structure in complicated crystals is applied to a non-cubic crystal and good agreement with experiment is found.  
N. M. B.

**Effects of chemical composition on X-ray lines.** H. H. ROSEBERRY and J. A. BEARDEN (Physical Rev., 1936, [ii], 50, 204—208).—The effect of combination with O<sub>2</sub> on the width, index of asymmetry and separation, and ratio of peak intensities of the  $\alpha$ -

doublet for Ti, Cr, Mn, Fe, and Zn, of the K-series emission lines was studied with a double-crystal spectrometer. The width of the  $\alpha$ -lines increased 3—35% and of the  $\beta$ -lines 4—30% except for the K $\alpha_1$  line of TiO<sub>2</sub> (3% decrease) and the  $\beta$ -lines of Mn (no change). No alteration of  $\gamma$ -line widths or of  $\alpha_1 \rightarrow \alpha_2$  separations was found. Asymmetries were unaffected except for TiO<sub>2</sub>  $\alpha$ -lines and K $\alpha_1$  and  $\beta$ -lines of MnO and Mn<sub>2</sub>O<sub>4</sub>. The ratios of peak intensities of the  $\alpha$ -lines were affected by changes of width caused by composition such that the ratio of areas remained 2:1.  
N. M. B.

**Intensity of X-ray spectrum lines of heavy elements.** H. S. W. MASSEY and E. H. S. BURHOP (Proc. Camb. Phil. Soc., 1936, 32, 461—470).—Mathematical. Intensities of lines resulting from transitions between K, L, and M shells are calc. for U, Au, and Sb.  
O. D. S.

**Intensities of X-ray reflexion from Bi crystals between 25° and 530° absolute.** R. B. JACOBS and A. GOETZ (Physical Rev., 1935, [ii], 47, 257; cf. A., 1935, 16).—Integrated intensities of Mo K $\alpha$  radiation from (111) of highly-purified Bi crystals have been measured.  
L. S. T.

**L Emission and absorption spectra of rhenium (75).** (MLLE.) Y. CAUCHOIS (Compt. rend., 1936, 203, 169—171; cf. A., 1928, 1294).— $\lambda\lambda$  are recorded and classified.  
J. G. A. G.

**L Spectra of iron, cobalt, nickel, and copper.** F. C. CHALKLIN (Proc. Roy. Soc., 1936, A, 155, 366—385).—The L spectra of Fe, Co, Ni, and Cu have been studied with a plane-grating vacuum spectrograph. The vals. of the energy levels are independent of the ferromagnetic condition of the metals. Anticathodes, when heated and free from oxidation, give the same results as previous workers have obtained using cold anticathodes. The L $\alpha$  lines possess an abnormal spread on the long-wave side, which is attributed to an energy spread in the level.  
L. L. B.

**Enhancement of certain L- and M-series X-ray satellite lines by the Auger effect.** F. R. HIRSH, jun. (Physical Rev., 1936, [ii], 50, 191—197; cf. this vol., 3).—Integrated relative energies of L $\beta_1$  satellites were measured photographically, and a marked relative intensity change at at. no. 40 was found. A theoretical study of satellite enhancement for the M-series shows qual. agreement with available data.  
N. M. B.

**L $\alpha$  Satellites of the elements 68, 70, and 71.** (MLLE.) Y. CAUCHOIS (Compt. rend., 1936, 203, 398—399).—The L $\alpha$  satellites of elements of at. no. 68, 70, and 71 have been observed. The L $\alpha_1$  band is degraded towards the violet, and is complex.  
A. J. M.

**L Spectrum of radium (88).** I. H. HULUBEI (Compt. rend., 1936, 203, 399—400).—The  $\lambda\lambda$  of the strongest lines in the X-ray L spectrum of Ra are given.  
A. J. M.

**Optical L spectra of elements potassium to chromium: K X, K XI, Ca XI, Ca XII, Sc XII, Ti XIII, V XIV, and Cr XV.** B. EDLÉN and F. TYRÉN (Z. Physik, 1936, 101, 206—213).  
A. B. D. C.



**Röntgen absorption spectra.** A. SANDSTRÖM (Nov. Acta Reg. Soc. Sci. Upsal., 1935, [iv], 9, No. 11, 88 pp.; Chem. Zentr., 1935, ii, 2494).—Data for  $\lambda$  in the *L* absorption spectra of elements from Cu to Te, and the *K* absorption spectra of Mg and Al, are given. The electronic transitions involved and the significance of complex absorption edges are discussed.

J. S. A.

**Forms of the X-ray absorption edges in metals and insulators.** T. MURO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 444—450).—For the absorption edge or its neighbourhood the absorption coeff. must be calc. by the Wigner-Seitz-Slater approximation method.

N. M. B.

**Mass absorption coefficients of monochromatic X-rays for Cellophane, aluminium, selenium, silver, cadmium, tin, antimony, and tellurium up to 10 Å.** H. H. BIERMANN (Ann. Physik, 1936, [v], 26, 740—760; cf. A., 1930, 982).—Apparatus for the production of intense monochromatic X-rays with  $\lambda$  up to 9.87 Å. is described. The mass absorption coeffs. ( $\mu/\rho$ ) of the above substances were determined for rays of  $\lambda$  1.66—9.87 Å. The  $C\lambda^n$  law is obeyed. The *K*-jump for Al, and the *L*-jumps for the other elements examined, are given. A. J. M.

**Mass absorption coefficients of monochromatic X-rays for selenium, silver, cadmium, tellurium, gold, lead, and bismuth up to about 2 Å.** K. SCHULZ (Ann. Physik, 1936, [v], 27, 1—14).—Mass absorption coeffs.,  $\mu/\rho$ , have been measured between 0.16 and 2.3 Å. The consts. *C* and *n* in  $\mu = C\lambda^n$  are tabulated on either side of the *K* edge for Se, Ag, Cd, and Te and of the *L<sub>I</sub>*, *L<sub>II</sub>*, and *L<sub>III</sub>* edges for Au, Pb, and Bi. Results are in agreement with those of Grosskurth (A., 1934, 824).

O. D. S.

**Measurement of shape and width of the Compton lines of gaseous neon, oxygen, and nitrogen, and of solid lithium, carbon, and sodium fluoride.** H. KAPPELER (Ann. Physik, 1936, [v], 27, 129—168).

O. D. S.

**Cloud chamber study of the Compton effect.** H. R. CRANE, E. R. GAERTTNER, and J. J. TURIN (Physical Rev., 1936, [ii], 50, 302—308).—To test the photon theory of scattering in the energy range 0.5—2.6 m.e.v., an experiment using radiation from a Th source scattered by celluloid in a cloud chamber is described. Out of 10,000 photographs, 300 electron-photon combinations were found, the angular and energy relations of which indicate the validity of the theory.

N. M. B.

**Experimental proof of the photon theory.** W. BOTHE and H. MAIERLEBNITZ (Z. Physik, 1936, 102, 143—155).—The coincidences between the Compton radiation and recoil electrons produced when filtered  $\gamma$ -rays from Th-C'' pass through a Cellophane film were studied with a counter tube. The results agree well with the photon theory of the Compton effect.

A. J. M.

**Effect of an electrostatic field on rate of vaporisation.** E. HUTCHINSON (Physical Rev., 1935, [ii], 47, 328).—The rate of vaporisation is calc. on the basis of a change in the binding forces of surface atoms of Mo in presence of an electric field.

L. S. T.

**Effect of temperature, degree of thoriation, and breakdown on field currents from tungsten and thoriated tungsten.** A. J. AHEARN (Physical Rev., 1936, [ii], 50, 238—253).—Electron field currents from thoriated W, with different degrees of thoriation, were independent of temp. The characteristic field current curve was independent of the degree of thoriation of the W filament. Breakdown phenomena and effects of heat-treatment are described in detail.

N. M. B.

**Relation between electron field emission and contact electromotive force for liquid mercury.** D. H. MOORE (Physical Rev., 1936, [ii], 50, 344—347).—The relation between contact e.m.f. and the impulsive potential necessary to initiate a vac. spark was studied for a liquid Hg cathode. The magnitude and time of application of the impulsive potential were determined by a cathode-ray oscillograph. For impure Hg no definite relation was found; for carefully distilled Hg the relation between the work function and breakdown field was in qual. but not in quant. agreement with theory.

N. M. B.

**Velocity distribution of atomic electrons by the method of electron impact.** G. E. M. JAUNCEY (Physical Rev., 1936, [ii], 50, 326—327; cf. A., 1934, 1282).—Mathematical.

N. M. B.

**After-effects produced on metallic surfaces by cathode-ray bombardment or by low-pressure gas discharges.** M. HATOYAMA and M. KIMURA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 681—691).—No after-effects were observed when Zn, Cu, Cd, Al, Ag, and Mg were bombarded in a vac. with high-speed electrons, but in air or H<sub>2</sub> low-energy electrons (< 50 volts) were emitted spontaneously. Similar effects were observed when using the metals as anodes in a discharge.

R. S. B.

**Energy distribution of secondary electrons from niobium.** L. J. HAWORTH (Physical Rev., 1936, [ii], 50, 216—219).—Energy distribution curves were obtained, and the no. of elastically reflected electrons was studied as a function of primary energy. Results show marked similarity to those for Mo (cf. A., 1935, 1047). The lower energy vals. involved in the various phenomena in the case of Nb are in agreement with its lower at. no. and larger lattice const.

N. M. B.

**Scattering of fast electrons by helium.** A. L. HUGHES and S. S. WEST (Physical Rev., 1936, [ii], 50, 320—325).—In view of the smaller scattering predicted by wave mechanics than by classical mechanics, scattering of 2000- and 4000-volt electrons by He atoms was investigated. The scattering is due to the nuclei (elastic scattering) and to the at. electrons (inelastic scattering) independently. The scattering ratio, compared with the vals. given by the two theories, agrees with the wave-mechanical theory.

N. M. B.

**Elastic scattering of fast electrons in mercury and agreement with Mott's theory.** W. E. STEPHENS (Physical Rev., 1935, [ii], 47, 255).—Agreement over the whole angular range for 2000 volts in Hg is not good.

L. S. T.

**Elastic scattering of slow electrons from organic molecules.** S. HILL and A. H. WOODCOCK

(Proc. Roy. Soc., 1936, A, 155, 331—344).—Measurements have been made on a group of gases ( $\text{CF}_4$ ,  $\text{CCl}_4$ , and  $\text{CBr}_4$ ) the mols. of which differ in size but have approx. spherically symmetrical outer potential contours. The results are reviewed in terms of a theoretical treatment which combines the theory of Faxen and Holtsmark with the interference theory developed by Debye for the scattering of X-rays.

L. L. B.

Variation of the mobility of gaseous ions with temperature. II. Cæsium and sodium ions in helium. A. F. PEAROE (Proc. Roy. Soc., 1936, A, 155, 490—498).—A temp. range of  $410^\circ$  abs. from the b.p. of  $\text{N}_2$  upwards was used. The mobility of the Cs ion at const.  $d$  passes through a max., and a similar max. probably occurs for the Na ion at a higher temp. The results are discussed in terms of the theories of Langevin and of Hassé and Cook (A., 1931, 1107).

L. L. B.

Ionisation of mercury vapour by positive sodium ions. R. N. VARNEY and W. C. COLE (Physical Rev., 1936, [ii], 50, 261).—Using a balanced space-charge method of detection (cf. A., 1935, 556), ionisation was observed for  $\text{Na}^+$  energies  $< 88 \pm 4$  volts. A corresponding val. for  $\text{Cs}^+$  is indicated at 59 volts.

N. M. B.

Production of slow positive potassium ion rays. H. POEVERLEIN (Ann. Physik, 1936, [v], 27, 92—96).—Apparatus to produce slow  $\text{K}^+$  ion rays of high intensity and uniform velocity is described.

O. D. S.

Light excitation in helium by collisions of positive potassium ions of 2500—8000 volts. H. BUMANN (Z. Physik, 1936, 101, 1—12).—A K-ion source giving up to  $2 \times 10^{-5}$  amp. was used to obtain He and K excitation functions.

A. B. D. C.

Velocity of atoms and ions projected from a wire exploded electrically. T. FUTAGAMI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 711—717).—The velocity ( $v$ ) was measured by the inclination of spectral lines, and amounts, at first, to 1—2 km. per sec.  $v_{\text{ion}} > v_{\text{atom}}$  and the initial  $v \propto (\text{at. wt.})^{-1/2}$ .

R. S. B.

Negative atomic ions. H. S. W. MASSEY and R. A. SMITH (Proc. Roy. Soc., 1936, A, 155, 472—489).—Processes leading to the formation of negative at. ions (direct radiative capture, dissociation of mols. on electron impact, collision processes with heavy atoms, extraction of electrons from metals), and those leading to the neutralisation of the ions (light absorption, ionisation by electrons and by heavy particles, neutralisation by collision with metal surfaces), are discussed. The absorption and emission of light by negative ions are not completely analogous to those by neutral atoms.

L. L. B.

Existence of negative ions according to the statistical model. H. JENSEN (Z. Physik, 1936, 101, 141—163).—Ionisation potential, and diamagnetic susceptibility and its decrease on crystal formation, are calc. from a modified Fermi equation.

A. B. D. C.

Positive-ray analysis of ions from a high-frequency spark. S. L. CH'U (Physical Rev., 1936,

[ii], 50, 212—215).—Results are given for a no. of metals and minerals as spark materials. The Dempster high-frequency spark method gives strong sources of multiply charged ions in almost all cases.

N. M. B.

History of the discovery of element 87, eka-cæsium. J. C. DE WIJS (Chem. Weekblad, 1936, 33, 515—519).—A review.

S. C.

Mass of the standard litre of ammonia gas. At. wt. of nitrogen. E. MOLES and J. SANCHE (Anal. Fís. Quím., 1934, 32, 931—953).—The mass of 1 litre of  $\text{NH}_3$  at  $0^\circ$  and 760 mm. ( $L_{760}$ ) is  $0.77142 \pm 0.00003$  g., that at 380 mm., corr. to 760 mm. ( $L_{760/380}$ ), is  $0.76562 \pm 0.00005$  g., and, by extrapolation, the limiting val. when  $p \rightarrow 0$  ( $L_{\text{lim}}$ ), corr. to 760 mm., is  $0.75982$  g. Hence the at. wt. of N is  $14.008 \pm 0.001$ .

D. R. D.

Relationship between the standard densities of nitrogen, carbon monoxide, and oxygen. At. wts. of carbon and nitrogen. E. MOLES and M. T. SALAZAR (Anal. Fís. Quím., 1934, 32, 954—978; cf. preceding abstract).—For CO,  $L_{760}$  is  $1.25001 \pm 0.00001$  g.,  $L_{760/380}$  is  $1.24975 \pm 0.00001$  g., and  $L_{\text{lim}}$  is  $1.24950$  g. For  $\text{O}_2$ ,  $L_{760}$  is  $1.42895 \pm 0.00001$  g.,  $L_{760/380}$  is  $1.42831 \pm 0.00001$  g., and  $L_{\text{lim}}$  is  $1.42767$  g. For  $\text{N}_2$ ,  $L_{760}$  is  $1.24049 \pm 0.00001$  g.,  $L_{760/380}$  is  $1.25022 \pm 0.00002$  g., and  $L_{\text{lim}}$  is  $1.24995$  g. Hence, the at. wt. of C is  $12.008 \pm 0.0005$  and that of N is  $14.0083 \pm 0.0002$ .

D. R. D.

Hyperfine structure of platinum isotopes. III. Relative frequency of platinum isotopes from hyperfine structure of some Pt  $\gamma$  lines. H. KOPFERMANN and K. KREBS (Z. Physik, 1936, 101, 193—205; cf. this vol., 916).—The relative frequency of  $^{194}\text{Pt}$  :  $^{195}\text{Pt}$  :  $^{196}\text{Pt}$  :  $^{198}\text{Pt}$  is as 19 : 20 : 13 : 5.

A. B. D. C.

Hyperfine structure and isotopy. H. KOPFERMANN (Naturwiss., 1936, 24, 561—567).—A lecture.

Ionic emission of alkali metals from glass melts and data from mass-spectrometric measurements of the relative frequencies of isotopes of lithium, potassium, and rubidium. H. BONDY and V. VANICEK (Z. Physik, 1936, 101, 186—192).—Relative isotope frequencies are:  $^7\text{Li}$  :  $^6\text{Li}$  12 : 1,  $^{39}\text{K}$  :  $^{41}\text{K}$  14 : 1. The frequency of Rb isotopes depends on the origin of the Rb.

A. B. D. C.

Masses of light atoms from transmutation data. H. BETHE (Physical Rev., 1935, [ii], 47, 633—634, 795).—Stability considerations require for  $^9\text{Be}$  an at. wt.  $< 9.0124$  as compared with the mass-spectroscopic val. 9.0154. This discrepancy and other difficulties connected with  $^{11}\text{B}$  and  $^{12}\text{C}$  can be resolved only on the assumption that the ratio He : O is incorrect. This also follows from the energy balance of nuclear transformations. All stability difficulties can be solved and all energy balances made to agree if  $^4\text{He}$  is assumed to be  $3.0 \pm 0.7$  parts in  $10^4$  heavier than hitherto supposed. At. wts. derived solely from transmutation data are ( $^{16}\text{O} = 16.0000$ ):  $^{12}\text{C}$  12.0085,  $^1\text{H}$  1.00807,  $^4\text{He}$  4.0033,  $^9\text{Be}$  9.0135,  $^{10}\text{B}$  10.0146,  $^{11}\text{B}$  11.0111,  $^{12}\text{C}$  12.0037,  $^{14}\text{N}$  14.0076, etc. L. S. T.

Abundance ratio of the isotopes of lithium. A. K. BREWER (Physical Rev., 1935, [ii], 47, 571—



572).—A re-determination with a new mass spectrograph gives  ${}^7\text{Li}/{}^6\text{Li}=11.60\pm0.06$  (cf. A., 1935, 140). The abundance ratio remains const. for cryst. emitters up to near the m.p., where the lighter isotope is emitted more readily than the heavier. L. S. T.

**Mass-spectrum analysis.** (1) Mass spectrograph. (2) Existence of isobars of adjacent elements. K. T. BAINBRIDGE and E. B. JORDAN (Physical Rev., 1936, [ii], 50, 282—296).—An improved instrument giving high resolving power, sensitivity, and dispersion is described. Singly or doubly ionised Ge, Cd, In, Sn, Te, Hg, Pb, and Bi were examined, using H-free ion sources. Proof was obtained for the existence of three apparently stable isobaric pairs  ${}^{113}\text{Cd}/{}^{113}\text{In}$ ,  ${}^{115}\text{In}/{}^{115}\text{Sn}$ , and  ${}^{123}\text{Sb}/{}^{123}\text{Te}$ . Isotopes  ${}^{115}\text{Cd}$ ,  ${}^{121}\text{Sn}$ ,  ${}^{197}\text{Hg}$ , and  ${}^{209}\text{Pb}$ , which have been reported as members of isobaric pairs, cannot be present to  $>1/8$ ,  $1/60$ ,  $1/2$ , and  $1/10$ , respectively, of the amounts given by Aston. The existence of  ${}^{205}\text{Pb}$  is doubtful. Stability conditions are discussed. N. M. B.

**Isotopes of cobalt and their radioactivity.** M. B. SAMPSON, L. N. RIDENOUR, and W. BLEAKNEY (Physical Rev., 1936, [ii], 50, 382).—In order to interpret the slow-neutron absorption of Co, a mass-spectrograph examination, using a mol. beam of  $\text{CoCl}_2$  ionised by slow electrons, was made.  ${}^{57}\text{Co}$  was found as the  $\text{CoCl}^+$  ion; peaks were observed at 92 ( ${}^{57}\text{Co}/{}^{35}\text{Cl}$ ), 94 ( ${}^{57}\text{Co}/{}^{37}\text{Cl}$  and  ${}^{59}\text{Co}/{}^{35}\text{Cl}$ ), and 96 ( ${}^{59}\text{Co}/{}^{37}\text{Cl}$ ). The abundance ratio  ${}^{57}\text{Co}/{}^{59}\text{Co}$  is approx.  $1/600\pm20\%$ ; assuming packing fraction  $-9$ , the at. wt. is 58.93. A Co cylinder, bombarded for nearly a month with neutrons from a Ra-Be source, exhibited a strong activity of half-life of the order 1 year; this activity explains the large slow-neutron cross-section of Co. Short-period activity is attributed to  ${}^{58}\text{Co}$ , formed by the capture of a neutron in  ${}^{57}\text{Co}$ , and the long-period activity to  ${}^{60}\text{Co}$ . N. M. B.

**Radioactivity determined by counter tubes and ion compensation amplifier.** C. B. MADSEN (Z. physik, 1936, 101, 72—76). A. B. D. C.

**Radioactive manganese as an indicator in testing for possible equilibria between several valencies of manganese.** M. J. POLISSAR (J. Amer. Chem. Soc., 1936, 58, 1372—1376).—Observations with radioactive Mn show that no exchange occurs in the pair-systems  $\text{MnO}_4'-\text{Mn}^{++}$ ,  $\text{MnO}_4'-\text{Mn}(\text{C}_2\text{O}_4)_2'$ ,  $\text{MnO}_4'-\text{MnO}_2$ , and  $\text{MnO}_2-\text{Mn}^{++}$ , but rapid, complete exchange occurs in  $\text{Mn}(\text{C}_2\text{O}_4)_2'-\text{Mn}^{++}$ . The significance of the observations is discussed. E. S. H.

**Stopping-power of mica for  $\alpha$ -particles.** W. E. BENNETT (Proc. Roy. Soc., 1936, A, 155, 419—434).—The stopping-power of mica has been determined by (1) measuring the velocities of the  $\alpha$ -particles of Th active deposit before and after they had passed through a sheet of mica, and (2) measuring the ranges of the incident and emergent  $\alpha$ -particles in an air chamber. The results show that no permanent data can be relied on to within 2—3%. L. L. B.

**Continuous  $\beta$ -[ray] spectrum of radium-E.** M. LECOIN (Compt. rend., 1936, 203, 171—173).—The range 0— $16^6$  e.v. has been studied. The mean energy

is  $2.5\times10^5$  e.v. and the probability of emission for low energies is small. J. G. A. G.

**$\beta$ -Ray spectrum of radium-E.** P. C. HO and M. H. WANG (Chinese J. Physics, 1936, 2, 1—9).—The  $\beta$ -ray spectrum of Ra-E has been investigated by means of an automatic cloud chamber. The spectrum is found to have an end-point at 7500  $H_p$ . The average energy per disintegration is estimated as  $4.01\times10^5$  e.v. O. D. S.

**Internal conversion coefficient for  $\gamma$ -rays.** H. R. HULME, N. F. MOTT, F. OPPENHEIMER, and H. M. TAYLOR (Proc. Roy. Soc., 1936, A, 155, 315—330).—The results obtained by previous authors in the theory of the internal conversion of  $\gamma$ -rays are discussed, and compared with experiment. The results support the hypothesis that soft  $\gamma$ -rays correspond with transitions between the states of a nuclear multiplet. L. L. B.

**Probability of  $\gamma$ -ray emission.** F. BLOCH and G. GAMOW (Physical Rev., 1936, [ii], 50, 260).—For at. nuclei, the reduction, by a factor of several thousands, of the probability of dipole transitions is explained by taking into account the exchange of charge between neutrons and protons. N. M. B.

**Continuous  $\gamma$ -radiation accompanying the  $\beta$ -decay.** F. BLOCH (Physical Rev., 1936, [ii], 50, 272—278).—Mathematical. Formulæ for spectral distribution and total intensity are developed for light elements. The relative energy liberated as radiation increases with increasing total energy, and for radioactive B is about 0.6%. N. M. B.

**Geiger-Nuttall relation.** K. C. KAR (Current Sci., 1936, 5, 17).—A wave-statistical basis is reported for the above relation. D. C. J.

**Resonance capture of slow neutrons.** H. H. GOLDSMITH and F. RASETTI (Physical Rev., 1936, [ii], 50, 328—331).—The energies of neutron groups selectively activating various elements have been measured by the B absorption method. Rh (3.9 min.), Rh (44 sec.), Ag (22 sec.), In (13 sec.), In (54 min.), Ir (19 hr.), and Au (2.7 days) show resonance capture for neutrons of energies 1—5 volts. Mn (2.5 hr.), Cu (5 min.), As (26 hr.), Br (18 min.), Ag (2.3 min.), I (25 min.), and Re (20 hr.) seem to be activated only by 30—85 volt neutrons. Gd and Sm may have resonance groups within the Cd absorption region (thermal energies). N. M. B.

**Neutron absorption in aqueous solutions.** W. H. FURRY (Physical Rev., 1936, [ii], 50, 381).—Mathematical. The theory of a simplified method, using only the velocity distribution of the neutrons, is developed. N. M. B.

**Diffusion of slow neutrons in flowing water.** P. HARTECK and F. KNAUER (Naturwiss., 1936, 24, 558).—The edge effect which limits the val. of previous determinations of the diffusion of slow neutrons in flowing  $\text{H}_2\text{O}$  has been avoided by making experiments in a canal. Neutrons are carried along by  $\text{H}_2\text{O}$  flowing with a velocity of a few m. per sec. Assuming that neutrons arrive at the Rh sheet, at which their activity is measured, only by thermal diffusion, the

diffusion const. was found to be  $3.5 \times 10^4$  and the mean life  $2 \times 10^{-3}$  sec. The mean free path was 0.4 cm.

A. J. M.

**Non-elastic collision cross-sections for slow neutrons.** G. BECK and L. H. HORSLEY (Physical Rev., 1935, [ii], 47, 510).—A discussion. L. S. T.

**Magnetic scattering of neutrons.** F. BLOCH (Physical Rev., 1936, [ii], 50, 259—260).—Mathematical. A basis for several suggested experimental methods of obtaining information on the magnetic moment of the neutron is deduced. N. M. B.

**Scattering of protons in collisions with neutrons.** W. D. HARKINS, D. M. GANS, M. KAMEN, and H. W. NEWSON (Physical Rev., 1935, [ii], 47, 511—512).—Data for neutron-proton collisions in  $C_2H_4$  and in  $H_2$  are recorded. L. S. T.

**Energy of the neutrons emitted from beryllium when bombarded by deuterons.** J. R. RICHARDSON and F. N. D. KURIE (Physical Rev., 1935, [ii], 47, 253—254).—This energy has been investigated by measuring the ranges and angles of projection of He recoil atoms in a neighbouring cloud chamber. The spectrum extends from  $< 1$  mv. to 10 mv. and possibly beyond. L. S. T.

**Resonance absorption of neutrons.** C. Y. CHAO and C. Y. FU (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 451—455).—The activity induced in Ag and I by photo-neutrons from a source surrounded by increasing thicknesses of paraffin increases to a max. at 2.5 cm. thickness and then decreases; for I, there is appreciable activity at zero thickness of paraffin. The total width of the Ag absorption band is approx.  $2 \times 10^4$  e.v. N. M. B.

**Passage of neutrons through matter.** C. H. COLLIE and J. H. E. GRIFFITHS (Proc. Roy. Soc., 1936, A, 155, 434—446).—The passage of neutrons through matter has been studied under conditions such that absorption coeffs. could be measured independently of scattering. Using Al and Si detectors, absorption cross-sections ( $1-1.4 \times 10^{-24}$  sq. cm.) were obtained which did not show a systematic increase with increasing at. no. I and Ag have a greatly enhanced probability of reacting with slow neutrons, and using these as detectors an increase in activity was found with all the elements examined except S and I. L. L. B.

**Secondary radiation emitted under the action of neutrons.** C. HAENNY (Compt. rend., 1936, 203, 173—175).—In presence of slow neutrons,  $\gamma$ -radiation ( $\times 10^6$  e.v.) is emitted by Gd (7—8), Cl (6), Cd (10), Hg (soft and  $> 15$ ), and Au. The transformations are discussed. J. G. A. G.

**Transmutation of sulphur by thorium-C'  $\alpha$ -particles.** C. J. BRASEFIELD and E. POLLARD (Physical Rev., 1936, [ii], 50, 296—301).—The protons emitted from S under bombardment by Th-C'  $\alpha$ -particles were resolved into three groups corresponding with nuclear energy changes  $-2.4 \pm 0.3$ ,  $-2.85 \pm 0.3$ , and  $-3.6 \pm 0.3$  m.e.v. The calc. mass of  $^{32}S$  is  $31.9812 \pm 0.0016$ . An excitation curve for proton emission obeys the Gamow penetration formula; from this the calc. nuclear radius of  $^{32}S$  is  $3.4 \pm 0.3 \times 10^{-13}$  cm. N. M. B.

**Metastable nuclei produced by the hard  $\gamma$ -rays from radium-B + C.** L. DEVOL (Physical Rev., 1935, [ii], 47, 325—326).—Al and Ni-walled counters enclosed in Pb glass were exposed to radiation from Ra-B + C filtered by 6.25 cm. of Pb. 10% of the discharges were apparently due to a secondary radiation associated with a decay period of the order  $1/2$  sec. L. S. T.

**Disintegration of beryllium by  $\gamma$ -rays and of boron by neutrons.** S. NISHIDA (Japan. J. Physics, 1936, 11, 9—11).—A preliminary report is given of an investigation of the reactions  $^9Be + h\nu \rightarrow ^8Be + ^1_0n$ ;  $^9Be + h\nu \rightarrow ^2_2He + ^7_3Li$ , and  $^{10}B + ^1_0n \rightarrow ^7_3Li + ^4_2He$ ;  $^{10}B + ^1_0n \rightarrow ^2_2He + ^8_4Be$  (cf. Taylor, A., 1935, 1297). N. M. B.

**$\gamma$ -Rays from the disintegration of beryllium by deuterons and protons.** H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 47, 782—783; cf. A., 1935, 1297).—The existence of the strong component at approx. 0.7 m.e.v. in the  $\gamma$ -radiation accompanying the neutrons obtained from Be bombarded by deuterons has been confirmed, and additional, but weaker,  $\gamma$ -ray lines up to 4 m.e.v. have been observed. Both neutrons and  $\gamma$ -rays probably arise from the reaction  $^9Be + D \rightarrow ^{10}B + ^1_0n + \gamma$ .  $\gamma$ -Ray lines at 2.2, 3.7, 4.8, and 6.0 m.e.v. are indicated in the energy spectra of negative electrons ejected from the cloud chamber by the  $\gamma$ -radiation from Be bombarded by protons. Assuming a stable mass for  $^9Be$ , the reaction involved appears to be  $^9Be + ^1H \rightarrow ^{10}B + \gamma$ . Referred to  $^{10}B = 10.0135$  and  $H^1 = 1.0078$ ,  $^9Be$  is  $> 9.0117$ . L. S. T.

**Energy levels of some light nuclei.** A. N. MAY and R. VAIDYANATHAN (Proc. Roy. Soc., 1936, A, 155, 519—532).—The disintegration of F, Na, and P by  $\alpha$ -particles from Ra-C has been studied by the method developed by Duncanson and Miller (A., 1934, 1184). The nuclei formed in these reactions,  $^{22}Ne$ ,  $^{26}Mg$ ,  $^{30}Si$ , and  $^{34}S$ , form a series in which each member would be obtained from the one before by the addition of an  $\alpha$ -particle, and experiment shows that this similarity in structure gives rise to a similarity in the level systems. L. L. B.

**Attempt to produce artificial radioactivity by an electron beam.** The behaviour of newly made Geiger-Müller counters. W. B. LEWIS and W. E. BURCHAM (Proc. Camb. Phil. Soc., 1936, 32, 503—505).—No radioactivity was detected in Al after bombardment with electrons at 300 kv. The activity of Geiger-Müller counters with newly cleaned surfaces is ascribed to ionisation accompanying oxidation. O. D. S.

**Short periods in artificial radioactivity.** M. E. NAHMIAS and R. F. WALLEN (Compt. rend., 1936, 203, 176—177).—Activity of Li bombarded by neutrons was not detected. A small effect was observed with B (cf. this vol., 772). J. G. A. G.

**Artificial production of radioactive elements.** A. I. ALICHANOV and A. I. ALICHANIAN (Uspechi Fiz. Nauk., 1935, 15, 281—314).—A review and discussion. CH. ABS. (e)

**Analysis of data on radioactivity induced by neutron bombardment.** C. N. WARFIELD and



A. E. RUARK (Physical Rev., 1935, [ii], 47, 700—701).—The 27 elements for which the isotope given by neutron bombardment is known are classified into three groups, viz., those activated by simple capture of a neutron, by capture of a neutron with emission of a proton, and by capture of a neutron with  $\alpha$ -emission. The rules concerning at no., the mass no., and at. no. — mass no. which then become apparent are defined. L. S. T.

Radioactivity caused by bombardment with neutrons. X. E. AMALDI, O. D'AGOSTINO, E. FERMI, B. PONTECORVO, and E. SEGRÈ (Ric. sci. Prog. tec., 1935, I, 6, 581—584; Chem. Zentr., 1935, ii, 3358).—The activity of Ag, V, and Al, induced by slow neutrons, increased as the temp. of the surrounding paraffin was lowered. Data are given for the relative ease of excitation of P, Si, Al, V, and Rh with neutrons from  $\text{CaF}_2 + \text{Rn}$ ,  $\text{Mg} + \text{Rn}$ , and  $\text{Al} + \text{Rn}$ . The production of neutrons by  $\gamma$ -rays is discussed. J. S. A.

Disintegration of beryllium, boron, and carbon by deuterons. T. W. BONNER and W. M. BRUBAKER (Physical Rev., 1936, [ii], 50, 308—314; cf. this vol., 264).—Bombardment was effected by 0.9 m.e.v. deuterons. For Be (cf. A., 1935, 1049), the energy of disintegration was  $4.25 \pm 0.2$  m.e.v.; lower energy groups due to excited  $^{10}\text{B}$  nuclei were observed, the corresponding energies being 3.7, 2.1, and 0.8 m.e.v. The reactions for B are:  $^{11}\text{B} + ^2\text{H} \rightarrow ^{12}\text{C} + n + Q_2$ ;  $^{11}\text{B} + ^2\text{H} \rightarrow ^3\text{He} + ^9\text{Be} + Q_3$ ;  $^{10}\text{B} + ^2\text{H} \rightarrow ^{12}\text{C} + n + Q_4$ , the second being the most probable, and giving rise to a group of neutrons with a continuous distribution of energies  $< 3$  m.e.v. The other disintegration energies are:  $13.5 \pm 0.3$ ,  $Q_2$   $9.1 \pm 0.2$ ,  $6.2 \pm 0.2$ ,  $Q_3$   $4.0 \pm 0.1$  m.e.v. The reactions for C are:  $^{12}\text{C} + ^2\text{H} \rightarrow n + Q_5$  and ; the former accounts for approx. 99% of the neutrons from C, and the latter for the remainder. Energies are:  $Q_5$   $-0.37 \pm 0.05$  and  $Q_6$   $5.2 \pm 0.4$  m.e.v. The calc. max. energy of the positrons from  $^{13}\text{N}$  is 1.16 m.e.v. A complete set of calc. masses of the light elements is tabulated. N. M. B.

Emission of negative electrons from boron bombarded by deuterons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 47, 887—888).—The  $\beta$ -ray spectrum obtained from B bombarded by deuterons is continuous with an upper energy limit of approx. 11 m.e.v. The probable reaction is  $^{11}\text{B} + \text{D} \rightarrow ^{12}\text{B} + ^1\text{H}$   $^{12}\text{C} + e^- + ^1\text{H}$ . In disintegrating,  $^{12}\text{B}$  loses an amount of mass  $\leq$  that corresponding with the upper limit of energy of the electron spectrum. L. S. T.

Emission of negative electrons from lithium and fluorine bombarded with deuterons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], 47, 971—972).—Energy distribution curves of negative electrons emitted from targets of  $\text{LiCl}$  and  $\text{CaF}_2$  bombarded by deuterons are reproduced. The probable reactions are  $^7\text{Li} + \text{D} \rightarrow ^8\text{Li} + ^1\text{H} \rightarrow ^8\text{Be} + e^- + ^1\text{H} \rightarrow ^4\text{He} + ^4\text{He} + e^- + ^1\text{H}$  and  $^{19}\text{F} + \text{D} \rightarrow ^{20}\text{F} + ^1\text{H} \rightarrow ^{20}\text{Ne} + e^- + ^1\text{H}$ , respectively. The half-life indicated for the active

constituent in the first reaction is  $0.5 \pm 0.1$  sec., and that for radio-F is  $12 \pm 2$  sec. L. S. T.

Chemical identification of the radioactive element produced from carbon by deuteron bombardment. L. N. RIDENOUR, D. M. YOST, and K. SHINOHARA (Physical Rev., 1935, [ii], 47, 253; cf. A., 1935, 559). L. S. T.

Barometer effect of ultra-radiation collisions. W. MESSERSCHMIDT (Physikal. Z., 1936, 37, 557).—The barometer effect is to be explained by the variation of  $\text{H}_2\text{O}$  content of the atm. An experiment is described to show the effect of  $\text{H}_2\text{O}$  on the no. of ultra-radiation collisions. A. J. M.

Heavy particle component of the cosmic radiation. R. B. BRODE, H. G. MACPHERSON, and M. A. STARR (Physical Rev., 1936, [ii], 50, 383).—A study of 8500 photographs of a Wilson cloud-chamber indicates that about 1% of the ionisation produced by cosmic rays at sea level is due directly to heavy particles; these may be  $\alpha$ -particles or protons, probably the latter. N. M. B.

Measurements of the angular distribution of cosmic-ray intensities in the stratosphere with Geiger-Müller counters. W. F. G. SWANN and G. L. LOCHER (Physical Rev., 1935, [ii], 47, 326). L. S. T.

Cosmic ray measurements under 30 m. of clay. D. H. FOLLETT and J. D. CRAWSHAW (Proc. Roy. Soc., 1936, A, 155, 546—558).—Proof is obtained that showers are produced under 30 m. of clay, and that the ratio (shower rate) : (vertical intensity) at that depth is of the same order as that at ground level; much of the radiation which penetrates 30 m. of clay must therefore consist of positive or negative electrons. L. L. B.

Soft primary corpuscular radiation as a shower producer. J. CLAY and A. VAN GEMERT (Physica, 1936, 3, 763—768; cf. A., 1936, 773).—The production of a shower in Pb layers from 0 to 14 cm. thick is found to coincide always with the passage of a particle through counters covering the top of the Pb sheet. Experiments in which Fe or Pb sheets are arranged in different positions above the shower counters indicate that the showers are chiefly produced in the lowest layers of the material. O. D. S.

Analysis of showers from cosmic rays by using their divergence. P. AUGER and (MME.) GRIVET-MEYER (Compt. rend., 1936, 203, 246—248).—By comparison of the nos. of collisions recorded by a Geiger counter at various distances from a single Pb screen, with and without a further Pb screen beyond the first, the effects of shower production and of absorption of shower-producing rays and of showers can be separated. J. W. S.

Shower groups in the cosmic radiation. J. C. STREET and R. T. YOUNG (Physical Rev., 1935, [ii], 47, 572—573).—The no. and rates of occurrence of the showers for different thicknesses of Pb above an ionisation chamber are recorded and discussed for three different localities. L. S. T.

Enhancement of cosmic-ray nuclear bursts by the presence of subsidiary material. C. G.

MONTGOMERY, D. D. MONTGOMERY, and W. F. G. SWANN (Physical Rev., 1935, [ii], 47, 512).

L. S. T.

Shower producing cosmic-ray primaries. J. H. SAWYER, jun. (Physical Rev., 1935, [ii], 47, 635).

L. S. T.

Connexion between cosmic-ray showers and bursts. W. EHRENBERG (Proc. Roy. Soc., 1936, A, 155, 532—545).—Experiments in which the recording of the ionisation current in a cosmic-ray ionisation chamber is controlled by triple coincidences of Geiger-Müller counters lead to the conclusion that bursts are showers measured by the ionisation they produce. Most of the showers produced in a Pb shield consist of far more particles than are necessary to operate a triple coincidence set.

L. L. B.

Problem of "swarms." G. BERNARDINI and D. BOCCIARELLI (Ric. sci. Prog. tec., 1935, 6, II, 83—90; Chem. Zentr., 1935, ii, 3633).— $>10\%$  of observed swarms are produced by the primary corpuscular radiation.

J. S. A.

Results of the Dutch cosmic-ray expedition 1933. VIII. Ionisation balance in the atmosphere. M. R. VAN DER LOEFF. IX. Ionisation balance for cosmic rays on the ocean. J. CLAY and M. R. VAN DER LOEFF (Physica, 1936, 3, 775—780, 781—796).—VIII. Theoretical. An expression for the ionisation balance is derived which takes account of the influence of large ions on measurements of ion no. and life.

IX. The ionisation balance on the open sea with clear sky is in accordance with the val. due to cosmic radiation alone, but experimental errors tend to make the measured val. too low.

O. D. S.

Flügge atomic nucleus model. K. UMEDA and Y. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 674—680).—The formation of at. nuclei from neutrons and protons is discussed.

R. S. B.

Radiationless transitions involving three-body collisions. R. A. SMITH (Proc. Camb. Phil. Soc., 1936, 32, 482—495).—Mathematical. The probability of the formation of negative ions by three-body collision between an atom and two electrons is calc. The process appears to be of little importance in discharges.

O. D. S.

Absorption coefficient of  $H^-$ . C. K. JEN (Chinese J. Physics 1936, 2, 38—42; cf. A., 1933, 547).—Mathematical. The absorption coeff. of negative H ions is calc. by wave mechanics to be of the order of magnitude of  $10^{-17} \text{ cm}^2$  from 17,000 to 1400 Å.

O. D. S.

Variational wave functions of doubly excited states of helium. T. Y. WU and S. T. MA (J. Chinese Chem. Soc., 1936, 4, 344—353).—The wave functions and energies of eight states of He are given.

J. G. A. G.

(A) Nuclear spin in isotopic mixtures. (B) Determination of the sign of nuclear magnetic moments by the method of atomic beams. I. I. RABI (Physical Rev., 1935, [ii], 47, 334, 338).—Nuclear spins and magnetic moments of the different

isotopes of a mixture can often be measured by means of at. beams.

L. S. T.

Nuclear magnetic moment of cobalt. K. R. MORE (Physical Rev., 1935, [ii], 47, 256; cf. A., 1934, 1279).—The nuclear  $g$ -factor is 0.77, giving 2.7 nuclear magnetons for the magnetic moment of Co.

L. S. T.

Nuclear spin and magnetic moment of  $^6\text{Li}$ . J. H. MANLEY and S. MILLMAN (Physical Rev., 1936, [ii], 50, 380; cf. this vol., 1039).—The spin of the  $^6\text{Li}$  nucleus and the hyperfine structure separation,  $\Delta\nu$ , of the  $^2S_{1/2}$  state were measured by the at. beam method of zero moments. The spin is  $2/2$ , and  $\Delta\nu$   $0.0077 \pm 0.0001 \text{ cm}^{-1}$ ; the calc. magnetic moment of  $^6\text{Li}$  is 0.85 nuclear magneton, the same val. as that reported for the deuteron.

N. M. B.

Magnetic moment of the  $^7\text{Li}$  nucleus. II. J. H. BARTLETT, jun., J. J. GIBBONS, jun., and R. E. WATSON (Physical Rev., 1936, [ii], 50, 315—319; cf. this vol., 653).—The calc. val., using a wave function due to James (cf. this vol., 774), is 3.33 nuclear magnetons.

N. M. B.

Tests of the validity of X-ray crystal methods of determining  $e$ . J. W. M. DU MOND and V. L. BOLLMAN (Physical Rev., 1936, [ii], 50, 383).—Investigations with calcite powder of grain size  $>2 \times 10^4 \text{ cm}$ . tend further to establish the validity of the X-ray crystal method.

N. M. B.

Attempt to calculate the number of energy levels of a heavy nucleus. H. A. BETHE (Physical Rev., 1936, [ii], 50, 332—341).—Mathematical.

N. M. B.

Relativity and nuclear forces. H. MARGENAU (Physical Rev., 1936, [ii], 50, 342—344).—Mathematical. An estimate of the relativity correction in nuclear problems is obtained.

N. M. B.

Forces between nuclear particles. W. V. HOUSTON (Physical Rev., 1935, [ii], 47, 260; cf. A., 1935, 1051).—Theoretical.

L. S. T.

Nuclear structure and the negative proton. E. C. WESTERFIELD and W. B. PIETENPOL (Physical Rev., 1935, [ii], 47, 325).—The negative proton (the anton) may be more fundamental to nuclear structure than hitherto supposed. The theory that nuclei are constructed of protons, antons, and a min. no. of neutrons is discussed in relation to structure of at. nuclei and known reactions of artificial and induced radioactivity.

L. S. T.

Nuclear reactions and their classification by atomic and isotopic numbers. W. D. HARKINS (Physical Rev., 1935, [ii], 47, 702—704).—Nuclear reactions are represented in a simple manner by means of diagrams connecting at. no. and isotopic no. Reactions given by a single type of projectile, neutron, proton, etc., are of relatively few simple types.

L. S. T.

Nuclear three- and four-particle eigenvalue problems. E. FEENBERG and S. S. SHARE (Physical Rev., 1936, [ii], 50, 253—257).—Mathematical. The determination of intranuclear forces from the mass defects of the H and He isotopes is investigated and approx. solutions are obtained.

N. M. B.



Connecting link between classical electromagnetic theory and wave mechanics *via* a derivation of the Schrödinger equations as a boundary value problem on the atom. L. T. DE VORE (Physical Rev., 1935, [ii], 47, 333). L. S. T.

Relativistic wave equations. P. A. M. DIRAC (Proc. Roy. Soc., 1936, A, 155, 447—459).—Wave equations for particles of spin  $>0.5$  quantum are formulated. L. L. B.

Townsend coefficients in nitrogen. D. Q. POSIN (Physical Rev., 1935, [ii], 47, 258).—Vals. are tabulated. L. S. T.

Forces acting on high-energy protons at collision. A. BRAMLEY (J. Franklin Inst., 1936, 222, 141—148).—Theoretical. The effect of a magnetic field on the interaction between relatively slow particles, such as protons, has been examined by the use of the Born-Infeld system of electrodynamics (A., 1935, 912). The interaction between protons at collision should have an upper limit dependent on the val. of  $b$ , the natural unit of electric intensity. Terms due to the effect of the magnetic field set up by the moving charges become of special importance when the relative velocity of the protons is  $>3\%$  of the velocity of light. Calculation of  $b$  for such protons gives a val. approx. the same as that for electrons, indicating that the mass of the proton is due to its spin rather than to its electrostatic field. A. J. M.

Theory of the photon and the relativistic wave-mechanics of the system. L. DE BROGLIE (Compt. rend., 1936, 203, 473—477).—Theoretical. D. C. J.

Neutrino theory of light. I. P. JORDAN (Z. Physik, 1936, 102, 243—252).—Mathematical. A. J. M.

Universal constants and atomic quantities. I. M. FREEMAN (Naturwiss., 1936, 24, 557).—Theoretical. A. J. M.

Theory of absorption spectra of insulating crystals. A. SMEKAL (Physikal. Z., 1936, 37, 554—556).—The ionisation of centres by the absorption of light is discussed. The theory of normal and abnormal centres and the displacement of the absorption spectrum on excitation is given, and compared with experiment. A. J. M.

Nature of "excited" colour centres. H. WOLFF (Physikal. Z., 1936, 37, 552—554).—The excitation of colour centres in synthetic rock-salt crystals to which a little  $\text{SrCl}_2$  has been added has been examined. The absorption spectrum of the unexcited colour centres was the same as that obtained for pure  $\text{NaCl}$ , exhibiting a max. at  $465 \text{ m}\mu$ . Irradiation within this band produced the excited centres, and there was not only the usual long-wave widening of the absorption spectrum, but also a reversible displacement of the max. towards the red. This displacement is dependent on the amount of  $\text{SrCl}_2$  added, but never exceeds  $10 \text{ m}\mu$ . The occurrence of excited centres is to be ascribed to the presence of small numbers of foreign atoms which produce a tension in the lattice. The effect was also noted when  $\text{NaNO}_3$  was added to  $\text{NaCl}$  in place of  $\text{SrCl}_2$ . Plastic deformation produces the same result. A. J. M.

Huggins' bands in the spectrum of the blue sky and the temperature of the atmospheric ozone. J. DUFAY (Compt. rend., 1936, 203, 383—386).—The absorption coeffs. of the Huggins bands of blue sky, photographed in the zenith when the sun is low, are intermediate between the absorption coeffs. of  $\text{O}_3$  at  $15^\circ$  and  $-80^\circ$ . R. S.

Transfer of rotational energy in molecular collisions. I. Elementary processes which lead to abnormal rotation of the  $\text{HgH}$  molecule. F. F. RIEKE (J. Chem. Physics, 1936, 4, 513—525; cf. A., 1930, 1083).—The effect of  $0.9\text{--}160 \text{ mm.}$  of  $\text{N}_2$  and  $0.7\text{--}17 \text{ mm.}$  of  $\text{H}_2\text{O}$  on the intensity distribution within the  $\text{HgH}$   $4017 \text{ \AA.}$  band has been determined by a photographic photometric method. The distribution of intensity is a function of  $[\text{N}_2]$  and  $[\text{H}_2\text{O}]$ , and the proportion of excited  $\text{HgH}$  with rotational energy  $>0.2$  volt is much  $>$  the thermal val. in all circumstances, in disaccord with published work. The nature of the collision process is discussed. The excess of rotation observed does not result from the reactions  $\text{Hg}^* + \text{H}_2 \rightarrow \text{HgH} + \text{H}$  and  $\text{Hg}^* + \text{H}_2\text{O} \rightarrow \text{HgH} + \text{OH}$ , but originates from two processes: (i) collisions of the second kind between unexcited  $\text{HgH}$  and metastable  $\text{Hg}$  atoms of which the excitation energy is taken up by the  $\text{HgH}$  partly as rotational and partly as electronic energy, and (ii) collisions of the second kind between normal  $\text{N}_2$  and highly excited  $\text{HgH}$  whereby part of the electronic and vibrational energy is converted into rotational energy of the  $\text{HgH}$ . There is only a small probability of rotational energy transfer in collisions between normal  $\text{N}_2$  or  $\text{H}_2\text{O}$  and  $\text{HgH}$  in the  $2\Pi_1$  ( $v=0$ ) state, but  $\text{H}_2\text{O}$  diminishes the average rotational energy by absorbing energy from  $\text{HgH}$  in highly excited states, thus transferring them to low rotational levels of the  $2\Pi_1$  ( $v=0$ ) state. J. G. A. G.

Band spectra of carbon deuteride. T. SHIDEI (Japan. J. Physics, 1936, 11, 23—34).—Using a low-pressure condensed discharge in presence of  $\text{D}_2\text{O}$  vapour and  $\text{CO}$ , the band spectra of  $\text{CD}$  have been photographed at high dispersion. Analyses are tabulated and data are discussed in relation to those for  $\text{CH}$ . N. M. B.

Symmetric C-D linking vibration in heavy acetylene. G. GLOCKLER and C. E. MORRELL (Physical Rev., 1935, [ii], 47, 569).—More prolonged exposure has given the other symmetrical valency frequency, at  $2700 \text{ \AA.}$  (cf. this vol., 407). L. S. T.

Absorption spectrum of  $\text{NH}$ . G. W. FUNKE (Z. Physik, 1936, 101, 104—112).—Analysis of the  $3360 \text{ \AA.}$  band gives the  $\text{NH}$  separation as  $1.035 \text{ \AA.}$  in the ground and activated levels. A. B. D. C.

Ultra-violet absorption spectrum of  $\text{ND}_3$ . A. B. F. DUNCAN (Physical Rev., 1935, [ii], 47, 886—887).—Spectra in the region  $2300$  to  $770 \text{ \AA.}$  have been obtained at various pressures of  $\text{ND}_3$ . The three  $0, 0$  bands of  $\text{ND}_3$  almost coincide with the corresponding bands of  $\text{NH}_3$ . The predissociation in progression 1 appears to start at approx. the same point in  $\text{ND}_3$  as in  $\text{NH}_3$ , but the rotational fine structure visible in  $\text{NH}_3$  is not apparent in  $\text{ND}_3$ . L. S. T.

**Band spectrum of MnH.** T. HEIMER (Naturwiss., 1936, 24, 521—522).—The strongest emission band, which is also the strongest absorption band, in the spectrum of MnH has its edge at 5680 Å., degraded towards the violet. Weaker bands at 6200 and 5205 Å. are 0—1 and 1—0 bands, respectively. There are further bands in the blue and violet. The MnH bands also occur in stellar spectra. A. J. M.

**Term scheme for gold deuteride.** T. HEIMER (Z. Physik, 1936, 101, 121—128).—The energy of dissociation for the  $^1\Sigma$  state is 3.7 volts.

A. B. D. C.

**Absorption spectra of solutions of iodine in carbon tetrachloride, titanium tetrachloride, and stannic chloride.** L. HOCK and W. KNAUFF (Z. anorg. Chem., 1936, 228, 209—212).—The spectra show max. absorption about  $\lambda$  520 m $\mu$ . No such max is observed in AsCl<sub>3</sub>.

E. S. H.

**Optical absorption of tellurium dichloride and oxychloride vapours.** M. KANTZER (Compt. rend., 1936, 203, 163—164).—TeCl<sub>2</sub> has 15 regularly spaced absorption bands between 3960 and 4358 Å. TeOCl<sub>2</sub> has 9 bands between 5015 and 5750 Å. The vapours are transparent outside these limits. J. G. A. G.

**Molecular spectra of metal halides.** K. BUTKOV (Acta Physicochim. U.R.S.S., 1935, 3, 205—217).—The ultra-violet absorption spectra and photodissociation of the following metal halide vapours are discussed: TlX, MX<sub>2</sub> (M=Hg, Cd, Zn, Pb, Sn), MX<sub>3</sub> (M=Bi, Pb), and M<sub>2</sub>X<sub>2</sub> (M=Au, Cu, Tl), where X=F, Cl, Br, I. For some of these substances new absorption data are recorded.

O. J. W.

**Energy levels of electrons in crystals.** P. TARTAKOVSKI (Acta Physicochim. U.R.S.S., 1935, 3, 340—344).—Electronic energy level diagrams for NaCl and KCl crystals, obtained from absorption spectra, are interpreted.

O. J. W.

**Behaviour of chlorine dioxide in carbon tetrachloride solution in dark and light. II. Behaviour in light.** R. LUTHER and R. HOFFMANN (Z. physikal. Chem., 1936, 177, 17—28; cf. A., 1931, 1377).—The absorption spectra in the violet and ultra-violet of ClO<sub>2</sub> and Cl<sub>2</sub>O in CCl<sub>4</sub> solution have been determined. ClO<sub>2</sub> has a regular band spectrum. After irradiation a CCl<sub>4</sub> solution of ClO<sub>2</sub> previously stabilised to darkness by washing with alkali decomposes in the dark according to  $-d[\text{ClO}_2]/dt = k[\text{ClO}_2]^{1/3}$ ; catalysis by Cl<sub>2</sub>O formed in the light is probably responsible, for Ba(OH)<sub>2</sub>·8H<sub>2</sub>O inhibits decomp. Photolysis of a ClO<sub>2</sub> solution in the light of a 'Uviol' lamp is a reaction of zero order; the Cl<sub>2</sub> formed has no effect.

R. C.

**Ultra-violet bands of beryllium oxide. II.** A. CICCONI (Ric. sci. Prog. tec., 1935, 6, II, 108—111; Chem. Zentr., 1935, ii, 3638).—Two singlet systems and a triplet system are identified.

J. S. A.

**Rotation analysis of the (1, 0)b<sup>3</sup> $\Sigma$ →a<sup>3</sup> $\Pi$  carbon monoxide band.** L. GERÖ (Z. Physik, 1936, 101, 311—322).

A. B. D. C.

**Rotation constants of the IV positive carbon monoxide bands.** R. SCHMID and L. GERÖ (Z. Physik, 1936, 101, 343—351).

A. B. D. C.

**Rotational analysis of the Ångström bands [of carbon monoxide] at  $\lambda$  6080 and 6620 Å.** R. K. ASUNDI (Proc. Indian Acad. Sci., 1936, 3, A, 554—561).—Full data are tabulated and discussed. There is probably predissociation (see following abstract).

N. M. B.

**Dissociation energy of carbon monoxide.** R. K. ASUNDI and R. SAMUEL (Proc. Indian Acad. Sci., 1936, 3, A, 562—565).—Experimental and theoretical objections to the low vals. (8.41 and 6.9 volts) generally reported for the dissociation energy of CO are discussed. The probable val. is 10.45 volts, or, if predissociation is proved, 9.57 volts. A val. of this order is supported by thermochemical data.

N. M. B.

**New band systems of selenous anhydride SeO<sub>2</sub>, selenium S<sub>2</sub>, and of tellurium Te<sub>2</sub> in the far ultra-violet.** C. S. PIATOW (Compt. rend., 1936, 203, 239—241; cf. A., 1935, 1443).—A third band system of SeO<sub>2</sub> has been found, which appears at 200° and comprises 10 bands between 2069 and 2195 Å., all degraded towards the red. The band system found previously has been extended from 2400 to 2200 Å. 20 bands of Se<sub>2</sub>, appearing at 230°, have been found between 1777 and 1939 Å., comprising two series with sharp and diffuse bands, respectively. At 430° the Te<sub>2</sub> spectrum shows a system of 30 bands at 1975—2107 Å.; at higher temp. a further system of 20 bands appears between this system and 2260 Å., whilst at about 640° a third system is found of 30 bands extending to 2495 Å. All the bands have sharp heads and are mainly degraded towards the violet.

J. W. S.

**Absorption spectrum of tervalent cerium salts.** T. Y. WU and A. T. KIANG (Chinese J. Physics, 1936, 2, 10—14).—The absorption spectra of aq. solutions of CeCl<sub>3</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> have been photographed between 2000 and 10,000 Å. A new broad absorption region was observed with centre about 2105 Å. No absorption was observed in the infra-red.

O. D. S.

**Spectrophotometric investigation of the hydrolysis of ferric salts.** J. CATHALA and J. CLUZEL (Compt. rend., 1936, 203, 401—403).—The absorption spectrum of solutions of Fe(NO<sub>3</sub>)<sub>3</sub> in buffers of known  $p_H$  was examined. The absorbing mols. appear to be complexes of Fe<sup>+++</sup> and Fe(OH)<sub>3</sub>.

A. J. M.

**Far ultra-violet absorption spectra and ionisation potentials of methyl bromide and chloride.** W. C. PRICE (Physical Rev., 1935, [ii], 47, 510).—The spectra in the region 1800—1000 Å. give ionisation potentials of 10.488 and 10.805 volts ( $\pm 0.002$  volt) for MeBr, and 11.17 and 11.25 volts ( $\pm 0.01$  volt) for MeCl.

L. S. T.

**Effect of temperature on absorption spectrum of ethyl iodide in the quartz ultra-violet.** A. HENRICI and G. MILAZZO (Z. physikal. Chem., 1936, B, 33, 201—228).—The effect of temp. and pressure on the spectrum down to 1950 Å. has been examined. It consists of two groups of bands. The first is characterised by a sequence of narrow singlet bands with an approx. separation of 17 cm.<sup>-1</sup> and by the marked effect of temp. on the probabilities of trans-



ition underlying the strongest bands; these are assigned to an upper state *B*, the probability of transition into which is the same as into the *B* state. The second group of bands leads from the ground state to the *B* term and forms groups of four, with the approx. intensity ratio 4:7:2:1. Compared with MeI (this vol., 8) the *B* term is shifted by 260 cm.<sup>-1</sup> towards shorter  $\lambda$ . R. C.

**Substitution and absorption band displacement. VIII. Dihalogenobenzenes.** H. CONRAD-BILLROTH and G. FORSTER (Z. physikal. Chem., 1936, B, 33, 311—318; cf. this vol., 1048).—The ultra-violet absorption spectra of dihalogenobenzenes in C<sub>6</sub>H<sub>11</sub> solution have been determined. Those containing only Cl and Br obey the rule previously formulated (A., 1933, 445), whilst with the I compounds there are discrepancies. The spectra of the I compounds have been resolved into the spectrum of the nucleus and that of the I, the former varying with the second substituent, and the latter not. R. C.

**Absorption spectrum of methyl ethyl ketone.** A. B. F. DUNCAN, V. R. ELLS, and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1936, 58, 1454—1456).—The absorption spectrum has been investigated at room temp. from the visible region down to 780 Å. The results are discussed and compared with data for COMe<sub>2</sub>. Four or five excited states explain the absorption regions. E. S. H.

**Photochemistry of nitrates, nitrites, and nitro-compounds. II.** C. H. PURKIS and H. W. THOMPSON (Trans. Faraday Soc., 1936, 32, 1466—1474; cf. this vol., 544).—Ultra-violet spectral data for Me, Et, isoamyl, and Bu<sup>n</sup> nitrites, dimethyl- and diethyl-nitrosoamine, *ON*-dimethylhydroxylamine, and chloronitrosopropane are recorded. MeNO<sub>2</sub> and EtNO<sub>2</sub> are decomposed by the radiation from a Hg lamp, yielding mainly N<sub>2</sub> and N<sub>2</sub>O as gaseous products; condensable products are also formed. E. S. H.

**Ultra-violet absorption spectrum of tyrosine.** K. FERAUD, M. S. DUNN, and J. KAPLAN (J. Biol. Chem., 1936, 114, 665).—The authors have been unable to repeat their observation (this vol., 135) of the bands in the ultra-violet absorption spectrum of tyrosine at 260, 254, 247, and 241 m $\mu$ . H. D.

**Absorption spectra of kephalin, lecithin, and selected antigens.** A. WADSWORTH and M. O'L. CROWE (J. Physical Chem., 1936, 40, 739—745).—Selective absorption in the regions 2850—2500 Å. and 2550—2200 Å. is common to kephalin, lecithin, and beef-heart antigens. The former range is near the absorption range of proteins. Complement-fixation and pptn. antigens differ in absorption, as do each when prepared in different ways. J. W. S.

**Absorption [spectra] of fluorescent substances in different solvents.** (MLLE.) G. BRAUN (J. Chim. phys., 1936, 33, 559—568).—The absorption by eosin, uranine, and rhodamine B in H<sub>2</sub>O, COMe<sub>2</sub>, EtOH, glycerol, C<sub>6</sub>H<sub>6</sub>, and binary mixtures has been investigated. The position and magnitude of the absorption max. vary with the solvent, and Beer's law is not always obeyed. Some of the dye solutions

contain an equilibrium mixture of coloured and colourless mols. J. G. A. G.

**Application of the diffraction grating to the photographic study of fluorescence spectra.** C. DHÉRE and O. BIERMACHER (Compt. rend. Soc. Biol., 1936, 112, 1144—1147).—The application to the spectrum of pyrroporphyrin and reference spectra for the infra-red and ultra-violet are described.

H. G. R.  
**Optical absorption of porphyrins. VI.** A. STERN, H. WENDERLEIN, and H. MOLVIG (Z. physikal. Chem., 1936, 177, 40—81; cf. this vol., 662).—The absorption spectrum of dissolved porphin has six bands in the visible and both it and the fluorescence spectrum vary little with the solvent. The absorption spectra of porphin, doubly-substituted porphyrins, and porphyrin fully substituted in nuclei I and II of the porphin system and not substituted in nuclei III and IV are of the phyllo-type, whilst porphyrins substituted only in nuclei I and III have spectra of the atio-type. Apparently in partly substituted porphyrins nuclei I and III have the same structure. The absorption curves of Cu salts of di-, tetra-, and octa-substituted porphyrins all have two bands, which are displaced towards the red by substitution. The curves are of two types, depending on the no. of substituents. In all these salts the state of combination of the Cu is the same. The absorption curves of  $\beta$  $\delta$ -di-iminoatiorporphyrin II and of a monoinimoatiorporphyrin resemble those of the corresponding porphyrins; apparently these have the porphyrin structure with *tert.* N in place of one and two methine bridges, respectively, in the porphin system. Introduction of Cu into the mol. of the Me<sub>4</sub> ester of  $\beta$  $\delta$ -di-iminocoproporphyrin II does not change the no. of absorption bands, and the effects on the absorption spectrum as a whole are similar to those of the introduction of Mg into the dihydroporphin system. 4:4'-Dimethyl-3:3'-diethylpyromethene-5:5'-diethylurethane has, in addition to a band in the blue, a band in the red, due to a labile H permitting the formation of a tautomeric form having a C:N group in special conjugation to the pyromethene system. R. C.

**Fluorescence of the chlorophyll series. Fluorescence and photodecomposition in solutions of phaeophorbide-*b* and methylphaeophorbide-*b*.** H. V. KNORR and V. M. ALBERS (Physical Rev., 1935, [ii], 47, 329; cf. this vol., 1129).—The fluorescence spectrum of phaeophorbide-*b* in anhyd. COMe<sub>2</sub> consists of an intense band, max. at 650 m $\mu$ , and a weaker band, max. at 678 m $\mu$ . As photodecomp. proceeds, the relative intensities of the individual bands vary considerably and an additional band, max. 654 m $\mu$ , appears. In the fluorescence of methylphaeophorbide-*b* in anhyd. COMe<sub>2</sub> three bands of approx. equal intensity have max. at 686, 651, and 640 m $\mu$ , respectively. After irradiation the intensity of the 686 and 640 m $\mu$  bands decreases almost to zero, and an additional band, max. 654 m $\mu$ , appears. This band is also present in the fluorescence spectrum of chlorophyll-*b*. L. S. T.

**Fluorescence of the chlorophyll series.**—See this vol., 1129.

**Low-frequency double vibrations of the deuterioammonias.** E. F. BARKER and M. MIGEOTTE (Physical Rev., 1935, [ii], 47, 702).—Pairs of absorption max. representing the zero branches of  $\nu_3$  for  $\text{NH}_3$ ,  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$ , and  $\text{ND}_3$  are recorded.

L. S. T.

**Absorption spectrum of aqueous solutions between 0.70 and 0.90  $\mu$ .** E. GANZ (Z. physikal. Chem., 1936, B, 33, 163—178).—Investigation of the effect of temp. and concn.,  $c$ , of solutes on the absorption bands of  $\text{H}_2\text{O}$  at 0.77 and 0.845  $\mu$  has confirmed the results previously published (this vol., 775). The  $\text{H}_2\text{O}$  absorbs like pure  $\text{H}_2\text{O}$  at a higher temp.,  $T$ ;  $T$  is the higher the larger is the anion of the dissolved salt. At the first max. the absorption approx.  $\propto$  the salt concn., and the position of the max. shifts towards the blue with increasing  $c$ , except at higher  $c$ , where its position does not alter. With increasing concn. of  $\text{HCl}$  the 0.77  $\mu$  band gradually disappears, whilst  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  sharpen it. In conc. aq.  $\text{NaOH}$  a sharp OH band is superimposed on the  $\text{H}_2\text{O}$  band at 0.74  $\mu$ . Aq.  $\text{NH}_3$  has a sharp max. at 0.80  $\mu$ .

R. C.

**Absorption spectrum of methyl alcohol vapour in the photographic infra-red.** R. M. BADGER and S. H. BAUER (J. Chem. Physics, 1936, 4, 469—473).—Regions of absorption were found at  $\lambda$  9500 and 7300 Å., corresponding with two harmonics of the O-H vibration, and at  $\lambda$  12,000 which is a harmonic of the C-H vibration. Under high dispersion, the bands at  $\lambda$  9500 and 7300 have a complex rotation structure. The interpretation of the spectrum is discussed, and further development of the theory of the torsion oscillator rotator is deemed necessary. J. G. A. G.

**Pressure effect in the HCN bands in the near infra-red.** S. D. CORNELL and W. W. WATSON (Physical Rev., 1936, [ii], 50, 279—281).—All the lines of the HCN absorption band at 1.04  $\mu$  are broadened equally by increase in gas pressure, contrary to the observations of Herzberg (cf. A., 1935, 281). The half-widths increase linearly with pressure at the rate of 0.56  $\text{cm}^{-1}$  per atm. Results indicate that broadening is due mainly to dispersion forces.

**Absorption spectra in the near infra-red of aniline derivatives.** (MME.) M. FREYMAN, R. FREYMAN, and P. RUMPF (Compt. rend., 1936, 203, 309—311).—The absorption spectra of  $\text{NH}_2\text{Ph}$  derivatives alone and/or in  $\text{CCl}_4$  have been measured. In each case the interval between the two characteristic bands due to the NH group is approx. 300  $\text{cm}^{-1}$ . In  $\text{CCl}_4$  all the bands are displaced towards higher frequencies. The influence of substituents is generally more marked in the *o*- than in the *m*- and *p*-positions.

C. R. H.

**Recording grating spectrometer. Application to absorption spectra of benzene derivatives in the region of 3000  $\text{cm}^{-1}$ .** P. LAMBERT and J. LECOMTE (Compt. rend., 1936, 203, 164—167).—Photographic records of the absorption spectra between 2500 and 3700  $\text{cm}^{-1}$  were obtained directly by means of an echelette spectrometer of high resolving power. The 3093, 3074, and 3037  $\text{cm}^{-1}$  bands in  $\text{C}_6\text{H}_6$  are slightly modified in  $\text{PhMe}$ ,  $\text{PhEt}$ ,

and  $\text{PhPr}$ , and displaced towards lower  $\nu$  in  $\text{PhBu}^{\text{B}}$  and isoamylbenzene. The intensity of the middle band at 3050  $\text{cm}^{-1}$  is its neighbours in  $\text{PhCl}$ ,  $\text{PhBr}$ , and  $\text{PhI}$ . The three  $\text{C}_6\text{H}_6$  bands do not coexist in the xylenes, and almost vanish in mesitylene and  $\psi$ -cumene.

J. G. A. G.

**Infra-red absorption of carbon disulphide at 4.57  $\mu$ .** J. A. SANDERSON (Physical Rev., 1936, [ii], 50, 209—211).—The transmission curve for the band was found by investigation with a Pfund stigmatic spectrometer. Rotational structure has been partly resolved, and consts. and data for *P* and *R* branches are given. An expression for the positions of the rotational lines is found. The location of the band centre at 2184.5  $\text{cm}^{-1}$  does not agree with that found by Bailey and Cassie (cf. A., 1931, 996).

N. M. B.

**Atomic polarisation and absorption of liquids in the extreme infra-red.** C. H. CARTWRIGHT and J. ERRERA (Acta Physicochim. U.R.S.S., 1935, 3, 649—684).—The abs. intensity of absorption in the infra-red (52—152  $\mu$ ) for polar liquids is generally for non-polar liquids,  $\text{H}_2\text{O}$  and  $\text{COMe}_2$  absorbing to the greatest degree. The data are discussed in relation to intermol. oscillation-vibrations and oscillation-rotations. From  $n$  data in the visible and extreme infra-red, at. polarisations were calc. and compared with existing data. The val. for  $\alpha$ -picoline affords no support for the existence of two tautomeric forms, as suggested by Rau *et al.* (cf. A., 1934, 943).

C. R. H.

**Raman spectrum and constitution of water.** M. MAGAT (Ann. Physique, 1936, [xi], 6, 108—193).—Data for the effect of temp. and the presence of electrolytes on the Raman spectra of  $\text{H}_2\text{O}$  are given, and, in conjunction with an analysis of the infra-red spectrum, frequencies are identified with the fundamental frequencies of the mol. A model for liquid  $\text{H}_2\text{O}$ , in conformity with mol. structure, is evolved, and from this are calc. heat of evaporation and energy of free rotation.

N. M. B.

**Raman spectra of some boron compounds.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 4, A, 74—81).—Full data are tabulated for  $\text{Me}$  and  $\text{Et}$  borate and for  $\text{BBr}_3$ . Results for the first-named differ widely from those of Joglekar (cf. this vol., 547). A pyramidal structure is postulated for the  $\text{B(OMe)}_3$  mol. Observed and calc. frequencies are in fair agreement.  $\text{BBr}_3$  shows two very intense lines and three very weak ones.  $\text{H}_3\text{BO}_3$  shows only one line, 875  $\text{cm}^{-1}$ , attributed to the totally symmetrical vibration of the mol.

N. M. B.

**Raman spectra of selenious acid and its sodium salts.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1936, 3, A, 533—543; cf. this vol., 136).—Data are tabulated for  $\text{H}_2\text{SeO}_3$  cryst., aq., and in  $\text{MeOH}$  at various concns., and for aq.  $\text{NaHSeO}_3$  and  $\text{Na}_2\text{SeO}_3$ . The solid gives 13 sharp and intense lines; on melting and in solution these lines broaden and undergo variations in frequency shift and intensity. The marked changes in the lines 706 and 597  $\text{cm}^{-1}$  are explained by postulating two types of mol.:  $\text{O:Se(OH)}_2$  and  $\text{O}_2\text{SeH}\cdot\text{OH}$  in dynamic equilibrium in the acid; the latter is predominant in the solid and in  $\text{MeOH}$



solution, and in aq. solution almost the whole of the acid is converted into the former type. The spectra at different concns. indicate that dissociation is weak, and that the proportion of mols. dissociated to  $\text{HSeO}_3'$  is almost const. throughout. The line  $895\text{ cm}^{-1}$  is assigned to  $\text{HSeO}_3'$  ions. Results are compared with those for  $\text{H}_2\text{SO}_3$ . Other lines are attributed to vibrations of definite mol. species by comparing them with those of the Na salts. N. M. B.

**Raman spectra of propylene and isobutane.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 527—532).—Data and analyses are tabulated and discussed in relation to polarisation. For  $\text{C}_3\text{H}_6$  the fundamental frequencies of the C chain are  $1648$  and  $920$  (valency type), and  $432\text{ cm}^{-1}$  (deformation frequency). The 14 additional lines are attributed to oscillations of the H atoms and are sharp. The isobutane lines are, in general, very broad and highly depolarised; the difference is probably due to the symmetry of the mol. which causes many of the vibrations to be degenerate. An interpretation with the help of polarisation data is given. There is a close similarity to the Raman spectrum of  $\text{CHCl}_3$ . N. M. B.

**Raman spectra of cyclopropane and ethylene oxide.** R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 4, A, 82—90; cf. Harris, this vol., 777).—Full data are tabulated, and the state of polarisation of the vibrational Raman lines is discussed. *cyclopropane* (I) shows 10 frequencies, and the four intense lines of the liquid have also been recorded in the vapour spectrum, with modified intensity. The Raman spectrum of  $(\text{CH}_2)_2\text{O}$  shows 10 frequencies, and closely resembles that of (I). N. M. B.

**Raman effect and dipole moment in relation to free rotation. V. Intramolecular potential of ethane derivatives.** S. MIZUSHIMA and Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 188—206; cf. this vol., 924).—Additional data for  $\text{C}_2\text{H}_5\text{ClBr}$  and  $\text{C}_2\text{Cl}_6$  are given and intramol. potential is discussed in detail. Results show no evidence of "free rotation" around C—C, but, in some cases, a "frozen rotation" without oscillatory mol. rotation of finite amplitude. The mutual energy effect between rotating groups is of the order  $kT$ ; hence a change in intramol. rotational state can be effected by a change in the state of aggregation. Normal vibrations of  $\text{C}_2\text{H}_5\text{ClBr}$  are calc. N. M. B.

**Raman effect. LVII. Five-membered rings. I. Raman spectra.** A. W. REITZ (Z. physikal. Chem., 1936, B, 33, 179—195).—The Raman spectra of *cyclopentane*, *cyclopentene*, *cyclopentadiene*, *thiophen*, *furan*, and *pyrrole* have been determined. The selection rules and types of vibration corresponding with the symmetry properties of a plane five-membered ring and the frequencies corresponding with the potential law for a valency-force system in such a ring have been worked out. R. C.

**Polarisation of Raman lines of formic acid, and formate and trichloroacetate ions.** J. GUPTA (Indian J. Physics, 1936, 10, 313—318).—The degree of depolarisation,  $\rho$ , of the stronger Raman lines of aq. solutions of  $\text{HCO}_2\text{H}$  (I),  $\text{HCO}_2\text{Na}$  (II), and

$\text{CCl}_3\cdot\text{CO}_2\text{Na}$  (III) has been determined. The  $1352$  line of (II) is much more polarised than the  $1398$  line of (I). These lines cannot therefore have their origin in the deformation oscillation of C—H in the  $\text{HCO}$  group.  $\rho$  for the  $1352$  line of (II) is approx. the same as that for the  $1330$  line of (III), indicating that they arise from the same mol. vibration. The  $1352$  line of (II), which is sharp and intense, is caused by the symmetrical oscillation of the ion  $(\text{C}\cdot\text{O})'$ , and this is confirmed by the fact that the  $1330$  line of (III) is strongly polarised, and the  $1650$  line of (III) is depolarised. A reversal of this behaviour is found in (I). The val. of  $\rho$  for the  $2735$  line of (II) is considerably  $>$  that of the  $2834$  line of (II), and hence these lines are due to two different modes of vibration of C—H. A. J. M.

**Raman spectra of deuterioacetones and methyl alcohol-d.** J. R. BATES, L. C. ANDERSON, and J. O. HALFORD (J. Chem. Physics, 1936, 4, 535).—Raman frequencies are tabulated for equilibrium solutions of the several deuterioacetones containing 0—91% of D. With increasing % of D, certain lines fade, whilst new lines appear. The  $1706\text{ cm}^{-1}$  line, ascribed to C=O, is unchanged, and there are six frequencies at  $2000$ — $2250\text{ cm}^{-1}$  with 91% of D, whereas  $\text{COMe}_2$  has only three at  $2900$ — $3000\text{ cm}^{-1}$ . The OD band in MeOD is at  $2500\text{ cm}^{-1}$  (cf. the OH band at  $3400\text{ cm}^{-1}$  in MeOH). J. G. A. G.

**Raman spectrum of deuterioacetaldehyde.** R. W. WOOD (J. Chem. Physics, 1936, 4, 536).—The wave no. differences of nine lines excited by the Hg line  $\lambda 4358$  are tabulated. J. G. A. G.

**Continuous spectrum observed in Raman scattering.** S. V. C. AIYA (Physical Rev., 1936, [ii], 50, 260—261).—An explanation is proposed. N. M. B.

**Doppler effect in light scattering in liquids. III. Polarisation of light transversely scattered by formic and acetic acids.** B. V. R. RAO (Proc. Indian Acad. Sci., 1936, 3, A, 607—609; cf. A., 1935, 1445).—The central undisplaced component of the triplet in the transversely scattered light shows appreciable depolarisation, differing from the case of non-associated liquids such as  $\text{CCl}_4$ , PhMe, and  $\text{CS}_2$  in which the central component is unobservable in the horizontal vibration of the transversely scattered light. Results indicate the presence of large non-rotating or immobile mol. clusters which depolarise the scattered light. N. M. B.

**Structure of the Rayleigh radiation of liquids.** K. BIRUS (Physikal. Z., 1936, 37, 548—549).—Polarisation determinations with Hg  $\lambda 4078\text{ Å}$  show that the scattered light consists of two parts, (1) a symmetrical triplet polarised in the direction of incidence, and (2) depolarised anisotropic radiation, degree of depolarisation  $6/7$ . A. J. M.

**Dispersion of depolarisation of Rayleigh scattering. I. Fatty acids.** R. S. KRISHNAN (Proc. Indian Acad. Sci., 1936, 3, A, 566—571).—Results of measurements are tabulated for  $\text{C}_6\text{H}_5$ ,  $\text{HCO}_2\text{H}$ ,  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ , and  $\text{Pr}^n\text{CO}_2\text{H}$ . The depolarisation factor for  $\text{C}_6\text{H}_5$  is const. over a wide range of  $\lambda$ ; for  $\text{HCO}_2\text{H}$  and  $\text{EtCO}_2\text{H}$  it increases, and for  $\text{AcOH}$

it decreases, towards the ultra-violet. The observed dispersion of depolarisation is probably due to the formation of large mol. groups in the fatty acids.

N. M. B.

**Distribution of luminescence carriers in gypsum crystals.** E. IWASE (Bull. Chem. Soc. Japan, 1936, 11, 475—479).—The fluorescence of gypsum crystals in ultra-violet light was of an "hour-glass" pattern. The impurities which cause the luminescence are supposed to be deposited during the growth of the crystal only at certain crystal faces.

C. R. H.

**Polarised fluorescence of organic dye solutions.** L. GRISEBACH (Z. Physik, 1936, 101, 13—22).—Degree of polarisation of fluorescent radiation excited by linearly polarised  $\lambda\lambda$  between 2330 and 5780 Å. was determined for fluorescein, eosin, rhodamine B, and aesculin in glycerol. Elliptically polarised  $\lambda\lambda$  did not give elliptically polarised fluorescence.

**Luminescence of frozen solutions of certain dyes.** F. G. WICK and C. G. THROOP (Physical Rev., 1935, [ii], 47, 329).—The effect on luminescent solutions of certain dyes of freezing and cooling to liquid air temp. has been determined. Marked changes in intensity and colour of the fluorescence occur and in some cases the frozen solutions are strongly phosphorescent.

L. S. T.

**Sharpness of coincidence with counter tubes.** W. CHRISTOPH (Physikal. Z., 1936, 37, 558—559).—An experiment for determining the "resolving power" of counter tubes is described.

A. J. M.

**Measurement of the number of colour centres in KCl crystals.** F. C. KLEINSCHROD (Ann. Physik, 1936, [v], 27, 97—107; cf. Pohl, A., 1935, 915).—The no. of colour centres is measured by chemical determination of the free metal atoms. This no. is greater by 24% than that calc. from the max. absorption coeff. and the half width of the  $F$  absorption band. Similar measurement for the  $U$  centres is in agreement with optical vals.

O. D. S.

**Photochemistry of crystals.** M. SAVOSTJANOVA (Acta Physicochim. U.R.S.S., 1935, 3, 345—354).—The photochemical behaviour of alkali and Ag halide crystals is discussed.

O. J. W.

**External photo-effect in alkali halides coloured by cathode rays.** E. ASMUS (Ann. Physik, 1936, [v], 26, 723—739).—Powdered NaCl, KCl, LiCl, and LiBr were coloured by irradiation with cathode rays and the external photo-effect was investigated with visible light. The photo-current ( $i$ ) at first increased with time ( $t$ ), but reached a max. and then slowly decreased. The time taken to reach the max. and the max.  $i$  itself varied with the intensity of the light. The  $i$ - $t$  curve was also studied for lights of different colours. The results can be explained by supposing that it is not the colour centres themselves which are responsible for the external photo-effect, but excited colour centres, which are produced by light absorbed in the  $F$  band.  $i \propto$  no. of excited colour centres.

A. J. M.

**New investigations with semi-conductors.** A. SCHULZE (Chem.-Ztg., 1936, 60, 545—547).—Recent

work on the semi-conducting properties of Si, C, Ti, Zr, Hf, Th, B, As, and Te is described.

A. J. M.

**Chemical condition of the photo-electrically active hydrogen absorbed in platinum and tantalum.** K. REGER (Z. Physik, 1936, 102, 156—162; cf. A., 1933, 441).—The photo-electric effect with Pt and Ta foils which had been treated with  $H_2$  was examined for samples of  $H_2$  of different purity and dryness. Electrolytic  $H_2$ , not specially purified, is photo-electrically active when absorbed by the foils, but this is not the case if the gas is freed from  $H_2O$ , at. H, and other impurities. Pure mol.  $H_2$  is not photo-electrically active. Traces of  $O_2$  appear to act catalytically in promoting the activity of  $H_2$ .

A. J. M.

**Migration of caesium on tungstic oxide.** L. FRANK (Trans. Faraday Soc., 1936, 32, 1403—1414).—The photo-electric effect of thin films of Cs on  $WO_3$  decreases with time. A study of the adsorption of such films at 125—400° abs. by a photo-electric method indicates that the decay of activity is due to migration of Cs atoms into the mass of  $WO_3$ . The activation energy connected with the migration has been calc.

E. S. H.

**Direction of rectifier action for excess- and defect-semi-conductors.** W. HARTMANN and W. SCHOTTKY (Naturwiss., 1936, 24, 558).—Sintered ZnO, an excess-semi-conductor, was deposited on Ag covered with a bakelite film. The arrangement acts as a rectifier, the direction of rectification being opposite to that when  $Cu_2O$ , a defect-semi-conductor, is used. This is in agreement with Schottky's theory (Z. tech. Physik, 1935, 16, 512).

A. J. M.

**Electrical breakdown in the cloud chamber.** H. RAETNER (Physikal. Z., 1936, 37, 560—562).—The first ionisation process preceding the passage of the spark takes place in "canals." The maintenance of the discharge at high pressures is due to photo-electrons.

A. J. M.

**Voltaic photo-effect in silver halides.** E. KIRILLOV, M. KITAIGORODSKI, and A. MOLCHANOV (Acta Physicochim. U.R.S.S., 1935, 3, 361—367).—Photovoltaic effects at a monocryst. AgCl surface and at a junction between polycryst. AgI and Ag or Au are described.

O. J. W.

**Electrification by friction.** F. MICHAUD (J. Chim. phys., 1936, 33, 546—558).—Theoretical. Electrification caused by friction and by blows arises from the thermo-electric effects of the temp. gradients produced. The theory explains some anomalies, and its consequences are discussed.

J. G. A. G.

**Ionic conductivity in solid salts.** W. SEITH (Z. Elektrochem., 1936, 42, 635—654).—A review.

**Mean values for the dipole moments of the harmonic and anharmonic oscillator in quantum mechanics.** R. P. BELL and E. A. GUGGENHEIM (Trans. Faraday Soc., 1936, 32, 1013—1017).—Theoretical.

O. J. W.

**Modern concept of the structure of anisotropic liquids and its foundation.** V. FREEDERICKSZ (Acta Physicochim. U.R.S.S., 1935, 3, 741—748).—Light scattering, variations in dielectric const. under the action of a magnetic field, orientation of electrical



dipole moments, and properties of thin films of anisotropic liquids are discussed. C. R. H.

**Dipole effect of viscous liquids at high frequencies.** C. SCHRECK (Physikal. Z., 1936, 37, 549—552; cf. Wien, this vol., 549).—The deviations from the Debye theory exhibited by conc. solutions of fructose at long  $\lambda$  may be supposed to be due to the existence in the solution of dipoles of different relaxation times. Calculations of dipole loss based on the assumption of 2 or 3 relaxation times give results in agreement with experiment over a considerable  $\lambda$  range. The effect of viscosity on dipole loss was investigated for glycerol solutions. The loss for given  $\lambda$  is a max. at a temp. in the neighbourhood of the f.p. The rate of increase of the loss with  $\lambda$  is different at different temp. A. J. M.

**Polarisation and dielectric constant of liquids.** J. WYMAN, jun. (J. Amer. Chem. Soc., 1936, 58, 1482—1486).—The empirical relation between polarisation and dielectric const.,  $p=(\epsilon+1)/8.5$ , is deduced from published data. E. S. H.

**Electric moments of molecules in liquids.** L. ONSAGER (J. Amer. Chem. Soc., 1936, 58, 1486—1493).—Theoretical. By analysis of the internal field, and dielectric const. of pure polar liquids, and of solutions, formulæ similar to Wyman's are obtained (cf. preceding abstract). E. S. H.

**Measurement of the dielectric constant of air at radio-frequencies.** L. G. HECTOR and H. L. SCHULTZ (Physical Rev., 1935, [ii], 47, 327).—The  $\epsilon$  of air at 900,000 cycles per sec. by the heterodyne-beat frequency method agrees closely with vals. obtained at low frequencies and with d.c. measurements. L. S. T.

**Refractivity and dielectric constant of carbon dioxide at high pressures.** P. O. JOHN (Phil. Mag., 1936, [vii], 22, 274—281).—Discussion of deviations from the Lorentz formula over a wide range of densities shows that, in conformity with the Raman-Krishnan theory of the anisotropic polarisation field in dense media, the anisotropy of the polarisation field increases progressively with increase in density, and, for any given density, the degree of anisotropy required to explain the deviations is the same for different  $\lambda\lambda$  of the incident light. N. M. B.

**Dielectric constants of gases and vapours.** V. M. KUBO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 179—187; cf. this vol., 924).—The dielectric const. of the vapour of  $\text{CH}_2(\text{OMe})_2$ , the mol. of which has two axes of free rotation, was measured for various temp., and used to calculate the dipole moment, which increases with rising temp. Theoretical investigation indicates that even at 200° the rotations are not perfectly free; the mol. executes rotational oscillations around the two axes of free rotation. The most stable configuration is that in which two Me are at opposite sides of the plane containing the central C and the two O. N. M. B.

**Dielectric coefficients of gases and vapours.** K. L. RAMASWAMY (Proc. Indian Acad. Sci., 1936, 4, A, 108—133).—Full data for the dielectric coeffs. measured at two or three temp. and the calc. electrical

moments are tabulated for MeF, MeCl, MeBr, MeI, EtCl,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , MeOH,  $\text{COMe}_2$ , MeCN,  $\text{Me}_2\text{O}$ ,  $\text{NH}_2\text{Me}$ , cyclopropane (I),  $(\text{CH}_2)_2\text{O}$ , and  $\text{C}_6\text{H}_6$ . (I),  $\text{C}_6\text{H}_6$ , and  $\text{CCl}_4$  are non-polar; the others have appreciable electric moments. Compressibilities at room temp. are determined from the variation of  $n$  with pressure. Results are compared with available data. N. M. B.

**Dipole moments of the alkali halides.** W. H. RODEBUSH (J. Chem. Physics, 1936, 4, 536).—The vals. published (this vol., 924) may be 10% too high. J. G. A. G.

**Dispersion determinations with decimetre waves.** M. VON ARDENNE, O. GROOS, and G. OTTERBEIN (Physikal. Z., 1936, 37, 533—544).—The first method of Drude, involving the determination of  $n$  for undamped waves of  $\lambda$  about 1 dm., was used to investigate the dispersion of  $\text{H}_2\text{O}$ , sucrose solutions, MeOH, EtOH, and glycerol. The dispersion bands often observed for  $\text{H}_2\text{O}$  were not found. The dispersion of sucrose solutions showed that  $n^2$  was the smaller the smaller was the concn. of  $\text{H}_2\text{O}$  in the solution. There was a variation of  $n^2$  with viscosity of the solution, which indicated that any anomalous dispersion in the case of  $\text{H}_2\text{O}$  must occur at  $\lambda$  about 1 cm. For MeOH anomalous dispersion just begins in the  $\lambda$  range 10—60 cm. The results for EtOH agree with the Debye theory, and give a mol. radius of 2.2 Å. The absorption max. of  $\text{PhNO}_2$  at  $\lambda$  6 m. found by Beck (A., 1933, 1103) and those of  $\text{Bu}^n\text{OH}$ ,  $\text{Bu}^s\text{OH}$ , and  $n\text{-C}_5\text{H}_{11}\text{OH}$  found by Krause (A., 1934, 1057) are not due to anomalous dispersion. The high frequency loss of  $\text{Bu}^n\text{OH}$ ,  $\text{Bu}^s\text{OH}$ , and  $n\text{-C}_5\text{H}_{11}\text{OH}$  increases with decreasing  $\lambda$ . A. J. M.

**Absorption in dipolar liquids in the region of 3—7 m. wave-length.** E. KEUTNER (Ann. Physik, 1936, [v], 27, 29—48).—The absorptions of Et, Pr, Bu, amyl, and hexyl alcohols, glycerol containing varying % of  $\text{H}_2\text{O}$ ,  $\text{PhNO}_2$ ,  $\text{PhCl}$ ,  $\text{COMe}_2$ , and  $\text{C}_6\text{H}_6$  are given between 15° and 35°. The results for the alcohols are in agreement with the Debye theory and vals. of the mol. radius, time of relaxation, and the const. determining the dispersion are calc. The vals. for glycerol and  $\text{PhNO}_2$  are not in agreement with the simple Debye theory. O. D. S.

**Anomalous behaviour of the dielectric constants of the higher organic acids near the f.p.** B. PIEKARA (Physikal. Z., 1936, 37, 624—627).—The freezing of stearic, palmitic, and oleic acids is accompanied by a sudden increase in the dielectric const. ( $\epsilon$ ), after which there is the normal decrease. The increase at the f.p. is not markedly altered by variation of the  $\lambda$  at which  $\epsilon$  is determined within the limits 200—3000 m. No anomaly in  $\epsilon$  was found in the case of  $\text{AcOH}$ ,  $\text{CH}_3\text{Cl}\cdot\text{CO}_2\text{H}$ , or octoic acid. A solution of palmitic acid in  $\text{C}_6\text{H}_{14}$  showed the anomaly, but it was spread over a wider temp. range, thus giving the temp.- $\epsilon$  curve a "hysteresis" loop. A. J. M.

**Polarity of chemical compounds. IX.** K. HIGASI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 766—786; cf. A., 1935, 568).—The dipole moments of  $\text{Pr}^s\text{OH}$  and  $\text{Bu}^s\text{OH}$  have been determined at 20° in  $\text{C}_6\text{H}_6$  ( $1.70_\epsilon$  and  $1.70_2 \times 10^{-18}$ , respectively) and in

$\text{CS}_2$  ( $1.48$  and  $1.41 \times 10^{-18}$ , respectively). The moments in  $\text{C}_6\text{H}_6$  are greater by  $0.13$  and  $0.07 \times 10^{-18}$ , respectively, than the vals. in the vapour, in agreement with the author's theory. The moments in  $\text{CS}_2$  and the results of Earp and Glasstone (this vol., 150) are explained.

R. S. B.

**Dielectric polarisation. XVII.** Dipole moments of some aromatic acid halides. **XVIII.** Dipole moments of the chlorides of some dicarboxylic acids. **XIX.** Dipole moments of some aromatic sulphonyl chlorides. G. T. O. MARTIN and J. R. PARTINGTON. **XX.** Dependence of polarisation and apparent moment of nitriles on solvent and temperature. E. G. COWLEY and J. R. PARTINGTON (J.C.S., 1936, 1175—1178, 1178—1182, 1182—1184, 1184—1194; cf. this vol., 408).—**XVII.** The following dipole moments ( $\mu$ ) in  $D$  at  $20^\circ$  and in  $\text{C}_6\text{H}_6$  solution are recorded:  $\text{BzCl}$ ,  $3.33$ ,  $\text{CH}_2\text{Ph}\cdot\text{COCl}$  (I),  $2.54$ ,  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COCl}$ ,  $2.00$ ,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COCl}$ ,  $2.03$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ ,  $1.11$ ,  $3:5\text{-(NO}_2)_2\text{C}_6\text{H}_3\cdot\text{COCl}$ ,  $1.20$ ,  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ ,  $3.81$ ,  $\text{BzBr}$ ,  $3.37$ . The fact that for  $\text{BzCl}$  is  $>$ , and for (I) is  $<$ , for  $\text{AcCl}$  or  $\text{EtCOCl}$  is in accord with the vals. for other  $\text{Bz}$  compounds. The results support the conclusions reached previously regarding the direction of the  $\text{COCl}$  group moment (this vol., 408).

**XVIII.**  $\text{C}_2\text{O}_2\text{Cl}_2$ ,  $\text{CH}_2(\text{COCl})_2$  (II),  $(\text{CH}_2\cdot\text{COCl})_2$  (III), and  $s$ -phthalyl chloride (IV) in  $\text{C}_6\text{H}_6$  at  $20^\circ$  give  $\mu$   $0.92$ ,  $2.80$ ,  $3.00$ , and  $5.12$ , respectively. These results are discussed in relation to the spatial configuration of the  $\text{COCl}$  groups, and the possibility of isomeric ring forms of (II) and (III) is discussed.  $\mu$  for the liquid form of (IV) confirms its symmetrical structure.

**XIX.**  $\text{PhSO}_2\text{Cl}$ ,  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ , and  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}$  in  $\text{C}_6\text{H}_6$  at  $20^\circ$  give  $\mu$   $4.47$ ,  $5.01$ , and  $3.23$ , respectively. The measured vals. are higher than the calc., but are in the same order.

**XX.** The polarisations and apparent moments of  $\text{PhCN}$  and  $\text{EtCN}$  have been measured in  $\text{C}_6\text{H}_{14}$ , cyclohexane,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , and  $\text{CS}_2$  and at various temp.  $\mu$  falls regularly with increasing dielectric const. of the solvent at const. temp., and for the same solvent decreases with fall in temp. The data are compared with the moments for the vapours by various formulæ, but the agreement between observed and calc. vals. is only approx.

J. W. S.

**Intermolecular force effects with the isomeric  $\beta\gamma$ -dibromobutanes.** H. G. TRIESCHMANN (Z. physikal. Chem., 1936, B, 33, 283—289).—The isomeride of lower b.p. (I) has a higher dielectric const. and smaller heat of vaporisation than the other (II). It is inferred that in (I) the intermol. force effects are  $<$  than in (II), and that (I) is therefore the *meso*-form and (II) the active form. The  $\beta$ -butylene of higher b.p. must then be the *cis*-form and that of lower b.p. the *trans*-form (cf. A., 1935, 825). (I) and (II) have the same dipole moment.

R. C.

**Dipole moments of benzoquinone, beryllium acetylacetonate, basic beryllium acetate, and *o*-nitrophenol.** H. O. JENKINS (J.C.S., 1936, 910—911).—The apparent dipole moments of  $\text{Be}$  acetylacetonate (I) and basic  $\text{Be}$  acetate (II) can be calc. from that of benzoquinone (III). From the given

equations the orientation polarisations of (III), (I), and (II) are predicted to be in the ratios of  $1:2:3$ ; experimental vals. are approx. in this ratio.

W. R. A.

**Dipole moments of nitrophenols.** H. O. JENKINS (J.C.S., 1936, 1049—1050).—The dipole moment of  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  in  $\text{C}_6\text{H}_6$  at  $25^\circ$  is  $3.11 D$ , in good agreement with previous data. Resonance effects or influence of the solvent may account for the fact that the electric moments of the substituted phenols increase in a direction contrary to the expected direction.

W. R. A.

**Inductive effects in the diphenyl series.** (MRS.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1936, 1130—1137).—The following dipole moments (in  $D$ ) are recorded in  $\text{C}_6\text{H}_6$  solution at  $25^\circ$ : 4-fluoro-,  $1.50$ , 4-chloro-  $1.56$ , 4-bromo-  $1.64$ , 2-nitro-  $3.80$ , 4-nitro-  $4.17$ , 4-amino-  $1.76$ , 4-acetamido-  $3.83$ , 4-nitro-4'-amino-  $6.46$ , 4-bromo-4'-amino-  $3.30$ , and 4-bromo-3'-nitro-4'-piperidino-diphenyl  $4.30$ ,  $\text{PhF}$   $1.47$ ,  $\text{PhCl}$   $1.54$ ,  $\text{PhBr}$   $1.55$ ,  $\text{PhNO}_2$   $4.03$ ,  $\text{NH}_2\text{Ph}$   $1.51$ ,  $\text{NHPhAc}$   $4.01$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$   $6.32$ ,  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$   $2.85$ , 4'-bromo-2'-nitro-1-phenylpiperidine  $4.29$ . The results indicate mesomerism in the disubstituted diphenyls and benzenes, whence it is concluded that the independent conjugation of the nuclei in  $\text{Ph}_2$  derivatives is not so complete as has generally been considered.

J. W. S.

**Dipole moment and molecular structure. XVII.** Dipole moments of azo-dyes and similar substances. **XVIII.** Dipole moments of substituted  $\alpha$ -methylstyrenes. E. BERGMANN and (Miss) A. WEIZMANN (Trans. Faraday Soc., 1936, 32, 1318—1326, 1327—1331; cf. this vol., 715).—**XVII.** Data for 24 compounds are recorded. The structures of *p*- and *o*-hydroxyazo-dyes are discussed in the light of the results. The "zwitterion" structure for the *p*-compounds is excluded by their relatively low dipole moments.

**XVIII.** Data for 10 compounds are recorded and discussed.

E. S. H.

**Discontinuous variations of the atomic volume in the solid state and at fusion.** G. DESTRIAU (J. Chim. phys., 1936, 33, 526—531).—The elements conform to the relation  $nC = K \times T \times (\text{at. vol.})$ , where  $C$  is approx.  $0.155$ ,  $K$  is the coeff. of cubical expansion of the solid,  $T^\circ$  abs. is the m.p., and  $n$  is an integer between 2 and 8 probably related to  $F'$  in Forrer's m.p. law (A., 1935, 1305). The change in g. at. vol. at fusion is  $\Delta V = n'C'$ , where  $n'$  is an integer and  $C'$  is approx.  $0.12$ .

J. G. A. G.

**Refractive index of gaseous heavy water.** C. CUTHBERTSON and M. CUTHBERTSON (Proc. Roy. Soc., 1936, A, 155, 213—217).—The vals. found for  $\mu$  of  $\text{D}_2\text{O}$ , 99.2% pure, for  $\lambda$   $5462.23$  and the dispersion  $\lambda\lambda$   $5462$ — $2968$  are expressed by  $\mu - 1 = (2.6756 \times 10^{27}) / (11,000 \times 10^{27} - n^2)$ ,  $n$  being the no. of vibrations per sec. for the  $\lambda$  in question. This gives a val. for  $\lambda$   $5462.23$  of  $0.0002501$ , against  $0.0002527$  for  $\text{H}_2\text{O}$ , and a flatter dispersion curve. The American observations on liquid  $\text{D}_2\text{O}$  are thus approx. confirmed for the gaseous form.

L. L. B.



**Anisotropy of the optical polarisation field in liquids.** IV, V. B. S. R. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 64—71, 72—73; cf. this vol., 780).—IV. The molar refractivity, measured at different temp., for  $\text{Bu}^\alpha\text{OH}$ ,  $\text{Et}_2\text{O}$ ,  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ , and  $\text{C}_7\text{H}_{16}$  increases (except for  $\text{Bu}^\alpha\text{OH}$ ) with temp., showing that the optical polarisation field is not of the Lorentz type but should be regarded as anisotropic. For  $\text{Bu}^\alpha\text{OH}$ , the molar refractivity first slightly increases and then diminishes, as for an associated liquid. For  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ , and  $\text{C}_7\text{H}_{16}$ , the ratio of the coeffs.  $p_2/p_1$ , constituting a measure of the anisotropy of the optical polarisation field, increases on ascending the series, and the deviations from the Lorentz law are similarly more marked. With rise of temp.  $p_2/p_1$  rapidly approaches unity in all cases except that of  $\text{Bu}^\alpha\text{OH}$ .

V. Vals. of  $p_2/p_1$  for 8 liquids are tabulated and plotted against temp. The curves fall into three classes: slow and regular fall in anisotropy of the optical polarisation field ( $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhNO}_2$ ); rapid and relatively large fall ( $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_7\text{H}_{16}$ ); abnormal and erratic variation ( $\text{AcOH}$ ,  $\text{BuOH}$ ) probably connected with the associating nature of the liquids.

N. M. B.

**Rotatory power of sugar hydrazones in relation to the stereochemical structure of the  $\alpha$ -carbon atom.**—See this vol., 1234.

**Rotatory dispersion.** XXIX. Absorption and circular dichroism of camphorquinone. T. M. LOWRY and (Miss) D. M. SIMPSON (J.C.S., 1936, 1156—1159).—The curve of the circular dichroism of camphorquinone in cyclohexane solution as a function of  $\lambda$  is roughly parabolic, with a rounded max. at 4700 Å. ( $\epsilon_r - \epsilon_i = 1.95$ ), but is steeper on the side of longer  $\lambda$ . The visible absorption band has a max. at 4780 Å., and there is another max. at 2650 Å. The principal component of the visible absorption is the optically active band, but the absorption band is less regular than that of the circular dichroism, and can be interpreted only by assuming the presence of optically inactive components on either side of the main component with max. about 4900 and 4230 Å., respectively.

J. W. S.

**Influence of solvents and of other factors on the rotation of optically active compounds.** XXXIII. Behaviour of  $\beta$ -octyl alcohol and of  $\beta$ -octyl acetate. T. S. PATTERSON and (Miss) G. M. HOLMES (J.C.S., 1936, 1007—1014).—The rotation of  $\beta$ -octyl acetate in  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$ , and Et cinnamate (I) has been studied. It is concluded that two regions of visibly anomalous dispersion would be exhibited by the  $T$ - $R$  curves if a sufficient range of temp. could be studied.  $\text{C}_6\text{H}_6$  displaces the  $T$ - $R$  curves to the left; the other solvents displace the curves to the right. Although  $\text{CS}_2$  and (I) have similar effects as regards rotation, they have opposite effects on the apparent mol. solution vol.

W. R. A.

**Constitution of formic acid and the formates.** T. S. WHEELER (Current Sci., 1936, 5, 17—18).—A reply to Halasyam (this vol., 412).

D. C. J.

**Constitution of complex metallic salts.** IV. Constitution of certain bridged dipalladium derivatives. Novel type of tautomerism. F. G.

MANN and D. PURDIE (J.C.S., 1936, 873—890).— $\text{NH}_4$  palladochloride reacts with the bisalkylphosphine- (and arsine-) palladium dichlorides  $[(\text{R}_3\text{P})_2\text{PdCl}_2]$  and  $[(\text{R}_3\text{As})_2\text{PdCl}_2]$  (this vol., 140), forming a new type of bridged di-Pd compound,  $[\text{R}_3\text{PPdCl}_2]_2$  and  $[\text{R}_3\text{AsPdCl}_2]_2$ . These compounds are markedly darker in colour and have generally higher m.p. than the parent substances; their mol. wt. in all solvents is twice that of the empirical formula. Corresponding members are isomorphous; the compounds have been prepared also with I,  $\text{NO}_2$ , and CNS instead of Cl. These compounds should exist as the unsymmetric form (I) and as *cis* and *trans* modifications of the symmetric form (II). In the solid state they exist in one form only, but in org. solvents an equilibrium mixture of (I) and (II) exists, since decisive reactions for both forms are given. These compounds are termed *dichlorobis(trialkyl-phosphine or -arsine)- $\mu$ -dichlorodipalladium*. Their reactions are described; dipole moment, crystallographic and parachor data have been obtained, and are discussed in relation to the structure of the mols.

W. R. A.

**Polarity and tautomerism.** V. RASUMOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 381—387; cf. A., 1935, 1348; this vol., 925).—Theoretical. Tautomeric changes in many org. and inorg. mols. are indicated, the occurrence of which is due to the bond electrons dividing their time between the attraction spheres of the atoms they join, the degree of inequality of division determining which shall be the more stable modification of the mol. concerned. In extreme cases ionisation results; in others, a given atom in a mol. is alternately positive and negative, so that acids and bases may become amphoteric.

R. C. M.

**Nature of the *trans*-effect.** A. GRUNBERG (Acta Physicochim. U.R.S.S., 1935, 3, 573—582).—Theoretical. In symmetrical complex ions of the type  $\text{PtCl}_4^{2-}$ , the anions are placed symmetrically around the cation, so that the effect of dipoles induced by reciprocal polarisation is neutralised. Substitution of a new anion disturbs the reciprocal polarisation, resulting in a dipole in the cation. *trans*-Effect appears when the central ion has strong polarisation properties, and is further influenced by all properties related to polarisation.

C. R. H.

**Action of the electric field on anisotropic liquids.** I. Motion of the liquid in the electric field. II. Orientation of the liquid in the electric field. V. FREDERICKS and V. ZVETKOV (Acta Physicochim. U.R.S.S., 1935, 3, 879—894, 895—912; cf. A., 1935, 1305).—I. The electric field induces an intensive motion in the liquid, which increases with the field strength. Experiments with films of varying thickness show that for a given field strength  $E$  the effect appears only when the thickness is  $>$  a certain val.  $z_0$  and  $z_0 E$  is a const. which increases with time. A magnetic field  $H$  parallel to the surface of the liquid and perpendicular to the electric field increases  $z_0$  but when parallel to the electric field and perpendicular to the surface,  $z_0$  is diminished.

II. The orienting action of the electric field has been determined by investigating the simultaneous action of electric and magnetic fields on a liquid layer of

thickness  $< z_0$ . Azoxyanisole (I) and *p*-acetoxybenzylideneazine are oriented perpendicular to the electric field according to Zocher's rule, whilst dibenzylideneazine and anisylidenebenzidine take up positions with the mol. axis parallel to the lines of force. The orienting effect depends on the dielectric anisotropy of the liquid, and the theoretical relation  $\alpha H^2 + \beta E^2 = 1/z_0^2$  is in good agreement with the experiments. The effect of a magnetic field  $H_e$  can be counteracted by an electric field  $E_e$ , the ratio  $H_e/E_e$  decreasing with temp. The diamagnetic anisotropy and the elasticity const.  $A$  of (I) have been calc. R. S.

**Bond strength in the hydrogen molecule.** Comparison of spectroscopic and wave mechanics data. H. BEUTLER and H. O. JÜNGER (Z. Physik, 1936, 101, 304—310).—Energy of dissociation of  $H_2$ , 36,100 cm.<sup>-1</sup>, energy of ionisation 124,425 cm.<sup>-1</sup>, and energy of dissociation of  $H_2^+$ , 21,366 cm.<sup>-1</sup>, are the same according to spectroscopic and wave-mechanics data. A. B. D. C.

**Second virial coefficient of heavy hydrogen.** K. SCHÄFER (Naturwiss., 1936, 24, 539).—The second virial coeff. of  $D_2$  was determined between 23° and 46° abs. It is approx. 20%  $>$  that of  $H_2$ . It is concluded that the intermol. force between two  $D_2$  mols. is the same as that between two  $H_2$  mols. Double mols.,  $D_4$  and  $H_4$ , of transitory existence, are formed by collision at low temp., the distance between the two mols. being  $>$  the distance between the atoms in the single mols. In the determination of permitted energy levels, the difference between *o*- and *p*- $H_2$  must be considered. There is a measurable difference between the virial coeffs. of these two forms of  $H_2$ . A. J. M.

**Modern representations of chemical combination.** H. FROMHERZ (Angew. Chem., 1936, 49, 429—437).—A brief elementary review of quantum mechanics and of the electronic structure of simple compounds. E. W. W.

**Form of [the] nitrous oxide molecule.** C. E. SUN and T. Y. WU (J. Chinese Chem. Soc., 1936, 4, 340—343).—The calc. binding energies for the mols. are: NON 144.6, NNO 197.6, OCO 248.5, and COO 202.2 kg.-cal., in agreement with a symmetrical mol. for  $CO_2$  and an asymmetric form for  $N_2O$ . J. G. A. G.

**Normal vibrations and the isotope effect of molecules of the type  $X_2Y_N$  with an *N*-fold axis of symmetry.** H. SCHIMMEL (J. Chem. Physics, 1936, 4, 508—512).—Mathematical. Frequencies, and shifts of frequency due to isotopes, are calc. in terms of the masses, geometrical consts. of the mol., and parameters of a general quadratic potential energy form, with sp. reference to the  $X_2Y_3$  mol. J. G. A. G.

**Electron affinity of bromine atoms from space-charge effects.** G. GLOCKLER and M. CALVIN (J. Chem. Physics, 1936, 4, 492—493; cf. A., 1935, 129).—The electron affinity of Br atoms determined by using a hot W filament in Br vapour is  $88 \pm 3.4$  kg.-cal. J. G. A. G.

**Transfer of translational and vibrational energy in oxygen as influenced by small im-**

purities of water or ammonia vapour. V. O. KNUDSEN and L. ORERT (Physical Rev., 1935, [ii], 47, 256).—For mol. collisions in  $O_2$ , the no. of transitions from the excited to the normal state per mol. per sec. is practically a linear function of  $[NH_3]$ , and a quadratic function of  $[H_2O]$  when these concns. are small. L. S. T.

**Collision frequency in solutions.** K. S. G. DOSS (Proc. Indian Acad. Sci., 1936, 4, A, 23—26).—An interpretation of a collision in solution is given on the basis of Wheeler's theory of liquids (cf. A., 1934, 1159). The expressions for the collision frequencies are similar to those obtained by other methods and used in interpreting the kinetics of reactions in solution. N. M. B.

**Collision mechanism and the primary photochemical process in solutions.** E. RABINOWITCH and W. C. WOOD (Trans. Faraday Soc., 1936, 32, 1381—1387).—Theoretical. E. S. H.

**X-Ray interference at the diamond as a wave-mechanics problem. II. Linear chains of atoms.** P. P. EWALD and H. HONL (Ann. Physik, 1936, [v], 26, 673—696; cf. this vol., 412).—Theoretical. The charge distribution in a linear chain of atoms is calc. A. J. M.

**Atomic forces of solid states. III.** W. WEN-PO (Phil. Mag., 1936, [vii], 22, 281—286; cf. this vol., 1052).—Mathematical. N. M. B.

**Quantum-mechanical calculation of the variation of lattice energy with lattice separation in the sodium chloride lattice.** R. LANDSHOFF (Z. Physik, 1936, 102, 201—228).—Mathematical. A general formula for the lattice energy of an alkali halide crystal is derived in terms of electrostatic interaction and exchange energies. Using the wave functions for  $Na^+$  and  $Cl^-$  calc. by Hartree and Fock, the lattice energy of the NaCl crystal is calc. A. J. M.

**Lattice theory of alkaline-earth carbonates. I. Lattice energy of crystals of aragonite type and their thermochemical applications.** B. Y. OKE (Proc. Indian Acad. Sci., 1936, 4, A, 1—10).—The lattice energies of the orthorhombic crystals aragonite,  $SrCO_3$ , and  $BaCO_3$  are calc. The stabilising forces other than the electrostatic attractions and repulsions of the charges are investigated with the help of compressibility measurements. The lattice energy vals. are verified by a thermochemical cyclic process. N. M. B.

**Energy levels of the asymmetrical rotator in the new quantum theory.** E. E. WITMER (Physical Rev., 1935, [ii], 47, 340).—Mathematical. L. S. T.

**Modification of the Heitler and London method.** C. ZENER (Physical Rev., 1935, [ii], 47, 334). L. S. T.

**Free and total surface energies and related quantities.** A. FERGUSON and S. J. KENNEDY (Trans. Faraday Soc., 1936, 32, 1474—1481).—Surface energy data for supercooled liquids at 0° abs. have been calc. from published work. E. S. H.

**Intensity of reflexion of X-rays from calcite.** P. E. TAHVONEN (Soc. Sci. fenn., Comm. phys.-



math., 1935, 8, No. 6, 1—84; Chem. Zentr., 1935, ii, 3637).—Intensities measured indicate a more ideal lattice than was found by Bragg. The effective absorption coeff. as measured by Bragg *et al.* gives too high vals. J. S. A.

**Study of the orientation of inclined aluminium wires and foil by means of Weissenberg's Röntgen goniometer.** J. PALACIOS and J. GARCÍA DE LA CUEVA (Anal. Fis. Quim., 1934, 39, 774—778; cf. A., 1935, 433).—The interference diagrams obtained with Al wire inclined at various angles to the axis of rotation of the apparatus are used to determine the orientation of the crystals. F. R. G.

**Supercooling.** A. GOETZ (Physical Rev., 1935, [ii], 47, 257; cf. A., 1935, 151).—In metals, supercooling is the more likely the more the lattice of the crystal differs from a close-packed configuration and the more groups of paracryst. qualities have been destroyed in the fused mass. L. S. T.

**Effect of sudden heating on the recrystallisation of metals.** U. YOSHIDA, S. NAGATA, and C. MITSUKI (Mem. Coll. Sci. Kyoto, 1936, 19, 169—180).—The grain no. is much greater when a thin Al plate is heated suddenly to a given temp. than when gradual heating is employed. C. W. G.

**Lattice constant of pure aluminium.** A. LEVINS and M. STRAUMANIS (Z. physikal. Chem., 1936, B, 33, 265—274).—The val. is  $4.04146 \pm 0.00003$  A. at  $25^\circ$  and  $4.04078 \pm 0.00002$  A. at  $18^\circ$ . The coeff. of expansion is  $23.13 \times 10^{-6}$ . R. C.

**Crystal structure of  $\beta$ -manganese.** T. A. WILSON (Physical Rev., 1935, [ii], 47, 332).— $\beta$ -Mn is cubic,  $a$  12.58 A.,  $d_{\text{calc.}}$  7.29; space-group  $O_h^2$ , with 160 atoms per cube. L. S. T.

**X-Ray studies on electro-deposited silver.** S. BASU and M. HUSSAIN (Indian J. Physics, 1936, 10, 267—274).—The effect of c.d. on the brightness and hardness of electro-deposited Ag films has been investigated by X-ray methods. The brightness, determined photographically, decreases with increase of c.d. The diffracted lines from 111, 200, and 311 planes are the most intense, and decrease in intensity with increasing c.d. The Brinell hardness of the deposit showed no relationship between degree of orientation of crystallites and hardness, but the breadth of X-ray lines increases with hardness. A. J. M.

**Polymorphic transformations of simple ionic lattices. II. Transformation of sodium chloride lattice into caesium chloride lattice.** G. WAGNER and L. LIPPERT (Z. physikal. Chem., 1936, B, 33, 297—303; cf. this vol., 416).—RbCl condensed from the vapour on TiCl at  $-190^\circ$  has the CsCl lattice with  $a_w$  3.74, A.,  $d$  3.80. At room temp. it changes to the NaCl lattice. R. C.

**Crystal structure of  $\text{Co}_9\text{S}_8$  and of pentlandite  $(\text{Ni,Fe})_9\text{S}_8$ .** M. LINDQVIST, D. LUNDQVIST, and A. WESTGREN (Svensk Kem. Tidskr., 1936, 48, 156—160).—Synthetic and recryst. specimens were prepared. The 111 line of cubic Co is faintly but clearly present in a prep. containing 46 at.-% S, but is absent from one with 48 at.-% S, while a few faint lines belonging to CoS are seen in the latter. In the  $\text{Co}_9\text{S}_8$  structure,

the S are in cubic close-packing, and the Co are located in the interstices. Photographs of  $\text{Co}_9\text{S}_8$  and pentlandite are almost identical; formula  $(\text{Ni,Fe})_9\text{S}_8$  is suggested for the latter. D. C. J.

**Crystalline structure of calcium sulphate dihydrate (gypsum).** J. PALACIOS and E. E. GAL-LONI (Anal. Fis. Quim., 1934, 32, 779—786).—A more detailed account of matter previously abstracted (this vol., 783). F. R. G.

**Lattice constant of topaz.** S. ELG (Z. Physik, 1936, 101, 113—116).—This is 4186.97 X.

A. B. D. C.

**Fine structure and transformations of alkali salts of long-chain fatty acids.** P. A. THIESSEN and J. STAUFF (Z. physikal. Chem., 1936, 176, 397—429; cf. A., 1933, 1004).—The unit cell of rhombic Na stearate (I) contains 8 mols. and has  $a$  8.04,  $b$  9.24,  $d$  12.25,  $c$  51.77 A.; space-group  $D_{2h}^2$ . Rhombic Na palmitate (II) has  $a$  8.06,  $b$  9.24,  $c$  47.70. In both the mols. are arranged along the  $c$  axis in pairs, one behind the other. On heating from room temp. (I) and (II) undergo irreversible transformation into a monoclinic  $\beta$ -form at  $52^\circ$  and  $42^\circ$ , respectively. The ordinary ( $\alpha$ ) forms are partly unstable, the sp. vols. and sp. heats being  $<$  those of the  $\beta$ -forms. The  $\beta$ -form of (I) has  $a$  7.80,  $b$  5.33,  $c$   $\sin \beta = 46.10$  A. and 4 mols. in the unit cell; probable space-group  $C_{2h}^2$ . The  $\beta$ -form of (II) has  $a$  7.83,  $b$  5.40,  $c$   $\sin \beta = 42.10$  A. The existence of  $\alpha$ - and  $\beta$ -forms is due to the ionic linking between the Na and the fatty acid residue, the  $\text{CO}_2\text{Na}$  constituting a dipole and the two forms corresponding with two orientations of the mol. dipoles in the double mol. In the  $\alpha$ -forms the lattice structure is determined by mol. cohesion forces, in the  $\beta$ -forms by these forces together with polar orienting forces. Above the genotypic transformation point the orientation effect is dominant. R. C.

**X-Ray scattering and the polarisation field of di-, tetra-, and deca-hydronaphthalene.** M. S. JEGLEKAR (Z. Physik, 1936, 101, 398—404).—The polarisation field for  $\text{C}_{10}\text{H}_{18}$  is less anisotropic than that for  $\text{C}_{10}\text{H}_8$  (cf. Krishnan and Rao, A., 1929, 1129). A. B. D. C.

**Comparison by X-ray diffraction of  $p$ -azoxy-anisole in liquid and liquid-crystalline phases.** H. R. LETNER and G. W. STEWART (Physical Rev., 1935, [ii], 47, 332; cf. this vol., 670). L. S. T.

**Geometrical and optical study of  $p$ -azoxyphenetole crystals.** P. CHATELAIN (Compt. rend., 1936, 203, 266—268).— $p$ -Azoxyphenetole crystals have  $a$  15.9,  $b$  5.42,  $c$  17.5 A.,  $\beta$   $94^\circ 20'$ ,  $d$  1.253. The unit cell contains 4 mols. Refractivity data are also recorded. J. W. S.

**X-Ray study of the phthalocyanines. II. Quantitative structure determination of the metal-free compound.** J. M. ROBERTSON (J.C.S., 1936, 1195—1209; cf. A., 1935, 813).—Bv comparison of the abs. measurements of corresponding reflexions of phthalocyanine and of its Ni derivative, the 300 significant phase consts. of the ( $h0l$ ) zones of the two compounds have been determined. Fourier analysis of the results determined two co-ordinates for each C and N in the structure and the regularity

of the projection indicate that the mol. is planar. The orientation of the mol. in the crystal is deduced and the third co-ordinate of the atoms calc. The results confirm Linstead's structure (A., 1934, 1114). The inner porphyrin nucleus comprises a closed system of 8 C and 8 N in a state of double linking—single linking resonance, with an interat. distance of  $1.34 \pm 0.03$  Å. This system is linked to the four  $C_6$  rings by C—C linking  $1.49 \pm 0.03$  Å. long, including a smaller % of double-linking character, these linkings being strained  $15^\circ$  from their normal positions. The whole mol. shows slight distortion from true tetragonal symmetry, probably owing to internal H—H linking between the two isoindole N atoms. In the crystal the planes of adjoining mols. are almost at right angles and the (min.) intermol. approach distance is 3.35 Å. The perpendicular distance between the mol. planes of parallel mols. is 3.38 Å. J. W. S.

**Diffraction of electrons by graphite.** G. I. FINCH and H. WILMAN (Proc. Roy. Soc., 1936, A, 155, 345—365).—Both artificial and natural graphite powders give many diffractions which do not seem to fit in with the structure deduced for graphite from X-ray data. These "extra" diffractions are not due to impurities or to lattice dimension deviations. Thin single crystals of graphite also give the "extra" diffractions, whereas thick crystals give Kikuchi line systems which confirm the assigned X-ray structure. It is concluded that the "extra" diffractions obtained with thin crystals are due to the fact that the graphite lattice, though unbounded in the cleavage plane direction, is limited in the other dimensions by the thinness of the crystal, so that diffractions of fractional  $l$  index and those normally forbidden by structure factor considerations can occur. Experimental evidence in support of this theory is adduced. L. L. B.

**Examination of cellulose by electron diffraction.** G. NATTA and M. BACCAREDDA (Atti R. Accad. Lincei, 1936, [vi], 23, 444—448).—Thin laminae of cellulose (I) from solutions prepared by dissolving (I) in 1% NaOH at 8 atm. pressure give an X-ray lattice of  $a$  8.60,  $b$  10.30,  $c$  8.07 Å.,  $\beta$   $82^\circ$ . Preps. from (I) in Schweitzer's reagent give similar data ( $a$  8.25 Å.), the vol. of the unit cell being  $672 \times 10^{-24}$  c.c. F. O. H.

**Intensity distribution in electron patterns.** K. LARK-HOROVITZ, H. J. YEARMAN, and J. D. HOWE (Physical Rev., 1935, [ii], 47, 331).—The intensity distribution in the electron diffraction patterns of thin films of Bi, Cd,  $Ca(OH)_2$ , Cu,  $Cu_2O$ , Au,  $Na_3N$ , Ni, W oxide, Zn, ZnO, and ZnS obtained with cathode rays from a 50—80-kv. gas discharge is discussed. L. S. T.

**Kikuchi envelopes.** M. VON LAUE (Physikal. Z., 1936, 37, 544—547).—Mathematical. A. J. M.

**Optical and electrical properties of thin metallic films at low temperatures.** T. FUKUROI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 663—673).—The decrease in electrical resistance on exposure to ultra-violet light has been studied at low temp. with films of Hg, Cd, and Zn condensed on glass and quartz, and is explained by the photo-electric effect of colloidal particles. R. S. B.

**Production of piezoelectricity by torsion.** R. E. GIBBS and L. C. TSIEN (Phil. Mag., 1936, [vii], 22, 311—322).—The production of piezoelectricity by torsion is considered for right circular cylinders of quartz cut with their axes parallel to the optic axis. Available data agree with the formula deduced. The Lindemann electrometer was suitable for the study of piezoelectricity and demonstrated the static development of vol. charges. Torsional oscillations have been produced in both hollow and solid cylinders, and were studied by the glow discharge, dust, and polarised light methods. N. M. B.

**Influence of tension, pressure, and torsion on longitudinal magnetostriction.** H. KIRCHNER (Ann. Physik, 1936, [v], 27, 49—69).—The influence of tension, pressure, and torsion on the saturated longitudinal magnetostriction  $\lambda$  of Ni containing 0.05% Be and alloys of Fe and Ni containing 15% and 50% Ni (0.5% Mn present as impurity) have been investigated. For Ni,  $\lambda$  increases to a limiting val.,  $1.5\lambda_0$ , with tension, decreases rapidly to zero with pressure, and decreases to a limiting val.,  $0.72\lambda_0$ , with torsion. O. D. S.

**Influence of elastic strains on the alternating current magnetisation curve.** H. LITTMANN (Ann. Physik, 1936, [v], 27, 186—200).—The influence of tension, torsion, and annealing on the  $\mu$ - $H$  curve at 50 Hz. of Ni, Ni-Fe alloys, and permalloy C has been investigated for longitudinal and circular magnetisation. Tension causes a decrease of  $\mu$  and a flattening of the  $\mu$ - $H$  curve for longitudinally magnetised Ni and circularly magnetised alloys, and an increase of  $\mu$ , at high field strength, in circularly magnetised Ni and longitudinally magnetised alloys. This is in agreement with the theory of Becker. O. D. S.

**Magnetic properties of nickel up to the Curie point.** W. SCHNABL (Ann. Physik, 1936, [v], 27, 169—185).—Permeability of Ni is measured at 0, 50, and 500 Hz. from room temp. to  $326^\circ$ . A dependence of magnetic losses on frequency is observed, not accounted for by eddy current losses. O. D. S.

**Magnetic anisotropy of nickel-cobalt single crystals.** J. W. SHIR (Physical Rev., 1936, [ii], 50, 376—379; cf. A., 1934, 1061).—The direction for easiest magnetisation changes from  $\langle 111 \rangle$  to  $\langle 100 \rangle$  as the Co content increases 3—10%, and changes back to  $\langle 111 \rangle$  when Co exceeds 20%. Anisotropy const. calc. for monocryst. and polycryst. specimens diverged beyond the limits of experimental error. N. M. B.

**Measurement of permeability by means of skin effect.** R. BECKER (Ann. Physik, 1936, [v], 27, 123—128; cf. Kreielsheimer, A., 1933, 76).—Theoretical. O. D. S.

**Ising's model of ferromagnetism.** R. PEIERLS (Proc. Camb. Phil. Soc., 1936, 32, 477—481).—O. D. S.

**Crystal structure and ferromagnetism of the transition metals.** U. DEHLINGER (Z. Metallk., 1936, 28, 117—121).—A crit. review of recent work and theories. A. R. P.

**Magnetic and electrostatic energy. Thermodynamics of magnetisation.** E. A. GUGGENHEIM



(Proc. Roy. Soc., 1936, A, 155, 49—70, 70—101).—Mathematical.

**Magnetisation curves of a superconducting sphere and ring.** D. SHOENBERG (Proc. Roy. Soc., 1936, A, 155, 712—726).—The magnetisation curve of a superconducting pure Pb sphere has been measured by the Faraday method. It consists of two straight lines, one of which corresponds with transition between the superconducting and normal states.

L. L. B.

**Galvomagentic effects in bismuth.** H. JONES (Proc. Roy. Soc., 1936, A, 155, 653—663).—Mathematical. The change of resistance in a magnetic field and the Hall coeffs. of Bi crystals are calc. The large galvomagentic effects observed are accounted for by the theory previously proposed to explain the diamagnetic properties of Bi (A., 1935, 153). Minute traces of impurity have a great effect on the galvomagentic properties.

L. L. B.

**Theory of constant paramagnetism. Application to manganese.** L. NÉEL (Compt. rend., 1936, 203, 304—306).—Mathematical. The occurrence of a break in the sp. heat curve of Mn at the same temp. (628° abs.) at which the susceptibility commences to vary with temp. is in agreement with the author's theory.

C. R. H.

**Permanent magnetisation of steel in the neighbourhood of a circuit carrying a rapid aperiodic discharge.** R. CHEVALLIER and M. LAPORTE (Compt. rend., 1936, 203, 302—304).—Near to the circuit steel needles are magnetised in the opposite sense to the field. On moving away from the circuit the magnetisation decreases and, after passing through a neutral point, increases in the same sense as the field. A few cm. from the circuit a max. val. is reached, followed by a decrease.

C. R. H.

**Influence of traces of slip planes on glow emission.** II. H. MAHL and D. SCHENK (Z. Physik, 1936, 101, 117—120; cf. this vol., 537).—Lines of different emissivity are visible on metal crystal surfaces with a layer of electropositive atoms, and these lines represent traces of slip planes.

A. B. D. C.

**Effect of recrystallisation on the emission of platinum.** F. SCHUBERT (Physikal. Z., 1936, 37, 595—598).—The degree of polarisation of radiation emitted from Pt after it had been heated to temp. above the recryst. temp. was investigated. The theoretical degree of polarisation is not reached as the emitted radiation contains a proportion of unpolarised radiation arising from the boundaries of the crystallites. If this is corr. by investigation of photomicrographs of the Pt surface, together with other phenomena, the experimental val. for the degree of polarisation agrees with that calc. from the known optical consts. of Pt. There is no effect of temp. on the optical consts. of Pt up to 1275°.

A. J. M.

**Optical properties of magnesium oxide.** R. T. BRICE and J. STRONG (Physical Rev., 1935, [ii], 47, 255—256).— $n$  has been measured for  $\lambda\lambda$  in the visible and ultra-violet; transmission limit, approx. 2200 Å. Windows of MgO in high-temp. furnaces withstand

etching by Li, Na, K, and Ca better than other materials.

L. S. T.

**Optical properties of sputtered metal films.** J. B. NATHANSON and H. S. SEIFERT (Physical Rev., 1935, [ii], 47, 328).—Comparison of computed and observed masses of Cu films, produced by sputtering in H<sub>2</sub>, indicates a higher  $u$  and/or lower  $d$  for the films compared with the metal in bulk.

L. S. T.

**Optical and electrical properties of thin metallic films at low temperature.** T. FUKUROI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 411—429).—The spectral reflectivity for light and the electrical conductivity at liquid air temp. of Hg, Cd, and Zn films condensed from vapours have been investigated, and the reflectivity result for Hg is compared with that based on a theory of spherical colloidal film particles.

N. M. B.

**Birefringence of potassium chloropalladite and potassium chloroplatinite.** D. P. MELLOR and F. M. QUODLING (J. Proc. Roy. Soc. New South Wales, 1936, 69, 167—170).—Both K<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> are optically negative and strongly birefringent,  $n$  being greater for a polarised ray with its electric vector in the plane of MX<sub>4</sub> than for the perpendicular polarised ray. This indicates a planar structure for MX<sub>4</sub> in these compounds, agreeing with results of X-ray analysis.

A. J. M.

**Elastic constants of alkali halides.** J. A. VASASTJERNA (Soc. Sci. fenn., Comm. phys.-math., 1935, 8, No. 9, 1—9; Chem. Zentr., 1935, ii, 3629—3630).—Theoretical. The compressibility of NaCl-type crystals is expressed as a function of the elastic consts.

J. S. A.

**Quantum theory calculations for alkali halide lattices.** H. JENSEN (Z. Physik, 1936, 101, 164—185).—Exchange energies are calc. by the statistical method for ion cores in alkali halide crystals. Born's repulsive forces arise from the Pauli principle rather than from electrostatic interaction. Lattice consts., compressibilities, and infra-red frequencies are deduced.

A. B. D. C.

**Modulus of elasticity of certain definite intermetallic compounds.** A. PORTEVIN and L. GUILLET, jun. (Compt. rend., 1936, 203, 237—239).—Intermetallic compounds are of two classes, those of metallic type (e.g., CuZn, Ag<sub>3</sub>Sb, and MgZn<sub>2</sub>) having elastic moduli approximating to the val. anticipated from the law of mixtures, and those of homopolar type (e.g., CuZn<sub>6</sub>, Cu<sub>31</sub>Sn<sub>8</sub>, and Cu<sub>9</sub>Al<sub>4</sub>) for which the moduli exceed considerably the val. anticipated theoretically.

J. W. S.

**Plasticity of metal crystals and its significance for the properties of metals.** G. WASSERMANN (Z. Ver. deut. Ing., 1936, 80, 283—287).—Deformation of metals is caused by the crystallographic process of translation and mechanical twinning. Examples are given to illustrate how knowledge of the properties of single crystals can help in elucidating and controlling the behaviour of materials.

R. B. C.

**Two forms of phosphorus pentachloride.** H. MOUREU, M. MAGAT, and G. WETROFF (Compt. rend.,

1936, 203, 257—259).— $\text{PCl}_5$  in a sealed vessel under its own v.p. melts over the range 159—160.5°, even when extremely pure. On cooling, crystals form at 157° but the temp. of arrest is always lower (148—154°). This behaviour is attributed to a mol. transformation at the m.p. This view is supported by the fact that the Raman spectrum of fused  $\text{PCl}_5$  shows seven frequencies distinct from those of the solid and not attributable to  $\text{PCl}_3$  or  $\text{Cl}_2$ . J. W. S.

The liquid state and theory of fusion. II. Theory of fusion and crystallisation. J. FRENKEL (Acta Physicochim. U.R.S.S., 1935, 3, 913—938; cf. A., 1935, 1062).—The continuity of the solid, liquid, and gaseous states is stressed, and a theory is outlined which points to a liquid  $\rightarrow$  solid  $pv$  curve of the same form as the van der Waals liquid  $\rightarrow$  gas curve. It is suggested that there is a lower crit. temp. below which the cryst. and amorphous phases cannot coexist. R. S.

Liquid state and the theory of fusion. J. FRENKEL (Acta Physicochim. U.R.S.S., 1935, 3, 633—648).—A detailed mathematical treatment of a theory previously outlined (cf. A., 1935, 1062). C. R. H.

Liquid state. W. H. RODEBUSH (Physical Rev., 1935, [ii], 47, 513). L. S. T.

Fatty acids and their esters. I. Cryoscopy and ebullioscopy of fatty acids. II. Mol. wts. of polymerised esters.—See this vol., 1229.

Electrical resistance of liquid helium. M. WOLFKE and W. H. KEESOM (Physica, 1936, 3, 823—824).—The resistance of liquid helium from 1.28° to 4.22° abs. is  $<10^{15}$  ohm.cm. O. D. S.

Electric conductivity of Rochelle salt single crystals under mechanical stress. F. SEIDL (Z. Physik, 1936, 101, 234—254).—The lowest sp. resistance at 24° is  $10^{13}$  to  $10^{14}$  ohm.cm.; this increases with mechanical strain of the crystal and with defects in the crystal. A. B. D. C.

Micro-resistance of superconductors. P. GRASSMANN (Physikal. Z., 1936, 37, 569—578).—The method of Onnes for the determination of very small resistances has been improved and used to find the resistance of superconductors at temp. below the transition point. The resistance of a film of Sn, 6.5  $\mu$  thick, on Cu is  $<10^{-14}R$  ( $R$ =resistance at room temp.), whilst that of a film of Pb, 3.5  $\mu$  thick, is  $<0.5 \times 10^{-15}R$ . For c.d. up to  $4 \times 10^5$  amp. per sq. cm. there was no perceptible decrease in current in this Pb film. There is, therefore, no additional effect causing loss of energy at high electron velocities. It is calc. that at least one atom in  $10^4$  must furnish a superconducting electron. A. J. M.

Magnetic transition curves of superconductors. R. FEIERLS (Proc. Roy. Soc., 1936, A, 155, 613—628).—Mathematical. An attempt is made to generalise the arguments of Gorter and Casimir (A., 1934, 480) to bodies of different shape, in particular to spheres and ellipsoids. The new feature of such bodies is that in an increasing external field superconductivity disappears gradually, the range of fields over which this process takes place being the greater, the greater

is the demagnetising factor of the body. The existence of a "transition state," intermediate between the superconducting and the normal states, is assumed. L. L. B.

Transition between the superconducting and normal state. I. Magnetic induction in mercury. K. MENDELSSOHN (Proc. Roy. Soc., 1936, A, 155, 558—570).—The change of induction from 0 to its normal val. of long-shaped Hg specimens when passing from the superconducting to the normal state has been found to be discontinuous. A more gradual change is observed on passing from the normal to the superconducting state. L. L. B.

Sound velocity in gas mixtures at high temperatures. H. PORITSKY and C. G. SURTS (Physical Rev., 1935, [ii], 47, 335).—Experimental vals. of the velocity in atm.-pressure arcs in air are interpreted in terms of temp. of the gas. L. S. T.

Sound absorption and velocity in mixtures. D. G. BOURGIN (Physical Rev., 1936, [ii], 50, 355—369; cf. A., 1933, 217).—Mathematical. The effects of collision excitation probabilities dependent on the internal energy specification of the impinging mols., transitions in both colliding members, triple and higher order collisions, and viscosity and conduction are considered with reference to sound propagation. The triple collision hypothesis for H—O—O<sub>2</sub> mixtures is discussed. Formulæ, in convenient form for application, for absorption and velocity in mixtures are deduced. N. M. B.

Dispersion of acoustic velocity in organic liquids. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 4, A, 17—22).—Data for acoustic velocities of 16 org. liquids, determined at about  $7 \times 10^6$  and  $20 \times 10^6$  cycles per sec., are tabulated. No dispersion in velocity was found. N. M. B.

Ultrasonic velocities in organic liquids. IV. Halogen compounds. V. Some related groups. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 3, A, 519—522; 4, A, 59—63; cf. this vol., 929).—IV. Data for ultrasonic velocities, at about  $7.32 \times 10^6$  frequency, for 15 aliphatic and aromatic halogen compounds, and calc. adiabatic compressibilities show, in general, that introduction of a heavier atom lowers acoustic velocity, and the presence of a double linking favours lowering of velocity.

V. Ultrasonic velocities and adiabatic compressibilities are tabulated for 2-, 3-, and 4-methylcyclohexanol, 2- and 4-methylcyclohexanone, *tert*.-C<sub>5</sub>H<sub>11</sub>.OH, *sec*.-octyl alcohol, mesitylene, CH<sub>2</sub>Ph<sub>2</sub>, decahydronaphthalene, *p*-cymene,  $\beta$ -picoline, MeCN, and PhNCS. The relation between sound velocities and chemical constitution is discussed. N. M. B.

Dependence on temperature of the absorption coefficients of ultrasonic waves in liquids. C. SORENSEN (Ann. Physik, 1936, [v], 27, 70—74; cf. this vol., 787).—Data are recorded for frequencies of 530—950 kHz. For COMe<sub>2</sub>, EtOH, PhMe, and xylene the absorption coeff.,  $\alpha$ , increases with  $T$ . For C<sub>6</sub>H<sub>6</sub>  $\alpha$  is independent of  $T$  at 950 kHz. and increases with  $T$  at 530 kHz. For H<sub>2</sub>O  $\alpha$  decreases with  $T$  less rapidly than is predicted by theory. O. D. S.



**Velocity of propagation of ultrasonic waves in colloidal solutions.** A. PASSINSKI (Acta Physicochim. U.R.S.S., 1935, 3, 779—782).—The velocity of propagation of ultrasonic waves in  $\text{Fe}_2\text{O}_3$  sol, a solution of crêpe rubber in  $\text{C}_6\text{H}_6$ , cellulose nitrate in  $\text{COMe}_2$ , and gelatin in  $\text{H}_2\text{O}$  is little different from that in the pure solvents  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{COMe}_2$ , and  $\text{H}_2\text{O}$ , respectively. R. S.

**Influence of ultrasonic waves on the process of solidification of molten metals.** S. SOKOLOV (Acta Physicochim. U.R.S.S., 1935, 3, 939—944).—The period of const. temp. in the solidification of Zn is diminished by ultrasonic waves and the rate of formation of crystals is accelerated. R. S.

**Constant paramagnetism. I, II. Diamagnetic compounds containing a transition element.** D. P. RAYCHAUDHURI and P. N. SENGUPTA (Indian J. Physics, 1936, 10, 245—251, 253—266).—I. The susceptibilities of  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{NaVO}_3$ ,  $\text{KMnO}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$  have been determined. The temp. coeff. of susceptibility is negative for  $\text{V}_2\text{O}_5$  and  $\text{KMnO}_4$ , but is positive for  $\text{K}_2\text{Cr}_2\text{O}_7$ . The const. at. susceptibilities of the elements from V to Mn depend on the no. of electrons in the  $d$  shell in a similar way to the dependence of the Bohr magneton no. for these elements. It is suggested that Fe, Co, and Ni will have const. paramagnetic at. susceptibility.

II. The mol. susceptibilities of a no. of co-ordination compounds containing transition elements have been collected. The at. susceptibility of the magnetogenic atom is not const., but is greater when the attached groups have a high dipole moment.

A. J. M.

**Magnetic properties of antimony.** D. SHOENBERG and M. Z. UDDIN (Proc. Camb. Phil. Soc., 1936, 32, 499—502).—The mass susceptibilities of Sb parallel and perpendicular to the trigonal axis,  $\kappa_3$  and  $\kappa_1$ , have been measured from 4° abs. to room temp.  $\kappa_1$  is independent of  $T$ .  $\kappa_3$  decreases with  $T$ . Both  $\kappa_1$  and  $\kappa_3$  are independent of field. O. D. S.

**Exaltation of the magnetism of ferric oxide by calcination in presence of ashless filter-paper.** C. COURTY (Compt. rend., 1936, 203, 369—371).—Magnetic determinations show the presence of about 0.002 mg. of Fe in the ash of a 50-mm. ashless filter-paper. R. S.

**Magnetism and cold-working in metals. I. Polycrystals.** S. R. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 37—53).—Cold-working causes a marked decrease in the diamagnetic susceptibility of Bi, a small decrease for Zn and Cd, and a decrease in the paramagnetic susceptibility of white Sn with a change of sign below a particular density. The nature of polycryst. metals is discussed and attention is drawn to a deformed boundary between the small crystals in the metal. Explanations of the susceptibility changes are offered on the basis of the distorted layer and the particle sizes of metallic colloidal powders (cf. A., 1935, 19). N. M. B.

**Paramagnetism of the  $\text{Mn}^{++}$  ion in the  $S$  state.** S. S. BHATNAGAR, M. B. NEVGI, and R. L. SHARMA (Phil. Mag., 1936, [vii], 22, 409—414).—From

measurements on anhyd. Mn acetate, formate, lactate, and oxalate, sp., mol., and ionic susceptibilities at 32°, 70°, and 122° are obtained and magneton vals. of  $\text{Mn}^{++}$  and the Mn salts are calc.; the vals. in the two cases are almost the same, and for  $\text{Mn}^{++}$  the simple Curie law is valid. N. M. B.

**Variations of the magnetic moment of the cobalt ion in the anhydrous chloride and in the mixed crystal systems  $\text{CoCl}_2\text{--CdCl}_2$  and  $\text{CoCl}_2\text{--MnCl}_2$ .** G. FOEX and C. FEHRENBACH (Compt. rend., 1936, 203, 307—309).—Data for the magnetic moment show a distinct break in the curves at approx. 137°, the variation in moment being 1 magneton. The transition temp. and variation in moment are independent of the amount of added  $\text{CdCl}_2$  or  $\text{MnCl}_2$ . C. R. H.

**Kelvin temperature of the ice point.** J. R. ROEBUCK (Physical Rev., 1936, [ii], 50, 370—375).—The val. of the ice point is calc. from data on the Joule-Thomson effect and coeffs. of vol. and pressure expansion. Results are: air 273.158, He 273.168,  $\text{N}_2$  273.125, A 273.10, and the most probable val.  $273.16 \pm 0.02$ . N. M. B.

**Comparison of platinum resistance thermometers with the helium gas thermometer in the range 14—90° absolute.** F. HENNING and J. OTTO (Physikal. Z., 1936, 37, 601—609).—The variation of the resistance of Pt with temp. may be expressed by an equation with five consts. A. J. M.

**F.p. of palladium.** F. H. SCHOFIELD (Proc. Roy. Soc., 1936, A, 155, 301—308).—The f.p. of Pd, determined by measuring the ratio of brightness of black-body radiators held at the f.p. of Pd and Au, is  $1554.4 \pm 1^\circ$ , confirming the val.  $1555^\circ$  recommended in the specification for the International temp. scale. L. L. B.

**Representation of specific heats as a function of temperature.** P. DROSSBACH (Z. Elektrochem., 1936, 42, 372—373).—Theoretical. O. J. W.

**Electronic heat capacities of platinum and of copper.** J. A. KOK and W. H. KEESOM (Physica, 1936, 3, 872).—Preliminary. Equations are given for  $C_v$  of Pt and Cu valid for  $T < 14^\circ$  and  $T < 5^\circ$ , respectively. The electronic heat capacity of Pt is several times, and of Cu 1.5 times, the val. calc. for free electrons. O. D. S.

**Effect of rotational distortion on the thermodynamic properties of water and other polyatomic molecules.** E. B. WILSON, jun. (J. Chem. Physics., 1936, 4, 526—528).—Mathematical. Correction terms to be added to the free energy, entropy, and heat capacity,  $C_v$ , calc. for rigid rotation to allow for rotational distortion of the mols. have been calc. for  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ . The correction for  $\text{H}_2\text{O}$  is approx. 0.5% of  $C_v$  and 0.032 e.u., but for heavy mols. the effect is quite small. J. G. A. G.

**Internal latent heat of vaporisation and orthobaric densities.** B. N. GREBENSCHTSCHIKOV (Bull. Univ. Asie Centrale, 1934, No. 19, 15—22).—The internal latent heat of vaporisation of a liquid is given by  $q - k(d_1 - d_2)^{n-1/3}$ , where  $k$  and  $n$  are consts., and  $d_1$  and  $d_2$  are the orthobaric densities of the liquid and vapour. R. T.

Internal and total latent heats of vaporisation of liquids, and their saturated vapour pressure. N. A. DE KOLOSOVSKI and A. ALIMOV (Bull. Univ. Asie Centrale, 1934, No. 19, 33—40).—Vals. are recorded for COMeEt, COMePr, MeI, EtI, EtBr, Et<sub>2</sub>CO, NH<sub>4</sub>Et, *cyclo*-hexane and -hexanone, and formulae connecting latent heat with v.p. and temp. are derived. R. T.

Application of kinetic theory to the problems of evaporation and sublimation of gases having more than one atom per molecule. H. A. GIDDINGS and P. D. CROUT (J. Math. Phys. Mass. Inst. Tech., 1936, 15, 124—178; cf. this vol., 558).—Mathematical. The conceptions developed previously are extended to polyat. gases, and comprehensive data and tables are furnished. J. W. S.

Volatility of red phosphorus. P. N. RAIKOV (Z. anorg. Chem., 1936, 228, 127—128).—No detectable volatilisation occurs at 100° and 0.5 mm. or on storage at room temp. for 1 year. E. S. H.

Vapour pressure of small drops and crystals. A. FRUMKIN and N. FUCHS (Acta Physicochim. U.R.S.S., 1935, 3, 783—790).—A kinetic derivation of the Kelvin equation for the v.p. of liquid droplets is given and the correction applicable to the equation in the case of cubical crystals has been derived. R. S.

Ruff's method for measurement of vapour pressures at high temperatures. Vapour pressures of zinc, cadmium, magnesium, calcium, strontium, barium, and aluminium fluorides. L. LE BOUCHER (Anal. Fis. Quím., 1934, 32, 1142—1156).—The v.p. of liquid ZnF<sub>2</sub>, CdF<sub>2</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>, and solid AlF<sub>3</sub> at different temp. have been measured by Ruff's spring-balance method. The calc. b.p./760 mm. are 1500°, 1748°, 2260°, 2500°, 2460°, and 2260° for the liquid fluorides, respectively; the calc. sublimation point for AlF<sub>3</sub> is 1260°. The curves log v.p.—1/T are straight lines which, in the case of the liquid fluorides, meet in a point when produced. The vals. of Trouton's const. are calc. L. A. O'N.

Evaporation from irregular surfaces. H. W. MELVILLE (Trans. Faraday Soc., 1936, 32, 1017—1020).—The effect of cracks in a surface on the v.p. (as determined by mol. distillation) is treated theoretically. If the condensation coeff. is 1 there is no increase in the rate of evaporation, but if it is <1 the rate of evaporation is increased by a relatively small factor, e.g., 1.3 for a condensation coeff. of 0.1. O. J. W.

Vapour pressure of red phosphorus. H. W. MELVILLE and S. C. GRAY (Trans. Faraday Soc., 1936, 32, 1026—1030; cf. this vol., 298).—The v.p. of red P has been redetermined by the method of evaporation in a vac. The vals. are given by  $\log_{10} p(\text{mm.}) = -4110/T + 1.1$ , and are about 10<sup>7</sup> times < the vals. obtained by the normal static method. The discrepancy is due to differences in the position of the equilibrium  $P_4 \rightleftharpoons 2P_2$ . O. J. W.

General physical foundations of real thermodynamics. V. JACZYNA, S. DEREVJANKIN, A. OBNORSKI, and T. PARFENTIEV (Z. Physik, 1936, 101,

77—85).—A discussion of the relations of quantum dynamics and thermodynamics. A. B. D. C.

Determination of the coefficient of accommodation from aspects of the temperature drop effect. H. S. GREGORY (Phil. Mag., 1936, [vii], 22, 257—265).—Mathematical. N. M. B.

Quantum theory of the non-ideal gas. I. Deviations from the classical theory. G. E. UHLENBECK and E. BETH (Physica, 1936, 3, 729—745).—Mathematical. An equation of state for a non-ideal gas is developed quantum-mechanically. The deviations from classical theory become important at low temp., below 75° abs. for He. O. D. S.

Proof of the selection theorem. V. JACZYNA (Z. Physik, 1936, 101, 139—140; cf. A., 1934, 1070). A. B. D. C.

Equations of state and thermodynamic functions for substances with variable specific heat. W. P. BOYNTON (Physical Rev., 1935, [ii], 47, 258).—Theoretical. L. S. T.

Time effects in the magnetic cooling method. I. W. HEITLER and E. TELLER. II. Conductivity of heat. H. FROHLICH and W. HEITLER (Proc. Roy. Soc., 1936, A, 155, 629—639, 640—652).—I. The time *t* necessary for the exchange of energy between the spins of a paramagnetic salt and the lattice vibrations has been calc. For the paramagnetic salts used hitherto for the magnetic cooling method, *t* is small enough for the successful application of the method for temp. >0.1—0.2° abs. and magnetic fields >1500 gauss, but rather too large for lower temp. and magnetic fields. For the nuclear spins in a diamagnetic insulating substance *t* is of the order of 10<sup>6</sup> years, whereas in a metal, *t* is, at 0.1° abs., of the order of 1 sec.

II. In paramagnetic salts at very low temp. the heat conductivity  $\lambda$  is due to the spins rather than to the lattice vibrations.  $\lambda$  (for Fe NH<sub>4</sub> alum)  $\propto T^{-2}$  or  $T^{-3/2}$ , approx., and at 0.06° abs. has a val. of the order 3 ergs per cm. sec. deg. L. L. B.

Thermal conductivity of electrets. G. GROETZINGER (Physikal. Z., 1936, 37, 589—592).—The thermal conductivity of beeswax, paraffin, and solid "cable oil" was determined first for the substances in the ordinary state, and then after they had been melted and allowed to cool in an electric field. The electrets formed by the latter process were found to possess a greater conductivity than the unpolarised substance. A. J. M.

Influence of magnetic fields on the heat conductivity of gases. II. Variation with angle between magnetic field and direction of heat flow. III. Variation with pressure at small gas pressures. H. SEFTLEBEN and J. PIETZNER (Ann. Physik, 1936, [v], 27, 108—116, 117—122; cf. A., 1933, 559).—II. The variation of the magnetic effect with the angle between lines of force and the direction of heat flow is found to be in good agreement with theory. The effect is greatest with magnetic field perpendicular to, and least with field parallel to, the direction of flow.

III. At pressures < 10 mm. the magnetic effect decreases with decreasing pressure, falling to zero



when mean free path is comparable with the dimensions of the containing vessel.

O. D. S.

**Dilatometric studies of pure liquids and azeotropic mixtures.** N. A. DE KOLOSOVSKI and E. N. IVANOVA (Bull. Univ. Asie Centrale, 1935, No. 20, 85—98).—The sp. vol.  $v$  at temp.  $t$  of a no. of liquids is given by  $v = v_0(1 + at + bt^2 + ct^3)$ , where  $v$  is the sp. vol. at  $0^\circ$ , and  $a$ ,  $b$ , and  $c$  are consts. Expressions connecting  $v$  with entropy, sp. heat, and thermodynamic potential are derived for a no. of pure liquids and azeotropic mixtures. The vol. changes associated with mixing the constituents of various azeotropic mixtures are shown to be positive or negative, depending on the temp., and are given by an expression in powers of  $t$ .

R. T.

(A) Thermal expansion of the crystal lattices of cadmium, osmium, and ruthenium. E. A. OWEN and E. W. ROBERTS. (B) Thermal expansion of beryllium. E. A. OWEN and T. L. RICHARDS (Phil. Mag., 1936, [vii], 22, 290—304, 304—311).—(A) Investigation by the X-ray method showed that Cd in the cast and sublimated forms has identical close-packed hexagonal structure;  $a$  2.9723<sub>8</sub>,  $c$  1.8853<sub>2</sub> Å. at  $18^\circ$ ,  $d$  8.646; the sublimated crystals showed a preferred orientation, the basal planes being perpendicular to the vapour stream direction. Expansion curves are given for the range 20—280°; the coeff. of expansion parallel to the hexagonal axis reaches a max. at about  $-160^\circ$  and then decreases continuously up to  $280^\circ$ , whilst the coeff. perpendicular to the axis increases over the range  $-220^\circ$  to  $280^\circ$ . At about  $250^\circ$  Cd is isotropic; there was no evidence of an allotropic change at  $60^\circ$ . Data for Os and Ru parallel and perpendicular to the hexagonal axis are given for the temp. range 20—600°. Coeffs. of linear expansion of Cd, Os, and Ru are tabulated.

(B) Be remained close-packed hexagonal over the range 20—550°;  $a$  2.2812<sub>4</sub>,  $c$  1.5682 Å. at  $20^\circ$ . Data for the coeff. of expansion of Be 99.8% pure are given for the range 20—550° along and perpendicular to the hexagonal axis; the coeff. in each case increases with rise of temp. Coeffs. of linear expansion are tabulated.

N. M. B.

**Expansion of copper from absolute zero to its m.p.** W. J. HARING and W. P. DAVEY (Physical Rev., 1935, [ii], 47, 337—338).—Total expansion has been measured from  $75^\circ$  to  $1356^\circ$  abs. and the curve extrapolated to  $0^\circ$  abs. The expansion from  $0^\circ$  abs. to the m.p. is 3.01% of the length at  $0^\circ$  abs. in agreement with the theory of melting of face-centred cubic substances. Expansion over this range is given by  $l_0(1 + \alpha t + \beta t^2)$  where  $\alpha$  and  $\beta$  are  $2.26 \times 10^{-5}$  and  $-2.44 \times 10^{-9}$ , respectively, between  $200^\circ$  and  $500^\circ$  abs., and  $2.08 \times 10^{-5}$  and  $1.66 \times 10^{-9}$ , respectively, between  $700^\circ$  and  $1200^\circ$  abs.

L. S. T.

**Atomic dimensions from the coefficients of compressibility and thermal expansion.** G. F. DJANG (J. Chem. Physics, 1936, 4, 530—532).—The equation of state for liquids and solids,  $p - K(V_T - V_0)/V_0 - RT/(V_T - V_0)$ , leads to  $\alpha/\beta = R/(V_T - V_0)$  where  $\beta$  and  $\alpha$  denote the coeffs. of compressibility and average thermal expansion, respectively,  $V_T$  and  $V_0$  are the mol. vols. at  $T^\circ$  abs. and  $0^\circ$  abs., respectively,  $R$  is the gas const.,  $p$  is the applied external pressure,

and  $K$  is an arbitrary const. The at. radii of a no. of elements calc. by means of the derived equation and the Loschmidt no. accord with vals. calc. from crystal data. The application of the equation to liquids and non-spherical mols. is discussed.

J. G. A. G.

**Compressibility coefficients of crystals.** V. ZDANOV (Z. Physik, 1936, 101, 86—92).—Morse's formula has been used to calculate the compressibility of Al, Fe, Cu, Ni, Ag, Au, Pt, NaCl, KCl, KBr, diamond, and ZnS crystals.

A. B. D. C.

**Viscosity of solids. Absorption frequencies of metals in the acoustic region.** K. BENNEWITZ and H. ROTGER (Physikal. Z., 1936, 37, 578—588).—The theory of viscosity of solids is treated from the point of view of the logarithmic decrement of periodic vibrations in the solid. The theory is tested by experiment over the frequency range 0.5—500 Hz.

A. J. M.

**Specific volume and gravity of solutions.** P. N. PAVLOV (Acta Physicochim. U.R.S.S., 1935, 3, 756—765).—Expressions are derived for the sp. gr. and sp. vol. of a solution and for the partial sp. gr. and sp. vol. of its components, and for the vol. changes which occur on dissolution.

C. R. H.

**Structure of solutions according to X-ray data.** V. DANILOV (Acta Physicochim. U.R.S.S., 1935, 3, 725—740).—X-Ray data for  $H_2O$  and Hg at low temp. are consistent with the view that at such temp. they are more akin to solids than to liquids. From intensity curves for 5*N*-HCl, 8*N*-HF,  $H_2O$ , 4.4*N*- and 8*N*-LiCl, it would seem, however, that in only a few cases do the data throw any light on the structure of solutions.

C. R. H.

**Magnetic susceptibility of aqueous nitric acid solutions.** S. P. RANGANADHAM and M. QURESHI (Z. physikal. Chem., 1936, B, 33, 290—296).—The susceptibility-concn. curve, which has been determined up to 64%  $HNO_3$ , is not linear and exhibits min. at  $HNO_3 \cdot 50H_2O$ ,  $HNO_3 \cdot 6H_2O$ ,  $HNO_3 \cdot 4H_2O$ , and  $2HNO_3 \cdot 5H_2O$ . The g.-ion susceptibility of the  $NO_3^-$  ion is  $-20.83 \times 10^{-6}$ . There is evidence for the depolymerisation of the  $H_2O$  at the higher concns.

R. C.

**Heats of mixing of anhydrous sulphuric and nitric acids.** R. DALMON (Compt. rend., 1936, 203, 250—252).—Data for the complete range of mixtures are recorded. With 1—8 wt.-%  $HNO_3$ , the heat liberated  $\propto$  the wt. of  $HNO_3$  added, indicating that the heat liberated  $\propto$  the quantity of  $N_2O_5$  formed (cf. this vol., 694).

J. W. S.

**Properties of metallic solutions.** V. K. SEMENTSCHENKO (Acta Physicochim. U.R.S.S., 1935, 3, 749—752).—The surface tension of amalgams of Pb, Sn, Ba, Li, Na, K, Rb, and Cs has been measured. The influence of the solute is determined by the difference between the "generalised moments" of solvent and solute.

C. R. H.

**Viscosity of sodium amalgams.** H. E. BENT and N. B. KEEVIL (J. Physical Chem., 1936, 40, 709—714).—The viscosities of liquid Na and Ag amalgams do not vary with time. No scum forms on Na amalgams in glass containers which have been baked

and evacuated. It is therefore improbable that Na amalgams are colloidal. J. W. S.

**Solidification diagram and electric conductivity of potassium-cæsium alloys.** E. RINCK (Compt. rend., 1936, 203, 255—257; cf. this vol., 559).—The liquidus and solidus curves show a sharp min. at  $-37.5^\circ$  for a 1:1 mixture. The conductivity isotherm for  $-39^\circ$  shows a min. at the same composition. The eutectic K+Cs is therefore a mixture and not a compound. No compound analogous to  $\text{Na}_2\text{Cs}$  could be detected. J. W. S.

**Thermal and electrical conductivities of copper alloys.** C. S. SMITH and E. W. PALMER (Amcr. Inst. Min. Met. Eng., Inst. Met. Div., 1935, Tech. Publ. 648, 19 pp.; cf. A., 1932, 157).—Thermal and electrical conductivities at  $20^\circ$  and  $200^\circ$  have been determined for binary alloys with Si, Al, Mn, or Ni and for various ternary alloys. In the binary alloys an increase in the amount of the second element in the  $\alpha$ -solid solution range decreases the conductivity and increases the Lorenz ratio. The thermal conductivity of the alloys increases with temp.

CH. ABS. (e)

**Thermal expansion of copper-beryllium alloys.** P. HIDNERT (J. Res. Nat. Bur. Stand., 1936, 16, 529—548).—The coeff. of expansion ( $\epsilon$ ) of Cu-Be alloys containing 1.33, 2.14, and 3.03% of Be has been determined at  $20$ — $300^\circ$ . In the expansion curves for the 1.33 and 2.14% alloys crit. regions appear due to structural changes which are accelerated by cold-working or tempering. The influence of Be on  $\epsilon$  is much  $<$  that on the tensile strength. R. S. B.

**Optical constants of copper-nickel alloys.** N. F. MOTT (Phil. Mag., 1936, [vii], 22, 287—290; cf. A., 1935, 1063).—The data reported by Lowery (cf. *ibid.*, 1065) are interpreted in terms of electronic configuration and are related to the magnetic properties of the alloys. N. M. B.

**Metals and alloys. XIX. Crystal structure of intermetallic phases MgAu and MgHg.** G. BRAUER and W. HAUCKE (Z. physikal. Chem., 1936, B, 33, 304—310; cf. this vol., 143).—These have the space-centred cubic lattice of  $\beta$ -brass. MgAu cryst. from an alloy with 48.7 at.-% Mg has  $a\ 3.259 \pm 0.001$  Å, and MgHg cryst. from an alloy with 50.8 at.-% Mg has  $a\ 3.443 \pm 0.002$  Å. Both are formed from their components with contraction, the amount of which is apparently related to the hardness of the alloys. MgHg does not obey Hume-Rothery's rule. R. C.

**Thread diagram of lead alloys.** W. HOFMANN (Naturwiss., 1936, 24, 507—508).—A Pb-Sb alloy (—% Sb) heated for 4 days at  $235^\circ$  gave a thread diagram when investigated by the X-ray method. After 2 weeks the Debye-Scherrer curves had become discontinuous, indicating that recrystallisation had occurred. A. J. M.

**Photo-electric effect of metallic alloys. II.** L. BELLADEN and G. GALLIANO (Annali Chim. Appl., 1936, 26, 263—266; cf. this vol., 420).—The photo-electric sensitivity curves of Cd-Sb and Cu-Sb alloys give max. vals. corresponding with  $\text{CdSb}$  and  $\text{Cu}_2\text{Sb}$ , respectively. F. O. H.

**Constitution of cadmium-tin alloys.** D. HANSON and W. T. PELL-WALPOLE (J. Inst. Metals, 1936, 59, Advance copy, 267—290).—The system has been re-examined by micrographic and electric resistance methods. A peritectic reaction occurs at  $223^\circ$  between  $\alpha$  (0.9% Cd) and liquid (3.7% Cd) to form a  $\beta$ -phase (1.9% Cd). At  $176^\circ$  the  $\beta$ -field extends from 3.9 to 5.7% Cd and below this temp. the solubility of both Cd and Sn in  $\beta$  decreases continuously to  $133^\circ$ , at which the  $\beta$  decomposes into the  $\alpha$ - $\gamma$  eutectoid (5% Cd). Thermal arrests previously observed at various intermediate temp. are attributed to hysteresis effects in connexion with the above changes. The solid solubility of Sn in Cd is 0.25% at the eutectic temp. ( $176^\circ$ ) and somewhat less at lower temp. A. R. P.

**Iron-chromium alloy system.** E. R. JETTE and F. FOOTE (Met. and Alloys, 1936, 7, 207—210).—Annealing of alloys approximating to FeCr leads under certain conditions to the formation of a new phase ( $\Sigma$ ), having a very complex structure. The transformation of  $\alpha$  into  $\Sigma$  does not occur when only a very small amount of impurity is present and the alloy is homogenised by a prolonged anneal at  $1300^\circ$ , but if the metal is cold-worked after annealing at high temp. and then reannealed at  $< 800^\circ$ , conversion of  $\alpha$  into  $\Sigma$  is practically complete in 2 days. This transformation is strictly reversible and is considerably accelerated by the presence of 0.09% Si in the alloy. The  $\Sigma$  phase is non-magnetic and very brittle; it appears to be a secondary solid solution and its transformation temp. is between  $775^\circ$  and  $800^\circ$ . A. R. P.

**Solid solutions of indium and lead.** N. AGEEV and V. AGEVA (J. Inst. Metals, 1936, 59, 235—242).—The system has been examined by X-ray and thermal analysis. There is no eutectic but a peritectic horizontal; liquid +  $\beta = \alpha$  at  $154^\circ$  extends from 0 to 38 at.-% Pb. The  $\alpha$ -In-rich solid solution extends to about 15 at.-% Pb at room temp. and to about 32 at.-% Pb at  $154^\circ$ . The  $\beta$ -Pb-rich solid solution extends to 62% In and its composition is unaffected by temp. changes. A. R. P.

**Magnetic susceptibility and change of state of hardenable aluminium-copper alloys.** H. AUER (Z. Metallk., 1936, 28, 164—175).—Measurements of the paramagnetic susceptibility  $\chi$  of Cu-Al alloys in the homogeneous and heterogeneous states afford a means of calculating the proportions of solid solution and  $\text{CuAl}_2$  in the alloy, i.e., of determining the solid solubility of Cu in Al at various temp. The vals. obtained in this way are  $20^\circ$ , 0.3;  $300^\circ$ , 0.5;  $400^\circ$ , 1.3;  $500^\circ$ , 4; and  $548^\circ$  (eutectic temp.) 5.65%. Measurements during ageing of quenched alloys show that the change in  $\chi \propto$  the enrichment of free Cu atoms in the lattice and is not subsequently affected by a remodelling of the lattice. The enrichment of the Cu atoms before and during the pptn. follows a simple exponential law,  $dc/dt = A \cdot D/t$ , where  $dc$  is the amount of Cu separating in time  $dt$  at  $T^\circ$ . The mechanism of pptn. is discussed at length with reference to the  $\chi$ -time, -temp., and -concn. curves obtained in the experimental work. A. R. P.



**Ternary system aluminium-magnesium-zinc ; region aluminium-Al-Mg<sub>3</sub>Zn<sub>3</sub>-MgZn<sub>2</sub>-Zn.** W. KOSTER and W. WOLF (Z. Metallk., 1936, 28, 155—158).—The section Al-Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub> forms a pseudo-binary system with a eutectic at 489°, Al 39, Mg 17, and Zn 44%; at the eutectic horizontal the solid solution extends to Al 76, Mg 7, and Zn 17% at the Al end and to Al 25, Mg 21, and Zn 54% at the other end. In the Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub>-MgZn<sub>2</sub> section the ternary compound is formed by a peritectic reaction at 535° and its field of homogeneity extends to Al 13, Mg 21, and Zn 66% on the MgZn<sub>2</sub> side. In the ternary Al-Mg-Zn system the eutectic and peritectic equilibria are displaced to lower temp. and terminate in the 4-phase equilibrium at 375°: liquid (Al 18, Mg 11, Zn 61%) + ternary compound (Al 16, Mg 20, Zn 64%) =  $\alpha$  (Al 71, Mg 4.5, Zn 24.5%) +  $\eta$  (Al 4, Mg 15.5, Zn 82.5%). At the Zn corner the Zn-rich eutectic contains Al 4 and Mg 2% at 350°. In the solid state the reaction  $\alpha' + \eta \rightleftharpoons \alpha + 0$  takes place at 325° and  $\alpha' \rightleftharpoons \alpha + 0 + \text{Zn}$  at 280°. A. R. P.

**Solubility of lithium in magnesium.** W. HOFMANN (Z. Metallk., 1936, 28, 160—163).—X-Ray examination shows the solubility of Li in Mg to be 5.7% irrespective of the temp. The  $d$  of the alloys falls with the Li content from 1.741 to 1.587 with 0—4.85% Li, but the Brinell hardness remains almost const. at 31.5—35. A. R. P.

**Behaviour of two non-miscible liquids illustrated by two wire models.** E. JANECKE (Angew. Chem., 1936, 49, 603—605).—Three-dimensional wire models are described which represent the phase relationships of various types of two-component liquid systems of incomplete miscibility as a function of temp. and pressure. J. W. S.

**Diffusion of hydrogen through iron and palladium.** W. R. HAM and J. D. SAUTER (Physical Rev., 1935, [ii], 47, 337).—The rate of diffusion of H<sub>2</sub> through Fe may be considerably modified by heat-treatment of the Fe in various atm.; e.g., Fe exposed to N<sub>2</sub> may have its diffusion rate for H<sub>2</sub> increased 10 to 15 times, but after baking out at higher temp. the diffusion curve regains its normal character. Diffusion isotherms for Fe and Pd are represented by  $r = A_1 p^{1.0}$  for slow rates and  $r = A_2 p^{0.5}$  for high rates. L. S. T.

**Equilibria in liquid mixtures and solutions. II. Solubility of carbonyl chloride in certain solvents at pressures less than atmospheric.** V. A. KIRIEV, S. I. KAPLAN, and K. I. VASNEVA (J. Gen. Chem. Russ., 1936, 6, 799—805).—Solubility data are recorded for COCl<sub>2</sub> in xylene at -15°, 0°, and 20°, in PhCl at 0°, in C<sub>6</sub>H<sub>6</sub>, PhMe, C<sub>2</sub>HCl<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, CCl<sub>4</sub>, and paraffin at 20°, for pressures < 1 atm. R. T.

**Influence of pressure on the solubility of gases.** A. MICHELS, J. GERVER, and A. BIJL (Physica, 1936, 3, 797—808).—Data are given for the solubility at 25° of CH<sub>4</sub> in H<sub>2</sub>O and aq. solutions of NaCl, LiCl, KCl, CaCl<sub>2</sub>, NaBr, NaI, sucrose, glucose, and CH<sub>3</sub>O at pressures between 40 and 450 atm. For H<sub>2</sub>O and aq. NaCl vals. are also recorded up to 150°. A general solubility formula is developed and discussed. O. D. S.

**Solubility of thorium in mercury.** W. G. PARKS and G. E. PRIME (J. Amer. Chem. Soc., 1936, 58, 1413—1414).—Hg dissolves about 0.014 at.-% of Th at 25°. E. S. H.

**Solubility of ammonium phosphates and formation of two liquid phases at higher temperatures.** E. JANECKE (Z. physikal. Chem., 1936, 177, 7—16).—Equilibrium conditions for the system NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub> have been determined up to 250° and 25% NH<sub>3</sub>. The diagram for the system H<sub>2</sub>O-NH<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub> has been derived up to 225° and 30% NH<sub>3</sub>; at higher temp. and [NH<sub>3</sub>] two liquid phases are present at equilibrium. R. C.

**Solubility in the system KCNS-H<sub>2</sub>O.** F. C. KRACEK (J. Washington Acad. Sci., 1936, 26, 307—313).—Data are recorded from 32° to the m.p., 176.8°, of KCNS. The transition KCNS II  $\rightarrow$  KCNS I occurs at 140.6°, and the calc. metastable m.p. of KCNS II is 171.6°. J. G. A. G.

**Physical studies of non-aqueous solvates. I. Solubility of magnesium bromide in ethyl ether.** H. H. ROWLEY (J. Amer. Chem. Soc., 1936, 58, 1337—1341).—Data for the range -20° to 30° are recorded. The presence of a small amount of H<sub>2</sub>O causes an increase in apparent solubility. The existence of MgBr<sub>2</sub>·3Et<sub>2</sub>O and MgBr<sub>2</sub>·2Et<sub>2</sub>O is confirmed. E. S. H.

**Interaction between ions and molecules in solutions.** P. GROSS (Acta Physicochim. U.R.S.S., 1935, 3, 583—592).—Data for the influence of glycine, CO(NH<sub>2</sub>)<sub>2</sub>, EtOH, COMe., and Pr<sup>o</sup>OH on the solubility in H<sub>2</sub>O of the sparingly sol. salts TiBrO<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>5</sub>Cl]S<sub>2</sub>O<sub>3</sub>, [Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]Fe(CN)<sub>6</sub>·0.5H<sub>2</sub>O, and LaCo(CN)<sub>6</sub>·4.5H<sub>2</sub>O are in agreement with the theory that the addition of neutral mols. alters the chemical potential of the ions by changing the dielectric const. and by solvation; the latter effect is independent of the concn. if the neutral mols. are very dil. and do not react with the ions. Debye's theory was tested by measuring the extinction coeff. of picrate ions in aq. EtOH. The val. of the coeff. increases with addition of H<sub>2</sub>O until in presence of approx. 0.9 mol. H<sub>2</sub>O the coeff. has the same val. as in pure H<sub>2</sub>O. This is attributed to sufficient dipolar mols. of H<sub>2</sub>O being present to surround completely the picrate ion. C. R. H.

**Crystallisation processes in potassium chloride solutions.** R. KOPPEN (Z. anorg. Chem., 1936, 228, 169—174).—In the crystallisation of aq. KCl the no. of nuclei formed varies with the degree of undercooling in a similar way to that observed by Tammann with melts. More nuclei are formed in KCl-NaCl solutions than in KCl for the same degree of undercooling. Spontaneous formation of nuclei is rapid in agitated solutions containing crystals, but very slow or absent in stationary solutions containing no crystals. E. S. H.

**Post-precipitation of zinc sulphide with mercuric sulphide.** I. M. KOLTROFF and R. MOLTZAU (J. Physical Chem., 1936, 40, 779—798).—HgS promotes post-pptn. of ZnS from acid solutions, the effect being  $\gg$  that of CuS. This is explained by a primary adsorption of ZnS on the HgS, with sub-

sequent pptn. of the latter. Substances which replace adsorbed  $\text{H}_2\text{S}$  or ions competing with  $\text{Zn}^{++}$  ions in their adsorption inhibit post-pptn. Very slow post-pptn. occurs in  $2N\text{-H}_2\text{SO}_4$ , although freshly pptd.  $\text{ZnS}$  dissolves at this acidity. Under these conditions the ppt. is of the aged form. Ageing of  $\text{HgS}$  decreases its effect in promoting post-pptn., probably owing to agglomeration of the particles and to the transformation from meta-cinnabar to cinnabar. The temp. of its pptn. has little effect on the activity of the  $\text{HgS}$ .  $\text{ZnS}$  post-pptd. with  $\text{HgS}$  cannot be completely extracted with  $3N\text{-HCl}$  at room temp. The  $\text{ZnS}$  penetrates the  $\text{HgS}$  lattice, yielding limited mixed crystal formation. The extent of post-pptn. diminishes greatly with decreasing partial pressure of  $\text{H}_2\text{S}$ .

J. W. S.

**Absorption of gases by mercury.** S. PRITZL (Tech. Phys. U.S.S.R., 1935, 2, 66—78; 5, 329—342).—Multiple distillation in vac. is necessary to remove all adsorbed gases. Org. compounds and org.  $\text{Hg}$  compounds are not removed by this means. Purified  $\text{Hg}$  in contact with air is freed from adsorbed gases by one distillation.  $\text{Hg}$  at  $150\text{--}200^\circ$  in contact with the vapour of benzene,  $\text{C}_6\text{H}_6$ , or  $\text{PhMe}$  at  $0.001\text{--}0.01$  mm. pressure rapidly forms  $\text{Hg}$  compounds, which are removed by passing the vapour through a hot tube. Adsorption of  $\text{H}_2$  on a  $\text{Hg}$  monocrystal in process of formation gives 0.6 of a unimol. layer.

CH. ABS. (e)

**Adsorption of gases by glass walls. XII. Ammonia on Jena glass.** Kinetics of the adsorption. M. CRESPI and V. ALEXANDRE (Anal. Fis. Quim., 1934, 32, 666—676; cf. A., 1926, 1002).—The apparatus previously used has been made more sensitive. The quantity of  $\text{NH}_3$  adsorbed by 1 sq. cm. of Jena glass at 760 mm. is  $15.4 \times 10^{-5}$  c.c., i.e., about one third the val. for ordinary glass. The correction to be applied to 1 litre of  $\text{NH}_3$  at 760 mm. contained in a spherical Jena glass vessel is  $5.6 \times 10^{-5}$  g. The results for  $p=50$  to 760 mm. agree with those calc. from Freundlich's equation. The velocity of adsorption at const. pressure is given by  $dy/dt = kx_e(y_e - y)/y$ , where  $y$  is the concn. at time  $t$ ,  $x_e$  the pressure, and  $y_e$  the equilibrium concn.  $k$  remains const. from 50 to 760 mm.

L. A. O'N.

**Kinetics of adsorption. II. Equations for the velocity of adsorption and their experimental verification.** M. CRESPI (Anal. Fis. Quim., 1934, 32, 639—657; cf. A., 1935, 587).—Equations for the velocity of adsorption are deduced. The relation between the velocity coeff. and the energy of activation of the gas, and also the derivation of Langmuir's isotherm from the equation of state of the gas in the two phases, are discussed theoretically. The equations are tested by reference to experimental results.

L. A. O'N.

**Sorption equilibria of methane, ethane, and propane with active carbon above and below the critical temperature.** E. WEINGAERTNER (Z. Elektrochem., 1936, 42, 599—606).—Deviations of the isotherms from straight lines in the linear region below the crit. temp. indicate the existence of a two-dimensional condensed phase. Above the crit.

temp., the quotient of the mol. heat of sorption and the abs. crit. temp. is approx. const. E. S. H.

**Adsorption by agate powders in relation to the artificial colouring of agates.** L. HOOK and O. BECKER (Kolloid-Beih., 1936, 44, 238—253).—The adsorption of  $\text{H}_2\text{O}$  vapour by powdered agates after different treatments (extraction with conc.  $\text{HCl}$ , 15%  $\text{NaOH}$ , light petroleum, conc.  $\text{HNO}_3$ , saturated aq.  $\text{Na}_2\text{CO}_3$ ) has been determined. Heats of adsorption have been measured. The surface of the different samples was measured by adsorption of methylene-blue.

E. S. H.

**Adsorption of electrolytes by crystalline surfaces. VI.** (MLLE.) L. DE BROUCKERE (Bull. Soc. chim. Belg., 1936, 45, 353—374; cf. A., 1932, 689; 1935, 359).—The  $\log x\text{-log } c$  curves ( $x$ =electrolyte adsorbed,  $c$ =concn. of solution) at  $25^\circ$  are plotted for  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ ,  $\text{CsCl}$ ,  $\text{NaBr}$ ,  $\text{KBr}$ ,  $\text{LiI}$ ,  $\text{NaI}$ , and  $\text{KI}$ , adsorbed on negatively-charged  $\text{BaSO}_4$  (pptd. in presence of excess of  $\text{SO}_4^{--}$ ), and for  $\text{RbCl}$ ,  $\text{CsCl}$ , and  $\text{LiI}$  on positively-charged  $\text{BaSO}_4$  (pptd. in presence of excess of  $\text{Ba}^{++}$ ). These, together with previous results, indicate that positively-charged  $\text{BaSO}_4$  adsorbs anions directly, and cations as a secondary layer, whilst the reverse is true when the  $\text{BaSO}_4$  is negative; the ions directly adsorbed form a unimol. layer. In solutions below  $0.01N$  ( $\text{BaSO}_4$  surface far from saturated) anions are adsorbed by positive  $\text{BaSO}_4$  in the order  $\text{Cl} < \text{Br} < \text{I}$ , whilst for negative  $\text{BaSO}_4$  the order is  $\text{Li} < \text{K}$ ,  $\text{K} < \text{Cs}$ , indicating that ionic deformation comes into play. R. C. M.

**Active oxides. C. Sorptive capacities of the active states through which needle iron ore passes during dehydration.** G. F. HUTTON and K. NEUMANN (Z. anorg. Chem., 1936, 228, 213—231; cf. this vol., 790).—Changes in the sorptive capacity for  $\text{MeOH}$  vapour indicate that the ore passes through four stages on dehydration: (1) homogeneous transformation of a single phase varying between  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3 \cdot 0.8\text{H}_2\text{O}$ , (2) separation into two phases of the  $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\alpha\text{-Fe}_2\text{O}_3$  types, between  $\text{Fe}_2\text{O}_3 \cdot 0.8\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3 \cdot 0.6\text{H}_2\text{O}$ , (3) further dehydration from 0.6 to  $0.2\text{H}_2\text{O}$ , (4) recrystallisation to anhyd.  $\alpha\text{-Fe}_2\text{O}_3$ .

E. S. H.

**Adsorption of barium hydroxide by humic acids.** K. I. SISKOV (Kolloid-Z., 1936, 76, 153—159).—Data for different preps. of humic acids show that the adsorptive power for  $\text{Ba}(\text{OH})_2$  can be used to characterise humic acids.

E. S. H.

**Laws governing the cation-exchanging properties of a precipitated aluminium silicate.** R. C. BACON (J. Physical Chem., 1936, 40, 747—761).—It is shown theoretically that the cation-exchange capacity of a colloidal  $\text{Al}$  silicate depends on the  $p_H$  of the solution and on the nature and concn. of the salts present. The conclusions have been tested for a specially prepared silicate. Most of the  $\text{Na}$  in this silicate is replaceable by an equiv. amount of  $\text{Ag}$ , but the remainder is non-exchangeable. The exchange capacity varies with the age of the sample. Its val. has been measured in presence of various salts ( $0.1N$ ) and at various  $p_H$  vals.

J. W. S.



Recovery of vapours of volatile solvents by adsorbents. III. Production of ethyl peroxide in the recovery of ethyl alcohol-ether vapour. E. V. ALEXEEVSKI and G. M. MOSKVIN (J. Appl. Chem. Russ., 1936, 9, 1010—1016).—Formation of Et peroxides does not occur when the vapour is adsorbed by or desorbed from active C in presence or absence of Fe or O<sub>2</sub>; only traces are formed after prolonged exposure of saturated adsorbent to atm. O<sub>2</sub>. R. T.

Study of adsorption in solution by means of cryoscopy. G. ODDO and E. CORSINI (Gazzetta, 1936, 66, 409—417).—By means of f.-p. measurements the adsorption of Pr<sup>2</sup>CO<sub>2</sub>H by animal C from aq. solution has been studied. The results do not agree with any of the usual adsorption formulæ, and the adsorbent manifests hysteresis phenomena. With C<sub>6</sub>H<sub>6</sub>, PhNO<sub>2</sub>, and AcOH as solvents there is no adsorption. The mechanism of the adsorption from H<sub>2</sub>O is considered to depend on the dissociation of adsorbed (H<sub>2</sub>O)<sub>2</sub> mols. O. J. W.

Effect of oxygen on the clean-up of phosphorus vapour by tungsten filaments. H. W. MELVILLE and S. C. GRAY (Trans. Faraday Soc., 1936, 32, 1020—1025; cf. this vol., 298).—When a W filament is covered with a layer of O atoms the dissociation of P<sub>4</sub> mols. on it is completely inhibited. Dissociation on a partly oxidised filament occurs entirely on the clean W surface. In the hetero-homogeneous reaction between P<sub>4</sub> and O<sub>2</sub> in presence of W, the surface of the latter is covered with a layer of P on the top of which are O atoms or O<sub>2</sub> mols. The evaporation of a lower oxide from this composite layer initiates the stable chain reaction. O. J. W.

Theory of the Freundlich isotherm. H. ZEISE (Acta Physicochim. U.R.S.S., 1935, 3, 163—164).—Polemical against Zeldovitch (cf. A., 1934, 1316).

A. J. M.

Statistical theory of adsorption with interaction between the adsorbed atoms. R. PEIERLS (Proc. Camb. Phil. Soc., 1936, 32, 471—476).—Mathematical. O. D. S.

Life period of particles in the adsorbed state. D. BLOCHINZEV and S. SCHECHTER (Acta Physicochim. U.R.S.S., 1935, 3, 767—778).—A formula applicable to light mols. adsorbed on a heavy adsorbent is given and the zero-point energy of the adsorbed particle has been calc. R. S.

Surface spreading and surface dissolution of positively adsorbed substances. T. F. FORD (J. Physical Chem., 1936, 40, 835—836).—All substances which lower the surface tension of H<sub>2</sub>O spread in the surface to form films, this spreading being an intermediate step in the process of dissolution. These materials introduced into a clean talc-dusted surface cause the production of a circular talc-free patch, which quickly contracts and disappears when the sol. material is withdrawn or totally immersed in the H<sub>2</sub>O. This surface spreading is a factor which probably hastens dissolution. J. W. S.

Measurement of molecular areas of cellulose from different sources by surface tension. II. J. K. CROWDHURY and T. P. BARDHAN (J. Indian

Chem. Soc., 1936, 13, 294—300).—Data for the surface tension,  $\gamma$ , of viscose solutions at concns. up to  $c=0.2\%$  have been applied to the calculation of the size of the cellulose mol. Assuming that a unimol. layer exists in the surface after  $\gamma$  has reached a const. val., the mol. area =  $RT \cdot d \log c/N \cdot d\gamma$  sq. cm. For cotton, jute, and bamboo cellulose the areas are respectively 571, 263.1, and 129.5 sq. Å. C. R. H.

Wetting characteristics of solids of low surface tension, such as talc, waxes, and resins. F. E. BARTELL and H. H. ZUIDEMA (J. Amer. Chem. Soc., 1936, 58, 1449—1454).—H<sub>2</sub>O and org. liquids of high surface tension form finite contact angles on waxes and resins in air, showing that the surface tension of the solids is low. The data obtained with talc confirm the Bartell-Osterhof equation relating adhesion tension and interfacial contact angles. E. S. H.

Rearrangement of molecules in plastic unimolecular films: pressure-area and potential relations for polycyclic compounds of the five-ring series. W. D. HARKINS, E. F. CARMAN, and H. E. RIES (J. Amer. Chem. Soc., 1936, 58, 1377—1383).—At const. area the pressure disappears almost entirely on keeping, due to shrinkage of the film. Thus the initial pressure appears to be of more significance than the final pressure. The shrinkage produces little effect on the surface potential. At film pressures of 8 dynes per cm. the apparent thickness of the films is approx. that to be expected if mols. with 5 rings stand on end. E. S. H.

Mechanism of the rise of hydrosols and coloured solutions through porous material. II. Influence of the constitution of hydrosols and coloured solutions on the rate of rise. A. BOUTARIC (Bull. Soc. Chim. biol., 1936, 18, 1147—1166; cf. this vol., 793).—The rise of solvent, sol particles, and coloured ions with time is expressed by  $y=At^m$ , in which  $m=0.5$  for the solvent and for negatively charged ions. For negatively charged particles the rise is independent of the concn., but with positively-charged particles it increases with the concn. Dialysis increases the rate of rise of positive particles, and decreases that of negative particles. A. L.

Electrocapillarity. IV. Interpretation of electrocapillarity data. S. R. CRAXFORD, O. GATTY, and H. A. C. MCKAY. V. Definition of surface tension. O. GATTY and H. A. C. MCKAY (Phil. Mag., 1936, [vii], 22, 359—402, 402—409; cf. A., 1935, 698).—IV. The general equation previously deduced is explained and applied to the typical systems Hg, Tl/NaCl, HCl, H<sub>2</sub>O, EtOH which include all electrocapillarity curves obtained by polarising the interphase; Hg, Tl/NaNO<sub>3</sub>, HNO<sub>3</sub>, Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, TiNO<sub>3</sub>, H<sub>2</sub>O, EtOH, in which the restriction of complete polarisability does not apply, and where the potential across the interphase is controlled by altering the composition of the solution; KI, MeNO<sub>2</sub>/KI, H<sub>2</sub>O, where the two solvents are not completely immiscible, and octyl alcohol, C<sub>8</sub>H<sub>17</sub>/octyl alcohol, H<sub>2</sub>O, where a capillary-active solute is distributed between two immiscible solvents. Electrocapillarity curves for NaCl solutions, the structure

of the double layer and the capacities of ions in the layer, dilution shifts, and sp. adsorption are considered. The effect of added non-electrolyte on the electrocapillarity curve and the curves of amalgams are examined.

V. A thermodynamic definition of surface tension is proposed and its relation to the properties of a "physical" surface within the interphase between the two phases is considered. N. M. B.

Adsorption of ovalbumin on collodion membranes. P. DOW (J. Gen. Physiol., 1936, 19, 907—916).—The adsorption of ovalbumin from 4 to 7% aq. solutions by collodion membranes resembles that of gelatin (cf. A., 1925, ii, 1054; 1926, 1100) in reaching apparent saturation vals., which show a max. at  $p_H$  5.0. More conc. solutions yield a different type of adsorption curve. Addition of NaCl to solutions of  $p_H > 5$  tends to diminish the effect of varying the  $p_H$ ; for  $p_H < 5$ , the adsorption is greatly increased. At 25° the adsorption is twice as great as at 1°.

F. A. A.

Saturation of non-volatile substances in aqueous solution. T. KUME (Proc. Imp. Acad. Tokyo, 1936, 12, 164—166).—It is shown that the empirical relation  $p_0/p = (Kn + n_0)/n_0$  where  $p_0$  and  $p$  are the v.p. of water and an aq. solution in which  $n_0$  and  $n$  are the no. of mols. of  $H_2O$  and solute, and  $K$  is a const. characteristic of a given solute, holds for saturated solutions over a large temp. range, and for  $n/n_0 = 0.03$  to 30.0.  $K$  varies with concn. and temp. for unsaturated aq. salt solutions, but becomes independent of temp. for any salt when  $S-X/X_s$  is used instead of concn.,  $X$  representing the concn. and  $X_s$  the corresponding solubility. D. C. J.

Association in solution. II. Determination of mol. wts. of fatty acids in benzene. J. MEISENHEIMER and O. DORNER (Annalen, 1936, 523, 299—301; cf. A., 1930, 1519).—As expected, the apparent mol. wts. of AcOH,  $PrCO_2H$ , stearic and myristic acid, determined cryoscopically in  $C_6H_6$ , decrease towards 1 as the concn. decreases. R. S. C.

Raoult depression in ordinary and heavy water. V. T. CHPLUNKER (Indian J. Physics, 1936, 10, 275—276).—According to Raoult's equation the dissolution of a salt in  $H_2O$  and  $D_2O$  tends to equalise their v.p., the effect being greater at higher temp. and concns. Hence the presence of a sol. salt reduces the efficiency of processes for separating  $H_2O$  and  $D_2O$  which depend on differences of v.p. McKay's theory (A., 1934, 626) of the deficiency of  $D_2O$  in the Dead Sea is criticised, and it is suggested that the high salt content hinders separation of  $D_2O$  and  $H_2O$ . A. J. M.

Fluorescing power of fluorescent solutions excited by ultra-violet radiation. A. BOUTARIC and J. BOUCHARD (Compt. rend., 1936, 203, 167—169).—Data are given for solutions of quinine sulphate, 2:6-OH- $C_{10}H_6SO_3H$ , and aesculin at several  $p_H$  vals. J. G. A. G.

Physico-chemical investigation of iodine solutions. J. A. FIALKOV (Acta Physicochim. U.R.S.S., 1935, 3, 711—724).—Sp. conductivities at 130° and 140° and thermal data for solutions of iodides in

liquid I, have been obtained. Alkali iodides and  $AlI_3$  dissociate to some extent, the simplest scheme being  $(MI)_n \rightleftharpoons (M_xI_{n-m})^m + mI^+$  ( $M$ =metal). The thermal data afford no evidence of polyiodide formation. C. R. H.

Equation of state for strong electrolytes and the virial law. B. N. FINKELSCHEIN (Acta Physicochim. U.R.S.S., 1935, 3, 753—755).—Mathematical. The Gibbs-Helmholtz formula is applied to the derivation of the virial law for strong electrolytes.

C. R. H.

Refraction in solutions of strong electrolytes. A. E. BRODSKI, J. M. SCHERSCHEVER, and N. S. FILIPPOVA (Acta Physicochim. U.R.S.S., 1935, 3, 685—692).—The  $n$  of conc. solutions of strong electrolytes is directly  $\propto$  the concn.,  $c$ . In dil. solutions  $n$  falls below that extrapolated from the data in conc. solutions, and for KCl  $n \propto \sqrt{c}$ . The data are considered to agree with Debye and Hückel's theory. In dil. solutions  $n$  was measured with an interferometer and good agreement with refractometer measurements was obtained. C. R. H.

Dielectric constants of solutions of electrolytes. E. FISCHER (Ann. Physik, 1936, [v], 26, 697—704; cf. A., 1935, 1318).—The dielectric consts. of dil. (0.0001—0.001N) aq. solutions of HCl and  $H_2SO_4$  have been determined. For such solutions the saturation effect plays little or no part.

A. J. M.

Optical behaviour of dissolved ions and its significance for the structure of solutions of electrolytes. IV. Range of validity of Lambert-Beer law in aqueous solutions of inorganic salts. G. KORTUM (Z. physikal. Chem., 1936, B, 33, 243—264; cf. this vol., 1066).—Apart from effects which are attributable to sp. interactions of dissolved ions and mols. with each other, the extinction coeff.,  $\epsilon$ , of a dissolved salt is a function of the  $n$  of the solution. Beer's law is therefore a limiting law valid only for very dil. solutions, the influence of  $n$  being negligible only below  $10^{-2}M$ . The absorption spectra of  $K_3Fe(CN)_6$ ,  $K_4Fe(CN)_6$ ,  $KNO_3$ , and  $K_2Cr_2O_7$  in aq. solution have been determined. For these salts and  $KNO_3$  and  $K_2CrO_4$  Beer's law is valid over a restricted concn. range for  $\lambda\lambda$  within some one absorption band; elsewhere there are notable deviations. With each salt and at all  $\lambda\lambda$ , however,  $\epsilon$  approaches a limiting val. at sufficiently high dilutions, which is determined solely by interaction between the ion and the solvent. This supports the view that the deviations from Beer's law are due, not to the deforming action of Coulomb forces in the ionic atm., but to interionic "chemical" forces or to the perturbed interaction of the ions with the solvent mols.

R. C.

Diffusion of copper sulphate in aqueous solutions of sulphuric acid. A. F. W. COLE and A. R. GORDON (J. Physical Chem., 1936, 40, 733—737).—Measurements at 18° indicate that for a given  $[H_2SO_4]$  the diffusion const.  $k$  of  $CuSO_4$  from aq.  $CuSO_4$  to aq.  $H_2SO_4$  is a linear function of the initial  $[CuSO_4]$ . For low  $[CuSO_4]$ ,  $k$  decreases almost linearly with increasing  $[H_2SO_4]$ , but for more conc.  $CuSO_4$



solutions, increase in  $[H_2SO_4]$  tends to decrease the dependence of  $k$  on  $[CuSO_4]$ . J. W. S.

**Disperse systems in gases.** R. WHYTLOW-GRAY (Trans. Faraday Soc., 1936, 32, 1042—1047).—A summary. J. G. A. G.

**Properties of aerocolloid systems, with regard to their dependence on methods of formation.** K. E. STUMPF and G. JANDER (Trans. Faraday Soc., 1936, 32, 1048—1055).—A crit. survey. J. G. A. G.

**Colloid synthesis by means of gaseous explosions and colloidal-chemical investigations on disperse systems so prepared.** N. SATA (Bull. Chem. Soc. Japan, 1936, 11, 443—455).—The general theory is discussed and some experimental observations are recorded. C. R. H.

**Sedimentation method of finding the number of particles in smokes.** R. WHYTLOW-GRAY, W. CAWOOD, and H. S. PATTERSON (Trans. Faraday Soc., 1936, 32, 1055—1059).—The particles settle on a specially prepared glass surface in a special holder and are counted by means of oblique illumination. The results accord with those given by other methods. J. G. A. G.

**Determination of size distribution in smokes.** H. S. PATTERSON and W. CAWOOD (Trans. Faraday Soc., 1936, 32, 1084—1088).—Circles and discs of different sizes from a graticule in the focal plane of the eyepiece appear superposed on the deposit as seen under a microscope, and permit the size of particles of  $1-25 \times 10^{-5}$  cm. radius to be determined. J. G. A. G.

**Size-frequency of particles in mineral dusts.** H. L. GREEN (Trans. Faraday Soc., 1936, 32, 1091—1098).—The data refer to dusts from flint, sandstone, hæmatite, shale, and asbestos. Most of the particles were of diameter  $< 2 \mu$ , but particles  $< 0.2 \mu$  were not found. The coagulation consts. are  $>$  for heterogeneous smokes. J. G. A. G.

**Cohesion between smoke particles.** R. S. BRADLEY (Trans. Faraday Soc., 1936, 32, 1088—1090).—Theoretical. The conditions under which cohesive forces just balance disruptive forces are considered. Impossibly high temp. would be necessary to disrupt particles of the size usual in smokes, but violent fanning leads to stationary states. J. G. A. G.

**Movement of dust or smoke particles in a temperature gradient.** W. CAWOOD (Trans. Faraday Soc., 1936, 32, 1068—1073).—The clear space observed around a hot body in a smoke is due to the kinetic effect on the smoke particles of the mols. moving in the temp. gradient. At the edge of the space, the smoke as a whole exerts an osmotic pressure opposing the kinetic effect. Experiments support the equations developed. J. G. A. G.

**Nature of the dispersoids in country and town air.** J. H. COSTE (Trans. Faraday Soc., 1936, 32, 1162—1171).—A general discussion. J. G. A. G.

**Determination of the mass and size of atmospheric condensation nuclei.** J. J. NOLAN and V. H. GUERRINI (Trans. Faraday Soc., 1936, 32, 1175—1179; cf., this vol., 425). J. G. A. G.

**Hygroscopic nuclei in formation of fog.** J. C. PHILIP (Trans. Faraday Soc., 1936, 32, 1182—1184; cf. A., 1934, 487).—An air-HCl stream was passed through 0.5N-NaOH containing 0.0009% of  $NEt_3$  and NaCl. When the  $[NaCl]$  was increased, it was found that the free HCl carried over decreases and the quantity of  $NEt_3$  increases slightly. These results confirm the views previously advanced (A., 1930, 855). J. G. A. G.

**Properties and behaviour of disperse systems of aqueous and other volatile particles, i.e., mist, cloud, hygroscopic nuclei, town and country fogs.** G. M. B. DOBSON (Trans. Faraday Soc., 1936, 32, 1149—1152).—A résumé. J. G. A. G.

**Nucleus in and growth of hygroscopic droplets.** H. KOHLER (Trans. Faraday Soc., 1936, 32, 1152—1161).—The  $[Cl^-]$  in rain drops is the same as in the droplets of fogs and clouds. In these the  $[Cl^-]$  is also independent of size, showing that such droplets are not obtained by direct condensation. The thermodynamics of condensation on hygroscopic nuclei are considered. J. G. A. G.

**Sulphuric acid mist.** A. DOOLEY and C. F. GOODEVE (Trans. Faraday Soc., 1936, 32, 1209—1218; cf. A., 1935, 40).—When a  $SO_3$ -air mixture was passed through a tube containing a drop of  $H_2O$ , there was a clear space between the drop and the reaction zone. This confirms a mechanism whereby mist is formed when  $SO_3$  is bubbled through  $H_2O$  or dil.  $H_2SO_4$ .  $H_2O$  and  $SO_3$  form  $H_2SO_4$  so rapidly (*loc. cit.*) that  $SO_3$ , as such, does not reach the  $H_2O$  surface, which is protected by a layer of  $H_2O$  vapour through which only a few  $H_2SO_4$  mols. penetrate. The gas phase therefore becomes supersaturated with  $H_2SO_4$ , and agglomerates or nuclei are formed and carried into a part containing excess of reactant, which is absorbed forming particles of strong light-scattering power. Curves show the manner in which the size of the initial  $H_2SO_4$  nucleus controls the change in droplet size with change of  $H_2O$  v.p. of the medium, and the technical importance is discussed. Pure  $H_2O$  is a better absorbent than conc.  $H_2SO_4$  for  $H_2SO_4$  mist. J. G. A. G.

**Sorption of fogs by liquids.** H. REMY [with W. SEEMANN, A. PANCERAM, and H. FRIEDLAND] (Trans. Faraday Soc., 1936, 32, 1185—1190; cf. A., 1935, 1314).—The dependence of the fall of concn. of a  $H_2SO_4$  fog on the height of the column of  $H_2O$ , KOH, or  $H_2SO_4$  ascended shows that turbulence inside the bubbles is the significant factor, and sedimentation plays no part. The absorptive powers of KOH and  $H_2SO_4$  solutions differ when of equal  $d$ , viscosity, surface tension, or v.p. J. G. A. G.

**Dust-free space surrounding hot bodies.** H. H. WATSON (Trans. Faraday Soc., 1936, 32, 1073—1081).—The thickness of the space increases as the 0.52 power of the temp. difference between the hot body and the ambient air, and inversely as the 0.61 power of the air pressure. The width of the space is independent of the nature and size of the dust particles, but depends on the shape and size of the hot body. The phenomenon is attributed to a differential mol.

bombardment on the particles in the very steep and variable temp. gradient near the hot body.

J. G. A. G.

**Coagulation of smoke by supersonic vibrations.** E. N. DA C. ANDRADE (Trans. Faraday Soc., 1936, 32, 1111—1115).—Theoretical. Spheres at rest in a vibrating medium attract one another if the line of centres is normal to the vibration vector. In the resulting coagulation process, the no. of particles decreases very rapidly initially and then progressively more slowly.

J. G. A. G.

**Experiments on coagulation by supersonic vibrations.** R. C. PARKER (Trans. Faraday Soc., 1936, 32, 1115—1119; cf. preceding abstract).—The rate of coagulation of MgO smoke in air vibrating at a frequency of 220 kc. per sec. accords with Andrade's theory.

J. G. A. G.

**Aggregation of suspended particles in gases by sonic and supersonic waves.** O. BRANDT and E. HIEDEMANN (Trans. Faraday Soc., 1936, 32, 1101—1110).—Photomicrographic and kinematographic observations show that the process of rapid coagulation by sonic waves of frequencies between 5 and 50 kc. per sec. takes place in the sound field. Flowing aerosols are coagulated and pptd. by sufficiently large sound intensities. The process occurs in two stages: in the first, the particles oscillate in the sound waves and aggregate by collision; in the second, the particles are so enlarged as no longer to oscillate, but describe irregular paths. The theory of the processes is discussed.

J. G. A. G.

**Influence of pressure on coagulation of ferric oxide smokes.** W. CAWOOD and R. WHYTLOW-GRAY (Trans. Faraday Soc., 1936, 32, 1059—1064; cf. A., 1933, 460).—The particulate vol.-time curves for the coagulation of  $\text{Fe}_2\text{O}_3$  aerosols prepared photochemically from  $\text{Fe}(\text{CO})_5$  in air at 760, 400, and 200 mm. are linear, but the slope increases as the pressure falls. The smokes formed at the lower pressures originate from primary particles larger than at 760 mm. The limitations of Smoluchowski's theory in these systems are discussed.

J. G. A. G.

**Effectiveness of the collisions of aerosol particles with solid walls.** N. FUCHS (Acta Physicochim. U.R.S.S., 1935, 3, 819—826).—Ultra-microscopic observations indicate that 10—25% of the collisions of aerosol particles with a glass or metal wall appear to be ineffective but it is shown that particles approaching within  $1\ \mu$  are counted as colliding, and that all actual collisions are effective.

R. S.

**Stability and charging of aerosols. II. Experimental.** N. FUCHS and I. PETRANOV (Acta Physicochim. U.R.S.S., 1935, 3, 827—838; cf. A., 1934, 959).—A method of unipolar charging of aerosols is described. The velocity of coagulation of such sols is  $>$  that of uncharged sols although there is an apparent increase in the dispersion due to the more rapid coagulation of the larger, highly charged particles. The coagulation curve of the charged aerosol is approx. linear and the coagulation velocity approx.  $\propto$  the square of the mean particulate charge in accordance with theory. The stability of an

aerosol with a bipolar charge is the same as that of the uncharged sol.

R. S.

**Rate of charging of droplets by an ionic current.** N. FUCHS, I. PETRANOV, and B. ROTZEIG (Trans. Faraday Soc., 1936, 32, 1131—1138).—A narrow cloud jet of oil droplets, 0.5—3  $\mu$  radius, was passed parallel to the axis of a cylindrical electric precipitator and the size and charge of the droplets were determined by the "oscillation" method. Results obtained with c.d. of  $3\text{--}10 \times 10^{-9}$  amp. per sq. cm. and charging times of 0.01—0.02 sec. agree with a theory in which effects due to diffusion of ions and to mirror-forces are neglected.

J. G. A. G.

**Solvation and determination of mol. wt. by the Svedberg ultracentrifuge.** W. D. LANSING and E. O. KRAEMER (J. Amer. Chem. Soc., 1936, 58, 1471—1473; cf. McBain, this vol., 441).—The error due to solvation in binary systems is independent of the partial sp. vols. of the components. The case of ternary systems in which combination occurs between the sedimenting component and one of the other two is discussed.

H. B.

**Solvation phenomena in caseinate and palmitate sols.** B. A. VILENSKI and V. A. PAVLOVA (Kolloid-Z., 1936, 76, 188—191).—The solubility of  $\text{PhOH}$  and  $\text{NH}_2\text{Ph}$  in K caseinate sols increases with the concn. of the sol; the solubility of  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , and  $\text{PhCl}$  is unchanged. The solubility of  $\text{C}_6\text{H}_6$  in K palmitate sols increases with the concn. of the sol. The observations are discussed in terms of solvation.

E. S. H.

**Relation between the viscosity and the concentration of cellulose nitrate solutions.** C. DE LEIZAOLA (Anal. Fis. Quim., 1934, 32, 1116—1123).—The  $\eta$  of solutions of cellulose nitrate (I) in  $\text{COMe}_2$  over the concn. range 2—40% is given by  $\log \eta = k \log c + m$ , where  $k$  is approx. const. (4.7—5.4) for all samples of (I), but varies with the temp., and  $m$  is a const. depending on the mol. wt. of the particular sample.

D. R. D.

**Role of dielectric constant, polarisation, and dipole moment in colloid systems. XVI. Swelling and solubility of cellulose acetate in ternary liquid mixtures.** W. L. H. MOLL (Kolloid-Z., 1936, 76, 200—210).—Data for  $d$ ,  $n$ , dielectric const., and mol. polarisation are recorded for the systems  $\text{EtOH-CHCl}_3\text{-H}_2\text{O}$ ,  $\text{EtOH-C}_6\text{H}_6\text{-H}_2\text{O}$ , and  $\text{EtOH-C}_6\text{H}_6\text{-COMe}_2$ . The swelling and solubility of cellulose acetate in the same mixtures have been determined; the results are discussed in the light of the above data.

E. S. H.

**Effect of emulsifier concentration on globule size and viscosity in emulsions.** C. L. WILSON and J. B. PARKE (Quart. J. Pharm., 1936, 9, 188—197).—Vals. of  $\eta$  for homogenised and non-homogenised emulsions of  $\text{C}_6\text{H}_6$  (concn. of 70%; cf. B., 1936, 75) dispersed in aq. Na oleate (vals. of  $\eta$  of which are given for 0.1—10.0%) indicate that homogenisation removes the irregularities occurring in  $\eta$  (excepting with low concns. of emulsifier) due to variations in globule-size of the disperse phase and in the emulsion itself.

F. O. H.



**Spinning properties of liquid systems.** H. ERBRING (Kolloid-Beih., 1936, 44, 171—237).—Apparatus for determining the spinning properties is described and results for different types of colloidal solutions are given. The connexion with  $\eta$ , surface tension, and liquid structure is discussed. In general, the property is at a max. in lyophilic colloid systems when separation of phases is occurring, e.g., in the sol-gel transformation. E. S. H.

**Velocity-gradient methods in rheology.** E. G. RICHARDSON (Physics, 1935, 6, 273—277).—Methods for determining  $\eta$  as a function of shear are discussed. Velocity gradients for starch in a  $\text{CCl}_4$ -paraffin mixture have been studied in a Couette-type viscosimeter with a hot wire. CH. ABS. (e)

**Osmotic pressure of gum arabic.** II. "Mol. wt." with different bases. H. B. OAKLEY (Trans. Faraday Soc., 1936, 32, 1360—1364; cf. A., 1935, 297).—At concns.  $\leq 0.3\%$  of gum the mean particle wt. of the salts formed with Li, Na, K, Ag, or Pb is  $220,000 \pm 10\%$ , and with Ca  $245,000 \pm 2\%$ . At  $< 0.3\%$  of gum, the particle wt. of Na gum increases, reaching 245,000 at  $0.15\%$ . E. S. H.

**Lyophilic colloids. XXVII. Mechanism of antagonism in mixtures of neutral salts in relation to the reversal of charge of phosphatides.** H. G. B. DE JONG, H. L. BOOIJ, and J. G. WAKKIE (Kolloid-Beih., 1936, 44, 254—284; cf. this vol., 29).—The antagonism of several neutral salt pairs in reversing the charge of a sol of EtOH-sol. soya-bean phosphatide (sensitised with triolein) has been examined. Antagonism occurs only when the reversal concn. of one salt is  $\leq 10$  times as great as that of the other neutral salt, and increases with the complexity and valency of the cations. The anion also plays a part. Antagonism is due mainly to the weakening of the adsorption of the more strongly adsorbed cation by the presence of the second salt. E. S. H.

**Highly purified negative reversed sols.** W. PAULI and M. ALPERN (Kolloid-Z., 1936, 76, 130—145).—Negatively-charged hydrosols of  $\text{Fe}(\text{OH})_3$  and  $\text{ThO}_2$  have been prepared by reversing the charge by adding multivalent anions. The charge on  $\text{Al}(\text{OH})_3$  sols cannot be reversed in the same way, but is reversed when NaOH is added. Negatively-charged  $\text{Fe}(\text{OH})_3$  and  $\text{ThO}_2$ , but not  $\text{Al}(\text{OH})_3$ , sols can be purified by electro-decantation. The purified negative sols show the same regularities towards coagulation by electrolytes as are observed with the corresponding positive sols. The interaction of purified positive and negative sols of the same substance has been studied. E. S. H.

**Ageing of hydrosols of ferric phosphate and vanadium pentoxide.** S. GHOSH and S. N. BANERJI (Bull. Acad. Sci. U.P., 1932, 2, 75—78).—On increasing the temp. of a dialysed  $\text{FePO}_4$  sol from  $30^\circ$  to  $60^\circ$  it was observed that  $\eta$  first decreases and then increases. The electrical conductivity increased steadily at a rate  $<$  that due to an electrolyte and the charge on the colloidal particles became lower. At  $60^\circ$  the adsorbed electrolyte is given up by the colloid. On heating  $\text{V}_2\text{O}_5$  sols  $\eta$  falls and the conductivity

and particle charge increase. The sol particles probably give rise to a mol. dispersion.

CH. ABS. (e)

**Relationship between  $\zeta$ -potential and stability in emulsions.** C. ROBINSON (Trans. Faraday Soc., 1936, 32, 1424—1425).—Ions adsorbed by the droplets may be redistributed as two droplets approach each other, leaving comparatively few ions on the opposing faces. The  $\zeta$ -potential may be so lowered at such points that coalescence may occur. E. S. H.

**Exact theory of coagulation of spherical particles arising from thermal agitation.** W. R. HARPER (Trans. Faraday Soc., 1936, 32, 1139—1144; cf. A., 1934, 960; 1935, 700).—Rigorous treatment leads to Smoluchowski's formula but the derivation by Smoluchowski's method is nevertheless open to criticism. The accord between theory and experiment shows that the different cohesive forces for different orientations of oleic acid mols. do not appreciably deform the droplets from the spherical shape. Stearic acid is a supercooled liquid in the early stages of coagulation. J. G. A. G.

**X-Ray studies of the coagulation process of colloidal gold. I. II. X-Ray experimental technique.** J. B. HALEY, K. SOELNER, and H. TERREY (Trans. Faraday Soc., 1936, 32, 1304—1312, 1312—1318).—I. Coagulation under the influence of electrolytes occurs in two stages: (a) formation of irregular agglomerates from the primary particles, (b) secondary crystallisation of the agglomerates. The rate of crystallisation depends on the electrolyte concn. in the region of slow coagulation, but is independent of electrolyte concn. in the region of rapid coagulation.

II. The technique involved in determining the particle size of coagulates in the above work is described. E. S. H.

**Electrolyte coagulation of weakly-solvated sols and electrolyte activity. IV. Arsenious sulphide sols in concentrated acids.** W. OSTWALD and H. A. WANNOW (Kolloid-Z., 1936, 76, 159—166; cf. this vol., 795).—The prep. of sols of  $\text{As}_2\text{S}_3$  in conc.  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{AcOH}$ ,  $\text{Ac}_2\text{O}$ , and  $\text{CCl}_3\text{CO}_2\text{H}$  is described. The stability of the sols, especially towards coagulation by  $\text{H}_2\text{O}$ , has been studied; coagulation follows when a certain degree of ionisation of the acid, as determined by conductivity measurements, is reached. The behaviour on adding  $\text{H}_2\text{O}$  is traced to displacement of the equilibrium between the homo- and hetero-polar structures of the acids. E. S. H.

**Change of refractive index in the coagulation of manganese dioxide sol. Step effect.** S. S. JOSHI and S. J. RAO (Kolloid-Z., 1936, 76, 145—149).—Curves representing the change of  $n$  with time in the coagulation of  $\text{MnO}_2$  sols by  $\text{HCl}$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Ce}(\text{NO}_3)_4$ , and  $\text{Th}(\text{NO}_3)_4$ , respectively, exhibit a series of steps. The actual variation of  $n$  depends on the nature of the coagulant and its concn. E. S. H.

**Coagulation of colloids. XII. "Zonal effect" in the change of refractivity during mutual coagulations.** S. S. JOSHI and K. P. N. PANIKKAR. XIII. "Zonal effect" in the opacity changes in

the coagulation of colloidal manganese dioxide. S. S. JOSHI and S. J. RAO (J. Indian Chem. Soc., 1936, 13, 309—311, 311—314).—XII. Coagulation of mixed colloidal solutions of  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  or  $\text{As}_2\text{O}_3$  offers further evidence for the existence of "zones of coagulation" (cf. this vol., 795).

XIII. The coagulation of colloidal  $\text{MnO}_2$  has been followed by measuring the increase in opacity by means of a thermopile and a low-resistance galvanometer. Zones of coagulation are practically absent in rapid coagulations, but with increasing dilution and slower coagulation the no. of zones and their duration increase. C. R. H.

Coagulation of alkaline silicic acid sols by lead acetate, copper acetate, lead nitrate, copper sulphate, and ferric chloride solutions. V. N. KRESTINSKAJA, O. S. MOLTSCHANOVA, and I. I. TARANENKO (Kolloid-Z., 1936, 76, 166—170).—Coagulation increases with increasing  $[\text{Pb}(\text{OAc})_2]$ , but decreases with increasing  $[\text{Pb}(\text{NO}_3)_2]$  or  $[\text{Cu}(\text{OAc})_2]$ .  $\text{CuSO}_4$  and  $\text{FeCl}_3$  coagulate the sols only between narrow limits of concn. The rôle of hydrolysis is discussed. E. S. H.

Coagulation of strongly-solvated sols by organic substances and salts. VII. Gelatin and starch sols. B. JIRGENSONS and A. JIRGENSONS (Kolloid-Z., 1935, 76, 182—187; cf. this vol., 426).—In the absence of salts, irregular series are observed in the flocculation of starch sols by  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Pr}^n\text{OH}$ , or  $\text{Pr}^o\text{OH}$ , and in the flocculation of gelatin sols by  $\text{Pr}^n\text{OH}$  and  $\text{Pr}^o\text{OH}$ . Small amounts of salts ( $\text{NaCl}$ ,  $\text{CaCl}_2$ , etc.) sensitise both sols to flocculation by alcohols and irregular series are no longer observed. With greater salt concn. and low alcohol concn. the sols are stabilised; stability increases with increasing salt concn. and decreasing concn. of colloid. The conditions for stability with definite concns. of alcohol and salts of different valencies have been determined. E. S. H.

Rhythmic turbidity in precipitation of barium sulphate. E. B. R. PRIDEAUX and G. E. L. CARTER (J.C.S., 1936, 1214—1219).—Suspensions of  $\text{BaSO}_4$  were made by adding to a mixture (5 min. old) of 10 c.c. of 0.01N- $\text{BaCl}_2$  and 100 c.c. of 0.01N- $\text{K}_2\text{SO}_4$  200 c.c. of  $\text{H}_2\text{O}$ , buffer solution, or dil. gelatin, mixing, and then adding the remaining 90 c.c. of  $\text{BaCl}_2$  to ensure that pptn. occurs on existing nuclei. With const. conditions, the mean turbidity increases with decrease of  $p_{\text{H}}$  vals. from 8 to 3. The gelatin has no sp. effect. The turbidity of these suspensions varies periodically with time, the amplitude being approx. 20% of the mean vals. The phenomenon is attributed to the periodic reversible transformation of cruciform aggregates of  $\text{BaSO}_4$  into simple prismatic crystals. J. G. A. G.

Liesegang rings in non-gelatinous media. I. V. GORE (Kolloid-Z., 1936, 76, 193—200).—Periodic structures have been obtained by the interaction of  $\text{KI}$  and  $\text{HgCl}_2$ , using as media sols prepared by peptising  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Zr}(\text{OH})_4$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , or  $\text{BaCO}_3$  ppts. E. S. H.

Rate of electrophoresis and electrical conductivity of hydrophobic colloids. A. J. RUTGERS

and J. T. G. OVERBEEK (Z. physikal. Chem., 1936, 177, 29—39).—The anomaly that for many sols the "free" particle charge,  $e$ , calc. from the rate of electrophoresis,  $v$ , is that calc. from the conductivity,  $\sigma$ , is discussed. A colloid particle is pictured as surrounded by a firmly adhering  $\text{H}_2\text{O}$  envelope ("Smoluchowski layer"), the counterions in which are freely mobile within the envelope; outside are the other counterions in free  $\text{H}_2\text{O}$ . On calculating  $v$  by applying Stokes' law, and correcting for the electrophoresis effect of the counterion atm., the usual Helmholtz-Debye-Huckel equation for  $v$  results,  $v$  being determined solely by the charge of the counterions in the free  $\text{H}_2\text{O}$ . Apparently, however, both groups of counterion participate in conduction with their full mobilities; the anomaly is therefore explained. For sols with high  $e$  almost all the counterions seem to be in the Smoluchowski layer. The various electrophoretic effects and their effect on  $\sigma$  are calc. R. C.

Cataphoretic velocity of colloidal particles during aggregation. I. J. N. MUKHERJEE, S. G. CHAUDHURY, and K. BHABAK (J. Indian Chem. Soc., 1936, 13, 372—389).—The cataphoretic velocity,  $v$ , of colloid particles in presence of electrolyte increases with time, i.e., with increased aggregation, this effect being the greater the higher is the valency of the pptg. ions.  $v$  for the supernatant suspension of a partly coagulated colloid is < that for the original colloid, whilst with  $\text{As}_2\text{S}_3$  sol  $v$  for the coagulate shaken with the supernatant liquid is the same as for the latter alone. These results are not in accord with current theories of cataphoresis, and an explanation based on Mukherjee's theory (A., 1933, 460, 1116; 1934, 729) is put forward. J. W. S.

Characterisation of starch by dispersoid analysis. O. LAMM (Naturwiss., 1936, 24, 508).—Starch is readily dispersed in solutions of  $\text{ZnCl}_2$  and  $\text{NaHgCl}_3$ , giving stable solutions which may be separated from the above reagents by dialysis. The dispersion proceeds to a definite limit, which is the same for both reagents. The diffusion const. and mol. wt. of a starch were determined, the latter amounting to  $4 \times 10^6$ . A. J. M.

Peptisation of wheat starch. A. G. KUHLMANN and O. N. GOLOSOVA (Kolloid-Z., 1936, 76, 223—227).—The degree of peptisation of starch in  $\text{H}_2\text{O}$  by adding the lower fatty acids or  $\text{KOH}$  has been determined. The chain length of the fatty acid has practically no influence, but the introduction of  $\text{OH}$  into the chain increases the degree of peptisation. The relation of peptisation to the behaviour on baking is discussed. E. S. H.

Electro-osmosis as a method of studying the process of peptisation of nickel and cobalt hydroxides. V. G. ZAPROMETOV and L. B. SMOLINA (Bull. Univ. Asie Centrale, 1935, No. 21, 29—37).—Peptisation of  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  in aq. alkaline sucrose and tartrate is followed by means of electro-osmotic measurements, involving determination of and  $\phi$ -potentials. R. T.

Lyotropic cation series in hydrophilic colloids. E. H. BUCHNER and C. S. B. DE GRUITER (Kolloid-Z.,



1936, 76, 173—175).—The swelling of gelatin in aq. CsCl, RbCl, KCl, NaCl, LiCl, and  $\text{NH}_4\text{Cl}$  and the softening point of gelatin gels containing the same salts have been determined. When the results are plotted against the lyotropic nos. of the cations, the curves show a min. and a max., respectively. It is probable that hydration and adsorption in the series are antibatic. The flocculation vals. of the alkali chlorides for gelatin solutions bear no relation to the lyotropic nos.; mixtures of NaCl and LiCl show antagonism in this respect. E. S. H.

**Influence of addition of sodium chloride on gelation.** R. REIGER and S. BACH (Kolloid-Z., 1936, 76, 178—182).—With increasing addition of NaCl the optical rotation and shear modulus of gelatin solutions are lowered. At concns.  $> 1N$ , the presence of NaCl influences only the initial stages of gelation. E. S. H.

**Lyophilic colloids. IX. Optical rotatory power of gelatin fractions.** S. M. LIEPATOV and I. N. PUTILOVA (Kolloid-Z., 1936, 76, 176—178; cf. A., 1935, 701, 932, 1320).—The fractions of gelatin obtained by extraction with  $\text{H}_2\text{O}$  at different temp. show different sp. rotation and have different temp. coeffs. of optical rotation. The optical differences are traced to different micellar structures; it is unlikely that isomerides of gelatin are present. E. S. H.

**Heat changes of egg-albumin.** B. A. VILENSKI and G. WEISSBERG (Kolloid-Z., 1936, 76, 191—193).—When egg-albumin is heated for about 2 hr. at  $57^\circ$ , the osmotic pressure rises to a max. and then falls to a val.  $<$  the original val. The heat-coagulation process occurs in two stages: (a) decomp. of the micelles with formation of colloidal substances, (b) formation of aggregates leading to visible pptn. E. S. H.

**Adsorption of proteins. Crystallised horse hæmoglobin.** (MLLE.) V. DEUTSCH (Compt. rend., 1936, 203, 182—184).—The absorption spectrum is altered by HCl, NaOH, aq.  $\text{NH}_3$ , and  $\text{Na}_2\text{PO}_4$ , but not by NaCl, KCl,  $\text{BaCl}_2$ , or  $\text{Na}_2\text{SO}_4$ . Three types of isotherms have been found for the adsorption of hæmoglobin by kaolin; according to the nature and concn. of the electrolyte the isotherms conform to the requirements of the Freundlich equation, show a min., or show a max. The adsorption is diminished by the cations in the order  $\text{Ba}^{++} < \text{Na}^+ < \text{K}^+$ . J. G. A. G.

**Adsorption of proteins. Horse serum-albumin.** (MLLE.) V. DEUTSCH (Compt. rend., 1936, 203, 252—254; cf. this vol., 676).— $0.1N$ -NaCl and  $-KCl$  scarcely affect the adsorption of the serum-albumin (I) by kaolin, but  $N$  solutions decrease it considerably.  $\text{BaCl}_2$  increases the adsorption, the effect with  $0.1N$ - $\text{BaCl}_2$  being  $>$  with  $1N$ .  $0.1N$ - $\text{Na}_2\text{SO}_4$  slightly increases the adsorption, but  $N$ - $\text{Na}_2\text{SO}_4$  decreases it. The salts scarcely alter the  $p_H$  of the solutions (initially 5.6). The adsorption of (I) is a max. at  $p_H$  5.1 and a min. at 3.4. The max. almost coincides with the isoelectric point of (I). J. W. S.

**Role of osmotic pressure in the phenomenon of imbibition.** D. KOHLER (Compt. rend. Soc. Biol.,

1936, 122, 1196—1198).—With a low concn. of electrolyte the coeff. of imbibition is increased or diminished according to the nature of the electrolyte; the rate of imbibition is not affected by the concn. H. G. R.

**Thixotropy of a suspension of Japanese acid earth.** B. TAMAMUSHI (J. Chem. Soc. Japan, 1935, 56, 778—780).—The suspension of the natural product is more thixotropic than that which is electrolysed. The effect of electrolytes was studied. CH. ABS. (e)

**Swelling pressure of isinglass in water and aqueous solutions.** H. FREUNDLICH and P. S. GORDON (Trans. Faraday Soc., 1936, 32, 1415—1424).—The swelling pressure,  $p$ , is related to the concn. of gel,  $\gamma$ , by  $p - p_0 = k\gamma^k$ , where  $p_0$  and  $k$  are consts. With  $0.2N$ -salt solutions, swelling in NaI or  $\text{NH}_4\text{CNS}$  is  $>$  in  $\text{H}_2\text{O}$ , but swelling is less in  $\text{Na}_2\text{SO}_4$ ,  $\text{BeCl}_2$ , or  $\text{La}(\text{NO}_3)_3$  than in  $\text{H}_2\text{O}$ . The order of effectiveness of the ions is that of the lyotropic series. The influence of electrolyte concn. is not simple, but  $k$  increases with the concn. Min. swelling is observed at  $p_H$  6.5, near the isoelectric point of isinglass. Swelling is reduced by sucrose or  $\text{CO}(\text{NH}_2)_2$ . E. S. H.

**Equilibrium constant of the system ethyl alcohol-acetic acid.** P. E. CORIA (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 67—75).—Contrary to Corso *et al.* (A., 1933, 125) the const. at  $120^\circ$  is  $1.31 + 4.86c$  where  $c$  is the initial  $[\text{AcOH}]$  relative to the total concn. F. R. G.

**Chlorination of sulphur by the action of carbon tetrachloride in presence of certain catalysts.** V. A. FOMIN (J. Gen. Chem. Russ., 1936, 6, 852—854).—The equilibrium at  $120^\circ$  in presence of Fe, Cu, or Al, or their anhyd. chlorides corresponds with  $6S + \text{CCl}_4 \rightleftharpoons \text{CS}_2 + 2S_2\text{Cl}_2$ . R. T.

**Hydrogen bridges in ice and liquid water.** M. L. HUGGINS (J. Physical Chem., 1936, 40, 723—731).—The evidence for the existence of H-bridges in liquid and solid  $\text{H}_2\text{O}$  and for their being asymmetrical is discussed. The partial freedom of orientation of the dipole which would be introduced by sufficiently small energy barriers accounts satisfactorily for the dielectric const. data. It is suggested that the  $\text{H}^+$  in  $\text{H}_2\text{O}$  is  $(\text{H}_2\text{O}-\text{H}-\text{OH}_2)^+$ . By slight rearrangement  $\text{H}_2\text{O}$  can be split off at one end of the ion and added at the other, with shift of charge. This, it is suggested, accounts for the high mobility of the  $\text{H}^+$  in aq. solution. It is also inferred that the  $\text{OH}^+$  is not bridged. A shift of the type  $\text{HOH} + \text{OH}^+ \rightarrow \text{HO}^+ + \text{HOH}$  should occur, but less readily than for a  $\text{H}^+$ , thus making the mobility smaller. J. W. S.

**Deuterium exchange equilibria in solution and the quinhydrone electrode.** S. KORMAN and V. K. LA MER (J. Amer. Chem. Soc., 1936, 58, 1396—1403).—Dissociation consts. of salicylic and acetic acids, quinol, and  $\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  and 92%  $\text{D}_2\text{O}$  have been determined. Except for salicylic acid, the ratio of the dissociation consts. in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  decreases as the const. increases. Advantages of using the quinhydrone electrode in preference to the  $\text{D}_2$  gas electrode are discussed. E.m.f. temp. coeffs. indicate that the difference in the heats of ionisation of AcOH

and AcOD may change sign at about 25°. The solubilities of benzoquinone, quinol, and deuterobenzoquinone in H<sub>2</sub>O and D<sub>2</sub>O have been determined.

E. S. H.

**Exchange of deuterium between deuterium hydroxide and ethyl alcohol.** W. J. C. ORR (Trans. Faraday Soc., 1936, 32, 1033—1037).—By using CaSO<sub>4</sub> to remove DOH from the reacting mixture the equilibrium const.,  $\alpha_{\text{H}}$ , of the reaction EtOH + HOD  $\rightleftharpoons$  EtOD + HOH has been found to be 1.11 at 25°. The velocity coeffs. for the backward and forward reactions are  $2.4 \pm 0.2 \times 10^{-6}$  and  $2.2 \pm 0.2 \times 10^{-6}$ , respectively (litres/g.-mol. sec.). These vals. indicate that the exchange proceeds ionically. From  $\alpha_{\text{H}}$  the ratio of the dissociation consts. of EtOH to EtOD in presence of 16% HOD is found to be 1.25.

O. J. W.

**Release of protons from molecular hydrogen with the aid of hydroxyl ions.** K. WIRTZ and K. F. BONHOEFFER (Z. physikal. Chem., 1936, 177, 1—6).—Exchange of H for D occurs at 100° between D<sub>2</sub>O and dissolved H<sub>2</sub> in presence of KOH, the OH<sup>-</sup> acting as catalyst, but there is little or no exchange in an acid or neutral medium.

R. C.

**Electrolytic dissociation of heavy water.** W. F. K. WYNNE-JONES (Trans. Faraday Soc., 1936, 32, 1397—1402).—E.m.f. determinations show that the ionic product of D<sub>2</sub>O at 25° is  $1.95 \times 10^{-15}$ . The heat of ionisation, calc. from the temp. coeff., is 940 g.-cal. > that of H<sub>2</sub>O.

E. S. H.

**Chemical theory of electrolytes.** M. USSANOVITSCH (Acta Physicochim. U.R.S.S., 1935, 3, 703—710).—The mass law has been applied to conc. solutions on the assumption that a linear relation exists between electrolyte concn. and electrical conductivity corr. for internal friction, and that the compounds formed between the components of a binary system are the true electrolytes.

C. R. H.

**Concentration and dissociation constant of each acid group in a mixture from the  $p_{\text{H}}$  titration curve.** J. O. BURTON and S. F. ACREE (J. Res. Nat. Bur. Stand., 1936, 16, 525—528).—The approx. calculation of the concn. and dissociation const. for each of the acid groups in a mixture from the titration curve is discussed and applied to experimental data for malonic acid, for which  $K_1 = 2.06 \times 10^{-3}$ . The method is of especial val. with plant and animal products.

R. S. B.

**Dissociation constants of malonic acid in its sodium salt solutions at 25° from electrometric titration measurements.** J. O. BURTON, W. J. HAMER, and S. F. ACREE (J. Res. Nat. Bur. Stand., 1936, 16, 575—593).—The electrometric titration curve has been determined at 25°. Corrections for liquid junction potential and interionic attraction are discussed, and the first and second thermodynamic dissociation consts. of malonic acid are calc. to be  $2.06 \times 10^{-3}$  and  $2.94 \times 10^{-6}$ , respectively. The variation of dissociation const. with ionic strength is discussed.

R. S. B.

**Dissociation constants and the basic titration of acetic acid in relation to water content of solvent.** S. KILPI (Z. physikal. Chem., 1936, 177,

116—130).—The dissociation const.,  $K$ , of an acid or base and the ionic product of the solvent,  $K_1$ , may be calc. from the potential jumps at the beginning of the titration and at the equiv. point or from the potentials as the beginning, at half-neutralisation, and at the equiv. point. For solutions of  $\text{o-NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$  in aq. AcOH  $K$  and  $K_1$  have been determined for solvents with 0.8—20% H<sub>2</sub>O; both fall rapidly with the [H<sub>2</sub>O] and the precision of titration with bases increases. Amines cannot be titrated in AcOH solution to which Ac<sub>2</sub>O has been added to effect dehydration, for they undergo acetylation, but satisfactory results are obtained in presence of Ac<sub>2</sub>O if a known amount of HClO<sub>4</sub> is added before adding the amine to the AcOH; excess of acid may be titrated back with a non-acetyltable base. R. C.

**Geometrical isomerism of strong bases.** A. GRUNBERG and D. RJAFTSCHIKOV (Acta Physicochim. U.R.S.S., 1935, 3, 555—572).—The *trans* form of  $\text{Pt}(\text{NH}_3)_2(\text{OH})_2$  is more alkaline than the *cis* form; the difference increases with the concn., and also in the presence of ions capable of forming complexes, the effect decreasing in the order I<sup>-</sup>, CNS<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>. Potentiometric titrations with a glass electrode give  $K_1 = 0.63 \times 10^{-7}$ ,  $K_2 = 1 \times 10^{-10}$  for the *trans* form and an average val.  $K = 0.16 \times 10^{-7}$  for the *cis* form.

C. R. H.

**Acid-base dissociation constants in mixtures, and their connexion with individual ion activities.** I. C. D. RIETZ (Svensk Kem. Tidskr., 1936, 48, 165—175).—A discussion of the above and related problems.

D. C. J.

**Potentiometric investigation of electrolytic dissociation. IV. Anion affinity of copper, zinc, cadmium, silver, and hydrogen ions.** E. FERRELL, J. M. RIDGION, and H. L. RILEY [in part with S. CHAMBERS] (J.C.S., 1936, 1121—1126).—Potentiometric data afford evidence of the formation of complex ions in certain of the following cases: Zn<sup>++</sup> with CNS<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-</sup>, NH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>, OAc<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>; Cd<sup>++</sup> and Ag<sup>+</sup> with CN<sup>-</sup>, CNS<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup>. The order of decreasing anion affinity is Ag<sup>+</sup> > Cu<sup>++</sup> > Cd<sup>++</sup> > Zn<sup>++</sup>. No evidence of complex ions of CN<sup>-</sup> and NH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> with H in which H has a covalency of 2 was obtained. Pt-black and pptd. Au dissolve in conc. aq. KCN and H<sub>2</sub> is evolved.

J. G. A. G.

**Solvation and complex formation in solutions of electrolytes.** V. FINKELSTEIN (Acta Physicochim. U.R.S.S., 1935, 3, 541—554).—Cryoscopic data for solutions of AsCl<sub>3</sub>, AsBr<sub>3</sub>, and SbCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> containing Et<sub>2</sub>O, AcOH, or PhNO<sub>2</sub> as solvating agent indicate that the lowering of f.p. oc the ratio of the mol. concns. of solvating agent and halide. The theoretical lowering, assuming absence of association, dissociation, and solvation, is > that found, the discrepancy increasing with the concn. of the solvating agent. Raman spectra of Et<sub>2</sub>O solutions of the same electrolytes afford no evidence for the formation of new compounds.

C. R. H.

**Two inorganic complexes having in solution an exceptionally high Verdet constant.** R. LUCAS and F. GALLAIS (Trans. Faraday Soc., 1936, 32, 973—975).—For saturated solutions of HgI<sub>2</sub>+KI



and of  $\text{BiI}_3 + \text{KI}$ , in which complex salts are present,  $[\alpha]$  is 18 to 28 times that of  $\text{H}_2\text{O}$ . O. J. W.

**Thermodynamics of chemical equilibria and reaction rates.** M. G. EVANS and M. POLANYI (Trans. Faraday Soc., 1936, 32, 1333—1360).—Theoretical. Subjects discussed include: linear relations between chemical free energies, thermodynamics of the transition state, linear relations accompanying structural changes, relation between entropies and heats of dissolution, collision factors in solution, influence of viscosity on bimol. reaction rate in solution, relations of energy and entropy based on the Nernst theorem, relevance of activation energies derived from energy surfaces. E. S. H.

**Activity coefficients of lithium chloride and potassium iodide in ethyl alcohol by the b.p. method.** J. N. PEARCE and M. L. McDOWELL (J. Physical Chem., 1936, 40, 845—852).—The b.p. elevations for 0.01—0.65*N* solutions of  $\text{LiCl}$  and 0.01—0.15*N* solutions of  $\text{KCl}$  in  $\text{EtOH}$  correspond closely with those which would be produced by undissociated solute mols. This is attributed to the existence of simple or chain ions in equilibrium with paired ions or quadrupoles, the formation of the latter being favoured by the low dielectric const. of  $\text{EtOH}$ . The activity of the  $\text{EtOH}$  is almost the same for equal concns. of  $\text{LiCl}$  or  $\text{KCl}$ , but the activity coeffs. of the ions of  $\text{KCl}$  are slightly  $>$  for those of  $\text{LiCl}$ . J. W. S.

**Specific thermodynamic properties of aqueous solutions of uni-univalent electrolytes.** E. A. GUGGENHEIM (Phil. Mag., [vii], 22, 322—336).—Formulae previously deduced (cf. A., 1935, 446) are applied to f.-p. data, and the osmotic and activity coeffs., for the chlorates, perchlorates, nitrates, formates, and acetates of  $\text{Li}$ ,  $\text{Na}$ , and  $\text{K}$ , are found to be in good agreement with experiment. For  $\text{NaCl}$  solutions e.m.f. data are also considered and results tabulated. General results for uni-univalent electrolytes are considered. N. M. B.

**Thermodynamics of silver fluoride-water mixtures.** W. J. HELD and K. JELLINEK (Z. Elektrochem., 1936, 42, 608—623).—Vals. are recorded for solubility, f.p.,  $d$ , mol. heat of mixing, heat of dilution, molar heat content, activity coeffs., v.p. of  $\text{H}_2\text{O}$  over the solutions, and free energy changes. E. S. H.

**Simple numerical relationships in binary eutectic mixtures.** D. STOCKDALE (Trans. Faraday Soc., 1936, 32, 1365—1369; cf. this vol., 151).—Published data for eutectics containing two salts with a common ion, and org. eutectics, give indefinite evidence. A plea for more exact data is urged. E. S. H.

**M.p. diagram of polycomponent systems. I—IV.** Y. KONISHI (J. Soc. Chem. Ind. Japan, 1936, 39, 209—211b).—A method is described by which the change of a given property (e.g., m.p.) with composition in polycomponent systems may be represented by rectangular co-ordinates, and illustrated by the systems  $\text{MgF}_2$ — $\text{BaF}_2$ — $\text{LiF}$  and  $\text{MgF}_2$ — $\text{BaF}_2$ — $\text{CaF}_2$ — $\text{LiF}$ . The lowest m.p. in the former is  $645^\circ$  with a wt. ratio of components =

1 : 1.65 : 0.73, and in the latter  $603^\circ$  with a ratio = 1 : 1.65 : 0.55 : 0.73. T. W. P.

**Isotherms of the system calcium oxide-water.** V. RODT (Z. anorg. Chem., 1936, 228, 175—177).—Data for  $20^\circ$  reveal only one hydrate,  $\text{CaO} \cdot \text{H}_2\text{O}$ . E. S. H.

**System methylamine-calcium chloride.** A. MAILLARD (Compt. rend., 1936, 302, 187—189).—The data refer to  $-16^\circ$  and  $24^\circ$ . Evidence for the formation of compounds represented by  $\text{CaCl}_2 \cdot x\text{NH}_2\text{Me}$  with  $x=2, 4, 6$ , and 8 has been obtained. J. G. A. G.

**Dissociation pressure of vanadium pentoxide.** N. NASU (J. Chem. Soc. Japan, 1935, 56, 666—669).—Measurements at  $220$ — $325^\circ$  lead to the following data:  $\text{V}_2\text{O}_5 = \text{V}_2\text{O}_4 + 0.5\text{O}_2$ ,  $\Delta H_{298} = 14,300$  g.-cal.,  $\Delta F_{298} = 7900$  g.-cal.,  $\Delta S = 15.6$  g.-cal. per degree;  $\text{V}_2\text{O}_5 + \text{H}_2 = \text{V}_2\text{O}_4 + \text{H}_2\text{O}$ ,  $\Delta H_{298} = -43,500$ ,  $\Delta F_{298} = -44,800$ ,  $\Delta S = -4.4$ . The lattice energy of  $\text{V}_2\text{O}_5$  is 9772 g.-cal. CH. ABS. (e)

**Solid-liquid equilibria in binary and ternary systems in which mixed crystals are formed. IV. (1) Camphor-bromocamphor. (2) Camphor-bromocamphor-borneol.** K. HRYNAKOWSKI, H. STASZEWSKI, and M. SZMYT (Z. physikal. Chem., 1936, 177, 95—102).—In the system camphor-bromocamphor there is complete miscibility in the solid state and the f.-p. curve has a min. Ternary mixed crystals are probably formed in the second system. It is suggested that ternary mixed crystals are formed in those ternary systems in which mixed crystals are formed in each of the three binary systems. R. C.

**Affinity. LXVII. Tensimetric analysis of higher palladium sulphides.** W. BILTZ and J. LAAR. **LXVIII. System manganese-sulphur; structure and synthesis of hauerite ( $\text{MnS}_2$ ).** W. BILTZ and F. WIECHMANN. **LXIX. System nickel monosulphide-nickel disulphide-sulphur.** W. BILTZ [with A. VOIGT, K. MEISEL, F. WEIRKE, and P. EHRLICH] (Z. anorg. Chem., 1936, 228, 257—267, 268—274, 275—296; cf. A., 1935, 1335).—LXVII. Thermal, tensimetric, and X-ray analyses confirm the existence of  $\text{Pd}_4\text{S}$ ,  $\text{Pd}_5\text{S}_2$ ,  $\text{PdS}$ , and  $\text{PdS}_2$ .

LXVIII. The S v.p. of  $\text{MnS}_2$  at different temp. has been determined. The conditions of synthesis of  $\text{MnS}_2$  from  $\text{MnS}$  and S are discussed.

LXIX. Tensimetric data show that no compound exists between  $\text{NiS}$  and  $\text{NiS}_2$ . The transformation temp. of  $\text{NiS}$  from trigonal to hexagonal is  $396^\circ$ . E. S. H.

**Relations of beryllium to the [zinc] group and the alkaline-earth metals. I.** W. SCHRODER [with E. NEUMANN and J. ALTDORF] (Z. anorg. Chem., 1936, 228, 129—159).—Equilibrium data for the systems  $\text{BeSO}_4$ — $\text{H}_2\text{O}$ ,  $\text{ZnSO}_4$ — $\text{H}_2\text{O}$ , and  $\text{BeSO}_4$ — $\text{ZnSO}_4$ — $\text{H}_2\text{O}$  at  $0$ — $100^\circ$  are recorded. E. S. H.

**Reduction equilibrium of metallic oxides. VII. Determination of the thermal diffusion effect in mixtures of hydrogen and oxygen.** Z. SHIBATA and H. KITAGAWA. **VIII. Effect of thermal diffusion on the determination of equilibrium constants in the systems  $\text{FeO} + \text{H}_2$ ,  $\text{Fe} + \text{H}_2\text{O}$  and  $\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{FeO} + \text{H}_2\text{O}$ .** Z. SHI-

BATA (J. Chem. Soc. Japan, 1935, 56, 722—735, 736—744; cf. A., 1933, 783).—VII. One end of the vessel containing the mixture was kept at room temp. and the other was heated to 721—1021°. The diffusion effect is discussed on the basis of the kinetic theory.

VIII. A crit. discussion. Thermochemical data are calc., account being taken of the effect of thermal diffusion. CH. ABS. (e)

System  $2\text{MnO}_3\cdot\text{SiO}_2 + \text{FeS}$ . A. S. GINZBERG, B. P. SELIVANOV, S. I. NIKOLSKI, and M. M. VOROVITSCH (Rep. Inst. Met. (Leningrad), 1933, No. 14, 111—115).—Inflection points in the heating curves are recorded and discussed. CH. ABS. (e)

Systems of sulphur and various metals. E. JÄNECKE (Z. Elektrochem., 1936, 42, 373—377).—Complicated systems of S and three metals can be represented by fairly simple diagrams when the ternary limiting systems are known. O. J. W.

Reciprocal salt pair  $(\text{K}_2\text{—Ca})(\text{Cl}_2\text{—SO}_4)$ . E. JÄNECKE and W. MÜHLHÄUSSER (Z. anorg. Chem., 1936, 228, 241—248).—Equilibrium in the fused mixture has been studied by thermal and microscopical methods. E. S. H.

Free energy of formation of more noble metal fluorides compared with other analogous metal halides. W. JAHN-HELD and K. JELLINEK (Z. Elektrochem., 1936, 42, 401—421).—From e.m.f. measurements the free energy, heat of formation, and entropy change in the formation of the following compounds at 25° have been calc.:  $\text{AgCl}$ ;  $\text{PbCl}_2$ ;  $\text{AgBr}$ ;  $\text{CuBr}$ ;  $\text{PbBr}_2$ ;  $\text{PbF}_2$ ;  $\text{AgF}\cdot 2\text{H}_2\text{O}$ ;  $\text{AgF}\cdot 4\text{H}_2\text{O}$ ;  $\text{CuF}_2\cdot 2\text{H}_2\text{O}$ ;  $\text{CdF}_2$ ;  $\text{ZnF}_2\cdot 4\text{H}_2\text{O}$ ;  $\text{NiF}_2\cdot 4\text{H}_2\text{O}$ ;  $\text{CoF}_2\cdot 4\text{H}_2\text{O}$ ;  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ ;  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ . The results are compared with those derived from equilibrium data in the reduction of the halides with H. Measurements of the  $\text{H}_2\text{O}$  v.p. over saturated  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  solutions, and of the  $\text{HBr}$  v.p. over 6*N*- $\text{HBr}$  solution at 15°, 25°, and 35° are recorded. O. J. W.

Electron affinity of free radicals. XI. Free energy of addition of sodium to ketones and unsaturated hydrocarbons. H. E. BENT and N. B. KEEVIL (J. Amer. Chem. Soc., 1936, 58, 1367—1371; cf. this vol., 1952).—Data for the addition of Na to  $\text{COPh}_2$ ,  $\text{CO}(\text{C}_6\text{H}_5\text{Ph})_2$ , fluorenone, tetraphenylcyclopentadienone,  $\text{C}_2\text{H}_2\text{Ph}_4$ , stilbene, and anthracene have been determined. With  $\text{COPh}_2$  the Na becomes attached to the O. E. S. H.

Solubility of non-electrolytes. III. Entropy of hydration. J. A. V. BUTLER and W. S. REID (J.C.S., 1936, 1171—1173).—Entropies of hydration,  $\Delta S$ , of ten monohydric aliphatic alcohols and five other compounds have been calc. Contrary to earlier views, the changes of  $\Delta F$  (free energy of hydration) and  $\Delta H$  (heat of hydration) are in opposite directions as the alcohol series is ascended.  $\Delta S$  for 17 gases and vapours has been calc. from solubility data.  $\Delta S$  is little influenced by the constitution of the solute mol., but depends mainly on the size. The solute mols. probably disorient  $\text{H}_2\text{O}$  to an extent which increases with the size, giving the solute an abnormally low partial entropy in the solution. J. G. A. G.

Thermochemistry of the alkali and alkaline-earth nitrites. M. DODÉ (Compt. rend., 1936, 203, 365—367).—The heats of formation and of dissolution are recorded for the nitrites of Li, Na, K, Ca, Sr, and Ba. R. S.

Secondary calibration substance for combustion calorimeter for gases and vapours. Heat of combustion of isopentane vapour. W. A. ROTH and H. PAHLKE (Angew. Chem., 1936, 49, 618—619).—*iso*Pentane vapour is recommended as a secondary standard. The heat of combustion at 20.5° is  $11,690 \pm 5$  g.-cal. per g. at const. vol., and  $11,722 \pm 5$  g.-cal. per g. at const. pressure. E. S. H.

Heats of dissolution and dilution of salts from extreme dilution to saturation. V. Barium chloride. E. SCHWARTZ and H. COBLANS (Z. physikal. Chem., 1936, 176, 430—443).—Thermal data are recorded for  $\text{BaCl}_2$  solutions. With increasing concn. the differential heat of dissolution passes through a min. and then through a max. In its thermochemical behaviour in solution  $\text{BaCl}_2$  resembles the Li rather than the K halides. R. C.

Heat of solvation of some univalent ions in water, methyl and ethyl alcohol. K. MISCHTSCHENKO (Acta Physicochim. U.R.S.S., 1935, 3, 693—702).—The heats of solvation of  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{KI}$ , and their ions in  $\text{H}_2\text{O}$ ,  $\text{MeOH}$ , and  $\text{EtOH}$  have been calc. from existing data for the integral heat of dissolution and from calc. vals. for the lattice energy, assuming that heat of dissolution = lattice energy + heat of solvation. The heat of solvation is approx. the same in  $\text{EtOH}$  as in  $\text{MeOH}$ , the val. in  $\text{H}_2\text{O}$  being slightly less. C. R. H.

Ionic radii and heat of hydration. A. VOET (Trans. Faraday Soc., 1936, 32, 1301—1304).—A linear relation exists between ionic radii and reciprocal heats of hydration of positive ions. An explanation, based on the electrostatic theory, is advanced. E. S. H.

Conductivity of the double sulphates of the magnesium series in aqueous solution. B. FEDOROV (Compt. rend., 1936, 203, 367—369).—The conductivity of the double salts  $\text{K}_2\text{M}^{\text{II}}(\text{SO}_4)_2$  ( $\text{M}^{\text{II}} = \text{Mg}$ ,  $\text{Zn}$ ,  $\text{Ca}$ ,  $\text{Cu}$ ,  $\text{Mn}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Ni}$ , or  $\text{Co}$ ) is < that of the sum of the conductivities of the component salts at all concns.  $> 0.0001M$ . R. S.

Electrical conductivities of aqueous solutions of sodium dodecyl sulphate and sodium hexadecyl sulphate at different temperatures. O. R. HOWELL and H. G. B. ROBINSON (Proc. Roy. Soc., 1936, A, 155, 386—406).—Data for the solutions have been obtained over a wide concn. range at 20° to 100°. The  $\Lambda\text{—}\sqrt{c}$  curves consist of three distinct parts: over the first, the fall in  $\Lambda$  is linear (as for a simple electrolyte), and the results are explained on the Debye-Huckel theory; over the second, the fall in  $\Lambda$  is very rapid and previous theories to account for this are shown to be untenable, and an anionic network is postulated which offers a satisfactory explanation; over the third,  $\Lambda$  rises to a small max. and falls again. Confirmation of the existence of micelles over the last range is afforded by the fact that the transport no.



of the anion retains its high val. of about 1. The ionic micelle is not highly charged, the charge probably being  $\geq 1$  or 2 units. It is suggested that the initial stage of micelle formation with  $C_{12}H_{25}\cdot SO_4Na$  probably involves  $Na^+ + [D_4Na_3]'$ . L. L. B.

**Conductivity of alkali-water-acetone solutions** [at  $0^\circ$ ]. W. H. HATCHER and C. T. MASON (Canad. J. Res., 1936, 14, B, 195—203).—The sp. conductivity,  $\kappa_w$ , of aq. NaOH and KOH is  $>$  that of aq.  $COMe_2$ -alkali. The sp. conductivity of the mixture,  $\kappa_m$ , is related to the viscosities,  $\eta_w$  and  $\eta_m$ , and the dielectric const.,  $\epsilon_w$  and  $\epsilon_m$ , of  $H_2O$  and the mixtures, respectively, thus  $\kappa_m = 1.08\kappa_w\eta_w\epsilon_m/\eta_m\epsilon_w$ .

J. G. A. G.

**Dispersion of electrical conductivity and dielectric constant in dilute solutions of strong electrolytes.** J. W. WILLIAMS and O. M. ARNOLD (Acta Physicochim. U.R.S.S., 1935, 3, 619—632).—Vals. of  $\kappa$  and  $\epsilon$  for strong electrolytes of several valency types in extremely dil. aq. solution are in satisfactory agreement with the Debye-Falkenhagen dispersion theory. The vals. of  $\epsilon$  indicate that any decrease in  $\epsilon$  resulting from saturation of the liquid mols. by the electric fields arising from the dissolved ions is small or even negligible. C. R. H.

**Determination of surface conductance from measurements on suspensions of spherical particles.** H. FRICKE and H. J. CURTIS (J. Physical Chem., 1936, 40, 715—722).—From the differences in the conductivity of solutions of KCl, HCl, and  $Na_2CO_3$  and of suspensions of glass and kaolin particles (diameter 0.6—3.4  $\mu$  in these solutions at 0.5—100 kc.), the surface conductivities of the particles have been calc. The results are compared with the vals. calc. on the assumption of a diffuse double layer, but the latter only partly explains the observations. There is also a surface capacity, indicating current transport at the solid surface, which may account for the variation of the surface conductivity with the frequency. J. W. S.

**Space-charge in a conducting electrolyte.** W. SCHRIEVER (Physical Rev., 1935, [ii], 47, 327).—Space-charges in the system  $Cu[0.0024N\cdot CuSO_4]Cu$  have been determined. L. S. T.

**Transference number of lanthanum chloride as a function of concentration.** G. JONES and L. T. PRENDERGAST (J. Amer. Chem. Soc., 1936, 58, 1476—1482).—Over the concn. range 0.0038—1.0M, the transference no. at  $25^\circ$  varies from about 0.47 to 0.30. Equations relating transference no. to concn. are discussed. E. S. H.

**Ionic transference numbers in Cellophane membranes.** T. TEORELL (J. Gen. Physiol., 1936, 19, 917—927).—The apparent cationic transport nos. for HCl, LiCl, NaCl, KCl, and  $NH_4Cl$  in Cellophane are all  $>$  the corresponding vals. in  $H_2O$ ; the relative cation mobilities show an increase of about 40%. F. A. A.

**Potentials of silver-zinc alloys.** G. I. PETRENKO and E. E. TSCHERKASCHIN (Z. Elektrochem., 1936, 42, 398—400).—Measurements of the p.d. of the cell  $Zn|N\cdot ZnSO_4|Ag-Zn$  alloy indicate that  $Ag_2Zn_3$  and  $AgZn$  are the only compounds formed. This agrees with thermal data. O. J. W.

**Amalgam concentration cells and electrodes of the second kind in non-aqueous solvents.** H. ULICH and G. SPIEGEL (Z. physikal. Chem., 1936, 177, 103—115).—Na amalgam dropping electrodes have been prepared giving a const. potential, independent of the rate of dropping, when the latter is sufficiently high, and the e.m.f. of amalgam concn. cells has been measured. With a  $COMe_2$ , MeOH, or  $C_5H_5N$  solution of NaI as electrolyte, the relation between the activity coeff.,  $f$ , and concn.  $c$ , for the Na in the amalgam is the same as when  $H_2O$  is the solvent, but with MeCN as solvent there are discrepancies. Attempts to prepare electrodes of the second kind having const. potentials in contact with solutions in  $COMe_2$ , MeCN, and  $C_5H_5N$  were unsuccessful. For NaCl solutions in MeOH, the relation between  $f$  and  $c$ , derived from concn. cell measurements, deviates at the highest dilutions from the Debye-Hückel theory. R. C.

**Phenomenon of induced dissolution of metals in solutions of neutral salts.** V. G. ZAPROMETOV (Bull. Univ. Asié Centrale, 1935, No. 21, 39—47).—The potential developed at a Pb plate in aq.  $CuSO_4$  at  $19^\circ$  has a max. val. for 0.07—0.1% solutions. Pptn. of  $PbSO_4$  from the solution is observed before deposition of Cu on the Pb; analogous results are obtained when  $K_2SO_4$ ,  $(NH_4)_2SO_4$ , or  $NiSO_4$  is substituted for  $CuSO_4$ , and when Cu is immersed in aq. KCNS,  $NH_4CNS$ ,  $Fe(CNS)_3$ ,  $Co(CNS)_2$ , or KCl. The process is conveniently studied by observing the potential changes at a Pt anode placed in a solution containing Cu or Pb and different salts. The mechanism consists in ionisation of the metal and formation of insol. salts. R. T.

**Thermodynamic derivation of diffusion potentials in concentrated solutions.** Z. SZABÓ (Naturwiss., 1936, 24, 539—540).—The method is based on the determination of the e.m.f. of non-isothermal cells. This gives the ratio of the ionic activities, from which the difference of electrode potentials may be calc. From this and the e.m.f. of the concn. cell with transport, the diffusion potential can be calc. A. J. M.

**Reduction-oxidation potential of flavins.**—See this vol., 1127.

**Oxidation-reduction potentials in non-aqueous solutions. II.** J. R. PARTINGTON and J. W. SKEEN (Trans. Faraday Soc., 1936, 32, 975—989; cf. A., 1935, 38).—E.m.f. measurements have been made with cells of the type Pt|oxidised salt+reduced salt+non-aq. solvent|reference electrode. Data are given for  $Cu(CNS)_2$ -CuCNS in  $C_5H_5N$ ,  $CuCl_2$ -CuCl in MeCN,  $FeCl_3$ -FeCl $_2$  in  $COMe_2$ , and  $Pb(OAc)_4$ -Pb(OAc) $_2$  in AcOH, and some results for other similar systems are given. Peters' formula can be applied quantitatively to several of these systems. In some cases unknown complexes are probably formed giving reproducible potentials which do not agree with the equation. In others indefinite potentials are indicated. O. J. W.

**Oxidation-reduction. XXII. Lapachol, lomatiol, and related compounds.** E. G. BALL (J. Biol. Chem., 1936, 114, 649—655).—The vals. of  $E'_0$  for lapachol, lomatiol, and a no. of synthetic 3-hydroxy-

2-alkyl-1:4-naphthaquinones at  $p_H$  1.1—12.6 are tabulated, together with the vals. of  $E_0$ ,  $p_{K_1}$ , and  $p_{K_2}$  at 30°. None of the compounds presents any advantages over phthiocol as an oxidation-reduction indicator. H. D.

**Influence of pressure on potential in relation to the depolarising effect of dissolved gases in the electrolysis of water.** III. V. SCHISCHKIN, J. DUBKOV, and E. KRASNOPOLSKAJA (Z. Elektrochem., 1936, 42, 631—635; cf. A., 1934, 1178).—Apparatus for the electrolysis of  $H_2O$  at pressures up to 200 kg. per sq. cm. is described. The change of p.d. with pressure is small and can be accounted for by the depolarising influence of dissolved gases. E. S. H.

**Polarographic investigations of anhydrous acetic acid solutions.** D. MACGILLAVRY (Trans. Faraday Soc., 1936, 32, 1447—1450).—Features of polarograms obtained with the dropping Hg cathode are compared with those for aq. solutions. With electrolytes in AcOH no breaks characteristic of the ions in solution are obtained and the presence of  $O_2$  does not cause max. E. S. H.

**Platinum electrode. I. Capacity of platinised platinum in different electrolytes and electro-motive behaviour of adsorbed hydrogen.** A. SEHLIGIN and A. FRUMKIN (Acta Physicochim. U.R.S.S., 1935, 3, 791—818; cf. A., 1934, 846).—The relation between the electrode potential  $\phi$  and the quantity of electricity  $Q$  passed has been studied with a large electrode surface and small c.d. The slope of the  $\phi$ - $Q$  curve is at first small (desorption of the adsorbed H), then becomes steeper (formation of the double layer), and finally decreases with the onset of oxidation. The H adsorption depends on the nature of the electrolyte, increasing in the order HBr, HCl,  $H_2SO_4$ , KOH. When the polarising current is interrupted,  $\phi$  remains const. or decreases slowly. If the polarising current is reversed in the "double layer region" hysteresis occurs which varies with the nature of the electrolyte.  $Q$  increases in the ratio 1:1.35 when the c.d. decreases from  $4.5 \times 10^{-4}$  to  $4.5 \times 10^{-6}$  amp. per sq. cm. There is a linear relation between the amount of adsorbed H, taken from the initial region of the  $\phi$ - $Q$  curve, and  $\log p_H$ . The results are discussed in relation to the nature of the adsorbed H layer. R. S.

**Cathode polarisation as a function of the current density in fused salts.** S. KARPATSOV and O. POLTORATSKA (J. Physical Chem., 1936, 40, 763—768).—The polarisation at C electrodes in fused  $PbCl_2$  and  $CdCl_2$  has been studied. The variation of the cathode potential ( $E$ ) with c.d. ( $i$ ) in the region of positive vals. of the potential is attributable to the slowness of diffusion of Pb or Cd atoms from the cathode into the fused electrolyte. For negative vals. of the potential,  $E = a - (RT/2F) \log i$ , where  $a$  is a const. J. W. S.

**Poisoning phenomena and hydrogen over-voltage.** M. G. RAEDER and K. W. NILSEN (Norges Tek. Hiskole Avh. til 25 Ars Jubileet, 1935, 263—279; Chem. Zentr., 1935, ii, 3640—3641).—In the electrolytic evolution of H, the active surface of the cathode plays the same rôle as in heterogeneous

catalysis. Evolution of H is considered to proceed preferentially at those points where the energy barrier between hydrated ions and neutral  $H_2$  mols. is lowest; these spots are occupied preferentially in the deposition of poisoning metals (e.g., Hg, As), thereby raising the val. of the energy barrier, and hence the overvoltage. J. S. A.

**Voltage-current curves obtained with an electrolytic cell and electric oscillations.** T. TERADA (Mem. Coll. Sci. Kyoto, 1936, A, 19, 57—64).—Curves for the p.d.-c.d. relation in a cell consisting of a Pt electrode in aq. HCl and a Pt wire which completes the circuit by touching the surface of the aq. HCl have been obtained. Definite stages in the curves are recognised and discussed. Electrical oscillations are produced. E. S. H.

**Anodic behaviour of gold-copper alloys in 5N-hydrochloric acid and 1N-sulphuric acid.** W. J. MULLER, H. FREISSLER, and E. PLETTERINGER (Z. Elektrochem., 1936, 42, 366—371).—In 5N-HCl all the Au-Cu alloys (0—100% Au) dissolve anodically at a c.d. of 2 amp. per sq. dm. without any passivity phenomena. From 100 to 50 at.-% Au the proportion of the two metals dissolved is the same as that present in the alloy. Between 50 and 30% Au the proportion of Cu dissolved increases, and below 30 at.-% Au only Cu goes into solution. In 1N- $H_2SO_4$  the alloys show passivity phenomena, and no Au is dissolved from any of the alloys. Cu is dissolved readily only up to 10 at.-% Au, and only in traces above 40 at.-% Au. O. J. W.

**Mechanism of electrolytic processes. III. Irreversible reductions.** W. M. LESLIE and J. A. V. BUTLER (Trans. Faraday Soc., 1936, 32, 989—998).—The mechanism of electrolytic reduction is discussed with special reference to the following examples, for which new measurements are recorded.  $COMe_2$ ,  $HCO_2Na$ , and  $C_5H_5N$  at Pb electrodes cause no significant displacement of the H overvoltage curve over the whole range, and these substances are reduced by free at. H.  $PhNO_2$  and  $PhCHO$  are reduced at a Hg electrode at more positive potentials than those at which H is liberated in their absence. These reductions are probably effected by direct transfer of electrons from the electrode, although reduction by absorbed H, liberated below the normal overvoltage, cannot be definitely excluded. In the reduction of  $C_5H_5N$  with a Pt electrode the H overvoltage is displaced in the negative direction; this is due to the adsorption of the substance on the electrode. O. J. W.

**Dimethylglycine buffer.** L. MICHAELIS and M. P. SCHUBERT (J. Biol. Chem., 1936, 115, 221—222).—The prep. of  $NMe_2 \cdot CH_2 \cdot CO_2Na$  (I) for use as a buffer in the range  $p_H$  8.6—9.6 is described and the  $p_H$  of (I)-HCl mixtures tabulated. H. D.

**Classifications of chemical reactions.** N. M. GOPSTEIN (Acta Physicochim. U.R.S.S., 1935, 3, 975—976).—A new derivation of Balandin's equation (cf. A., 1935, 1348) is given. R. S.

**Reaction isotherm and its deduction by means of the equilibrium box.** A. BANCHEFFI (Gazzetta, 1936, 66, 370—374).—A discussion of the methods



used in various text-books of physical chemistry to derive the max. work of a chemical reaction.

O. J. W.

**Kinetics of explosive reactions.** C. N. HINSHELWOOD (Z. Elektrochem., 1936, 42, 445—449).—A lecture.

E. S. H.

**Combustion processes and explosions in the gaseous phase.** M. BODENSTEIN (Z. Elektrochem., 1936, 42, 439—445).—A lecture.

E. S. H.

**Optical investigations on flames.** K. F. BONHOEFFER (Z. Elektrochem., 1936, 42, 449—457).—A lecture describing published work on hydrocarbon,  $H_2$ , and CO flames.

E. S. H.

**Ignition and flame propagation.** W. JOST (Z. Elektrochem., 1936, 42, 461—467).—Published work is discussed.

E. S. H.

**Flames of light and heavy hydrogen.** K. CLUSIUS and H. GUTSCHMIDT (Z. Elektrochem., 1936, 42, 498).—The effect of convection on the propagation of combustion of  $H_2$  and  $D_2$  in  $O_2$  with and without inert gases ( $N_2$ , He, A, Ne) is demonstrated.

E. S. H.

**Detonation.** R. BECKER (Z. Elektrochem., 1936, 42, 457—461).—A lecture on the characteristics of detonation and combustion in gaseous mixtures.

E. S. H.

**Determination of explosion limits of chlorine-hydrogen mixtures.** A. WEISSWEILER (Z. Elektrochem., 1936, 42, 499—503).—The explosion limits, determined by a photographic method, lie between 6 and 84.5%  $H_2$ . At the lower limit the pressure curve shows a marked, superimposed detonation wave. A similar phenomenon has been observed in  $H_2$ - $O_2$  and  $H_2$ -air mixtures.

E. S. H.

**Spectrographic method of studying the thermal decomposition of ozone.** E. VASSY (Compt. rend., 1936, 203, 403—406).—The variation with temp. of the absorption coeff. of  $O_3$  has been determined quantitatively. A knowledge of this variation enables the concn. of  $O_3$  in a mixture to be determined spectrographically. The decomp. of  $O_3$  at  $115^\circ$  is at first bimol., but after about 10 hr. deviations from the bimol. equation occur owing to desorption of  $O_3$  from the walls of the containing vessel.

A. J. M.

**Homogeneous unimolecular decomposition of gaseous alkyl nitrites. VII. Effect of chemical configuration on the reaction rate.** E. W. R. STEACLE, S. KATZ, S. L. ROSENBERG, and W. McF. SMITH (Canad. J. Res., 1936, 14, B, 268—274).—The rate of decomp. of alkyl nitrites, which is determined by the primary reaction  $RO\cdot NO = RO + NO$ , is suitable for examining the effect of chemical constitution on reaction rate. The method of Kassel is used to derive expressions for the rate of reaction at high and low pressures, and the relative rates of reaction of members of an homologous series. The Kassel theory is in good agreement with experiment in the case of the alkyl nitrites, but does not explain why the rate of decomp. increases as the series is ascended. The factors determining this increase are considered.

A. J. M.

**Thermal decomposition of dioxan.** P. GROSS and H. SUESS (Monatsh., 1936, 68, 207—214).—The thermal decomp. of dioxan has been studied at  $459$ — $534^\circ$  and  $50$ — $600$  mm., the main reaction being  $C_4H_8O_2 = 2CO + C_2H_6 + H_2$ , accompanied by  $C_4H_8O_2 = 2CO + 2CH_4$ . The unimol. reaction coeff. ( $k$ ) is almost independent of surface/vol. ratio, and is given by  $k = 3.20 \times 10^7 e^{-37.650/RT} / [1 + 4.95 \times 10^{-6} e^{37.650/RT} / p]$  sec.<sup>-1</sup> ( $p$  in dynes per sq. cm.;  $R$  in g.-cal.). The departure from the simple theory of homogeneous gas reactions is perhaps due to the presence of two or more reactions. The decomp. of  $Me_2CO_3$  at  $450^\circ$  into  $H_2 + CO + CO_2 + CH_4$  at  $184$ — $244$  mm. is heterogeneous to a considerable extent; the reaction  $Me_2CO_3 + H_2O = 2MeOH + CO_2$  at  $305^\circ$  is almost entirely heterogeneous.

R. S. B.

**Pyrogenic condensation of hydrocarbons. V. Kinetics of polymerisation of hexanes.** M. S. NEMTZOV and A. V. POLETAEV (J. Gen. Chem. Russ., 1936, 6, 892—897).—The energy of activation of the reaction of polymerisation of  $\Delta^3$ - $n$ -hexene (I) at  $350$ — $400^\circ$  is  $38,000 \pm 1000$ , and the velocity coeff. is given by  $\log k = 9.07 - 38,000/4.57T$ . The velocity of polymerisation of  $\gamma$ -methyl- $\Delta^3$ -pentene (II) is half as great as that of (I). The products are chiefly the di- and tri-merides. (I) is more stable than (II).

R. T.

**Kinetics of the thermal decomposition of alkylene oxides. I. Ethylene oxide.** H. W. THOMPSON and M. MEISSNER (Trans. Faraday Soc., 1936, 32, 1451—1460).—The reaction products are mainly  $CH_4$  and CO. The reaction is approx. first order. The unimol. velocity coeff. falls with decreasing initial pressure in the same way as in other quasi-unimol. decomp., and the plot of  $k$  against the initial pressure has a segmented appearance. The reaction is homogeneous; there is no evidence of the propagation of reaction chains. The energy of activation at the higher pressures is about  $53,000$  g.-cal., falling slightly as the initial pressure is lowered.

E. S. H.

**Influence of temperature on inflammation limits of combustible vapours in air.**—See B., 1936, 728.

**Upper temperature limit of explosion of explosives.**—See B., 1936, 910.

**Gaseous explosions. Critical initial temperature for maximum rate of pressure rise.** W. A. PEARL and G. G. BROWN (Ind. Eng. Chem., 1936, 28, 1058—1065).—Bomb experiments indicate that the crit. initial temp. ( $T'$ ), at which the rate of pressure rise on explosion is a max., depends on the composition of the products of combustion and the diluents. Explosive mixtures giving products having heat capacities with low temp. coeffs. are characterised by high  $T'$ , and the greater is the C : H ratio of the fuel, the lower is  $T'$ . In all cases, increasing the diluent, or excess of  $O_2$  or fuel, raises  $T'$ , whilst increasing the excess of  $H_2$  fuel raises  $T'$  relatively much < increasing the hydrocarbon fuel.  $T'$  under conditions of const. initial pressure is < at const. initial  $d$  for both theoretical and near theoretical mixtures containing small concns. of diluent  $N_2$ . For mixtures containing concns. of diluent  $N_2$  < that of

air,  $T$  at const. initial pressure is  $>$  at const. initial  $d$ . Similar relations are found in gasoline engine tests.

H. C. M.

**Mechanism of hydrocarbon combustion.** A. R. UBBELOHDE (Z. Elektrochem., 1936, 42, 468—471).—A lecture.

E. S. H.

**Induction time and ignition temperature of methane-oxygen mixtures.** H. SACHSSE (Z. Elektrochem., 1936, 42, 504).—The induction period, when  $\text{CH}_4$  and  $\text{O}_2$  (2 : 1) are passed through a quartz tube at 850—950°, has been measured. A chain mechanism is proposed.

E. S. H.

**Mechanism of oxidation of hydrocarbons.** W. JOST, L. (FRHR.) VON MUFFLING, and W. ROHRMANN (Z. Elektrochem., 1936, 42, 488—497).—Mainly a discussion of published work. Experiments on the oxidation of paraffins, naphthenes, and olefines are described. The results support earlier work. There are sharp pressure limits of explosion at const. temp., and at certain compositions wide temp. ranges in which explosion does not occur. The action of anti-knock agents is discussed.

E. S. H.

**Explosive oxidation of methane.** N. KOBOSOV, J. KASARNOVSKI, and L. KASHTANOV (Acta Physicochim. U.R.S.S., 1935, 3, 857—878).—The yield of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{H}_2$  per cu.m. of  $\text{CH}_4$  consumed in an equimol. mixture of  $\text{CH}_4$  and  $\text{O}_2$  is independent of pressure up to 3.70 atm. and is unaffected by the nature of the wall or the diameter of the vessel, although the amount of  $\text{CH}_4$  oxidised is less in narrow vessels. The influence of additions of  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  is in agreement with thermodynamic requirements. The explosion temp. calc. from the water-gas equilibrium data agrees closely with that calc. from sp. heat data, and it is inferred that equilibrium is attained in the explosion. If  $\text{H}_2\text{O}$  is present initially  $\text{CH}_2\text{O}$  and  $\text{EtOH}$  are formed and equilibrium is not attained. The reaction forms a suitable source of  $\text{H}_2$  for the  $\text{NH}_3$  synthesis.

R. S.

**Synthesis of hydrogen sulphide.** D. PORRET (Helv. Chim. Acta., 1936, 19, 680—694).—The reaction between  $\text{H}_2$  and  $\text{S}$  has been studied at 307° and 343° by a static method and at 450° and 500° by a dynamic method. At the lower temp. the rate  $\propto [\text{H}_2][\text{S}]^{\frac{1}{2}}$ . In this temp. range  $[\text{S}_2]$  is also  $\propto [\text{total S}]^{\frac{1}{2}}$ . At the higher temp. both  $\text{S}_8$  and  $\text{S}_2$  may react with  $\text{H}_2$ . The rate is  $>$  that calc. from the activation energy (52,000 g.-cal.). The reaction is not a normal bimol. reaction and may involve chains initiated by a process such as  $\text{H}_2 + \text{S}_2 = \text{H}_2\text{S} + \text{S}$ , or heterogeneously.

H. J. E.

**Theory of electrokinetic effects in solution; reactions between ions.** E. A. MOELWYN-HUGHES (Proc. Roy. Soc., 1936, A, 155, 308—315).—Bimol. reactions in solutions have normal velocity when  $k = Ze^{-E_A/RT}$ .  $E_A$  is the energy of activation (Arrhenius) and  $Z$  is a theoretical collision frequency. The abnormality in the reaction rate is determined by the term  $P$  in  $k = PZe^{-E_A/RT}$ . The abs. magnitude of the velocity is considered, and attempts are made to interpret the experimental vals. of  $P$  as high as  $10^8$  and as low as  $10^7$ . The deviation from normal behaviour is attributed to electrostatic

attraction. Debye and Huckel's expression is introduced and theoretical equations are obtained for  $P$  and the variation of  $E_A$  with temp. and ionic strength.

L. L. B.

**Influence of the solvent on the kinetics of bimolecular reactions in solutions.** B. I. SVESHNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 61—65).—Theoretical. The influence of viscosity on the velocity coeff. is related to the mean life of the activated state.

R. S.

**Interaction of sodium formate and sodium hydroxide.** A. A. BALANDIN and L. C. FREIDLIN (J. Gen. Chem. Russ., 1936, 6, 868—872).—The reaction between  $\text{HCO}_2\text{Na}$  (I) and  $\text{NaOH}$  commences at 210°, and proceeds at high velocity at 250°. In presence of the theoretical amount of  $\text{NaOH}$  it is represented as  $(\text{I}) + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2$ , whilst in presence of excess of (I), and at  $>270^\circ$ , the reaction  $2(\text{I}) \rightarrow \text{Na}_2\text{C}_2\text{O}_4$  (II) +  $\text{H}_2$  takes place. (II) also reacts at  $>260^\circ$  as follows:  $(\text{II}) + 2\text{NaOH} \rightarrow 2\text{Na}_2\text{CO}_3 + \text{H}_2$ .

R. T.

**Kinetics of the oxidation of formic acid by iodic acid.** E. ABEL and A. BILDERMANN (Monatsh., 1936, 68, 215—232).—The reaction  $5\text{HCO}_2\text{H} + 2\text{HIO}_3 = \text{I}_2 + 5\text{CO}_2 + 6\text{H}_2\text{O}$  has been studied at 60°. I is an inductor owing to the reaction  $\text{I}_2 + \text{HCO}_2\text{H} = \text{CO}_2 + 2\text{HI}$  (a), followed by  $\text{HIO}_3 + 5\text{HI} = 3\text{I}_2 + 3\text{H}_2\text{O}$  (b). For (a)  $d(\text{CO}_2)/dt = 1.0 \times 10^2 [\text{I}_2][\text{HCO}_2\text{H}]$ , where  $t$  is in min. and concn. in mol. per litre.  $\text{HOI}$  formed by hydrolysis of I reacts  $(\text{HOI} + \text{HCO}_2\text{H} = \text{CO}_2 + \text{H}_2\text{O} + \text{HI})$  according to  $d(\text{CO}_2)/dt = 5.7 \times 10^2 [\text{HOI}][\text{HCO}_2\text{H}]\{1 + 5.7[\text{HCO}_2\text{H}]\}$ . The reaction between  $\text{HCO}_2\text{H}$  and  $\text{HIO}_3$  is expressed as a function of the subsidiary reactions, and is compared with the reaction between  $\text{HIO}_3$  and  $\text{H}_2\text{C}_2\text{O}_4$  (cf. A., 1935, 587).

R. S. B.

**Kinetics of saponifications of iodoacetic acid by sodium hydroxide and by certain alkaline buffer solutions.** R. BRDIČKA (J. Gen. Physiol., 1936, 19, 899—906).—The bimol. velocity coeffs. of the rate of hydrolysis of iodoacetic acid increase with the ionic strength of the solution. In borate buffer solutions, the reaction is unimol.; at  $>11.2$  the coeffs.  $\propto [\text{OH}^-]$ , and at  $p_H < 11.2$  they  $\propto [\text{borate}]$ .

F. A. A.

**Mechanism of thermal poly-condensation reactions.** H. DOSTAL and R. RAFF (Monatsh., 1936, 68, 188—201, 247—250).—(A) The general theory of poly-condensations is discussed and is applied to the reactions between succinic acid (I) and  $(\text{CH}_2\text{OH})_2$  (II) and  $(\text{C}_2\text{H}_4\text{OH})_2$  at 110—150° in dioxan. The relative quantity of condensation =  $1 - (1 + at/2)^{-2}$ , where  $a$  is a reaction coeff.; there is no induction period. The reaction velocity for (II) varies for the first 10 hr. with approx. the second power of the concn., and then with a lower power. The temp. coeff. and influence of medium are discussed.

(B) The reaction between (I) and (II) has been further studied, leading to a revised val. of the activation energy. The influence of the solvent is small.

R. S. B.

**Thermal mutarotation of *d*-galactose, *l*-arabinose, and *d*-talose.** H. S. ISBELL and W. W.



PIGMAN (J. Res. Nat. Bur. Stand., 1936, 16, 553—554).—Aq. solutions of galactose (I), arabinose (II), and talose (III) were cooled rapidly from 25° to 0° and the change with time of  $\alpha$  was observed. The thermal mutarotation consists of (a) a rapid change due to a change in concn. of the labile constituents, and (b) a slow change due to a disturbance in the equilibrium of  $\alpha$ - and  $\beta$ -isomerides. The heats of activation for the reactions (a) and (b) for (I), (II), and (III) are respectively (a) 15,040, 14,700, and 12,750; (b) 17,130, 16,800, and 15,820 g.-cal. per g.-mol. The ordinary mutarotations of (I) and (II) are in agreement with published vals. For  $\alpha$ -d-talose (previously undetermined)  $[\alpha]^{20} = 9.3 \times 10^{-0.0263t} + 37.9 \times 10^{-0.126t} + 20.8$ ;  $[\alpha]_D^{25} = 9.8 \times 10^{-0.00362t} + 27.5 \times 10^{-0.0255t} + 25.2$ , where  $t$ —time. R. S. B.

**Specificity of salt effect in some ionic reactions.** L. SMITH [with B. OLIN] (Z. physikal. Chem., 1936, 177, 131—157).—The rates of hydrolysis at 25° by NaOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub> of chloro-substituted hydroxycarboxylic acids, acetyl- and benzoyl-citric acids, and bromotricarballic acid have been determined, the acid anion (I) and OH<sup>-</sup> being in equiv. concns. of 0.004—0.03M; the chloride or nitrate of the base was present in some cases. The Bronsted-Debye-Hückel equation  $\log(k/k_0) = z_A z_B \sqrt{\mu}$ , where  $k$  is the bimol. velocity coeff. in a medium of ionic strength  $\mu$ , and  $z_A, z_B$  are valencies, is not, in general, valid. This discrepancy is partly due to the salt action being affected by the constitution of (I) and the sp. properties of the metal ion, and complex formation may also play some part. Dibasic acids exhibit greater ionic effects than monobasic acids, and in some cases configuration plays a part. In some reactions Na<sup>+</sup> ions have a negative salt effect, whilst bivalent ions have a normal positive effect. The temp. coeffs. of some of the reactions have been measured. The dissociation consts. of some of the acids have been determined from conductivity measurements. R. C.

**Kinetics of decomposition of the  $\gamma$ -bromobutyrate ion in neutral and in alkaline solution.** E. F. CALDIN and J. H. WOLFENDEN (J.C.S., 1936, 1239—1241).—The decomp. of Na  $\gamma$ -bromobutyrate in neutral and NaOH solutions has been investigated at 0—25° by conductivity measurements. In neutral solution, lactonisation takes place, not by a pseudo-unimol. mechanism involving collisions with solvent mols., but by a truly unimol. ionisation process of which the heat of activation is 32,500 g.-cal. and the velocity requires  $\approx 7$  internal degrees of freedom of the mol. In alkaline solution, lactonisation is followed by a bimol. reaction of the lactone with OH<sup>-</sup>. The temp. coeff. of the bimol. reaction leads to a heat of activation of 6450 g.-cal. and a  $P$ -factor of  $10^{-7}$ . J. G. A. G.

**Hydrolysis of monochloroacetate ion in light and heavy water.** O. RETZ (Z. physikal. Chem., 1936, 177, 85—94).—Hydrolysis by OH<sup>-</sup> is about 20% more rapid in D<sub>2</sub>O than in H<sub>2</sub>O. In acid and neutral solution both CH<sub>3</sub>Cl·CO<sub>2</sub><sup>-</sup> (I) + H<sub>2</sub>O  $\rightarrow$  OH·CH<sub>2</sub>·CO<sub>2</sub>H (II) + Cl<sup>-</sup> and 2(I) CH<sub>2</sub>Cl·CO<sub>2</sub>·CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> (III) + Cl<sup>-</sup>; (III) + H<sub>2</sub>O  $\rightarrow$  (II) + (I) are retarded in D<sub>2</sub>O by about 8%. This retard.

ation is probably purely a solvent effect and not directly connected with the reaction mechanism. R. C.

**Hydration rate of methylethylethylene [ $\beta$ -methyl- $\Delta^2$ -butene] in aqueous solutions of acids.** Y. P. LIU and T. C. WEI (J. Chinese Chem. Soc., 1936, 4, 297—304; cf. A., 1934, 1312).—The rate of hydration of CH<sub>2</sub>:CMeEt to CMe<sub>2</sub>Et·OH by dil. HNO<sub>3</sub> at 25° and 35° and const. ionic strength is unimol. with respect to each reactant. At const. [HNO<sub>3</sub>], the rate is increased by adding KNO<sub>3</sub>. The temp. coeff. is 3.21 corresponding with the energy of activation 21.04 kg.-cal. The rate of hydration of the olefines is in the order isobutene > CH<sub>2</sub>:CMeEt > CHMe:CMe<sub>2</sub>, probably owing to steric effects. The catalytic effect of 0.1M-acids on the hydration of CH<sub>2</sub>:CMeEt at 25° is in the order H<sub>2</sub>SO<sub>4</sub> > HCl > HClO<sub>4</sub> > HBr > HNO<sub>3</sub> > C<sub>6</sub>H<sub>5</sub>Me·SO<sub>3</sub>H > H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> > AcOH. J. G. A. G.

**Application of the chain theory of chemical change to certain enzyme reactions.**—See this vol., 1296.

**Kinetics of reaction between -SH groups and iodoacetic acid.**—See this vol., 1291.

**Kinetics of polymerisation and poly-condensation reactions.** H. MARK (Chem. Weekblad, 1936, 33, 514—515).—A lecture. S. C.

**Application of Hahn's emanation method to investigation of reactions in solid state.** III. R. JAGITSCH (Z. physikal. Chem., 1936, B, 33, 196—200).—For the formation of PbSiO<sub>3</sub> from PbO and SiO<sub>2</sub> at 500—700°, followed by the above method, the unimol. law is valid. At 500—640° the velocity coeff.,  $k$ , is at first determined by the rate of diffusion of the PbO to the SiO<sub>2</sub>, but after a time abruptly assumes a lower val., being now determined by the rate of diffusion of the PbO through the PbSiO<sub>3</sub>. At 700°, however,  $k$  remains const. throughout, being determined by the rate of diffusion of the PbO to the SiO<sub>2</sub>. R. C.

**Corrosion.**—See B., 1936, 743, 744.

**Theories of corrosion. II. Distribution of corrosion.** J. E. O. MAYNE (J.C.S., 1936, 1095—1098).—The distribution of corrosion of rectangular steel specimens partly immersed in 0.1N-KCl departs progressively from Evans' "ideal distribution" as the thickness is increased, until, with specimens of square cross-section, there is no preferential corrosion at the edges, consistent with the distribution of corrosion being governed by alkali distribution. The corrosion of a composite steel plate of two laminæ separated by insulating material, partly immersed at an angle of 45° in 0.1N-KCl, follows Evans' "ideal distribution," but the attack on the upper surface is > on the lower. When the aq. KCl contains 0.1 of the saturation val. of CO<sub>2</sub>, the distribution of corrosion of the upper surface is not affected, but the whole of the lower surface is attacked, indicating that the alkali concn. at the upper surface is > at the lower surface, and supporting the view that total O<sub>2</sub> supply governs the amount of corrosion. J. G. A. G.

**Reactions of atomic oxygen with halogen salts of mercury.** S. ROGINSKI and A. SCHECHTER (Acta

Physicochim. U.R.S.S., 1935, 3, 219—222).—At. O reacts with  $\text{HgX}_2$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ), more readily at 200—300°. The heats of activation for  $\text{HgCl}_2$  and  $\text{HgI}_2$  are approx. 3000 and 6000 kg.-cal., respectively. All the reactions are accompanied by a sharp and intense fluorescence. O. J. W.

**Dissolution of magnesium oxide in magnesium sulphate solutions.** (MLLE.) M. L. DELYON (Bull. Soc. chim., 1936, [v], 3, 1632—1638).—The curve relating amount dissolved with time for  $\text{MgO}$  in aq.  $\text{MgSO}_4$  shows a regular initial increase to a max. val., a period during which little or no further dissolution occurs, and then a period of pptn. of oxysulphate. The solubility, defined by the max. amount of  $\text{MgO}$  absorbed,  $\propto$  the  $[\text{MgSO}_4]$ . Rise in temp. increases the solubility and accelerates the formation of oxysulphate. Optimum conditions for the production of the latter are deduced. J. W. S.

**Attack of aluminium by chlorine.** I. M. G. EVANS (Mem. Manchester Phil. Soc., 1934—1935, 79, 13—28).—The velocity of attack of Al foil by  $\text{Cl}_2$  at 134—254° and 100—600 mm. is independent of the pressure and has an apparent energy of activation of 2000 g.-cal. During attack large crystals of Al are broken up and the X-ray powder photograph becomes sharper. The kinetics of the reaction are discussed. R. S. B.

**Mechanism of combustion of graphite at different temperatures.** II. V. N. PERTZOV and M. C. KARAPETJANTZ (J. Appl. Chem. Russ., 1936, 9, 1269—1277).—The reaction  $\text{C} + \text{O} \rightarrow \text{CO}_2$  proceeds at low velocity at <600°; at >600° the C is surrounded by a zone of burning CO, as a result of which the  $[\text{O}_2]$  of the atm. in contact with the C falls, and the velocity of combustion of the C correspondingly diminishes. A second break is observed at 800—850°, at which  $\text{O}_2$  is entirely absent from the atm. surrounding the C, the reaction taking place at the surface being  $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ . R. T.

**Kinetics and heat of adsorption of ethylene by platinum.** E. B. MAXTED and C. H. MOON (Trans. Faraday Soc., 1936, 32, 1375—1381).—In the slow secondary adsorption that follows the immediate primary process, the ratio of the vol. adsorbed to the square root of the time is const. The mol. heat of adsorption of  $\text{C}_2\text{H}_4$  by Pt is 9 kg.-cal. E. S. H.

**Rate of dissolution of paraformaldehyde.**—See this vol., 1232.

**Induced and catalysed reactions.** F. FEIGL (Oesterr. Chem.-Ztg., 1936, 39, 139—140).—A lecture.

**Causes of decomposition of hydrogen peroxide, and the stabilisation of perhydrol.**—See B., 1936, 884.

**Effect of nitrate ions on the systems  $\text{Zn}^\circ/\text{Ni}^{+++}$  in water and  $\text{Zn}^\circ/\text{Ni}^\circ$  in water.** A. OLIVERIO and O. BELFIORI (Rend. sem. fac. sci. Univ. Cagliari, 1933, 3, 51—55).—Traces of  $\text{NO}_3^-$  retard the pptn. of Ni from its salts by Zn and also the reaction  $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{++} + \text{H}_2$ . Large amounts of  $\text{NO}_3^-$  lead to the formation of basic Zn and Ni salts. The passive effect produced by  $\text{NO}_3^-$  is due to the ion itself and not to its reduction products ( $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ).

CH. ABS. (e)

**Stabilisation of diazo-compounds in solution.**—See B., 1936, 779.

**Mechanism of autoxidation of hydrocarbons in the liquid phase.** M. N. MICHAILOVA and M. B. NEIMAN (J. Gen. Chem. Russ., 1936, 6, 821—838).—The velocity of oxidation  $v$  of cracking benzene  $\propto$  partial  $\text{O}_2$  pressure, temp., and liquid-gas interface, and inversely  $\propto$  concn. of inhibitor ( $\alpha\text{-C}_{10}\text{H}_7\text{OH}$ ). The length of the induction period  $\propto 1/v$ , and is smaller in presence than in absence of light, active centres being formed only at the surface in the latter case, and also in the bulk of the liquid in the former. The action of inhibitors consists in interrupting oxidative chain reactions taking place in the bulk of the liquid. Oxidation does not take place in the gaseous phase at low temp. R. T.

**Ascorbic acid as catalyst in oxidation of unsaturated fats.**—See this vol., 1303.

**Induction effect of ascorbic acid on oxidation of sugar.**—See this vol., 1304.

**Contact question as an equilibrium problem.** R. SCHENCK (Angew. Chem., 1936, 49, 649—653).—The sp. characteristics of mixed catalysts, and the action of promoters, are related to the influence of solid reactions on the heterogeneous equilibria obtaining between the catalyst and a gaseous component. Thus with mixtures of oxides, addition of an oxide capable of mixed crystal or compound (e.g., spinel) formation considerably affects the equilibrium  $\text{O}_2$  pressure of the system (cf. A., 1930, 43). Similar effects in reduction reactions are shown by the equilibrium  $\text{H}_2\text{S}-\text{H}_2$  ratio over  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  or  $\text{PbS}-\text{Sb}_2\text{S}_3$  mixtures, and by the  $\text{CH}_4-\text{H}_2$  ratio over Mn-Cu alloys. J. S. A.

**Stable platinum alloys as catalysts of oxidation of ammonia.**—See B., 1936, 832.

**Surface reactions at very low pressures.** III. **Platinum-iodine.** C. NOGAREDA (Anal. Fis. Quím., 1934, 32, 658—665; cf. A., 1935, 711, 941).—A Pt wire is attacked by I atoms at 1200—1350°, affording  $\text{PtI}_2$ . The reaction is strongly endothermic, of zero order, and in accordance with a mechanism of limiting adsorption. A sublimated Pt layer adsorbs at 0° a limiting unimol. I film, stable to about 100°. A reduced Pt layer adsorbs only about half this amount of I. A simultaneous attack by I atoms on the wire and on the reduced Pt layers has been observed above 1200°. L. A. O'N.

**Evolution of sulphur dioxide and trioxide from calcium sulphate treated with chlorine in presence of a catalyst.** P. P. BUDNIKOV and E. I. KRETSCH (J. Appl. Chem. Russ., 1936, 9, 995—1009).—Decomp. of  $\text{CaSO}_4$  in presence of  $\text{Cl}_2$  commences at 800—850° in absence, and at 700—750° in presence, of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , or  $\text{SiO}_2$ . The activity of catalysts at 900—950° falls in the order  $\text{NiSO}_4 > \text{CuSO}_4 > \text{MnCl}_2 > \text{MnO}_2 > \text{MgSO}_4 > \text{Fe}_2\text{O}_3 > \text{KCl}$ . Decomp. commences at 450—500° for 4 : 1 C- $\text{CaSO}_4$  mixtures, and is completed after 1 hr. at 700°. Addition of steam to the  $\text{Cl}_2$  has no effect on the reaction. Max. velocity of decomp. is found for 1 : 4 mol.  $\text{CaSO}_4$ - $\text{SiO}_2$  mixtures, the best effect being given by amorphous  $\text{SiO}_2$ .

R. T.



**Vanadium catalysts for sulphuric acid production.**—See B., 1936, 737.

**Amorphous and crystalline oxide hydrates and oxides. XXVII. Catalytic decomposition of hydrogen peroxide and the "active positions" of the amorphous ferric hydroxides and the products of their ageing.** A. KRAUSE [with D. KANIOWSKA] (Ber., 1936, 69, [B], 1982—1990; cf. this vol., 947).—The roentgenographically amorphous ortho-Fe<sup>III</sup> hydroxides (I) decompose H<sub>2</sub>O<sub>2</sub> fairly rapidly, the change being of the first order. Slowly and rapidly ageing, non-ageing, freshly prepared, and aged specimens are equally active because they all readily unite with Ag. H replaceable by Ag in the ortho-hydroxides must be regarded as active in Wieland's sense; H<sub>2</sub>O<sub>2</sub> can therefore cause dehydrogenation whereby it becomes decomposed. The chemistry of the process which involves the intermediate production of a labile Fe<sup>III</sup> peroxide is discussed. When suitable treatment causes (I) to lose its power of uniting with Ag, the catalytic activity is very considerably diminished. The amorphous condition and the "ageing activity" are not related directly with the catalytic decomp. of H<sub>2</sub>O<sub>2</sub>. "Active positions" may also be present in cryst. Fe<sup>III</sup> hydroxides if the necessary OH contain H replaceable by Ag. A fresh, almost yellow product showing distinctly the interferences of goethite united readily with Ag and accelerated the decomp. of H<sub>2</sub>O<sub>2</sub>, but further ageing in *N*- and 0.5*N*-NaOH destroyed both types of activity. The product thus formed, (α-Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O)<sub>n</sub>, is identical in these properties with Bohm's autoclaved material, from which it differs in apparent *d* and solubility in 1.4*N*-H<sub>2</sub>SO<sub>4</sub>. The use of C<sub>5</sub>H<sub>5</sub>N in the prep. of (I) appears to cause somewhat lessened activity. Decomp. of H<sub>2</sub>O<sub>2</sub> depends greatly on [H<sup>+</sup>] and proceeds most rapidly in alkaline solution. The increasingly intense decomp. of H<sub>2</sub>O<sub>2</sub> during the hydrolysis of Fe<sup>III</sup> salts is due to the production of basic salts the mols. of which are laden with OH groups. In addition to active positions of the "first rank" which must be regarded as identical with H atoms and cause marked decomp. of H<sub>2</sub>O<sub>2</sub>, there exist centres of the "second rank" which are probably related to the colloid-chemical properties of (I). H. W.

**Reaction zones in the reduction of magnetite and hæmatite with hydrogen.** G. TSCHUFAROV and E. TATIEVSKAJA (Acta Physicochim. U.R.S.S., 1935, 3, 957—974).—The reaction is autocatalytic. The change in porosity with temp. and degree of reduction has been studied and related to the reaction rate. Magnetite is less porous than hæmatite, but below 600° the rate of reduction is faster. Above this temp. the porosity and the rate of reduction decrease rapidly in both cases. Microscopical investigations show the presence of the layers α-Fe-Fe<sub>3</sub>O<sub>4</sub> in the case of magnetite, and α-Fe-Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> in the case of hæmatite, whilst FeO could not be detected, and it is suggested that Fe<sub>3</sub>O<sub>4</sub>→Fe is the rate-determining process. The rate of advance of the reduction zone is linear below 500°, and the activation energy for hæmatite is 15,700 g.-cal. R. S.

**Platinum electrode as a catalyst for the activation of hydrogen.** M. CALVIN (Trans. Fara-

day Soc., 1936, 32, 1428—1436).—The rate of the reaction D<sub>2</sub>+H<sub>2</sub>O→HD+HDO, catalysed by a Pt electrode in neutral and acid solutions, is reversibly retarded by small cathodic polarisations, but not increased by anodic polarisation up to 0.7 volt. Higher anodic polarisation inhibits the reaction irreversibly. The observations are discussed.

E. S. H.

**Thiol compounds as catalysts for the decomposition of sodium azide by iodine.** E. FRIEDMANN (J. pr. Chem., 1936, [ii], 146, 179—192).—Qual. and quant. study is made of the effect of 19 S compounds on the decomp. of NaN<sub>3</sub> by I. SH compounds cause much immediate decomp., linked with the reaction 2RSH→I<sub>2</sub>→R<sub>2</sub>S<sub>2</sub>+2HI, followed by a further slow decomp., linked with the reaction R<sub>2</sub>S<sub>2</sub>+5I<sub>2</sub>+6H<sub>2</sub>O→2RSO<sub>3</sub>H+10HI. Disulphides effect only the slower decomp. Sulphides are without action. CS(NH<sub>2</sub>)<sub>2</sub>, 4-methylthiohydantoin, and [NH<sub>2</sub>-C(NH)<sub>2</sub>-S]<sub>2</sub> cause the same violent decomp. as do SH compounds. The no. of mols. of NaN<sub>3</sub> decomposed varies greatly with the nature of the S compound, the ratio of the wts. of S compound and NaN<sub>3</sub>, and the concns. A chain mechanism is proposed. R. S. C.

**Catalytic reduction of carbon monoxide at ordinary pressures. VII. Influence of alkali content on the iron-copper catalyst.** S. KODAMA and K. FUJIMURA. **VIII. Influence of the proportions of the two metals in the iron-copper catalyst.** K. FUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 272—279, 280—284; cf. B., 1935, 132).—VII. The reaction between CO and H<sub>2</sub> (1:2) has been studied at approx. 270° on an Fe-Cu (1:1) catalyst in presence of 0—0.05 mol. of Na<sub>2</sub>CO<sub>3</sub> per mol. of Fe. The Na<sub>2</sub>CO<sub>3</sub> increases the initial activity of the catalyst, but the rate of decrease in activity is > in the absence of Na<sub>2</sub>CO<sub>3</sub>. The Na<sub>2</sub>CO<sub>3</sub> increases the yield of hydrocarbons of high mol. wt.

**VIII.** The reaction between CO and H<sub>2</sub> (1:1) has been studied at approx. 270° on Fe-Cu catalysts (5:1, 3:1, and 1:2). The yield of benzene is unaffected by alteration in the Fe:Cu ratio, but the gas contraction is highest with the 1:2 catalyst.

R. S. B.

**New method of preparing catalysts.** L. FAUCONNAU (Compt. rend., 1936, 203, 406—407).—Cu and Co of high catalytic activity may be obtained from Devarda's alloy (Al-Cu-Zn) and Co<sub>2</sub>Al<sub>3</sub>, respectively, by repeated treatment with NaOH, washing with H<sub>2</sub>O and EtOH by decantation, and storing under EtOH. The catalysts will aid the dehydrogenation of primary and sec. alcohols. In the case of hydrogenations, the two catalysts give, in general, different results.

A. J. M.

**Catalytic action of copper oxide in the combustion of hydrogen. II.** G. TEDESCHI (Gazzetta, 1936, 66, 417—420; cf. this vol., 570).—Further experiments confirm the view that in the combustion of H<sub>2</sub>-O<sub>2</sub> mixtures the CuO acts as an O<sub>2</sub>-carrier.

O. J. W.

**Reduction of copper oxide and stannic oxide with Sarmasel natural gas.** C. CANDEA and J.

KÜHN (Petroleum, 1936, 32, No. 35, 11—14; cf. A., 1935, 592).—Reduction of CuO by natural gas (98.6% CH<sub>4</sub>) begins at 400° and is complete at 720°. Below 600° CH<sub>4</sub> is oxidised to CO<sub>2</sub> only, and very little H<sub>2</sub> is liberated. Above 600° CO appears and H<sub>2</sub> rises to 6.5%. C is deposited at all temp., its amount being independent of the degree of reduction  $r$ . Cu catalyses the decomp. of CH<sub>4</sub>, the H<sub>2</sub> formed then reducing CuO. Reduction of SnO<sub>2</sub> begins at 700°, and is complete at 910°;  $r$  is but little dependent on the rate of streaming of the CH<sub>4</sub>. Little C is deposited. The gases are low in H<sub>2</sub>, but contain unsaturated hydrocarbons (I). Sn has little catalytic effect on the CH<sub>4</sub> decomp., but promotes the formation of (I).

J. S. A.

**Catalytic interchange of hydrogen with water and alcohol.** D. D. ELEY and M. POLANYI (Trans. Faraday Soc., 1936, 32, 1388—1397).—The rate of the first step in the at. interchange in presence of Pt-black has been determined by the use of the para-H<sub>2</sub> conversion and the D<sub>2</sub>+H<sub>2</sub>=2HD reaction. The rate-determining step is the splitting of H<sub>2</sub>, which is influenced by the nature and acidity of the liquid. The products of dissociation of H<sub>2</sub> cannot be homopolar H atoms, but must be H<sup>+</sup> ions or H atoms in a strongly polarised state, e.g., participating in a Pt-H linking.

E. S. H.

**Activation of specific bonds in complex molecules at catalytic surfaces. I. Carbon-hydrogen linking in methane and methane-d<sub>4</sub>.** K. MORIKAWA, W. S. BENEDICT, and H. S. TAYLOR (J. Amer. Chem. Soc., 1936, 58, 1445—1449).—CH<sub>4</sub> undergoes exchange with D<sub>2</sub>, CD<sub>4</sub>, and D<sub>2</sub>O on active Ni catalysts at <138°. At 184° the rate of reaction with CH<sub>4</sub> decreases in the order CD<sub>4</sub>>D<sub>2</sub>>D<sub>2</sub>O. The activation energies of reaction with CD<sub>4</sub> and D<sub>2</sub> are ~19 and ~28 kg.-cal., respectively. The rate-determining step is ascribed to the activation of the C-H linking of CH<sub>4</sub>.

E. S. H.

**Reduction of carbon dioxide to higher hydrocarbons.**—See B., 1936, 727.

**Nitration of benzene.**—See B., 1936, 779.

**Activation of hydrogen by phthalocyanine and copper phthalocyanine. I.** M. CALVIN, E. G. COCKBAIN, and M. POLANYI. **II.** M. CALVIN, D. D. ELEY, and M. POLANYI (Trans. Faraday Soc., 1936, 32, 1436—1443, 1443—1446).—I. Crystals of phthalocyanine (I) and Cu phthalocyanine (II) can activate H<sub>2</sub>. They show at. interchange with H<sub>2</sub>, catalyse the at. interchange between H<sub>2</sub> and H<sub>2</sub>O (activation energy 6 kg.-cal.), and catalyse the formation of H<sub>2</sub>O from H<sub>2</sub> and O<sub>2</sub> (activation energy 18 kg.-cal.).

**II.** The conversion of para-H<sub>2</sub> into normal H<sub>2</sub> is catalysed by (I) and (II), the activation energies being 5700 and 5000 g.-cal., respectively. The positive temp. coeff. shows that the reaction involves a disruption of the H-H linking by chemisorption.

E. S. H.

**Promoter action of platinic chloride on Raney nickel catalyst.**—See this vol., 1237.

**Catalytic transformations of heterocyclic compounds.**—See this vol., 1264.

**Electrolytic oxidation of graphite in fused alkali.** V. SIHVONEN and K. VOHLONEN (Suomen

Kem., 1936, 9, A, 67—69).—A cylinder of purest natural graphite is used as anode, immersed in either molten NaOH or a mixture of NaOH and KOH, at 500° approx. No org. compounds are found after electrolysis. The carbonate produced and the H<sub>2</sub> evolved correspond closely with that calc. from the current consumption. The bearing of the results on theories of the combustion of graphite is discussed.

D. C. J.

**Oxidation of cobalt amalgam.** F. P. DWYER and J. W. HOGARTH (J. Proc. Roy. Soc. New South Wales, 1936, 69, Part 2, 105—110).—Co amalgam is prepared by electrolysis of aq. CoSO<sub>4</sub> at various c.d. In all cases the isolated compound is Co<sub>2</sub>Hg<sub>3</sub>. Rapid atm. oxidation causes the separation of a fine, black powder, Co<sub>2</sub>O, which subsequently decomposes into CoO and Co in pyrophoric condition. The oxidation product has powerful reducing properties.

E. A. R.

**Corrosion protection of iron.**—See B., 1936, 888.

**Electrolytic removal of iron from solutions of aluminium salts.**—See B., 1936, 738.

**Alkaline plating baths containing ethanolamines.**—See B., 1936, 746.

**Rate of linear crystallisation KG<sub>1</sub> of silver peroxide deposited at the anode.** A. GLAZUNOV and L. SCHLEICH (Coll. Czech. Chem. Comm., 1936, 8, 306—312).—The linear velocity of crystallisation of anodic Ag<sub>2</sub>O<sub>2</sub> deposit from AgNO<sub>3</sub> solutions obeys the same laws as similar cathodic deposits. The rate of crystallisation increases with c.d. and with decreasing electrolyte concn.

C. R. H.

**Electrolysis of solutions of titanium salts.** (MME.) H. EMMANUEL-ZAVIZZIANO and M. HAISSINSKY (Compt. rend., 1936, 203, 161—163).—Electrolysis of Ti(SO<sub>4</sub>)<sub>2</sub> in 0.1N-H<sub>2</sub>SO<sub>4</sub> containing Na<sub>2</sub>SO<sub>4</sub> affords, with a Au-Hg, Ag-Hg, or Pt cathode, pertitanic acid, with a Zn cathode, a basic Ti<sup>IV</sup> salt, and with a Pb cathode, Ti<sup>III</sup> or TiO in an atm. of H<sub>2</sub> or if the electrolyte contains I<sup>-</sup> and has been exactly neutralised with aq. NH<sub>3</sub>.

J. G. A. G.

**Electrolytic formation of sodium perborate.** I. R. MATSUDA (Bull. Chem. Soc. Japan, 1936, 11, 456—464).—In the electrolysis of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution to form NaBO<sub>3</sub>, the presence of Na<sub>2</sub>CO<sub>3</sub> was indispensable. The current efficiency was not impaired by dispensing with the diaphragm. The influence of K<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and KCl was investigated. Electrolysis of metaborate solutions resulted in poor yields of NaBO<sub>3</sub>.

C. R. H.

**Oxidation processes at the cathode.** O. K. KUDRA and K. N. IVANOV (J. Physical Chem., 1936, 40, 769—777).—The powder-like deposits of Cu, Zn, Cd, and Ag formed at cathodes during electrolysis of aq. solutions of their salts at high c.d. are dispersed and contain oxides, formed by secondary oxidation at the cathode. The oxide content depends principally on the oxidising capacity of the anion present, but also on the readiness of oxidation of the metal deposited. Cu, Cd, Cu<sub>2</sub>O, and ZnO so produced have greatly enlarged lattices, due to absorption of H<sub>2</sub>, but Zn and Ag have normal parameters. It is considered that the formation of spongy deposits



during electrolysis of Cd and Zn solutions at very low and at very high c.d. is associated in each case with oxidising conditions at the cathode. J. W. S.

**Electrolytic tantalum plating of metals.**—See B., 1936, 842.

**Electrochemistry of polonium.**—See B., 1936, 842.

**Electrolytic oxidation of sodium arsenite.**—See B., 1936, 788.

**Electrolysis of organic substances in non-aqueous media.** II.—See this vol., 1091.

**Preparation of aniline.**—See this vol., 1103.

**Dependence of anodic oxidation reactions on the electrode material in organic electrolyses.** E. TOMMILA (Suomen Kem., 1936, 9, A, 76—78).—Experiments with alcohols,  $\alpha\beta$ -glycols, and  $\alpha$ -OH-acids in alkaline solution using Fe, Ni, and Pt anodes are described. Polished Pt, but not Fe and Ni, anodes give rise to chain fission. H. N. R.

**Fixation of atmospheric nitrogen.**—See B., 1936, 832.

**Becquerel effect at oxidised copper electrodes. Unidirectional layer photocells and photogalvanic cells.** A. GOLDMANN (Acta Physicochim. U.R.S.S., 1935, 3, 303—334).—The electrical processes in CuO rectifiers and photo-electric cells can be represented by formulae which hold also for polarisation and photogalvanic cells. O. J. W.

**Chain photochemical reactions.** N. SEMENOV (Acta Physicochim. U.R.S.S., 1935, 3, 245—246).—A discussion of previous work. O. J. W.

**Photochemical reactions in solutions.** E. SCHPOLSKI (Acta Physicochim. U.R.S.S., 1935, 3, 255—256).—Discussion of previous work. O. J. W.

**Photodissociation of complex molecules.** A. TERENIN (Acta Physicochim. U.R.S.S., 1935, 3, 181—194).—The localisation of the electronic transition, the interaction of separate parts of the mol., and the distribution of the absorbed energy during the optical excitation and dissociation of polyat. mols. are discussed. O. J. W.

**Induced predissociation in the kinetics of photochemical reactions.** V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1935, 3, 203—204).—A discussion of previous work. O. J. W.

**Action of inhibitors in the photochemical dissociation of hydrogen peroxide.** B. DAIN and A. SCHWARZ (Acta Physicochim. U.R.S.S., 1935, 3, 291—302).—The inhibition by ketones of the photochemical decomp. of  $H_2O_2$  has been studied and the mechanism of the inhibiting action is discussed. O. J. W.

**Possible correlation between the intensity of cosmic radiation and the velocity of certain chemical reactions.** J. REBOUL (Compt. rend., 1936, 203, 245—246; cf. this vol., 943).—Sheets of Zn and Cd cause slightly greater action on a photographic plate in their close proximity when exposed to cosmic radiation than when enclosed in a Pb screen 20 cm. thick, and also slightly greater action when on a tower 20 cm. high than when in a deep cave. The effect is

attributed to the formation of  $H_2O_2$  through secondary emission from the metal under the action of cosmic radiation. J. W. S.

**Kinetics of halogen atom recombination, and in particular the significance of convection.** E. RABINOWITSCH (Z. physikal. Chem., 1936, B, 33, 275—282).—Contrary to the suggestion of Hilferding and Steiner (this vol., 293), convection currents played a negligible part in the author's experiments on the optical dissociation of  $Br_2$  mols. (*ibid.*, 788). The optically determined recombination consts. of  $Br + Br + X \rightarrow Br_2 + X$  are probably more trustworthy than these authors' vals. R. C.

**Photo-sensitisation of films of potassium by means of hydrogen.** R. C. L. BOSWORTH (Trans. Faraday Soc., 1936, 32, 1369—1375).—Monat. films of K on W do not react with  $H_2$  at temp. < volatilising point, but react with at. H to form a "WKH" surface, which can absorb more K to give a sensitive "WKHK" surface. A more sensitive surface is obtained by depositing K on a "WH" surface. E. S. H.

**Photochemical oxidation of carbon monoxide in the Schumann region.** B. POPOV (Acta Physicochim. U.R.S.S., 1935, 3, 223—244).—The oxidation of CO by at. O produced by the photodissociation of  $O_2$  in the region  $\lambda < 1750$  A. has been studied at 0.1 mm. and at low temp. The reaction is heterogeneous and has a very small energy of activation. Contrary to the case of the oxidation of CO by O produced by discharge, the efficiency of collisions on the wall is large, and is explained by the participation of excited O' atoms ( $^1D$ ) together with normal O atoms in the reaction, which proceeds according to  $CO_{ads} + O' \rightarrow CO_2$ . O. J. W.

**Photochemical oxidation of nitrogen.** V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1935, 3, 247—253).—Experiments on the photochemical oxidation of N and of CO by O, and of CO by NO, as well as on the photodissociation of NO, are described. The addition of CO and  $H_2$  to the mixture of  $N_2 + O_2$  increases the yield of NO, during the photochemical oxidation. The mechanism of this is discussed. O. J. W.

**Theory of photochemical reactions and chemiluminescence in solutions.** B. SVESHNIKOV (Acta Physicochim. U.R.S.S., 1935, 3, 257—268).—The theory of the quenching of fluorescence in solutions is discussed, particularly with regard to the influence of the viscosity of the solvent. Some experiments described indicate that there is a decrease of the quenching of excited mols. in aq. glycerol solutions with increase of viscosity. O. J. W.

**Rôle of oxygen in photo-sensitisation in solutions.** II. E. V. SCHPOLSKI and A. A. ILJINA (Acta Physicochim. U.R.S.S., 1935, 3, 269—289; cf. this vol., 809).—The effect of  $O_2$  on Eder's reaction has been studied, using eosin and  $FeCl_3$  as fluorescent and non-fluorescent sensitizers, respectively. The presence or absence of  $O_2$  influences the sensitisation process considerably, but it is not possible to conclude whether  $O_2$  is indispensable for the photo-sensitisation

in the reaction studied. The influence of  $\text{Na}_2\text{SO}_3$  on the rate of the sensitised reaction is also described.

O. J. W.

**Alteration of lead oxides by light and pressure.** J. HOFFMANN (Z. anorg. Chem., 1936, 228, 160—168).—The influence of visible light, Ra radiations, and pressure on the appearance of  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ , and  $\text{PbO}_2$  is described.

E. S. H.

**Oxidation reactions under the influence of light.** H. J. SCHUMACHER (Z. Elektrochem., 1936, 42, 522—529).—Published work is reviewed and the reactions are classified in three groups: the light is absorbed by (1)  $\text{O}_2$ , (2) the mol. undergoing oxidation, or (3) a foreign mol. (sensitised reactions).

E. S. H.

**Photochemical investigations in the extreme ultra-violet.** W. GROTH (Z. Elektrochem., 1936, 42, 533—535).—A modified Xe lamp, in which the resonance lines at 1295 and 1469 Å. are obtained free from C or other lines, is described. Preliminary experiments on photochemical reactions of  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{O}_2$  are reported.

E. S. H.

**Optical sensitisation of silver halides. IV. Chain mechanism of the optical sensitisation of silver bromide.** J. I. BOKINIK and Z. A. ILJINA (Acta Physicochim. U.R.S.S., 1935, 3, 383—396; cf. A., 1933, 35).—A method for determining the "sensitising yield" in the sensitisation of unprotected AgBr sols by erythrosin is described. The "yield" represents the ratio of Ag deposited to the amount of dye adsorbed. It is independent of the amount of dye adsorbed, but is influenced by the  $p_{\text{H}}$  of the sol and, within certain limits,  $\propto$  the time of illumination. Some suggestions concerning the behaviour of the sensitising mol. during photolysis are made.

O. J. W.

**Optical sensitisation of photochemical reactions in solids.** A. J. RABINOVITSCH (Acta Physicochim. U.R.S.S., 1935, 3, 368—382).—Previous work on the action of sensitisers in photochemical reactions is reviewed. Curves showing the sensitising action of erythrosin and other dyes on AgBr are recorded. It is suggested that in solid systems the energy evolved in the photo-oxidation of the adsorbed sensitiser by atm.  $\text{O}_2$  is utilised in the decomp. of the crystals.

O. J. W.

**Influence of polarised light on silver halides coloured by colloids (Weigert effect).** S. TSCHERDINCEV (Acta Physicochim. U.R.S.S., 1935, 3, 355—360).—The dichroism of cryst. plates of AgCl, coloured by exposure to light, has been studied. Absorption curves are given.

O. J. W.

**Photographic reversal with monochromatic and heterogeneous X-rays.** K. PROSAD, S. BASU, and B. N. GHOSH (Z. Physik, 1936, 102, 259—271).—Photographic reversal and multiple reversal have been studied using heterogeneous X-rays from Cu, Fe, and Pt anticathodes, and monochromatic X-rays obtained by spectral decomp. with NaCl and calcite crystals. With Cu and Pt as anticathodes, two reversal ranges were found, but monochromatic rays gave only one reversal during an exposure time of 10 hr. The causes of reversal are discussed. Part of the blackening curve can be explained by the Blair-Leighton theory

4 K

that the formation of the latent image is the result of a reversible chemical decomp. (A., 1932, 1006).

A. J. M.

**Photochemical studies. XXIII. Photochemical decomposition of acetone vapour near 1900 Å. Comparison with the decomposition at longer wave-lengths.** J. P. HOWE and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1936, 58, 1404—1412; cf. this vol., 944).—The quantum yield is independent of the radiation intensity over wide limits, increases with decreasing  $\text{CO Me}_2$  pressure to a limiting val. 0.65, increases on addition of  $\text{N}_2$ ,  $\text{CO}_2$ , or  $\text{C}_2\text{H}_6$ , and is apparently increased by the action of excited Hg. Fluorescence was not detected. The results are discussed.

E. S. H.

**Primary process of the light-rearrangement of o-nitrobenzaldehyde.** L. KUCHLER and F. PATAT (Z. Elektrochem., 1936, 42, 529—532).—The quantum yield in the gaseous phase at 4 mm. pressure is  $0.75 \pm 0.07$ . Addition of  $\text{N}_2$  gives a quantum yield of 0.5 at 1 atm. in agreement with the val. obtained when the reaction occurs in solution.

E. S. H.

**Study of kinetics of a photochemical reaction by means of ultra-violet spectrophotometry. Decomposition of vitamin-A.** P. DUBOULEZ (J. Chim. phys., 1936, 33, 532—545).—Rates of transformation of the reactant and the products are deduced from a series of spectrophotometric curves. The decomp. of vitamin-A by  $\lambda$  3650 Å. does not follow the same course in EtOH as in  $\text{C}_6\text{H}_{14}$ .

J. G. A. G.

**Emission of radiation by chemical reactions.** R. AUDUBERT (J. Chim. phys., 1936, 33, 507—525).—Details are given of results already summarised (this vol., 778, 407). In addition the approx. spectral distribution of the ultra-violet light emitted during the several reactions has been determined. The intensity of the radiation emitted when pyrogallol and  $\text{Na}_2\text{S}_2\text{O}_4$  are oxidised varies approx. parallel with the corresponding instantaneous rate of  $\text{O}_2$  absorption.

J. G. A. G.

**Action of X-rays on glucose.**—See this vol., 1094.

**Reduction and oxidation by ultra-violet-irradiated sugar.**—See this vol., 1094.

**Photochemical reaction of polyatomic molecules as represented by carbonyl compounds.** R. G. W. NORRISH (Acta Physicochim. U.R.S.S., 1935, 3, 171—177).—A summary of previous work. The transfer of energy in mols. by an internal process analogous to a "collision of the second kind" is discussed.

O. J. W.

**Photochemical polymerisation of butadiene.** V. K. NIKIFOROV and P. M. RUNTZO (Acta Physicochim. U.R.S.S., 1935, 3, 335—339).—Commercial gaseous butadiene polymerises when exposed to the light of a quartz-Hg lamp, but with the pure liquid substance there is no polymerisation. The mechanism of polymerisation processes is discussed.

O. J. W.

**Photo-reduction of fluorescent substances by visible light.** J. WEISS (Trans. Faraday Soc., 1936, 32, 1331—1332).—Published work (cf. this vol., 11) is discussed.

E. S. H.



Use of photographic films as a means of measuring  $\gamma$ -ray dosage. R. PAYNE-SCOTT (J. Cancer Res. Comm. Sydney, 1936, 7, 170—175).—Doses of  $\gamma$ -rays may be measured by means of the darkening of photographic films exposed to the rays and developed under standard conditions. The error varied from 4 to 12% according to the type of film. W. O. K.

Photographic action of slow protons. R. KOLLATH (Ann Physik, 1936, [v], 26, 705—722).—The photographic activity of protons of 30—1000 volts with regard to Schumann plates has been determined. In experiments with gelatin plates and films there was considerable halation, due to the positive charge imparted to the plate, but Schumann films on Ag gave satisfactory results. The reciprocity law was obeyed. Blackening increases with the proton intensity, but not linearly. The relative sensitivity of the Schumann plate to protons of various energies was determined, and the abs. sensitivity to 350-volt protons was calc. to be  $0.25 \times 10^8$  per coulomb per sq. cm. The sensitivity of Schumann plates to electrons and protons was compared. The plates have the same sensitivity to slow protons and slow electrons of the same energy. A. J. M.

Exchange between di- and tri-hydroxybenzenes and heavy water.—See this vol., 1104.

Reactions between dry inorganic salts. III. E. B. THOMAS [with L. J. WOOD] (J. Amer. Chem. Soc., 1936, 58, 1341—1344; cf. A., 1935, 832).—In 57 of the 60 possible reactions between the fused halides of Li, Na, K, Rb, and Cs, (1) the reactions proceed in such a direction that the average cube edge of the stable pair is < that of the reciprocal pair, (2) the sum of the heats of formation of the stable pair is > that of the reciprocal pair, (3) the stable pair has the cation of greater at. wt. united with the anion of greater at. wt. and the cation of smaller at. wt. united with the anion of smaller at. wt. E. S. H.

Metallic alkoxides. P. BRUN (Compt. rend., 1936, 203, 315—316).—Dry alcohols were added to dry  $\text{Et}_2\text{O}$  into which dipped two electrodes, one of Pt, the other of the metal to be studied, and the current produced was measured. For the same alcohol K reacted more vigorously than Na, with the production of a greater current. MeOH was more reactive than EtOH. With an alcohol concn. of 1 mol. per litre the current was of the order of  $50 \times 10^{-8}$  amp. The reaction between alcohols and amalgams was also studied. C. R. H.

Thermal decomposition of simple and complex cyanides in the formation of alkali metals, especially potassium. B. ORMONT and B. A. PETROV (Monatsh., 1936, 68, 171—187).—The thermal decomp. of  $\text{K}_4\text{Fe}(\text{CN})_6$  in a vac. gives a few % of K at  $600^\circ$  and 50—80% at  $900^\circ$ , due partly to the capture of electrons by  $\text{K}^+$  ions, but mainly to the reactions  $\text{K}_4\text{Fe}(\text{CN})_6 = 4\text{KCN} + \text{FeC}_2 + \text{N}_2$ ,  $4\text{KCN} = 4\text{K} + 4\text{C} + 2\text{N}_2$ . No  $\text{K}_3\text{Fe}(\text{CN})_6$  is formed.  $\text{K}_3\text{Fe}(\text{CN})_6$  decomposes at  $400\text{—}500^\circ$ :  $\text{Fe}(\text{CN})_6''' + 3\text{K} = 3\text{K} + \text{FeC}_2 + 4\text{C} + 3\text{N}_2$ ,  $3\text{K}_3\text{Fe}(\text{CN})_6 + 3\text{K} = 3\text{K}_4\text{Fe}(\text{CN})_6$ . The  $\text{FeC}_2$  formed as above and by the decomp. of  $\text{H}_4\text{Fe}(\text{CN})_6 \cdot 2\text{Et}_2\text{O}$  is not a compound, but contains

an intimate mixture of  $\alpha$ -Fe and graphite. In presence of  $\text{N}_2$ , up to approx. 90 mm., the velocity of decomp. of  $\text{K}_4\text{Fe}(\text{CN})_6$  at  $900^\circ$  decreases, owing to the formation of labile Fe nitrides.  $\text{Li}_4\text{Fe}(\text{CN})_6$  gives some Li on heating, and a mixture of equal quantities of Na and K salts gives NaK. R. S. B.

Salt hydrates. R. DUBRISAY and J. LEFOL (Compt. rend., 1936, 203, 248—250).—The dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (with excess of  $\text{H}_2\text{O}$ ) in presence of  $\text{P}_2\text{O}_5$  and at 8 mm. pressure has been studied. A sharp break in the wt.-time curve is found at  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , but a steady decrease is then found to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Replacement of the  $\text{P}_2\text{O}_5$  by  $\text{H}_2\text{SO}_4\text{—H}_2\text{O}$  mixture of  $\text{H}_2\text{O}$ -v.p. 0.85 mm. decreases the velocity of dehydration considerably, and after 10 days the wt. remains const. and corresponding with  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . In presence of  $\text{P}_2\text{O}_5$  this dehydrates to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Rehydration curves have also been traced. J. W. S.

Double iodides of copper and ammonium. (Mlle.) D. MONTAGNON (Compt. rend., 1936, 203, 325—327).— $\text{NH}_4\text{Cl}$  and KI were added to an aq.  $\text{NH}_3$  solution of  $\text{Cu}(\text{OH})_2$ , and, according to the conditions of heating the mixture,  $\text{Cu}_2\text{I}_2 \cdot 3\text{NH}_4\text{I} \cdot \text{NH}_3\text{OI} \cdot 6\text{H}_2\text{O}$  and  $\text{CuI}_2 \cdot 3\text{NH}_3 \cdot 11\text{H}_2\text{O}$  were formed. The latter compound absorbed  $\text{H}_2\text{O}$  and  $\text{NH}_3$  to form  $\text{CuI}_2 \cdot 5\text{NH}_3 \cdot 3\text{H}_2\text{O}$ . C. R. H.

Concentrated copper sulphate solution gives on impure iron, polished and deprived of active dust, a phenomenon recalling that of Evans for rust. P. RONCERAY (Bull. Soc. chim., 1936, [v], 3, 1687—1689).—The effect produced by a drop of aq.  $\text{CuSO}_4$  (25—30%) on clean Fe is, unlike the Evans effect, due to spreading of the drop. The Fe in the exterior of the zone is attacked most, due to the production of a Cu-Fe cell. If active dust remains on the surface this effect is replaced by the Evans effect. J. W. S.

Basic phosphates of bivalent metals. I. Basic magnesium phosphate. R. KLEMENT (Z. anorg. Chem., 1936, 228, 232—240).—Hydrolysis of  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  yields  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Mg}_3(\text{PO}_4)_2 \cdot 0.33\text{Mg}(\text{OH})_2 \cdot 9\text{H}_2\text{O}$ , or  $\text{Mg}_3(\text{PO}_4)_2 \cdot \text{Mg}(\text{OH})_2 \cdot 9\text{H}_2\text{O}$ , according to the hydrolytic agent. E. S. H.

Preparation of calcium and sodium hydrogen sulphides. I. N. OSTROVSKI and I. L. SCHERESCHEVSKI (J. Appl. Chem. Russ., 1936, 9, 1214—1220).— $\text{H}_2\text{S}$  is passed into a 20% suspension of CaO at  $20^\circ$ , with stirring, when the solution at saturation contains 38.5% of  $\text{Ca}(\text{SH})_2$ . 39% aq. NaSH is obtained from this solution by adding anhyd.  $\text{Na}_2\text{CO}_3$  at room temp. The reaction is not affected by admixture of 5% of  $\text{CO}_2$  to the  $\text{H}_2\text{S}$ . R. T.

Active oxides. XCVI. Temperature increments of the intermediate processes in the combination of zinc oxide with ferric oxide. G. F. HUTTON, M. EHRENBERG, and H. KITTEL (Z. anorg. Chem., 1936, 228, 112—126; cf. this vol., 441).—Determinations of  $d$ , hygroscopicity, and magnetic susceptibility have been carried out with mixtures of powdered  $\text{ZnO}$  and  $\text{Fe}_2\text{O}_3$ , after heating at different

temp. for definite intervals. Intermediate steps are identified. E. S. H.

**Precipitation of mercuric iodide.** P. G. PATER-NOSRO (Rev. Fac. Cienc. Quim. La Plata, 1935, 10, 11—18).—The formation of  $\text{HgI}_2$  from solutions of  $\text{HgCl}_2$  and KI has been studied under various conditions of concn. and temp. The most perfect and readily filtered crystals are obtained by mixing boiling 0.02*N* solutions. F. R. G.

**Mercurous salts and their amido-compounds.** II. E. GLEDITSCH and T. F. EGIDIUS (Z. anorg. Chem., 1936, 228, 249—254; cf. this vol., 574).— $\text{Hg}_2\text{NH}_2\text{Cl}$  is a single compound, stable at room temp. when dry. In presence of aq.  $\text{NH}_3$  it decomposes into  $\text{HgNH}_2\text{Cl} + \text{Hg}$ . Similar observations hold for  $\text{Hg}_2\text{NH}_2\text{NO}_3$ . E. S. H.

**Boron hydrides. XXIV. Borane salts.** A. STOCK and H. LAUDENKLOS (Z. anorg. Chem., 1936, 228, 178—192; cf. this vol., 172).—The prep. of  $\text{Na}_2\text{B}_2\text{H}_6$ ,  $\text{CaB}_2\text{H}_6$ ,  $\text{Na}_2\text{B}_4\text{H}_{10}$ ,  $\text{K}_2\text{B}_2\text{H}_6$ ,  $\text{K}_2\text{B}_4\text{H}_{10}$ , and  $\text{K}_2\text{B}_5\text{H}_9$  is described. When heated at 170° the salts containing  $\text{B}_2\text{H}_6$  remain unaltered; the others lose  $\text{H}_2$ , forming  $\text{K}_2\text{B}_4\text{H}_8$ ,  $\text{Na}_2\text{B}_4\text{H}_8$ , and  $\text{K}_4\text{B}_{10}\text{H}_{16}$ . When heated at 450° the salts containing  $\text{B}_2$  or  $\text{B}_4$  give compounds of the type  $\text{M}_2\text{B}_4\text{H}_6$  or  $\text{M}_2\text{B}_4\text{H}_4$ ;  $\text{K}_2\text{B}_5\text{H}_9$  gives  $\text{K}_2\text{B}_5\text{H}_3$ . Treatment with HCl generally yields the alkali chloride and the corresponding borane;  $\text{K}_2\text{B}_4\text{H}_{10}$  gives  $\text{K}_2\text{B}_4\text{H}_5\text{Cl}_5$ . X-Ray diagrams of the above salts are compared. E. S. H.

**Preparation and properties of aluminium periodate dodecahydrate.** V. BIBER, A. VNUKOVA, and N. KONSCHIN (J. Gen. Chem. Russ., 1936, 6, 873—879).—Freshly pptd.  $\text{Al}(\text{OH})_3$  and  $\text{HIO}_4$  yield  $\text{Al}(\text{IO}_4)_3 \cdot 12\text{H}_2\text{O}$ , for which crystallographic and solubility data are recorded. R. T.

**Hydrogenation of aluminium nitride by active hydrogen.** N. I. KOBOSEV, B. V. JEROFEEV, and V. M. SAVINA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 389—392).— $\text{NH}_3$  and an Al hydride are formed when  $\text{H}_2$ , or  $\text{N}_2 + 3\text{H}_2$ , is led over AlN (formed by the action of  $\text{NH}_3$  on Al powder at 800—900°) in a discharge tube immersed in liquid air. The reaction must be due to at. H, for which it is suggested as a test; mol.  $\text{H}_2$  has no action on account of the high energy val. of AlN. The Al hydride obtained decomposes spontaneously outside the discharge zone. R. C. M.

**Basic gallium nitrate.** N. A. PUSHIN and R. D. ŽIVADINOVITSCH (Z. anorg. Chem., 1936, 228, 255—256).—The prep. and properties of  $\text{Ga}(\text{OH})_2\text{NO}_3$ ,  $\text{Ga}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$  are described. E. S. H.

**Gallium compounds. I.** P. NEOGI and S. K. NANDI (J. Indian Chem. Soc., 1936, 13, 399—403).—When  $\text{Ga}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , freshly pptd. from  $\text{Ga}(\text{NO}_3)_3$  with  $\text{NaHCO}_3$ , is dried in a vac. it yields the compound  $\text{Ga}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , insol. in org. acids. Dissolution of freshly pptd.  $\text{Ga}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  in the respective acids and crystallisation of the solutions in a vac. yields Ga d-, l-, meso-, and r-tartrates  $\text{Ga}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 4\text{H}_2\text{O}$ , basic Ga acetate  $4\text{Ga}(\text{OAc})_3 \cdot 2\text{Ga}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , basic formate  $\text{Ga}(\text{HCO}_2)_3 \cdot \text{Ga}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (I), oxalate  $\text{Ga}_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$  (hygroscopic), lactate  $\text{Ga}(\text{C}_3\text{H}_5\text{O}_3)_3 \cdot 2\text{H}_2\text{O}$ , citrate  $\text{Ga}(\text{C}_6\text{H}_6\text{O}_7)_3 \cdot 3\text{H}_2\text{O}$ , malate  $\text{Ga}_2(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 3\text{H}_2\text{O}$ , H

phosphite  $\text{GaH}_3(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ , and H hypophosphite  $\text{GaH}_3(\text{PO}_2)_2$ . Action of  $\text{Ga}(\text{NO}_3)_3$  on the Na salt yields basic Ga acetate  $\text{Ga}(\text{OAc})_3 \cdot 3\text{Ga}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , phosphite  $\text{GaPO}_3 \cdot \text{H}_2\text{O}$ , hypophosphite, and (I). Ga d- and l-tartrates have  $[\alpha] +20.3^\circ$  and  $-20.0^\circ$ , respectively. J. W. S.

**Mechanism of oxidation of carbon.** V. SIVONEN (Svensk Kem. Tidskr., 1936, 48, 185—202).—A lecture.

**Carbon obtained by dehydration of carbohydrate.** G. R. LEVI and A. BARONI (Atti R. Accad. Lincei, 1936, [vi], 23, 441—443).—C prepared from inositol, quebrachitol, glucose, or sucrose by heating at 200° with  $\text{ZnCl}_2$ -HCl cannot be differentiated by the method of Hofmann and Frenzel (A., 1930, 875); the rates of formation of  $\text{CO}_2$  by  $\text{K}_2\text{Cr}_2\text{O}_7$ - $\text{H}_3\text{PO}_4$  at 100°, however, are characteristically different (cf. Balfour and Riley, this vol., 178). F. O. H.

**Activated charcoal. II. Purification by washing with water and by activation.** S. ROYCHOUDHURY, S. K. NANDI, and J. K. BANERJEE (J. Indian Chem. Soc., 1936, 13, 410—418; cf. A., 1931, 1226).—Alternate washing and activation at 800° leads to the removal of the negative charge of a suspension of the charcoal in  $\text{H}_2\text{O}$ . Electrolytes are liberated from the charcoal during each washing. After washing with HCl, the latter cannot be entirely removed at 800°/10 mm., although the charge on the particles is zero. Some samples of very pure charcoal showed a positive charge. Addition of NaOH or NaCl increases the charge on negatively charged particles, whilst HCl and  $\text{H}_2\text{SO}_4$  produce a negative charge on isoelectric charcoal. J. W. S.

**Minimum temperature of oxidation of silicon.** C. BEDEL (Compt. rend., 1936, 203, 323—325).—The min. temp. of oxidation of Si in dry  $\text{O}_2$  is approx. 850° and is certainly  $<800^\circ$ . In the presence of  $\text{H}_2\text{O}$  vapour oxidation begins at approx. 430°. C. R. H.

**Behaviour of titanium dioxide on heating and its behaviour towards ferric, sodium, and magnesium oxides.** E. JUNKER (Z. anorg. Chem., 1936, 228, 97—111).— $\text{TiO}_2$  has m.p. about 1800°. At higher temp. dissociation occurs. The heat of reaction of  $0.5\text{Ti}_2\text{O}_3 + 0.5\text{O}_2 = \text{TiO}_2$  is 99,000 g.-cal. The transformation temp. of rutile into brookite is 1300°.  $\text{TiO}_2$  reacts with C in presence of CO at  $>870^\circ$  forming  $\text{Ti}_2\text{O}_3$ ; at temp.  $>$  m.p.,  $\text{Ti}_2\text{O}_3$  and TiC are formed. Equilibrium in the system  $\text{Ti}_2\text{O}_3$ -TiC has been studied.  $\text{TiO}_2$  is reduced to  $\text{Ti}_2\text{O}_3$  when heated in  $\text{H}_2$ ; in  $\text{N}_2$  some  $\text{Ti}_2\text{O}_3$  is formed by dissociation.  $\text{Ti}_2\text{O}_3$  has m.p. about 1900°. The m.p. of  $\text{TiO}_2$ - $\text{Ti}_2\text{O}_3$  mixtures have been determined. The system  $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$  has been investigated. Ilmenite has m.p. about 1350°. The  $\text{TiO}_2$ -rich end of the  $\text{TiO}_2$ - $\text{Na}_2\text{O}$  equilibrium diagram has been investigated and the existence of  $\text{Na}_2\text{O} \cdot 3\text{TiO}_2$  confirmed. M.p. data for the system  $\text{TiO}_2$ - $\text{Ti}_2\text{O}_3$ -MgO have been determined. E. S. H.

**Titanium. I. Preparation of  $\text{TiNCl}$ ,  $\text{TiCl}_4$ .** II. Action of oxygen on titanium tetrachloride under the influence of the silent electrical discharge. III. Formation of titanium di-iodide



from titanium tetrachloride and potassium iodide, and attempts to convert it into titanium iodoform. L. HOCK and W. KNAUFF (Z. anorg. Chem., 1936, 228, 193—199, 200—203, 204—208).—I.  $TiNCl_4$  has been prepared by the action of the silent electrical discharge on  $TiCl_4$  and  $N_2$ .

II. The yellow reaction product consists of a mixture of  $TiCl_4$  and  $TiO_2$ .

III.  $TiCl_4$  and KI yield  $TiI_2$ .  $TiI_2$  and HI do not yield  $TiHI_3$ . E. S. H.

**Generalised prototropy.** C. PREVOST (Bull. Soc. chim., 1936, [v], 3, 1666—1673).—The possibility is propounded that a proton may be liberated from the atom to which it is normally bound by co-valency and be attached to an atom with a lone pair of electrons. This phenomenon, called generalised prototropy, will not cause isomerism but renders the mol. susceptible to reagents. It is used to explain diverse oxidations, e.g.,  $H\cdot PO(OH)_2 \rightarrow P(OH)_3 \rightarrow O:P(OH)_3$ ,  $RCHO \rightarrow RC:OH \rightarrow RCO_2H$ ,  $CHCl_3 \rightarrow CCl_2\cdot Cl\cdot H \rightarrow O:CCl_2\cdot Cl\cdot H$ ,  $COCl_2 + HCl$ . A similar migration of Me, termed methylenic dehydration, is applied thus:  $CR_3\cdot CH_2\cdot OH \rightarrow CR_3\cdot CH \rightarrow CR_2\cdot CHR$ ; by analogy the mechanism,  $CHR_2\cdot CH_2\cdot OH \rightarrow CHR_2\cdot CH \rightarrow CR_2\cdot CH_2$ , is proposed. R. S. C.

**New type of vanadyl salicylate.**—See this vol., 1107.

**Reaction of arsenious oxide with oxides of heavy metals at high temperatures.** I. M. DUBROVIN (J. Appl. Chem. Russ., 1936, 9, 1049—1056).— $As_2O_3$  begins to combine with  $ZnO$  at  $250^\circ$ , and at  $400^\circ$  the production of  $Zn_3(AsO_3)_2$  is at a max.;  $As^V$  is absent. At  $500^\circ$   $As^{III}$  and  $As^V$  are present in approx. equal amounts, but the total As content is at a min. owing to volatilisation. Mixtures heated at  $600^\circ$  contain only  $As^V$ ; with rising temp. above  $600^\circ$  the rate of combination rises to a max. at  $700^\circ$ , thereafter remaining const. Formation of  $Pb_3(AsO_3)_2$  commences at  $250^\circ$ , and is associated with oxidation to  $Pb_3(AsO_4)_2$  (I) at  $250$ — $300^\circ$ ; with rising temp. the amount of combined As falls to a min. at  $350$ — $450^\circ$  (loss of  $As_2O_3$  by volatilisation), whilst at  $450$ — $800^\circ$  the product consists exclusively of (I). Combination, associated with oxidation of  $As^{III}$  to  $As^V$ , takes place between  $Fe_2O_3$  and  $As_2O_3$  at  $225^\circ$ , and is at a max. at  $250^\circ$ . With rising temp. above  $250^\circ$  the amount of combined As falls to a min. at  $500^\circ$ , due to thermal decomp., and then rises to a const. level at  $600$ — $700^\circ$ , when exclusively  $As^V$  is present. R. T.

**Conductometric titrations of the isomeric chromic chlorides with silver nitrate.** N. H. LAW (Trans. Faraday Soc., 1936, 32, 1461—1465).—In aq. solution the violet compound yields  $3Cl'$ . The pale green compound yields  $2Cl'$ , except in solutions of  $p_H$  approx. 5, when all the  $Cl$  is ionised. The dark green compound yields  $1Cl'$  in strongly acid solutions, but with increasing  $p_H$  the ionisable  $Cl$  increases, ionisation eventually becoming complete. E. S. H.

**Chromous and chromic ammines.** J. H. BALTHUS, jun., and J. C. BAILLAR, jun. (J. Amer. Chem. Soc., 1936, 58, 1474—1476).—The prep. and

properties of  $[Cr en_3]Cl_3 \cdot 3.5H_2O$ ,  $[Cr en_2]Br_3 \cdot 3H_2O$ ,  $[Cr(NH_2\cdot CHMe\cdot CH_2\cdot NH_2)_3]Cl_3 \cdot H_2O$ ,  $[Cr\{(CHMe\cdot NH_2)_2\}_3]I_3$ ,  $[Cr_4(OH)_6 en_6]Br_6 \cdot 4H_2O$ , and  $[Cr(C_5H_5N)_2]Cl_2$  are described. Corresponding  $Cr^{II}$  compounds (except the  $C_5H_5N$  derivatives) cannot be isolated from aq. solution, as they rapidly oxidise to  $Cr^{III}$ . E. S. H.

**Molybdenum chlorohydrin and normal glycol molybdate.** J. BYÉ (Compt. rend., 1936, 203, 321—323).—The solubility of  $MoO_3$  in  $HCl$  has been investigated. Extraction of the solution with  $Et_2O$  yields an indefinite compound  $MoO_3 \cdot 2HCl \cdot 2Et_2O + xEt_2O$ . The excess of  $Et_2O$  is easily liberated and under the action of light and moisture the compound loses the combined  $Et_2O$  and becomes blue. In the decomp. products  $MeCHO$  and  $EtOAc$  have been detected. If  $(CH_2)_2O$  is bubbled through an  $Et_2O$  solution of  $MoO_3 \cdot 2HCl$ , normal glycol molybdate is pptd. C. R. H.

**Hydrates of manganese sulphate.** E. RENCKER and P. DUBOIS (Compt. rend., 1936, 203, 185—187).—The existence of hydrates containing 7, 5, 4, 3, and 1 mols. of  $H_2O$  of crystallisation is confirmed; other hydrates reported are probably mixtures.

J. G. A. G.

**The Evans effect is produced on impure iron and is caused by active dust.** P. RONCEBAY (Bull. Soc. chim., 1936, [v], 3, 1661—1668).—The Evans effect (A., 1922, ii, 814; 1924, ii, 599) is associated with active dust left during polishing, the dust being more active in contact with aq.  $NaCl$  than in contact with  $H_2O$ . The effect occurs with impure as well as pure Fe. The thickness of rust in the three zones  $\propto$  the extent of attack in these zones, and therefore contradicts the view that the  $FeCl_2$  migrates towards the exterior alkaline zone. The presence of active dust on even carefully cleaned surfaces is considered to explain the divergent conclusions of various investigators. J. W. S.

**Rhodium chloride,  $RhCl_3$ .** J. MEYER and M. KAWCZYK (Z. anorg. Chem., 1936, 228, 297—300).— $RhCl_3$  can exist in a yellow, ionisable, or brown, non-ionisable form. The analogy with  $Cr^{III}$  compounds is discussed. E. S. H.

**Chromatographic analysis.** A. H. COOK (Chem. and Ind., 1936, 724—726).—A review.

**Determination of  $p_H$  values by the hydrogen and antimony electrodes.** A. T. WILLIAMSON and W. G. OAKES (J. Text. Inst., 1936, 27, T199—203).—A modified rocking H electrode which is simple in construction and rapid in action is described. A  $N_2$ -filled Sb electrode for which  $E = 0.049 + 0.0589p_H$  for solutions containing or free from  $Cl'$  is also described. A. G.

**Determination of the  $p_H$  of natural waters and solutions.** T. T. COCKING (Ind. Chem., 1936, 12, 375—376).—The use of colorimetric methods for natural and condenser waters, paper, soils, and coloured solutions is described. C. W. G.

**Comparison of the glass and quinhydrone electrodes for the measurement of the activity of the hydrogen ion in sucrose solutions.** H. P.

CADY and J. D. INGLE (J. Physical Chem., 1936, 40, 837—843).—The quinhydrone electrode gives a changing potential when the electrode is left in contact with the HCl-quinhydrone solution for long periods, and so gives untrustworthy results in measuring the H<sup>+</sup> activity in sucrose solutions during inversion. The glass electrode yields reproducible results which indicate that this activity remains const. throughout the inversion of sucrose by HCl. J. W. S.

Micro-thermoconductivity method for the determination of para-hydrogen and deuterium. D. D. ELEY and J. L. TUCK (Trans. Faraday Soc., 1936, 32, 1425—1428).—Apparatus and technique are described. E. S. H.

Determination of moisture. See B., 1936, 768.

Determination of moisture by means of calcium carbide. P. M. ORSHEGROVSKI and K. B. CHAIT (J. Appl. Chem. Russ., 1936, 9, 1141—1143).—Commercial CaC<sub>2</sub> contains a small amount of H<sub>2</sub>O, and evolves C<sub>2</sub>H<sub>2</sub> when heated. In determining the H<sub>2</sub>O content of substances by means of CaC<sub>2</sub> the latter should be previously heated until C<sub>2</sub>H<sub>2</sub> evolution ceases. R. T.

Electroanalysis and indirect macro-electroanalysis of anions using three electrodes. J. GUZMAN and L. QUINTERO (Anal. Fís. Quím., 1934, 32, 800—806).—Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Fe(CN)<sub>6</sub><sup>4-</sup>, and Fe(CN)<sub>6</sub><sup>3-</sup> may be determined to within 0.2% by quant. conversion into their Ag salts, the Ag being determined by Guzman's three-electrode method, using a cathode of Ag-plated brass and an anode of passive Fe wire (cf. A., 1935, 949). F. R. G.

Determination of halides in photographic materials.—See B., 1936, 763.

Qualitative reaction for bromates. F. L. HAHN (Mikrochem., 1936, 20, 236—238).—BrO<sub>3</sub><sup>-</sup> can be detected in presence of KClO<sub>3</sub> and KBr by the greenish-yellow colour which develops on addition of fluorescein, boiling, and making alkaline. R. S.

Absorption of gases and vapours. Determination of traces of volatile bromides. F. L. HAHN (Mikrochem., 1936, 20, 239—243).—Air containing the vapour is passed through a heated SiO<sub>2</sub> tube with H<sub>2</sub>O, and the HBr in the condensate is determined colorimetrically. R. S.

Determination of fluorine.—See B., 1936, 766.

Rapid determination of oxygen in atmospheric gases. A. KLING and M. CLARAZ (Compt. rend., 1936, 203, 319—321).—To 5 c.c. of a solution containing FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 2 g. and tartaric acid 20 g. per litre, and sufficient methylene-blue to colour, are added 5 c.c. of N-NaOH. The gaseous mixture is bubbled through this solution at a known rate until the blue, which acts as oxidation-reduction indicator, is decolorised, and the vol. of gas passed is noted. The apparatus is calibrated by means of known O<sub>2</sub> mixtures. An accuracy of 0.5% is claimed. C. R. H.

Determination of sulphide-sulphur in pyrites.—See B., 1936, 884.

Use of spot-reactions in the identification of substances soluble with difficulty in acids. F.

FEIGL (Mikrochem., 1936, 20, 198—208).—Spot-reactions are described for insol. sulphides, insol. sulphates, Ag halides, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrCl<sub>3</sub>, MnO<sub>2</sub>, PbO<sub>2</sub>, WO<sub>3</sub>, W, Mo, SiO<sub>2</sub>, Si, Sb<sub>2</sub>O<sub>5</sub>, insol. fluorides, SnO<sub>2</sub>, and Sn<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>. R. S.

Rapid dynamic method of determining sulphur dioxide in air. D. N. FINKELSCHTEIN (J. Appl. Chem. Russ., 1936, 9, 1347—1358).—Gurevitch's colorimetric method, depending on absorption of SO<sub>2</sub> in acid aq. BaCrO<sub>4</sub>, boiling, and pptn. of unchanged BaCrO<sub>4</sub> by NH<sub>3</sub>, followed by colorimetric determination of (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> remaining in solution, gives approx. correct results only for 0.05—0.5 mg. of SO<sub>2</sub>. SO<sub>2</sub> (<0.005 mg.) can be determined with satisfactory accuracy by adding 25 ml. of 5% KClO<sub>3</sub>, 3 ml. of 0.1N-KI, and 1 ml. of 0.05N-KIO<sub>3</sub>, and titrating after 45 min. with 0.002N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Alternatively, the H<sub>2</sub>SO<sub>4</sub> produced from SO<sub>2</sub> and aq. KClO<sub>3</sub> is titrated with 0.004N-KOH (Me-red) to *p*<sub>H</sub> 6. A procedure for rapid sampling of air is described. R. T.

Volumetric determination of sulphate.—See B., 1936, 766.

Sulphuric acid as a disperse phase in town air. J. H. COSTE and G. B. COURTIER (Trans. Faraday Soc., 1936, 32, 1198—1201).—A condensation method, whereby filters are avoided, for determining the H<sub>2</sub>SO<sub>4</sub> in air is described. Air freed from SO<sub>2</sub> was almost saturated with H<sub>2</sub>O and passed through an ice-cooled flask, where the large droplets, formed on nuclei of H<sub>2</sub>SO<sub>4</sub>, condensed. Dust and smoke particles passed through the flask. London air contains 1—20 × 10<sup>-6</sup> g. of free H<sub>2</sub>SO<sub>4</sub> per cu.m. High [H<sub>2</sub>SO<sub>4</sub>] was found during calm and foggy conditions and, also, in general, when [SO<sub>2</sub>] was high. J. G. A. G.

Determination of carbon disulphide.—See B., 1936, 869.

Bromometric determination of thiocyanates. Application to micro-analysis and analysis of thiocyanate complexes. E. KAHANE and R. COUPECHOUX (Bull. Soc. chim., 1936, [v], 3, 1588—1595).—Treadwell and Mayr's method (A., 1916, ii, 264) for the determination of CNS<sup>-</sup> (treatment with KBr and KBrO<sub>3</sub>, addition of KI, and titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) gives good results if the KI is added as soon as possible after the KBrO<sub>3</sub>. 0.001 g. of KCNS can be determined in this way to within ±2%. The method can also be used for determination of Reinecke's salt or similar complexes. J. W. S.

Determination of selenium in steel.—See B., 1936, 793.

Determination of tellurium in steel.—See B., 1936, 840.

Determination of nitrates in presence of nitrites and certain organic compounds. A. S. VETROV (J. Appl. Chem. Russ., 1936, 9, 1158—1167).—2.5 ml. of 18N-NaOH and 5 ml. of 5N-CO(NH<sub>2</sub>)<sub>2</sub> are added to 20 ml. of meat extract, the solution is heated, and 3 ml. of 18N-H<sub>2</sub>SO<sub>4</sub> are added. The solution is boiled for 5 min. with 3 ml. of 18N-NaOH and excess of KMnO<sub>4</sub>. Excess of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> and 10 ml. of 18N-H<sub>2</sub>SO<sub>4</sub> are then



added, followed by 115 ml. of HCl ( $d$  1.115), air is expelled from the flask by passing  $\text{CO}_2$ , and 3 ml. of 1%  $(\text{NH}_4)_2\text{MoO}_4$  are introduced. The solution is then distilled in a stream of  $\text{CO}_2$ , collecting the issuing gases under aq. NaOH, and the  $\text{HNO}_3$  content of the original extract is derived from the vol. of NO collected. R. T.

Determination of ammoniacal nitrogen in seawater. O. GÓMEZ IBÁÑEZ (Anal. Fis. Quím., 1934, 32, 897—898).—The  $\text{NH}_3\text{-N}$  at various depths at Eddystone has been found by Wattenberg's method of direct Nesslerisation in presence of  $[\text{-CH(OH)CO}_2\text{H}]_2$  to vary from 30 to 0 mg. per cu. m. between February and April. F. R. G.

Determination of phosphates in waters.—See B., 1936, 766.

Analysis of superphosphates.—See B., 1936, 738.

Rapid determination of phosphorus in stainless steels.—See B., 1936, 793.

Progress of the formation of the arsenical mirror in the Marsh apparatus and the determination of small quantities of arsenic. J. GANGL and J. VAZQUEZ SANCHEZ (Anal. Fis. Quím., 1934, 32, 876—890).—The usual form of the Marsh apparatus does not give quant. results. It is essential to use Zn dust to produce sufficient nascent H, and subsequently to boil the liquid for 10 min. to expel all the  $\text{AsH}_3$ , using a spiral quartz tube of 0.2 mm. internal diameter to collect the As, which is then dissolved in ICl and the liberated I titrated in presence of KCN with 0.001M-KIO<sub>3</sub> (for amounts of As up to 1 mg.). The influence of salts on the formation of  $\text{AsH}_3$  has been investigated. The use of special absorbents in the apparatus is unnecessary. F. R. G.

Determination of boron in glass.—See B., 1936, 789.

Determination of silica in iron ores.—See B., 1936, 792.

Determination of carbon dioxide in air. Y. KAUKO and T. YLI-UOTILA (Suomen Kem., 1936, 9, A, 71—72).—An improvement on the usual absorption method for the determination of  $\text{CO}_2$  in air is described. Results obtained by this method are more exact and also give higher abs. vals. D. C. J.

Determination of total carbonic acid in water. A. PEKKARINEN (Suomen Kem., 1936, 9, A, 70—71).—Methods are briefly discussed. D. C. J.

Determination of the total carbonic acid of carbonate solutions. Y. KAUKO, V. MANTERE, and T. YLI-UOTILA (Suomen Kem., 1936, 9, A, 65—67).—Air is passed at a measured rate up a column containing glass beads, and down which the carbonate solution, acidified in its course, passes at a measured rate. The accuracy of the method is limited only by that of the determination of the  $\text{CO}_2$  content of the air used. D. C. J.

Micro-determination of carbon dioxide and hydrogen in elementary analysis. Volumetric determination of carbon dioxide. J. LINDNER [in part with V. RANK] (Mikrochem., 1936, 20, 209—

224).—The absorption of  $\text{CO}_2$  in alkali and  $\text{Ba(OH)}_2$ , and the influence of excess of air are discussed. Suitable sizes of absorption apparatus are given, and errors arising in the titration or from rubber connexions are considered. R. S.

Photo-electric turbidimeter and alkaline titration method for determination of small amounts of hydrocyanic acid. E. T. BARTHOLOMEW and E. C. RABY (J. Assoc. Off. Agric. Chem., 1936, 19, 472—476).—The use of the turbidimeter facilitates the detection of the end-point of the titration. Maceration of the material should take place in a closed vessel; otherwise HCN is lost. The distillate should be clarified with  $\text{PbCO}_3$  to prevent reduction of  $\text{AgNO}_3$  by volatile org. substances. E. C. S.

Detection and determination of hydrogen cyanide.—See B., 1936, 861.

Determination of free cyanide in cadmium-plating solutions.—See B., 1936, 890.

Gravimetric determination of sodium. J. C. CANESSA (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 87—93).—Kahane's method (A., 1930, 726) is more trustworthy in presence of  $\text{Cl}^-$  and  $\text{NO}_3^-$  than of  $\text{SO}_4^{2-}$ . F. R. G.

Determination of total alkali metals in water.—See B., 1936, 766.

Use of formaldehyde for the elimination of ammonia and of ammonium salts. III. Decomposition of ammoniacal complexes by formaldehyde. Determination of metals in solutions containing ammonia or ammonium salts by alkali hydroxides or carbonates. A. HEMMELEK (Annali Chim. Appl., 1936, 26, 240—248; cf. this vol., 303).—The method is applicable to metals (e.g., Ag, Cu, Cd, Zn, Ni, Co) with salts insol. in  $\text{H}_2\text{O}$  but sol. in aq.  $\text{NH}_3$ . Addition of  $\text{CH}_2\text{O}$  to solutions in aq.  $\text{NH}_3$  converts the latter into  $(\text{CH}_2)_6\text{N}_4$  and permits pptn. of the metal as hydroxide or carbonate. F. O. H.

Analysis of calcium fluoride.—See B., 1936, 833.

Causes of contamination of precipitates. I. Precipitation processes in which barium compounds are involved. Z. KARAOGLANOV (Z. anal. Chem., 1936, 106, 129—146; cf. A., 1918, ii, 239, 241).—The author's published work on the pptn. of  $\text{BaSO}_4$  and  $\text{BaCrO}_4$  is discussed. The variability of composition and the nature of the ions co-pptd. in presence of foreign electrolytes are considered to be due to secondary reactions accompanying pptn., leading to the formation of mixed salts, e.g.,  $\text{Ba(KSO}_4)_2$ ,  $(\text{BaCl})_2\text{SO}_4$ . J. S. A.

Sensitive reagents for detection and determination of magnesium. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 224).—A correction (cf. this vol., 1082). *p*-Nitrobenzenediazoaminobenzene gives a strong carmine absorption colour with  $\text{Mg(OH)}_2$ . J. S. A.

Determination of magnesium in glass.—See B., 1936, 884.

Electroanalysis and macro-electroanalysis of zinc with three electrodes. J. GUZMAN and J. S. D'ANGLADA (Anal. Fis. Quím., 1934, 32, 1053—

1066).—A galvanised Fe cathode gave satisfactory results with  $\text{NH}_3$ -Zn solutions containing  $\text{SO}_4^{''}$ ,  $\text{HCO}_2'$ ,  $\text{C}_2\text{O}_4^{''}$ , tartrate, and  $\text{CN}'$  (with a passive Fe anode), and with Zn solutions containing free  $\text{AcOH}$  (with a steel anode). The results are most accurate with the ammoniacal cyanide solutions. The three-electrode indicator potential method is recommended.

D. R. D.

**Micro-reactions of lead.** I. M. KORENMAN and S. S. MESSONSENK (Mikrochem., 1936, 20, 189—193).—The micro-characterisation of  $\text{PbCl}_2$ ,  $\text{PbI}_2$ , and  $\text{K}_2\text{CuPb}(\text{NO}_2)_6$  in presence of other salts is described, and the optimum concns. of  $\text{HCl}$ ,  $\text{KI}$ , and  $\text{H}_2\text{SO}_4$ , respectively, are given.

R. S.

**Determination of lead in pyrites.**—See B., 1936, 833.

**Gravimetric determination of copper by hexamethylenetetramine.** A. HEMMELER (Annali Chim. Appl., 1936, 26, 237—240).—Cu is pptd. by  $(\text{CH}_3)_6\text{N}_4$  (or  $\text{NH}_3 + \text{CH}_2\text{O}$ ), the ppt. being incinerated and weighed as  $\text{CuO}$ . Ag and Zn salts must first be separated, the former being reduced to Ag and the latter partly pptd. by  $(\text{CH}_2)_6\text{N}_4$ .

F. O. H.

**Colour reaction of copper and urobilin.** G. BERTRAND and L. DE SAINT-RAT (Compt. rend., 1936, 203, 140—143).—Urobilin in 60% EtOH gives with  $>0.0001$  mg. of Cu in 1 ml. of 60% EtOH containing  $\text{NaOAc}$  a permanent pink colour which is sp. for Cu and can be used to determine Cu colorimetrically in admixture with other elements and radicals without preliminary separation.

**2:7-Diaminodibenzfuran as a reagent for copper.** E. F. BRAU (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 43—45).—2:7-Diaminodibenzfuran with  $\text{CuSO}_4$  in presence of  $\text{KCN}$ ,  $\text{KCNO}$ , or  $\text{NH}_4\text{CNS}$  gives a blue ppt.

F. R. G.

**Electroanalysis and macro-electroanalysis of copper with three electrodes.** J. GUZMAN and A. SARABIA (Anal. Fis. Quím., 1934, 32, 910—917; cf. A., 1935, 723).—Satisfactory results have been obtained with  $\text{NH}_3$ -Cu solutions containing  $\text{HCO}_2'$ ,  $\text{BO}_3^{''}$ ,  $\text{OAc}'$ ,  $\text{C}_2\text{O}_4^{''}$ , and citrate, and for acid Cu solutions containing  $\text{HCO}_2'$ ,  $\text{NO}_2'$ ,  $\text{SO}_4^{''}$ ,  $\text{PO}_4^{''}$ , and  $\text{OAc}'$ .

D. R. D.

**Determination of copper in brass etc.**—See B., 1936, 889.

**Determination of copper.** I. JOLSON (Z. anal. Chem., 1936, 106, 157—167).—Cu<sup>++</sup> in absence of a great excess of  $\text{NH}_4$  salts is reduced to Cu<sup>+</sup> by means of  $\text{N}_2\text{H}_4$  or  $\text{NH}_2\text{OH} + \text{aq. NH}_3$ . Cu<sup>+</sup> is pptd. by  $\text{C}_2\text{H}_2$  as  $\text{Cu}_2\text{C}_2$ , which is kept in suspension by adding gelatin as protective colloid. The suspension is titrated with 1% or 0.1% aq.  $\text{KCN}$ , being decolorised and converted quantitatively into  $\text{K}_2\text{Cu}(\text{CN})_3$ . In presence of Fe or Zn, 5 g. of  $\text{Na}_4\text{P}_2\text{O}_7$  per 100 c.c. are added. For the determination of Cu in melts from sulphide ores, the material is dissolved in  $\text{HCl} + \text{HNO}_3 + \text{KClO}_3$ , and the solution is evaporated to dryness. Flotation gangue is dissolved similarly, but for the titration of Cu a large excess of  $\text{Na}_4\text{P}_2\text{O}_7$  is necessary. Slags from Cu smelting are evaporated down successively with  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ .

J. S. A.

**Induced reduction by silver ion for rapid detection of mercuric, silver, and stannous ions.** N. A. TANANAIEV (Z. anal. Chem., 1936, 160, 167—170).—In presence of a small amount of Ag,  $\text{HgCl}_2$  and  $\text{Hg}_2\text{Cl}_2$  are reduced inductively by  $\text{SnCl}_2$  in acid solution. The reaction may be used for a drop test for Ag, Hg, or (much less sensitive) Sn. Fe<sup>++</sup> should be absent.

J. S. A.

**Colorimetric determination of minute amounts of mercury in organic matter.** N. STRAFFORD and P. F. WYATT (Analyst, 1936, 61, 528—535).—Org. matter is decomposed by hot  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ , using an aq.  $\text{NaOH}$  trap and also one containing aq.  $\text{H}_2\text{S}$ ,  $\text{CuSO}_4$  and paper pulp. The mixed acid and alkaline liquids are neutralised with aq.  $\text{NH}_3$ , oxidised with  $\text{KMnO}_4$ , and the contents of the  $\text{H}_2\text{S}$  trap added. The solution is treated with  $\text{H}_2\text{S}$ , the ppt. washed with  $\text{H}_2\text{S}-\text{H}_2\text{O}$  and then  $\text{COMe.}$ , and free S is removed by  $\text{CS}_2$ . The dry, mixed sulphides are oxidised with  $\text{H}_2\text{SO}_4-\text{HNO}_3$ , a slight excess of aq.  $\text{NH}_3$  is added followed by an excess of  $\text{HNO}_3$ , and the liquid is electrolysed. The Hg on the cathode is dissolved in  $\text{HNO}_3$  and determined colorimetrically with *p*-dimethylaminobenzylidenerrhodanine. The method is considered to be more satisfactory than the colloidal sulphide and the diphenylcarbazide and diphenylcarbazone methods, the disadvantages of which are discussed.

E. H. S.

**Quantitative separation of aluminium and beryllium.** J. DEWAR and P. A. GARDINER (Analyst, 1936, 61, 536—538).—If the Al is not greatly in excess of the Be present, a slight modification of Britton's method (B., 1922, 273) gives accurate results.

E. H. S.

**Colorimetric determination of aluminium with hæmatoxylin.** M. T. GOLUBEVA (J. Appl. Chem. Russ., 1936, 9, 1144—1149).—Hatfield's method (A., 1924, ii, 350) gives satisfactory results with coloured as well as colourless hæmatoxylin. It serves for determination of 0.025—0.6 mg. of Al per litre of  $\text{H}_2\text{O}$  (error  $\pm 5\%$ ); Ca and Mg affect the colour obtained. Low results are obtained when the Al is in the form of hydroxide.

R. T.

**Colorimetric determination of aluminium by means of alizarin-red S.** A. P. MUSAKIN (J. Appl. Chem. Russ., 1936, 9, 1340—1346).—The greatest difference between the intensity of coloration of aq. Na alizarinsulphonate (I) alone and in presence of Al<sup>+++</sup> is at  $p_H$  3.6. 25 mg. of (I) should be taken per mg. of  $\text{Al}_2\text{O}_3$  present. Fe<sup>+++</sup> is removed by adding 1 ml. of 32%  $\text{KCN}$  per 3 ml. of a solution, and extracting with  $\text{C}_5\text{H}_{11}\text{OH}$  (2 successive 1-ml. portions). The colorations remain unchanged for 15 days.

R. T.

**Rational analysis of clays.**—See B., 1936, 834.

**Microchemical test for gallium with morin.** G. BECK (Mikrochem., 1936, 20, 194—197).—Ga may be detected in presence of Al if  $\text{NaF}$  is added, when only the green Ga fluorescence appears. The limiting quantities detectable and the reactions of other salts are given.

R. S.

**Direct photo-electrometric determination of manganese and chromium in the flame.** J.



HEYES (Z. Elektrochem., 1936, 42, 532).—The intensity of the spectral lines is determined by means of a photo-electric cell. The sensitivity is comparable with that of the photographic method.

E. S. H.

Micro-determination of manganese in steel.—See B., 1936, 839.

Determination of traces of iron. J. A. GUY (Chem. and Ind., 1936, 642).—Traces of Fe were determined by dissolving in dil.  $\text{H}_2\text{SO}_4$  and making pink with 0.01N- $\text{KMnO}_4$ . The excess of  $\text{KMnO}_4$  was decolorised with dil.  $\text{H}_2\text{O}_2$ , after which the normal colorimetric method with  $\text{NH}_4\text{CNS}$  was used.

C. R. H.

Electrometric analysis. Depolarimetry and galvanimetry. J. GUZMAN and A. RACANO (Anal. Fis. Quím., 1934, 32, 899—909).—Modifications of the authors' method (A., 1935, 948) for use in determining  $\text{Fe}^{\text{II}}$  and  $\text{H}_2\text{O}_2$  by means of  $\text{KMnO}_4$ ,  $\text{OCl}^-$  by means of  $\text{AsO}_3^-$  and  $\text{Fe}^{\text{II}}$ , and  $\text{H}_2\text{O}_2$  and  $\text{Fe}(\text{CN})_6^{4-}$  by means of  $\text{Ce}(\text{SO}_4)_2$  are described.

D. R. D.

Photometric determination of iron in used engine oils.—See B., 1936, 866.

Separation of iron, aluminium, and chromium from manganese, cobalt, and nickel with pyridine. E. A. OSTROUMOV (Z. anal. Chem., 1936, 106, 170—176).—Pptn. of Fe, Cr, and Al as hydroxides from dil.  $\text{HCl}$  or  $\text{HNO}_3$  solution by means of 20% aq.  $\text{C}_5\text{H}_5\text{N}$  at 60—70°, in presence of  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ , affords a quant. separation from Mn, Co, and Ni with one pptn. Large amounts of  $\text{SO}_4^{2-}$  should not be present.

J. S. A.

Micro-silicate analysis. II. Determination of iron, aluminium, magnesium, calcium, titanium, and manganese. K. SCHOKLITSCH (Mikrochem., 1936, 20, 247—253).—Fe and Al, and, later, Mg, are separated as 8-hydroxyquinoline compounds, Ca as  $\text{CaC}_2\text{O}_4$ , and Mn is determined colorimetrically. (Cf. A., 1935, 1472.)

R. S.

Argentometric studies. IV. Determination of ferricyanide. O. TOMÍČEK and M. K. HUBROVA (Coll. Czech. Chem. Comm., 1936, 8, 293—305).—The potentiometric titration of  $\text{K}_3\text{Fe}(\text{CN})_6$  with  $\text{AgNO}_3$  in neutral solution was carried out with an accuracy of 0.2%. The sensitivity of the electrode, which consisted of Ag foil soldered to Pt wire, was increased by the addition of  $\text{HNO}_3$  or, better,  $\text{EtOH}$ . The presence of salts of  $\text{NH}_4$ , Na, K, Ca, Sr, Ba, Mg, Al, and Pb lowered the results. In the presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ , titration gives  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{K}_3\text{Fe}(\text{CN})_6$ . If, however, the solution is made acidic with  $\text{H}_2\text{C}_2\text{O}_4$  and the  $\text{K}_4\text{Fe}(\text{CN})_6$  pptd. with  $\text{Pb}(\text{NO}_3)_2$ , the filtered solution can be titrated with  $\text{AgNO}_3$ .  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{KCNS}$  can be titrated consecutively,  $\text{AgCNS}$  being pptd. before the  $\text{Ag}_3\text{Fe}(\text{CN})_6$ . The solubility of  $\text{Ag}_3\text{Fe}(\text{CN})_6$  was calc. as  $4 \times 10^{-5}N$ , and the solubility product  $[\text{Ag}^+]^3 \times [\text{Fe}(\text{CN})_6^{3-}]$  as  $8.4 \times 10^{-19}N$ .

C. R. H.

Potentiometric determination of cobalt and manganese.—See B., 1936, 840.

Electroanalysis and macro-electroanalysis of nickel with three electrodes. J. GUZMAN and G. GARCÍA (Anal. Fis. Quím., 1934, 32, 923—930).—

Guzman's method is applied successfully to  $\text{NH}_3$ -Ni solutions containing  $\text{PO}_4^{3-}$ ,  $\text{BO}_3^{3-}$ ,  $\text{HCO}_3^-$ ,  $\text{OAc}^-$ , and  $\text{C}_2\text{O}_4^{2-}$ . Anodes of passive Fe and cathodes of brass may be employed.

D. R. D.

Determination of chromium.—See B., 1936, 744, 839, 840.

Mechanism of the benzidine reaction for chromium. L. KÜHLBERG (Mikrochem., 1936, 20, 244—246).—The sensitivity of the benzidine-blue test for  $\text{Cr}_2\text{O}_7^{2-}$  is increased by addition of  $\text{H}_2\text{O}_2$ . Greater sensitivity is attained with *o*-tolidine +  $\text{H}_2\text{O}_2$ . Possible mechanisms are discussed.

R. S.

Separation and determination of tungsten and molybdenum. H. YAGODA and H. A. FALES (J. Amer. Chem. Soc., 1936, 58, 1494—1501).— $\text{MoS}_3$  can be pptd. quantitatively in aq. solution in presence of  $\text{HCO}_2\text{H}$  by reaction with saturated aq.  $\text{H}_2\text{S}$  at 0°. Separation from W is effected by adjusting the  $p_H$  to 2.9 by means of a buffer mixture of  $\text{HCO}_2\text{NH}_4$ , tartaric acid, and  $\text{HCO}_2\text{H}$ .

E. S. H.

Separation of small amounts of tin in presence of antimony and arsenic. N. J. TSCHERVIAKOV and E. A. OSTROUMOV (Ann. Chim. Analyt., 1936, [iii], 18, 201—207).—Sn, Sb, and As are separated from Cu, Bi, etc. by pptn. with  $\text{Na}_2\text{S}$ , and are repptd. from the solution by addition of  $\text{AcOH}$ . The sulphides are dissolved in *N*- $\text{HCl}$  at 30—40°, and Sn is pptd. by a large excess of cupferron at > 5°.

J. S. A.

Colorimetric determination of germanium. I. P. ALIMARIN and B. N. IVANOV-EMIN (J. Appl. Chem. Russ., 1936, 9, 1334—1339).—The distillate obtained by heating the mineral in a stream of  $\text{Cl}_2$  is decolorised by aq.  $\text{NaHSO}_3$ , a small excess of Br is added, and the solution is again made colourless with  $\text{NaHSO}_3$ . The  $[\text{HCl}]$  is adjusted to 6N,  $\text{H}_2\text{S}$  is passed, and the ppt. is collected after 24 hr., washed, and dissolved in 1%  $\text{NaOH}$ . The solution is heated with  $\text{H}_2\text{O}_2$ , excess of which is decomposed by boiling, and  $\text{H}_2\text{O}$  is added to a known vol. 5%  $(\text{NH}_4)_2\text{MoO}_4$  and  $\text{HNO}_3$  to 0.15—0.35N are added to a portion of solution, the vol. is made up to 25—50 ml., and the yellow coloration is compared with that given by a standard solution, or with aq. picric acid (I) [10 mg. of (I) per litre correspond with 7.48 mg. of  $\text{GeO}_2$  per 100 ml.]. The method permits the determination of 1 p.p.m. of Ge. Org. acids, Se, F',  $\text{PO}_4^{3-}$ , and  $\text{SiO}_3^{2-}$  interfere, as does also  $\text{As}^V$  when present in large amount.

R. T.

Determination of vanadium in the field. A. S. KOMAROVSKI (Mikrochem., 1936, 20, 161—162).—The method of Tananaev and Pantschenko, as described by Silbermintz and Florenzki (A., 1935, 1474), is inapplicable in presence of  $\text{CrO}_4^{2-}$ ,  $\text{ClO}_3^-$ ,  $\text{MnO}_4^-$ , etc.

R. S.

Determination of antimony in copper.—See B., 1936, 889.

Determination of gold with gaseous hydrogen phosphide and filter-paper. N. D. COSTEANU (Bull. Soc. chim., 1936, [v], 3, 1527—1530).—A filter-paper soaked in aq.  $\text{AuCl}_3$  and then exposed to  $\text{PH}_3$  turns dark blue, owing to production of colloidal Au.

The intensity of coloration  $\propto$  the [Au] of the solution, and can be compared with standards. 25-mg. test samples only are required for determination of Au in jewellery etc. J. W. S.

Detection of small amounts of platinum in minerals, alloys, precipitates, etc. Separation and concentration of platinum by precipitation with tellurium. S. K. HAGEN (Mikrochem., 1936, 20, 180—188).—The alkaline solution is treated with KI and AcOH. A reddish-brown or rose colour appears if Pt<sup>++++</sup> is present. Te, pptd. from solutions containing NaTeO<sub>2</sub> by treatment with SO<sub>2</sub>, separates Pt, Au, Se, Mo, and Hg from the other metals. Pt may then be detected as above. R. S.

Precision thermostat for the temperature regulation of a room. T. DEIGHTON (J. Sci. Instr., 1936, 13, 298—300).—Two connected expansion chambers control a heater of very small heat capacity. One is controlled by the room temp. and the other by the heater itself, thus taking up the lag at once. Temp. variation is  $< 0.01^\circ$ . C. W. G.

Simplified and accurate process for the calculation of heat loss in calorimetric determinations. H. MOSER (Physikal., 1936, 37, 529—533).—A method of determining the heat loss during the course of a calorimetric experiment involves the use of the Regnault-Pfaundler formula instead of the more usual, but less accurate, Langbein formula. A. J. M.

Cryogenic laboratory of the California Institute of Technology. II. A. GOETZ (Rev. Sci. Instr., 1936, [ii], 7, 307—318; cf. A., 1935, 1212).—A description is given of the He liquefaction plant, separate "stations" for particular types of experiments, details of the station for X-ray spectroscopy at low temp., and equipment for potentiometric measurements. N. M. B.

Photo-electric colorimeter. I. M. DILLER (J. Biol. Chem., 1936, 115, 315—322). H. D.

Stabilised photo-electric colorimeter with light filters. K. A. EVELYN (J. Biol. Chem., 1936, 115, 63—75).—The construction of a direct-reading, single photo-cell colorimeter of exceptional stability is described. H. G. R.

Photo-electric colorimeter for determining carbon dioxide in air.—Sec B., 1936, 861.

Spectropolarimeter for the Schumann region. R. SERVANT (Compt. rend., 1936, 203, 311—312).—The apparatus previously described has been modified to permit the use of lower  $\lambda\lambda$  (cf. this vol., 697). C. R. H.

Optical difficulties with the cylindrical cataphoresis cell. A. M. BUSWELL and T. E. LARSON (J. Physical Chem., 1936, 40, 833—834).—To obtain illumination at the correct depth in the Mattson cell (A., 1933, 349) the light beam should enter the liquid at a depth of  $0.377R$  from the top, where  $R$  is the radius of the cell. J. W. S.

Ultra-violet solution light filters. W. V. BHAGWAT (Bull. Acad. Sci. U.P., 1932, 2, 67—74).—Aq. CoCl<sub>2</sub> (3.66 mol.) + Ni(NO<sub>3</sub>)<sub>2</sub> (2.08 mol.) transmits

$\lambda\lambda$  3307—3598 Å.; aq. CoCl<sub>2</sub> (3.66 mol.) transmits  $\lambda\lambda$  2618—4063 and 7100—7600 Å. CH. ABS. (e)

Investigation of Raman spectra by means of a photo-electric counter. V. KUDRJAVEVA (Acta Physicochim. U.R.S.S., 1935, 3, 613—618).—Apparatus, consisting essentially of a photo-electric counter placed behind the second slit of a monochromator, enables the dependence of the intensity of the scattered light on  $\lambda$  to be determined. It can also be used for measuring the relative intensity and change in intensity of single Raman lines. C. R. H.

Technique of photographic spectrophotometry of solutions. H. VON HALBAN, G. KORTUM, and B. SZIGETI (Z. Elektrochem., 1936, 42, 628—631).—Modified technique is described. E. S. H.

Sputtering of large-aperture Fabry-Perot interferometer mirrors. S. TOLANSKY and E. LEE (J. Sci. Instr., 1936, 13, 261—263).—Directions for obtaining deposits of large area, uniform thickness, and high reflecting power are given. C. W. G.

Continuous absorption spectra: experimental methods. R. G. AICKIN (J. Proc. Austral. Chem. Inst., 1936, 3, 206—212).—A review.

Measurement of optical densities of smoke stains on filter-papers. A. S. G. HILL (Trans. Faraday Soc., 1936, 32, 1125—1131).—A photo-electric cell method is described. J. G. A. G.

Apparatus for preparing microphotometer records of electron diffraction photographs. C. DEGARD and W. VAN DER GRINTEN (Rev. Sci. Instr., 1936, [ii], 7, 319).—An arrangement is described for rotating the plate at 600—1000 r.p.m. while the record is being made; this obviates emulsion grain and dust effects and gives a fine smooth curve. N. M. B.

Correction of gas refractometer reading for temperature and pressure change. Z. TUZI and H. OOSIMA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 718—729).—The correction for temp. and pressure of the gas refractometer, used as an indicator of explosive gas, is calc., and agrees with experimental results. R. S. B.

Objective microphotometry. P. KRUMHOLZ (Mikrochem., 1936, 20, 227—235).—A microphotometer in which 1 c.c. of solution can be tested is described. Standard absorption curves for blue, green, and yellow filters are given. R. S.

Combined transparent photo-cathodes. P. GORLICH (Z. Physik, 1936, 101, 335—342).—Cs alloys are used to give transparent red-sensitive photo-cathodes; the long- $\lambda$  limit can be extended by sensitisation with O<sub>2</sub>. The quantum efficiency is large when the second alloy component is Bi or Sb. A. B. D. C.

Apparatus for spectroscopic chemical analysis. J. L. GRING and G. L. CLARK (Rev. Sci. Instr., 1936, [ii], 7, 305—306).—An electrode stand holding four pairs of electrodes simultaneously, and an improved apparatus for producing an under-water spark, are described. N. M. B.

Machine for drawing pole-figures directly from X-ray diffraction patterns. D. McLACHLAN, jun.



(Rev. Sci. Instr., 1936, [ii], 7, 301—304).—The construction and use of a simple instrument for drawing stereographic pole figures are described. N. M. B.

**Ultrasonic stroboscope.** E. HIEDEMANN and K. H. HOESCH (Z. Physik, 1936, 102, 253—258).—Ultrasonic stroboscopes may be constructed employing the following principles: the production of artificial double refraction in substances by ultrasonic waves, and the modulation of light by such waves. Several stroboscopes are described, and their use is demonstrated. A. J. M.

**Simplifications in step and inversion potentiometers.** J. GUZMAN and A. ARA (Anal. Fis. Quím., 1934, 32, 1067—1076).—Zn, Al, Sb, Cu, Ag, Hg, Au, Pd, or Pt in  $N\text{-KCl}$  or  $\text{-K}_2\text{SO}_4$  is used as intermediate electrode. D. R. D.

**Graduated electrical resistances.** J. GUZMAN (Anal. Fis. Quím., 1934, 32, 918—922).—Simple resistances for use in potentiometry are described. D. R. D.

**Emanation electroscope.** B. A. SPICER (J. Sci. Instr., 1936, 13, 263—267).—The ionising effect of  $\beta$ -rays is used, and 0.001—3.0 millicuries of Rn can be measured. C. W. G.

**Double amplifying apparatus for the detection of individual electrons in thermal emission.** E. H. WINKLER (Physikal. Z., 1936, 37, 557—558). A. J. M.

**Primary and secondary image in the electron microscope.** II. Investigation of structure by electron diffusion. H. BOERSCH (Ann. Physik, 1936, [v], 27, 75—80; cf. *ibid.*, 26, 631).—A method whereby the crystal structure of small selected areas of the object can be investigated in the electron microscope is described. O. D. S.

**Second-order focussing for the mass spectrograph.** W. W. SAWYER (Proc. Camb. Phil. Soc., 1936, 32, 453—460).—Mathematical. Conditions are calc. for the lay-out of a mass spectrograph with second-order focussing. O. D. S.

**Speed control for small direct-current motors.** L. G. HOXTON (Science, 1936, 84, 187—188). L. S. T.

**Wilson cloud-chamber of simple construction.** H. NEUERT (Physikal. Z., 1936, 37, 629—630).—Details are given for constructing a simple, portable cloud-chamber. A. J. M.

**Simple Wilson cloud-chamber.** H. BAUER (Physikal. Z., 1936, 37, 627—629).—The apparatus is described. A 50%  $\text{EtOH-H}_2\text{O}$  mixture is recommended for the chamber liquid. A. J. M.

**Stability of standard cells.** P. VIGOREUX (J. Sci. Instr., 1936, 13, 297—298).—Temp. variation from  $-8^\circ$  to  $60^\circ$  does not affect the e.m.f. of Cd cells containing acid, provided constant temp. is maintained just before and during measurement. C. W. G.

**Photo-electric methods of measuring the velocity of rapid reactions.** I. General principles and controls. F. J. W. ROUGHTON and G. A. MILLIKAN. II. Simple apparatus for rapid  $p_{\text{H}}$  and other changes requiring 200 c.c. or more of each reagent. F. J. W. ROUGHTON. III.

**Portable micro-apparatus applicable to an extended range of reactions.** G. A. MILLIKAN (Proc. Roy. Soc., 1936, A, 155, 258—269, 269—276, 277—291).—I. An optical method of analysis of the moving fluid has been devised in the Hartridge-Roughton rapid reaction apparatus, rendering it more economical in the use of fluid. This is accomplished by the use of photo-electric cells. More accurate and extensive tests of the efficiency of mixing and character of flow down the observation tube have been made.

II. A photo-electric method for analysing the colour of the streaming fluid in various parts of the observation tube is described. The method has been applied to the colour changes of indicators, and rapid  $p_{\text{H}}$  changes may be followed. Under good conditions an accuracy of 0.01—0.02  $p_{\text{H}}$  is obtained. The method is used for the determination of the velocity coeffs. of the reaction (1)  $\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  and (2)  $\text{CO}_2 + \text{OH}' \rightarrow \text{HCO}_3'$ , and the vals. obtained agree with those given by other methods.

III. The continuous-flow apparatus has been modified to adapt it for reactions involving any kind of colour change, small quantities of material, and easy transport. It is proved to be adequate to deal with processes the half reaction time of which is  $>0.0005$  sec. L. L. B.

**Contact potential difference.** C. W. OATLEY (Proc. Roy. Soc., 1936, A, 155, 218—234).—Details are given of a new method of measuring contact p.d., which depends on the known relation between anode voltage and crit. magnetic field in a magnetron, when electrons from the filament just fail to reach the anode. The method enables the contact potential of a given surface to be measured with respect to a hot W filament. Results are given for Zn and Mo surfaces. L. L. B.

**U-Tube method of measuring electrophoresis.** A. L. ROBERTS and J. C. CARRUTHERS (J. Physical Chem., 1936, 40, 703—708).—Measurements made by the U-tube method, uncorr. for the electro-osmotic flow of the medium, agree satisfactorily with those made by the microscopic cell method where such corrections must be introduced. J. W. S.

**Electro-osmotic measurements.** A. VAŠIČEK (Chem. Listy, 1936, 30, 173—175).—Apparatus and methods are described. R. T.

**Determination of the Curie point of ferromagnetic substances.** L. BERGMANN (Physikal. Z., 1936, 37, 547—548).—A hollow cylinder of the material under investigation carries a thermo-couple and is placed in a double coil. One coil magnetises the specimen, whilst the other is connected to a low-frequency amplifier. The specimen is heated above the Curie point, and allowed to cool in the apparatus while it is intermittently heated by focussing on it the rays from a small arc lamp. When the sample cools to the Curie point the intermittent heating causes variations in the magnetisation which are observed by means of the amplifier. The val. obtained for Ni was  $345^\circ$ , and for monel metal  $110^\circ$ . A. J. M.

**Automatic titration burette.** E. BAYER (Chem.-Ztg., 1936, 60, 726). J. S. A.

**Macro-micro-burette and precision micro-pipette.** J. GUZMAN (Anal. Fis. Quím., 1934, 32, 1129—1134).—A macro-micro-burette and precision micro-pipette suitable for electrometric titration are described.  
L. A. O'N.

**Absorber of CO<sub>2</sub> for currents of atmospheric air.** A. A. RICHTER (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 291—293; cf. A., 1902, ii, 682).—The air is forced through a pressed glass filter into a glass tower containing 0.02*N*-NaOH and 2—5 drops of BuOH; this yields an intense foam with a very large absorptive surface. Reproducible results are obtained if the current has a speed of 30—40 litres per hr.  
R. C. M.

**Separation of gaseous isotopes by diffusion.** D. E. WOOLDRIDGE and W. R. SMYTHE (Physical Rev., 1936, [ii], 50, 233—237).—The design, use, and results of tests with a 34-member Hertzian type apparatus are described. Marked enrichments of <sup>13</sup>C<sup>1</sup>H<sub>4</sub> from CH<sub>4</sub> and <sup>15</sup>N from N<sub>2</sub> were obtained (cf. this vol., 574, 772).  
N. M. B.

**Dilatometer for wide range of temperature.** H. SCHLÜTER (Chem.-Ztg., 1936, 60, 717).  
J. S. A.

**Apparatus for determination of the apparent volume and of the volume of voids.**—See B., 1936, 769.

**Method of measuring the net density of a substance which dissolves a little in a liquid.** U. YOSHIDA, S. MATANO, and M. WATANABE (Mem. Coll. Sci. Kyoto, 1936, 19, 161—168).—The following wts. are determined: a sealed evacuated tube containing the specimen, the tube filled with a liquid of known *d*, the tube alone. From these data and the vol. of the sealed tube the *d* of the solid can be calc.  
C. W. G.

**Accurate pycnometer.** J. M. CLAVERA and F. MORENO MARTIN (Anal. Fis. Quím., 1934, 32, 690—697).—A pycnometer and apparatus for filling are described.  
L. A. O'N.

**Rotary dialyser of large capacity.** G. FLORENCE and D. VINCENT (Bull. Soc. Chim. biol., 1936, 18, 1167—1169).  
A. L.

**Pouring from vessels.** H. KEIM (Chem.-Ztg., 1936, 60, 664).—The glass rod, used as an aid in pouring from beakers etc., is bent at an angle of 45° about 1 cm. from its end.  
E. S. H.

**Active hydrogen, oxygen, and nitrogen at pressures up to 20 mm.** P. HARTECK [with E. ROEDER] (Z. Elektrochem., 1936, 42, 536—538).—Apparatus and procedure for activating H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> at higher pressures than heretofore are described.

Preliminary observations on reduction and oxidation reactions are reported.  
E. S. H.

**Volumetric adsorption methods.** F. DURAU (Z. Physik, 1936, 101, 27—67).—Errors due to temp., pressure, adsorption by glass walls, solubility of the adsorptive in grease, vol. changes due to compression by the atm., and deviations from the gas laws have been empirically determined. The volumetric method is also developed for use with org. vapours.  
A. B. D. C.

**Hydrogen sulphide apparatus.** F. MORENO MARTIN (Anal. Fis. Quím., 1934, 32, 891—892).—A delivery tube terminating in a hook carrying a porous porcelain basket containing sulphide passes through the mouth of a bell jar which is placed inside a slightly wider jar of acid.  
F. R. G.

**Apparatus for obtaining hydrogen sulphide.** F. E. RAURICH SAS (Anal. Fis. Quím., 1934, 32, 1007—1010).—A large apparatus for the prep. and storage of H<sub>2</sub>S is described.  
D. R. D.

**Apparatus for distillation.** H. I. COOMBS (Biochem. J., 1936, 30, 1586—1587).—The apparatus is made of Pyrex, and is suitable for the distillation of conc. acids.  
F. A. A.

**Apparatus for fractional vacuum distillation of small amounts of high-boiling mixtures.** E. KLENK (Z. physiol. Chem., 1936, 242, 250—252).—The apparatus described is especially suitable for distillation of <0.5 g. of high-boiling fatty acids and their esters.  
W. McC.

**Fractional distillation columns.**—See B., 1936, 768, 819.

**Plastics in instrument design.** H. W. ROWELL (J. Sci. Instr., 1936, 13, 277—282).—Many applications are described, together with information as to methods of working.  
C. W. G.

**Production of metallic films.** R. V. JONES (J. Sci. Instr., 1936, 13, 282—288).—A method of preparing metal foil 0.1 μ thick by rolling is described. The electrical properties of rolled foil are superior to those of samples prepared by other methods.  
C. W. G.

**Motor-driven circulating pump.** G. BARR (J. Sci. Instr., 1936, 13, 300—302).—A glass bell is raised and lowered through a Hg seal, and, dipping continuously in Hg in a vessel in which it is itself enclosed, circulates gas through valves by double action.  
C. W. G.

**Lecture experiment in combustion chemistry.** H. ULICH (Angew. Chem., 1936, 49, 619—620).—The experiment demonstrates the influence of pressure on the reaction of H<sub>2</sub> with O<sub>2</sub>.  
E. S. H.

## Geochemistry.

**Variations in the atmospheric dust content due to micro-atmospheric influences.** R. MELBAU (Trans. Faraday Soc., 1936, 32, 1270—1272).—Very small (micro-atm.) differences of temp., humidity, and of air currents lead to high concns. of fog and dust at unexpected places.  
J. G. A. G.

**Influence of urban conditions on the circulation of electricity through the atmosphere.** F. J. W. WHIPPLE (Trans. Faraday Soc., 1936, 32, 1203—1209).—Diurnal variations of the resistance of the atm. are correlated with the formation of ions and smoke from the combustion of fuel.  
J. G. A. G.



**Fog along the Meuse valley.** J. FIRKET (Trans. Faraday Soc., 1936, 32, 1192—1196).—A summary of the scientific report on the fog disaster of Dec. 1—5, 1930; toxic effects are attributed to  $\text{SO}_2$  and  $\text{SO}_3$ .

J. G. A. G.

**Emanation content of hot springs and artesian wells in the Peiping area.** Y. K. HSU and Y. M. HSIEH (Chinese J. Physics, 1936, 2, 106—116).—The Th- and Ra-emanation contents of a no. of hot springs and artesian wells have been measured.

O. D. S.

**Geological significance of thermophilic bacteria.** A. SCHLOEMER (Chem. Erde, 1936, 10, 667—670).—Sinter deposited by the agency of bacteria in the hot ( $40$ — $50^\circ$ ) springs at Aachen contains  $\text{CaCO}_3$  61.35,  $\text{SiO}_2$  29.74,  $\text{Fe}_2\text{O}_3$  3.15%. Sinter deposited by the hotter ( $60$ — $70^\circ$ ) springs in the Burtscheid suburb contains  $\text{CaCO}_3$  99.82%.

L. J. S.

**Chemical characteristics of some Jugoslavian lakes.** K. HOLL (Arch. Hydrobiol., 1935, 28, 437—442; Chem. Zentr., 1935, ii, 3493).—Analytical data are recorded.

J. S. A.

**Mineral water from the Graf Ludwigstorff iodine-sulphur spring at Bad Deutsch-Altenburg.** J. GANGL and R. POSEGA (Wien. klin. Woch., 1935, 48, 1157—1160).—Analyses are recorded.

H. J. E.

**Analyses of mineral water of Marano Equo [Italy].** A. FOSCHINI and B. ROSSI (Annali Chim. Appl., 1936, 26, 270—282).—Data are given for inorg. and gaseous constituents, radioactivity, and physico-chemical consts.

F. O. H.

**Enrichment of heavy water in glacier ice and melting diagram of system  $\text{H}_2\text{O}$ — $\text{D}_2\text{O}$ .** A. EUCKEN and K. SCHAFER (Nachr. Ges. Wiss. Göttingen, 1935, [ii], 1, 109—125; Chem. Zentr., 1935, ii, 3741).—The enrichment of  $\text{D}_2\text{O}$  in glacier ice is the greater the smaller is the amount of the original ice remaining—e.g., in the narrow pointed tongues of deep valley glaciers with large basins—and may attain 50%. The m.p. diagram of the system  $\text{D}_2\text{O}$ — $\text{HDO}$ — $\text{H}_2\text{O}$  is calc. from the m.p. and latent heats,  $L$ , on the assumption that  $L/T$  rises regularly from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$ . The m.p. of  $\text{HDO}$  is extrapolated from the m.p. of  $\text{H}_2\text{O}$  low in D as  $2.50^\circ$ . The enrichment of  $\text{D}_2\text{O}$  in the solid phase is calc. and compared with experimental vals.

J. S. A.

**Gas occurrence in southern Daghestan.** J. G. IVASCHTSCHENKO and E. A. PODALKO (Azer. Neft. Choz., 1934, No. 11—12, 38—44).—Analyses are given.

CH. ABS. (e)

**Natural gases in Azerbaidshan.** L. POTOLOVSKI and V. BUINITZKAJA (Azer. Neft. Choz., 1934, No. 11—12, 25—28).—Five types of gas occur: (1)  $\text{CH}_4$  with little  $\text{CO}_2$  and  $\text{N}_2$  and traces of He; (2)  $\text{CH}_4$  with  $> 43\%$   $\text{N}_2$ ,  $> 0.15\%$  He, and some  $\text{CO}_2$ ; (3)  $\text{CH}_4$  and  $\text{N}_2$  with 9—30%  $\text{CO}_2$  and considerable He; (4)  $\text{N}_2$ , with considerable He; (5)  $\text{CO}_2$ .

CH. ABS. (e)

**Application of  $VEK$  in geochemistry.** A. E. FERSMAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 393—396; cf. A., 1935, 1305).—Since  $VEK$  (amount of energy, per unit valency, released by an

ion in forming a heterovalent or at. crystal lattice) should (theoretically) decrease, for cations and anions, with increasing alkalinity or acidity, respectively, it should be a useful measure of these properties; tabulated vals. of  $VEK$  in general support this argument (those for cations being compared with the pptn.  $\mu_n$ ) except in the case of cations from subsidiary groups in the periodic table. Possible geochemical applications are outlined. R. C. M.

**Electrical conductivity of rocks.** (MME.) F. BAYARD-DUCLAUX (Ann. Physique, 1936, [xi], 6, 5—107).—Data obtained by using a Wheatstone bridge method, the specimen being held at various high pressures between two metallic electrodes, are given for a no. of rocks from various localities. Results are reported for a study of the variation of resistance with p.d., time of passage of current, temp., and state of desiccation of the specimen, and for the effect of saturating the specimens with distilled or salt  $\text{H}_2\text{O}$ , and for the humidity of the surrounding air. The electrolytic conductivity of specimens between electrolytes as anode and cathode is described, and theoretical considerations are discussed.

N. M. B.

**Lattice of uraninite.** A. SCHOEP and V. BILLIET (Bull. Soc. géol. Belg., 1935, 58, 198—206; Chem. Zentr., 1935, ii, 3491—3492).—Uraninite from both Shinkolobere and Katanga is identical with synthetic  $\text{UO}_2$ . The face-centred cubic lattice has  $a$  5.47 Å.

J. S. A.

**Crystalline uraninite from Kasolo-Shinkolobwe.** R. VAN AUBEL (Publ. Congo belge, 1934—1935, 42—48).—The length of the edge of the unit cube was 4.67 Å. Elements detected spectroscopically are recorded.

H. J. E.

**Radioactivity of bituminous shale.** I. N. A. ORLOV and L. M. KURBATOV (Chim. Tverd. Topl., 1934, 5, 525—527).—The  $\text{U}_3\text{O}_8$  content of samples from a deposit near the river Popovka was 0.21% (deduced from the  $\alpha$ -activity). In an  $\text{HCl}$  extract the Ra content was  $16.5 \times 10^{-12}$  g. per g. of shale. The Th was  $12.5 \times 10^{-5}$  g. per g. of shale.

CH. ABS. (e)

**Determination of the gas content of horizons by the radioactivity of the minerals.** A. SNARSKI (Azer. Neft. Choz., 1934, No. 11—12, 28—34).—A review.

CH. ABS. (e)

**Significance of quantitative microanalyses of radioactive minerals for measurement of geological time.** F. HECHT and E. KROUPA (Z. anal. Chem., 1936, 106, 82—103).—Results are recorded for complete microanalyses of uraninites, pitchblendes, thorianite, monazite, and allanites, using 20—40 mg. of hand-picked material or a single crystal for each analysis. Good agreement of the U : Pb ratio with that determined macroanalytically shows the applicability of rock microanalysis to the determination of geological age.

J. S. A.

**Pleochroic (radioactive) haloes, their distribution in rocks and variability.** M. STARK (Chem. Erde, 1936, 10, 566—630).—The minerals composing rocks of all kinds and of different geological ages were examined for pleochroic haloes. These

are not always present, and they are affected by changes in the rocks. They do not afford a trustworthy indication of the age of a rock, but they give some idea of the distribution of radioactive elements.

L. J. S.

**Melilite-basalt from Westberg [Hesse-Nassau], an assimilation product of ultrabasic rocks.** T. ERNST (Chem. Erde, 1936, 10, 631—666).—Nodules of olivine and pyroxene present in this rock are relics of fragments of ultrabasic rocks brought up with the magma from depth: they are not segregation products as previously thought. Analyses are given of the rock and of the pyroxene, and the composition of the original magma is calc. The composition appears to have been only slightly affected by the assimilation of sedimentary rocks into which the magma was intruded.

L. J. S.

**Origin of the Passau [Bavaria] graphite deposits.** A. MAUCHER (Chem. Erde, 1936, 10, 539—565).—The presence of V, up to 0.1% (together with Ni, Co, Cu, Cr), is taken to indicate that the graphite is of org., probably algal, origin (like the bitumen of the Black Sea), with subsequent profound modification by metamorphic processes.

L. J. S.

**Origin of quartz in the Bavarian Pfahl.** F. HEGEMANN (Chem. Erde, 1936, 10, 521—538).—The large bodies of massive quartz ( $\text{SiO}_2$  95–11%) present in this zone of dislocation are of hydrothermal origin.

L. J. S.

**Arsenic in Upper Carboniferous and Permian sediments in Silesia and Bohemia.** K. HOEHNE and W. E. PETRASCHECK (Chem. Erde, 1936, 10, 475—478).—Ironstones and shales contain 0.1–0.74%  $\text{As}_2\text{O}_5$ , the larger amounts being from localities nearer the Riesengebirge granite mass (whence the As was derived), and in materials richer in Fe and C.

L. J. S.

**Mineral paragenesis of gravel ores in Outokumpu and Polvijärvi districts.** H. VAYRYNEN (Bull. Comm. géol. Finlande, 1935, No. 109, 19 pp.; Chem. Zentr., 1935, ii, 3492).—The Outokumpu deposits probably originated above the crit. temp. of the  $\text{H}_2\text{O}$  solutions, but below the equilibrium temp. of the reaction  $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$ . Polvijärvi deposits originated under hydrothermal conditions not much above 400°.

J. S. A.

**Blockite, a new selenium ore from Bolivia.** R. HERZENBERG and F. AHLFELD (Zentr. Min., 1935, A, 277—279; Chem. Zentr., 1935, ii, 3492).—A mineral approximating to  $(\text{Ni,Cu})\text{Se}_2$  is described.

J. S. A.

**Coprolites from North African phosphates.** L. CAYEUX (Compt. rend., 1936, 203, 217—219).—These coprolites consist of  $\text{Ca}_3(\text{PO}_4)_2$  and have no action on polarised light. They are free from mineral or org. inclusions.

J. W. S.

**Characteristics of the activity and the peculiar product "sara-isi" of the Aso volcano.** M. NAMBA (Mem. Coll. Sci. Kyoto, 1936, 19, 131—159).—Analyses are given.

C. W. G.

**Romerite from Pfaffenreuth, Obpf.** B. GOSNER and K. DREXLER (Zentr. Min., 1935, A, 267—270).—The composition is  $\text{SO}_3$  38.40,  $\text{Fe}_2\text{O}_3$  19.55,

$\text{Al}_2\text{O}_3$  1.4,  $\text{FeO}$  0.78,  $\text{MgO}$  0.14,  $\text{CaO}$  0.62,  $\text{H}_2\text{O}$  31.17%.

H. J. E.

**Lithiferous pegmatite from Goyás (Lalin).** I. PARGA-PONDAL and M. DE LA E. FRAGA-PADIN (Anal. Fis. Quím., 1934, 32, 1011—1020).—The pegmatite is a mixture containing albite (53%), spodumene (22%), quartz (19%), and small proportions of orthoclase, muscovite, anorthite, and magnetite. The pegmatite contains 1.20%  $\text{Li}_2\text{O}$ , present entirely in the spodumene ( $\text{Li}_2\text{O}$  5.55%). Complete analyses of the pegmatite, spodumene, and muscovite are given.

D. R. D.

**Kasolite.** V. BILLIET and W. F. DE JONG (Natuurwetensch. Tijds., 1936, 18, 261—265).—X-Ray and chemical examination show that kasolite,  $\text{PbO} \cdot \text{UO}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ,  $d$  6.46, forms monoclinic crystals,  $a : b : c = 1.8953 : 1 : 0.9575$ ,  $\beta = 75^\circ 18'$ .

S. C.

**Crystalline chalky rocks of Kivu.** J. THOREAU (Bull. Acad. roy. Belg., 1936, [v], 22, 753—757).—A description and results of analyses [RONCHESNE] of some of these rocks are given.

D. C. J.

**Behaviour of coloured agates in ultra-violet light.** K. OBENAUER (Deut. Golschmiede-Ztg., 1935, 38, 384—385; Chem. Zentr., 1935, ii, 3644).—Agates dyed with org. dyes fluoresce brightly; those coloured with metal compounds, and also true lapis lazuli, are not fluorescent.

J. S. A.

**Origin of tektite surfaces.** V. ROSICKY (Zentr. Min., 1935, A, 270—277; Chem. Zentr., 1935, ii, 3644).—The surface formations are attributed to chemical corrosion after reaching the earth.

J. S. A.

**Olivine lumps of basalt as fragments of older olivine rocks.** T. ERNST (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1935, [ii], 1, 147—154; Chem. Zentr., 1935, ii, 3644).—Petrographic evidence is advanced.

J. S. A.

**Paragenetic relations and mode of formation of minerals and pseudomorphs of the Wendelstein range, Nürnberg.** S. KLEIN (Zentr. Min., 1935, A, 231—242; Chem. Zentr., 1935, ii, 3644).—Petrographic data are given for minerals from the arkose layers from the Frankish keuper deposits.

J. S. A.

**Micro-plankton in the phosphates of Tunis and eastern Algeria.** L. CAYEUX (Compt. rend., 1936, 203, 477—480).—A systematic study of the numerous diatoms found in phosphate grains in the main beds of the above localities has been made.

D. C. J.

**Relations of bodies of the sepiolite-attapulgite series to the phyllic silicates of the mica type.** J. DE LAPPARENT (Compt. rend., 1936, 203, 482—484).—Data have been collected in support of the above relation.

D. C. J.

**Sepiolites.** H. LONGCHAMON and G. MICEON (Compt. rend., 1936, 203, 431—433).—Examination of three further samples of fibrous texture visible to the unaided eye confirms the composition and structure described previously (A., 1935, 842, 1099). The interpretation proposed by de Lapparent (this vol., 957), attributing to them a phyllite structure, is criticised.

J. W. S.



**Meteoric iron from the province of Granada.** J. DORRONSORO and F. MORENO MARTÍN (Anal. Fis. Quim., 1934, **32**, 1111—1115).—A meteorite weighing 134 g. contained Fe 91.500, Ni 7.162, Co 0.426,  $\text{SiO}_2$  0.645, S 0.127, C 0.122, P 0.028%, and traces of Mg, Ge, and Ag. D. R. D.

**Magnetite deposit near Humacao, Puerto Rico.** R. J. COLONY and H. A. MAYERHOFF (Trans. Amer. Inst. Min. Met. Eng., 1935, **115**, 247—272).—The magnetite is directly associated with andesitic and dioritic intrusions. It is of contact replacement origin. Analyses and petrographic data are given.

CH. ABS. (e)

**Iron ores of Hunan.** C. C. TIEN, H. C. WANG, and T. Y. LIU (Geol. Survey Hunan, 1934, Mem. Ser., A, **1**, 124 pp.).—The ores are described. Analyses are given.

CH. ABS. (e)

**Origin of Siegerland spathic iron ore veins by lateral secretion.** H. BREDDIN (Glückauf, 1935, **71**, 821—830; Chem. Zentr., 1935, ii, 3492).—The veins are considered to be derived by aq. deposition from  $\text{FeCO}_3$  in neighbouring rocks, from which thermal  $\text{H}_2\text{O}$  was expelled during pressure metamorphism.

J. S. A.

**Optical properties, densities, and degree of corrosion of the alumino-magnesian titanomagnetites.** G. JOURAVSKY (Compt. rend., 1936, **203**, 373—375; cf. this vol., 1089).—The reflective power and  $d$  diminish whilst the velocity of corrosion by HCl increases with increase of Fe content. R. S.

**Dickite from St. Louis County, Missouri.** V. T. ALLEN (Amer. Min., 1936, **21**, 457—459).

L. S. T.

**Mineral formation in system  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ .** W. NOLL (Jahrb. Min. Beil.-Bd., 1935, A, **70**, 65—115; Chem. Zentr., 1935, ii, 3368; cf. this vol., 584).—No reaction takes place between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in adsorption mixtures at room temp., but under hydrothermal conditions reaction is rapid. Cryst. phases formed are bohmite (I); bayerite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (unstable); corundum (II); kaolin; a pyrophyllite  $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$  (III); montmorillonite and an Al silicate (IV), described by Schlapfer and Niggli, probably a sillimanite.  $\text{SiO}_2$  remains amorphous at all temp. Kaolin is formed at  $<400^\circ$ , with all ratios of  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2$ , any excess of  $\text{Al}_2\text{O}_3$  crystallising as (I). (III) is formed at  $>400^\circ$  where  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2 > 1 : 2$ ; where  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2 > 1 : 2$  (IV) is formed at  $500^\circ$ . (II) crystallises from pure  $\text{Al}_2\text{O}_3$  at  $500^\circ$ , addition of  $\text{SiO}_2$  leading to (I). The formation of dickite, nacrite, and halloysite under special conditions is discussed.

J. S. A.

**Three kaolins.** D. BELJANKIN and V. IVANOVA (Zentr. Min., 1935, A, 298—308; Chem. Zentr., 1935, ii, 3753).—Russian occurrences of normal kaolin, hydrokaolin, and halloysite are described. J. S. A.

**Bolivian minerals.** V. Franckeite. F. AHLFELD, H. HIMMEL, and W. KLEBER (Zentr. Min., 1935, A, 292—298; Chem. Zentr., 1935, ii, 3752—3753).—Crystallographic data are given. J. S. A.

**Occurrence of large zircon needles in a basic pegmatite [near Mellen, Wisconsin].** R. WILCOX (Amer. Min., 1936, **21**, 459).

L. S. T.

**Inclusions in puzzuolanas of middle Aniense valley.** A. SCHERILLO (Period. Min., 1935, **6**, 169—178; Chem. Zentr., 1935, ii, 3735).—Inclusions of limestone, lava, and a homogeneous leucitic magma of volcanic origin are described. J. S. A.

## Organic Chemistry.

**Problem of dissymmetric synthesis.** F. M. JAEGER (Chem. Weekblad, 1936, **33**, 522—533).—A lecture. S. C.

**Interpretation of the rules of fission.** O. SCHMIDT (Ber., 1936, **69**, [B], 1855—1862).—It is shown that there is strong evidence for ascribing a considerable content of kinetic energy, and hence a considerable velocity, to the loosely bound valency electrons of the double linking and, in a greater degree, to the non-coupled valency electrons of radicals; further, that the points of fission in a chain alternate with points at which fission does not occur. Exact proof is afforded that in linkings which are in the neighbourhood of the dissociation point the spin of the non-coupled valency electrons alternates and the phenomenon is propagated throughout the entire chain. The mechanism of fission is discussed.

H. W.

**Generalised prototropy.**—See this vol., 1218.

**Light reactions of halogens with organic compounds of the aliphatic series.** H. J. SCHUMACHER (Angew. Chem., 1936, **49**, 613—617).—Published work is reviewed. E. S. H.

**Mechanism of oxidation of hydrocarbons.**—See this vol., 1209, 1211.

**Hydrogen value as a means for measuring unsaturation.** W. J. C. DE KOK, H. I. WATERMAN, and H. A. VAN WESTEN (J.S.C.I., 1936, **55**, 225—228t).—Apparatus for hydrogenation using Pd or Pt on active C as catalyst is described. Pd cannot be used with aromatic compounds and with Pt hydrogenation of ethylenic linkings proceeds much faster than that of  $\text{C}_6\text{H}_6$  rings. F. R. S.

**Hydration rate of  $\beta$ -methyl- $\Delta^2$ -butene.**—See this vol., 1210.

**Reaction of free cyanogen with butadiene.** E. MÜLLER and A. FREYTAG (J. pr. Chem., 1936, [ii], **146**, 58—60).—Reaction occurs so rapidly when butadiene is passed into CNS in  $\text{Et}_2\text{O}$  that polymerisation is avoided. The  $\alpha\delta$ -dithiocyanobutene thus formed in 80% yield combines with Br in AcOH and  $\text{Cl}_2$  in  $\text{CCl}_4$  to  $\beta\gamma$ -dibromo-, m.p.  $142^\circ$ , and  $\beta\gamma$ -dichloro- $\alpha\delta$ -dithiocyanobutane. H. W.

**Photochemical polymerisation of butadiene.**—See this vol., 1215.

**Azeotropic mixture of acetylene and ethane at atmospheric pressure.** W. A. McMILLAN (J. Amer. Chem. Soc., 1936, 58, 1345).—The mixture, b.p.  $-94.5 \pm 0.1^\circ$ , contains  $40.75 \pm 0.25\%$   $C_2H_2$  and  $59.25 \pm 0.15\%$   $C_2H_6$ . H. B.

**Identification of ethyl alcohol.** M. NICLOUX (Compt. rend., 1936, 203, 16—19; cf. this vol., 535).—Duclaux's method (cf. A., 1896, ii, 504) is used to determine the composition of solutions containing  $AcOH$  (I) and  $Pr^oCO_2H$  (II), obtained by oxidising the corresponding alcohols.  $BuOH$  when oxidised affords (II) and (I) in the ratio of 3 : 1, so that knowing (II) and (I),  $[BuOH]$  and  $[EtOH]$  can be calc. Error  $\pm 5$ — $10\%$ .  $EtOH$  containing 16% of  $BuOH$  was extracted from a putrefying corpse after 55 days. J. L. D.

**Determination of ethyl alcohol.** T. E. FRIEDMANN and R. KLASS (J. Biol. Chem., 1936, 115, 47—61).—After distillation from  $Na_2WO_4$ ,  $HgSO_4$ , and  $Ca(OH)_2$ ,  $EtOH$  is oxidised with alkaline  $KMnO_4$ , the excess of which is titrated. H. G. R.

**Metallic alkoxides.**—See this vol., 1216.

**Simplified condensation with sodium ethoxides.** ( $\beta\zeta$ -Dimethyl- $\Delta^4$ -heptenol.) G. FESTER and D. PUCCI (Ber., 1936, 69, [B], 2017—2018).—The prep. of  $NaOEt$  in suitable form by gradual addition of abs.  $EtOH$  to  $Na$  under ligroin, b.p.  $100$ — $120^\circ$ , is described. Methylheptenone,  $CH_2Cl \cdot CO_2Et$ , and  $NaOEt$  afford  $Et \alpha\beta$ -oxido- $\beta\zeta$ -dimethyl- $\Delta^4$ -octenoate, whence dimethylheptenol and  $\beta\zeta$ -dimethyl- $\Delta^4$ -heptenol (I). (I) when esterified with  $AcCO_2H$  and then treated with  $NH_2 \cdot CO \cdot NH \cdot NH_2$  gives the *semicarbazone*,  $C_{13}H_{23}O_3N_3$ , m.p.  $100^\circ$ . (I) is not identical with yacarol (A., 1934, 509). H. W.

**Organic electrolyses.**—See this vol., 1214.

**Esterification of glycerol with chloroacetic acid and trichloroacetic acid.** J. HELGESON and E. H. SHAW, jun. (Proc. S. Dakota Acad. Sci., 1935, 14, 22—26).—The process is a series of bimol. reactions. CH. ABS. (r)

**Sugar alcohols. V. Chemical constitution and sweet taste.** C. J. CARR, F. F. BECK, and J. C. KRANTZ, jun. (J. Amer. Chem. Soc., 1936, 58, 1394—1395).—The anhydrides of various alcohols (e.g., glycerol, arabitol, mannitol, sorbitol, dulcitol) are generally devoid of sweet taste. There is no significant relationship between sweetness and the no. of C atoms or OH groups in the alcohols. H. B.

**Synthesis of *dl*-arabitol.** R. LESPIEAU (Compt. rend., 1936, 203, 145—146).— $\alpha$ -Chloro- $\Delta^4$ -pentinene- $\gamma\delta$ -triol (A., 1928, 989) affords a  $Ac_3$  derivative, b.p.  $149.5$ — $150.5/9$  mm., reduced ( $H_2$ -Pd) to  $\gamma\delta$ -triacetoxy- $\Delta^4$ -pentene, b.p.  $148$ — $149/14$  mm., which with  $AgClO_4 \cdot OsO_4$  affords pentitol  $\alpha\beta\gamma$ -triacetate, converted into *dl*-arabitol penta-acetate, m.p.  $96$ — $96.5^\circ$  (cf. A., 1934, 891). J. L. D.

**Thermal decomposition of ethylene oxide.**—See this vol., 1208.

**Decomposition of alkyl nitrites.**—See this vol., 1208.

**Molybdenum chlorohydrin and normal glycol molybdate.**—See this vol., 1218.

**Xylitol penta-acetate.** G. BERTRAND (Compt. rend., 1936, 203, 143—144; cf. A., 1892, i, 28).—The acetate (prep. described), m.p.  $60^\circ$ , is optically inactive. J. L. D.

**Organic sulphur compounds. IV. Molecular compounds of sulphides with mercuric chloride.** L. BERMEO and J. J. HERRERA (Anal. Fis. Quím., 1934, 32, 682—689).— $R_2S$  with  $HgCl_2$  in  $EtOH$  gives a ppt. of the mol. compound. The following compounds were prepared:  $(CH_2Ph)_2S \cdot HgCl_2$ , m.p.  $136^\circ$ ,  $(CH_2 \cdot CH_2Ph)_2S \cdot 2HgCl_2$ , m.p.  $101^\circ$ ,  $(CH_2 \cdot CH_2 \cdot CH_2Ph)_2S \cdot 2HgCl_2$ , m.p.  $120^\circ$ ,  $(CHMePh)_2S \cdot HgCl_2$ , m.p.  $110$ — $112^\circ$ . F. R. G.

**Preparation of alkanesulphonyl chlorides.** T. B. JOHNSON and J. M. SPRAGUE (J. Amer. Chem. Soc., 1936, 58, 1348—1352).—Partly a more detailed account of work previously reviewed (this vol., 974). Good yields of  $AlkSO_2Cl$  are obtained when  $SAlk \cdot C(NH) \cdot NH_2 \cdot HX$  [ $X = Cl$  (I),  $NO_2$ ,  $OAc$ ,  $SO_3$ ] are treated with  $Cl_2$  in  $H_2O$  at  $<15^\circ$ ; when  $X$  is  $Br$  the product is contaminated with  $AlkSO_2Br$  (which can be similarly prepared using  $Br$ ). (I) can be conveniently prepared from  $AlkOH$ ,  $CS(NH_2)_2$ , and  $HCl$ ; isolation is not necessary. The following are new: *S*-isopropylisothiocabamide hydrobromide, m.p.  $76$ — $78^\circ$ ; *S*-*n*-heptylisothiocabamide hydrobromide, m.p.  $92$ — $94^\circ$ , and acetate, m.p.  $136$ — $137^\circ$ ;  $\beta$ -phenylethylisothiocabamide hydrochloride, m.p.  $113$ — $114^\circ$ ; *SS*-ethylene-diisothiocabamide hydrochloride, m.p.  $247$ — $248^\circ$ , and acetate, m.p.  $157$ — $158^\circ$ ; *n*-heptane-, b.p.  $124$ — $126/9$  mm., and  $\beta$ -phenylethane-, b.p.  $121$ — $123/3$  mm., m.p.  $32$ — $33^\circ$ , -sulphonyl chlorides; *n*-heptane-, m.p.  $74$ — $75^\circ$ , and  $\beta$ -phenylethane-, m.p.  $121.5$ — $122.5^\circ$ , -sulphonamides. H. B.

**Determination of mol. wts. of fatty acids in benzene.**—See this vol., 1197.

**Reaction of esters with ammonia.** H. E. FRENCH, O. H. JOHNSON, and E. RATEKIN (J. Amer. Chem. Soc., 1936, 58, 1346—1347).— $NH_3 \cdot Ac$  (69.7, 68.8, 18.6, and 2.9%) and  $NH_3 \cdot OAc$  (6.1, 7.7, 4.8, and 2.1%) are formed from *n*-, *iso*-, *sec*-, and *tert*- $BuOAc$ , respectively, with aq.  $EtOH \cdot NH_3$  (40 wt.-%  $EtOH$  in  $H_2O$  saturated with  $NH_3$  at  $25$ — $30^\circ$ ) at  $25^\circ$  after 120, 120, 120, and 360 hr., respectively. No reaction occurs with gaseous  $NH_3$  at  $100^\circ$  under pressures up to 8 atm. H. B.

**Interaction of sodium formate and sodium hydroxide.**—See this vol., 1209.

**Chloroformates.** A. PERRET and J. BIECHLER (Compt. rend., 1936, 203, 84—87).— $ClCO_2CH_2Cl$ ,  $ClCO_2CHCl_2$ ,  $ClCO_2CCl_3$ , and  $CO(CCl_3)_2$  react with  $NaI$  and  $NaBr$  in  $COMe_2$  liberating halogen. The reactivity of the first three substances increases with the no. of substituted  $Cl$  atoms. C. R. H.

**Decomposition of the  $\gamma$ -bromobutyrate ion.**—See this vol., 1210.

**Fatty acids and their esters. I. Cryoscopy and ebullioscopy of fatty acids.** H. N. BROCKLESBY. II. Mol. wts. of polymerised esters. H. N. BROCKLESBY. III. Iodine values by the bromine vapour method. H. N. BROCKLESBY and K. F. HARDING (Canad. J. Res., 1936, 14, B, 222—230,



231—236, 237—242).—I. Ebullioscopically, and cryoscopically in  $C_6H_6$ , saturated fatty acids show decreasing degree of association up to lauric acid; above this, degree of association remains substantially const. Unsaturation decreases the tendency of fat acids of the same C content to associate.

II. Allowing for effect of solute on dissociation of the solvent, raw linsced oil gives normal mol. wts. by b.-p. and f.-p. methods. Polymerised oils and esters behave similarly and hence cannot be assumed to be associated.

III. A modified Br-vapour method, which allows the determination of substitution, is described. The unsaturation of conjugated and non-conjugated materials can be determined satisfactorily, but owing to substitution that of oxidised or polymerised esters cannot.

F. C. B. M.

**Chloro-iodo-derivatives of linoleic and linolenic acids and dichlorodi-iodo-derivative of linolenic acid.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1936, 39, 219—220b).—Linoleic acid (1 mol.) and ICl (1 mol.) in AcOH give  $\lambda$ -(chloroiodo)- $\Delta^6$ -octadecenoic acid, converted by  $O_3$  into azelaic and nonenoic acids. Linolenic acid (1 mol.) and ICl (1 mol.) yield  $\nu$ -(chloroiodo)- $\Delta^{6,8}$ -octadecadienoic acid, which with  $O_3$  gives MeCHO,  $CO_2$ , azelaic and hexenoic acids. With 2 mols. of ICl,  $\lambda,\nu$ -(dichlorodi-iodo)- $\Delta^6$ -octadecadienoic acid is obtained.

E. W. W.

**Occurrence of new highly unsaturated fatty acids,  $C_{26}H_{40}O_2$  and  $C_{26}H_{42}O_2$ , in tunny oil.** S. UENO and C. YONESE (Bull. Chem. Soc. Japan, 1936, 11, 437—442).—The fatty acids from the oil of tunny fish, fractionated as Me esters at 4 mm., and then through their Na salts (in  $COMe_2$ ), yield, in addition to sciodonic, nisinic, and clupanodonic acids, an acid which is hydrogenated to cerotic acid; from neutralisation and I vals., and from analysis of its polybromide, it is regarded as a mixture of *thynnac acid*,  $C_{26}H_{40}O_2$  (with six double linkings), and *shibic acid*,  $C_{26}H_{42}O_2$  (five double linkings).

E. W. W.

**Synthesis of  $\alpha$ -hydroxy- and  $\alpha$ -amino-decoic acid from the oxidation product of oleic acid.** Y. KOBATA (J. Agric. Chem. Soc. Japan, 1935, 11, 709—714).—Nonaldehyde (I) (by ozonolysis of oleic acid) is converted, through its  $NaHSO_3$  compound, into the *cyanohydrin*, m.p. 149—149.5°, which is hydrolysed to  $\alpha$ -hydroxydecoic acid (II), m.p. 69.5—70°. (I), with  $NH_3$ -MeOH followed by HCN and then HCl, yields  $\alpha$ -aminodecoic acid, m.p. 219—221°, yielding (II) with  $HNO_2$ .

CH. ABS. (r)

**Sulphonated oils. XXVII. Preparation and properties of pure salts of the sulphuric ester of  $\alpha$ -hydroxystearic acid.** K. NISHIZAWA (J. Soc. Chem. Ind. Japan, 1936, 39, 234b).— $\alpha$ -Hydroxystearic acid (I), isolated from the regenerated fatty acid from the interaction of olive oil and conc.  $H_2SO_4$ , was converted into its sulphuric ester (II) by the action of  $ClSO_3H$  in  $Et_2O$  at  $0 \pm 1^\circ$ . The K H salt of (II) was used to prepare the  $K_2$ ,  $Na_2$ ,  $(NH_4)_2$ , Na H, and  $NH_4$  H salts. Measurements were made at 25° of the relative viscosities and relative surface tensions against air and against kerosene of the aq. solutions of these six salts. The results indicate the

identity of (I) with the hydroxystearic acid isolated from "Plastabitol V."

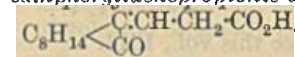
F. R.

**Mechanism of thermal poly-condensation reactions.**—See this vol., 1209.

**$\beta\gamma$ -Dihydroxypropylmalonic ester and its propyl homologue.** R. M. LEEKLEY and E. M. SHAW, jun. (Proc. S. Dakota Acad. Sci., 1935, 14, 27—28).—Et ( $\beta\gamma$ -dihydroxypropyl)-(*di*-p-nitrobenzoate, m.p. 170—171°) and propyl-( $\beta\gamma$ -dihydroxypropyl)-(*di*-p-nitrobenzoate, m.p. 166—168°) -malonate are described.

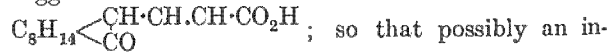
CH. ABS. (r)

**Unsaturated acids from hydroxymethylene compounds.** W. BORSCHÉ and J. NIEMANN (Ber., 1936, 69, [B], 1993—1998).—Condensation of Et hydroxymethylenepropionate with  $CH_2(CO_2H)_2$  (I) in  $C_6H_5N$  at 100° gives *trans*- $\alpha$ -methylglutaconic acid, m.p. 144°, whilst Et  $\gamma$ -cyano- $\alpha$ -methylbutenoate, b.p. 133—137°/15 mm., is obtained with  $CN \cdot CH_3 \cdot CO_2H$  (II). Similarly Et hydroxymethylenephylacetate (III) affords  $\alpha$ -phenylglutaconic acid, m.p. 166—167° ( $Me_2$  ester, b.p. 180—182°/15 mm.), hydrogenated (Pd) to  $Me_2$   $\alpha$ -phenylglutarate, b.p. 178—179°/13 mm., which is hydrolysed and then converted by distillation into  $\alpha$ -phenylglutaric anhydride, m.p. 93°, which when distilled gives  $CO_2$ , phenylsacrotonic acid (IV), and some  $\alpha$ - $C_{10}H_7 \cdot OH$ . (III) and (II) yield Et  $\gamma$ -cyano- $\alpha$ -phenyl- $\Delta^2$ -butenoate, b.p. 183—187°/19 mm., transformed by  $NaOH$ - $MeOH$ - $H_2O$  into phenylisocrotononitrile, m.p. 61—62°, and some (IV). Et  $\gamma$ -cyano- $\alpha$ -phenylbutyrate has m.p. 132°. Hydroxymethylene-camphor and (I) give an acid (V),  $C_{13}H_{18}O_3$ , m.p. 104—106° ( $Me$  ester, b.p. 180—181°/18 mm.), (?)  $\beta$ -3-camphorylidenepropionic acid,



constitution is sug-

gested by the ready ozonolysis of it and the corresponding ketone to camphorquinone, but its ready decarboxylation to 3-ethylidenecamphor, b.p. 224—226°/764 mm., and its conversion by conc.  $H_2SO_4$  or  $SOCl_2$  into the lactone,  $C_{13}H_{16}O_2$ , m.p. 62—63°, suggest the alternative structure



stance of allyl tautomerism is presented. The liquid portions remaining in the prep. of (V) give a substance,  $C_{13}H_{17}O_2Cl$ , b.p. 117—119°/13 mm., when treated with  $SOCl_2$ . Camphorylidenepropionitrile has b.p. 188—192°/16 mm., m.p. 72°. Formylfluorene [2:4-dinitrophenylhydrazones, m.p. 208° (decomp.)] and (I) yield  $\beta$ -9-fluorenylidenepropionic acid, m.p. 202—203°. Attempts to use the  $OH \cdot CH$  derivatives of  $CH_2Ph \cdot CO_2Et$ ,  $CH_2Ph \cdot CN$ , or camphor with  $\beta$ - $C_{10}H_7 \cdot NH_2$  in the synthesis of cinchoninic acids gave only 2-methyl-5:6-benzocinchoninic acid obtained without their participation; the *enamines*  $CN \cdot CPh \cdot CH \cdot NH \cdot C_{10}H_7$ , m.p. 190—191°, and  $C_{10}H_{14}O \cdot CH \cdot NH \cdot C_{10}H_7$ , m.p. 186—187°, are obtained incidentally.

H. W.

**Decapentaene- $\alpha\kappa$ -dicarboxylic acid.** R. KUHN and C. GRUNDMANN (Ber., 1936, 69, [B], 1979—1981).—Addition of  $Et_2C_2O_4$  and Et  $\Delta^{5,7}$ -decatetraenoate to  $RbOEt$  in  $Et_2O$  gives  $Et_2$  oxalodecatetraenoate, m.p. 147° ( $Rb$  derivative), the Ac derivative of which is

reduced by Al-Hg in Et<sub>2</sub>O to the corresponding H<sub>2</sub>-compound, converted by cold KOH-MeOH into Me<sub>2</sub>Δ<sup>27,28</sup>-*decapentaene-α,κ-dicarboxylate* CO<sub>2</sub>Me[CH:CH]<sub>5</sub>·CO<sub>2</sub>Me, m.p. 223° (Berl), which with conc. H<sub>2</sub>SO<sub>4</sub> slowly gives the characteristic carotenoid colour reaction. *Decapentaene-α,κ-dicarboxylic acid* has m.p. 229—230° (decomp.) when rapidly heated above 220°. Rb cannot be replaced by K in the condensation.

H. W.

**Preparation of diethoxysuccinic esters.** M. MEYER (Compt. rend., 1936, 203, 189—192; cf. A., 1933, 491).—Et<sub>2</sub> sodioethoxymalonate (I) with Et<sub>2</sub> bromoethoxymalonate, b.p. 132°/15 mm. [prepared from (I) and Br], in boiling PhMe affords Et<sub>4</sub> α,β-diethoxyethanetetra-carboxylate, b.p. 154°/1 mm., hydrolysed to the acid, which loses 2 CO<sub>2</sub> to give a mixture of stereoisomeric diethoxysuccinic acids. The mixed Bu esters, b.p. 140—141°/3.5 mm., with N<sub>2</sub>H<sub>4</sub> afford the *dl*- and *meso*-hydrazides, m.p. 194° and 242°, identical with those derived from *dl*- and *meso*-tartaric acid, respectively.

J. L. D.

**Oxidation of the methyl group in the animal body.** R. KUHN, F. KÖHLER, and L. KÖHLER (Z. physiol. Chem., 1936, 242, 171—197; cf. A., 1933, 1325; Hildebrandt, A., 1901, ii, 180).—After administration of β<sub>2</sub>-dimethylheptadiene (I), geranic acid (II), geraniol (III), and citral (IV) to rabbits their urine contains α,ζ-dimethylhexadiene-α,ζ-dicarboxylic acid (V), m.p. 193—194°, which, with PtO<sub>2</sub>-H<sub>2</sub> yields α<sub>2</sub>-dimethylsuberic acid (VI), b.p. 165—167°/0.4 mm. (*bis*-*p*-bromophenacyl ester, m.p. 110.5—111.5°). (II), (III), and (IV) also yield thus d-α<sub>2</sub>-dimethylhexadine-α,ζ-dicarboxylic acid, m.p. 102.6—103.6° (corr.), [α]<sub>D</sub><sup>25</sup> +15.25° in 2*N*-NaOH, which, treated in AcOH with O<sub>3</sub> and then Pt-H<sub>2</sub>, yields AcCO<sub>2</sub>H. Similarly Me β-methyl-β-hexylacrylate (VII) is converted in the body into β-methylazelaic acid (VIII), b.p. 173—175°/0.002 mm. (*bis*-*p*-bromophenacyl ester, m.p. 93—96°), and Me β-methyl-β-nonylacrylate (IX) into β-methylbutene-α,γ-dicarboxylic acid (X), b.p. 145—150°/0.001 mm. (*bis*-*p*-bromophenacyl ester, m.p. 95—97°). For the synthesis of (VI) *dl*-3-methylcyclohexanone is treated with EtOAc and Na giving *dl*-6-acetyl-3-methylcyclohexanone, which with alkali gives *dl*-ζ-acetyl-β-methylhexoic acid, b.p. 150°/8 mm., and this with PtO<sub>2</sub>-H<sub>2</sub> in AcOH gives *dl*-ζ-hydroxy-β-methylcyclooctoic acid, b.p. 155.5°/6 mm., which, with HBr, in AcOH, gives the corresponding bromo-acid, b.p. 143—144°/6 mm., the Me ester of which in PhMe with KCN followed by hydrolysis with KOH gives (VI). (V) in Et<sub>2</sub>O with a trace of I, irradiated with ultra-violet light, undergoes *cis*-*trans*-rearrangement, yielding a form of m.p. 123.8—124.2°. (V) in EtOAc treated with O<sub>3</sub> and then with Pt-H<sub>2</sub> gives AcCO<sub>2</sub>H, lävulaldehyde, and CHO·CO<sub>2</sub>H. Me hexyl ketone in C<sub>6</sub>H<sub>6</sub> with CH<sub>2</sub>Br·CO<sub>2</sub>Me and Zn gives the Me ester, b.p. 123.5°/20 mm., of an acid from which H<sub>2</sub>O is eliminated by ZnCl<sub>2</sub> and Ac<sub>2</sub>O at 155—160° to give (VII), b.p. 100—102°/18 mm. Similarly Me nonyl ketone gives (IX), b.p. 108—109°/3 mm., Et ζ-acetylhexoate, b.p. 83—84°/0.4 mm., with CH<sub>2</sub>Br·CO<sub>2</sub>Et gives an Et<sub>2</sub> ester, b.p. 130—132°/0.5 mm., which yields (VIII), Et lävulate gives first Et<sub>2</sub> β-hydroxy-β-

4 L

methyladipate, b.p. 92.5°/0.01 mm., and then (X), and Et δ-acetylvalerate gives β-methylhexene-α<sub>2</sub>-dicarboxylic acid (XI), m.p. 100—101° (corr.), b.p. 145—147°/0.005 mm. (*bis*-*p*-bromophenacyl ester, m.p. 102—103°). (XI) is not found in the urine of rabbits given (IX). Et cyclopentanone-2-carboxylate in PhMe with Na and AcCl gives Et 2-acetylcyclopentanone-2-carboxylate, b.p. 103.5—105°/3.3 mm. β-Bromo- and β-iodo-heptadecane with CHNa(CO<sub>2</sub>Et)<sub>2</sub> give the Et<sub>2</sub> ester, b.p. 180—182°/0.3 mm., of β-heptadecylmalonic acid, m.p. 86.5—87°, which at 180—200° gives β-methylstearic acid, m.p. 48.5—49° [Me ester (XII), b.p. 148—149°/0.4 mm.]. The urine of rabbits given (XII) yields an oil possibly containing a dicarboxylic acid. The biological oxidation of Me is a general reaction not confined to ω-Me and probably takes place always in the stages ·CH<sub>2</sub>· → ·CH<sub>2</sub>·OH → ·CHO → ·CO<sub>2</sub>H. The ease and extent of the oxidation vary with the nature of the substance, the animal concerned, and the method of administration.

W. McC.

**Colour reaction for organic acids and detection of small quantities of citric acid.** R. CASARES (Anal. Fis. Quim., 1936, 34, 594—596).—Agaric acid gives a characteristic violet-brown colour, *d*-, *l*-, and *meso*-tartaric acid, but not esters, give the green colour, in the Ac<sub>2</sub>O-C<sub>6</sub>H<sub>5</sub>N colour reaction for org. acids (cf. Fürth and Herrmann, A., 1935, 1516). Pyridine tartrate, m.p. 124°, gives a red colour with Ac<sub>2</sub>O. 0.015 mg. of citric acid may be detected by the reaction.

L. A. O'N.

**Production of citric acid.** F. KNOOP and C. MARTIUS (Z. physiol. Chem., 1936, 242, 1).—AcCO<sub>2</sub>H mixed with oxalacetic acid in aq. Na<sub>2</sub>CO<sub>3</sub> and then oxidised with H<sub>2</sub>O<sub>2</sub> gives in 20—30 hr. a 35% yield of Ca citrate. This synthesis probably occurs in the animal organism and possibly the reverse process also.

W. McC.

**Decomposition of ascorbic acid in acid and alkaline solution.** A. CARTENI and A. MORELLI (Boll. Soc. ital. Biol. sperim., 1936, 11, 158—160).—The stability at 37° decreases rapidly with increasing *p*<sub>H</sub> from 4.93 to 9.64.

F. O. H.

**Derivatives of glycuronic acid. VII. Synthesis of aldobionic acids.** R. D. HOTCHKISS and W. F. GOEBEL (J. Biol. Chem., 1936, 115, 285—292; cf. A., 1935, 1483).—Diisopropylidenegalactose, Me 1-α-bromo-2 : 3 : 4-triacetylglycuronate (I), and Ag<sub>2</sub>O in dry Et<sub>2</sub>O give the Me ester, m.p. 112.5—114°, [α]<sub>D</sub><sup>25</sup> -6.8° in CHCl<sub>3</sub>, of 1 : 2 : 3 : 4-diisopropylidenegalactose-6-β-2' : 3' : 4'-triacetylglycuronide, which, when hydrolysed first by Ba(OH)<sub>2</sub> and then by 0.02*N*-H<sub>2</sub>SO<sub>4</sub>, gives galactose-6-β-glycuronide, identical with that obtained from gum acacia (cf. Challinor *et al.*, A., 1931, 465). This confirms the structure of (I). (I) and β-glucose 1 : 2 : 3 : 4-tetraacetate give similarly Me β-gentiobionate heptaacetate, m.p. 198—199°, [α]<sub>D</sub><sup>25</sup> -11° in CHCl<sub>3</sub>, converted by Ac<sub>2</sub>O-ZnCl<sub>2</sub> into the α-compound, m.p. 201—202°, [α]<sub>D</sub><sup>25</sup> +48.4°.

R. S. C.

**tert.-Butylthiolacetic acid and related compounds.** N. HELLSTROM and T. LAURITZSON (Ber., 1936, 69, [B], 2003—2006).—Bu<sup>t</sup>Br evolves gas and



consumes alkali when heated with  $\text{SNa}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$  or  $\text{SNa}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me-}p$  and does not appear to react with  $\text{SNa}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$  in  $\text{H}_2\text{O}$  or  $\text{EtOH-H}_2\text{O}$ .  $\text{Bu}^n\text{OH}$  and  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  in  $2N\cdot\text{HCl}$  at  $100^\circ$  give *tert*-butylthiolacetic acid (I), b.p.  $107\text{--}109/2$  mm. (compound  $\text{SBu}^n\cdot\text{CH}_2\cdot\text{CO}_2\text{HgCl}_2$ , m.p.  $86\text{--}89^\circ$  and decomp.  $175\text{--}177^\circ$  after re-solidification); under these conditions  $\text{Pr}^n\text{OH}$ ,  $\text{Pr}^i\text{OH}$ ,  $\text{Bu}^n\text{OH}$ , and  $\text{Bu}^i\text{OH}$  do not react. (I) is transformed by  $\text{SOCl}_2$  into the corresponding chloride, b.p.  $68\text{--}70/6$  mm., converted by  $\text{NH}_2\text{Ph}$  in  $\text{C}_6\text{H}_6$  into *tert*-butylthiolacetanilide, m.p.  $80\text{--}81^\circ$  (corresponding sulphoxide, m.p.  $146\cdot5\text{--}147\cdot5^\circ$ ), and by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  into *tert*-butylthiolacet-*p*-toluidide, m.p.  $87\text{--}88^\circ$ . Cautious oxidation of (I) with  $\text{H}_2\text{O}_2$  in  $\text{COMe}_2$  at  $3\text{--}4^\circ$  gives the corresponding sulphoxide, m.p.  $110\text{--}111^\circ$ . Treatment of  $\text{SBu}^n\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$  with  $\text{H}_2\text{O}_2$  yields  $\text{Bu}^n\text{SH}$ , b.p.  $64\text{--}65^\circ$ , in 60% yield. H. W.

**Fission of disulphides by alkali. III. Fission of dithiodiacetic acid with alkali.** A. SCHÖBERL (Ber., 1936, 69, [B], 1955; cf. A., 1933, 1276).—A claim for priority against Kharasch *et al.* (this vol., 631) and Shinohara *et al.* (A., 1934, 761). H. W.

**Keratin. Hydrolysis of disulphide compounds.** A. SCHÖBERL (Collegium, 1936, 412—421).—Disulphides,  $(\text{-SR})_2$ , are hydrolysed by  $\text{NaOH}$  to  $\text{RSH}$  and  $\text{RS}\cdot\text{OH}$ , which may then form  $\text{RSH}$  and  $\text{RSO}_2\text{H}$  or  $\text{RSO}_3\text{H}$ , respectively.  $(\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{S})_2$  is converted into  $\text{OH}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  first and subsequently into  $\text{H}_2\text{S}$  and  $\text{CHO}\cdot\text{CO}_2\text{H}$ . Na salts of the disulphides are hydrolysed by boiling in neutral solution. Cystine is decomposed by boiling with  $\text{NaOH}$  into cysteine,  $\text{H}_2\text{S}$ , and  $\text{NH}_3$  but there must be the intermediate formation of  $\text{R}\cdot\text{SO}_2\text{H}$ -type acids followed by that of  $\text{CHO}\cdot\text{CO}_2\text{H}$  type. Cystine is rendered more sensitive to  $\text{NaOH}$  by substituting the  $\text{NH}_2$  groups. Wool is a typical disulphide compound sensitive to boiling  $\text{H}_2\text{O}$  or  $\text{NaOH}$ . D. W.

**Selenodicarboxylic acids and diselenodicarboxylic acids.** A. FREDGA (Uppsala Univ. Arsskr., 1935, No. 5, 232 pp.).—Se is determined in org. compounds by digestion with  $\text{H}_2\text{SO}_4\text{--HNO}_3$ , followed by pptn. of the Se (weighed as such) with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ . *dl-αα'*-Selenodipropionic acid (I), m.p.  $147\text{--}148^\circ$  (from  $\text{K}_2\text{Se}$  and  $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ ), is resolved by means of its *brucine* salt; the *d*-(II) and *l*-acids have m.p.  $123\cdot5\text{--}124\cdot5^\circ$ ,  $[\alpha]_D^{25} \pm 234^\circ$ ; the *meso*-acid, isolated from the mother-liquors from (I), has m.p.  $128\text{--}129^\circ$  (*quinine* salt). *dl-ββ'*-Selenodipropionic acid, m.p.  $147\cdot5\text{--}148^\circ$  (*Ag* and *Pb* salts), is prepared similarly. *dl-αα'*-Selenodibutyric acid, m.p.  $100\text{--}101^\circ$ , is resolved by means of the *brucine* salt; the *d*-acid has m.p.  $76\text{--}77^\circ$ ,  $[\alpha]_D^{25} + 201\cdot9^\circ$ ; the *meso*-acid has m.p.  $84\text{--}85^\circ$  (*brucine* salt). Hydrolysis of the product from  $\text{K}_2\text{Se}$  and  $\text{CMe}_3\text{Br}\cdot\text{CO}_2\text{Et}$  yields *αβ'*-selenodisobutyric acid, m.p.  $154\text{--}155^\circ$ . *meso-αα'*-Selenobisphenylacetic acid has m.p.  $178\text{--}179^\circ$  (*quinine*, *strychnine*, and *Ag* salts); the *dl*-acid, m.p.  $153\cdot5\text{--}154\cdot5^\circ$ , is resolved, through the *strychnine* and *quinine* salts, into the *d*- and *l*-acids, m.p.  $144\text{--}145^\circ$ ,  $[\alpha]_D^{25} \pm 534^\circ$ . Oxidation of (II) yields *l-αα'*-seleninylidipropionic acid,  $[M]_D^{25} - 34\cdot5^\circ$ . The following are prepared similarly: *d-αα'*-seleninylidibutyric acid,  $[M]_D^{25} + 173\cdot5^\circ$ ; *l-αα'*-seleninylbisphenylacetic acid,

$[M]_D^{25} - 2262^\circ$ ; *l-tetrahydroselenophenoxide-αα'*-dicarboxylic acid,  $[M]_D^{25} - 535\cdot5^\circ$ . The following are prepared by direct halogenation: (*dibromoseleno*)-diacetic, *-di-α-propionic*, and *-di-β-propionic acids*; (*di-iodoseleno*)-diacetic, m.p.  $124^\circ$ . and *-αβ'*-diisobutyric, m.p.  $137^\circ$ , acids.  $\text{Se}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$  and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  afford the compound,

$\text{CO} < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} > \text{Se}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , m.p.  $177^\circ$  (*Pb* and *Ag* salts). *dl-αα'*-Diselenodipropionic acid, m.p.  $85\text{--}88^\circ$ , is resolved, though the *brucine* salt, into the *d*- and *l*-acids, m.p.  $86\cdot5\text{--}87\cdot5^\circ$ ,  $[\alpha]_D^{25} \pm 254^\circ$ ; the *meso*-acid has m.p.  $108\cdot5\text{--}109\cdot5^\circ$ . *meso-αα'*-Diselenodipropionic acid has m.p.  $71\text{--}73^\circ$  (*strychnine* salt), and *ββ'*-diselenodipropionic acid, m.p.  $137^\circ$ . *dl-αα'*-Diselenodibutyric acid is resolved, by means of the *quinidine* and *morphine* salts, into the *d*- and *l*-acids, m.p.  $50\text{--}52^\circ$ ,  $[\alpha]_D^{25} \pm 293^\circ$ . *d-αα'*-Diselenobisphenylacetic acid, m.p.  $160\text{--}165^\circ$ ,  $[\alpha]_D^{25} + 446\cdot1^\circ$ , is obtained from the *dl*-acid by means of the *strychnine* salt. *meso*- and *dl*- (III) *-αα'*-Diselenocyanate-adipic acids are prepared from the corresponding *αα'*-dibromoadipic acids and  $\text{KCNSe}$ . (III) is cyclised (*K* salt and  $\text{H}_2\text{SO}_4$ ) to *meso*-cyclotetramethylenediseleno-*αα'*-dicarboxylic acid, m.p.  $172\text{--}176^\circ$ . The appropriate diseleno-acid and  $\text{N}_2\text{O}_4$  afford *d-α-seleninophenylacetic acid*, m.p.  $93^\circ$ ,  $[M]_D^{25} + 1020^\circ$ , and *l-αα'*-diseleninoadipic acid,  $[M]_D^{25} - 63\cdot5^\circ$ . Shaking the appropriate diselenodicarboxylic acid with  $\text{Hg}$  affords *mercuribis-(α-selenopropionic)* (*d*- and *l*-forms,  $[\alpha]_D^{25} + 2\cdot8^\circ$  and  $-2\cdot4^\circ$ ), *-(α-selenobutyric)*, and *-(α-selenoisobutyric)* acid. Solubilities and dissociation consts. are given for most of the acids described. CH. ABS. (r)

**Kinetics of the reactions of polymeric aldehydes. I. Rate of dissolution of paraformaldehyde.** J. LÖBERING (Ber., 1936, 69, [B], 1844—1854).—Measurements of the rate of dissolution of paraformaldehyde show that the formula for a unimol. change is applicable. The influence of  $[\text{H}^+]$  and  $[\text{OH}^-]$  is similar to that observed by Hess in the depolymerisation of  $(\text{CH}_2\text{O})_n$  in  $\text{H}_2\text{O}$ . The temp. coeff. increases with rising temp. The rate of dissolution is therefore governed by that of depolymerisation. H. W.

**Aldolase. I. Aldol condensation of dihydroxyacetonephosphoric acid with acetaldehyde. II. Aldol condensation of dihydroxyacetone with glyceraldehyde.** O. MEYERHOF, K. LOHMANN, and P. SCHUSTER (Biochem. Z., 1936, 286, 301—318; 319—335).—I. In dialysed or inactivated yeast or muscle extract an aldolase is present which condenses dihydroxyacetonephosphoric acid (I), arising from hexose diphosphate, with  $\text{MeCHO}$  with the formation of a methyltetrose phosphate (II),  $[\alpha]_D^{25} + 1\cdot8^\circ$  (cryst. *Ag* salt,  $\text{C}_5\text{H}_9\text{O}_6\text{P}\cdot\text{Ag}_2\cdot\text{H}_2\text{O}$ ;  $[\alpha]_D^{25}$  for  $\text{Na}_2$  salt  $+14\cdot7^\circ$ ,  $\text{Na H}$  salt  $+5\cdot1^\circ$ ). The same product can be obtained using undialysed maceration extract in presence of  $\text{NaF}$ , glucose, and  $\text{MeCHO}$ . The reaction of formation of (II) is reversible and obeys the mass law. (II) is hydrolysed by alkali, gives but little  $\text{AcCHO}$  on acid hydrolysis, gives with acid  $\text{KMnO}_4$  phosphoglycollic acid (III),  $\text{MeCHO}$ , and  $\text{CO}_2$ , with  $\text{H}_2\text{O}_2$  in alkaline solution (III) and  $\text{HCO}_2\text{H}$ , and with phosphatase is hydrolysed to the free methyl-

tetrose (osazone, m.p. 165—167°). (II) is therefore  $\text{Me}[\text{CH}(\text{OH})]_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{PO}_3\text{H}_2$ .

II. Under similar conditions, *d*-glyceraldehyde with (I) gives *d*-fructose-1-phosphoric acid (IV), free acid  $[\alpha]_D -52.5^\circ$ , whilst *r*-glyceraldehyde gives an equimol. mixture (V) of (IV) and *l*-sorbitol-1-phosphate, isolated as Ba and brucine mixed salts but not separated completely. The rotation, hydrolysis curve, and production of glucosazone after dephosphorylation of (IV) identified it with the ester obtained by Tanko and Robison (A., 1935, 660) from hexose diphosphate by partial dephosphorylation with bone phosphatase. The free sugars from (IV) and (V) were 90 and 45% fermentable, respectively, the latter corresponding with the non-fermentability of *l*-sorbitol.

P. W. C.

**Transformation of carboxylic acids into aldehydes.** C. GRUNDMANN [with F. BAR and H. TRISCHMANN] (Annalen, 1936, 524, 31—48).—The synthesis follows the lines,  $\text{R} \cdot \text{COCl} \rightarrow \text{R} \cdot \text{CO} \cdot \text{CHN}_2 \rightarrow \text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{OAc} \rightarrow \text{OH} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{OH} \rightarrow \text{R} \cdot \text{CHO} + \text{CH}_2\text{O}$ . It is not successful for the prep. of  $\alpha$ -unsaturated aldehydes. Thus stearyl chloride is converted by  $\text{CH}_3\text{N}_2$  into  $\alpha$ -diazononadecan- $\beta$ -one, m.p. 69°, transformed by AcOH at 70° into  $\beta$ -ketononadecyl acetate, m.p. 72° (Berl); this is reduced by  $\text{Al}(\text{OPr}^i)_3$  in  $\text{Pr}^i\text{OH}$  to nonadecane- $\alpha$ - $\beta$ -diol, m.p. 85°, oxidised by  $\text{Pb}(\text{OAc})_4$  in  $\text{AcOH} \cdot \text{C}_6\text{H}_6$  to stearaldehyde, m.p. 63°. Oleyl chloride similarly gives  $\beta$ -keto- $\Delta^8$ -nonadecenyl acetate, b.p. 172—174°/0.06 mm., m.p. 21°, reduced and hydrolysed by  $\text{Al}(\text{OPr}^i)_3$  to  $\Delta^8$ -nonadecene- $\alpha$ - $\beta$ -diol, b.p. 158—161°/0.005 mm., whence olealdehyde, b.p. 108—110°/0.01 mm. (2:4-dinitrophenylhydrazones, m.p. 67—68°).  $\Delta^8$ -Undecenoic acid is converted by  $\text{SOCl}_2$  into the corresponding chloride, b.p. 119°/10 mm., which yields crude  $\alpha$ -diazododecen- $\beta$ -one, m.p. about 16°, whence  $\beta$ -keto- $\Delta^8$ -dodecenyl acetate, m.p. 52°,  $\Delta^8$ -dodecene- $\alpha$ - $\beta$ -diol, m.p. 48°, and undecenaldehyde, b.p. 101—103°/10 mm. (2:4-dinitrophenylhydrazones, m.p. 91° (Berl); semicarbazone], which forms a dimeride, m.p. 26°, when exposed to air. *d*-Citronellal acid gives  $\beta$ -keto- $\alpha$ -dimethyl- $\Delta^7$ -octenyl acetate, b.p. 140—141°/10 mm.,  $[\alpha]_D +5.1^\circ$ , reduced  $[\text{Al}(\text{OPr}^i)_3]$  to  $\delta$ -dimethyl- $\Delta^7$ -octene- $\alpha$ - $\beta$ -diol, b.p. 156—160°/14 mm., whence *d*-citronellal, b.p. 102—105°/12 mm.,  $[\alpha]_D +9.6^\circ$  (2:4-dinitrophenylhydrazones, m.p. 76.5°).  $\text{COPh} \cdot \text{CHN}_2$  affords phenylglycol, m.p. 67°, and thence PhCHO. Elaidic acid (I) is converted into  $\alpha$ -diazononadecan- $\beta$ -one, m.p. 53°,  $\beta$ -keto- $\Delta^8$ -nonadecenyl acetate, m.p. 62°,  $\Delta^8$ -nonadecene- $\alpha$ - $\beta$ -diol, m.p. 50°, and elaidaldehyde, m.p. 33° (semicarbazone, m.p. 92°; 2:4-dinitrophenylhydrazones, m.p. 90°), oxidised by  $\text{Ag}_2\text{O}$  to (I).  $\Delta^8$ -Hexenyl chloride gives  $\beta$ -keto- $\Delta^8$ -heptenyl acetate, b.p. 112—115°/12 mm., reduced by Na-Hg in aq. MeOH to  $\Delta^8$ -hepten- $\alpha$ - $\beta$ -diol, b.p. 122—124°/12 mm., whence  $\Delta^8$ -hexenaldehyde (2:4-dinitrophenylhydrazones, m.p. 147°). Dihydropyruconyl dichloride gives  $\alpha$ -bisdiazononadecene- $\beta$ - $\gamma$ -dione, m.p. 75°, whence  $\alpha$ -diacetoxy- $\Delta^8$ -octene- $\beta$ - $\gamma$ -dione (II), m.p. 91°, transformed by Br in  $\text{CHCl}_3 \cdot \text{CCl}_4$  into  $\delta$ -dibromo- $\alpha$ -diacetoxyoctane- $\beta$ - $\gamma$ -dione, m.p. 110° (decomp.), which with warm  $\text{C}_6\text{H}_5\text{N}$  yields  $\alpha$ -diacetoxy- $\Delta^7$ -octadiene- $\beta$ - $\gamma$ -dione, m.p. 133°. Reduction of (II) by Na-Hg in aq. dioxan yields non-cryst.  $\alpha$ - $\beta$ -tetra-acetoxy- $\Delta^8$ -octene, oxidised by

$\text{Pb}(\text{OAc})_4$  in AcOH to readily polymerised dihydropyruconaldehyde [*di*-*p*-nitrophenylhydrazones, m.p. 237° (decomp.)].  $\text{CHPh} \cdot \text{CH} \cdot \text{COCl}$  and  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  afford the very unstable 5-diazoacetyl-4-phenylpyrazoline, m.p. 80—81° (decomp.). H. W.

**Constitution of the coloured compound characteristic of the Rothera, Engfeldt, and Raurich Sas reaction of acetone.** F. E. RAURICH SAS (Anal. Fis. Quím., 1934, 32, 985—1006; cf. this vol., 1140).—The colour is attributed to a mixture of  $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})(\text{NH}_2)] \cdot \text{H}_2\text{O}$  and  $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\{\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2\}_2\text{CO})] \cdot 2\text{H}_2\text{O}$ , of which the latter is isolated from  $\text{COMe}_2$  with conc.  $\text{NH}_3$  and 10%  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$  and is decomposed to  $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  and  $\text{Na}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{OH})(\text{H}_2\text{O})]$ . The function of  $(\text{NH}_4)_2\text{SO}_4$  in the reaction combines dehydration, catalysis, and salting out.  $\text{CN}'$  is determined by distilling the sample in a current of  $\text{CO}_2$  with dil.  $\text{H}_3\text{PO}_4$  into 0.1*N*- $\text{AgNO}_3$  in dil.  $\text{HNO}_3$ , followed by titration with 0.1*N*- $\text{KCN}$ . F. R. G.

**Constitution of the coloured compounds formed in Rimini's reaction for acetone and some of its variations.** F. E. RAURICH SAS (Anal. Fis. Quím., 1934, 32, 1187—1216).—The complexes formed by  $\text{COMe}_2$ ,  $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ , and amines are discussed. The following are isolated:  $\text{NH}_2\text{Me}$  gives  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{NHMe} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})_2] \cdot 2\text{H}_2\text{O}$ ;  $\text{NHMe}$  yields  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{NHMe})_2] \cdot \text{H}_2\text{O}$ ;  $\text{NH}_2\text{Et}$  gives  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{NHEt} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})_2] \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{NHEt} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})(\text{NH}_2\text{Et})] \cdot \text{H}_2\text{O}$ ;  $(\text{CH}_2 \cdot \text{NH})_2$  produces  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})] \cdot \text{H}_2\text{O}$  and  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{CH}_2 \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ac})_2] \cdot 2\text{H}_2\text{O}$ , whilst piperazine gives  $\text{Na}_2[\text{Fe}(\text{CN})_4(\text{C}_4\text{H}_{10}\text{N}_2)] \cdot 1.2\text{H}_2\text{O}$ . F. R. G.

**Electrolytic reduction of organic compounds at the dropping mercury electrode.** II. A. WINKEL and G. PROSKE (Ber., 1936, 69, [B], 1917—1929; cf. this vol., 709).—Measurements are recorded for many diketone-compounds, saturated dicarboxylic acids, OH-CO substances, halogen derivatives of PhCHO, and phenolic aldehydes. The magnitude of the potential displacement cannot be quantitatively given since it depends on the abs. val. of the reduction potential. The relative activity of the individual groups is readily deduced. Activating groups arranged in order of decreasing effect are  $\text{CH}_2\text{I}$ ,  $\text{CH}_2\text{Br}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{C}_{10}\text{H}_7$  (*k*), Ph (*k*), Ac,  $\text{CO}_2\text{H}$ ,  $\text{C}_6\text{H}_4\text{Cl-o}$ ,  $\text{C}_6\text{H}_4\text{Cl-m}$ ,  $\text{C}_6\text{H}_4\text{Cl-p}$ ,  $\text{C}_6\text{H}_4\text{Br-m}$ ,  $\text{C}_6\text{H}_4\text{Br-p}$ ,  $\text{CH}_2 \cdot \text{OH}$ ,  $\text{CH}_2\text{Ac}$  whereas stabilising groups are Me,  $\text{NH}_2$ , OH. The activity of groups *k* is due exclusively to the conjugated double linkings caused by introduction of the groups into the reducible mol. The most active conjugation is shown by compounds with quinonoid structure. Repeated introduction of a substituent increases its effect but the degree does not correspond with the no. of substituents. A correlation of reduction potential with absorption and Raman spectrum is indicated. H. W.

**Thermal mutarotation of *d*-galactose, *l*-arabinose, and *d*-talose.**—See this vol., 1209.



Colour reaction of hexoses and their polymerides, and its application to colorimetric determination of glucose in blood. M. Pozzi-Escot (J. Pharm. Chim., 1936, [viii], 24, 121).—A claim of priority in respect of the reaction described by Sanchez (this vol., 709). W. O. K.

Hydrolysis of acetylated carbohydrates. G. ZEMPLÉN, A. GERECs, and I. HADÁCSY (Ber., 1936, 69, [B], 1827—1829).—Zemplén's method can be applied in cases in which the Ac derivative and parent substance are insol. in the medium. Thus cellulose acetate (38% OAc) is completely hydrolysed with about 6% of the amount of Na (in boiling MeOH) which is required for complete removal of Ac as NaOAc. The process is little influenced by the duration of heating, greatly by the amount of Na. The method can also be used with reducing sugars which are very sensitive to warm alkali; thus cellobiose octa-acetate is hydrolysed at room temp. by NaOMe in MeOH (about half the amount necessary if CHCl<sub>3</sub> is used) to cellobiose in 85% yield. H. W.

Rotatory power of sugar hydrazones in relation to the stereochemical structure of the  $\alpha$ -carbon atom. II. E. VOTOČEK and Z. ALLAN. III. E. VOTOČEK and O. WICHTERLE (Coll. Czech. Chem. Comm., 1936, 8, 313—321, 322—326; cf. A., 1931, 938).—II. *p*-Tolylhydrazine with CH<sub>2</sub>PhCl at 140—145° affords *p*-tolylbenzylhydrazine, m.p. 37—38° (hydrochloride), and some benzaldehyde-*p*-tolylbenzylhydrazone, m.p. 137—138°. The *p*-tolylbenzylhydrazones (m.p. in parenthesis) of the following are prepared: *d*-xylose (96—97°; [ $\alpha$ ]<sub>D</sub> -22.5°); *d*-arabinose (170—171°; [ $\alpha$ ]<sub>D</sub> +9.6°); *l*-rhamnose (129—130°; [ $\alpha$ ]<sub>D</sub> -11°); *l*-fucose (183°; [ $\alpha$ ]<sub>D</sub> +33.3°); *d*-glucose (169.5—170.5°; [ $\alpha$ ]<sub>D</sub> -23.2°  $\rightarrow$  -18.6° in 24 hr.); *l*-mannose (160—161°; [ $\alpha$ ]<sub>D</sub> +31.6°); and *d*-galactose (160.5—161.5°; [ $\alpha$ ]<sub>D</sub> -9.0°); all rotations are in MeOH. The *p*-tolylbenzylhydrazones of glyoxal and *d*-fructose have m.p. 221° and 132—133°, respectively. The *p*-tolylbenzylhydrazones of the following are prepared: *o*-, m.p. 118—119°, *m*-, m.p. 151°, and *p*-OH-C<sub>6</sub>H<sub>4</sub>-CHO, m.p. 173—174°; anisaldehyde, m.p. 132—133°; vanillin, m.p. 152—153°; piperonal, m.p. 143°. The *p*-tolylbenzylhydrazones of the sugars follow Hudson's rule and can be used to determine the stereochemical configurations at the  $\alpha$ -C.

III. NPhPh-NH<sub>2</sub> with CH<sub>2</sub>Ph-CH<sub>2</sub>Cl at 145—160° affords phenyl- $\beta$ -phenylethylhydrazine, m.p. 54—56° (hydrochloride). The phenyl- $\beta$ -phenylethylhydrazones (I) of the following are prepared (m.p. in parenthesis): PhCHO (109°); *d*-arabinose (140—142°; [ $\alpha$ ]<sub>D</sub> +1.5°); *l*-rhamnose (121°; [ $\alpha$ ]<sub>D</sub> -9.95°); *l*-fucose (179°; [ $\alpha$ ]<sub>D</sub> +7.4°  $\rightarrow$  +6.3° in 20 hr.); *d*-glucose (142°; [ $\alpha$ ]<sub>D</sub> +5.2°); *d*-mannose (157°; [ $\alpha$ ]<sub>D</sub> +18.1°); and *d*-galactose (157°; [ $\alpha$ ]<sub>D</sub> +2.7°  $\rightarrow$  +7.0° in 3 days); all rotations are in MeOH. The "benzyl rule" (see above) cannot be applied to (I). J. L. D.

Acetylation of carbohydrates. Catalytic acetylation of glucose with small amounts of perchloric acid. D. KRUGER and W. ROMAN (Ber., 1936, 69, [B], 1830—1834).—Glucose (I) is not acetylated by AcOH-Ac<sub>2</sub>O in absence of a catalyst at low

temp. but the  $\alpha$ -penta-acetate is readily produced in the presence of very small amounts of HClO<sub>4</sub>. The behaviour of (I) is essentially similar to that of cellulose. Since reaction occurs to only a very limited extent with AcOH in presence of a catalyst or dehydrating agent, acetylation is due to Ac<sub>2</sub>O and the change is ROH+Ac<sub>2</sub>O=ROAc+AcOH; free H<sub>2</sub>O is not intermediately produced. Reaction is considered to proceed through a "crit. complex" of catalyst, acetylating agent, and reactive group. H. W.

Photochemical reactions in the *o*-nitrobenzylidenacetals series. X. Benzylideneacetals of sugars and glucosides. I. TANASESCU and M. IONESCU. XI. Benzylideneacetals of sugars and glucosides. Their transformation into diastereoisomerides. I. TANASESCU and E. CRACIUNESCU (Bull. Soc. chim., 1936, [v], 3, 1511—1517, 1517—1527; cf. this vol., 593).—X. Glucose, *o*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CHO, and P<sub>2</sub>O<sub>5</sub> at 40—50° give 1:2:4:6- or 1:3:4:6-di-*o*-nitrobenzylideneglucose, m.p. 125—130°, [ $\alpha$ ] 0°, stable to hydrolysing and acylating agents, converted in CHCl<sub>3</sub> or C<sub>6</sub>H<sub>6</sub> by light into 1:2- or 1:3-*o*-nitrobenzylideneglucose 4-*o*-nitrosobenzoate (I), m.p. 145°, [ $\alpha$ ] 0°, the presence of the free 6-OH being proved by formation of a 6-benzoate, m.p. 145°, -benzene-, m.p. 145°, and -*p*-toluene-sulphonate, m.p. 140°, and that of the NO by condensation to yield a phenylazo-, m.p. 124°, and dimedon derivative, m.p. 163°. Similarly are obtained 2:3:4:6-di-*o*-nitrobenzylidene- $\alpha$ -methylglucoside, m.p. 95—100°, and 2:3-*o*-nitrobenzylidene- $\alpha$ -methylglucoside 4-*o*-nitrosobenzoate, m.p. 135°. Di-*m*-nitrobenzylideneglucose, m.p. 105—110°, is stable to light.

XI. Di-*o*-nitrobenzylidene-glucose, -mannose, and -galactose give in light the same NO-compound (I) owing to inversion, and with Dimroth's reagent all give galactose (characterised as osazone). Di-*o*-nitrobenzylidene- $\alpha$ -mannoside, m.p. 125—130°, gives 2:3-*o*-nitrobenzylidene- $\alpha$ -methylmannoside 4-*o*-nitrosobenzoate, m.p. 117°. R. S. C.

Two forms of methylated derivatives of sorbose. G. ARRAGON (Bull. Soc. Chim. biol., 1936, 18, 1336—1343).—Methylation of methylsorbose gave two pentamethylsorbosides, (I) b.p. 48—49°/10<sup>-4</sup> mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -31.5° in MeOH and (II), b.p. 48—49°/10<sup>-4</sup> mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -11.8° in MeOH. On hydrolysis (I) gave tetramethylsorbose (III), b.p. 51°/10<sup>-4</sup> mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +4.9° in MeOH and (II) tetramethylsorbose (IV), b.p. 51°/10<sup>-4</sup> mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +3.6° in MeOH. Treatment of either (III) or (IV) with Ag<sub>2</sub>O and MeI gave the Me<sub>5</sub> derivative from which it was derived by hydrolysis; with Me<sub>2</sub>SO<sub>4</sub> only (II) was obtained. The mol. refractions of the compounds suggest that they have ring structures. H. D.

Influence of the aglucone on rate of hydrolysis of  $\beta$ -glucosides by emulsin.—See this vol., 1297.

Synthesis of glucosides. I—III. K. SISO (J. Soc. Chem. Ind. Japan, 1936, 39, 217—218b).—I. II. The reaction of PhOH etc. with sugar acetates in presence of *p*-C<sub>6</sub>H<sub>4</sub>Me-SO<sub>3</sub>H to form phenolglucosides is facilitated by working at very high vac., when AcOH is removed as liberated. In this way,  $\beta$ -

glucose penta-acetate with PhOH gives  $\beta$ -phenol-glucoside tetra-acetate (70%) (also obtained using  $\text{ZnCl}_2$ ); with quinol, arbutin penta-acetate (60%); with  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , helicin acetate; and with  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , salicylic acid  $\beta$ -glucoside acetate.

III. Sucrose octa-acetate with PhOH and  $\text{ZnCl}_2$  yields  $\alpha$ -phenolglucoside tetra-acetate. E. W. W.

**Non-hydrolysable  $\beta$ -glucoside.** S. VEIBEL and E. NEILSEN (Compt. rend., 1936, 203, 126—128).—Acetobromoglucose with  $\text{Bu}^n\text{OH}$  and  $\text{Ag}_2\text{CO}_3$  affords *trimethylcarbinol- $\beta$ -d-glucoside tetra-acetate*, m.p. 145—146° (corr.),  $[\alpha]_D^{20}$  —19.3° in EtOH, converted ( $\text{NaOMe}$ ) into the *glucoside*, m.p. 164—166°,  $[\alpha]_D^{20}$  —19.0° in  $\text{H}_2\text{O}$ , which is hydrolysed ( $k=2\times 10^{-4}$ ) at 0.005 times the rate of  $\beta$ -methylglucoside ( $k=3.9\times 10^{-2}$ ).

J. L. D.

**$\beta$ -d-Glucosides of caffeic and ferulic acids.** B. HELFERICH and F. VORSATZ (J. pr. Chem., 1936, [ii], 145, 270—272).—The prep. of  $\beta$ -d-glucosido-caffeic acid ( $+\text{H}_2\text{O}$ ), m.p. 145°, (anhyd.)  $[\alpha]_D^{20}$  —80° in  $\text{H}_2\text{O}$  and —114° in 0.5N-NaOH (cf. A., 1935, 489), and of  $\beta$ -d-glucosidoferulic acid, m.p. 231—232°,  $[\alpha]_D^{20}$  —41.5° in  $\text{C}_6\text{H}_5\text{N}$  ( $\text{Ac}_4$  derivative,  $[\alpha]_D^{20}$  —32.9° in  $\text{CHCl}_3$ ) (cf. A., 1934, 1003), by the modified Knoevenagel method (this vol., 1251) is described.

H. G. M.

**Thevetin.** R. C. ELDERFIELD (J. Biol. Chem., 1936, 115, 247—252).—Thevetin (I),  $\text{C}_{29}\text{H}_{44}\text{O}_{13}$  (cf. lit.), softens at 193—194°, decomp. 210°, affords glucose with hot 3%  $\text{H}_2\text{SO}_4$ , and with  $\text{NaOH-MeOH}$  gives *isothetvetin*, sinters at 180°, decomp. 200—210°,  $[\alpha]_D^{20}$  —60° in  $\text{C}_6\text{H}_5\text{N}$ ; this is hydrolysed by 2%  $\text{HCl}$  to *isothetvetogenin*,  $\text{C}_{23}\text{H}_{34}\text{O}_8$ ,  $+\text{H}_2\text{O}$ , sinters at 170°, decomp. about 220°, and with  $\text{NaOBr}$  gives *isothetvetinic acid* (not obtained pure), which is hydrolysed by  $\text{HCl}$  to *isothetvetogenic acid*,  $\text{C}_{23}\text{H}_{34}\text{O}_9$ , decomp. 120—130°. These reactions, the nitroprusside reaction, and absorption of 1  $\text{H}_2$  on hydrogenation support the formula assigned above to (I). Most of the derivatives form gels except in presence of mineral salts.

R. S. C.

**Characterisation of starch by dispersoid analysis.**—See this vol., 1201.

**Hemimethylcellulose.** R. PIWONKA (Ber., 1936, 69, [B], 1965—1968; cf. this vol., 971).—Treatment of ramie fibres with 4.12N-NaOH and  $\text{CuCl}_2$  and of the product (I) with  $\text{Me}_2\text{SO}_4$  gives a hemimethylcellulose, hydrolysed (Irvine-Hirst) to a methylmethylglucoside (II), b.p. 156°/0.1 mm. Treatment of (II) with 5% aq.  $\text{HCl}$  and then with  $\text{NHPh}\cdot\text{NH}_2$  in  $\text{AcOH}$  gives a methylglucosazone, m.p. 178—180°, showing that Me is not present at position 2. Oxidation of (II) with  $\text{HNO}_3$  ( $d$  1.2) and esterification of the product gives *Et<sub>2</sub> methylsaccharate*, b.p. 161°/2 mm., and *Et methylsaccharolactonate*, b.p. 184°/1.5 mm., m.p. 103—104°,  $[\alpha]_D^{20}$  +8.1°. It follows therefore that the sugar derivatives contain Me at 3 and that in the methylation of (I) the entry of Me into the glucose group of cellulose occurs exclusively in this position.

H. W.

**Alkaline decomposition of cellulose nitrate.** I. QUANTITATIVE. W. O. KENYON and H. LE B. GRAY (J. Amer. Chem. Soc., 1936, 58, 1422—1427).—

Hydrolysis (1—20%  $\text{NaOH}$ ) of cellulose nitrate (I) at 30—60° gives a little  $\text{Na}_2\text{CO}_3$ , much  $\text{NaNO}_2$ , and some reducing substances (II). The production of  $\text{CO}_2$  and (II) is related to time, temp., alkali concn., and ratio of  $\text{NaOH}$  to (I). Quant. data are given.

H. B.

**System methylamine-calcium chloride.**—See this vol., 1204.

**Optical rotations in homologous series of aliphatic amines.** P. A. LEVENE and R. E. MARKER [with M. KUNA] (J. Biol. Chem., 1936, 115, 267—274).—Amines,  $\text{NH}_2\cdot[\text{CH}_2]_m\cdot\text{CHMe}\cdot[\text{CH}_2]_n\cdot\text{Me}$ , exactly resemble the corresponding alcohols in variations of  $[M]$ , but their hydrochlorides resemble the corresponding acids.  $[M]$  given below are max.  $[M]^{25}$  (homogeneous) unless otherwise stated. *d*- $\beta$ -Methyl-*n*-valeronitrile and  $\text{H}_2$ -Raney Ni in  $\text{MeOH}$  give *d*- $\gamma$ -methyl-*n*-amylamine,  $[M]$  +10.9° in 44%  $\text{EtOH}$  (hydrochloride,  $[M]$  +9.85° in  $\text{H}_2\text{O}$ ). Similarly are prepared *d*- $\delta$ -methyl-*n*-hexyl-, b.p. 80°/90 mm.,  $[M]$  +11.7° (hydrochloride,  $[M]$  +13.2° in  $\text{H}_2\text{O}$ ), *d*- $\epsilon$ -methyl-*n*-heptyl-,  $[M]$  +16° in 60%  $\text{EtOH}$  (hydrochloride,  $[M]$  +15.7° in  $\text{H}_2\text{O}$ ), *d*- $\delta$ -methyl-*n*-heptyl-, b.p. 165°,  $[M]$  +0.68°, *l*- $\beta$ -methyl-*n*-hexyl-,  $[M]$  —16.4° in  $\text{Et}_2\text{O}$  (hydrochloride,  $[M]$  —18.2° in  $\text{MeOH}$ ), *l*- $\gamma$ -methyl-*n*-heptyl-, b.p. 65—66°/14 mm.,  $[M]$  —1.72° (hydrochloride,  $[M]$  +2.13° in  $\text{MeOH}$ ), *l*- $\delta$ -methyl-*n*-octyl-, b.p. 75—77°/13 mm.,  $[M]$  —0.78° (hydrochloride,  $[M]$  —0.63° in  $\text{MeOH}$ ), *l*- $\epsilon$ -methyl-*n*-nonyl-, b.p. 92°/15 mm.,  $[M]$  —0.75° (hydrochloride,  $[M]$  —1.15° in  $\text{MeOH}$ ), and *l*- $\zeta$ -methyl-*n*-decyl-amine, b.p. 113°/15 mm.,  $[M]$  —2.44° (hydrochloride,  $[M]$  —3.47° in  $\text{H}_2\text{O}$ ).

R. S. C.

**Identification of hexamethylenetetramine and ammonia.** G. BOUVILLOUX (J. Pharm. Chim., 1936, [viii], 24, 58—64).— $(\text{CH}_2)_6\text{N}_4$  may be used to identify  $\text{CH}_2\text{O}$ , phenols, piperonal, and iodides.

F. N. W.

**Determination of choline.** I. SAKAKIBARA and T. YOSINAGA (J. Biochem. Japan, 1936, 23, 211—239).—The following methods were investigated: pptn. by  $\text{HgCl}_2$  from  $\text{EtOH}$  solution and determination (Kjeldahl) of N in the ppt.; pptn. by  $\text{AuCl}_3$  in  $\text{EtOH}$  and determination of N in the ppt.; Levene-Ingvaldsen method (A., 1920, ii, 713); Roman's method (A., 1930, 752). None of these methods is applicable to choline (I)-lecithin (II) mixtures. Attempts to remove (II) by  $\text{COMe}_2$ , or salts  $[\text{MgCl}_2, \text{CaCl}_2, \text{Fe}(\text{OH})_3, \text{Fe citrate}]$  and their mixtures indicated the following method: (II) is pptd. by aq.  $\text{Fe citrate}$  followed by aq.  $\text{Fe citrate-Fe}(\text{OH})_3$ , the ppt. is separated, and (I) is determined in the filtrate by Roman's method.

F. O. H.

**Colorimetric micro-determination of choline and acetylcholine.** F. J. R. BEATTIE (Biochem. J., 1936, 30, 1554—1559; cf. Kapfhammer *et al.*, A., 1930, 1464).—Choline (I) and acetylcholine (II) are pptd. as reineckate, the colour of which, after dissolution in  $\text{COMe}_2$ , is compared with that of a standard, but (II) is best hydrolysed to (I) before determination. Carnitine, but not other common biological material, interferes. 0.03 mg. of (I) (concn. 0.003%) can be determined with an error of  $\pm 3\%$ .

W. McC.



**Action of hypochlorites on amino-acids and proteins. Effect of acidity and alkalinity.** N. C. WRIGHT (Biochem. J., 1936, 30, 1661—1667).—Between  $p_H$  6 and 11 the quantity of Cl capable of liberating I from KI in a 0.014% NaOCl solution decreases with the amount of glycine (I) added and reaches zero at a concn. of approx. 0.005%; with greater concns. the available Cl increases  $\propto$  the concn. of (I). The rate of this increase depends on the  $p_H$  attaining a max. at  $p_H$  8.8. At very acid  $p_H$  the available Cl never falls to zero and no subsequent rise with increasing concn. of (I) occurs. Cystine produces only the decrease with the amount added and no subsequent rise; in alkaline solution the reaction is associated with polysulphide formation. The fact that large quantities of  $NH_2$ -acid cause a smaller reduction in available Cl than small quantities is explained by assuming that NaOCl in low concn. acts as a chlorinating agent and only as an oxidant when present in relative excess. The behaviour of caseinogen and gelatin under the same conditions showed similarities to that of the  $NH_2$ -acids; in addition a ppt. was formed with gelatin which on treatment with KI liberated I. The purely oxidative theory of NaOCl action of Norman (this vol., 595) is criticised. H. D.

**Interaction of ethyl  $\alpha$ -chlorocrotonate and dimethylamine.** J. C. ROBERTS (J.C.S., 1936, 1169—1170).—Et  $\alpha$ -bis(dimethylamino)butyrate, b.p. 89°/3 mm., 91°/6 mm. [monohydrochloride, m.p. 117°; picrate, m.p. 147°; platinichloride, m.p. 180° (decomp.)], is prepared from Et  $\alpha$ -chlorocrotonate (1 mol.) and  $NHMe_2$ -abs. EtOH. Attempts to prepare the dimethiodide of the base failed. J. T. A.

**Preparation and activation of homoaspartic acid.** P. PFEIFFER and E. HEINRICH (J. pr. Chem., 1936, [ii], 146, 105—112).— $CH_3Ac \cdot CO_2Et$ ,  $(NH_4)_2CO_3$ , and KCN in 50% EtOH under  $CO_2$  at 70—80°/20 atm. afford Et 5-methylhydantoin-5-acetate, m.p. 138° [corresponding amide, m.p. 252° (decomp.)], and hydrazide, m.p. 104—105°, converted by boiling 40% KOH into  $\beta$ -aminopropane- $\alpha$ -dicarboxylic (homoaspartic) acid (I), m.p. 233° (decomp.) [hydrochloride, m.p. 212° (decomp.)]; Ca (also +3H<sub>2</sub>O), Ba (also +4H<sub>2</sub>O), Pb (also +2H<sub>2</sub>O), and Cu (also +3H<sub>2</sub>O) salts; Ac derivative, m.p. 156—157°; corresponding diamide, m.p. 173°. (I) and NaNO<sub>2</sub> in HCl yield  $\beta$ -hydroxypropane- $\alpha$ -dicarboxylic acid, m.p. 119°. Resolution of (I) by strychnine in H<sub>2</sub>O gives the corresponding d-acid, m.p. 240°,  $[\alpha]_D^{20} +3.55^\circ$  in H<sub>2</sub>O [strychnine salt (also +2H<sub>2</sub>O), decomp. about 302° after becoming discoloured at 210°,  $[\alpha]_D^{24} -28.67^\circ$ ], and the l-acid,  $[\alpha]_D -3.66^\circ$  in H<sub>2</sub>O. H. W.

**Resolution of dl-lysine.** C. P. BERG (J. Biol. Chem., 1936, 115, 9—15).—dl-Lysine yields l-(+)-lysine d- (I), m.p. 245—246°,  $[\alpha] +16.41^\circ$ , and l-camphorate, m.p. 239—240°,  $[\alpha] +0.35^\circ$ , and d-(−)-lysine d-, m.p. 239—240°,  $[\alpha] -0.38^\circ$ , and l-camphorate (II), m.p. 245—246°,  $[\alpha] -16.39^\circ$ , and thence l-(+)-lysine and d-(−)-lysine dihydrochloride, m.p. 201—202°,  $[\alpha] -15.65^\circ$ . (I) and (II) are the less sol. salts. M.p. are corr. and  $[\alpha]$  are  $[\alpha]_D^{20}$  in H<sub>2</sub>O. R. S. C.

**Determination of creatinine with sodium 3:5-dinitrobenzoate.** W. D. LANGLEY and M.

EVANS (J. Biol. Chem., 1936, 115, 333—341).—Procedure similar to that of Benedict and Behre (this vol., 1013) is described. H. D.

**Reversible transfer of phosphate between the adenylic acid system and phosphagens.** H. LEHMANN (Biochem. Z., 1936, 286, 336—343).—Tables and curves show that the reversible esterification of adenylypyrophosphoric acid with arginine or with creatine (I) to give respectively adenosine diphosphate (II) + argininephosphoric acid or (II) + creatine phosphate (III) follow the mass law and give bimol. equilibrium consts. The same probably holds for (II) + (I) giving adenylic acid + (III). P. W. C.

**Diamino-acid, canavanine. IV. Constitution of canavanine and canaline.** M. KITAGAWA and A. TAKANI (J. Biochem. Japan, 1936, 23, 181—185).—Dibenzoylcanaline with 7% HCl at 100° affords  $\alpha$ -benzoylcanaline, m.p. 150°, which on keeping with O-methylisocarbamide in MeOH at room temp. (Kapfhammer and Muller, A., 1934, 876) yields  $\alpha$ -benzoylcanavanine. The properties of normal and guanidated O-hydroxylamineacetic acid (from condensation of benzhydroximic acid and  $CH_2Br \cdot CO_2Et$ ; cf. Werner, A., 1893, i, 510) confirm the indication of the above synthesis that canaline is  $NH_2O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$  and canavanine is  $NH_2 \cdot C(NH_2) \cdot NH \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$  (cf. A., 1934, 993). F. O. H.

**Synthesis of peptides containing cystine and glutamine; possible bearing on the structure of insulin. Amide nitrogen of insulin.** C. R. HARRINGTON and T. H. MEAD (Biochem. J., 1936, 30, 1598—1611).—Neither glutaminylcysteine (I) nor cysteylglutamine (II), in either the reduced or the oxidised forms, has hypoglycaemic activity. They resemble insulin in the lability of the amide-N, but their S is more stable to alkali. Insulin appears to have 34 amide groups per mol., indicating about 30% of glutamic acid. In the syntheses of (I) and (II), it is found that the intermediate compounds crystallise more readily as cysteine rather than cystine derivatives, and also that benzylcarboxyl esters are more convenient than benzyl esters, owing to the readier removal of the group with  $PH_4I$ . In the synthesis of (I), S-benzylcysteine and  $CH_2Ph \cdot COCl$  in 2M-NaOH give, on acidification, N-carbobenzylxy-S-benzylcysteine (III), m.p. 93—95°, which, converted into the acid chloride and added to  $\gamma$ -Et glutamate and  $NEt_3$  in H<sub>2</sub>O, gives  $\gamma$ -Et N-carbobenzylxy-S-benzylcysteylglutamate, m.p. 88°. Treatment with aq.  $NH_3$  and acidification yields N-carbobenzylxy-S-benzylcysteylglutamine, m.p. 188—189°, reduction of which with Na in liquid  $NH_3$  yields cysteylglutamine, which after purification via the  $Cu^I$  mercaptide has  $[\alpha]_{5461}^{20} +6.6^\circ$ . Oxidation with  $H_2O_2$  yields cystylglutamine,  $[\alpha]_{5461}^{20} -13.9^\circ$ . (III) is also obtained by Zn-Cu reduction of N-carbobenzylxycystine in EtOH- $H_2SO_4$  to N-carbobenzylxycysteine, m.p. 82°, which with  $CH_2PhBr$  in alkaline solution gives (III). In the synthesis of (II), N-carbobenzylxycystyl chloride with  $CH_2Ph \cdot OH$  gives the  $CH_2Ph$  ester, which with  $PH_4I$  in AcOH is converted into cysteine benzyl ester hydriodide, m.p. 139° (decomp.). This with N-carbobenzylxyglutamic anhydride in dry  $CHCl_3$  in presence

of  $\text{NHET}_2$  gives *N*-carbobenzyloxy- $\alpha$ -glutamylcysteine benzyl ester (IV), m.p. 148°, which with  $\text{CH}_2\text{PhBr}$  in  $\text{CHCl}_3\text{-NHET}_2$  gives *N*-carbobenzyloxy- $\alpha$ -glutamyl-S-benzylcysteine benzyl ester, m.p. 144°. This, after conversion into the acid chloride, gives the amide, m.p. 182°, and after removal of the substituent groups by Na in liquid  $\text{NH}_3$ , yields glutamylcysteine, decomp. 197°,  $[\alpha]_{5461} -9.8^\circ$ . Oxidation with  $\text{H}_2\text{O}_2$  gives glutamylcystine,  $[\alpha]_{5461} -119^\circ$ . Other substances described include glycine benzyl ester hydrochloride (V), m.p. 139–140°, from glycyl chloride hydrochloride and  $\text{CH}_2\text{Ph-OH}$  in  $\text{Et}_2\text{O}$ ; *N*-carbobenzyloxyglycylglycine benzyl ester, m.p. 167–168°, by removal of  $\text{HCl}$  from (V) and treatment with *N*-carbobenzyloxyglycyl chloride. Using instead the acid chloride from  $\alpha$ -benzyl *N*-carbobenzyloxyglutamate, the  $\alpha$ -benzyl ester of *N*-carbobenzyloxy- $\gamma$ -glutamylglycine benzyl ester, m.p. 104–105°, results. The acid chloride from *N*-carbobenzyloxyaspartic acid  $\alpha$ -benzyl ester, in  $\text{CHCl}_3$ , added with aq.  $\text{NaOH}$  to glycine, yields *N*-carbobenzyloxy- $\beta$ -aspartylglycine, m.p. 153°; the same acid chloride with cystine  $\text{Et}$  ester hydrochloride in  $\text{C}_6\text{H}_5\text{N}$  gives  $\alpha$ -benzyl-*N*-carbobenzyloxy- $\beta$ -aspartylcystine *Et* ester, m.p. 160°. (IV) with  $\text{CH}_2\text{N}_2$  at 0° gives  $\gamma$ -methyl-*N*-carbobenzyloxy- $\alpha$ -glutamyl-S-methylcysteine benzyl ester, m.p. 85–86°.

F. A. A.

**Alkyl- and aryl-amides and -carbamides as hypnotics.** E. H. VOLWILER and D. L. TABERN (J. Amer. Chem. Soc., 1936, 58, 1352–1354).—The following acids are prepared from the appropriate  $\text{CRR}'(\text{CO}_2\text{H})_2$ ; their derivatives are generally obtained by standard methods:  $\beta$ -methylhexoic acid, b.p. 208–210°/755 mm. (chloride, b.p. 83–85°/60 mm.);  $\alpha$ -bromo- $\beta$ -methylhexoic acid (chloride, b.p. 110–120°/40 mm.; amide, m.p. 112–114°; methylamide, m.p. 90°);  $\beta$ -methyl- $\alpha$ -ethylhexoic acid, b.p. 225–230°/755 mm. (chloride, b.p. 103–108°/45 mm., 190°/755 mm.; amide, m.p. 97–98°; methylamide; allylamide; diethylamide);  $\alpha$ -bromo- $\beta$ -methyl- $\alpha$ -ethylhexoic acid (chloride, b.p. 138–150°/50 mm.; amide);  $\beta$ -methylallylhexoic acid, b.p. 195–200°/755 mm. (chloride, b.p. 190–195°/755 mm.; amide, m.p. 90–91°);  $\beta$ -methyl- $\alpha$ -butylhexoic acid, b.p. 185–190°/55 mm. (chloride, b.p. 140°/55 mm.; amide, m.p. 97–98°);  $\alpha$ -ethylheptioic acid, b.p. 232–238°/750 mm. (chloride, b.p. 195–200°/750 mm.; amide, m.p. 96°);  $\beta$ -methyl- $\alpha$ -ethylvaleric acid (allylamide;  $\alpha$ -Br-derivative chloride, b.p. 130–135°/50 mm.);  $\alpha$ -isopropylbutyric acid (methylamide, m.p. 72–75°; ethylamide; allylamide, m.p. 58–60°);  $\alpha$ -phenyl- $\Delta^2$ -pentenoic acid (amide, m.p. 63°);  $\alpha\beta$ -diethylvaleric acid (amide, m.p. 123–125°). The requisite acyl chloride and an excess of  $\text{CO}(\text{NH}_2)_2$  at 110–135° give  $\beta$ -methylhexoyl, m.p. 180°,  $\alpha$ -bromo-methylhexoyl, m.p. 108–110°,  $\beta$ -methyl- $\alpha$ -ethylhexoyl, m.p. 133°,  $\alpha$ -bromo- $\beta$ -methyl- $\alpha$ -ethylhexoyl,  $\beta$ -methyl- $\alpha$ -allylhexoyl, m.p. 123°,  $\beta$ -methyl- $\alpha$ -butylhexoyl, m.p. 123°,  $\beta$ -methyl- $\alpha$ -ethylvaleryl, m.p. 172°,  $\alpha$ -phenyl- $\Delta^2$ -pentenoyl, m.p. 133–134°,  $\alpha\beta$ -diethylvaleryl, m.p. 148–150°, and  $\alpha$ -ethylheptoyl, m.p. 130°. carbamide.  $\alpha$ -Phenylbutyramide and diethylmalonalloylamic acid have m.p. 85–87° and 105°, respectively. Pharmacological data for some of the compounds are given.

H. B.

**Synthetic substrates for protein-digesting enzymes.** M. BERGMANN and W. F. ROSS (J. Amer. Chem. Soc., 1936, 58, 1503).— $\epsilon$ -Carbobenzyloxyamino- $\alpha$ -hippurylamidohexoamide (I), m.p. 212° (from the Me ester and  $\text{MeOH-NH}_3$ ), is reduced catalytically to  $\epsilon$ -amino- $\alpha$ -hippurylamidohexoamide (II) (hydrochloride, m.p. 248°), which is hydrolysed by tryptic proteinase (prep.: Waldschmidt-Leitz and Purr, A., 1929, 1338) at 8.8 to  $\text{NH}_2\text{Bz-CH}_2\text{-CO}_2\text{H}$ , lysine, and  $\text{NH}_3$ . (I) is similarly unaffected. Papain-HCN at  $pH$  5 hydrolyses one peptide linking of (II).

H. B.

**Micro-determination of carbamide without distillation.** F. RAPPAPORT and M. GUTMANN (Klin. Woch., 1935, 14, 1325–1326; Chem. Zentr., 1935, ii, 3553).— $\text{CO}(\text{NH}_2)_2$  is converted by urease into  $\text{NH}_4$  salts;  $\text{NH}_3$  is then determined by an indirect iodometric method.

H. N. R.

**Structure of carbamide.**—See this vol., 298.

**Fission (sulpholysis) of carbamide by sulphuric acid.** Simple preparation of amidosulphonic acid and imidosulphonates. P. BAUMGARTEN (Ber., 1936, 69, [B], 1929–1937).— $\text{CO}(\text{NH}_2)_2$  and excess of 100%  $\text{H}_2\text{SO}_4$  at 130–140° give  $\text{CO}_2$ ,  $\text{NH}_2\text{-SO}_3\text{H}$  (I), and  $\text{NH}_4\text{HSO}_4$ :  $\text{CO}(\text{NH}_2)_2 + \text{OH}\text{-SO}_3\text{H} = \text{NH}_2\text{-CO}_2\text{H}$  (II) + (I) and (II) =  $\text{NH}_3 + \text{CO}_2$ . The yield of (I) diminished with increasing amount of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_7$  is produced either according to  $\text{CO}(\text{NH}_2)_2 + 4\text{H}_2\text{SO}_4 = \text{CO}_2 + 2\text{NH}_4\text{HSO}_4 + \text{H}_2\text{S}_2\text{O}_7$  or (I) +  $\text{H}_2\text{SO}_4 = \text{NH}_4\text{HS}_2\text{O}_7$ , the latter change being realisable with (I) as initial material. Sulpholysis occurs more readily with fuming  $\text{H}_2\text{SO}_4$  and is then preceded by sulphonation of  $\text{CO}(\text{NH}_2)_2$  to  $\text{NH}_2\text{-CO-NH-SO}_3\text{H}$ , the intermediate production of which enables 2 mols. of (I) to be formed from 1 mol. of  $\text{CO}(\text{NH}_2)_2$ , instead of 1 mol. as when  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  is employed; this yield is nearly attained when the acid has the approx. constitution  $\text{H}_2\text{S}_2\text{O}_7$ . With oleum containing less  $\text{SO}_3$  the yield of (I) declines even when an excess of  $\text{SO}_3$  is present. The strongly exothermic reaction between  $\text{CO}(\text{NH}_2)_2$  and  $\text{H}_2\text{S}_2\text{O}_7$  is very violent;  $\text{CO}(\text{NH}_2)_2$  should therefore be first dissolved in  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  or conc.  $\text{H}_2\text{SO}_4$ , the necessary amount of conc. oleum is then added with cooling, and the mixture is cautiously heated.  $\text{CO}(\text{NH}_2)_2\text{-H}_2\text{SO}_4$  (III) is decomposed at 140°;  $3(\text{III}) \rightarrow 2\text{CO}_2 + \text{NH}(\text{SO}_3\text{NH}_4)_2 + \text{CO}(\text{NH}_2)_2\text{-NH}_4\text{HSO}_4$ . Better yields (about 80%) of  $\text{NH}(\text{SO}_3\text{H})_2$  [best isolated as the  $(\text{NH}_4)_3$  or  $\text{K}_3$  salt] are obtained when  $\text{H}_2\text{SO}_4$  is added,  $4(\text{III}) + \text{H}_2\text{SO}_4 = 4\text{CO}_2 + 2\text{NH}(\text{SO}_3\text{NH}_4)_2 + (\text{NH}_4)_2\text{SO}_4$ . (I) and  $\text{NH}_2\text{-SO}_3\text{NH}_4$  give  $\text{NH}(\text{SO}_3\text{NH}_4)_2$ . H. W.

**Synthesis of  $\alpha$ -bromoisovalerylcarbamide.** T. ICHIKAWA (J. Pharm. Soc. Japan, 1935, 55, 727–731).— $\alpha$ -Bromoisovaleryl bromide and  $\text{CO}(\text{NH}_2)_2$  yield  $\alpha$ -bromoisovalerylcarbamide, m.p. 153–154°.

CH. ABS. (r)

**Reduction of nitroguanidine. VI. Promoter action of platonic chloride on Raney nickel catalyst.** E. LIEBER and G. B. L. SMITH (J. Amer. Chem. Soc., 1936, 58, 1417–1419).—The rate of reduction of nitroguanidine (in  $\text{H}_2\text{O}$ ) and of castor oil, linseed oil,  $\text{PhNO}_2$ , and  $\text{PhCHO}$  (in 95%  $\text{EtOH}$ ) by  $\text{H}_2$  and Raney Ni (I) is considerably accelerated by addition of a little  $\text{PtCl}_4$  immediately before hydrogen-



ation begins. The following reaction occurs between (I) and  $\text{H}_2\text{PtCl}_6$ :  $3\text{Ni} + 2\text{H}^+ + \text{PtCl}_6^{--} \rightarrow 3\text{Ni}^{++} + \text{Pt} + \text{H}_2 + 6\text{Cl}^-$ . H. B.

Optical rotations and rotatory dispersions in homologous series of aliphatic nitriles. P. A. LEVENE, A. ROTHEN, and R. E. MARKER [with M. KUNA] (J. Biol. Chem., 1936, 115, 253—266).—Variation of  $[\alpha]_D$  in the series,  $\text{CN} \cdot [\text{CH}_2]_m \cdot \text{CHMe} \cdot [\text{CH}_2]_n \cdot \text{Me}$ , is analogous to that in the corresponding carboxylic acid series, except for an irregularity when  $m=1$ . Rotatory dispersions are usually small, but probably always anomalous.  $[\alpha]$  given below are max.  $[\alpha]_D^{25}$  (homogeneous) unless otherwise stated. *l*- $\alpha$ -Methyl-*n*-butyric acid affords the nitrile, b.p. 127°,  $[\alpha] -24.7^\circ$ , by way of the chloride and amide. *d*- $\gamma$ -Methyl-*n*-hexylic bromide and KCN in aq. EtOH give *d*- $\beta$ -methyl-*n*-valeronitrile, b.p. 154°,  $[\alpha] +8.67^\circ$ . *d*- $\gamma$ -Methyl-*n*-hexoic acid gives the chloride, b.p. 80°/50 mm.,  $[\alpha] +19^\circ$ , and thence the amide,  $[\alpha] +19.1^\circ$  in 75% EtOH, and nitrile, b.p. 105°/100 mm.,  $[\alpha] +16.7^\circ$ . *d*- $\delta$ -Methyl-*n*-hexylic bromide gives *d*- $\delta$ -methyl-*n*-heptonitrile, b.p. 115—133°/98—100 mm.,  $[\alpha] +17.3^\circ$ . *l*- $\delta$ -Methyl-*n*-heptoic acid gives the chloride, b.p. 82°/30 mm.,  $[\alpha] -6.78^\circ$ , and nitrile, b.p. 125°/100 mm.,  $[\alpha] -2.01^\circ$ . *d*- $\alpha$ -Methyl-*n*-hexoic acid gives the nitrile, b.p. 75—77.5°/20 mm.,  $[\alpha] +50.5^\circ (+52.5^\circ \text{ in } \text{C}_7\text{H}_{16})$ . *d*- $\gamma$ -Methylheptic acid gives the nitrile, b.p. 48—52°/0.5 mm.,  $[\alpha] +5.97^\circ (+6.86^\circ \text{ in } \text{C}_7\text{H}_{16})$ . *d*- $\gamma$ -Methylheptyl bromide gives *d*- $\gamma$ -methyl-octonitrile, b.p. 119—120°/30 mm.,  $[\alpha] -2.44^\circ (-2.63^\circ \text{ in } \text{C}_7\text{H}_{16})$ . *l*- $\delta$ -Methyl-*n*-nonoic acid gives the chloride, b.p. 111°/14 mm.,  $[\alpha] -3.47^\circ$ , and amide,  $[\alpha] -1.6^\circ$  in 75% MeOH. *l*- $\delta$ -Methyl-*n*-octyl bromide gives *l*- $\delta$ -methyl-*n*-nononitrile, b.p. 96—102°/12 mm.,  $[\alpha] -5.32^\circ (-5.44^\circ \text{ in } \text{C}_7\text{H}_{16})$ . *l*- $\epsilon$ -Nonan- $\alpha$ -ol gives *l*- $\epsilon$ -methyl-*n*-nonyl bromide, b.p. 110°/15 mm.,  $[\alpha] -5.3^\circ$ , and *l*- $\epsilon$ -methyl-*n*-deconitrile, b.p. 116—118°/15 mm.,  $[\alpha] -1.95^\circ (-1.95^\circ \text{ in } \text{C}_7\text{H}_{16})$ . R. S. C.

Polymerisation of  $\alpha$ -methylacrylonitrile. E. MERTENS and M. FONTEYN (Bull. Soc. chim. Belg., 1936, 45, 438—444).—The optimum temp. of polymerisation is 64°; no polymerisation occurs at <60° or >69°. Hot 60%  $\text{HNO}_3$ , alone of many acids, reacts probably by oxidation.  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$  polymerise the nitrile. A series of physical properties of the polymeride is given. J. L. D.

Action of hydrogen fluoride on diazoheptane. C. L. TSENG and T. S. HO (J. Chinese Chem. Soc., 1936, 4, 335—339).—*n*-Heptylcarbamide (modified prep.) with  $\text{HNO}_2$  yields nitrosoheptylcarbamide, m.p. 69.2—72.2°, which with 50% aq. KOH (<1°) gives diazoheptane. The latter with anhyd. HF forms  $\Delta^8$ -heptene. F. N. W.

Chromous and chromic ammines.—See this vol., 1218.

Use of organo-sodium compounds in organic syntheses. G. V. TSCHELINCEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 269—273).—A survey. J. T. A.

Aromatisation of cyclopentane homologues and paraffins in presence of platinised charcoal. B. A. KASANSKI and A. F. PLATE (Ber., 1936, 69,

[B], 1862—1869).—In contrast with the behaviour of cyclopentane and its Me, Et, and Pr derivatives *n*-butylcyclopentane is converted by passage over Pt-C in  $\text{H}_2$  at 300—310° into (?)  $\delta$ -methyloctane and *o*- $\text{C}_6\text{H}_4\text{MeEt}$ . The formation of aromatic substances is more pronounced when  $\text{H}_2$  is replaced by  $\text{N}_2$  or  $\text{CO}_2$  whereas less paraffin is produced. Similar observations are recorded with *sec*-butyl- and *iso*amylcyclopentane. The possibilities are discussed that aromatisation is due to preliminary production of a six-membered ring from the side-chain followed by fission of the cyclopentane ring or that aliphatic hydrocarbons are first produced and are transformed into aromatic derivatives. In support of the latter view it is shown that *p*-xylene is formed from diisobutyl, hydrocarbons oxidised to BzOH and *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  result from *n*-octane, and that *m*-cymene is produced from diisomyl. H. W.

Oxidation of cyclohexane by hydrogen peroxide. G. DUPONT and R. DULOU (Compt. rend., 1936, 203, 92—94).—In  $\text{Et}_2\text{O}$  containing  $\text{OsO}_4$ , cyclohexane is oxidised by  $\text{H}_2\text{O}_2$ , though in anhyd.  $\text{Et}_2\text{O}$  the reaction is slow. MeCHO and AcOH are the principal products. C. R. H.

Contact transformations of allylcyclohexene, cyclohexylallene, and cyclohexylallylene. R. J. LEVINA and D. M. TRACHTENBERG (J. Gen. Chem. Russ., 1936, 6, 764—773).— $\beta\gamma$ -Dibromopropylcyclohexane and quinoline yield allylcyclohexane (I), b.p. 155—156°/755 mm.  $\Delta^1$ -Allylcyclohexene (II) in presence of C-Pt at 200° in  $\text{CO}_2$  yields PhPr and propylcyclohexane, probably by way of  $\Delta^2$ -propenyl- $\Delta^1$ -cyclohexene and propyl- $\Delta^{1,5}$ -cyclohexadiene. (I), under similar conditions, yields  $\Delta^2$ -propenyl- $\Delta^1$ -cyclohexene, which isomerises to (II), and this undergoes further changes as above.  $\gamma$ -cyclohexyl- $\Delta^2$ -propinane isomerises to (I), and this further as above. R. T.

Triple linkings in carbon rings, and the possible structure of the simpler cyclic hydrocarbons of the formula  $\text{C}_n\text{H}_{2n-4}$ . A. E. FAVORSKI [with M. F. SCHOSTAKOVSKI and N. A. DOMININ] (J. Gen. Chem. Russ., 1936, 6, 720—731).—cyclopentanone (I) and  $\text{PCl}_5$  yield a mixture of  $\text{Cl}_2$  and  $\text{Cl}_2$ -derivatives, converted by heating at 40° with 20% KOH in EtOH into chloro- $\Delta^1$ -cyclopentene, b.p. 111—113°, which with Br in  $\text{CHCl}_3$  gives 1-chloro-1:2-dibromocyclopentane, and this yields 1:2-dibromo- $\Delta^1$ -cyclopentene (II), b.p. 78°/5 mm., when warmed with KOH-EtOH. (II), when heated with Na in  $\text{Et}_2\text{O}$ , affords tri(trimethylene)benzene and the di-, tri-, and tetra-merides of  $\Delta^{1,3}$ -cyclopentadiene. Suberone, when treated similarly to (I), yields successively chloro- $\Delta^1$ -cycloheptene, b.p. 58—59°/12 mm., 1-chloro-1:2-dibromocycloheptane, b.p. 105—108°/2 mm., 1-chloro-2-bromo- $\Delta^1$ -cycloheptene, b.p. 80—82°/2 mm.,  $\Delta^{1,2}$ -cycloheptadiene, b.p. 118—119°, tri(pentamethylene)benzene, and unidentified polymerides. R. T.

Rule for substitution in the benzene series. J. C. MCGOWAN (Chem. and Ind., 1936, 607—608).—A substituent, *A*, promotes *o/p*- or *m*-substitution in  $\text{C}_6\text{H}_6$  according to whether the mesomeric effect causes it to resist or assist, respectively, dissociation

of a proton from the compound  $\text{AOH}$ . The following rule expresses this relation. Substitution in the compound  $\text{PhA}$  by cationoid reagents will give largely *o*- and *p*-derivatives if  $K = [\text{AO}^-][\text{H}^+]/[\text{AOH}]$  (measured in dil. aq. solution at room temp.) is  $< 10^{-7}$ , and will give largely the *m*-derivative if  $K$  is  $> 10^{-5}$  g.-mol. per litre.

R. S. C.

Is the methyl group attached to the benzene nucleus positive or negative? W. HUNTENBURG (J. pr. Chem., 1936, [ii], 145, 229—234).—A general discussion of the polarity of  $\text{Me}$  attached to the  $\text{C}_6\text{H}_5$  nucleus and a criticism of the view of Rosenmund (this vol., 105).

H. G. M.

**Constitution and reactivity. XVIII. Condition of the individual positions in the molecule of nitrobenzene.** K. LAUER and R. ODA (J. pr. Chem., 1936, [ii], 146, 61—64).—The nitration of  $\text{PhNO}_2$  by  $\text{KNO}_3$  in 84%, 89%, 95%, and 100%  $\text{H}_2\text{SO}_4$  has been studied. The results are discussed in relation to Hückel's formulation of  $\text{PhNO}_2$ .

H. W.

**Photochemistry of nitro-compounds.**—See this vol., 1178.

**Behaviour of certain aromatic compounds at the anode, in solutions of potassium nitrate.** C. B. MEDINSKI (Acta Univ. Asiae Med., 1933, [vi], No. 6, 3—7).—Nitration in the anode chamber by "nascent"  $\text{HNO}_3$  is applicable only to insol. substances, others being oxidised under these conditions. The velocity of nitration is  $>$  with  $\text{HNO}_3\text{--H}_2\text{SO}_4$ , and that of oxidation  $>$  that of nitration.

R. T.

**Aliphatic substitution and the Walden inversion.** E. D. HUGHES, F. JULIUSBURGER, A. D. SCOTT, B. TOPLEY, and J. WEISS (J.C.S., 1936, 1173—1175).—Since the abs. rate of racemisation of *d*- $\text{CHPhMeBr}$  in  $\text{COMe}_2$  containing  $\text{LiBr}$  agrees, within experimental error, with the abs. velocity of substitution of  $\text{Br}$  for  $\text{Br}$  in  $\alpha$ -phenylethyl bromide, b.p.  $88^\circ/12$  mm., it is concluded that 90% of the mol. act of substitution lead to stereochemical inversion in this reaction.

J. T. A.

**Polymerisation. II. Properties, mechanism of formation, and constitution of di- and polystyrenes.** J. RISI and D. GAUVIN (Canad. J. Res., 1936, 14, B, 255—267; cf. this vol., 196).—The Br-method of McIlhenny (A., 1900, ii, 178) is used to determine the degree of unsaturation of polymerides. Distyrene-I (I), obtained from  $\text{CHPh:CH}\cdot\text{CO}_2\text{H}$  by  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$  (1 : 1.5) (II) (A., 1883, 475), contains 30% of saturated isomeride (III). The similar product (IV), obtained in 65% yield from  $\text{CHPh:CH}_2$  (V) and (II), contains 50% of (III). The distyrene (VI) of Stocmer and Kootz (A., 1929, 55) is completely saturated. Staudinger's distyrene (VII) (A., 1935, 740) contains only 7% of (III); his tristyrene (VIII) contains 25% of a saturated compound. When further heated with (II), (I) gives more (III) and not an unsaturated isomeride as previously supposed; under these conditions (IV) also gives a little more (III) and (VII) is completely polymerised, but (VIII) is scarcely affected. The polystyrenes obtained from (V) by  $\text{SbCl}_5$  and probably by heat or  $\text{H}_2\text{SO}_4$  are completely saturated. (V) with  $\text{SbCl}_5$  in  $\text{C}_6\text{H}_6$  in the

dark at room temp. gives polystyrenes, m.p.  $60^\circ$  (mol. wt. 636) and  $90\text{--}92^\circ$  (mol. wt. 1335), and by Staudinger's method (*loc. cit.*) gives 10—15% of an unsaturated distyrene and solid polystyrenes, m.p.  $70\text{--}72^\circ$  (mol. wt. 827) and  $53\text{--}55^\circ$  (mol. wt. 566). With  $\text{SnCl}_4$  (I) and (IV) undergo 50% of polymerisation and much cyclisation, but (VI) is unaffected. At  $210\text{--}215^\circ$  (4 days) (I) gives 10% of a polymeride, (VII) gives 50%, and (VIII) 55% thereof; cyclisation does not occur. Hence fission of the di- and trimerides precedes polymerisation, a conclusion confirmed by production of 8% of (VI) from (VIII) at  $210\text{--}215^\circ$ . Mixtures of di- with poly-styrenes and of (III) with (VII) or (VIII) behave at  $210\text{--}215^\circ$  as do the constituents, so that polymerisation is a chain reaction and does not occur in stages. (I) and (IV) are  $\text{CHPh:CH}\cdot\text{CHPhMe}$ , (III) is 1-phenyl-3-methyl-hydrindene, polystyrene is  $\text{CHPh:CH}\cdot[\text{CHPh}\cdot\text{CH}_2]_x\cdot\text{CHPhMe}$ , and polymerisation is stopped by cyclisation of the terminal linking giving  $\text{CHPh}\langle\text{CH}_2\text{C}_6\text{H}_5\rangle\text{CH}\cdot\text{CH}_2\cdot[\text{CHPh}\cdot\text{CH}_2]_x\cdot\text{CHPhMe}$ . The formulae of (VII) and (VIII) are unknown.

R. S. C.

**Organic sulphur compounds. V. New sulphide and its derivatives.** L. BERMEJO and J. J. HERRERA. VI. Preparation and study of  $\alpha$ -phenylpropyl sulphide. L. BERMEJO, J. J. HERRERA and F. M. PANIZO (Anal. Fis. Quím., 1934, 32, 1106—1110, 1182—1186).—V.  $\text{CHPhMeCl}$  with  $\text{K}_2\text{S}$  in  $\text{EtOH}$  yields di- $\alpha$ -phenylethyl sulphide, f.p.  $< 23^\circ$  (sulphoxide, an oil; sulphone, m.p.  $135^\circ$ ), purified through its  $\text{HgCl}_2$  compound (cf. this vol., 1229).

VI.  $\text{CHPhEt}\cdot\text{OH}$  with  $\text{SO}_2\text{Cl}$  gives  $\alpha$ -phenylpropyl chloride, b.p.  $117\text{--}120^\circ/33$  mm., converted as above into the sulphide, b.p.  $190\text{--}192^\circ/12$  mm. (compound with  $2\text{HgCl}_2$ , decomp.  $95^\circ$ ; sulphoxide, m.p.  $45\text{--}46^\circ$ ; sulphone, m.p.  $60^\circ$ ).

F. R. G.

**Azido-derivatives of acetylenic hydrocarbons.** V. A. KUZMIN and S. G. FRIDMAN (Mem. Inst. Chem. Ukrain. Acad. Sci., 1936, 3, 61—76).— $\text{CPh:C}\cdot\text{CPh}_2\text{Cl}$  (I) and  $\text{NaN}_3$  in  $\text{COMe}$ , (20 hr. at the b.p.) yield  $\text{CPh:C}\cdot\text{CPh}_2\text{N}_3$ , m.p.  $165\text{--}170^\circ$  [dibromide, m.p.  $187\text{--}190^\circ$ ; dichloride, m.p.  $180^\circ$  (decomp.)], not decomposed by aq.  $\text{H}_2\text{SO}_4$ . By using  $\text{CPh:C}\cdot\text{CPh}_2\text{Cl}$  in place of (I), an unstable oil, probably containing  $\text{CPh:C}\cdot\text{CMe}_2\text{N}_3$ , is obtained.

R. T.

**Inductive effects in the diphenyl series.**—See this vol., 1183.

**Preparation of 3 : 4-dibromodiphenyl.** F. H. CASE (J. Amer. Chem. Soc., 1936, 58, 1249—1251).—4-Bromo-3-nitrodiphenyl, b.p.  $210\text{--}215^\circ/6$  mm. (from the 4- $\text{NH}_2$ -derivative), is reduced ( $\text{EtOH}\text{--}\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ ) to 4-bromo-3-aminodiphenyl, m.p.  $97\text{--}98^\circ$  [Ac derivative (I), m.p.  $127^\circ$ ], converted (Sandmeyer) into 3 : 4-dibromodiphenyl (II), b.p.  $192\text{--}195^\circ/5$  mm. 2-Bromo-5-nitrodiphenyl, m.p.  $80\text{--}81^\circ$  (from 5 : 2- $\text{NO}_2\text{--C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Cl}$ ,  $\text{C}_6\text{H}_6$ , and aq.  $\text{NaOH}$  at  $< 5^\circ$ ), is similarly reduced and then acetylated to 2-bromo-5-acetamidodiphenyl (III), m.p.  $162\text{--}163^\circ$ . The (I) and (II) of Blakey and Scarborough (A., 1928, 165) are (III) and impure 2 : 5-dibromodiphenyl, respectively; the latter with  $\text{Cu}\text{--}\text{Mg}$  alloy followed by  $\text{CO}$ , gives 2-bromodiphenyl-5-carboxylic and diphenyl-



2:5-dicarboxylic acids, whilst oxidation affords 2:5- and only a little 3:4- $C_6H_3Br_2 \cdot CO_2H$ . The product from 3:4- $C_6H_3MeBr \cdot N_2Cl$ ,  $C_6H_6$ , and aq. NaOH is oxidised (aq.  $KMnO_4$ ) to 4-bromodiphenyl-3-carboxylic acid, m.p. 194—195°; 4:3- $C_6H_3MeBr \cdot N_2Cl$  similarly leads to 3-bromodiphenyl-4-carboxylic acid, m.p. 179—180°. H. B.

Action of magnesium on homonuclear dibromodiphenyls. F. H. CASE (J. Amer. Chem. Soc., 1936, 58, 1246—1249).—The amount of  $C_6H_5Ph(MgBr)_2$ , determined by yield (quoted) of  $Ph_2$  on hydrolysis, from Mg (2 atoms) and the following dibromodiphenyls increases in the order 3:5- (I) (26%), 2:5- (II) (39%), and 2:4- (III) (56%); with Cu-Mg alloy the yields are 35.1, 68.8, and 77.9%, respectively. 3:4-Dibromodiphenyl does not react. The  $C_6H_5Ph$  recovered when (II) and (III) are treated with Mg (1 atom) is oxidised to  $o$ - $C_6H_4Br \cdot CO_2H$  showing that the 2-Br is less readily attacked. 2:5- $C_6H_5Ph(MgBr)_2$ , obtained using Cu-Mg, with  $CO_2$ , gives diphenyl-2:5-dicarboxylic acid, m.p. 274—275°; the 3:5-compound affords an impure product. (I) and (II) with 1 atom of Mg followed by  $CO_2$  give 3-bromo-, m.p. 177—178°, and 2-bromo-, m.p. 247—248° (lit. 242—243°), -diphenyl-5-carboxylic acid, respectively. (III), prepared by deamination of its 5- $NH_2$ -derivative, has b.p. 174—176°/7 mm. H. B.

2-Bromo-9-nitrofluorene and 2:2'-dibromo-9:9'-dinitro-9:9'-difluorenyl. C. DALE and R. L. SHRINER (J. Amer. Chem. Soc., 1936, 58, 1502).—The previously described (this vol., 197) normal form (m.p. 170°) of 2-bromo-9-nitrofluorene (I) is 2:2'-dibromo-9:9'-dinitro-9:9'-difluorenyl (II), m.p. 175° (corr.). (II) is obtained in good yield from the K salt of (I) and I (1 mol.) and in small amount when the *aci*-form of (I) is heated with EtOH. H. B.

Discrepant behaviour of anthracenes of different origin towards sulphuryl chloride. M. A. ILJINSKI and B. I. AFREMOV (Ber., 1936, 69, [B], 1824).—An anthracene (I) of 94—96% purity from Kuznezsk (Siberia) was readily and almost quantitatively converted by  $SO_2Cl_2$  in  $CCl_4$  into 9:10-dichloroanthracene, whereas an apparently similar product (II) from Donez (Ukraine) remained unchanged. Reaction occurred readily with (I) and (II) in xylene and (I) and (II) were similarly oxidised to anthraquinone. Purification of (I) and (II) by treatment with superheated steam followed by crystallisation from EtOH and xylene yielded products differing somewhat in appearance and in which the differing behaviour towards  $SO_2Cl_2$  in  $CCl_4$  persisted. H. W.

Hydrogenation of anthracene. E. I. PROKOPETZ and V. N. CHADSHINOV (Chim. Tverd. Topl., 1935, 6, 347—353).—Hydrogenation in presence of  $MoS_3$  at 100—120 atm. is described; 1:2:3:4-tetrahydro-, 1:2:3:4:5:6:7:8-octahydro-, and perhydro-anthracenes are produced, together with a mixture of naphthene hydrocarbons, b.p. 39—150°. CH. ABS. (r)

Synthesis of phenanthrene and hydrophenanthrene derivatives. III. Hydrocarbons of the chrysene, acechrysene, and 3:4-benzphen-

anthrene series; 1:2-benzpyrene derivatives. L. F. FIESER, M. FIESER, and E. B. HERSHBERG (J. Amer. Chem. Soc., 1936, 58, 1463—1468).—3:4-Dihydrophenanthrene-1:2-dicarboxylic anhydride and  $(CH_2 \cdot CH)_2$  in dioxan at 160—180° give 1:2:3:6:15:16-hexahydrochrysene-15:16-dicarboxylic anhydride (I), m.p. 143.5—144°, which when fused with KOH affords hydrochrysenes [containing dihydrochrysene, m.p. 223—226° (when regenerated from the *picrate*, m.p. 142—144°), repeated crystallisation of which from AcOH yields chrysene (II)], which are dehydrogenated (Se at 300—310°) to (II). 4:5-Dimethylchrysene, m.p. 215—215.3°, is similarly obtained from the 4:5- $Me_2$  derivative (this vol., 203) of (I). 3:4-Dihydronaphthalene-1:2-dicarboxylic anhydride and cyclopentadiene and cyclohexadiene at 100° give 1:4-endomethylene-, m.p. 158—159° (decomp. to original components), and 1:4-endoethylene-, m.p. 137—138°, -1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, respectively, which are reduced ( $H_2$ ,  $PtO_2$ , AcOH) to the 1:2:3:4:9:10:11:12-octahydro-derivatives, m.p. 156—156.5° and 135—135.5°, respectively. KOH-fusion and dehydrogenation of the product from 2:3-dimethyl-1:4:9:10:11:12-hexahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride (improved prep.; cf. *loc. cit.*) affords 6:7-dimethyl-3:4-benzphenanthrene, m.p. 94.5—95° (*picrate*, m.p. 143—144°); the parent benzphenanthrene could not be prepared similarly. 1:2:3:4:9:10:11:12-Octahydro-5:6-benzphenanthrene-11:12-dicarboxylic anhydride, m.p. 182—183.2°, is obtained by reduction of the  $H_6$ -derivative (improved prep.; cf. *loc. cit.*). 5:6-Tetramethylene-1:2:3:4-tetrahydro-8:9-acephenanthrene, m.p. 148.6—149°, prepared by reduction [ $H_2$  (3000 lb.),  $PtO_2$ , EtOH, 200°] of its 1-CO-derivative (A., 1933, 67), is completely destroyed on attempted dehydrogenation. Et  $\gamma$ -3-acenaphthylbutyrate,  $Et_2C_2O_4$ , and KOEt give (method: A., 1935, 1495) *Et\_2*  $\alpha$ -oxalyl- $\gamma$ -3-acenaphthylbutyrate, m.p. 83—85°; the crude product is converted by 80%  $H_2SO_4$  at 70—80° into 3:4-dihydro-8:9-acephenanthrene-1:2-dicarboxylic anhydride (III), m.p. 229—232° (previous softening; in quartz) [corresponding *Et\_2* ester, m.p. 140.2—140.6°, formed with some (III) when cyclisation is effected with 82%  $H_2SO_4$ +AcOH], which with  $(CH_2 \cdot CH)_2$  and  $(CH_2 \cdot CMe)_2$  affords 1:2:3:6:15:16-hexahydro-8:9-acechrysene-15:16-dicarboxylic anhydride (IV), m.p. 189—189.3°, and its 4:5- $Me_2$  derivative (V), m.p. 187.5—188°, respectively. KOH-fusion of (V) furnishes a  $H_6$ -derivative, m.p. 193.5—194.5°, of 4:5-dimethyl-8:9-acechrysene, m.p. 222.6—223.1°; (IV) similarly yields a dihydro-8:9-acechrysene, m.p. 153.2—153.5°, attempted dehydrogenation (Se at 300—310°) of which gives an isomeride (?), m.p. 181—182°. Me  $\gamma$ -1-acenaphthylbutyrate and  $Et_2C_2O_4$  lead (as above) to 3:4-dihydro-5:10-aceanthrene-1:2-dicarboxylic anhydride, m.p. 276—277°, whilst Et  $\gamma$ -1-pyrenylbutyrate, m.p. 48.5—49°, similarly affords *Et\_2*  $\alpha$ -oxalyl- $\gamma$ -1-pyrenylbutyrate, m.p. 106—107°, and then (by cyclisation) 1':2'-dihydro-1:2-benzpyrene-3':4'-dicarboxylic anhydride, m.p. 338—340° (decomp.). This is dehydrogenated (S in quinoline) to 1:benzpyrene-3':4'-dicarboxylic anhydride, m.p. 380

382°, which appears to have no carcinogenic activity. All m.p. are corr. H. B.

[Perylene tribromide.] K. BRASS and E. CLAR (Ber., 1936, 69, [B], 1977—1979).—A reply to Zinke et al. (this vol., 1102). H. W.

Reversible oxidisability of organic compounds. *iso*Oxybis-(*p*-bromophenyl)diphenylnaphthacene. L. ENDERLIN (Compt. rend., 1936, 203, 192—194; cf. A., 1930, 1173; 1934, 649).—*o*:11-Di-*p*-bromophenyl-6:12-diphenylnaphthacene 6:11-peroxide, C<sub>42</sub>H<sub>26</sub>O<sub>2</sub>Br<sub>2</sub> (dissociable), with MgI<sub>2</sub> in Et<sub>2</sub>O at room temp. affords the isomeric, non-dissociable, 5:12, 6:11-dioxide, m.p. 258°, which is reduced (Fe or Zn-AcOH) partly to naphthacene, but is unaffected by RMgI. The change probably occurs as a result of a rupture of the O-O linking followed by an allyl change with elimination of MgI<sub>2</sub> to give a structure similar to that of the photo-oxide of anthracene (cf. A., 1935, 1488). J. L. D.

Influence of electric moment on the number of molecules of base fixed by a salt. II. A. ARLOV (Bull. Soc. chim., 1936, [v], 3, 1673—1682; cf. A., 1935, 182, 1448).—The following compounds, prepared by mixing the constituent Co di- and tri-chloroacetates and amines in EtOH solution, are described: [R=(CCl<sub>3</sub>·CO)<sub>2</sub>Co; X=(CHCl<sub>2</sub>·CO)<sub>2</sub>Co]: R<sub>4</sub>NH<sub>4</sub>Ph; R<sub>4</sub>(*o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); R<sub>4</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); R<sub>4</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); R<sub>4</sub>(*o*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); R<sub>4</sub>(*p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); R<sub>4</sub>(*o*-OEt·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); R<sub>4</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>); R<sub>4</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>); R<sub>4</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>); R<sub>4</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>); R<sub>4</sub>(*p*-C<sub>6</sub>H<sub>4</sub>I·NH<sub>2</sub>); X<sub>5</sub>NH<sub>4</sub>Ph; X<sub>5</sub>2NH<sub>4</sub>Ph; X<sub>2</sub>(*o*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); X<sub>2</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); X<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>); X<sub>2</sub>(*o*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); X<sub>2</sub>(*p*-OMe·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); X<sub>2</sub>(*o*-OEt·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); X<sub>2</sub>(*p*-OEt·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>); X<sub>2</sub>(*o*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>); X<sub>2</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>); X<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>); X<sub>2</sub>(*m*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>); X<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub>); X<sub>2</sub>(*m*-CN·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>). The rule found previously relating the dipole moment of the substituent group in NH<sub>2</sub>Ph with the no. of mols. of base co-ordinated by Ni salts holds also for the Co compounds. J. W. S.

Organic molecular compounds. II. III. Compounds of phenols with some synthetic cyclic oxides. G. M. BENNETT and R. L. WAIN (J.C.S., 1936, 1108—1114, 1114—1120; cf. A., 1929, 436).—II. The prep. of the following is described: 3:5-dinitrobenzonitrile (I), m.p. 127°; 5-nitroisophthalyl chloride (II), m.p. 66—68°; 5-nitro-1:3-dicyanobenzene (III), m.p. 205°; trimelic acid trichlorobenzene (IV), m.p. 35—37°, b.p. 213°/13 mm.; *s*-tricyanobenzene (V), m.p. 261—263° (corr.); 5-nitro-1:3-bis-methylthiolbenzene, m.p. 92° [disulphoxide, m.p. 176—185°, presumably a mixture of stereoisomerides; disulphone (VI), m.p. 214°]. Mol. compounds obtained from the following components are described. All are 1:1 compounds except those marked \*, which are 2:1 compounds of the components in the order given. M.p. are given in parentheses. 3:5:1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>Me and  $\alpha$ - (120°) and  $\beta$ - (88—90°) C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, benzidine (99—102°), *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>

(72°), C<sub>10</sub>H<sub>8</sub> (77—80°), acenaphthene (85—87°), phenanthrene (117—119°), *s*-C<sub>6</sub>H<sub>3</sub>(OMe)<sub>3</sub> (71—73°); (I) and  $\alpha$ - (166—169°) and  $\beta$ - (109—113·5°) C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, benzidine\* (161—163°), NPhMe<sub>2</sub> (71—73°), NH<sub>2</sub>Ph (87°), *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> (96—98°), C<sub>10</sub>H<sub>8</sub> (123°), acenaphthene (148—150°), phenanthrene (107—108°), fluorene\* (128—130°), Ph<sub>2</sub>\* (96—99°), anthracene\* (151—153°), *s*-C<sub>6</sub>H<sub>3</sub>(OMe)<sub>3</sub> (81—82°), PhMe (41—94°), C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub> (92—97°); 3:5:1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·COCl and C<sub>10</sub>H<sub>8</sub> (127°), anthracene (130—151°), acenaphthene (149—151°), NPhMe<sub>2</sub>; 3:5:1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·NH<sub>2</sub> and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (149°), acenaphthene (148—150°); (III) and  $\alpha$ - (147—149°) and  $\beta$ - (105—107·5°) C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, benzidine\* (173°), *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> (62°), NH<sub>2</sub>Ph (95—170°), acenaphthene (156—160°); (II) and acenaphthene (139—143°), phenanthrene (134—137°), anthracene (122—154°); (VI) and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (139—172° indef.), NH<sub>2</sub>Ph (126°); (V) and  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> (165—167°), benzidine [168° (decomp.)]; (IV) and C<sub>10</sub>H<sub>8</sub> (97—101°), acenaphthene (134—137°), phenanthrene (129—131°), anthracene (120—152°), fluorene (75—77°), NPhMe<sub>2</sub> (34—82°). Thermal analysis of the system 2:4:1-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CN- $\beta$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> revealed a stable 1:1 compound, congruent m.p. 135°. The function of the polar groups in complex formation is discussed. One of the nuclear C of the NO<sub>2</sub>-compound (or other acceptor mol.) is considered to act as the acceptor in the formation of a link with the other component (donor) (cf. loc. cit.).

III. Some dicarboxylic esters with excess of MgMeI give ditertiary glycols, readily dehydrated by H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O to cyclic oxides. Thus *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>Me)<sub>2</sub> (VII) gives *aaa'*-*α*-tetramethylphthalan (VIII), m.p. 71—72°; Me,  $\beta$ -phenylglutarate gives 4-phenyl-2:6-dimethylheptane-2:6-diol, m.p. 70—71°, dehydrated to 4-phenyl-2:2:6:6-tetramethyltetrahydropyran (IX), m.p. 57·5°; Me<sub>2</sub> phenylsuccinate gives 3-phenyl-2:5-dimethylhexane-2:5-diol, m.p. 61—62°, dehydrated to 3-phenyl-2:2:5:5-tetramethyltetrahydrofuran, m.p. 39—40°; and Me<sub>2</sub> diphenate gives 2:2'-di-( $\alpha$ -hydroxyisopropyl)diphenyl, m.p. 139°, dehydrated to the cyclic oxide (X)  $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{CMe}_2 \\ \text{C}_6\text{H}_4\cdot\text{CMe}_2 \end{matrix} > \text{O}$ , m.p. 90—91·8°. (VII) with

MgMeI-Et<sub>2</sub>O (instead of C<sub>6</sub>H<sub>6</sub>) gives a *hydroxyisopropylphenyl Me ketone*, m.p. 108—111°. These cyclic oxides do not yield compounds with HCl, BF<sub>3</sub>, or HClO<sub>4</sub>, but the thermal diagrams for systems of these oxides and certain phenols showed the formation of mol. compounds (mol. proportions and m.p. in parentheses): (a) (VIII) with  $\alpha$ - (1:1; m.p. 92·6°) and  $\beta$ - (2 oxide:1 naphthol; congruent m.p. 79·3°) C<sub>10</sub>H<sub>7</sub>·OH, *p*-C<sub>6</sub>H<sub>4</sub>Br·OH (1:1; m.p. 54·3°), *p*-C<sub>6</sub>H<sub>4</sub>I·OH (1:1; m.p. 51·8°), *o*- (1:1; m.p. 85·5°) (2 oxide:1 phenol; congruent m.p. 88·5°) and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, *p*-xylol (1:1; m.p. 40·5°), but not with *s*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>·OH, *s*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>·OH, CH<sub>3</sub>·Ph·CO<sub>2</sub>H, or *o*-C<sub>6</sub>H<sub>4</sub>Me·CO<sub>2</sub>H. (b) (IX) with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OH (1:1; m.p. 69°), *o*- (1:1, m.p. 78°) (2 oxide:1 resorcinol; congruent m.p. 67·5°) and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, but no stable compound with  $\beta$ -C<sub>10</sub>H<sub>7</sub>·OH. (c) (X) with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·OH [2 oxide:1 naphthol; incongruent m.p. 76° (unstable)], but none with *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>. These results support the view that increase in the basicity of O by ring formation and the rigidity of the struc-



tures of the cyclic oxides favour the formation of mol. compounds. The extent of dissociation on melting is estimated in two cases. H. G. M.

**Halogenation of phenolic ethers and anilides.** VII. Method of determining proportions of *o*- and *p*-isomerides in a mixture. B. JONES (J.C.S., 1936, 1231—1234; cf. this vol., 719).—A method suitable for use in nuclear chlorination reactions, depending on the determination of the difference in velocities of substitution of *o*- and *p*-isomerides, is outlined and applied to NHPAc, NHPbZ, and PhSO<sub>2</sub>-NHPh. Controlled addition of Cl<sub>2</sub> (1 mol.) to the anilide yields a mixture of *o*- and *p*-isomerides which is analysed by determining its velocity of further chlorination and observing the coincidence of the velocity with that of an artificial mixture of known composition. F. N. W.

**Mechanism of N-halogenoacylanilide rearrangements.** R. P. BELL (J.C.S., 1936, 1154—1156; cf. A., 1935, 1209).—The rearrangement of NBrPhAc (I) in PhCl catalysed by CCl<sub>3</sub>·CO<sub>2</sub>H involves intramol. migration of halogen only, as no free Br is observed. (I) and HBr react instantly and completely in PhCl to form NHPAc and Br, and under these conditions it is impossible to tell whether formation of *p*-bromoacetanilide is due to migration or nuclear halogenation. F. N. W.

**Alkylthiolacet-anilides, -*p*-toluidides, and the corresponding thionyl compounds.** N. HELLSTROM and T. LAURITZSON (Ber., 1936, 69, [B], 1999—2003).—For identification, the alcohol is converted by PBr<sub>3</sub> into the corresponding bromide, which is heated in EtOH and alkali with *thiolacetanilide*, m.p. 109.5—110°, from SH·CH<sub>2</sub>·CO<sub>2</sub>H and NH<sub>2</sub>Ph in N<sub>2</sub> at 150°, or *thiolacet-p-toluidide*, m.p. 125—126°; the products may then be oxidised by H<sub>2</sub>O<sub>2</sub> to the corresponding sulfoxides. Compounds SR·CH<sub>2</sub>·CO·NHPh are described, the m.p. of the corresponding sulfoxides being placed in parentheses: R=Me, m.p. 77—78° (136—137°); Et, m.p. 58—59° (160—161°); Pr<sup>a</sup>, m.p. 55.5—56° (137.5—138°); Pr<sup>β</sup>, m.p. 66.5—67° (157—158°); Bu<sup>a</sup>, an oil (m.p. 143.5—144°); *sec*.-Bu, an oil (127—128°); Bu<sup>β</sup>, m.p. 45—46° (145—146°). The analogous substances SR·CH<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>4</sub>Me-*p*, have been prepared: R=Me, m.p. 102—103° (173—174°); Et, m.p. 81—82° (174—175°); Pr<sup>a</sup>, m.p. 78—79° (147—148°); Pr<sup>β</sup>, m.p. 65—66° (148—149°); Bu<sup>a</sup>, m.p. 61—62° (146—147°); *sec*.-Bu, m.p. 56—57° (145—146°); Bu<sup>β</sup>, m.p. 85—86° (141—142°). (Cf. this vol., 1231.) H. W.

**M.p. curve of *o*-anisidine and *o*-chloroaniline mixtures.** S. AOYAMA and I. MORITA (J. Pharm. Soc. Japan, 1933, 53, 1089—1093).—Pure *o*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub> has a double m.p.,  $\alpha$ -form, m.p. —11.92°, and  $\beta$ -form, m.p. —1.78°. The m.p. curve for mixtures with pure *o*-anisidine (I), b.p. 90—91°/4 mm., is given; there are two eutectics, m.p. —16.8° [25% of (I)] and —13.0° [68.63% of (I)].

CH. ABS. (r)

**Absorption [spectra] of anils of aliphatic ketones.** (MME.) P. RAMART-LUCAS and (MLLE.) M. MONTAGNE (Bull. Soc. chim., 1936, [v], 3, 916—

918).—The ultra-violet absorption spectra of the anil (I) of COEt<sub>2</sub>, of its isomeride,  $\gamma$ -anilino- $\Delta^2$ -pentene (II), of  $\gamma$ -anilinopentane and its Ac derivative, and of  $\gamma$ -(*N*-phenylacetamido)- $\Delta^2$ -pentene have been determined in hexane or EtOH. No conclusions can be reached concerning the existence in hexane solutions of (I) of its tautomeride (II).

H. G. M.

**Absorption in the ultra-violet and structure of anils and  $\alpha$ -ethylenic amines.** (MME.) P. RAMART-LUCAS and M. J. HOCH (Bull. Soc. chim., 1936, [v], 3, 918—929; cf. preceding abstract).—The prep. of the following is described (cf. A., 1935, 336): *Ph Bu<sup>a</sup> ketone-anil*, b.p. 160—161°/15 mm., and *p-methoxyanil*, m.p. 61°, b.p. 196—198°/15 mm., *Ph  $\alpha$ -dimethylamyl ketone-anil*, b.p. 200—202°/25 mm., and *p-methoxyanil*, b.p. 221—222°/17 mm., *Ph phenyltert-butyl ketone-anil*, b.p. 229—230°/23 mm., *cis*-, m.p. 86° (cf. lit.), and *trans*-, m.p. 105°, *-deoxybenzoinanil*. The absorption spectra of the foregoing imines and of the following have been determined: the anils derived from COMeEt, COEt, COPhEt, COPhMe, COPr<sup>a</sup>, COPh<sub>2</sub>, PhCHO, Me nonyl ketone, cyclohexanone, and 3-methylcyclohexanone: the *o*-, *m*-, and *p*-methyl- and *o*- and *p*-methoxy-anils from COPr<sup>a</sup>; the *p*-methylanils from COPh<sub>2</sub> and Me nonyl ketone; the *p*-methoxyanils from COPhMe and PhCHO; NMePh·CET·CHPr<sup>a</sup>, NMePh·CPh·CH<sub>2</sub>, NEtPh·CPh·CH<sub>2</sub>, NMePh·CH·CHPh, NMePh·CPh·CHPh, and 1-methylanilino- $\Delta^1$ -cyclohexene. The spectra do not permit the detection of the tautomeride NHR·CR'·CR''R''' in solutions of NR·CR'·CHR'R''' (cf. A., 1934, 1336). The spectra of the trialkylacetophenones and diaryl ketones present anomalies attributed to deformation of the valency angles of >C=N-. H. G. M.

**Nitroamines. VI. 3:6-Dinitrophenylnitroamine.** E. MACCIOTTA (Rend. Semin. Fac. Sci. R. Univ. Cagliari, 1934, 4, 143—144; Chem. Zentr., 1935, ii, 3647; cf. A., 1933, 387).—Treatment of 3:6-dinitroaniline with HNO<sub>3</sub>, followed by Ac<sub>2</sub>O, yields 3:6-dinitrophenylnitroamine, isolated as Ag salt. H. N. R.

**Alkaline fusion. I. Fusion of potassium sulphanilate.** N. N. VOROSHOV and M. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1936, 6, 880—883).—K sulphanilate and KOH (1:10 mol.) at 350—355° (45 min.) yield almost exclusively *p*-OH·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H (77% yield). R. T.

**N-Methylanilides.** J. RODRÍGUEZ VELASCO (Anal. Fís. Quím., 1934, 32, 807—814).—NPhMeAc with NaOEt yields NHPHMe and PrCO<sub>2</sub>H, indicating the intermediate formation of NPhMe·COPr. The behaviour of NPhMeAc with MgCl·CH<sub>2</sub>Ph is in agreement with Maxim (A., 1926, 837), and that of NPhMe·CO·CH·CHPh with MgPhBr concordant with Maxim *et al.* (A., 1928, 1004). F. R. G.

**Positive reaction of glass on *o*-tolidine.** D. W. HORN (Amer. J. Pharm., 1936, 108, 324—325).—*o*-Tolidine gives a yellow colour, as does Cl<sub>2</sub>, in contact with glass, but not when the glass is washed with dil. HCl. When bottles which do not give the

test are heated with  $H_2O$  under pressure they become active.

J. L. D.

**Stereoisomerism due to restricted rotation about a single bond.** II. 8-Nitro-*N*-benzenesulphonyl-1-naphthylglycine and analogous compounds. H. C. TUAN, T. T. HSU, and E. I. F. HSÜ (J. Chinese Chem. Soc., 1936, 4, 131—141).—The rate of racemisation of 1-8-nitro-*N*-benzenesulphonyl-1-naphthylglycine in EtOH, NaOH, and AcOH has been determined. 6-Nitro-*N*-benzenesulphonyl-2:4-dimethylaniline and  $CH_2Br \cdot CO_2Et$  give *Et* 6-nitro-*N*-benzenesulphonyl-2:4-dimethylanilinoacetate, m.p. 93—95°, hydrolysed to *N*-benzenesulphonyl-6-nitro-2:4-dimethylphenylglycine, m.p. 212°, the cinchonine salt, m.p. 218° (decomp.), of which shows no mutarotation. 6-Bromo-*N*-benzenesulphonyl-2:4-dimethylaniline, m.p. 155—156°, and  $CH_2Br \cdot CO_2Et$  afford 6-bromo-*N*-benzenesulphonyl-2:4-dimethylphenylglycine, m.p. 196—197°, which does not form crystalline salts. 2:4:6-Tribromo-3-acetamidohydrocinnamic acid, decomp. 267°, gives a quinine salt, m.p. 180—183°, which does not show mutarotation. It is concluded that Br, Me, and  $NO_2$  are not large enough to cause restricted rotation in this type of compound.

F. R. S.

**Manufacture of substituted aminochrysenes.**—See B., 1936, 874.

**Diacetyl derivative of 2:6-tolylenediamine.** E. ROSTOV'TZEVA (J. Appl. Chem. Russ., 1936, 9, 1116).—*NN'*-Diacetyl-2:6-tolylenediamine melts at 310—311°, and not, as stated by Green and Lawson (J.C.S., 1891, 59, 1017), at 202°.

R. T.

**Preparation of certain 2:3-naphthalene derivatives.** H. H. HODGSON and R. L. ELLIOTT (J.C.S., 1936, 1151—1154).—Nitration of 2-iodo-*NN'*-diacetyl-1:4-naphthylenediamine (I) gives the corresponding 2- $NO_2$ -derivative (II), m.p. 309° (lit. 295°), which when refluxed with  $H_2SO_4$ -EtOH- $H_2O$  gives 2-nitro-1:4-naphthylenediamine, m.p. 241°. The ease of displacement of halogen in the 2-halogen compounds corresponding with (I) by  $NO_2$  is in the order  $I > Cl > Br$ , whilst prolonged reaction gives 2:3-dinitro-*NN'*-diacetyl-1:4-naphthylenediamine (III), m.p. above 360°, hydrolysed by  $H_2SO_4$ -EtOH to the free diamine, m.p. 207°. Reduction of (II) and (III) by  $SnCl_2$ -HCl-EtOH gives the stannichlorides of the corresponding 2- $NH_2$ - and 2:3-( $NH_2$ )<sub>2</sub>-compounds. (III) when boiled with 20% aq. NaOH gives 2:3-dinitro-1:4-dihydroxynaphthalene, m.p. 357°, methylated to the corresponding 1:4-(*OMe*)<sub>2</sub>-compound, m.p. 190°. Nitration of 4-chloro- and of 4-bromo-*NN'*-diacetyl-1:2-naphthylenediamine gives the corresponding 4-chloro-3-nitro-, m.p. 208° (oxidised by alkaline  $KMnO_4$  to phthalic acid), and 4-bromo-3-nitro-, m.p. 195°, compounds, respectively, whilst nitration of the 4-I-analogue gives 4-nitro-*NN'*-diacetyl-1:2-naphthylenediamine, m.p. 124°. 3-Chloro-aceto-1-naphthalide with diacetylorthonitric acid or conc.  $HNO_3$  yields 3-chloro-2-nitroaceto-1-naphthalide, m.p. 225°, hydrolysed by  $H_2SO_4$ -EtOH- $H_2O$  to the amine (IV), m.p. 149°. Nitration above 30° gives 2:3-dinitroaceto-1-naphthalide, m.p. 275.5°. 3-Bromo-2:3-dinitroaceto-1-naphthalide, m.p. 235°, and 3-iodo-

(VI), m.p. 250° (Ac derivative, m.p. 298°), 2-nitro-1-naphthylamine were similarly prepared. (IV), (V), and (VI) when diazotised below 20° and then boiled with EtOH give, respectively, 3-chloro-2-nitronaphthalene, m.p. 79°, and the corresponding 3-Br-, m.p. 84° (lit. 82—83°), and 3-I-, m.p. 105° (lit. 89—89.5°), compounds. Diazotisation above 20° leads to the formation of complex azo-products, m.p. 145° from (IV), and m.p. 165° from (VI).

H. G. M.

**Magenta series.** II. Higher basic members. J. T. SCANLAN (J. Amer. Chem. Soc., 1936, 58, 1427—1429; cf. A., 1935, 973).—4:4'-Diamino-3:5:3':3''-tetramethyl-, -3:5:3':5':3''-penta-methyl-, and -3:5:3':5':3''-hexamethyl-fuchsonimonium chlorides [magenta IV, V, and VI, respectively; termed below (IV), (V), and (VI), respectively] are identified by absorption spectra and analysis of their carbinol bases. The data obtained (below) confirm the view (*loc. cit.*) that the " $CH_2O$  process" for the prep. of magenta involves fission of the diaminodiphenylmethane. (IV) is prepared (details: *loc. cit.*) from 4:4'-diamino-3:5:3':5'-tetramethyldiphenylmethane (I) [from *m*-2-xylylene hydrochloride (II) and 40%  $CH_2O$  in dil. HCl at 70—75°], *o*- $C_6H_4Me \cdot NH_2$ , *o*- $C_6H_4Me \cdot NH_2 \cdot HCl$ , *o*- $C_6H_4Me \cdot NO_2$ , and  $FeCl_2 \cdot 4H_2O$ . (V) is obtained from 4:4'-diamino-3:3'-dimethyldiphenylmethane, *m*-2-xylylene (III), (II), nitro-*m*-xylene (or *o*- $C_6H_4Me \cdot NO_2$ ), and  $FeCl_2 \cdot 4H_2O$  or from (II), (III), *m*-4-xylylene, nitro-*m*-xylene, and  $FeCl_2 \cdot 4H_2O$ . (VI) is prepared from (I), (II), (III), *o*- $C_6H_4Me \cdot NO_2$ , and  $FeCl_2 \cdot 4H_2O$ .

H. B.

**Azoformamides.** II. Action of hydrochloric and hydrobromic acids on naphthaleneazoformamides. R. JUSTONI (Gazzetta, 1936, 66, 375—379).— $\beta$ - $C_{10}H_7 \cdot N_2 \cdot CO \cdot NH_2$  and conc. HCl yield 1-chloro- $\beta$ -naphthylsemicarbazide, m.p. 168.5° (decomp.), also obtained from 1:2- $C_{10}H_6Cl \cdot NH_2$  by way of 1-chloro- $\beta$ -naphthylhydrazine hydrochloride. Action of conc. HBr similarly gives 1-bromo- $\beta$ -naphthylsemicarbazide, m.p. 158° (decomp.). These compounds are oxidised by  $HNO_2$  to 1-chloro-, m.p. 190—191° (decomp.), and 1-bromo- $\beta$ -naphthaleneazoformamide, m.p. 197—198° (decomp.). Action of HBr on the last yields 1:6-dibromo- $\beta$ -naphthylsemicarbazide, m.p. 173—174° (also obtained from 1:6:2- $C_{10}H_5Br_2 \cdot NH_2$ ), and thence 1:6-dibromo- $\beta$ -naphthaleneazoformamide, m.p. 212° (decomp.).

E. W. W.

**Azo-compounds of fuchsin.** G. ODDO, M. RUSSO, and A. RODRIGUEZ (Gazzetta, 1936, 66, 405—409).—Completely diazotised fuchsin couples with PhOH to give 4:4':4''-tri-*p*-hydroxybenzeneazo-3-methyltriphenylmethane, m.p. 180°, of which the  $Ac_3$  derivative, decomp. 90°, is oxidised to the  $Ac_3$  derivative, decomp. 110—120°, of 4:4':4''-tri-*p*-hydroxybenzeneazo-3-methyltriphenylcarbinol, decomp. 160°. With  $NPhMe_2$ , (I) yields 4:4':4''-tri-*p*-dimethylaminobenzeneazo-3-methyltriphenylmethane, decomp. 145°, m.p. 258° (monohydrochloride), which gives the corresponding carbinol, decomp. 140°, m.p. 260° (Ac derivative, decomp. 132°, m.p. 150°).

E. W. W.

**Reaction of selenium dioxide with arylhydrazines.** J. J. POSTOVSKI, B. P. LUGOVKIN, and



G. T. MANDRIK (Ber., 1936, 69, [B], 1913—1916).—The action of  $\text{SeO}_2$  on aq. solutions of the hydrochlorides of  $\text{NHPh}\cdot\text{NH}_2$ , *p*-bromo- and *m*-nitrophenylhydrazine, and 1- and 2-naphthylhydrazine gives Se and the corresponding diazonium chloride.  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$  gives  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot p'$  and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_3$ .  $\text{NPh}_2\cdot\text{NH}_2$  affords  $\text{NHPh}_2$  and  $\text{N}_2$ .

**Aromatic nitro-derivatives. VIII. 1-Bromo-3:4-dinitrobenzene.** A. MANGINI (Gazzetta, 1936, 66, 343—350).—1:3:4- $\text{C}_6\text{H}_3\text{Br}(\text{NO}_2)_2$  (I) with  $\text{NH}_3$  gives *o*-bromo-2-nitroaniline (Ac derivative, new m.p. 140—141°; Bz derivative, m.p. 122—123°), and with  $\text{N}_2\text{H}_4$ , 5-bromo-2-nitrophenylhydrazine (II), m.p. 159.5—160° (Ac, m.p. 205—206°, and Bz, m.p. 197.5—198.5°, derivatives), which can be converted into  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ . (II) with  $\text{PhNCS}$  furnishes 4-phenyl-1-(5'-bromo-2'-nitrophenyl)isothiosemicarbazide, m.p. 186.5—187.5°; with  $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , *p*-aminoacetophenone-5-bromo-2-nitrophenylhydrazone, m.p. 195.5—196.5°; and with  $\text{ClCO}_2\text{Et}$ , Et *o*-bromo-2-nitrophenylhydrazoformate, m.p. 130—131°, converted by  $\text{NH}_3\text{-EtOH}$  into 1-(5'-bromo-2'-nitrophenyl)semicarbazide, m.p. 233—234° (decomp.), also obtained from (I). Action of  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$  on (I) or of  $\text{PhNCO}$  on (II) yields 4-phenyl-1-(5'-bromo-2'-nitrophenyl)semicarbazide, m.p. 236—237°. E. W. W.

**Interaction of arylsulphonylphenylhydrazines with bromine.** F. BELL (J.C.S., 1936, 1242—1244). *p*-Toluenesulphonylphenylhydrazine (I) with Br in  $\text{CHCl}_3$  gives 4-bromophenylhydrazine *p*-toluenesulphonate, m.p. 212°, and *p*-toluenesulphonyl-2:4-dibromophenylhydrazine, m.p. 166°, which with Br in  $\text{C}_5\text{H}_5\text{N}$  yields 2:4-dibromobenzenediazonium *p*-toluenesulphonate, m.p. 128°. Benzenesulphonyl-2:4-dibromoanilide, m.p. 128°, is obtained by bromination of the 4-Br compound. (I) and Br in  $\text{C}_5\text{H}_5\text{N}$  for a short time yield benzenediazonium *p*-toluenesulphonate, decomp. 93°, and after 2 days, form di-*p*-toluenesulphonylphenylhydrazine, m.p. 194°. 4-Bromophenylhydrazine (II) and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  give *p*-toluenesulphonyl-4-bromophenylhydrazine, m.p. 144°, brominated to 4-bromobenzenediazonium *p*-toluenesulphonate, decomp. 124°. Benzenesulphonylphenylhydrazine and Br in  $\text{CHCl}_3$  afford benzenesulphonyl-2:4-dibromophenylhydrazine, m.p. 177°, converted by Br in  $\text{C}_5\text{H}_5\text{N}$  into 2:4-dibromobenzenediazonium sulphinate, decomp. 98°. (II) and  $\text{PhSO}_2\text{Cl}$  yield benzenesulphonyl-4-bromophenylhydrazine, m.p. 140°, converted by Br in  $\text{C}_5\text{H}_5\text{N}$  into 4-bromobenzenediazonium benzenesulphonate. F. R. S.

**Inversion of isodiazotates into normal diazotates.** A. BRIVEC (Gazzetta, 1936, 66, 374).—This reaction (cf. this vol., 328—329) can be brought about by action of  $\text{CO}_2$  in the absence of light. E. W. W.

**Direct benzylation of monohydric phenols with benzyl chloride in presence of phosphorus pentoxide.** K. A. ANDRIANOV (J. Gen. Chem. Russ., 1936, 6, 846—851).— $\text{PhOH}$ ,  $\text{CH}_3\text{PhCl}$ , and  $\text{P}_2\text{O}_5$  in  $\text{PhMe}$  (130—135°; 8 hr.) yield *o*- and *p*-benzyl and dibenzyl-phenol. Under similar conditions *o*-cresol affords 6-benzyl- and 4:6-dibenzyl-*o*-cresol, *m*-cresol gives benzyl-, m.p. 95°, and dibenzyl-*m*-cresol,

m.p. 130—134°, and *p*-cresol yields benzyl-, b.p. 206—208°/17 mm., and dibenzyl-*p*-cresol, b.p. 250—260°/30 mm. R. T.

**Pyrolysis of chlorophenols.** F. BELL (J.C.S., 1936, 1244).—Pyrolysis of  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$  gives some diphenylene dioxide (*d*-nitro-derivative, m.p. 257°), whilst  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$  gives some 3:6-dichlorodiphenylene oxide and a phenolic substance, m.p. 83°, together with other unidentified phenolic substances.

H. G. M.

**Nitration of phenols in chloroform.** E. BARONI and W. KLEINAU (Monatsh., 1936, 68, 251—260).— $\text{HNO}_3$  (*d* 1.4) is added to phenols in  $\text{CHCl}_3$  at 20°, the following being obtained in the yields stated: *o*- (26%) and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  (61%); 3:5-dinitro-*o*-cresol (88%); 4- (25%) and 6-nitro-*m*-cresol (43%); 3:5-dinitro-*p*-cresol (87%); 4:6-dinitro-2- (93%) and 2:6-dinitro-4-cyclohexylphenol (94%); 5-nitrosalicylic acid (99%); 3-nitro-4-hydroxybenzoic acid (75%) (with some 2:4-dinitrophenol); 2:4-dinitro- $\alpha$ -naphthol (yield variable). R. S. C.

**Preparation of thymol from *m*-cresol. III. Properties of the mixture of *m*-cresol and thymol.** K. ONO and M. IMOTO (J. Soc. Chem. Ind. Japan, 1936, 39, 215b).—The m.p. of mixtures of *m*-tolyl- and thym-oxyacetic acid (which form a eutectic at 91° with 25.7% of the latter), and  $d^4$  of mixtures of *m*-cresol and thymol, are expressed graphically. E. W. W.

**Rearrangement of phenyl allyl ethers. [I. Phenyl pentenyl ethers.]** W. M. LAUER and W. F. FILBERT. II. Phenyl crotyl ether. W. M. LAUER and H. E. UNGNADE (J. Amer. Chem. Soc., 1936, 58, 1388—1392, 1392—1393).—I. Repeated saturation of  $\text{CH}_2\text{CH}\cdot\text{CH}\cdot\text{Et}\cdot\text{OH}$  with dry  $\text{HCl}$  at 0° gives approx. equal amounts of  $\gamma$ -chloro- $\Delta^a$ -pentene, b.p. 50—50.2°/150 mm., and  $\alpha$ -chloro- $\Delta^b$ -pentene (I), b.p. 62—63.2°/146—149 mm., which with  $\text{PhOH}$  and anhyd.  $\text{K}_2\text{CO}_3$  in  $\text{COMe}_2$  afford Ph  $\alpha$ -ethylallyl (II), b.p. 92—93°/15 mm. [with (III)], and Ph  $\Delta^b$ -pentenyl ether (III), b.p. 118.6°/20 mm., respectively. (II) and (III) are oxidised ( $\text{KMnO}_4$ , aq.  $\text{COMe}_2$ ) to  $\text{OPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  and  $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , respectively. (II) heated in  $\text{NPhEt}_2$  rearranges to the expected *o*- $\Delta^b$ -pentenylphenol, b.p. 131—132.5°/16 mm. [phenylcarbamate, m.p. 67—68°; Me ether, b.p. 143—145°/35 mm. (ozonolysis product,  $\text{EtCHO}$ )], also obtained from  $\text{NaOPh}$  and (I) in  $\text{C}_6\text{H}_6$ . (III) similarly rearranges unexpectedly to *o*- $\alpha$ -methyl- $\Delta^b$ -butenylphenol (IV), b.p. 125—127°/16 mm. (phenylcarbamate, m.p. 108.5—109.5°), also formed by rearrangement of Ph  $\alpha$ -methyl- $\Delta^b$ -butenyl ether (Claisen *et al.*, A., 1925, i, 656) [which is oxidised ( $\text{KMnO}_4$ , aq.  $\text{COMe}_2$ ) to  $\text{OPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ ]. Ozonolysis of the Me ether, b.p. 135—136°/35 mm., of (IV) gives  $\text{CH}_2\text{O}$ ,  $\text{MeCHO}$ , and  $\alpha$ -*o*-anisylpropaldehyde (?) (semicarbazone, m.p. 162.2—162.6°; 2:4-dinitrophenylhydrazone, m.p. 123—125°; corresponding acid, m.p. 100—101°). *o*- $\alpha$ -Methyl- $\Delta^b$ -butenylphenoxyacetic acid, m.p. 128—130°, is oxidised ( $\text{KMnO}_4$ , aq.  $\text{COMe}_2$ ) to  $\alpha$ -*o*-carboxymethoxyphenylpropionic acid (V), m.p. 170—171°. *o*- $\Delta^b$ -Pentenylphenoxyacetic acid has m.p. 108.5—110°.

II. *o*- $\alpha$ -Methylallylphenol (Claisen and Tietze, A.,

1926, 1241), obtained by rearrangement of  $\text{CHMe}:\text{CH}:\text{CH}_2\cdot\text{OPh}$  [oxidised ( $\text{KMnO}_4$ , aq.  $\text{COMe}_2$ ) to  $\text{OPh}:\text{CH}_2\cdot\text{CO}_2\text{H}$ ], with  $\text{CH}_2\text{Cl}:\text{CO}_2\text{H}$  and aq.  $\text{NaOH}$  gives *o*- $\alpha$ -methylallylphenoxycetic acid, m.p. 120—120.5°, which is oxidised to (V) (above). This result supports the constitution assigned to (IV) (above).

H. B.

**Identification of phenolic ethers as picrates.** O. L. BARIL and G. A. MEGRIDICHIAN (J. Amer. Chem. Soc., 1936, 58, 1415—1416).—The ether (1 mol.) is treated with picric acid (1.05 mols.) in  $\text{CHCl}_3$  and the (1 : 1) picrate recrystallised from  $\text{CHCl}_3$  (hydrolysis often occurs with  $\text{EtOH}$ ). The picrates of the following are new:  $\text{PhOMe}$ , m.p. 79—81°;  $(\text{CH}_2\text{Ph})_2\text{O}$ , m.p. 77—78°;  $\text{CH}_2\text{Ph}:\text{OMe}$ , m.p. 115—116°;  $\text{PhOBu}^t$ , m.p. 110—112°; *o*- $\text{C}_6\text{H}_4(\text{OEt})_2$ , m.p. 69—71°; *o*-, m.p. 118—119.5°, *m*-, m.p. 113—114°, and *p*-, m.p. 88—89°; *o*- $\text{C}_6\text{H}_4\text{Me}:\text{OMe}$ ; *o*-, m.p. 117.5—118.5°, *m*-, m.p. 114—115°, and *p*-, m.p. 110—111°; *o*- $\text{C}_6\text{H}_4\text{Me}:\text{OEt}$ ; eugenol, m.p. 62—63°; eugenol Me ether, m.p. 114—115°; isoeugenol, m.p. 46—47.5°; *p*- $\text{OH}:\text{C}_6\text{H}_4\text{OMe}$ , m.p. 43—44°; *p*- $\text{C}_6\text{H}_4(\text{OMe})_2$ , m.p. 47—48°;  $\alpha$ -, m.p. 127—127.5°, and  $\beta$ -, m.p. 113—113.5°;  $\text{C}_{10}\text{H}_7\text{OMe}$ ;  $\alpha$ -, m.p. 107—108°, and  $\beta$ -, m.p. 99—100.5°;  $\text{C}_{10}\text{H}_7\text{OEt}$ ; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{Ph}$ , m.p. 84—84.5°;  $\text{PhOEt}$ , m.p. 91—92°;  $\text{Ph}_2\text{O}$ , m.p. 108—110°; 1 : 2 : 3- $\text{C}_6\text{H}_3(\text{OMe})_3$ , m.p. 78.5—80°; *m*- $\text{OH}:\text{C}_6\text{H}_4\text{OMe}$ , m.p. 68—69.5°; *m*- $\text{OH}:\text{C}_6\text{H}_4\text{OEt}$ , m.p. 105—106°; *m*- $\text{C}_6\text{H}_4(\text{OMe})_2$ , m.p. 56—58°; *m*- $\text{C}_6\text{H}_4(\text{OEt})_2$ , m.p. 108—109°; safrole, m.p. 104—105.5°; isosafrole, m.p. 74—75°;  $\text{CPh}_3\text{OMe}$ , m.p. 56—57.5°. Some of the picrates are unstable in air.

H. B.

***o*-Phenylene sulphate or sulphurylpyrocatechol.** L. DENIVELLE (Compt. rend., 1936, 203, 194—196).— $\text{SO}_2\text{Cl}_2$  with the  $\text{Na}_1$ -derivative of pyrocatechol in dry  $\text{C}_6\text{H}_6$  at 0° affords a chloropyrocatechol (cf. A., 1894, i, 368; 1911, i, 729) and *o*-hydroxyphenyl chlorosulphonate (not purified), which is easily hydrolysed, and with hot  $\text{C}_5\text{H}_5\text{N}$  affords *o*-phenylene sulphate (I), m.p. 47° (cf. A., 1926, 1244). Thionylpyrocatechol (A., 1927, 354) cannot be oxidised to (I).

J. L. D.

***C*-Alkylresorcinols. II. Synthesis of polyalkylresorcinols.** R. C. SHAH and P. R. MEHTA (J. Indian Chem. Soc., 1936, 13, 358—367).—4 : 6-Diethylresorcinol (A., 1929, 821) in dry  $\text{Et}_2\text{O}$  containing  $\text{HCl}$  (gas) with  $\text{Zn}(\text{CN})_2$  affords a ketimine hydrochloride, decomposed by hot  $\text{H}_2\text{O}$  to give 2 : 6-dihydroxy-3 : 5-diethylbenzaldehyde (I), m.p. 68—70° (*p*-nitrophenylhydrazone, m.p. 217—219°), which with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and piperidine at room temp. affords *Et* 5-hydroxy-6 : 8-diethylcoumarin-3-carboxylate, m.p. 155—157°, and with dry  $\text{HCl}$  (gas) and 5 : 6-dimethoxy-1-hydrindone (II) in dry  $\text{EtOAc}$  is converted into 5-hydroxy-5' : 6'-dimethoxy-6 : 8-diethyl-2 : 3(3' : 2')-indenobenzopyrylium chloride, m.p. 209—210° (perchlorate, m.p. 155—158°). (I) with  $\text{Zn-Hg}$  in dil.  $\text{HCl}$  at 100° affords 2-methyl-4 : 6-diethylresorcinol, m.p. 51—53° (*di-p*-nitrobenzoyl derivative, m.p. 161—162°). Reduction ( $\text{Zn-Hg}$ ;  $\text{HCl}$ ) of orsacetophenone ( $\text{Bz}_2$  derivative, m.p. 97—98°) affords 5-methyl-4-ethylresorcinol (III) ( $\text{Hg}$  derivative; *di-p*-nitrobenzoyl derivative, m.p. 173—174°), converted through the ketimine into 4 : 6-dihydroxy-2-methyl-3-ethylbenzaldehyde (IV), m.p. 161—162° (*p*-nitrophenylhydrazone, m.p. 255—257°), the structure of which is proved by its conversion by  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and piperidine into *Et* 7-hydroxy-5-methyl-6-ethylcoumarin-3-carboxylate, m.p. 165—167°, which exhibits a strong fluorescence in conc.  $\text{H}_2\text{SO}_4$ . (IV) with (II) in dry  $\text{EtOAc}$  containing dry  $\text{HCl}$  affords 7-hydroxy-5' : 6'-dimethoxy-5-methyl-6-ethyl-2 : 3(3' : 2')-indenobenzopyrylium chloride, m.p. >300° (perchlorate, m.p. >315°). (IV) with  $\text{CH}_2\text{Ac}:\text{CO}_2\text{Et}$  containing piperidine at room temp. gives a product which with dil.  $\text{HCl}$  affords a pyrylium salt,  $\text{C}_{24}\text{H}_{25}\text{O}_5\text{Cl}$ , m.p. 295—298°, probably as a result of the condensation of the 3-acetylcoumarin first formed with a second mol. of (IV). (III) with malic acid in 85%  $\text{H}_2\text{SO}_4$  affords 7-hydroxy-5-methyl-6-ethylcoumarin, m.p. 211—212°, and with  $\text{CH}_2\text{Ac}:\text{CO}_2\text{Et}$  in 85%  $\text{H}_2\text{SO}_4$  it gives 5-hydroxy-4 : 7-dimethyl-6-ethylcoumarin, m.p. 187—189°. (III) with  $\text{Zn-Hg}$  and dil.  $\text{HCl}$  at 100° affords 5 : 6-dimethyl-4-ethylresorcinol, m.p. 145—146° (*di-p*-nitrobenzoyl derivative, m.p. 224—225°), and by the Hoesch reaction gives 2 : 4-dihydroxy-6-methyl-5-ethylacetophenone (V), m.p. 107—108° ( $\text{Bz}_2$  derivative, m.p. 61—63°; phenylhydrazone, m.p. 197—198°; ketimine hydrochloride, m.p. 237—238°), which with  $\text{Zn-Hg}$  in dil.  $\text{HCl}$  at 100° gives 5-methyl-4 : 6-diethylresorcinol (VI), m.p. 80° (*di-p*-nitrobenzoyl, m.p. 243—245°, and  $\text{Ac}_2$ , m.p. 69—70°, derivatives), converted as above into 2 : 6-dihydroxy-4-methyl-3 : 5-diethylbenzaldehyde (VII), m.p. 117—118° (*p*-nitrophenylhydrazone, m.p. 224—225°), which with  $\text{CH}_2(\text{CO}_2\text{Et})_2$  and piperidine gives *Et* 5-hydroxy-7-methyl-6 : 8-diethylcoumarin-3-carboxylate, m.p. 181—183°, thus confirming the structure of (V). (VII) with (II) in dry  $\text{EtOAc}$  containing  $\text{HCl}$  affords 5-hydroxy-5' : 6'-dimethoxy-7-methyl-6 : 8-diethyl-2 : 3(3' : 2')-indenobenzopyrylium chloride, m.p. 153—154° (perchlorate, m.p. 240—241°). (VII) with  $\text{Zn-Hg}$  in dil.  $\text{HCl}$  containing  $\text{EtOH}$  at 100° affords 2 : 5-dimethyl-4 : 6-diethylresorcinol, m.p. 107—108° (*di-p*-nitrobenzoyl derivative, m.p. 257—259°) (cf. A., 1933, 953). (VI) with malic acid and  $\text{CH}_2\text{Ac}:\text{CO}_2\text{Et}$  in 85%  $\text{H}_2\text{SO}_4$  affords, respectively, 5-hydroxy-7-methyl-6 : 8-diethylcoumarin, m.p. 183—185°, and 5-hydroxy-4 : 7-dimethyl-6 : 8-diethylcoumarin, m.p. 179—180°.

J. L. D.

**Characterisation of quinols. I.** TSUKERVANIK (Bull. Univ. Asie Centrale, 1934, No. 19, 49—60).—Toluquinol and  $\text{Br}$  in  $\text{CHCl}_3$  yield the dibromide, an oil, readily decomp. to yield 2-chloro-5-methylquinol; the tetrabromide, m.p. 138°, prepared similarly, yields di- and tri-bromo-*p*-cresol when heated above the m.p., whilst when it is heated with  $\text{H}_2\text{O}$  the product is 2 : 6-dibromo-5-methylquinol. The di-, m.p. 93° (decomp.), and tetra-chloride, m.p. 143°, prepared analogously, behave similarly to the above bromides, but are more stable. Xyloquinol dibromide, m.p. 108°, tetrabromide, m.p. 138°, dichloride, m.p. 112°, and tetrachloride, an oil, yield unidentified quinols when heated.

R. T.

**Relative directive powers of groups of the forms RO and  $\text{RR}'\text{N}$  in aromatic substitution.** X. Nitration of 4-*tert*-butoxyanisole and 4-*isopropoxy*anisole. L. J. GOLDSWORTHY (J.C.S., 1936, 1148—1150; cf. A., 1931, 479).—The nitration



of 4-*tert*.-butoxyanisole (I), b.p. 112°/10 mm. and 220°/737 mm., prepared by refluxing *p*-OH·C<sub>6</sub>H<sub>4</sub>·OMe (II), Bu<sup>γ</sup>Br, K<sub>2</sub>CO<sub>3</sub>, and COMe<sub>2</sub>, and of 4-isopropoxyanisole, b.p. 103°/12 mm., prepared by refluxing (II), KOH, Pr<sup>β</sup>I, and MeOH, has been studied. The resulting 2- and 3-NO<sub>2</sub>-derivatives are hydrolysed by conc. HCl-AcOH to 2- and 3-nitro-4-methoxyphenol, which are readily separable, thus permitting the calculation of the relative directive powers of OBU<sup>γ</sup> (328) and OPr<sup>β</sup> (229) (OMe—100). These results accord with the theory of Allan *et al.* (A., 1926, 397). A little 2:6-dinitro-4-methoxyphenol was found in the nitration product of (I).  
H. G. M.

**Desmotropy of the phenols as exemplified by Clemmensen reduction.** J. MADINAVEITIA (Anal. Fis. Quím., 1934, 32, 1100—1105).—Unlike the OH-derivatives of C<sub>6</sub>H<sub>6</sub>, those of C<sub>10</sub>H<sub>8</sub> are reduced by Zn-Hg and HCl to hydrocarbons. Differing velocities of reduction of various naphthols are interpreted as due to the presence of differing amounts of the keto-forms. 2-Methyl-1:4-naphthaquinone in Et<sub>2</sub>O is reduced (Zn, 2*N*-H<sub>2</sub>SO<sub>4</sub>) and the product with anhyd. HCN, HCl, and ZnCl<sub>2</sub> gives 1:4-dihydroxy-2-methyl-3-naphthaldehyde, m.p. 195° [*Ac* derivative, m.p. 168°; 2:4-dinitrophenylhydrazone, m.p. 245°; diphenylsemicarbazone, m.p. 215° (previous softening)], reduced to 2:3-dimethyltetrahydronaphthalene. Similarly 2-methyl- and 2:3-dimethyl-1:4-naphthaquinone are reduced to 2-methyl- and 2:3-dimethyl-tetrahydronaphthalene respectively. α-C<sub>10</sub>H<sub>7</sub>·OH is reduced more slowly and β-C<sub>10</sub>H<sub>7</sub>·OH much more slowly to tetrahydronaphthalene. PhOH, *m*- and *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>, and 1:4:2:5-C<sub>6</sub>H<sub>2</sub>MePr<sup>β</sup>(OH)<sub>2</sub> are not reduced.  
F. R. G.

**Manufacture of condensation products from phenols, formaldehyde, and amines.**—See B., 1936, 684.

**Manufacture of *p*-*N*-*sec*.-alkylaminophenols and other substituted phenols and their salts.**—See B., 1936, 685.

**Manufacture of arylaminophenols.**—See B., 1936, 780.

**Manufacture of halogenated alkenylphenols.**—See B., 1936, 824.

**Preparation of β-formalkylamino-α-*p*-anisylpropanes.**—See B., 1936, 874.

**Manufacture of unsymmetrical dialkyl or alkylaralkyl derivatives of resorcinol.**—See B., 1936, 875.

**Pyrogallol compounds of wood tar.** H. SCHULZ (Ber., 1936, 69, [B], 1870—1873).—Acetylation of a fraction, b.p. 269—271°/760 mm., of wood tar and subsequent distillation yields a viscous liquid from which 2-acetoxy-1:3-dimethoxy-5-ethylbenzene, m.p. 70° (Br<sub>2</sub>-derivative, m.p. 113°), slowly separates. It is hydrolysed to 5-ethylpyrogallol 1:3-Me<sub>2</sub> ether, b.p. 272—274° (Bz derivative, m.p. 114°), the constitution of which is established by its oxidation to 2:6-dimethoxy-*p*-benzoquinone, m.p. 255°, and its demethylation to 5-ethylpyrogallol, m.p. 86—87° (acetate, m.p. 90°). Similar treatment of a wood tar fraction, b.p. 256—260°/760 mm., affords pyrogallol 1-Me ether [4:5:6-Br<sub>3</sub>-derivative, m.p.

111°; Br<sub>1</sub>-, m.p. 138.5°, Br<sub>2</sub>-, m.p. 148°, and Br<sub>3</sub>-, m.p. (?) 121°, -derivatives of 1:2:3-OMe·C<sub>6</sub>H<sub>3</sub>(OAc)<sub>2</sub>]. Analogously the fraction, b.p. 264—266°/760 mm., gives 4:5-diacetoxy-*m*-tolyl Me ether, m.p. 88°, hydrolysed to 5-methylpyrogallol 1-Me ether, m.p. 68°, which immediately reduces AgNO<sub>3</sub> (corresponding 1-Et ether, m.p. 116°); it is obtained synthetically from 5-methylpyrogallol, Me<sub>2</sub>SO<sub>4</sub>, and NaOH. 5-Methylpyrogallol 2-Me ether, m.p. 138° (acetate, m.p. 121°), is described.  
H. W.

**9-Acetamido-2:3:4:6-tetramethoxyphenanthrene.** T. M. SHARP (J.C.S., 1936, 1234—1236).—Trimethylgallaldehyde with conc. H<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> (1:9) (20 min.; -8°) yields 2-nitro-3:4:5-trimethoxybenzaldehyde (I), m.p. 76—77°, together with some 2:6-dimethoxy-*p*-benzoquinone and 4:5-dinitro-1:2:3-trimethoxybenzene. (I) with *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·CO<sub>2</sub>Na and Ac<sub>2</sub>O (135°; 8 hr.) affords 2-nitro-3:4:5-trimethoxy-α-*p*-methoxyphenylcinnamic acid, m.p. 170—171°, which with NH<sub>2</sub>-aq. FeSO<sub>4</sub> (1 hr.; 100°) gives the dimorphous 2-NH<sub>2</sub>-compound, m.p. 167—168° and 159°, which in turn with aq. H<sub>2</sub>SO<sub>4</sub>-NaNO<sub>2</sub> affords 2:3:4:6-tetramethoxyphenanthrene-9-carboxylic acid (II), m.p. 172—173°, and a compound, m.p. 162—163°. The crude hydrazide of the Et ester of (II) with 3-8*N*-EtOH-HCl and amyl nitrite yields the azide, which on refluxing with MeOH is converted into the urethane, which with 10% MeOH-KOH (65°; 3.5 hr.) yields 9-amino-2:3:4:6-tetramethoxyphenanthrene, m.p. 157—159° (*Ac* derivative, m.p. 152—153°).  
F. N. W.

**Action of ethyl diazoacetate on thiophenols.** E. MULLER and A. FREYTAG (J. pr. Chem., 1936, [ii], 146, 56—57).—Addition of CHN<sub>2</sub>·CO<sub>2</sub>Et to PhSH at 80° gives Et phenylthiolacetate, b.p. 147.6°/12 mm. Et *p*-tolylthiolacetate, b.p. 157°/14 mm., is obtained similarly.  
H. W.

**Anthrylmercapturic acid.**—See this vol., 1019.

**Action of sodium acetylide on cyclic ketones.** I. Synthesis of 1-acetylenylcyclohexanol. R. J. LEVINA and E. I. VINOGRADOVA (J. Appl. Chem. Russ., 1936, 9, 1299—1302).—cycloHexanone and CNa;CH in Et<sub>2</sub>O give 1-acetylenylcyclohexanol (55% yield), converted by H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> at 120—140° into Δ<sup>1</sup>-cyclohexenylacetylene.  
R. T.

**Hydrogenation of phenylated carbinols.** P. A. LEVENE [with M. KUNA] (J. Biol. Chem., 1936, 115, 275—277).—Although hydrogenation (PtO<sub>2</sub>) of CHPhMe·OH in AcOH gives much PhEt and little cyclohexylmethylcarbinol (I), and the Ph is unaffected in MeOH, (I) is the main product in MeOH-AcOH (9:1). Change of catalyst is without effect. Other Ph derivatives are hydrogenated in MeOH even under pressure without affecting the Ph. The conclusions of Levene *et al.* (A., 1930, 1178) are confirmed.  
R. S. C.

**Compounds related to phenacetin.** (MISS) B. N. KATRAK (J. Indian Chem. Soc., 1936, 13, 334—336).—From *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·ONa and CH<sub>2</sub>Cl·CH<sub>2</sub>·OH was prepared *p*-nitro-β-hydroxy-, m.p. 101—102° (*Ac*, m.p. 85—87°, Bz, m.p. 116°, and salicyl derivatives, m.p. 133°), converted by PCl<sub>5</sub> into β-chloro-*p*-nitro-phenetole, m.p. 67—68°. *p*-Acetamido-, m.p.

116—117° (*Ac* derivative, m.p. 130°), *o*-, b.p. 180—182°/4 mm. (*Ac*, b.p. 201—202°/4 mm. and *Bz* derivatives, m.p. 75—76°), and *m*-nitro- $\beta$ -hydroxyphenetole, m.p. 90—91°, were prepared from the corresponding phenoxide. F. R. S.

**Synthesis of 2 : 4-dihydroxymethylanisole and of some derivatives.** R. QUELET and M. ANGLADE (Compt. rend., 1936, 203, 262—264).—PhOMe with CH<sub>2</sub>O saturated with HCl gas at 0° affords a product which when treated similarly, but at 75°, gives 2 : 4-dichloromethylanisole (I), m.p. 66°, oxidised (KMnO<sub>4</sub>) to 4-methoxyisophthalic acid (A., 1929, 65). (I) with NaOAc in hot AcOH affords 2 : 4-diacetoxymethylanisole, m.p. 47—48°, hydrolysed (20% EtOH-KOH at room temp.) to 2 : 4-dihydroxymethylanisole, m.p. 100—101° (phenylcarbamate, m.p. 152°; Me<sub>2</sub>, Et<sub>2</sub>, Pr<sub>2</sub>, Bu<sub>2</sub>, and diisooamyl ethers, b.p. 155°/18 mm., 166°/16 mm., 183°/17 mm., 178°/6 mm., and 188°/7 mm., respectively). J. L. D.

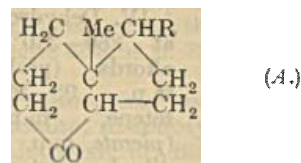
**Lederer-Manasse reaction. Synthesis of vanillyl alcohol.** G. GOETHALS (Natuurwetensch. Tijds., 1936, 18, 249—255).—Guaiacol and CH<sub>2</sub>O react in NaOH solution to give vanillyl alcohol, 1-methoxy-2 : 4-di(hydroxymethyl)phenol, m.p. 105—106° (dibromide, m.p. 127—127.5°), and 4 : 4'-dihydroxy-3 : 3'-dimethoxy-5 : 5'-di(hydroxymethyl)diphenylmethane, m.p. 146.5—147° (dibromide, m.p. 181—183°). S. C.

**$\beta$ -Cholesterol.** E. A. EVANS, jun., and R. SCHOENHEIMER (J. Biol. Chem., 1936, 115, 17—18).—The portion of " $\beta$ -cholesterol" (I) (A., 1932, 844) not pptd. by digitonin affords  $\Delta^2$ -cholestadiene and is epiallocholesterol (II). (II) and dihydrocholesterol give a mol. compound identical with (I), but with const. m.p. 154°; the m.p. 160° previously (A., 1908, i, 164) reported for (I) is probably due to the presence of cholesterol pinacone. R. S. C.

**Constitution of cholesterol. XII. Isomerisation by monochloroacetic acid.** F. PIRRONE (Gazzetta, 1936, 66, 398—404).—Cholesterol and CH<sub>2</sub>Cl-CO<sub>2</sub>H mixed in CHCl<sub>3</sub> and exposed to sunlight, or fused together at 125—155°, yield an isocholesterol (metacholesterol ?) (I), m.p. 139—140°, and its monochloroacetate (II), m.p. 159—161°, which with Br in AcOH gives a dibromodihydro-derivative, m.p. 110—111°. (II) is converted by NaOAc into (I): it is not affected by NH<sub>3</sub>. With Ac<sub>2</sub>O (I) and (II) give a product of which the m.p. is not depressed on admixture with that derived from cholesterol or its *Ac* derivative. E. W. W.

**Constitution of vitamin-D<sub>2</sub>. II.** A. WINDAUS and W. GRUNDMANN (Annalen, 1936, 524, 295—299; cf. this vol., 69).—Oxidation of vitamin-D<sub>2</sub> (I) by KMnO<sub>4</sub> yields small amount of HCO<sub>2</sub>H, whilst small quantities of CH<sub>2</sub>O are obtained by its ozonisation. The results are not considered to establish the presence of :CH<sub>2</sub> since somewhat similar experience results with ergosterol from which :CH<sub>2</sub> is absent. From the KMnO<sub>4</sub> oxidation a ketone, C<sub>19</sub>H<sub>32</sub>O (semicarbazone, m.p. 222°; oxime, m.p. 107°), is isolated, which is hydrogenated (spongy Pd in Et<sub>2</sub>O) to the ketone of

Windaus *et al.* (*loc. cit.*) and hence has the constitution A (R=CHMe·CH:CH·CHMePr <sup>$\beta$</sup> ).



Ozonisation of (I) in AcOH and fission of the ozonide with steam affords the acid (*A* with R=CHMe·CO<sub>2</sub>H), m.p. 124°. These results with those of Heilbron *et al.* (A., 1935, 1036, 1235) are considered to support the author's formulation of (I). The contrary views of Bernal *et al.* (A., 1935, 1120) are not explained.

H. W.

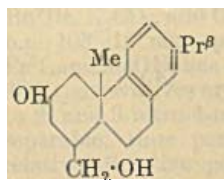
**Oestrogenic activity of synthetic polycyclic compounds.** J. W. COOK, E. C. DODDS, and W. LAWSON (Proc. Roy. Soc., 1936, B, 121, 133—141).—Tests for oestrogenic activity have been carried out with 18 diols, prepared by the action of Grignard reagents on polycyclic quinones. Substances of higher activity than 9 : 10-dihydroxy-9 : 10-di-*n*-propyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene have not been found. In the dibenzanthracene series the effects of branching and cyclisation of the alkyl-group have been studied. Diols with polynuclear skeletons other than dibenzanthracene may show some activity. In the 9 : 10-dihydroxy-9 : 10-di-alkyl- (or -aryl)-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene series, the isopropyl, m.p. 288—290°, allyl-, m.p. 210—211°, isobutyl-, m.p. 212°, cyclopentyl-, m.p. 281—282°, cyclohexyl-, m.p. 279—280°, and phenyl-, m.p. 346°, compounds were prepared. In the corresponding 9 : 10-dihydroanthracene series the allyl-, m.p. 111—112°, *n*-propyl-, m.p. 171—172°, *n*-butyl-, m.p. 158°, *n*-amyl-, m.p. 179—180°, and cyclopentyl-, m.p. 216°, compounds were prepared. Other new substances prepared were 9 : 10-dihydroxy-9 : 10-di- $\alpha$ -naphthyl-9 : 10-dihydrophenanthrene, m.p. 265—266°, 1 : 2-dihydroxy-1 : 2-di-*n*-propyl-, m.p. 145°, and -di-*n*-amyl-1 : 2-dihydrochrysene, m.p. 107—108°, 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10 : 1' : 2' : 3' : 4'-hexahydro-1 : 2-benzanthracene, m.p. 230—231°, 9 : 10-dihydroxy-9 : 10-di-*n*-butyl-, m.p. 154°, and -9 : 10-diphenyl-9 : 10 : 1' : 2' : 3' : 4'-hexahydro-2 : 3-benzanthracene, m.p. 222—223°. 1-Hydroxy-1 : 2 : 3 : 4-tetrahydrophenanthrene, m.p. 100—101° (acetate, m.p. 63—64°), was obtained by hydrogenation of the corresponding keto-compound. Further hydrogenation gave *s*-octahydrophenanthrene. E. A. H. R.

**Constituents of hinokiol. II. Comparison of hinokin and cubebinolide. III. Constitution of hinokiol. IV. Structure of hinokiol.** S. KEIMATSU and T. ISHIGURO (J. Pharm. Soc. Japan, 1935, 55, 96—99, 99—105, 186—195).—II. Comparison of derivatives leads to the conclusion that hinokin is identical with cubebinolide (Steer, Annalen, 1840, 36, 331). Diphenylhinokin has m.p. 138°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —172.4° in CHCl<sub>3</sub>.

III. Reduction of hinokiol (HI-red P) yields a substance (I), C<sub>19</sub>H<sub>32</sub>, b.p. 320—335°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +5.50°, containing one double linking, and another substance, b.p. 290—310°, also obtained by further reduction of



(I). Dehydrogenation (Se at 280—320°) of (I) gives retene (?), m.p. 95—98°.



IV. Dehydrogenation (Se at 280—340°) of hinokiol affords (probably) retene, m.p. 98—99°, hydroxyretene, m.p. 176—177° (picrate, m.p. 176—177°), and dihydroxyretene, m.p. 234—235°. Adopting the mol.

formula  $C_{19}H_{28}O_2$  for hinokiol, the appended structure is suggested.

CH. ABS. (r)

**Sterols and bile acids.** U. WESTPHAL (Chem. Ztg., 1936, 60, 774—777).—A review.

**Fixed oil of poke root.**—See this vol., 1306.

**Seed oil of *Cuscuta reflexa*, Roxb.**—See this vol., 1166.

**cycloHexane series.** II. Formation of isomeric arylaminocyanomethylcyclohexanes in the condensation of the cyanohydrins of the methylcyclohexanones with arylamines. M. W. BUKSHI, R. D. DESAI, R. F. HUNTER, and M. HUSSAIN (J.C.S., 1936, 1159—1161; cf. this vol., 846).—Condensation of 4-methylcyclohexanone cyanohydrin with  $NH_2Ph$ ,  $p-C_6H_4Br.NH_2$ ,  $o-$  (I),  $m-$ , and  $p-C_6H_4Me.NH_2$ ,  $\alpha-$  and  $\beta-C_{10}H_7.NH_2$  yields [with the exception of (I)] pairs of isomeric arylaminocyanomethylcyclohexanes  $CHMe \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CN} \\ \text{C} \cdot \text{NHR} \end{smallmatrix}$ . The

following are described, with the corresponding carboxylic acids and their amides, the recorded m.p. being for the A and B forms, respectively:  $R=Ph$ , m.p. 107° and 92—93° [A amide, m.p. 166° (lit. 161°); B amide, m.p. 174°; A acid, m.p. 186° (lit. 179°)];  $p-C_6H_4Br$ , m.p. 126° and 88—89° (amides, m.p. 178° and 158°; A acid, m.p. 184°);  $p-$ , m.p. 104° and 79° (amides, m.p. 155° and 145°),  $m-$ , m.p. 115° and 82—83° (amides, m.p. 137—138° and 117—118°),  $o-C_6H_4Me$ , m.p. 100° (amide, m.p. 143°);  $\alpha-$ , m.p. 151—152° and 165° (amides, m.p. 138° and 204°),  $\beta-C_{10}H_7$ , m.p. 152° and 132° (amides, m.p. 270° and 205°). The 3-methyl compounds are obtained similarly:  $Ph$ , m.p. 75° and 95° (amides, m.p. 97° and 92°);  $p-C_6H_4Br$ , m.p. 88—89° (amide, m.p. 137°);  $p-$ , m.p. 78° (amide, m.p. 165°),  $o-C_6H_4Me$ , m.p. 86°;  $\alpha-$ , m.p. 137° (amide, m.p. 169°), and  $\beta-C_{10}H_7$ , m.p. 136° (amide, m.p. 186°); and the following 2-methyl compounds:  $R=Ph$ , m.p. 126° and 88° (amides, m.p. 128° and 147°; A acid, m.p. 187°);  $p-C_6H_4Br$ , m.p. 99° (amide, m.p. 154°);  $p-$ , m.p. 140° (amide, m.p. 185°),  $m-$ , m.p. 101° (amide, m.p. 112°), and  $o-C_6H_4Me$ , m.p. 121°;  $\alpha-$ , m.p. 118°, and  $\beta-C_{10}H_7$ , m.p. 110—111° and 105° (A amide, m.p. 178°).

F. N. W.

**Mechanism of amination by sodamide.** II. Formation of unsubstituted aromatic amidines by the action of sodamide on aromatic nitriles. A. KRSSANOV and I. POLJAKOVA (Bull. Soc. chim., 1936, [v], 3, 1600—1606; cf. this vol., 198).— $NaNH_2$  and aromatic nitriles give amidines, best isolated as carbonates, thus proving that reaction of  $NaNH_2$  also with  $C_5H_5N$  and Schiff's bases occurs by addition to the C.N. The following are prepared, best in  $PhMe$  at 150°. Benz. [carbonate, m.p. 91—94°;

platinichloride, m.p. 192—194° (corr.); salicylate, m.p. 200—203°; picrate, m.p. 228—232° (cf. lit.)],  $p$ -tolu. [carbonate, m.p. 118—122°; picrate (I) (prep. in  $C_6H_6$ ), decomp. 219°; salicylate, m.p. 210—220°; platinichloride, m.p. 198° (cf. lit.)], and  $\beta$ -naphth-amidine, m.p. 133—136° (lit. 145°) [carbonate, m.p. 128—132°; platinichloride, m.p. 199—202° (cf. lit.)].  $MeCN$  and  $NaNH_2$  react violently, but no amidine could be isolated. Crystallisation of (I) from  $EtOH$  gives  $\omega$ -ethoxytolualdimine picrate. Cornell's salts (A., 1929, 173) were probably mixtures of nitriles and sodalkamides. R. S. C.

**p-Phenylphenacyl esters of organic acids.** T. L. KELLY and E. A. MORISANI (J. Amer. Chem. Soc., 1936, 58, 1502—1503).—The following are prepared by the method of Drake *et al.* (A., 1932, 745):  $p$ -phenylphenacyl  $m-$ , m.p. 155°, and  $p-$ , m.p. 160°, -bromo-,  $o-$ , m.p. 123°,  $m-$ , m.p. 154°, and  $p-$ , m.p. 160°, -chloro-,  $o-$ , m.p. 143°,  $m-$ , m.p. 147°, and  $p-$ , m.p. 171° (sealed tube), -iodo-,  $o-$ , m.p. 140°, and  $m-$ , m.p. 153°, -nitro-, and  $p$ -cyano-, m.p. 165°, -benzoates;  $o-$ , m.p. 146°,  $m-$ , m.p. 193°, and  $p-$ , m.p. 192°, -nitrocinnamates; diphenylacetate, m.p. 111°. H. B.

**Synthesis of derivatives of s-diphenylethane related to materials occurring naturally.** I. **Synthesis of ring system proposed for calciferol.** S. NATIELSON and S. P. GOTTFRIED (J. Amer. Chem. Soc., 1936, 58, 1432—1438).—Benzylidenephthalide [from  $CH_2Ph.CO_2H$  and  $o-C_6H_4(CO_2O)$  at  $>240^\circ$ ; cf. Org. Synth., 1933, 13, 10] is reduced (Na-Hg, aq. KOH) to benzylphthalide, m.p. 61°, which when dissolved in  $EtOH-KOH$ , the  $EtOH$  subsequently evaporated, and the residue heated at 180°, gives stilbene- $o$ -carboxylic acid, m.p. 160°. This is reduced (Na-Hg on aq. Na salt) to  $o$ - $\beta$ -phenylethylbenzoic [s-diphenylethane- $o$ -carboxylic] acid, m.p. 130° [chloride (I), b.p. 202°/20 mm., m.p. 50—55°, obtained from  $SOCl_2$  and the Hg-free acid only; Et ester (II), b.p. 205°/18 mm.; anilide (III), m.p. 137°, from (I) and  $NH_2Ph$  at 90° or the acid and  $NH_2Ph$  at  $<240^\circ$ ]. (I) and  $NaOAc$  in  $Ac_2O$  at 180° afford  $o$ - $\beta$ -phenylethylbenzoic acetic anhydride, m.p. 95°, whilst reduction (Na and  $Bu^oOH$  in  $PhMe$ ) of (II) gives products, b.p. 177°/20 mm. and 195°/20 mm. (III) and  $PCl_5$  followed by anhyd.  $SnCl_2$  in  $Et_2O-HCl$  give a complex,  $C_{21}H_{20}NCl_3Sn$ , decomp. 213°, hydrolysed (dil. HCl) to  $o$ - $\beta$ -phenylethylbenzaldehyde (IV) (phenylhydrazone, m.p. 95°), which with  $CH_2(CO_2H)_2$  and  $C_5H_5N$  at 90° yields  $o$ - $\beta$ -phenylethylcinnamic acid (V), m.p. 149—150°, reduced (Na-Hg, aq.  $Na_2CO_3$ ) to  $\beta$ - $o$ -phenylethylphenylpropionic [s-diphenylethane- $o$ - $\beta$ -propionic] acid (VI), m.p. 110—111°. (IV),  $Ac_2O$ , and  $NaOAc$  or  $KOAc$  at 180—200° give some (V) and (mainly)  $o$ - $\beta$ -phenylethylbenzylidene diacetate, m.p. 85°, which with  $NaOAc$  and  $AcOH$  at 200° affords (V). The chloride, b.p. 155—165° (bath)/0.002—0.004 mm., of (VI) with  $AlCl_3$  in light petroleum yields 4- $\beta$ -phenylethyl-1-indanone, not obtained cryst. [oxime, m.p. 135°, reduced (Na,  $EtOH$ ) to 1-amino-4- $\beta$ -phenylethylindane (hydrochloride, m.p. 192°)], reduced (Clemmensen) to 4- $\beta$ -phenylethylindane, b.p. 115—120°/0.0001 mm., which has the ring-system proposed (lit.) for calciferol and tachysterol. H. B.

Esters of triphenylpropionic acid and their application to the identification of alcohols. A. GARCÍA BANUS and F. BOQUÉ (Anal. Fis. Quim., 1935, 33, 72—80).— $\text{MgCl} \cdot \text{CH}_2\text{Ph}$  and  $\text{RCHO}$  (R is Ph or  $p\text{-C}_6\text{H}_4\text{OMe}$ ) with  $\text{CHPhCl} \cdot \text{COCl}$  yield  $\text{CHPhCl} \cdot \text{CO}_2\text{CHR} \cdot \text{CH}_2\text{Ph}$ , which when distilled at 20 mm. gives  $\text{CHPh} \cdot \text{CHR}$  and  $\text{CH}_2\text{PhCl}$ .  $\text{CPh}_2 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$  (improved prep.) with  $\text{SOCl}_2$  gives the *chloride*, m.p. 94°, which with  $\text{MgCl} \cdot \text{CH}_2\text{Ph}$  and  $\text{PhCHO}$  yields the  $\alpha\beta$ -diphenylethyl ester, m.p. 114°, and with  $\text{MgPrBr}$  and  $\text{COMeEt}$  the  $\beta$ -methyl- $\beta$ -ethylbutyl ester, m.p. 170° (also obtained from  $\text{CMeEtPr} \cdot \text{OH}$ ), and with the appropriate alcohol gives the following esters:  $\text{Pr}^\alpha$ , m.p. 109°,  $\text{Pr}^\beta$ , m.p. 138°,  $\text{Bu}^\alpha$ , m.p. 99°,  $\text{Bu}^\beta$ , m.p. 84°, *amyl*, m.p. 92.5°, *isoamyl*, m.p. 72°, *sec.-amyl*, m.p. 114°, *sec.-isoamyl*, m.p. 63°,  $[\alpha]_D + 85.4^\circ$  in  $\text{EtOH}$ ,  $\alpha$ -methylbutyl, m.p. 60°, *hexyl*, m.p. 92°, *heptyl*, m.p. 95.5°, *octyl*, m.p. 74°, *nonyl*, m.p. 77°, *decyl*, m.p. 78°, *undecyl*, m.p. 93.5°, *dodecyl*, m.p. 88°, *cetyl*, m.p. 62°, *octadecyl*, m.p. 70°,  $\alpha$ -ethylpropyl, m.p. 104°, *allyl*, m.p. 108°, *Ph*, m.p. 124°, *bornyl*, m.p. 173°, *benzyl*, m.p. 117°, *menthyl*, m.p. 138°,  $[\alpha]_D - 96.5^\circ$  in  $\text{EtOH}$ . The *menthylamine* salt has m.p. 125°,  $[\alpha]_D - 33^\circ$  in dil.  $\text{EtOH}$ . F. R. G.

Manufacture of aromatic or heterocyclic carboxylic acid amides of high mol. wt.—See B., 1936, 875.

Action of acetylene on ethyl acetoacetate in presence of mercury salts. B. CIOCCA and (SIGNA.) M. SCATTOLA (Gazzetta, 1936, 66, 394—398).— $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{Et}$  treated with  $\text{C}_2\text{H}_2$  under slight pressure in  $\text{H}_2\text{SO}_4$  containing Hg salts reacts violently, after an induction period, and gives  $\text{Et } 2:6\text{-dimethyl-}\Delta^2\text{-cyclohexen-4-one-1-carboxylate}$ ,  $\text{Et}_2 2:4\text{-dimethyl-}\Delta^4\text{-cyclohexen-6-one-1:3-dicarboxylate}$ , and  $\text{Et ethylideneacetoacetate}$ . E. W. W.

Modification of the Clemmensen method of reduction. E. L. MARTIN (J. Amer. Chem. Soc., 1936, 58, 1438—1442).—Improved results in the reduction of many  $\beta$ -aroylpropionic acids by the Clemmensen method are often obtained by addition of a layer of  $\text{PhMe}$  to the reaction mixture. The same modification is advantageous in the reduction (Zn dust, aq.  $\text{NaOH}$ ) of anthrones to anthracenes. It is suggested that Clemmensen reduction occurs thus:  $\text{CO} \rightarrow \text{CH}(\text{OH})$ ,  $\text{CHCl} \rightarrow \text{CH}_2$ ; this view is supported by the ready production of  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  from  $\gamma$ -phenyl- $\gamma$ -butyrolactone.

$\beta$ -m-Nitrobenzoylpropionic acid, m.p. 162—164° (*Me* ester, m.p. 68—69°), from  $\text{CH}_2\text{Bz} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ,  $\text{HNO}_3$  (d 1.5), and conc.  $\text{H}_2\text{SO}_4$  at  $-10^\circ$  to  $0^\circ$  and then at  $15^\circ$ , is reduced (aq.  $\text{NH}_4\text{HS}$  at  $<50^\circ$ ) to the *m-NH*<sub>2</sub>-derivative, m.p. 131—132° [*hydrochloride*, m.p.  $>250^\circ$  (decomp.) (all m.p. except this are corr.)], converted (diazo-method) into  $\beta$ -m-hydroxybenzoylpropionic acid, m.p. 144—145° [*semicarbazone*, m.p. 198—200°; *Me* ether, m.p. 107—108° (lit. 110—111°), reduced (as above) in small quantities to  $\gamma$ -m-anisylbutyric acid (60% yield)].  $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  similarly leads to  $\beta$ -3-nitro-, m.p. 148—150° (*Me* ester, m.p. 50—51°),  $\beta$ -3-amino-, m.p. 148—149° [*hydrochloride* (+ $\text{H}_2\text{O}$ )],

m.p. 144—146°,  $\beta$ -3-hydroxy-, m.p. 172—173° (*semicarbazone*, m.p. 188—190°), and  $\beta$ -3-methoxy-, m.p. 120—121° (*semicarbazone*, m.p. 172—173°), 4-methylbenzoylpropionic acids and thence  $\gamma$ -3-methoxy-4-methylphenylbutyric acid, m.p. 70—71° (86% yield).

H. B.

Ultra-violet absorption spectra of thyroxine, thyronine, tyrosine, di-iodotyrosine, and thyroglobulin. L. J. HEIDT (J. Biol. Chem., 1936, 115, 223—225).—The spectra were all sufficiently similar to prevent a differential detection of these substances spectrographically.

H. D.

Octylsalicylic acid.—See B., 1936, 685.

6-Nitro- and 6-amino-2:3-hydroxynaphthoic acid.—See B., 1936, 686.

Manufacture of a new 5-hydroxyhydrindene-carboxylic acid and derived amides.—See B., 1936, 825.

Preparation of lithocholic acid from cholesterol. R. SCHOENHEIMER and (MISS) F. BERLINER (J. Biol. Chem., 1936, 115, 19—24).—The dibromide of *Me* 3-hydroxy- $\Delta^5$ -cholenate and  $\text{CrO}_3$  give a product, which with  $\text{NaI} \cdot \text{MeOH}$  affords *Me*  $\Delta^4$ -cholen-3-onate (I) (55% yield), m.p. 125° [*semicarbazone*, m.p. 229° (decomp.)], hydrolysed to the corresponding acid (II), m.p. 185—186°, the absorption spectrum (max. at 240  $\text{m}\mu$ ) of which proves the position of the ethylenic linking. With  $\text{H}_2$ - $\text{PtO}_2$  in  $\text{EtOH} \cdot \text{Et}_2\text{O}$  (I) gives 80% of *Me* lithocholate and 20% of *Me* 3-hydroxyallocholate, separable by digitonin. With  $\text{H}_2$ -Pd (II) gives a difficulty separable mixture of much 3-keto- with a little 3-ketoallocholic acid. Thus hydrogenation of the CO occurs solely in such a way that the OH formed is *trans* to the H in position 5.

R. S. C.

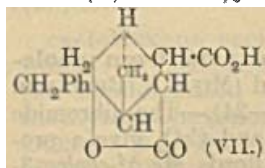
Synthesis of *dl-cis*- and *-trans*-1-isopropylcyclopropane-1:2-dicarboxylic acids and a resolution of the *cis*-acid. Synthesis of umbellulanic acid. S. K. RANGANATHAN (Current Sci., 1936, 5, 20, and J. Indian Chem. Soc., 1936, 13, 419—425).— $\text{CH}_2\text{CPr}^\beta \cdot \text{CO}_2\text{Et}$  and  $\text{CHN}_2 \cdot \text{CO}_2\text{Et}$  give  $\text{Et}_2$   $\alpha$ -isopropyl- $\Delta^1$ -pyrazoline-3:5-dicarboxylate, b.p. 158°/1 mm., which at 200° loses to form the mixed  $\text{Et}_2$  ester of *dl-trans*-1-isopropylcyclopropane-1:2-dicarboxylic acid (cf. this vol., 993), from which ( $\text{AcCl}$ ) the *cis-anhydride*, b.p. 140°/20 mm., and *cis*-acid (*p-tolil*, m.p. 89°) are obtained (cf. *loc. cit.*). The *d-cis*-acid is isolated through the *brucine* salt (+9 $\text{H}_2\text{O}$ ),  $[\alpha]_D^{20} - 25.63^\circ$  in  $\text{EtOH}$ , and the *l-cis*-acid (*umbellulanic acid*) through the *cinchonidine* salt.

E. W. W.

Introduction of substituents into the cyclopentadiene nucleus. I. 1- and 2-Benzylcyclopentadiene. K. ALDER and H. HOLZRICHTER (Annalen, 1936, 524, 145—180).—*cyclopentadiene* in  $\text{C}_6\text{H}_6$  is treated successively with K and  $\text{CH}_2\text{PhCl}$  giving unchanged material, a mixture (I) of 1-,  $\text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{C} \cdot \text{CH}_2\text{Ph}$ , and 2-benzylcyclopentadiene,  $\text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{C} \cdot \text{CH}_2\text{Ph}$ , and *dibenzylcyclopentadiene* (II),  $\text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{C} \cdot \text{CH}_2\text{Ph}$ , b.p. 200—210°/13 mm., which readily passes into a *dimeride*, m.p. 88°. (I) does not yield  $\text{Ph}_2$  when



heated with Se at 300°, thus excluding the possibility of the presence of cyclohexadiene derivatives. Treatment of (I), b.p. 115—120°/13 mm., after being depolymerised by heating for some time at 115°, with maleic anhydride in dry Et<sub>2</sub>O affords 3-benzyl-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride (III), m.p. 123° [corresponding acid (IV), m.p. 165° (decomp.)], and 4-benzyl-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride (V), m.p. 80°, best isolated through the Na<sub>2</sub> salt of the corresponding acid (VI), m.p. 154—155° (decomp.). Catalytic hydrogenation of (V) (colloidal Pd) yields 4-benzyl-3:6-endomethylenehexahydrophthalic acid, m.p. 153°, whereas (VI) in presence of PtO<sub>2</sub> gives 4-cyclohexylmethyl-3:6-endomethylenehexahydrophthalic acid, m.p. 159° (decomp.). Oxidation of (V) with 4% KMnO<sub>4</sub> gives BzOH and *cis-cis-cis-cis*-cyclopentane-1:2:3:4-tetracarboxylic acid. (V) with 50% H<sub>2</sub>SO<sub>4</sub> at room temp. gives the lactonic acid (VII), m.p. 189° (*Me* ester, m.p. 126°), isomerised by NaOMe to the

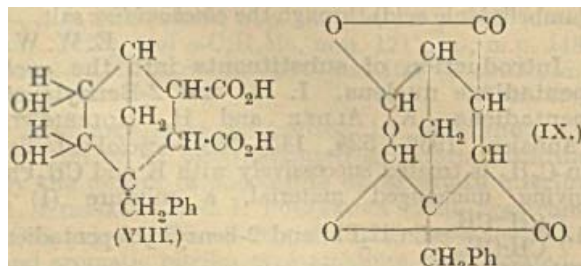


156°, also obtained by the action of CH<sub>3</sub>Ph·MgCl on trans-4-keto-3:6-endomethylene-

hexahydrophthalic acid, thus establishing the position of the CH<sub>2</sub>Ph. Ozonisation of (V) in EtOAc at 0° and treatment of the solution with H<sub>2</sub>-Pd-CaCO<sub>3</sub> gives the "O<sub>5</sub> substance," C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>, m.p. 203—204°, and (?) CH<sub>2</sub>Ph·CO<sub>2</sub>H.

Hydrogenation of (IV) (colloidal Pd) yields 3-benzyl-3:6-endomethylenehexahydrophthalic acid, m.p. 169° (decomp.) (anhydride, m.p. 83°), whereas in presence of PtO<sub>2</sub> 3-cyclohexylmethyl-3:6-endomethylenehexahydrophthalic acid, m.p. 144—145° (anhydride, m.p. 81°), is produced. Treatment of (III) with boiling MeOH gives two *Me* H esters, m.p. 165° and m.p. 114°, respectively, thus proving that CH<sub>2</sub>Ph is unsymmetrically placed with respect to

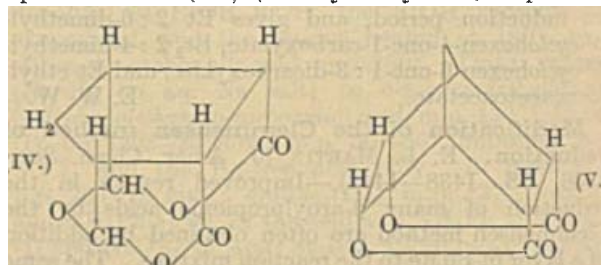
$\begin{matrix} \text{C}=\text{CO} \\ \text{C}=\text{CO} \end{matrix} \text{O}$  and establishing the constitution of (III). Either ester is transformed by CH<sub>3</sub>N<sub>3</sub> into the non-cryst. *Me*<sub>3</sub> ester, isomerised by NaOMe and then hydrolysed to the *trans*-acid, C<sub>16</sub>H<sub>16</sub>O<sub>6</sub>, m.p. 204—205°. (III) and 50% H<sub>2</sub>SO<sub>4</sub> give the lactonic acid, m.p. 239—240° (*Me* ester, m.p. 86°). With PhN<sub>3</sub> in EtOAc (III) yields the hydrotriazole, m.p. 239°. (III) with 4% KMnO<sub>4</sub> gives *cis-cis-cis-cis*-1-benzylcyclopentane-1:2:3:4-tetracarboxylic acid, m.p. 197° (*mono*-, m.p. 216°, and *di*-, m.p. 161°, -anhydride); milder conditions lead to the (OH)<sub>4</sub>-acid, (VIII), m.p. 216°



(decomp.) (*mono*-, m.p. 132°, and *di*-, m.p. 111°, -acetyl anhydride), and (IX), oxidised to a stereo-isomeric 1-benzylcyclopentane-1:2:3:4-tetracarb-

oxylic acid, m.p. 232°, transformed by AcCl only into a monoanhydride, m.p. 234—235°. The formation of 1- and 2-CH<sub>2</sub>Ph derivatives in place of the expected 5-compound is explained by assuming K cyclopentadiene to be heteropolar with a symmetrically constituted anion. (I) with (C·CO<sub>2</sub>H)<sub>2</sub> in Et<sub>2</sub>O gives a mixture of 3- and 4-benzyl-3:6-endomethylene- $\Delta^{1:4}$ -dihydrophthalic acids, best separated from one another by partial hydrogenation (colloidal Pd) of their Na salts to 4-benzyl-3:6-endomethylene- $\Delta^1$ -tetrahydrophthalic acid (X), m.p. 217—218° (anhydride, m.p. 99—100°, and its adduct, C<sub>22</sub>H<sub>19</sub>O<sub>3</sub>N<sub>3</sub>, m.p. 155°, with PhN<sub>3</sub>), and the corresponding 3-CH<sub>2</sub>Ph acid, m.p. 185—186° (anhydride, m.p. 63—64°, and its adduct, m.p. 206°). Further hydrogenation (PtO<sub>2</sub>) of (X) gives the acid, m.p. 159°, derived from (VI), thus establishing the constitution and proving that the union of H to the double linking of (X) takes place in the *exo* position. Addition of maleic anhydride to (II) gives the compound, C<sub>28</sub>H<sub>22</sub>O<sub>4</sub>, m.p. 190°. H. W.

Oxidation of double linkings. I. Oxidation of *endo-cis*-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic acid. K. ALDER and S. SCHNEIDER (Annalen, 1936, 524, 189—202).—Oxidation of *endo-cis*-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic acid (I) by 4% KMnO<sub>4</sub> without particular precautions gives *cis-cis-cis-cis*-cyclopentane-1:2:3:4-tetracarboxylic acid (II), m.p. 195° (decomp.), converted by boiling AcCl into the dianhydride, m.p. 222°. Under milder conditions and in alkaline solution the products are 4:5-dihydroxy-3:6-endomethylenehexahydrophthalic acid (III) (diacetyl-anhydride, m.p. 161—



162°) and the neutral O<sub>5</sub> substance (IV), m.p. 263° (decomp.), which is the main product when oxidation is effected in acid solution. (IV) is neutral, and indifferent towards CH<sub>2</sub>N<sub>2</sub>, boiling Ac<sub>2</sub>O, and cold aq. Na<sub>2</sub>CO<sub>3</sub>. When dissolved in hot aq. Na<sub>2</sub>CO<sub>3</sub> it is oxidised by KMnO<sub>4</sub> to (II). It is therefore regarded as formed by threefold loss of H<sub>2</sub>O from the hydrated form of 3:5-dialdehydocyclopentane-1:2-dicarboxylic acid. The conclusion is supported by the observation that it is converted by NHPh·NH<sub>2</sub> into the diphenylhydrazonodiphenylhydrazide, m.p. 224—225°, of this acid and is formed by the treatment of (III) with Pb(OAc)<sub>4</sub> in AcOH and by the ozonisation of (I). Oxidation of *endo-cis*-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride by Pb(OAc)<sub>4</sub> in AcOH gives the dilactone (V), m.p. 266°. (I) and 30% H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>-AcOH afford 4-hydroxy(*endo*)-5-hydroxy(*exo*)-*cis*-3:6-endomethylenehexahydrophthalic acid (corresponding lactone and its *Ac* derivative, m.p. 150—151°, and *Ac Me* ester, m.p. 65°). H. W.

**cycloHexane series. III. 1-Carboxy-3:3-dimethylcyclohexane-1-acetic acid.** R. D. DESAI, M. O. FAROOQ, and R. F. HUNTER (J.C.S., 1936, 1162—1163).—1-Carboxy-3:3-dimethylcyclohexane-1-acetic acid (I), m.p. 166° (effervescence) (Ba, Ca, Pb, and Cu salts; anhydride, m.p. 67°; anilic acid, m.p. 205°; anil, m.p. 132°), together with its imide, m.p. 204°, an amic acid, m.p. 145° [hydrolysed to (I)], and a compound, m.p. 85—86°, result from the hydrolysis (conc. HCl; 48 hr.) of the dinitrile obtained by the interaction of aq. KCN and Et 3:3-dimethylcyclohexylidene-1-cyanoacetate, b.p. 155—157°/14 mm. [from 3:3-dimethylcyclohexanone (II) and CN·CH<sub>2</sub>·CO<sub>2</sub>Et in presence of piperidine and Na<sub>2</sub>SO<sub>4</sub> (48 hr.; 100°)]. (II) with aq. KCN and NaHSO<sub>3</sub> affords 1-hydroxy-1-cyano-3:3-dimethylcyclohexane, b.p. 128—129°/15 mm., which with CN·CHNa·CO<sub>2</sub>Et (24 hr., room temp., and 2 hr., 100°) yields Et 1-cyano-3:3-dimethylcyclohexane-1-α-cyanoacetate, b.p. 190—191°/15 mm., hydrolysed (HCl; 48 hr.) to (I). F. N. W.

**Diene synthesis. I. Direct differentiation of cyclic penta- and hexa-dienes.** K. ALDER and H. F. RICKERT (Annalen, 1936, 524, 180—189).—The readiness of addition of PhN<sub>3</sub> to the simpler cyclopentadienes (I) is much > to cyclohexadienes (II), but the difference in rate tends to disappear in the presence of heavy substituents. Adducts of (I) and maleic anhydride (III) dissociate into their components when heated whereas those of (II) afford (·CH<sub>2</sub>·CO)<sub>2</sub>O and a C<sub>6</sub>H<sub>6</sub> derivative. With complex derivatives of (I) decomp. frequently occurs with liberation of H, which converts (III) into (·CH<sub>2</sub>·CO)<sub>2</sub>O, so that the isolation of the latter is not a certain criterion of the presence of (II). A safer guide is found in (·C·CO<sub>2</sub>R)<sub>2</sub>, the adducts of which with (I) dissociate when distilled into their components, which re-unite in the receiver giving esters which are hydrolysed to acids identical with those obtained by the direct union of (I) with (·C·CO<sub>2</sub>H)<sub>2</sub>. Derivatives of (II) when distilled yield C<sub>6</sub>H<sub>4</sub> and ester of phthalic acid or its derivatives readily identified after hydrolysis. The following transformations are cited: α-phellandrene to 4-methylphthalic acid; cyclohexadiene to o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, also obtained from trans-1:2-dihydrophthalic acid; 2-benzylcyclopentadiene to 4-benzyl-3:6-endomethylene-Δ<sup>1,4</sup>-dihydrophthalic acid, m.p. 232°, identified by partial hydrogenation (colloidal Pd) to 4-benzyl-3:6-endomethylene-Δ<sup>1</sup>-tetrahydrophthalic acid, m.p. 218°. H. W.

**Reaction of phthalic anhydride with glycerol.** A. I. KOGAN (J. Appl. Chem. Russ., 1936, 9, 1070—1081).—Condensation of o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O with glycerol leads to the production of a series of esters, with, in presence of excess of glycerol, condensation between OH-groups; in the latter case the mol. wt. rises more rapidly with time of heating than in the former.

R. T.

**Derivatives of tert.-alcohols. Hydrogen phthalates.** W. A. FESSLER and R. J. SHRINER (J. Amer. Chem. Soc., 1936, 58, 1384—1386).—CR<sub>3</sub>·O·MgBr and o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O (I) or its derivatives in Et<sub>2</sub>O-dioxan at 0—55° give 36—66% of the CR<sub>3</sub>H phthalate. The following are described: Bu<sup>n</sup>H

phthalate, m.p. 85.5—86.5°, 3-nitrophthalate, decomp. 145°, and tetrabromophthalate, decomp. 147°; Bu<sup>i</sup>, decomp. 142°, tert.-amyl, decomp. 126°, CEt<sub>3</sub>, decomp. 145°, CPr<sup>n</sup><sub>3</sub>, decomp. 138°, CBu<sup>n</sup><sub>3</sub>, decomp. 112°, and tri-n-amylcarbinyl, decomp. 102°, H tetra-chlorophthalates. o-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>CHPh<sub>2</sub> is obtained in 74% yield from CHPh<sub>2</sub>·O·MgBr and (I); CHPh<sub>2</sub>·OH and (I) at 110° give 18%. OBu<sup>n</sup>·MgBr (+0.5Et<sub>2</sub>O) is isolable from Bu<sup>n</sup>OH and MgEtBr in Et<sub>2</sub>O. H. B.

**2:4-Dinitrophenylhydrazides.** J. CEREZO and E. OLAY (Anal. Fis. Quím., 1934, 32, 1090—1099).—2:4-Dinitrophenylhydrazine heated with org. acids and 5N-H<sub>2</sub>SO<sub>4</sub> gives 2:4-dinitrohydrazides; those of the following acids are new: formic, m.p. 183—184° (decomp.); CH<sub>2</sub>Cl·CO<sub>2</sub>H, m.p. 199—200°; CH<sub>2</sub>Ph·CO<sub>2</sub>H, m.p. 177° (decomp.); CH<sub>2</sub>Ph·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 196—197°; stearic, from stearyl chloride, m.p. 120° (softens 116°). The derivatives of dibasic acids are of three types, normal monohydrazides [A], bishydrazides [B], and cyclic monohydrazides,

R<CO>N·NH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub> [C]. Derivatives of the following are described: malonic acid, type [A], m.p. 185—186° (decomp. to give the corresponding aceto-derivative); succinic, type [C], m.p. 269—270° (decomp.), also from the aceto-hydrazide and succinic acid; glutaric, type [B], m.p. 253—254°; phthalic, type [C], m.p. 268—269° (decomp.), also from the aceto-hydrazide and phthalic acid, converted by successive treatment with N-NaOH and N-HCl into type [A], which reverts to type [C] at 120—130°; 3-nitrophthalic, type [C], m.p. 249—250°; 3:6-dihydroxyphthalic, type [A], m.p. 277—278°, giving type [C] at 150°; phthalamic, from phthalimide, m.p. 298—299°. Derivatives could not be obtained from lactic, p-toluic, salicylic, cinnamic, iso- and terephthalic, tartaric, citric, and camphoric acids.

F. R. G.

**Improvement in the synthesis of hydroxycinnamic acids.** F. VORSATZ (J. pr. Chem., 1936, [ii], 145, 265—269).—The Knoevenagel synthesis of hydroxycinnamic acids from the appropriate hydroxy-aldehyde, CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>N, and a little C<sub>5</sub>H<sub>11</sub>N (or better, in some cases, NH<sub>2</sub>Ph) gives yields up to > 80%, provided the temp. does not exceed 80° for mono- and 60° for di-hydroxycinnamic acids. Daphnetin-3-carboxylic acid, prepared in this way (temp. 37°), had m.p. 272° (cf. A., 1934, 79). H. G. M.

**Preparation of some esters. II. F. ADICKES** (J. pr. Chem., 1936, [ii], 145, 235—242; cf. A., 1931, 822).—The prep. of the following is described: [C(CO<sub>2</sub>Et)<sub>2</sub>]<sub>2</sub>, Et fluorene-9-carboxylate, HCO<sub>2</sub>Pr, o-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>CH<sub>2</sub>Ph)<sub>2</sub>, Et<sub>2</sub> α-diphenylethylene-ββ-di-carboxylate, m.p. 71—72°, b.p. 175°/high vac. [from CPh<sub>2</sub>Cl<sub>2</sub> or CPh<sub>2</sub>Br<sub>2</sub>, b.p. 170—180°/13 mm. (cf. lit.), and Na (or, better, Mg) derivative of CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub>], hydrolysed by MeOH-KOH to the acid, m.p. 194—195°, Me<sub>3</sub> phenylmethanetricarboxylate, m.p. 84.5°, b.p. 141—142°/0.9 mm., and p-tolyl-9-fluorenylsulphone, m.p. 224—225°. An improved prep. of 9-bromofluorene from fluorene through Et 9-bromofluorene-9-glyoxylate is described. H. G. M.

**Unsaturated aralkyl ketones. III. Polymorphism of ethyl p-methoxycinnamoylpyruv-**



ate. E. FRIEDMANN (J. pr. Chem., 1936, [ii], 145, 341—352; cf. this vol., 1254).—*Et p-methoxycinnamoylpyruvate*, prepared from  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ ,  $\text{Et}_2\text{C}_2\text{O}_4$ , and  $\text{NaOEt}$ , exists in polymorphic forms, m.p.  $93^\circ$  (stable) and  $89^\circ$ , respectively, which differ slightly in colour and adsorption and in that hydrogenation of the former is slightly faster. Both forms give the same acid when hydrolysed. The stable form absorbs 6.27 and the unstable 5.68 mols. of  $\text{H}_2$  in 30 hr., but the reason for this excess is not evident.

R. S. C.

**1:4-Bridging of diethyl succinosuccinate.** P. C. GUHA (Current Sci., 1936, 5, 19—20).—The Na derivative of  $\text{Et}_2$  succinosuccinate and  $(\text{CH}_2\text{Br})_2$  yield the  $\text{Et}_2$  ester (I), m.p.  $112^\circ$ , of 1:4-endoethylene-cyclohexa-2:5-dione-1:4-dicarboxylic acid, m.p.  $274^\circ$ . With  $\text{KOH}\cdot\text{MeOH}$ , (I) gives *hexane- $\alpha\beta\epsilon\zeta$ -tetracarboxylic acid*, m.p.  $170^\circ$ , and with neutral  $\text{KMnO}_4$ , an acid, m.p.  $150^\circ$ . Using  $\text{CH}_2(\text{CH}_2\text{Br})_2$ , the  $\text{Et}_2$  ester, m.p.  $132^\circ$  of 1:4-endotrimethylenecyclohexa-2:5-dione-1:4-dicarboxylic acid, m.p.  $238^\circ$ , is similarly prepared. The *disemicarbazones* of the esters and acids are prepared.

E. W. W.

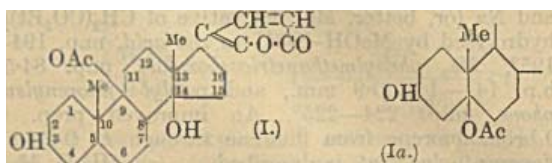
**Diveratrylacetic acid and triveratrylmethane.** P. DREYFUSS and F. SERRA (Rend. Semin. Fac. Sci. R. Univ. Cagliari, 1934, 4, 139—142; Chem. Zentr., 1935, ii, 3650).—3:4-Dimethoxymandelonitrile with veratrole and  $\text{H}_2\text{SO}_4$  yields *diveratrylacetoneitrile*, m.p.  $147^\circ$ , hydrolysed ( $\text{KOH}\cdot\text{EtOH}$ ) to *diveratrylacetic acid*, m.p.  $114^\circ$ . Condensation ( $\text{H}_2\text{SO}_4\text{-AcOH}$ ) of veratrole and veratraldehyde affords *triveratrylmethane*, m.p.  $142.5^\circ$ .

H. N. R.

**Oxidation of bisphenylpyruvic [ $\alpha$ -hydroxy- $\gamma$ -keto- $\beta$ -phenyl- $\alpha$ -benzylglutaric] acid.** J. JARROUSE (Compt. rend., 1936, 203, 259—261).—Oxidation of bisphenylpyruvic acid with  $\text{KMnO}_4$  in  $\text{NaOH}$  affords  $\alpha$ -hydroxydibenzyl ketone (I), m.p.  $114^\circ$  (cf. A., 1934, 523) (erroneously described as an aldehyde; cf. this vol., 73), and  $\text{H}_2\text{C}_2\text{O}_4$ . Ph  $\alpha$ -hydroxy- $\beta$ -phenylethyl ketone (J.C.S., 1914, 105, 1589) with dil.  $\text{NaOH}$  affords (I), and when oxidised gives  $\text{CH}_2\text{Ph}\cdot\text{COBz}$ , as does (I).

J. L. D.

**Toad poisons. IX. Questions of constitution.** H. WIELAND, G. HESSE, and R. HUTTEL [in part with H. BEHRINGER] (Annalen, 1936, 524, 203—222; cf. A., 1935, 749).—A new, mainly chromatographic, method of isolating bufotalin (I) and the subsidiary poisons from the dried secretion is described. The absorption spectrum of (I) indicates the presence of three, mutually conjugated double linkings as expressed by (I). This view harmonises with the production of  $\text{CHO}\cdot\text{CO}_2\text{H}$  by the ozonolysis of acetylbufotalin and the almost complete identity of the absorption spectra of (I) and scillariden A (II) for which Stoll has established the same skeleton.

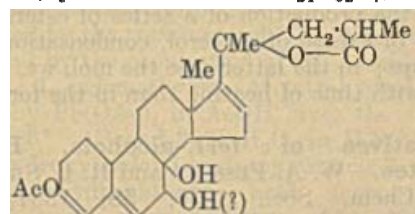


Further, (I) and (II) appear to suffer similar fission by  $\text{KOH}\cdot\text{MeOH}$  and in the case of bufotalinin (III) the

corresponding *Me* ester, m.p.  $210\text{--}211^\circ$ , of the enolcarboxylic acid is obtained cryst. The presence of *tert.* OH at  $\text{C}_{14}$ , is rendered probable by the results of the alkaline fission of bufotalone and the analogy of the reaction with those of strophanthidin and scillaren. The *sec.* OH at  $\text{C}_{13}$  is not established with certainty but is placed there in analogy with the bile acids and sterols. The ready hydrolysis of (I) by cold  $\text{HCl}$  and the optical behaviour of bufotaliene indicates  $\text{OAc}$  attached to  $\text{C}_9$ . Bufotoxin has the same absorption spectrum as (I) and hence the same arrangement of double linkings. The increment of 1  $\text{H}_2\text{O}$  in it is due to firmly bound  $\text{H}_2\text{O}$  of crystallisation. It has therefore the structure (I) or (Ia) and the OH at  $\text{C}_{14}$  is esterified by the residue of suberylarginine. The absorption spectrum of bufotalidin (IV) shows the presence of the same, doubly-unsaturated lactone group as in (I) which is opened by  $\text{KOH}\cdot\text{MeOH}$  with formation of the *Me* ester, m.p.  $237^\circ$ , of the enolcarboxylic acid. When catalytically hydrogenated it absorbs 3  $\text{H}_2$  and yields a saturated acid. It does not contain  $\text{OMe}$  or  $\text{OAc}$ , and has  $[\alpha]_D +0.78^\circ$  in 80%  $\text{EtOH}$ ; it contains 1 OH and one double linking more than (I), but their location remains undecided. The separation of (III) from (IV) is difficult on account of its instability and the great firmness with which it retains solvent of crystallisation. (III) has the composition  $\text{C}_{24}\text{H}_{30}\text{O}_6$ , is without definite m.p., and has  $[\alpha]_D +14.14^\circ$  in 80%  $\text{EtOH}$ . It does not contain  $\text{OAc}$ . The *Ac* derivative has m.p.  $247^\circ$ . The ultra-violet absorption spectrum shows it to contain the same absorbing groups as (I) and (IV). The presence of two active H at  $28^\circ$  and of three at  $95^\circ$  in (III) is indicated. Since a stepwise action of (III) towards  $\text{MgMeI}$  is also observed it appears that two *sec.* OH and one *tert.* OH groups are present whereas the nature of the fourth O is undetermined. It absorbs  $>4 \text{ H}_2$  and therefore contains four double linkings or three double linkings and CO. The absorption spectra of gamabufogenin and arenobufogenin resemble those of (I), (III), and (IV) so that they belong to the same structural type.

H. W.

**Constituents of "senso." V. Constitution of  $\psi$ -bufotalin.** S. IKAWA (J. Pharm. Soc. Japan, 1935, 55, 748—757).—Deacetyltetrahydromethyl- $\psi$ -bufotalonic acid (*Me*<sub>1</sub> ester, m.p.  $95\text{--}97^\circ$ ) is ozonised to deacetyltetrahydromethyl- $\psi$ -bufotalonic peroxide and deacetyltetrahydromethyl- $\psi$ -bufotalonolactone,  $\text{C}_{19}\text{H}_{28}\text{O}_5$  (diacetate, m.p.  $111\text{--}113^\circ$ ; *Et*<sub>2</sub> acetal, m.p.  $91\text{--}92^\circ$ ). Ozonolysis of *Me* deacetyltetrahydro- $\psi$ -bufotalinate (I) yields a *keto-aldehyde*,  $\text{C}_{20}\text{H}_{30}\text{O}_8$ , m.p.  $114\text{--}116^\circ$ , and a *ketonic acid*,  $\text{C}_{23}\text{H}_{33}\text{O}_6\cdot\text{CO}_2\text{H}$ , which, when heated, yields a *dilactone*,  $\text{C}_{24}\text{H}_{32}\text{O}_7$ , decomp.



$172\text{--}174^\circ$  (oxime, m.p.  $180\text{--}181^\circ$ ). Se-dehydrogenation of (I) yields 3'-methyl-1:2-cyclopentenophen-

anthrene, m.p. 123—124°, the picrate of which is also obtained from the dehydrogenation product from  $\psi$ -bufotalin bromide. The appended structure is suggested for  $\psi$ -bufotalin.

CH. ABS. (r)

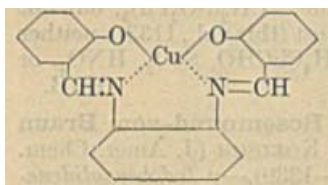
**Dihydroresorcinols.** III. Condensation of *p*-methoxystyryl methyl and ethyl ketone with ethyl ethane- $\alpha\alpha\beta$ -tricarboxylate. E. FRIEDMANN (J. pr. Chem., 1936, [ii], 146, 79—87).—Treatment of  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$  with *p*-methoxystyryl Me ketone and  $\text{NaOEt}$  in  $\text{EtOH}$  at 115° yields *Et*<sub>2</sub> 2-*p*-anisylcyclohexane-4 : 6-dione-1-carboxylate-1-acetate, b.p. 243°/11 mm., m.p. 82.5°, which could not be hydrogenated ( $\text{Pd}-\text{BaSO}_4$  in  $\text{EtOH}$  at 20°). It is hydrolysed by aq.  $\text{NaOH}$  at room temp. to *Et* 1-carboxy-2-*p*-anisylcyclohexane-4 : 6-dione-1-acetate, m.p. 134°, decarboxylated at 140—160° to *Et* 2-*p*-anisylcyclohexane-4 : 6-dione-1-acetate, m.p. 71—72°, which probably exists in two cryst. forms. Similarly, *p*-methoxystyryl *Et* ketone affords *Et*<sub>2</sub> 2-*p*-anisyl-5-methylcyclohexane-4 : 6-dione-1-carboxylate-1-acetate, b.p. 243—245°/11 mm., whence *Et* 1-carboxy-2-*p*-anisyl-5-methylcyclohexane-4 : 6-dione-1-acetate, m.p. 127° (decomp.), and *Et* 2-*p*-anisyl-5-methylcyclohexane-4 : 6-dione-1-acetate, m.p. (indef.) 59—62°, apparently a mixture of isomerides. H. W.

Comparison of the action of the Grignard reagent on thiodiazolines and thioacylhydrazines. H. WUYTS and (Mlle.) A. LACOURT (Bull. Soc. chim. Belg., 1936, 45, 445—453; cf. A., 1933, 498, 831; 1935, 1360).—Thiodiazolines are unchanged in dry  $\text{Et}_2\text{O}$  by  $\text{MgMeI}$  or  $\text{MgEtBr}$  in excess at room temp. if the 2 position is unsubstituted. Benzaldehyde- $\beta$ -thiobenzoyl-, *o*-tolualdehyde- $\beta$ -*o*-toluoyl-, and *p*-tolualdehyde- $\beta$ -*p*-toluoyl- $\beta$ -methylhydrazones (I) with  $\text{MgMeI}$ ,  $\text{MgMeI}$ , and  $\text{MgEtBr}$ , respectively, in dry  $\text{Et}_2\text{O}$  at room temp., followed by hydrolysis, afford oily products (+ $\text{HgCl}_2$ , m.p. 99°, 83°, and 195°, respectively) which contain 1 labile H as well as S. (I) with  $\text{MgMeI}$  gives a compound, m.p. 98° (+ $\text{HgCl}_2$ , m.p. 87°), which does not react with  $\text{Ac}_2\text{O}$  or  $\text{BzCl}$ . Analysis indicates that in each case two alkyl groups have been introduced into the mol. Benzaldehydephenylmethylhydrazone is unaffected by  $\text{MgMeI}$  in boiling  $\text{Pr}_2\text{O}$ , whereas benzaldehydephenylhydrazone affords  $\text{NH}_2\text{Ph}$  and  $\text{COPhMe}$ .  $\alpha$ -Naphthaldehydephenylmethylhydrazone is unaffected by  $\text{MgMeI}$  in boiling  $\text{Pr}_2\text{O}$ .

J. L. D.

**Polyatomic co-ordinate valency rings with meta- and para-condensation.** P. PFEIFFER and H. PFITZNER (J. pr. Chem., 1936, [ii], 145, 243—256; cf. A., 1933, 824).—The Schiff's bases (apparently new; m.p. in parentheses) of  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  with the following diamines form co-ordinated Cu compounds by reaction with  $\text{Cu}(\text{OAc})_2$ : *o*- (164°), *m*- (109—110°), and *p*- (212°)  $\cdot\text{C}_6\text{H}_4(\text{NH}_2)_2$ ; 2-hydroxy- (162—163°), 1-methoxy- (165°) 3 : 5-phenylenediamine; 1 : 4- (141°), 1 : 5- (219—220°), and 2 : 7- (202°) naphthylenediamine; 3 : 3'-dimethyl- (202°) and 3 : 3'-dimethoxy- (162°) 4 : 4'-diaminodiphenylhydrazine (213°); 2 : 4-toluylenediamine (109°); 1 : 4'- (136°) and 4 : 4'- (256°) diaminodiphenyl. The properties of the complex with the last of these bases depends on the mode of prep. Resorcyalde-

hyde,  $\text{Ni}(\text{OAc})_2$ , and 3 : 5-diaminobenzoic acid give a Ni complex of the appropriate Schiff's base, and a Ni complex from the second of the above Schiff's bases is described. Most of these complexes are new (cf. *loc. cit.*). Mol. wt. determinations (b.p. elevation of  $\text{CHCl}_3$  or f.p. depression of  $\beta$ -naphthaquinoline or acridine; mol. f.p. depression const. 12.4° and 12.0°, respectively) on suitable



complexes show that only the *o*-diamine complexes have the simple unimol. structure (as inset), whilst those of the *m*-phenylene and benzidine series have a bi-

mol. structure with two metallic atoms. This accords with stereochemical requirements. H. G. M.

Reactions of aldoxime derivatives with bases. III. Reactions of geometrically isomeric acetyl-3 : 4-methylenedioxybenzaloximes with amines. C. R. HAUSER and E. JORDAN (J. Amer. Chem. Soc., 1936, 58, 1419—1422; cf. this vol., 332).—Acetyl- $\alpha$ -3 : 4-methylenedioxybenzaloxime with  $\text{NH}_2\text{Bu}^a$ ,  $\text{NH}_2\text{Ph}$ ,  $\text{NH}_2\text{Et}$ , or piperidine gives an almost quant. yield of the  $\alpha$ -oxime;  $\text{C}_5\text{H}_5\text{N}$  and  $\text{NEt}_3$  have little or no effect. Acetyl- $\beta$ -3 : 4-methylenedioxybenzaloxime with  $\text{NH}_2\text{R}$  and  $\text{NHR}_2$  affords the  $\beta$ -oxime (practically the sole product with weak bases and at <0° with strong bases) and/or 3 : 4-methylenedioxybenzonitrile (which is the sole product with  $\text{NR}_3$ ); analogous results are obtained with aq. solutions of the amines. H. B.

**Ketimine dyes and related compounds.** J. D. REID and D. F. J. LYNCH (J. Amer. Chem. Soc., 1936, 58, 1430—1432; cf. A., 1933, 826).—4 : 4'-*Di-n-butyl*-, m.p. 45° (all m.p. are corr.), 4 : 4'-*tetra-n-propyl*-, b.p. 260°/7 mm. [*dipicrate*, decomp. 175° (sinters at 165°)], and 4 : 4'-*tetra-n-butyl*-, b.p. 270—280°/6 mm. (*dipicrate*, m.p. 156°), -diaminodiphenylmethane are prepared from 40%  $\text{CH}_2\text{O}$  and  $\text{NHPhBu}^a$ ,  $\text{NPhPr}^a$ , and  $\text{NPhBu}^a$ , respectively, in dil.  $\text{HCl}$  at 90°. *p*-*Di-n-propylaminobenzoic acid*, m.p. 142°, is obtained from  $\text{NPhPr}^a$  and  $\text{COCl}_2$ . 4-*Di-n-propylaminobenzophenone*, m.p. 100°, is prepared from  $\text{NPhPr}^a$ ,  $\text{NHBzPh}$ , and  $\text{POCl}_3$  at <200°; the 4- $\text{NBu}^a$ -derivative could not be similarly obtained. *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$  (I),  $\text{NH}_2\text{Ph}$ , and  $\text{NH}_2\text{Ph}\cdot\text{HCl}$  at 160—180° give 4-aminobenzophenoneanil, m.p. 154° [*hydrochloride* (II), m.p. >400° (sinters about 275—280°)]. Repeated treatment of (II) in  $\text{EtOH}$  with gaseous  $\text{NH}_3$  affords a little 4-aminobenzophenoneimine (3 : 5-dinitrobenzoate, m.p. 198°), better obtained from (I) and  $\text{PCl}_5$  in  $\text{PhMe}$  followed by liquid  $\text{NH}_3$ . 4-Dimethyl- and 4-diethylaminobenzophenoneimine (3 : 5-dinitrobenzoates, m.p. 214° and 141°, respectively) are similarly formed from *p*- $\text{NAlk}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ ,  $\text{POCl}_3$  (not  $\text{PCl}_5$ ), and  $\text{NH}_3$  in  $\text{PhMe}$ . The *Bz* derivative, m.p. 165°, of 4 : 4'-tetraethylaminobenzophenoneimine, prepared using  $\text{Bz}_2\text{O}$  in  $\text{C}_6\text{H}_6$ , is an indicator (yellow  $\rightarrow$  blue;  $p_H$  4—5.2). The 3 : 5-dinitrobenzoates of  $\text{NPhEt}_2$ ,  $\text{NPhPr}^a$ ,  $\text{NPhBu}^a$ , and  $\text{NHPbBu}^a$  have m.p. 120°, 118°, 104°, and 98.5°, respectively. H. B.

**Michael condensation.** IV. Active methylene group in sulphones. R. CONNOR, C. L. FLEMING,



jun., and T. CLAYTON (J. Amer. Chem. Soc., 1936, 58, 1386—1388).— $p$ -C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·CH<sub>2</sub>Ph (I) undergoes the Michael condensation; with CHPh·CH·COPh and MeOH—NaOMe in C<sub>6</sub>H<sub>6</sub>  $\alpha$ -benzoyl- $\gamma$ - $p$ -toluenesulphonyl- $\beta$ - $\gamma$ -diphenylpropane, stereoisomeric forms, m.p. 139—141° (corr.) and 197—197.5° (corr.), results. (I) thus resembles deoxybenzoin (II). (I) and (II) do not react with CHPh·CH·CO<sub>2</sub>Me. CH<sub>2</sub>(SO<sub>2</sub>Ph)<sub>2</sub>, but not (I), gives a positive HgCl<sub>2</sub> test (this vol., 1133); neither reacts with PhCHO,  $p$ -C<sub>6</sub>H<sub>4</sub>Cl·CHO, SeO<sub>2</sub>, HNO<sub>3</sub>, or isoamyl nitrite. H. B.

**Applications of the Rosenmund-von Braun nitrile synthesis.** C. F. KOELSCH (J. Amer. Chem. Soc., 1936, 58, 1328—1330).— $p$ -Iodobenzylidene-phthalide, m.p. 172—173° [from  $p$ -C<sub>6</sub>H<sub>4</sub>I·CH<sub>2</sub>·CO<sub>2</sub>H,  $o$ -C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)<sub>2</sub>O, and a little NaOAc at 225—235°], is converted by MeOH—NaOMe into 2- $p$ -iodophenyl-1:3-indanedione, colourless and reddish-violet forms, both m.p. 145—146° (red melt), which with MgPhBr gives 3-phenyl-2- $p$ -iodophenylindone (I), m.p. 141—143°. (I) and CuCN at 240° (cf. von Braun and Manz, A., 1931, 1044) afford 3-phenyl-2- $p$ -cyanophenylindone, m.p. 142—144°.  $\alpha$ -Diphenyl- $\beta$ - $p$ -iodophenylpropan- $\beta$ -ol, m.p. 117—117.5° (from  $p$ -C<sub>6</sub>H<sub>4</sub>I·CO<sub>2</sub>Et and CH<sub>2</sub>Ph·MgCl), is dehydrated (AcOH—H<sub>2</sub>SO<sub>4</sub>) to the propylene, m.p. 92—92.5°, which with Br in boiling AcOH gives 1-phenyl-2- $p$ -iodophenylindene (II), m.p. 184—185°, and (probably)  $\alpha$ -bromo- $\alpha$ -diphenyl- $\beta$ - $p$ -iodophenylpropylene, m.p. 165—168° (decomp.). (II) and PhCHO in EtOH—NaOEt afford 3-phenyl-2- $p$ -iodophenyl-1-benzylideneindene, m.p. 173—174°, oxidised (CrO<sub>3</sub>, AcOH) to (I). 2-Phenyl-1:3-indanedione and  $p$ -C<sub>6</sub>H<sub>4</sub>Br·MgBr give 2-phenyl-3- $p$ -bromophenylindone, m.p. 172—174°, which with CuCN at 250° yields 2-phenyl-3- $p$ -cyanophenylindone, m.p. 184—187°. The mixture of phthalides from CH<sub>2</sub>Ph·CO<sub>2</sub>H, 4-bromophthalic anhydride, and a little NaOAc at 220—240° is converted by MeOH—NaOMe into 5-bromo-2-phenyl-1:3-indanedione, colourless and violet-black forms, both m.p. 166—167° (red melt), which with MgPhBr affords 5- (III), m.p. 167—168°, and 6- (IV), m.p. 192—194°, -bromo-2:3-diphenylindones. (III) is oxidised (CrO<sub>3</sub>, AcOH) to 4-bromo-2-benzoylbenzoic acid, whilst (IV) and CuCN at 250° give 6-cyano-2:3-diphenylindone, m.p. 209—211°.

Diphenyl- $p$ -bromobenzylcarbinol, m.p. 124—126° (from  $p$ -C<sub>6</sub>H<sub>4</sub>Br·CH<sub>2</sub>·MgBr and COPh<sub>2</sub>), is converted by Br in AcOH into  $\beta$ -diphenyl- $\alpha$ - $p$ -bromophenylvinyl bromide, m.p. 109—110°, which is resinified by CuCN at 240°. CPh<sub>2</sub>·CPh·CN is similarly obtained in quant. yield from CPh<sub>2</sub>·CPhBr, whilst  $\alpha$ -phenyl- $\beta$ -diphenyl-nevinyl bromide (A., 1932, 1024) affords  $\alpha$ -phenyl- $\beta$ -diphenyleneacrylonitrile, m.p. 188—189°. H. B.

**Halogen analogues of adrenaline and ephedrine.** III. Derivatives of propiophenone and general discussion. R. P. EDKINS and W. H. LINNELL (Quart. J. Pharm., 1936, 9, 203—229).—4-Hydroxypropiophenone, m.p. 149° (prepared by action of AlCl<sub>3</sub> on EtCO<sub>2</sub>Ph in CS<sub>2</sub>), is nitrated to the 3-NO<sub>2</sub>-derivative, m.p. 66°, reduced to the 3-NH<sub>2</sub>-compound (hydrochloride, m.p. 217°) in poor yield; this yields through the diazo-compounds 3-chloro-4-hydroxypropiophenone, m.p. 79° (Bz compound, m.p.

107.5°), which on nitrosation and reduction affords 3-chloro-4-hydroxy- $\alpha$ -aminopropiophenone hydrochloride, m.p. 138.6°. 4-Chloropropiophenone, m.p. 35.8° (4-Br-compound, m.p. 47°), prepared from PhCl and (EtCO)<sub>2</sub>O, with HCl and Bu nitrite yields 4-chloro-oximinopropiophenone, m.p. 114° (4-Br-compound, m.p. 133.6°), reduced (SnCl<sub>2</sub>—HCl) to 4-chloro- $\alpha$ -aminopropiophenone hydrochloride, m.p. 259° (4-Br-compound, m.p. 252°).  $\alpha$ -Aminopropiophenone hydrochloride, m.p. 187°, obtained from oximinopropiophenone, is hydrogenated to norephedrine. The stability of the aminoketones towards NaOH and EtOH—KOH has been determined and it is shown that there is no obvious relationship between the stabilities of the substances and their toxicity or pharmacological activity. F. R. S.

**Unsaturated aralkyl ketones.** I. Anisylidenemethyl methyl, [ethyl,] and  $n$ -propyl ketones. E. FRIEDMANN. II.  $o$ -Tolylidenebenzylidene- and di- $o$ -tolylidene-acetone. E. FRIEDMANN and W. E. VAN HEYNINGEN (J. pr. Chem., 1936, [iii], 145, 321—336, 337—340).—I.  $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·CHO (I), when shaken with 10% NaOH and COMe<sub>2</sub>, COMeEt, or COMePr for 3, 16, or 11 days, respectively, gives about 50% yields of 4-methoxystyryl Me ketone (II), m.p. 73—74°, b.p. 176—177°/11 mm. (2:4-dinitrophenylhydrazones, m.p. 229°), 4-methoxystyryl Et (III), b.p. 180—181°/11 mm., m.p. 61° (oxime, +H<sub>2</sub>O, m.p. 105°; 2:4-dinitrophenylhydrazones, m.p. 200—201°), and  $Pr^a$  ketone (IV), b.p. 170—189°/11 mm., m.p. 40—41° (2:4-dinitrophenylhydrazones, m.p. 190°). Hydrogenation (Pd—BaSO<sub>4</sub>; EtOH) gives pure saturated ketones if continued until the reaction slows down, which occurs only after absorption of rather >2 H; cessation of reaction after absorption of exactly 2 H leaves some unsaturated ketone. Thus are prepared anisylacetone, b.p. 150—151°/9 mm. (2:4-dinitrophenylhydrazones, m.p. 145°, clears at 149—150°),  $\beta$ -anisylethyl Et (V), b.p. 160—162° (2:4-dinitrophenylhydrazones, m.p. 103—104°), and  $Pr^a$  ketone, b.p. 170—172°/9 mm. (2:4-dinitrophenylhydrazones, transparent at 104°, m.p. 112—114°). (I), CH<sub>3</sub>(CO<sub>2</sub>H)<sub>2</sub>, and piperidine in C<sub>5</sub>H<sub>5</sub>N give  $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·CH·CH·CO<sub>2</sub>H (52% yield), m.p. 175°, clears at 192° (cf. lit.), reduced by Na—Hg to  $p$ -OMe·C<sub>6</sub>H<sub>4</sub>·[CH<sub>2</sub>]<sub>2</sub>·CO<sub>2</sub>H (74.1%), the Ca salt, +2H<sub>2</sub>O, of which with (EtCO<sub>2</sub>)<sub>2</sub>Ca at 305° gives a poor yield of (V). The relative rates of hydrogenation and solubilities in olive oil or mixtures thereof with OMe·CH<sub>2</sub>·CH<sub>2</sub>·OH are (II) > (III) > (IV). (II), (III), and (IV) spread well on H<sub>2</sub>O at  $p_H$  7.5, having a surface potential of about 400 mv. M.p. are corr.

II.  $o$ -OMe·C<sub>6</sub>H<sub>4</sub>·CHO and NaOH—aq. EtOH with CHPh·CH·COMe or COMe<sub>2</sub> give 2'-methoxy-2-methyldistyryl, m.p. 61—62°, and 2:2'-dimethyldistyryl ketone, m.p. 99°, respectively, which with 2:4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH·NH<sub>2</sub> give pyrazoline derivatives, m.p. 193° and 202.5°, respectively. R. S. C.

**Phenyl mesityl diketone** [2:4:6-trimethylbenzil]. H. H. WEINSTOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 1233—1236).—2:4:6-Trimethylbenzil (I), m.p. 136—137° (oxime, m.p. 155°; 2:4-dinitrophenylhydrazones, m.p. 232—232.5°),

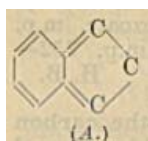
now prepared (cf. A., 1934, 525) by oxidation ( $\text{SeO}_2$ , dioxan, little  $\text{H}_2\text{O}$ ) of  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$  (*p*-chlorobenzylidene derivative, m.p.  $141^\circ$ ), does not react with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in EtOH or AcOH, is oxidised (30%  $\text{H}_2\text{O}_2$ , dioxan) to  $\text{BzOH}$  and  $s\text{-C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ , and with  $\text{MgPhBr}$  gives 2:4:6-trimethylbenzoyl-diphenylcarbinol, m.p.  $169.5\text{--}170^\circ$ . (I) is reduced (Zn, AcOH) to 2:4:6-trimethylbenzoin (II) (designated 2':4':6'- in A., 1935, 1499),  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OH}$ , m.p.  $101\text{--}102^\circ$  [phenylcarbamate, m.p.  $160\text{--}161^\circ$ ; attempted prep. of 2:4-dinitrophenylhydrazones gives that of (I)], and 2':4':6'-trimethylbenzoin (III),  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}(\text{OH})\cdot\text{COPh}$ , m.p.  $93.5\text{--}94^\circ$  (phenylcarbamate, m.p.  $141\text{--}142^\circ$ ; 2:4-dinitrophenylhydrazone, m.p.  $211.5\text{--}212^\circ$ ); more vigorous reduction (Zn, AcOH) of (I)—(III) affords Ph 2:4:6-trimethylbenzyl ketone (IV), m.p.  $163.5\text{--}164^\circ$  (phenylhydrazone, m.p.  $104\text{--}105^\circ$ ; 2:4-dinitrophenylhydrazone, 2 forms, m.p.  $163^\circ$  and  $190^\circ$ ), also obtained by reduction of (I) with Zn+aq. EtOH-KOH or Sn+EtOH-conc. HCl and of (II) with Sn+HCl. (IV) is synthesised from  $s\text{-C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\cdot\text{COCl}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{AlCl}_3$ . Oxidation ( $\text{SeO}_2$ ) of (IV) gives (I), whilst treatment with an excess of  $\text{MgEtBr}$  or  $\text{MgPr}^n\text{Br}$  affords  $\beta\gamma$ -dihydroxy- $\beta\gamma$ -diphenyl- $\alpha\delta$ -dimesitylbutane, m.p.  $241\text{--}242^\circ$ . (I) is converted by aq. MeOH-KOH into phenylmesitylglycollic acid (+MeOH), m.p.  $87\text{--}89^\circ$ , (+EtOH), m.p.  $84\text{--}85^\circ$  (Me ester, m.p.  $111\text{--}111.5^\circ$ ), reduced (P, I or Zn, AcOH) to  $s\text{-C}_6\text{H}_2\text{Me}_3\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ .

H. B.

**1:2-Diketo-3-phenylhydrindene.** C. F. KOELSCH (J. Amer. Chem. Soc., 1936, 58, 1321—1324).—3-Phenylhydrindone,  $\text{BuO}\cdot\text{NO}$ , and conc. HCl in 95% EtOH give 2-oximino-3-phenylhydrindone, m.p.  $198\text{--}203^\circ$  (decomp.) (Me ether, m.p.  $148\text{--}149^\circ$ ), hydrolysed ( $\text{AcCO}_2\text{H}$ , AcOH, and aq. HCl) to the violet 1:2-diketo-3-phenylhydrindene (I), dimorphous, both m.p.  $140\text{--}147^\circ$  [quinoxaline, m.p.  $169\text{--}172^\circ$ , from  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ], which is oxidised (3%  $\text{H}_2\text{O}_2$ , 0.5N-NaOH) to diphenylmethane- $\alpha\alpha$ -dicarboxylic acid, m.p.  $171\text{--}172^\circ$  (decomp.). (I) does not give a colour with  $\text{FeCl}_3$  [oxidation to a compound,  $\text{C}_{30}\text{H}_{18}\text{O}_4$ , m.p.  $200\text{--}205^\circ$  (decomp.) (darkens at  $180^\circ$ ), occurs], but it appears to exist completely in the enolic form (i.e., 2-hydroxy-3-phenylindone; not an *o*-quinonoid form). Methylation ( $\text{Me}_2\text{SO}_4$ , N-NaOH) of (I) thus gives the unstable 2-methoxy-3-phenylindone, m.p.  $67\text{--}68^\circ$  (oxime, m.p.  $184\text{--}186^\circ$ ), which is reduced (Zn dust, AcOH) to 2-methoxy-3-phenylhydrindone, m.p.  $96\text{--}98^\circ$ , whilst (I) and  $\text{MgPhBr}$  afford 1-hydroxy-2-keto-1:3-diphenylhydrindene, m.p.  $195\text{--}200^\circ$  (decomp.), which is oxidised ( $\text{CrO}_3$ , AcOH) to  $o\text{-C}_6\text{H}_4\text{Bz}$ , and is reduced (HI, AcOH) to 2-keto-1:3-diphenylhydrindene, m.p.  $169^\circ$  (decomp.). (I) and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$  give 1-hydroxy-2-keto-3-phenyl-1-benzylhydrindene, m.p.  $155\text{--}157^\circ$ . 3-Bromo-1:2-diketo-3-phenylhydrindene (II), m.p.  $77\text{--}79^\circ$  [from (I) and Br in  $\text{CCl}_4$ ], and MeOH lead to 2:2:3-trimethoxy-3-phenylhydrindone, m.p.  $102\text{--}103^\circ$ , hydrolysed ( $\text{AcOH}\text{--}\text{H}_2\text{SO}_4$ ) to 1:2-diketo-3-methoxy-3-phenylhydrindene, m.p.  $86\text{--}87^\circ$  [hydrate, m.p.  $115\text{--}120^\circ$  (loss of  $\text{H}_2\text{O}$ ); quinoxaline]. 2:2:3-Triethoxy-3-phenylhydrindone, m.p.  $89\text{--}90^\circ$  [from (II) and EtOH], is similarly hydrolysed to 1:2-diketo-3-ethoxy-3-phenylhydrindene, m.p.  $102\text{--}$

$103^\circ$ . Replacement of the enolisable H of (I) by OAlk thus activates the 2-CO. H. B.

**Attempted synthesis of compounds containing the isoindene nucleus.** C. F. KOELSCH (J. Amer. Chem. Soc., 1936, 58, 1331—1333).—Compounds containing the isoindene nucleus (A) could not be prepared. 2-Anisyl-1:3-indanedione, m.p.  $152\text{--}154^\circ$



(from phthalide and  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  in EtOH-NaOEt), and  $\text{MgPhBr}$  in PhMe give 3-phenyl-2-anisylindone (I), m.p.  $117\text{--}118^\circ$ , demethylated (40% HBr, AcOH) to 3-phenyl-2-p-hydroxyphenylindone, m.p.  $163\text{--}165^\circ$  (benzoate, m.p.  $145^\circ$ ), which with  $\text{MgPhBr}$  in  $\text{C}_6\text{H}_6$  affords 1-hydroxy-1:3-diphenyl-2-p-hydroxyphenylindene, m.p.  $196\text{--}197^\circ$ . This could not be dehydrated (heat; AcOH); AcOH- $\text{H}_2\text{SO}_4$  gives amorphous material. 3-Phenyl-2-p-cyanophenylindone is hydrolysed (dil.  $\text{H}_2\text{SO}_4$ ) to the 2-p-carbamyl, m.p.  $248\text{--}254^\circ$  (decomp.), and 2-p-carboxy-derivatives (II), m.p.  $212\text{--}214^\circ$ . The Me, m.p.  $167\text{--}168^\circ$ , and Et ester, m.p.  $120\text{--}121^\circ$ , of (II) or 3-phenyl-2-p-benzoylphenylindone, m.p.  $169\text{--}171^\circ$  [from the chloride of (II) and  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$ ], with  $\text{MgPhBr}$  (excess) give 1-hydroxy-1:3-diphenyl-2-p- $\alpha$ -hydroxybenzylhydrindene. This and its  $\text{Me}_2$  ether (?) and chloride (?) with Zn and AcOH-conc. HCl afford 1:3-diphenyl-2-p-benzhydrilphenylindene, m.p.  $173\text{--}175^\circ$ , which is oxidised ( $\text{CrO}_3$ , AcOH) to  $o\text{-C}_6\text{H}_4\text{Bz}$  and  $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{OH}$ .  $\alpha\gamma$ -Diphenyl- $\beta$ -anisylpropan- $\beta$ -ol, m.p.  $93\text{--}94^\circ$  (from Me anisate and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ ), is dehydrated (AcOH- $\text{H}_2\text{SO}_4$ ) to the propylene, m.p.  $82\text{--}83^\circ$ , which is converted by Br in boiling AcOH into 1-phenyl-2-anisylindene, m.p.  $120\text{--}122^\circ$ . This and PhCHO with EtOH-NaOEt in  $\text{Pr}^n\text{OH}$  give 3-phenyl-2-anisyl-1-benzylideneindene, m.p.  $188\text{--}190^\circ$ , also obtained by dehydration (AcOH- $\text{H}_2\text{SO}_4$ ) of the carbinol from (I) and  $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ . H. B.

**Derivatives of 1:3-diketohydrindene.** W. H. HUNTER and E. C. YACKEL (J. Amer. Chem. Soc., 1936, 58, 1395—1396).—2-Benzoyl-1:3-indanedione (I) is cleaved by Br in AcOH at  $100^\circ$  (bath) to  $\text{BzOH}$  and 2:2-dibromo-1:3-indanedione (II), m.p.  $178\text{--}179^\circ$ . (I) and  $\text{HNO}_3$  (d 1.5) in conc.  $\text{H}_2\text{SO}_4$  at  $-5^\circ$  give 2-m-nitrobenzoyl-1:3-indanedione, m.p.  $228\text{--}229^\circ$  (decomp.), which is similarly cleaved to (II) and  $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . The Na (III) and Ag (IV) derivatives of Et 1:3-indanedione-2-carboxylate with AcCl give the readily hydrolysable Et 3-acetoxyindone-2-carboxylate, m.p.  $77\text{--}78^\circ$ ; (IV) [not (III)] and  $\text{BzCl}$  in  $\text{C}_6\text{H}_6$  afford the 3-benzoyloxy-ester, m.p.  $146\text{--}148^\circ$  (Hantzsch and Gajewski, A., 1912, i, 870). (III) and  $\text{BzCl}$  alone at  $80^\circ$  give a compound,  $\text{C}_{14}\text{H}_{10}\text{O}_4$ , m.p.  $140\text{--}141^\circ$ . H. B.

**Diphenacylfluorene; its relationship to fluor-enylideneacetophenone.** C. DUFRAISSE and A. P. DE CARVALHO (Bull. Soc. chim., 1936, [v], 3, 882—884).—Fluorenone (I),  $\text{COPhMe}$  (II),  $\text{Et}_2\text{O}$ , and  $\text{NaNH}_2$  give 9:9-diphenacylfluorene (cf. this vol., 208) (dioxime, m.p.  $214\text{--}215^\circ$ ), which decomposes at  $230^\circ$  into (II) and  $\omega$ -fluorenylideneacetophenone (A., 1930, 1437), also obtained direct from (I), (II), EtOH, and HCl. H. G. M.



**Sterols. VI. Synthetic preparation of oestrone (theelin).** R. E. MARKER, O. KAMM, T. S. OAKWOOD, and J. F. LAUCIUS (J. Amer. Chem. Soc., 1936, 58, 1503—1504).—Dehydroncoergosterol is reduced (Na, amyl alcohol) to the phenolic *tetrahydrodehydroncoergosterol*, m.p. 170.5—171.5°; acetylation, oxidation ( $\text{CrO}_3$ ), and hydrolysis ( $\text{EtOH-NaOH}$ ) of the resultant neutral product gives oestrone, m.p. 259—261.5°,  $[\alpha]_D^{25} +159^\circ$  in  $\text{EtOH}$  [benzoate, m.p. 205—207°; semicarbazone ( $+0.5\text{H}_2\text{O}$ ), m.p. 252—253°]. H. B.

Possible methods of synthesis of the carbon skeleton present in sterols, bile acids, sexual hormones, and plant heart poisons. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1936, 3, 317—343).—Six methods for the synthesis of the skeleton present in female sexual hormones and three methods for the male sexual hormones have been suggested.

F. R. S.

**Dihydroresorcinols. I. Hydrolysis of dihydroresorcinolcarboxylic esters. II. Autoxidation of dihydroresorcinol derivatives.** E. FRIEDMANN (J. pr. Chem., 1936, [ii], 146, 65—70, 71—78).—I. Dihydroresorcinolcarboxylic esters are readily hydrolysed by cold aq. alkali and subsequent decarboxylation of the acids gives the corresponding dihydroresorcinols in excellent yield. Thus Et 2-*p*-anisylcyclohexane-4 : 6-dione-1-carboxylate affords 1-*p*-anisylcyclohexane-3 : 5-dione, m.p. 181°, in 86—100% yield; it is reduced by Zn-Hg and boiling 5*N*-HCl to *p*-anisylcyclohexane, b.p. 141—144°/11 mm.  $\text{CHNa}(\text{CO}_2\text{Et})_2$  and *p*-methoxystyryl Et ketone afford Et 2-*p*-anisyl-5-methylcyclohexane-4 : 6-dione-1-carboxylate, m.p. 119—120°, hydrolysed and decarboxylated to 4-*p*-anisyl-1-methylcyclohexane-3 : 5-dione, m.p. 201—202°, whence 4-*p*-anisyl-1-methylcyclohexane, b.p. 156—159°/11 mm.

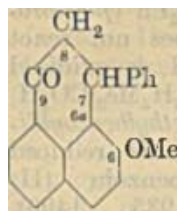
II. Condensation of *p*-methoxystyryl Me ketone with  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and NaOEt in EtOH affords 1-cyano-2-*p*-anisylcyclohexane-4 : 6-dione (I), m.p. 207° (decomp.) after becoming red (Na derivative; corresponding *O*-Me ether, m.p. 171°). Similarly, *p*-methoxystyryl Et ketone affords 1-cyano-2-*p*-anisyl-5-methylcyclohexane-4 : 6-dione (II), m.p. 173° (*O*-Me ether, m.p. 195—196°). The presence of Me at  $\text{C}_5$  decreases the readiness of autoxidation and catalytic hydrogenation. H. W.

**Synthesis of 2 : 4-dihydroxybenzophenone.** R. C. SHAH and P. R. MEHTA (J. Indian Chem. Soc., 1936, 13, 368—371).— $\text{NHPhBz}$  and  $m\text{-C}_6\text{H}_4(\text{OH})_2$  (I) in presence of  $\text{ZnCl}_2$  and  $\text{POCl}_3$  at 130—140° afford a product which with boiling 2*N*-NaOH is converted into 2 : 4-dihydroxybenzophenone (II).  $\text{NH}_2\text{Bz}$  reacts similarly, but  $\text{PhCN}$  is a by-product. (I) with  $\text{BzOH}$  and  $\text{ZnCl}_2$ ,  $\text{SnCl}_4$ , or  $\text{P}_2\text{O}_5$  gives a poor yield of (II).

J. L. D.

**periNaphthindene [phenalene] series. I. Condensation of  $\beta$ -naphthol with cinnamic acid.** C. F. KOELSCH (J. Amer. Chem. Soc., 1936, 58, 1326—1328).— $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  in boiling  $\text{AcOH-H}_2\text{SO}_4$  give 4-phenyl-3 : 4-dihydro-5 : 6-benzocoumarin, m.p. 115—116°, methylated ( $\text{Me}_2\text{SO}_4$ , 10% NaOH) to  $\beta$ -phenyl- $\beta$ -2-methoxy-1-naphthylprop-

ionic acid, m.p. 168—170°, the chloride of which with  $\text{AlCl}_3$  in  $\text{C}_6\text{H}_6$  affords 9-keto-6-methoxy-7-phenyl-7 : 8-dihydroperinaphthindene (I), m.p. 144—145° (oxime, m.p. 207—211°). (I) is demethylated (40% HBr, AcOH) to the 6-*OH*-derivative (II), m.p. 191—193° (sinters at 185°); oxidation ( $\text{CrO}_3$ , AcOH) gives 6a-hydroxy-6 : 9-diketo-7-phenyl-6 : 6a : 7 : 8-tetrahydroperinaphthindene ( $+ \text{H}_2\text{O}$ ), m.p. 105—110° (decomp.), m.p. (anhyd.) 160—163° (darkening), which is readily reduced (alkaline  $\text{Na}_2\text{S}_2\text{O}_4$ ) to (II). H. B.



**Tetramethoxyfluorene-carboxylic acid and the "red substance."** P. DREYFUSS (Rend. Semin. Fac. Sci. R. Univ. Cagliari, 1934, 4, 135—138; Chem. Zentr., 1935, ii, 3651—3652).—Condensation of veratrole with veratroylformic acid yields 2 : 3 : 6 : 7-tetramethoxyfluorene-9-carboxylic acid (monohydrate), which is decarboxylated to 2 : 3 : 6 : 7-tetramethoxyfluorene, oxidised to 2 : 3 : 6 : 7-tetramethoxyfluorenone (see below). H. N. R.

**2 : 3 : 6 : 7-Tetramethoxyphenanthraquinone.** A. OLIVERIO (Rend. Semin. Fac. Sci. R. Univ. Cagliari, 1934, 4, 126—129; Chem. Zentr., 1935, ii, 3651).—2 : 3 : 6 : 7-Tetramethoxyphenanthraquinone (improved prep.) [quinoxaline derivative, m.p. 270—271° (decomp.)] on distillation with CaO yields 2 : 3 : 6 : 7-tetramethoxyfluorenone, m.p. 202—208°, identical with the "red substance" of Vanzetti (A., 1927, 462). H. N. R.

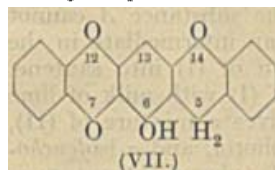
**Synthesis of plumbagin.** J. SAENZ DE BURUAGA and F. VERDU (Anal. Fís. Quím., 1934, 32, 830—837; cf. A., 1933, 1053; Witanowski, A., 1935, 420, 1375; Feiser *et al.*, this vol., 728).—2-Methyl- $\alpha$ -naphthaquinone (A., 1930, 91) with  $\text{H}_2\text{SO}_5$  yields 5-hydroxy-2-methyl- $\alpha$ -naphthaquinone identical with plumbagin, together with, probably, the 3-*OH*-derivative, m.p. 164—167°. F. R. G.

**Constitution and reactivity. XVII. Action of hydrogen sulphates during sulphonation.** K. LAUER and Y. HINATA (J. pr. Chem., 1936, [ii], 145, 287—290; cf. this vol., 1239).—The velocity of sulphonation of anthraquinone by 89.5 and 95.8%  $\text{H}_2\text{SO}_4$  and 3.2% oleum with varying amounts of  $\text{KHSO}_4$  at 150—220° is measured.  $\text{KHSO}_4$  decreases the reaction velocity with conc. acid, but with more dil. acid the first additions cause an increase. Sulphonation is probably due to an unknown pyrosulphate and its hydrate. R. S. C.

**Introduction of side-chains into anthraquinones.** C. MARSCHALK, F. KENIG, and N. OUROUSOFF (Bull. Soc. chim., 1936, [v], 3, 1545—1575).—The leuco-compounds of aminoanthraquinones with  $\text{CH}_2\text{O}$  or, better,  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$  in alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  in absence of  $\text{O}_2$  give sol. compounds with  $\text{CH}_2\cdot\text{SO}_3\text{Na}$  vicinal to the  $\text{NH}_2$ ; reduction by glucose or warm  $\text{Na}_2\text{S}_2\text{O}_4$  changes this substituent to Me and affords after re-oxidation aminomethylantraquinones (Me vicinal to  $\text{NH}_2$ ), which are usually the first products actually isolated. Hydroxyanthraquinones with aldehydes in hot alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  in absence of  $\text{O}_2$  give *vic*-hydroxy-aryl- or -alkyl-anthraquinones (A). In some cases and under certain conditions  $\text{CH}_2\text{O}$  or

$\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$  gives  $\text{H}_2\text{O}$ -sol. salts,  $\text{R}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$  [e.g.,  $\text{K}_2$  anthrarufin-2 : 6-di(methylsulphonate)]; these are stable to  $\text{Na}_2\text{S}_2\text{O}_4$ , are converted into (A) only by fusion with alkali, and thus are not intermediates in the formation of the latter, in contrast to the amino-anthraquinone reaction. In the absence of  $\text{O}_2$  or of an excess of  $\text{Na}_2\text{S}_2\text{O}_4$  quinizarin and  $\text{CH}_2\text{O}$  give directly a little 2 : 3-dimethylquinizarin (I); in the complete absence of  $\text{Na}_2\text{S}_2\text{O}_4$  (and of air) much di-3-quinizarinylmethane, m.p. 296—297°, and a little 2-methylquinizarin (I), m.p. 178—179°, are obtained. The normal reaction of hydroxy-quinones is thus to form first the carbinols,  $\text{X}\cdot\text{CHR}\cdot\text{OH}$  ( $\text{R}$ =alkyl, aralkyl, or  $\text{H}$ ;  $\text{X}$ =leucohydroxyanthraquinonyl); the  $\text{CH}\cdot\text{OH}$  is then reduced to  $\text{Me}$  by the 9 : 10-( $\text{OH}$ )<sub>2</sub>; the resultant methylquinones are reduced again to the leuco-compounds by the excess of  $\text{Na}_2\text{S}_2\text{O}_4$  and are finally isolated as quinones only after re-oxidation.  $\text{CH}_2\text{O}$  is more reactive than are other aldehydes. Thus quinizarin gives the  $\text{Me}_2$  compound, but only the mono-Et or  $-\text{CH}_2\text{Ph}$  compounds; these latter products react further with  $\text{CH}_2\text{O}$  to give mixed alkyl derivatives. Similarly 2-hydroxyanthraquinone reacts with only one mol. of  $\text{PhCHO}$ , but with 2 of  $\text{CH}_2\text{O}$ . The quinones described below are prepared by the above-mentioned reactions. (I), m.p. 253° ( $\text{Ac}_2$  derivative). 1-Hydroxy-2-methyl- and -2-benzyl-, 1-amino-2-methyl-, m.p. 202°, 1 : 5-diamino-2 : 6-dimethyl- (III) [converted by diazo-reactions into 2 : 6-dimethylantraquinone or its 2 : 6-( $\text{OH}$ )<sub>2</sub>-derivative], 5-chloro-1-amino-2-methyl-, m.p. 213° (with  $\text{HNO}_3$  gives an indazole derivative), 8-chloro-1-amino-2-methyl-, and 1 : 8-diamino-2 : 7-dimethyl-anthraquinone (IV), m.p. 223° (block). (IV) is also obtained by nitration and subsequent reduction of 2 : 7-dimethylantraquinone, gives (diazo-reactions) the 1 : 8-( $\text{OH}$ )<sub>2</sub>-compound, m.p. 216—217° (cf. lit.), and 2 : 3-dimethylantraquinone (V), and, when treated with  $\text{S}_2\text{Cl}_2$ - $\text{PhNO}_2$  and then with  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$  and finally sulphonated gives a blue acid dye, as also does (II); when nitrated and then reduced it gives a substance dyeing cellulose acetate bluish-violet. 2-Ethyl-, m.p. 168—169° (oxidised by  $\text{H}_3\text{BO}_3$ - $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$  at 140—143° to quinizarin-2-carboxylic acid), 2-methyl-3-ethyl-, m.p. 173—174° (oxidised to quinizarin-2 : 3-dicarboxylic acid), 2-butyl-, m.p. 125°, 2-benzyl-, m.p. 180—181° (very readily sulphonated), 2-benzyl-3-methyl-, m.p. 211°, 2-o-chlorobenzyl-, m.p. 183—184°, 2-p-tolylmethyl-, m.p. 177—178°, and 2-furfurylmethyl-quinizarin, m.p. 165—166°. 2 : 6-Dimethylanthrurufin, m.p. 240—241° ( $\text{Ac}_2$  derivative, m.p. 284—285°), also obtained (diazo-reaction) from (III). 2 : 7-Dimethylchrysazin, m.p. 216—217° ( $\text{Ac}_2$  derivative, m.p. 222—223°), also obtained from (IV). 1-Hydroxyanthraquinone-2-acetic acid (from  $\text{CHO}\cdot\text{CO}_2\text{H}$ ), m.p. 236—237° (block), when distilled, gives 1-hydroxy-2-methylantraquinone, affords 1-keto-5 : 6-phthaloyl-1 : 2-dihydrobenzofuran (VI) by treatment with  $\text{Ac}_2\text{O}$ , a substance,  $\text{C}_{16}\text{H}_{10}\text{O}_3$ , by the action of  $\text{SOCl}_2$ - $\text{PhNO}_2$  at 100° [also obtained similarly from (VI)], and by nitration and reduction a ? 4- $\text{NH}_2$ -derivative, which gives with  $\text{Al}(\text{OH})_3$  a violet lake, not fast to light. Quinizarin-2-acetic acid, m.p. 248—250°, gives similarly 2-methylquinizarin, with  $\text{H}_2\text{SO}_4$  an acid, which gives

a mordant dye, and with  $\text{H}_2\text{SO}_4$ - $\text{MnO}_2$  an orange acid; with  $\text{S}_2\text{Cl}_2$ - $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ - $\text{H}_2\text{SO}_4$  it gives a dye, as does (IV). 1-Hydroxy-2-o-carboxybenzyl-anthraquinone with  $\text{AlCl}_3$ - $\text{NaCl}$  at 150° gives impure 6-hydroxy-7 : 12 : 14-triketo-5 : 7 : 12 : 14-tetrahydro-



pentacene (VII). 2-o-Carboxybenzylquinizarin with  $\text{H}_2\text{SO}_4$ ,  $\text{ClSO}_3\text{H}$ , or  $\text{AlCl}_3$ - $\text{NaCl}$  at 140° gives 6 : 13-dihydroxy-7 : 12 : 14-triketo-5 : 7 : 12 : 14-tetrahydropentacene [cf. (VII)], oxidised by  $\text{MnO}_2$ - $\text{H}_2\text{SO}_4$  to 6 : 13-dihydroxypentacene-7 : 12 : 5 : 14-diquinone, also obtained from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  and leucoquinizarin. 4-Chloro-1-aminoanthraquinone loses the  $\text{Cl}$  during reaction with  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ - $\text{Na}_2\text{S}_2\text{O}_4$ . (V) and  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  at  $-10^\circ$  give 1-nitro- and thence ( $\text{Na}_2\text{S}$ ) 1-amino-2 : 3-dimethyl-anthraquinone, m.p. 211°, which with oleum (2—3%  $\text{SO}_3$ )-paraformaldehyde- $\text{HNO}_3$  affords a  $\text{NO}_2$ -compound, reduced ( $\text{Na}_2\text{S}$ ) to 1 : 4-diamino-2 : 3-dimethyl-anthraquinone; with  $\text{MnO}_2$ - $\text{H}_2\text{SO}_4$  this gives (I), which is also obtained from 2-methylquinizarin (VIII) and  $\text{CH}_2\text{O}$ - $\text{Na}_2\text{S}_2\text{O}_4$ . 2 : 2'-Diquinizarin and  $\text{KOH}$ - $\text{Na}_2\text{S}_2\text{O}_4$ - $\text{CH}_2\text{O}$  at 95° give 3 : 3'-dimethyl-2 : 2'-diquinizarin, m.p.  $>320^\circ$ , reduced to (VIII) by  $\text{Na}_2\text{S}_2\text{O}_4$  in aq.  $\text{C}_6\text{H}_5\text{N}$  at 40—50°. The benzyl-anthraquinones mentioned are sulphonated by 98%  $\text{H}_2\text{SO}_4$  at room temp. or 100° to give dyes, which give bluish-red lakes with  $\text{Al}(\text{OH})_3$ . The quinizarin derivatives with  $\text{HCl}$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Zn}$  dust, and primary aromatic amines give 1-hydroxy-4-anilino-derivatives, which give dyes when sulphonated. Sulphonation of the carboxybenzyl and pentacene compounds leads to dehydration and often oxidation.

R. S. C.

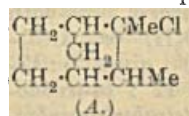
**2-Deuterocamphane.** E. BILLMANN, K. A. JENSEN, and B. BAK (Ber., 1936, 69, [B], 1947—1949; cf. this vol., 855).—Further experiments show that the decomp. of  $\text{Mg}$  *l*-bornyl chloride (I) with  $\text{H}_2\text{O}$  gives dextrorotatory camphane preps. (II) which do not lose their optical activity when crystallised repeatedly. In contrast with earlier experiences, crude (II) are dextrorotatory instead of levorotatory, and the sign persists in spite of repeated crystallisation of the initial material. The production of (II) is hence a complex process, and the previous results are rendered uncertain. Parallel decomp. of (I) by  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , respectively, appear to yield identical products but the yields with  $\text{D}_2\text{O}$  are considerably  $<$  with  $\text{H}_2\text{O}$ .

**Chlorination of camphane.** A. GANDINI (Gazzetta, 1936, 66, 357—365).—Camphane (I) in  $\text{CHCl}_3$  treated in sunlight with 1  $\text{Cl}_2$  gives mainly bornyl chloride (II); (I) with 2  $\text{Cl}_2$ , or (II) in  $\text{CCl}_4$  with 1  $\text{Cl}_2$ , gives 2 : 3-dichlorocamphane (III), m.p. 126—126.5°, b.p.  $>220^\circ$  (decomp.) (of which a small amount is also obtained in the first reaction), oxidised by  $\text{KMnO}_4$  to *i*-camphoric acid, and to an acid, m.p. 100—101°. The structure of (III) is shown by its dechlorination ( $\text{Na}$  in  $\text{Et}_2\text{O}$ ) to bornylene, and its formation from the latter and  $\text{Cl}_2$ . E. W. W.

True constitution of camphenyl and 4-methylcamphenyl chloride and a stereois-



meric  $\alpha$ -fenchocamphorol. G. KOMPPA and G. A. NYMAN (Ber., 1936, 69, [B], 1813—1820).—The "camphenilyl chloride" (I) obtained from camphenilol (II) by the action of  $\text{PCl}_5$  in light petroleum is very resistant towards 0.5*N*-KOH-EtOH at 20°, so that Cl is completely *sec*. The substance A cannot



therefore be an intermediate in the transformation of (I) into santene. Hydrolysis of (I) with milk of lime at 50—60° gives a mixture of (II),  $\beta$ -fenchocamphorol, and  $\alpha$ -isofenchocamphorol (III), m.p. 132—133° (phenylurethane, m.p. 115—116°), oxidised to apocamphoric (IV) and apofenchocamphoric (V) acid and camphenilone. (I) is not therefore a normal derivative of (II), but is formed by change in the C skeleton, and consists mainly of apobornyl chloride. apocyclene hydrochloride is hydrolysed to a mixture of alcohols oxidised to (IV) and (V) and from which (III) is isolated by crystallisation. The non-identity of (III) and the  $\alpha$ -fenchocamphorol obtained by alkaline reduction of the corresponding ketone is established by the non-identity of the corresponding *H* phthalates, m.p. 168—169° and 166.5—167.5°, respectively, which show depression in mixed m.p. 4-Methylcamphenilol is similarly converted into the "chloride," which with milk of lime gives a (?) hydrocarbon and, mainly, *dl*-epiborneol, m.p. 179—181° (phenylurethane, m.p. 94—95°), oxidised to *dl*-camphoric acid. H. W.

**Physical identity of enantiomers. II. (a) Rotatory dispersion of *d*-, *l*-, and *dl*-oximinocamphor and their sodium derivatives. (b) Differences in the physiological action of *d*-, *l*-, and *dl*-forms of sodio-oximinocamphor.** B. K. SINGH and S. PRASAD (Proc. Indian Acad. Sci., 1936, 3, A, 586—593).—1-Oximinocamphor is obtained in the stable form, m.p. 152°, and unstable form, m.p. 114°, by the action of  $\text{C}_6\text{H}_{11}\text{ONO}$  on Na and *l*-camphor at 0°. The *dl*-compound, m.p. 108°, is similarly obtained from *dl*-camphor. The rotatory dispersions of *d*- and *l*-oximinocamphor in  $\text{C}_6\text{H}_6$ , EtOH, and  $\text{CHCl}_3$  and of their Na derivatives in  $\text{H}_2\text{O}$  are recorded, as are the physiological activities of *d*-, *l*-, and *dl*-sodio-oximinocamphor. F. N. W.

**Different reaction velocities of enantiomers with a common optically active reagent. I. New reactions of *d*- and *l*-camphor-10-sulphonyl chlorides.** A. S. GALLOWAY and J. READ (J.C.S., 1936, 1219—1222).—*d*-Camphor-10-sulphonyl chloride (I) and *p*-aminoacetanilide give the *Ac* derivative, m.p. 136—137°,  $[\alpha]_D +40.5^\circ$  in  $\text{CHCl}_3$ , hydrolysed to mono-*d*-camphor-10-sulphonyl-*p*-phenylenediamine (II), m.p. 185°,  $[\alpha]_D +41.1^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . *p*-Acetamidophenyl *d*-camphor-10-sulphonate, m.p. 79°,  $[\alpha]_D +34.1^\circ$  in  $\text{CHCl}_3$ , is similarly obtained and is hydrolysed to the *p*-aminophenyl compound (III) m.p. 102—103°,  $[\alpha]_D +42.3^\circ$  in  $\text{CHCl}_3$ . (I) and (II) form *di*-*d*-, m.p. 188°,  $[\alpha]_D +52.3^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ , and *d*-camphor-10-sulphonyl-*p*-phenylenediamine, m.p. 206°,  $[\alpha]_D \pm 0.0^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ ; in this reaction, the proportion of *D*-*d* and *L*-*d* forms from the *d*- and *l*-forms of (I) is 58 : 42. *d*- and *l*-forms of (I) react with (III) to give *p*-*d*-, m.p. 133°,  $[\alpha]_D +69.9^\circ$  in  $\text{CHCl}_3$  and *p*-*l*-camphor-10-sulphonamidophenyl *d*-camphor-10-sul-

*phonate*, m.p. 135°,  $[\alpha]_D -2.4^\circ$  in  $\text{CHCl}_3$ , in the proportion 61 : 39. F. R. S.

**Homologues of the camphor group. X. Benzyldenecamphane, a dehydration product of *tert*-benzylbornyl alcohol.** S. S. NAMETKIN and M. K. STRUGATSKI (J. Gen. Chem. Russ., 1936, 6, 862—867).—*tert*-Benzylbornyl alcohol and anhyd.  $\text{KHSO}_4$  (150—160° : 3 hr.) yield benzyldenecamphane, m.p. 25° [wrongly identified by Haller *et al.* (A., 1906, i, 440) as  $\beta$ -benzylcamphene], also obtained synthetically from phenylbornylcarbinol by heating with K in PhMe, and treating the alkoxide so formed with  $\text{CS}_2$ , adding MeI to the ppt. of xanthate obtained, and decomp. the Me ester at 160°. R. T.

**New methods in stereochemistry. III. New optically active reagents for ketones and aldehydes.** A. S. GALLOWAY and J. READ (J.C.S., 1936, 1222—1225).—*p*-Hydroxynitrosomethylaniline and *d*-camphor-10-sulphonyl chloride give *p*-*d*-camphor-10-sulphonoxy-nitrosomethylaniline, m.p. 115°,  $[\alpha]_D +40.0^\circ$ , hydrolysed to the -methylaniline, m.p. 67—68°,  $[\alpha]_D +44.5^\circ$ , and reduced (Zn-AcOH) to the -phenyl- $\alpha$ -methylhydrazine, m.p. 45—46° (benzylidene, m.p. 138°, and *p*-nitrobenzylidene derivatives, m.p. 200°). *l*-Menthylamine and *p*- $\text{C}_6\text{H}_4\text{MeSO}_2\text{Cl}$  yield *p*-toluenesulphonbenzyl-*l*-menthylamide, m.p. 96—97°,  $[\alpha]_D -39.9^\circ$ , which with  $\text{HNO}_2$  gives benzyl-*l*-menthyl-nitrosoamine, m.p. 52°,  $[\alpha]_D -2.5^\circ$ . *p*-Nitrobenzyl-*l*-menthylamine, m.p. 53°,  $[\alpha]_D -89.4^\circ$  (*p*-toluenesulphonyl derivative, m.p. 115°,  $[\alpha]_D -49.3^\circ$ ), with AcOH and  $\text{NaNO}_2$  forms *p*-nitrobenzyl-*l*-menthyl-nitrosoamine, m.p. 132°,  $[\alpha]_D +17.6^\circ$ , reduced (Zn-AcOH) to the *p*-*NH*<sub>2</sub>-compound, m.p. 88°,  $[\alpha]_D +21.8^\circ$ . Et *l*-menthylglycine and  $\text{N}_2\text{H}_4$  yield *l*-menthylglycine-hydrazide,  $[\alpha]_D -57.7^\circ$ , which gives acetone-, m.p. 55°,  $[\alpha]_D -52.5^\circ$ , and *l*-menthone-*l*-menthylglycine-hydrazone,  $[\alpha]_D -69.1^\circ$ , and the benzylidene derivative of benzaldehyde-*l*-menthylglycinehydrazone, m.p. 158°,  $[\alpha]_D -266.9^\circ$ . Et *d*-neomenthylglycine, b.p. 139—141°/11 mm.,  $[\alpha]_D +32.7^\circ$ , with  $\text{N}_2\text{H}_4$  gives *d*-neomenthylglycinehydrazide, m.p. 51°,  $[\alpha]_D +40.0^\circ$ , which affords acetone-, m.p. 79.5°,  $[\alpha]_D +24.5^\circ$ , benzaldehyde-, m.p. 110°,  $[\alpha]_D +20.8^\circ$ , *l*-menthone-, m.p. 102—103°,  $[\alpha]_D -9.0^\circ$ , and *dl*-menthone-*d*-neomenthylglycinehydrazone, m.p. 98—99°,  $[\alpha]_D +9.3^\circ$ . All rotations are in  $\text{CHCl}_3$ . F. R. S.

**Sesquiterpene series. III. Synthesis of 1 : 10-dimethyl-7-isopropyldecyl-2-one.** A. E. BRADFIELD, E. R. JONES, and J. L. SIMONSEN (J.C.S., 1936, 1137—1143).—*l*-Tetrahydracarvone, condensed with  $\text{CH}_2\text{Cl-CH}_2\text{-CO}_2\text{Et}$ , gave fractions, b.p. 172—182°/14 mm. (I) and b.p. 182—240°/14 mm. (II). From (I), following hydrolysis, a liquid acid (semicarbazone, m.p. 186—187°) was obtained, corresponding with  $\text{CHPr}^a < \begin{array}{c} \text{CH}_2\text{---CH}_2 \\ | \\ \text{CH}_2\text{---CO} \end{array} > \text{CMe-}[\text{CH}_2]_2\text{-CO}_2\text{Et}$ . (I) with  $\text{Et}_2\text{C}_2\text{O}_4$  gave a neutral substance (III) and an oil (IV) extracted from the acidified mother-liquors. (III) gave rise to more of (I), whilst (IV), when heated, lost CO, yielding Et 3-carbetoxy-1-methyl-4-isopropylcyclohexan-2-one-1- $\beta$ -propionate, b.p. 186—189°/4 mm.,  $[\alpha]_{5461} -82^\circ$  (semicarbazone, m.p. 155°), which on hydrolysis and re-esterification gave Et 1-methyl-4-isopropylcyclohexan-2-one-1- $\beta$ -propionate (V), b.p.

174°/11 mm.,  $[\alpha]_{5461} -112^\circ$ , the parent acid of which gives the semicarbazone, m.p. 186—187°, above. (V) with  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and Zn yielded a main fraction, b.p. <185°/10 mm., and a small fraction b.p. 185—220°/10 mm. Further treatment of the main fraction with the same reagents yielded ultimately a product, b.p. 170—220°/11 mm., and from the fraction boiling up to 190°/11 mm. a 2:4-dinitrophenylhydrazone, m.p. 187—189°. Catalytic reduction of the whole condensation product, led to two fractions, (A) b.p. up to 175°/10 mm., and (B) 175—220°/10 mm., the former of which gave a ketone, b.p. 165—170°/16 mm. (2:4-dinitrophenylhydrazone identical with the above), reduced catalytically to 1:10-dimethyl-7-isopropyldecal-2-one (VI), b.p. 146—155°/11 mm., m.p. 102—103°,  $[\alpha]_{5461} +22.2^\circ$ , [semicarbazone, m.p. 210°; 2:4-dinitrophenylhydrazone, m.p. 221—223° (decomp.)]. In the total distillate some hydrocarbon was apparently present. (VI) when treated with  $\text{MgMeI}$  and then dehydrogenated with Se gave an oil, b.p. 130—160°/14 mm., the picrate and  $s\text{-C}_6\text{H}_5(\text{NO}_2)_3$  derivatives of which had m.p. and mixed m.p. identical with those of 1:2:7- $\text{C}_{10}\text{H}_5\text{Me}_2\text{Pr}^{\text{a}}$ . Et 1:3-dimethylcyclohexan-2-one-3-carboxylate, b.p. 115—116°/16 mm., gives a semicarbazone, m.p. 181°, in the prep. of which 2-carbamyl-3-keto-7:9-dimethyl-3:4:5:6:7:9-hexahydroindazole, m.p. 144—147°, was obtained as by-product. Et 3-carbethoxy-1:3-dimethylcyclohexan-2-ol-2-acetate, b.p. 172—173°/17 mm. (from the above ketone,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ , and Zn), with  $\text{SOCl}_2$  gave Et 3-carbethoxy-1:3-dimethylcyclohexylidene-2-acetate (VII), b.p. 159°/13 mm., which was hydrolysed to acids, m.p. 148—150°, and m.p. 120—121°, together with the H ester (?). Re-esterification, following hydrolysis, yielded a lactonic acid, m.p. 194—195° (Et ester, b.p. 174—176°/11 mm.), and an isomeric lactonic acid, m.p. 128—129°. Reduction of (VII), in two stages, gave Et 3-carbethoxy-1:3-dimethylcyclohexane-2-acetate, b.p. 155°/12 mm., and 1:3-dimethyl-3-hydroxymethyl-2- $\beta$ -hydroxyethylcyclohexane (VIII), b.p. 150—180°/15 mm. (diacetate, b.p. 136—137°/4 mm.), with an unsaturated alcohol. A by-product in the prep. of (VIII) was 3-carboxy-1:3-dimethylcyclohexane-2-acetic acid, m.p. 185°. 6-Methyl-3:4:5:8-tetrahydrocoumaran-1:2-dione (?), b.p. 170—178°/12 mm., m.p. 139—140°, was obtained from distillation residues of Et 1-methylcyclohexan-2-one-3-carboxylate, and 2-methylcyclohexyl-1-methylcyclohexan-2-one-3-carboxylate, b.p. 181—182°/19 mm. (semicarbazone, m.p. 152—153°; 2:4-dinitrophenylhydrazone, decomp. 109—110°), from by-products of  $\text{Et}_2\text{C}_2\text{O}_4$  condensation. J. T. A.

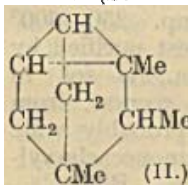
**Catalytic dehydration of  $\beta$ -fenchyl alcohol.** N. J. TOIVONEN (Suomen Kem., 1936, 9, A, 72—73).—By heating with kaolin to 200°,  $\beta$ -fenchyl alcohol yields  $\beta$ -fenchene; under similar conditions  $\alpha$ -fenchyl alcohol is dehydrated much less readily to a mixture of fenchene and methylsantene. H. N. R.

**Action of isomerisation catalysts on tricyclic hydrocarbons of the terpene series.** N. J. TOIVONEN (Suomen Kem., 1936, 9, A, 75—76).—cycloFenchene is readily polymerised on keeping with

Florida earth; tricyclene and apocyclene are scarcely attacked by this reagent even under drastic conditions.

H. N. R.

**Racemisation of methylsantene.** N. J. TOIVONEN (Suomen Kem., 1936, 9, A, 73—75).—After purification, the methylsantenes obtained by dehydration of  $\alpha$ -fenchyl alcohol (I) with Florida earth and with  $\text{ZnCl}_2$  are optically inactive; a mechanism is suggested to account for this. A tricyclic terpene, b.p. 154—155°, possibly (II), is produced in small amount in the dehydration of (I) with kaolin. H. N. R.



**Primary resin acids.** K. KRAFT (Annalen, 1936, 524, 1—13).—The filtrates obtained after removal of pimaric acids as  $\text{NH}_4$  salts from the crude acids from the resin of *Pinus palustris* are treated with  $\text{CO}_2$  and the liberated acids are again purified through the  $\text{NH}_4$  salts followed by crystallisation, whereby proabietic acid (I),  $\text{C}_{20}\text{H}_{30}\text{O}_2$ , m.p. 159—160°,  $[\alpha]_{\text{D}} +11.5^\circ$  in 96% EtOH, is obtained. It is also obtained from French galipot. It is isomerised by  $\text{HCl}$ -EtOH at room temp. to abietic acid (II), and comparison of the  $[\alpha]_{\text{D}}$ -t graph thus observed with that for the isomerisation of *l*-pimaric acid (III) indicates that it is probably an intermediate product in the latter change. The transformation of (I) and (III) into (II) by boiling AcOH indicates a common C skeleton. The absorption spectrum of (III) indicates the probable presence of three conjugated double linkings (cf. A., 1935, 1372), but treatment of dihydro-*l*-pimaric acid with  $\text{BzO}_2\text{H}$  shows the presence therein of a single double linking, whilst two only are observed in (II) and (III). Probably these are present in the same ring. Ozonisation of (III) does not give  $\text{CH}_2\text{O}$ , indicating thus the absence of terminal  $\text{CH}_2$ . The view that the majority of the sapic acids are mixtures of (III) and *d*-pimaric acid requires modification in view of the isolation of (I). Probably the no. of primary resin acids does not exceed four. H. W.

**Ammoresinol.** H. RAUDNITZ, F. PETRU, E. DIAMANT, K. NEURAD, and K. LANNER (Ber., 1936, 69, [B], 1956—1961).—According to analyses and determinations of mol. wt., diacetylammoresinol (I), m.p. 102—103°, is  $\text{C}_{28}\text{H}_{34}\text{O}_6$ . It contains 2 Ac; hence ammmoresinol (II), m.p. 111°, is  $\text{C}_{24}\text{H}_{30}\text{O}_4$ , confirmed by analysis and mol. wt. determinations. Hydrogenation ( $\text{PtO}_2$  in AcOH) of (I) at 50° yields diacetylhexahydroammoresinol (III), m.p. 64°, unaffected by Br or  $\text{C}(\text{NO}_2)_4$ . Ozonolysis of (I) gives 0.8 mol. of  $\text{COMe}_2$  1:1  $\text{CMe}_2$ . Oxidation of (III) by  $\text{KMnO}_4$  in  $\text{COMe}_2$  affords  $\beta\gamma$ -dimethylundecan- $\kappa$ -one (semicarbazone, m.p. 97°),  $\gamma$ -hydroxy- $\gamma\lambda$ -trimethyldecylolactone (IV), b.p. 130—135°/0.2 mm.,  $\beta$ -resorecylic and 2-hydroxy-4-acetoxybenzoic acid. (IV) is stable to  $\text{SOCl}_2$ . Moderated oxidation of (II) with  $\text{CrO}_3$  gives a saturated acid,  $\text{C}_{20}\text{H}_{20}\text{O}_8$ , m.p. 199°, and an unsaturated neutral substance,  $\text{C}_{22}\text{H}_{26}\text{O}_5$ , m.p. 99°. When heated in a high vac. (I) is decomposed with evolution of gas whereas (II) affords a hydrocarbon,  $\text{C}_{13}\text{H}_{22}$ , b.p. 64°/0.08 mm.



No evidence of a fourth, difficultly saturated double linking is obtained (cf. Spath *et al.*, this vol., 1118).

H. W.

**Rhodocladonic acid.** G. KOLLER and H. HAMBURG (*Monatsh.*, 1936, 68, 202—206).—Rhodocladonic acid,  $C_{16}H_{10}O_8 \cdot OMe$ , decomp. 250—300° (Ac. derivative, m.p. 216—218°), is best purified by sublimation at 210—230°/0.008 mm., is sol. in  $NaHCO_3$  etc., and, when repeatedly recryst. from AcOH, gives an Ac derivative. It is probably a Me tetrahydroxy-hydroxymethylantraquinonecarboxylate.

R. S. C.

**Spirilloxanthin.**—See this vol., 1155.

**Dracorubin, the red pigment of dragon's blood.** I. H. BROCKMANN and R. HAASE (*Ber.*, 1936, 69, [B], 1950—1954).—Powdered Indian dragon's blood is extracted with boiling  $C_6H_6$ ; the cold, filtered extract is treated with picric acid and the ppt. is decomposed with  $KOH-MeOH-H_2O$ . The crude pigment is purified by adsorption with  $Al_2O_3$  thus giving dracorubin (I),  $C_{19}H_{14}O_8$ , m.p. 315° (Berl) (also +0.5  $CHCl_3$  and +1  $MeOH$ ) (picrate; hydrochloride; perchlorate). It does not contain N,  $CMc_2$ , OMe, or active H. Oxidation with  $CrO_3$  (Kuhn) affords 1.7 mol. of acid. (I) is moderately stable to dil.  $KOH-EtOH$  but prolonged boiling with conc. solutions causes decolorisation with production of  $BzOH$  and  $COPhMe$ . Hydrogenation (Pt in  $MeOH$  or  $EtOAc$ ) causes decolorisation and ceases after absorption of 1  $H_2$  and (I) is regenerated from the solution by air. In AcOH decolorisation occurs after absorption of 2  $H_2$  and after that of 5  $H_2$  a colourless product, m.p. 242°, is produced. (I) closely resembles 2-phenylbenzopyran derivatives.

**New pterins.** C. SCHOPF and E. BECKER (*Analen*, 1936, 524, 49—123).—Examination of *Appias nero*, F., *Catopsilia argante*, F., *Euchloe cardamines*, and *Colias edusa* shows the presence of xanthopterin (I), erythropterin (II), and guanopterin (III), whilst in addition to leucopterin (IV) and (I), chrysopterin (V) is isolated from *Gonepteryx rhamni*, L. After a preliminary extraction of the wings with  $Et_2O$  and  $EtOH$  the pterins are isolated and purified by repeated fractional extraction with dil.  $NH_3$  and fractional pptn. or extraction with acid. Chromatographic analysis is useful only for identification or enrichment. They and their derivatives have no definite m.p. and proof of homogeneity rests on absorption spectrum and elementary analysis, particularly the determination of N (Kjeldahl-Friedrich), and isolation of individuals from various sources. They appear to form a complex natural group containing 19 C per mol. in the case of (I), (III), and (IV) and probably also of (II) and (V). The very high N content is characteristic. The individuality of the pterin preps. cannot generally be guaranteed and in some cases there is distinct evidence that they are mixtures of isomerides or closely allied substances.

(II) is obtained from *A. nero*, *E. cardamines*, *C. argante*, *Col. edusa*, and *G. rhamni* and is best freed from (I) by crystallisation from 0.1N-HCl. Analyses of the products thus obtained are not very concordant and are best expressed by  $C_{19}H_{17-18}O_{8-10}N_{13-11}$  in

which  $xO + yN = 20$  or 21. In spite of this uncertainty a peculiar group is at any rate concerned; this is characterised by red colour, relatively low N content, and violet-blue fluorescence in 0.5N-AcOH. (II) is much better adsorbed by (I) by  $Al_2O_3$  from dil. aq. HCl or HCl-MeOH. The solubility of (II) in  $H_2O$  is considerable. It does not give cryst. salts with acids or alkalis. The alkaline-earth salts are very sparingly sol. in hot  $H_2O$  and separation of (II) from (I) by hot aq.  $Ba(OH)_2$  is therefore possible. The Ag and Fe salts are very dark ppts.  $HNO_3$  (conc. and 1 : 1) readily decomposes (II) and the residues do not give the murexide reaction. (II) tends to pass into a dark violet, amorphous transformation product probably of high mol. wt. The absorption spectra of various samples of (II) do not show good concordance.

(I) is best purified by repeated crystallisation of the  $\beta$ -Ba salt (VI), re-analyses of which agree with  $C_{19}H_{14}O_8N_{16}Ba_3$ ; for (I)  $C_{19}H_{14}O_8N_{12}$  is most probable. Analyses and X-ray diagrams of the Ba salt obtained from *A. nero*, *C. argante*, and *S. rhamni* are identical, and preps. of (I) from these sources have identical absorption spectra. As far as can be judged an identical material is derived from *E. cardamines* and *Col. edusa* so that (I) appears chemically homogeneous. During the isolation of (I) from *C. argante* a more acidic isomeride is obtained, converted by aq.  $Ba(OH)_2$  into (VI). During the isolation of (VI) from crude (I) the formation of a dark brown, very sparingly sol. Ba salt is observed from which (V),  $C_{19}H_{16}O_8N_{14}$ , purified through the Na salt, is obtained. Probably it is derived from (I) by replacement of 2 NH by 2 O. Its solution in 0.5N-AcOH has a violet-blue fluorescence. It is more strongly adsorbed than (I) by  $Al_2O_3$  from very dil. aq. HCl, but the difference is less marked from HCl-MeOH.

(III), first observed in *E. cardamines*, is separated from (II) and (IV) by its readier solubility in most acids and from (V) and (I) by its ready solubility in aq.  $Ba(OH)_2$  and purified through the very sparingly sol. sulphate,  $C_{19}H_{22}O_4N_{20} \cdot 2H_2SO_4$ , from which NaOAc liberates it. It is  $C_{19}H_{22}O_4N_{20}$  or, after desiccation at 120°/high vac.,  $C_{19}H_{20}O_3N_{20}$ . Fluorescence is not shown by it or its solutions. It is adsorbed by Frankonit KL. The Ag salt is stable in boiling solution. It does not give the "lepidoporphyrin" reaction when warmed with 20%  $H_2SO_4$  or the murexide reaction with  $HNO_3$ . The absorption spectrum has a single max. at 284  $m\mu$ , probably corresponding with a pyrimidine nucleus.

The possible constitution of the pterins is discussed.

H. W.

**Acetylation of lignin, and its isolation from wood.** II. F. KOMAROV and G. FILMONOVA (*J. Appl. Chem. Russ.*, 1936, 9, 1096—1105).—Acetylation of lignin (I) prepared by the König, Willstätter, and Freudenberg methods gives products yielding respectively 33, 31, and 26.7% of AcOH, whilst the acetylated products of resinification of fructose yield <15% of AcOH. It is concluded that the differences are due to slight modifications of (I) arising from differences in the extraction procedures, but are not due to production of (I) from sugars.

**Ursolic acid. III. Acid from the leaves of *Rhododendron hymenanthos*, Makino.** S. KUWADA and T. MATSUKAWA (J. Pharm. Soc. Japan, 1933, 53, 1065—1070).—Extraction of the leaves with Et<sub>2</sub>O affords  $\beta$ -ursolic acid (I), m.p. 290—291° (decomp.) (acetate, m.p. 294—295°; Me ester of acetate, m.p. 245—246°; Me ester of benzoate, m.p. 215—216°). (I) gives a Me ester, m.p. 230°, with Me<sub>2</sub>SO<sub>4</sub> or, after treatment with alkali, with CH<sub>2</sub>N<sub>2</sub>; with CH<sub>2</sub>N<sub>2</sub> (I) yields another Me ester, m.p. 170—172°.

CH. ABS. (r)

**Bitter constituents of colombo root. III. F. WESSELY, K. SCHÖNOL, and W. ISEMANN** (Monatsh., 1936, 68, 274).—A minor correction (cf. this vol., 995).

R. S. C.

**Bitter principles of colombo root. V. K. FEIST, R. BRACHVOGEL, and W. VOLKSEN** (Annalen, 1936, 523, 289—294; cf. this vol., 730).—COMe<sub>2</sub> is formed from columbin and 50% KOH at about 270°. The K compound of carboxyiso-V-columbin, isolated impure as intermediary product in the prep. of this compound, with Me<sub>2</sub>SO<sub>4</sub>—5% aq. KOH gives the Me ether, C<sub>20</sub>H<sub>21</sub>O·OMe, m.p. 241°. When merochamanthic acid Me ether, m.p. 248°, is distilled with Zn dust, it yields 1 : 2 : 5-C<sub>10</sub>H<sub>14</sub>Me<sub>3</sub> and a trace of a phenol.

R. S. C.

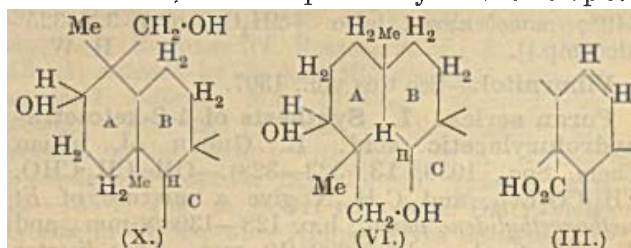
**Constitution of acid sapogenins. X. Hederagenin and oleanolic acid.** Z. KITASATO [with C. SONE and H. SHISHIDO] (Acta Phytochim., 1936, 9, 43—60; cf. A., 1935, 1126).—The following oxidations by CrO<sub>3</sub> in AcOH are recorded: diacetyl-hederagenin to *ketodiacetylhederagenin* (I), m.p. 217° or (+H<sub>2</sub>O) m.p. 162° [Me ester (II), m.p. 237°]; acetyloleanolic acid to *ketoacetyloleanolic acid* (II), m.p. 278° (Me ester, m.p. 237°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +99.2° in CHCl<sub>3</sub>); hederagenin acid to *ketohederagenic acid*, m.p. 275° (decomp.) [Me ester, m.p. 237°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +149.2° in CHCl<sub>3</sub>]; Me<sub>2</sub> hederagenonedicarboxylate to Me<sub>2</sub> *ketohederagenonedicarboxylate*, m.p. 165—166°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +53.7° in CHCl<sub>3</sub>; Me acetyloleanolate to Me *ketodehydroacetyloleanolate*, m.p. 195°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —8.4° in CHCl<sub>3</sub>. The following conversions are effected with HBr—AcOH: (I) to  $\psi$ -ketohederagenin, m.p. >300°; (III) to  $\psi$ -keto-oleanolic acid, m.p. 267—271° (decomp.); ketodiacetylhederageninlactone (IV) to *isoketodiacetylhederagenin* (V), m.p. 275—279°; ketoacetyloleanolactone to *isoketoacetyloleanolic acid* (VII), m.p. 324—330° (Me ester, m.p. 216°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +25.7° in CHCl<sub>3</sub>). The following reductions with Na—Hg are described: (IV) to ketodehydrohederagenin, m.p. >300°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —11.6° in CHCl<sub>3</sub>; ketoacetyloleanolactone to Me ketodihydro-oleanolate, m.p. 198—200°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —19.6° in CHCl<sub>3</sub>;  $\psi$ -ketodiacetylhederagenin to dehydrohederageninlactone;  $\psi$ -ketodiacetylhederagenin Me ester to dehydrohederagenin Me ester, m.p. 219—220° (Ac<sub>2</sub> derivative, m.p. 199°, [ $\alpha$ ]<sub>D</sub> —124.5°); Me  $\psi$ -ketoacetyloleanolate to Me *dehydro-oleanolate*, m.p. 175°; (V) to *isodehydrohederagenin* (Ac<sub>2</sub> derivative, m.p. 247—250°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +222.1°, and its Me ester, m.p. 140—145°, [ $\alpha$ ]<sub>D</sub> +223.3° in CHCl<sub>3</sub>); (VI) to *isodehydro-oleanolic acid* (Ac derivative, m.p. 235°); (V) to *dehydrodiacetylhederagenin*, m.p. 212—215°, after loss of H<sub>2</sub>O of crystallisation at 152°, [ $\alpha$ ]<sub>D</sub> —122.2° in CHCl<sub>3</sub>;

(III) to *dehydroacetyloleanolic acid* (Ac derivative, m.p. 205°, [ $\alpha$ ]<sub>D</sub> —105.9° in CHCl<sub>3</sub> and its Me ester, m.p. 224°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —115.4° in CHCl<sub>3</sub>); (III) to *isodehydrodiacetylhederagenin* Me ester and impure dehydrodiacetylhederagenin Me ester; oleanolic acid to oleanylenic acid (Me ester, m.p. 136—140°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +119.2° in CHCl<sub>3</sub>).

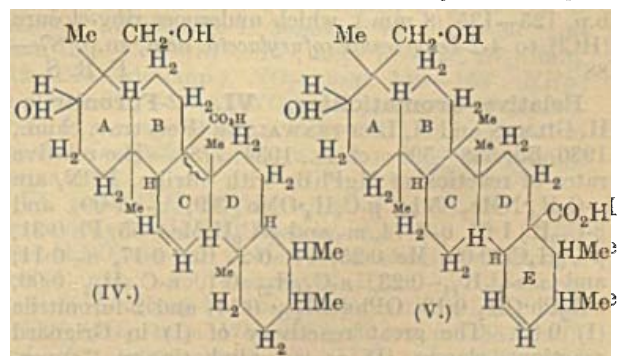
Hedratricarboxylic acid is converted by boiling conc. HCl—MeOH into the Me H<sub>2</sub> ester, m.p. 185°, and by KOH—Me<sub>2</sub>SO<sub>4</sub> followed by HCl—MeOH into the Me<sub>3</sub> ester (VII), m.p. 124°, also obtained by use of CH<sub>2</sub>N<sub>2</sub>. Regulated hydrolysis of (VII) affords the Me<sub>2</sub> H ester. Oxidation of the Me ester of hederagenonedicarboxylomonolactone with CrO<sub>3</sub>—conc. H<sub>2</sub>SO<sub>4</sub>—AcOH yields the Me<sub>2</sub> ester of hedratricarboxylomonolactone, m.p. 170°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> ±0° in CHCl<sub>3</sub>, also obtained from (VII) and HBr—AcOH at room temp., and the monolactone of the Me<sub>3</sub> ester of a tetracarboxylic acid, m.p. 195°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> —23.9° in CHCl<sub>3</sub>.

H. W.

**Constitution of acid sapogenins. XI. Z. KITASATO** (Acta Phytochim., 1936, 9, 61—74).—The conditions of Ruzicka's dehydrogenations are regarded as too drastic to form a completely trustworthy guide to the structure of hederagenin (I) and oleanolic acid (II) and attempts are made to deduce their constitutions from oxidative observations. The presence of the group  $\cdot\text{CMe}(\text{CH}_2\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot$  in ring A is established and the behaviour of hedratricarboxylic acid towards esterification and of its esters towards hydrolysis combined with that of the Me ester of hederagenonedicarboxylomonolactone towards CrO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in AcOH establishes the possibilities (X) and (VI) for the rings A and B. The presence of a sec.-OH in (II) is established, with the probability that it occupies



the same position as in (I). Reasons are advanced for assigning structure (III) to the ring containing the



double linking and CO<sub>2</sub>H and the results combined with the application of the isoprene rule indicate the constitution (IV) or (V) for (I).

H. W.



**Constitution of acid sapogenins. XII. Z. KITASATO** [with H. SHISHIDO] (*Acta Phytochim.*, 1936, 9, 75—82).—Oxidation of Me *isoketo-oleanolate* with  $\text{CrO}_3\text{--H}_2\text{SO}_4$  in AcOH affords *Me\_3 isoketo-oleanoltricarboxylate*, m.p. 219—220°,  $[\alpha]_D^{25} -16.4^\circ$  in  $\text{CHCl}_3$ , whilst similar treatment of its Ac derivative yields a small amount of substance, m.p. 278°, and much unchanged materials without any tricarboxylic acid or dicarboxylolactone expected on the basis of Ruzicka's formulation (this vol., 477). On the other hand, oxidation of Me *ketoacetyloleanolate* affords the lactone of Me, *acetyloleanoldicarboxylate* (I), m.p. 202—204°,  $[\alpha]_D^{25} +14.8^\circ$  in  $\text{CHCl}_3$ , also obtained from hydroxyacetyl-oleanolactone and identical with Ruzicka's product, so that his scheme is devoid of experimental basis. (I) is hydrolysed by KOH—MeOH to *oleanolpenta-carboxylic acid* (*Me\_5* ester, m.p. 205°,  $[\alpha]_D^{25} -15.5^\circ$  in  $\text{CHCl}_3$ ). Oxidation of dehydro- or  $\psi$ -*keto-diacetyl-hederagenin* Me ester gives substances,  $\text{C}_{35}\text{H}_{55}\text{O}_8$ , m.p. 165° (m.p. 235° after desiccation), and  $\text{C}_{35}\text{H}_{55}\text{O}_7$ .

H. W.

**Constitution of jegosapogenin. II. C. SONE** (*Acta Phytochim.*, 1936, 9, 83—88; cf. A., 1934, 1223).—Jegosapogenol (I) is shown to contain one primary OH (probably esterified by tiglic acid in jegosapogenin), one *sec.* OH, and two acylatable *tert.* OH. Oxidation of tri-bromojegosapogenin with  $\text{CrO}_3$  in AcOH gives the compound,  $\text{C}_{35}\text{H}_{53}\text{O}_6\text{Br}_3$ , m.p. 251° (decomp.). Treatment of (I) with  $\text{Pb}(\text{OAc})_4$  in AcOH gives the *aldoketone*,  $\text{C}_{30}\text{H}_{46}\text{O}_5$ , m.p. 208° (decomp.) (also  $+1\text{H}_2\text{O}$ ) [*dioxime*, m.p. 242° (decomp.)], oxidised by  $\text{CrO}_3$  in AcOH to the *ketolactone*,  $\text{C}_{30}\text{H}_{42}\text{O}_5$  (also  $+1\text{H}_2\text{O}$ ), m.p. 325° (decomp.) from  $\text{CHCl}_3\text{--MeOH}$ , m.p. 351° (decomp.) from EtOAc [*monoxime*, m.p. 298—300° (decomp.) (also  $+1\text{H}_2\text{O}$ ); *monoacetate*, m.p. 348—349°; *monobenzoate* (also  $+2\text{H}_2\text{O}$ ), m.p. 320—325° (decomp.)].

H. W.

**Viburnitol.**—See this vol., 1307.

**Furan series. I. Synthesis of 4-2-ketotetrahydrofurylacetic acid. R. GHOSH** (*J. Indian Chem. Soc.*, 1936, 13, 323—328).— $\text{OMe}\cdot\text{CH}_2\cdot\text{CHO}$ ,  $\text{CH}_2(\text{CO}_2\text{Et})_2$ , and  $\text{C}_5\text{H}_{11}\text{N}$  give a mixture of *Et methoxyethylidene mono-*, b.p. 128—130°/8 mm., and *di-malonate*, b.p. 190—200°/10 mm. The di-ester with HCl yields  $\beta$ -*methoxymethylglutaric acid*, b.p. 184—190°/4 mm. (*anhydride*, m.p. 77—78°; *Et* ester, b.p. 125—135°/8 mm.), which undergoes ring-closure (HCl) to 4-2-ketotetrahydrofurylacetic acid, m.p. 87—88°.

F. R. S.

**Relative aromaticities. VI. 2-Furonitrile. H. GILMAN and M. LICHTENWALTER** (*Rec. trav. chim.*, 1936, 55, 588—590; cf. A., 1934, 778).—The relative rates of reaction of  $\text{MgPhBr}$  with nitriles,  $\text{RCN}$ , are  $p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$  5.1,  $p\text{-C}_6\text{H}_4\cdot\text{OMe}$  3.9,  $\alpha$ - 1.09, and  $\beta\text{-C}_{10}\text{H}_7$  1.64,  $o$ - 1.74,  $m$ - and  $p\text{-C}_6\text{H}_4\cdot\text{Me}$  0.55,  $\text{Ph}$  0.31,  $p\text{-C}_6\text{H}_4\cdot\text{Cl}$  0.09,  $\text{Me}$  0.25,  $\text{Pr}^i$  0.2,  $\text{Bu}^i$  0.17,  $n$ - 0.11, and *iso*- $\text{C}_5\text{H}_{11}$  0.23,  $n\text{-C}_{11}\text{H}_{23}$  0.1,  $n\text{-C}_{17}\text{H}_{35}$  0.09,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2$  0.13,  $\text{OPh}\cdot[\text{CH}_2]_3$  0.11, and 2-furonitrile (I) 0.02. The great reactivity of (I) in Grignard reactions classes (I) as an aliphatic or "super-aliphatic" compound, whereas other reactions class it as "super-aromatic." The reality of "relative aromaticities" is thus doubtful.

R. S. C.

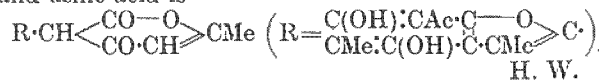
**Catalytic reduction of 2-furylpropylcarbinol. H. KONDO and K. TAKEDA** (*J. Pharm. Soc. Japan*, 1935, 55, 734—740).—Furylpropylcarbinol (I) (*phenylurethane*, m.p. 79.5°) is hydrogenated ( $\text{PtO}_2$ ; 2.5  $\text{H}_2$ ) to *tetrahydrofurylpropylcarbinol*, b.p. 84—88°/12 mm. (*phenylurethane*, m.p. 89°), and octane-8 $\epsilon$ -diol (*bisphenylurethane*, m.p. 193—194°), which is also obtained by hydrogenation of dipropenylethylene. Hydrogenation of (I) with Pd—C gave a substance, b.p. 95—100°/20 mm., and another substance, b.p. 120—125°/20 mm.

CH. ABS. (r)

**Furan and pyrrole derivatives from sugars and ethyl acetoacetate. Relation of the mechanism of this reaction to antiketogenesis. F. GARCÍA GONZÁLEZ** (*Anal. Fís. Quím.*, 1934, 32, 815—829; cf. this vol., 972).—The compound described by West (A., 1927, 1173) as Et dextrosecycloacetate is *Et 5-methyl-2- $\alpha\beta\gamma\delta$ -tetrahydroxybutylfuran-4-carboxylate* (*mono-*, b.p. 155—175°/0.2 mm., and *di-isopropylidene*, b.p. 150—160°/0.2 mm.,  $[\alpha]_D^{20} -10.9^\circ$  in  $\text{CHCl}_3$ , derivatives), oxidised ( $\text{H}_2\text{O}_2$  or  $\text{KMnO}_4$ ) to 5-methylfuran-2:4-dicarboxylic acid, m.p. 270—275° (decomp.) (*dichloride*, b.p. 133—135°/14 mm., m.p. 25—26°; *diamide*, m.p. 210—211°; *dianilide*, m.p. 196—197°; *Me\_2* ester, m.p. 61—62°); this sublimes with loss of  $\text{CO}_2$  at 270—280° to yield 2-methylfuran-3-carboxylic acid (*amide*, m.p. 90°; *anilide*, m.p. 111—112°).

F. R. G.

**Lichen substances. LXIX. Usnic acid. I. Y. ASAHINA and M. YANAGITA** (*Ber.*, 1936, 69, [B], 1646—1649).—Oxidation of usnetic (I) or pyrrousnic acid with 3%  $\text{H}_2\text{O}_2$  in 3% KOH gives 4:5-dicarboxy-3-methylfuran-2-acetic acid, m.p. 251—252° (decomp.) after becoming discoloured at about 220°, the *Me\_3* ester, b.p. 193—195°/10 mm., 162°/2 mm., of which gives an *oximino*-derivative, hydrolysed and dehydrated by  $\text{Ac}_2\text{O}$  at 120° to 2-cyano-3-methylfuran-4:5-dicarboxylic acid (II), m.p. 171—172° after softening at about 165° and m.p. 260° after re-solidification. Decarboxylation of (II) by Cu powder in quinoline at 210° and subsequent hydrolysis of the nitrile yields 3-methylfuran-2-carboxylic acid, thus establishing the position of Me and  $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . Since decarboxusnic acid, formed from (I) by elimination of  $\text{COMe}_2$ , condenses with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  to the substance  $\text{C}_{23}\text{H}_{23}\text{O}_4\text{N}_2$  (*hydrochloride*, decomp. 274—275° after softening at 260°), it is  $\text{R}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$  and usnic acid is



H. W.

**Addition of iodine to coumarin derivatives. W. RUZICZKA** (*Monatsh.*, 1936, 68, 233—236).—Coumarin, osthol, and ostruthin absorb 0.1985, 0.0601, and 0.0898 mol., respectively, of I.

R. S. C.

**Synthesis of coumarin derivatives. I. T. SAKAI and C. KATO** (*J. Pharm. Soc. Japan*, 1935, 55, 691—704).—4-Methyl-daphnetin [*Me\_2* ether (I), m.p. 132°; *diacetate*, m.p. 178°; *dibenzoate*, m.p. 178°; *dibenzyl ether*, m.p. 157°] yields 3-bromo-4-methyl-daphnetin (II), m.p. 254—255°, and 3:4-dibromo-4-methyl-daphnetin, m.p. 265° [*Me\_2* ether (III), m.p. 138—139°; *dibenzoate*, m.p. 198—199°; *dibenzyl ether*, m.p. 151—152°]. Bromination of (I) gave the *Me\_2* ether

(IV), m.p. 166—167° (*dibenzoate*, m.p. 184—185°; *dibenzyl ether*, m.p. 148—149°), of (II). (III) with KOH yields 3-bromo-6:7-dimethoxy-4-methylcoumaran-2-carboxylic acid (V), m.p. 248°; (IV) similarly yields 6:7-dimethoxy-3-methylcoumarone-2-carboxylic acid, m.p. 188°, whilst the *dibenzoate* of (II), under these conditions, yields 6:7-dibenzoyloxy-3-methylcoumarone-2-carboxylic acid, m.p. 123°, converted into *Et* 6:7-dihydroxy-3-methylcoumarone-2-carboxylate, m.p. 191—192°. The *dibenzyl ether* of (II) similarly yields 6:7-dibenzoyloxy-3-methylcoumarone-2-carboxylic acid, m.p. 184—185°. (V) with HCl in a sealed tube yields a substance,  $C_{22}H_{24}O_6$ , m.p. 127—128°, whilst with  $MgMeBr$  it yields 6-hydroxy-7-methoxy-3-methylcoumarone (?), b.p. 119—122°/1 mm., converted into 6-benzoyloxy-7-methylcoumarone, m.p. 144—145°.

CH. ABS. (r)

Optically active flavanones. II. Optical resolution of hydroxyflavanones. S. FUJISE and A. NAGASAKI (Ber., 1936, 69, [B], 1893—1896; cf. A., 1935, 91).—Treatment of *dl*-demethoxymatteucinol (I) in  $C_6H_5N$  with *l*-menthoxyacetyl chloride (II) in  $C_6H_6$  and repeated crystallisation of the product from MeOH affords *l*-demethoxymatteucinol *l*-menthoxyacetate, m.p. 125—125.5°,  $[\alpha]_D -51.6^\circ$ , which becomes partly racemised when hydrolysed. Similarly, (I) and (II) (2 mols.) give *d*-demethoxymatteucinol *di-l*-menthoxyacetate, m.p. 118—119°,  $[\alpha]_D -81.3^\circ$  in  $COMe_2$ , whence the partly racemised *d*-compound. 7-Hydroxyflavanone and (II) yield *d*-7-hydroxyflavanone *l*-menthoxyacetate, m.p. 96—97°,  $[\alpha]^{14.5} -30.0^\circ$ , whence *d*-7-hydroxyflavanone, m.p. 181—182°,  $[\alpha]_D^{17} +33.3^\circ$ .

H. W.

Anthocyanin of the blue blossoms of *Hyalcinthus orientalis*.—See this vol., 1307.

Spectrographic investigations of the blue pigments of the benzopyrylium type. V. Relationships between the absorption of light and hydroxyl or sugar substitution in the 2-phenylbenzopyrylium pigments. K. HAYASHI (Acta Phytochim., 1936, 9, 1—24).—The following general conclusions are reached. As frequently observed with hydroxyflavones, OMe is spectroscopically similar to OH in the same position. With cyanidin and delphinidin derivatives replacement of OH of the benzopyrylium nucleus by OMe has a more or less hypsochromic effect.  $HO_2CH_2$  behaves similarly to two corresponding vicinal OH or OMe groups. Introduction of acyl or aroyl into flavones is an important method of elucidating their constitution because of the pronounced optical effect but has less significance with anthocyanidins since it does not invariably yield a homogeneous product and not infrequently involves change of structure. Apart from a slight alteration in the shape of the graph, nuclear Me has the same optical effect as H.

Benzopyrylium pigments with a single OH in the benzopyrylium nucleus (I) generally show bands *i* (frequency 1800—2300), *iv* (3400—3800), and *v* (4000—4100) and it is characteristic of the group that *iv* never becomes divided. OH at 5 has a bathochromic effect on *i* and the complete curve becomes more hypsochromic. The influence of 2 OH in (I) is discussed. Introduction of a single OH into

the side Ph (II) causes resolution of *iv* into two bands. Hypsochromism of *i* and *iv* increases in the sequence,  $2' < 3' < 4'$ . Only the pigment with 4'-OH shows the band *iii* (2600—3200) and *v*. Two OH (OMe) groups in (II) generally exert a marked bathochromic effect on *i* and the otherwise usually small and therefore indistinct *iv* becomes better developed and is never divided. *i* is unchanged by alteration of the position of three or four OH (OMe) groups in (II) and *iv* usually consists of a homogeneous, very small band. Introduction of OH at 3 causes bathochromic displacement of *i* by 180—200 units and sometimes induces fission of *iv*; it has no pronounced influence on the other bands. The sugar residue at 3 or 5 in the flavylum mol. appears to exert a not unimportant, diffuse influence on the absorption spectrum. Generally the changes introduced in the spectrum of flavylum derivatives by the position and no. of substituents are not very marked and somewhat complex so that proof of constitution is not so readily secured as with the flavones. Nevertheless the moderately purified aglucone of an unknown anthocyanin can thus be assigned to its anthocyanidin type. The prep. of  $\omega$ -methoxyresacetophenone and its condensation with  $\beta$ -resorcaldehyde to 7:2':4'-trihydroxy-3-methoxyflavylum chloride are described.

H. W.

Thermal decomposition of dioxan.—See this vol., 1208.

1:3-Dioxins. V. Preparation of  $\alpha\beta$ -naphtho-1:3-dioxin and comparison with 1:8-naphtho-1:3-dioxin. M. C. CARNERO and F. CALVET. VI. Condensation of *p*-hydroxybenzoic acid with formaldehyde at low temperatures. M. N. MEJUTO and F. CALVET (Anal. Fis. Quím., 1934, 32, 1157—1167, 1168—1181).—V. 4'-Nitro- $\alpha\beta$ -naphtho-1:3-dioxin (cf. Borsche *et al.*, A., 1904, i, 415) (I) reduced by Zn and HCl yields 4'-amino- $\alpha\beta$ -naphtho-1:3-dioxin, m.p. 107—110° (hydrochloride, decomp. about 225°), which on diazotisation and decomp. of the product with  $SnCl_2$  in KOH yields  $\alpha\beta$ -naphtho-1:3-dioxin, m.p. 35—37° (picrate m.p. 133—135°); this in AcOH with conc.  $HNO_3$  yields (I) and in  $COMe_2$  with  $KMnO_4$  gives  $\alpha\beta$ -naphtho-4-keto-1:3-dioxin, m.p. 65—70° characterised by hydrolysis (dil. NaOH) to 1:2-OH- $C_{10}H_6$ - $CO_2H$ . 1:8- $C_{10}H_6(OH)_2$  in  $COMe_2$  with  $Me_2SO_4$  and dil. NaOH yields 1':8'-naphtho-1:3-dioxin, m.p. 29—30° (picrate, m.p. 135—137°; Br-, m.p. 70—72°; Br<sub>3</sub>-, m.p. 212—214° (decomp.),  $NO_2$ -, m.p. 146—148°;  $NH_2$ -, m.p. 93—95°; 4:5(?)-( $NO_2$ )<sub>2</sub>-, m.p. 198—200° (hydrolysed to a compound, m.p. 218—220°, and reduced to the diamine hydrochloride, m.p. about 310° {decomp.}), derivatives].

VI. *p*-OH- $C_6H_4$ - $CO_2H$  with 2 mols. of para-formaldehyde (I) (cf. Epstein, A., 1910, i, 117) in conc.  $H_2SO_4$  at -15° yields 1:3-benzdioxin-6-carboxylic acid (I), m.p. >350°; excess of (II) at -10° produces 8:8'-di-(6-carboxy-1:3-benzdioxin)methane (III), m.p. >320° ( $Me_2$ , m.p. 175—178°, *Et*<sub>2</sub>, m.p. 138—140°, and *Pr*<sub>2</sub> esters, m.p. 109—111°; *Ag* salt), and 8-hydroxymethyl-1:3-benzdioxin-6-carboxylic acid (IV), m.p. 229—230° (*Me* ester, m.p. 116—118°; *Ac* derivative, m.p. 192—194°). Further action of (I)



on (II) yields (III). 6:1:3-OH·C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>H)<sub>3</sub> with (I) gives (IV). *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H with CH<sub>2</sub>Cl·OH and ZnCl<sub>2</sub> yields 8-chloromethyl-1:3-benzodioxin-6-carboxylic acid, m.p. 201—203°, which with H<sub>2</sub>O gives (IV). (II) in COMe<sub>2</sub> with KMnO<sub>4</sub> yields 4-keto-1:3-benzodioxin. (IV) hydrolysed (2*N*-NaOH) and oxidised (KMnO<sub>4</sub>) yields *Me phenol*-2:4:6-tricarboxylate, m.p. 143—145°, hydrolysed to 1:2:4:6-OH·C<sub>6</sub>H<sub>2</sub>(CO<sub>2</sub>H)<sub>3</sub> (cf. Ullmann *et al.*, A., 1909, i, 590). F. R. G.

**Furylfuran and its derivatives.** II. H. KONDO, H. SUZUKI, and K. TAKEDA (J. Pharm. Soc. Japan, 1935, 55, 741—747).—Reduction (Pd-C) of 2:2'-difuryl (I) affords 2-furyldihydrofuran (II), b.p. 55—60°/8 mm., and a substance, b.p. 95—108°/8 mm. (maleic anhydride adduct, C<sub>12</sub>H<sub>12</sub>O<sub>5</sub>, m.p. 94.5—95°). Hydrogenation (PtO<sub>2</sub>) of a mixture of (I), (II), and furyltetrahydrofuran yields octahydro-2:2'-difuryl, b.p. 77—80°/13 mm., octane- $\alpha$ -diol, m.p. 60°, and a substance, b.p. 120—124°/13 mm. CH. ABS. (r)

**Correlation of toxicity with optical activity of *Derris* derivatives.**—See this vol., 1295.

**Possibility of dynamic isomerism in certain heterocyclic compounds.** E. W. McCLELLAND and C. E. SALKELD (J.C.S., 1936, 1143—1148).—

The compounds  $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{NR}$  (I),  $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{C(NR)}\text{S}$  (II) [R=Me, CH<sub>2</sub>·CH<sub>2</sub>·OH, Ph, NH<sub>2</sub>, or NHPh; (II) R=OH, OMe, or NH·CO<sub>2</sub>C<sub>6</sub>H<sub>11</sub>, and C·NR=C(SH)·NH·NH·CO·NH<sub>2</sub>] have been hydrolysed (HCl) to 2:2'-dithiobenzoic acid and (in most cases) 2-dithiobenzoyl and this is in accord with the equilibrium, (I)  $\rightleftharpoons$  (II). It is suggested that the compounds, (I) or (II), which on treatment with H<sub>2</sub>S give  $\text{C}_6\text{H}_4\langle\text{S}\rangle\text{S}$  and are oxidised to saccharins

are an equilibrium mixture of the two forms, whilst those [(II), R=OH, OMe] which do not react with H<sub>2</sub>S and are oxidised to a sulphone have the structure (II). The oxime, m.p. 208°, of 2:3-dithiosulphindene (III), is oxidised (H<sub>2</sub>O<sub>2</sub>) to a sulphone, m.p. 177°, and the *O-Me ether* of the oxime, m.p. 55°, is oxidised to the corresponding sulphone, m.p. 135°. (III) condenses with NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·OH to a substance, m.p. 107° (*Ac* derivative, m.p. 64.5°), with N<sub>2</sub>H<sub>4</sub> to a product, m.p. 125° (with ClCO<sub>2</sub>Et gives a product, m.p. 96°), with NHPh·NH<sub>2</sub> to a solid, m.p. 106°, with semicarbazide to a compound, m.p. 205—212° (with *iso*-C<sub>6</sub>H<sub>11</sub>·OH gives *isoamyl* 1-keto-2:3-dithiobenzohydrazone- $\beta$ -carboxylate, m.p. 105°). The following have been synthesised: 2-methylthiobenzomethylamide, m.p. 140°; 2-methylthiobenzo-, m.p. 71°, and 2-methylthiobenzo-NS-di-methylthioamide, m.p. 68.5°; 2-methylthiobenzomethylamidoxime, m.p. 194°; and 2-methylthiobenzodimethylamide, b.p. 168—170°/10 mm., and -thioamide, m.p. 83°. H<sub>2</sub>Se in EtOH reduces (I) (II) (R=Me) to a thiol, which on methylation (Me<sub>2</sub>SO<sub>4</sub>) gives mainly SMe·C<sub>6</sub>H<sub>4</sub>·C(NMe)·SMe, whilst reduction in Et<sub>2</sub>O and methylation (CH<sub>2</sub>N<sub>2</sub>) yields SMe·C<sub>6</sub>H<sub>4</sub>·CS·NHMe. The significance of the results is discussed.

F. R. S.

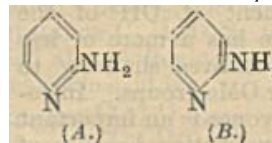
**Syntheses by means of magnesylpyrroles.** Series II. XXII. B. ODDO and G. ACUTO (Gaz-

zetta, 1936, 66, 380—386).—The Mg derivative of 2:5-dimethylpyrrole reacts with CO<sub>2</sub>, ClCO<sub>2</sub>Et, and COCl·CH<sub>2</sub>·CO<sub>2</sub>Et, respectively, to form 2:5-dimethylpyrrole-3-carboxylic acid and its Et ester, and *Et* 2:5-dimethylpyrrole-3- $\beta$ -ketopropionate (I), m.p. 62°. (I) is hydrolysed to 3-acetyl-2:5-dimethylpyrrole, and with NHPh·NH<sub>2</sub> yields 1-phenyl-3-(2':3'-dimethyl-3'-pyrryl)pyrazolone, decomp. 247—252°. The Mg derivative of 2:4-dimethylpyrrole and CO<sub>2</sub> give 2:4-dimethylpyrrole-5-carboxylic acid, m.p. 137° (decomp.). E. W. W.

**Catalytic transformations of heterocyclic compounds.** V. Transformation of furan into 1-phenyl-, 1-*o*-tolyl-, and 1-*p*-tolyl-pyrrole. J. K. JURIEV (Ber., 1936, 69, [B], 1944—1948; cf. this vol., 858).—Mixtures of furan with excess of NH<sub>2</sub>Ph, *o*- and *p*-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> when passed over Al<sub>2</sub>O<sub>3</sub> at 465° afford 1-phenyl-, m.p. 61—62°, 1-*o*-tolyl-, b.p. 114°/12 mm., and 1-*p*-tolyl-, m.p. 79—79.5°, -pyrrole respectively in 24%, 40.6%, and 21% yield. Crude furan, b.p. 205—210°, obtained by pyrolysis of pyromucic acid, may be employed. H. W.

**Nitration with nitrogen dioxide.** II. Nitration of pyridine and quinoline. P. SCHORGEN and A. TOPTSCHIEV (Ber., 1936, 69, [B], 1874—1877; cf. A., 1934, 996).—Nitration of C<sub>5</sub>H<sub>5</sub>N vapour by N<sub>2</sub>O<sub>4</sub> in presence of CO<sub>2</sub> proceeds best at 115—120° and gives 3-nitropyridine in 7—10% yield; irradiation with ultra-violet light is without influence. The same yield is obtained at 220—230° whereas at 300—330° violent explosions take place which are also observed with C<sub>5</sub>H<sub>5</sub>N and liquid N<sub>2</sub>O<sub>4</sub> at room temp. Pyridine nitrate, m.p. 117—118°, and nitrite (+1H<sub>2</sub>O), m.p. 58—60°, are described. Quinoline and N<sub>2</sub>O<sub>4</sub> afford 7-nitro- (optimal temp. 95—100°) and 5:7-dinitro- (best at 155—160°) -quinoline. H. W.

**Structure of 2-amino- and 2:6-diaminopyridine.** Hydrolysis of the amino-group in 2-aminopyridine. 2:6-Diamino- and 2-amino-6-hydroxy-pyridine and 7-amino-2-hydroxy-4-methyl-1:8-naphthyridine. O. A. SEIDE and A. T. TITOV (Ber., 1936, 69, [B], 1884—1893).—Evidence is adduced, based mainly on hydrolysis,



that the structure *A* in preference to *B* should be assigned to 2-aminopyridine (I). (I) and 2:6-diaminopyridine (II) are unchanged by conc. aq. or alcoholic alkali at 130° and 2-amino-6-hydroxypyridine (III), m.p. 214° (also +1H<sub>2</sub>O) [hydrochloride (also +1H<sub>2</sub>O); sulphate (C<sub>5</sub>H<sub>6</sub>ON<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub> and +1H<sub>2</sub>O; picrate], and 7-amino-2-hydroxy-4-methyl-1:8-naphthyridine (IV) do not evolve NH<sub>3</sub> when boiled with 10% NaOH. (I) and 70% H<sub>2</sub>SO<sub>4</sub> do not interact at 15° whereas (IV) suffers considerable hydrolysis; (II) rapidly and quantitatively loses 1 NH<sub>3</sub> whilst (III) gives NH<sub>3</sub> probably with opening of the C<sub>5</sub>H<sub>5</sub>N ring. H<sub>2</sub>SO<sub>4</sub>+NaHSO<sub>3</sub> rapidly attacks (II), involving the ring N; under like conditions (I) and 2-pyridone (V) are somewhat affected. (III) is converted by an excess of cold Ac<sub>2</sub>O into the *Ac*. derivative, m.p. 162—163° (decomp.), which does not give a colour

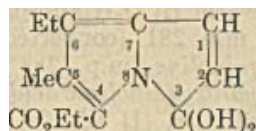
with  $\text{FeCl}_3$  or react with diazo-compounds but is readily halogenated or nitrated. It is hydrolysed by hot  $\text{H}_2\text{O}$  to 2-acetamido-6-hydroxypyridine, m.p.  $213^\circ$ , which gives an intense red-brown colour with  $\text{FeCl}_3$  and closely resembles (V) in acidity. H. W.

**Pyridylmethylamines.** R. GRAF [with G. PERATHONER and M. TATZEL] (J. pr. Chem., 1936, [ii], 146, 88—104).—Reduction of 2-cyanopyridine with  $\text{Cr}(\text{OAc})_2$  and aq. KOH yields 2-pyridylmethylamine (I), b.p.  $82^\circ/12$  mm. [platinichloride,  $\text{C}_6\text{H}_8\text{N}_2\cdot\text{H}_2\text{PtCl}_6\cdot 3\text{H}_2\text{O}$ , m.p.  $245^\circ$ ; aurichloride,  $\text{C}_6\text{H}_8\text{N}_2\cdot 2\text{AuCl}_3$ , m.p.  $186^\circ$ ; picrate, m.p.  $162^\circ$  (decomp.); dihydrobromide, m.p.  $234^\circ$ ; Bz derivative, b.p.  $235^\circ/11$  mm., m.p.  $53^\circ$ ; p-nitrobenzoyl, m.p.  $136^\circ$ , reduced by Sn and HCl in EtOH to the p-aminobenzoyl, m.p.  $94^\circ$ , derivative]. When preserved (I) passes partly into pyridine-2-aldehyde, also obtained from it by the action of  $\text{PhNO}$  in EtOH or of  $\text{SOCl}_2$  in  $\text{Et}_2\text{O}$ . Treatment of (I) with  $\text{AgNO}_2$  in 0.5N-HCl affords 2-pyridylmethyl alcohol, b.p.  $105^\circ/12$  mm. (picrate, m.p.  $158^\circ$ ; platinichloride, m.p.  $177^\circ$ ; p-nitrobenzoate, m.p.  $92^\circ$ , reduced to the p-aminobenzoate, m.p.  $79$ — $80^\circ$ ). Similarly 3-cyanopyridine gives 3-pyridylmethylamine, b.p.  $102$ — $103^\circ/14$  mm. [dihydrochloride, m.p.  $219$ — $220^\circ$ ; platinichloride, decomp. about  $280^\circ$ ; aurichloride, m.p.  $201$ — $202^\circ$  (decomp.) after darkening; p-nitrobenzoyl derivative, m.p.  $188$ — $189^\circ$ ]. 3-Cyano-6-methylpyridine yields the very hygroscopic 6-methyl-3-pyridylmethylamine (II), b.p.  $118$ — $120^\circ/14$  mm., m.p.  $63^\circ$  [dihydrochloride, m.p.  $247^\circ$  (decomp.) when rapidly heated; platinichloride, decomp.  $240^\circ$  after darkening at  $220^\circ$  in preheated bath; aurichloride ( $+1\text{H}_2\text{O}$ ), m.p.  $199^\circ$  in closed capillary; Bz derivative, m.p.  $121$ — $122^\circ$ ; p-nitrobenzoyl derivative, m.p.  $171^\circ$ ]. (II) and  $\text{NaNO}_2$  in  $\text{H}_2\text{SO}_4$  afford 6-methyl-3-pyridylmethyl alcohol, b.p.  $140^\circ/11$  mm. (hydrochloride, m.p.  $102^\circ$ ; p-nitrobenzoyl derivative, m.p.  $136$ — $138^\circ$ ). (II) and  $\text{SOCl}_2$  in  $\text{Et}_2\text{O}$  give 6-methylpyridine-3-aldehyde [phenylhydrazone, m.p.  $143$ — $144^\circ$ , or ( $+1\text{H}_2\text{O}$ ) m.p. about  $115^\circ$  after softening at  $98^\circ$ ]. 4-Cyanopyridine gives 4-pyridylmethylamine, b.p.  $103^\circ/11$  mm. [platinichloride, m.p.  $>300^\circ$  after darkening at  $260^\circ$ ; aurichloride, m.p.  $190^\circ$ ; monohydrobromide, m.p.  $240^\circ$  (decomp.); Bz derivative, m.p.  $240^\circ/11$  mm., m.p.  $108^\circ$ ]. Pyridine-4-aldehydephenylhydrazone has m.p.  $175^\circ$ . 4-Pyridylmethyl alcohol b.p.  $140$ — $142^\circ/12$  mm., m.p. about  $40^\circ$ , gives a hydrochloride, m.p.  $164^\circ$  (decomp.), platinichloride, m.p.  $220^\circ$ , and aurichloride, m.p.  $138^\circ$ . 2:6-Dicyanopyridine, m.p.  $123^\circ$ , is reduced to 2:6-diaminomethylpyridine (trihydrochloride, decomp.  $250^\circ$  after darkening at  $230^\circ$ ; platinichloride; aurichloride, decomp.  $180^\circ$  after darkening; Bz derivative, m.p.  $190^\circ$ ), apparently accompanied by 6-methyl-2-pyridylmethylamine. 2-Cyanoquinoline affords 2-quinolylmethylamine, b.p.  $104^\circ/10$  mm. (dihydrochloride, m.p.  $205^\circ$ ; platinichloride, decomp.  $220$ — $225^\circ$ ). 2:3:5:6-Tetrachloro-4-cyanopyridine, m.p.  $138^\circ$ , affords 2:3:5:6-tetrachloro-4-pyridylmethylamine, m.p.  $62$ — $63^\circ$  (monohydrochloride, decomp.  $265^\circ$  after darkening when rapidly heated). 2:4:6-Trichlorobenzonitrile yields 2:4:6-trichlorobenzylamine, m.p.  $62^\circ$  (hydrochloride, m.p.  $247^\circ$ ).

[With W. LANGER.] Me nicotinate is converted

into 3-pyridyldimethylcarbinol, b.p.  $130^\circ/11$  mm., m.p.  $53^\circ$  (benzoate, m.p.  $53^\circ$ , and its hydrochloride; p-nitrobenzoate, m.p.  $157^\circ$ , reduced to the p-aminobenzoate, m.p.  $130^\circ$ ). H. W.

**Derivatives of a dicyclic condensed ring system formed from two pyrrole rings [pyrrolizine].** F. MICHEEL and W. KIMPEL (Ber., 1936, 69, [B], 1990—1993).—Treatment of 5-carbethoxy-4-methyl-3-ethylpyrrole-2-vinyl- $\omega\omega$ -dicarboxylic acid,  $\text{C}(\text{CO}_2\text{Et})\cdot\text{NH}>\text{C}\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})_2$ , with boiling  $\text{Ac}_2\text{O}$

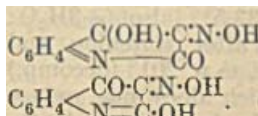


(I.)

affords  $\text{CO}_2$  and Et 3:3-dihydroxy-5-methyl-6-ethylpyrrolizine-4-carboxylate (I), m.p.  $234$ — $235^\circ$  (decomp.), which is unchanged when heated in xylene, and does not react with  $\text{NH}_4\text{OH}$  or  $\text{NHPh}\cdot\text{NH}_2$  or yield an Ac derivative with  $\text{Ac}_2\text{O}$ . Its structure is deduced from its transformation by 0.2N-NaOH-MeOH into 3-hydroxy-3-methoxy-5-methyl-6-ethylpyrrolizine-4-carboxylic acid, m.p.  $242^\circ$ . Et 3-hydroxy-3-ethoxy-5-methyl-6-ethylpyrrolizine-4-carboxylate, m.p.  $127.5^\circ$ , is described. H. W.

**Oxidation of acetyltetrahydroquinolinesulphonic acids.** K. V. BOKIL (J. Indian Chem. Soc., 1936, 13, 404—409).—Quinoline-8-sulphonic acid (prep. described) with Sn-HCl affords tetrahydroquinoline-8-sulphonic acid, the K salt of which with  $\text{Ac}_2\text{O}$  at  $135$ — $140^\circ$  affords K N-acetyltetrahydroquinoline-8-sulphonate ( $+1.5\text{H}_2\text{O}$ ), which with aq. 5%  $\text{KMnO}_4$  at room temp. affords mainly  $\text{K}_2$  2-oxalvalacetamido-3-carboxybenzenesulphonate (I) ( $+0.5\text{H}_2\text{O}$ ) and some  $\text{K}_1$  salt. (I) with boiling dil. HCl affords K 2-oxalamido-3-carboxybenzenesulphonate ( $+1.5\text{H}_2\text{O}$ ). K N-acetyltetrahydroquinoline-5-sulphonate ( $+1\text{H}_2\text{O}$ ) with aq.  $\text{KMnO}_4$  at room temp. affords mainly  $\text{K}_2$  2-acetamido-6-sulphobenzoylformate (II) ( $+1.5\text{H}_2\text{O}$ ) and some  $\text{K}_1$  3-acetamido-2-carboxybenzenesulphonate ( $+1\text{H}_2\text{O}$ ) and  $\text{K}_1$  3-amino-2-carboxybenzenesulphonate ( $+1\text{H}_2\text{O}$ ). (II) with warm conc. HCl affords K isatin-4-sulphonate. J. L. D.

**Nitroso-derivative of 4-hydroxycarbostyryl.** A. MEYER and P. HEIMANN (Compt. rend., 1936, 203, 335—337).—The product (I) of the nitrosation of 4-hydroxycarbostyryl (II) separates from EtOH or from  $\text{H}_2\text{O}$  if the solution is rapidly cooled to about  $15^\circ$  in yellow, thermolabile crystals which pass into the red variety at about  $100^\circ$ . From aq. solution at  $>40^\circ$  thermostable yellow crystals, m.p.  $251^\circ$ , separate which lose  $1\text{H}_2\text{O}$  when dried at  $140^\circ$ ; it cannot be diazotised. Since CO cannot be detected in (I) by  $\text{NH}_2\text{OH}$  or  $\text{NHPh}\cdot\text{NH}_2$  and (I) is fixed by metallic mordants the formulæ  $\text{C}_6\text{H}_4\cdot\text{N}=\text{C}(\text{OH})\cdot\text{C}(\text{NO})\cdot\text{OH}$  or



are suggested in place of  $\text{C}_6\text{H}_4\cdot\text{N}=\text{C}(\text{OH})\cdot\text{C}(\text{NO})\cdot\text{OH}$ . (II) is transformed in alkaline solution into 2-hydroxy-4-methoxyquinoline, m.p.  $271^\circ$ , the NO-derivative, m.p.  $220^\circ$ , of which forms greenish-yellow crystals, unchanged by heat and with slight affinity for metallic mordants. (I) yields a Na salt, converted by  $\text{CoCl}_2$  in  $\text{H}_2\text{O}$  into the complex,



$C_9H_5O_3N_2Co(OH)_2$ , giving with HCl the substance  $(C_9H_5O_3N_2)_3Co$ . The salt,  $(C_9H_5O_3N_2)_2Na$ , is described. H. W.

**Halogenation of oxidation products of 2:4-dihydroxyquinoline.** A. MEYER and P. HEIMANN (Compt. rend., 1936, 203, 264—266).—At room temp. 2:4-dihydroxyquinoline (I) in  $HCO_2H$  containing the theoretical amount of Br affords a  $Br_1$ -derivative, m.p. 199° (converted by  $PBr_5$  into a  $Br_3$ -derivative, m.p. 276°, in which 1 Br is in the aromatic nucleus, and when oxidised affords 2:4-dihydroxyquinolinic acid), and with excess of Br in warm  $HCO_2H$  affords 3-bromo-2:4-dihydroxyquinoline, m.p. 281° (converted by  $PBr_5$  into 2:3:4-tribromoquinoline, m.p. 288°, and oxidised to 3-bromo-2:4-dihydroxyquinolinic acid, m.p. 240°). In boiling  $C_6H_6$  with Br, (I) affords a  $Br_1$ -derivative, m.p. 241°. J. L. D.

**Manufacture of 3-aminoquinoline derivatives.**—See B., 1936, 876.

**Azo-dyes from quinolonemethides.** E. KOENIGS and H. BUEREN (J. pr. Chem., 1936, [ii], 146, 119—128).—Gradual addition of quinaldine methosulphate and 2N-NaOH to  $PhN_2Cl$  at 3° gives 1-methyl-2-benzeneazomethylene-1:2-dihydroquinoline, m.p. 141° [hydrochloride, m.p. 241° (decomp.)]; coupling takes 1—2 min. after each addition. Similarly are prepared 1-methyl-2-anisole-p-, m.p. 185° (hydrochloride, m.p. 245°), -phenetole-p-, m.p. 178° (hydrochloride, m.p. 239°), -naphthalene-1'- (hydrochloride, m.p. 242°), -p-aminobenzene- (dihydrochloride, m.p. 242°), -2'-hydroxy-4'-methylquinoline-7'- [hydrochloride, m.p. 252° (decomp.)], and -2'-ethoxy-4'-methylquinoline-7'-azomethylene-1:2-dihydroquinoline (hydrochloride, m.p. 247°), 6-methoxy-1-methyl-2-benzene- (hydrochloride, m.p. 263°), -anisole-p- (hydrochloride, m.p. 258°), and -naphthalene-1'-azomethylene-1:2-dihydroquinoline (hydrochloride, m.p. 256°), 1:6-dimethyl-2-naphthalene-1'-azomethylene-1:2-dihydroquinoline (hydrochloride, m.p. 245°), 1-methyl-2-di-(anisole-p-azo)methylene-1:2-dihydroquinoline (hydrochloride, m.p. 183°), 1-methyl-4-benzene- [hydrochloride, m.p. 246° (decomp.)] and -naphthalene-1'-azomethylene-1:4-dihydroquinoline [hydrochloride, m.p. 256° (decomp.)]. 7-Amino-2-ethoxy-4-methylquinoline, m.p. 106°, is prepared from the 2-Cl-base and NaOEt at 130°. R. S. C.

**7-Hydroxyquinoline-8-aldehyde.** L. KOCHANŠKA and B. BOBRANŠKI (Ber., 1936, 69, [B], 1807—1813).— $m-NO_2 \cdot C_6H_4 \cdot NH_2$  is converted (Skraup) into 7-nitroquinoline, reduced by Fe powder and conc. HCl at 110—120° to 7-aminoquinoline, which is transformed by conc. HCl at 200° into 7-hydroxyquinoline (I), m.p. 239° after becoming black at 200°. (I), very conc. aq. NaOH, and  $CHCl_3$  afford 7-hydroxyquinoline-8-aldehyde (II), m.p. 133—133.5° [also +  $3H_2O$ ; phenylhydrazone, m.p. 181.5° after softening and darkening at 175°; oxime (III), m.p. 201° (decomp.) after darkening at 195°], which does not reduce Fehling's solution and only slowly darkens  $Ag_2O \cdot NH_3$ . (III) is transformed by boiling  $Ac_2O$  into 8-cyano-7-hydroxyquinoline, m.p. 240°, which with NaOH and  $Me_2SO_4$  yields 8-cyano-7-methoxyquinoline (IV), m.p. 140—141°. 8-Nitro-7-methoxyquinoline (V) is reduced to 8-amino-7-methoxyquinoline, trans-

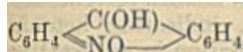
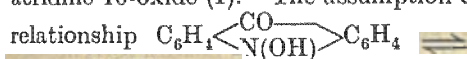
formed through the diazo-compound into (IV), which is very resistant towards acid and alkali. Treatment with a large excess of conc. HCl at 170° causes hydrolysis and subsequent loss of  $CO_2$  with production of (I). Boiling conc. HCl transforms (V) into 8-nitro-7-hydroxyquinoline, m.p. 252—253° (decomp.) after darkening at 220°, the constitution of which is established by its conversion into 7-chloro-8-nitroquinoline, m.p. 185°. 8-Nitro-7-hydroxyquinoline, KI, red P, and boiling HI give 8-aminoquinoline, m.p. 65°. H. W.

**Action of iodine monochloride solutions on heterocyclic bases.** K. GLEU and W. JAGEMANN (J. pr. Chem., 1936, [ii], 145, 257—264).—Solutions of ICl in HCl, prepared from  $KIO_3$ , KI, and HCl, with bases form salts of  $HICl_2$ , some of which lose HCl when washed. Thus  $C_5H_5N$  forms  $C_5H_5N \cdot HICl_2$  and  $C_5H_5N \cdot ICl$ ; quinoline gives  $C_9H_7N \cdot HICl_2$  and  $C_9H_7N \cdot ICl$ , m.p. 157°; isoquinoline gives  $C_9H_7N \cdot HICl_2$ , m.p. 155°, and  $C_9H_7N \cdot ICl$ , m.p. 158°; acridine gives  $C_{13}H_9N \cdot HICl_2$ , m.p. 220°, stable to  $H_2O$ ; o-phenanthroline gives  $C_{12}H_8N_2 \cdot HICl_2$ , m.p. 167°, stable to  $H_2O$ ; and p-phenanthroline gives  $C_{12}H_8N_2 \cdot 2HICl_2 \cdot 2H_2O$ , m.p. 197°. Under similar conditions 8-hydroxyquinoline gives its 5-I- and 5:7-I<sub>2</sub>-derivatives, 8-aminoquinoline its 5-I-, m.p. 125°, and 5:7-I<sub>2</sub>-, m.p. 151°, derivatives, 5-hydroxyquinoline its 8-I-, m.p. 153°, and 6:8-I<sub>2</sub>-, m.p. 134° (decomp.), derivatives; 5- and 6-aminoquinoline give, respectively, their iodochloride, m.p. 198°, and iodochloride hydrochloride, m.p. 206°, and 6-hydroxyquinoline its iodochloride, m.p. 252° (decomp. from 225°). H. G. M.

**Action of phosphorus pentachloride on derivatives of diphenylamine.** R. R. GOODALL and W. O. KERMACK (J.C.S., 1936, 1163—1166).—Cyclisation of 4-methoxy- and 4-chloro-diphenylamine-2'-carboxylic acid is effected by refluxing with  $PCl_5$  in  $PhCl$  (8 hr.; 130°) forming 5-chloro-3-methoxy-, m.p. 148—149° (lit. 152—153°), and 3:5-dichloroacridine (I) m.p. 196—198°, respectively. (I) with boiling aq. HCl gives 3-chloroacridine, m.p. 398°, and with  $PhOH \cdot KOH$  (2 hr.; 100°) affords 3-chloro-5-phenoxyacridine, m.p. 144—145°. 2:4-Dichloro-, 2:5-dichloro-, and 2-bromo-4-methyldiphenylamine-2'-carboxylic acid, m.p. 191° (from  $o-C_6H_4Cl \cdot CO_2K$ , 3-bromo-p-toluidine, and Cu-bronze at 150° during 4 hr.), similarly treated undergo substitution prior to ring-closure to form 2:4:4'-trichloro-, m.p. 188—189° [acid, m.p. 270° (identical with that obtained from 2:5- $C_6H_3Cl_2 \cdot CO_2K$  (II), 2:4- $C_6H_4Cl_2 \cdot NH_2$ , and Cu-bronze in  $C_6H_{11} \cdot OH$  at 150° during 6 hr.)]; Me ester, m.p. 124°; Ph ester, m.p. 108—109°]; a mixture of 2:5:4'- (III) and 2:4:5-trichloro- (?); and 4'-chloro-2-bromo-4-methyldiphenylamine-2'-carboxylic chloride [acid, m.p. 235—237° (identical with that obtained from (II), 3-bromo-p-toluidine, and Cu-bronze), respectively. Pure (III), m.p. 125—126°, is obtained from the corresponding acid, m.p. 254—255°, which results from the interaction of (II), 2:5- $C_6H_3Cl_2 \cdot NH_2$ , and Cu-bronze. F. N. W.

**Acridones. IX. Acridine 10-oxide and 5-hydroxyacridine 10-oxide.** I. TANASESCU and E. RAMONTIANU (Ber., 1936, 69, [B], 1825—1826).—

*ms*-Chloroacridine is oxidised by  $\text{BzO}_2\text{H}$  to 5-chloroacridine 10-oxide, hydrolysed by alkali to Kliegl's "N-hydroxyacridone" which therefore is 5-hydroxyacridine 10-oxide (I). The assumption of tautomeric

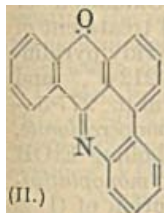


is invalidated by the observation that the absorption spectrum of (I) is the same in abs. EtOH as in alkaline solution and that a change of structure does not therefore accompany salt formation.

H. W.

**Anthraquinone derivatives** [carbazoles and acridines].—See B., 1936, 780.

**Benzosemiflavanthrene. I. Reduction.** C. F. KOELSCH (J. Amer. Chem. Soc., 1936, 58, 1325—1326).—N-o-Diphenylphthalimide, m.p. 165—166° [from o-C<sub>6</sub>H<sub>4</sub>Ph·NH<sub>2</sub> and o-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>O at 200°], is converted by ZnCl<sub>2</sub> at 275°/1 min. into o-9-phenanthridylbenzoic acid (I), m.p. 268—270° (decomp.) (Me ester, m.p. 150—151°), which when distilled with Cu(OAc)<sub>2</sub> gives 9-phenylphenanthridine. (I) and conc. H<sub>2</sub>SO<sub>4</sub> at 160° afford benzosemiflavanthrene (II), m.p. 221—222°, which is of little use as a dye. Reduction of (II) with alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> affords the H<sub>2</sub>-derivative (III) (O → OH; N → NH), m.p. 197°; SnCl<sub>2</sub> and AcOH-HCl lead to the deoxy-derivative (IV) [(III) with :O=H<sub>2</sub>]. Treatment of (III) with Ac<sub>2</sub>O, BzCl-C<sub>5</sub>H<sub>5</sub>N, or boiling aq. HCl causes disproportionation to (II) and (IV). (IV) is converted by HNO<sub>2</sub> into (II).



H. B.

**γ-Ethylidenecanaline.**—See this vol., 1297.

**1-Phenyl-2:3-dimethyl-5-pyrazolone and its 4-dimethylamino-derivative.**—See B., 1936, 908.

**Alkoxyphenyliminazoles.**—See B., 1936, 907.

**Di- and tri-alkylbarbituric acids.** H. A. SHONLE and W. J. DORAN (J. Amer. Chem. Soc., 1936, 58, 1358—1359).—The following are generally prepared from  $\text{CRR}'(\text{CO}_2\text{Et})_2$  and  $\text{CO}(\text{NH}_2)_2$  or  $\text{NHAlk}\cdot\text{CO}\cdot\text{NH}_2$  in EtOH-NaOEt: 5-methyl-5-isoamyl-, m.p. 124.5—125.2° (lit. 108°), -5-n-hexyl-, m.p. 168—169°, -5-α-methylamyl-, m.p. 173—174°, and -5-β-ethylhexyl-, m.p. 132—132.5°; 5-α-methylamyl-5-allyl-, b.p. 218—220°/7 mm.; 5-n-propyl-5-β-methylbutyl m.p. 129—130.5°; 1:5-dimethyl-5-n-amyl-, m.p. 108—109°, -5-isoamyl m.p. 106—107°, -5-α-methylbutyl-, m.p. 116—117°, -5-α-methylamyl-, b.p. 180°/3 mm., -5-n-hexyl- [decomp. on attempted distillation to N-α-methyloctoyl-N'-methylcarbamide (?), b.p. 189°/3 mm., m.p. 63—64°], and -5-β-ethylhexyl- [decomp. when kept at room temp. to N-α-methyl-γ-ethyloctoyl-N'-methylcarbamide (?), m.p. 65—70°]; 1-methyl-5-ethyl-5-n-propyl-, m.p. 94.5—95°, -5-iso-butyl-, m.p. 90—91°, -5-sec.-butyl-, m.p. 94—95°, -5-n-amyl-, b.p. 155—156°/1 mm., -5-α-methylbutyl-, b.p. 188—190°/7 mm., and -5-β-ethylhexyl-; 1-methyl-5-α-methylbutyl-, b.p. 148—150°/1 mm., and -5-α-methylamyl-5-allyl-; 1:5-diethyl-5-isoamyl-, b.p. 192—194°/13 mm. and -5-α-methylbutyl-, b.p. 148—150°/1 mm., -barbituric acids. Pharmacological data are

given. Et methylisoamyl-, b.p. 103—104°/3 mm., methyl-n-hexyl-, b.p. 125°/3.5 mm., methyl-α-methylamyl-, b.p. 126°/6 mm., α-methylamylallyl-, b.p. 139°/5 mm., methyl-β-ethylhexyl-, b.p. 126°/1.5 mm., methyl-n-amyl-, b.p. 99°/8 mm., methyl-α-methylbutyl-, b.p. 124°/10 mm., and n-propyl-β-methylbutyl-, b.p. 100°/1 mm., -malonates are prepared usually using the AlkBr.

H. B.

**N-Alkyl- and N-aryl-substituted barbituric acids.** D. L. TABERN and E. H. VOLWILER (J. Amer. Chem. Soc., 1936, 58, 1354—1356).—The following are generally prepared from  $\text{CR}_2(\text{CO}_2\text{Et})_2$  or  $\text{CN}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$  and  $\text{NHR}'\cdot\text{CO}\cdot\text{NH}_2$ : 1:5-dimethyl-5-α-methylbutyl-, m.p. 105—108°, -5-α-ethylpropyl-, -5-cyclohexenyl-, -5-sec.-butyl-, m.p. 81—83°, -5-isopropyl-, m.p. 113—114°, -5-β-ethylbutyl-, m.p. 98—100°, -5-α-methylamyl-, and -5-α-γ-dimethylbutyl-; 1-methyl-5-ethyl-5-α-methylbutyl-, α-ethylpropyl-, -sec.-butyl-, -isopropyl-, m.p. 124—125°, and -β-ethylbutyl-, m.p. 63—65°; 1-methyl-5-sec.-butyl-5-allyl-; 5-methyl-1-ethyl-5-α-methylbutyl-, -sec.-butyl-, and -isopropyl-, m.p. 106—107°; 1:5-diethyl-5-isopropyl-; 5-methyl-5-α-methylbutyl-1-allyl-; 5-methyl-5-sec.-butyl-1-β-methylallyl-, m.p. 130°; 1-phenyl-5-ethyl-5-α-methylbutyl-; 5:5-diethyl-1-sec.- and -tert.-butyl-, m.p. 83—85° and 98°, respectively; 1-n-butyl-5-sec.-butyl-; 5-methyl-5-α-methylbutyl-1-n- and -tert.-butyl-; 5-α-γ-dimethylbutyl-, m.p. 235°; 5-methyl-, m.p. 205°, and 5-ethyl-, m.p. 175°, -5-α-γ-dimethylbutyl-barbituric acids. Some of the acids show promise as short-acting intravenous hypnotics and anaesthetics.

H. B.

**Phenyl nitrogen substitution and reactivity in barbituric acid series.** D. NIGHTINGALE and L. C. MORRIS (J. Amer. Chem. Soc., 1936, 58, 1469—1470; cf. A., 1932, 283; Cope, *ibid.*, 523).—5:5-Dibromobarbituric acid (I) reacts rapidly with  $\text{NH}_2\text{Ph}$  in EtOH to give p-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub> and 5-bromobarbituric acid (II) [stable  $\text{NH}_2\text{Bu}^a$  salt, obtained similarly in 73% yield from (I) and  $\text{NH}_2\text{Bu}^a$ ]. 5:5-Dibromo-1-phenylbarbituric acid (III) reacts more slowly yielding p-C<sub>6</sub>H<sub>4</sub>Br·NH<sub>2</sub> and 5-bromo-1-phenylbarbituric acid (IV) [unstable  $\text{NH}_2\text{Bu}^a$  salt, m.p. 110—120° (decomp.), when prepared from (IV); obtained less pure in small yield from (III) and  $\text{NH}_2\text{Bu}^a$  in C<sub>6</sub>H<sub>6</sub> (not EtOH)]. Cryst. products could not be similarly obtained from 5:5-dibromo-1:3-diphenylbarbituric acid (V). (I) or (II) with  $\text{NHR}\cdot\text{CS}\cdot\text{NH}_2$  gives 9-phenyl-, m.p. 240° (decomp.), 9-o-tolyl-, m.p. 275° (decomp.), and 9-allyl-, m.p. 270° (decomp.), -8-thio-ψ-uric acids; (III) or (IV) similarly affords 1-phenyl-, m.p. >300° [from  $\text{CS}(\text{NH}_2)_2$ ], 1:9-diphenyl-, m.p. 280° (decomp.), and 1-phenyl-9-allyl-, m.p. >300°, -8-thio-ψ-uric acids, whilst (V) and 5-bromo-1:3-diphenylbarbituric acid do not react to any appreciable extent. (III) and (V) with α-C<sub>10</sub>H<sub>7</sub>·NH·NH<sub>2</sub>·HCl in EtOH give 1-phenyl-, m.p. 292°, and 1:3-diphenyl-, m.p. 303°, -allozan-α-naphthylhydrazones, respectively. 1-Phenyl- and 1:3-diphenyl-barbituric acids appear to react with  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  and  $\text{NHPh}\cdot\text{CH}\cdot\text{NPh}$  at about the same rate (cf. this vol., 864).

H. B.

**Mechanism of the narcosis induced by hypnotics. II. Synthesis of coloured derivatives of**



phenobarbital [5-phenyl-5-ethylbarbituric acid]. A. E. PIERCE and M. M. RISING (J. Amer. Chem. Soc., 1936, 58, 1361—1363; cf. A., 1933, 958).—Nitration (method: Bousquet and Adams, A., 1930, 351) of phenobarbital gives 60% of 5-*m*-nitrophenyl- (I), new m.p. 283—284°, and some 5-*p*-nitrophenyl-, m.p. 216—217°, -5-ethylbarbituric acid. (I) is reduced (Adams) to the 5-*m*-aminophenyl derivative (II), m.p. 208—209°, converted (diazo-method) into the 5-*m*-hydroxyphenyl derivative (III) (+2H<sub>2</sub>O), m.p. (anhyd.) 199.5—200°, which has no hypnotic activity. Diazotised (II) coupled with *m*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, (II), and (III) affords pharmacologically inactive dyes, m.p. 221—222°, decomp. 210°, and decomp. about 280°, respectively. A method for the micro-determination of diazoamino-N is described. H. B.

5-Ethyl-5-β-ethylhexylbarbituric acids.—See B., 1936, 860.

Homologues of histamine and their pharmacological actions. Y. TAMAMUSHI (J. Pharm. Soc. Japan, 1933, 53, 1080—1088).—2-Methyl-5-hydroxymethylglyoxaline-4-carboxylic acid is converted by SOCl<sub>2</sub> into 2-methyl-5-chloromethylglyoxaline-4-carboxylic acid hydrochloride, which, with KCN, yields 2-methyl-5-cyanomethylglyoxaline-4-carboxylic acid, m.p. 224°, reduced (Na—EtOH) to 2-methyl-5-(β-aminoethyl)glyoxaline-4-carboxylic acid hydrochloride (I), decomp. 237°, accompanied by 2-methylglyoxaline-4-carboxylic-5-acetic acid, decomp. 242°. (I), when heated, yields 2-methyl-5-β-aminoethylglyoxaline hydrochloride, m.p. 217°, which is 1.3 times as active, physiologically, as histamine. CH. ABS. (r)

Synthesis of *d*-carnosine, the enantiomorph of the naturally occurring form. Its depressor effect on the blood pressure. V. DU VIGNEAUD and M. HUNT (J. Biol. Chem., 1936, 115, 93—100).—*l*-Histidine with Ac<sub>2</sub>O—aq. NaOH at 50—55° affords acetyl-*l*-histidine and thence (hydrolysis; resolution by the *d*-tartrate; esterification) *d*-histidine *Me* ester dihydrochloride, m.p. 197° (corr.), [α]<sub>D</sub><sup>20</sup> —9.8° in H<sub>2</sub>O, which yields carbobenzyloxy-*d*-carnosine, m.p. 161° (corr.), [α]<sub>D</sub><sup>24</sup> —11° in H<sub>2</sub>O, and thence *d*-carnosine (I), m.p. 260°, [α]<sub>D</sub><sup>20</sup> —20.4° in H<sub>2</sub>O (hydrochloride, m.p. 245°). *dl*-Carnosine (II), m.p. 260°, and *l*-carnosine hydrochloride, m.p. 245°, are prepared. (I), (II), and *l*-carnosine (III) are crystallographically identical, as are the *d*- and *l*-hydrochlorides. (I) is without effect on the blood pressure of anaesthetised cats or rabbits. (II) has half the effect of (III). R. S. C.

Optically active di- and tetra-methylspiro-5:5-dihydantoin. (SIR) W. J. PORE and J. B. WHITWORTH (Proc. Roy. Soc., 1936, A, 155, 1—11).—*l*-spiro-5:5-Dihydantoin (I) (A., 1932, 171) and Et<sub>2</sub>O—CH<sub>2</sub>N<sub>2</sub> in COMe<sub>2</sub> give 3:7-dimethyl- (II), m.p. 307—308° (decomp.) (softens at 300°), [α]<sub>D</sub><sup>20</sup><sub>461</sub> —100.7° in MeOH, or tetramethyl- (III), m.p. 188—189°, [α]<sub>D</sub><sup>17</sup><sub>461</sub> —36.4° in MeOH, -*l*-spiro-5:5-dihydantoin. 3:7-Dimethyl-*d*-spiro-5:5-dihydantoin (IV), m.p. 307—308° (decomp.) (softens at 300°), [α]<sub>D</sub><sup>17</sup><sub>461</sub> +100.9° in MeOH [1:9-Bz<sub>2</sub>, m.p. 168—169°, [α]<sub>D</sub><sup>13</sup><sub>461</sub> +187.1° in COMe<sub>2</sub>, and 1:9-Ac<sub>2</sub>, m.p. 183—184°, [α]<sub>D</sub><sup>13</sup><sub>461</sub> —15.7° in COMe<sub>2</sub>, derivatives, obtained by

methylation (Et<sub>2</sub>O—CH<sub>2</sub>N<sub>2</sub>) of the 1:9-Bz<sub>2</sub>, m.p. 307—308° (decomp.) (darkens at 280°), and 1:9-Ac<sub>2</sub>, m.p. 262—263°, derivatives, respectively, of *d*-spiro-5:5-dihydantoin (V), are slowly hydrolysed by MeOH to (IV)], can be similarly prepared from (V). The rotatory dispersions of (I)—(V) in neutral solvents are normal and nearly congruent, indicating ketonic structures. (II) undergoes enolisation in aq. NaOH; hydrolysis to 3:8-dimethylallantoin (which appears to exist in cold aq. NaOH in an optical form, but becomes racemic during isolation or in warm solution) then occurs. The absence of racemisation during methylation of (I) and (V) or their acyl derivatives indicates great configurational stability. 1:9-Dibenzoyl-*dl*-spiro-5:5-dihydantoin is similarly methylated to the 1:9-Bz<sub>2</sub> derivative, m.p. 196—197°, of 3:7-dimethyl-*dl*-spiro-5:5-dihydantoin, m.p. 297—298° (1:9-Ac<sub>2</sub> derivative, m.p. 175—176°; similarly prepared), further methylated to the tetramethyl-*dl*-dihydantoin, m.p. 225—226°; these results prove the constitutions assigned to (II), (III), and (IV). H. B.

3-Pyridylpyridinium salts. P. BAUMGARTEN (Ber., 1936, 69, [B], 1938—1944).—Oxidation of C<sub>5</sub>H<sub>5</sub>N with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in H<sub>2</sub>O at 100° and treatment of the product with 20% HClO<sub>4</sub> gives 2-pyridylpyridinium monoperchlorate, m.p. 211.5—212.5°, and 3-pyridylpyridinium diperchlorate (I), m.p. 277.5—280° (slight decomp.) after softening [monoperchlorate, m.p. 170—172°, obtained from (I) and boiling EtOH or by aq. NaHCO<sub>3</sub>; dihydrochloride (II); monoplaticchloride, decomp. >300°]. The constitution of (I) is established by its hydrolysis by alkali to the compound 3-C<sub>5</sub>H<sub>4</sub>N·N:CH:CH:CH:CH:CH·ONa (III), transformed by NH<sub>2</sub>Ph and HCl into glutaconaldehydianil hydrochloride and 3-aminopyridine (IV). Addition of conc. HCl to the solution of (III) causes production of glutacondialdehyde (V) and α-3-pyridyl-amino-ε-3-pyridylimino-Δ<sup>α</sup>-pentadiene, isolated as the perchlorate dihydrochloride, m.p. 158° [corresponding trihydrochloride (VI) (+0.5H<sub>2</sub>O), m.p. 175—176°]. In HCl (III) and (IV) yield (VI), which passes in hot solution into (II) and (IV). H. W.

Preparation and physiological properties of some 2-phenyl-4:5:6:7-tetrahydroisindazolones. J. LEE and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 691—694).—2-Phenyl-4:5:6:7-tetrahydroisindazol-3-one (I) with Me<sub>2</sub>SO<sub>4</sub> and Et<sub>2</sub>SO<sub>4</sub> affords the 1-*Me*, m.p. 105.5—106.5°, and 1-*Et* derivative, m.p. 108—110°, respectively. Methylation of the 6-*Me* derivative yields the 1:6-*Me*<sub>2</sub> derivative, m.p. 105—106°. Et 3-methylcyclohexanone-6-carboxylate with NPh·NH<sub>2</sub> gives 2-phenyl-5-methyl-4:5:6:7-tetrahydroisindazol-3-one, m.p. 198—201°, methylation of which affords the 1:5-*Me*<sub>2</sub> derivative, m.p. 110—110.5°. Et 3-methylcyclohexanone-2-carboxylate with NPh·NH<sub>2</sub> yields the phenyl-hydrazone, m.p. 136—138°, which with Na affords the 7-*Me* derivative of (I), m.p. 176°. (I) with NaOEt followed by CH<sub>2</sub>·CBr·CH<sub>2</sub>·Br gives the 1-β-bromoallyl derivative (unstable oil). The above compounds possess antipyretic activity and moderate toxicity (rats, mice). F. O. H.

Reaction of certain diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid. XV. Derivatives of 2'-nitro-4'-methylbenzene-2-naphthol-1-diazosulphonate and synthesis of 2-(2'-nitro-4'-methylphenylamino)isoindolinone-3-acetic acid. F. M. ROWE, A. S. HAIGH, and A. T. PETERS (J.C.S., 1936, 1098—1108; cf. this vol., 737).—The previous investigations have been extended to compounds derived from *m*-nitro-*p*-toluidine (I). 2 : 1-OH·C<sub>10</sub>H<sub>6</sub>·SO<sub>3</sub>Na and diazotised (I) give 2'-nitro-4'-methylbenzene-3-naphthol-1-diazosulphonate, which with Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O gives Na 1-(2'-nitro-4'-methylbenzeneazo)- $\beta$ -naphthaquinone-1-sulphonate (II). This when treated with NaOH and then HCl gives Na benzaldehyde-2'-nitro-4'-methylphenylhydrazide- $\omega$ -sulphonate-2- $\beta$ -acrylic acid (III), which with boiling HCl·H<sub>2</sub>O gives benzo-2'-nitro-4'-methylphenylhydrazide-2- $\beta$ -acrylic acid (IV), m.p. 224—244° with ring-closure and partial decomp., and 2-(2'-nitro-4'-methylphenylamino)isoindolinone-3-acetic acid (V), m.p. 248° [Me ester (VI), m.p. 167°; anilide, m.p. 258°], also obtained by boiling the former acid with H<sub>2</sub>O, EtOH, AcOH, or PhNO<sub>2</sub>, or better by refluxing the mixture of these two acids with Ac<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N, and treating the resulting 2 : 5-diketo-3-(2'-nitro-4'-methylphenyl)isoindolinopyrazolidocoline (VII), m.p. 233°, with warm conc. H<sub>2</sub>SO<sub>4</sub> and then pouring on to ice. (VII) can also be obtained from (V) with Ac<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N, PCl<sub>3</sub>, or SOCl<sub>2</sub>, and is reduced by Fe-AcOH to 2 : 5-diketo-3-(2'-amino-4'-methylphenyl)isoindolinopyrazolidocoline (VIII), m.p. 233° [Ac<sub>2</sub> derivative (IX), m.p. 194°]. Neither (VII) nor (VIII) reacts with *p*-nitrophenylhydrazine. (VIII) when refluxed (4 hr.) with PhMe and PCl<sub>3</sub>, or when heated to the b.p. with dil. H<sub>2</sub>SO<sub>4</sub> and then basified, gives 2 : 2'-anhydro-2 : 5-diketo-3-(2'-amino-4'-methylphenyl)isoindolinopyrazolidocoline (X), m.p. 242° [sulphate (XI), m.p. 269° (decomp.); picrate, m.p. 239°]. *o*-Carboxycinnamionitrile when treated successively with PCl<sub>5</sub> at 100° and (after removal of POCl<sub>3</sub>) *m*-nitro-*p*-tolylhydrazine in CHCl<sub>3</sub> gives benzo-2'-nitro-4'-methylphenylhydrazide-2- $\beta$ -acrylonitrile, m.p. 201° from PhMe, which with MeOH-HCl gives (VI), hydrolysed to the acid. (VII), (V), or (IV) when refluxed with aq. NaOH-EtOH is converted into 1-hydroxy-6-methyl-1 : 2 : 3-benzotriazole (cf. J.C.S., 1922, 121, 720) and a little *o*-carboxycinnamic acid (good prep. described), m.p. 205° with conversion into phthalideacetic acid, m.p. 152° [diamide, m.p. 228° (cf. lit.); dianilide, m.p. 172°], also obtained when *o*-cyanocinnamic acid is boiled with aq. HCl. *o*-Cyanocinnamic acid (*allo* or *trans*) when refluxed with aq. NaOH gives isoindolinone-3-acetic acid, m.p. 182° (amide, m.p. 221°), also obtained when *o*-carboxycinnamdiamide is refluxed with aq. NaOH. (V) or (VII) is reduced by aq. NaOH-Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to 2-(2'-amino-4'-methylphenylamino)isoindolinone-3-acetic acid (XII), m.p. 185° (decomp.) [Me ester hydrochloride, m.p. 204° (decomp.)], which does not form an Ac derivative, but yields (IX), and gives (X), instead of an anilide, in presence of PCl<sub>3</sub> and PhMe. (XII) with cold 10% H<sub>2</sub>SO<sub>4</sub> and NaNO<sub>2</sub> gives 2-(5'-methyl-1' : 2' : 3'-benzotriazolyl)isoindolinone-3-acetic acid, m.p. 253° (amide, m.p. 214°; anilide, m.p. 221°; Me ester). (X) or (XI) but not (XII) when refluxed with dil. H<sub>2</sub>SO<sub>4</sub> gives 2-(2'-aminophenylamino)isoindolinone-3-

acetic acid lactam, m.p. 231° (picrate, m.p. 226°). Na H 3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine-1-sulphonate-4-acetate is obtained (a) when (II) is kept at room temp. for 2 days and then acidified, (b) when (III) is kept similarly with 20% NaOH or heated (sealed vessel; 150°; 6 hr.), and is converted by boiling aq. HCl into 1-hydroxy-3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine-4-acetic acid (XIII), m.p. 233° [Me ester, m.p. 169°; N-Me ether, 1-keto-3-(2'-nitro-4'-methylphenyl)-2-methyltetrahydrophthalazine-4-acetic acid, m.p. 187—188° (decomp.)], which when refluxed (66 hr.) with Ac<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>N gives (VII), and is reduced by Fe-AcOH-H<sub>2</sub>O to the corresponding 2'-NH<sub>2</sub>-acid (XIV), m.p. 180—200° (impure) [lactam (XV), m.p. 282—284°]. (XV) is stable to hot mineral acids (cf. lower homologue and its 4'-Cl-derivative, this vol., 737) and is not reduced (SnCl<sub>2</sub>, Sn-HCl, or Zn-H<sub>2</sub>SO<sub>4</sub>) to 5-methyl-*o*-benzylenebenzimidazole. (XIV) or (XV) with acid dichromate gives a substance m.p. 311—313° (decomp.); 2'-amino-3-phenyl-4'-methylphthalaz-1-one-4-acetic acid lactam or 2'-amino-3-phenyl-4' : 4'-dimethylphthalaz-1-one were not obtained (cf. loc. cit.). (XIII) when refluxed with aq. H<sub>2</sub>SO<sub>4</sub> gives 2'-nitro-3-phenyl-4'-methylphthalaz-1-one (XVI), m.p. 256—258°, which when heated (120°) with PhNO<sub>2</sub>-Me<sub>2</sub>SO<sub>4</sub> gives the 1-OMe-derivative, m.p. 119—121° from MeOH and m.p. 115—117° from EtOH, decomposed by heat but without formation of 4-keto-1-methoxy-3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine. (XIII) is oxidised by aq. KMnO<sub>4</sub> to 1 : 4-diketo-3-(2'-nitro-4'-methylphenyl)-tetrahydrophthalazine, m.p. 286—288°, of which the Ag salt, when refluxed with EtI·C<sub>6</sub>H<sub>5</sub>, gives 4-keto-1-ethoxy-3-(2'-nitro-4'-methylphenyl)-3 : 4-dihydrophthalazine, m.p. 185° (contains C<sub>6</sub>H<sub>6</sub> of cryst.). (XIII) is oxidised by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O to 2'-nitro-3-phenyl-4' : 4'-dimethylphthalaz-1-one (XVII), m.p. 236°, the Me derivative of which could not be purified. Reduction of (XVI) and (XVII) with aq. Na<sub>2</sub>S does not give the corresponding NH<sub>2</sub>-compounds. H. G. M.

Synthesis of pyrroles with attached isocyclic ring. A. TREIBS [with F. DORNBERGER, A. ALBRECHT, C. G. SCHRODER, H. REINECKE, and H. EMMERICH] (Annalen, 1936, 524, 285—294; cf. A., 1935, 870).—Gradually addition of a mixture of cyclohexene  $\psi$ -nitrosite and Zn dust to a boiling solution of CH<sub>2</sub>Ac·CO<sub>2</sub>Et in AcOH affords Et 2-methyl-4 : 5 : 6 : 7-tetrahydroindole-3-carboxylate (I), m.p. 133° (yield 35%), and octahydrophenazine (II); possibly the change occurs through the NH<sub>2</sub>-ketone but the imino-amine is also possible. 1 : 2-Dioximes can also be used in this variation of Knorr's synthesis; thus (CMe·N·OH)<sub>2</sub> and CH<sub>2</sub>Ac·CO<sub>2</sub>Et give Et 2 : 3 : 5-trimethylpyrrole-4-carboxylate, m.p. 103—105°. The very unstable cyclopentene  $\psi$ -nitrosite, m.p. 69—70°, passes into Et 4 : 5-cyclopenteno-2-methylpyrrole-3-carboxylate, m.p. 146°, and dicyclopentenopyrazine, m.p. 88—89°, in poor yield. CH<sub>2</sub>Cl·CHO and cyclohexanone in NH<sub>3</sub> give 4 : 5 : 6 : 7-tetrahydroindole (III), m.p. 55°. A more suitable initial material is chlorocyclohexanone, which with CH<sub>2</sub>Ac·CO<sub>2</sub>Et and 10% NH<sub>3</sub> at 60—70° affords (I) (best method of prep.) and with Et<sub>2</sub>C<sub>2</sub>O<sub>4</sub> gives 3-carbethoxy-4 : 5 : 6 : 7-tetrahydroindole-1-carboxylic acid (IV), m.p. 212°



(decomp.). Hydrolysis of the latter with boiling 10% KOH involves loss of  $\text{CO}_2$  and gives 4 : 5 : 6 : 7-tetrahydroindole-3-carboxylic acid (V), m.p.  $201^\circ$  (decomp.) [Et ester, m.p.  $78^\circ$ , also obtained by treatment of (IV) with HCl in boiling EtOH or by decarboxylation of (IV) at  $230^\circ$ ]. At  $210^\circ$ , (V) passes into (III). The substance,  $\text{C}_{20}\text{H}_{27}\text{O}_4\text{N}_3$  or  $\text{C}_{20}\text{H}_{29}\text{O}_4\text{N}_3$ , m.p.  $240^\circ$  (decomp.), is obtained as by-product of the prep. of (IV). (II) and Br in  $\text{H}_2\text{O}$  give a very unstable *perbromide*,  $\text{C}_{12}\text{H}_{16}\text{N}_2\cdot 2\text{Br}_2$ , converted by short treatment with  $\text{COMe}_2$  into *octahydrophenazine dihydrobromide*, decomp.  $210^\circ$ , and by more prolonged treatment into the *monohydrobromide*, decomp.  $160^\circ$ . A complex acid, (?)  $\text{C}_{22}\text{H}_{32}\text{O}_6\text{N}_2$ , m.p.  $194^\circ$  (decomp.), is obtained as by-product of the prep. of (IV).

H. W.

Modern purine chemistry, facts and explanations. H. BILTZ (J. pr. Chem., 1936, [ii], 145, 65—228).—A comprehensive review; the interpretation of results is based on the electronic theory of valency and stereochemical considerations.

H. G. M.

Synthesis of urobilin (urobilin-IX $\alpha$ ) and its isomerides urobilin-III $\alpha$  and -XIII $\alpha$ . W. SIEDEL and E. MEIER (Z. physiol. Chem., 1936, 242, 101—132).—Aldehydoneoxanthobilirubinic acid with colloidal Pd in 0.1N-NaOH and  $\text{H}_2$  gives *aldehydoneobilirubinic acid* (I), m.p.  $228^\circ$  (corr.), and similarly *aldehydoneoxanthobilirubinic acid* gives *aldehydoneobilirubinic acid* (II), m.p.  $242^\circ$  (corr.). (I) mixed with *isoneobilirubinic acid* (III) in AcOH and treated with 2N-HCl under  $\text{N}_2$  at  $70$ — $80^\circ$  gives urobilin (IV), m.p.  $177^\circ$  (corr.) [hydrochloride, m.p.  $199$ — $200^\circ$ ; hydrobromide, m.p.  $200$ — $201^\circ$  (corr.)], also obtained in 25% yield from mesobilirubinogen (V) by heating in AcOH at  $70$ — $80^\circ$  for 30 min. Similarly (II) with neobilirubinic acid (VI) gives (IV). (III) in  $\text{HCO}_2\text{H}$  at  $70$ — $80^\circ$  with  $\text{Ac}_2\text{O}$  gives urobilin-III $\alpha$ , m.p.  $183^\circ$  (corr.) [hydrochloride, m.p.  $203^\circ$  (corr.)]. (I) with (VI) in AcOH and (VI) with  $\text{HCO}_2\text{H}$  and  $\text{Ac}_2\text{O}$  give urobilin-XIII $\alpha$  (VII), m.p.  $176^\circ$  (corr.) [hydrochloride, m.p.  $192^\circ$  (corr.); hydrobromide, m.p.  $194^\circ$  (corr.)]. Mesobilirubin-IX $\alpha$  obtained during the production of (IV) from (V) has m.p.  $301^\circ$  (corr.). The constitution and properties of stercobilin (VIII),  $\text{C}_{33}\text{H}_{46}\text{O}_6\text{N}_4$ , very closely resemble those of (IV), but (VIII) is derived from urobilinogen by a more complicated process. Fuming  $\text{HNO}_3$  gives with (IV) hydrochloride a substance (IX) probably derived from methylethylmaleimide (X), and with (VII) hydrochloride (IX) and (X).  $\text{H}_2\text{SO}_4$ - $\text{CrO}_3$  give with (VII) hydrochloride (IX) and two other substances. (VII) hydrochloride with colloidal Pd and  $\text{H}_2$  in 0.1N-NaOH and with Na-Hg gives mesobilirubinogen-XIII $\alpha$ , m.p.  $194^\circ$ . (I) with  $\text{CH}_2\text{N}_2$  gives a substance, m.p.  $176^\circ$ , but no Me ester.

W. McC.

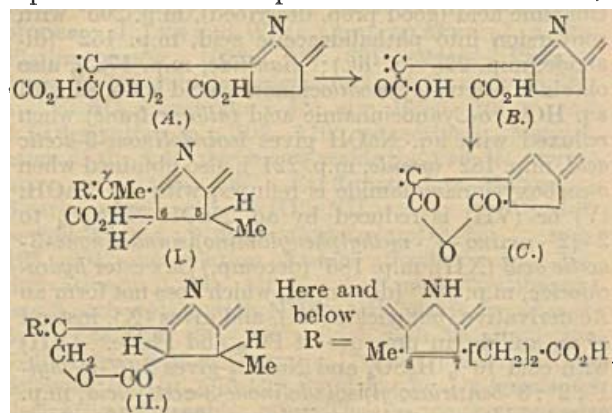
Porphyrins. XXXVII. Constitution of *Spirographis-hæmin*. H. FISCHER and C. VON SEEMANN (Z. physiol. Chem., 1936, 242, 133—157; cf. this vol., 1128, 1273; Warburg *et al.*, A., 1932, 292).—10.6 kg. of *S. Spallanzanii* yielded 260 mg. of the  $\text{Me}_2$  ester of *Spirographis-hæmin* (I). Treatment of the corresponding porphyrin (II) with HI in air results in a shift towards blue in the spectrum

and the product yields no oxime. The oxime of (II) yields the corresponding nitrile on boiling with  $\text{Ac}_2\text{O}$ . The  $\text{Me}_2$  ester of (II) reacts with  $\text{CHN}_2\cdot\text{CO}_2\text{Me}$  and the product (III) yields an oxime (IV). In (III) the spectrum is shifted towards red, but in (IV) towards blue. The product of hydrogenation ( $\text{Pd-H}_2$ ) of the  $\text{Me}_2$  ester of (II) has m.p.  $242$ — $243^\circ$  and is identical with 1 : 2 : 3 : 5 : 8-pentamethyl-4-ethylporphyrin-6 : 7-dipropionic acid and hence (II) is 2-aldehydo-1 : 3 : 5 : 8-tetramethyl-4-vinylporphyrin-6 : 7-dipropionic acid. The  $\text{Me}_2$  ester of (I) fused with resorcinol yields deuteroporphyrin-IX. 6-Aldehydopyrroporphyrin Me ester in  $\text{HCO}_2\text{H}$  treated with  $\text{Pd-H}_2$  and then oxidised with air gives the corresponding 6-Me derivative, m.p.  $247$ — $248^\circ$ .

W. McC.

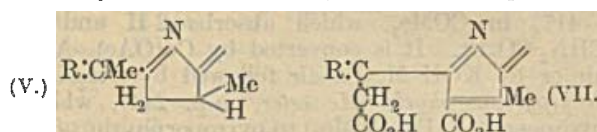
Hydrogenated benzisotetrazoles.—See B., 1936, 825.

Chlorophyll. LXIX. Chlorophyll-b. VIII. Purpurins, rhodins, and rhodinoporphyrins from chlorophyll-b. Analogies between chlorophyll-a and -b. H. FISCHER and K. BAUER (Annalen, 1936, 523, 235—284; cf. A., 1935, 763; this vol., 1128).—Many reactions of chlorophyll-b derivatives are reported analogous to those in the -a series, there being no differences except sometimes in conditions and yields, due to the 3-CHO of the -b derivatives. This CHO causes a shift of absorption towards the red and differences in  $\text{Et}_2\text{O}$  colour. Substances with Me at 3,  $\text{CH}_2\cdot\text{CO}_2\text{H}$ , Me,  $\text{CO}_2\text{H}$ , or H at  $\gamma$ , and H or  $\text{CO}_2\text{H}$  at 6 belong to the chlorin type (green  $\text{Et}_2\text{O}$  colour, broad spectrum); substances which are similar except that they have CHO instead of Me at 3 are rhodins (red  $\text{Et}_2\text{O}$  colour, narrow spectrum), but are converted into substances of chlorin type by masking of the CO, *e.g.*, by oximation. Unstable rhodins or chlorins exist in the hydrate form (A), which reverts to the CO form when the  $\text{CO}_2\text{H}$  is esterified; this assumption explains the ready formation of anhydride-purpurins, which occurs by loss of  $\text{HCO}_2\text{H}$  as shown in the partial formulæ (A)—(C). *cyclo*Propanecarboxylates formed by reaction of the  $\text{CH}\cdot\text{CH}_2$  with  $\text{CHN}_2\cdot\text{CO}_2\text{Me}$  are called below “D-products”; spectrographic evidence of this reaction or of oximation, without isolation of the products, is reported below as “positive D- or O-reaction,”

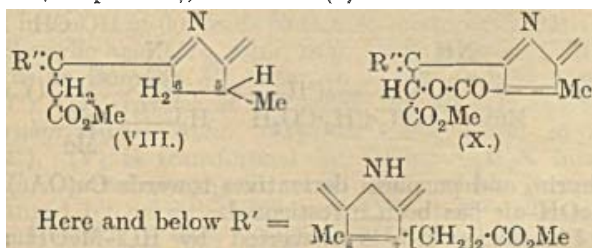


respectively.  $[\alpha]$  are  $[\alpha]_{6900}^{0-7300}$  in  $\text{COMe}_2$ . The D-product of the  $\text{Me}_2$  ester of rhodin-g<sub>7</sub> gives an

oxime,  $C_{36}H_{33}O_5N_5(OMe)_4$ , m.p. 229°, which in boiling  $C_5H_5N$  gives a *pyrophosphoribide-b* derivative,  $C_{37}H_{33}O_4N_5(OMe)_2$ , m.p. 278°; decarboxylation has occurred and this can thus no longer be ascribed to the vicinity of the  $CH:CH_2$  and  $CHO$  in the *-b* series, since in this case the  $CH:CH_2$  and  $CHO$  were masked. Rhodin-*g*, in hot  $C_5H_5N$  gives 30–60% of rhodin-*g*<sub>5</sub> (I) and 10% of rhodin-*g*<sub>5</sub>- $\gamma$ -hydroxymethyl-lactone (II) [*Me* ester, m.p. 215°,  $[\alpha] -431^\circ$  (*Cu* salt, m.p. 162°; *oxime*, m.p. 235°; *D-product*, m.p. 240°)], which decomposes at 230° to yield a little 3-demethyl-3-formylphyllporphyrin (III). The *Me*<sub>2</sub> ester (IV), m.p. 180°,  $[\alpha] -566^\circ$  [*Cu*, m.p. 191°,  $[\alpha] -515^\circ$  (with HI gives a little rhodoporphyrin-*g*<sub>6</sub>), and *Zn* salt], of (I) gives an oxime, m.p. 214°, which with  $Ac_2O-KOAc$  gives the nitrile,  $C_{33}H_{31}O_2N_5(OMe)_2$ , m.p. 181° (*Cu* salt, m.p. 188°,  $[\alpha] -629^\circ$ ). Rhodinporphyrin-*g*<sub>5</sub>,  $C_{33}H_{32}O_3N_4(OMe)_2$  (analysed), purified by the *Fe* salt, m.p. 286°, with  $HI-AcOH-O_2$  gives a substance, the *Me* ester,  $C_{33}H_{31}O_3N_4(OMe)_3$ , m.p. 214°, of which gives no oxime; the *Fe* salt of rhodin-*g* *Me*<sub>3</sub> ester gives similarly a substance, esterified to rhodin-*g*<sub>8</sub> *Me*<sub>4</sub> ester. Phæophorbide-*b* and  $NaOMe-C_5H_5N$  at 140–150° give rhodoporphyrin and traces of phyllo- and pyrrro-porphyrins; (IV) gives a little phylloporphyrin. (II) resists acylation and alkaline hydrolysis and was not obtained from rhodin-*g*-ester, but with  $HI$  in  $N_2$  gives rhodinporphyrin-*g*<sub>5</sub> and a little -*g*<sub>6</sub>.  $C_5H_5N$ -degradation of chlorin-*e*<sub>6</sub>, analogous to that of (I), gives similarly chlorin-*e*<sub>4</sub> and 3% of chlorin-*e*<sub>4</sub>- $\gamma$ -hydroxymethyl-lactone [cf. formula (II)], m.p. 166° (*D*-reaction positive); the lactone with  $HI$  gives chloroporphyrin-*e*<sub>4</sub> very rapidly. (I), m.p. 212°, at 225° gives 1 mol. of  $CO_2$ , rhodin-*g*<sub>3</sub> (V),  $C_{32}H_{31}O_3N_4$  (decomposes entirely on attempted further decarboxylation; *Me* ester, m.p. 243°,  $[\alpha] -428^\circ$ ; positive *O*- and *D*-reactions), and (III), m.p. 233° [negative *D*-reaction; also obtained by short heating of (I) with  $HI$  at 70°, and in 2% yield with (V) by decarboxylation of rhodin-*g* (VI); *oxime*, m.p. 244°].

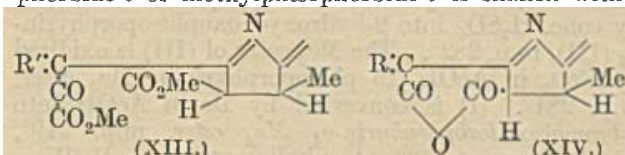


(VI) in boiling  $HCO_2H$  gives rhodinporphyrin-*g*<sub>3</sub> (*Me* ester, m.p. 230°, and *oxime*, m.p. 275°, give negative *D*-reactions). Chlorin-*e* gives similarly a 5% yield of a *phyllporphyrin* (*Me* ester, m.p. 227°). (VI) and cold  $HCl-MeOH$  give 60% of rhodin-*g*<sub>7</sub> (VII),  $C_{34}H_{32}O_7N_4$ , the *Me*<sub>2</sub> ester, m.p. 274°,  $[\alpha] -230^\circ$  (*Cu* salt, m.p. 246°), of which (a) at about 285° or in

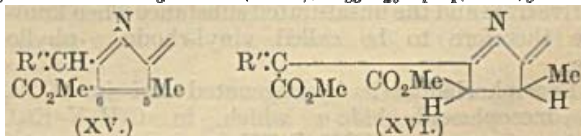


boiling  $Ph_2$  gives  $CO_2$  and 5% of isorhodin-*g*<sub>5</sub> *Me*<sub>2</sub> ester (VIII), m.p. 255°,  $[\alpha] -424^\circ$  [positive *O*- and

*D*-reactions; with  $HI$  at 70° and subsequently  $CH_2N_2$  gives a *porphyrin* (IX),  $C_{33}H_{32}O_3N_4(OMe)_2$ , m.p. 253°, and (b) with  $HI$  at 60° gives *rhodinporphyrin-g-lactone Me*, ester (X),  $C_{34}H_{30}O_5N_4(OMe)_2$ , m.p. 258°, a *porphyrin* (XI),  $C_{34}H_{32}O_5N_4(OMe)_2$ , m.p. 268° [also obtained by decarboxylation of (X) by melting], and a little (IX). The *O*-reactions of (IX), (X), and (XI) are positive, the *D*-reactions negative. When phæophorbide-*b* or methylphæophorbide-*b* is shaken with



20%  $KOH-PrOH-Et_2O$ , there are formed a trace of (VI) and, nearly quantitatively, an unstable rhodin (XII), which, when esterified ( $CH_2N_2$ ), changes its type and yields *b-phæopurpurin-7 Me*<sub>3</sub> ester (XIII),  $C_{34}H_{29}O_5N_4(OMe)_3$ , m.p. 252°,  $[\alpha] +481^\circ$  (*D*-reaction positive; *oxime*, m.p. 238°; a *dioxime* is indicated spectrographically, but could not be isolated); cold, acid hydrolysis of this ester gives a stable purpurin acid, which was not, however, isolated crystalline. If (XIII) is repeatedly evaporated in  $Et_2O$  and then heated at 130° or kept for months in  $Et_2O$ , a 35% yield of *b-phæopurpurin-18* (XIV),  $C_{33}H_{30}O_6N_4$ , m.p. >360° (previous decomp.),  $[\alpha] +340^\circ$  [*Me* ester, m.p. 282°, spectrographically identical with (XIV), both before and after hydrolysis; *D*- and *O*-reactions positive], is obtained. (XII) and  $HCl-Et_2O-MeOH$  give (XIII). With  $KOH-PrOH$ , rhodin-*g* *Me*<sub>3</sub> ester or pure phæophytin-*b* gives (XIII) quantitatively, but (VI) and chlorin-*e* are largely unchanged, and mixtures of phæophytin-*a* and -*b* or chlorophyllide-*a* and -*b* give mixtures of phæopurpurin-7 and -18. Rhodin-*g*-oxime gives the oxime of (XIII). Phæophorbide-*b* and  $KOH-MeOH$  give (VI), but no (XIII). (XIII) in hot  $C_5H_5N$  gives a good yield of 3-demethyl-3-formyl- $\psi$ -verdoporphyrin (XV),  $C_{34}H_{28}O_3N_4(OMe)_2$ , m.p. 250° (*O*-reaction positive; also obtained with another product by 20%  $HCl$ ), which with  $CHN_3 \cdot CO_2Me$  gives the *D-product*, m.p. 228° (*O*-reaction positive). (XIV) and  $KOH-MeOH$  give *b-chlorin-p*<sub>6</sub>, which with  $CH_2N_2$  yields the *Me*<sub>3</sub> ester (XVI),  $C_{33}H_{29}O_4N_4(OMe)_3$ , m.p.



261°,  $[\alpha] +249^\circ$  (*D*- and *O*-reactions positive). In hot  $C_5H_5N$  (XIV) is largely decomposed, but gives a little *b-rhodoporphyrin-g-carboxylic anhydride* and a *porphyrin*, also obtained from (XVI) by  $HI$ . The  $CO-CO_2Me$  of (XIII) is removed by boiling with 20%  $KOH-PrOH$  for 3 min.; *b-rhodochlorin* (XVII) [*Me*<sub>3</sub> ester,  $C_{35}H_{30}O_3N_4(OMe)_2$ , m.p. 198°,  $[\alpha] -230^\circ$ , =the 5 : 6- $H_2$ -derivative of (XV); *O*- and *D*-reactions positive] and a little (XV) are obtained. (XIII) or (XVII) with  $HI$  give a poor yield of *b-rhodoporphyrin*,  $C_{32}H_{30}O_3N_4(OMe)_2$ , m.p. 218° (*O*-reaction positive; *D*-reaction negative).

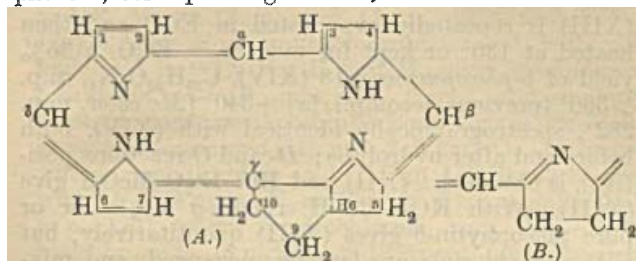
R. S. C.

**Chlorophyll. LXX.** Partial synthesis of phæoporphyrin-*a*<sub>5</sub> and phylloerythrin. H.



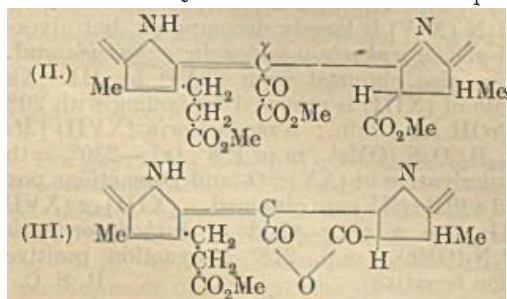
FISCHER and H. KELLERMANN (Annalen, 1936, 524, 25—30; cf. A., 1935, 1382).—*iso*Chlorin- $e_4$  Me<sub>2</sub> ester is converted by protracted hydrogenation (Pd in AcOH) with subsequent re-oxidation of any leuco-compound formed into *isochlorophorphyrin-e<sub>4</sub>* Me<sub>2</sub> ester (I) and thence into the *hæmin* (II), C<sub>35</sub>H<sub>35</sub>O<sub>4</sub>N<sub>4</sub>FeCl, m.p. 289°, from which Fe could be removed only with difficulty. The product obtained from (II), CHCl<sub>3</sub>·OEt, and SnBr<sub>4</sub> is transformed by conc. H<sub>2</sub>SO<sub>4</sub> into 9-hydroxydeoxophæorphyrin- $a_5$  (III), m.p. 282°. The Me<sub>2</sub> ester of (III) is oxidised by CrO<sub>3</sub> in AcOH to phæorphyrin- $a_5$  Me<sub>2</sub> ester, m.p. 281°. (I) is converted by Br in AcOH into 6-bromoisochlorophorphyrin- $e_4$  Me<sub>2</sub> ester, m.p. 249°, which passes at 252° into phylloerythrin. H. W.

Chlorophyll. LXXI. Mesopurpurin, vinyl-chlorin, and their derivatives. H. FISCHER, K. HERRLE, and H. KELLERMANN (Annalen, 1936, 524, 222—250).—To distinguish between H<sub>2</sub>-derivatives in which the atoms are added to the vinyl group and those in which they are added to the porphin nucleus it is proposed to introduce the term phorbin, corresponding with A, for the fundamental



nucleus of chlorophyll. Phorbin derivatives with Et at 2 receive the prefix "meso." The open form obtained by removal of the *isocyclic* ring, B, is termed chlorin, the names thus coinciding with those of the older nomenclature. With purpurins and rhodins it is proposed where necessary to use the prefix "meso" to denote the saturation of the vinyl group, thus causing a change of nomenclature among synthetic phyllo-, pyrro-, and rhodo-chlorins. The use of "meso" for porphyrins is not contemplated since it would be required for nearly all known derivatives and the unsaturated substance when known are therefore to be called vinyl-rhodo-, -phyllo-, etc.

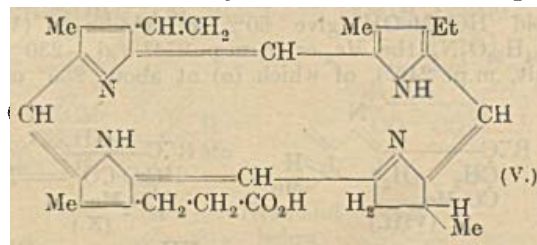
Phæophorbide- $a$  is hydrogenated (Pd in COMe<sub>2</sub>) to mesophæophorbide- $a$  which, in C<sub>5</sub>H<sub>5</sub>N-Et<sub>2</sub>O, is transformed by KOH-PrOH into mesopurpurin-7



(I), the Me ester (II), m.p. 215°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> +210° in COMe<sub>2</sub>, of which passes when heated above its m.p.

or boiled with C<sub>5</sub>H<sub>5</sub>N into rhodoporphyrin Me<sub>2</sub> ester; as by-product, *mesopurpurin-18* (III), m.p. 266°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> +1210° in 25% HCl, is obtained. When heated at about 290° (III) passes into rhodoporphyrin- $\gamma$ -carboxylic anhydride ester, m.p. 256°, [ $\alpha$ ]  $\pm 0^\circ$ , further identified by successive hydrolysis and treatment with CH<sub>2</sub>N<sub>2</sub>, whereby the Me<sub>2</sub> ester, m.p. 252°, is obtained. Under similar conditions (III) is transformed into *mesochlorin-p<sub>6</sub>* Me<sub>2</sub> ester, m.p. 201°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> +334° in COMe<sub>2</sub>. When heated with KOH in PrOH (I) loses the ·CO·CO<sub>2</sub>H residue and passes into *mesorhodochlorin* (IV), C<sub>32</sub>H<sub>36</sub>O<sub>4</sub>N<sub>4</sub>, m.p. (indef.) 275°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -364° in COMe<sub>2</sub> (Cu salt, m.p. 298°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -676° in COMe<sub>2</sub>), which affords rhodoporphyrin when heated at 250° or treated with HI, PhOH, or (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>; the corresponding Me<sub>2</sub> ester (Cu salt, m.p. 196°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -242° in COMe<sub>2</sub>) has m.p. 176°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -299° in COMe<sub>2</sub>. During the thermal conversion of chlorins into porphyrins H<sub>2</sub> does not appear to be liberated, but pyrrole is produced. (IV) passes in boiling AcOH into *mesopyrrochlorin*, C<sub>31</sub>H<sub>34</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 229°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -536° in COMe<sub>2</sub> (Me ester), converted when heated at 229° or treated with Cu(OAc)<sub>2</sub>-AcOH-air into pyrroporphyrin, also obtained by means of KOH-MeOH.

The chlorin- $f$  Me<sub>2</sub> ester of Conant *et al.* (A., 1931, 368), now designated *rhodochlorin* Me<sub>2</sub> ester, has m.p. 207°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -458° in COMe<sub>2</sub>. It is unchanged when heated above its m.p., or treated with boiling C<sub>5</sub>H<sub>5</sub>N or with (·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub> and *m*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> or PhOH, but is converted by HI into rhodoporphyrin and by mild alkaline degradation or by Cu(OAc)<sub>2</sub>-AcOH-air into  $\psi$ -verdroporphyrin. It readily adds CHN<sub>2</sub>·CO<sub>2</sub>Et giving the product, C<sub>37</sub>H<sub>42</sub>O<sub>6</sub>N<sub>4</sub>, m.p. 198°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -302° in COMe<sub>2</sub>, which is isomerised by HI in AcOH to "*D.E.E.*- $\psi$ -verdroporphyrin ester," m.p. 244°. Free rhodochlorin in C<sub>5</sub>H<sub>5</sub>N is transformed by boiling AcOH into pyrro- and rhodo-porphyrin and *pyrrochlorin* (V), C<sub>31</sub>H<sub>34</sub>O<sub>2</sub>N<sub>4</sub>, m.p. 220°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -417° in COMe<sub>2</sub>, which absorbs 2 H and adds CHN<sub>2</sub>·CO<sub>2</sub>Et. It is converted by Cu(OAc)<sub>2</sub>-AcOH-air or by KOH-MeOH-air followed by CH<sub>2</sub>N<sub>2</sub> into *vinylpyrroporphyrin* Me ester, m.p. 244°, which is hydrogenated (Pd-COMe<sub>2</sub>) to pyrroporphyrin. Treatment of 2-deethylvinylpyrroporphyrin Me ester with CHN<sub>2</sub>·CO<sub>2</sub>Et causes displacement of the spectrum towards the blue. (V) has therefore the annexed structure. The stability of numerous chlorin, por-



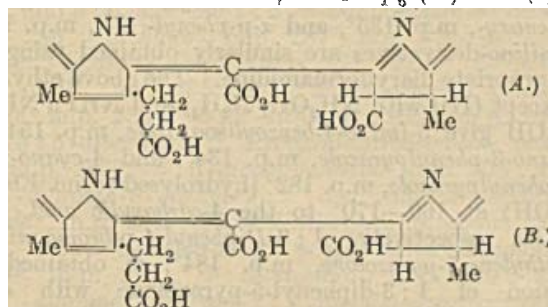
phyrin, and purpurin derivatives towards Cu(OAc)<sub>2</sub>-AcOH-air has been investigated.

Phæopurpurin-7 is converted by HCl-MeOH at 0° into *purpurin* Me<sub>2</sub> ester, m.p. 178°. Mesochlorin- $e_6$  passes above its m.p. into mesophyllochlorin, m.p. 147°, [ $\alpha$ ]<sub>690-730</sub><sup>20</sup> -392° in COMe<sub>2</sub>, the ester of which

is converted by Br in  $\text{CHCl}_3$ -AcOH into the compound,  $\text{C}_{33}\text{H}_{38}\text{O}_2\text{N}_4\text{Br}_2$ , m.p.  $150^\circ$ ,  $[\alpha]_{\text{D}}^{20} -580^\circ$  in  $\text{COMe}_2$ .

H. W.

**Chlorophyll. LXXII.** Isomerism between chlorin- $p_6$  and  $\psi$ -chlorin- $p_6$  and their derivatives. Elucidation of the pyrrole structure of ring III of chlorophyll. H. FISCHER and K. KAHR (Annalen, 1936, 524, 251—268).—Treatment of mesophaeophorbide- $a$  in 1% NaOH with air at  $50^\circ$  and of the product with  $\text{CH}_2\text{N}_2$  gives meso- $\psi$ -chlorin  $Me$  ester, m.p.  $190^\circ$   $[\alpha]_{\text{D}}^{20} -168^\circ$  in  $\text{COMe}_2$ . Whereas chlorin- $p_6$  (I) and mesochlorin- $p_6$  are readily converted into their anhydrides, the change can be effected in the  $\psi$ -series to a minimal degree only in the case of the vinyl compound and not at all with the meso-derivative. The only possible explanation lies in the assumption that the two "superfluous" H atoms are attached to  $\text{C}_{(5)}$  and  $\text{C}_{(6)}$ , thus leading to the constitutions A and B for  $\psi$ -chlorin- $p_6$  (II) and (I).

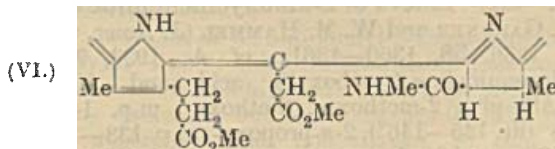


(I) and (II) are transformed by HI into different rhodoporphyrin- $\gamma$ -carboxylic acids; the  $\text{Me}_3$  ester of that derived from (I) is transformed by conc.  $\text{H}_2\text{SO}_4$  into the green rhodoporphyrin- $\gamma$ -carboxylic anhydride whereas that from (II) gradually suffers total decomp. The results are explained by assuming the formation of a double linking between  $\text{C}_{(5)}$  and  $\text{C}_{(6)}$  in the one case and a wandering of the double linkings in the second instance. Similar relationships obtain between derivatives of (I) and (II). Thus *D.E.E.*-phaeophorbide- $a$  (III) is converted by  $\text{KOH}$ - $\text{PrOH}$  into *D.E.E.*-phaeopurpurin-18 (III) ( $Me$  ester,  $\text{C}_{38}\text{H}_{38}\text{O}_7\text{N}_4$ , m.p.  $211^\circ$ ,  $[\alpha]_{\text{D}}^{20} +104^\circ$  in  $\text{COMe}_2$ ) and *D.E.E.*-phaeopurpurin-7 (V) ( $Me_4$  ester,  $\text{C}_{40}\text{H}_{44}\text{O}_8\text{N}_4$ , m.p.  $195^\circ$ ,  $[\alpha]_{\text{D}}^{20} +303^\circ$  in  $\text{COMe}_2$ ), the former of which is transformed by  $\text{KOH}$ - $\text{MeOH}$  into *D.E.E.*-chlorin- $p$  (V) ( $Me$  ester  $\text{C}_{38}\text{H}_{44}\text{O}_8\text{N}_4$ , m.p.  $220^\circ$ ,  $[\alpha]_{\text{D}}^{20} +411^\circ$  in  $\text{COMe}_2$ ), re-convertible into (IV). Under the action of  $\text{NaOH}$ -air, (III) passes into *D.E.E.*- $\psi$ -chlorin- $p_6$  (VII) ( $Me$  ester, m.p.  $191^\circ$ ,  $[\alpha]_{\text{D}}^{20} -208^\circ$  in  $\text{COMe}_2$ ), also obtained by addition of  $\text{CHN}_2\cdot\text{CO}_2\text{Et}$  to  $\psi$ -chlorin- $p_6$  ester). Isomerisation of (VI) by colourless HI in AcOH at  $60^\circ$  leads to *D.E.E.*-rhodoporphyrin- $\gamma$ -carboxylic acid ( $Me_4$  ester, m.p.  $232^\circ$ ), whereas (VII) gives an isomeric  $Me_4$  ester, m.p.  $232^\circ$  (mixed m.p.  $217^\circ$ ). (IV) passes at  $280$ — $290^\circ$  into *D.E.E.*-rhodoporphyrin- $\gamma$ -carboxylic anhydride ( $Me_2$  ester, m.p.  $204^\circ$ ). (V) is transformed by boiling  $\text{C}_5\text{H}_5\text{N}$  into *D.E.E.*- $\psi$ -verdoporphyrin, m.p.  $246^\circ$ , which is unchanged by colourless HI in AcOH at  $60^\circ$ . Treatment of (III) with  $\text{KOH}$ - $\text{MeOH}$ - $\text{C}_5\text{H}_5\text{N}$ - $\text{MgO}$  at  $160^\circ$  affords *D.E.E.*-phyllorophyrin ( $Me$  ester, m.p.  $207.5^\circ$ ), whereas *D.E.E.*-pyrro- ( $Me$  ester, m.p.  $187^\circ$ ) and *D.E.E.*-rhodo-porphyrin ( $Me$  ester, m.p.  $245^\circ$ )

are derived from (III) and  $\text{KOH}$ - $\text{MeOH}$ - $\text{C}_5\text{H}_5\text{N}$  at  $185^\circ$  and  $125^\circ$ , respectively.

H. W.

**Chlorophyll. LXXIII.** New ring fission of phaeophorbide- $a$  and phaeoporphyrin- $a_5$ . H. FISCHER and S. GOEBEL (Annalen, 1936, 524, 269—284; cf. A., 1935, 362).—Treatment of phaeoporphyrin- $a_5$  (I) with  $\text{Mg}$ - $\text{MgEtBr}$  in  $\text{MeOH}$ - $\text{C}_5\text{H}_5\text{N}$  yields phaeoporphyrin- $a_5$ -phyllin (II),  $\text{C}_{35}\text{H}_{34}\text{O}_5\text{N}_4\text{Mg}$ , transformed by  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  into the  $Me_2$  ester, decomp. about  $220$ — $310^\circ$ , and by  $\text{CHMeN}_2$ + $\text{EtOH}$  into the  $Et_2$  ester (III), decomp. about  $220$ — $310^\circ$ . (III) is decomposed by 10%  $\text{HCl}$  to phaeoporphyrin- $a_5$   $Et_2$  ester (IV), m.p.  $272^\circ$ ; with  $\text{NH}_2\text{OH}$  it gives an oxime, whence the oxime of (IV) and ultimately (I); with  $\text{Ba(OH)}_2$  it gives chloroporphyrin- $e_6$ , identified as the tri-ester, m.p.  $242^\circ$ . The catalytic hydrogenation ( $\text{PtO}_2$  in dioxan) of (II) and of ethylchlorophyllide (improved prep.) is described.  $\text{Mg}$  is introduced similarly into phylloerythrin (V) giving the substance,  $\text{C}_{34}\text{H}_{34}\text{O}_3\text{N}_4\text{Mg}$ , which could not be obtained by decarboxylation of (II) in boiling  $\text{C}_5\text{H}_5\text{N}$ . The successful introduction of  $\text{Mg}$  into phaeophytin- $a$  necessitates the addition of phytol which could not be satisfactorily removed. Methylphaeophorbide- $a$  in  $\text{NH}_2\text{Me}$ - $\text{COMe}_2$  at room temp. affords the methylamide (VI), m.p.  $234^\circ$ , whereas  $\text{NH}_3$  in  $\text{C}_5\text{H}_5\text{N}$  gives the corresponding amide, m.p.  $195^\circ$ . Treatment of phaeophorbide- $a$  with  $\text{NH}_3$ - $\text{MeOH}$  and of the product with  $\text{CH}_2\text{N}_2$  affords a substance, m.p.  $139$ — $162^\circ$ , degraded by HI to chloroporphyrin- $e_6$  6-amide, m.p.



$278^\circ$ , identical with the product obtained from (I); it is transformed by  $\text{PhOH}$  at  $160^\circ$  into (I), by anhyd.  $\text{H}_2\text{C}_2\text{O}_4$  or 20%  $\text{HCl}$  at  $80^\circ$  (V), and by 33%  $\text{HCl}$ - $\text{MeOH}$  into chloroporphyrin- $e_4$  and - $e_6$ . (I) and  $\text{NHPh}\cdot\text{NH}_2$  or  $\text{NH}_2\text{Ph}$  give the corresponding phenylhydrazide ( $Me$  ester, m.p.  $259^\circ$ ) and (?) anilide. Phaeophorbide- $a$ , suspended in  $\text{MeOH}$ , is converted by  $\text{COCl}_2$  into a mixture of methylphaeophorbide- $a$  and chlorin- $e_6$  tri-ester, the latter being exclusively obtained when it is treated with 1%  $\text{KOH}$ - $\text{MeOH}$  in presence of  $\text{C}_5\text{H}_5\text{N}$ .

[With HAARER.] Passage of  $\text{COCl}_2$  through a suspension of (I) and geraniol in  $\text{CHCl}_3$  gives the corresponding geranyl ester,  $\text{C}_{45}\text{H}_{52}\text{O}_5\text{N}_4$ , m.p.  $194^\circ$ ; the corresponding menthyl, m.p.  $254^\circ$ , bornyl, m.p.  $243^\circ$  after softening, and dimethylaminoethyl, m.p.  $247^\circ$  (decomp.), esters are obtained similarly.

H. W.

**Fluorescence of the porphyrins.**—See this vol., 1048.

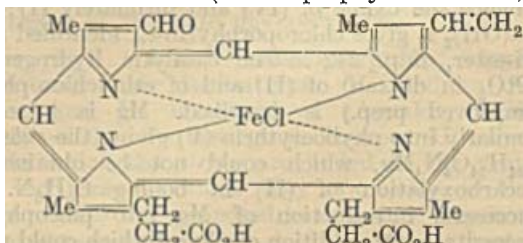
**Optical absorption of porphyrins. VI.** See this vol., 1178.

**Colour reaction of copper and urobilin.**—See this vol., 1221.

**Spirographis-haemin.** H. FISCHER and C. VON SEEMANN (Angew. Chem., 1936, 49, 461—462).—*Spirographis*-haemin (I) (A., 1932, 292) gives spectrum



displacements suggesting the presence of  $\cdot\text{CH}:\text{CH}_2$ . Interaction with  $\text{CHN}_2\cdot\text{CO}_2\text{Et}$  (II) causes, however, a displacement towards the red, but as Warburg's oxime (*loc. cit.*) can be converted into a nitrile, the presence of a CHO (responsible for this anomalous behaviour) is suggested, and is confirmed by conversion of the latter into  $\text{CO}_2\text{H}$ . When the product from (I) and (II) is treated with  $\text{NH}_2\text{OH}$ , a spectrum displaced towards the blue is observed. Catalytic hydrogenation of (I) gives 1 : 2 : 3 : 5 : 8-pentamethyl-4-ethylporphin-6 : 7-dipropionic acid (A., 1930, 1450),  $\cdot\text{CHO}$  and  $\cdot\text{CH}:\text{CH}_2$  being converted into Me and Et, respectively. The resorcinol-melt of (I) yields deuterohæmin-IX-ester (deuteroporphyrin-IX-ester)



(A., 1928, 1385). (I) is thus the Fe derivative of 2-aldehyde-1 : 3 : 5 : 8-tetramethyl-4-vinylporphin-6 : 7-dipropionic acid, and has the annexed structure. (Cf. also this vol., 1271.) E. W. W.

**Hæmatins of cytochrome-A.**—See this vol., 1287.

**Local anæsthetics containing the morpholine ring. III. Esters of 2-alkoxycinchonic acids.** J. H. GARDNER and W. M. HAMMEL (J. Amer. Chem. Soc., 1936, 58, 1360—1361; cf. A., 1933, 960).—2-Chloroquinoline-4-carboxylic acid and  $\text{AlkOH}\cdot\text{NaOAlk}$  give 2-methoxy-, 2-ethoxy-, m.p. 142–2–143.8° (lit. 145–146°), 2-n-propoxy-, m.p. 138–139.4° (lit. 136°), and 2-n-butoxy-, m.p. 96.6–97.6° (lit. 111°), -quinoline-4-carboxylic acids [*chlorides*, m.p. 45.6–46.5°, 86–86.5°, 54–55°, and 35.5–37.5°, respectively;  $\beta$ -4-morpholine-ethyl esters, m.p. —, 44–46°, — (*hydrochlorides*, m.p. 198–199°, 147°, 150.6–151.2°, and 150.5–151.4°, respectively);  $\gamma$ -4-morpholinepropyl esters, m.p. —, 57–58°, — (*hydrochlorides*, m.p. 155–160°, 157°, 174.7–175.6°, and 149.2–149.6°, respectively)]. All m.p. are corr. The ester hydrochlorides are local anæsthetics.

H. B.

**N-p-Aminophenylmorpholine and naphthylaminophenylmorpholine.**—See B., 1936, 876.

**Aliphatic polyamines. II.** J. VAN ALPHEN (Rec. trav. chim., 1936, 55, 669–674; cf. this vol., 999).—When crude 2-phenyl-1 : 3-di-( $\beta$ -benzylidene-aminoethyl)tetrahydroglyoxaline is reduced with Na-EtOH and the resulting crude oily  $(\text{CH}_2\text{Ph})_2$  derivative is heated with EtOH-HCl, there are formed PhCHO and NN'-di-( $\beta$ -benzylaminoethyl)ethylenediamine, (anhyd.) an oil and  $+\text{H}_2\text{O}$ , m.p. 58° [*tetrahydrochloride*, m.p. 250–290° (decomp.), -*picrate*, m.p. 209°, and -*oxalate*, m.p. 270–280° (decomp.)];  $(\text{NO})_4$ , m.p. 136°, Bz, m.p. 196°, *tetra-phenylcarbamide*, m.p. 194°, and -*phenylthiocarbamide* derivative, m.p. 197°. This base with  $\text{CS}_2$  gives s-di-(2-thio-3-benzyltetrahydroquinazolin-1-yl)ethane, m.p. 167°, with the appro-

priate aldehyde in EtOH yields s-di-(2-phenyl-, m.p. 181°, -2-p-anisyl-, m.p. 165°, -(2-3' : 4'-methylenedioxyphenyl-, m.p. 170°, and -(2-2'-furfuryl-3-benzyltetrahydroquinazolin-1-yl)ethane, m.p. 142°, and with the  $\text{NaHSO}_3$  compound of  $(\text{CHO})_2$  in hot  $\text{H}_2\text{O}$  gives a cherry-red colour. R. S. C.

**Reactions of methylene derivatives containing cyanide, thiocyanate, or sulphonyl radicals.** C. E. GROTHAUS and F. B. DAINS (J. Amer. Chem. Soc., 1936, 58, 1334–1336).—The reactivity of the  $\text{CH}_2$  in  $\text{C}_6\text{H}_4\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$  ( $\text{R}=\text{H}$ , *p*-Br) (and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ ) resembles that of  $\text{CH}_2\cdot\text{Bz}\cdot\text{CO}_2\text{Et}$  and is  $>$  that of  $\text{COPh}\cdot\text{CH}_2\cdot\text{CNS}$  and still  $>$  that of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COPh}$ . Phenacyl cyanide (*CHPh*, m.p. 85°, and *p*-dimethylaminoanilo-, m.p. 128°, derivatives) and  $\text{NHPh}\cdot\text{CH}\cdot\text{NPh}$  (I) in xylene at 120° give  $\alpha$ -anilino- $\beta$ -cyano- $\beta$ -benzoylthiophene, m.p. 159°; the  $\alpha$ -o-, m.p. 167°, and -*p*-, m.p. 185°, -*chloro*-,  $\alpha$ -*p*-bromo-, m.p. 205°,  $\alpha$ -o-ethoxy-, m.p. 138°,  $\alpha$ -*p*-phenoxy-, m.p. 135°, and  $\alpha$ -*p*-phenyl- (II), m.p. 161°, -anilino-derivatives are similarly obtained using the appropriate diarylformamidine. The above ethylenes [except (II)] with  $\text{NH}_2\text{OH}$ ,  $\text{N}_2\text{H}_4$ , and  $\text{NHPh}\cdot\text{NH}$ , in EtOH give 5-imino-4-benzoylisooxazole, m.p. 154°, 4-cyano-3-phenylpyrazole, m.p. 134°, and 4-cyano-1 : 5-diphenylpyrazole, m.p. 182° [hydrolysed (conc. EtOH-KOH) at 160–170° to the 4-carboxylic acid, m.p. 173°], respectively. 1 : 3-Diphenyl-4-*p*-bromoanilino-methylene-5-pyrazolone, m.p. 184°, is obtained by fusion of 1 : 3-diphenyl-5-pyrazolone with di-*p*-bromophenylformamidine. *p*-Bromophenacyl cyanide, m.p. 159° (from the chloride and NaCN in EtOH), and (I) at 150° afford  $\alpha$ -anilino- $\beta$ -cyano- $\beta$ -*p*-bromobenzoylthiophene, m.p. 143°; this and the  $\alpha$ -*p*-bromoanilino-derivative, m.p. 209°, with  $\text{NH}_2\text{OH}$ ,  $\text{N}_2\text{H}_4$ , and  $\text{NHPh}\cdot\text{NH}$  give 5-imino-4-*p*-bromobenzoylisooxazole, m.p. 195°, 4-cyano-3-*p*-bromophenylpyrazole, m.p. 195°, and 4-cyano-1-phenyl-5-*p*-bromophenylpyrazole, m.p. 212°, respectively. Phenacyl thiocyanate and (I) in xylene at 160° afford 2-imino-5-benzoyl-3-phenyl-2 : 3-dihydrothiazole, m.p. 257°, probably by rearrangement of the intermediate  $\alpha$ -anilino- $\beta$ -thiocyano- $\beta$ -benzoylthiophene; the 3-*p*-chloro-, m.p. 204°, and -*p*-bromo-, m.p. 214°, -phenyl derivatives are obtained similarly. Phenacyl *p*-tolyl sulphone (*CHPh* derivative, m.p. 142°; phenylhydrazone, m.p. 188°) and (I) in xylene at 180–190° give  $\alpha$ -anilino- $\beta$ -benzoyl- $\beta$ -*p*-toluenesulphonylthiophene (III), m.p. 208° [ $\alpha$ -o-, m.p. 187°, and -*p*-, m.p. 217°, -*chloro*- and  $\alpha$ -*p*-bromo- (IV), m.p. 210°, -anilino-derivatives]. (III) and (IV) with  $\text{NHPh}\cdot\text{NH}$  give 4-*p*-toluenesulphonyl-1 : 5-diphenylpyrazole, m.p. 164°; no reaction occurs with  $\text{NH}_2\text{OH}$  or  $\text{N}_2\text{H}_4$ .  $\alpha$ -Anilino- $\beta$ -cyano- (V), m.p.  $>260^\circ$ , and - $\beta$ -carbethoxy-, m.p. 114–115°, - $\beta$ -*p*-nitrophenylthiophenes are formed from (I) and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$  and  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , respectively. (V) does not react with  $\text{NH}_2\text{OH}$ .

H. B.

**Arylaminomethylbenzthiazyl sulphides.**—See B., 1936, 849.

**By-products of thiolbenzthiazole synthesis.** W. COCKER (J.S.C.I., 1936, 55, 228 $\pi$ ).—Benzthiazole is an impurity in technical thiolbenzthiazole (I) prepared from  $\text{NH}_2\text{Ph}$ ,  $\text{CS}_2$ , and S under certain con-

ditions. It is largely responsible for the usually unpleasant odour of (I). It forms well-defined crystals which hydrolyse in  $H_2O$ .

**Thiolbenzthiazole.** F. M. HAMER (Chem. and Ind., 1936, 682; cf. preceding abstract).—Benzthiazole has a not unpleasant odour resembling that of quinoline. H. W.

**5-Chloro- and 5-bromo-1-methylbenzthiazole and certain dyes prepared from them.** B. BEILSEN and (Miss) F. M. HAMER (J.C.S., 1936, 1225—1231).—**5-Bromo-1-methylbenzthiazole**, m.p. 86—87° (cf. Bogert and Naiman, A., 1935, 1386), obtained by oxidation of 4-bromothioacetanilide, gives an *ethobromide*, m.p. 197°, *etho-p-toluenesulphonate*, and *ethiodide* (I), m.p. 214° (decomp.). The following dyes have been prepared from (I), the *ethiodide*, m.p. 239° (decomp.), of 5-chloro-1-methylbenzthiazole, and other salts: **5:5'-dichloro-**, m.p. 288°, and **5:5'-dibromo-2:2'-diethylthiacyanine iodide**, m.p. 286°; **5-chloro-**, m.p. 287°, and **5-bromo-2:1'-diethyl-2'-cyanine iodide**, m.p. 278—279°; **5-chloro-**, m.p. 250°, and **5-bromo-2:2'-diethylthia-1'-cyanine iodide**, m.p. 253°; **5:5'-dichloro-iodide**, m.p. 292°, and **5:5'-dibromo-2:2'-diethylthiacarbocyanine bromide**, m.p. 283°; **5:5'-dichloro-iodide**, m.p. 303°, and **5:5'-dibromo-8-methyl-2:2'-diethylthiacarbocyanine bromide**, m.p. 280°; **5:5'-dichloro-**, m.p. about 258°, and **5:5'-dibromo-2:2':8-triethylthiacarbocyanine iodide**, m.p. 273°; **5:5'-dichloro-**, m.p. 270°, and **5:5'-dibromo-8-phenyl-2:2'-diethylthiacarbocyanine iodide**; **5:5'-dichloro-**, m.p. 278°, and **5:5':9-trichloro-2:2'-diethylthiacarbocyanine iodide**, m.p. 267°; **5:5'-dibromo-2:2'-diethylthiacarbocyanine p-toluenesulphonate**, m.p. 230°; **5:5':9-tribromo-2:2'-diethylthiacarbocyanine bromide**, m.p. 228°; **5:5'-dichloro-2:2'-diethylthiacarbocyanine iodide**, m.p. 227°; and **5:5'-dibromo-2:2'-diethylthiacarbocyanine p-toluenesulphonate**, m.p. about 184°. The absorption spectra of the compounds have been examined. M.p. of the dyes are also decomp. points.

F. R. S.

**Thiazoles obtained by direct thiocyanogenation.** R. Q. BREWSTER and F. B. DAINS (J. Amer. Chem. Soc., 1936, 58, 1364—1366).—Treatment of  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , **3:4:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·NH<sub>2</sub>**, *m*-4-xylylene, **2:4:1-C<sub>6</sub>H<sub>3</sub>BrMe·NH<sub>2</sub>**, **4:2:1-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·NH<sub>2</sub>**,  $p\text{-C}_6\text{H}_4\text{Me·NH·Et}$ ,  $p\text{-C}_6\text{H}_4\text{Me·NH·CH}_2\text{Ph}$ , and  $p\text{-C}_6\text{H}_4\text{Me·NHMe}$  with  $\text{NH}_4\text{CNS}$  and Br in AcOH at <10° gives **5-nitro-1-imino-**, m.p. 252°, **4-nitro-1-imino-5-methyl-**, m.p. 257°, **1-imino-3:5-dimethyl-**, m.p. 140°, **3-bromo-1-imino-5-methyl-**, m.p. 211°, **5-nitro-1-imino-3-methyl-**, m.p. 280°, **1-imino-5-methyl-2-ethyl-** (I), m.p. 106° (*hydriodide*), **1-imino-2-benzyl-5-methyl-** (II), m.p. 80°, and **1-imino-2:5-dimethyl-** (III), m.p. 51° (*hydriodide*), **1:2-dihydrobenzthiazoles**, respectively. (I), (II), and (III) are also obtained by alkylation ( $\text{EtI}$ ,  $\text{CH}_2\text{PhCl}$ ,  $\text{MeI}$  in EtOH) of **1-imino-5-methyl-1:2-dihydrobenzthiazole** (IV).  $\text{NH}_2\text{Ph}$  and (IV) at 220° give **1-anilo-5-methyl-1:2-dihydrobenzthiazole**, m.p. 167°; **5-bromo-1-anilo-**, m.p. 188°, **1-p-tolylimino-5-methoxy-**, m.p. 160°, and **1-p-methoxy-**, m.p. 160°, **1-p-nitro-** (V), m.p. 272°, **1-p-acetamido-** (VI), m.p. 220°, and **1-p-chloro-anilo-** (VII), m.p. 197°, **5-**

**methyl-1:2-dihydrobenzthiazoles** are similarly prepared. (V) is reduced ( $\text{Sn}$ ,  $\text{HCl}$ ) to **1-p-aminoanilino-5-methylbenzthiazole**, m.p. 147°, also obtained by hydrolysis (15%  $\text{HCl}$ ) of (VI). (IV) heated at 270°/30 min. gives **di-(5-methyl-1-benzthiazolyl)amine**, m.p. 278°. (VI) and (VII) are also prepared from  $p\text{-C}_6\text{H}_4\text{Me·NH·CS·NH·C}_6\text{H}_4\text{R}$ -*p* ( $\text{R} = \text{NHAc}$  and  $\text{Cl}$ , respectively) and Br in  $\text{CHCl}_3$ ; similarly,  $p\text{-C}_6\text{H}_4\text{Me·NH·CS·NH·Et}$  gives **1-ethylimino-5-methyl-1:2-dihydrobenzthiazole**, m.p. 133°;  $p\text{-C}_6\text{H}_4\text{Me·NH·CS·NEt}_2$  affords **1-diethylamino-5-methylbenzthiazole**, an oil (picrate, m.p. 174°; *platini-chloride*);  $p\text{-C}_6\text{H}_4\text{Me·NH·CS·NH·CH}_2\text{Ph}$  furnishes **1-benzylimino-5-methyl-1:2-dihydrobenzthiazole**, m.p. 159°;  $p\text{-C}_6\text{H}_4\text{Br·NH·CS·NHPh}$  and  $(p\text{-C}_6\text{H}_4\text{Br·NH})_2\text{CS}$  yield **1-p-bromoanilo-**, m.p. 210°, and **5-bromo-1-p-bromoanilo-**, m.p. 256°, **1:2-dihydrobenzthiazole**, respectively. H. B.

**Cause of the red precipitate of bismuth salts with bismuthiols.** J. V. DUBSKÝ and A. OKAC (Chem. Obzor, 1935, 10, 83—84, 107—108, 123—125; Chem. Zentr., 1935, ii, 3383—3384).—Such ppts.

$$\begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{S} \backslash \\ | \quad \text{S} < \quad \text{C} \cdot \text{S} \backslash \\ \text{N} = \text{C} \cdot \text{C} \cdot \text{C} \end{array} \text{Bi}$$
 are produced only when compounds of the type shown can be formed. H. N. R.

**Photochemical behaviour of thiodiazoline derivatives.** I. LIFSCHITZ and W. FROENTJES (Reo. trav. chim., 1936, 55, 753—760).—18 isomerides of **2:2:5-trisubstituted  $\Delta^4$ -1:3:4-thiodiazolines**,

$\text{CR} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NR} \end{array}$ , are possible,  $\text{R}'$  is asymmetric.

When solutions of **3:5-diphenyl-2- $\alpha\beta\gamma\delta\epsilon$ -pentahydroxyamyl- $\Delta^4$ -1:3:4-thiodiazolines** (from galactose or arabinose and  $\text{SH·CPh·N·NHPh}$ ) are kept in the dark,  $\alpha$  slowly decreases, but never reaches 0. The ultraviolet absorption does not change, so that only racemisation occurs, being probably complete except for the sugar residue. Illumination greatly accelerates change of  $\alpha$  in MeOH, which falls to a min. (sometimes with change of sign), rises to a max., and then falls again, the changes being the more rapid the more dil. is the solution; this reaction is complex, probably consisting of racemisation, followed by oxidation of the  $\text{CH}_2\text{·OH}$  to  $\text{CHO}$  (development of reducing power), and decomp. of the heterocyclic nucleus. R. S. C.

**Antineuritic vitamin.** V. R. GREWE (Z. physiol. Chem., 1936, 242, 89—96; cf. this vol., 253).—Acetamidine (I) boiled in EtOH for several hr. with *Et* ethylenemalonate gives the *Et* ester (II) [*hydrochloride*, m.p. 205° (decomp.)] of **4-hydroxy-2:6-dimethyldihydropyrimidine-5-carboxylic acid**, m.p. 294° (decomp.). (II) in  $\text{C}_6\text{H}_5\text{N} + \text{CHCl}_3$  gives with 2 Br in  $\text{CHCl}_3$  at 0° the *Et* ester (III), m.p. 164°, of **4-hydroxy-2:6-dimethylpyrimidine-5-carboxylic acid**, m.p. 220° (decomp.) (*Me* ester, m.p. 160—162°), and (III) boiled with excess of  $\text{POCl}_3$  gives an oil which, with  $\text{NH}_3$  in EtOH at 80—100°, yields ***Et* 4-amino-2:6-dimethylpyrimidine-5-carboxylate**, m.p. 129°. (I) with ethoxymethylenemalononitrile gives **4-amino-5-cyano-2-methylpyrimidine**, m.p. 249°, which, treated in AcOH with gaseous  $\text{HCl}$  and then shaken with  $\text{H}_2$  in presence of  $\text{Pd-C}$ , yields **4-amino-2-methyl-5-aminomethylpyrimidine** (IV), identical with the



base  $C_6H_{10}N_4$  obtained from the vitamin by oxidation with  $BaMn_2O_8$ . When 4-amino-2-methyl-5-bromomethylpyrimidine [from (IV) by substitution of  $CH_2Br$  for  $CH_2NH_2$ ] in  $H_2O$  is saturated with  $NaHSO_3$ , treated with excess of  $SO_2$ , and heated at  $100^\circ$  for 2 hr. Br is replaced by  $SO_3H$  giving Williams' compound  $C_6H_9O_3N_3S$ , m.p.  $>350^\circ$  (this vol., 1159). W. McC.

**Structure of aneurin and thiochrome.** F. BERGEL and A. R. TODD (Nature, 1936, 138, 76).—A preliminary note (cf. Williams, A., 1935, 504; this vol., 1159). L. S. T.

**Synthesis of vitamin- $B_1$ .** R. R. WILLIAMS and J. K. CLINE (J. Amer. Chem. Soc., 1936, 58, 1504—1505).—6-Hydroxy-2-methyl-5-ethoxymethylpyrimidine (from Et  $\alpha$ -aldehydo- $\beta$ -ethoxypropionate and  $NH_2CMeNH$ ) is converted through the 6-Cl- into the 6- $NH_2$ -derivative, which with  $HBr$  gives 6-amino-2-methyl-5-bromomethylpyrimidine. This and 4-methyl-5- $\beta$ -hydroxyethylthiazole afford the bromide and thence the chloride (I), m.p.  $232-234^\circ$ , of vitamin- $B_1$ . (I) is identical (absorption; activity) with the natural chloride (II), m.p.  $246^\circ$  (mixed m.p.  $242-244^\circ$ ). (II) is often a mixture of stereoisomerides. (See preceding abstract.) H. B.

**Dihydrionicotyrine, 1-methyl-2-3'-pyridylpyrroline.** II. A. G. OOSTERHUIS and J. B. WIBAUT (Rec. trav. chim., 1936, 55, 727—729; cf. A., 1933, 77).—Dihydrionicotyrine (I) (*loc. cit.*) is resolved by way of the  $\alpha$ -bromocamphor- $\alpha$ -sulphonate [that of the d-base (II), m.p.  $115^\circ$ ], giving (II) (*dipicrate*, m.p.  $163-164^\circ$ ,  $[\alpha]_D^{25} +16^\circ$  in EtOH). (I) is thus 1-methyl-2-3'-pyridyl- $\Delta^3$ - or  $\Delta^4$ -pyrroline. Neither the dihydrionicotyrine nor the idonicotyrine of Pictet *et al.* (A., 1898, i, 688) could be prepared. R. S. C.

**Alkaloids of jaborandi leaves.** X. Synthesis and isomerisation of *r*-pilocarpine. N. A. PREOBRASHENSKI, A. M. POLJAKOVA, and V. A. PREOBRASHENSKI (Ber., 1936, 69, [B], 1835—1837).—*r*-Pilocypyl  $CHN_2$  ketone, m.p.  $113-113.5^\circ$  (corresponding 1-compound, m.p.  $105-107^\circ$ ), is converted by  $Ag_2O$  in abs. EtOH into Et *r*-homopilocate, b.p.  $116-118^\circ/0.5$  mm. (corresponding d-ester, b.p.  $106-108^\circ/0.01$  mm.,  $[\alpha]_D^{25} +64.26^\circ$  in  $C_2H_5Cl_4$ ; l-ester, b.p.  $115-117^\circ/0.5$  mm.,  $[\alpha]_D^{25} -94.33^\circ$  to  $[\alpha]_D^{20} -64.17^\circ$  in  $C_2H_5Cl_4$ ). *r*-Homopilocate acid, m.p.  $106-107^\circ$ , is converted through the corresponding chloride into *r*-homopilocypyl  $CHN_2$  ketone, m.p.  $60-62^\circ$  (corresponding d-ketone, m.p.  $80-81^\circ$ ), transformed by dry HCl in  $Et_2O$  into *r*-homopilocypyl  $CH_2Cl$  ketone (I), m.p.  $64-64.5^\circ$  (corresponding l-ketone, m.p.  $82.5-83.5^\circ$ ,  $[\alpha]_D^{25} -102.06^\circ$  in  $C_2H_5Cl_4$ ). (I) and  $C_6H_4(CO)_2NK$  in EtOH give *r*-homopilocypyl phthalimidomethyl ketone, m.p.  $142.5-143^\circ$ , hydrolysed by boiling HCl (1:1) to *r*-homopilocypyl  $CH_2NH_2$  ketone (*hydrochloride*, m.p.  $163-164^\circ$ ), which with KCNS affords *r*-2-thiopilocarpidine, m.p.  $203-204^\circ$ , oxidised to the corresponding base, whence *r*-pilocarpine nitrate (II), m.p.  $139-140^\circ$ . Treatment of (II) with NaOEt in EtOH gives *r*-isopilocarpine. H. W.

**$\alpha$ -Nicotine, 1-methyl-2-2'-pyridylpyrrolidine.** II. Relation between pharmacological action and chemical constitution in the nicotine group.

A. G. OOSTERHUIS and J. B. WIBAUT (Rec. trav. chim., 1936, 55, 729—736; cf. A., 1933, 1312).—The prep. of *dl*- $\alpha$ -nicotine (I) is improved. Previous data are confirmed (cf. A., 1934, 787); a small amount of a by-product (*picrate*, m.p.  $148^\circ$ ) is obtained. The pharmacological properties of (I) (mostly reported elsewhere) are detailed. (I) is less toxic than nicotine (II). Consideration of the action of other  $C_5H_5N$  derivatives shows that the lowering effect of (I) on blood-pressure as compared with the raising due to (II) is caused by the  $\alpha$ -position of the pyrrolidine nucleus in (I) and its  $\beta$ -position in (II). R. S. C.

**Cotarnine series.** VI. Condensation of cotarnine with carbonyl chloride. B. B. DEY and (Miss) P. L. KANTAM. VII. Action of sulphuric acid on cotarnine: formation of methylenebisphenol-betaine of 6:7-dihydroxy-8-methoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide. B. B. DEY and T. K. SRINIVASAN (J. Indian Chem. Soc., 1936, 13, 281—283, 337—344).—VI. Cotarnine (I),  $COCl_2$ , and NaOH form cotarnomethylcarboxyl chloride, m.p.  $106^\circ$  (*anil*, m.p.  $132^\circ$ ), which could not be hydrolysed to the acid. It forms Et, m.p.  $100^\circ$  (*oxime*, m.p.  $129^\circ$ , and its *Ac* derivative, m.p.  $127^\circ$ ; *phenylhydrazone*, m.p.  $120^\circ$ ), and Me cotarnomethylcarboxylate, m.p.  $139^\circ$ . 5-Bromocotarnomethylcarboxyl chloride, m.p.  $142^\circ$  (*anil*, m.p.  $149^\circ$ ), similarly forms an Et ester, m.p.  $90^\circ$  (*oxime*, m.p.  $155^\circ$ ; *phenylhydrazone*, m.p.  $165^\circ$ ).

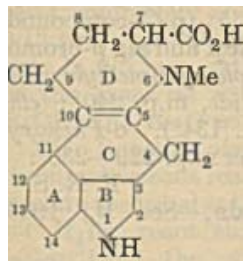
VII. (I) and 90%  $H_2SO_4$  at room temp. for 3 days give the methylenebisphenol-betaine of 6:7-dihydroxy-8-methoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide ( $+H_2O$ ) (II), m.p.  $308^\circ$  (decomp.) [*dihydrochloride*, m.p.  $200^\circ$  (decomp.); *mono*-, m.p.  $222^\circ$ , and *dinitrate*, m.p.  $93^\circ$ ; *platinichloride* ( $+H_2O$ ), m.p.  $198^\circ$  (decomp.); *dipicrate*, m.p.  $230^\circ$  (decomp.); *monomethiodide* ( $+H_2O$ ), m.p.  $220^\circ$  (decomp.); *monomethiodide*, m.p.  $222^\circ$ ]. The monomethiodide and NaOH form (II), but demethylation (HI) of (II) yields the methylenebisphenol-betaine of 6:7:8-trihydroxy-2-methyl-3:4-dihydroisoquinolinium hydroxide, m.p.  $275^\circ$  (decomp.) [*dihydrochloride*, m.p.  $220^\circ$  (decomp.); *dinitrate*, m.p.  $195^\circ$  (decomp.)]. Methylation ( $Me_2SO_4$ ) of (II) leads to the methylenebisphenol-betaine of 7-hydroxy-6:8-dimethoxy-2-methyl-3:4-dihydroisoquinolinium hydroxide, m.p.  $268^\circ$  (decomp.) [*dihydrochloride*, m.p.  $191^\circ$  (decomp.); *dinitrate*, m.p.  $235^\circ$  (decomp.); *platinichloride*, m.p.  $248^\circ$  (decomp.); *picrate*, m.p.  $114^\circ$ ; *dimethiodide* (III), m.p.  $180^\circ$  (decomp.)]. (III) is reduced ( $Zn-H_2SO_4$ ) to methylenebis-6:7:8-trimethoxy-2-methyl-1:2:3:4-tetrahydroisoquinoline, m.p.  $201^\circ$ . F. R. S.

**Alkaloids of ergot.** VI. Ergometrine. S. SMITH and G. M. TIMMS (J.C.S., 1936, 1166—1169; cf. A., 1935, 1256).—Ergometrine (I), decomp.  $195-197^\circ$ ,  $[\alpha]_{D^{461}}^{25} +520^\circ$  in  $CHCl_3$ , forms a *hydrochloride*, decomp.  $175-180^\circ$ , *hydrobromide*, *perchlorate*, decomp.  $225^\circ$ , *nitrate*, decomp.  $235^\circ$ ,  $[\alpha]_{D^{461}}^{25} +361^\circ$  in  $H_2O$ , and *H sulphate*, decomp.  $250^\circ$ ; it has little or no pharmacological or clinical action. Hydrolysis of (I) and of ergometrine (II) with HCl affords *d*- $NH_2CHMeCH_2OH$  and of (I) with KOH-MeOH yields lysergic acid. (I) and (II) are interconvertible by acids or alkalis and it is suggested that physiological

activity may be dependent largely on the configuration of the lysergic acid group, although other forms of isomerism susceptible to facile reversibility cannot be excluded from consideration. F. R. S.

**New alkaloid and an acid salt from ergot, and an acid derived from the salt.** G. W. HOLDEN and G. R. DRIVER (Quart. J. Pharm., 1936, 9, 230—234).—During the manufacture of ergotamine, a phenolic alkaloid, *ergomonamine*,  $C_{19}H_{19}O_4N$ , m.p. 132—132.5° (*picrate*, m.p. 163—164°), has been obtained. From ergot, an acid *K salt*,  $C_7H_9O_{11}NK$  (?), has been isolated, from which the Ag salt gives *citergic acid*,  $C_6H_8O_{10}$ , m.p. 157—158° ( $Ac_4$  derivative, m.p. 128—129°); the acid is probably  $\alpha\beta\gamma$ -tetrahydroxypropane- $\alpha\beta\gamma$ -tricarboxylic acid. F. R. S.

**Ergot alkaloids. XI. Isomeric dihydrolysergic acids. Structure of lysergic acid.** W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1936, 115, 227—238; cf. this vol., 742).—Ergotamine with  $H_2$ -PtO<sub>2</sub> in AcOH absorbs 1.8 H<sub>2</sub> to give an oily product, hydrolysed to  $\gamma$ -*dihydrolysergic acid* (I), decomp. 300—330°,  $[\alpha]_D^{25} + 32^\circ$  in  $C_6H_5N$ , the oily *Me* ester of which with Na-BuOH gives  $\gamma$ -*dihydrolysergol*, m.p. about 255° (decomp. from 234°),  $[\alpha]_D^{25} + 33^\circ$  in  $C_6H_5N$ . Ergotamine and ergine absorb 1.67 and 1.6 H<sub>2</sub>, respectively, to give oily products,  $[\alpha]_D^{25} + 382^\circ$  in  $CHCl_3$  and  $+332^\circ$  in MeOH, respectively, hydrolysed to (I). Ergotamine absorbs about 3 and ergotamine 1.6 H<sub>2</sub> (to give a product with  $[\alpha]_D^{25} - 140^\circ$  in  $CHCl_3$ ); hydrolysis of the products gives  $\alpha$ -*dihydrolysergic acid* (II) [obtained from lysergic acid (III) and not previously given the prefix], also obtained from ergometrine (IV). Hydrogenation of (III) gives a mixture of (I) and (II). The *Me* ester (V) of (II) with Na-BuOH gives  $\alpha$ -*dihydrolysergol*. *Me* lysergate mutarotates in hot MeOH (only oils were isolated), but (V) is stable; similarly dihydroergometrine does not mutarotate, whereas (IV) does. The ethylenic linking is thus involved in mutarotation. These and other facts are discussed on the basis of the annexed formula for (III). The positions of the CO<sub>2</sub>H and ethylenic linking



are uncertain but probable. Position 4 for the CO<sub>2</sub>H is improbable, because (III) sublimes largely unchanged. Mutarotation involves alternation of the ethylenic linking between positions 9—10, 10—5, and/or 4—5, or less probably permanent migration of this linking. R. S. C.

**Senecio alkaloids. III. Degradation of platynecine to heliotridane.** R. KONOVALOVA and A. OREKHOV (Ber., 1936, 69, [B], 1908—1913; cf. A., 1935, 764, 1387).—Platynecine (I) is converted by BzCl in  $C_6H_5N$  into *dibenzoylplatynecine* (*hydrochloride*, m.p. 228—230°), which could not be hydrogenated (PtO<sub>2</sub>). Monobenzoylplatynecine (II) is not dehydrated by P<sub>2</sub>O<sub>5</sub> in  $C_6H_6$  or boiling PhMe and is transformed by conc. H<sub>2</sub>SO<sub>4</sub> at room temp. into anhydroplatynecine (III). Gradual addition of SOCl<sub>2</sub> to (II) yields *monobenzoylplatynecine chloride* (IV),  $C_{15}H_{28}O_2NCl$ , m.p. 73—74° (*picrate*, m.p. 185—186°;

*picrolonate*, m.p. 198—199°; *hydrochloride*, m.p. 203—204°; *hydriodide*, m.p. 176—177°). (IV) retains Cl very firmly and is not affected by Zn dust and Mg powder with HCl, AcOH, or HI or by catalytic H (Pt or Pd). Alkaline reduction causes removal of Bz with production of (III). (IV) is indifferent to boiling quinoline. PCl<sub>3</sub>, POCl<sub>3</sub>, and PCl<sub>5</sub> dehydrate (I) exclusively whereas SOCl<sub>2</sub>, distilled over cottonseed oil, gives *platynecine dichloride* (V),  $C_8H_{13}NCl_2$ , m.p. 63—64° (*hydrochloride*, m.p. 186—187°; *picrate*, m.p. 205—206°), in very small yield. (V) is resistant to catalytic hydrogenation (Pt or Pd) but is converted by Na and EtOH to a mixture of saturated and unsaturated bases hydrogenated to heliotridane, b.p. 169—171°/750 mm.,  $[\alpha]_D - 52.91^\circ$  in EtOH.

H. W.

**Structure of aconitine.** W. FREUDENBERG (Ber., 1936, 69, [B], 1962—1965; cf. this vol., 618).—Aconitine (I) is converted by dry distillation with Ba(OH)<sub>2</sub> into NH<sub>2</sub>Et, identified as 2:4-dinitroethylaniline. Demethylation of (I) followed by treatment of the residue according to Willstätter and Utzinger gives EtI, which is not obtained similarly from oxonitine (II). (I) contains 3 active H, corresponding with 3 identified OH groups, whereas (II) contains 4. The additional H in (II) is therefore probably united to N and takes the place of Et in (I). The additional O in (II) indicates a vicinal CO and confers its lactam character on (II). Oxidation of (I) and (II) with CrO<sub>3</sub> gives 3 and 2 mols. of volatile acid, respectively (2 or 1 AcOH + 1 BzOH). Assuming (I) to have the mol. formula  $C_{34}H_{47}O_{11}N$ , its constitution may be resolved into  $C_{19}H_{19}(NEt)(OH)_3(OMe)_4(OAc)(OBz)$ . The fundamental base is therefore  $C_{19}H_{26}NH$ , and the fundamental hydrocarbon is  $C_{20}H_{30}$  contrasted with a paraffin  $C_{20}H_{42}$ . Determination of the no. of double linkings by catalytic micro-hydrogenations shows the presence of three in (I) and (II) but none in aconine (III). Therefore in (I) and (II) the Bz group is perhydrogenated and (III) does not contain a double linking. The H deficit in  $C_{20}H_{30}$  can therefore be explained only by assuming the presence of six perhydrogenated rings. H. W.

**Addition of organomagnesium halides to  $\psi$ -codeine types. II. Preparation of nuclear alkylated morphine derivatives.** L. SMALL, H. M. FITCH, and W. E. SMITH (J. Amer. Chem. Soc., 1936, 58, 1457—1463; cf. this vol., 490).—Dihydrothebaine (I) [prepared by reduction (H<sub>2</sub>, colloidal Pd, 3*N*-AcOH, little conc. HCl) of thebaine] added slowly (Soxhlet) to an excess of MgMeI gives the phenolic *methylidihydrothebainone* (II), m.p. 192—193°,  $[\alpha]_D^{25} - 20.5^\circ$  in EtOH [*hydrochloride*, m.p. (vac.) 283—285° (decomp.); *methiodide*, m.p. (vac.) 212—216°; *oxime*, m.p. (vac.) 244°; *Ac* derivative, m.p. 179—179.5°], and some of the phenolic *isomethylidihydrothebainone* (III), m.p. 168—168.5°,  $[\alpha]_D^{25} - 57^\circ$  in EtOH [*oxime*, m.p. (vac.) 191—192°; *Ac* derivative, m.p. 157—158°]. The production of (II) and (III) from (I) involves fission of the O ring, hydrolysis (probably during isolation) of the enol *Me* ether group at C<sub>6</sub>, and addition of Me (at ? C<sub>5</sub>, and C<sub>7</sub>). (II) and Br in AcOH followed by aq. NaOH give a little



*bromomethylidihydrothebainone*, m.p. (vac.) 207—208° (decomp.) [debrominated to (II)], and (mainly) *bromomethylidihydrocodeinone* (IV), m.p. 143.5—145°. Reduction ( $\text{H}_2$ , Pd, 2*N*-AcOH, KOAc) of (IV) gives *methylidihydrocodeinone*, m.p. 144—144.5°,  $[\alpha]_D^{20}$  -146.9° in EtOH [*methiodide*, m.p. (vac.) 246—248°; *enol acetate*, m.p. 191.5—194.5°], which condenses with  $\text{Et}_2\text{C}_2\text{O}_4$  in EtOH-NaOEt to a glyoxylic acid [*hydrochloride*], is reduced ( $\text{H}_2$ , PtO<sub>2</sub>, EtOH) to *methylidihydrocodeine* (V) (+ $\text{H}_2\text{O}$ ), m.p. 98—102°, m.p. (anhyd.) 85—88°,  $[\alpha]_D^{24}$  -84.8° in EtOH [*hydrochloride*, m.p. (vac.) 286—287°; *methiodide*, m.p. (vac.) 269—271°], and is demethylated (48% HBr) to *methylidihydromorphine*, m.p. (vac.) 243—245° (sinters at 235°),  $[\alpha]_D^{24}$  -140.7° in EtOH [*hydrochloride*, m.p. (vac.) 315—318° (decomp.)], which is reduced (Adams) to *methylidihydromorphine* (VI), m.p. 206—207°,  $[\alpha]_D^{24}$  -92.9° in EtOH [*hydrochloride*, m.p. (vac.) 316—317° (decomp.)]; *hydriodide*, m.p. (vac.) 289—291°. (VI), which could not be prepared by demethylation of (V), is methylated ( $\text{CH}_3\text{N}_2$ ) to (V). Bromoisomethylidihydrocodeinone [from (III) and Br in AcOH followed by aq. NaOH] is debrominated [as for (IV)] to *isomethylidihydrocodeinone*, m.p. 144—145°,  $[\alpha]_D^{24}$  -179.4° in EtOH (*enol acetate*, m.p. 123—124°), which appears to condense with  $\text{Et}_2\text{C}_2\text{O}_4$  (cryst. products not isolable). H. B.

**Strychnos alkaloids. LXXXIX. iso-Forms of dihydro-brucine and -strychnine and their benzylidene derivatives.** H. LEUCHS and A. DORNOW (Ber., 1936, 69, [B], 1838—1844).—Analyses of *isodihydrobrucine* I,  $[\alpha]_D^{20}$  -165° in abs. EtOH, after desiccation at 110° or 130°/15 mm., agree with  $\text{C}_{23}\text{H}_{28}\text{O}_4\text{N}_2$ ; it contains 1 active H (Zerevitinov) and its *Ac* derivative is passive towards MgMeI in PhOMe. The *hydrobromide*,  $[\alpha]_D^{20}$  -167°, and *methiodide*,  $[\alpha]_D^{15}$  -48.1° in 90% AcOH, are described. The base does not react with PhCHO in EtOH containing NaOEt. Oxidation of it by  $\text{Ba}(\text{MnO}_4)_2$  in  $\text{COMe}_2$  gives a substance,  $\text{C}_{23}\text{H}_{28}\text{O}_5\text{N}_2$ , decomp. 315°,  $[\alpha]_D^{15}$  +63.5° in  $\text{CHCl}_3$  (*hydrobromiae*, m.p. about 65°, or after desiccation, decomp. about 325°,  $[\alpha]_D^{20}$  +29° in  $\text{H}_2\text{O}$ ; *acetate*, m.p. 260—265° (decomp.),  $[\alpha]_D^{20}$  +40.8° in  $\text{CHCl}_3$ ), whereas  $\text{CrO}_3$  in 3.6*N*- $\text{H}_2\text{SO}_4$  transforms it into a compound, (?)  $\text{C}_{15}\text{H}_{20}\text{O}_5\text{N}_2$ . *isodihydrobrucine* II is transformed by PhCHO and NaOEt in EtOH into *isobenzylidenedihydrobrucine* (*methiodide*, m.p. 195° and 264°), where as *isodihydrobrucine* III (I) is isomerised to base I. (I) contains 1 active H (Zerevitinov) which is not present in its acetate. It affords a *hydrobromide*, decomp. >330° after darkening at 260°,  $[\alpha]_D^{20}$  +17.5°; it does not absorb H (Pt in 2*N*-AcOH), is stable towards  $\text{KMnO}_4$ , and is oxidised by  $\text{CrO}_3$  to a substance, (?)  $\text{C}_{16}\text{H}_{20}\text{O}_6\text{N}_2$ . *isodihydrostrychnine* (II) (*acetate*,  $[\alpha]_D^{20}$  +33.5° in 90% AcOH) contains 1 active H. It is transformed by PhCHO-EtOH-NaOEt into *isobenzylidenedihydrostrychnine*, m.p. 186°, and appears to be isomerised by NaOMe in MeOH at 100° to a substance,  $[\alpha]_D^{20}$  -110° in EtOH; oxidation with  $\text{KMnO}_4$  gives indefinite results. Treatment of the base with  $\text{Ba}(\text{MnO}_4)_2$  in warm  $\text{COMe}$ , possibly affords *isodihydrostrychnine* II, m.p. 248°,  $[\alpha]_D^{20}$  -48° to -60°. Hydrogenation of (II) gives a substance, m.p. 228°,  $[\alpha]_D^{20}$  -23.7° in 90%

AcOH, which contains 1 active H, gives a *methiodide*, m.p. about 310° (decomp.),  $[\alpha]_D^{20}$  -5° in 90% AcOH, and an *Ac* derivative (*perchlorate*, m.p. about 60°, decomp. 105°,  $[\alpha]_D^{20}$  -2.6° in AcOH); it does not condense with PhCHO. H. W.

**Emetine camphorsulphonate.** C. A. GRAU (Bull. Sci. pharmacol., 1935, 42, 452—456; Chem. Zentr., 1935, ii, 3676).—*Emetine d-camphorsulphonate* is therapeutically preferable to the hydrochloride.

H. N. R.

**South American curare.** F. W. FREISE (Pharm. Ztg., 1936, 81, 818—820; cf. this vol., 534).—Curare preps. (analytical data given) afford an alkaloid *macoubeine*,  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{N}_2 \cdot 4\text{H}_2\text{O}$ , decomp. 185°,  $[\alpha]_D^{20}$  -55.5° in EtOH, containing 1 OMe, the toxic dose of which in various animals is 0.05—0.10 mg. per kg., the time of appearance of the symptoms being independent of the dose.

F. O. H.

**Arsonic acids of diphenylene oxide and diphenyl ether.** W. C. DAVIES and C. W. OTHERN (J.C.S., 1936, 1236—1239).—Mercuration of diphenylene oxide yields 1-acetoxymercuridiphenylene oxide, which with  $\text{CaCl}_2$  gives the 1-HgCl-compound, converted by  $\text{AsCl}_3$  into *diphenylene oxide-1-arsinic acid monohydrate*, m.p. 186—188° (decomp.). 2-Amino-diphenylene oxide hydrochloride on diazotisation and addition of  $\text{As}_2\text{O}_3$  gives *diphenylene oxide-2-arsinic acid monohydrate*, m.p. 385° (*Ba* salt); the -3-*acid monohydrate*, m.p. 213—214° (*Ba* salt), is similarly prepared and may also be obtained from diphenylene oxide and  $\text{AsCl}_3$  in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$  with  $\text{AlCl}_3$ . *p*-Nitrodiphenyl oxide after reduction is converted into *p-phenoxyphenyl-arsinic acid*, m.p. 365°, which yields the -*dichloroarsine*, m.p. 66°; the arsine cannot be cyclised. The acid is brominated to *p-bromo-p-arsinodiphenyl ether*, m.p. 354—355° (*p-Cl*-compound, m.p. 375°, and its *Ba* salt).  $\text{AsMe}_2\text{I}$  and  $\text{Mg } p$ -bromodiphenyl ether give *p-phenoxyphenyldimethylarsine*, b.p. 189—190°/10 mm. (*methiodide*, m.p. 240°; *ethiodide*, m.p. 237°; *di-iodide*, m.p. 134°). *o*-Phenoxyphenyltrimethylarsonium iodide has m.p. 229—230°.

F. R. S.

**Organic arsenic compounds.**—See B., 1936, 908.

**Smooth conversion of compounds  $\text{HgRX}$  into compounds  $\text{HgR}_2$ .** H. GILMAN and M. M. BARNETT [and, in part, R. H. KIRBY] (Rec. trav. chim., 1936, 55, 563—566).—Compounds  $\text{HgRX}$  ( $\text{R}=\text{aryl}$ ) are converted rapidly and in excellent yield into  $\text{HgR}_2$  and Hg by  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2\text{OH}$ , or  $\text{NH}_2\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  (slowly) (or their salts with  $\text{Na}_2\text{CO}_3$ ) in hot EtOH. Good yields are also obtained with mixtures of  $\text{HgRX}$  and  $\text{HgR}_2$ . If R is alkyl, yields are less good; the yield is 90% with *N*-ethyl-2-acetoxymercuricarbazole. With  $\text{N}_2\text{H}_4$   $\text{PbPh}_2\text{Cl}$  gives slowly 74% of  $\text{PbPh}_4$ , also obtained from  $\text{PbPh}_2\text{Cl}_2$  in 53.5% yield with much of an amorphous substance.  $\text{SnPh}_3\text{Cl}$  and  $\text{SnPh}_3\text{I}$  with  $\text{N}_2\text{H}_4$  give a little  $\text{SnPh}_4$  and much  $\text{SnPh}_3\cdot\text{OH}$ .  $\text{SnPh}_2\text{I}_2$  gives a little  $\text{SnPh}_3\cdot\text{OH}$  and (?)  $\text{SnPh}_2\text{O}_2$ . The mechanism of the reaction is uncertain.

R. S. C.

**Phenyl mercurinitrates.**—See B., 1936, 825.

**Relative reactivities of organo-metallic compounds.** X. LITHIUM and magnesium [compounds]. H. GILMAN and M. LICHTENWALTER [and, in part, R. H. KIRBY]. XI. Grignard reagents. H. GILMAN, (MISS) E. L. ST. JOHN, (MISS) N. B. ST. JOHN, and M. LICHTENWALTER [and, in part, L. L. HECK]. XII. Competitive reactions of some compounds, RHal, with magnesium. (MISS) E. L. ST. JOHN and N. B. ST. JOHN (Rec. trav. chim., 1936, 55, 561—563, 577—585, 585—588; cf. this vol., 1004).—X.  $\text{MgPhBr}$  reacts slowly with  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$  (3-8 hr.) and  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$  (5-15 hr.) to give >90 and 60% of  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$  and  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , respectively (cf. A., 1926, 914; 1904, i, 925). The only remaining qual. difference between Mg and Li compounds is thus reaction of the latter with olefines, and even the former may react slowly. Comparisons of Mg and Li compounds are carried out better using  $\text{Mg}\cdot\text{R}$  than  $\text{MgRHal}$ .  $\text{PhCN}$  reacts (to disappearance of the colour test) in 0.07 hr. with  $\text{LiMe}$  and 2.8 hr. with  $\text{MgMe}_2$ .

XI. The times of reaction (to disappearance of the colour test) of 41 Mg organohalides with  $\text{PhCN}$  are determined. There is a sharp differentiation of alkyl from the more reactive aryl groups and general (but not complete) parallelism with the ease of reaction of the Pb and Hg compounds, but none with other Grignard reactions. 2:4:6- $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{MgBr}$  and  $\text{PhCN}$  give a ? ketimine, m.p. 260—261° (containing Br and N), hydrolysed to  $\text{C}_6\text{H}_4\text{Me}_3\cdot\text{COPh}$ . I accelerates many of the reactions and catalytic effects are also observed in some cases with  $\text{PbEt}_4$ ,  $\text{PhCl}$ ,  $\text{CuCl}$ ,  $\text{PhBr}$ , and xylene, but not  $\text{PhMe}$ . Mixed Grignard reagents behave as the sum of the individuals.  $\text{Et}_2$  fumarate and maleate react very fast with  $\text{MgBu}^+\text{Br}$  and  $\text{MgPhBr}$ .  $\text{EtOBz}$  and  $\text{COPh}$  react completely with 1 mol. of  $\text{MgPhBr}$  in 0.1 and 0.13 hr., respectively, but  $\text{EtOBz}$  reacts with 2 mols. only in 0.5 hr., and similar phenomena are observed in the stepwise and complete reaction of  $\text{PhOBz}$ ,  $\text{BzOH}$ , and  $\text{Bz}_2\text{O}$  with  $\text{MgPhBr}$ .

XII. Reaction of an alkyl halide with Mg accelerates the simultaneous reaction of an aryl halide, which may explain the usual catalytic effect of the former.  $m$ - and  $p$ - $\text{C}_6\text{H}_4\text{Br}_2$  react slightly,  $m$ - and  $p$ - $\text{C}_6\text{H}_4\text{Cl}_2$  much, faster than the corresponding  $o$ -compound under comparable conditions. R. S. C.

**Organoselenium compounds.** VI. S. KEMATSU, K. YOKOTA, and I. SATODA (J. Pharm. Soc. Japan, 1933, 53, 994—1046).— $\text{PhSeNa}$  and  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  give  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SePh}$  in 25% yield. Treatment of the appropriate Grignard compound with Se affords *selenopyrocatechol O-Me ether* (I), b.p. 79—80°, *selenoresorcinol O-Me ether*, b.p. 81°, and *selenoquinol O-Me ether* (II), b.p. 78°, oxidised ( $\text{FeCl}_3$ ) to *bis-o*-, m.p. 90°,  $m$ -, m.p. 194°, and  $p$ -, m.p. 53.5°, *-methoxyphenyl diselenide*, respectively. Treatment of (I) with alkyl halides yields the following *O-Me selenoalkyl ethers* (III): *Me*, m.p. 30°; *Et*, b.p. 91—92°; *Pr*<sup>a</sup>, b.p. 102—103°; *Pr*<sup>β</sup>, b.p. 91—92°; *Bu*<sup>a</sup>, b.p. 106°; *Bu*<sup>β</sup>, m.p. 28.5°; *isoamyl*, b.p. 111°; *hexyl*, b.p. 131.5°. Corresponding (II) derivatives: *Me*, b.p. 93°; *Et*, b.p. 94.5°; *Pr*<sup>a</sup>, b.p. 99°; *Pr*<sup>β</sup>, b.p. 97.5°; *Bu*<sup>a</sup>, b.p. 116°; *Bu*<sup>β</sup>, b.p. 102.5°;

*isoamyl*, b.p. 107°; *hexyl*, b.p. 128°. (III) with  $\text{RMgI}$  yields the following *monoselenopyrocatechol selenoalkyl ethers*: *Me*, b.p. 53°; *Et*, b.p. 68.5°; *Pr*<sup>a</sup>, b.p. 81°; *Pr*<sup>β</sup>, b.p. 75°; *Bu*<sup>a</sup>, b.p. 93°; *Bu*<sup>β</sup>, b.p. 76°; *isoamyl*, b.p. 85°; *hexyl*, b.p. 103—104°. Corresponding *quinol derivatives*: *Me*, b.p. 108°; *Et*, b.p. 113°; *Pr*<sup>a</sup>, b.p. 116°; *Pr*<sup>β</sup>, b.p. 117°; *Bu*<sup>a</sup>, b.p. 123°; *Bu*<sup>β</sup>, b.p. 127°; *hexyl*, m.p. 35°. Methoxydiazonium chlorides couple with Na methoxyselenophenoxides to yield bis(methoxyphenyl) diselenides, which are demethylated by means of  $\text{RMgI}$ ; in this way the following *Ph<sub>2</sub> selenides* are prepared: *bis-m-hydroxy*-, m.p. 91°; *bis-m-methoxy*-, b.p. 169°/1 mm.; *bis-2-hydroxy*-, m.p. 126°; *bis-2-methoxy*-, m.p. 81°; *bis-2-ethoxy*-, b.p. 163°/1 mm.; *bis-2-benzoyloxy*-, m.p. 74°; *bis-2-acetoxy*-, m.p. 92°; 2:4'-*dihydroxy*-, m.p. 76°; 2:4'-*dimethoxy*-, b.p. 171°/1 mm.; 2:4'-*diethoxy*-, m.p. 106°; 2:4'-*diacetoxy*-, m.p. 56°; 2:4'-*dibenzoyloxy*-, m.p. 102°; 2:3'-*dihydroxy*-, m.p. 88.5°; 2:3'-*dimethoxy*-, m.p. 75°; 3:4'-*dihydroxy*-, m.p. 110°; 3:4'-*dimethoxy*-, b.p. 153°/1 mm. When heated  $o\text{-(OMe}\cdot\text{C}_6\text{H}_4\cdot\text{Se})_2\text{Pb}$  affords  $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SeMe}$  and a substance, m.p. 186°. Dimethoxydiazonium chlorides condense with  $\text{PhSeNa}$ , and treatment of the products with  $\text{RMgI}$  yields: 2-*phenylselenoresorcinol Me<sub>2</sub> ether*, m.p. 78.5—79°, *Me<sub>1</sub> ether*, b.p. 147—148°/0.5 mm., *monoacetate*, m.p. 60°, *diacetate*, m.p. 63°; *phenylselenoquinol Me<sub>2</sub> ether*, m.p. 43°, *Me<sub>1</sub> ether*, b.p. 165°/1 mm., *dibenzoate*, m.p. 147°; *phenylselenopyrocatechol*, b.p. 176°/1 mm., *Me<sub>2</sub> ether*, m.p. 63°, *Me<sub>1</sub> ether*, b.p. 166—167°/1 mm. The method is also adapted to the prep. of salicylic acid derivatives: the following are described: 5-*phenylselenosalicylic acid* (IV), m.p. 167.5°; *Me 5-benzylideneamino-salicylate*, m.p. 61° (*Ac derivative*, m.p. 106°); *Me 5-aminoacetylsalicylate* (V), m.p. 102°; *Me 5-phenylselenoacetylsalicylate*, m.p. 70°. Diazotised (V) with  $\text{KSeCN}$  affords *Me 5-(selenocyano)acetylsalicylate*, m.p. 69°, which is hydrogenated to *Me o-acetylselenoquinolcarboxylate*, b.p. 137—138°/2.5 mm. This is oxidised to *Me bis-p-acetoxyphenyl diselenide bis-m-carboxylate*, m.p. 90°, hydrolysed to *bis-(m-carboxy-p-hydroxyphenyl) diselenide*, m.p. 231.5°. Treatment of the *Me ester* of (IV) and its isomerides with  $\text{Pb(OAc)}_2$ , followed by  $\text{MeI}$  and by hydrolysis, affords *o*-, m.p. 180—181° (*Me ester*, m.p. 65°),  $m$ -, m.p. 122° (*Me ester*, b.p. 105—106°/3.5 mm.), and  $p$ -, m.p. 174° (*Me ester*, m.p. 83°), *-methylselenobenzoic acid*. *o*-, m.p. 94°,  $m$ -, m.p. 39°, and  $p$ -, m.p. 98°, *-Methoxyphenyl-α-naphthyl selenide* are obtained by condensation of the appropriate anisidine diazonium salt with  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{SeNa}$ . With  $\text{MeMgI}$  these yield *o*-, m.p. 95°,  $m$ -, m.p. 71°, and  $p$ -, m.p. 98°, *-hydroxyphenyl α-naphthyl selenide*. 4:1- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$  and  $\text{PhCHO}$ , followed by  $\text{Ac}_2\text{O}$ , yield 4-*benzylideneamino-α-naphthyl acetate*, m.p. 90°; with  $\text{HCl}$  this affords 4-*amino-α-naphthyl acetate hydrochloride*, m.p. 216°. This is diazotised and coupled with  $\text{PhSeNa}$ : hydrolysis affords 4-*phenylseleno-α-naphthol*, m.p. 75° (*acetate*, m.p. 78.5°; *Et ether*, m.p. 107°). Methoxynaphthylidiazonium chlorides and  $\text{PhSeNa}$ , followed by  $\text{RMgI}$ , afford 2-*phenylseleno-α-naphthol*, m.p. 65° (*Me ether*, m.p. 63°), and 1-*phenylseleno-β-naphthol*, m.p. 79° (*Et ether*, m.p. 63°). *Ph 3-pyridyl selenide*, b.p. 128°/1.5 mm., is obtained similarly. CH. ABS. (r)



Optical activity of derivatives of quadrivalent tellurium containing two identical negative radicals. I. T. M. LOWRY and F. HUTHER. II. (Miss) M. G. TER HORST (Rec. trav. chim., 1936, 55, 688—696, 697—711).—I.  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{TePhBr}_2$  and Ag  $\alpha$ -bromocamphor- $\pi$ -sulphonate (2 mols.) in  $\text{COMe}_2$  give the disulphonate (I), which with  $\text{H}_2\text{O}$  affords phenyl- $p$ -tolyltelluronium hydroxy- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m.p. between  $105^\circ$  and  $150^\circ$ , which exhibits downward mutarotation. In MeOH a similar salt is obtained, m.p. between  $150^\circ$  and  $180^\circ$ , exhibiting upward mutarotation. Crystallisation to const. m.p. ( $180^\circ$ ) gives the *dl*-compound, exhibiting no mutarotation. Each salt with NaOH gives phenyl- $p$ -tolyltelluronium dihydroxide, mutarotating rapidly in the same direction as the parent salt; both active forms and the *dl*-form melt at  $148^\circ$  and there are no depressions on admixture.  $\text{Te}^{\text{IV}}$  compounds with two identical negative groups thus have optical activity.

II. (I), the dibromide and di-iodide [prep. from (I) by KBr or KI], and diphenyltelluronium di- $\alpha$ -bromocamphor- $\pi$ -sulphonate and dibromide show very rapid mutarotation.  $\alpha$  observed are very small, but the changes are considered definite. Jaeger's theory that the tetrahedron of  $\text{Te}^{\text{IV}}$  is irregular is thus supported.

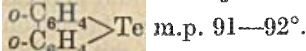
R. S. C.

Organo-metallic compounds. I. Aromatic tellurium compounds. L. REICHEL and E. KIRSCHBAUM (Annalen, 1936, 523, 211—223).—Various types of  $\text{Te}^{\text{IV}}$  compounds are prepared.

$[\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{TeMeEt}]^+$  and  $\text{C}_6\text{H}_5\text{Mo}\cdot\text{TePhO}$  give rise to optical activity, but only in combination with optically active anions etc. Dry  $\text{TeCl}_4$  (prep. in 60—75% yield described) and  $\text{PhOEt}$  or  $\text{PhOMe}$  in dry  $\text{CCl}_4$  give *p*-phenetyl- (cf. A., 1926, 83), m.p.  $184^\circ$ , and *p*-anisyl-tellurium trichloride, m.p.  $182^\circ$ , converted by  $\text{H}_2\text{O}$  into *p*-phenetyl- and *p*-anisyl-tellurium oxychloride, both decomp.  $400\text{—}500^\circ$ , which with  $\text{Ag}_2\text{O}$  regenerate the ethers, but with hot 70—80% NaOH give *p*-phenetyl- and *p*-anisyl-tellurous acid,  $\text{RTeO}_2\text{H}$ , both m.p. indef., and with  $\text{K}_2\text{S}_2\text{O}_5$  give *di*-*p*-phenetyl, m.p.  $109^\circ$ , and -anisyl ditelluride (I),  $\text{R}_2\text{Te}_2$ , m.p.  $60^\circ$ .  $\text{TeCl}_4$  and  $\text{PhOH}$  decompose at  $150\text{—}180^\circ$ , but at about  $90^\circ$  or in hot  $\text{CCl}_4$  give *p*-hydroxyphenyltellurium trichloride, m.p.  $233^\circ$  (cf. Rust. A., 1898, i, 137), converted by  $\text{H}_2\text{O}$  into the oxychloride, m.p. indef. (decomp.), by 2*N*-NaOH into *p*-hydroxyphenyltellurous acid (II), m.p. indef. (decomp.), and by  $\text{K}_2\text{S}_2\text{O}_5$  into *di*-*p*-hydroxyphenyl ditelluride (III), m.p.  $93^\circ$ . With  $\text{HNO}_3$  (1 mol.)  $\text{—H}_2\text{SO}_4$  (II) gives the 2- $\text{NO}_2$ -acid, m.p.  $221^\circ$  (decomp.), with 2 mols. the 2:6-dinitro-acid, reducible to the  $\text{NO}_2$ -, m.p.  $150^\circ$  (decomp.), and  $(\text{NO}_2)_2$ -derivative (IV), m.p.  $153^\circ$  (decomp.), respectively, of (III). (II) and  $\text{HNO}_3$  (3 mol.)  $\text{—H}_2\text{SO}_4$  give the mixed anhydride,  $(\text{NO}_2)_2\text{C}_6\text{H}_4(\text{OH})\cdot\text{TeO}\cdot\text{O}\cdot\text{NO}_2$ , giving (IV) with hot 20%  $\text{H}_2\text{SO}_4$ , but not reduced to a ditelluride.  $\text{NHPhAc}$  and  $\text{TeCl}_4$  alone at  $115^\circ$  or in hot  $\text{CCl}_4$  give a product, reduced to *di*-*p*-acetanilide ditelluride, decomp.  $172^\circ$ . The  $\text{NO}_2$ -compounds cannot be reduced to  $\text{NH}_2$ -derivatives and no products are obtained from  $\text{TeCl}_4$  and  $\text{NH}_2$ -compounds. (I) and hot MeI give *p*-anisylmethyltellurium di-iodide (V) and *p*-anisyl dimethyltellurium iodide [also obtained

from (V), MeI, and  $\text{K}_2\text{S}_2\text{O}_5$ ]. (V) and alkaline  $\text{K}_2\text{S}_2\text{O}_5$  give anisyl Me telluride, b.p.  $150\text{—}152^\circ/20\text{ mm.}$ , which with EtI gives *p*-anisylmethylthyltelluronium iodide, m.p.  $168^\circ$  [also obtained from (V), EtI, and  $\text{K}_2\text{S}_2\text{O}_5$ ]; the *d*-bromocamphor- $\pi$ -sulphonate, m.p.  $149^\circ$ , of the corresponding *l*-cation is obtained with  $[\text{M}]_D +198.58^\circ$  in  $\text{CHCl}_3$ , whence  $[\text{M}]_D$  for the cation is  $-71.42^\circ$ . The *d*-camphor- $\beta$ -sulphonate, m.p.  $93^\circ$ , of *d*-Ph *p*-tolyl telluroxide is obtained with  $[\text{M}]_D +450.5^\circ$  in  $\text{COMe}_2$ . Both salts give *dl*-compounds when the active acid is removed. R. S. C.

Diphenylene telluride. C. COURTOT and M. G. BASTANI (Compt. rend., 1936, 203, 197—199; cf. A., 1934, 1119).— $\text{TePh}_2\text{O}$  is not cyclised with  $\text{NaNH}_2$ , nor does diphenylene sulphone react with Te. The diazonium chloride of  $o\text{-C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$  with  $\text{HgCl}_2$  affords diphenyl *o*-mercuric chloride, m.p.  $165\text{—}167^\circ$ , which resists cyclisation.  $\text{Ph}_2$  with  $\text{TeCl}_4$  at  $140\text{—}165^\circ$  affords diphenylene telluride dichloride (I) (decomp. about  $200^\circ$ ) (a little dibromide, decomp.  $210\text{—}220^\circ$ , is formed with  $\text{TeBr}_4$ ), hydrolysed to diphenylenetellurine, decomp.  $230\text{—}240^\circ$ , which with hot H halides gives dihalogenated compounds. (I) with  $\text{KHSO}_3$  affords diphenylene telluride,



J. L. D.

Rotatory power of gelatin fractions.—See this vol., 1202.

Ultimate analysis of organic substances from combustion in a bomb calorimeter. P. J. MERKUS and A. H. WHITE (Proc. Amer. Gas Assoc., 1934, 991—1001).—Combustion is carried out in a bomb containing  $\text{O}_2$ . The analysis is based on pressure measurements.

CH. ABS. (e)

Micro-determination of carbon dioxide and hydrogen in elementary analysis.—See this vol., 1220.

Semi-micro-combustion method for determining nitrogen in organic compounds. C. F. H. ALLEN and D. M. YOUNG (Canad. J. Res., 1936, 14, B, 216—221).—A modified Dumas method requiring 20—30 mg. of org. compound is described. Pure  $\text{CO}_2$ , obtained by heating  $\text{NaHCO}_3$  and stored over Hg, is passed at a controlled speed through the combustion tube. The % of N is determined to within  $\pm 0.2$ .

J. G. A. G.

Iodometric micro-determination of nitrogen. S. MORGULIS and A. F. FRIEDMAN (Bull. Soc. Chim. biol., 1936, 18, 1074—1080).—The described method is suitable for the micro-determination of N in  $\text{NH}_4$  salts and  $\text{CO}(\text{NH}_2)_2$ , but not for Kjeldahl digests.

A. L.

Volumetric adsorption methods.—See this vol., 1225.

Analysis of organic substances by means of the Raman effect. W. HANLE and F. HEIDENREICH (Physikal. Z., 1936, 37, 594—595).—The conditions under which the Raman spectrum of a mixture of org. substances may be used to discover the constituents of the mixture are discussed. A mixture of  $\text{C}_6\text{H}_6$  and dioxan was particularly considered, the ratio of the intensities of two neighbouring

lines in the Raman spectrum, one due to  $C_6H_6$ , the other to dioxan, being determined for mixtures of different compositions. A. J. M.

**Basic titration of acetic acid.**—See this vol., 1203.

**Step-wise separation and useful effect. Construction of separation diagrams.** J. P. TREUB (Chem. Weekblad, 1936, 33, 496—500).—A mathematical discussion and practical illustration of the separation of solid and liquid fatty acids by step-wise freezing and pressing at progressively increased temp. The separation is illustrated by f.-p. curves. S. C.

**Relation between emulsion technique and analytical and organic chemistry.** A. STEIGMANN (Phot. Ind., 1936, 34, 963—966).—The possible use of the effects of a given substance on photographic emulsions, as an aid in analysis, is reviewed. Many substances, e.g., of the cystine group, show well-defined results, but the reactions are not generally sp. The prep. of a new desensitising compound, "cyclocystine," is described. J. L.

**Colour reaction for aromatic amines.** T. YAMANAKA (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 43).—Pure  $NH_2Ph$  gives a dark green colour and  $NH_2Ph$  containing  $>1\%$   $C_6H_4Me \cdot NH_2$  a dark or reddish-brown colour, when warmed with dil.  $H_2SO_4$  and a few drops of  $NH_4VO_3$  and  $KClO_3$  solutions. The presence of 0.01—1% of  $C_6H_4Me \cdot NH_2$  in  $NH_2Ph$  is detected by removing the  $NH_2Ph$  by Lewy's method, warming the  $HCl$  solution with a few drops of  $NH_4VO_3$  and *p*-tolylenediamine solutions and finally with a few drops of aq.  $KClO_3$ , when a bluish-violet or violet colour develops; in the absence of  $C_6H_4Me \cdot NH_2$  the colour is scarlet or purple-red. Methods are also given for the detection of  $PhNO_2$  in  $NH_2Ph$ . W. O. K.

**Volumetric determination of the xylidine isomerides with bromide-bromate solution.** B. P. FEDOROV and A. A. SPRISKOV (Z. anal. Chem., 1936, 105, 412—418).—Titration of commercial xylidine (I) with  $KBr-KBrO_3$  solution (II) results in the formation of  $Br_1$ -derivatives of the *m*- and  $Br_2$ -derivatives of the *o*- and *p*-isomerides. The (I) is dissolved in 95%  $EtOH$ , previously treated with  $HCl$  gas until 8 g. per 100 c.c. has been absorbed, (II) is added until a permanent brown colour persists, and, after addition of  $KI$ , the excess of (II) is determined by titration with  $Na_2S_2O_3$ . A. R. P.

**Determination of phenols.** R. W. STOUGHTON (J. Biol. Chem., 1936, 115, 292—298).—5 drops of  $H_2SO_4$  and 2 drops of  $HNO_3$  are added to 6 c.c. of an  $AcOH$  solution of the phenol; the mixture is warmed until the colour is fully developed (2—10 min.), diluted with 5—10 c.c. of  $H_2O$ , treated with 15 c.c. of conc. aq.  $NH_3$ , and made up to 50 c.c. The yellow colour is matched against that given by a standard (1:6000) solution of the same phenol. Phenols in biological material are first isolated by distillation of the acid ( $H_3PO_4$ ) solution in steam and extraction of the distillate thrice with  $Et_2O$ . Phenols containing also a CO do not respond to the test. The colour depends on formation of a NO-compound;  $HNO_2$

leads to a similar colour in a few sec., but side-reactions alter the shade. R. S. C.

**Specificity of the phenol reagent of Folin and Ciocalteu for determination of tryptophan.** E. SCHILD and C. ENDERS (Biochem. Z., 1936, 286, 220—224).—The reaction with this reagent is due to the reducing power of the tested substance and is not sp. A table gives a series of substances found in physiological fluids and natural products which give positive reactions. The reaction gives untrustworthy results with protein hydrolysates, wort, and beers. P. W. C.

**Determination of phenol and cresols in presence of each other.** V. MIKLASCHESKAYA (Chim. Tverd. Topl., 1934, 5, 553—558).—On heating to 80° with  $KMnO_4$  and dil.  $H_2SO_4$   $PhOH$  is oxidised to  $CO_2$  and  $H_2O$ , whilst cresol forms  $CO_2$ ,  $H_2O$ , and  $AcOH$ . The  $KMnO_4$  reduced and the  $AcOH$  formed are determined volumetrically. CH. ABS. (e)

***m*-Chlorobenzhydrazide as a reagent for the identification of aldehydes and ketones.** P. P. T. SAH and C. S. WU (Sci. Rept. Nat. Tsing Hua Univ., 1936, 3, 443—449).—*m*-Chlorobenzhydrazide, m.p. 157—158°, obtained from *m*- $C_6H_4Cl \cdot CO_2Et$  and  $N_2H_4 \cdot H_2O$ , may be used to prepare the *m*-chlorobenzoylhydrazones of the following:  $MeCHO$ , m.p. 154—155°,  $EtCHO$ , m.p. 124—125°,  $Pr^iCHO$ , m.p. 156—157°,  $Pr^sCHO$ , m.p. 160—161°, *n*-valeraldehyde, m.p. 152—153°,  $PhCHO$ , m.p. 118°, *m*- $NO_2 \cdot C_6H_4 \cdot CHO$ , m.p. 209—210°, *o*-, m.p. 207—208°, and *p*- $OH \cdot C_6H_4 \cdot CHO$ , m.p. 247—248°,  $CHPh \cdot CH \cdot CHO$ , m.p. 208—209°, furfuraldehyde, m.p. 184—185°,  $COMe_2$ , m.p. 97°, cyclopentanone, m.p. 172—173°, cyclohexanone, m.p. 138—139°,  $COPhMe$ , m.p. 150—151°, *p*- $C_6H_4Cl \cdot COMe$ , m.p. 159—160°, *p*- $C_6H_4Br \cdot COMe$ , m.p. 206—207°, *p*- $C_6H_4Me \cdot COMe$ , m.p. 211—213°,  $COPh_2$ , m.p. 146—148°, styryl Me ketone, m.p. 171—172°, pinacolin, m.p. 144—145°, and lævulic acid, m.p. 155—156°. F. R. S.

**Hydrazines.** V. *m*-Tolylhydrazine as a reagent for the identification of aldehydes and ketones. VI. Identification of sugars by means of the three isomeric tolylhydrazines. P. P. T. SAH and C. Z. TSEU (Sci. Rept. Nat. Tsing Hua Univ., 1936, 3, 403—407, 409—416).—V. The *m*-tolylhydrazones of the following have been prepared:  $PhCHO$ , m.p. 97—98°, *o*-, m.p. 140—141°, and *p*- $OH \cdot C_6H_4 \cdot CHO$ , m.p. 151—152°, *m*-, m.p. 123—124°, and *p*- $NO_2 \cdot C_6H_4 \cdot CHO$ , m.p. 106—107°, styryl Me ketone, m.p. 97—98°. *Et* lævulate, m.p. 102°, lævulic acid, m.p. 133°,  $CHPh \cdot CH \cdot CHO$ , m.p. 131—132°,  $COPh_2$ , m.p. 49—50°, and *o*- $C_6H_4Br \cdot COMe$ , m.p. 90—91°.

VI. The following hydrazones and osazones are insol.: *d*-galactose-*o*-, m.p. 176—177°, *p*-, m.p. 156°, and *m*-, m.p. 153—154°, *d*-mannose-*p*-, m.p. 190°, and *l*-arabinose-*p*-, m.p. 159—160°, and *m*-tolylhydrazones, m.p. 157°; *d*-glucose-*p*-, m.p. 195—196°, *m*-, m.p. 177—178°, and *o*-, m.p. 204—205°, *d*-mannose-*p*-, m.p. 196°, *m*-, m.p. 177—178°, and *o*-, m.p. 204—205°, *d*-galactose-*p*-, m.p. 193°, and *o*-, m.p. 165°, *lactose*-*p*-, m.p. 208—209°, *o*-, m.p. 207—208°, and *m*-, m.p. 189—190°, *maltose*-*p*-, m.p. 159°, *m*-, m.p. 156°, and *o*-, m.p. 169°, *l*-arabinose-*p*-,



m.p. 176—177°, and -o-, m.p. 133°, d-xylose-p-, m.p. 175—176°, -m-, m.p. 157—158°, and -o-tolyl-*osazone*, m.p. 98—99°. F. R. S.

**Reagent for oxidising substances.** P. PRATESI and R. CELEGHINI (*Gazzetta*, 1936, **66**, 365—370).—3 : 6-Dibromo-2 : 5-bis-(2' : 4'-dimethyl-1'-pyrryl)-quinol (this vol., 999), of which the prep. is described in detail, is a sensitive reagent for peroxides; thus with  $\text{H}_2\text{O}_2$ ,  $\text{BzO}_2\text{H}$ ,  $o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ,  $\text{MeEtO}_2$ ,  $\text{Bz}_2\text{O}_2$ ,  $(\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO})_2\text{O}_2$ ,  $(o\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO})_2\text{O}_2$ , and  $(o\text{-CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO})_2\text{O}_2$ , in  $\text{C}_5\text{H}_5\text{N}$ , the intense blue colour of the benzoquinone is formed. The reagent will detect 0.05 mg. of  $\text{BzO}_2\text{H}$ , and shows its formation during the autoxidation of  $\text{PhCHO}$ , and that of peroxides in the autoxidation of terpenes and styrenes. The quinol also reacts with benzo-, tolu-, thymo-, and 2 : 5-dibromobenzo-quinone, and, in  $\text{EtOH}$  or dioxan, detects  $\text{Fe}^{+++}$  ( $< 0.002$  mg., and even in the presence of many other substances),  $\text{Fe}(\text{CN})_6^{+++}$ ,  $\text{Cl}'$ , and  $\text{Br}'$  in  $\text{H}_2\text{O}$ . In  $\text{EtOH}$ ,  $\text{EtOAc}$ , and dioxan the reagent is less sensitive to org. peroxides than in  $\text{C}_5\text{H}_5\text{N}$ . E. W. W.

**Structure of simple nucleic acids. IV. Determination of furfuraldehyde in pyrimidyl acids.** H. STREUDEL (*Z. physiol. Chem.*, 1936, **242**, 100).—The two cytosylic acids and uracilic acid give no furfuraldehyde when treated by Hoffman's method (cf. A., 1927, 687). W. McC.

**Reaction of quinine with various phenols.** R. LABES and K. WEDELL (*Arch. exp. Path. Pharm.*, 1936, **182**, 249—261).—The pptn. of quinine (I) by  $\text{PhOH}$ ,  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ , trichlorophenol, and picric acid depends on the hydrophobic nature of groups substituted in  $\text{PhOH}$  and only to a limited extent on  $[\text{H}']$ . The ease of pptn. of (I) from very dil. solution is discussed with reference to its action on biological processes in which phenolic substances are concerned. F. O. H.

**Solubility products of strychnine with various phenols.** (Chemical constitution and biochemical action.) R. LABES and F. LU (*Biochem. Z.*, 1936, **286**, 232—247).—Strychnine gives difficultly sol. reaction products with a large no. of investigated phenolic derivatives, in the formation of which the mass law is obeyed and for which solubility products can be determined. The latter are the smaller, i.e., extend to greater dilutions, the greater is the no. of hydrophobic groups substituted in the phenol. The effect is maintained down to concns. of alkaloid which are pharmacologically active. Detection of alkaloids by means of picric acid is a special case of this reaction. P. W. C.

**Titration of alkaloids in anhydrous media.** G. N. THOMAS (*J. Pharm. Chim.*, 1936, [viii], **24**, 162—173).—A criticism of various methods. The author concludes that his method (B., 1935, 1117) offers advantages over the others (error is  $\pm 0.1\%$ ). J. N. A.

**Determination of methionine in proteins.** H. D. BAERNSTEIN (*J. Biol. Chem.*, 1936, **115**, 25—32).—After hydrolysis and demethylation with  $\text{HI}$ , homocysteine is oxidised with  $\text{Na}_2\text{S}_4\text{O}_6$  (reaction is sp. for oxidation of  $\cdot\text{SH}$ ) and the  $\text{Na}_2\text{S}_2\text{O}_3$  formed titrated with  $\text{KIO}_3\text{--HIO}_3$  (I). Cysteine must be determined also, preferably with (I). Methionine may be also determined by absorption of  $\text{MeI}$  during the process and gives satisfactory results if  $\text{Et}_2\text{O}$ ,  $\text{EtOH}$ , and fat are absent. Glucose yields no volatile I' under the prescribed conditions. H. G. R.

**Sulphur distribution in proteins. II. Combined methods for determination of cystine, methionine, and sulphates in hydriodic acid digests.** H. D. BAERNSTEIN (*J. Biol. Chem.*, 1936, **115**, 33—36).—The distribution of S in 11 proteins (average recovery 96.9%) by the new system of analysis (cf. preceding abstract) is described. H. G. R.

## Biochemistry.

**Blood-gases in pneumectomised animals.** J. ENSELME, M. DARGENT, and D. CHEVASSU (*Bull. Soc. Chim. biol.*, 1936, **18**, 1352—1355).—Pneumectomy in the rabbit is followed by an increased  $\text{O}_2$ -capacity and haemoglobin content of the blood. H. D.

**Insulin-decomposing power of erythrocytes.** F. ROSENTHAL, I. FRIEDHEIM, and R. NAGEL (*Klin. Woch.*, 1935, **14**, 603—606; *Chem. Zentr.*, 1935, ii, 3536).—The reaction between insulin and haemolysed human erythrocytes is examined *in vitro*. A. G. P.

**Extraction of lipins from red blood cells.** E. M. BOYD (*J. Biol. Chem.*, 1936, **115**, 37—45).—After haemolysis with an equal vol. of  $\text{H}_2\text{O}$ , the cells are extracted with  $\text{EtOH}\text{--Et}_2\text{O}$  (25—30 vols. per 1 vol. of cells) without heating. The val. obtained from oxalated is  $>$  that from defibrinated blood. H. G. R.

**Cholesterol content of blood corpuscles.** G. LAROCHE and A. GRIGAUT (*Compt. rend. Soc. Biol.*, 1936, **122**, 1253—1255).—The cholesterol content of red cells is approx. 1.5 g. per litre, being  $<$  that of the plasma. H. G. R.

**Preservation of erythrocytes with naphthalene-1 : 6-disulphonate.** H. GOLDIE (*Compt. rend. Soc. Biol.*, 1936, **122**, 1218—1221).—Erythrocytes of sheep can be preserved for serological reactions for  $< 4$  months in a 0.5—0.75% solution of the Na salt. H. G. R.

**Daily variation in eosinophile numbers in blood; influence of adrenaline.** I. DJAVID (*Klin. Woch.*, 1935, **14**, 930—931; *Chem. Zentr.*, 1935, ii, 3400).—Regular variations are recorded. These are unaffected by adrenaline. A. G. P.

**Absorption spectra of oxyhaemoglobin of some Vertebrata.** T. TUTSCHOLSKI and A. WOŁOSZCZUK (*Acta phys. Polon.*, 1934, **3**, 271—278).—The absorption spectra of oxyhaemoglobin from man, guinea-pig, and frog show identical structure. The absorption intensity varies with the source. CH. ABS. (p)

Reaction of cyanide with the hæmocyenin of *Limulus polyphemus*. O. H. PEARSON (J. Biol. Chem., 1936, 115, 171—177).—CN' reacts with oxyhæmocyenin, removing O and forming a rather stable cyanohæmocyenin, in which 4 CN are associated with 2 Cu. The reaction is reversed by dialysis. The relative affinities of salt-free hæmocyenin for O and CN' are approx. 5:1. J. N. A.

Determination of the isoionic point of hæmoglo-bin and total serum-proteins. M. LÉVY, S. MIGNON, and A. NETTER (Bull. Soc. Chim. biol., 1936, 18, 1311—1324).—The dialysis method for the determination of the isoionic points of proteins (Sandor, this vol., 1008) is applied to (human) total serum-proteins and hæmoglo-bin, giving mean normal vals. of  $p_H$  5.35 and 7.09, respectively. Variations are observed in pathological conditions. H. D.

Serum-proteins during anaphylactic state [in man]. AUBRY, THIODET, and RIBERE (Bull. Soc. Chim. biol., 1936, 18, 1356—1360).—An increase in the albumin/globulin ratio occurs. H. D.

Flocculation of globulin in diluted serum. M. DOLADILHE and C. MOREL (Compt. rend. Soc. Biol., 1936, 122, 1310—1311).—[H'] is the chief factor causing the flocculation of globulin on dilution and may be stabilised by the addition of NaHCO<sub>3</sub>. H. G. R.

Lipin-protein complexes and ageing of blood-serum. B. DELAGE (Bull. Soc. Chim. biol., 1936, 18, 1304—1310).—Aseptic horse serum, kept at 0° for periods up to one year, shows a progressive decrease in the lipins extractable by cold EtOH-Et<sub>2</sub>O. The quantity extractable increases to a max. with increasing [EtOH] in the mixture. H. D.

Blood-fibrin. Protein structure. M. BERGMANN and C. NIEMANN (J. Biol. Chem., 1936, 115, 77—85).—Fibrin (ox) on hydrolysis yields arginine (I) 7.5%, histidine 2.5%, lysine 10.1%, glutamic acid 14.0%, aspartic acid (II) 5.3%, and proline (III) 4.9%, (I), (II), and (III) being produced in equiv. amounts. The distribution of the NH<sub>2</sub>-acids follows one of two arithmetical series. H. G. R.

Mechanism of spontaneous hydrolysis of the organic phosphorus of blood *in vitro*. G. DE TONI and G. GRAF (Biochim. Terap. sperim., 1935, 22, 395—410; Chem. Zentr., 1935, ii, 3670).—The increase in inorg. P during autolysis of blood *in vitro* is due entirely to phosphatase, and does not occur when the action of the enzyme is prevented by addition of CCl<sub>3</sub>·CO<sub>2</sub>H. A. G. P.

Blood plasma-cholesterol and -phospholipin-phosphorus in rats following partial hepatectomy or ligation of the bile duct. A. CHANUTIN and S. LUDEWIG (J. Biol. Chem., 1936, 115, 1—7).—After partial hepatectomy a decrease in cholesterol (I) esters occurred on the 1st day, returning to normal on the 2nd day, when an increase in free (I) was noted. Free (I) is increased and (I) esters are normal in rats with ligated bile duct; in all cases phospholipin-P  $\propto$  the concn. of free (I). H. G. R.

Blood-phospholipin as a transport mechanism. R. G. SINCLAIR (J. Biol. Chem., 1936, 115,

211—220).—The elaidic acid (I) content of plasma-phospholipins (II) rises rapidly after ingestion of (I) (as mixed glyceride), indicating that (II) enter into the transport of fatty acids. Only after 2 days' continuous feeding of (I) does it appear in the erythrocyte-(II). H. D.

Selenium as catalyst in determination of non-protein-nitrogen in blood. F. REIS and H. H. POWERS (J. Lab. Clin. Med., 1935, 20, 1204—1206).—Technique for examining Folin-Wu blood filtrates is described. CH. ABS. (p)

Histamine or a similar substance in rabbits' blood. B. TARRAS-WAHLBERG (Klin. Woch., 1935, 14, 1285—1287; Chem. Zentr., 1935, ii, 3402).—The blood contains  $0.5 \times 10^{-6}$  g. per c.c. of histamine (I) or a substance exhibiting the biological reactions of (I). A. G. P.

Aminoacidæmia and the action of hypotensive substances. G. DE NITO (Boll. Soc. ital. Biol. sperim., 1936, 11, 160—161).—Hypotensive substances decrease the blood-NH<sub>2</sub>-acid level by increasing the deaminating activity of the blood as shown by deamination of glycine. F. O. H.

Influence of various substances on the change of state of uric acid in the serum. I, II. Y. NUKITA (Folia Pharmacol. Japon., 1935, 20, 30—37).—I. Protein in the serum stabilises uric acid (I). In presence of Na and Mg salts (I) separates less readily from serum. K<sub>2</sub>SO<sub>4</sub> and KCNS have a similar influence, but KCl, KNO<sub>3</sub>, CaCl<sub>2</sub>, and CaSO<sub>4</sub> have the reverse effect.

II. The action of serum-protein is unaltered by purification by electrodialysis. CH. ABS. (p)

Content of nitrogenous degradation products in the serum of ungulates. A. URBAIN and R. CAHEN (Compt. rend., 1936, 203, 342—345).—The urea content of the serum of non-ruminants is approx. const. for the same species and is <0.5 g. per litre. Great variations from animal to animal are found among ruminants; the content is about 0.4 g. for oxen and reaches 0.7 g. for goats and camels. Uric acid is present in very small amount in comparison with that in human serum. The total non-protein-N is very low. H. W.

Reduced glutathione in the blood of ungulates. A. URBAIN, R. CAHEN, and M. A. PASQUIER (Compt. rend. Soc. Biol., 1936, 122, 1210—1211).—In the ruminants individual variations in the same species were observed. The val. for domestic *Caprinæ* is similar to that of man, but it is greater in the *Camelidæ* and *Cervidæ*. H. G. R.

Determination of urea in blood. C. A. SAGASTUME and R. A. CRESPI GHERZI (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 47—49).—The authors' reagent (see this vol., 1288) with Na<sub>2</sub>SO<sub>4</sub> in place of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is recommended for deproteinisation of blood prior to determination of urea. F. R. G.

Composition of elk's blood. J. BRUGEMANN (Z. physiol. Chem., 1936, 242, 169—170).—The following vals. (mg. per 100 c.c.) were obtained with the blood of a female (1 year): total N 3136—3864, residual N 19—50, sugar (I) 34—58, lactose (II) 19—38,



Na 170—326, Cl 337—390. In the plasma the (I) and (II) vals. were 62—87 and 20—36, respectively, and the alkali reserve was 44—66 vols. per 100 vols. In the serum the Ca, P, Na, and Cl vals. were 8.2—9.8, 6.5—11.2, 367—433, and 305—369, respectively.

W. McC.

Has orally-administered saccharin an influence on blood-sugar? F. FISCHLER and A. SCHROTER (Deut. med. Woch., 1935, 61, 1354—1358; Chem. Zentr., 1935, ii, 3536).—No effect was observed.

A. G. P.

Effect of hypertonic, intra-arterial injections on blood-sugar. A. BAUDOUIN, J. LEWIN, and E. AZÉRAD (Compt. rend. Soc. Biol., 1936, 122, 1193—1195).—Hypoglycæmia was induced.

H. G. R.

Glycæmia and its regulation in carbohydrate metabolism. A. TURLETTI (Rass. clin. Terap. Sci. affini, 1935, 34, 152—171; Chem. Zentr., 1935, ii, 3405).—The opposing influences of insulin and adrenaline are utilised.

A. G. P.

[Hypo]glycæmia and increased temperature produced by external factors. M. SENDRAIL and L. TAMELET (Compt. rend. Soc. Biol., 1936, 122, 1262—1264).—With dogs kept at a temp. between 45° and 50°, the blood-sugar falls during the first 10 min. and then increases; the temp. of the animal reached 42.5° in 45 min.

H. G. R.

Colorimetric determination of glucose in blood.—See this vol., 1234.

Influence of lactic acid on the determination of blood-ketones. G. W. SCHWARZBERG (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 105—112).—The presence of normal amounts of lactic acid in blood does not affect the determination of ketones.

F. R. G.

Exchange of sodium, potassium, and calcium between erythrocytes and plasma and content of these elements in plasma and serum. G. M. STREFF (Z. physiol. Chem., 1936, 242, 1—14; cf. Waelsch *et al.*, A., 1935, 1142).—In human and sheep's blood no appreciable amount of Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>++</sup> passes from erythrocytes to plasma or *vice versa* within 2 hr. after drawing.

W. McC.

Blood-sulphur. H. R. DALÓ (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 77—85).—The SO<sub>4</sub><sup>++</sup>-S and total S contents of the deproteinised blood of normal persons are 0.002—0.003 and 0.0045—0.0065%, respectively. Diabetes or tuberculosis does not affect, but uræmia increases, these vals.

F. R. G.

Spectrographic determination of lead in blood. K. CRUSE and H. SCHUBERT (Z. anal. Chem., 1936, 105, 241—256).—100 c.c. (0.01—0.1 mg. Pb) of blood are ashed at 500°, H<sub>2</sub>SO<sub>4</sub> being added. Pb is deposited electrolytically at 70°, with low c.d. on a pure Sn cathode (0.1 to 0.5 g., according to the amount of Pb), from a solution of the ash in aq. NH<sub>4</sub> tartrate of  $p_H$  6.2—6.4. The cathode is melted in a H<sub>2</sub> atm., and Pb is determined in its spark spectrum by the logarithmic sector method. Sources of subjective error in this method are discussed.

J. S. A.

Vasoconstrictive substance in blood, with special reference to high blood pressure. L. HANTSCHMANN (Z. ges. exp. Med., 1935, 96, 442—

467; Chem. Zentr., 1935, ii, 3401).—The constrictive action of blood and of various biological preps. is examined in relation to blood pressure and other disturbances.

A. G. P.

Interferometry of the refraction of blood-serum as a function of the concentration. R. JONNARD (Compt. rend., 1936, 203, 124—126; cf. this vol., 1038).—For 7 normal human sera,  $n$  varies from 1.349025 to 1.351320, but the rate of decrease of  $n$  with dilution (100—20%) with H<sub>2</sub>O varies from case to case. As the concn. approaches 20%, rabbit or horse serum shows a break in the curve, below which the relationship is not linear, probably corresponding with the flocculation of globulins.

J. L. D.

Interferometry of the refraction of serum in presence of foreign substances. R. JONNARD (Compt. rend. Soc. Biol., 1936, 122, 1305—1307).—On adding sugar to serum the observed increase in  $n$  is always > the calc. val.

H. G. R.

Interferometry of the refraction of serum in presence of electrolytes. R. JONNARD and F. ZUCKERKANDL (Compt. rend. Soc. Biol., 1936, 122, 1315—1316).— $n$  is increased by KCl and decreased by NaCl; in pathological cases the effect of KCl is more considerable.

H. G. R.

Modification in bactericidal power of blood by sodium citrate. P. CARNOT and H. LAVERGNE (Compt. rend. Soc. Biol., 1936, 122, 1249—1252).—The bactericidal power is decreased by 1—2% of Na citrate.

H. G. R.

Double mechanism of adenosine triphosphate stabilisation in cells. I. Reticulocytes. V. ENGELHARDT and M. LIUBIMOVA. II. Nucleated avian erythrocytes. V. ENGELHARDT and A. BAJEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 329—330, 331—333).—I. The maintenance of supplies of adenosine triphosphate (I) in the cells is effected by glycolysis and by respiration, both processes operating simultaneously. Inhibition of either process causes only a partial breakdown, but inhibition of both processes leads to complete disappearance of (I).

II. Inhibition of glycolysis results in increased NH<sub>3</sub> production, 50—80% of which is derived from (I). With deficient respiration the NH<sub>3</sub> produced is 10—20% > could be accounted for by decomp. of (I).

A. G. P.

Sensitising action of the leaf pigments, chlorophyll, carotene, and xanthophyll. F. M. KUEN and K. PURINGER (Biochem. Z., 1936, 286, 196—203).—Ethylchlorophyllide and EtOH extracts of green plants (*e.g.*, spinach) act photodynamically on red blood cells in the spectral range 296—579 m $\mu$ . EtOH extracts of *Selaginella* did not, but COMe<sub>2</sub> extracts and the pure chlorophyll (I) prep. therefrom did, show similarly strong sensitising action. The carotene (II) of *Selaginella* leaves acts similarly in the range 280—435 m $\mu$ , the action being < that of (I) in the longer  $\lambda$ . Xanthophyll and carrot-(II) act similarly to leaf-(II).

P. W. C.

**Pancreatic hæmolysin.** R. D. DE LA RIVIÈRE, N. KOSOVITCH, and S. ISHII (Compt. rend. Soc. Biol., 1936, 122, 1170—1173).—The hæmolysin is insol. in EtOH but sol. in Et<sub>2</sub>O and COMe<sub>2</sub>; it is not affected by boiling and is adsorbed on kaolin.

H. G. R.

**Chemistry of blood coagulation. I. Determination of inhibition of blood clotting. Methods and units. II. Inhibition of blood clotting by substances of high mol. wt.** E. CHARGAFF, F. W. BANCROFT, and M. STANLEY-BROWN (J. Biol. Chem., 1936, 115, 149—154, 155—161).—I. In determining the inhibitory activity of substances towards clotting of chicken plasma, the following conditions must be observed: (a) the reaction vol. is kept const., (b) the plasma is disturbed as little as possible, (c) the time taken for one determination is 6—10 min. The "inhibitor-unit" is the smallest amount of inhibitor which raises the clotting time of 0.1 c.c. of plasma to 4 times its normal val. at 30° under described conditions.

II. Na cellulose monosulphate is inactive, whilst cellulose disulphate and K polyvinyl sulphate are active (250 units per mg.). The Na salt of the naturally occurring galactansulphuric acid has an activity of 30 units per mg. Agar agar and the sp. polysaccharide from type III pneumococci are inactive. A substance, to act as inhibitor, must be H<sub>2</sub>O-sol., of high mol. wt., and contain combined H<sub>2</sub>SO<sub>4</sub> or possibly other acid groups of similar strength.

**Protective action of "germanin" (Bayer 205) on coagulation of blood-proteins.** V. KOCIAN (Arch. exp. Path. Pharm., 1936, 182, 313—316).—Pptn. of blood-proteins by tannic acid, CuSO<sub>4</sub>, or OsO<sub>4</sub> or coagulation at 60° is retarded by germanin; coagulation by AcOH, however, is enhanced. Coagulation occurs less readily with blood from young than from old persons; sex has no influence.

F. O. H.

**Stabilisation of fibrinogen in blood-plasma.** A. FISCHER (Enzymologia, 1936, 1, 81—84).—Clotting of purified fibrinogen by lipins is not inhibited by heparin. Addition of serum restores the inhibition.

E. D. Y.

**Group-specific A-substance in human urine and animal tissue.** K. FREUDENBERG, O. WESTPHAL, and P. GROENEWOUD (Naturwiss., 1936, 24, 522).—From human urine derived from blood group A, a product has been isolated, five times as active as that previously obtained, slightly dextrorotatory, containing galactose and Ac groups but not acetylglucosamine or uronic acids. In the urine of individuals of the O-group a similar substance, serologically inactive, poorer in C and richer in N than the A-substances and laevorotatory, is found. Purified A-factor from cattle or pig tissue may be detected serologically in amounts of  $5 \times 10^{-10}$  g. Its composition differs from that of the product obtained by Landsteiner (J. Exp. Med., 1936, 63, 185) from horse saliva. Hexose and Ac groups are present but not amino-hexose or uronic acids. Its properties are similar to those of the substances from human urine.

W. O. K.

**Immunochemistry of pyridine and its derivatives.** E. BERGER and H. ERLÉNMEYER (Klin. Woch., 1935, 14, 536—537; Chem. Zentr., 1935, ii, 3402).—Substitution by aliphatic side-chains does not change the serological action of C<sub>5</sub>H<sub>5</sub>N (I). Quinoline and nicotine behave similarly to (I). Hydrogenation, e.g., to piperidine, completely alters the reaction with antiserum.

A. G. P.

**Anti-complementary action of the urine of pregnant and of normal women.** L. GRIMARD (Compt. rend. Soc. Biol., 1936, 122, 1288—1290).—Normal urines of any origin have an anti-complementary action of variable intensity, generally < that of the serum.

H. G. R.

**Chemistry of anaphylactic shock.** A. SPITZ and A. HOCHWALD (Arch. exp. Path. Pharm., 1936, 182, 384—389).—Anaphylactic shock in dogs due to injection of horse serum is partly or completely inhibited by ascorbic acid (I). The sensitisation and shock are accompanied by increased residual C (II), sugar, and lactic acid levels of the blood [of these only (II) is affected by injection of (I)] and a decreased content of hydrolysable substances. The increase in (II) is a common but not essential symptom of shock.

F. O. H.

**Neutralising action of carbon disulphide on tetanus toxin *in vitro*.** L. VELLUZ (Compt. rend., 1936, 203, 471—472).—Freshly distilled CS<sub>2</sub> inactivates the toxin and the mixture may be injected without subsequent infection. The immunogenic ability of the mixture is retained. The reaction is unaffected by  $p_{H}$  (6—8) or by reduced pressure. CS<sub>2</sub> has no action on diphtheria toxin.

A. G. P.

**Chemical composition of teeth. IV. Calcium, magnesium, and phosphorus contents of the teeth of different animals. Mechanism of calcification.** M. M. MURRAY (Biochem. J., 1936, 30, 1567—1571; cf. this vol., 878).—The Mg and P contents of the ash of rodents' (rabbit, hare, guinea-pig, rat) teeth are > and the Ca content < those of human and dogs' teeth. In rodents the molars and incisors have different compositions. The Ca : P ratios vary from 1.75 (rats' incisors) to 2.09 (human dentine) the variations being due chiefly to alterations in Ca content coincident with changes in Mg content. When Mg is calc. as Ca the Ca : P ratios differ less. The wide variations in the mineral composition of teeth and of different tissues in the same tooth indicate that calcification is an active and sp. cell process and not merely a pptn. from saturated or supersaturated solutions of a salt of const. composition dependent on the ionic composition of the blood-plasma.

W. McC.

**Separation of enamel, dentine, and cementum.** P. J. BREKHUS and W. D. ARMSTRONG (J. Dental Res., 1935, 15, 23—29).—The fat-free material is dried, crushed, and separated by flotation in CHBr<sub>3</sub>-EtOH (5 : 1 vols.) having  $d_{20}^{25}$  2.53. Enamel sinks and the crude dentine (floating) is further separated from cementum by use of a flotation mixture having  $d_{20}^{25}$  2.04 (cementum floats). Enamel and dentine, thus prepared, contained Ca 34.3, 27.2, and P 17.5, 12.95%, respectively.

CH. ABS. (p)



**Mineral composition of bone.** M. COPPO (Arch. int. Pharm. Ther., 1935, 50, 328—331; Chem. Zentr., 1935, ii, 3534).—The composition of rabbit bones is comparable with that of human bones except that the Na and K contents are higher. The mineral composition of different bones from the same individual is more uniform than that of the same bone from different individuals. Vals. for compact are practically the same as those for spongy bones. During demineralisation, the Ca content falls and that of Mg increases irrespective of the cause of demineralisation. The % of  $H_2O$ , Na, K, and P is unchanged.

A. G. P.

**Relation between the magnesium of muscle and chronaxie.** R. WOLFF, M. RANGIER, and A. BOURQUARD (Compt. rend., 1936, 203, 414—416).—The amount of Mg in relation to dry wt. in the gastrocnemius, tibialis anterior, and semimembranosus muscles of the frog is nearly const. for each muscle, and an increase in Mg corresponds with a decrease in chronaxie. There is a close relation between intensity of glycolysis and functional activity of the muscle. Similar results are found for the muscles of *Astacus fluviatilis*. In spite of their higher chronaxie these contain more Mg than those of the frog.

J. N. A.

**Iron and copper in the liver and spleen of children of various ages.** E. LESNÉ, P. ZIZINE, and S. B. BRISKAS (Compt. rend. Soc. Biol., 1936, 122, 1271—1274).—In the foetal stage the liver and spleen contain a reserve of Cu and Fe and as growth proceeds the Cu val. decreases.

H. G. R.

**Composition of an intestinal concretion (enterolith) of a horse.** R. A. ROBINSON (New Zealand J. Sci. Tech., 1936, 18, 65—66).—The enterolith contained 53% of mineral matter consisting largely of struvite (probably), with smaller amounts of bobierrite and vivianite. No acid radical other than  $PO_4'''$  was present.

A. G. P.

**Composition of vesical calculi.** L. T. KYA (Chinese Med. J., 1936, 50, 797—806).—Of 42 calculi, 16 were composed principally of uric acid, 3 of  $PO_4'''$ , 4 of  $C_2O_4''$ , and 1 of cystine, whilst 18 were mixed stones.

W. O. K.

**Physiology of fur-bearing animals. I, II.** R. NESENI (Deut. tierarztl. Woch., 1934, 42, 643—644; 1935, 43, 241—243; Chem. Zentr., 1935, ii, 3398—3399).—Data are given concerning the digestive enzymes, contents of stomach and intestines, gall, liver, and fat of the silver and blue fox, nutria, etc.

A. G. P.

**Isoelectric point of animal tissues. III. Striped muscle. IV. Mouse erythrocytes.** G. YASUZUMI (Folia Anat. Japon., 1935, 13, 55—61, 332—342).—Data are recorded and the influence of different fixatives is examined.

Ch. Abs. (p)

**Isolation of acetic acid from mammalian liver.** R. P. COOK and K. HARRISON (Biochem. J., 1936, 30, 1640—1643).—AcOH was isolated as the 2:4-dinitrophenylhydrazide from fresh ox liver, together with the *osazone*, m.p. 175° (decomp.), of a substance of empirical formula  $C_8H_{12}O_6$ . The compound represents the major, if not the entire, part of the

$HSO_3$ -binding compounds of liver extract. Glucosazone was not detected.

P. W. C.

**Reducing substance in brain. I. Chemical tests. A. BONSIGNORE. II. Biological assay.** A. BONSIGNORE and C. ARDY (Boll. Soc. ital. Biol. sperim., 1936, 11, 92—94, 94—96).—The properties of ascorbic acid (I) added to brain-tissue indicate that the reducing substance titrated by 2:6-dichlorophenol-indophenol is (I); this is confirmed by feeding normal brain-tissue to scorbutic guinea-pigs.

F. O. H.

**Glycogen content of ascarids. I. A. SMORODINCEV and K. BEBESCHIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 189—191).**—The glycogen (I) and lipin contents of female ascarids were > those of males. Differences in ash, total dry matter, and protein were smaller. All vals. tended to be smaller in *Taenia rhynchus saginatus* and still smaller in *Taenia solium* and *Diphyllobothrium latum*. On a dry-matter basis the (I) of *T. saginatus* was > that of ascarids. The protein of the latter was the more active.

A. G. P.

**Chitobiose octa-acetate from beetles.** L. ZECHMEISTER and I. PINCZÉSI (Z. physiol. Chem., 1936, 242, 97—99).—Chitin (I) from the wing-covers of the cockchafer (*Melolontha vulgaris*) yields the octa-acetate (II) with  $Ac_2O$ . (I) from the wings, thorax, and head of cantharides (*Lytta vesicatoria*) yields less pure (II) which is purified by treatment with NaOMe. Direct acetylation of cantharides yields impure (II).

W. McC.

**Liberation from the spinal cord of a substance similar to acetylcholine [during electrical stimulation].** B. MINZ (Compt. rend. Soc. Biol., 1936, 122, 1214—1216).

H. G. R.

**Physical chemistry of lipins. V. Behaviour of kephalin from human brain towards acids and bases.** M. SPIEGEL-ADOLF (Biochem. J., 1936, 30, 1536—1541).—1 g. of purified kephalin (I) in presence of excess of HCl neutralises 0.0086—0.0088 ml. of *N*-HCl. A (I)-HCl compound is pptd. when the [HCl] is further increased. The  $\eta$  of (I) solutions first decreases when HCl is added, but later increases before flocculation occurs. (I) can be pptd. by centrifuging only when the stage of increasing  $\eta$  has been reached. (I) also neutralises NaOH, the binding capacity increasing with [NaOH]. In fresh solutions of (I) with increasing [NaOH]  $\eta$  passes through a max. After 24 hr.  $\eta$  decreases steadily as [NaOH] is increased.

W. McC.

**Chemistry of insects. III. Wax of *Psylla bursi*.** B. K. BLOUNT (J.C.S., 1936, 1241—1242).—The wax, m.p. 89.6—90.1°, consists of an ester of the  $C_{30}$  acid with  $C_{30}$  alcohol, each component containing about 5% of the  $C_{28}$  compound. No paraffin is present.

F. R. S.

**Absorption spectra of kephalin, lecithin, and selected antigens.**—See this vol., 1178.

**Highly unsaturated fatty acids,  $C_{25}H_{40}O_2$  and  $C_{26}H_{42}O_2$ , in tunny oil.**—See this vol., 1230.

**Adsorption of proteins. Crystallised horse-haemoglobin. Horse serum-albumin.**—See this vol., 1202.

Flavins in the vitellin and shell of silkworm eggs and in the tegument of yellow silkworms. C. MANUNTA (Boll. Soc. ital. Biol. sperim., 1936, 11, 50—51).—The pigment of yellow silkworms is extracted (together with protein which is removed by  $\text{Na}_2\text{WO}_4\text{-AcOH}$ ) by 40% aq.  $\text{COMe}_2$  at 40—50° but not by abs.  $\text{COMe}_2$ ,  $\text{EtOH}$ , or  $\text{C}_6\text{H}_6$  (cf. A., 1932, 871). F. O. H.

Constituents of the retina. II. Visual purple. Reaction mechanism of the bleaching [of visual purple] by light. III. Vitamin-C content of the retina. O. BRUNNER and W. KLEINAU. IV. Flavins of the retina. O. BRUNNER and E. BARONI (Monatsh., 1936, 68, 244—246, 261—263, 264—273; cf. this vol., 97).—II. Visual purple is bleached by light at the same speed in the absence or presence of  $\text{O}_2$  or  $\text{Na}_2\text{S}_2\text{O}_4$ . Bleaching is thus not due to oxidation.

III. Determination of vitamin-C by 2:6-dichlorophenol-indophenol is best effected at exactly  $p_{\text{H}}$  2.5; glutathione and cysteine do not then interfere. Each retina of ox, pig's, and sheep's eyes contains 0.105, 0.026, and 0.04 mg., respectively, of -C. The titration is equally sharp at  $p_{\text{H}}$  7, so that SH-compounds are absent.

IV. Lactoflavin, lumiflavin, lumichrome, and creatinine (and, after decomp.,  $\text{NMc}_3$ ) are isolated from retina and choroid of ox and pigs' eyes. R. S. C.

Hæmatins of cytochrome-A. J. ROCHE and M. T. BENEVENT (Compt. rend., 1936, 203, 128—130).— $\text{C}_2\text{H}_5\text{N}$  extracts of various animal and vegetable tissues which contain cytochrome-A (I) or  $\text{-A}_1$  exhibit with  $\text{NaHS}$  or cystine an absorption band at 584—586  $m\mu$ , probably due to the hæmochromogen of (I). A and  $\text{A}_1$  do not co-exist, so their similar absorption at 585  $m\mu$  is probably due to a common group. Extracts of *B. coli communis*, rich in  $\text{A}_1$  and  $\text{A}_2$ , show also ill-defined bands at 600—605  $m\mu$  and 620—625  $m\mu$ . By a modification of Negelein's method (A., 1934, 96), a new hæmatin (II) is isolated from horse's heart-muscle, reduced to a hæmochromogen with bands at 580, 530, and 425  $m\mu$  (very similar to the bands of Warburg's "respiratory enzyme"), and converted by dil.  $\text{NaOH}$  into Negelein's hæmatin. (II) is probably the prosthetic group of cytochrome A and  $\text{A}_1$ . J. L. D.

Nature of the carbohydrate in lactalbumin. M. SØRENSEN (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 8, 123—128).—Fractionation of lactalbumin (I) gives one fraction very rich in carbohydrate. The nature and amount of this carbohydrate were determined by the orcinol method; it proved not to be galactose (II) as found by Sørensen and Haugaard (A., 1933, 731), but to be either lactose or, more probably, (II)+mannose, in which case the final (I) fraction contained 7.02% of carbohydrate. An explanation is given of the former error.

E. A. H. R.

Comparison between copper and iodometric methods for determining sugar in human milk. M. BERRY (Compt. rend. Soc. Biol., 1936, 122, 857—858).—The val. obtained by the iodometric is > that obtained by Bertrand's method, the deviations with human being > those with other milks. H. G. R.

Refraction of buffalo's and goat's milk sera obtained with copper sulphate. I. ZLATEFF (Z. Fleisch-Milchhyg., 1935, 45, 402—405; Chem. Zentr., 1935, ii, 3594).—The refractometer no. for Cu serum from buffalo's milk is 40.9—44.9 and for goat's milk 38—40.5; corresponding vals. for  $\text{CaCl}_2$  sera are 39.6—43.3 and 36.6—38.9. The influence of various factors on these vals. is discussed. H. N. R.

Active biological factor in cow's milk. R. SASAKI and N. ANDO (J. Agric. Chem. Soc. Japan, 1936, 12, 684—698).—The poor appearance of the fur of rats produced by excess of Ca in bread diets can be corr. by feeding cow's milk. J. N. A.

Transmission of vitamin-A from parents to young in mammals. V. Vitamin-A and carotenoid contents of human colostrum and milk. W. J. DANN (Biochem. J., 1936, 30, 1644—1651).—Single samples of human colostrum were obtained shortly after secretion commenced and those of early milk several days later. The diet was poor during pregnancy and liberal after delivery. The vitamin-A and carotenoid (I) contents of the colostrum were of the same order as in cows but could not be correlated with the age, number of birth, or length of time after birth until the colostrum was obtained. The -A and (I) contents of the early milk were for cow's milk. The -A content of colostrum was not increased by regular ingestion of cod-liver oil during pregnancy. The ratio of the amounts of -A in colostrum and early milk in 70% of cases was < 3 (small relative to the ratio for the cow). Colostrum can have no function in the provision of reserve supplies of -A at birth.

P. W. C.

Hæmostatic action of maternal milk. A. SOLE (Klin. Woch., 1935, 14, 1354—1359; Chem. Zentr., 1935, ii, 3402).—The coagulating principle is associated with the fat particles and separates with these. The prep. of an active milk powder is described. It has a local action only. A. G. P.

Chemical constitution of exudates and transudates. I. Protein and glucose. II. Calcium, sodium, and chlorine. E. STOLFI (Boll. Soc. ital. Biol. sperim., 1936, 11, 3—5, 5—8).—I. Polleri's work (Pathologica, 1926, 18, 287) is not confirmed. The lowest protein (I) content is found in the spermatocyst; in symptomatic hydrocele it is in essential hydrocele. The concn. of (I) in the plasma is slightly > that in the pleuritic and peritoneal exudates.

II. The Na contents are irregular. The Cl' in transudates is considerably, and in exudates slightly, > in the plasma. The Ca contents are diminished in exudates and transudates; in the latter the non-diffusible Ca is low. E. P.

Action of organ extracts on mesobilirubinogen (urobilinogen). I. Effect of aqueous glycerol extract of liver. G. OLIVA (Minerva med., 1935, II, 205—208). CH. ABS. (p)

Amino-acids and free choline in bile. E. F. W. MULLER (Z. physiol. Chem., 1936, 242, 201—203).—Fresh human bile treated with aq.  $\text{CuSO}_4$  and  $\text{Ba(OH)}_2$  yields glycine, tyrosine, lysine, and a mixture of valine and leucine together with some impure substances (including possibly arginine and histidine).



Bile also contains free choline ( $\leq 100$  mg. per 100 c.c.) in amount equiv. to the lecithin content.

W. McC.

**Metal content of gallstones and bile.** E. MULLER (Biochem. Z., 1936, 286, 182—185).—The ash of human bile contains Fe, Mn, Al, and Ni but, unlike gallstones, does not contain Cu, Pb, Cr, Zn, and Co.

P. W. C.

**New interpretation of results of the conventional titration of gastric juice.** L. MARTIN (Amer. J. Digest. Dis. Nutrition, 1934, 1, 330—332).—Titration of the juice to the lemon-yellow end-point of Topfer's indicator measures free HCl, acid combined with gastric proteins ( $\text{Cl}'$ ,  $\text{PO}_4'''$ ), and free  $\text{H}_3\text{PO}_4$ .

CH. ABS. (p)

**Antipeptic influence of gastric mucin.** E. A. ZAUS and L. S. FOSDICK (Amer. J. Digest. Dis. Nutrition, 1934, 1, 177—178).—The antipeptic action of the commercial mucin (I) disappears after 3 hr. incubation *in vitro*, but is increased by incubation at  $37^\circ$  in a pepsin solution. This is ascribed to hydrolysis of (I) with liberation of a substance resembling mucoitin- or chondroitin-sulphuric acid. The Ca salt of the last-named has a marked antipeptic effect.

CH. ABS. (p)

**Determination of sodium in urine by sedimentation.** E. BROUWER (Z. physiol. Chem., 1936, 241, 135—141).— $\text{PO}_4'''$  is removed from urine (2 c.c.) by shaking with CaO, and Na is pptd. by the method of Butler *et al.* (A., 1931, 1342) and determined with sufficient accuracy by a sedimentation procedure. The usual K contents do not interfere but control determinations must be made occasionally.

W. McC.

**Application of diphenylthiocarbazone (dithizone) to the determination of lead in urine.** F. MORRIS (Analyst, 1936, 61, 465—471).—500 c.c. of urine are treated with 10 c.c. of conc. aq.  $\text{NH}_3$ , and after keeping overnight, the ppt. is collected and ashed at  $500^\circ$ . The residue is dissolved in 20 c.c. of 10% HCl, filtered hot, and the filtrate treated with 10 c.c. of 60% aq.  $\text{NH}_3$  citrate and 5 c.c. of 10% aq. KCN, after which the solution is made just alkaline with aq.  $\text{NH}_3$ . It is shaken with 5-c.c. portions of a 0.05% solution of dithizone (I) in  $\text{CHCl}_3$  until the  $\text{CHCl}_3$  extracts show no pink colour after washing with 5 c.c. of 1% aq. KCN and 5 c.c. of 2% aq.  $\text{NH}_3$ . Free (I) is removed from the  $\text{CHCl}_3$  by repeated shaking with this solution, and finally the  $\text{CHCl}_3$  solution is shaken with 15 c.c. of 0.1N-HCl, the green colour produced, due to free (I), being compared colorimetrically with standards (cf. A., 1934, 381).

J. W. S.

**Determination of albumin in urine.** C. A. SAGASTUME and R. A. CRESPI GHERZI (Rev. Fac. Cienc. Quim. La Plata, 1935, 10, 7—10; cf. A., 1935, 884).—Albumin is pptd. by a solution of 50 g. of  $(\text{NH}_4)_2\text{SO}_4$ , 3 g. of PhOH, and 10 g. of sulphosalicylic acid in 100 g. of  $\text{H}_2\text{O}$ , and centrifuged (1500 r.p.m.) for 2 min. The method is more exact than that of Aufrecht.

F. R. G.

**Chemical basis of the Ehrlich diazo-reaction with urine.** III. P. SACHS (Z. physiol. Chem., 1936, 242, 19—22; cf. this vol., 502).—The fraction

of the crude dye (from the diazonium salt of 2:4- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}_2$  and urine) sol. in  $\text{Et}_2\text{O}$  and aq.  $\text{Na}_2\text{CO}_3$  and that ( $\text{C}_{12}\text{H}_8\text{N}_2\text{Cl}_4$ ) sol. in  $\text{Et}_2\text{O}$  but insol. in aq. NaOH and  $\text{Na}_2\text{CO}_3$  have no biological significance, the second probably being derived from the reagent. The fraction insol. in  $\text{Et}_2\text{O}$  when treated with fuming  $\text{HNO}_3$  and then with *p*-cresol (I) yields the original diazonium compound coupled with (I) and an orange-red substance,  $\text{C}_{28}\text{H}_{22}\text{O}_4\text{N}_2$ , m.p.  $200\text{--}201^\circ$ , containing a (I) residue. The corresponding substance  $\text{C}_{21}\text{H}_{16}\text{O}_3$  with which (I) couples to give the dye is probably not a pathological product.

W. McC.

**Ascites and retention of sodium.** W. KLODT and C. DIENST (Arch. exp. Path. Pharm., 1936, 182, 262—267).—The serous fluid of ascites has a mol. content of  $\text{Na}^+$   $>$  that of  $\text{Cl}'$ , the concns. being approx. equal to those in the serum. Palliative treatment includes restricted ingestion of  $\text{Na}^+$ . The phenomenon is due to diminished excretion of  $\text{Na}^+$  following disturbances of the  $\text{H}_2\text{O}$  threshold in cardiac and renal diseases.

F. O. H.

**Treatment of epidermophytosis of feet and hands with benzoic acid preparations.** H. O. LOOS (Arch. Dermatol. Syphilis, 1935, 173, 109—116; Chem. Zentr., 1935, ii, 3674).—The antimycotic action of Me, Et, Pr, and benzyl *p*-hydroxybenzoates increases in the order named. Nipasol (Pr ester) gives good results with mycosis of feet.

A. G. P.

**Effect of parathyroid hormone on heat stroke. Changes in blood-sugar and calcium and potassium contents of serum.** E. SANFILIPPO and S. RICCA (Biochim. Terap. sperim., 1935, 22, 411—420; Chem. Zentr., 1935, ii, 3669).—Hyperglycæmia following heat stroke in rabbits is more marked after pretreatment with parathyroid hormone. Treated animals showed lowered blood-Ca level in the initial and increased blood-K in the final phase.

A. G. P.

**Lipin-phosphorus content of hypertrophied heart and kidney in the rat.** S. LUDEWIG and A. CHANUTIN (J. Biol. Chem., 1936, 115, 327—332). The theory that the phospholipin (I) content of an organ is directly related to its activity is investigated. Hypertrophy of the heart or kidney in the rat, induced by unilateral nephrectomy, is not associated with an increased % of (I) in these organs.

H. D.

**Magnesiæmia in hypothalamic-hypophyseal diseases. I. Blood-magnesium. II. Parallelism between hypermagnesiæmia and hyperprolactinuria in hypophyseopathy. III. Variations in magnesiæmia and prolactinuria on X-irradiation of the pituitary gland in hyperpituitarism.** L. CANNAVO and G. FRADDA (Boll. Soc. ital. Biol. sperim., 1936, 11, 194—196, 196—197, 198).—I. Hyperpituitarism in man is accompanied by hypermagnesiæmia and hypopituitarism by occasionally slight hypomagnesiæmia. The P level follows a parallel course whilst Ca is approx. const.

II. Hypermagnesiæmia is accompanied by increased levels of gonadotropic hormone in blood and urine.

III. The abnormally high serum-Mg and urinary prolactin levels are diminished (cf. A., 1935, 543).

F. O. H.

**Cirrhosis of the liver.** I. Etiology, symptomatology, liver-function tests and gastric juice findings. II. Calcium, total proteins, sugar, and chloride distribution in various body-fluids. C. F. WANG (Chinese Med. J., 1936, 50, 891—902, 903—910).—II. The average serum-Ca (8.56 mg. per 100 c.c.) is < normal. The sugar contents of ascitic, pleural, and oedematous fluids are > those of the blood and cerebrospinal fluid, these latter being within the normal range. W. O. K.

**Fluorine as a specific for the parathyroid.** M. CALLAM (Münch. med. Woch., 1935, 82, 1534—1535; Chem. Zentr., 1935, ii, 3400).—Use of 1% solution of NaF in certain diseases is described. A. G. P.

**Calcium and phosphorus metabolism in pituitary basophilism.** R. H. FREYBERG and R. L. GRANT (Arch. Int. Med. 1936, 58, 213—228).—The P and Ca metabolism was not characteristic of hyperparathyroidism, but there was a low concn. of P in the serum, and a low urinary and high faecal excretion of P. Sufficient Ca and P was not absorbed to allow their retention, although there was a great need of  $\text{Ca}_3(\text{PO}_4)_2$ . Administration of vitamin-D hardly affected absorption and retention of Ca, but there was good utilisation of Ca when it was injected intravenously. J. N. A.

**Glycæmia following scalding and traumatic shock.** G. STOLFI (Boll. Soc. ital. Biol. sperim., 1936, 11, 8—11).—Traumatic shock or scalding in rabbits produces hyperglycæmia. F. O. H.

**Cause of hyperglycæmia following traumatic shock.** I. Blood-glycolysis. II. Liver-glycogen and cellular oxidation. G. STOLFI (Boll. Soc. ital. Biol. sperim., 1936, 11, 106—107, 107—109).—I. Traumatic shock only slightly diminishes blood-glycolysis.

II. Cellular dehydrogenation diminishes in brain and heart but increases in liver, kidney, and muscle (rabbit). Hepatic glycogenolysis, however, is the main cause of the hyperglycæmia. F. O. H.

**Effect of alkaline therapy for peptic ulcer on utilisation of dietary iron in regeneration of hæmoglobin.** F. KELLOGG and S. R. METTIER (Arch. Int. Med., 1936, 58, 278—284).—No significant increase in hæmoglobin (I) occurred during alkaline therapy and restriction of Fe intake, but addition of foods rich in Fe increased the no. of erythrocytes, but not (I). Cessation of alkaline therapy caused an increase in (I). Alkalinisation of the upper part of the gastro-intestinal tract interferes with the utilisation of dietary Fe for the synthesis of (I), but not with the material needed for formation of erythrocytes. J. N. A.

**Relations between [mitogenetic] radiation, catalase action, and respiration intensity during development of *Bombyx mori*, L.** K. YAMAFUGI and S. GORO (Bull. Agric. Chem. Soc. Japan, 1936, 12, 90—93).—During embryonic evolution there is no exact parallel between respiration intensity and catalase (I) activity. The mitogenetic radiation from the egg is connected with colour changes in the egg, and also with a strong (I) activity and a weak respiration intensity.

Radiation is a min. at the stages when the colour of the egg is still yellow, and the (I) content low and when the worm emerges and respiration and (I) activity reach a max. The respiration of the cocoon is very small compared with that of the larva and moth, but the (I) activity is much greater, and the mitogenetic radiation is also at a max. During the change of larva to moth, the radiation is intermittent. J. N. A.

**Respiration of brain.** T. F. DIXON and A. MEYER (Biochem. J., 1936, 30, 1577—1582).—The  $\text{O}_2$  uptake of the minced striate body, globus pallidus, cerebellar cortex, cornu ammonis, hypothalamus, and medial parts of the thalamus of ox brain is scarcely if at all increased by addition of glucose or lactate but is constantly and greatly increased if slices of these parts are used. The metabolic activity of the cerebellar cortex is > that of any other part of the brain. W. McC.

**Production of a [growth]-inhibiting substance in tissue cultures.** L. NATTAN-LARRIER and L. GRIMARD (Compt. rend. Soc. Biol., 1936, 122, 1187—1190).—Development of old cultures is arrested by the production of an inhibiting substance which can act *in vivo*. H. G. R.

**Relation between the minimum protein requirement and the base content of human diet.** C. ROSE (Z. ges. exp. Med., 1935, 96, 793—798; Chem. Zentr., 1935, ii, 3403).—The N balance was positive on a basic and negative on an acidic diet. An adequate base content in the food is necessary for the effective utilisation of protein. A. G. P.

**Effect of diet on phosphate compounds in the liver of dogs.** E. FLOCK, J. L. BOLLMAN, and F. C. MANN (J. Biol. Chem., 1936, 115, 179—199).—A method for the separation and determination of total, acid-sol., phospholipin-, and residual  $\text{PO}_4'''$  in hepatic tissue is described. The total  $\text{PO}_4'''$  in livers of normal dogs on a regular kennel diet varied from 241 to 318 mg. of P per 100 g. of moist tissue. Using a standard balanced diet, the range was 226—270 mg. The acid-sol.  $\text{PO}_4'''$  was similar for the two diets, whilst diets rich in protein, carbohydrate, or fat and fasting gave normal  $\text{PO}_4'''$  vals., but a high-fat diet for < 20 days reduced the total  $\text{PO}_4'''$ . The greatest decrease occurred in the acid-sol. (especially glycerophosphoric acid and an extremely sol. unknown  $\text{PO}_4'''$ ), and the smallest in the phospholipin fraction. With a const. diet, the composition of the livers of individual dogs at different times remained approx. const. If a diet high in fat be replaced by one high in carbohydrate, the normal composition of the liver was quickly restored. J. N. A.

**Protein lost by the various organs and tissues of the body during a fast.** T. ADDIS, L. J. POO, and W. LEW (J. Biol. Chem., 1936, 115, 111—116).—The % protein-loss (in rats fasted for 1 week) was distributed as follows, the proportion of the original protein being in parentheses: muscle, skin, and skeleton 62 (8), liver 16 (40), alimentary tract, pancreas, and spleen 14 (18—28), blood 6 (18—28), kidneys 1 (18—28), heart 0.5 (18—28), other organs 0.5. The testicles and adrenals lost no protein,



whilst the prostate and seminal vesicles lost 29 and the brain 5% of their initial protein content.

H. G. R.

**Protein-loss from liver during a two-day fast.** T. ADDIS, L. J. POO, and W. LEW (J. Biol. Chem., 1936, 115, 117—118; cf. preceding abstract).—The liver (rat) lost 20% of its original protein, whilst all other organs and tissues combined lost only 4%. This supports the hypothesis that the liver contains a store of reserve protein.

J. N. A.

**Photosensitisation of animals in S. Africa.** VIII. Biological formation of phyloerythrin in digestive tracts of various domesticated animals. J. I. QUIN, C. RIMINGTON, and G. C. S. ROETS (Onderstepoort J. Vet. Sci., 1935, 4, 463—478).—Formation of phyloerythrin (I) from chlorophyll (II) in the digestive tract is due to symbiotic infusoria and bacteria. The (I) content of sheep faeces is probably related to the (II) content of the food plant.

CH. ABS. (p)

**Synthesis of uric acid in the avian organism: hypoxanthine as intermediary metabolite.** N. L. EDSON, H. A. KREBS, and A. MODEL (Biochem. J., 1936, 30, 1380—1385).—In pigeons two tissues are necessary for uric acid (I) synthesis. 30% of the  $\text{NH}_3$  which is bound in presence of lactate and pyruvate by the liver appears as hypoxanthine (II) and is isolated as such. In the kidney and pancreas (II) is oxidised to (I), xanthine oxidase (III) acting as catalyst. The kidney and pancreas do not bind  $\text{NH}_3$  and the amount of (I) produced by liver, kidney, and pancreas separately is small. Liver produces (I) in the absence of kidney when (III) (from milk) is added. Probably in other birds also (II) is an intermediate in (I) production.

W. McC.

**Degradation of dimethylaniline in herbivora.** F. HORN (Z. physiol. Chem., 1936, 242, 23—28; cf. this vol., 514).—In rabbits  $\text{NPhMe}_2$  subcutaneously injected is converted into  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$ , which is excreted conjugated with glucuronic acid in the urine. Possible  $\text{NHPHMe}$  is an intermediate product in the process and small amounts of it are sometimes found. Administration of  $\text{NPhMe}_2$  does not lead to production of  $\text{NPhMe}_2\text{O}$  or of methæmoglobin.

W. McC.

**Post-mortem transformation of barbituric derivatives into hydrocyanic compounds.** P. R. ORELLA (Rev. Fac. Cienc. Quím. La Plata, 1935, 10, 51—60).—Contrary to Kohn-Abrest *et al.* (A., 1930, 369) when veronal, luminal, or prominal was orally administered to dogs, no HCN or HCN derivatives were detected in the organs or viscera. The presence of CNS' in man is attributed to the use of mustard or tobacco.

F. R. G.

**Cholesterol feeding and fat metabolism.** R. P. COOK (Biochem. J., 1936, 30, 1630—1636).—With rats maintained on synthetic diets, cholesterol (I) feeding causes a decreased growth rate and a fatty liver only when the diet contains fat. With fat-free diets there is no effect due to absence of absorption. Guinea-pigs are very susceptible to the action of (I) and fatty livers are produced without adding fat to the stock diet. There is a marked decrease in the

depot fat, the action of (I) being in part the mobilisation of fat in the liver.

P. W. C.

**Respiration and ketogenesis in the "cholesterol" fatty liver.** R. P. COOK and N. L. EDSON (Biochem. J., 1936, 30, 1637—1639).—Rats given a fat-free diet + cholesterol (I) for short periods failed to develop fatty livers. The livers gave normal respiration vals. and on adding  $\text{PrCO}_2\text{Na}$  (II) the normal  $\text{O}_2$  uptake and ketone (III) formation. Guinea-pigs also presented a normal metabolism. After feeding (I) for longer periods to rats the liver tissue had a significantly lower respiration both in presence and absence of (II), whilst with guinea-pigs there was no significant change of respiration but (III) formation in presence of (II) was decreased. Spontaneous (III) formation in (I) fatty liver is < in livers of rats starved for 24 hr. The changes in respiration and (III) formation in these fatty livers are small.

P. W. C.

**Synthesis of cholesterol in living organisms.** H. L. BROSE (J. Cancer Res. Comm. Sydney, 1936, 7, 134—136).—A discussion of the *in vivo* synthesis of cholesterol from oleic acid (cf. Minovici *et al.*, A., 1934, 552).

W. O. K.

**Biological oxidation of dibasic and  $\omega$ -oxidation of monobasic fatty acids.** F. P. MAZZA (Boll. Soc. ital. Biol. sperim., 1936, 11, 143—145).—Org. dibasic acids [saturated (excepting glutaric) and unsaturated (with certain exceptions)] are readily oxidised (without production of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ ) by liver and kidney tissues, the latter being more active in  $\omega$ -oxidation (cf. Verkade and Lee, A., 1935, 242, 390) of monobasic acids and their esters. Suberic acid appears to yield a  $\gamma$ -diketone.

F. O. H.

**Biological oxidation of saturated dibasic fatty acids.** F. P. MAZZA (Boll. Soc. ital. Biol. sperim., 1936, 11, 157—158).— $\beta\beta'$ -Diketoadipic acid is oxidised and decarboxylated by liver and kidney tissue, the latter producing traces of  $\text{H}_2\text{C}_2\text{O}_4$ ; adipic acid yields traces of  $\text{Ac}_2$  with kidney but with neither tissue is  $\text{H}_2\text{C}_2\text{O}_4$  formed. The processes are discussed with reference to  $\beta$ - and  $\omega$ -oxidation.

F. O. H.

**Nutritive value of pentosan. III. Decomposition of xylan by intestinal bacteria.** H. IWATA (J. Agric. Chem. Soc. Japan, 1936, 12, 587—594).—Micro-organisms in the alimentary tract of man and higher animals decompose xylan (I) into xylose, lactic acid,  $\text{PrCO}_2\text{H}$ ,  $\text{AcOH}$ , and  $\text{HCO}_2\text{H}$ , together with  $\text{CO}_2$  and traces of  $\text{H}_2$ .  $\text{EtOH}$ ,  $\text{MeCHO}$ , and  $\text{CH}_4$  are not produced. The protein synthesised by these organisms from (I) and  $\text{NH}_4$  phosphate is similar to a plant-protein.

J. N. A.

**Assimilation of carbohydrates (starch and its hydrolysis products) in infants under six months on an artificial or mixed diet.** P. ARMAND-DELILLE, MENTZER, and URBAIN (Compt. rend. Soc. Biol., 1936, 122, 1212—1213).—Cooked starch, up to 30 g. per day, is assimilated by infants of 3—6 months.

H. G. R.

**Utilisation of sugars in experimental diabetes.** T. CARN and J. HOUGET (Compt. rend., 1936, 203, 130—132; cf. this vol. 749).—The vastus externus

of pancreatectomised dogs when tetanised has a normal content of reducing substances and lactic acid (I). The blood- and liver-(I) are normal, but the liver-sugar is diminished. After exercise, muscle-glucose and -(I) decrease and blood- and liver-(I) increase. With diabetic dogs, the peripheral utilisations of glucose and carbohydrate storage in muscle are normal but glycogen storage in the liver is very slight.

J. L. D.

#### Action of metals on carbohydrate metabolism.

I. U. SAMMARTINO (Arch. Farm. sperim., 1936, 61, 209—236).—The blood-sugar of normal rabbits is unaltered by intravenous injection of aq. NaCl; that of aq. chlorides of K, Rb, Cs, or Sr has an irregular effect, either increasing or decreasing the level, whilst that of aq. LiCl, CaCl<sub>2</sub>, and, more consistently, BaCl<sub>2</sub>, produces hypoglycaemia.

F. O. H.

Combustion of ethyl alcohol during perfusion of the liver. N. FIESSINGER, H. BÉNARD, J. COURTIAL, and L. DERMER (Compt. rend. Soc. Biol., 1936, 122, 1255—1258).—After a rapid decrease, due to diffusion, EtOH destroyed  $\propto$  the time and is not affected by the addition of 2:4-dinitrophenol. Addition of KCN inhibits the combustion, which recommences at a lower rate on adding Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

H. G. R.

Oxidation of the methyl group in the animal body.—See this vol., 1231.

Metabolism of iodine. III. Uptake from surrounding air by man. H. LÖHR (Arch. exp. Path. Pharm., 1936, 182, 132—140; cf. this vol., 358).—The blood-I of men in an atm. containing I (e.g., the air near patients painted with tincture of I) increases up to 6—7 times ( $167.2 \times 10^{-6}\%$ ) the normal val. within 1 hr.; the absorption is mainly through the lungs, that through the skin being much smaller. The increase persists for approx. 5 days.

F. O. H.

Chemical processes during cell division. II. Nature and kinetics of the reaction between -SH groups and moniodoacetic acid. L. RAPKINE (J. Chim. phys., 1936, 33, 493—506; cf. A., 1931, 115; 1933, 1039).—The -SH of denatured reduced egg-white (I) reacts quantitatively with 1 mol. of CH<sub>2</sub>I-CO<sub>2</sub>Na (II), liberating 1 HI. -SH determined by a direct method, in which the indicator (Na nitroprusside) is added 30—40 min. after mixing (I) with (II) at 50° and  $p_H$  7.5, accords with the val. given by Hopkins' method. Under similar conditions, the rate of reaction of (II) increases in the order (I) < glutathione (III) < cysteine and the rates increase with rise of temp. The reaction with (III) increases rapidly as the  $p_H$  is raised to >6.

J. G. A. G.

Right vagus nerve and hypoglycaemic action of ultra-violet irradiation. E. MARTINI and E. RONCALLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 77—79).—Section of the right vagus or sciatic nerve in rabbits depresses the hypoglycaemic action of irradiation (this vol., 238).

F. O. H.

Glycaemia and ketosis in rabbits due to X-ray lesions of the anterior pituitary lobe. L. CANNANO and S. LA MONACA (Boll. Soc. ital. Biol. sperim., 1936, 11, 35—36).—Cell destruction of the anterior

lobe due to intensive X-irradiation of the pituitary produces a slight hyperglycaemia but the alimentary glycaemia curve is unchanged. The effect on ketonuria is variable (cf. A., 1935, 543).

F. O. H.

Effect of short electric waves on sterol colloids. W. M. MALISOFF and F. A. STENBUCK (J. Biol. Chem., 1936, 115, 87—91).—Waves of the order of 5 m. have a coarsening effect on colloidal preps. of cholesterol or its acetate which is independent of temp. and increases with age of the colloid and time of exposure.

H. G. R.

Action of ultra-violet rays on starch solution. T. ISEMURA (J. Chem. Soc. Japan, 1935, 56, 772—778).—The initial stage of decomp. of starch by diastase was hydrolysis of amylose and amylo-pectin. Decomp. by exposure to ultra-violet light involved oxidation as well as hydrolysis of amylophosphoric ester.

CH. ABS. (p)

Biochemical and biological changes produced by high pressures. M. A. MACHEBŒUF and J. BASSET (Bull. Soc. Chim. biol., 1936, 18, 1181—1191).—The cells of higher animals and bacteria are killed, enzymes are inactivated, certain cancer cells lose their power of transplantation, certain immunity reactions are destroyed, and serum-globulin is coagulated by pressures up to 20,000 atm. The pressures required to inactivate bacteria may form a basis for their differentiation.

H. D.

Influence of hydrogen-ion concentration and of salinity on eggs of *Eugraulis encrasicholus*, L. S. S. ELIZAROVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 255—260).—In variety *maeoticus* eggs survive a salinity <5.36 g. per 1000 g. and  $p_H$  >6.52. Eggs of variety *ponticus* develop in the range 8—21 salinity and  $p_H$  6.9—8.9.

A. G. P.

Adaptation of cutaneous tactile receptors. IV. Electrolyte content of frog skin. M. A. RUBIN. V. Release of potassium from frog skin by mechanical stimulation. H. HOAGLAND and M. A. RUBIN. VI. Inhibitory effects of potassium and calcium. H. HOAGLAND (J. Gen. Physiol., 1936, 19, 935—937, 939—942, 943—950).—IV. The skin of *Rana pipiens* contains K 132, Na 91, Ca 302, Mg 4.4, Cl 172, S 33, and P 337 mg. per 100 g. of wet tissue.

V. K is liberated from the epithelial cells of frog skin on stimulation by an interrupted air-jet; Ca<sup>++</sup>, PO<sub>4</sub><sup>'''</sup>, and Cl<sup>'</sup> are not liberated under these conditions.

IV. The adaptation to stimulation by an interrupted air-jet of single freely branching axon endings in frog skin is hastened by Ringer's solutions containing 15-fold excess of K or Ca. K acts more rapidly than Ca, and the K effect, but not the Ca effect, is reversible in normal Ringer's solution. Recovery from Ca inhibition can be effected by K-rich solutions. K, but probably not Ca, is involved in the adaptation of the tactile nerve endings in frog skin.

F. A. A.

Absorption of drugs from human skin. A. R. BLISS, jun. (J. Amer. Pharm. Assoc., 1936, 25, 694—701).—Inunction with ointments containing Me salicylate, I, I+KI, or KI is followed by absorption of the drug (as indicated by presence in the urine)



to a varying extent. I is not absorbed from aq. preps. nor is quinine hydrochloride from ointments. The fatty base of the ointment has no influence on absorption. F. O. H.

**Permeability of tissue cells.** H. GROSSFELD (Biochem. Z., 1936, 286, 193—195).—Dil. aq.  $\text{NH}_3$  permeates normal tissue cells (heart, stomach, liver, etc. of chick embryos) *in vitro* quickly,  $\text{NaHCO}_3$  much more slowly, and  $\text{NaOH}$  and  $\text{KOH}$  hardly at all.  $\text{NH}_4\text{Cl}$  and  $\text{Na}_3\text{PO}_4$  in presence of Ringer's solution permeate very slowly but in absence of Ringer's solution very quickly and cause considerable swelling. In absence of Ringer's solution, urea permeates much more quickly into the cells than does glucose. P. W. C.

**Calcium, phosphorus, and the alkali reserve in rachitic osteopathy produced by strontium.** G. NATUCCI (Biochim. Terap. sperim., 1935, 22, 385—389; Chem. Zentr., 1935, ii, 3671).—Oral administration of Sr lactate to young rabbits produced changes in bones of a rachitic nature, hypercalcaemia, and a lowering of the P level and alkali reserve of the blood. A. G. P.

**Relationship of tissue-iodine to glycogen.** A. STURM and H. ERTNER (Biochem. Z., 1936, 286, 204—212).—During electric stimulation of rabbit muscle, glycolysis is accelerated by I', inorg. I taking part in glycogen degradation and becoming organically bound as  $\text{H}_2\text{O}$ -sol. protein-I (I). The increase of liver-glycogen during the action of insulin is accompanied by a decrease of (I) and an increase of inorg. I. The probable close relationship of (I) with the thyroglobulin of thyroid gland is discussed. P. W. C.

**Relation between chemical constitution and physiological action of organic compounds. I. Action of benzene, toluene, xylene, and mesitylene on white mice.** V. VLASSOPOULOS (Praktika, 1935, 10, 32—41; Chem. Zentr., 1935, ii, 3405—3406).—Physiological action (reflex stimulus, convulsions, paralysis) is weaker as the mol. is more symmetrical, e.g.,  $\text{PhMe} > \text{C}_6\text{H}_6$ ,  $\text{PhMe} > \text{xylene} > \text{mesitylene}$ . A. G. P.

**Action of camphor on the heart system.** B. KADYKOV and I. LEWIN (Arch. int. Pharm. Ther., 1935, 50, 298—314; Chem. Zentr., 1935, ii, 3542).—A. G. P.

**Action of octinum in increasing blood pressure.** E. ETTINGER and L. POPPER (Klin. Woch., 1935, 14, 575—576; Chem. Zentr., 1935, ii, 3406).—The mechanism of the action of octinum (methyl-octenylamine) is examined. A. G. P.

**Skatole and tissue cultures.** J. VERNE and P. KUBIKOWSKI (Compt. rend. Soc. Biol., 1936, 122, 1155—1156).—Skatole, at very low concn., augments the growth of fibroblasts and renal cells. H. G. R.

**Blood-sugar and glutathione content of blood and tissues after administration of glutathione.** J. DRISCH (Arch. exp. Path. Pharm., 1936, 182, 301—312).—Parenteral administration of glutathione (I) temporarily increases the blood-sugar in rabbits, the injected (I) being mostly excreted (partly reduced) within 15 min. The content of oxidised (I) in the lungs increases and that of reduced (I) in the intestine

decreases; the muscle content is unaffected whilst the liver shows a slight decrease. Continuous injection is not followed by storage in the organs. (I) has no significant effect on the action of insulin or adrenaline; it probably directly affects blood-glycolysis. F. O. H.

**Action of phloridzin on muscular glycogenolysis.** J. K. PARNAS, W. MEJBAUM, and B. SOBCHUK (Compt. rend. Soc. Biol., 1936, 122, 1148—1152).—Phloridzin suppresses primarily the formation of hexose monophosphate and also the oxidation-reduction of phosphotriose. H. G. R.

**Chemistry, pharmacology, and chemotherapy of thiazyl substances.** E. MENEGHETTI (Boll. Soc. ital. Biol. sperim., 1936, 11, 189—191).—A preliminary discussion. F. O. H.

**Theory and pharmacological and chemotherapeutic action of auxochromes. I. B. BREYER** (Boll. Soc. ital. Biol. sperim., 1936, 11, 191—194).—A résumé of the theories of Diltthey and Wizinger (A., 1926, 1163; 1927, 764; 1928, 627; 1932, 1127) and a discussion of their possible significance in biological action. F. O. H.

**Chemical constitution and pharmacological action. Quinoline-4-carboxylic acids.** S. BERLINGOZZI and G. DONATELLI (Boll. Chim. farm., 1936, 75, 381—389).—Isatoic acid with  $\omega$ -anilino-acetophenone in  $\text{EtOH-NaOH}$  affords 3-anilino-2-phenylquinoline-4-carboxylic acid (cf. A., 1924, i, 314, 1345; 1927, 674, 1086, 1087). The action of this and other derivatives (*ibid.*) of quinoline-4-carboxylic acid (I) on blood- and urine-uric acid indicates a slight increase of uric acid excretion due to (I) following substitution of OH or  $\text{NH}_2$  at 3 and a decrease following that of OPh and  $\text{C}_6\text{H}_5\text{NHAc}$  at 3 and 6, respectively. F. O. H.

**Effect of diethylaminomethylbenzdioxan on diuresis.** E. ZUNZ and F. JOURDAN (Ann. physiol. physicochim Biol., 1934, 10, 880—886; Chem. Zentr., 1935, ii, 3406).—The diuretic action of  $\text{H}_2\text{O}$ ,  $\text{NaCl}$ , and urea is restricted. A. G. P.

**Action of diethylaminomethyl- (F. 883) and piperidomethyl-3-benzdioxan on the circulatory system.** G. DE VLEESCHOUWER (Arch. int. Pharm. Ther., 1935, 50, 251—295; Chem. Zentr., 1935, ii, 3539—3540).—Experiments with chloralised dogs are recorded. The mutual effects of these and other drugs are examined. A. G. P.

**Toxicity and antipyretic action of *d*-glucono-*p*-phenetidine.** H. A. BRAUN and G. F. CARTLAND (J. Amer. Pharm. Assoc., 1936, 25, 615—618).—*d*-Glucono-*p*-phenetidine (I) has a toxicity < that of acetophenetidine (II), the min. lethal dose in rats being >50 and 2 g. per kg., respectively. Methæmoglobin formation occurs with (II) but not (I). The antipyretic action of (I) in febrile rabbits is < that of (II) (cf. Hamburger, A., 1934, 691). F. O. H.

**Action of (A) arsenicals on glycolysis of the isolated rabbit's heart, (B) atoxyl on enzymic glucose degradation, and (C) glucose on lipin degradation due to atoxyl in the artificially-circulated heart.** B. TANZI (Boll. Soc. ital. Biol. sperim., 1936, 11, 129—130, 131, 131—132).—(A)

0.002*M*- $\text{Na}_3\text{AsO}_4$  or 0.005*M*-atoxyl diminishes whilst 0.01*M*- $\text{Na}_3\text{AsO}_4$  increases lactic acid (I) production, probably respectively due to inhibition and stimulation of glycolysis.

(b) Atoxyl (0.005*M*) in the perfusing glucose-Ringer's solution depresses the aerobic or anaerobic formation of (I).

(c) Glucose does not influence the decomp. of lipins due to atoxyl. F. O. H.

**Experimental anæmias and their suitability for the assay of anti-anæmic preparations. III. Collargol-saponin anæmia in rabbits for the assay of injected liver extracts.** P. GOTTLIBE (Arch. exp. Path. Pharm., 1936, 182, 91—97; cf. this vol., 1014).—Active liver preps. injected into rabbits in which anæmia has been induced by injection of collargol-saponin increase the erythrocyte count and hence such animals are suitable for the assay of anti-anæmic preps. F. O. H.

**Influence of oxidation-reduction dyes on conditions of disturbed respiration. I. Thionine and methæmoglobin[forming] poisons.** F. HAUSCHILD (Arch. exp. Path. Pharm., 1936, 182, 118—131).—The pharmacology of thionine (I) was investigated in rats; the min. lethal dose is 10 mg. per 100 g. body-wt. whilst luminal has an antagonistic action. (I) inhibits the toxicity of methæmoglobin-forming (e.g.,  $\text{NaNO}_2$ ,  $\text{NH}_2\text{Ph}$ ,  $\text{NHPh}\cdot\text{OH}$ ) poisons, probably by acting as  $\text{O}_2$ -transporter in place of the affected hæmoglobin. F. O. H.

**"Vagotropine" of Viale. (A) Origin. (B) Nature. (C) Relation to vagotropic substance of Loewi and acetylcholine.** B. BARTOLINI (Boll. Soc. ital. Biol. sperim., 1936, 11, 83—85, 86—88, 88—91).—(A) Vagotropine (I) is of uniform occurrence in the dog's organs.

(b) (I) is org., sol. in EtOH, not extracted from serum by  $\text{CHCl}_3$  or  $\text{Et}_2\text{O}$ , and does not occur in filtrates from pptn. of sera by  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  or phosphotungstic acid; a non-protein character, however, is indicated by its non-pptn. by tannic acid.

(c) The vagotropic substance of Loewi, but not (I), is probably identical with acetylcholine (cf. A., 1929, 1326). F. O. H.

**Intravenous administration of egg-lecithin and carbohydrate metabolism.** M. TESTOLIN and A. CHINAGLIA (Rass. Clin. Terap., 1935, 34, 124—137; Chem. Zentr., 1935, ii, 3405).—Egg-lecithin increases carbohydrate tolerance, and thus facilitates the utilisation of sugar by increasing both consumption and storage by the liver. A. G. P.

**Specific depressor substance of secretions of the human prostate and seminal vesicles.** U. S. VON EULER (Klin. Woch., 1935, 14, 1182—1183; Chem. Zentr., 1935, ii, 3535).—The substance "prostaglandin" is isolated from dialysed EtOH extracts of the tissues or secretions. It is acidic and differs in some respects from the active material previously isolated from other body-fluids. Its physiological activity is unaffected by atropine. A. G. P.

**Alkyl- and aryl-amides and -carbamides as hypnotics.**—See this vol., 1237.

**Antagonism of narcotics to cardiazole.** O. GROS and H. T. A. HAAS (Arch. exp. Path. Pharm., 1936, 182, 348—362).—The action of various narcotics in diminishing the lethal effect of administration of 15 mg. per 100 g. of cardiazole to rats was investigated. The ratio of narcotic dose (from the "side-position" reaction) to protective dose is 4—6 for all the narcotics examined. The anomalous behaviour of chloral hydrate and avertin is discussed. F. O. H.

**Pernocton-urethane. Therapy of combination of hypnotics.** G. PIOTROWSKI (Arch. exp. Path. Pharm., 1936, 182, 243—248).—Pernocton (I) and urethane (II) produce hypnosis (i.e., sleep for 30—45 min.) with subcutaneous injection of respectively 0.045—0.050 and 0.9—1.20 g. per kg. in rabbits and guinea-pigs. The effect of mixtures of (I) and (II) is purely additive (cf. Lendle, A., 1927, 1219), hence both have the same site of action (pons and mid-brain). F. O. H.

**Toxicity of barbital derivatives.** I. JONES and E. V. LYNN (J. Amer. Pharm. Assoc., 1936, 25, 597—601).—The min. lethal doses of amytal, barbital, dial, neonal, pentobarbital, phanodorm, and phenobarbital, administered orally and intraperitoneally to rabbits, are tabulated. F. O. H.

**Increased veronal excretion due to alkalis.** H. SALZER and R. FISCHER (Arch. exp. Path. Pharm., 1936, 182, 170—177).—The total excretion of veronal administered to rabbits is increased by intravenous injection of  $\text{NaHCO}_3$ , which raises the urinary  $p_{\text{H}}$  from 4.5 to 7—8. The mechanism is probably one of inhibition of tubular re-absorption in the kidneys and increased excretion of the Na salt. The toxicity is also correspondingly modified. F. O. H.

**Local anaesthetics containing the morpholine ring.**—See this vol., 1274.

**Quantitative relationships between the basic and other components of pancreatic secretion.** R. K. S. LIM, S. M. LING, A. C. LIU, and I. C. YUAN (Chinese J. Physiol., 1936, 10, 475—491).—Data are given for the total base,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  contents,  $p_{\text{H}}$  and vol. of the pancreatic juice secreted by dogs under chloralose anaesthesia after stimulation by the introduction of aq. glucose into the duodenum. The results indicate that the juice consists of three independent secretions containing, respectively, (a) 0.174*N*- $\text{NaHCO}_3$ , (b) 0.174*N*- $\text{NaCl}$ , and (c)  $\text{HCl}$ , mucus, and enzymes. The chief constituent is (a) along with a proportional quantity of (b) and a small but const. val. of (c). The pancreatic  $\text{NaHCO}_3$  and gastric  $\text{HCl}$  are both secreted at cons. isosmotic with the blood. W. O. K.

**Dependence of infiltration of anaesthetics on their chemical nature or on composition of biological substrate.** A. PATANIA (Boll. Soc. ital. Biol. sperim., 1936, 11, 202—204).—The rate of absorption of anaesthetics by the skin of amphibia depends on the chemical nature of the anaesthetic. F. O. H.

**Assay of aphrodisiacs by Glaser and Haempel's fish method.** E. GLASER and A. KONYA (Arch. exp. Path. Pharm., 1936, 182, 219—238).—The



activities of various preps. (e.g., yohimbine, cantharidin) as indicated by tests on fish (A., 1932, 308) and their relation to sex-hormonal action are discussed.

F. O. H.

**Folinerin, a new cardiac drug from leaves of *Nerii oleander*.** F. FLURY and W. NEUMANN (Klin. Woch., 1935, 14, 562—564; Chem. Zentr., 1935, ii, 3542).—This cryst. glucoside (low mol. wt.) exerts the same action on the frog heart as does digitalis, is less sensitive to acids, permanent in storage, and easily resorbed.

A. G. P.

**Heart treatment with the pure glucoside of *Scilla*.** F. BACH and A. BERR (Deut. med. Woch., 1935, 61, 1591—1594; Chem. Zentr., 1935, ii, 3406).—The glucoside is effective on digitalis-refractory hearts.

A. G. P.

**Pigeon bio-assays and diuretic tests of digitalis substances.** A. J. LEHMAN (J. Amer. Pharm. Assoc., 1936, 25, 611—615).—Min. emetic and fatal doses (pigeon) and min. fatal doses (cat) are tabulated. Cessation of urinary flow in pigeons is unsatisfactory as a method of assay.

F. O. H.

**Potency of eleven crystalline cardiac principles from plants.** K. K. CHEN, A. L. CHEN, and R. C. ANDERSON (J. Amer. Pharm. Assoc., 1936, 25, 579—590).—The potency of convallatoxin,  $\beta$ -antiarin, ouabain, cymar, scillaren-A, digoxin, digitoxin, erythrophlein sulphate, thevetin (cat unit  $0.92 \pm 0.035$  mg. per kg., i.e., > that previously reported), uzarin, and gitoxin were determined by the cat unit, frog min. systolic dose, and cat min. emetic dose. Emetic action is not related to cardiac action. Relationship between chemical structure and pharmacological activity is discussed.

F. O. H.

**Evaluation of cardio-active glucosides by means of frogs.** K. FROMHERZ (Arch. exp. Path. Pharm., 1936, 182, 55—71).—The use of standard preps. of *g*- (I) and *k*-strophanthin (II), convallatoxin (III), digitoxin, and total-glucoside extracts of *Digitalis* and *Adonis* was investigated by the lethal-dose method in 8500 frogs. With different standards, an error up to 25—33% (average  $\pm 10\%$ ) occurs, but by using a definite standard the error is diminished, e.g., (I) to (II) and (III) to (II) give respective average errors of  $\pm 6.5$  and  $\pm 5.6\%$ . Slight deviations from the Trevan dose-mortality characteristic and the significance of body-wt. and other factors in the assay are discussed.

F. O. H.

**Distribution, elimination, and accumulation of strophanthidin and the activity of its esters.** L. LENDLE (Arch. exp. Path. Pharm., 1936, 182, 72—86).—When tested on frogs, the esters (acetate, isovalerate, phenylpropionate, etc.) are less active than strophanthidin (I) and  $\frac{1}{2}$ — $\frac{1}{3}$  as active as *k*-strophanthin (II), whilst with the isolated frog's heart, the activities of the esters approx. equal that of (II). Comparative data for the toxicities, rate of elimination, distribution in cardiac and peripheral tissues, and cumulative action indicate no significant basic differences in mode of action between (I) and (II).

F. O. H.

**Effects of colchicine and related substances on cell division.** A. M. BRUES and A. COHEN (Biochem. J., 1936, 30, 1363—1368).—Mitosis in the regenerating liver of rats (after partial hepatectomy) is arrested by subcutaneous injection of colchicine (optimal dose 1.0—2.0 mg. per kg.), the effect occurring only within certain limits of dosage. Octahydro-colchicine, *N*-acetylcolchinal and its Me ether, colchinal Me ether hydrochloride, and the corresponding carbinol act similarly but considerably higher doses of them are required. Di- and tri-methyl-colchicinic acid are without effect in sub-lethal or lethal doses.

W. McC.

**Vagus[-stimulating] substances.** W. STRAUB and J. SCHOLZ (Arch. exp. Path. Pharm., 1936, 182, 331—339).—The use of a double cannula connected to two heart preps. in demonstrating the humoral transference of vagal action indicates that the esterase-inhibitory action (a controlling factor in the stimulation due to substances of the choline ester type) of prostigmine (I) is > that of eserine; the bearing of the constitution of these two drugs on this difference is discussed. HCN resembles (I) in its inhibition of esterase.

F. O. H.

**Influence of certain salts on morphine toxicity and narcosis in mice and rats.** J. M. ORT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 593—597).—The characteristic action of morphine is not significantly altered by simultaneous injection of aq.  $\text{NaH}_2\text{PO}_4$ , NaCNS, or NaCl; the results do not support Bancroft's theory of anaesthesia (A., 1931, 1932).

F. O. H.

**Prolongation of the local anaesthetic action of morphine-cocaine by calcium.** G. MATSCHULAN and C. AMSLER (Arch. exp. Path. Pharm., 1936, 182, 87—90).—Pre-injection of guinea-pigs with Ca gluconate prolongs the local anaesthesia following injection of cocaine-morphine mixtures. The mechanism of the phenomenon is discussed.

F. O. H.

**Relations between chemical constitution, pharmacological action, and therapeutic uses of the harmine group of alkaloids.** T. A. GUNN (Arch. int. Pharm. Ther., 1935, 50, 379—396; Chem. Zentr., 1935, ii, 3540).—The qual. action of harmine (I) is not changed by reduction to the  $\text{H}_2$ - or  $\text{H}_4$ -derivative. Introduction of Me or OMe has little effect. Substitution of OMe by phenolic OH modifies the convulsive action and decreases the effect on protozoa and to a smaller extent on mammals. Substitution of Me by Et etc. produces no fundamental change in the action. Ethylharmol is as toxic as (I) to protozoa: nonylharmol has a slower effect. The dilating action is more marked in the higher esters (highest in amyl compound).

A. G. P.

**Relation between pharmacological action and chemical constitution in the nicotine group.**—See this vol., 1276.

**Oxidation-reduction phenomena and functional activity of nervous tissue.** M. MITOLO (Atti R. Accad. Lincei, 1936, [vi], 23, 453—458).—Hyperexcitability (induced by strychnine or PhOH) of the reflex processes in toads and rats increases the

power of the central nervous tissue to reduce 2:6-dichlorophenol-indophenol. F. O. H.

**Strychnine. VI. Variation in physiological action.** J. C. WARD, J. C. MUNCH, and F. E. GARLOUGH (J. Amer. Pharm. Assoc., 1936, 25, 590—593).—Commercial preps. of "chemically-pure" strychnine show marked differences in toxicity which could not be correlated with variations in chemical or physical properties and are not changed by recrystallisation. F. O. H.

**Action of poisons on the isolated heart-muscle strip of frog. II. Alkaloids and their parent substances.** K. MEZEY and H. STAUB (Arch. exp. Path. Pharm., 1936, 182, 183—204).—The min. effective concn., type of action, reversibility (*i.e.*, return of sensitivity on washing with Ringer's solution), and mutual antagonism and synergism of 35 alkaloids and of  $C_5H_5N$ , piperidine, pyrrole, quinoline, and indole were investigated in rhythmically-stimulated frog's heart-strip preps. F. O. H.

**Relationship between diffusion of alkaloids through blood-vessels and their ultrafilterability through artificial membranes.** M. VOGT (Arch. exp. Path. Pharm., 1936, 182, 112—117).—Some alkaloids, *e.g.*, atropine and scopolamine, readily diffuse from aq. NaCl through Cellophane membranes which to others, *e.g.*, quinine and bulbocapnine, are only slightly permeable; the presence of serum diminishes the diffusibility of both groups. The bearing of the data on processes of absorption and permeation in the organism is discussed. F. O. H.

**Effect of veratrine and atropine on the tonus of skeletal muscle.** M. LAPORTA (Arch. Sci. biol., 1933, 19, 249—265; Chem. Zentr., 1935, ii, 3673).

A. G. P.

**Effect of adrenaline, atropine, and ergotamine on the excitability of the irido-dilatory sympathetic system.** D. BOLSI and F. VISINTINI (Boll. Soc. ital. Biol. sperim., 1934, 9, 253—255).

R. N. C.

**Halogen analogues of adrenaline and ephedrine. III.**—See this vol., 1254.

**Acetylcholine and eserine.** F. ZINNITZ (Arch. exp. Path. Pharm., 1936, 182, 340—347).—The action of acetylcholine (I) on blood-pressure etc. is prolonged but not intensified by prior injection of eserine (II); the latent period is also increased. The effect, which is reversible, is due to the esterase-inhibitory action of (II) diminishing the rate of hydrolysis of (I).

F. O. H.

**Effect of sympathomimetic and parasympathomimetic substances on the chemical processes producing the energy of muscular contraction. I. Effect of adrenaline, pilocarpine, and potassium on the formation of lactic acid and decomposition of phosphagen.** D. NACHMANSOHN, J. WAIZER, and R. LIPMANN (Bull. Soc. Chim. biol., 1936, 18, 1207—1231).—Adrenaline in concns. of  $1-2 \times 10^{-4}\%$  at  $pH$  7.2 immediately increases the lactic acid (I) formation of resting anaerobic muscle (frog); phosphagen (II) resynthesis is induced only after some time and is independent of the [P] in the Ringer's solution. In fatigued muscle,

4 P

however, resynthesis of (II) runs parallel with formation of (I); poisoning the muscle with  $CH_3I-CO_2H$  prevents this resynthesis. These effects are not observed with guinea-pig's muscle. At  $pH$  6.4, (I) formation is less rapid and the (II) changes depend on the [P] in the Ringer's solution. At  $pH$  8.0, resynthesis and decomp. of (II) are retarded. Pilocarpine and  $K^+$  accelerate both formation of (I) and decomp. of (II). H. D.

**Effect of certain substances on phosphate compounds in the liver of dogs.** E. FLOCK, J. L. BOLLMAN, and F. C. MANN (J. Biol. Chem., 1936, 115, 201—206).—Injection of adrenaline produced no change in the acid-sol.  $PO_4'''$ , whilst administration of thyroxine, phloridzin, and  $CCl_4$  over intervals for a few days did not produce extremely fatty livers or low vals. for  $PO_4'''$  unless used with a fatty diet. In these dogs, as well as in depancreatised dogs deprived of insulin, only when the liver became extremely fatty were the vals. for  $PO_4'''$  reduced to < normal. J. N. A.

**Toxicity of fish-liver oil and the antitoxic effect of yeast. II. Antitoxic effect of alcoholic extract of yeast.** I. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 590—594; cf. A., 1935, 233).—The food consumption and growth of rats on a diet containing 15% of cod-liver oil were increased by the addition of 50% aq. EtOH extract of yeast, but not quite so markedly as by that of yeast itself.

W. O. K.

**Comparison of toxicity and general effects of natural, *dl*-, and *l*-camphor on the rat.** R. HAZARD and R. LARDÉ (J. Pharm. Chim., 1936, [viii], 24, 149—154; cf. A., 1935, 526).—When injected intraperitoneally (in oil) into white rats, the order of toxicity and lethal action is  $l > dl > d$ . J. N. A.

**Correlation of toxicity with optical activity of *Derris* derivatives.** R. S. CAHN (J.S.C.I., 1936, 55, 259—260r).—Since *dl*-dihydrodeguelin (I) is less toxic to mosquito larvae than one tenth of its wt. of the *l*-form (II) (Fink and Haller, J. Econ. Entom., 1936, 29, 595), either the biological results are very inaccurate (possibly owing to different rates of agglomeration of suspensions of the two forms), or (I) and (II) are *cis-trans* ring isomerides. Such isomerisation may be caused by alkali. The connexion (*cf. loc. cit.*) of differences in toxicity with optical isomerism and of the toxicity of the non-rotenone portion of *Derris* extract with the presence of (II) therein is thus not proved. R. S. C.

(A) Spectrographic determination of blood-lead; its value in diagnosis of lead poisoning. (B) Plasma-cell partition of blood-lead in clinical lead poisoning. H. BLUMBERG and T. R. MCN. SCOTT (Bull. Johns Hopkins Hosp., 1935, 56, 276—293, 311—316).—(A) Blood is ashed and burnt on graphite electrodes. Non-pathological blood shows 0.005—0.1 mg. and pathological blood >0.2 mg. of Pb per 100 c.c.

(B) In cases of blood poisoning approx. 90% of the blood-Pb was in the cells or the clot. The cell fraction contained <50% of the non-pathological Pb. Isotonic NaCl does not remove Pb from cells separated from serum. CH. ABS. (p)



Toad poisons.—See this vol., 1252.

Snake poisons. F. MICHEEL (Chem.-Ztg., 1936, 60, 753—755).—A review.

Nature and action of enzymes. H. ALBERS (Angew. Chem., 1936, 49, 448—455).—A review.  
E. W. W.

Application of the chain theory of chemical change to certain enzyme reactions. E. A. MOELWYN-HUGHES (Acta Physicochim. U.R.S.S., 1935, 3, 593—612).—A consideration of the characteristics of chain reactions leads to the view that among enzyme reactions only enzymic oxidation can be examined in the light of the chain theory. Simple mathematical treatment leads to the conclusion that the Michaelis const. is inversely  $\propto$  the average length of the chain. The theory is applied to the oxidation of luciferin, catalysed by luciferase, and purine bases, catalysed by xanthine-oxidase.  
C. R. H.

Nature of autolysis. H. HAEHN (Woch. Brau., 1936, 53, 259—263).—A review.  
I. A. P.

Origin and significance of blood-serum enzymes. L. A. CRANDALL, jun. (Amer. J. Digest. Dis. Nutrition, 1935, 2, 230—235).—A review.

CH. ABS. (p)  
Biochemistry of *Bombyx mori*, L. XVI. K. YAMAFUJI (Biochem. Z., 1936, 286, 225—228).—Curves are given showing changes in the catalase (I), peroxidase, invertase, tyrosinase, maltase, amylase, lipase, and protease activity and in the mitogenetic effect of the blood during the various stages of metamorphosis. In both cases a close relationship exists between (I) activity and mitogenetic effect.  
P. W. C.

Enzymes of trypanosomes. B. J. KRIJGSMAN (Natuurwetensch. Tijds., 1936, 18, 237—241).—*T. evansi* contains cathepsin, carboxy- and aminopolypeptidase, and dipeptidase but no lipase, carbohydrazase, or protease. It lives entirely on simple substances in the blood-stream and needs enzymes only for the synthesis of protoplasm. Toxins produced by this trypanosome are amines produced by the decarboxylation of  $\text{NH}_2$ -acids.  
S. C.

Digestive enzymes of *Anemonia sulcata*. M. SAVIANO (Boll. Soc. ital. Biol. sperim., 1936, 11, 145—146).—The endoderm contains tributyrase and trypsin but not lipase, amylase, or pepsin.  
F. O. H.

Determination of enzyme concentration in duodenal fluids. C. W. LUEDERS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 224—229).—Methods for trypsin, lipase, and amylase are described.

CH. ABS. (p)  
Isolation and properties of the indophenol-oxidase from yeast cells and heart muscle. S. YAMAGUCHI, H. TAMIYA, and Y. OGURA (Acta Phytochim., 1936, 9, 103—106).—Indophenol-oxidase, isolated from yeast cells or heart muscle and free from cytochrome and haemochromogen, is indifferent towards CO; its action is greatly restricted by  $\text{CN}^-$ .  
H. W.

Haematin and peroxidase of fig sap. J. B. SUMNER and S. F. HOWELL (Enzymologia, 1936, 1, 133—134).—Fig. sap is a rich source of peroxidase,

preps. of which contain no free haematin, but reduced haematin may be present.  
E. D. Y.

The Schardinger enzyme and xanthine-oxidase of milk. D. MICHLIN, A. JEMELJANOV, and M. SOLOVJEVA (Enzymologia, 1936, 1, 151—155).—The two enzymes vary similarly during lactation and appear to be identical.  
E. D. Y.

Diffusion of the dehydrogenase of higher fatty acids in various organs. F. P. MAZZA (Boll. Soc. ital. Biol. sperim., 1934, 9, 298—299; Chem. Zentr., 1935, ii, 3396; cf. A., 1935, 782).—Kidney sections placed in Ringer- $\text{PO}_4^{'''}$  buffer ( $p_{\text{H}}$  7.4) until the  $\text{O}_2$  consumption has decreased considerably show a marked increase in  $\text{O}_2$  consumption on addition of Na palmitate. There is no corresponding production of  $\text{CO}_2$ .  
A. G. P.

Amino-acid dehydrogenase. II. Activator of proline dehydrogenase. N. B. DAS (Biochem. J., 1936, 30, 1617—1621).—An activator (cf. this vol., 894) of proline dehydrogenase (I) of pig's kidney is present in baker's yeast and can be adsorbed on acid clay, frankonit, and animal C from faintly acid solution, but not by kaolin or  $\text{Al}(\text{OH})_3$   $\text{C}_\gamma$  (Willstatter), is pptd. by  $\text{AgNO}_3$  and  $\text{Hg}(\text{OAc})_2$ , is not inactivated by  $\text{HNO}_2$ ,  $\text{H}_2\text{O}_2$ , or aeration, is not extracted by  $\text{Et}_2\text{O}$  from alkaline solution, and is pptd. by  $\text{EtOH}$ . Lactoflavin is incapable of activating (I).  
P. W. C.

Aminodehydrogenases of the animal body. B. KISCH (Enzymologia, 1936, 1, 97—106).—Preps. of  $\alpha$ -aminodehydrogenases from liver and kidney of various animals contain three different enzymes. A relationship exists between their activity (optimum  $p_{\text{H}}$  7.0—7.6) and the C-chain length of the substrate. Quinone models for two of the types are suggested. Liver preps. are less active than kidney preps.  
E. D. Y.

Effect of glutathione and other substances on the inactivation of catalases. G. W. MARKS (J. Biol. Chem., 1936, 115, 299—314).—The inactivation of mussel-catalase (I) is a unimol. reaction, and of a large no. of substances studied,  $\text{MeOH}$ ,  $\text{EtOH}$ , and  $\text{KCN}$  decrease, and ascorbic acid (II) and glutathione (III) increase,  $k$ . Dialysis of mussel-(I) preps. to remove (II) and (III), however, has no effect on their stability. The p.d. at a Pt electrode decreases linearly with time although this change is not directly correlated with the course of inactivation. Ox kidney-(I) is made unstable by (III) and this condition is similar to unstable mussel-(I).  
H. D.

Catalase activation in living cells. K. YAMAFUJI (Enzymologia, 1936, 1, 120—124).—Ultra-violet irradiation of *Saccharomyces ellipsoideus*, *S. rosa*, and, notably, *S. colliculosa* increases the catalase activity (up to 25 times). The effect is less evident in presence of glucose or koji-agar.  
E. D. Y.

Influence of antiseptics on amylolytic actions. M. VAN HAUWAERT (Natuurwetensch. Tijds., 1936, 18, 187—190).—Small amounts of  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ , xylene,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ , or  $\text{COMe}_2$  have practically no effect on the saccharification of starch by diastase but  $\text{CHI}_3$  reduces the rate considerably.  
S. C.

**Purification of koji amylase by precipitation.** N. TAKETOMI and S. TAKEDA (Bull. Waseda Appl. Chem. Soc., 1935, 25, 11—15).—Aq. amylase (I) concentrates can usually be pptd. by addition of EtOH (2 vols.) or COMe<sub>2</sub> (0.55 vol.). Treatment with suitable proportions of EtOH-COMe<sub>2</sub> (1 : 2 vol.) dissolves (I) but ppts. invertase and protein. Further impurities in (I) may be pptd. by Pb(OAc)<sub>2</sub> or BaCl<sub>2</sub>.  
CH. ABS. (p)

**Amylase activity as a racial characteristic in silkworms.** K. YAMAFUJI, I. HIRAIWA, and S. GOTO (Biochem. Z., 1936, 286, 229—231).—The amylase content of the digestive juices and blood of European strains of *Bombyx mori* is extremely small compared with that of Japanese and Chinese strains; the former also show a smaller survival rate when exposed to unfavourable conditions of growth.

P. W. C.

**Blood-amylase and body-strength of some strains of silkworms.** K. YAMAFUJI and S. GOTO (Bull. Agric. Chem. Soc. Japan, 1936, 12, 75—77).—With three new strains during the fifth larval stage the amylase content of the blood increased daily, that in females being generally > that in males. The resistance of the worms to conditions of unfavourable growth varied considerably, that of the females being always slightly < that of the males.  
J. N. A.

**Rates of digestion of starches and glycogen and their bearing on chemical constitution. I. Action of amylases on starches and glycogen.** G. E. GLOCK (Biochem. J., 1936, 30, 1386—1396).—Determinations of achromic point, residual polysaccharide, total reducing power, and reducing power after pptn. of dextrans indicate the course of digestion of potato-, wheat-, maize-, and rice-starch and glycogen (I) by pancreatic amylase, and of wheat-starch and (I) by salivary amylase and malt-diastase. The rates of degradation are different for the different starches, each of which, however, is hydrolysed more rapidly than (I). Glucose is not produced except with high concns. of amylase and the reducing sugar which constitutes the end-product is not maltose or isomaltose.  
W. McC.

**Enzymic power of dead human livers and kidneys.** V. GETREUER and G. OBERSOHN (Z. ges. exp. Med., 1935, 96, 51—59; Chem. Zentr., 1935, ii, 2542).—The kidneys exhibit a diastatic action which oscillates in potency; it is uninfluenced by disease, and is regularly distributed between the cortex and the medulla. Glycogen is high in the kidneys in some cases of diabetes mellitus. The secondary enzymic power is uninfluenced by diabetes or previous treatment with insulin (I). The liver enzymes are less potent than the kidney enzymes normally, but are more potent in Basedow's disease and necrosis of the pancreatic fat tissue; in diabetes they are slightly more potent or of equal potency, and are inhibited by (I).  
R. N. C.

**Comparison of methods for determining diastase in duodenal fluid.** C. R. SCHMIDT, H. GREENGARD, and A. C. IVY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 618—627).—Willstätter's hypiodite titration is best suited for clinical analysis. Amylolytic activity (duodenal drainage fluid) is

optimal at  $p_H$  6.8. Maltase in the fluid is insufficient to cause variation of results in a starch substrate at  $p_H$  6.8. MgSO<sub>4</sub> (up to 5%) and bile do not affect amylolytic activity as determined by a modified Willstätter procedure.  
CH. ABS. (p)

**Invertase. III. Elution from adsorbents.** N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1936, 39, 206B; cf. this vol., 243).—Invertase (I) adsorbed on activated C is eluted partly by aq. NH<sub>3</sub> at  $p_H$  9.2; the eluate contains neither proteins nor reducing sugars. From Al(OH)<sub>3</sub> or activated clay (I) is readily eluted by 0.2% aq. NH<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> at  $p_H$  7.0—7.3; if adsorption on clay is carried out above 30°, elution is difficult.  
J. L. D.

**Influence of the aglucone on the rate of hydrolysis of  $\beta$ -glucosides by emulsin.** S. VEIBEL and F. ERIKSEN (Compt. rend., 1936, 203, 390—392).—The rate of hydrolysis of  $\beta$ -glucosides by emulsin is in the order Me < Et < Pr <sup>$\alpha$</sup>  > Pr <sup>$\beta$</sup>  < Bu > trimethylcarbinol < *d*-methylbutylcarbinol. The arrangement of the groups in the mol. is of importance. The introduction of two Me increases the rate of hydrolysis, but the presence of a third Me almost stops hydrolysis. *d*-Methylbutylcarbinol- $\beta$ -*d*-glucoside is hydrolysed approx. 15,000 times as quickly as trimethylcarbinol- $\beta$ -*d*-glucoside.  
J. N. A.

**Baicalinase, an enzyme which hydrolyses flavone glycuronides. III.** T. MIWA (Acta Phytochim., 1936, 9, 89—102; cf. A., 1932, 650).—Although baicalin is unaffected by technical emulsin (*loc. cit.*), it (and scutellarin) are hydrolysed by freshly-prepared emulsin from the seeds of *Prunus armeniaca*, var. *Ansu*, Maxim, or from bitter almonds. The probability that the hydrolysis of flavone glycuronides and  $\beta$ -glucosides is effected by specifically different  $\beta$ -glucosidases of emulsin is strengthened by the following observations. The ratio of the activity of glycuronide to glucoside fission varies with the purification of the enzyme. These actions vary independently when the enzyme is treated with adsorbents. Various harmful influences (increased [H<sup>+</sup>]; increased temp.; ultra-violet irradiation) influence the actions in differing degrees.  
H. W.

**Canavanine. V. Natural occurrence of  $\gamma$ -ethylidenecanaline, the condensation product between canaline and acetaldehyde, during the enzymic hydrolysis of canavanine.** M. KITAGAWA, K. SAWADA, and Y. HOSOKI (J. Agric. Chem. Soc. Japan, 1935, 11, 539—544; cf. A., 1934, 993).—Canavanine, with a pig-liver extract at 37°, affords canaline and  $\gamma$ -ethylidenecanaline, C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>, m.p. 233—234°,  $[\alpha]_D^{25}$  -8.96° in H<sub>2</sub>O (also from canaline and MeCHO), hydrogenated to a  $\gamma$ -hydroxy- $\alpha$ -amino acid, C<sub>4</sub>H<sub>9</sub>O<sub>3</sub>N, m.p. 204°.  
CH. ABS. (r)

**Enzymic synthesis of alkylglucosides.** S. VEIBEL (Enzymologia, 1936, 1, 124—132).—The synthetic activity of emulsin is shown for 8 alcohols by the optical method. Equilibrium consts. and heats of reaction are given.  
E. D. Y.

**Hepatic origin of serum-lipase.** N. FIESSINGER and A. GAJDOS (Enzymologia, 1936, 1, 145—150).—Serum-lipase is decreased in liver disease, increased



by parenteral administration of liver-lipase, and unchanged after pancreatectomy. E. D. Y.

**Method of enzymic ester synthesis.** E. A. SYM (Enzymologia, 1936, 1, 156—160).—Na gallate and bile salts catalyse the esterification of oleic acid + cholesterol,  $\text{PrCO}_2\text{H}$  + cyclohexanol, etc. in  $\text{C}_6\text{H}_6$  or  $\text{CCl}_4\text{--H}_2\text{O}$ . E. D. Y.

**Isolation from beef pancreas of crystalline trypsinogen, trypsin, a trypsin inhibitor, and an inhibitor-trypsin compound.** M. KUNITZ and J. H. NORTHROP (J. Gen. Physiol., 1936, 19, 991—1007; cf. A., 1935, 785).—Detailed methods for the prep. of trypsinogen, trypsin (I), a substance which inhibits (I), and an inhibitor-(I) compound are given. The inhibitor appears to be a polypeptide, mol. wt. 6000, low in C and N compared with proteins. A solution of (I)+inhibitor is inactive in the  $p_{\text{H}}$  range 7.0—3.0, but becomes active at  $p_{\text{H}}$  1.0; this action is reversible and takes about  $\frac{1}{2}$  hr. to reach completion. The inhibitor also inhibits chymotrypsin, but less markedly. F. A. A.

**Proteolytic enzymes in the uterine fluid of selachians.** M. SAVIANO (Boll. Soc. ital. Biol. sperim., 1936, 11, 146—148).—The uterine fluid of *Torpedo ocellata* and *T. marmorata* contains a peptic type whilst that of *Mustelus laevis* contains a tryptic type of protease. F. O. H.

**Activity of cathepsin and dipeptidases of the tissues of regenerating and normally-developing liver of birds.** V. N. ORECHOVITSCH (Biochem. Z., 1936, 286, 248—253).—Cathepsin (I) and dipeptidase (II) activities of normal and regenerating liver of hens and pigeons and of developing embryo chicks are tabulated. With hens, both tissues have the same (I) and (II) activity. With chick embryos, the liver-(I) activity is only 47% on the 13th day but by the 15th day reaches the adult val. whereas the (II) activity shows a max. on the 15th day. In pigeons, the liver-(II) activity is much more const. than in hens and increases considerably with regenerating tissue. P. W. C.

**Error due to blood-arginase in the urease method of determining blood-urea.** A. B. ANDERSON and S. L. TOMPSETT (Biochem. J., 1936, 30, 1572—1576).—The urea (I) content of human blood determined by incubation with a conc. solution of urease (II) (cryst. or from soya or Jack bean) is too high because (II) is attacked by arginase (III) in the corpuscles. (III) is inactivated by incubation at 37—50° for 10 min. after addition of acid and is activated by  $\text{Co}^{++}$ , which produces an increase of up to 100% in the apparent (I) content. When conc. (II) solutions are incubated with liver-(III) a similar production of  $\text{NH}_3$  occurs. For accurate determination of blood-(I) plasma should be used. W. McC.

**Structure of urea with reference to its deamination and synthesis by urease.** W. R. FEARON (Biochem. J., 1936, 30, 1652—1660).—Studies of zymolysis of urea (I) in presence of trapping agents, e.g., Ba, Ca, and Pb salts, semicarbazide, etc., and of the synthesis of (I) by urease (II) from  $\text{NH}_4$  carbonate-carbamate indicate that in the (I)-(II)

system, (I) reacts in the unsymmetrical or *iso*-form with the formation of  $\text{NH}_3$  and  $\text{NH}_2\cdot\text{CO}_2\text{H}$ . The high dielectric const. of (I) supports the suggestion that (I) is largely present in the zwitterionic form  $^+\text{NH}_3\cdot\text{C}(\text{NH})\cdot\text{O}^-$ . P. W. C.

**Distribution of urease in dog's stomach.** K. LINDERSTRÖM-LANG and A. S. ØHLSEN (Enzymologia, 1936, 1, 92—95).—Urease is situated in the surface layers of the mucosa of the fundus and pylorus in cells which stain with mucicarmine. The gastric mucosa of pigs is inactive. E. D. Y.

**Enzymic amylolysis. VI. Colour produced in dephosphorylated potato-starch by iodine.** M. SAMEC, E. WALDSCHMIDT-LEITZ, and K. MAYER (Z. physiol. Chem., 1936, 242, 165—168; cf. this vol., 111).—Potato-starch dephosphorylated with amylophosphatase from barley and kidney-phosphatase does not differ appreciably from the untreated starch as regards the colour produced with I. W. McC.

**Effect of  $\alpha$ -amino-acids and magnesium on the activity of kidney- and intestinal phosphatases.** O. BODANSKY (J. Biol. Chem., 1936, 115, 101—110).— $\alpha\text{-NH}_2$ -acids prevent inactivation of the phosphatases whilst Mg increases the initial velocity of reaction. The velocity, at optimal concn. of glycine and Mg,  $\propto$  the concn. of the enzyme. Prolonged dialysis inactivates the enzymes. H. G. R.

**Phosphatases. V. Influence of buffer composition on the course of the activity- $p_{\text{H}}$  curves of phosphoesterases. VI. Presence in animal organs of a second phosphoesterase active in acid solution.** E. BAMANN and W. SALZER (Biochem. Z., 1936, 286, 143—146, 147—159; cf. A., 1935, 402).—V. The form of the  $p_{\text{H}}$ -activity curves for the action of spleen-phosphoesterase, extracted with dil.  $\text{AcOH}$ , on Na  $\beta$ -glycerophosphate varies considerably with varying concn. of citrate ions, only one clearly defined max. being obtained with const. citrate ion concn. and two max. with Sørensen's buffer mixture.

VI. The differences in the  $p_{\text{H}}$ -activity curves for animal phosphatases according to the method of prep., substrate, etc. are due partly to the buffer effect but chiefly to the fact that two esterases having optima at  $p_{\text{H}}$  4 and 5.5, respectively, are present to differing extents. Urine contains only the enzyme of optimum  $p_{\text{H}}$  5.5. The amount of the enzyme of optimum  $p_{\text{H}}$  4 can be decreased by adsorption methods and it can be selectively destroyed by the action of alkali. The enzyme of optimum  $p_{\text{H}}$  5.5 is not identical with that of the red cells since the organ-enzyme attacks preferentially  $\beta$ -glycerophosphate and is not activated by  $\text{Mg}^{++}$  whilst the red cell-enzyme has an optimum  $p_{\text{H}}$  6.4, reacts preferentially with  $\alpha$ -glycerophosphate, and is activated by  $\text{Mg}^{++}$ . The animal organism thus possesses four different isodynamic non-sp. phosphatases, one of optimum  $p_{\text{H}}$  9. No evidence could be obtained for the existence of an enzyme of optimum  $p_{\text{H}}$  2.9—3.2. P. W. C.

**Synthesis of phospho-*d*-tartaric acid and its decomposition by phosphatase.** C. NEUBERG and W. SCHUCHARDT (Enzymologia, 1936, 1, 39—47).—

$\text{POCl}_3$  with *d*-tartaric acid in quinoline affords the acid, which is hydrolysed by taka-phosphatase ( $p_{\text{H}}$  optima at 4.0 and 5.7). E. D. Y.

**Variations in the phosphomonoesterase content of milk in relation to the progress of lactation.** S. J. FOLLEY and H. D. KAY (*Enzymologia*, 1936, 1, 48—54).—The concn. of milk-phosphatase increases during lactation whilst the total daily phosphatase content is max. 180 days after parturition. Serum-phosphatase shows no parallel changes.

E. D. Y.

**Inactivation of milk-phosphatase.** S. HERSCHDORFER (*Enzymologia*, 1936, 1, 96).—Slow cooling after heat-inactivation permits partial regeneration of the enzyme.

E. D. Y.

**Phosphatase of bones.** A. ROSSI (*Boll. Soc. ital. Biol. sperim.*, 1933, 8, 714—719; *Chem. Zentr.*, 1935, ii, 3397).—A prep. of phosphatase (I) from dog bones showed optimum activity at  $p_{\text{H}}$  7.0—8.55, decreasing rapidly at  $>9.5$ .  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{F}^-$  decreased the action of (I), which did not attack lecithin.

A. G. P.

**Phosphatase in subcutaneous tissue of dogs.** F. CEDRANGOLO (*Bol. Soc. ital. Biol. sperim.*, 1936, 11, 140—141).—An enzyme is present hydrolysing glycerophosphate, activated by  $\text{Mg}^{++}$ , and inhibited by  $\text{Na}_3\text{AsO}_4$ ,  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ , or  $\text{NaF}$ .

F. O. H.

**Effect of nucleophosphatase on thymus nucleohistone.** G. SCHMIDT (*Enzymologia*, 1936, 1, 135—141).—Hydrolysis is markedly increased after digestion of the natural nucleic acid with crude pancreas extract but not with pure trypsin.

E. D. Y.

**Heterophosphatase.** E. BAUER (*Z. physiol. Chem.*, 1936, 242, 29—39).—The heterophosphatase (I) of bottom yeast is not identical with Albers' phosphatase from top yeast,  $\alpha$ -glycerophosphatase (II), or pyrophosphatase although (I) possibly acts together with (II). Activation of (I) with  $\text{Mg}^{++}$  is optimal with  $[\text{Mg}^{++}]$  0.01—0.001*M*. When fructose (III) is the P acceptor, the activity of (I) is very low at  $p_{\text{H}}$  4.3—7.0. (I) produces mono-esters with glucose and (III). (I) appears not to esterify galactose and ribose and to esterify mannose more easily than glucose.

W. McC.

**Effect of autolysis on phosphate compounds in the liver of dogs.** E. FLOCK (*J. Biol. Chem.*, 1936, 115, 207—210).—Autolysis of the liver-tissue at room temp. for 15 min. hydrolyses labile nucleotide with production of inorg.  $\text{PO}_4'''$ . During 4 hr. autolysis there is a further but slower increase in inorg.  $\text{PO}_4'''$  due to breakdown of more stable acid-sol. esters. Occasionally there is an increase due to breakdown of the residual or nucleic acid fraction. The phospholipids are unchanged.

J. N. A.

**Enzymic hydrolysis of lactoflavinphosphoric acids.** H. RUDY (*Z. physiol. Chem.*, 1936, 242, 198—200).—Lactoflavinphosphoric acid (I), prepared by vigorous action of  $\text{POCl}_3$  on lactoflavin (II), in addition to lacking growth-promoting properties is much more slowly hydrolysed by glycerol extract of rat's intestine than are the acids from heart and yeast and the acid (III) obtained from (I) by gentle action of  $\text{POCl}_3$ , although the final extent of hydrolysis is the

same in all cases. The acids from heart and yeast and (III) are hydrolysed at the same rate.  $\alpha$ -Glycerophosphatase (IV) attacks these three equally rapidly but (I) much more slowly.  $\beta$ -Glycerophosphatase acts does (IV). Cytoflavin (V) from heart is identical with the acid from yeast. Interaction of (II) with  $\text{POCl}_3$  produces phosphoric esters not identical with (V).

W. McC.

**Aldolase.**—See this vol., 1232.

**Enzymes of lactic acid fermentation and glycogenolysis.** R. LOHMANN (*Arch. exp. Path. Pharm.*, 1936, 182, 239—242).—Muscle-pulp from animals showing muscle-glycogenolysis [indicated by creatinuria (Brentano, A., 1932, 83)] has a lactic acid (I) production (normal or increased by caffeine) similar in velocity and extent to that of muscle from normal animals. Hence the enzymes producing (I) are not influenced by depletion of muscle-glycogen.

F. O. H.

**Separation of glyoxalase activity and glycolytic activity by means of radium radiation.** H. G. CRABTREE (*Biochem. J.*, 1936, 30, 1622—1629).—The anaerobic glyoxalase (I) activity of normal and tumour rat tissue is measured. All tissues including pancreas showed considerable activity, particularly tumour tissue, with which the activity was of the same order as the anaerobic glycolysis. Ra radiation applied at low temp. to these tissues suppressed the anaerobic glycolysis almost completely whilst (I) activity was unaffected. Total suppression with rat retina (the most sensitive tissue) was effected in 1—2 hr.

P. W. C.

**Activation and inhibition of zymoheaxase.** E. BAUER (*Z. physiol. Chem.*, 1936, 242, 15—18; cf. this vol., 894).—The inactivation of zymoheaxase (I) solutions on diluting is not due to destruction of (I) but to heavy metals, since elimination of metals and activation (at first  $\propto$  amount of activator) follow addition of KCN,  $\text{H}_2\text{S}$ , cysteine, glutathione, and activator from muscle. Inactivation is produced by  $\text{Cu}^{++}$  (irreversible),  $\text{Ag}^+$ ,  $\text{Hg}^{++}$ , and  $\text{Zn}^{++}$ . Activation is not (or at least not exclusively) due to production of a cyanohydrin or similar compound.

W. McC.

**Alcoholic fermentation in the intact enzyme system of the yeast cell and in the disorganised zymase system.** I. R. NILSSON and F. ALM (*Biochem. Z.*, 1936, 286, 254—278).—The influence of various  $[\text{PO}_4''']$  and temp. on the course of the fermentation curve is investigated using fresh and dried yeast. Without  $\text{PO}_4'''$  addition the course is approx. the same for both yeasts, but with dried yeast or maceration juice on adding  $\text{PO}_4'''$  a deflexion in the curve which is independent of sugar concn. or  $[\text{PO}_4''']$  occurs when 50% of the added sugar has been fermented to  $\text{CO}_2$ . Similar results are obtained with sucrose, the deflexion being more clearly defined at  $40^\circ$  than at  $30^\circ$  and corresponding with the max. of phosphorylation although 28% of the added  $\text{PO}_4'''$  is still unesterified. Hexose diphosphate is probably not a normal intermediate product during fermentation with the intact cell, the velocity of its fermentation being small. Schemes are given for the reactions occurring with varying amounts of  $\text{PO}_4'''$ .

P. W. C.



**Phosphorylation in living yeast.** M. G. MACFARLANE (Biochem. J., 1936, 30, 1369—1379).—During the fermentation of sugar the acid-sol.  $\text{PO}_4'''$  of fresh brewery yeast first decreases, then remains fairly const., and finally regains the original level when fermentation ceases. The compound produced by the disappearing  $\text{PO}_4'''$  is possibly acid-insol. A method for the successive extraction of P compounds from fresh yeast is described. Aq.  $\text{CCl}_3\text{-CO}_2\text{H}$  extract of fresh yeast contains  $\text{PO}_3'$  but apparently not hexose mono- or di-phosphate. Approx. 30% of the total P of yeast is present as a complex containing Fe, a nucleic acid (I) (possibly ribonucleic), and  $\text{PO}_3'$ . The complex may be identical with Kossel's plasmic acid (A., 1893, i, 680). The  $\text{PO}_3'$  of the (I) fraction is converted into  $\text{PO}_4'''$  during the autofermentation of yeast in presence of PhMe.

W. McC.

**Influence of the substrate on the respiration of and fermentation by yeast cells.** W. LIBBRECHT (Natuurwetensch. Tijds., 1936, 18, 84).—Increase in the pressure of  $\text{O}_2$  inhibits the fermentation of glucose and  $\text{AcCO}_2\text{H}$ . With  $\text{AcOH}$ ,  $(\text{CH}_2\text{-CO}_2\text{H})_2$ , and  $\text{EtOH}$  there is a slight inhibitive action, whilst with lactic acid fermentation is increased. This inhibition is the greater, the more easily the substrate ferments under atm. pressure.

D. R. D.

**Alcoholic fermentation of various sugars.** G. AMADIO (Annali Chim. Appl., 1936, 26, 258—262).—Determinations of  $\text{EtOH}$ , glycerol, acidity, and  $\text{CO}_2$  formed by the action of *Saccharomyces cerevisiae*, Hansen, and of *S. ellipsoideus*, Hansen, indicate that glucose, fructose, galactose (I), sucrose, maltose, mannose, and raffinose (II) are readily fermented except that (I) is unattacked and (II) only to the extent of approx.  $\frac{1}{3}$  by *S. ellipsoideus*.

F. O. H.

**Phytochemical reduction of triketopentane.** C. NEUBERG and W. M. CAHILL (Enzymologia, 1936, 1, 142—144).—Yeast reduces  $\text{COAc}_2$  to *s*-dimethylglycerol.

E. D. Y.

**Nitrogen assimilation of yeast.** VII. Ability of yeast to assimilate amino-acids. N. NIELSEN (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 16, 395—425; cf. this vol., 1026).—N assimilation is determined by the decrease of N in solution, not by the growth of the yeast, as the latter does not necessarily depend on assimilation of N. Addition of a growth-promoting factor, e.g., beer wort, is essential. Of the 27  $\text{NH}_2$ -acids examined, 12 are completely assimilated and 8 are not assimilated. Partial assimilation is due, in *dl*-mixtures, to assimilation of one stereoisomeride only, and with *l*-tryptophan, *l*-histidine, and *d*-arginine to the assimilation of the  $\text{NH}_2\text{-N}$  only.

E. A. H. R.

**Relationship between the metabolism of yeast and lactic acid bacteria and the oxidation-reduction potential of the medium.** A. J. KLUYVER and J. C. HOOGERHEIDE (Enzymologia, 1936, 1, 1—21).— $E_h$  at  $p_H$  5.2 of suspensions of *Saccharomyces cerevisiae* depends on the nature of oxidation-reduction dye added. Nile-blue and chloraphin (0.001%) give characteristic  $E_h$  for yeast of  $-43$  mv. These dyes cause no marked change in anaerobic

glycolysis;  $E_h$  is const. and independent of dye concn. Vals. for other yeast strains vary from  $-27$  to  $-43$  mv. In aerobic glycolysis,  $E_h$  is a function of R.Q. and not  $Q_{O_2}$  (cf. A., 1934, 1138). 18 types of lactic acid bacteria give  $r_H$  vals. of 5—6 in milk cultures with universal reduction-oxidation mixture.

E. D. Y.

**Biological role of hydroxylamine.** IV. Utilisation of hydroxylamine salts by *Aspergillus niger*. V. Production of hydroxylamine by *A. niger* at the expense of nitrate- and ammonia-nitrogen. M. LEMOIGNE, P. MONGUILLON, and R. DESVEAUX (Bull. Soc. Chim. biol., 1936, 18, 1291—1296, 1297—1303; cf. this vol., 639).—IV.  $\text{NH}_2\text{OH}$  retards the growth of *A. niger* only in concns. of  $<0.1$ — $0.2\%$ . The mould grown in a medium of  $\text{NH}_4\text{NO}_3$  produces  $\text{NH}_2\text{OH}$  and even when the latter is the only source of N, synthesis of protein occurs with evolution of  $\text{NH}_3$ .

V. *A. niger* can form  $\text{NH}_2\text{OH}$  by oxidation of  $\text{NH}_3$  or reduction of  $\text{NO}_3'$ ; various theories concerning the role of  $\text{NH}_2\text{OH}$  in the synthesis of proteins are discussed.

H. D.

**Isolation and identification of *B. coli*.** G. MONTALDO (Boll. Soc. ital. Biol. sperim., 1936, 11, 181).—The characteristic appearance of colonies of *B. coli* grown in neutral or slightly alkaline 30% lactose-agar containing 0.005—0.01% of Congo-red is described.

F. O. H.

**Formation of alcohol from pentoses.**—See B., 1936, 758.

**Acetone-butanol fermentation.** IX. Isolation of organism. B. ROKUSHO (J. Agric. Chem. Soc. Japan, 1936, 12, 639—649).—The organism (isolated from corn and apparently a strain of *Clostridium acetobutylicum*) ferments many sugars and polysaccharides, but not Ca lactate, inulin, glycerol, isodulcitol, trehalose, or melibiose. From corn, rice, and millet it produces 10—11% of  $\text{COME}_2$ , 20—22% of  $\text{BuOH}$ , and traces of  $\text{EtOH}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and org. acids. It utilises animal or vegetable protein, peptone, glutamic acid, and  $\text{NH}_4$  salts. It reduces  $\text{NaNO}_2$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , methylene-blue, and Me-red.

J. N. A.

**Synthesis of cellulose by *Acetobacter xylinum* from various polyalcohols.** Y. KHOUVINE (Bull. Soc. Chim. biol., 1936, 18, 1325—1335).—The yield of cellulose by *A. xylinum* cultured in media containing different polyalcohols ( $\text{C}_3$ — $\text{C}_7$ ) was highest with arabitol (I) and least with erythritol,  $\alpha$ - and  $\beta$ -glucoheptitol, and perseitol. In the  $\text{C}_6$  group, dulcitol (II) and mannitol (III) were more productive than sorbitol. The ratio of  $\text{CO}_2$  produced to  $\text{O}_2$  consumed corresponded with that required for combustion of the alcohol in the case of (I), (II), and (III) whereas in the other cases,  $\text{O}_2$  was apparently used chiefly in the synthetic processes. In general the yield of ketose corresponded with 80—90% of the alcohol consumed. In the case of heptitols, a substance which reduced alkaline Cu reagent in the cold without giving a  $\text{NaHSO}_3$  compound was present in addition to the expected ketose.

H. D.

**Nodule-bacteria. X. Influence of stimulating substances, especially alkaloids, on growth and morphology of nodule-bacteria.** A. ITANO and A. MATSUURA (J. Agric. Chem. Soc. Japan, 1936, 12, 604—621).—Guanidine (I), morphine hydrochloride (II), and anthraquinone were not harmful to growth;  $C_5H_5N$  and strychnine were slightly toxic, whilst quinine and, to a smaller extent, brucine and quinine prohibited growth. No correlation occurred between concn. of stimulant and degree of morphological variation. Caffeine was most effective in producing large bacteroids in all strains of bacteria, whilst (I) and (II) were effective only in certain cases. J. N. A.

**Morphology and physiology of soil *Azotobacter*.** S. WINOGRADSKY (Compt. rend., 1936, 203, 10—13; cf. A., 1932, 437).—*Azotobacter* (I) grown on  $SiO_2$  gel can utilise not only sugars but alcohols, and fatty acids (and their salts) with 2—4 C, which are end products of fermentation, and in the absence of  $NH_3$ - or  $NO_3$ -N grow to the exclusion of other bacterial strains. Benzoates are not utilised probably because of their low concn. in soil. Different strains of (I), though belonging to the same subgroup, show considerable adaptability to, and divergence in, their choice of nutrient media, and by making cultures of different composition with respect to the source of C, pure strains of (I) are obtained. J. L. D.

**Decomposition of adenine compounds by bacteria.** C. LUTWAK-MANN (Biochem. J., 1936, 30, 1405—1412).—Fresh and sterilised (PhMe) suspensions of *B. coli* (and certain other bacteria) aerobically and anaerobically deaminate adenosine (I) and adenine (II) and deaminate and dephosphorylate adenosinetriphosphoric acid (III) (optimal  $pH$  7.2) and muscle- (IV) and yeast-adenylic acid (V) with production of hypoxanthine but not of ribose. Dephosphorylation probably precedes deamination in (III) and (IV). The decomp. of (III) is accelerated, but that of (I) and (IV) is unaffected by  $Mg^{++}$ . The decomp. of (V) proceeds at a different rate from that of (IV) especially with *B. coli* grown in aq. glucose. NaF and  $CH_2I-CO_2H$  do not inhibit the decomp. of (III), (IV), and (V). (I) is more rapidly deaminated (optimal  $pH$  8.8) than (II) and than other (II) derivatives. Deamination of (I) and (II) is stimulated by  $PO_4'''$  (and  $AsO_4'''$ ), that of (II) being very incomplete (20%) in absence of  $PO_4'''$ . (III), but not adenylic acid, occurs in *B. coli*. W. McC.

**Spectrum of light emitted by *Photobacterium phosphoreum* and by some chemiluminescent reactions.** J. G. EYMERS and K. L. VAN SCHOUWENBURG (Enzymologia, 1936, 1, 107—119).—The spectral energy distribution of the bacterium is independent of external conditions and identical with that of dimethyldiacridyl nitrate during oxidation and fluorescence. Data for 3-aminophthalhydrazide are also given. E. D. Y.

**Geological significance of thermophilic bacteria.**—See this vol., 1226.

**Extraction of bacteriophage *coli* (S) by ether.** J. VOET (Compt. rend. Soc. Biol., 1936, 122, 1248—1249).—The lytic principle is insol. in  $Et_2O$ . H. G. R.

**Action of heavy water on bacteria.** K. HANSEN and E. BLEGEN (Klin. Woch., 1935, 14, 1113; Chem. Zentr., 1935, ii, 3351).—92—94%  $D_2O$  showed no sign of toxic action on staphylococci or typhus bacilli in 70 days. J. S. A.

**Avidity of solusalvarsan.** R. SCHNITZER (Wien. med. Woch., 1935, 85, 1063—1065; Chem. Zentr., 1935, ii, 3406).—Solusalvarsan acts on trypanosomes which have low sensitivity towards other As compounds as a result of As fixation. A. G. P.

**Chemistry of the ductless glands.** E. C. DODDS (Chem. and Ind., 1936, 642—646).—A lecture.

**Chemical structure in relationship to hormone and biological activity.** E. C. DODDS (Helv. Chim. Acta, 1936, 19, Spec. No., 49—58).—A lecture.

**Biochemistry of the germinal gland hormones.** A. BUTENANDT (Naturwiss., 1936, 24, 529—536, 545—552).—A lecture.

**Subconjunctival iron deposits after adrenaline injections.** T. GUNDERSON (Amer. J. Ophthalmol., 1934, 17, 807—808).—The deposits remaining at the site of injections consist of complex salts formed from  $FeCl_3$  and adrenaline (I). Fe is dissolved from hypodermic needles by (I) hydrochloride ( $pH$  5.6).

CH. ABS. (p)

**Hormone content of the pituitary of the blue whale (*Balaenoptera Sibbaldii*).** III. Growth hormone. J. VALSO (Klin. Woch., 1935, 14, 1183—1184; Chem. Zentr., 1935, ii, 3668; cf. A., 1935, 1544).—The growth hormone content per unit wt. of anterior pituitary is of the same order as that in cattle. A. G. P.

**Evaluation of the thyrotropic hormone of the human pituitary.** R. MÜLLER, H. EITEL, and A. LOESER (Klin. Woch., 1935, 14, 1296; Chem. Zentr., 1935, ii, 3399—3400).—The presence of the hormone in the human pituitary is demonstrated (guinea-pig test). The amount is not related to age or sex, or to the structure of the thyroid, but is high in certain diseases. A. G. P.

**Effect of sex hormones on the vitamin-C content of the adrenals and liver of guinea-pigs.** J. MOSONYI (Z. physiol. Chem., 1936, 242, 158—164).—The vitamin-C content of these organs of male guinea-pigs is reduced 30—40% by injection of the male hormone (I) and that of the organs of females is equally reduced by injection of follicular hormone (II). (I) has no effect on the -C content in females but (II) has a considerable reducing effect on the -C content of male organs. W. McC.

**Influence of menformone treatment on the urinary elimination of the male hormone.** F. DINGEMANSE [with H. BORCHARDT] (Acta Brev. neerl. Physiol., 1935, 5, 94—97; Chem. Zentr., 1935, ii, 3668).—Administration of menformone to man had no influence on the amount of male hormone in the urine. A. G. P.

**Effect of the crystalline male hormone on the histological structure of the comb in capons.** F. DESSAU (Acta Brev. neerl. Physiol., 1935, 5, 94; Chem. Zentr., 1935, ii, 3668).—Application to the



comb of androsterone or testosterone for 14 days stimulated its growth. A. G. P.

**Action of various male hormones on hypophysectomised animals.** J. FREUD (Acta Brev. neerl. Physiol., 1935, 5, 97—98; Chem. Zentr., 1935, ii, 3668).—Androsterone, with or without an uncharacterised substance (X) from testicles, has no action on hypophysectomised castrated male rats. Dihydroandrosterone and a conc. testosterone prep. produced positive effects which were intensified by addition of X. A. G. P.

**Effect of male sex hormone on respiration of sex-organs in castrated rats.** Y. WANG, H. WU, and C. Y. CHOU (Chinese J. Physiol., 1936, 10, 403—405).—The respiration rates (measured on surviving tissue after decapitation) of the seminal vesicles, preputial gland, and prostate of rats are lower in castrated than in normal rats but are increased (especially in the seminal vesicles) by prior administration of male sex hormone. W. O. K.

**Bi-sexual hormone (dehydroandrosterone).** D. VAN STOLK and H. PÉNAU (J. Pharm. Chim., 1936, [viii], 24, 155—162).—4 mg. of dehydroandrosterone (I) when injected simultaneously with  $1 \times 10^{-6}$  g. of folliculin (II) into castrated rats completely masked the action of (II). The active threshold for (I) is approx. 2 mg. for rats standardised to  $1.5 \times 10^{-6}$  g. of (II). Transformation of male into female hormones by dehydrogenation is not effected in the ovary. The constitution and physiological action of some sex hormones are discussed. J. N. A.

**Action of follicular hormone on bones. I. Variation in weight. II. Calcium content.** E. LIPPMAHN and U. DACHA (Boll. Soc. ital. Biol. sperim., 1936, 11, 79—81, 81—82).—I. Injection of large doses of the hormone into rabbits fed on diets rich in Ca increases the content of org. matter (loss on ashing) in the bones; with diets poor in Ca, the results are inconclusive.

II. With both diets, the bone-Ca tends to increase. F. O. H.

**Follicular content of urine in childbed.** G. TATA (Russ. Clin. Terap. Sci. affini, 1935, 34, 115—123; Chem. Zentr., 1935, ii, 3399).—A direct relationship is indicated between the *post partum* elimination of folliculin and the reappearance of menstruation. A. G. P.

**Acid-hydrolysable combined form of pregnandiol in human pregnancy urine.** A. D. ODELL and G. F. MARRIAN (Biochem. J., 1936, 30, 1533—1535).—Bu<sup>4</sup>OH extract of the urine after washing with aq. NaOH contains combined pregnandiol (I) insol. in Et<sub>2</sub>O. The complex is stable to hot alkali but is hydrolysed by hot acid. The best yield of crude free (I) was obtained by heating for 2 hr. at 120° at  $p_H$  1.5. (I) is slowly decomposed by prolonged boiling in aq. acid. W. McC.

**Urine of ovariectomised women contains only the auxogenic factor.** E. GUYÉNOT, E. HELD, A. MOZKOWSKA, and H. DE STOUTZ (Compt. rend. Soc. Biol., 1936, 122, 1152—1154). H. G. R.

**Synthetic preparation of oestrone (theelin).**—See this vol., 1256.

**Oestrogenic activity of synthetic polycyclic compounds.**—See this vol., 1247.

**Blood-lactic acid following administration of insulin in cats without the adrenal medulla.** A. H. SCOTT and B. N. BERG (J. Biol. Chem., 1936, 115, 163—169).—The blood-lactic acid curve closely follows that of the blood-sugar. J. N. A.

**Relation of the adrenal medulla to the effect of insulin on purine metabolism.** P. S. LARSON and G. BREWER (J. Biol. Chem., 1936, 115, 279—284; cf. A., 1935, 790).—Adrenalectomy prevents the increased excretion of allantoin by dogs due to injection of insulin, but is without influence on that due to adrenaline injection. H. D.

**Glucagon, the hyperglycæmia-producing substance of the pancreas.** M. BÜRGER and W. BRANDT (Z. ges. exp. Med., 1935, 96, 375—397; Chem. Zentr., 1935, ii, 3401).—The initial increase in blood-sugar caused by technical preps. but not by cryst. insulin (I) is due to glucagon (II). A conc. prep. of (II) is described. (II) is similar to (I) in physical and chemical properties and composition, but differs from it in not being inactivated by NaOH or cysteine. A. G. P.

**Influence of insulin on experimental lipæmia.** A. I. LEWIN (Z. ges. exp. Med., 1935, 96, 532—547; Chem. Zentr., 1935, ii, 3400—3401).—Administration to dogs of cholesterol (I) in vegetable oil increases the lipin content of the blood with accompanying hypercholesterolaemia. The latter diminishes after cessation of (I) treatment or on administration of insulin (II). In normal lipæmia and hypercholesterolaemia large dosages of (I) are necessary to produce this effect. An antagonistic action between blood-sugar and -(I) is indicated. No evidence of the conversion of fat into carbohydrate in the blood under these conditions was obtained. A. G. P.

**Habituation to insulin.** F. MAINZER and W. JOEL (Wien. klin. Woch., 1935, 48, 1040—1043; Chem. Zentr., 1935, ii, 3669—3670).—During insulin cures the dosage is necessarily increased. Initial symptoms of overdosage do not appear at later stages even with larger doses. The blood-sugar curve returns more quickly to normal. After interruption of treatment carbohydrate tolerance is lowered, although the hypoglycæmia produced by insulin and the rapidity of its appearance are not affected by acclimatisation. A. G. P.

**Variations in the chlorine content of the blood and nervous system [of rabbits] under the influence of insulin.** J. GARCIA-BLANCO and C. MASA (Anal. Fis. Quím., 1934, 32, 1021—1027).—The Cl content of the blood increases markedly, whereas that of the centre of the brain and that of the cerebellum increase only slightly and that of the cerebral cortex not appreciably. D. R. D.

**Synthesis of peptides. Structure and amide-nitrogen of insulin.**—See this vol., 1236.

**Thyroid function and detection of thyroid hormone in pregnancy.** (A) W. NEUWEILER. (B) K. J. ANSELMINO and F. HOFFMANN (Arch. Gynakol., 1935, 159, 574—579, 580—584; Chem. Zentr., 1935, ii, 3669).—(A) The work of Anselmino

and Hoffmann (A., 1935, 1270) is criticised. Hyperthyroidism is not a normal condition of pregnancy. Increased production by the thyroid is conditioned by the greater hormone requirement in pregnancy.

(B) A reply. A. G. P.

**Occurrence in the thyroid gland of a substance containing iodine and having antithyroxine activity.** I. ABELIN (Biochem. Z., 1936, 286, 160—181).—A peptone containing I and free from thyroxine was isolated from the Ba(OH)<sub>2</sub>-hydrolysate of thyroid gland tissue. The substance is extremely active, causes lowering of basal metabolism and general improvement of hyperthyroidised animals, can be given orally, and on further degradation yields di-iodotyrosine. The effect cannot be explained by I content. P. W. C.

**Heart size during and after feeding thyreoidin.** K. SECHER and J. VESTERDAL-JORGENSEN (Acta med. Scand., 1935, 86, 76—81; Chem. Zentr., 1935, ii, 3400).—Heart-wt. increases 4—8% during feeding of thyreoidin and slowly regains normal wt. on cessation of feeding. A. G. P.

**Combined action of thymus and irradiated ergosterol and the thymus of ergosterol-treated animals on experimental rickets.** M. MESSINI (Boll. Soc. ital. Biol. sperim., 1932, 7, 941—944; Chem. Zentr., 1935, ii, 3671).—Simultaneous administration of thymus extract accelerated the curative action of ergosterol (I). Thymus from animals pretreated with (I) was more active than that of normal animals, in respect of improved Ca fixation. A. G. P.

**Healing of bone fractures in relation to the effect of thymus and the lime-fixing vitamin.** M. MESSINI and M. COPPO (Boll. Soc. ital. Biol. sperim., 1932, 7, 947—950; Chem. Zentr., 1935, ii, 3671).—Thymus deficiency retards healing and its absence prevents the beneficial action of irradiated ergosterol. A. G. P.

**Occurrence of callicrein in salivary glands and saliva.** E. WERLE and P. VON RODEN (Biochem. Z., 1936, 286, 213—219).—Submaxillary saliva always contains callicrein (I) in considerable amounts, the amount in man and dog being < and in pig, ox, and cat > that in the respective pancreatic juice. (I) is present in smaller amounts in parotid and sublingual saliva, and is absent from parotid saliva of ox. P. W. C.

**Antigonadotropic action of epiphysan.** P. ENGEL (Wien. klin. Woch., 1935, 48, 1160—1161; Chem. Zentr., 1935, ii, 3401).—Epiphysan, from the pineal body of cattle, contains 80 rat units of the hormone per ampoule. A. G. P.

**Changes in carotene-vitamin-A economy in myxoedema and in cretins.** H. WENDT (Munch. med. Woch., 1935, 82, 1679—1681; Chem. Zentr., 1935, ii, 3670).—In human hyperthyrosis there is a marked decrease in carotene (I) and (especially) vitamin-A in serum. Vals. increase after administration of I, or after thyroid operation. In exophthalmic goitre administration of large amounts of -A induce considerable wt.-increases and a return of basal exchange to nearly normal vals. In myxo-

dema the transition of (I) into -A is disturbed when large amounts of (I) are given. In cretins serum-A is low. A. G. P.

**Carotene and vitamin-A.** B. BOTTA (Boll. Soc. ital. Biol. sperim., 1932, 7, 907—911; Chem. Zentr., 1935, ii, 3670).—Pure carotene possesses, in itself, all the biological properties of vitamin-A. A. G. P.

**Microscopical detection of vitamin-A in animal tissues. Paraplasmaic liver-cell inclusions.** III. F. R. VON QUERNER (Klin. Woch., 1935, 14, 1213—1217; Chem. Zentr., 1935, ii, 3670—3671).—Fatty inclusions in liver parenchyma, adrenals, pituitary, and retinal fat globules contain a microscopically fluorescent substance, destroyed by ultraviolet light and generally exhibiting spectral properties resembling those of vitamin-A. None occurs in rats receiving an -A-free diet. It is regarded as a storage form corresponding with factor A. A. G. P.

**Blood-sugar level in avitaminosis-A.** B. BOTTA (Boll. Soc. ital. Biol. sperim., 1932, 7, 912—916; Chem. Zentr., 1935, ii, 3670).—A vitaminosis-A probably induces a change in carbohydrate metabolism. A. G. P.

**Hypervitaminosis-B.** V. Complement action of the blood. L. BUTTURINI and R. VAILATI. VI. Cholesterolæmia. VII. Glycolytic activity of the blood. L. BUTTURINI and D. PENSOTTI. VIII. Variations in glycæmia. A. ALLEGRI (Boll. Soc. ital. Biol. sperim., 1936, 11, 36—39, 39—40, 41—42, 42—45).—V. Hypervitaminosis-B in rabbits due to crude vitamin-B preps. has an anti-complementary action in hæmolysis; cryst. -B, however, is ineffective.

VI. Blood-cholesterol is increased up to >100% by administration of large amounts of -B.

VII. Blood-glycolysis increases to a varying extent.

VIII. Blood-sugar either rises or falls, alimentary hyperglycæmia is intensified and accelerated, whilst adrenaline hyperglycæmia (especially with large doses) is diminished. F. O. H.

**Effect of extra supply of vitamin-B<sub>1</sub> on children.** M. ISHII (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 581—589).—Addition of purified vitamin-B<sub>1</sub> to the normal diet of children slightly increased the rate of growth. W. O. K.

**Synthesis of vitamin-B<sub>1</sub>.**—See this vol., 1276.

**Mechanism of formation of vitamin-C in the [eye] lens.** H. K. MÜLLER (Klin. Woch., 1935, 14, 1498—1499; Chem. Zentr., 1935, ii, 3671).—Synthesis of -C in the lens probably involves phosphorylation of sugar under the influence of glutathione. A. G. P.

**Ascorbic acid as catalyst in the oxidation of unsaturated fats.** P. HOLTZ (Arch. exp. Path. Pharm., 1936, 182, 98—108).—Autoxidation of linseed oil (emulsified with aq. gum) is accelerated by addition of normal (but not oxidised) ascorbic acid (I). The effect, which at  $p_H$  7.4 is > that at  $p_H$  5.0, is inhibited by HCN and also by CuSO<sub>4</sub>, the *per-se* accelerating action of which is also inhibited. The disappearance of the inhibitory action of reduced (I)+CuSO<sub>4</sub> with time is explained by the high catalytic activity of oxidised (I)+CuSO<sub>4</sub>. The



bearing of the results on *in-vivo* processes is discussed. F. O. H.

**Induction effect of ascorbic acid on the oxidation of sugar.** P. HOLTZ (Arch. exp. Path. Pharm., 1936, 182, 109—111).—The spontaneous oxidation of fructose, glucose (in presence of Cu), and glyceraldehyde in neutral  $\text{PO}_4'''$  buffer is accelerated by presence of ascorbic acid, the action of which, however, is not truly catalytic as it is itself at least partly oxidised. F. O. H.

**Ratio of dehydroascorbic to ascorbic acid in tissues after administration of thyroxine.** E. MARTINI and F. COPELLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 73—74).—Administration of thyroxine to guinea-pigs decreases the ascorbic acid and increases the dehydroascorbic acid content of liver and adrenals. F. O. H.

**Ratio of dehydroascorbic to ascorbic acid in the heart after administration of parasympatheticotropic substances.** F. COPELLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 75—77).—The ratio is decreased (in guinea-pigs) by parasympathetic stimulants (*e.g.*, acetylcholine) and increased by paralytics (*e.g.*, atropine) (cf. this vol., 375). F. O. H.

**Vitamin-C content of Szechwan fruits and vegetables.** Y. T. CHANG and H. B. COLLIER (Chinese J. Physiol., 1936, 10, 435—443).—The methods of Birch *et al.* (A., 1933, 646) and Bessey and King (A., 1934, 227) have been applied to the determination of the ascorbic acid (I) content of various fruits and vegetables. The "hairy pear" (*Actinidia chinensis*) is considerably richer in (I) than the various citrus fruits. W. O. K.

**Fate of dehydroascorbic acid in the organism.** M. BULOW (Z. physiol. Chem., 1936, 242, 40—42).—Oxidised ascorbic acid (I) injected into guinea-pigs on a diet poor in (I) is reduced in the organism and stored there or excreted in the urine. In some of the organs the increase in the (I) content after injection of reduced (I) is < that after injection of oxidised (I). W. McC.

**Passage of vitamin-C into the cerebrospinal fluid and the aqueous humour.** H. GOLDMANN and W. BUSCHKE (Klin. Woch., 1935, 14, 1326; cf. Tatsumi *et al.*, this vol., 1033). R. N. C.

**Avitaminosis-C and pregnancy.** M. LAPORTA and E. RINALDI (Boll. Soc. ital. Biol. sperim., 1936, 11, 141—143).—Pregnant guinea-pigs are unable to synthesise vitamin-C (cf. Mouriquand and Schoen, Compt. rend., 1933, 197, 203). F. O. H.

**Have sucklings a specialised vitamin-C metabolism?** U. HÄHN (Z. Kinderheilk., 1935, 57, 442—445; Chem. Zentr., 1935, ii, 3404).—Urinary elimination of vitamin-C following a diminished intake affords no evidence of a specialised -C metabolism or auto-synthesis. A. G. P.

**Blood-serum, -protein, and vitamin-C.** E. SCHNEIDER and E. WIDMANN (Klin. Woch., 1935, 14, 1454—1456; Chem. Zentr., 1935, ii, 3404).—Therapeutic administration of vitamin-C lowers (but not regularly) the globulin-N and increases the albumin-N of blood without decrease in sedimentation

rate. Serum of young contains more -C than that of old animals. Hypovitaminosis is not always detectable by serum analysis. Thyrotropic hormone given with -C increases the size and wt. of the adrenals by development of the medulla. A. G. P.

**Decomposition of ascorbic acid.**—See this vol., 1231.

**Chemical determination of vitamin-C.** Z. KOŁODZIEJSKA (Arch. Chem. Farm., 1934, 1, 244—252).—Tillmans' reagent gives results in agreement with biological assay for a no. of fruit juices. In some juices, oxidising and reducing agents other than ascorbic acid may vitiate results, and biological methods are necessary. CH. ABS. (p)

**Formation of vitamin-D by cathode rays.** R. M. HOFFMAN and F. DANIELS (J. Biol. Chem., 1936, 115, 119—130).—Ergosterol (I) acquires antirachitic properties when subjected to high-voltage cathode rays. The effect due to accompanying X- and ultra-violet rays is small. The cathode rays also have a strong destructive action and the antirachitic potencies produced are considerably < those from ultra-violet irradiation. One high-velocity electron produces <1 mol. of vitamin-D, but decomposes about 80 mols. of (I). Anomalous effects in the early stages of activation support the view the (I) is changed into an isomeride prior to vitamin formation. J. N. A.

**Spectrographic evaluation of solutions of vitamin-D in fats.** L. FUCHS [with Z. BECK] (Pharm. Presse, 1935, 40, 411—416, 432—440, 447—449; Chem. Zentr., 1935, ii, 3671—3672).—Ultra-violet absorption spectra are examined. Preps. are preferably dissolved in benzine or 96% EtOH. Storage in air-filled vessels for 12—14 months results in 15—19% loss of activity of the solutions. Solutions in sesame oil cannot be analysed directly by this method; the interfering substance (sesamin) is removed by triple extraction with an equal vol. of 90% AcOH. With >0.3 mg. of -D per g. of oil the method becomes inaccurate. In the presence of white P, solutions of -D lost little activity during 6 months. A. G. P.

**Constitution of vitamin-D<sub>2</sub>.**—See this vol., 1247.

**Poplar bud.** G. BRUCH and E. H. WIRTH (J. Amer. Pharm. Assoc., 1936, 25, 672—682).—The morphology and histology of the buds of *Populus balsamifera*, *P. nigra*, and *P. candicans* are described. The leaf-buds are more sol. in EtOH than are the flower-buds. F. O. H.

**Frost-hardening with living cells. I. Osmotic and bound-water changes in relation to frost-resistance and the seasonal cycle.** J. LEVITT and G. W. SCARTH (Canad. J. Res., 1936, 14, C, 267—284).—The plasmolytic method is utilised to determine the osmotic pressure and the non-osmotically active portion of the cell content. Cabbage cells probably contain no bound H<sub>2</sub>O. In cells of *Catalpa* the non-active fraction occupies a relatively larger proportion of the vacuole than of the protoplasm, and its increase in the vacuole during hardening is the principal characteristic of the process. High osmotic vals. in woody plants during winter are due

not only to production of sugar from starch but also to increased bound  $H_2O$ . The latter operates by preventing the freezing of the vacuole rather than by minimising the dehydration of protoplasm.

A. G. P.

Living geranium leaf emits a fluorescent radiation which extends in the infra-red to 830  $m\mu$ . C. DHERE and O. BIERNACHER (Compt. rend., 1936, 203, 412—414; cf. A., 1935, 671).—Repetition of the previous experiment using an infra-red plate gives a band with axis at  $\lambda$  740; longer exposure gives another brilliant band with axis at  $\lambda$  812 and extending to 830.5.

J. N. A.

Hydrogen-ion phenomena in tobacco. J. CALVERT (J. Austral. Inst. Agric. Sci., 1936, 2, 83—84).—Buffer curves of aq. extracts of cured leaves and of expressed sap of fresh leaves are recorded. Differences between curves for Australian and American tobaccos are shown.

A. G. P.

Role of potassium and phosphorus in the assimilation of different forms of nitrogen by plants.—See B., 1936, 708.

Absorption of manganese by plants. II. Toxicity of manganese to various species. C. OLSEN (Compt. rend. Trav. Lab. Carlsberg, 1936, 21, No. 9, 129—145; cf. A., 1934, 1048).—In  $H_2O$  cultures growth inhibition by Mn occurs at threshold concns. of 0.5—62.5 mg. per litre according to the species of plant. Plants frequently absorb larger amounts of Mn from nutrients containing low than from those containing high [Mn]. Stimulative effects on maize are shown by 0.1—12.5 mg. of Mn per litre. Toxic effects of Mn on *Hordeum distichum* were more marked at  $pH$  4.0 than at  $pH$  6.0. The role of Mn in controlling the flora of acid soils, and the antagonism of Mn and Ca in plant nutrition, are discussed.

A. G. P.

Nitrogen metabolism of the apple fruit. III. Effect on the composition of the fruit of injecting nitrogenous compounds into the tree. A vacuum extractor. A. C. HULME and W. A. ROACH (Biochem. J., 1936, 30, 1397—1404; cf. this vol., 531).—Injection of solutions of  $NH_4NO_3$ , urea, or asparagine (I) into apple trees resulted in increased total N content and altered N distribution (increase chiefly in non-protein N) in the fruit. Fruit stored at 9.5° after detaching from trees injected with aq.  $NH_4NO_3$  or (I) did not synthesise protein whereas fruit from untreated trees synthesised considerable amounts. A rapid continuous vac. extractor of the Soxhlet type is described.

W. McC.

Comparative action of acetaldehyde vapour on the cellular structure and sugar content of some vegetable tissues. M. MASCRÉ and R. R. PARIS (Compt. rend., 1936, 203, 113—115; cf. A., 1920, i, 584).—The syringoside (I) content of privet leaves in an atm. saturated with acetaldehyde (II) is unchanged during 1 hr., but the concn. of sugar (III) increases 10%. Subsequent exposure to air for 3 hr. causes (I) to decrease by 50% and (III) to return to normal. Similar results are obtained with *Aucuba* and cherry-bay leaves, but prolonged exposure to (I) vapour abolishes the effect. The results closely

parallel the changes in cell structure (Mascre, this vol., 1165), and suggest the interdependence of the destruction of chondriosomes and the initiation of enzymic hydrolysis.

J. L. D.

*m*-Dinitrobenzene as indicator of the respiration of animal and vegetable cells. S. C. J. OLIVIER and K. EBES (Rec. trav. chim., 1936, 55, 723—726).—Gurevitch's colour reaction for detecting respiration and the production of colour by Zn-Cu reduction fail if the *m*- $C_6H_4(NO_2)_2$  (I) used is pure. *o*- (II) and *p*- $C_6H_4(NO_2)_2$  (III) give the reaction strongly in both cases and its success hitherto is due to the presence of the isomerides as impurities in the (I) used. 1 : 3 : 5- $C_6H_4(NO_2)_3$  gives no colour. The colour given by (II) is intensified by the presence of (I). The test is valid if the (I) is replaced by 0.01 g. of (II) or (III). It is also a test for the purity of (I).

R. S. C.

Cell respiration and carbon dioxide assimilation in heavy water. K. SHIBATA and A. WATANABE (Acta Phytochim., 1936, 9, 107—114).—Respiration of *Chlorella ellipsoidea* and yeast cells takes place more slowly in 86%  $D_2O$  than in  $H_2O$  and  $CO_2$  assimilation is affected similarly. The results support the theory that the processes involve activation of  $H_2O$  mols. which is more readily effected than that of  $D_2O$  mols.

H. W.

(A) Intensity of geotropic reaction as a quantitative index of the content of growth-promoting substance [in plants]. (B) Growth-promoting substance and the formative action of light on vegetation in plants. V. M. KATUNSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 237—240, 241—243).—(A) Went's coleoptile technique has low sensitivity (error  $\pm 20\%$ ), largely due to lack of uniformity in the flow of growth substance (I) from the agar block to the coleoptile. More satisfactory results are obtained by placing the block symmetrically on the cut stump and, after 2—4 hr., placing the stump in a horizontal position (in darkness) and measuring the geotropic curvature.

(B) Brief exposure (1—2 min.) of etiolated oat coleoptiles to light rapidly lowered their (I) contents, which were not greatly altered by more prolonged exposure. Short exposures at intervals indicated a regeneration of (I) during darkened periods. Development of plants was directly related to the decrease in (I) caused by exposure. Etiolation is characterised by an over-production of (I), and may be controlled in glass-house practice by short-period illumination.

Plant growth-substances. XX. Production of crystalline biotin from egg-yolk. F. KOGL and B. TONNIS. XXI. Isolation of bios-I (*meso*-inositol) from yeast. F. KOGL and W. VAN HASSELT (Z. physiol. Chem., 1936, 242, 43—73, 74—80; cf. this vol., 1163).—XX. The fraction of bios-II which is adsorbed by C yields cryst. biotin (I), m.p. 148°, an  $NH_2$ -acid (or its Me ester) which stimulates the growth of yeast at dilutions of  $1 : 4 \times 10^{11}$ . (I), which yields an inactive acetate and benzoate, is obtained from the dried yolk of Chinese duck's eggs (1.1 mg. from 250 kg.; 1.8% of that present) by pptn., adsorption on animal C, elution with  $COMe_2$  and aq.



NH<sub>3</sub>, and distillation in a high vac. (b.p. 185—250°/0.001 mm.). The activity is not affected by catalytic hydrogenation but is increased by *meso*-inositol and by filtrates from the C adsorption.

XXI. Extract of autolysed yeast treated with Pb(OAc)<sub>2</sub> followed by purification with C and fractional pptn. with EtOH yields a syrup having high bio-I activity. The syrup treated with Ac<sub>2</sub>O followed by hydrolysis and re-acetylation with AcBr gives *meso*-inositol hexa-acetate, also obtained from purified extract of plasmolysed yeast by treatment with AcBr.

W. McC.

Action of oestrogenic substances on plant growth.—See B., 1936, 708.

Physiology of the incubation period in rust infections. A. I. GRETSCHUSCHNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 245—247).—Following infection of oats with rust, photosynthesis increased during the first few days and subsequently declined to a low level until after the appearance of pustules. The respiratory coeff. was low before sporulation, after which it increased abruptly. Intensification coincides with the appearance of urea in tissues. Fat formation in assimilatory cells was not observed.

A. G. P.

Toxins of rust (*Puccinia*). A. I. GRETSCHUSCHNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 335—339).—The active toxin of rust consists principally of urea and NH<sub>3</sub>. Direct introduction of NH<sub>3</sub> into leaves depresses, and that of urea intensifies, photosynthesis. Toxin extracts favour or retard photosynthesis according to the concn. applied. Both NH<sub>3</sub> and urea increase the respiratory discharge of CO<sub>2</sub>. The effects of toxin excretion on plant metabolism are such as to prevent the mutual poisoning of the symbiotic organisms.

A. G. P.

Physiology of spike disease of sandal. B. N. SASTRI (Proc. Indian Acad. Sci., 1936, 3, B, 444—459).—Tissue fluids of resistant varieties are characterised by low acidity and poor oxidase activity.

A. G. P.

Composition of (A) *Artemisia terre-alba*. L. DANILEVSKI. (B) *A. salina*. G. V. LAZUREVSKI. (C) *A. juncea*. (D) *A. turanica*. Z. MANULKIN (Acta Univ. Asiae Med., 1935, No. 9, 5—8, 9—11, 12—13, 14—16).—(A) The air-dry plant contains H<sub>2</sub>O 8.6, hemicellulose (I) 22.2, cellulose (II) 20.2, lignin (III) 10.2, protein 4.2, ash 3.25, Et<sub>2</sub>O-sol. 6.4 [including essential oil 0.74% (cineole 8, cumene 6, borneol 7%)], H<sub>2</sub>O-sol. 21.8 (including santonin 1, tannin 6, and carbohydrates 9.9%), and EtOH-sol. substances 2.7%.

(B) The air-dry plant contains H<sub>2</sub>O 11.2, (I) 20.6, (II) 23.2, (III) 5.8, ash 4.6, Et<sub>2</sub>O-sol. 8.2 (including essential oil 0.45, wax 0.9, and resin 6.4%), H<sub>2</sub>O-sol. 22.4 (including tannin 3.6, reducing sugars 2.3, protein 1.35, and salts 1.8%), and EtOH-sol. substances 5.2%.

(C) and (D) The air-dry leaves of *A. juncea* and *turanica* contain respectively H<sub>2</sub>O 8.62 and 10.32, (I) 9.6 and 11.8, (II) 11.8 and 11.8, (III) 8.5 and 7.7, ash 5.37 and 5.79, Et<sub>2</sub>O-sol. 11.3 and 14.1 (including 1.05 and 0.69% of essential oil), H<sub>2</sub>O-sol. 27.3 and 27.3 (including reducing sugars 2.24 and 4.01, protein 5.75

and 6.37, salts 3.54 and 2.63, tannin 2.7 and 2.2%), and EtOH-sol. substances 2.5 and 1.9%.

R. T.

Root nodule bacteria of some tropical leguminous plants. I. Cross-inoculation with *Vigna sinensis*. O. N. ALLEN and E. K. ALLEN (Soil Sci., 1936, 42, 61—77).—Tests with a no. of tropical strains are recorded. The versatility of the cowpea group is emphasised.

A. G. P.

Composition of *Artemisia scopariaeformis*. G. LAZUREVSKI (Bull. Univ. Asie Centrale, 1934, No. 19, 41—48).—The air-dry leaves contain H<sub>2</sub>O 12.8, hemicellulose 13.3, cellulose 12.7, lignin 7.2, ash 5.3, H<sub>2</sub>O-sol. 34 (including tannins 6, salts 4.4, reducing sugars 2.2%), Et<sub>2</sub>O-sol. 12 [including essential oil 1.2 (*d*- $\alpha$ -pinene 4,  $\beta$ -pinene 30, myrcene 10%), wax 1, and resin 7.2%], and EtOH-sol. substances 5.14%.

R. T.

Degradation of pyrethrin in chrysanthemum flowers (*C. cinerariaefolium*). F. KIRIGIN (Arh. Hemiju, 1936, 10, 12—20).—An apparent fall in pyrethrin I+II content, as determined chemically, takes place during 4 months of storage; this effect is due to oxidation of accompanying unsaturated acids, and to diminished solubility of pyrethrins in light petroleum. After 20 months of storage about 45% of the insecticidal activity is lost in the dried flowers, and somewhat less in pyrethrum powder.

R. T.

Composition of (A) *Psoralea drupacea*, B., and of the oil pressed from its seeds, (B) roots of *Ferula pseudoreosolinum*, Lipsky. I. TSUKERVANIK and V. BERSUTSKI (Bull. Univ. Asie Centrale, 1935, No. 21, 49—54, 55—68).—(A) The air-dry leaves contain hemicellulose (I) 7.7, cellulose (II) 9.2, lignin (III) 5.5, protein 16.8, ash 9.7, H<sub>2</sub>O-sol. 24, Et<sub>2</sub>O-sol. substances 13.8%, the roots contain 8.9% of H<sub>2</sub>O-sol. products, and the seeds contain (I) 6.8, (II) 8.3, (III) 4.1, ash 6.0, H<sub>2</sub>O-sol. 23.5, EtOH-sol. 2.1, and Et<sub>2</sub>O-sol. substances 15.4%. The Et<sub>2</sub>O extract of the seeds yields a fatty oil, containing saturated (palmitic, stearic) 8, and unsaturated acids (oleic, linoleic, linolenic) 80, resins 4.1, and unsaponifiable 5.0%.

(B) [with C. V. BRUTZEVA and B. I. AJZIKOVITSCH]. The air-dry root contains (I) 11, (II) 12.4, (III) 4.3, pentosans 6.4, pectins 9.6, starch 7.19, mono- 2.11, and di-saccharides 8.86, protein 7.37, ash 5.82, H<sub>2</sub>O-sol. 29.6, EtOH-sol. 1.9, and Et<sub>2</sub>O-sol. substances 15.9% [including resin 12.63 (acids, including podocarpic, 6.1, phenols 62.5, and neutral constituents 29.5%), essential oil 3.3 (*d*- $\alpha$ -pinene 90, *d*- $\beta$ -phellandrene 5%)].

R. T.

Fixed oil of poke root. S. W. GOLDSTEIN and G. L. JENKINS (J. Amer. Pharm. Assoc., 1936, 25, 636—641).—Fractionation of the fatty oil (*d*<sub>4</sub><sup>20</sup> 0.9209, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +13°, *n*<sub>D</sub><sup>20</sup> 1.4741, acid val. 71.97, sap. val. 139.43, ester val. 67.46, I val. 69.14) obtained by petrol extraction of roots of *Phytolacca americana* yields fatty acids (arachidic 5.91, palmitic 8.63, margaric 4.19, hydroxymyristic, 0.72%; also oleic and acids of low mol. wt.), hentriacontane, a sterol-like compound C<sub>23</sub>H<sub>40</sub>O, m.p. 107—108°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +70.0° in CHCl<sub>3</sub>, containing no OH, and *phytolaccasterol*, C<sub>30</sub>H<sub>50</sub>O, H<sub>2</sub>O, m.p. 169—170°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +35.0° in CHCl<sub>3</sub> (Ac derivative, m.p. 183—183.5°).

F. O. H.

**Phytochemistry of *Monarda pectinata*, Nutt. I. [Dried] herb.** J. B. BURT (J. Amer. Pharm. Assoc., 1936, 25, 602—606).—Data are tabulated of the H<sub>2</sub>O content, fractions sol. in org. solvents, H<sub>2</sub>O, acid, and alkali, and ash constituents of flower, leaf, stem, and root. F. O. H.

**Composition of pineapples.** J. C. BODENSTEIN (Union S. Africa Dept. Agric. Forestry Sci. Bull., 1936, No. 153, 14 pp.).—Analyses are recorded. Sucrose is the principal sugar in the juice, and the ratio, fructose/glucose is approx 0.8. A negative correlation is established between the K and Ca contents of the ash of the whole fruit. A. G. P.

**Capillary distribution of plant constituents.** See B., 1936, 812.

**Iron in vegetable ashes.** G. BERTRAND (Compt. rend., 1936, 203, 371—372).—The occurrence of small nodules of Fe in vegetable ashes is attributed to local reduction. R. S.

**Iodine content of some marine algae of the Shantung coast.** T. H. TANG, F. C. KOÜ, and P. S. TANG (Chinese J. Physiol., 1936, 10, 377—378).—The I content of 14 marine algae varies from 16.8 to 462.0 p.p.m. (calc. on dry wt.). W. O. K.

**Unsaponifiable matter of algal fats. II. Pelvesterol from *Iligikia fusiformis* (Harv.), Okam.** K. SHIRAHAMA (J. Agric. Chem. Soc. Japan, 1936, 12, 521—522).—The crude fat gave 9% of pelvesterol, m.p. 122°,  $[\alpha]_D -39.6^\circ$  (acetate, m.p. 118.5°,  $[\alpha]_D -44.1^\circ$ ; propionate, m.p. 105—106°,  $[\alpha]_D -43.1^\circ$ ). The absorption spectrum of the sterol in EtOH shows narrow bands at 295, 282.5, and 273, a wide band at 260, and a wider band at 250 m $\mu$ . J. N. A.

**Balsam pear-seed oil.** Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1936, 39, 220—221B).—Trichosanic acid (A., 1935, 960) has been separated from the oil. T. W. P.

**Lipins of fenugreek (*Trigonella foenum graecum*).** B. N. SASTRI and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1936, 3, A, 513—518).—Fractions containing a phospholipin allied to sphingomyelin, a lecithin forming a complex with CdCl<sub>2</sub>, a C<sub>5</sub>H<sub>5</sub>N-sol. and an insol. galactolipin have been isolated from fenugreek. F. N. W.

**Production of citric acid.**—See this vol., 1231.

**Odoriferous principle of green tea. VII. Constituents of tea oil.** S. TAKEI, Y. SAKATO, and M. ONO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 626—634).—Oil from green tea contains *n*-octyl alcohol (I), geraniol (II), and an alcohol, C<sub>5</sub>H<sub>12</sub>O (4'-iododiphenylurethane, m.p. 147°), probably  $\beta$ -methylbutan- $\alpha$ -ol. The ester fraction, on hydrolysis, yields (I), (II), and octoic acid. (Cf. this vol., 125.) W. O. K.

**Constituents of mulberry tree bark. I.  $\alpha$ -Amyrin.** M. OKU (J. Agric. Chem. Soc. Japan, 1936, 12, 555—559).—The unsaponifiable matter of the bark contains  $\alpha$ -amyrin. J. N. A.

**Constituents of horse-chestnut seeds. I. Nutritive value.** R. SASAKI and M. KANDATSU (J. Agric. Chem. Soc. Japan, 1936, 12, 675—683).—Treatment of powdered whole seeds with dil. Na<sub>2</sub>CO<sub>3</sub>

removes toxic substances (e.g., glucosides), and the product can then be used as a constituent of the diet of rats, which maintain normal growth. J. N. A.

**Extraction of a crystalline substance, viburnitol, from leaves of *Viburnum tinus*, L.** H. HÉRISSEY and G. POIROT (Compt. rend., 1936, 203, 466—468).—The hot-H<sub>2</sub>O extract of leaves is hydrolysed by boiling with dil. H<sub>2</sub>SO<sub>4</sub> and neutralised. Sugars are removed by yeast fermentation and the liquor is defecated with Pb(OAc)<sub>2</sub>. Further addition of ammoniacal Pb subacetate produces a ppt. from which is obtained viburnitol, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, m.p. 180—181°,  $[\alpha]_D -49.5^\circ$ . It is probably a cyclic polyhydroxy-compound. A. G. P.

**Phytochemistry of *Monarda pectinata*, Nutt. II. Volatile oil.** J. B. BURT (J. Amer. Pharm. Assoc., 1936, 25, 682—687).—The crude oil,  $d^{25}_4$  0.9496,  $n^{25}_D$  1.5070, from the fresh, flowering herb contains 77.68 vol.-% of phenols, fractionation of which yields carvacrol: the non-phenolic fraction yields a CHO-free oil,  $d^{24}_4$  0.97264,  $n^{25}_D$  1.4806,  $[\alpha]_D^{25} +0.759^\circ$ . F. O. H.

**Lomatol and lapachiol.**—See this vol., 1119.

**Some naturally occurring pigments of biochemical interest.** P. KARRER (Helv. Chim. Acta, 1936, 19, Spec. No., 33—48).—A lecture.

**Anthocyanin of the blue blossoms of *Hyacinthus orientalis*.** K. HAYASHI (Acta Phytochim., 1936, 9, 25—33).—Extraction of the blossoms with 1% HCl-MeOH and treatment of the extract with aq. Pb(OAc)<sub>2</sub> ppts. the Pb salt, which is decomposed with 10% HCl-MeOH. Addition of Et<sub>2</sub>O to the filtrate from the PbCl<sub>2</sub> causes separation of hyacin chloride (I), decomp. 188° after softening at 185°, which closely resembles delphin chloride from *Salvia patens*. It is hydrolysed to 2 mols. of glucose and 1 mol. of delphinidin chloride. The absorption spectrum of (I) is identical with that of awobanin-A chloride from *Commelina* blossoms. H. W.

**Anthocyanin pigments of *Pharbitis nil*.** T. KATAOKA (Acta Phytochim., 1936, 9, 35—42).—Details are given of the isolation of pelargonin from red *Pharbitis* blossoms and of its hydrolysis to pelargonidin (formerly designated pharbitidin). Similarly the pink-violet blossoms yield pæonin chloride; the terms cyanilin and cyanilidin are therefore superfluous. H. W.

**Brilliant blue F.C.F., a new dye for diagnostic gastrointestinal studies.** A. C. TAYLOR (Amer. J. Digest. Dis. Nutrition, 1934, 1, 239).—A preliminary report. CH. ABS. (p)

**Modified Wright's method for staining blood smears.** W. N. STEIL (Stain Tech., 1936, 11, 99—100).—The technique with Wright's stain has been modified to give uniform results. H. G. R.

**Aniline-blue collagen stain.** F. B. MALLORY (Stain Tech., 1936, 11, 101—102).—Phosphotungstic acid is used in place of phosphomolybdic acid and the time of staining increased. H. G. R.

**Filter of Pyrex glass and stainless steel for use with Seitz filter-pads.** B. C. J. G. KNIGHT and P. FIDES (Biochem. J., 1936, 30, 1138—1139).—



The apparatus, which avoids contamination of the filtrate with toxic metals, is described. W. O. K.

[Method for] micro-extraction of tissues *in vacuo* at the normal temperature of the animal. R. PANNIER (Compt. rend. Soc. Biol., 1936, 122, 1216—1218). H. G. R.

Determination of chlorides in biological materials. V. COLLIER, jun. (J. Biol. Chem., 1936, 115, 239—245).—Tissue is digested with KOH, acidified with  $\text{HNO}_3$ , and re-digested with KOH until clear; the solution is neutralised and  $\text{Cl}^-$  determined by Fajans' method of titrating with  $\text{AgNO}_3$  with dichlorofluorescein as indicator (A., 1924, ii, 776). H. D.

Determination of chloride in body-fluids by direct titration. C. F. M. ROSE (Biochem. J., 1936, 30, 1140—1146).— $\text{Cl}^-$  is determined in urine (decolorised with C and diluted by titration with  $\text{AgNO}_3$  with eosin-dichlorofluorescein (I) as indicator. Fluids of low protein content, e.g., milk, cerebrospinal fluid, and gastric juice, are titrated at the isoelectric point of the protein directly with (I) as indicator. With whole blood and serum the protein must be removed before titration preferably by heating in  $\text{AcOH-NaOAc}$  buffer solution. W. O. K.

Electrometric determination of iodine in blood and tissues. H. PAAL and G. MOTZ (Klin. Woch., 1935, 14, 1291—1293; Chem. Zentr., 1935, ii, 3353).—The method, although fairly accurate, is troublesome and tedious. H. N. R.

Microdetermination of lead in normal and pathological tissues. F. GALLEGU Y GÓMEZ (Anal. Fis. Quim., 1935, 33, 937—941).—The org. matter contained in 0.5—1.0 g. of dried material is decomposed with  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ , and the resultant  $\text{PbSO}_4$  removed in a centrifuge, washed with aq. EtOH, dissolved in ammoniacal  $\text{NH}_4$  tartrate, and saturated with  $\text{H}_2\text{S}$ . The amount of Pb is determined colorimetrically as  $\text{PbS}$ . The error is <0.6%. Epitheliomas and carcinomas of dogs and cats which have been treated with Pb compounds have Pb contents > normal. F. R. G.

Spectrographic micro-determination of zinc [in plant material]. A. P. VANSELOW and B. M. LAURANCE (Ind. Eng. Chem. [Anal.], 1936, 8, 240—242).—The plant ash is dissolved in dil. HCl, 2 mg. of Cd as  $\text{CdSO}_4$  are added, CdS and ZnS are pptd. with  $\text{H}_2\text{S}$  at  $p_{\text{H}}$  3, and the mixed ppt. is examined spectrographically, using Cd as internal standard. The range is about 1—100 p.p.m. and the error usually 10—20%. E. S. H.

Determination of non-protein-nitrogen of tissue. M. D. MEZINCESCU and F. SZABO (J. Biol. Chem., 1936, 115, 131—138).—A method, based on extraction of the minced tissue with dil.  $\text{CCl}_3\text{-CO}_2\text{H}$  for 3 hr. at  $0^\circ$ , is described. Data obtained are compared with those by Janney's method (A., 1916, ii, 460). J. N. A.

Determination of nitrogen partition in tissues. G. B. AYRES and M. LEE (J. Biol. Chem., 1936, 115, 139—148).—Sol. proteins, albumins, and globulins are determined in a KCl-buffer extract, whilst glucose,  $\text{NH}_2$ -acids,  $\text{NH}_3$ , creatine, creatinine, reduced glutathione, urea, uric acid, allantoin, and non-protein-N

are determined in an aq.  $\text{H}_2\text{WO}_4$  extract. Determinations of glycogen, Ca, P, S, total N, fat, cystine, cysteine, methionine, ash, and  $\text{H}_2\text{O}$  are made on other samples of the tissue. Details of the methods are given. J. N. A.

Determination of residual carbon in biological fluids. W. KOCHOLATY (Biochem. Z., 1936, 286, 186—192).—A method is described and used for C determinations in various org. substances and in phosphotungstic acid filtrates of blood and urine. P. W. C.

Determination of alcohol in forensic chemistry. D. C. VUCETICH (Rev. Fac. Cienc. Quim. La Plata, 1935, 10, 37—42).—5 c.c. of liquid containing EtOH with 40 c.c. of saturated aq. picric acid in a Schloesing-Aubin apparatus are slowly distilled to half vol. into 5 c.c. of  $\text{H}_2\text{SO}_4$ . 5 c.c. of the distillate are mixed with 30 c.c. of  $\text{H}_2\text{SO}_4$  and 30 c.c. of 0.1N- $\text{K}_2\text{Cr}_2\text{O}_7$  and rapidly boiled for 5 min. When cold, the solution is diluted, KI added, and the mixture is titrated with 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ . Solutions containing 0.1% of EtOH may be determined with an error of 1%. F. R. G.

Diffusion methods in qualitative micro-analysis. Detection of acetone and alcohol in biological liquids. W. R. FEARON and D. A. WEBB (Analyst, 1936, 61, 539—540).—The Conway vapour diffusion apparatus (A., 1933, 654) adapted to the detection of  $\text{COMe}_2$  (using Nessler's reagent in the inner compartment) and EtOH [using  $\text{K}_2\text{CrO}_4\text{-HNO}_3$  (cf. A., 1932, 718)] in urine, blood, and similar liquids is a very sensitive and accurate method. E. H. S.

Colorimetric determination of reduced glutathione. T. SO (Kitasato Arch. Exp. Med., 1935, 12, 243—264).—The nitroprusside method is less influenced by various factors than is the I method. CH. ABS. (p)

Micro-colorimetric determination of benzene in blood and urine. S. J. PEARCE, H. H. SCHRENK, and W. P. YANT (U.S. Bur. Mines., Rept. Invest., 1936, No. 3302, 8 pp.).—The  $\text{C}_6\text{H}_6$  is removed by aeration from the sample of blood or urine and collected in a mixture of fuming  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  which converts it into  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ . The acid mixture is neutralised, extracted with 10-c.c. of  $\text{COMeEt}$ , and 1.5 c.c. of 40% NaOH is added to the extract. The reddish-purple colour which develops  $\propto$  concn. of  $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ . The method is sensitive to 0.001 mg. of  $\text{C}_6\text{H}_6$ , and has an accuracy of about  $\pm 10\%$  over a range of 0.01—0.9 mg. in 10-c.c. samples. W. O. K.

Creatine-creatinine determinations according to Folin. L. BOHUNKA (Kozl. osszehas. elet. Kortan Korebol, 1935, 26, 163—166).—Colour comparisons should be made immediately and the ratio of alkali : picric acid should be 1 : 3. Creatine changes to creatinine (I) within 15 min. at  $135^\circ$ . (I) does not decompose at this temp. CH. ABS. (p)

Determination of choline.—See this vol., 1235.

Determination of haemoglobin as globin picrate. A. BOLLIGER (Austral. J. Exp. Biol., 1936, 14, 97—99).—After pptn. of globin picrate with alcoholic picric acid, excess is titrated with methylene-blue. H. G. R.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

NOVEMBER, 1936.

### General, Physical, and Inorganic Chemistry.

Width of stellar hydrogen lines. P. ROSSIER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 85—86).—Widths are approx. const. and independent of the brightness of the star and of its temp. over 7000—14,000°. N. M. B.

Spectroscopic determination of [atomic] mass of deuterium from the Balmer series. A. HAGENBACH and H. GARTNER (Helv. phys. Acta, 1935, 8, 314—315; Chem. Zentr., 1935, ii, 3885).—The Balmer lines excited in the vapour of 58% heavy  $H_2O$  have satellites of shorter  $\lambda$  which are due to D. From their Rydberg const.,  $M_D/M_H=1.996$ . J. S. A.

Extension of the absorption spectrum of the hydrogen molecule. J. J. HOPFIELD (Physical Rev., 1935, [ii], 47, 788—789).—Discrete absorption lines have been observed as far as 738 Å. in  $H_2$  at low pressures. L. S. T.

Stark effect with the helium line  $\lambda$  4686. B. KULLENBERG (Z. Physik, 1936, 102, 423—427).—The Stark effect for the He line  $\lambda$  4686 Å. has been investigated for fields up to 40 kv. per cm. A. J. M.

Spectra of helium by high-frequency excitation. M. PETERSEN and H. CARL (Physical Rev., 1935, [ii], 47, 803).—Conditions of enhancement of certain singlet lines have been ascertained. L. S. T.

Spreading in the first positive bands of nitrogen. E. T. S. APPLEYARD (Proc. Physical Soc., 1936, 48, 763—771).—An experiment is described to distinguish between the theories of Maxwell (cf. A., 1932, 1185) and of Skinner (cf. A., 1933, 893) for the secondary excitation responsible for the production of spreading. The resonance radiation of N emitted from an electron beam is passed through a thin celluloid window which holds back metastable atoms; results show that part, or possibly the whole, of the secondary excitation of the first positive bands is due to collisions of the second kind with mols. in the  $a^1\Pi$  state, supporting Skinner's theory. N. M. B.

Energy of metastable nitrogen molecules. H. HAMADA (Sci. Rep. Tohoku, 1936, 25, 217—226).—From the intensity distribution in bands attributed to the metastable  $A^3\Sigma N_2$  mol., the energy of metallic spectra excited by this mol., and the intensity distribution in bands in the afterglow of active N, it is deduced that the concn. of mols. in low vibrational states among the metastable mols. is small. It is suggested that the high concn. of mols. in states  $v''=7-8$  can be deduced from the Franck-Condon principle. O. D. S.

Origin of the afterglow in active nitrogen. G. CARIO and U. STILLE (Z. Physik, 1936, 102, 317—330).—An apparatus for photography of the band systems of the N afterglow under various conditions of pressure and discharge is described. Effects of wall activation and pressure are discussed with reference to the Cario-Kaplan theory. L. G. G.

Nuclear magnetic moment of  $^{23}Na$ . L. A. WILLS and G. BREIT (Physical Rev., 1935, [ii], 47, 704—705).—A discussion. L. S. T.

Magnetic moment of the  $^{23}Na$  nucleus. W. E. SHOUPP, J. H. BARTLETT, jun., and C. G. DUNN (Physical Rev., 1935, [ii], 47, 705—706).—A discussion. This moment is probably about 2.5—3.1 nuclear magnetons. L. S. T.

Alkali-metal films transparent in the Schumann region. W. H. WATSON and D. G. HURST (Canad. J. Res., 1936, 14, A, 153—157; cf. this vol., 1039).—Na films on fluorite are transparent to  $\lambda < 2100$  Å., but show some absorption in the range 1400—1250 Å. K films show weak absorption from 1700 Å., the intensity of absorption increasing with decreasing  $\lambda$ . No evidence of transparency with Li films has been obtained. J. W. S.

Alternating intensities in the spectrum of  $P_2$ . F. A. JENKINS (Physical Rev., 1935, [ii], 47, 783). L. S. T.

Spectra of phosphorus, P II, P III, P IV. H. A. ROBINSON (Physical Rev., 1935, [ii], 47, 799; cf. this vol., 397). L. S. T.

Deep terms in ions of the isoelectronic sequence Cl I to Mn IX. S. G. WEISSBERG and P. G. KRUGER (Physical Rev., 1935, [ii], 47, 798).—Vals. of deep terms and ionisation potentials are tabulated. L. S. T.

Molecular spectra of the sulphur group. B. ROSEN and F. BOUFFIQUX (Bull. Acad. roy. Belg., 1936, [v], 22, 885—893).—The broad emission bands of  $Te_2$  vapour reported by Désirant (cf. this vol., 1040) were photographed and analysed to longer  $\lambda$ ; they resolve into narrow bands degraded towards the red. Intensity fluctuations are discussed. The new infra-red band system of  $S_2$  (cf. *ibid.*, 537) photographed at high dispersion showed that certain of the narrow bands are groups of lines of S I. An analysis of 7 bands of  $S_2$  is given. New measurements of the complex bands in the red part of the principal system of  $S_2$  are reported (cf. *ibid.*, 127). N. M. B.

Lifetimes of potassium doublets  $\lambda$  4047—4 and  $\lambda$  3447—6. D. SINCLAIR and H. W. WEBB (Physical Rev., 1936, [ii], 50, 440—445).—The life-



times were measured by the a.c. excitation method; a special NaH vac. photo-cell was used to measure the radiation from a K cell containing a hot cathode and two anodes. The K v.p. range was  $4 \times 10^{-5}$ – $10^{-2}$  mm. The respective lifetimes, accurate to 1%, were  $3.79 \times 10^{-7}$  and  $8.50 \times 10^{-7}$  sec. Radiation emitted after electron excitation followed a simple exponential law. No change of lifetime was found for the whole pressure range; this could be accounted for by assuming that only 10% of each of the  $\lambda\lambda$  groups is re-emitted at the same  $\lambda$ . N. M. B.

**Term analysis of the first spectrum of vanadium (V I).** W. F. MEGGERS and H. N. RUSSELL (J. Res. Nat. Bur. Stand., 1936, 17, 125–192).—Complete tables of the lines and terms of the V I spectrum are given, and the electronic configurations responsible for the observed terms have been identified in nearly all cases. The ionisation potential of neutral V atoms is calc. to be 6.71 volts. O. J. W.

**Connexion between the deep terms of the elements of the iron series.** M. A. CATALAN and M. T. ANTUNES (Z. Physik, 1936, 102, 432–460).—The expression for the energy of spectral terms based on the Slater method is discussed, and the energy of terms of certain configurations is calc. Empirical relationships between observed term vals. are discussed. A. J. M.

**Connexion between the Rydberg numbers of the deep terms in the iron series.** M. A. CATALAN and F. POGGIO (Z. Physik, 1936, 102, 461–479).—The observed abs. term vals. and Rydberg nos. for the  $3d^m4s$  and  $3d^m4s^2$  configurations are compared with those calc. from Catalan and Antunes' formula (see above), and a no. of empirical rules are derived. A. J. M.

**Absorption processes in the halogen spectra.** R. S. MULLIKEN (J. Chem. Physics, 1936, 4, 620–621).—The interpretation of the absorption continuum of  $\text{Br}_2$  preferred by Acton *et al.* (this vol., 1167) may apply to that of  $\text{Cl}_2$ , but is inapplicable to that of  $\text{I}_2$ . The transition  $^1\text{I} \leftarrow ^1\Sigma^+$  is not so weak in the halogens as hitherto supposed. J. G. A. G.

**Third spectrum of krypton.** C. J. HUMPHREYS (Physical Rev., 1935, [ii], 47, 799–800).—The spectrum characteristic of the  $\text{Kr}^{++}$  ion has been selected from the various Kr spectra excited in a Geissler tube discharge. 369 lines extending from 2100 to 7400 Å. have been classified as arising from 88 levels of Kr III. L. S. T.

**Hyperfine structure of Y II lines.** P. G. KRUGER and C. N. CHALLACOMBE (Physical Rev., 1935, [ii], 47, 509).—Data are tabulated. A nuclear moment of  $\frac{1}{2}$  is indicated for Y. L. S. T.

**Quenching of cadmium resonance radiation (3261) by hydrogen.** H. C. LIPSON and A. C. G. MITCHELL (Physical Rev., 1935, [ii], 47, 638).

L. S. T.

**Ultra-violet  $\text{I}_2$  fluorescence.** D. T. WARREN (Physical Rev., 1935, [ii], 47, 642).

L. S. T.

**Intensity distribution in the line emission spectrum of caesium.** F. L. MOHLER (J. Res. Nat. Bur. Stand., 1936, 17, 45–54).—The intensity dis-

tribution in the *S*, *D*, and *F* series of the Cs emission spectrum has been measured. For the *D* series intensity measurements have also been made for a columnar discharge, and for the 5466 and 5503 Å. lines the intensity variation with current and pressure is described. D. J. W.

**Paschen-Back effect in the hyperfine structure of the caesium resonance line  $\lambda 8522$  Å.** H. KOPFERMANN and H. KRÜGER (Z. Physik, 1936, 102, 527–533).—The Paschen-Back effect was investigated in the case of 16 field-parallel components of the Cs I line,  $\lambda 8522$  Å. ( $6^2S_1 - 6^2P_{3/2}$ ) using a magnetic field of 9700 Gauss. The nuclear moment of Cs is  $7/2$ . A. J. M.

**Wave-length measurements in the spectra of the neodymium arc and the standard Pfund iron arc.** G. R. HARRISON and W. W. BARTLETT (Physical Rev., 1935, [ii], 47, 799). L. S. T.

**Near infra-red spectrum of mercury. I.** O. MASAKI, K. KOBAYAKAWA, and T. MORITA (J. Sci. Hiroshima Univ., 1936, 6, 291–297).—The spectrum was photographed with supersensitised plates, and full data and classifications are tabulated. N. M. B.

**Line absorption of mercury vapour for individual hyperfine structure components of the 2537 Å. line.** K. ZUBER (Helv. phys. Acta, 1935, 8, 370–380; Chem. Zentr., 1935, ii, 3890).—Assuming that the mean life of the  $2^3P_1$  level is the same for all isotopes, the results accord with the fine structure scheme of Schüler and Keyston. J. S. A.

**Stepwise fluorescence in mercury vapour: the 3650 line.** L. A. TURNER (Physical Rev., 1935, [ii], 47, 807). L. S. T.

**Isotope effect of ionised mercury hydrides ( $\text{HgH}^+/\text{HgD}^+$ ).** S. MROZOWSKI (Z. Physik, 1936, 102, 545–547).—The results of Hori *et al.* (this vol., 1168) are not sufficiently accurate to warrant the conclusion that there are deviations from the usual isotope formula in the case of the ionised Hg hydrides. A. J. M.

**Zeeman effect of the lead line  $6p^2\ ^3P_2 - 6p.7s\ ^3P_1$  ( $\lambda 4058$  Å.).** S. SATÔ (Sci. Rep. Tôhoku, 1936, 25, 207–216). O. D. S.

**Deep terms in the spectra of Pb v and Bi VI.** G. K. SCHOEPPLE (Physical Rev., 1936, [ii], 50, 538–542; cf. A., 1935, 424; Mack, *ibid.*, 1292).—Full data for  $\lambda\lambda$ , classifications, energy levels, and transitions are tabulated for 69 terms involving 205 lines of Pb v, and 40 terms involving 94 lines of Bi VI. N. M. B.

**Paschen-Back effect. -S-P multiplets in strong fields.** P. JACQUINOT (Physical Rev., 1936, [ii], 50, 573).—The resolution of the *s* components reported by Green (cf. this vol., 653) had been previously effected (cf. A., 1935, 423). N. M. B.

**Distribution of the energy in the extreme ultra-violet of the solar spectrum.** W. W. COBLENTZ and R. STAIR (J. Res. Nat. Bur. Stand., 1936, 17, 1–6).—The distribution of energy in the extreme ultra-violet of the solar spectrum within and outside the earth's atm. has been calc. It seems

incorrect to assume that the radiation is similar to that of a black body at 6000° abs. Apparatus is described for measuring the spectral quality and total intensity of ultra-violet solar radiation by means of a photo-electric cell and filter radiometer transported aloft in sounding balloons. O. J. W.

**Ultra-violet absorption spectrum of Nova Herculis 1934.** H. E. GREEN (Month. Notices Roy. Astron. Soc., 1935, 95, 694—704).—Lines of Fe II, Ti II, Cr II, V II, and Mn II were identified.

CH. ABS. (c)

**Arcs in inert gases. III.** G. E. DOAN and W. C. SCHULTE (Physical Rev., 1935, [ii], 47, 783—784).—The non-arcing phenomenon reported (A., 1934, 935) for low-current arcs also obtains in high-current welding arcs. In A of <99.0% purity, crater formation and penetration do not occur. L. S. T.

**Processes at the cathode of arc discharges.** O. BECKEN and K. SOMMERMEYER (Z. Physik, 1936, 102, 551—561).—Two types of discharge at C and W cathodes are described, which are regarded as due to thermal and auto-electronic emission respectively. O. D. S.

**Condensed discharge.** Z. BAY (Z. Physik, 1936, 102, 507—526).—Short-lived collisions of high intensity were produced in H<sub>2</sub>, N<sub>2</sub>, Ne, and Ne-Hg mixture by the condensed discharge, and the electrical and spectral properties of the discharge were investigated. Very high c.d. were obtained, and the resulting spectra showed corresponding variations with c.d. A. J. M.

**Gas reactions in silent discharge at atmospheric pressure. I. New type of screened point discharge with transition of strong current form of discharge to a weaker.** P. A. THIESSEN and H. BARTEL (Z. tech. Physik, 1935, 16, 285—293; Chem. Zentr., 1935, ii, 3891).—The discharge characteristics are described. J. S. A.

**Photographic effective wave-length.** P. ROSIER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 83—85).—Differences between visual and micro-photometric measurements of the distances of diffraction spectra from the central image and resulting differences of  $\lambda\lambda$  are examined mathematically. N. M. B.

**Precision X-ray wave-length measurements.** L. G. PARRATT (Physical Rev., 1935, [ii], 47, 882—883).—A discussion. L. S. T.

**Energies of X-ray photoelectrons.** L. W. ALVAREZ (Physical Rev., 1935, [ii], 47, 636).—New vals. of these energies favour the crystal rather than the grating scale of X-ray  $\lambda$  (cf. this vol., 1040). L. S. T.

**Absorption of X-rays in the wave-length range 50 to 200 X.** M. T. JONES and T. R. CUYKENDALL (Physical Rev., 1935, [ii], 47, 643).—Absorption coeffs. in this range have been measured for C, Na, Al, K, Ni, Cu, Nb, Mo, Ag, Sn, Ta, and Pb. L. S. T.

**Production of X-radiation by very fast electrons.** E. McMILLAN (Physical Rev., 1935, [ii], 47, 801).—As indicated by theory, radiation is emitted by paraffin, Al, and Pb when they stop the  $\beta$ -particles

given by active <sup>32</sup>P or by Cl activated by deuteron bombardment. L. S. T.

**K $\beta$  Spectra of chlorine and sulphur.** H. TAZAKI (J. Sci. Hiroshima Univ., 1936, 6, 299—305).—Using LiCl, NaCl, and KCl on a Cu, and S and K<sub>2</sub>SO<sub>4</sub> on an Al, anticathode, the spectra were photographed with long exposure, revealing many fine spark lines of Cl and new lines of S. Full  $\lambda\lambda$  and  $\nu/R$  and  $\sqrt{\nu}/R$  vals. are tabulated, and semi-Moseley diagrams are given and discussed. N. M. B.

**Relationships between atomic number and effect of chemical binding on the K $\alpha_{1,2}$  doublet of some of the lighter elements.** N. G. JOHNSON (Z. Physik, 1936, 102, 428—431; cf. A., 1935, 908).—The effect of chemical binding on the K $\alpha_{1,2}$  lines of <sup>12</sup>Mg and <sup>13</sup>Al has been investigated. With the compounds used there is a displacement of the lines, compared with the positions of those of the free elements, towards shorter  $\lambda\lambda$ , the effect being a max. in the case of the fluorides Na<sub>3</sub>AlF<sub>6</sub> and MgF<sub>2</sub>. The displacements for the oxides of elements of at. no. 12—16 (Mg—S) when plotted against at. no. lie on a smooth, almost rectilinear curve. A similar curve is obtained for fluorides. A. J. M.

**New lines in the K series spectrum of tungsten.** J. C. HUDSON, H. G. VOGT, and A. H. ARMSTRONG (Physical Rev., 1935, [ii], 47, 809). L. S. T.

**Widths of certain L-absorption edges.** A. E. SANDSTROM (Phil. Mag., 1936, [vii], 22, 497—513).—The effect of thickness of absorbing screen, time of exposure, and the broadening effect of the spectrograph on the width of the L-absorption edges of some elements has been examined. The full widths of the L<sub>II</sub> and L<sub>III</sub> and some L<sub>I</sub> edges of elements between Zn and Te were measured, together with their asymmetry. The latter was, in most cases, very pronounced. Curves are given showing the variation of the width of the edge with at. no. The L<sub>II</sub> and L<sub>III</sub> curves have the same shape, but the few points obtained for L<sub>I</sub> edges seem to require a different curvature. A. J. M.

**L Spectra of radium (88).** H. HULUBEI (Compt. rend., 1936, 203, 542—543; cf. this vol., 399).—Emission and absorption lines of the L spectra of Ra have been determined and the electron levels tabulated. R. S.

**K Spectra and conductivity electrons of solid and liquid aluminium.** J. FARINEAU (Compt. rend., 1936, 203, 540—541).—The  $\alpha$  bands and the short-wave limits of the  $\beta$  bands of solid and liquid Al are the same, but the structure of the bands is different in liquid Al. It is suggested that the M electrons are only loosely bound and subject to perturbations connected with the lattice structure. R. S.

**Calculation of the X-ray energy level widths of Au (79).** E. RAMBERG and F. K. RICHTMYER (Physical Rev., 1935, [ii], 47, 644; cf. A., 1935, 138).—L. S. T.

**Form and breadth of Compton lines.** H. KAPPELER (Helv. phys. Acta, 1935, 8, 314; Chem. Zentr., 1935, ii, 3361).—Data are given for N, Ne,



Li, C, and NaF. The form of the Compton line is dependent on the nature of the scattering particle.

J. S. A.

**Auger effect for Au (79) and the origin of certain L-satellites in X-ray spectra.** E. RAMBERG and F. K. RICHTMYER (Physical Rev., 1935, [ii], 47, 805).

L. S. T.

**Radiative Auger effect.** F. BLOCH and P. A. ROSS (Physical Rev., 1935, [ii], 47, 884—885).

L. S. T.

**Photo-electric properties of zinc.** C. F. DE VOE (Physical Rev., 1936, [ii], 50, 481—485).—The work function of a vac.-distilled Zn surface, corresponding with the long-wave limits 2900—2930 Å., was 4.24 volts at  $1.5 \times 10^{-8}$  mm. pressure, and decreased, with rise of air pressure, to a min. at about  $10^{-6}$  mm. and then increased. He and N<sub>2</sub> had no effect to pressures of 3 mm. and  $10^{-3}$  mm., respectively.

N. M. B.

**Free path of conductivity electrons.** A. PAPAETROU (Z. Physik, 1936, 102, 539—544).—The Bloch method of calculating electrical conductivity from the interaction between electrons and heat waves is simplified by avoiding the use of an integral equation.

A. J. M.

**Passage of fast electrons through matter.** H. J. BHABHA and W. HEITLER (Nature, 1936, 138, 401).—The probability for production of secondary electrons when a fast primary electron passes through varying thicknesses of matter has been calc. A primary electron of  $2 \times 10^9$  e.v. passing through a thickness equiv. to 1.6 cm. of Pb produces, on the average, 2 positive and 2 negative electrons with energies  $> 2 \times 10^7$  e.v.

L. S. T.

**Properties of an electron which rolls without slipping and of radius varying inversely as the velocity.** T. V. IONESCU (Compt. rend., 1936, 203, 537—539).—The properties of free and orbital electrons can be accounted for.

R. S.

**Positive and neutral rays. IV. Effective cross-sections for neutralisation.** A. ROSTAGNI (Nuovo Cim., 1935, [ii], 12, 134—153; Chem. Zentr., 1935, ii, 3362).—For the neutralisation of A<sup>+</sup>, Ne<sup>+</sup>, and He<sup>+</sup> in A, Ne, and He, respectively, the effective cross-section rises with decreasing velocity of the ions to a max. between 20 and 30 volts, and then decreases for low velocities.

J. S. A.

**Absorption and diffusion of positive rays in gases.** A. ROSTAGNI (Atti R. Accad. Sci. Torino, 1935, I, 70, 472—486; Chem. Zentr., 1935, ii, 3362).—Data are given for A<sup>+</sup>, Ne<sup>+</sup>, and He<sup>+</sup> in A, Ne, and He, respectively.

J. S. A.

**Potential for light excitation in mercury by collisions with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>.** O. HENLE and W. MAURER (Physikal. Z., 1936, 37, 659—661; cf. this vol., 1167).—The potentials required for the appearance of lines due to alkali metals in the light caused by collision of the ions with Hg have been determined. The potentials at which the various lines appear are: Hg < 500, Li<sup>+</sup> and Na<sup>+</sup> > 9000, K<sup>+</sup> > 9000, Rb<sup>+</sup> < 9000, Cs<sup>+</sup> about 1400 volts.

A. J. M.

**Filament sources of positive ions.** J. P. BLEWETT and E. J. JONES (Physical Rev., 1936, [ii], 50, 464—468).—Efficient filament sources of alkali-metal ions were obtained by heating synthetic alkali Al silicates. Studies of emission of the Li sources as a function of composition show that β-eucryptite, Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>, is the most satisfactory. Ions of Mg, Ca, Sr, Ba, Al, Ga, In, Ti, V, Mn, Y, and Ce are emitted when the oxide of the respective metal is raised to white heat on a W filament. Mass-spectrograph analyses of ion beams were made; for Al, negative ions of mass 27, probably Al<sup>-</sup>, were observed.

N. M. B.

**Approximate numerical values of the atomic field and radial wave functions of the silver ion.** (MISS) M. M. BLACK (Mem. Manchester Phil. Soc., 1934—1935, 79, 29—33).—Calculations of the approx. at. field and wave functions of Ag<sup>+</sup> have been computed by the method of self-consistent field.

R. S. B.

**Products of ionisation in methane.** J. A. HIPPLE, jun., and W. BLEAKNEY (Physical Rev., 1935, [ii], 47, 802).—The ions CH<sub>4</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, CH<sub>2</sub><sup>+</sup>, CH<sup>+</sup>, C<sup>+</sup>, H<sub>2</sub><sup>+</sup>, and H<sup>+</sup> have been observed by the usual mass-spectrograph method. Excepting H<sub>2</sub><sup>+</sup>, which may be an impurity, these ions are primary products. The appearance potentials are 13.7, 14.7, 15.7, 23, 27, —, and 31 volts, respectively. No negative or doubly-charged ions were observed. CD<sub>4</sub> and CHD<sub>3</sub> show characteristics similar to CH<sub>4</sub>.

L. S. T.

**Separation of isotopes by centrifuging.** J. W. BEAMS and F. B. HAYNES (Physical Rev., 1936, [ii], 50, 491—492).—The possibility of adapting a new air-driven centrifuge, giving "velocity separation" as well as centrifugal separation, is investigated by experiments on N<sub>2</sub>-CO<sub>2</sub> mixtures, relative to rotor speed and design. A change in *d* of fractions of CCl<sub>4</sub> was observed.

N. M. B.

**Production of helium of mass three?** H. D. SMYTH, G. P. HARNWELL, W. BLEAKNEY, and W. W. LOZIER (Physical Rev., 1935, [ii], 47, 800—801).—A discussion of doubts concerning the interpretation of previous results (this vol., 301).

L. S. T.

**Oxygen isotopes.** W. BLEAKNEY and J. A. HIPPLE, jun. (Physical Rev., 1935, [ii], 47, 800).—Mass-spectrographic analyses of > 100 samples of O<sub>2</sub> from various sources give vals. of <sup>16</sup>O : <sup>18</sup>O around 500. Commercial O<sub>2</sub> varies in isotopic concn. from tank to tank, suggesting that refinements of some at. wt. determinations are meaningless without a simultaneous isotopic analysis. Fractionation of the O isotopes produced by electrolysis of H<sub>2</sub>O is approx. 1.01.

L. S. T.

**Chemical differences between nitrogen isotopes.** H. C. UREY and A. H. W. ATEN, jun. (Physical Rev., 1936, [ii], 50, 575; cf. Ogawa, this vol., 1079).—Preliminary results of attempted separations by fractionation and exchange reaction methods are reported.

N. M. B.

**Mass-spectrograph analysis of beryllium.** W. BLEAKNEY, J. P. BLEWETT, R. SHERR, and R. SMOLUCHOWSKI (Physical Rev., 1936, [ii], 50, 545—546).—A new ion source for positive-ray analysis was developed

in the form of a mol. beam from a hot oven; ions were produced in the beam by electron impact and focussed on the slit of the mass spectrograph by electric fields. Application to Be revealed only  $^9\text{Be}$ . The upper limit for  $^8\text{Be}$  was 1 part in 10,000.

N. M. B.

**Mass-spectrograph study of Ba, Sr, In, Ga, Li, and Na.** M. B. SAMPSON and W. BLEAKNEY (Physical Rev., 1935, [ii], 50, 456—460).—Using a  $180^\circ$ -type mass-spectrograph of 22 cm. radius with 1400 gauss magnetic field, an analysis was made of the ions from coated filaments. Peaks for Sr at 84, comprising 0.5% of the total Sr current, and for Ba at 134, comprising 1.8% of the total Ba current, are interpreted as new Sr and Ba isotopes. A third isotope of In was not found. Relative abundances of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  were 38.8% and 61.2%, respectively.  $^6\text{Li}$  and  $^{23}\text{Na}$ , reported by Brewer (cf. this vol., 918), were not confirmed.

N. M. B.

**Variations of the at. wts. of terrestrial elements.** V. I. VERNADSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 129—133).—A review and discussion of the isotopic compositions of elements.

A. J. E. W.

**Ranges of particles emitted by samarium.** L. LEWIN (Nature, 1936, 138, 326).—In addition to  $\alpha$ -particles of 1.150 cm. range, ionising particles of 0.13 cm. range contributing approx. 35% of the total ionisation due to  $\alpha$ -particles are emitted by Sm.

L. S. T.

**Emission of protons by samarium.** J. A. BEARDEN and W. R. KANNE (Physical Rev., 1935, [ii], 47, 639).—Two groups of  $\alpha$ -particles (cf. this vol., 130) differing in range by 2 mm., but no proton emission (cf. A., 1934, 713), have now been detected.

L. S. T.

**Diffusion of radioactive atoms.** J. A. GRAY and J. F. HINDS (Physical Rev., 1935, [ii], 47, 813).—The relative rates of deposit of Ra-D, -E, and -F on plates placed above a source of Ra-(D+E+F) from Rn have been compared with the equilibrium vals. These atoms diffuse through thin metal foils, the Ra-E more easily than -D and -F.

L. S. T.

**Excitation curves for fluorine and lithium.** L. R. HAFSTAD, N. P. HEYDENBURG, and M. A. TUVE (Physical Rev., 1936, [ii], 50, 504—514; cf. A., 1935, 1296, 1297).—Results are given of observations of increased accuracy, using a corona-free, 10,000-megohm voltmeter-resistor for voltage measurements, on the  $\alpha$ -particles from Li and the  $\gamma$ -rays from Li and F, when bombarded with protons of energies up to 1000 kv. A weak multiplet structure in F is indicated in the region 500—700 kv., with a broad but fairly prominent "resonance" at 650—700 kv.

N. M. B.

**$\alpha$ -Activity excited in cerium and caesium by neutrons.** E. FUNFER (Physikal. Z., 1936, 37, 693—694).—Contrary to Dopel (this vol., 659) no marked activity could be excited in Ce (using  $\text{CeO}_2$ ) or in Cs (using  $\text{CsCl}$ ) by bombardment with neutrons.

A. J. M.

**High-frequency parallel rod method for the determination of  $\alpha$ -ray speeds.** T. R. WILKINS,

W. RAYTON, and H. ST. HELENS (Physical Rev., 1935, [ii], 47, 812).

L. S. T.

**$\alpha$ -Ray and proton tracks in photographic emulsions.** T. R. WILKINS, W. RAYTON, and H. ST. HELENS (Physical Rev., 1935, [ii], 47, 812).— $\alpha$ -Ray and proton tracks showing Rutherford scattering have been observed; an analysis of the tracks observed when collimated  $\alpha$ -rays fall on a  $\text{H}_2\text{CrO}_4$ -sensitised emulsion has been made.

L. S. T.

**$\alpha$ -Particle scattering by deuterons and protons.** H. MARGENAU and E. POLLARD (Physical Rev., 1935, [ii], 47, 640).—For  $\alpha$ -particle collision with protons anomalous scattering is detected at the range of a 1.7 cm.  $\alpha$ -particle; for D the  $\alpha$ -particle range is 1.3—1.6 cm.

L. S. T.

**Precise measurement of three radium-B  $\beta$ -particle energies.** F. T. ROGERS, jun. (Physical Rev., 1936, [ii], 50, 515—523; cf. Scott, A., 1934, 1284).—Vals. of  $H_\rho$ , where  $H$  is the magnetic field required to produce a radius  $\rho$  of curvature of path, measured for the three most intense Ra-B  $\beta$ -particle lines by a precise magnetic spectrograph method, are 1406.0, 1671.1, and 1931.5 gauss cm., accurate to 1 part in 3000, and the corresponding energies are  $1.512 \times 10^5$ ,  $2.044 \times 10^5$ , and  $2.610 \times 10^5$  e.v.

N. M. B.

**Scattering of  $\gamma$ -rays.** R. S. SHANKLAND (Physical Rev., 1936, [ii], 50, 571).—Experiments previously described (cf. this vol., 265) are extended with modified apparatus.

N. M. B.

**$\gamma$ -Radioactivity with continuous spectrum. New unitary field theory.** E. C. G. STUECKELBERG (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 64—69).—Energy considerations are discussed. A new field theory, analogous to that of Born, uses spinors instead of vectors, and considers the electron, neutrino, proton, and neutron as different quantum states of a single elementary particle.

N. M. B.

**Neutron effects in a photographic emulsion.** D. W. MUELLER and H. A. BARTON (Physical Rev., 1935, [ii], 47, 796; cf. A., 1935, 1441).—The proton and  $\alpha$ -particle tracks produced by the passage of neutrons through photographic emulsions have been investigated.

L. S. T.

**Absorption cross-sections of thermal neutrons.** C. T. ZAHN, E. L. HARRINGTON, and S. GOUDSMIT (Physical Rev., 1936, [ii], 50, 570).—The back scattering of slow neutrons from a thick layer is measured by immersing a detector foil in a liquid and comparing the activity caused by the neutrons for the bare foil with that when the neutrons have been screened on one side. Hence the absorption cross-sections can be calc. (cf. Bayley, below). Approx. results are obtained with dil. Cd salt solutions.

N. M. B.

**Diffusion of slow neutrons.** D. S. BAYLEY, B. R. CURTIS, E. R. GAERTNER, and S. GOUDSMIT (Physical Rev., 1936, [ii], 50, 461—463).—The effect of Ag, Cu, C, and Cd on the diffusion in  $\text{H}_2\text{O}$  of slow neutrons, as indicated by the decrease of activity of Rh and Ag foil detectors, was investigated and plotted. The interpretation of data on the back



scattering of neutrons (cf. Mitchell, this vol., 541) is discussed. N. M. B.

**Behaviour of slow neutrons at different temperatures.** E. AMALDI and E. SEGRE (Physical Rev., 1936, [ii], 50, 571).—Measurements of the reflexion coeff. of paraffin for thermal neutrons show that the result is the same at liquid air and at room temp. Hence the mean free path and mean life of the neutrons in paraffin cannot be independent of their velocity, and scattering is not isotropic. N. M. B.

**Bragg reflexion of slow neutrons.** D. P. MITCHELL and P. N. POWERS (Physical Rev., 1936, [ii], 50, 486—487).—Using large MgO single crystals, data for relative reflexion and scattering indicate that the observed reflexion of slow neutrons is in accord with the Bragg relation between their de Broglie  $\lambda$  and the grating space of the crystals. N. M. B.

**Influence of temperature on the "groups" of slow neutrons.** A. ARSENJEWA-HEIL, O. HEIL, and C. H. WESTCOTT (Nature, 1936, 138, 462).—The radioactivity induced in Ag at 20°, 77°, and 290° abs. by slow neutrons of different energies, the A, B, and C groups of Amaldi and Fermi, has been determined. All three groups are affected by changes in temp. The assumption that the absorption coeff. of B varies inversely as the velocity of the neutrons is erroneous. L. S. T.

**Absorption of neutrons in silver and cadmium.** N. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 235—236).—The absorption of neutrons in Ag remains practically unchanged with increased thickness of paraffin whereas in Cd there is a steady increase. The region of intense absorption in Ag begins when the velocity of the neutrons is substantially  $>$  in the corresponding region in Cd. W. R. A.

**Absorption of thermal neutrons in silver at low temperatures.** V. FOMIN, F. G. HOUTERMANS, I. V. KURTSCHATOV, A. I. LEIPUNSKI, L. SCHUBNIKOV, and G. SCHTSCHEPKIN (Nature, 1936, 138, 326—327).—Data obtained at 20.4°, 77°, and 290° abs. are discussed in relation to a Maxwellian distribution for the energies of the neutrons. L. S. T.

**Nuclear reactions due to neutrons of 2 m.e.v. energy.** E. T. BOOTH and C. HURST (Nature, 1936, 138, 367—368).—No appreciable activity was observed when Mn, Cr, Al, Zn, Si, Fe, Ni, Ca, and Mg were bombarded for periods varying from 20 min. to 6 hr. by neutrons of approx. 2 m.e.v. energy obtained by bombarding D<sub>2</sub> with D ions. L. S. T.

**Scattering of neutrons by protons.** M. A. TUBE and L. R. HAFSTAD (Physical Rev., 1936, [ii], 50, 490—491).—Corr. measurements for 600—1200 kv. neutrons from C, with precautions to eliminate the effect of any neutrons of energy  $<$ 300 kv., agree with the predictions of Wigner's formula. N. M. B.

**Nuclear chemistry and the scattering of protons in collisions with neutrons.** D. M. GANS and W. D. HARKINS (Physical Rev., 1935, [ii], 47, 795—796). L. S. T.

**Capture and scattering of neutrons.** H. A. BETHE (Physical Rev., 1935, [ii], 47, 640).—Theoretical. L. S. T.

**Scattering of fast neutrons by heavy nuclei.** C. H. FAY (Physical Rev., 1936, [ii], 50, 560—567; cf. Dunning, A., 1935, 1186).—Mathematical. An investigation neglecting polarisation indicates that effects due to this are small. N. M. B.

**Neutron absorption of boron and cadmium at low temperatures.** V. FOMIN, F. G. HOUTERMANS, A. I. LEIPUNSKI, L. B. RUSINOV, and L. V. SCHUBNIKOV (Nature, 1936, 138, 505).—The effect of temp. on the absorption of neutrons in Fermi's group C by B and Cd using the 2.3 min. Ag activity as detector has been measured. The absorption curve of Cd has a selective character. L. S. T.

**Effect of hydrocarbons at low temperatures on slow neutrons.** W. F. LIBBY and E. A. LONG (Physical Rev., 1936, [ii], 50, 575—576).—Ag targets were bombarded with slow neutrons passed through paraffin cylinders or through a thickness of *n*-heptane. Ag activities plotted against temp. for the range 25—300° abs., obtained by the gradual warming of liquid H<sub>2</sub>, support the assumptions that the neutrons are at the temp. of the hydrocarbon, and that the proton capture and Ag capture cross-sections are  $\propto 1/(\text{neutron velocity})$ . N. M. B.

**Bond effect in the action of protons on neutrons.** W. F. LIBBY and E. A. LONG (Physical Rev., 1936, [ii], 50, 577).—The slowing power of protons on slow neutrons was investigated with liquid and solid H<sub>2</sub>, paraffin, and AcOH, using Ag targets (cf. preceding abstract). There is a nearly identical Ag activity whether the Dewar flask is filled with low-temp. H<sub>2</sub> or with a solution of the same proton density at room temp. Results indicate that the neutrons are cooled to a mean temp.  $\sim$  150° abs., and the expected increase in Ag activity is nearly offset by the increase in capture by protons. N. M. B.

**Resonance energy of cadmium for neutron capture.** E. SEGRE and C. T. ZAHN (Physical Rev., 1936, [ii], 50, 577—578).—The results of Powers (cf. *ibid.*, 49, 650) and of Rasetti (cf. this vol., 264) are considered in terms of the Breit-Wigner formula for the cross-section involved. An approx. resonance energy of 0.05<sub>5</sub> volt and a half-width of about the same val. are deduced. N. M. B.

**Resonance levels for absorption of neutrons.** J. ROTBLAT (Nature, 1936, 138, 545).—The ionisation currents due to slow neutrons from Po+Be produced in a B-coated chamber have been measured in absence and presence of absorbers of Cd, Cd+Ag, Au, and I as KI, and the resonance levels of the neutrons calc. L. S. T.

**Names of and symbols for the artificially radioactive elements.** G. M. PETTY (Science, 1936, 84, 183).—The prefix *radio-* and symbol *ra-* are suggested. L. S. T.

**Symbols for the artificially radioactive elements.** S. C. LIND (Science, 1936, 84, 228—229).—Rd is suggested as a prefix for the natural radioactive elements and "rd-" for the artificial ones. L. S. T.

Analysis of the data on radioactivity induced by neutron bombardment. C. N. WARFIELD (Physical Rev., 1935, [ii], 47, 796—797).—Eight generalisations are put forward. L. S. T.

Correlation of nuclear disintegration processes. M. S. LIVINGSTON and R. D. EVANS (Physical Rev., 1935, [ii], 47, 795; cf. this vol., 919).—The known artificial nuclear transformations and natural radioactive processes are classified under one of 14 generalised type reactions. The 200 or more reactions can be represented diagrammatically. L. S. T.

Radio-helium. T. BJERGE (Nature, 1936, 138, 400).—Bombardment of finely-pptd  $\text{Be}(\text{OH})_2$  by neutrons from  $\text{Be}+\text{Rn}$  produces a radioactive gas of half-period approx. 1 sec. in the  $\text{Be}(\text{OH})_2$  (cf. this vol., 773). The gas is  $^3\text{He}$  or possibly  $^4\text{He}$ . L. S. T.

$\beta$ -Ray spectrum of radio-helium. T. BJERGE and K. J. BROSTROM (Nature, 1936, 138, 400).—The energy distribution of radio-He (cf. preceding abstract) has been measured. The upper limit of the spectrum is probably  $3.7 \pm 0.5$  m.e.v. Probable reactions are  $^7\text{Be} + \frac{1}{2}n \rightarrow ^7\text{He} + ^4\text{He}$  and  $^6\text{He} \rightarrow ^3\text{Li} + e^-$ . L. S. T.

Low-voltage disintegration of lithium with lithium. C. A. WHITMER and M. L. POOL (Physical Rev., 1935, [ii], 47, 795).— $\alpha$ -Particles are produced by bombardment of a Li target with multiply-charged Li ions accelerated by a potential of approx. 120 kv.  $\text{LiOH}$  and  $\text{LiOD}$  give a larger yield than pure Li, but a Be target gives no results. L. S. T.

(A) Deuteron-induced radioactivities. J. J. LIVINGOOD. (B) Deuteron-induced radioactivity in tin. J. J. LIVINGOOD and G. SEABORG (Physical Rev., 1936, [ii], 50, 425—434, 435—439).—(A) Bombardment of elements with 5-m.e.v. deuterons gave the following results: commercial Cu decays with half-life  $130 \pm 10$  days, emitting  $\gamma$ -rays and very slow electrons; Zn emits electrons with half-lives  $97 \pm 10$ ,  $25 \pm 2$ ,  $12 \pm 1$ , and  $1 \pm 0.3$  hr., the third being probably due to radio- $^{64}\text{Cu}$ ; Sb gives electron activities with half-lives  $50 \pm 4$  days,  $68 \pm 2$  and  $24 \pm 2$  hr.; corresponding results for Ru are  $46 \pm 3$ ,  $11 \pm 2$  days,  $39 \pm 1$  and  $4 \pm 1$  hr. Bi yields electrons of 5 days half-life and  $\alpha$ -particles increasing in no. to a const. val. after 3 weeks; this is interpreted as the synthesis of Ra-E thus:  $^{209}\text{Bi} + ^2\text{H} \rightarrow ^{210}\text{Bi}$  (i.e.,  $\text{Ra-E} + ^1\text{H}$ ), followed by its decay to Po and thence to Pb.

(B) Sn was bombarded with 5-m.e.v. deuterons and chemically analysed for transmutation into radioactive In, Sn, and Sb isotopes. The In fraction shows strong electron emission of  $26 \pm 2$  hr. half-life and a very weak activity of half-life probably several months. The Sn ppt. emits an intense electron group of half-life  $28 \pm 2$  hr. and a weak activity as for In. Two Sb isotopes are formed with half-lives  $13.3 \pm 1$  hr. and  $112 \pm 30$  days. Short period activities from bombarded Sn are of  $12 \pm 2$  and  $45 \pm 5$  min. half-life. Absorption curves in Al are given and possible transmutations discussed. N. M. B.

Radioactive isotopes of bromine. C. H. JOHNSON and F. T. HAMBLIN (Nature, 1936, 138, 504).—

After exposure to neutrons for 1 week liquid Br gives an activity of approx. 24 hr. half-period. AgBr pptd. from irradiated aq.  $\text{NH}_4\text{Br}$  gives a similar effect. The reactions  $^{79,81}\text{Br} + \frac{1}{2}n \rightarrow ^{79,81}\text{Sc} + ^1\text{H}$  or  $^{76,83}\text{As} + ^4\text{He}$  are excluded. This activity is probably due to another radioactive isotope of Br or to an excited Br nucleus, since it has not been possible to separate it from the 18 min. and 4.2 hr. activities observed by Fermi *et al.* Possible reactions are discussed. L. S. T.

Measurement of single corpuscular rays in presence of intense  $\gamma$ -rays. H. POSE (Z. Physik, 1936, 102, 379—407).—A description is given of apparatus used for the investigation of nuclear transformations brought about with  $\alpha$ -particles. Results obtained with Al are similar to those of Duncanson and Miller (A., 1934, 1284). A. E. M.

Specific ionisation of cosmic radiation. M. G. E. COSYNS (Nature, 1936, 138, 284).—Sp. ionisations of cosmic rays in  $\text{H}_2$ , He, and A are recorded. L. S. T.

Measurements of cosmic ray intensity in a deep [coal] mine. J. BARNÓTHY and M. FORRO (Nature, 1936, 138, 325, 399).—Cosmic rays penetrate a layer equiv. to a thickness of 1500 m. of  $\text{H}_2\text{O}$ , corresponding with particles of an energy  $> 10^{12}$  e.v. L. S. T.

Search for protons in the primary cosmic-ray beam. C. G. MONTGOMERY, D. D. MONTGOMERY, W. E. RAMSEY, and W. F. G. SWANN (Physical Rev., 1936, [ii], 50, 403—407).—Measurements of ionisation spurts above an assigned size are an indication of the presence of charged particles towards the end of their range. Results indicate an upper limit of the no. of protons as 5% of the total no. of cosmic rays at sea level. N. M. B.

Variation of cosmic ray intensity with sidereal time. B. F. J. SCHONLAND, B. DELATIZKY, and J. P. GASKELL (Nature, 1936, 138, 325). L. S. T.

Longitude effect of cosmic radiation. M. S. VALLARTA (Physical Rev., 1935, [ii], 47, 800; cf. A., 1935, 560). L. S. T.

Structure of cosmic rays. II. B. TRUMPY (Z. Physik, 1936, 102, 691—696).—No confirmation is obtained of the results of Hilgert and Botha (cf. this vol., 658) that by passage of cosmic rays through coal photons are formed which produce showers in Pb. O. D. S.

Angular distribution and number of pairs (C-rays) produced by cosmic ultra-radiation in lead. B. PUSCHER (Physikal. Z., 1936, 37, 661—663).—A curve is given showing the angular distribution of C-rays in terms of coincidences per hr. at different angles. The max. occurs at  $7-12^\circ$ . A. J. M.

Production of cosmic ray showers. A. BRAMLEY (Science, 1936, 84, 206—207).—Theoretical. L. S. T.

Absorption analysis of the Hoffmann collisions. J. BOGGILD and A. KARKOV (Naturwiss., 1936, 24, 588—589).—An experiment described indicates that the collisions are accompanied by a soft radiation. A. J. M.



**Dependence of burst production on atomic number.** C. G. MONTGOMERY and D. D. MONTGOMERY (Physical Rev., 1936, [ii], 50, 490; cf. this vol., 133).—Investigation of bursts originating in small thicknesses of Mg, Fe, Sn, and Pb shows that the rate of production of bursts  $\propto$  (at. no.)<sup>2</sup>. Results indicate that the nuclei remain intact under the impact of cosmic rays, and that the building-up process involved in burst formation is not one of pair production. N. M. B.

**Production and absorption of cosmic-ray showers [in lead].** R. H. WOODWARD and J. C. STREET (Physical Rev., 1935, [ii], 47, 800). L. S. T.

**Absence of cosmic rays from Nova Lacertæ.** BARNÓTHY and M. FORRÓ (Nature, 1936, 138, 544—545). L. S. T.

**Interaction of the neutron and proton.** Y. NISHINA, S. TOMONAGA, and H. TAMAKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 61—69).—Mathematical. Experimental results are explained on the basis of simultaneous Heisenberg exchange forces and Majorana forces. N. M. B.

**Energy states of valency electrons in some metals. I. (2) Absolute values of some X-ray levels of zinc.** M. SATÔ (Sci. Rep. Tôhoku, 1936, 25, 197—201).—Theoretical. Energy levels calc. for Zn are: *K* term 711.880 Ryd., valency electrons *E*<sub>1</sub> 0.960, *E*<sub>2</sub> 0.840, *E*<sub>3</sub> 0.600, *E*<sub>4</sub> 0.581, *E*<sub>5</sub> 0.545, and *E*<sub>6</sub> 0.021 crystal Ryd. units. O. D. S.

**Coulomb energy of <sup>3</sup>He.** S. S. SHARE (Physical Rev., 1936, [ii], 50, 488—489).—Mathematical. The difference in binding energies of <sup>3</sup>H and <sup>3</sup>He is approx. equal to the calc. Coulomb, energy, supporting the view that, except for the Coulomb repulsion between protons, the neutron-neutron and proton-proton attractions are equal. N. M. B.

**Electric quadrupole moment of the nucleus <sup>123</sup>I.** (A) T. SCHMIDT. (B) S. TOLANSKY (Nature, 1936, 138, 404—405, 405).—(A) The <sup>123</sup>I nucleus has a negative electric quadrupole moment  $< -0.5 \times 10^{-24}$ , the negative sign indicating that the charge distribution is flattened in the direction of the spin axis.

(B) The moment suggested can only be considered tentative. L. S. T.

**Nuclear states and moments.** D. R. INGLIS (Physical Rev., 1935, [ii], 47, 813; cf. A., 1935, 278).—A discussion. L. S. T.

**Relation between hyperfine structure and atomic nuclei.** H. SCHULER and H. KORSCHING (Z. Physik, 1936, 102, 373—378).—Certain rules for the building up of at. nuclei are formulated from a consideration of hyperfine structure data. The relative abundance of isotopes of all elements for which the data are available conforms to these rules.

H. C. G.

**Dependence of nuclear forces on spin.** C. F. VON WEINSACKER (Z. Physik, 1936, 102, 572—602).—Mathematical. The dependence of nuclear forces on the spin orientation of protons and neutrons is investigated. O. D. S.

**Magnetic moment of the proton.** H. HONL (Naturwiss., 1936, 24, 637—638).—Theoretical. It is shown that the magnetic moment of the proton is about 3 nuclear magnetons (1 nuclear magneton = 1 Bohr magneton/1840). A. J. M.

**Gyromagnetic properties of the hydrogens.** J. M. B. KELLOGG, I. I. RABI, and J. R. ZACHARIAS (Physical Rev., 1936, [ii], 50, 472—481).—The nuclear moments of the proton and deuteron were measured by the method of at. beams, independently of at. velocity distribution, and the signs of the moments by the method of non-adiabatic transitions in a weak magnetic field. Results are:  $\mu_H$  2.85 ± 0.15;  $\mu_D$  0.85 ± 0.03 nuclear magnetons; signs of both moments are positive. N. M. B.

**Conservation of energy in radiation processes.** E. J. WILLIAMS and E. PICKUP (Nature, 1936, 138, 461—462).—Further experiments on the production of photo-electrons in A by X-rays confirm the light-quantum theory and the applicability of conservation principles to X-radiation processes (cf. this vol., 660). L. S. T.

**Energy levels of light nuclei.** G. BECK (Physical Rev., 1935, [ii], 47, 809—810).—Theoretical. L. S. T.

**Nature of energy states in solids.** F. H. SPEDDING (Physical Rev., 1936, [ii], 50, 574).—In view of discrepancies arising from the application of the theory for the behaviour of energy levels of an atom subjected to the electric fields of other atoms in a cryst. solid, as developed by Penny (cf. A., 1932, 985) and Frank (cf. this vol., 19), results of a spectroscopic study of the energy levels of Nd, Sm, Er, and Dy are reported. Energy level separations as found from absorption spectra are compared with those predicted by theory. N. M. B.

**Interaction of heavy nuclear particles.** D. IVANENKO and A. SOKOLOV (Nature, 1936, 138, 246).—Theoretical. L. S. T.

**Correlation between electromagnetic theory and wave mechanics.** L. T. DEVORE (Physical Rev., 1935, [ii], 47, 638). L. S. T.

**Approximate determination of the atomic wave functions of chromium.** A. PORTER (Mem. Manchester Phil. Soc., 1934—1935, 79, 75—81).—Calculations for Cr and Cr<sup>++</sup> have been made using the differential analyser. R. S. B.

**Validity of X-ray crystal methods of determining *e*.** J. W. M. DUMOND and V. L. BOLLMAN (Physical Rev., 1936, [ii], 50, 524—537).—Measurements with extremely finely powdered calcite give conclusive evidence in favour of the X-ray crystal method. The val. of *e* is 4.799 ± 0.007. Several new unexplained crystal diffraction effects are described.

N. M. B.

**Application of the Franck-Condon principle to continuous absorption spectra of diatomic molecules.** H. TRIVEDI (Proc. Acad. Sci. U.P., 1935, 4, 59—70).—Theoretical. CH. ABS. (e)

**Determination of the atmospheric transparency coefficients for different spectral rays and the density of atmospheric ozone.** N. P.

LUGIN (J. Geophys. U.S.S.R., 1935, 5, 58—76).—Transparency data and vals. for the  $[O_3]$  are given.

CH. ABS. (e)

**Isotopes and molecular asymmetry.** T. IRDALE (Nature, 1936, 138, 292).—It is suggested that asymmetric mols. containing Me and F should be examined for optical resolution.

L. S. T.

**Absorption spectrum of hydrogen peroxide vapour.** R. S. SHARMA (Proc. Acad. Sci. U.P., 1934, 4, 51—58).—The ultra-violet absorption spectrum of 3, 10, and 30% aq.  $H_2O_2$  terminates abruptly at 2055 Å., corresponding with  $H_2O_2 + 136.1$  kg.-cal. =  $2H + O_2$ . The recombination spectrum corresponds with  $H + HOO - H_2O_2 + 59.6$  kg.-cal. CuO in the absorption tube became reddish, showing the presence of at. H.

CH. ABS. (e)

**Spectroscopic investigation of chemical reactions of OH in the electric discharge.** A. A. FROST and O. OLDENBERG (Physical Rev., 1935, [ii], 47, 788).—OH produced by the electric discharge through  $H_2O$  vapour has a lifetime of the order of  $\lambda$  sec. The chief process by which OH disappears is indicated to be the three-body process  $OH + OH + M \rightarrow H_2O_2 + M$ .

L. S. T.

**Ultra-violet absorption spectra of the deutero-ammonias.** W. S. BENEDICT (Physical Rev., 1935, [ii], 47, 641).—Spectrograms of  $NH_3$  containing varying amounts of D have been obtained over a wide range of temp. and pressure. Vibrational analyses have been made for  $NH_3$ ,  $NH_2D$ ,  $NHD_2$ , and  $ND_3$ .

L. S. T.

**Band system of copper deuteride.** M. A. JEPPESEN (Physical Rev., 1936, [ii], 50, 445—449).—Full data and analysis of the system photographed at high dispersion are tabulated and constns. are evaluated. The electronic isotope displacement of CuD relative to CuH is  $19\text{ cm}^{-1}$ .

N. M. B.

**Pressure effect on the C band of strontium hydride.** R. F. HUMPHREYS and W. R. FREDRICKSON (Physical Rev., 1936, [ii], 50, 542—545; cf. A., 1935, 1443).—At low  $H_2$  pressures the emission spectrum of the 3808 Å. band of SrH shows a sharp break-off at  $R(18)$ , but at high pressures the lines extend to  $R(49)$ . Perturbations due to resonance and predissociation are present. Frequency assignments are tabulated, and electronic configurations and probable dissociation energies are discussed.

N. M. B.

**Band spectrum of silicon fluoride.** R. M. BADGER and C. M. BLAIR, jun. (Physical Rev., 1935, [ii], 47, 881).—A re-examination of the violet spectrum obtained in the Si fluoride discharge reveals two systems with considerable overlapping. Previous conclusions (A., 1927, 1005) are invalidated. The emitter is probably SiF.

L. S. T.

**Absorption spectra of the vapours of sulphur monochloride and thionyl chloride and their constitutions.** H. TRIVEDI (Proc. Acad. Sci. U.P., 1935, 4, 263—268).—The ultra-violet absorption spectra of both  $S_2Cl_2$  and  $SOCl_2$  show two bands at 2740, 2135 and 2980, 2040 Å., respectively. The differences in energy between the beginnings of the

bands correspond with that between the 3P and 1D states of S (for  $S_2Cl_2$ ) and of O (for  $SOCl_2$ ). The structures are  $S:S:Cl_2$  and  $O:S:Cl_2$ .

CH. ABS. (e)

**Band system of TiCl.** A. E. PARKER and A. H. PARKER (Physical Rev., 1935, [ii], 47, 812).—The four-headed band system extending from 4340 to 3730 Å. has been analysed.

L. S. T.

**Band spectrum of arsenic oxide and lead oxide.** E. N. SHAWHAN and F. MORGAN (Physical Rev., 1935, [ii], 47, 199; cf. A., 1935, 562).—The band spectrum of AsO has been investigated in emission and in absorption. Two systems of double double-headed bands have been analysed.

L. S. T.

**Far ultra-violet absorption spectra and ionisation potentials of the alkyl halides.** I. [Methyl halides.] II. [Ethyl and higher halides.] W. C. PRICE (J. Chem. Physics, 1936, 4, 539—547, 547—551).—I. The absorption spectra of MeI, MeBr, and MeCl have been photographed in the region 2000—1000 Å. The bands are due to excitation of non-binding electrons in the halogen atoms, and the ionisation potentials deduced from the Rydberg series are: MeI 9.49 and 10.11 volts, MeBr 10.49 and 10.80, and MeCl 11.17 and 11.25, in general accord with theory (cf. A., 1935, 562). The vibrational nature of the bands is discussed and the three spectra are correlated.

II. The Rydberg series found in the range 2000—1000 Å. lead to the ionisation potentials EtI 9.30 and 9.88, and EtBr 10.24 and 10.56 volts. Other halides gave very diffuse bands, and continuous absorption from C-C and C-H linkings interfered. The ionisation potentials of consecutive members of the homologous series probably diminish asymptotically to a limiting val.

J. G. A. G.

**Mutual optical effect of neighbouring colour carriers in a molecule.** H. FROMHERZ, W. AUMULLER, and C. O. STROTHER (Z. Elektrochem., 1936, 42, 680).—For dihalogenated paraffins with at least one  $CH_2$  between the halogen (Br or I) atoms, the light absorption is const. and equal to the sum of the absorptions of the individual groups. When the halogen atoms are nearer, and especially when they are the same, the absorption band shifts towards longer  $\lambda$ . This effect is increased when the H near the halogens is replaced by alkyl.

J. W. S.

**Light absorption and tautomerism of uric acid.** H. FROMHERZ and A. HARTMANN (Z. Elektrochem., 1936, 42, 687).—The absorption spectrum of uric acid has been measured in pure  $H_2O$  and in presence of excess of  $HClO_4$  and of NaOH, comparison being made with the absorption spectra of substituted uric acids of definite keto- and enol forms. The results indicate that in  $H_2O$  or acid, uric acid is in the keto-form, but addition of a little NaOH shifts the absorption bands towards longer  $\lambda$ , corresponding with the enol form. This is a halochromatic effect due to dissociation of a H atom, and is compared with the change in absorption between dissociated and undissociated  $CO_2H$  groups.

J. S.

**Influence of substituents on the ultra-violet absorption spectra of simple and double-linking**



conjugated benzene chromophores. M. PESTEMER, T. LANGER, and F. MANCHEN (Monatsh., 1936, 68, 326—348).—The absorption spectra of  $\text{BzCl}$ ,  $\text{CHPhCl}_2$ ,  $\text{CPhCl}_3$ , styrene,  $\text{COPhMe}$ , and  $\text{PhCHO}$  and of their  $\text{NH}_2$ -,  $\text{CN}$ -, and  $\text{NO}_2$ -substitution products have been studied in the region 25,000—50,000  $\text{cm}^{-1}$ , and compared with those of  $\text{C}_6\text{H}_6$  and  $\text{PhMe}$  compounds. The effect of the substituents on both the *A* (38,500—43,400  $\text{cm}^{-1}$ ) and *B* (49,000—52,000  $\text{cm}^{-1}$ ) bands of the conjugated systems  $\text{Ph}\cdot\text{C}\cdot\text{C}$  and  $\text{Ph}\cdot\text{C}\cdot\text{O}$  is to shift them towards longer  $\lambda$ , the effects being in the order  $p > m > o$ . This is the same order as the effect of substituents on the *B* band for  $\text{PhMe}$ , but the reverse of that for the *A* band. The relative effects of the  $\text{NH}_2$ - and of the  $\text{NO}_2$ - and  $\text{CN}$ -groups are in accord with their respective negative and positive characters. J. W. S.

**Absorption spectra of anils of aliphatic ketones. Absorption in the ultra-violet and structure of anils and  $\alpha$ -ethylenic amines.**—See this vol., 1242.

**Optical absorption of the porphyrins. VII.** A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1936, 177, 165—192; cf. this vol., 1178).—Introduction of vinyl groups into the dihydroporphyrin system (I) shifts the absorption max. towards the red and at times intensifies them, but does not alter the type of the absorption curve.  $\gamma$ -Substitution with weak chromophoric groups has little effect. Introduction of a CO at 3 causes the curve to change to the "rhodin" type, band I of the spectrum being depressed and shifted towards the blue. Oximation raises band I and shifts it towards the red. CO at 6 does not give rise to the rhodin type of curve. It is inferred that nucleus III differs in structure from nuclei I and II, and has no double linking at 5:6, and that in this nucleus are located the optically active centres of the system (cf. A., 1935, 1383). Chlorin  $p_6$  and pseudochlorin  $p_6$  have different absorption curves and are in some way stereoisomeric. The purpurins and rhodins seem to have the (I) framework. Mg in (I) only displaces the fluorescence bands towards the red. R. C.

**Ultra-violet absorption spectra of thyroxine, thyronine, tyrosine, di-iodotyrosine, and thyroglobulin.**—See this vol., 1249.

**Gossypol.** R. GRÜNBAUMÓWNA and L. MARCHLEWSKI (Biochem. Z., 1936, 286, 295—296).—An absorption curve of gossypol acetate showing max. at 3780 and 2390 Å. and a min. at 3220 Å. is given. P. W. C.

**Nuclear vibration bands of solid carbon dioxide.** W. DAHLKE (Z. Physik, 1936, 102, 360—372).—Apparatus for determining the absorption of thin layers of solid  $\text{CO}_2$  at about 100° abs., throughout the spectrum from the visible to 17  $\mu$  is described. Three absorption bands are obtained similar to the rotation-vibration bands found in the gas. The possibility of mol. rotation in solid  $\text{CO}_2$  is discussed. A. E. M.

**2.73  $\mu$  Absorption band in fused silica.** D. G. DRUMMOND (Nature, 1936, 138, 248—249).—The view that this band is due to  $\text{CO}_2$  contamination is favoured (cf. this vol., 921). L. S. T.

**Diffuse infra-red transmission of solids.** J. D. HARDY and C. MUSCHENHEIM (Physical Rev., 1935, [ii], 47, 789). L. S. T.

**Fundamental absorption bands of the deutero-ammonias.** M. V. MIGOTTE and E. F. BARKER (Physical Rev., 1936, [ii], 50, 418—424; cf. *ibid.*, 1935, [ii], 47, 892).—The four fundamental vibration bands of  $\text{ND}_3$  were observed in infra-red absorption,  $\nu_3$  being double as in  $\text{NH}_3$ ; the parallel frequencies are:  $\nu_1 = 2420$ ,  $\nu_3 = 749.2$  and  $745.8$ , the perpendicular are:  $\nu_2 = 2556$ ,  $\nu_4 = 1191.3$   $\text{cm}^{-1}$ . The rotational structure of  $\nu_3$  is completely resolved. The moments of inertia of  $\text{ND}_3$  are:  $C = 8.985 \times 10^{-40}$  with respect to the symmetry axis, and  $A = 5.397 \times 10^{-40}$  g.  $\text{cm}^2$  for any perpendicular axis. The height of the mol. pyramid is  $0.360 \times 10^{-8}$ , and distance between D atoms  $1.645 \times 10^{-8}$  cm. The potential curve is discussed. N. M. B.

**Vibrational levels of cyclopropane.** G. W. KING, R. T. ARMSTRONG, and L. HARRIS (J. Amer. Chem. Soc., 1936, 58, 1580—1584).—The infra-red absorption and Raman spectra have been determined, and the results are discussed. E. S. H.

**Absorption spectrum of heavy methane ( $\text{MeD}$ ) in the photographic infra-red.** W. H. J. CHILDS and H. A. JAHN (Nature, 1936, 138, 285).—The absorption spectrum of  $\text{MeD}$  from 12,000 to 6000 Å. shows none of the lines of  $\text{CH}_4$ . A region of intense absorption extends from 8350 to 9000  $\text{cm}^{-1}$  with a strong, broad max. at 8617  $\text{cm}^{-1}$ . Similarities with the spectrum of  $\text{CH}_4$  are pointed out. L. S. T.

**Infra-red absorption spectra of acetic acid and acetic anhydride.** E. K. PLYLER and E. S. BARR (Physical Rev., 1935, [ii], 47, 793; cf. this vol., 34). L. S. T.

**Raman effect. LX. Polarisation measurements. 1. Experimental method.** A. W. REITZ (Z. physikal. Chem., 1936, B, 33, 368—386).—The sources of error in polarisation measurements are discussed, and suitable apparatus and the experimental technique described. R. C.

**Raman spectra and the latent heat of fusion of non-associated substances.** C. J. PHILLIPS (Physical Rev., 1935, [ii], 47, 792).—When applied to 38 org. and inorg. substances in the cryst. and liquid states, the relation  $\lambda = mNh_c/JML_f$ , when  $m$  is 1, 2, . . . and  $L_f$  is the latent heat of fusion, gives  $\lambda\lambda$  which agree closely with the observed infra-red absorption bands. The relation apparently holds only for non-associated substances. In glass the  $\text{SiO}_2$  group may vibrate independently to a certain extent. L. S. T.

**Raman spectrum of thiophosphoryl chloride.** V. N. THATTE (Nature, 1936, 138, 468—469).—Prominent shifts in the Raman spectra of  $\text{POCl}_3$  and  $\text{PSCl}_3$  are compared. The slight reduction in the vals. for the latter is attributed to substitution of O by S. L. S. T.

**Raman effect in solutions of magnesium sulphate of varying concentrations.** E. M. COON and E. R. LAIRD (Physical Rev., 1935, [ii], 47, 889).—Any change in frequency due to concn. ( $N$  to  $4.5N$ ) is  $\lambda > 1$  or 2 wave nos. L. S. T.

**Raman effect and molecular structure.** L. SIMONS (Finska Kem. Medd., 1936, 45, 77—97).—A review, with special reference to  $C_6H_6$ .

M. H. M. A.

**Raman spectrum of deuterioethanol.** S. MIZUSHIMA, Y. MORINO, and G. OKAMOTO (Bull. Chem. Soc. Japan, 1936, 11, 553).—Raman lines closely corresponding with those of EtOH have been observed. The band  $3370 \pm 80$   $cm^{-1}$ , attributed to the -OH linking, is displaced to  $2510 \pm 50$   $cm^{-1}$  in EtOD.

R. S.

**Raman effect of heterocyclic compounds of the dioxan type.** L. MÉDARD (J. Chim. phys., 1936, 33, 626—630; cf. A., 1934, 1289).—The Raman spectra of dioxan (I), dichlorodioxan, thioxan (II), dithian (III), and morpholine have been determined. The vibration frequency of  $CH_2$  is determined by linking to O or S since the  $CH_2$  line 1415 of (III) and the corresponding lines 1445—1460 of (I) appear at 1415—1452 in (II). Lines attributable to the cyclic structure are absent, in agreement with the aliphatic properties of the compounds.

R. S.

**Modification of the Raman spectrum of dioxan by dissolved materials.** A. SIMON and F. FÉHÉR (Z. Elektrochem., 1936, 42, 688—691).—Polar solutes modify the Raman spectrum of dioxan, the CO-frequencies being diminished and the CH-frequencies raised. The changes are due to electrostatic effects and not to formation of mol. compounds. The shape of the solute mol. and the type and location of its dipole have a greater influence than the magnitude of the dipole moment or the deformability of the mol. The results are discussed with reference to Raman frequencies in complicated mols. and in binary mixtures.

J. W. S.

**Raman spectra and the structure of benzene.** G. DUPONT and R. DULOU, with (in part) V. DESREUX (Bull. Soc. chim., 1936, [v], 3, 1639—1661).—The principal Raman frequencies and their relative intensities are tabulated for *cyclo*-hexane and -hexene,  $C_6H_6$ , PhMe, PhEt, PhPr, *o*-, *m*-, and *p*-xylene, *m*-, *p*-, and *o*-cymene,  $\psi$ -cymene, mesitylene, thiophen, *alloo*cimene, PhOH,  $NH_2Ph$ ,  $p$ - $C_6H_4EtOMe$ ,  $p$ - $C_6H_4PrOMe$ , eugenol, *isoeugenol*, dihydroeugenol, saffrole, *isosaffrole*, and dihydrosaffrole. It is concluded that in  $C_6H_6$  a form predominates which may be represented by a formula of hexagonal symmetry, e.g., the Stark-Pauli formula, and is responsible for the aromatic properties, but a second form, corresponding with Kekulé's formula, is also present in small quantities.

J. W. S.

**Raman spectrum of heavy benzene  $C_6D_6$ .** R. W. WOOD (Physical Rev., 1935, [ii], 48, 488; cf. A., 1935, 1189).

L. S. T.

**Raman spectra and vibrations of di- and tetra-deutero benzene.** O. REDLICH and W. STRICKS (Monatsh., 1936, 68, 374—382; cf. this vol., 663, 922).—The Raman spectra of *o*- and *m*- $C_6H_4D_2$  and of a mixture of the  $C_6H_2D_4$  isomerides have been determined. The frequencies calc. from the valency energy model of  $C_6H_6$  differ considerably from the observed frequencies, but a generalised model is developed which is in satisfactory accord for  $C_6H_6$ ,

$p$ - $C_6H_4D_2$ , 1:2:4:5- $C_6H_2D_4$ , and  $C_6D_6$ . The Ca salt of polycarboxylic acids of  $C_6H_6$  when heated with  $Ca(OH)_2$ , yields only a mixture of isomerides.

J. W. S.

**Raman spectrum of hydroxyquinol trimethyl ether.** S. FRIED and B. SUSZ (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 124—126; cf. Kohlrausch, A., 1935, 146).—Raman data for 1:2:4- $C_6H_3(OMe)_3$  are reported.

N. M. B.

**Raman spectra of *cis*- and *trans*-isoeugenol.** E. PERROTET and B. SUSZ (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 120—124; cf. this vol., 923).—Raman frequencies for the pure commercial substance (80% *trans*, 20% *cis*) and for the two isomerides are tabulated. *iso*Eugenol contains all the frequencies of these two forms with the exception of 1629  $cm^{-1}$ . The vals. for *trans* show an approx. const. difference from those for *cis*, the former being the higher.

N. M. B.

**Raman effect. LVIII. Raman spectra of organic substances. Nitrogen compounds. I. Simple amines.** K. W. F. KOHLRAUSCH. LIX. Raman spectra of organic substances. Nitrogen compounds. II. Amino- and hydroxy-acetic acids and esters. L. KAHOVEC and K. W. F. KOHLRAUSCH (Monatsh., 1936, 68, 349—358, 359—373).—LVIII. The Raman spectra of  $NH_2Me$ ,  $NH_2Et$ ,  $NH_2Pr^a$ ,  $NHMe_2$ , and  $NMe_3$  have been determined and compared with those of  $Me_2O$ ,  $Me_2S$ , and  $MeOEt$ .

LIX. The Raman spectra of  $NH_2 \cdot CH_2 \cdot CO_2H$  and its Me, Et,  $Pr^a$ , and  $Bu^a$  esters,  $(NH_2)_2CH \cdot CO_2H$  and its Me and Et esters,  $OH \cdot CH_2 \cdot CO_2H$  and its Me, Et,  $Pr^a$ , and  $Bu^a$  esters,  $NH_2 \cdot CH(OH) \cdot CO_2H$  and its Me and Et esters,  $EtCO_2H$  and its  $Pr^a$  and  $Bu^a$  esters,  $CH_2Cl \cdot CO_2H$ , and  $CH_2Br \cdot CO_2H$  have been determined in the solid state and/or in aq. solution.

J. W. S.

**Raman spectrum of piperidine.** S. M. MITRA (Z. Physik, 1936, 102, 697—699).—A new line at  $\Delta\nu=1451$  is observed in this spectrum.

O. D. S.

**Excitation of Raman spectra of substances with the aid of "optical catalysers."** K. PRASAD and D. K. BHATTACHARYA (Nature, 1936, 138, 510—511).—The method used for glass (this vol., 270) has been extended to  $H_2O$ , MeOH, EtOH,  $COMe_2$ ,  $C_5H_5N$ , and aq.  $HNO_3$ , traces of  $KMnO_4$  being added to produce absorption bands in these media. The importance of the new technique for the study of Raman spectra is discussed.

L. S. T.

**Raman spectra of gallic acid, of its derivatives, and of tannin.** B. SUSZ and S. FRIED (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 69—74; cf. A., 1935, 1446).—Raman data are recorded and discussed for pyrogallol, gallic acid, Me gallate, Me trimethylgallate, triacetyl gallic acid, and tannin.

N. M. B.

**Induced ultra-violet fluorescence and its release by visible light.** O. GLASSER and I. E. BEASLEY (Physical Rev., 1935, [ii], 47, 570).—The ultra-violet fluorescence of certain substances following exposure to X- or  $\gamma$ -radiation is found to persist for unexpectedly long periods of time. It is markedly increased when the irradiated compounds are exposed to visible light. Of the 25 substances examined, NaCl, KCl, rock-salt, and fluorite crystals showed



these effects most clearly. Impurities inhibit the subsequent induction of the fluorescence. L. S. T.

**Scintillations of zinc sulphides in  $\alpha$ -rays.** G. DESTRIAU (J. Chim. phys., 1936, 33, 587—625; cf. A., 1931, 1108).—ZnS screens free from Canada balsam have been prepared from a suspension of ZnS in EtOH. Using a Po source, it has been shown that the no. of scintillations—distance curve varies with the specimen of ZnS. For a given specimen, the curvature is the sharper the smaller is the ZnS crystal and the richer the crystal in phosphorogen. Whilst the concn. of phosphorogen runs parallel to the [Cu], there is no direct proportionality, and only a part of the Cu appears to be active. Theoretical curves in agreement with the experimental results have been derived and the influence of crystal size, concn. of phosphorogen, and the no. of centres excited by an  $\alpha$ -particle have been investigated. The view that scintillations involving only one active centre are visible is discussed in relation to data on the min. of visual perception. The mean duration of the scintillations, determined microscopically by a rotating-disc method, increases with the concn. of active phosphorogen and is a max. in crystals of approx. 27  $\mu$ , but there is no relation between the sensitivity to  $\alpha$ -rays and phosphorescent power of ZnS. The effect of infra-red light, and the relation between the sensitivity to  $\alpha$ -rays, X-rays, and triboluminescence, are discussed. Only one specimen of ZnS showed luminescence in the electric field. R. S.

**Fluorescence of the salts of tervalent europium in aqueous solutions.** J. LARIONOV and A. SEIDEL (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 115—118).—Fluorescence spectrum data are given. Three narrow bands in the red occur only with solutions containing  $\text{SO}_4^{2-}$ , and are ascribed to  $\text{Eu}^{+++}$ . One narrow band and two broad bands in the blue-ultra-violet region are of general occurrence: the latter coincide with bands observed in solutions of Ce and Y earth salts. A. J. E. W.

**Effect of visible light on the ultra-violet fluorescence of various compounds previously irradiated with Röntgen or  $\gamma$ -rays.** O. GLASSER and I. E. BEASLEY (Physical Rev., 1935, [ii], 47, 789).—The ultra-violet fluorescence of NaCl, KCl, NaBr, rock-salt, and fluorite crystals following exposure to X- or  $\gamma$ -radiation is markedly increased by exposure to visible light. With NaCl the emitted radiation has a max. near 2450 Å. L. S. T.

**Luminescence of calcite. I. Fluorescence spectrum of Japanese calcite in ultra-violet light.** E. IWASE and T. KURONUMA. II. Thermoluminescence. III. Alteration of the fluorescence spectrum by previous heating. E. IWASE (Bull. Chem. Soc. Japan, 1936, 11, 513—522, 523—528, 528—538).—I. All specimens did not fluoresce but band max. were observed at 625—635, 460—470, 515—520, and 560—570 m $\mu$ . Calcites from mineral veins gave a reddish-orange fluorescence, whilst stalactitic calcites gave a whitish fluorescence.

II. A no. of thermoluminescence bands have been determined, but no relation between thermoluminescence and fluorescence could be obtained.

III. The fluorescence of white-fluorescing calcites is affected by previous heating, whilst that of the orange-red type is not. Bands in the Arakawa calcite can be attributed to the presence of rare-earth metals. R. S.

**Fluorescence of chlorophyll in its relation to photochemical processes in plants and organic solutions.** J. FRANCK and R. W. WOOD (J. Chem. Physics, 1936, 4, 551—560; cf. A., 1935, 681).—Chlorophyll, illuminated in org. solutions, behaves as though excited chlorophyll,  $\text{HChph}^*$ , which is free from adsorbed mols., has a small probability of fluorescing and a greater probability of pre-dissociating into a H and monodehydrochlorophyll. The products of dissociation react with any  $\text{O}_2$  present unless  $\text{O}_2$ -acceptors, RH, are also present which take up the excitation energy by collision of the second kind or by intramol. energy exchange within a complex  $\text{HChphRH}$  (I) and protect  $\text{HChph}$  (II) against oxidation, whilst the RH is oxidised after initial formation of H and R or  $\text{HChphR}$  (III). The change of intensity of the fluorescence with period of illumination in presence of  $\text{O}_2$  and certain acceptors is interpreted in terms of the inferred properties of the complexes (III) and (I). The fluorescence of (III) is  $>$  that of (I). Determinations of the similar variations in the intensity of fluorescence with time of illumination of living leaves in presence of  $\text{O}_2$  (cf. A., 1935, 1038) are consistent with photosynthesis and photo-oxidation of org. substances adsorbed to (II) taking place in the plant, but (II) is not itself photo-oxidised. The "light saturation" of photosynthesis *in vivo* may arise from photo-oxidation. The time of half life of (III) is approx. 0.02 sec.

J. G. A. G.

**Emission of aromatic compounds containing the carbonyl group.** N. PRILESHAeva (Acta Physicochim. U.R.S.S., 1935, 3, 195—201).—In the fluorescence of PhCHO and CPhMe vapours the excitation is primarily localised in the  $\text{C}_6\text{H}_6$  ring, whereas the subsequent emission is localised in the CO group. O. J. W.

**Biologically active radiation. III. Supposed photographic detection of earth rays according to Dobler.** B. ROMEIS, J. WÜST, and J. WIMMER (Strahlenther., 1935, 54, 114; Chem. Zentr., 1935, ii, 3745).—No satisfactory evidence of the photographic action of "earth rays," or of their being electromagnetic radiation of about 1 mm.  $\lambda$ , has been brought forward by Dobler. J. S. A.

**Photo-electric threshold of uranium, calcium, and thorium treated with limited amounts of oxygen.** H. C. RENTSCHLER and D. E. HENRY (Physical Rev., 1935, [ii], 47, 807).—A shift in the photo-electric threshold towards the longer  $\lambda$  occurs when surfaces of Th, U, or Ca react with a small amount of  $\text{O}_2$ . L. S. T.

**Photo-electric primary current in an alternating field in potassium bromide crystals containing colour centres.** A. NAUMANN (Ann. Physik, [v], 27, 233—242).—The photo-electric conductivity of crystals of KBr containing electrically formed colour centres has been measured for alternating

currents of frequency between  $10^2$  and  $10^5$  sec.<sup>-1</sup> Ohm's law is obeyed. The conductivity increases with frequency to a saturation val. The ratio conductivity/light absorbed is of the same order of magnitude for the saturation conductivity and for the static conductivity determined at much lower light intensity. It is deduced that the mobility of the photochemically produced electrons is not reduced by the block structure of the crystal. O. D. S.

**Analysis of photo-electric data.** R. J. CASHMAN and N. C. JAMISON (Physical Rev., 1936, [ii], 50, 568—569; cf. Fowler, A., 1931, 1106).—The comparative results of plotting photo-electric current per quantum of light absorbed or per unit intensity of incident radiation are examined. N. M. B.

**Correlation of secondary electron emission with photo-sensitivity and the thermionic effect.** A. DOBROJUBSKI (Z. Physik, 1936, 102, 626—628).—Photocell layers Cs—Cs<sub>2</sub>O—Ag, Ag<sub>2</sub>O—Ag, and Cs—Ag<sub>2</sub>O—Ag were considered. O. D. S.

**Nature of the barrier plane in the cuprous oxide photovoltaic cell.** J. W. BALLARD and E. D. WILSON (Physical Rev., 1935, [ii], 47, 794). L. S. T.

**Colouring and luminescence of crystals under the influence of Becquerel rays.** K. PRZIBRAM (Z. Physik, 1936, 102, 331—352).—A general review of modern work on the colour and luminescence of crystals produced naturally or artificially by pressure or by radioactive emission. Attention is given to the fluorites, alkali halides, and bivalent rare earths. H. C. G.

**Electrical observations during the formation and re-formation of colour centres in potassium bromide and chloride crystals.** G. GLASER (Ann. Physik, 1936, [v], 27, 217—232).—Measurements have been made of the spectral distribution of the photo-electric current in sensitised crystals of KBr and KCl during the photochemical formation of colour centres. No correlation was found between this and the absorption spectrum associated with the *U*-centres. It was correlated with the absorption spectrum of the "X-centres," which underlies that of the *U*-centres, and is similar in form to that of the pure crystal. It is deduced that the photo-electric current is a secondary effect due to the illumination of X-centres, which probably result from foreign mols. in the crystal. O. D. S.

**Ionisation of liquids by X-rays.** L. S. TAYLOR and F. L. MOHLER (Physical Rev., 1935, [ii], 47, 805).—An extension of previous work (A., 1935, 148) to CS<sub>2</sub>, ligroin, tetrahydronaphthalene, and their mixtures. L. S. T.

**Structure of electrolytic oxide films.** H. BETZ (Z. Physik, 1936, 102, 548).—The breakdown potential of Ta<sub>2</sub>O<sub>5</sub> films determined by Rummel (this vol., 923) is the val. obtained by Just (A., 1933, 555). A. J. M.

**Structure of electrolytic oxide films.** T. RUMMEL (Z. Physik, 1936, 102, 549).—A reply to Betz (preceding abstract). A. J. M.

**Measurement of low conductivities and dipole losses with long waves.** C. SCHROECK (Ann. Physik, 1935, [v], 27, 261—284).—A method is described by which conductivities of the order of  $10^{-13}$  ohm<sup>-1</sup> cm.<sup>-1</sup> and dipole losses in liquids can be measured at  $\lambda$  from 170 to 18,000 m. The dielectric const. is determined simultaneously. Data are given of the dipole losses in this region of PrOH, BuOH, and amyl alcohol, glycerol, and aq. solutions of sucrose and fructose. The dielectric const. of mixtures of EtOH and C<sub>6</sub>H<sub>6</sub> is determined and the mol. polarisation of EtOH calc. O. D. S.

**Electric properties of crystals. I, II.** (SIR) W. BRAGG (Proc. Roy. Inst., 1936, 29, 225—230, 290—295).—Lectures.

**Reactivity in solid state at ordinary temperature. II.** A. SERRA (Period. Min., 1935, 6, 179—183; Chem. Zentr., 1935, ii, 3743; cf. A., 1935, 716).—The electrical conductivity of Cu, Fe, Ag, Ni, and Pb wires was increased by contact with finely powdered realgar, Sb glance, Cu glance, haverite, marcasite, and pyrolusite. Sb glance in contact with Ag foil produces a stain of Ag<sub>2</sub>S. J. S. A.

**Influence of electric moment on the number of molecules of base fixed by a salt.**—See this vol., 1241.

**Theory of dielectric polarisation.** J. G. KIRKWOOD (J. Chem. Physics, 1936, 4, 592—601).—A mol. treatment of the polarisation of a non-polar dielectric in a homogeneous field shows that small but significant deviations from the Clausius-Mosotti formula are to be expected. The magnitudes of the corrections are discussed. J. G. A. G.

**Dielectric constant for pure liquid and solid substances. I.** K. HØJENDAHL (Kem. Maanedssbl. nord. Handelsbl. kem. Ind., 1935, 16, 53—55; Chem. Zentr., 1935, ii, 3748).—Vals. are recorded for C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>. J. S. A.

**Peculiarities of dielectric constant versus pressure curves for vapours.** J. D. STRANATHAN (Physical Rev., 1935, [ii], 47, 794).—For H<sub>2</sub>O vapour deviation of the  $(\epsilon-1)/(\epsilon+2)$ -pressure curve from linearity is due not to conductivity but to adsorption on the insulator surfaces and the consequent increase in polarisation contributed by these additional mols. L. S. T.

**Polar properties of 1:4- and 1:2-dihydronaphthalene.** Polar character of the tetralin molecule. M. PUCHALIK (Acta phys. polon., 1934, 3, 179—185; Chem. Zentr., 1935, ii, 3370).—The dipole moment of 1:4- and of 1:2-dihydronaphthalene is  $1.4 \times 10^{-18}$  e.s.u. The polar asymmetry of the tetralin mol. is thus to be attributed mainly to a change in the C<sub>6</sub>H<sub>4</sub> nucleus. H. N. R.

**Liquid propane.** Electrical conductance and dielectric constant. G. GLOCKLER and R. E. PECK (J. Chem. Physics, 1936, 4, 624).—The conductivity is  $< 5 \times 10^{-13}$  ohm<sup>-1</sup> at 1 kilocycle between -90° and 15°. The dielectric const. at 0° is 1.61 and the temp. coeff. -0.00124. J. G. A. G.

**Molecular rotation in solid aliphatic alcohols.** C. P. SMYTH and S. A. MCNEIGHT (J. Amer. Chem.



Soc., 1936, 58, 1597—1600).—The dielectric consts. of solid MeOH, Bu<sup>n</sup>OH, and *n*-octyl alcohol (I) have been determined from liquid-air temp. to the m.p. There is evidence of dipole rotation in MeOH between 159.9° abs. and the m.p. Absence of dipole rotation in Bu<sup>n</sup>OH and (I) and the absence of transitions in many other alcohols show that OH does not rotate inside the mol., but the whole MeOH mol. rotates above the transition point (159.9° abs.).

E. S. H.

**Non-rotation of molecules in a number of solids.** S. A. McNEIGHT and C. P. SMYTH (J. Amer. Chem. Soc., 1936, 58, 1718—1722).—The dielectric consts. of solid NH<sub>2</sub>Me, Et<sub>2</sub>O, COMe<sub>2</sub>, CPh<sub>2</sub>, and succinic acid have been determined over a wide range of temp. and frequency. Mol. rotation cannot be postulated.

E. S. H.

**Molecular rotation of solid arsine and other hydrides.** C. P. SMYTH and S. A. McNEIGHT (J. Amer. Chem. Soc., 1936, 58, 1723—1728).—Dielectric consts. and sp. conductances of solid HCN and H<sub>2</sub>Se have been determined from liquid-air temp. to the m.p., and those of AsH<sub>3</sub> from liquid-H<sub>2</sub> temp. to the b.p. over the frequency range 0.5—50 kilocycles. Solid HCN shows no mol. rotation; H<sub>2</sub>Se mols. rotate freely even at liquid-air temp.; AsH<sub>3</sub> rotates freely down to 32.1° abs., where a transition, accompanied by anomalous dispersion, occurs. The mols. rotate the more readily the smaller are their dipole moments.

E. S. H.

**Indication of a decrease in the polarisability of a non-polar molecule by pressure.** A. MICHELIS, C. MICHELIS-VERAAT, and A. BIJL (Nature, 1936, 138, 509—510).—Graphs showing the relation between the Clausius-Mosotti function *P*, which  $\propto$  the polarisability of the mol., and *d*, the pressure, and the change in kinetic energy of the internal motion of the mols.,  $\Delta K$ , are reproduced from calculations based on recent isotherm data for CO<sub>2</sub>. The decrease of *P* with an increase in pressure and in  $\Delta K$  is practically linear.

L. S. T.

[Refractometry.] W. GEFFCKEN (Z. physikal. Chem., 1936, B, 33, 405).—Errors in previous papers (A., 1929, 1233; 1931, 905) are corr.

R. C.

**Refractive indices of ordinary and heavy ammonia.** O. E. FRIVOLD, O. HASSEL, and S. RUSTAD (Nature, 1936, 138, 330).—*n* for ND<sub>3</sub>, determined for various  $\lambda$  between 4358 and  $6562.9 \times 10^{-8}$  cm., is slightly  $< n$  for NH<sub>3</sub>.

L. S. T.

**Refractometric studies in normal methyl ketones.**—See this vol., 1363.

**Optical properties of non-polar liquids.** H. MUELLER (Physical Rev., 1936, [ii], 50, 547—559).—Mathematical. A theory of refraction, Kerr effect, and light scattering is developed from considerations of the quasi-cryst. grouping of neighbouring mols., the anisotropy of the Lorentz forces, and potential barriers of various heights. Results are applied to C<sub>6</sub>H<sub>6</sub>. Hindered rotation and cybotactic grouping suffice to explain deviations from classical theory.

N. M. B.

**Kerr constants of the hydrogen halide gases.** C. H. D. CLARK and E. C. HUMPHRIES (Nature,

1936, 138, 248).—Calc. vals., which appear to support the theory previously advanced (this vol., 1051), are given.

L. S. T.

**Kerr effect with nitrotoluene.** F. GABLER and P. SOKOB (Naturwiss., 1936, 24, 570).—The effect of temp. on the Kerr const., *B*, of *o*- and *m*-C<sub>6</sub>H<sub>4</sub>Me·NO<sub>2</sub>, at  $\lambda$  5461 Å. has been determined, and is expressed by empirical equations.

A. J. M.

**Polarisation of light and some technical applications.** A. F. C. POLLARD (Nature, 1936, 138, 311—314).

L. S. T.

**Magnetic rotation of lanthanum and neodymium chlorides in aqueous solution.** C. M. MASON, R. D. GRAY, and G. L. ERNST (J. Amer. Chem. Soc., 1936, 58, 1600—1604).—Data are recorded for  $\lambda$  5893 and 5460.8 Å. at 10—50° and compared with corresponding data for Al. The Verdet consts. of the solutions have been calc.; those for NdCl<sub>3</sub> vary linearly with 1/*T*. Mol. rotations of aq. NdCl<sub>3</sub> vary with temp. according to  $(T - 32.6)D = -790.1$ .

E. S. H.

**Calculation of the polarisation ellipsoid of a molecule.** T. NEUGEBAUER (Z. Physik, 1936, 102, 305—316).—A method for calculating change in polarisability of an ion due to external influence is described. Anomalies in the calc. polarisabilities parallel and perpendicular to the long axis of a mol. are due to incorrect application of methods for spherically symmetrical ions.

L. G. G.

**Structure of benzene. I. Problem and experimental method.** W. R. ANGUS, C. R. BAILEY, C. K. INGOLD, and C. L. WILSON. II. Direct introduction of deuterium into benzene and the physical properties of hexadeuterobenzene. C. K. INGOLD, C. G. RAISIN, and C. L. WILSON. (Appendix: Vapour pressure of hexadeuterobenzene. C. R. BAILEY and B. TOPLEY.) III. Raman spectra of liquid benzene and hexadeuterobenzene. W. R. ANGUS, C. K. INGOLD, and A. H. LECKIE. IV. Infra-red absorption spectra of liquid and gaseous benzene and hexadeuterobenzene. C. R. BAILEY, J. B. HALE, C. K. INGOLD, and J. W. THOMPSON. V. Fluorescence spectra of benzene and hexadeuterobenzene vapour. VI. Resonance emission spectrum of benzene and hexadeuterobenzene. C. K. INGOLD and C. L. WILSON. VII. Coincidental frequencies in the infra-red and Raman spectra of benzene and hexadeuterobenzene. VIII. Assignment of vibration frequencies of benzene and hexadeuterobenzene. W. R. ANGUS, C. R. BAILEY, J. B. HALE, C. K. INGOLD, A. H. LECKIE, C. G. RAISIN, J. W. THOMPSON, and C. L. WILSON (J.C.S., 1936, 912—915, 915—925, 925—931, 931—941, 941—954, 955—966, 966—971, 971—987).—I. The difficulty of reconciling the transformations of the aromatic nucleus with its stability is discussed. Although Pauling and Wheland's theory (A., 1934, 15) is successful in bringing the stability of the ring into line with its chemical transformations, it cannot explain certain difficulties, the most important of which is the appearance of identical frequencies in the Raman and infra-red spectra (see VII). Experimental methods for the

investigation are outlined. Since substitution of D for H does not alter nuclear changes, only effects arising from changes in at. masses influence vibration frequencies, and definite numerical relationships between the frequencies of corresponding normal vibrations of two isotopically related mols. are calculable if some mol. model is assumed. Only  $C_6H_6$  and  $C_6D_6$  are discussed; a scheme is given for investigating other D-substituted benzenes.

II. The exchange reaction,  $PhH + DO \cdot SO_3D \rightarrow PhD + HO \cdot SO_3D$  is utilised to prepare  $C_6D_6$  containing only 1% of  $C_6D_5H$ . Data for m.p., b.p., mol. vol., and mol. refraction for  $C_6D_6$  and for a series of partly deuterated benzenes are given and discussed. V.p. measurements with a differential tensimeter are recorded. A statistical treatment of the v.p. difference of isotopic mols. is developed to explain the higher v.p. of  $C_6D_6$ .

III. Raman spectra of  $C_6H_6$  and  $C_6D_6$  are obtained and compared with previous data. Peak and integrated intensities of the principal lines have been measured photometrically and are correlated by photographing an artificial mixture of 50 mols.-% of  $C_6H_6$  and  $C_6D_6$ . Polarizations of all the principal lines are recorded. The  $C_6H_6$  spectrum has 8 strong lines (fundamentals), 14 weak lines, 16 very weak lines, and 4 satellites of the strong line at  $992\text{ cm}^{-1}$ . For  $C_6D_6$ , 7 strong (fundamental) and 19 weak lines are found.

IV. To make comparison more trustworthy, the same samples of  $C_6H_6$  and  $C_6D_6$  were examined as vapour and as liquid between 1 and  $22\mu$ .  $C_6H_6$  vapour has 15 and liquid  $C_6H_6$  24 bands. Previous data are discussed and differences between results are explained, particularly for three bands previously recorded, but not now confirmed, for the vapour; these three bands, however, appear in the liquid  $C_6H_6$  spectrum.  $C_6D_6$  vapour gives 16 bands, liquid  $C_6D_6$  27. Mappings of the complete spectra, contours of strong bands, intensities, and  $P$ - $R$  and doublet separations are given and discussed.

V. The ideal case for the production of fluorescence and resonance spectra is outlined and experimental arrangements are detailed. The fluorescence spectra of both vapours are given and microphotometric intensities and series assignments are recorded. The spectra are accounted for by assuming 3 electron levels and 2 vibration frequencies; numerical formulæ are given.

VI. The resonance spectrum of  $C_6H_6$  falls into sections of  $989\text{ cm}^{-1}$  and 9 such sections are discussed; the eight component frequency differences are derived from which the series assignment of band max. is made. The corresponding spectrum of  $C_6D_6$  comprises sections each  $944\text{ cm}^{-1}$  in length and has 7 component frequency differences. Correlation of the  $C_6H_6$  and  $C_6D_6$  bands leads to a satisfactory pairing, 4 pairs being definitely identifiable. The other 3 pairs and a non-paired low frequency are provisionally characterised as fundamentals, inactive both in Raman and infra-red spectra.

VII. If the benzene mol. is a plane, regular hexagon and, therefore, has a centre of symmetry, selection rules forbid the appearance of the same frequencies in both infra-red and Raman spectra. Several coincident frequencies reported previously had led

to the conclusion that the mol. could not be a plane, regular hexagon. A table of 18 suggested coincidences in  $C_6H_6$  and 12 in  $C_6D_6$  is compiled from data in III and IV. By comparing Raman frequencies with infra-red frequencies of liquid  $C_6H_6$  more coincidences are found than with those of the vapour. Cohesive forces in the liquid deform the mol. sufficiently to cause a breakdown in strict selection rules and strong Raman frequencies appear in the liquid infra-red spectra but not in the vapour; strong infra-red frequencies appear faintly in Raman spectra: frequencies, inactive in both, appear fairly strongly in liquid infra-red, feebly in Raman, and are absent from infra-red vapour spectra. All the suggested coincidences are discussed and no evidence for the absence of a centre of symmetry is obtained.

VIII. In the theory of point groups the symbol which represents the symmetry classification of a plane, regular, hexagonal benzene model is  $D_{6h}$ ; those for the Kekulé and trigonally puckered models are  $D_{3h}$  and  $D_{3d}$ , respectively. The symmetry classifications of the vibrations of the three models are developed. Benzene has 20 normal modes of vibration. The  $D_{6h}$  model has 4 active in infra-red only, 7 active in Raman spectrum only (two polarised), and 9 forbidden in both spectra. For the  $D_{3h}$  model, there should be 8 fundamentals in the infra-red, 14 in Raman spectrum (4 polarised), and 7 common to both; whilst the  $D_{3d}$  model requires 8 in infra-red, and 9 in Raman spectra (4 polarised). By Teller's product theorem the products of the frequencies of vibrations of the same symmetry class for two isotopically related mols. are in a ratio which can be expressed as a function of the masses of the atoms and the moments of inertia. The numerical vals. for the ratios are given for the  $D_{6h}$  model. Experimental data are analysed and frequencies assigned for this model. Raman spectra give 7 strong lines (2 polarised); infra-red give 4 prominent bands: these are the allowed fundamentals. On applying Teller's product rule to these, very good agreement between calc. and observed ratios is found. The order of magnitude of the nine inactive frequencies is discussed and tentative vals. are given. The selection rules which govern the appearance of overtones and combination tones in these spectra are reviewed and assignments of the majority of the observed frequencies are made. The spectroscopic investigation of benzene, thus far, supports the  $D_{6h}$  model; there is no definite indication in favour of the  $D_{3d}$  structure. The Kekulé model fails to explain the facts.

W. R. A.

Structure of benzene. IX. Direct observation of the fluorescence spectra of benzene and hexadeuterobenzene vapour in the region of absorption. C. L. WILSON (J.C.S., 1936, 1210—1214; see preceding abstract).—The fluorescence spectra of  $C_6H_6$  and  $C_6D_6$ , excited by the Hg 2537 Å. line, have been measured at 0.1—0.3 mm., the resonance spectra being quenched by presence of  $N_2$  (760 mm.). The frequencies and relative intensities of the lines in the region 2577—2667 Å. are recorded. The results are in accord with previous data.

J. W. S.



**Investigation of the binding properties of benzene by physical methods.** R. KREMANN (Naturwiss., 1936, 24, 632—635).—A review of the application of physical methods to the study of the linkings in the  $C_6H_6$  mol. A. J. M.

**Structure and properties of mononuclear and polynuclear phenanthroline-ferric complexes.** A. GAINES, jun., L. P. HAMMETT, and G. H. WALDEN, jun. (J. Amer. Chem. Soc., 1936, 58, 1668—1674).—The analysis, hydration, conductivity, acid-base properties, magnetic susceptibility, and diffusibility of the brown, cryst. substance prepared by reaction of phenanthroline (I) and  $FeCl_3$  are consistent with the view that it is tetraphenanthrolinediol-diferric chloride. Other compounds probably exist in the mother-liquor. The low magnetic susceptibility suggests the partial neutralisation of the magnetic moments of the two Fe, and is evidence of a polynuclear structure. The magnetic susceptibility of the blue triphenanthroline- $Fe^{III}$  complex ion = approx. that of  $Fe(CN)_6^{4-}$ . Stable (I) complexes, the composition of which has been established in the solid state, may add more (I) in solution, forming secondary complexes of lower stability. E. S. H.

**Structure of the chlorine monoxide molecule.** R. POHLMAN and H. J. SCHUMACHER (Z. Physik, 1936, 102, 678—683).—An alternative interpretation of the infra-red measurements of absorption of  $Cl_2O$  by Bailey and Cassie (cf. A., 1933, 1228). O. D. S.

**Valency and molecular structure.** R. F. HUNTER and R. SAMUEL (Nature, 1936, 138, 411—413). L. S. T.

**Transition of covalency to electrovalency.** R. F. HUNTER and R. SAMUEL (Chem. and Ind., 1936, 733—740).—From consideration of potential energy relations in diat. mols. with at. binding, ionic binding, and hydrated ions, it is shown that covalency may pass over into electrovalency when the energy min. of the covalent and electrovalent states are sufficiently close for external forces (lattice energy, energy of solvation, van der Waals forces) to cause an intersection with the at. binding curve. The tendency for transition is dependent on the difference,  $J-E$ , between the ionisation energy of the cation  $J$ , opposing ionisation, and the electron affinity  $E$  of the anion, favouring ionisation. For compounds with a const. negative ion (e.g.,  $Cl^-$ ), the transition from covalency to electrovalency, as shown by the m.p., b.p., conductivity and hydrolysis of chlorides, runs strictly parallel to the variation of  $J$ . J. S. A.

**Energy of formation of "cyclol" molecules.** D. M. WRINCH (Nature, 1936, 138, 241—242).—Calculations of the approx. energy of formation of cyclol mols. from polypeptides (cf. this vol., 619) indicate that the linking process is facilitated if the appropriate groups are in the form  $\cdot C(OH) \cdot N \cdot$ , and that certain enzymes operate directly on the substrate by imposing this form on some of its  $\cdot CO \cdot NH \cdot$  groups. L. S. T.

**Energy of formation of "cyclol" molecules.** F. C. FRANK (Nature, 1936, 138, 242; cf. preceding abstract).—Estimation of the energy balance of the

linking process postulated for proteins by Wrinch (this vol., 619) indicates the necessity for assuming the existence of an additional source of energy similar to that provided by the strain in the side-chain cross-linkings found in keratin. Hydration also provides part of the necessary additional energy and helps to explain certain properties of proteins observed in degeneration and denaturation. L. S. T.

**Relation of the states of the carbon atom to its valency in methane.** H. H. VOGEL (J. Chem. Physics, 1936, 4, 581—591).—Resonance of  $C^{IV}$  with other valency configurations raises the stability of  $CH_4$  to a val. slightly  $>$  that calc. from the Pauling-Slater configuration. The relative energies of  $CH$ ,  $CH_2$ ,  $CH_3$ , and  $CH_4$  are 4.0, 8.0, 12.1, and 17.0 volts and thus there is no indication that  $CH_2$  is specially stable. This conclusion is discussed. J. G. A. G.

**Orbital valency according to an extended Heitler-London method.** G. NORDHEIM (Physical Rev., 1935, [ii], 47, 803—804).—An extension of the Heitler-London theory of chemical linking is developed to take into account not only the ground states but also the lowest excited states of the composing atoms. Directional properties of valency in polyat. mols. are explained. L. S. T.

**Intramolecular forces between bound atoms.** W. ALTAR (Physical Rev., 1935, [ii], 47, 804; cf. A., 1935, 1192). L. S. T.

**Provisional computation of the plane vibration frequencies of symmetrical deuterioethylenes.** C. MANNEBACK and A. VERLEYSSEN (Nature, 1936, 138, 367).—Calc. vibration spectra of  $C_2D_4$  and the three isomerides  $C_2D_2H_2$  are tabulated. L. S. T.

**Relation between the energy saturation and polarity of molecules.** V. RASUMOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 21—27; cf. this vol., 925).—The "energy saturation" of mols.  $\propto$  the degree and duration of approach of the valency electrons to the individual at. in the mols.; the tendency to ionise is inversely, and to partake in addition reactions directly,  $\propto$  the energy saturation. These concepts are applied to some facts in org. chemistry. R. C. M.

**Significance of the new quantum theory in chemistry.** E. HUCKEL (Z. Elektrochem., 1936, 42, 657—662).—A general survey. J. W. S.

**Elements of the quantum theory.** VII. van der Waals forces. VIII. Perturbation theory. IX. Helium atom. X. Hydrogen molecule. XI. Slater-Pauling theory of valency linkings. S. DUSHMAN (J. Chem. Educ., 1935, 12, 581—586; 1936, 13, 32—38, 84—92, 132—140, 179—187, 287—294, 330—333, 333—338, 385—393; cf. this vol., 134). L. S. T.

**Vibrational frequencies of molecules.** H. G. HOWELL (Nature, 1936, 138, 290; cf. this vol., 1052). L. S. T.

**Free energies.** T. W. DAVIS (J. Chem. Educ., 1936, 13, 376). L. S. T.

**Transfer of rotational energy.** F. F. RIEKE (Physical Rev., 1935, [ii], 47, 788). L. S. T.

**Phenomena of the exchange of wave energy in collisions of molecules.** V. KONDRATEEV (*Uspechi Fiz. Nauk.*, 1934, 14, 982—1008).—A review.

CH. ABS. (e)

**Range of action of surface forces.** B. DERJAGUIN (*Nature*, 1936, 138, 330—331).—Bowden and Bastow's data (*A.*, 1935, 819) do not refute the author's findings that films of  $H_2O$   $< 1.5 \times 10^{-5}$  cm. thick have great rigidity.

L. S. T.

**Parachor.** R. LAUTIE (*Bull. Soc. chim.*, 1936, [v], 3, 1689—1691).—The parachor is shown to follow the formula  $[P] = 0.316P_c V_c$ , where  $P_c$  is expressed in atm. This relation also follows from Aten's formula (*A.*, 1935, 1059). The crit. temp. can be deduced from the parachor.

J. W. S.

**Parachor and the structure of formic acid.** S. K. RAY (*J. Indian Chem. Soc.*, 1936, 13, 484—485).—Published data are consistent with the structure.

E. S. H.

**Steady performance of Geiger-Müller counters.** B. DASANNACHARYA and G. S. RAO (*Nature*, 1936, 138, 289).

L. S. T.

**Characteristics of Geiger-Müller counters filled with different gases.** C. L. HAINES (*Physical Rev.*, 1935, [ii], 47, 791).

L. S. T.

**Application of the Geiger point-counter to the measurement of small X-ray intensities.** M. PAHL and A. FAESSLER (*Z. Physik*, 1936, 102, 562—571).—Apparatus for measuring the intensity of X-rays, of high sensitivity below  $\lambda$  800 X, is described.

O. D. S.

**Improved numerical method of two-dimensional Fourier synthesis for crystals.** H. LIPSON and C. A. BEEVERS (*Proc. Physical Soc.*, 1936, 48, 772—780).—Mathematical.

N. M. B.

**Reduction of space-groups.** F. SEITZ (*Physical Rev.*, 1935, [ii], 47, 810).

L. S. T.

**Structure-factor graphs for crystal analysis.** W. L. BRAGG (*Nature*, 1936, 138, 362—363).—The use of contoured graphs for determining the configuration of atoms in crystals from X-ray data is explained and illustrated. The analysis of at. positions can thus be expedited.

L. S. T.

**Tables for the determination of crystals.** A. K. BOLDIREV and V. V. DOLIVO-DOBROVOLSKI (*Z. Krist.*, 1936, 93, 321—367).—A summary of a forthcoming set of tables for the identification of crystal specimens from their crystallographic data. For each class of crystals, in the key the crystals are arranged in order of the polar distances of their faces [*i.e.*, angle between (001) and the perpendicular to the face] for all commonly occurring faces; in the sequel they are described fully. The process of identification is thus (1) measurement, (2) determination of the crystal class, (3) determination of the polar distance for each observed form, (4) search for corresponding vals. in the table, (5) confirmation from the details given.

B. W. R.

**Classification of crystal structures with defect lattices.** L. W. STROCK (*Z. Krist.*, 1936, 93, 285—311).—For "ideal solids" all positions in a theoretical

lattice are occupied by similar particles. If this condition is not fulfilled, there is a "defect lattice," varying in degree from the ideal solid to a state where the lattice of one kind of particle is completely destroyed. A classification is made on this basis of such defect lattices and detailed examples are given; it includes not only those defect lattices which are directly measurable by X-rays, but also the larger micro-lattices.

B. W. R.

**Theory of crystal growth.** R. KAISCHEV (*Z. Physik*, 1936, 102, 684—690).—The equation previously developed (*cf. A.*, 1934, 946) can be deduced kinetically.

O. D. S.

**Oxide layer on a polished surface.** L. H. CALLENDER (*Nature*, 1936, 138, 291).—Dobinski's results for Cu (this vol., 1055) are confirmed by experiments on polished Al (*B.*, 1927, 724).

L. S. T.

**Fourier analyses of X-ray patterns of phosphorus.** N. S. GINGRICH and R. HULTGREN (*Physical Rev.*, 1935, [ii], 47, 808; *cf. A.*, 1935, 919).

L. S. T.

**Crystal structure of black phosphorus.** R. HULTGREN and B. E. WARREN (*Physical Rev.*, 1935, [ii], 47, 808; *cf. A.*, 1935, 919).

L. S. T.

**X-Ray determination of residual atomic lattice deformation in pressed duralumin.** F. F. KOSOLAPOV and E. F. BACHMETEV (*Vestn. Metalloprom.*, 1934, 14, No. 3, 76—82).—Crystallites with dimensions  $> 10^{-1}$  cm. comprise the chief portion of the deformed duralumin. The change in the X-ray diagram is due to lattice distortion, which disappears at 200° (15 min.—1 hr.) or 300° (30 sec.).

CH. ABS. (e)

**Change of elastic parameters of single crystals of iron by heating.** K. NAKAMURA (*Sci. Rep. Tôhoku*, 1936, 25, 364—380).—The natural frequency of longitudinal and of torsional vibration of a no. of single crystals of Fe has been measured at intervals from 20° to 560°.

O. D. S.

**Intensity of X-rays reflected from zinc.** C. ZENER and S. BILINSKY (*Physical Rev.*, 1936, [ii], 50, 489; *cf. this vol.*, 273).—Discrepancies between calc. and experimental vals. of the consts. in the expression for the temp. dependence of the intensity are discussed.

N. M. B.

**Anisotropy in the atomic vibrations of zinc crystals.** I. Evidence from X-ray scattering. II. Diffuse scattering of X-rays from single crystals. G. E. M. JAUNCEY and W. A. BRUCE. III. (0002) and (1010) reflexions of Mo  $K\alpha$  X-rays from powdered zinc. R. D. MILLER and E. S. FOSTER, jun. (*Physical Rev.*, 1936, [ii], 50, 408—412, 413—416, 417—418).—I. A comparison of results of intensity measurements of the various reflexions of Cu  $K\alpha$  X-rays from powdered Zn crystals (*cf. Brindley, this vol.*, 3, 15, 538) and measurements on the diffuse scattering of X-rays from single crystals shows that the anisotropy of the thermal vibrations is previously supposed. The root mean square thermal displacements of the atoms are 0.172 and 0.093 Å. along and perpendicular to the *c* axis, respectively. The anisotropy almost explains the anomalous at. structure factor vals.  $F'$ , as modified



by thermal vibrations, for the (0002) and (1010) reflexions, and indicate some asymmetry in the electron structure of the atoms of the Zn crystal.

II. Experiments varying  $S$  with  $\psi$ , the orientation angle, for a fixed scattering angle  $\phi$ , and varying  $S$  with  $\phi$  for two fixed vals. of  $\psi$  confirm Zener's formula (cf. this vol., 273) for the Debye-Waller  $M$ , in the temp. factor  $e^M$  for hexagonal crystals, and the consts.  $a$  and  $b$  in the expression for  $M$ . Results give a higher anisotropy,  $a-b=1.66$ , than Brindley's val. 0.785.

III. The ratio of the  $F$  vals. for the two reflexions is 0.891, using an ionisation method, agreeing with Brindley's val. 0.894 for Cu  $K\alpha$  X-rays, using a photographic method. N. M. B.

**Asymmetry in metallic zinc and cadmium.** H. HERRMANN (Nature, 1936, 138, 290).—Certain discrepancies in the X-ray scattering factors of Zn and Cd (cf. this vol., 412) are ascribed to the asymmetry of the atoms rather than to that in the lattice vibrations. L. S. T.

**Asymmetry in metallic zinc and cadmium.** G. W. BRINDLEY (Nature, 1936, 138, 290—291).—A reply to Herrmann (cf. preceding abstract). The view that the lattice vibrations are responsible for the asymmetry is maintained. L. S. T.

**Eddy arrangement of micro-crystals in metallic wire caused by drawing.** T. FUJIWARA and Y. SEIKI (J. Sci. Hiroshima Univ., 1936, 6, 307—312).—Investigations for Al and W wires were made by X-ray radiographs and microscopically. N. M. B.

**Soft X-rays and photo-electrons from nickel at different temperatures.** S. R. RAO (Current Sci., 1936, 5, 73—74).—The photo-electric efficiencies ( $E$ ) of Cu and Ni when exposed to soft X-rays (applied potentials 100—150 volts) are independent of temp. in the range 30—500°.  $E$  for the 110 face of Ni is 12% < that of polycryst. Ni, this, it is suggested, being associated with the distortion of the crystal surface during bombardment. The soft X-ray emission from well degassed Ni increases with rise of temp., the rate of increase also increasing with rise of temp. No abrupt change was observed at the Curie point. It is concluded that the increase in secondary electron emission observed by Hayakawa (A., 1934, 233) at the Curie point and at potentials above a crit. val. is due to increasing nos. of electrons returning. J. W. S.

**Osmiridium.** III. O. E. ZVJAGINTZEV and B. K. BRUNOVSKI (Z. Krist., 1936, 93, 229—237).—Rotation and Laue photographs of osmiridium show a type of fibre structure in which the single crystal is divided into blocks set at angles up to  $\pm 10^\circ$  from each other. On this basis certain anomalous reflexions in the Laue picture are explained (cf. A., 1935, 440). B. W. R.

**Precision measurement of the lattice constant of very pure tantalum.** M. C. NEUBURGER (Z. Krist., 1936, 93, 312—313).— $a_0=3.2959 \pm 0.0003$  A. at 20°. B. W. R.

**Precision measurement of the lattice constant of very pure vanadium.** M. C. NEUBURGER (Z.

Krist., 1936, 93, 314—315).— $a_0=3.0338 \pm 0.0003$  A. at 25°. B. W. R.

**Crystal structure of heat-treated tungsten filaments.** R. P. BIEN (Physical Rev., 1935, [ii], 47, 806).—Well-aged filaments showed large crystals, up to 3 cm. in length, extending across the entire diameter of the filament. L. S. T.

**$\alpha$ - and  $\beta$ -Ice.** N. SELJAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 227).—Orientations of  $\alpha$ - and  $\beta$ -ice crystals to the normal to the  $H_2O$  surface on which ice formation takes place are given from 0.5° to 10°. W. R. A.

**X-Ray analysis of vitreous  $B_2O_3$ .** B. E. WARREN and O. MORNINGSTAR (Physical Rev., 1935, [ii], 47, 808).—The X-ray scattering curve is that of a typically amorphous pattern showing four peaks. The distribution curve obtained from a Fourier analysis shows peaks at 1.4 and 2.38 A. for the B—O and O—O distances, respectively. A triangular co-ordination with each B linked to 3 O and each O to 2 B is indicated. L. S. T.

**Amorphous and crystalline oxide hydrates and oxides.** XXVIII. X-Ray structure and catalytic properties of silver ferrite. A. KRAUSE, Z. ERNST, S. GAWRYCH, and W. KOCAY (Z. anorg. Chem., 1936, 228, 352—356; cf. this vol., 947, 1080).—The crystal structures of various preps. of  $AgFeO_2$  are similar and show rhombohedral symmetry. The catalytic decomp. of  $H_2O_2$  by  $AgFeO_2$  is relatively slow. J. W. S.

**Crystal structure of cuprous ferrite.** W. SOLLER and A. J. THOMPSON (Physical Rev., 1935, [ii], 47, 644).— $CuFeO_2$ , rhombic,  $a$  5.96 A.,  $\alpha$  29° 26', one mol. per unit cell, space-group  $D_{3d}^3$ , is the only one of several forms of Cu ferrites which is slightly magnetic compared with the cubic form of  $Cu^{II}$  ferrite. L. S. T.

**Lattice constant of sodium chloride and rock-salt.** M. STRAUMANIS and A. IEVINŠ (Z. Physik, 1936, 102, 353—359).—The lattice const. of pure NaCl is  $5.6273 \pm 0.0000_2$  A. at 18°. Three specimens of natural rock-salt from different localities all give the val.  $5.6276_8 \pm 0.0000_3$  A. at 18°. From measurements between 18° and 67°, the coeff. of expansion is  $40.5 \times 10^{-6}$ . A. E. M.

**Crystal structure of germanium disulphide.** W. H. ZACHARIASEN (J. Chem. Physics, 1936, 4, 618—619).— $GeS_2$  crystals are orthorhombic; the unit cell,  $a$  11.66,  $b$  22.34,  $c$  8.86 A., contains 24 mols., and the space-group is  $Fdd$  ( $C_{2h}^{10}$ ). Each Ge is linked tetrahedrally with four S. The angle between two linkings is 103° and the Ge—S distance is 2.19 A. J. G. A. G.

**Interatomic distances in orpiment, realgar, sodium sulphoantimonate enneahydrate, and calcium mercuric bromide.** W. V. MEDLIN (J. Amer. Chem. Soc., 1936, 58, 1590—1592).—In orpiment and realgar the distance between As and S agrees with the sum of the corresponding covalent radii. In  $Na_3SbS_4 \cdot 9H_2O$  the Sb—S distance is < the sum of the covalent radii. Indefinite results were obtained with  $CaHgBr_4$ . E. S. H.

**Crystal structure of cupric chloride dihydrate.** D. HARKER (Z. Krist., 1936, 93, 136—145).— $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  is orthorhombic,  $a_0$  7.38,  $b_0$  8.04,  $c_0$  3.72 Å., space-group  $Pbmn$ . The structure is found from intensity measurements. The Cu atoms are attached to 2 Cl and 2 O by covalent linkings directed to corners of a square. A similar square formation must occur in  $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ . B. W. R.

**Crystal structure of ammonium chlorobromiodide.** R. C. L. MOONEY (Physical Rev., 1935, [ii], 47, 807—808).—The unit cell, containing 4 mols., has  $a$  6.14,  $b$  5.58,  $c$  10.03 Å.; space-group  $Pmcn$  ( $V^{16}$ ). Parameters for  $\text{NH}_4$ , Cl, I, and Br are given. The atoms lie in planes perpendicular to the  $x$ -axis and separated by a distance  $a/2$ . The halogen atoms are associated in a strictly linear group with I at the centre. The distance between I and Br atoms in a group agrees with the sum of the at. radii of I and Br as found in  $\text{I}_2$  and  $\text{Br}_2$  from band spectra.  $\text{NH}_4$  is co-ordinated with 4 Cl at a distance of 3.34 Å., 4 Br at one of 3.63 Å., and 2 I at one of 3.79 Å.

L. S. T.

**Crystal structure of thallium trithionate,  $\text{Tl}_2\text{S}_3\text{O}_6$ .** J. A. A. KETELAAR and J. K. SANDERS (J. Chem. Physics, 1936, 4, 621).— $\text{Tl}_2\text{S}_3\text{O}_6$  crystals are monoclinic and the unit cell,  $a$  13.20,  $b$  7.45,  $c$  7.58 Å.,  $\beta$  91.0°, contains 4 mols. The space-group is  $(C2/c)$ . The crystals are not isomorphous with  $\text{K}_2\text{S}_3\text{O}_6$ . J. G. A. G.

**X-Ray investigation of the structure of ultramarine-blue and its reaction products.** E. PODSCHUS, U. HOFMANN, and K. LESCHEWSKI (Z. anorg. Chem., 1936, 228, 305—333).—Ultramarine (I) has a cubic structure with a space-group  $T_d$ , similar to that of sodalite, hauynite, and nosean (cf. A., 1929, 749). The S is in a polysulphide state, probably with some in an ionic form. The structures of the Li and Ag substitution products are similar, but in the latter the position of the Ag ions is not quite ideal. The "sulphate-product" obtained by oxidising (I) has a lattice with space-group  $T_d$ . The S atoms are responsible for the colour of (I). J. W. S.

**X-Ray diffraction pattern of liquid and solid glycerol films.** K. LARK-HOROVITZ and E. P. MILLER (Physical Rev., 1935, [ii], 47, 813; cf. A., 1935, 18).—The apparent sharpening of diffracted lines at lower temp. is due to inhomogeneous radiation. None was observed at room temp. and at  $-80^\circ$ . This agrees with the view that the mols. in solid glycerol are distributed at random similarly to mols. in liquids. L. S. T.

**Physical investigation of phenyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylvinyl sulphone.** H. E. BENT, E. S. LARSEN, and H. BERMAN (J. Amer. Chem. Soc., 1936, 58, 1522—1523).—Crystallographic and solubility (in  $\text{C}_6\text{H}_6$  and  $\text{MeOH}$ ) data are recorded and compared with corresponding data for Ph  $\alpha$ -hydroxy- $\beta\beta$ -diphenylpropenyl sulphone. The compounds may be identical. E. S. H.

**Lattice structure of condensed aromatic hydrocarbons and their molecular compounds with trinitrobenzene.** E. HERTEL and H. W. BERGK (Z. physikal. Chem., 1936, B, 33, 319—333).—2 : 3-

Benanthracene (I) crystallises in the triclinic system with  $I_a$  7.94,  $I_b$  6.02,  $I_c$  13.5 Å., and 2 mols. in the unit cell. Perylene (II) crystallises in the monoclinic system with  $I_a$  10.3,  $I_b$  10.8,  $I_c$  13.6 Å., space-group  $C_{2h}^2$ , and 4 mols. in the unit cell. The lattice structures of the 1 : 1 mol. compounds of (II) and pyrene with  $\text{C}_6\text{H}_5(\text{NO}_2)_3$  (III) have been examined. (I) forms no mol. compound with (III). The lattices of the 1 : 1 mol. compounds of (III) with  $\text{C}_6\text{H}_6$  and  $\text{PhMg}$  are able to take up small amounts of (I). An apparatus for vac. sublimation in a const. gas current is described. R. C.

**Absorption edges in the X-rays patterns of native and mercerised cellulose.** W. A. Sisson, G. L. CLARK, and E. A. PARKER (J. Amer. Chem. Soc., 1936, 58, 1635—1638).—Diffracted general radiation from the 002 and 101 planes in native and the 101 plane in mercerised cellulose produces Br and Ag absorption edges similar in appearance to diffraction lines on the X-ray negative. Absorption edges correspond with some, but not all, of the large interferences reported for cellulose. No spacings  $>$  the cellulose unit cell were found. E. S. H.

**Shape and properties of thread-like molecules in solution and in the elastic solid state.** W. KUHN (Z. Elektrochem., 1936, 42, 692; cf. A., 1934, 959; this vol., 785).—The mean distance between the ends of a long chain mol. is  $aZ$ , where  $Z$  is the no. of members in the chain and  $a$  is a const. The valency angle and nature of the free rotation modify the val. of  $a$ . The modulus of elasticity of rubber-like materials  $\propto 1/Z$ , and so can be used to determine the mol. wt. of the mols. J. W. S.

**Elementary lattice of crystallised caoutchouc.** K. H. MEYER and W. LOTMAR (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 61—62; cf. Mark, A., 1928, 1178).—Previous data are corr. The lattice is slightly monoclinic, with  $a$  8.54,  $b$  8.20,  $c$  12.65 Å.,  $\beta$  83°, space-group probably  $C_{2h}^2$ . N. M. B.

**Electron diffraction by transmission through thin silica glass films.** L. R. MAXWELL and V. M. MOSLEY (Physical Rev., 1935, [ii], 47, 330—331).—The electron diffraction pattern obtained by transmission of 25—38-kv. electrons through thin films of  $\text{SiO}_2$  glass is described. L. S. T.

**Structure of thin metal layers.** R. RIEDMILLER (Z. Physik, 1936, 102, 408—416).—The determination of lattice const. of Ni, Au, and Ag by electron diffraction through films vaporised on collodion is described. Various errors are eliminated by photographing a reference pattern simultaneously, and measuring the patterns microphotometrically. The effect of air and  $\text{H}_2$  on the films is studied. Lattice const. by this method are about 1%  $>$  by X rays. L. G. G.

**Structure of some metallic deposits on a copper single crystal as determined by electron diffraction.** W. COCHRANE (Proc. Physical Soc., 1936, 48, 723—735).—Ni, Cu, Zn, Cd, Ag, Cr, and Co were deposited electrolytically on etched Cu single-crystals and the structure of the deposits was found by electron diffraction. At small c.d. the layers are oriented except in the case of Zn and Cd. Irregul-



arities (lines and spots) in the Ni and Co patterns are accounted for by assuming repeated twinning on (111) planes. N. M. B.

Gerlach's thermomagnetic electromotive force in some ferromagnetic alloys. N. YAMANAKA (Sci. Rep. Tôhoku, 1936, 25, 174—183).—The e.m.f. produced by the application of a longitudinal magnetic field in a wire down which there is a temp. gradient has been measured for Ni, nichrome, ipvar, and superinvar. The effect for the alloys is  $<$  for Ni. When the temp. is  $<$  Curie point the e.m.f. increases with magnetic field and with temp., tending to a saturation val. O. D. S.

Time lag in the magnetisation of soft iron in the upper portion of the hysteresis loop. J. ÔKUBO and N. YAMANAKA (Sci. Rep. Tôhoku, 1936, 25, 163—173).—Measurements have been made of the time variation of magnetic induction in soft iron and Fe-Si-Al alloys after removal of a magnetising current under conditions where  $\mu$  was nearly const. O. D. S.

Magnetic viscosity at different points of the magnetisation curve. A. MITKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 175—177).—The best conditions for the observation of the effect of magnetic history on magnetic viscosity are obtained, the magnetisation curve for an iron ring being found by the method of reversals. The viscosity reaches a max. on the steepest part of the curve and decreases exponentially with time. The effect of magnetic history on subsequent viscosity is most marked in weak fields, becoming imperceptible with increase of magnetic field. W. R. A.

Ferromagnetism of iron alloys. M. FALLOT (Ann. Physique, 1936, [xi], 6, 305—387).—The law of the approach to saturation magnetisation as a function of  $T^{3/2}$  near  $0^\circ$  abs. is verified. A special apparatus for liquefying small quantities of  $H_2$  for magnetisation experiments, and a recording apparatus for the determination of Curie points, are described. Mean at. moments and Curie points for alloys of Fe with Si, Al, Cr, V, Au, Sn, Pt, and Mn were determined and their variations with the nature and proportion of the added element are discussed. The at. moment of Fe depends on the foreign atoms surrounding the Fe atom in the lattice. N. M. B.

Hall coefficients of alkali metals. C. ZENER (Physical Rev., 1935, [ii], 47, 636).—Theoretical. L. S. T.

Determination of the optical anisotropy constants of absorbing crystal sections from polarisation observations in perpendicularly reflected light. M. BEREK (Z. Krist., 1936, 93, 116—135).—Mathematical. B. W. R.

Optical studies on organic crystals. I. K. S. SUNDARARAJAN (Z. Krist., 1936, 93, 238—248).—A summary of measurements of principal refractive indices and directions of optic axes for 14 aromatic hydrocarbons. The results are discussed in relation to the mol. positions already known from X-ray and magnetic methods. B. W. R.

Effect of crystal boundaries on test specimens consisting of several large crystals. G. SEUMEL (Z. Krist., 1936, 93, 249—283).—The behaviour of test-rods containing several large crystals is studied under strain, the normal polycryst. metal being regarded as the limiting case of such measurements. B. W. R.

Slip, twinning, and cleavage in silicon ferrite (4.17% Si). C. S. BARRETT (Physical Rev., 1935, [ii], 47, 809).—Repeated bending causes cleavage on cube planes [100], and hammering causes twinning (Neuman bands) on icositetrahedral planes [112]. Slip occurs only on rhombic dodecahedral planes [110]. L. S. T.

Crystalline symmetry and shear constants of Rochelle salt. T. TASCHKE and H. OSTERBERG (Physical Rev., 1936, [ii], 50, 572).—Interferometer studies of patterns due to shear modes of vibration excited by alternating electric fields of frequency 20—200 kc. per sec. show that, for 12 specimens, the cryst. symmetry is hemihedric with no transitions to the hemimorphic class in the temp. range  $0$ — $40^\circ$ . Frequency-temp. curves show negative temp. coeffs. for all three shear modes; all curves show anomalies near  $23.5^\circ$ . N. M. B.

Temperature variation of the elastic moduli of NaCl, KCl, and MgO. M. A. DURAND (Physical Rev., 1936, [ii], 50, 449—455; cf. Balamuth, A., 1934, 836).—The principal adiabatic and isothermal elastic moduli and elastic consts. were measured over  $270$ — $480^\circ$  abs. for NaCl,  $80$ — $280^\circ$  abs. for KCl, and  $80$ — $560^\circ$  abs. for MgO. The Debye characteristic temp. of these at  $80^\circ$  abs., calc. from the adiabatic elastic consts., are  $320^\circ$ ,  $246^\circ$ , and  $946^\circ$  abs., respectively. The variation of isothermals with temp. is evaluated and discussed. N. M. B.

High-pressure transitions of bismuth [and antimony]. P. W. BRIDGMAN (Physical Rev., 1935, [ii], 47, 427—428; cf. this vol., 146).—The transition parameters of Bi have been determined at high pressures. Two new modifications of Bi, each denser than the liquid, exist. The transition line between ordinary Bi (I) and the first high-pressure modification (II) is linear and passes through the points  $80^\circ$ , 23,250 kg. per sq. cm. and  $180^\circ$ , 17,850 kg. per sq. cm.; that between (II) and the second high-pressure Bi (III) is also linear and passes through  $80^\circ$ , 26,400 kg. per sq. cm. and  $180^\circ$ , 22,950 kg. per sq. cm. The triple point liquid-(I)-(II) occurs at  $184.0^\circ$  and 17,600 kg. per sq. cm. Estimated vals. for the triple point liquid-(II)-(III) are approx.  $187.0^\circ$  and 22,700 kg. per sq. cm. Sb shows no new modifications in the range examined. L. S. T.

Glassy state of arsenic. W. E. McCORMICK and W. P. DAVEY (Physical Rev., 1935, [ii], 47, 330).—In pure  $H_2$  below  $100^\circ$ , As vapour condenses to an amorphous (X-rays) powder of small particle size; between  $100^\circ$  and  $130^\circ$ , a mixture of powder and coherent sheet, and between  $130^\circ$  and  $250^\circ$  non-cryst. coherent sheet or glass, is obtained. Above  $250^\circ$ , the deposit is distinctly cryst. to X-rays. L. S. T.

Transformation of fluids into the glassy state. H. EBERT (Glastech. Ber., 1935, 13, 73—77; Chem.

Zentr., 1935, ii, 3812).—Glass, when cooled below the transformation interval, behaves as a frozen phase. The transformation curve does not afford decisive evidence of a transformation of higher order. J. S. A.

Osmotic mol. wt. determination for large molecules. G. V. SCHULZ (Z. Elektrochem., 1936, 42, 692).—The mol. wt. ( $M$ ) of large mols. can be calc. from their osmotic pressure ( $p$ ) in solution by the formula  $p = RTc/M(1 - cs)$  ( $c$  = concn.,  $s$  = vol. occupied in solution by 1 g. of solute).  $s$  is related to  $p$  by  $p - ks^v$ , where  $k$  and  $v$  are swelling consts. independent of mol. wt. and determinable for smaller mols. of known mol. wt. The vals. of  $M$  calc. from these equations are independent of concn. and are in accord with vals. deduced from viscosity and ultrafilter methods. The variation of  $p$  with  $c$  indicates that no mol. aggregation occurs at higher concn.

J. W. S.

Bismuth crystals. II. Variation of thermoelectric power in transverse magnetic fields. E. GRUNEISEN and J. GIELESSEN (Ann. Physik, 1936, [v], 27, 243—255; cf. this vol., 930).—The effect of transverse magnetic field on the thermoelectric power of couples of Bi crystals with metals unaffected by the field has been investigated at  $0^\circ$ ,  $-183^\circ$ , and  $-195^\circ$ , with respect to the direction of the field and of the crystal axis. For  $Bi_{II}$  at low temp. the thermoelectric power is increased by the magnetic field to an extent varying with the direction of the field. For  $Bi_I$  at low temp. the thermoelectric power is increased or decreased according to the direction of the field. In both  $Bi_{II}$  and  $Bi_I$  the thermoelectric power is affected by reversal of the field. The thermoelectric power of a  $Bi_{II}$ - $Bi_I$  couple at  $-183^\circ$  and  $-195^\circ$  is calc.

O. D. S.

Free path and thermoelectric effects. L. W. NORDHEIM (Physical Rev., 1935, [ii], 47, 794).—A general expression for the mean free path of electrons in metals is derived.

L. S. T.

Destruction of superconductivity by electric current and magnetic field. L. SCHUBNIKOV (Nature, 1936, 138, 545—546).—The data plotted for Sn show that as a necessary condition of superconductivity the magnetic field should be zero in the whole of the vol. and its effective tangential component should be  $\geq$  a crit. val. at any point of the surface of the superconductor.

L. S. T.

New phenomenon in the superconducting transition of tin and tantalum. F. B. SLSBEE, F. G. BRICKWEDDE, and R. B. SCOTT (Physical Rev., 1935, [ii], 45, 794).—With large currents, passage from the superconducting to the normal resisting condition is accompanied by a spontaneous, transitory increase in resistance followed by a slower return.

L. S. T.

Electron theory in metals of any crystal form. M. KOHLER (Ann. Physik, 1936, [v], 27, 201—216).—Mathematical. Theory of electrical conductivity, thermoelectric effect, and the galvanomagnetic phenomena is generalised for metals of any crystal form.

O. D. S.

Effect of electric field on the heat current in gases. H. SENFTLEBEN and W. BRAUN (Z. Physik, 1936, 102, 480—506).—A thin wire heated in an electric field gives out more heat than without the field. The effect was investigated in A and O<sub>2</sub> (non-polar gases) and in EtCl (polar), with variation of pressure, external temp., and temp. of wire. In all cases the effect varied with the square of the field strength, pressure, and temp. of wire. The val. decreased rapidly with increase of external temp. The effect in polar gases is  $>$  in non-polar gases. It can be explained as a supplementary convection due to variations in electrostriction, and offers a method of determining the latter in gases. A. J. M.

(A) Magnetic properties of chromium. L. F. BATES and A. BAQI. (B) Magnetic properties of amalgams. L. F. BATES and L. C. TAI (Proc. Physical Soc., 1936, 48, 781—794, 795—809).—(A) The magnetic susceptibility of pure Cr prepared from Cr amalgam was investigated over the temp. range  $90$ — $620^\circ$  abs. The mass susceptibility is almost const.; the mean susceptibility is  $3.08 \times 10^{-6}$  e.m.u. per g. at room temp. The effects of impurities are considered in detail, and thermal and magnetic data are discussed on the basis of modern theories of paramagnetism.

(B) The magnetic susceptibilities of a series of amalgams of known concn. of Bi, Cr, Cu, and Mn were studied at room temp. by the Gouy method, the drop-wt. method being untrustworthy for amalgams. The apparent at. susceptibilities in dil. amalgams were: Mn,  $0.137$ ; Bi,  $133 \times 10^{-6}$ ; Cr,  $23 \times 10^{-6}$ ; Cu,  $-7.3 \times 10^{-6}$  e.m.u. Metals diamagnetic in the solid state were paramagnetic in dil. amalgams, with the possible exception of Cu. N. M. B.

Paramagnetism of the rare-earth sulphates at low temperatures. L. C. JACKSON (Proc. Physical Soc., 1936, 48, 741—746).—Measurements of magnetic susceptibilities of powdered octahydrated sulphates of Yb, Dy, and Er are plotted from room temp. to  $14^\circ$  abs. Results are discussed in terms of the cryst.-field theory of Penny (cf. A., 1932, 985). Measurements on  $Nd_2(SO_4)_3 \cdot 8H_2O$  support Gorter (cf. *ibid.*, 448) against Selwood (cf. A., 1933, 1002).

N. M. B.

Acoustical studies. V. Collision efficiencies of deuterium and hydrogen in exciting the lower vibrational states of ethylene. W. T. RICHARDS. VI. Behaviour of formic and acetic acid vapours. C. O. STROTHER and W. T. RICHARDS (J. Chem. Physics, 1936, 4, 561—566, 566—569; cf. A., 1934, 588).—V. Sound velocity data in  $C_2H_4$ - $D_2$  mixtures show that a  $H_2$ - $C_2H_4$  collision is eight times as effective as a  $D_2$ - $C_2H_4$  collision in producing transitions in the lower vibrational states of  $C_2H_4$ . The origin of this difference may be found in the uniquely small moment of inertia of  $H_2$ .  $C_3H_8$  behaves as an inert gas in  $C_2H_4$ - $C_3H_8$  mixtures. The claim to have found rotational dispersion in  $H_2$  is withdrawn.

VI. Thermal decomp. of formic acid at  $60^\circ$  prevents accurate sound velocity measurements. Data for AcOH at  $85$ — $115^\circ$  show that the rate of dissociation of the double mols. is  $> 10^4$  sec.<sup>-1</sup> at  $85^\circ$  and 174 mm.

J. G. A. G.



**Propagation of sound in partly dissociated gases.** H. O. KNESER and O. GAULER (Physikal. Z., 1936, 37, 677—684).—Theoretical. The effect of partial dissociation of a gas on the velocity of waves of short and of long  $\lambda$ , respectively, through it is discussed, and applied to the case of  $\text{N}_2\text{O}_4$  and  $2\text{NO}_2$ .  
A. J. M.

**Current, breakdown, and supersonic vibrations in dielectric liquids.** W. MEYER (Z. Physik, 1936, 102, 279—304).—The influence of supersonic vibrations on the conductivity and dielectric strength of  $\text{C}_6\text{H}_{14}$ ,  $\text{PhCl}$ ,  $\text{Et}_2\text{O}$ ,  $\text{CCl}_4$ ,  $\text{PhMe}$ , and  $\text{COMe}_2$  has been investigated. Results are affected by the nature of the electrode surfaces and by the presence of dissolved gas and other impurities in the liquids. The incidence of supersonic vibrations causes a general increase in conductivity and a decrease in dielectric strength.  
H. C. G.

**Intensity measurements in the diffraction of light by ultrasonic waves.** F. H. SANDERS (Canad. J. Res., 1936, 14, A, 158—171).—The relative intensities in the various orders of the diffraction pattern produced when light is passed through a liquid carrying ultrasonic waves have been measured for various ultrasonic intensities and for both progressive and standing wave-fields. The variation with intensity is in accord with the theory of Raman and Nath (this vol., 148, 555).  
J. W. S.

**Absorption of ultrasonic waves by liquids.** P. BIQUARD (Ann. Physique, 1936, [xi], 6, 195—304; cf. this vol., 417).—Using the method of measuring the radiation pressure exerted on an obstacle or an optical method based on diffraction, the absorption in  $\text{H}_2\text{O}$  and several org. liquids of ultrasonic waves of frequency  $(4-11) \times 10^6$  was investigated. Absorption coeffs. differed widely from theoretical predictions and the law of proportionality of absorption to  $v^2$  was not always obeyed. Various explanations are discussed.  
N. M. B.

**Absorption of ultrasonic waves in liquids and related optical phenomena.** L. MANDELSTAM and M. LEONTOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 111—114).—Theoretical. The dependence of the absorption coeff. of ultrasonic waves in liquids on frequency and other factors is discussed, and related to the diffraction of light in the transmitting liquid.  
A. J. E. W.

**Thermal and caloric equation of state of condensed hydrogen isotopes. I. Determination of magnitudes of state.** E. BARTHOLOME (Z. physikal. Chem., 1936, B, 33, 387—404).—The results of measurements of the isothermal compressibility of liquid  $\text{H}_2$  and  $\text{D}_2$  at 16—21° abs. agree with Eucken's equation of state for a condensed substance (A., 1934, 946); the compressibility falls rapidly with increasing pressure. From measurements of the change in vol. on melting under pressure, part of the fusion curve has been traced, and the latent heats of fusion have been calc. The mol. vol. at 0° abs. of  $\text{H}_2$  and  $\text{D}_2$  are calc. to be 22.9 and 20.3 c.c., respectively. The characteristic temp. of the Debye sp. heat function are 105° and 97° for solid  $\text{H}_2$  and  $\text{D}_2$ , respectively, the deviation of the ratio of these vals.

from the theoretical val.  $\sqrt{2} : 1$  being attributed to the anharmonicity of the potential curve of solid  $\text{H}_2$ . From  $C_p$  for the liquids, compressibilities have been calc. The results obtained have been used to construct pressure-vol.-temp. and enthalpy-pressure-temp. diagrams for  $\text{H}_2$  and  $\text{D}_2$ .  
R. C.

**Determination of heat capacities and heat capacity ratios of gaseous hydrogen cyanide and hydrogen sulphide.** W. A. FELSING and G. W. DRAKE (J. Amer. Chem. Soc., 1936, 58, 1714—1717).—Heat capacities have been determined at 30—148° for HCN and 30—110° for  $\text{H}_2\text{S}$  with an accuracy of approx. 1%.  $C_p/C_v$  has been determined at 30—75° for HCN and at 10—75° for  $\text{H}_2\text{S}$  with an accuracy of approx. 0.2%.  
E. S. H.

**Thermodynamic properties of methane.** W. C. EDMISTER (Ind. Eng. Chem., 1936, 28, 1112—1116).—Vals. of  $(dc_p/dP)_T$ ,  $c_p - c_v$ , Joule-Thomson coeff.,  $S$ , enthalpy, and  $\alpha = RT/P - V$  for  $\text{CH}_4$  at pressures 1 to 120 atm. and temp. —70° to 200° have been calc. from existing compressibility and sp. heat data.  
C. R. H.

**Effect on the fundamental units of volume and temperature of the variable isotopic composition of water.** E. H. RIESENFELD and T. L. CHANG (Physikal. Z., 1936, 37, 690—692).—The effect of the variability in composition of  $\text{H}_2\text{O}$  from different sources on the accuracy of the definition of the litre and of the Centigrade degree is discussed, and it is concluded that owing to the difficulty of obtaining pure  $^1\text{H}_2^{16}\text{O}$  it would be unwise to alter the present definitions. It would, however, be an advantage to specify the source and treatment of the  $\text{H}_2\text{O}$  referred to in the definitions.  
A. J. M.

**Density and compressibility of solid hydrogen and deuterium at 4.2° absolute.** H. D. MEGAW and F. SIMON (Nature, 1936, 138, 244).—Approx. vals. of  $d$ , compressibility, and thermal expansion of H and D at 4.2° abs. have been determined in order to show the effect of zero-point energy.  
L. S. T.

**Density and coefficient of expansion of liquid gallium over a wide range of temperature.** W. H. HOATHER (Proc. Physical Soc., 1936, 48, 699—707).—Accurate data for  $d$  and coeff. of expansion for the temp. range 30—1000°, obtained by a dilatometric method, are reported. An equation for vol. increase with temp. is found. The calc. mean coeff. of expansion (32.38—310°) is  $118.7 \times 10^{-6}$ .  
N. M. B.

**Density of hydrocarbon gases and vapours at high temperature and pressure.** W. B. KAY (Ind. Eng. Chem., 1936, 28, 1014—1019).— $P$ ,  $V$ , and  $T$  data on eleven petroleum hydrocarbon mixtures are correlated with similar data on pure hydrocarbons by means of the theory of corresponding states. For the mixtures,  $P_r$  and  $T_r$  are related to a "pseudocrit. point," which is the crit. point of the pure compound of which the  $P$ ,  $V$ ,  $T$  relations in the superheated region are identical with those for the mixture.  
C. R. H.

**Reduced volume at the b.p. and additivity.** R. LAUTIE (Bull. Soc. chim., 1936, [v], 3, 1595—1600).

—The reduced density at the b.p. ( $T^\circ$  abs.) is not const. but varies according to  $d_c/d_e = 2.23 + 0.1861 \log T_e - 8.03 \times 10^{-5} T_e$  to within 2.5%. J. W. S.

**Vapour pressure of potassium chloride and caesium iodide crystals.** V. DIETZ (J. Chem. Physics, 1936, 4, 575—580).—The v.p. determined by means of a modified abs. manometer are for KCl,  $\log_{10} \text{ dynes} = -11,300/T + 13.461$  between  $847^\circ$  and  $936^\circ$  abs. and for CsI,  $\log_{10} P_{\text{dynes}} = -10,360/T + 13.793$ , at  $767$ — $847^\circ$  abs., from which the heats of sublimation are 51,800 and 47,500 g.-cal. per mol., respectively. Effusion experiments show that the mols. are not associated. J. G. A. G.

**Vapour pressure curves and triple points in the temperature range  $14$ — $90^\circ$  abs.** F. HENNING and J. OTTO (Physikal. Z., 1936, 37, 633—638).—Data for the v.p. curves of  $\text{H}_2$ , Ne,  $\text{O}_2$ , and  $\text{N}_2$  between the triple point and the b.p. have been obtained using the He gas thermometer. Empirical equations expressing variation of v.p. with temp. are given. For Ne the v.p. of the solid is also given. The triple points are:  $\text{H}_2$   $13.96^\circ$ , 54.1 mm., Ne  $24.56^\circ$ , 325 mm., N,  $63.145^\circ$ , 94.6 mm.,  $\text{O}_2$   $54.33^\circ$ , 1.2 mm. (all temp. abs.). A. J. M.

**Derivation of the equation  $PV = RT$ .** L. McCULLOCH (J. Chem. Educ., 1936, 13, 393—394). L. S. T.

**Generalised high-pressure properties of gases.** K. M. WATSON and R. L. SMITH (Nat. Petroleum News, 1936, 28, No. 27, 29—36).—Methods which are simpler than the ordinary thermodynamic formulæ are derived for calculating the effect of pressure on heat content, heat capacities, and the Joule-Thomson coeff. from the activity coeffs. Plots of the authors' correlations of compressibility factor ( $PV/RT$ ) and activity coeffs. are presented. R. B. C.

**Joule-Thomson coefficient of oxides of carbon.** T. C. HUANG, F. LIN, and C. Y. FU (Z. Physik, 1936, 102, 422).—A correction (this vol., 930). For CO read  $\text{CO}_2$ . H. C. G.

**Thermal conductivity of deuterium.** C. T. ARCHER (Nature, 1936, 138, 286—287).—Vals. obtained for the thermal conductivity at  $0^\circ$  of  $\text{D}_2$  prepared by two different methods from 99.95%  $\text{D}_2\text{O}$  are 0.000308<sub>2</sub> and 0.000307<sub>8</sub> g.-cal. per cm. per sec. per degree. L. S. T.

**Thermal conductivity of gases with free convection.** W. WEIZSACKER (Physikal. Z., 1936, 37, 641—650).—The effect of pressure on the free convection of  $\text{CO}_2$ , A,  $\text{H}_2$ , He, and air for small temp. differences has been investigated. The convection disappears at a temp. characteristic for each gas. A. J. M.

**Viscosity of deuterium.** H. C. TORREY (Physical Rev., 1935, [ii], 47, 644—645).—Rankine's method gives for the ratio  $\eta_{\text{D}_2} : \eta_{\text{H}_2}$   $1.410 \pm 0.03$ , yielding  $124.4 + 2.5$  micropoises for the  $\eta$  of  $\text{D}_2$  at  $23.0^\circ$ . The mol. cross-sections of the H isotopes effective in  $\eta$  thus differ by  $<2\%$ . L. S. T.

**Physical properties of water and other fluids.** R. L. DAUGHERTY (Trans. Amer. Soc. Mech. Eng., 1935, 57, 193—196).— $\eta$  data for  $\text{H}_2\text{O}$  and various

liquids are represented graphically.  $P$ — $V$ — $T$  data and vol. modulus of elasticity and sp. heat data for  $\text{H}_2\text{O}$  are given. CH. ABS. (e)

**Fluidity and molecular complexity.** E. C. BINGHAM and C. E. COOMBS (Physical Rev., 1935, [ii], 47, 645).—Formulæ connecting fluidity and mol. complexity are discussed for normal org. compounds. L. S. T.

**Effect of an electric field on the viscosity of eolotropic liquids.** Y. BJORNSTAHL (Physics, 1935, 6, 257—264).—An oscillating-disc viscosimeter with connexions for applying a field parallel to the axis of the instrument was used.  $\eta$  increased with increase of either an a.c. or a d.c. field, probably owing to orientation of swarms. A change in electrical conductivity with shear was found. CH. ABS. (e)

**Viscosity of aqueous solutions. III. Calculation of the viscosity of mixed solutions.** A. BANCHETTI (Gazzetta, 1936, 66, 446—451; cf. A., 1935, 693).—The validity of various formulæ for calculating the viscosity of mixed solutions has been examined for solutions of  $\text{NaCl} + \text{HCl}$ ,  $\text{NaCl} + \text{KCl}$ , and  $\text{HCl} + \text{KCl}$ . O. J. W.

**Viscosity of supersaturated solution of sucrose.** J. COUMOU (Chem. Weekblad, 1936, 33, 542—544).—For supersaturated solutions (75%) of sucrose at  $20^\circ$   $\eta$  decreases to a const. val. on keeping for 2—3 hr. and increases when the solution is vigorously stirred. S. C.

**Binary liquid systems in which compounds are formed.** E. ANGELESCU and C. EUSTATIU (Z. physikal. Chem., 1936, 177, 263—276).—Mixtures of aromatic amines with fatty acids at  $25^\circ$  have been studied. The contraction on mixing,  $\phi$ , may be represented by  $\phi = Kx^a(1-x)$ , where  $x$  is the mol. fraction and  $K$  and  $a$  are consts. The relation between the viscosity,  $\eta$ , and vol. composition of the mixtures may be represented by McLeod's equation (Trans. Faraday Soc., 1924, 19, 6, 17). is a max. for a mixture containing a greater proportion of acid than corresponds with the composition of the compounds indicated by thermal analysis, a discrepancy which is ascribed to the acids being more highly associated than the amines. Neither the mol. surface energy nor the parachor follows the additive law, but each may be represented by  $P = [P_1x + P_2(1-x)](1 - K'\phi)$ , where  $P$  is the parachor or mol. surface energy and  $K'$  a const. which is the greater the more capillary active is the acid. The mol. refraction is approx. additive, but  $n$  deviates from additivity, the deviation being a max. for a mixture of one mol. of amine with two mols. of acid. R. C.

**Properties of metallic solutions. I.** V. K. SEMENTSCHENKO (Acta Physicochim. U.R.S.S., 1936, 4, 695—704; cf. this vol., 1192).—The surface tension of amalgams of Mg, Co, Zn, Cd, Ag, Ca, Sr, Pb, Sn, Ba, Li, Na, K, Rb, and Cs has been determined for various concns. There is good agreement with the theory of generalised moments. The effect of minute quantities of impurities on the mechanical properties of metals and alloys, and that of surface-active metals on the mutual solubility of two metals



are discussed. The action of promoters may be explained on the theory. A. J. M.

**Diffusion constant and valency of silver in liquid silver amalgam.** K. SCHWARZ and R. STOCKERT (*Monatsh.*, 1936, 68, 383—368).—The diffusion const. of Ag in Ag amalgam at 16° is  $1.1 \times 10^{-5}$  sq. cm. per sec., in accord with the bivalency of Ag in these amalgams. J. W. S.

**Heat content and heat of formation of molten alloys.** H. O. VON SAMSON-HIMMELSTJERNA (*Z. Metallk.*, 1936, 28, 197—202).—The heat contents of Pb-Bi alloys at 400°, 500°, and 600°, Sn-Bi, Pb-Sn, and Pb-Cd alloys at 500°, Pb-Ag alloys at 1000°, and Pb-Sn-Bi alloys at 500° have been determined. The max. heats of alloying calc. from these figures are at 500°: Pb-Bi +1000, Bi-Sn +530, Pb-Sn -250 and Cd-Pb -480 g.-cal. per g.-atom; and at 1000° Pb-Ag -800 g.-cal. per g.-atom. The heats of formation of solid Ag-Zn alloys lie on two straight lines intersecting at  $\text{Ag}_2\text{Zn}_3$ , and those of solid Cu-Zn alloys on straight lines intersecting at  $\text{Cu}_2\text{Zn}_3$ ; calculations of the heat of formation of these alloys at 1000° show that these compounds exist in the liquid state but are strongly dissociated unless a large excess of either component is present. The heats of alloying of Cu and Ni and of Ni and Fe at 1500—1600° vary only slightly from the heats of formation of the corresponding solid solutions. A. R. P.

**Relation between the thermal and electrical conductivities of copper alloys.** C. S. SMITH (*Physical Rev.*, 1935, [ii], 48, 166—167).—When thermal conductivity is plotted against electrical conductivity at the same temp., the results for all Cu alloys can be represented by a single curve, regardless of composition within wide limits and also of structure or heat-treatment. The curves for 20° and 200° differ in slope, but intersect at approx. the same point on the thermal conductivity axis. All results both at 20° and 200° lie on a single curve when thermal conductivity is plotted against electrical conductivity  $\times$  abs. temp. L. S. T.

**Hall effect and some other physical constants of alloys. V. Antimony-silver series.** W. G. JOHN and E. J. EVANS (*Phil. Mag.*, 1936, [vii], 22, 417—435).—The resistivity, temp. coeff. of resistance, thermo-electric power,  $d$ , and Hall coeff. of Sb-Ag alloys have been determined over the complete composition range. The property-composition curves afford no evidence for the existence of a solid solution at the Sb end of the series. Sharp negative max. occur in the thermo-electric power and Hall coeff. curves at 72% Ag, but  $X$ -ray analysis shows no sign of a phase change at this composition. A. J. M.

**Magnetic susceptibilities of the silver-lead, silver antimony, and silver-bismuth series of alloys.** G. O. STEPHENS and E. J. EVANS (*Phil. Mag.*, 1936, [vii], 22, 435—445).—The  $d$  and mass susceptibilities ( $\chi$ ) of Ag-Pb, Ag-Sb, and Ag-Bi alloys have been determined. Annealing has little effect on  $\chi$  for Ag-Pb alloys, which represent a series of mechanical mixtures throughout the whole composition range. In the Ag-Sb alloys no indication is found of the existence of a solid solution at the Sb

end of the system (cf. preceding abstract). The existence of a solid solution of Bi in Ag up to a concn. of 5.7% Bi is shown. All the alloys examined were diamagnetic. A. J. M.

**Longitudinal magneto-resistance effect at various temperatures in nickel-copper alloys.** H. MASUMOTO and Y. SHIRAKAWA (*Sci. Rep. Tohoku*, 1935, 25, 105—127).—The magneto-resistance of Ni-Cu alloys rises with increasing Cu content to a max. at 10% (−195°), 6% (0°), and 4% Cu (100°) and then falls rapidly, reaching zero at 47% (−195°), 33% (0°), and 23% Cu (100°). The max. in the curves is much more pronounced at temp. below 0° than at higher temp. A. R. P.

**Quantum theory of electrical conductivity of alloys in superlattice state.** T. MUTO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, 30, 99—120).—Theoretical. An expression is derived which connects the influence of temp. and composition on the resistance with the superlattice order of the alloy. Comparison with published results for the Cu-Au system shows fair agreement. J. S. A.

**Diffusion experiments as means of simple micrographic detection of compound formation between alloy components in three- and multi-component systems.** M. BOSSHARD (*Aluminium*, 1935, 17, 477—481; *Chem. Zentr.*, 1935, ii, 3972—3973).—A cone of the basis metal with one alloy component is pressed into a corresponding seating in a block of an alloy of the basis metal with the second alloying component. After several days just below the solidus temp. the region of the interface is examined micrographically for evidence of diffusion. In the following combinations the changes indicated were so detected: Al-Si: Al-Fe,  $\text{Al}_3\text{Fe} \rightarrow \text{Al}_x\text{Fe}_y\text{Si}_z$  (probably  $\text{Al}_6\text{Fe}_2\text{Si}_3$ ); Al-Si: Al-Mn, MnSi formed; Al-Cr: Al: Si,  $\text{Al}_2\text{Cr} \rightarrow \text{CrSi}$ , with vol. contraction; Al-Fe: Al-Cu,  $\text{Al}_3\text{Fe} \rightarrow \text{Al}_2\text{Cu}_2\text{Fe}$ ; Al-Ni: Al-Cu,  $\text{Al}_5\text{NiCu}_2$  or Al-NiCu<sub>2</sub> formed; Al-Cu: Al-Mg,  $\text{Al}_6\text{Mg}_4\text{Cu}$  formed. J. S. A.

**Stability of cementite.** K. HONDA, K. IWASE, and K. SANO (*Sci. Rep. Tohoku*, 1936, 25, 202—206).—Theoretical. The solubility curve of graphite in austenite is deduced from the equilibrium const. of the reactions: austenite (C-rich) +  $\text{CO}_2$  = austenite (C-poor) + 2CO, and  $\text{C} + \text{CO}_2 = 2\text{CO}$ . The solubility of graphite above 925° is > that of cementite; it is inferred that cementite is stable above this temp. O. D. S.

**System iron-zinc.** J. SCHRAMM (*Z. Metallk.*, 1936, 28, 203—207).—The system has been examined by  $X$ -ray, thermal, and magnetic analysis and by micrographical methods. At 20° there are four stable phases:  $\eta$  (hexagonal Zn-rich solid solution,  $\delta$  (hexagonal "FeZn<sub>2</sub>"),  $\Gamma$  (cubic "FeZn<sub>3</sub>" with 52 atoms in the unit cell), and  $\alpha$  (Fe-rich solid solution). The eutectic point is 419.4°, 0.09% Fe and < 0.03% of Fe dissolves in Zn at the eutectic temp. The  $\delta$ -field extends from 6.3 to 11.5% Fe at 20° and from 5.8 to 11.5% Fe at 419° and the  $\Gamma$ -field from 20 to 27% Fe at 20—600°. The peritectic horizontal at 780° extends from 54 to 19% Fe, and that at 668° from 20 to 4% Fe, whilst the eutectoid horizontal at 623°

extends from 80 to 27% Fe;  $\alpha$ -Fe dissolves 20% Zn at 623°, 10% at 450°, and 8% at 20°, but  $\gamma$ -Fe dissolves a max. of 46% Zn at 780°. The compositions of the  $\delta$ - and  $\Gamma$ -phases are not in agreement with any of the formulæ previously proposed. A. R. P.

**Equilibrium diagram of magnesium-rich magnesium-manganese binary system.** H. SAWAMOTO (Suiv.-Shi, 1935, 8, 763—768; cf. this vol., 559).—The new  $\beta$ -phase in the Mg-Mn system is a solid solution of the compound  $\text{Mg}_6\text{Mn}$ , which is formed by the peritectic reaction at 726°.

CH. ABS. (e)

**Phase relationships in the nickel-tin system.** E. FETZ and E. R. JETTE (J. Chem. Physics, 1936, 4, 537).—With increasing % of Sn, a new phase appears at  $\text{Ni}_3\text{Sn}$  which coexists at 25—35.5 at.-% Sn with a phase (I) having a NiAs-structure. (I) exists alone at 35.5—45 at.-% Sn, but at 40 at.-% Sn and below 500° gives place to a deformed modification. Three new phases,  $\eta$ ,  $\theta$ , and  $\epsilon$ , exist at 51, 54, and 56—62 at.-% Sn, respectively. The  $\zeta$ -phase coexists with the Sn-phase above 62 at.-% Sn. The solubility of Ni in Sn is very small. J. G. A. G.

**Phase equilibria in hydrocarbon systems.** XVI. Solubility of methane in four light hydrocarbons. B. H. SAGE, D. C. WEBSTER, and W. N. LACEY (Ind. Eng. Chem., 1936, 28, 1045—1047).—The solubility of  $\text{CH}_4$  in  $n\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_6\text{H}_{14}$ , cyclohexane, and  $\text{C}_6\text{H}_6$  and the sp. vols. of the mixtures have been determined at 100°, 160°, and 220° F. and at total pressures between 400 and 3000 lb. per sq. in. C. R. H.

**Solubility of calcium  $\beta$ -methylbutyrate in water.** D. F. HOUSTON (J. Res. Nat. Bur. Stand., 1936, 17, 55—58).—Solubilities at 0—100° are recorded. The results indicate a transition from the penta- to the hemi-hydrate at 36.5°. O. J. W.

**Solubility of sodium carbonate in aqueous ammonia.** E. I. ACHUMOV and E. A. EZEROVA (J. Appl. Chem. Russ., 1936, 9, 1173—1177).—Solubility data are recorded, for the system  $\text{Na}_2\text{CO}_3\text{--NH}_3\text{--H}_2\text{O}$ , at 0°, 10°, and 20°. R. T.

**Equilibrium in fluoride systems. I. Solubility of cryolite in aqueous solutions of iron and aluminium salts at 25°.** F. J. FRERE (J. Amer. Chem. Soc., 1936, 58, 1695—1697).—Solubility data for  $\text{Na}_3\text{AlF}_6$  in aq.  $\text{Fe}^{\text{III}}$  and Al chloride, nitrate, and sulphate are recorded. Solubility is greatest in the Al salt solutions. Double salts appear to be formed. E. S. H.

**Sodium silicofluoride and aluminium fluoride, and their solubility in water and hydrofluoric acid.** N. S. NIKOLAEV, N. A. IVANOV, and S. G. KOLTIPIN (J. Appl. Chem. Russ., 1936, 9, 1183—1190).—The solubility of  $\text{Na}_2\text{SiF}_6$  and  $\text{AlF}_3\cdot 5\text{H}_2\text{O}$  (I) rises with increasing [HF] and temp. Anhyd.  $\text{AlF}_3$  is obtained by drying (I) at 300°. R. T.

**Solubility of naringin in water.** G. N. PULLEY (Ind. Eng. Chem. [Anal.], 1936, 8, 360).—Data for 6—75° are recorded. Solubility increases little with rise of temp. below 45°, but increases rapidly at >45°.

**Relative vapour pressure and aqueous solubility of the solid-solution system  $\beta$ -naphthol-naphthalene.** R. WRIGHT and N. E. WALLACE (J.C.S., 1936, 1279—1283).—The solubility of solid solutions of  $\beta\text{-C}_{10}\text{H}_7\text{-OH}$  (I) and  $\text{C}_{10}\text{H}_8$  (II) in  $\text{H}_2\text{O}$  at 25°, 65°, and 78° has been determined. At 25° the max. solubility occurs with approx. 50% (I), but at higher temp. the solubility rises with increase in the proportion of (I) until at approx. 80% it rises suddenly to the val. for pure (I). The ratio of the v.p. of (II) in solid solution to that of pure (II) is const. over definite composition ranges at 30° and 55°, indicating the presence of two solid phases in these regions, but this constancy disappears at higher temp. C. R. H.

**Laws of separation out of traces of foreign substances during crystallising out of precipitates.** N. RIEHL (Z. physikal. Chem., 1936, 177, 224—234).—Theoretical. In slow crystallisation from a supersaturated solution the ratio,  $r$ , of the micro-component (I) to the macrocomponent (II) in the crystal as a whole  $\propto$  the ratio of the concns.  $c_1$  and  $c_2$  in the solution at equilibrium. This can be explained only by supposing that in a layer of mols. deposited on the growing crystal  $r=c_1/c_2$ , at first, but subsequently this is altered by kinetic exchange between crystal and solution. For rapid crystallisation from supersaturated solution in presence of many crystal nuclei the Doerner-Hoskins equation (A., 1925, ii, 381) is valid for the relation between the initial and final vals. of  $c_1$  and  $c_2$ ; this may be explained by supposing that owing to the abnormally high solubility of the nuclei there is metastable equilibrium between the liquid and solid phases. R. C.

**Equations for diffusion of gases through metals.** W. R. HAM (Physical Rev., 1935, [iii], 47, 645). L. S. T.

**Diffusion of hydrogen through highly degassed palladium.** J. D. SAUTER and W. R. HAM (Physical Rev., 1935, [ii], 47, 645; cf. this vol., 1194).—Results obtained with highly degassed Pd are recorded. L. S. T.

**Diffusion in zeolitic solids.** M. H. HEY (Phil. Mag., 1936, [vii], 22, 492—497).—The equations derived in the kinetic theory of zeolitic diffusion previously put forward (A., 1935, 1345) are applied to analcime- $\text{NH}_3$  (I) and Pd- $\text{H}_2$  (II). The calc. diffusion const. of (I) is  $(1.2+0.7)\times 10^{-8}$  sq. cm. per sec., agreeing with the val. given by Tiselius (this vol., 153), whilst that of (II) agrees with the val. given by Jost *et al.* (A., 1935, 1200). A. J. M.

**Sorption processes on diamond and graphite. I. Reactions with hydrogen. II. Reactions of diamond with oxygen, carbon dioxide, and carbon monoxide.** R. M. BARRER (J.C.S., 1936, 1256—1261, 1261—1268).—I. Isothermals for the chemisorption of  $\text{H}_2$  by diamond (I) correspond with a large heat of sorption, the estimated val. being 58 kg.-cal. per g.-mol. compared with 45 kg.-cal. per g.-mol. for sorption by graphite. A comparison of the energy of activation-% saturation curves for (I), graphite, and charcoal indicates that only (I) approaches the ideal adsorbent which consists of perfect crystals



and for which the energy is const. for all degrees of saturation. The admission of  $O_2$  prevents the chemisorption of  $H_2$  by forming a stable oxide film on the (I).

II. At  $-78^\circ$  the sorption of  $O_2$  by (I) is nearly all physical. As the temp. is raised chemisorption becomes more pronounced, the  $O_2$  being retained as a film. At  $244-370^\circ$ , with further admission of  $O_2$ ,  $CO_2$  is liberated, and at still higher temp. the  $O_2$  film begins to decompose,  $CO_2$  and  $CO$  being formed.  $CO_2$  is reduced by (I) to  $CO$ , a small proportion of which is considered to be retained as a film.

C. R. H.

**Porosity and sorption properties of activated charcoal.** M. DUBININ and E. SAVERINA (Acta Physicochim. U.R.S.S., 1936, 4, 647-674).—A series of activated charcoals, prepared by activation of sugar-C at  $850^\circ$  and  $1000^\circ$ , has been used in the investigation of the adsorption of org. acids, PhOH, methylene-blue, Congo-red, and I from aq. solution and the data have been applied to estimate the porosity of the adsorbent. The adsorption isotherms of  $C_6H_6$  vapour at  $20^\circ$  and  $50^\circ$ , and of MeOH vapour at  $20^\circ$ , on outgassed C were determined at pressures from  $10^{-4}$  mm. to the saturation pressure. The adsorption depends on the activation process, and, for the substances used, agrees well with the Polanyi adsorption potential theory.

A. J. M.

**Activated adsorption of hydrogen and carbon monoxide on zinc oxide. Effect of water vapour.** R. L. BURWELL, jun., and H. S. TAYLOR (J. Amer. Chem. Soc., 1936, 58, 1753-1755).— $H_2O$  vapour minimises surface reduction of ZnO catalysts and is strongly adsorbed from gas mixtures by those fractions of ZnO surfaces to which the gas mixture first has access. Saturation of ZnO surfaces with  $H_2O$  vapour inhibits markedly the activated adsorption of  $H_2$  and CO.

E. S. H.

**Adsorption of iodine on quartz glass at temperatures up to  $1000^\circ$ .** P. HOLEMANN (Z. Elektrochem., 1936, 42, 680).—From the v.d. obtained by vaporisation of known amounts of I in vessels with varying areas of internal surface, the adsorption of I on fused  $SiO_2$  has been studied at  $150-1000^\circ$  and at v.d.  $1.7-3.3 \times 10^{-5}$  g. per c.c. The amount adsorbed ( $A$ )  $\propto$  the v.d. At  $150-400^\circ$  and  $850-1000^\circ$   $A \propto 1/T$ . It is concluded that for the lower temp. interval the adsorption is mol., and for the upper is at.; the heats of adsorption calc. from the proportionality factors are 1.2 and 15 kg.-cal. per g.-mol., respectively. The no. of "active centres" decreases with rising temp. and is less for at. than for mol. adsorption.

J. W. S.

**Adsorption of silver and iodide ions by freshly-precipitated silver iodide. Isoelectric point of the fresh precipitate.** I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Chem. Soc., 1936, 58, 1528-1533).—The isoelectric point of freshly-pptd. AgI is  $p_{Ag}$  6.0. At the equivalence potential the excess of adsorbed  $I^-$  is 0.09% of the total I in the ppt. Adsorption of  $Ag^+$  or  $I^-$  by the fresh ppt. is in accordance with  $\Delta X - K \log C$  in the  $p_{Ag}$  range 4-7.2;  $I^-$  is more strongly adsorbed than  $Ag^+$ . The theoretical ratio

KI:Ag is found in potentiometric titration if the end-point is taken at the isoelectric point instead of at the equivalence potential, and if a correction is applied for excess of  $Ag^+$  in solution.

E. S. H.

**Adsorption of barium salts by barium sulphate from solutions in 50% ethyl alcohol.** I. M. KOLTHOFF and W. M. MACNEVIN (J. Amer. Chem. Soc., 1936, 58, 1543-1546).—Adsorption of Ba salts from 50% EtOH is  $>$  from  $H_2O$ ; the Freundlich adsorption isotherm is followed. In a series of Ba salts there is no simple relation between adsorbability and solubility.  $KBrO_3$  gives equiv. adsorption of cations and anions.  $Ca(BrO_3)_2$  is adsorbed as  $Ca(OH)BrO_3$ .

E. S. H.

**Adsorption at the interface between two fluids. II. Adsorption of five dyes at a paraffin-water and at an air-water interface.** C. W. GIBBY and C. C. ADDISON (J.C.S., 1936, 1306-1313).—No adsorption of methylene-blue (I), orange-II (II), Congo-red, Mc-orange, or Bordeaux-extra (III) at an air- $H_2O$  interface can be detected. (III) is more adsorbed on a light paraffin- $H_2O$  interface than on a  $C_6H_6$ - or a PhCl- $H_2O$  interface, the other four dyes being less adsorbed on paraffin than on  $C_6H_6$  or PhCl. The adsorption curves for (I) and (II) at all three liquid-liquid interfaces rise with the concn. and finally become horizontal. The curves for the other three dyes pass through a max. and then fall towards zero.

C. R. H.

**Adsorption of barium chloride from acidic and basic silica sols.** Z. BERESTNEVA and V. KARGIN (Acta Physicochim. U.R.S.S., 1936, 4, 675-694).—The Ba-amalgam electrode may be employed for the determination of the activity of  $Ba^{++}$  in  $SiO_2$  sols. It has been used to study the adsorption of  $Ba^{++}$  from  $BaCl_2$  solution by  $SiO_2$  sols at  $p_H$  4.7-11.4. There is no adsorption at  $p_H < 8$ . The exchange adsorption on coagulation of  $SiO_2$  sols has also been examined. The  $[Na^+]$  in alkaline  $SiO_2$  sols remains practically const. during the coagulation by  $BaCl_2$ .

A. J. M.

**Statistical mechanical treatment of adsorption phenomena of gases in organic liquids.** I, II. S. HAMAI (Sci. Rep. Tohoku, 1936, 25, 344-356, 357-363; cf. Hildebrand, this vol., 818).—I. Vals. of the const.  $b$  in Hildebrand's general solubility equation are calc. statistically and compared with those derived from experimental data. Agreement is not generally satisfactory for solutions of  $CO_2$  and  $N_2O$  in org. liquids, but solutions of  $CO_2$  in  $CS_2$  are exceptional.

II. For solutions of HCl in various org. liquids agreement is best for the more symmetrical and less polar solvents.

O. D. S.

(A) Theoretical basis of calculating work of adsorbents, in particular as applied to fractionation of mixtures of gases or vapours. M. DUBININ and S. JAVITSCH. (B) Dynamics of sorption of mixtures of vapours. M. DUBININ and M. CHRENOVA (J. Appl. Chem. Russ., 1936, 9, 1191-1203, 1204-1213).—(A) The adsorption coeff.  $\alpha$  of one vapour by another is shown theoretically to be given by  $\alpha = (C_1' - C_1)/C_2$ , where  $C_1'$  is the concn. of one vapour in the issuing air during the period

preceding appearance of the second vapour, and  $C_1$  and  $C_2$  are the initial concns. of the vapours.

(B) The above equation is shown to hold in the case of air containing EtOH and PhMe vapours passed through active C at 20°.

R. T.

**Ageing of surfaces of solutions. I. Study of variation of surface tension of solutions with time by the ring method.** K. S. G. DOSS and B. S. RAO. **II. Activated accumulation of solute molecules.** K. S. G. DOSS (Proc. Indian Acad. Sci., 1936, 4, A, 11—16, 97—107; cf. this vol., 284).—I. An automatic device for the construction of quartz helical springs is described. The spring is used for measuring the max. pull in the determination of the surface tension of PhMe by the ring method, and the effect of time has been investigated for several liquids. No consistent or reproducible variations were found and the ring method is considered to be unsuitable.

**II.** An application of the Langmuir-Adam surface pressure technique is described. A fresh surface of benzopurpurin solution shows a fall of surface tension with time; on producing mechanically an overcrowding of solute mols. in the surface, a rise of surface tension with time is found. The measured rate of accumulation of mols. at the surface is very slow and is accounted for on the basis of activated accumulation. This postulate throws light on the time variation of surface tension, the high temp. coeff., and the manifestation of surface pressure. The observations may be applied to the measurement of the efficacy of a substance as a stabiliser of foam.

N. M. B.

**Kinetics of selective wetting and surface reactions on metals in presence of electrolytes. I.** D. MRLIS and P. REHBINDER (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 123—128).—The spreading of drops of electrolyte solutions on metal plates immersed in  $C_6H_6$  has been studied by observing changes in the contact angle. Spreading is due to hydrophilisation of the surface by corrosion products accumulating at the perimeter of the drop; corrosion of the metal by the drop can thus be studied. Fatty acid in the  $C_6H_6$  phase inhibits spreading owing to adsorption on the metal surface.

A. J. E. W.

**Union with complement as a surface reaction.**

**I. Surface tension and adsorption. Model experiments with caffeine solutions.** F. SEELICH (Biochem. Z., 1936, 286, 396—407).—Curves show the surface tension at various  $H_2O$ -non-miscible org. substance (paraffin,  $C_6H_6$ ,  $NPhMe_3$ , oleic acid, etc.) interfaces when varying amounts of caffeine are added and the relation between surface tension and adsorption is investigated. The bearing of the observations on biological surface reactions is discussed.

P. W. C.

**Studies of unimolecular films by the ripple method. I, II.** J. SAMESHIMA and T. SASAKI (Bull. Chem. Soc. Japan, 1936, 11, 539—546, 547—552).—I. The relation between mol. area and amplitude of ripple has been determined by the const. surface area method for palmitic (I), stearic, myristic (II), and oleic acids (III), tetradecyl alcohol (IV), and palmitonitrile (V), and the results are in agreement with surface pressure data. The damping action

of the film increases with the vibration frequency of the wave-source (tuning fork), in accordance with hydrodynamical theory. It is suggested that the damping action of oil on ocean waves is due to the subsidence of ripples, entailing a diminution in the resistance to the wind.

**II.** Oleic and lauric acids, (I)—(V) tripalmitin, triolein, ricinoleic acid, and Et palmitate have been studied using const. oil quantity and varying surface area. The compression and expansion curves show hysteresis with an acid medium, which is attributed to inclination of the mols. in the expanded state. The mol. wt. of mastic, calc. from the area at which the ripples subside, is approx. 3600.

R. S.

**Multimolecular films.** W. D. HARKINS and R. J. MYERS (J. Amer. Chem. Soc., 1936, 58, 1817—1819).—Multimol. liquid films of stearic, oleic, myristic, and pentadecic acid have been obtained by thickening the films with a liquid paraffin (nujol) of low volatility.

E. S. II.

**Contact potentials of reversible soluble films of lauric acid.** R. T. FLORENCE, R. J. MYERS, and W. D. HARKINS (Nature, 1936, 138, 405—406).—The changes in surface pressure and in the contact potential when the surface of a solution of lauric acid is swept clean of its adsorbed film and the acid allowed to accumulate at the surface by diffusion from the interior of the solution have been determined. The results indicate the importance of the time factor in the determination of  $\gamma$  for solutions of surface-active materials, and the unsuitability of dynamic methods for materials which require considerable time for equilibrium in the surface.

L. S. T.

**Electrical properties of films of  $\omega$ -bromohexadecic acid.** M. GEROVICH and A. FRUMKIN (J. Chem. Physics, 1936, 4, 624).—Films of the acid on the surface of a solution containing 0.01N-KCl and  $10^{-4}$ N-HCl show a large negative interfacial potential owing to the orientation of C-Br linkings. By increasing the acidity of the solution to  $10^{-3}$ N-HCl, the surface pressure is decreased markedly and the potential is changed to a small positive val. probably owing to a change of film structure.

J. G. A. G.

**Unimolecular layers of chlorophyll.** W. SJOERDSMA (Nature, 1936, 138, 405).—A 3:1 mixture of the *a* and *b* modifications forms unimol. layers on  $H_2O$ , 0.01N- and 0.1N- $H_2SO_4$ . The limiting area per mol. at zero compression is  $124 \text{ \AA}^2$ , and at 26 dynes per cm. the film becomes multimol. On  $H_2O$  in equilibrium with  $CO_2$  at atm. pressure the mols. appear to require more space, the limiting area being  $132 \text{ \AA}^2$ . NO has no such effect.

L. S. T.

**Permeability of membranes. III. Ionic permeability of non-aqueous liquid layers.** K. H. MEYER, H. HAUPTMANN, and J. F. SIEVERS. **IV. Analysis of structure of vegetable and animal membranes.** K. H. MEYER and J. F. SIEVERS (Helv. Chim. Acta, 1936, 19, 948—962, 987—995; cf. this vol., 1065).—III. Diffusion potentials across layers of  $NH_2Ph$ ,  $PhOH$ , *m*-cresol, and  $CH_3Bu^aOH$  have been measured at 20° and the mobilities of the participating ions calc. Diffusion is determined by



the mobilities and solubilities of the ions in the non-aq. liquid and there is no selectivity. Partition coeffs. of ions have been determined potentiometrically and published data are discussed.

IV. Diffusion potentials between KCl solutions across vegetable (bracts of *Iris amoena*) and animal (skin of *Bombinator igneus*) membranes have been measured. The former contains acids of high mol. wt. and is permeable to cations, whilst the latter shows only slight permeability. These, and similar data relating to membranes studied by other workers, are used to elucidate their structure. Accumulation of K<sup>+</sup> in plants is not due to selective solubility in lipins, but to its greater facility of passage through what is essentially a fine-meshed sieve. F. L. U.

Statistical evaluation of sieve constants in ultrafiltration. J. D. FERRY (J. Gen. Physiol., 1936, 20, 95—104).—The sieve const. is evaluated in terms of the calibrated membrane porosity and the particle size. H. G. R.

Viscosity nomograph for salt solutions. D. S. DAVIS (Chem. Met. Eng., 1936, 43, 485).—A nomograph from which  $\eta$  at 25° of 0.1—1.0*N* solutions of 38 salts can be read is published. W. L. D.

Viscosity of dilute solutions: technique and measurements with solutions of hydrocarbons. K. H. MEYER and A. VAN DER WYK (Kolloid-Z., 1936, 76, 278—289).—Systematic errors and the corresponding corrections in the determination of  $\eta$  of dil. solutions are discussed. The sp.  $\eta$  of dil. (<1%) solutions of higher hydrocarbons in CCl<sub>4</sub> has been determined with special reference to changes in constitution, concn., and temp. In these series  $\eta$  is not a function of the length of the dissolved mol., but varies in a complicated way with constitution. The variation of  $\eta$  with temp. and concn. shows that the dissolved mols. cannot be regarded as rod-like particles. E. S. H.

High-frequency loss and molecular properties of polar solutions. G. MARTIN (Physikal., 1936, 37, 665—667).—The high-frequency loss for dil. solutions of polar substances in non-polar solvents has been determined in order to verify the dipole theory of high-frequency loss. The dielectric loss for *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>  $\propto \mu^2$ , as required by theory. The extrapolated loss at infinite dilution for Pr<sup>o</sup>OH, *n*-C<sub>8</sub>H<sub>17</sub>·OH, and *n*-C<sub>16</sub>H<sub>33</sub>·OH increases with the no. of C in the mol. The effect of  $\eta$ , investigated for solutions of *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> in C<sub>6</sub>H<sub>14</sub>, C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>, and decalin, the relaxation time being plotted against  $\eta$ , shows that Stokes' law holds in the calculation of relaxation time even for particles of mol. size, if an inner  $\eta$  is assumed, which differs from that determined by macroscopic methods. In non-polar liquids this mol. is a function of the ordinary  $\eta$  and the mol. vol. A. J. M.

Interdiffusion of acid and base in aqueous solution. C. V. KING and W. H. CATHCART (J. Amer. Chem. Soc., 1936, 58, 1639—1642).—Diffusion coeffs. of HCl and NaOH in presence of NaCl have been determined over a wide concn. range. In the interdiffusion of HCl and NaOH in aq. NaCl the diffusion coeffs. are unchanged if sufficient NaCl is present

initially; in the porous-disc cell the diffusion rates are increased since the concn. gradients become sharper because of neutralisation within the disc. Limitations of the porous-disc cell are demonstrated. E. S. H.

Diffusion of magnesium chloride and nitrate in aqueous solution. L. W. ÖHOLM (Finska Kem. Medd., 1936, 45, 71—76).—Diffusion data are compared with vals. for other properties of the solutions. M. H. M. A.

Viscosities and densities of dilute aqueous solutions of weak electrolytes (*o*-nitrobenzoic acid). A. BANCHETTI (Annali Chim. Appl., 1936, 26, 351—356).— $d$  varies almost linearly with the concn. ( $c$ ) and the variation of  $\eta$  is given by  $\eta - 1 = ac^b$ , where  $a$  and  $b$  are consts. L. A. O'N.

Condition of electrolytes in aqueous solutions. A. H. W. ATEN (Chem. Weekblad, 1936, 33, 555—562).—A lecture. S. C.

Physical characterisation of dissolved ions. II. F.p. and conductivity of very dilute aqueous solutions of alkali halides. J. LANGE (Z. physikal. Chem., 1936, 177, 193—212; cf. A., 1934, 596).—The f.p. and conductivity of solutions of the chlorides and iodides of Li, Cs, and K at 0.001—0.1*N* have been determined. Up to 0.05*N* the results can be expressed by  $1 - f_0 = 0.37\sqrt{c} + B_0c$  (f.p.) and  $1 - f_\infty = (0.219 + 29.5/\Delta_0)\sqrt{c} + B_\infty c$  (conductivity). For all the salts  $B_0$  and  $B_\infty$  are negative and approx. equal, indicating complete dissociation. Each consists essentially of a negative and a positive component. The negative component arises from the finite size of the ions in the sense of the Debye-Hückel theory, varies little from one ion to another, and has the same val. for  $B_0$  as for  $B_\infty$ . The positive component originates in the mutual attraction of the ions owing to the short-period perturbations of the movements of the electrons, on the lines of London's theory (A., 1931, 149), and can be approx. calc. by means of this theory; it is greater for  $B_\infty$  than for  $B_0$ . R. C.

Hydrochloric and hydrobromic solutions of the salts of cobalt, copper, and bivalent nickel. P. JOB (Ann. Chim., 1936, [xi], 6, 97—144; cf. A., 1935, 582).—Solutions of salts of Co, Cu, and Ni in aq. HCl, HBr, and NaBr have been studied spectrographically. For the Co solutions the absorption is independent of the anion and  $\propto [\text{Co}^{2+}]$  for a fixed concn. of acid. The  $\lambda$ - and [HCl]-absorption curves show max., whilst the absorption becomes const. when [HCl] > 13 mols. per litre. The results can be accurately reproduced on the assumption that an intermediate complex CoCl<sup>+</sup> and a blue complex CoCl<sub>2</sub><sup>+</sup> are formed. HBr solutions show similar properties, the blue colour appearing, however, at a slightly greater concn. The absorption of Cu<sup>2+</sup> in aq. HBr increases with the [HBr] to a limiting val. at 10 mols. per litre. Two complexes CuBr<sup>+</sup> and CuBr<sub>2</sub><sup>+</sup> are probably formed. The activity coeffs. of NaBr, determined by comparison of the absorption of NaBr and HBr solutions containing Cu<sup>2+</sup>, agree with the results of Harned and Douglas. Solutions of Ni<sup>2+</sup> in HBr resemble those of Co<sup>2+</sup> in HBr and contain the coloured complexes NiBr<sub>2</sub><sup>+</sup> and NiBr<sub>4</sub><sup>2-</sup>. The equilibrium consts. have been calc. in each case and the stabilities of the

complexes compared.  $\text{CuBr}'$  is more stable than  $\text{CoBr}'$ , whilst  $\text{CoBr}_3'$  is less stable than  $\text{CoCl}_3'$ .

R. S.

**Molecular state of red rhenium chloride in solution.** F. W. WRIGGE and W. BILTZ (*Z. anorg. Chem.*, 1936, 228, 372—382).—The mol. wt. of anhyd.  $\text{ReCl}_3$  (prepared by sublimation in a vac.), calc. from the depression of the f.p. of  $\text{AcOH}$ , corresponds with  $\text{Re}_3\text{Cl}_6$ . The dialysis coeff. of its  $\text{HCl}$  solutions indicates that it exists as  $\text{HReCl}_4$  in these solutions. The absorption spectrum of anhyd.  $\text{ReCl}_3$  in  $\text{AcOH}$ , dioxan,  $\text{H}_2\text{SO}_4$ , or  $\text{HCl}$  has a max. at about 5100 Å., and a min. at about 4500 Å. Solutions of  $\text{ReCl}_3 \cdot 2\text{H}_2\text{O}$  (obtained by exposure of  $\text{ReCl}_3$  to moist air) in  $\text{AcOH}$  or dioxan show two absorption max. at about 5000 and 5400 Å., respectively. The structures of the anhyd. and hydrated salts are discussed. J. W. S.

**Light pressure and Brownian movement.** M. SATO (*Sci. Rep. Tohoku*, 1935, 28, 156—162).—The results obtained for the light pressure and mean square of the displacement of a Brownian particle from Planck's radiation law are in good agreement with those derived from Glaser's theory of corpuscular gas (cf. *Z. Physik.*, 1935, 94, 677). A. R. P.

**Rheopexy in bentonite.** E. A. HAUSER and C. E. REED (*J. Amer. Chem. Soc.*, 1936, 58, 1822).—Fractionation (by high-speed centrifuge) of dispersions of bentonite in  $\text{H}_2\text{O}$  gives completely amicromic fractions which exhibit rheopexy (A., 1935, 933). H. B.

**Behaviour of aerosols in the acoustic field. II. Behaviour of suspended matter in oscillating gases at sonic and ultra-sonic frequencies.** O. BRANDT (*Kolloid-Z.*, 1936, 76, 272—278; cf. this vol., 794).—The rate of aggregation of the particles (0.2—1.7  $\mu$  diameter) in stationary and streaming aerosols of liquid paraffin has been determined for different frequencies by measurement of the rate of fall of the particles and by optical means.

E. S. H.

**Effect of an electric field on the intensity of the Tyndall light for different forms of colloidal particles.** H. UERLINGS (*Physikal. Z.*, 1936, 37, 655—657).—The effect of an electric field on the Tyndall light from  $\text{V}_2\text{O}_5$ , blue Au, benzopurpurin, and  $\text{Fe}(\text{OH})_3$  sols (all having non-spherical particles) and from Ag, red Au, and mastic sols (with spherical particles) has been examined. The electric field increases the intensity of the light for the former group of sols when the lines of force and the direction of vibration of the electric vector coincide, and the direction of observation is mutually perpendicular to this, and to the direction of the incident light. Sols with spherical particles show no increase in the intensity of the Tyndall light on application of the field.

A. J. M.

**Structures and forces in colloidal systems.** H. FREUNDLICH (*Proc. Roy. Inst.*, 1936, 29, 232—252).—A lecture.

**Relations between molecular size, statistical molecular structure, and elastic properties of highly-polymerised substances.** W. KUHN (*Kolloid-Z.*, 1936, 76, 258—271; cf. this vol., 785).—Theoretical.

E. S. H.

**Determination of the specific weights of cellulose solutions. Estimation of the specific weights of the double compounds of cellulose derivatives with organic solvents.** W. KUMICHEL and C. TROGUS (*Cellulosechem.*, 1936, 17, 97—102).—From *d* measurements of solutions of cellulose nitrates in  $\text{COMe}_2$  and in 4-methylcyclohexanone (I) the sp. vols. of the compounds have been estimated. The vals. found agree with those given by *X*-ray measurements if the unit cell in  $\text{COMe}_2$  contains 10  $\text{C}_6$  units, whilst that in (I) contains 6  $\text{C}_6$  units and 6 mols. of solvent (at 20—30°) and 10  $\text{C}_6$  units and 20 mols. of solvent (at 18°).

A. G.

**Lyophilic colloids. III. Micelle composition.** H. KROEPFELIN (*Rev. Fac. Sci. Univ. Istanbul*, 1936, 1, 70—76).— $\text{Et}_2\text{O}$  solutions of rubber show an increased Tyndall effect on addition of small amounts of  $\text{EtOH}$  or  $\text{COMe}_2$  contrary to the theory which is presented. The Tyndall effect increases more slowly than the concn.

R. S.

**Colloid synthesis by vapour explosions and the colloid-chemical investigation of the disperse systems obtained.** N. SATA (*Bull. Chem. Soc. Japan*, 1936, 11, 481—503; cf. this vol., 1198).—Dust, burnt cork, and passage through filter-paper stabilise the Hg sol obtained by the vapour explosion method.  $\text{Na}_2\text{SO}_3$  coagulates the sol whilst the stability increases to a max. with increasing  $[\text{Na}_2\text{S}]$  owing to the formation of stabilising complexes. A similar stability max. obtained with  $\text{NaI}$  is ascribed to the formation of  $\text{HgI}$ , which gives a green colour in presence of Hg. The concn. range of stabiliser giving max. stability is diminished by irradiation with ultra-violet light, and more so in the case of  $\text{Na}_2\text{S}$  than  $\text{NaI}$ . Se sols have been prepared by the vapour explosion method and the influence of stirring and shaking investigated.  $\text{O}_2$  increases the stability of the sol by reacting with adsorbed  $\text{SeH}_2$ . S sols, similarly prepared, are unstable.

R. S.

**Coagulation of colloids. XIV. Coagulation of colloidal arsenious sulphide by mercuric chloride. Inadmissibility of viscosity and transparency as general criteria of coagulation.** S. S. JOSHI and S. S. KULKARNI (*J. Indian Chem. Soc.*, 1936, 13, 439—447; cf. this vol., 795).—No over-all change of *n* or opacity is observed during coagulation by  $\text{HgCl}_2$ , although normal variations in these properties occur during coagulation by  $\text{CdCl}_2$  or  $\text{KCl}$ . These properties do not depend only on the charge, shape, and size of the disperse particles, but on macroscopic properties of the system as a whole.

E. S. H.

**Variation of cataphoretic velocity of colloidal particles during coagulation. II.** J. N. MUKHERJEE, S. G. CHAUDHURY, and J. SEN-GUPTA (*J. Indian Chem. Soc.*, 1936, 13, 428—438; cf. this vol., 1201).—The variation of electrophoretic velocity with time has been determined for sols of  $\text{As}_2\text{S}_3$ ,  $\text{V}_2\text{O}_5$ , Se,  $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ ,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , and  $\text{Fe}(\text{OH})_3$  in presence of various electrolytes. The % increase of velocity is the greater the higher are the concn. of the pptg. electrolyte and the valency of the pptg. ion. The effect also depends on the nature of the sol and of the electrolyte and on the electrolyte content of the



sol and thus runs parallel with the effect on the rate of coagulation. E. S. H.

**Ionic interchange in stearic acid sols and the mechanism of coagulation.** T. R. BOLAM and A. I. S. DUNCAN (J.C.S., 1936, 1317—1324).—The coagulation of stearic acid (I) by  $\text{H}_2\text{SO}_4$  and sulphates has been followed; the coagulative effect decreases in the order  $\text{H}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ . The  $\text{H}^+$  liberated from (I) by ionic interchange increases with increasing salt concn., the tendency of the cations to displace  $\text{H}^+$  being  $\text{Mg}^{++} > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . The data support the view that the surface mols. of (I) particles dissociate like a weak acid. C. R. H.

**Liesegang rings in non-gelatinous media.** II. V. GORE (Kolloid-Z., 1936, 76, 330—333; cf. this vol., 1201).—The formation of periodic structures by diffusion of an electrolyte into sols of metal hydroxides, peptised by another electrolyte, is described. The results support the periodic-coagulation theory.

E. S. H.

**Sensitising effect of small amounts of alkali on silicic acid sol.** V. N. KRESTINSKAJA and N. E. NATANSON (Kolloid-Z., 1936, 76, 313—321).—Experiments on coagulation with  $\text{NaCl}$  and titration with  $\text{HCl}$  show that small amounts of  $\text{NaOH}$  produce complex silicates, which sensitise the sol to electrolyte coagulation, but with increasing amounts of  $\text{NaOH}$  the product is  $\text{Na}_2\text{SiO}_3$ , which stabilises the sol.

E. S. H.

**Oxidation and reduction reactions of colloidal substances.** IV. Theory of structure of aggregates of colloid particles. V. N. SKVORZOV (Kolloid-Z., 1936, 76, 322—330; cf. A., 1935, 1208).—The rate of reaction of mono- and poly-disperse sols of  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$  with  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{SO}_4$  has been determined. From the results it is inferred that the disperse particles have a zonal structure. Practically monodisperse Mn oxide sols can be prepared by inoculation with a nuclear Au sol.

E. S. H.

**Colloidal potassium complexes.** R. KELLER (Kolloid-Z., 1936, 76, 334—337).—The physiological effects of  $\text{K}^+$  and combined K in a negatively-charged colloid are contrasted.

E. S. H.

**Molecular and colloid solubility of acid and salt dyes, especially benzopurpurin.** I. Dissolution of acid dyes in sodium hydroxide. W. O. OSTWALD and R. WALTER (Kolloid-Z., 1936, 76, 291—313).—Benzopurpurin acid is shown by X-ray analysis to be microcryst.; the crystallites are of about colloid dimensions. The solubility of the dye acid in aq.  $\text{NaOH}$  is in accordance with the solid-phase rule, reaching a max. for medium amounts of the dye. With increasing  $[\text{NaOH}]$  the max. is displaced in the direction of increased solubility and increased amount of solid phase. Dissolution by salt formation occurs only when excess of  $\text{NaOH}$  is present.

E. S. H.

**Swelling pressure and van der Waals force.** G. V. SCHULZ (Naturwiss., 1936, 24, 589; cf. A., 1932, 225, 570).—The dependence of the consts.  $k$  and  $v$  in  $p = ks^v$  ( $p$  is swelling pressure, and  $s$  is swelling vol.) on the dispersion medium, and their independence of the mol. wt. of the solute make it probable that

swelling and the co-vol. of substances in solution are related to the van der Waals forces between solvent and solute. Assuming this to be true, it is possible to calculate the val. of the force, and a quant. law of force is derived by employing solvation potentials.

A. J. M.

**Syneresis.** III. G. ROSSI and G. SCANDELLARI (Gazzetta, 1936, 66, 459—464; cf. this vol., 935).—The liquid resulting from the syneresis of agar-agar gels containing non-electrolytes is more conc. with respect to these substances than the original gel. The results are discussed.

O. J. W.

**Molecular state of proteins in mixtures and concentrated solutions.** K. O. PEDERSEN (Nature, 1936, 138, 363).—The addition of a protamine (clupein) to serum-albumin lowers the sedimentation const., probably owing to dissociation into mols. of one eighth the original size. Haemoglobin is also dissociated in presence of other proteins and clupein.

L. S. T.

**Denaturation and hydration of proteins.**—See this vol., 1404.

**Limiting high-temperature rotational partition function of non-rigid molecules.** VI. The methanol equilibrium. L. S. KASSEL (J. Chem. Physics, 1936, 4, 493—496).—The entropy of  $\text{MeOH}$  and the equilibrium const. for  $\text{MeOH}$  synthesis are calc. for two mol. models: (i) with free rotation around the  $\text{CO}$  linking and (ii) with a torsional oscillation of frequency  $700 \text{ cm}^{-1}$  about that linking. The evidence favours (ii) but does not exclude (i).

J. G. A. G.

**Thermal separation of gas mixtures and its significance in the measurement of chemical equilibria; measurement data for the systems  $\text{H}_2$ - $\text{H}_2\text{S}$  and  $\text{Ag}$ - $\text{S}$ - $\text{H}$ .** N. G. SCHMAHL and W. KNEPPER (Z. Elektrochem., 1936, 42, 681—686).—A thermal diffusion effect has been observed with  $\text{H}_2$ - $\text{H}_2\text{S}$  mixtures, the effect increasing with increasing temp. difference between different parts of the container and with increasing pressure. The effect at  $20^\circ$  and  $400^\circ$  is a max. with about 40%  $\text{H}_2\text{S}$  and amounts to about 6% difference in  $[\text{H}_2\text{S}]$  between the two regions. Errors which may be introduced in the measurement of thermal equilibria of gases and solids when portions of the vessels are at different temp. are emphasised. Measurements on the equilibrium  $2\text{Ag} + \text{H}_2\text{S} \rightleftharpoons \text{Ag}_2\text{S} + \text{H}_2$ , corr. for this effect, indicate that discrepancies previously encountered are associated with the use of  $\text{Ag}$  in thread and powder form, and that these differ in heat content by  $153.1 \text{ g.-cal. per atom}$ .

J. W. S.

**Theory of concentrated solutions.** XIII. Aqueous solutions of organic compounds. M. EWERT (Bull. Soc. chim. Belg., 1936, 45, 493—515).—Partial v.p.-composition data are recorded for mixtures of 16 org. liquids with  $\text{H}_2\text{O}$ , and are used in calculating activity coeffs. The data are discussed on the basis of thermodynamic theory.

H. J. E.

**Isotope exchange between water and some organic compounds.** M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 465—474).—From experiments with org. compounds it is con-

cluded that the isotopic replacement of D atoms occurs only when these are linked to O or N. No replacement was observed with  $\text{CHCl}_3$ ,  $\text{Et}_2\text{O}$ , and  $\text{PhCHO}$ . For the remaining compounds the distribution quotients, *i.e.*, the ratios between the at. concn. of D in the total exchangeable H in the compound, and the at. concn. of D in the total H in the  $\text{H}_2\text{O}$ , were  $\text{NH}_2\text{Ph}$ , 1.11;  $\text{PhOH}$ , 1.07; pyrrole, 0.88;  $\text{BzOH}$ , 1.0;  $\text{CH}_2\text{Ph}\cdot\text{OH}$ , 1.10. C. R. H.

Isotopic exchange between aniline hydrochloride and heavy water. M. HARADA and T. TITANI (Bull. Chem. Soc. Japan, 1936, 11, 554—556).—The equilibrium  $\text{NH}_2\text{PhCl} + 3\text{D}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{D}_3\cdot\text{ND}_3\text{Cl} + 3\text{H}_2\text{O}$  is established at  $60^\circ$  after 3 hr. Replacement of the H of  $\text{NH}_2\text{PhCl}$  occurs immediately, but when  $\text{ND}_3\text{PhCl}$  is heated alone to  $160^\circ$ , D wanders into the nucleus. R. S.

Properties of pentadeuterobenzoic acid,  $\text{C}_6\text{D}_5\cdot\text{CO}_2\text{H}$ . H. ERLIENMEYER and A. EPPRECHT (Nature, 1936, 138, 367).—Vals. recorded are  $K^{25}_{25}$   $6.6 \times 10^{-5}$ , mol. heat of combustion 761,380 g.-cal., and solubility 0.34 g. per 100 c.c. of  $\text{H}_2\text{O}$  at  $18^\circ$ . L. S. T.

Primary and secondary dissociation constants of malonic, succinic, and glutaric acids by potentiometric titration. W. L. GERMAN and A. I. VOGEL (J. Amer. Chem. Soc., 1936, 58, 1546—1549).—Data obtained at  $25^\circ$ , using the quinhydrone electrode, are recorded. The calc. primary dissociation consts. agree within 2—4% with those determined by conductivity. E. S. H.

Ionisation constant of hydrazinium hydroxide. G. C. WARE, J. B. SPULNIK, and E. C. GILBERT (J. Amer. Chem. Soc., 1936, 58, 1605—1606).—Ionisation consts. of  $\text{N}_2\text{H}_5^+$  as an acid and of  $\text{N}_2\text{H}_5\text{OH}$  as a base have been determined at  $15^\circ$ ,  $25^\circ$ , and  $35^\circ$  with the aid of the glass electrode. E. S. H.

Polyhalides. IV. Formation and dissociation of polyhalides of ammonium and substituted ammonium bases. S. K. RAY and R. R. BHATTACHARYA (J. Indian Chem. Soc., 1936, 13, 456—463; cf. A., 1934, 599).—The conditions of formation and dissociation of  $\text{NH}_4\text{ClBr}_2$ ,  $\text{NH}_4\text{ClI}_2$ ,  $\text{NH}_4\text{BrI}_2$ ,  $\text{NH}_4\text{Br}_3$ ,  $\text{NH}_4\text{I}_3$ ,  $\text{NMe}_4\text{I}_3$ , and  $\text{C}_5\text{H}_5\text{NEtBrI}_2$  in aq. media and the solubility of I in  $\text{NEt}_4\text{I}$ ,  $\text{NEt}_4\text{Br}$ , and  $\text{C}_5\text{H}_5\text{NEtI}$  and of Br in  $\text{NEt}_4\text{Br}$  and  $\text{C}_5\text{H}_5\text{NEtBr}$  at  $25^\circ$  or  $30^\circ$  have been determined. The degree of dissociation of  $\text{NEt}_4\text{Br}$  at  $25^\circ$  and of  $\text{C}_5\text{H}_5\text{NEtBr}$  at  $30^\circ$  has been calc. from conductivity measurements. E. S. H.

Equilibrium between isopropyl alcohol and acetone in presence of alcohol-dehydrogenase. Oxido-reduction potential of the system  $\cdot\text{CH}(\text{OH})\cdot \rightleftharpoons \cdot\text{CO}\cdot$ . R. WURMSER and S. FILITTI-WURMSER (J. Chim. phys., 1936, 33, 577—586; cf. this vol., 936).—The attainment of equilibrium has been followed potentiometrically from both sides. It is shown, by comparison of the normal potential  $E_0$  with that of other  $\cdot\text{CH}(\text{OH})\cdot$   $\cdot\text{CO}\cdot$  systems, that introduction of  $\cdot\text{CO}$  into  $\text{Pr}^\beta\text{OH}$  increases  $E_0$  by +0.078 volt, whereas  $E_0$  decreases as the ratio  $\text{NH}_2/\text{CO}$  increases. R. S.

Equilibrium constants in terms of activities (cryoscopic). V. *p*-Toluidine *o*-chlorophenoxide and *p*-chlorophenoxide in benzene and in *p*-dichlorobenzene. W. R. BURNHAM and W. M. MADGIN (J.C.S., 1936, 1303—1306).—The activity coeffs. for  $\text{C}_6\text{H}_6$  and  $\text{p-C}_6\text{H}_4\text{Cl}_2$  solutions of the undissociated complexes *p*-toluidine *o*- (I) and *p*-chlorophenoxide (II) at concns. up to 0.05 mol. have been determined cryoscopically. The average vals. for the dissociation consts. are 20.95 and 8.66 for (I) and 48.39 and 16.54 for (II) in  $\text{C}_6\text{H}_6$  and  $\text{p-C}_6\text{H}_4\text{Cl}_2$ , respectively. Each complex is formed exothermally, the heats of formation being —4200 g.-cal. for (I) and —3500 g.-cal. for (II). In discussing dipolar influences and chelation the vals. have been compared with those previously obtained for similar phenol-base complexes. C. R. H.

Alkali-hydrolysis and dissociation constants of diketopiperazines and aniline peptides. M. ODA (J. Biochem. Japan, 1936, 23, 241—266).—The rates of hydrolysis of diketopiperazines (I) or  $\text{NH}_2\text{Ph}$  peptides by 0.5*N*-NaOH are not related to the corresponding rates of enzymic hydrolysis. Electrometric titration indicates that (I) which are hydrolysed by carboxypolypeptidase exist at  $p_H$  8 as negatively-charged anions; this probably facilitates formation of enzyme-substrate complexes. Basic and, for the last three, acidic dissociation consts. are given for glycol derivatives of  $\text{NH}_2\text{Ph}$ , *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ , *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ , and *o*-, *m*-, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . F. O. H.

Dissociation pressure of magnesium chloride hexahydrate. K. SANO (Sci. Rep. Tôhoku, 1936, 25, 184—186).—Dissociation pressures of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  between  $50^\circ$  and  $110^\circ$  are given by  $\log P_{\text{H}_2\text{O}} = 3473.25/T + 11.2195$ . For  $\text{MgCl}_2\cdot 6\text{H}_2\text{O} = \text{MgCl}_2\cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ .  $\Delta H_{298} = 32146$  g.-cal.,  $\Delta F_{298} = 9070$  g.-cal., and  $\Delta S_{298} = 77.44$  e.u. O. D. S.

Dissociation pressure of copper sulphate pentahydrate. F. SCHACHERL and O. BĚHOŮNEK (Nature, 1936, 138, 406; this vol., 1070).—Dissociation pressures of  $\text{CuSO}_4\cdot 5\text{D}_2\text{O}$  at  $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ ,  $50^\circ$ , and  $60^\circ$  are 4.4, 9.9, 21.0, 42.1, and 80.9 mm., respectively. L. S. T.

Thermal transitions of copper sulphate pentahydrate: molecular rotation and the dehydration of hydrates. T. I. TAYLOR and H. P. KLUG (J. Chem. Physics, 1936, 4, 601—607).—The heating curve of  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  (I) from  $-75^\circ$  to  $160^\circ$  has been determined by a differential thermocouple method at 690 mm. Small abrupt changes in heat capacity shown at  $29^\circ$ ,  $35^\circ$ , and  $53.7^\circ$  are attributed to a change from oscillatory to rotational movement of the  $\text{H}_2\text{O}$  mols. in the crystal. Dehydrations at  $96.5^\circ$ ,  $102^\circ$ , and  $113^\circ$  correspond with the formation of the tetra-, tri-, and mono-hydrates, respectively. A view of the mechanism of dehydration of (I) by heat, based on mols. acquiring sufficient vibrational-rotational energy to break from the crystal lattice, is shown to accord with the cryst. structure (cf. A., 1934, 1296). J. G. A. G.

System calcium oxide-ferric oxide. B. TAVASCI (Annali Chim. Appl., 1936, 26, 291—300).—The system has been studied micrographically and the



results compared with those of Sosman and Merwin (A., 1916, ii, 618). The existence of  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ , and the decomp. of the latter at  $1216^\circ$  are confirmed, but  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3$ , decomp. at  $1227^\circ$  into  $\text{Fe}_2\text{O}_3$  + liquid, is also found. The eutectic, m.p.  $1203^\circ$ , has the approx. composition  $3\text{CaO} \cdot 4\text{Fe}_2\text{O}_3$  and consists of a mixture of  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and  $\text{CaO} \cdot 2\text{Fe}_2\text{O}_3$ .  
L. A. O'N.

**System potassium dichromate-sodium dichromate.** A. LEHRMAN, H. SELDITCH, and P. SKELL (J. Amer. Chem. Soc., 1936, 58, 1612—1615).—The liquidus curve is of the simple eutectic type.  $\text{Na}_2\text{Cr}_2\text{O}_7$  has m.p.  $356.7 \pm 1.0^\circ$ . The transition point of  $\text{K}_2\text{Cr}_2\text{O}_7$  has been redetermined as  $241.6 \pm 1.0^\circ$ .  
E. S. H.

**System  $\text{Zn}[\text{Hg}(\text{CNS})_4]$ - $\text{Cu}[\text{Hg}(\text{CNS})_4]$ .** M. STRAUMANIS and E. ENCE (Z. anorg. Chem., 1936, 228, 334—340).— $\text{Zn}[\text{Hg}(\text{CNS})_4]$  forms a continuous series of mixed crystals with  $\text{Cu}[\text{Hg}(\text{CNS})_4]$  from solutions with a  $\text{Cu}:\text{Cu}+\text{Zn}$  ratio  $> 38.5\%$ . The  $\text{Zn}[\text{Hg}(\text{CNS})_4]$  crystal lattice is expanded proportionately to the  $[\text{Cu}]$ . On crystallising mixtures with  $\text{Cu}:\text{Cu}+\text{Zn}$  ratios  $> 40\%$ , green crystals of  $\text{Cu}[\text{Hg}(\text{CNS})_4]$ , free from Zn, are also obtained.  
J. W. S.

**Solid-liquid equilibria in systems of organic components. V. Systems consisting of *o*-, *m*-, and *p*-aminophenol.** K. HRYNAKOWSKI and M. SZMYT (Z. physikal. Chem., 1936, 177, 306—316).—The f.-p. diagrams of the ternary and three binary systems have been obtained. *p*- and *m*-Aminophenol combine in equimol. proportions to form an incongruently melting compound. Activity coeffs. in the melts have been calc. The mol. attractive forces increase in the order *o*- < *m*-aminophenol.  
R. C.

**Ternary systems. XXI. Lead nitrate, ammonium nitrate, and water at  $25^\circ$ .** A. E. HILL and N. KAPLAN (J. Amer. Chem. Soc., 1936, 58, 1644—1645).—The solubility of  $\text{Pb}(\text{NO}_3)_2$  is increased by  $\text{NH}_4\text{NO}_3$ , but < by  $\text{KNO}_3$ . No double salts have been found as solid phases.  
E. S. H.

**Systems  $\text{MCl}_2$ - $\text{HCl}$ - $\text{H}_2\text{O}$ . II. System  $\text{CdCl}_2$ - $\text{HCl}$ - $\text{H}_2\text{O}$ .** D. I. KUZNETZOV and A. A. KOSHUCHOVSKI (J. Appl. Chem. Russ., 1936, 9, 1178—1182).—Solubility data are recorded for  $25^\circ$ . The solid phases are  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $2.5\text{H}_2\text{O}$ ,  $2\text{CdCl}_2 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ , and  $\text{CdCl}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ .  
R. T.

**Systems lithium chloride-water-ethyl alcohol and lithium bromide-water-ethyl alcohol.** J. P. SIMMONS, H. FREIMUTH, and H. RUSSELL (J. Amer. Chem. Soc., 1936, 58, 1692—1695).—Equilibrium data at  $25^\circ$  are recorded. The solid phases recognised are  $\text{LiCl}$ ,  $\text{LiCl} \cdot \text{H}_2\text{O}$ ,  $\text{LiBr}$ ,  $\text{LiBr} \cdot \text{H}_2\text{O}$ , and  $\text{LiBr} \cdot 2\text{H}_2\text{O}$ . No alcoholates were detected.  
E. S. H.

**Reduction equilibrium of silver sulphide by hydrogen.** K. SANO (Sci. Rep. Tohoku, 1936, 25, 186—196).—The equilibrium const. for  $\text{Ag}_2\text{S} + \text{H}_2 = 2\text{Ag} + \text{H}_2\text{S}$  between  $490^\circ$  and  $660^\circ$  is expressed by  $\log K_p = 11.7/T - 0.741$ . The heat of reaction, change in free energy, and entropy change are  $\Delta H_{298} 2726$  g.-cal.,  $\Delta F_{298} 1896$  g.-cal.,  $\Delta S_{298} = 2.79$  e.u., respectively. For  $2\text{Ag} + \text{S}(\text{rhombic}) = \text{Ag}_2\text{S}(\text{rhombic})$ ,  $\Delta H_{298}$

$= -7486$  g.-cal.,  $\Delta F_{298} = -9736$  g.-cal., and  $\Delta S_{298} = 7.55$  e.u.  
O. D. S.

**Effect of structure on reactions of organic compounds. Temperature and solvent influences.** L. P. HAMMETT (J. Chem. Physics, 1936, 4, 613—617).—The heat and free energy of ionisation of an org. acid are not equally affected by a substituent. The entropy of ionisation of derivatives of  $\text{BzOH}$  varies in a manner which is predictable from the dielectric const.,  $\epsilon$ , of the solvent and is closely correlated with the effect of a change of  $\epsilon$  on the relative strengths of the substituted and unsubstituted acids. Aliphatic acids do not show similar relations and this is probably connected with their less rigid structure. Other equilibria and reaction rates are similarly considered.  
J. G. A. G.

**Thermodynamic properties of phosphorus compounds.** T. F. ANDERSON and D. M. YOST (J. Chem. Physics, 1936, 4, 529—530).—Raman spectrum, electron diffraction, and equilibrium data lead to the following standard virtual entropies (g.-cal. per  $1^\circ$ ):  $\text{P}$  (solid, white)  $10.55$ ,  $\text{P}_4$  (gas)  $66.88$ ,  $\text{PCl}_3$  (gas)  $74.7$ ,  $\text{PCl}_3$  (liquid)  $52.8$ ,  $\text{PCl}_5$  (gas)  $87.7$ , and  $\text{PCl}_5$  (solid)  $40.8$ ; the corresponding standard free energies of formation are  $0$ ,  $585$ ,  $-63,570$ ,  $-64,650$ ,  $-72,540$ , and  $-77,950$  g.-cal., respectively.  
J. G. A. G.

**Atomic heats of formation and bond energies.** F. G. SOPER (J.C.S., 1936, 1126—1130).—Linking energies calc. from the at. heats of formation of org. compounds are only approx. const., the increment in heat of formation between successive members of a homologous series (due to formation of one C-C and two C-H linkings) varying with the nature of the series. However, if the at. heats of formation are corr. for the intramol. potential energy arising from coulombic attractions and repulsions between the constituent atoms (calc. from the dipole moments of the linkings) the linking energies are more nearly const. for the paraffin, alcohol, and alkyl halide series.  
J. W. S.

**Heat capacity of aqueous solutions of barium chloride.** C. M. WHITE (J. Amer. Chem. Soc., 1936, 58, 1615—1620).—Modified apparatus and technique, increasing the precision to  $\pm 0.01\%$ , are described. Data are recorded for  $0.003$ — $0.3M$ - $\text{BaCl}_2$  at  $25^\circ$ . The apparent mol. heat capacity is related linearly to  $[\text{BaCl}_2]^{\frac{1}{2}}$ .  
E. S. H.

**Heat capacity and entropy of barium chloride dihydrate from  $15^\circ$  to  $300$  abs. Heat of dissolution of barium chloride dihydrate. Entropy of barium ion.** O. L. I. BROWN, W. V. SMITH, and W. M. LATIMER (J. Amer. Chem. Soc., 1936, 58, 1758—1759).—The entropy of  $\text{Ba}^{++}$ , calc. from the above determinations, is  $2.2$  e.u.  
E. S. H.

**Heat capacity of aqueous solutions of carbamide and mannitol.** C. M. WHITE (J. Amer. Chem. Soc., 1936, 58, 1620—1623).—Data for  $0.01$ — $1.0M$  solutions with a precision of  $\pm 0.01\%$  are recorded. The apparent mol. heat capacities are related linearly to  $\sqrt{M}$ .  
E. S. H.

**Heats of dissolution of salts in heavy water.** E. LANGE and W. MARTIN (Z. Elektrochem., 1936,

42, 662—668).—The heats of dissolution ( $L$ ) of alkali halides in  $D_2O$  and  $H_2O$  have been measured. The difference in  $L$  for the same salt in  $D_2O$  and  $H_2O$  ( $\Delta L$ ) varies with both anion and cation. The results are explained by assuming that  $L$  is not only produced by the electrostatic effects but is also modified by van der Waals forces and by an absorption of energy in creating space in the solvent for the solute mols.

J. W. S.

**Thermochemistry of titanium oxides. II. Thermochemical calculations.** N. NASU (J. Chem. Soc. Japan, 1935, 56, 659—666; cf. this vol., 682).—The following data are deduced:  $2TiO_2 + H_2 = Ti_2O_3 + H_2O$ ,  $\Delta H_{298} = 4700$  g.-cal.,  $\Delta F_{298} = 5280$  g.-cal.,  $\Delta S_{298} = 1.95$  g.-cal. per  $1^\circ$ ;  $Ti_2O_3 + \frac{1}{2}O_2 = 2TiO_2$ ,  $\Delta H_{298} = -62,530$  g.-cal.,  $\Delta F_{298} = -59,770$  g.-cal.,  $\Delta S_{298} = -9.26$  g.-cal. per  $1^\circ$ ;  $2Ti + 1.5O_2 = Ti_2O_3$ ,  $\Delta H_{298} = -388,070$  g.-cal.;  $2TiO_2 + CO = Ti_2O_3 + CO_2$ ,  $\Delta F_{298} = -6220$  g.-cal. The lattice energy of  $Ti_2O_3$  is 3569 kg.-cal.

CH. ABS. (e)

**Thermal data. VI. Heats of combustion and free energies of seven organic compounds containing nitrogen.** H. M. HUFFMAN, E. L. ELLIS, and S. W. FOX (J. Amer. Chem. Soc., 1936, 58, 1728—1733; cf. A., 1935, 304).—The heats of combustion at const. vol. of *d*-alanine, *l*-asparagine, *l*-asparagine monohydrate, *l*-aspartic acid, *d*-glutamic acid, creatinine, and creatine have been determined at  $25^\circ$ . The heats of formation and free energies are calc.

E. S. H.

**Heats of combustion and formation of dibutyl and diamyl phthalates.** H. R. AMBLER (J.S.C.I., 1936, 55, 291—292T).—The vals. recorded are, respectively,  $7396 \pm 10$  and  $7713 \pm 10$  g.-cal. per g. at const. pressure. These vals. agree with those derived from the structure of the compounds, but not with vals. in the literature (cf. Schmidt, B., 1934, 1085).

**Single linking energies. III. C-C linking in diphenyldidiphenylene-ethane.** H. E. BENT and J. E. CLINE (J. Amer. Chem. Soc., 1936, 59, 1624—1627; cf. this vol., 291).—The heat of oxidation of diphenyldidiphenylene-ethane is about 20 kg.-cal. < that of  $C_6Ph_6$ . Steric hindrance is < with  $C_6Ph_6$ , and the free radical formed by dissociation, phenylfluoryl, has more resonance energy than  $CPh_3$ .

E. S. H.

**Thermodynamic extension of the diffusion equation.** U. DEHLINGER (Z. Physik, 1936, 102, 633—640).—The Fick diffusion equation is shown to be the special case for ideal mixtures of the author's general diffusion equation (cf. A., 1933, 896). By means of the general equation the probability of change of position is calc. for Au-Ni mixtures from the results of Jédule (*ibid.*, 1006). The probability is greater in the mixed crystals than in either pure phase.

O. D. S.

**Conductance of salts (potassium acetate) and the dissociation constant of acetic acid in deuterium oxide.** V. K. LA MER and J. P. CHITTUM (J. Amer. Chem. Soc., 1936, 58, 1642—1644).—The Walden const. increases linearly by 1.93% in passing from  $H_2O$  to  $D_2O$  for KOAc and KCl. From the data

4 s

the dissociation consts. of weak acids in  $D_2O$  can be calc. with the aid of conductivity data. The dissociation const. of AcOH ( $0.55 \times 10^{-5}$  in pure  $D_2O$ ) shows a marked negative deviation from linearity on passing from  $H_2O$  to  $D_2O$ .

E. S. H.

**Hydrogen cyanide. VIII. Conductivity of electrolytes in anhydrous hydrogen cyanide. Some univalent salts at  $18^\circ$ .** J. E. COATES and E. G. TAYLOR (J.C.S., 1936, 1245—1256).—The  $\Lambda$  of 21 salts has been measured from 0.0001N to 0.002N, and the ionic mobilities have been calc. on the basis of Walden's rule. In most cases  $\Lambda_c - \Lambda_o - x\sqrt{C}$ , although for LiCl, LiNO<sub>3</sub>, and LiCNS the val. of  $x$  is > that calc. from the Debye-Hückel-Onsager equation on account of incomplete dissociation. The calc. dissociation consts. for these salts are respectively 0.11, 0.07, and 0.043.

C. R. H.

**Electrochemical investigation of the ternary system: aluminium bromide-silver and copper halides in ethyl bromide, ethylene dibromide, and benzene.** V. A. PLOTNIKOV and E. J. GORENBEIN (Acta Physicochim. U.R.S.S., 1936, 4, 775—790).—The electrical conductivity of the systems AgX-AlBr<sub>3</sub> and CuX-AlBr<sub>3</sub> (X=Cl, Br, I) in EtBr, C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub> has been determined. The sp. conductivity increases with the concn. of halide at first rapidly, and then more slowly, attaining vals. of  $10^2$  in conc. solutions. The conductivity in C<sub>6</sub>H<sub>6</sub> is > that in C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub> for solutions of the same mol. concn., although the dielectric const. ( $\epsilon$ ) of C<sub>6</sub>H<sub>6</sub> is < that of C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>. Similarly the conductivity in EtBr is only twice as great as that in C<sub>6</sub>H<sub>6</sub> although  $\epsilon$  of EtBr is four times that of C<sub>6</sub>H<sub>6</sub>, and the dipole moment ( $\mu$ ) of EtBr is considerable. It is concluded that the chemical and electrochemical activity of a solvent is not completely characterised by  $\mu$ , and that  $\epsilon$  is not the principal const. on which the electrical conductivity of a solution depends. Electrolysis of the above solutions gave Ag and Cu<sup>+</sup> at the cathode, and Br at the anode, the best deposit being obtained when X=Cl. The decomp. potentials of the Cu<sup>+</sup> and Ag halides in the above solutions were determined.

A. J. M.

**Streamline scattering in electrolytes.** W. KANGRO and K. M. WAGNER (Z. Elektrochem., 1936, 42, 669).—The current distribution within and outside the space between the electrodes has been determined. Within the electrode zone the relations are complicated, but for the region outside this zone a streamline scattering const. can be calc. which varies little with the ionic strength or chemical nature of the ions, but is dependent on the conductivity and total c.d. With an angular cathode the distribution within the electrode zone deviates from ideal distribution in a manner analogous to that in the outer region.

J. W. S.

**Normal potential of the silver-silver bromide electrode from  $5^\circ$  to  $40^\circ$ .** B. B. OWEN and L. FOERING (J. Amer. Chem. Soc., 1936, 58, 1575—1577).—Data have been obtained by comparison with the Ag-AgCl electrode in Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solutions. The Ag-AgBr (fused) electrode is highly reproducible.

E. S. H.



**Potential of mercury electrodes in solutions of salts of other metals.** T. ERDEY-GRÚZ and P. SZARVAS (Z. physikal. Chem., 1936, 177, 277—291; cf. A., 1935, 706).—The potential,  $E$ , of stationary and dropping Hg electrodes in  $O_2$ -free solutions containing salts of other metals and no Hg ions has been measured. For the stationary electrode  $E$  is determined by the concn. of the anions present, and is given approx. by  $E = E_0 + k \log a_{\pm}$ , where  $a_{\pm}$  is the mean ionic activity of the solution. With increase in the capillary activity of the anion  $E$  becomes more negative and more definite. It must therefore be supposed that  $E$  is due to the adsorption of the anion on the Hg; the above relation indicates that Freundlich's isotherm is valid for the adsorption. The adsorbed anion induces a positive charge on the Hg surface, which is therefore left negatively charged by detachment of drops. This negative charge lessens the adsorption of anions until ultimately at a quite small rate of dropping the surface charge,  $Q$ , becomes zero, and  $E$  assumes a const. val. which does not change with further increase in the rate of dropping. In the ordinary Paschen dropping electrode the  $E$  corresponding with zero  $Q$  is reached in the same way, and Hg ions play no part in establishing this val. of  $E$  (cf. A., 1933, 128). R. C.

**Electrode potentials of dilute amalgams.** T. ERDEY-GRÚZ and A. VAZSONYI-ZILAHY (Z. physikal. Chem., 1936, 177, 292—305).—The potentials,  $E$ , of stationary and dropping amalgam electrodes of concn.  $c$  in solutions free from Hg ions and  $O_2$  but containing ions of the metal in the amalgam,  $M$ , have been measured. At concn. up to a certain crit. concn.  $c_1$  ( $\sim 10^{-6}$  g.-ion per litre)  $E$  at a stationary electrode is independent of  $c$  and approx. the same as  $E$  for a pure Hg electrode in that particular electrolyte. As  $c$  rises above  $E$  begins to be influenced by the  $M$  ions, but varies with  $c$  much more rapidly than corresponds with Nernst's electrode potential formula. From a concn.  $c_2$  ( $10^{-6}$ — $10^{-4}$  g.-ions per litre) onwards the relation between  $E$  and  $c$  follows this formula. A dropping electrode behaves similarly to a stationary electrode, except that  $c_2$  is usually higher. It may be supposed that at concns. up to  $c_1$ ,  $E$  is determined solely by the adsorption of the foreign ions present in solution (cf. preceding abstract). Between  $c_1$  and  $c_2$   $E$  is determined by the distribution of  $M$  ions between the solution and the electrode and also by all the other ions present. R. C.

**Potential differences at metal-vapour, vapour-liquid, and liquid-metal interfaces of partially immersed electrodes.** C. G. FINK and R. C. DEHMEL (Trans. Electrochem. Soc., 1936, 70, Preprint 23, 245—284).—Apparatus is described for determining the p.d. across the vapour between the exposed portion of a partly immersed electrode and the surface of the solution into which it dips. Experiments with Cu, Au, and Pt electrodes in  $M$  solutions of their salts gave the following vals. for the p.d.: in presence of  $O_2$  at 1 atm. pressure, Cu +0.175 (temp. 22°), Au -0.33 (26.9°), Pt -0.19 volt (21.1°); in the absence of  $O_2$  the vals. at the same temp. are: Cu -0.151, Au -0.839, Pt -0.76 volt. When  $O_2$  is introduced the ratio of change in

solution potential to change in p.d. existing across the vapour phase in the case of Cu and Au is approx. 1:100, but is nearer unity for Pt.  $O_2$  causes the solution potential of each metal to become less anodic. In cells having Cu or Au electrodes equilibrium potential is rapidly established, but much less quickly in the case of bright Pt electrodes. Natural atm. ionisation is insufficient to render the p.d. across the vapour phase important as a factor in electrode corrosion. J. W. C.

**Polarographic studies with the dropping mercury cathode. LX. Influence of buffers and cations on the electro-reduction of fumaric and maleic acids.** E. VOPIČKA (Coll. Czech. Chem. Comm., 1936, 8, 349—365).—In HCl and in AcOH-NaOAc buffers the "half-wave potential" depends on the  $p_H$ , and remains const. over a wide range of concn. of maleic and fumaric acids. The former is reduced at more positive potentials than is the latter. In LiOH the "half-wave potential" becomes more positive with increase of  $p_H$  and in presence of  $Ca^{++}$  the fumarate ion is reduced at more positive potentials than is the maleate ion. C. R. H.

**$p_H$  values of some alkaline products.** A. T. WILLIAMSON and W. G. OAKES (J. Text. Inst., 1936, 27, T197—198).—The following  $p_H$  vals. are recorded for 0.2% solutions with H and Sb electrodes: NaOH, 12.69;  $Na_2SiO_3 \cdot 5H_2O$ , 11.94;  $Na_3PO_4 \cdot 12H_2O$ , 11.67;  $Na_2CO_3$ , 11.17;  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ , 10.11;  $Na_2B_4O_7 \cdot 10H_2O$ , 9.15;  $NaHCO_3$ , 8.43. A. G.

**Electrochemical reduction potential of pyrrole-aldehyde.** G. B. BONINO and G. SCARAMIELLI (Ric. sci. Prog. tecn., 1935, 6, II, 111—112; Chem. Zentr., 1935, ii, 3897).—The reduction potential of pyrrole-aldehyde (I) is 1.254 volts and that of PhCHO 1.054 volts; in accordance with conclusions from Raman spectra, the results suggest that (I) is not enolic in structure. H. N. R.

**Influence of pressure on the electrode potential in the electrolysis of water. IV.** V. SCHUSCHKIN and E. KARNAUCH (Z. Elektrochem., 1936, 42, 693—695; cf. A., 1934, 1178).—Sudden increase of pressure from 1 to 100 kg. per sq. cm. slightly diminishes the cathode potential at a Ni electrode in 5N-NaOH, whilst release of the pressure increases it again, especially at low c.d. The effect is  $> 0.008$  volt. A similar but smaller effect is observed for the anode potential at Ni and for the cathode potential at Fe electrodes. It is inferred that the decrease in overpotential forms only a small part in the change of p.d. observed in the electrolysis of  $H_2O$  under pressure. J. W. S.

**Chemical polarisation of the hydrogen electrode by oxygen and the problem of electrolytic corrosion protection.** A. E. LORCH (Trans. Electrochem. Soc., 1936, 70, Preprint 15, 173—178).—The H electrode has been polarised by introducing  $O_2$  into the stream of  $H_2$ ; if  $i$  is the current required to polarise the electrode to the same extent as the  $O_2$  it is found that  $i = k[O_2]$ , when  $k$  is an approx. const. The current equiv. of the  $[O_2]$  is const. over a wide range of p.d. The bearing on protection from electrolytic corrosion is discussed. R. S. B.

**Overvoltage ; effect of fusion of the cathode and the effect of temperature on gas polarisation.** A. BUTTS and W. A. JOHNSON (Trans. Electrochem. Soc., 1936, 70, Preprint 19, 205—220).—From the variation of voltage with time and temp. at const. c.d. for cells containing Pt anodes and Wood's metal or Ga cathodes in 25%  $\text{H}_2\text{SO}_4$  it has been shown that no change in polarisation occurs on melting or freezing the cathode, so that H overvoltage is independent of internal physical structure or total energy content of the cathode. Changes in voltage occur with Wood's alloy which has not reached equilibrium, and sharp changes occur with liquid Ga. The H overvoltage is  $0.63 \pm 0.05$  volt at  $70\text{--}85^\circ$  on Wood's metal and  $0.60 \pm 0.05$  volt at  $25\text{--}30^\circ$  on Ga.

R. S. B.

**Mechanism of the electrolytic liberation of hydrogen at palladium and platinum.** L. KANDLER and C. A. KNORR (Z. Elektrochem., 1936, 42, 669).—The difference in form of the c.d.-cathode potential curve in the electrolysis of 2N- $\text{H}_2\text{SO}_4$  with Pt or Pd electrodes when (a) no gas, (b)  $\text{N}_2$ , and (c)  $\text{H}_2$  is passed through the cathode vessel during the measurement is attributed to the back reaction  $\text{H}_2 \rightarrow 2\text{H}$ , which occurs to a considerable extent in presence of excess of  $\text{H}_2$ , but is inappreciable when the  $\text{H}_2$  is swept away with  $\text{N}_2$ .

J. W. S.

**Difficulties encountered in the determination of the decomposition potential of molten salts.** P. DROSSBACH (Trans. Electrochem. Soc., 1936, 70, Preprint 18, 201—204).—The neglect of the influence of dispersed metal by many previous investigators leads to errors, owing to the development of a polarisation p.d. If anodic and cathodic regions are not separated current efficiency decreases rapidly with rise in temp. and thermodynamic formulæ cannot be applied to determine the heat of reaction. Polarisation processes are discussed.

R. S. B.

**Drop of potential in the metallic electrodes of certain electrolytic cells.** C. SNOW (J. Res. Nat. Bur. Stand., 1936, 17, 101—124).—Theoretical. Formulæ are derived for the drop of potential in thin metallic electrodes used for the measurement of the electrolytic resistance of solutions.

O. J. W.

**Simultaneous discharge of copper and hydrogen in solutions of complex cyanic salts.** O. ESSIN and A. MATANZEV (J. Chim. phys., 1936, 33, 631—639; cf. this vol., 32).—The discharge of Cu in solutions containing  $\text{CuCN} \cdot 1.5\text{KCN}$  is accompanied only by a concn. polarisation due to diminution in  $[\text{Cu}(\text{CN})_2^-]$  and accumulation of  $\text{CN}^-$  near the cathode. The current distribution between Cu and  $\text{H}^+$  discharged simultaneously is in agreement with a theoretical equation.

R. S.

**Co-deposition of metals of the same valency in acid solutions.** W. G. PARKS and I. M. LE BARON (Trans. Electrochem. Soc., 1936, 70, Preprint 21, 235—239).—For the metal pairs Zn—Cd, Cu—Cd, Ni—Cu, Zn—Cu, and Ag—Tl in solutions of  $p_{\text{H}}$  5, the limiting % concn. in solution at which the added metal is alone deposited varies linearly with log c.d. The respective effects of difference in electrode potential

and in equiv. wt. of the two metals on the limits of co-deposition are discussed.

J. W. C.

**Passivity of iron and steel in nitric acid solutions.** K. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 981—1054).—Potentiometric data at  $70^\circ$  indicate that activation of Fe occurs by reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$ . Passivation is hindered by  $\text{CO}(\text{NH}_2)_2$ , due to removal of  $\text{HNO}_2$ , and facilitated by  $\text{AgNO}_3$ , which forms  $\text{HNO}_2$  in presence of Fe.  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  hinder passivation.

J. S. A.

**Energy of activation.** C. H. MACGILLAVRY (Chem. Weekblad, 1936, 33, 582—593).—A review.

S. C.

**Reaction rates of non-isothermal processes.** J. SHERMAN (Ind. Eng. Chem., 1936, 28, 1026—1031).—Mathematical. Reaction rates are derived for various time-temp. relations.

C. R. H.

**Explosion diagram.** E. M. BRUINS (Chem. Weekblad, 1936, 33, 566—570).—A mathematical analysis of various types.

S. C.

**Detonation of gaseous mixtures.** J. BRETON (Ann. Off. nat. Combust. liq., 1936, 11, 487—546).—Mixtures of known composition of  $\text{O}_2$  or air with  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{C}_3\text{H}_8$ , isobutane,  $\text{C}_2\text{H}_2$ , or  $\text{Et}_2\text{O}$  were passed through a glass tube and detonated with Hg fulminate, photographs of the passage of the wave front being taken on a revolving cylinder. The detonation range in relation to the % of combustible gas in the mixture, and the max. rate of propagation, in m. per sec., with the corresponding mixture composition, are given for each of the above mixtures. The lower limit of detonation of  $\text{CO-O}_2$  mixtures was considerably lower when a small amount of  $\text{H}_2$  was added. An increase of the initial pressure extended the detonation range of  $\text{H}_2\text{-O}_2$  or  $\text{H}_2\text{-air}$  mixtures. Mixtures in the vicinity of the upper or lower limit produced helicoidal explosive waves. The photographic method enabled a study to be made of the non-luminous phenomena and of the mechanism of rupture of the glass tube as the explosive wave passed.

R. B. C.

**Propagation of explosion condensation through air.** L. THOMPSON (Physical Rev., 1935, [ii], 47, 811).—The velocity and intensity functions as affected by the quantity of explosive detonated and by the distance from the centre of the pulse at the instant of disintegration have been investigated.

L. S. T.

**Latent energy in explosions.** W. T. DAVID and A. S. LEAH (Phil. Mag., 1936, [vii], 22, 513—523).—The heat loss and pressure reached in explosions of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{C}_5\text{H}_{12}$  (vapour),  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$  with  $\text{O}_2$  or air, in different proportions, and at initial pressures of 0.25, 0.5, and 1 atm. have been determined. The amount of incomplete combustion increases as the initial pressure of the inflammable mixture decreases and is considerable at pressures  $< 1$  atm. This incomplete combustion is due to long-lived latent energy left in the exploded gases, which varies with the nature of the combustible gas, the nature of the diluent gas, and the pressure of the mixture before explosion.

A. J. M.



**Measurements of flame velocity by a modified burner method.** F. A. SMITH and S. F. PICKERING (J. Res. Nat. Bur. Stand., 1936, 17, 7—43).—The velocity of propagation of flame in mixtures of air with various combustible gases has been studied by means of the Bunsen-burner method. Data are given on the effect of varying the size of the air-inlet, of changing the velocity of flow of the mixture from the burner, of changing the composition of the mixture, and of different methods of measuring the flame and of calculating the results. Apparatus is described and the limitations of the method are discussed. O. J. W.

**Period of induction of cold flames in pentane-oxygen mixtures.** B. AIVAZOV and M. NEUMANN (Z. physikal. Chem., 1936, B, 33, 349—367).—The equation  $\tau = Ae^{v/T} [(a+b/d^2)/(1+[N_2]/p)]^2 (p-p_0)^2$  has been obtained empirically for the relation between the period of induction of the cold flame,  $\tau$ , temp.,  $T$ , vessel diameter,  $d$ , pressure,  $p$ , min. pressure at which a cold flame is formed,  $p_0$  ( $A$ ,  $\gamma$ ,  $a$ ,  $b$ —const.). MeCHO and NO<sub>2</sub> reduce both  $\tau$  and  $p_0$ . To explain the formation of cold flames it is suggested that the oxidation of hydrocarbons is a slowly developing chain reaction in which there is intercation of the chains, and that the reaction follows the equation  $dn/dt = -gn + fn$ , where  $n_0$  is the no. of active centres formed in 1 sec.,  $v$  the length of the primary chain,  $g$  the chain-breaking factor, and  $f$  the chain-branching factor, and  $f'n^2$  takes account of the chain interaction;  $f'$  is very small. At low pressures  $g > f$  and the reaction is stationary, whilst at higher pressures  $f > g$  and the reaction is autoaccelerated. This theory accounts for the above experimental relation. R. C.

**Reaction between ammonia and carbon dioxide.** T. YOSHIDA (Proc. Imp. Acad. Tokyo, 1936, 12, 191—194).—H<sub>2</sub>O vapour is necessary for the interaction of NH<sub>3</sub> and CO<sub>2</sub>. The data indicate that the reaction is of the second order and has a negative temp. coeff. C. R. H.

**Relative rates of combination of hydrogen and deuterium with ethylene.** A. WHEELER and R. N. PEASE (J. Amer. Chem. Soc., 1936, 58, 1665—1668).—In the homogeneous reaction near 500° the rate of reaction for H<sub>2</sub> is 2.5 times that for D<sub>2</sub>; in the catalytic reaction over Cu at 0° the rate for H<sub>2</sub> is twice that for D<sub>2</sub>. Exchange reactions are unimportant. E. S. H.

**Reactions of deuterium atoms with methane and ethane.** E. W. R. STEACIE and N. W. F. PHILLIPS (J. Chem. Physics, 1936, 4, 461—468).—The D atoms were produced by the discharge tube method and by photosensitisation with Hg. The activation energies of the reactions with CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are 11.7 and 6.3 kg.-cal., respectively (cf. A., 1935, 457). Experiments with CH<sub>3</sub>-C<sub>2</sub>H<sub>5</sub> mixtures show that the reaction C<sub>2</sub>H<sub>5</sub>+CH<sub>3</sub>=C<sub>2</sub>H<sub>4</sub>+CH<sub>4</sub> does not occur under the conditions. The mechanisms are discussed, and the measured activation energy, 6.3 kg.-cal., is that of the reaction D+C<sub>2</sub>H<sub>6</sub>=C<sub>2</sub>H<sub>5</sub>+HD; hence the process H+C<sub>2</sub>H<sub>6</sub>=Et+H<sub>2</sub> has approx. the same energy of activation. The bearing

of these results on the theory of free radical chains is discussed. J. G. A. G.

**Prototropy in relation to the exchange of hydrogen isotopes. I. Rates of isomerisation and of hydrogen isotope exchange in unsaturated nitriles.** C. K. INGOLD, E. DE SALAS, and C. L. WILSON (J.C.S., 1936, 1328—1334).—The rate of interconversion of  $\Delta^1$ -cyclohexenyl- (I) and cyclohexylidene- (II) -acetonitrile in 0.1N-NaOEt-EtOD has been compared with the rates of isotopic exchange between (I), (II), and the system (I) (II) and the medium at 25°. Rapid isotopic interchange (too great to be measured) of 2 H of (I) with D from the medium is followed by slow conversion of (I) into (II), which is in turn more rapid than H exchange between (II) and the medium, and is accompanied by a diminution in the D content of the total nitrile (I)+(II). Contrary to Kandiah *et al.* (A., 1929, 1294), the equilibrium proportion of (II) is indistinguishable from 100%. Analysis of the system (I)  $\xrightleftharpoons[k_2]{k_1}$  mesomeric ions  $\xrightleftharpoons[k_4]{k_3}$  (II) shows that  $k_1 \gg k_2$ ,  $k_3 \gg k_4$ , and  $(k_1/k_2)$

$(k_3/k_4)$ , the equilibrium val. of the ratio (D : H ratio in one exchanging position in the nitrile)/(D : H ratio in the exchanging position in EtOH) being 0.67. The lower D content of (II) than of (I) is explained by the fact that of the two positions concerned in exchange in each nitrile both of these in (I) and only one in (II) attain isotopic equilibrium with the medium, the second position in (II) being filled irreversibly, H<sup>+</sup> being taken up 4.1 times as fast as D<sup>+</sup>. H<sup>+</sup> is withdrawn from the nitrile 2.75 times as fast as D<sup>+</sup> by the OEt<sup>-</sup> ions of the medium. J. W. B.

**Homogeneous unimolecular decomposition of gaseous alkyl nitrites. VI. Decomposition of *n*-butyl nitrite.** E. W. R. STEACIE and W. McF. SMITH (J. Chem. Physics, 1936, 4, 504—507; cf. this vol., 33).—The rate of decomp. of 4—43 cm. of Bu<sup>o</sup>O·NO at 170—212° has been determined by the pressure changes. The reaction is unimol. and homogeneous, and the primary step is BuNO<sub>2</sub>=BuO+NO, but the reaction is not simple, as some tarry matter is also formed. The temp. coeff. leads to the energy of activation 36,000 kg.-cal. approx. Comparison shows that at 189.9°,  $k_{Me \cdot Et \cdot Pr \cdot Bu} = 0.97 : 1.89 : 3.95 : 3.70 : 8.88 \times 10^{-4}$  (cf. A., 1935, 938). J. G. A. G.

**Decomposition of azomethane. III. Effect of inert gases.** D. V. SICKMAN and O. K. RICE (J. Chem. Physics, 1936, 4, 608—613; cf. this vol., 684).—Kinetic data at 290° and 310° for Me<sub>2</sub>N<sub>2</sub>—"inert" gas mixtures afford relative activating efficiencies,  $\alpha$ , from which the following activating efficiencies per collision are calc.: Me<sub>2</sub>N<sub>2</sub> 1.00, N<sub>2</sub> 0.21, CO 0.13, CH<sub>4</sub> 0.20, H<sub>2</sub>O 0.46, CO<sub>2</sub> 0.25, D<sub>2</sub> 0.37, and He 0.07. The uniquely low val. for He suggests that exchange of vibrational energy between mols. is more probable than the transition of translational to vibrational energy. The val. of  $\alpha$  varies with pressure in mixtures of Me<sub>2</sub>N<sub>2</sub> with H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>, and Me<sub>2</sub>N<sub>2</sub> initiates a chain decomp. in *iso*-C<sub>4</sub>H<sub>10</sub>. J. G. A. G.

**Thermal decomposition of acetone.** J. R. HUFFMAN (J. Amer. Chem. Soc., 1936, 58, 1815—

1816).—The unimol. rate coeff. falls at low pressures in accordance with theory based on a free-radical chain mechanism. E. S. H.

**Kinetics of an inverse diene synthesis in the pure liquid state.** (A) B. S. KHAMBATA and A. WASSERMANN. (B) A. WASSERMANN (*Nature*, 1936, 138, 368, 369; cf. this vol., 684).—(A) Between 100° and 150° the decomp. of dicyclopentadiene in the pure liquid state follows the Arrhenius equation, and the rate const. is  $3 \times 10^{13} e^{-35400/RT}$  sec.<sup>-1</sup> in agreement with the const. in paraffin.

(B) Activation energies and temp.-independent factors are given. L. S. T.

**Velocity of hydrolysis of chlorine.** E. A. SHILOV and S. M. SOLODUSHENKOV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 3, 15—19; cf. A., 1935, 939).—Measurements were made at 1.2° and 18° by Hartridge and Roughton's flowing stream method (A., 1923, ii, 744) using Schmidt's mixing arrangement (A., 1929, 919); changes of concn. were followed conductometrically. The direct determination gave vals. of the velocity coeff.  $m$  in the equation  $-d[Cl_2]/dt = m[Cl_2] - n[HOCI][H^+][Cl^-] = 125$  at 1.2° and =700 at 18°, in good agreement with those given by the chlorination of PhOH (cf. A., 1926, 831).

R. C. M.

**Decomposition of fluosilicate ion in aqueous and in aqueous salt solutions.** A. G. REES and L. J. HUDLESTON (*J.C.S.*, 1936, 1334—1338).—The decomp. of  $SiF_6^{2-}$  in alkaline solution is unimol., the mechanism being:  $SiF_6^{2-} = SiF_4 + 2F^-$  (slow),  $SiF_4 + 3H_2O = 4HF + H_2SiO_3$  (rapid), followed by neutralisation of the acid.  $k$  is unaffected by alkali concn. or presence of added electrolyte. The degree of initial dissociation of the  $SiF_6^{2-}$  ( $R_0$ ) is deduced, and  $K = a_{SiF_4} a_{F^-} / a_{SiF_6^{2-}}$  calc. Added electrolyte decreases  $R_0$  owing to the increase of ionic strength of the solution, in quant. agreement with theory. A. J. E. W.

**Kinetic and equilibrium measurements of the reaction  $2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$ .** A. V. HERSHEY and W. C. BRAY (*J. Amer. Chem. Soc.*, 1936, 58, 1760—1772).—Rate measurements at 25° and ionic strength 0.09 in aq. solutions containing  $H^+$ ,  $Fe^{+++}$ ,  $Fe^{++}$ ,  $I^-$ ,  $I$ ,  $K^+$ , and  $NO_3^-$  have been determined and evaluated. Intermediate compounds involved are discussed. Equilibrium data have been determined.

E. S. H.

**Kinetics of the reaction between ferric and stannous perchlorates in acid solution.** M. H. GORIN (*J. Amer. Chem. Soc.*, 1936, 58, 1787—1795).—Determinations of rate at 55° and 70° give no evidence of a direct reaction between  $Fe^{+++}$  and  $Sn^{++}$ . The rate-determining step for the reduction of  $Fe^{+++}$  is  $Fe(OH)_2^+ + Sn^{++}$ . When the hydrolysis equilibria are maintained the rate law is  $d(Fe^{++})/dt = 2k_3 k_1 k_2 (Fe^{+++})(Sn^{++}) / (H^+)^2$  when  $[Fe^{+++}]$  is high compared with  $[Sn^{++}]$ . The hydrolysis equilibria have been studied in the light of the above rate law. E. S. H.

**Influence of solvents on reaction velocity. Interaction of pyridine and methyl iodide and benzoylation of *m*-nitroaniline.** N. J. T. PICKLES and C. N. HINSHELWOOD (*J.C.S.*, 1936, 1353—1357).—The bimol. reactions between  $C_5H_5N$  and  $MeI$ ,

and between  $BzCl$  and  $m\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$ , have been examined using various solvents, and vals. of  $k$  and the activation energy  $E$  obtained. The influence of the nature of the solvent on the consts.  $P$  and  $E$  in the equation  $k = PZ e^{-E/RT}$  ( $Z$  = collision no.) is discussed,  $Z$  being assumed const. For active solvents,  $E$  remains nearly const.,  $P$  varying in approx. parallelism with the dipole moment of the solvent. For inert solvents  $E$  increases. Variations in  $P$  are discussed. A. J. E. W.

**Kinetics of acid and alkaline hydrolysis of esters.** W. B. S. NEWLING and C. N. HINSHELWOOD (*J.C.S.*, 1936, 1357—1361).—Vals. of  $k$  and the activation energy  $E$  for the acid and alkaline hydrolysis of a no. of esters in aq.  $COMe_2$  solution have been obtained, and are discussed in relation to the equation  $k = PZ e^{-E/RT}$  (cf. preceding abstract). For a given ester,  $P$  is approx. const. for acid and alkaline hydrolysis, suggesting analogous mechanisms. Possible mechanisms are discussed. Results for  $P$  are not in accord with Soper's entropy change relation.

A. J. E. W.

**Reaction kinetics of acid hydrolysis of phenolic ethers.** R. P. GHASWALLA and F. G. DONNAN (*J.C.S.*, 1936, 1341—1346).—The acid hydrolysis of eight substituted anisoles and four substituted phenetoles by  $HCl$  and  $HBr$  has been investigated. The reactions are pseudo-unimol. with acid in excess, and formally of the third order with equiv. acid and ether,  $[HCl]^2$  occurring in the equation for  $k$ . This may be due to the formation of an intermediate oxonium compound the decomp. of which determines  $k$ , or to the acid functioning as undissociated mols. The effect of nuclear substituents on  $k$  is discussed.

A. J. E. W.

**Reaction of paraformaldehyde with cyanide.**—See this vol., 1362.

**Inflammation of dust clouds.**—See B., 1936, 964.

**Initial velocities of reduction of hæmatite and magnetite with hydrogen.** G. I. TSCHUFAROV and B. D. AVERBUCH (*Z. physikal. Chem.*, 1936, B, 33, 334—348; cf. this vol., 570).—The initial rate of reduction,  $v$ , in  $H_2$  at 0.001—0.1 mm. and at 300—800° has been determined. If a piece of magnetite is repeatedly heated in  $H_2$  so that reduction proceeds a stage further each time,  $v$  at a given  $H_2$  pressure increases with the no. of heatings, showing that reduction is autocatalysed. In the earlier stages of the reaction there is a period of induction which increases with fall in the temp. or  $H_2$  pressure. These observations are accounted for if it is supposed that reaction begins at active centres on the oxide surface, and when reaction occurs at a centre several new ones are formed. Above 600° the active surface is reduced by recrystallisation of the active centres, resulting in  $v$  being much smaller than at lower temp.

R. C.

**Autoxidation of unsaturated hydrocarbons.** I. P. PANJUTIN, L. HINDIN, and O. VASILJEEVA (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 2, 183—186).—An EtOH solution of  $KI$  and conc.  $H_2SO_4$  was mixed with  $C_6H_6$  and kept in the dark for 4 hr. The amount of unchanged  $KI$  was determined by means of oxid-



ation with  $\text{Fe}^{\text{III}}$  salts. Liberated I was absorbed in KI and titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ . The peroxide no. in g. of I is calc. from a formula. W. R. A.

**Kinetics of rapid reactions. II. Starch iodide.** H. VON HALBAN and H. EISNER (Helv. Chim. Acta, 1936, 19, 915—927; cf. A., 1935, 1082).—Measurements by the streaming method of the rate of decolorisation of starch iodide by sulphite (I) or thiosulphate (II) indicate that at 25° the rate-determining process is the reaction between I and the reducing agent, the dissociation of the complex being immeasurably rapid. The observed rates decrease with increasing age of the complex and are, *ceteris paribus*, higher for (II) than for (I). The speed of reaction with (I) increases, and with (II) decreases, with increase of  $[\text{H}^+]$ . F. L. U.

**Kinetics of heterogeneous organic reactions. II. Reaction between benzyl chloride and solid silver nitrate in the presence of inert diluents.** M. V. NABAR and T. S. WHEELER (Proc. Indian Acad. Sci., 1936, 4, A, 91—96; cf. A., 1935, 1466).—The presence of dry  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  inhibits the reaction, the effect of  $\text{Et}_2\text{O}$  being most marked. The rate of reaction  $\propto$  the surface of  $\text{AgNO}_3$  present, but is independent of the initial amount of a given mixture of  $\text{CH}_2\text{PhCl}$  and diluent. Results can be reproduced by a kinetic equation based on the assumption that the rate of reaction for a given initial mixture of  $\text{CH}_2\text{PhCl}$  and diluent depends only on the surface of the  $\text{AgNO}_3$ . The effect of the diluent may be due to adsorption on the  $\text{AgNO}_3$  surface. N. M. B.

**Autocatalysis in chemistry and biology.** A. MITTASCH (Chem.-Ztg., 1936, 60, 793—794).—A review.

**Influence of nitric oxide on the thermal decomposition of dimethyl ether. Gaseous catalysis.** P. F. GAY and M. W. TRAVERS (Nature, 1936, 138, 546—547; cf. this vol., 825, 1072).—Small amounts of NO reduce the rate of the thermal decomp.  $\text{Me}_2\text{O} = \text{CH}_3 + \text{CH}_3\text{O}$ , but larger amounts rapidly increase it. The reaction of NO with  $\text{Me}_2\text{O}$  gives rise to processes resulting in the formation of a short-lived intermediate which can decompose in two different ways. The oxidations can be represented by the equations  $\text{Me}_2\text{O} + \text{O} \rightarrow \text{OMe} \cdot \text{CH}_2 \cdot \text{OH}$  (I)  $\rightarrow (\text{CH}_3 + \text{CO}_2 + \text{H}_2)$  or  $(\text{CH}_3 + \text{CO} + \text{H}_2\text{O})$  and  $(\text{I}) + \text{O} \rightarrow \text{OMe} \cdot \text{CH}(\text{OH})_2 \rightarrow (\text{CH}_3 + \text{CO}_2 + \text{H}_2\text{O})$  or  $(\text{MeOH} + \text{CO} + \text{H}_2\text{O})$ . L. S. T.

**Ozone as an oxidising catalyst. XIII. Rate of transformation of systems obtained by ozonisation of aldehydes.** E. BRINER and A. LARDON (Helv. Chim. Acta, 1936, 19, 1062—1074; cf. this vol., 1075).—The system  $\text{PhCHO}$  (I)— $\text{BzO}_2\text{H}$  (II) is transformed into  $\text{BzOH}$  at approx. the same rate as is that obtained by ozonisation of (I), whence it is inferred that the peroxide formed in the latter reaction is (II). In support of this, the speed of the reaction between (I) and (II) is greater in  $\text{C}_6\text{H}_{14}$  than in  $\text{CCl}_4$ , corresponding with the higher proportion of (II) formed in the former solvent by ozonisation. The speed of reaction between  $\text{MeCHO}$  and  $\text{AcO}_2\text{H}$ , and the proportion of the latter formed by ozonisation, are greater in  $\text{CCl}_4$  than in  $\text{C}_6\text{H}_{14}$ . The course of the

transformation cannot be represented by any of the usual equations, and the process is considered to depend on chain reactions. F. L. U.

**Rates of some acid- and base-catalysed reactions, and dissociation constants of weak acids in "heavy" water.** J. C. HORNEL and J. A. V. BUTLER (J.C.S., 1936, 1361—1366).—The rates of hydrolysis in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  of  $\text{MeOAc}$ , acetal (I), and  $\text{CH}(\text{OEt})_3$  (II) in acid solution, and of diacetone alcohol in alkaline solution have been determined by observing changes in  $n$  or  $\eta$ . Acid hydrolysis of (I) or (II) was used to determine the ratio of the dissociation consts. of some weak acids in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  ( $K_D/K_H$ ). This ratio increases as  $K$  increases; this is interpreted by a modification of Halpern's theory (A., 1935, 1203),  $K_D/K_H$  being determined mainly by the force const. between the proton and the acid anion. A. J. E. W.

**Catalytic decomposition of diazoacetate ion in aqueous solution.** C. V. KING and E. C. BOLINGER (J. Amer. Chem. Soc., 1936, 58, 1533—1542).—The reaction of  $\text{CHN}_2 \cdot \text{CO}_2^-$  with  $\text{H}_2\text{O}$  is extremely sensitive to general acid catalysis. The mol. catalytic const. for  $\text{H}^+$ ,  $3.57 \times 10^8$  at 25°, is the highest recorded for any reaction. The mol. catalysis consts. decrease with increasing base or acid concn. There is a linear relation between the mol. consts. and the reciprocal of the base concn., except at low vals. of base concn. Mol. acid consts. at high base concn. agree with the Bronsted theory. Salt effects are described in relation to the mechanism. E. S. H.

**Catalytic action of lactoflavin-5'-phosphoric acid.**—See this vol., 1418.

**Application of transition state method to the heterogeneous reaction on hydrogen electrode; absolute calculation of isotopic interchange reaction velocity, cathodic and anodic currents, and isotopic separation factor.** G. OKAMOTO, J. HORIUTI, and K. HIROTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 223—251).—The transition state method has been applied to the calculation of abs. reaction velocities for the H-Ni electrode, the rate-determining step being  $\text{H}_2 + 2\text{Ni} \rightarrow 2\text{H-Ni}$ . The authors' experimental results for anodic and cathodic currents, separation factor for H and D, velocity of interchange of H and D in  $\text{H}_2\text{O}$ , and temp. coeffs. of these processes, together with the relative adsorption velocities of  $\text{H}_2$  and  $\text{D}_2$  on Ni, and overvoltage, are successfully accounted for. The (110) plane of Ni is the most active, and activation of the catalyst probably consists in increasing the extent of the (110) plane, not the no. of active centres. R. S. B.

**Activation of specific linkings in complex molecules at catalytic surfaces. II. Carbon-hydrogen and carbon-carbon linkings in ethane and ethane-d.** K. MORIKAWA, W. S. BENEDICT, and H. S. TAYLOR (J. Amer. Chem. Soc., 1936, 58, 1795—1800; cf. this vol., 1213).—The exchange reaction between  $\text{C}_2\text{H}_6$  and  $\text{D}_2$  on a Ni catalyst occurs at lower temp. (100—130°) than that required for the reaction to yield  $\text{CH}_4$  (160—300°). The formation of  $\text{CH}_4$  has been studied kinetically; the surface reaction is

inhibited by  $H_2$ . At low  $[H_2]$  the side reactions  $2C_2H_6 = C + 3CH_4$  and  $C + 2H_2 = CH_4$  may predominate. The reaction of  $C_2H_6$  with  $H_2$  in presence of Ni, forming  $CH_4$ , has an activation energy approx. 43 kg.-cal.; the corresponding val. for the reaction with  $D_2$  is approx. 0.5 kg.-cal. higher. The activation energy of dissociative adsorption at the C-C linking is deduced to be  $>$  that of the C-H linking. The prep. of  $C_2D_6$  is described. E. S. H.

Water-gas reaction at a platinum surface at low pressure. G. M. SCHWAB and K. NAICKER (Z. Elektrochem., 1936, 42, 670—673).—The reaction between  $CO_2$  and  $H_2$  on a heated Pt wire has been studied at pressure of 0.01—0.1 mm. The temp. coeff. of the velocity of reaction ( $v$ ) of an equimol.  $H_2SO_4$ -dried mixture at 1300—1500° indicates a heat of activation of 35 kg.-cal. per mol. Excess of  $CO_2$  has little effect on the reaction, which is unimol., but shows an initial period of autocatalysis which disappears when CO is initially present in the reaction vessel. This effect is attributed to preformation of active centres. When the gases are  $P_2O_5$ -dried there is no autocatalysis and the reaction is of zero order, CO has a retarding effect, whilst excess of  $H_2$  is without effect. When the gases are dried to a  $H_2O$ -v.p. of  $2 \times 10^{-4}$  mm. by immersion in a bath at  $-90^\circ$ ,  $v$  has a very high temp. coeff. between 700° and 800°, and above about 900° remains const. at a high val. This indicates that with  $P_2O_5$ -dried gases there is a retardation of the reaction, attributed to poisoning of the active centres. J. W. S.

Kinetics of ammonia synthesis on technical iron catalyst.—See B., 1936, 985.

Catalytic methanisation of carbon monoxide in industrial gases.—See B., 1936, 915.

[Catalytic] preparation of ethyl alcohol from ethylene.—See B., 1936, 918.

[Catalytic] preparation of hydrocarbons of the butadiene series from alcohols.—See B., 1936, 970.

[Catalytic] synthesis of acetic acid.—See B., 1936, 970.

Mechanism of [catalytic] hydrogenation of naphthalene.—See B., 1936, 971.

Preparation of nickel-kieselguhr catalysts.—See B., 1936, 986.

Catalytic hydrolysis of *p*-dichloro- and *p*-dibromo-benzene by steam.—See B., 1936, 970.

Structure of the electric double layer of platinised platinum and velocity of hydrogenation of benzene in a liquid medium. B. FORESTI (Gazzetta, 1936, 66, 464—475; cf. following abstract).—The rate of hydrogenation of  $C_6H_6$  suspended in solutions of KCl of varying  $p_H$  and in presence of platinised Pt has been measured. There is a max. velocity at about  $p_H$  0, which corresponds with the  $p_H$  at which the Pt electrode has zero charge.

O. J. W.

Relation between the activity of the hydrogen ions of the medium and velocity of hydrogenation of benzene and of oxygen in a liquid medium and in presence of platinum. B. FORESTI (Gaz-

zetta, 1936, 66, 455—459).—The rate of hydrogenation of O and of  $C_6H_6$  suspended in aq. solutions in presence of platinised Pt is greatly influenced by the  $p_H$  of the solution, especially when the Pt catalyst is very active.

O. J. W.

Temperature coefficient of the electrolytic separation of the hydrogen isotopes. H. F. WALTON and J. H. WOLFENDEN (Nature, 1936, 138, 468).—The temp. variation of the electrolytic separation of the H isotopes at Hg and Ag cathodes has been measured at c.d.  $>$  1 milliamp. per sq. cm. At Ag, the separation coeff. falls with a rise in temp., whilst that at Hg is practically unchanged. Addition of  $\alpha$ -naphthaquinoline, which might be expected to inhibit any catalytic mechanism, lowers the coeff. markedly in both cases, and changes the sign of the temp. coeff.

L. S. T.

Electrolytic preparation of silver salts.—See B., 1936, 1000.

Electrodeposition of cadmium.—See B., 1936, 997.

Theory of electrodeposition of chromium.—See B., 1936, 997.

Influence of various acid radicals on chromium [plate] hardness.—See B., 1936, 997.

Electrodeposition of molybdenum.—See B., 1936, 997.

Causes of electrochemical corrosion of iron and its alloys in moist aerated media.—See B., 1936, 994.

Electrolytic production of ferro-vanadium.—See B., 1936, 996.

Effect of addition of cadmium salts to nickel-plating baths.—See B., 1936, 997.

Electroplating of antimony.—See B., 1936, 997.

Europium. H. N. MCCOY (J. Amer. Chem. Soc., 1936, 58, 1577—1580).—The electrolytic reduction of  $Eu^{+++}$  to  $Eu^{++}$  is described. The reduction potential of the  $Eu^{+++}$ ,  $Eu^{++}$  electrode is 0.4313 volt. In solutions of  $Eu^{++}$  complete absorption of visible light occurs below 4480 Å.; the bands of the absorption spectrum of  $Eu^{+++}$  solutions are not shown. The stability of  $Eu^{++}$  solutions to oxidation has been investigated. Cryst.  $EuSO_4$  is stable in air. Iodometric methods for the determination of Eu are described.

E. S. H.

Electrochemical investigations with  $\alpha$ -hydroxy-acids. E. TOMMILA (Ann. Acad. Sci. Fennicae, 1936, A, 46, 1—95; cf. A., 1935, 960).—The electrolytic oxidation of a no. of aliphatic and aromatic  $\alpha$ -OH-acids in 2—5*N*-NaOH solution and with bright and platinised Pt, Ni, and Fe anodes has been investigated. With Ni and Fe anodes the reaction proceeds almost independently of anode potential, yielding almost exclusively the corresponding  $\alpha$ -keto-acids, whilst at Pt anodes it yields mainly  $CO_2$  and the next lower aldehyde. Under special conditions  $H_2$  and hydrocarbons can be formed at a bright Pt anode, this phenomenon being least common with the lower members of the series. For each  $\alpha$ -OH-acid there are two separate regions of oxidation potential,



corresponding with decomp. with and without  $O_2$  evolution, respectively. In some cases periodic oscillation between the two potentials is observed.

J. W. S.

**Polarographic studies with the dropping mercury cathode. LXI. Effect of buffer solutions on the reaction of proteins.** R. BRDIČKA (Coll. Czech. Chem. Comm., 1936, 8, 366—376).—The catalytic effect of ovalbumin, peptone, and cysteine in lowering the over-potential of the deposition of H ions has been investigated in buffer solutions. The presence of cystine nuclei in the protein is considered essential for the catalytic action.

C. R. H.

**Chemical action of electric discharges. XI. Production of nitric oxide by the electric arc at high frequency in mixtures of nitrogen and oxygen at reduced pressure.** E. BRINER, B. SIEGRIST, and H. PAILLARD (Helv. Chim. Acta, 1936, 19, 1074—1079; cf. this vol., 571).—Yields of  $HNO_3$  >500 g. per kw.-hr. have been obtained from equimol. mixtures of  $N_2$  and  $O_2$  by combining the use of a high-frequency arc ( $10^7$  cycles) with reduction of the gas pressure to about 70 mm. Such yields are due to the much smaller min. energy required to maintain a stable discharge. Under the conditions stated excess of  $O_2$  in the mixture and addition of Li to the electrodes have a less favourable influence.

F. L. U.

**Kinetics of recombination of iodine atoms.** E. RABINOWITCH and W. C. WOOD (J. Chem. Physics, 1936, 4, 497—504; cf. this vol., 398, 437).—The equilibrium  $I_2 + h\nu \rightarrow I + I$ ,  $I + I \rightarrow I_2$  in the presence of added gases is heterogeneous at low pressures. The atoms recombine mainly by diffusion to the walls, and the dissociation increases with rising pressure. At higher pressures, sp. for the added gas (e.g., 250 mm. in He, 40 mm. in  $CO_2$ ) there is a fairly sharp transition and the recombination becomes homogeneous. The walls have practically no effect at pressures > the transition val., and the dissociation  $\propto$  (light intensity) $^{\frac{1}{2}}$  and (pressure) $^{-\frac{1}{2}}$ , in accordance with the theory for recombination by three-body collisions. The velocity coeffs. of the reaction  $I + I + X \rightarrow I_2 + X$  for the different added gases, X, are calc., and the order of efficiency in promoting recombination is  $He < A < H_2 < N_2 < O_2 < CH_4 < CO_2 < C_6H_6$ . At atm. pressure, one binary collision of I atoms in 530 leads to recombination in He, but one in 50 is fruitful in  $CO_2$  (cf. this vol., 801).

J. G. A. G.

**Photochemical reduction of nitrates.** R. CULTRERA (Gazzetta, 1936, 66, 440—446).—When aq. solutions of  $HNO_3$  or of metallic nitrates are exposed to sunlight, or to the light of a C arc or of a quartz Hg lamp, some reduction to  $NO_2'$  takes place. With the Hg lamp radiation reduction to  $NH_3$  may also occur. In both reactions  $O_2$  is evolved. The effect of various factors on the amount of reduction products formed has been studied.

O. J. W.

**Theory of desensitisation.** LUPPO-CRAMER (Z. wiss. Phot., 1936, 35, 197—200).—AgBr-collodion emulsions (not dye-sensitised) are scarcely desensitised by the usual dyes. This fact was used by Weber (this vol., 808) for his theory of desensitisation as a

process of oxidation of chemical or optical sensitising substances. Previous work by the author has, however, shown that the latent image of collodion emulsions is resistant to bleaching and other reactions. The facts are therefore more in accord with the older theory that desensitisation is a process of oxidation of at. Ag to Ag ions.

J. L.

**Influence of grain size, separation, and distribution on the capability of enlargement of photomicrographs of biological objects.** F. BUCHTHAL and G. G. KNAPPEIS (Z. wiss. Phot., 1936, 35, 177—192).—The characteristics of the grains of nine emulsions have been determined by photomicrographs of single-grain layers within the emulsion and by microphotometric records of density. No definite relation between any characteristic and the capability of enlargement could be found. The methods of measurement and the results obtained are fully discussed.

J. L.

**Colloid substrate in photosynthesis.** M. COPPSAROW (Nature, 1936, 138, 509).

L. S. T.

**Photochemical decomposition of methane.** P. A. LEIGHTON and A. B. STEINER (J. Amer. Chem. Soc., 1936, 58, 1823).— $H_2$  and unsaturated hydrocarbons (probably  $C_2H_4$ ) are produced when  $CH_4$  is irradiated with the light transmitted by a thin fluorite window from a H $_2$  discharge tube.

E. S. H.

**Photochemical oxidation of methane, methyl chloride, and methylene chloride sensitised by chlorine.** W. BRENSCHKE and H. J. SCHUMACHER (Z. physikal. Chem., 1936, 177, 245—262).—When a mixture of  $Cl_2$  and  $O_2$  with  $CH_4$ ,  $MeCl$ , or  $CH_2Cl_2$  is irradiated with light of  $\lambda$  436 m $\mu$  the principal products are HCl and CO; small amounts of  $COCl_2$ ,  $H_2O$ , and less volatile org. compounds are also formed. The reaction has a chain mechanism and a quantum yield referred to CO formation rising from about 80 to 800 in the order  $CH_4 < MeCl < CH_2Cl_2$ . From  $CH_4$  and  $MeCl$  reaction proceeds by way of  $MeCl$  and  $CH_2Cl_2$ , and  $CH_2Cl_2$ , respectively. Up to the formation of  $CH_2Cl_2$  there is little oxidation of the hydrocarbon radicals participating in the chains.  $CH_2Cl_2$ , however, forms by collision with a Cl atom the  $CHCl_2$  radical, which reacts with  $O_2$  to give CO and HCl, some peroxide of short life being an intermediate product; after a period of induction the velocity of this reaction becomes const.

R. C.

**Action of ultra-violet light on halogenated hydrocarbons.**—See this vol., 1358.

**Behaviour of iodine in sensitised decompositions of gaseous organic compounds.** R. F. FAULL and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1936, 58, 1755—1758).—Spectroscopic evidence shows that the [I] during sensitised decomp. of gaseous  $Et_2O$ ,  $MeCHO$ ,  $PrCHO$ ,  $(CH_3)_2O$ ,  $MeOH$ ,  $HCO_2Me$ , or  $CH_2O$  is very low. Definite chemical reactions are involved in the decomp.

E. S. H.

**Photochemical formation of peroxides. VI. Oxidation of formic acid in ultra-violet light by molecular oxygen.** Photochemical formation of performic acid. R. CANTIENT (Helv. Chim. Acta, 1936, 19, 1153—1158; cf. this vol., 1091).—Peroxide

is formed in both anhyd. and aq.  $\text{HCO}_2\text{H}$  in presence of  $\text{O}_2$  on exposure to ultra-violet light of short  $\lambda$ . The peroxide (I), which is not  $\text{H}_2\text{O}_2$ , is assumed to be performic acid. In presence of  $\text{HCO}_2\text{H}$  (I) decomposes at a rate which increases with its concn., so that a steady concn. is attained, which in the aq. acid is never  $>0.75\%$  in consequence of the strong ultra-violet absorption. F. L. U.

**Mechanism of decomposition. I. Vapour-phase photolysis of acetic acid. II. Photolysis of formic acid.** M. BURTON (J. Amer. Chem. Soc., 1936, 58, 1645—1654, 1655—1657).—I. During photolysis, H atoms, but no free Me radicals, are formed. The production of at. H is favoured slightly by decrease in  $\lambda$ ; none is produced at  $\lambda > 2300 \text{ \AA}$ . Energies of activation for two reactions involving AcOH and H atoms have been calc. A free-radical mechanism is put forward. The detection of H atoms in presence of free Me is described.

II. No H is produced during photolysis of  $\text{HCO}_2\text{H}$ ; a mechanism for the production of OH is formulated. A reaction with a fairly low energy of activation occurs between H and  $\text{HCO}_2\text{H}$ . Experiments with MeCHO show CHO to be a stable radical at room temp. E. S. H.

**Photo-rearrangement of o-nitrobenzaldehyde to o-nitrobenzoic acid.** L. KUHLER and F. PATAT (Monatsh., 1936, 68, 275—289).—The quantum yield in the photo-conversion of  $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  into  $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  in the vapour phase is  $>$  for this reaction in solution (cf. A., 1931, 1251; 1935, 48), but is  $<1$ . The mechanism of the reaction is discussed. J. W. S.

**Photochemical deamination of amino-acids in water solution.** C. WEIZMANN, E. BERGMANN, and Y. HIRSHBERG (J. Amer. Chem. Soc., 1936, 58, 1675—1678).—Glycine, alanine, betaine, and aspartic acid are hydrolysed in aq. solution under the influence of ultra-violet light, yielding corresponding OH-acids. The kinetics and quantum yields of the reactions have been determined and a mechanism is suggested. E. S. H.

**Photochemical studies. XXIV. Photochemical chlorination of dichlorobenzenes.** C. F. FISK and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1936, 58, 1707—1714).—The rates of photochemical chlorination of o-, m-, and p- $\text{C}_6\text{H}_4\text{Cl}_2$  are equal. The rate  $\propto$  the light intensity at low intensities, but  $\propto$  some power of the intensity between 0.5 and 1.0 at higher intensities. The rate is independent of  $[\text{Cl}_2]$ , but  $\propto$   $[\text{C}_6\text{H}_4\text{Cl}_2]$ . The mechanism is discussed. E. S. H.

**Chemical reactions produced by ionisation processes. I. Ortho-para hydrogen conversion by  $\alpha$ -particles.** H. EYRING, J. O. HIRSCHFELDER, and H. S. TAYLOR (J. Chem. Physics, 1936, 4, 479—491).—Theoretical. The processes occurring in a gas ionised by  $\alpha$ -particles are considered. In  $\text{H}_2$ , approx. one ion in 5—9 is associated with a mol. Stable states of  $\text{H}_2^-$  exist, but the probability of formation is very small. Most neutralisation processes involve  $\text{H}_3^+$ , and 2—3 H atoms are produced, corresponding with 3—4 H atoms per ion pair formed. At. H is responsible for the large ratio of para- $\text{H}_2$

converted with respect to ions produced by  $\alpha$ -particles (cf. this vol., 171). H atoms are removed only slowly by the process  $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$  compared with the speed of recombination at the wall of the vessel, and Hg atoms are not effective. The results accord with the data (*loc. cit.*). J. G. A. G.

**Radiochemical synthesis and decomposition of hydrogen bromide.** H. EYRING, J. O. HIRSCHFELDER, and H. S. TAYLOR (J. Chem. Physics, 1936, 4, 570—575).—Theoretical. A mechanism is developed whereby the variations of yield per ion pair with change of  $[\text{H}_2]$ ,  $[\text{Br}_2]$ , and  $[\text{HBr}]$  are accounted for quantitatively (cf. this vol., 688). In pure  $\text{H}_2$  six H atoms are formed per ion pair, whilst in pure HBr six mols. are decomposed. In equal mixtures of  $\text{Br}_2$  and HBr, an electron forms a negative ion from HBr more frequently than from  $\text{Br}_2$ . J. G. A. G.

**Separation of isotopes.** G. CHAMPETIER (Bull. Soc. chim., 1936, [v], 3, 1701—1727).—A lecture.

**Exchange between sodium iodide and ethyl iodide.** D. E. HULL, C. H. SCHIFFLETT, and S. C. LIND (J. Amer. Chem. Soc., 1936, 58, 1822—1823).—Exchange between radioactive NaI and EtI in EtOH at  $100^\circ$  is demonstrated. E. S. H.

**Preparation of magnesium hypochlorite.**—See B., 1936, 986.

**Graduated [thermal] decomposition of barium dihydrogen oxalate dihydrate measured by the emanation method.** B. SAGORTSCHEV (Z. physikal. Chem., 1936, 177, 235—240).—There are formed successively  $\text{BaH}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ ,  $\text{BaH}_2\text{C}_2\text{O}_4$ ,  $4\text{BaC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4$  (decomp. above  $210^\circ$ ),  $\text{BaC}_2\text{O}_4$ , and  $\text{BaCO}_3$ . R. C.

**Mercuric halides, cyanide, and thiocyanate.** K. BRAND and I. TURCK (Pharm. Zentr., 1936, 77, 591—593).— $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ,  $\text{HgI}_2$ , and  $\text{Hg}(\text{CN})_2$  crystallise with 2,  $\text{Hg}(\text{SCN})_2$  with 1 mol. of dioxan of crystallisation which is readily lost in air. Dioxan is a good solvent for recrystallisation of  $\text{HgI}_2$ . R. S. C.

**Base-exchanging properties of synthetic aluminosilicate materials.**—See B., 1936, 986.

**Recent developments in the chemistry of the rare-earth group.** B. S. HOPKINS (J. Chem. Educ., 1936, 13, 363—368).—An address. L. S. T.

**Separation of yttrium from the yttrium earths.** H. C. FOGG and L. HESS (J. Amer. Chem. Soc., 1936, 58, 1751—1753).—Y is separated by fractional pptn. with  $\text{CO}(\text{NH}_2)_2$  at  $90$ — $95^\circ$ . E. S. H.

**Extraction of indium from cylindrite, chalcopyrite, and metallic tin.** F. M. BREWER and E. BAKER (J.C.S., 1936, 1290—1294).—Sn in metallic Sn is pptd. as  $\text{SnS}_2$ , and In subsequently co-pptd. with  $\text{Al}(\text{OH})_3$ ; alternatively, treatment with  $\text{Cl}_2$  volatilises Sn as  $\text{SnCl}_4$ , leaving In in the residue. Cu and Fe in chalcopyrite are pptd. with nitroso- $\beta$ -naphthol (I); some In is carried down, and separation is poor with low In content, making this source inconvenient. Pb, Sn, and Sb in cylindrite (an analysis of which is given) are pptd. as sulphides. In is then pptd. (with Fe and Zn) as hydroxide; Fe is separated with (I), and  $\text{Zn}(\text{OH})_2$  dissolved out with aq.  $\text{NH}_3$ .



Treatment with  $\text{NaHSO}_3$  gives In basic sulphite. Elimination of traces of Fe is troublesome.

A. J. E. W.

**Concentration of the carbon isotope.** H. C. UREY, A. H. W. ATEN, jun., and A. S. KESTON (J. Chem. Physics, 1936, 4, 622—623).—The % of  $^{13}\text{C}$  was increased from 1.06 to 1.36 by using  $\text{CO}_2$  and aq.  $\text{KHCO}_3$  containing carbonic anhydrase in a counter-current fractionating column apparatus.

J. G. A. G.

**Corrosion of silica by chlorine.**—See B., 1936, 989.

**Properties of the oxides of nitrogen. V. Combustion in the system nitric anhydride-ozone.** J. T. LEMON and T. M. LOWRY (J.C.S., 1936, 1409—1412).—Mixtures of  $\text{N}_2\text{O}_5$  and ozonised  $\text{O}_2$  (7—8%  $\text{O}_3$ ) contain a blue gas, probably  $\text{NO}_3$ . The mixture ignites at  $<100^\circ$ , burning with a characteristic blue flame and producing  $\text{N}_2\text{O}_4$ . The  $\text{NO}_3$  appears to burn in  $\text{O}_3$  with liberation of  $\text{O}_2$ :  $\text{NO}_3 + \text{O}_3 = \text{NO}_2 + 2\text{O}_2$  or  $2\text{NO}_3 = 2\text{NO}_2 + \text{O}_2$ . Once the combustion is initiated, a reaction such as  $\text{N}_2\text{O}_5 + \text{O}_3 = 2\text{NO}_2 + 2\text{O}_2$  may occur.

A. J. E. W.

**Nitrosyl of A. Angeli.** L. CAMBI (Ber., 1936, 69, [B], 2027—2033; cf. Oddo *et al.*, this vol., 460).—Anhyd.  $\text{MeCHO}$ ,  $\text{EtCHO}$ ,  $\text{Pr}^\text{c}\text{CHO}$ , and  $\text{BuCHO}$  do not react with  $\text{Na}_2\text{N}_2\text{O}_3$ ; Angeli's reaction with formation of  $\text{NaNO}$ , and  $\text{OH}\cdot\text{CR}\cdot\text{N}\cdot\text{ONa}$  is immediately induced by a little  $\text{H}_2\text{O}$ . In anhyd. media  $\text{PhSO}(\text{OH})\cdot\text{N}\cdot\text{ONa}$  (I) reacts immediately with  $\text{MeCHO}$  and  $\text{EtCHO}$ :  $(\text{I}) \rightarrow \text{R}\cdot\text{SO}_2\text{Na} + \text{NaNO}$  and  $\text{NaNO} + \text{R}\cdot\text{CHO} \rightarrow \text{OH}\cdot\text{CR}\cdot\text{N}\cdot\text{ONa}$ . After removal of the excess of aldehyde, the salt-like residue does not give the reactions characteristic of Piloty's acid (II). With  $\text{MeCHO}$  and  $\text{EtCHO}$  (II) yields compounds thus:  $\text{R}\cdot\text{CHO} + 2\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{OH}$  (III)— $\text{H}_2\text{O}$  whereas with  $\text{Pr}^\text{c}\text{CHO}$  a mixture of  $\text{Pr}^\text{c}\text{CHO} + 2(\text{III})$ — $\text{H}_2\text{O}$  and  $\text{Pr}^\text{c}\text{CHO} + (\text{III})$ — $\text{H}_2\text{O}$  results. These are decomposed in complex manner by alkali, giving  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and traces of  $\text{NO}$  and yielding products containing N and S (including  $\text{PhSO}_2\text{H}$ ), but no hydroxamic acids. Their formation therefore does not involve Angeli's reaction. (II) and  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$  do not interact appreciably during several days. (II) appears unchanged by  $\text{PhCHO}$  in anhyd.  $\text{Et}_2\text{O}$ .  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  and (II) slowly yield a brown resin and a colourless, cryst. material which does not give hydroxamic acids with alkali. Contrary to Oddo, therefore, it is concluded that Angeli's hypothesis of nitrosyl as an unsaturated radical logically connects the reactions of widely differing substances which only share the ability to afford  $\text{HNO}$  when decomposed. Nitrosyl therefore belongs to the group of free radicals and is comparable with  $\text{NH}\cdot\text{NPh}$  and  $\cdot\text{NPh}$ . In gaseous and liquid systems the formation of  $\text{HNO}$  as intermediate has frequently been observed.

H. W.

**Preparation of chemically pure phosphoric acid.**—See B., 1936, 930.

**Metaphosphoric acids.** R. SALIH (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 77—84).— $\text{H}_6(\text{PO}_3)_6$  has been prepared by the action of  $\text{H}_2\text{S}$  on  $\text{Pb}_3(\text{PO}_3)_6$ . It is inferred from titration curves that four of the acidities are strong and two are weak.

R. S.

**Pyridinium vanadate.** S. KATZOFF and R. ROSEMAN (J. Amer. Chem. Soc., 1936, 58, 1785—1786).—The prep. and properties of  $(\text{C}_5\text{H}_6\text{N})_3\text{V}_5\text{O}_{14}\cdot\text{H}_2\text{O}$  are described.

E. S. H.

**Concentration of the oxygen isotopes.** H. C. UREY, G. B. PEGRAM, and J. R. HUFFMAN (J. Chem. Physics, 1936, 4, 623).—By means of a 35-ft. fractionating column with alternate cones rotating, the ratio of the O isotopes in  $\text{H}_2\text{O}$  was changed by a factor of three.

J. G. A. G.

**Preparation of amidosulphonic acid and imido-sulphonates.**—See this vol., 1237.

**Reactions in which metal atoms are exchanged between a gaseous and a solid phase.** G. BECKER, E. HERTEL, and C. KASTER (Z. physikal. Chem., 1936, 177, 213—223).—If  $\text{H}_2$  charged with  $\text{HCl}$  is passed over Cr and then over Fe at  $950^\circ$  the  $\text{CrCl}_2$  first formed reacts with the Fe:  $\text{Fe} + \text{CrCl}_2 = \text{FeCl}_2 + \text{Cr}$ . The Cr atoms formed on the surface of the Fe diffuse inwards, and new crystallites with a body-centred cubic lattice and consisting of a solid solution of Cr in Fe, apparently free from C, grow inwards from the surface; the depth of penetration may reach 1 mm. In the spaces between the Cr-Fe crystallites and between these and the Fe crystallites C accumulates, forming a eutectic alloy containing Cr 5, C 5, Fe 90%. Cr may be introduced into Ni and Co by a process similar to the above.

R. C.

**Effect of molecular nitrogen on molybdenum at high temperatures.** P. TURV and S. KRAUSZ (Nature, 1936, 138, 331).—Heating Mo wires electrically in  $\text{N}_2$  at  $1300^\circ$  raises the yield point and increases the extension of the wire under load. Cold-worked wires react more slowly with  $\text{N}_2$  than annealed. Deformation of nitrided wires restores the properties possessed prior to nitriding, but deformed nitrided wires revert to the nitrided stage after flashing even in A for 1—2 sec. Electrical resistivity is unaltered by nitriding. Heating in  $\text{H}_2$  or in a vac. denitrates the wires. Contamination of the wire surface by C and the presence of traces of  $\text{O}_2$  and/or  $\text{H}_2\text{O}$  vapour in the gas retard penetration of  $\text{N}_2$  into the wire.

L. S. T.

**Preparation and determination of elementary fluorine.** W. T. MILLER, jun., and L. A. BIGELOW (J. Amer. Chem. Soc., 1936, 58, 1585—1589).—Apparatus and procedure for the prep. of  $\text{F}_2$  and determination by absorption in Hg are described.

E. S. H.

**Complex nickel compounds. I. Formation and solvation of nickelous chloride in some non-aqueous liquids.** D. R. CHESTERMAN and A. S. NICKELSON (J.C.S., 1936, 1300—1302).—The reaction between Ni and  $\text{HCl}$  dissolved in various org. solvents has been studied. The reaction is more vigorous when the solvent is  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{Pr}^\text{c}\text{OH}$ ,  $\text{Pr}^\text{t}\text{OH}$ , or  $\text{AcOH}$  than when it is  $\text{Et}_2\text{O}$ ,  $\text{MeOAc}$ , or  $\text{EtOAc}$ . No reaction takes place in  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{PhNO}_2$ , or light petroleum. The following compounds were isolated:  $\text{NiCl}_2\cdot\text{MeOH}$ ;  $\text{NiCl}_2\cdot 2\text{MeOH}$ ;

$\text{NiCl}_2\cdot\text{EtOH}$ ;  $2\text{NiCl}_2\cdot\text{Pr}^\text{c}\text{OH}$ ;  $2\text{NiCl}_2\cdot\text{Pr}^\text{t}\text{OH}$ ;

$2\text{NiCl}_2\cdot\text{AcOH}$ ;  $\text{NiCl}_2\cdot\text{AcOH}$ ;  $\text{NiCl}_2\cdot\text{Et}_2\text{O}$ ;

$2\text{NiCl}_2\cdot\text{MeOAc}$ .

C. R. H.

**Affinity. LXX. Combination of palladium and phosphorus.** G. WIEHAGE, F. WEIBKE, and W. BILTZ [with K. MEISEL and F. WIECHMANN] (*Z. anorg. Chem.*, 1936, 228, 357—371).—Heating of Pd sponge in P vapour at 600—700° yields  $\text{PdP}_2$ . Thermal analysis of the system Pd— $\text{PdP}_2$  indicates the existence of a very stable *tripalladium phosphide*,  $\text{Pd}_3\text{P}$ , the compound  $\text{Pd}_5\text{P}_2$ , and a  $\beta$ -mixed crystal phase of mean composition  $\text{Pd}_5\text{P}$ . M.p., v.p., and X-ray measurements indicate no compounds between  $\text{Pd}_5\text{P}_2$  and  $\text{PdP}_2$ . The physical properties of Pd—P alloys of various compositions are described.

J. W. S.

**Co-ordination compounds of platinous halides with unsaturated substances.**—See this vol., 1369.

**Application of statistics to quantitative analysis.** A. A. BENEDETTI-PICHLER (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 373—377).—A discussion.

E. S. H.

**Calculation of mean error in conductometric titration.** J. MIKA (*Z. anal. Chem.*, 1936, 106, 248—261).—A method for the convenient calculation of the true equivalence point, subjective errors being eliminated, is developed.

J. S. A.

**Isohydric indicator method [for  $p_H$  determination].** S. STENE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 398—399).—Modified procedure is described.

E. S. H.

**Use of adsorption indicators in acidimetry and alkalimetry.** S. N. ROY (*J. Indian Chem. Soc.*, 1936, 13, 486—487).— $\text{HNO}_3$  or  $\text{AcOH}$  can be determined by titration with  $\text{NaOH}$  in presence of  $\text{Pb}(\text{NO}_3)_2$  and fluorescein or eosin. A slight excess of alkali ppts.  $\text{Pb}(\text{OH})_2$ , which adsorbs fluorescein or eosin, giving characteristic, coloured dye complexes.

E. S. H.

**Micro-determination of active hydrogen with deuterium oxide.** R. J. WILLIAMS (*J. Amer. Chem. Soc.*, 1936, 58, 1819—1820).—The substance is dissolved in  $\text{D}_2\text{O}$ , evaporated to dryness, and the increase of wt. due to replacement of active H by D determined. Results are given for hydroxyproline and  $\text{CO}(\text{NH}_2)_2$ .

E. S. H.

**Determination of hydrogen, carbon monoxide, and methane.**—See B., 1936, 931.

**Qualitative micro-analysis by electrolysis and spectrography.** Analysis of a mine water.—See B., 1936, 1022.

**Significance of spectrum analysis for water-works.**—See B., 1936, 1022.

**Titration of chloride ion with mercuric nitrate solutions, using diphenylcarbazide indicator.** I. ROBERTS (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 365—367).—Within a definite range of  $[\text{H}^+]$ , the procedure gives an accuracy of about 0.3%.  $\text{HgO}$  can be used as a primary standard in the prep. of the  $\text{Hg}(\text{NO}_3)_2$  solutions.

E. S. H.

**Accuracy of the potentiometric iodide-silver titration.** I. M. KOLTHOFF and J. J. LINGANE (*J. Amer. Chem. Soc.*, 1936, 58, 1524—1528).—The error is 0.1% at room temp., 0.048% at 70°, and 0.017% at 90°. At the equivalence potential the ppt. con-

tains an excess of  $\text{I}^-$ , due to adsorption. Titration at 90° is recommended.

E. S. H.

**Determination of microgram quantities of iodine.** R. H. HAMILTON, jun. (*J. Amer. Chem. Soc.*, 1936, 58, 1592—1594).— $\text{IO}_3^-$  can be reduced quantitatively in hot alkaline solution by  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ . KI can be extracted with EtOH from a saturated solution of  $\text{K}_2\text{CO}_3$ .

E. S. H.

**Determination of free and combined iodine in [pharmaceutical] iodine preparations.**—See B., 1936, 1016.

**Micro-determination of iodine and iodides.** G. ENDRES and L. KAUFMANN (*Z. physiol. Chem.*, 1936, 243, 144—148).—The procedure (A., 1935, 1167) used for the determination of  $\text{NH}_2\text{OH}$  has been adapted for the determination of  $10^{-5}$ — $10^{-4}N$ -I (error about 2%) and of  $\text{I}^-$  in concns.  $>10^{-5}N$ , the concn. of the dye produced being determined by means of a photometer. In the determination of  $\text{I}^-$  the liberated  $\text{I}_2$  must be separated from excess of  $\text{I}^-$  by distillation. The concn. of the dye should be  $>2 \times 10^{-5}$  mol. per litre.

W. McC.

**Micro-determination of fluorine. Elimination of effect of chloride.** W. D. ARMSTRONG (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 384—387).—Modified procedure, based on titration with  $\text{Th}(\text{NO}_3)_4$ , but using aq. instead of alcoholic solutions, is described. The F contents of dental enamel, dentine, and inorg. phosphates have been determined.

E. S. H.

**Sodium hyposulphite solutions for the absorption of oxygen.** D. QUIGGLE (*Ind. Eng. Chem. [Anal.]*, 1936, 8, 363).— $\text{Na}_2\text{S}_2\text{O}_4$  solutions are unstable; only freshly-prepared solutions are useful for  $\text{O}_2$  absorption.

E. S. H.

**Determining oxygen in boiler-feed water.**—See B., 1936, 911.

**[Detection of] nitrous and nitric acids in drinking water.**—See B., 1936, 957.

**Determination of nitrites in presence of nitrates and of certain organic substances.**—See B., 1936, 985.

**Benzidine phosphomolybdate and its use for the colorimetric determination of phosphoric acid.** H. ETIENNE (*Bull. Soc. chim. Belg.*, 1936, 45, 516—538).—Benzidine phosphomolybdate has the formula  $3\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot 2\text{H}_3\text{PO}_4 \cdot 24\text{MoO}_3 \cdot 22\text{H}_2\text{O}$ . The P is pptd. in this form in HCl solution and the ppt. is dissolved by heating with 2% aq.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ . The resulting blue solution is matched against standards prepared from pure phosphomolybdic acid by treating with aq.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ . 0.2—1.5 mg. of P per 100 c.c. may be determined. As does not interfere. Details are given for the determination of P in cast Fe, steel, minerals, red Cu, and bronze.

H. J. E.

**Modifications of the Gutzeit method for determination of arsenic.** H. F. CROSSLEY (*J.S.C.I.*, 1936, 55, 272—276T).—The Gutzeit apparatus is modified by the provision of a water cooling-jacket around the staining chamber and a suitable stand to ensure rigidity. Optimum conditions have been determined.



Rapid colorimetric determination of silicon in steel.—See B., 1936, 994.

Volumetric determination of potassium by the sodium cobaltinitrite method. K. SUZUKI and M. KENJO (Rept. Govt. Sugar Exp. Sta., Formosa, 1935, No. 2, 45—55; Internat. Sugar J., 1936, 38, 270).—A modification of the Jendrassik and Takacs method (cf. A., 1935, 134) is described; the cobaltinitrite ppt. separated by centrifuging is dissolved in  $\text{H}_2\text{SO}_4$ , treated with dil. aq.  $\text{KMnO}_4$ , KI added, and the liberated I titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ . J. P. O.

Determination of sodium in high aluminous material. H. V. CHURCHILL, R. W. BRIDGES, and A. L. MILLER (Ind. Eng. Chem. [Anal.], 1936, 8, 348—349).—Modified procedure, using  $\text{NH}_4\text{F}$  as fusion reagent, is described. E. S. H.

Rapid evaluation of sodium silicate.—See B., 1936, 931.

Sensitiveness of magnesium uranyl acetate reagent to sodium and potassium. C. H. GREENE (Ind. Eng. Chem. [Anal.], 1936, 8, 399—400).—The influence of the vol. ratio of reagent and test solutions and of the addition of EtOH has been investigated. E. S. H.

Determination of sodium and potassium in insoluble silicates. C. C. MILLER and F. TRAVES (J.C.S., 1936, 1390—1394).—The silicate is decomposed by the Lawrence Smith method. Na is pptd. as Na Zn uranyl acetate (cf. A., 1928, 859). Ca interferes, and double pptn. is necessary. K is determined as  $\text{KClO}_4$  after removal of Ca, Na, and  $\text{SO}_4^{2-}$ , preferably by preliminary pptn. of K Na cobaltinitrite, which is treated with  $\text{HClO}_4$ , and interfering perchlorates are extracted with  $\text{EtOAc}-\text{Bu}^\circ\text{OH}$ . A. J. E. W.

Quantitative separation of lithium, with reference to its determination in insoluble silicates. C. C. MILLER and F. TRAVES (J.C.S., 1936, 1395—1399).—Li may be determined as Li Zn uranyl acetate,  $\text{LiZn}(\text{UO}_2)_3(\text{OAc})_9 \cdot 6\text{H}_2\text{O}$ . Conditions for complete pptn. are crit. Na interferes, and is removed by extracting  $\text{LiCl}$  and  $\text{CaCl}_2$  from the mixed anhyd. chlorides with isoamyl alcohol or  $\text{COMe}_2$ ; with the former double pptn. is advisable, owing to interference of Ca when present in large quantity. A procedure is given for the determination of Na, K, and Li in silicates (cf. preceding abstract). A. J. E. W.

Qualitative analysis of the alkaline-earth and alkali groups. C. H. GREENE (Ind. Eng. Chem. [Anal.], 1936, 8, 346—348).—A system suitable for laboratory classes is described. E. S. H.

Test-tube flame test applied to the rarer elements. A. R. CLARK (J. Chem. Educ., 1936, 13, 383—384; cf. A., 1935, 1093).—Characteristic flames or residues given by Li, Rb, Cs, Au, Be, B, Sc, In, Tl, Ti, Zr, Ge, Mo, U, Se, and Te are described and sensitivities recorded. The method is especially applicable to a final identification after the usual group separations. L. S. T.

Determining hardness of water.—See B., 1936, 1022.

Qualitative analysis of the ammonia and ammonium sulphide groups and of phosphoric acid. W. FISCHER, W. DIETZ, K. BRUNGER, and H. GRIENEISEN (Angew. Chem., 1936, 49, 719—731).—An excess of Fe is added, and then aq.  $\text{NH}_3$ . The ppt. is dissolved in  $\text{HCl}$ , Fe is extracted with  $\text{Et}_2\text{O}$ , and Zr, Ti, La, and any co-pptd. Zn, Mn, Co, Ni, Ca, etc. are then pptd. with  $\text{NaOH}+\text{H}_2\text{O}_2$ . Cr, V, and U are pptd. by treating the filtrate with  $\text{HCl}$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ , and  $\text{NaOH}$  successively. P and W are pptd. from the remaining solution by means of  $\text{BaCl}_2$ . Subsequent separations of the sub-groups so obtained follow usual lines. The scheme is expeditious and minimises the loss by adsorption on earlier ppts. of elements present in small amounts. J. S. A.

Analysis of cations of third and second [fourth] groups in presence of phosphate ion. V. J. PETRASCHENJ (Z. anal. Chem., 1936, 106, 241—243).—After pptn. of the second analytical group,  $(\text{NH}_4)_2\text{S}$  and  $(\text{NH}_4)_2\text{HPO}_4$  are added. The ppt. is redissolved in dil.  $\text{HCl}$ , and Cr and Mn are oxidised completely either by  $\text{Na}_2\text{CO}_3+\text{Br}-\text{H}_2\text{O}$ , or by  $\text{Na}_2\text{O}_2$ . The ppt. is treated with  $\text{AcOH}$  to dissolve Mg, Ca, Sr, and Ba. Subsequent separations are orthodox. J. S. A.

Spectrographic micro-determination of zinc. A. P. VANSELOW (Ind. Eng. Chem. [Anal.], 1936, 8, 400).—A correction (cf. this vol., 1308). E. S. H.

Electrolytic micro-determination of zinc and its application to brass. P. WENGER, C. CIMERMAN, and G. TSCHANUN. Volumetric micro-determination of zinc. C. CIMERMAN and P. WENGER (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 113—116, 116—119).—Practical details are described; calc. and experimental results are in agreement. N. M. B.

Preparation and some analytical applications of 2:7-diaminofluorine. E. L. NINO and F. CALVERT (Anal. Fis. Quím., 1934, 32, 698—701).—An improvement of the technique of Schmidt *et al.* (A., 1931, 1045) is described. The use of 2:7-diaminofluorene (I) is preferred to  $\text{H}_2\text{S}$  for detection of Cd after removal of Cu by means of  $\text{KCNS}$ . In a solution containing 0.2—0.6% of Zn with added EtOH the Zn is determined by addition of (I) in EtOH; the ppt. is dried at  $90^\circ$ . The error is  $>1$  part in 1000. (I) is suitable for the detection of blood peroxidases (cf. Schmidt *et al.*, A., 1932, 242) but not for determination of Zn in presence of Al or of Cd or Cu. F. R. G.

Cause of contamination of precipitates. II. Precipitation processes involving lead salts. Z. KARAOGLANOV (Z. anal. Chem., 1936, 106, 262—272; cf. this vol., 1220).—Further data for Pb salts are reviewed, and advanced in support of the author's theory of contamination by secondary reaction products. The known compounds  $\text{Pb}(\text{OH})\text{X}$  ( $\text{X}=\text{Cl}$ , Br, I, CNS) are considered to be such secondary products. Their formation involves the partly ionised complexes  $\text{PbX}^+$  and the degree of contamination follows the extent to which such complexes are present in solution; e.g., contamination with  $\text{PbBr}_2 > \text{PbCl}_2 > \text{Pb}(\text{CNS})_2 > \text{PbI}_2 > \text{Pb}(\text{OAc})_2 = 0$ . J. S. A.

**Determination of metallic copper in cuprous oxide-cupric oxide mixtures.** L. C. HURD and A. R. CLARK (Ind. Eng. Chem. [Anal.], 1936, 8, 380—382).— $\text{Cu}_2\text{O}$  is sol. in cold aq.  $\text{NH}_3$ ,  $\text{CuO}$  is slightly sol., and  $\text{Cu}$  insol. Addition of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  causes reduction of any  $\text{Cu}^{++}$  entering the solution and prevents reaction between  $\text{Cu}^{++}$  and  $\text{Cu}$ . In a  $\text{CO}_2$  atm. the  $\text{Cu-CuO}$  mixture may be isolated and  $\text{Cu}$  determined by direct dissolution in  $\text{FeCl}_3 + \text{HCl}$ , followed by titration with  $\text{K}_2\text{Cr}_2\text{O}_7$ . E. S. H.

**Electrolytic application of hydrobromic acid test for copper.** G. W. BAKER (Analyst, 1936, 61, 603—604).—0.0002 mg. of  $\text{Cu}$  per sq. mm. on a steel surface may be detected by using the steel as anode, with a Pt wire cathode tipped with cotton-wool which is moistened with aq.  $\text{KBr}$ . Traces of  $\text{Cu}$  produce a purple-red stain. J. S. A.

**Determination of mercury in air and absorption of mercury vapour by means of metallic gold.** V. MAJER (Coll. Czech. Chem. Comm., 1936, 8, 339—348).—Air is passed at a known rate through glass tubing containing Au leaf. One end of the tubing is then sealed and the other drawn out into a fine capillary. On distilling, the  $\text{Hg}$  condenses in the capillary and is dissolved in  $\text{Cl}_2\text{-H}_2\text{O}$  and either determined colorimetrically or reprecipitated on Fe wire, redistilled in a fine capillary, and determined microscopically. The determination of  $\text{Hg}$  by condensing in liquid air has also been investigated. C. R. H.

**Effect of aluminium on the flame spectra of the alkaline earths. Determination of aluminium.** R. L. MITCHELL and I. M. ROBERTSON (J.S.C.I., 1936, 55, 269—272).—The presence of Al reduces the intensity of the flame emission lines of Ca and Sr. This reduction depends on the relative amounts of Ca and Sr present; with sufficient Sr in the solution, Al does not appreciably affect the Ca emission and *vice versa*. The Ca or Sr depression may be used as an indication of the amount of Al present.

**Separation and determination of aluminium and zinc.** F. H. FISHER and J. M. SMITH, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 349—350).—Al is pptd. as Li aluminate from solutions containing  $\text{NH}_4\text{OAc}$ ; Zn is determined in the filtrate as  $\text{Zn}_2\text{P}_2\text{O}_7$ . E. S. H.

**Arc spectrographic determination of indium in minerals, and association of indium with tin and silver.** F. M. BREWER and E. BAKER (J.C.S., 1936, 1286—1290).—Known sources of In are reviewed. The In content of certain Sn, Sb, Ag, Zn, Mn, and Fe minerals, and of specimens of Sn, Cd, and  $\text{CdO}$ , has been determined spectrographically by the persistence method. Sn ores, particularly sulphides (cylindrite, 0.1—1% In; franckeite, max. 0.1% In), and commercial Sn contained appreciable quantities of In, suggesting a fairly general association of In with Sn. Association in other cases is more sp. Some chalcocopyrite samples contained an estimated max. of 0.1% In. A. J. E. W.

**Chemical concentration of gallium, indium, thallium, germanium, and rhenium, in their determination in oxide and sulphide ores.**—See B., 1936, 931.

**Determination of ferrocyanide ion by means of luteocobaltamine chloride.** W. A. HYNES, M. G. MALKO, and L. K. YANOWSKI (Ind. Eng. Chem. [Anal.], 1936, 8, 356—357).— $\text{Fe}(\text{CN})_6^{4-}$  is determined by igniting the pptd.  $[\text{Co}(\text{NH}_3)_6]_4[\text{Fe}(\text{CN})_6]_3$  and weighing the residue as  $8\text{Co}_3\text{O}_4 + 9\text{Fe}_2\text{O}_3$ . The procedure is suitable in absence of  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{VO}_3^-$ . E. S. H.

**Macro-detection of cobalt.** I. F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 239—244).—1 part of Co in presence of 1000 parts of Fe may be detected as  $(\text{NH}_4)_2\text{Co}(\text{CNS})_4$ , which may be extracted with  $\text{C}_5\text{H}_5 \cdot \text{OH} + \text{Et}_2\text{O}$ , by adding  $\text{NaNH}_4\text{HPO}_4$  until the  $\text{Fe}(\text{CNS})_3$  coloration is destroyed. Decolorisation with  $\text{KHF}_2 + \text{aq. NH}_3$  is applicable, but less sensitive. J. S. A.

**Oxidation-reduction indicators for use with dichromate.** II. S. COHEN [with R. E. OESPER] (Ind. Eng. Chem. [Anal.], 1936, 8, 364—365).—The prep. and use as indicators of  $\text{NHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ ,  $\text{NHPh} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_3\text{Na}$ , and Na diphenylbenzidine-monosulphonate are described. E. S. H.

**Determination of chromium, vanadium, and molybdenum in silicate rocks.** E. B. SANDELL (Ind. Eng. Chem. [Anal.], 1936, 8, 336—341).—After decomp. of the rock with  $\text{Na}_2\text{CO}_3$  in the usual way, V is determined with phosphotungstic acid after separation from Cr with 8-hydroxyquinoline (I). In neutral or slightly acid solutions,  $\text{V}^{5+}$  reacts with (I) to give a compound which can be extracted from the aq. solution with  $\text{CHCl}_3$ , whereas  $\text{Cr}^{VI}$  does not react and remains in the aq. layer. Diphenylcarbazide is used as the reagent for Cr, after separation from V. Mo is determined by the  $\text{SnCl}_2\text{-KCNS-Et}_2\text{O}$  procedure without previous separation. The method is suitable for determining 0.001% of Cr or V, and 0.0001% of Mo in a 1-g. sample. E. S. H.

**Determination of chromium and iron in tanning solutions and in leather.**—See B., 1936, 948.

**Reducing action of mercury. II. Stability of quinquevalent molybdenum solutions. Determination of molybdenum by reduction with mercury and titration with ceric sulphate.** N. H. FURMAN and W. M. MURRAY, jun. (J. Amer. Chem. Soc., 1936, 58, 1689—1692; cf. this vol., 574).— $\text{Mo}^V$  solutions are sufficiently stable in air at room temp. to be used in analytical procedures which are completed in a few hr.  $\text{Mo}^{VI}$  is quantitatively reduced to  $\text{Mo}^V$  by shaking with Hg in presence of 2—3.5N-HCl.  $\text{Mo}^V$  can be titrated with  $\text{Ce}(\text{SO}_4)_2$  at room temp., using the o-phenanthroline- $\text{Fe}^{2+}$  complex indicator. E. S. H.

**Precipitation of uranium, and its separation from alkaline-earth metals by means of pyridine.** E. A. OSTROUMOV (Z. anal. Chem., 1936, 106, 244—248).— $\text{C}_5\text{H}_5\text{N}$  ppts. U quantitatively as  $\text{H}_2\text{UO}_7$  from solutions of  $\text{UO}_2^{2+}$  salts. The presence of  $\text{NH}_4$  salts is advantageous; in presence of much  $\text{SO}_4^{2-}$  a large excess of  $\text{C}_5\text{H}_5\text{N}$  is necessary. Separation from Ca, Sr, and Ba is quant. J. S. A.

**Use of nitrophenylarsinic acid as a reagent for tin.** B. TOUGARINOFF (Bull. Soc. chim. Belg., 1936, 45, 542—544).— $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$  (0.8% aq. solu-



tion) gives a white flocculent ppt. with  $\text{Sn}^{\text{IV}}$  in  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  solution on boiling. 0.0001 g. of  $\text{Sn}$  may be detected in 20 c.c. of solution.  $\text{Hg}^{\text{II}}$ ,  $\text{Cu}$ ,  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Mn}$ ,  $\text{Fe}$ ,  $\text{Cr}$ ,  $\text{Zn}$ ,  $\text{Ba}$ ,  $\text{Sr}$ ,  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{Bi}$ , and  $\text{Sb}$  do not interfere. H. J. E.

**Colorimetric determination of titanium.** M. SCHENK (Helv. Chim. Acta, 1936, 19, 1127—1135).—Substances containing a phenolic OH give with  $\text{Ti}^{\text{IV}}$  in conc.  $\text{H}_2\text{SO}_4$  in intense red coloration. The intensity decreases with time after 2 hr. The use of  $o\text{-OH-C}_6\text{H}_4\text{-CO}_2\text{H}$  permits the determination of  $\text{Ti}$  in solutions containing 0.2—40 mg. of  $\text{TiO}_2$  per litre. The reaction is not affected by other cations, but  $\text{HNO}_3$  and  $\text{HNO}_2$  must be absent. Operative details are given. F. L. U.

**Special reaction of N. A. Tananaev and A. V. Tananaeva for zirconium.** I. P. ALIMARIN (Z. anal. Chem., 1936, 106, 276—279).—The reaction, in a more sensitive form, was described by Lundell and Knowles (A., 1920, ii, 60). J. S. A.

**Detection of minute quantities of thorium in common materials.** R. D. EVANS, G. D. FINNEY, A. F. KIP, and R. MUGELE (Physical Rev., 1935, [ii], 47, 791—792).—The Th emanation flow-technique is inherently inefficient. Four new methods involving counting of  $\alpha$ - or  $\gamma$ -rays have been developed. Applied to a series of Sierra Nevada igneous intrusive rocks they indicate that the  $\text{Th}:\text{U}$  ratio is  $>$  previously supposed. L. S. T.

**Determination of bismuth as phosphate.** W. C. BLASDALE and W. C. PARLE (Ind. Eng. Chem. [Anal.], 1936, 8, 352—353).—The procedure is accurate when pptn. is from solutions which contain no  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , and are approx. 0.2M with respect to  $\text{HNO}_3$ , and approx. 0.065M with respect to  $(\text{NH}_4)_2\text{HPO}_4$ .  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Ca}^{2+}$  do not interfere;  $\text{Cd}^{2+}$  and especially  $\text{Pb}^{2+}$  interfere. Co-pptn. of basic salts is avoided by adjusting  $[\text{H}^+]$  and pptg. from a hot solution and digesting for 1 hr. at  $80^\circ$ . E. S. H.

**Separation and determination of bismuth with gallic acid.** L. KIEFT and G. C. CHANDLEE (Ind. Eng. Chem. [Anal.], 1936, 8, 392).—Pptn. with gallic acid at  $70^\circ$  serves to separate and determine  $\text{Bi}$  in 3% aq.  $\text{HNO}_3$  in presence of  $\text{Pb}$ ,  $\text{Cd}$ ,  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Al}$ ,  $\text{Cr}$ ,  $\text{Fe}$ ,  $\text{Ni}$ ,  $\text{Ba}$ ,  $\text{Ca}$ ,  $\text{Na}$ , and  $\text{K}$ , but not  $\text{Sb}$ ,  $\text{Hg}$ ,  $\text{Sn}$ , or  $\text{Ag}$ . E. S. H.

**Analytical chemistry of tantalum, niobium, and their mineral associates.** XXXII. Phosphorus, vanadium, and a tannin precipitation series. W. R. SCHOELLER and H. W. WEBB (Analyst, 1936, 61, 585—590).—(a) Small amounts of  $\text{P}$ , carried down with  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  on tartaric hydrolysis, are separated by fusion with  $\text{NaOH}$  followed by extraction with aq.  $\text{NaCl}$ .  $\text{Na}_3\text{PO}_4$ , but no  $\text{Ta}$  or  $\text{Nb}$ , dissolves. (b)  $\text{V}$  may be separated from  $\text{Ti}$  and  $\text{Ta}$  by twofold pptn. with tannin (I) from  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution half-saturated with  $\text{NH}_4\text{Cl}$ .  $\text{Ti}$  and  $\text{Ta}$  are first pptd. by (I);  $\text{V}$  only on addition of excess of  $\text{NH}_3$ . Pptn. of  $\text{Nb}$  does not occur, or is incomplete.  $\text{V}$  is separated from  $\text{Ta}$  and  $\text{Nb}$  in tartrate solution, by addition of (I)+ $\text{NH}_4\text{OAc}$  to the neutralised  $(\text{NH}_3)$  filtrate from the tartaric hydrolysis of  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ . The ppt. is fused with  $\text{KHSO}_4$ , extracted

with (I)+ $\text{H}_2\text{SO}_4$ , and repptd. by addition of cinchonine hydrochloride.  $\text{V}$  in the filtrate is pptd. on adding  $\text{NH}_4\text{OAc}$ . (c) Pptn. by (I), in decreasing acidity of solution, follows the order  $\text{Ta}$ ,  $\text{Ti}$ ,  $\text{Nb}$ ,  $\text{V}$ ,  $\text{Fe}$ ,  $\text{Zr}$ ,  $\text{Hf}$ ,  $\text{Th}$ ,  $\text{U}$ ,  $\text{Al}$ . Neighbouring metals cannot be separated by fractional pptn. with (I).

J. S. A.

**Determination of iridium by titration with potassium ferrocyanide.** A. A. GRUNBERG and J. L. MICHELIS (Compt. rend. Acad. Sci. U.R.S.S., 1936, 2, 179—181).—By titration in  $\text{H}_2\text{SO}_4$  solution,  $\text{Ir}^{\text{IV}}$  in the form of  $(\text{IrCl}_6)^-$  can be determined with as great accuracy as by Mohr's salt. W. R. A.

**Portable aradiant convection pyrometer.** F. T. BARR and R. F. BERGER (Ind. Eng. Chem. [Anal.], 1936, 8, 393—395).—Apparatus and technique are described. E. S. H.

**Sensitive thermo-regulator.** L. D. GOODHUE (Ind. Eng. Chem. [Anal.], 1936, 8, 387).—Sensitivity is increased by employing the principle of the differential manometer. A range of  $0.05^\circ$  is sufficient to make and break the electrical contact. E. S. H.

**Platinum resistance thermometer as a secondary temperature standard between  $14^\circ$  and  $90^\circ$  abs.** F. HENNING and J. OTTO (Physikal. Z., 1936, 37, 639—641).—For the calibration of a Pt resistance thermometer, five fixed points are required, according to the equation previously derived (this vol., 1190). Suitable points are the normal b.p. of  $\text{O}_2$ , the triple point of  $\text{H}_2$ , the normal b.p. of  $\text{H}_2$ , the triple point of  $\text{N}_2$ , and the  $\beta$ - $\gamma$  transition point of  $\text{O}_2$ . The comparison of the resistance ratios of different Pt thermometers with each other is considered. A. J. M.

**Gas furnace with temperature control.** D. VAN DUYN (Chem. Weekblad, 1936, 33, 562).—The inner tube of a van den Berg furnace (A., 1934, 162) is enclosed in a brass tube provided with a hole for carrying a thermocouple. Uniform temp. from  $500^\circ$  to  $800^\circ$  can be obtained. S. C.

**Determination of thermal expansion of liquids when observation is hindered by the temperature bath.** A. LAMBERTZ (Chem.-Ztg., 1936, 60, 755—756).—An Archimedean method is described, the change in apparent wt. of a submerged glass body being determined. J. S. A.

**Limiting sensitivity of a radiometer depending on the principle of the gas thermometer.** M. VEINGEROV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 119—122).—A radiometer operating by the thermal expansion of gas heated by incident radiation is theoretically more sensitive than other types of instrument. A. J. E. W.

**S.N.P. Photo-densimeter [photometer].** A. FAURE and PALLU (Ann. Falsif., 1936, 29, 393—401). E. C. S.

**Christiansen filters as polarisers.** H. W. FARWELL (Physical Rev., 1936, [ii], 50, 486).—Fibres of viscose and silk, wound on a frame, were used as doubly refracting crystals, and, immersed in  $\text{CS}_2$ - $\text{C}_6\text{H}_6$ , transmitted green polarised light horizontally and blue polarised perpendicularly. N. M. B.

**Frames for protecting and repairing Lovibond colour glasses.** E. FREYER (Oil and Soap, 1936, 13, 234—235).—Whole or broken glasses are mounted in light Al slide-holders, with a central window.

E. L.

**Simplified and improved cell for liquids in the interferometer.** J. W. McBAIN, T. F. FORD, and G. F. MILLS (Rev. Sci. Instr., 1936, [ii], 7, 341—342).—The cell is of block Ag, bored with two tunnels to contain the liquid and carry the light rays; it is suitable for small quantities of liquid, and evaporation difficulties are obviated.

N. M. B.

**[Quantitative] spectrum analysis using emission spectra.** J. E. MILLS (J. Proc. Austral. Chem. Inst., 1936, 3, 245—250).—The technique of the Gerlach internal standard method is described.

J. S. A.

**Apparatus for rapid study of absorption and rotatory power in the ultra-violet.** P. GESTEAU (J. Pharm. Chim., 1936, 24, [viii], 201—209).—An ultra-violet spectrograph with polariser attachments is described. It may be employed either for quant. absorption measurements or for determination of  $\alpha$ .

W. O. K.

**Anomalous diffraction gratings.** U. FANO (Physical Rev., 1936, [ii], 50, 573; cf. Wood, this vol., 128; Strong, *ibid.*, 399).—Theoretical.

N. M. B.

**Method for accurate titrations.** D. B. PALL (Canad. J. Res., 1936, 14, B, 299—300).—A colour comparator is described in which the two tubes on the one side contain  $H_2O$  and the coloured solution undergoing titration, respectively, whilst those on the other side contain a solution buffered to the required endpoint  $p_H$  and the indicator, and the original solution, without indicator, respectively. The light used is filtered to the colour of the indicator in the buffered tube. The apparatus is of particular use in titration of weak acids with weak bases in coloured solutions.

J. W. S.

**$\gamma$ -Ray sensitivity of tube counters and the measurement of the thorium content of rocks.** R. D. EVANS and R. A. MUGELE (Physical Rev., 1935, [ii], 47, 427).—Factors affecting sensitivity are discussed. The feeble  $\gamma$ -radiation from the radioactive impurities in ordinary granitic rocks can be directly measured with the highly-sensitised counters described.

L. S. T.

**Counter-controlled cloud chambers.** J. C. STREET and E. C. STEVENSON (Rev. Sci. Instr., 1936, [ii], 7, 347—353).—The design and operation of two cloud chambers of the pneumatic rubber diaphragm type are described. One is cylindrical for use with a large electromagnet, and the other is a rectangular one of wood for cosmic-ray shower studies. The expansion ratio is determined by the separation of rigid diaphragm stops.

N. M. B.

**Check valve for wash bottles.** F. H. SMITH (Ind. Eng. Chem. [Anal.], 1936, 8, 400).

E. S. H.

**Gas-absorption vessels.** W. M. MARTIN (Ind. Eng. Chem. [Anal.], 1936, 8, 395—396).—A scrubber and a quant. absorption vessel are described.

E. S. H.

**Spindle for insulating wires.** J. M. STURTEVANT (Ind. Eng. Chem. [Anal.], 1936, 8, 341).

E. S. H.

**Apparatus for production of metallic adsorption powders under nitrogen and other gases.** F. DURAU (Physikal. Z., 1936, 37, 684—688).—An apparatus for the prep. of powders of hard or soft metals for adsorption and catalysis is described.

A. J. M.

**Sensitive manostat for low pressures and its application to the adsorption of hydrogen and deuterium on copper.** T. SOLLER, S. GOLDWASSER, and R. A. BEEBE (J. Amer. Chem. Soc., 1936, 58, 1703—1706).—Apparatus for the control of gas pressures to  $\pm 0.005$  mm. at any pressure is described. Provision is made for the continuous reading of the vol. of gas entering the system during adsorption. The rates of adsorption of  $H_2$  and  $D_2$  by Cu at  $0^\circ$  and 2.63 mm. are in the ratio 3.35 : 1; the difference in activation energies of adsorption is 0.48 kg.-cal. The temp. inversion in the ratio of adsorbability of  $H_2$  and  $D_2$  has been confirmed.

E. S. H.

**Apparatus for dialysis, electrodialysis, osmosis, electro-osmosis, filtration, and electro-filtration.** MEMBRANFILTER G.M.B.H. (Chem.-Ztg., 1936, 60, 767).

E. C. S.

**Pneumatic trough.** W. H. POWERS and J. WACLAWIK (J. Chem. Educ., 1936, 13, 375).

L. S. T.

**Vacuum centrifuge.** E. G. PICKELS (Physical Rev., 1935, [ii], 47, 797).—Developments and improvements are outlined (cf. *ibid.*, 336).

L. S. T.

**Centrifuging in rotating hollow cylinders.** M. SCHLESINGER (Nature, 1936, 138, 549—550).—A new technique for the fractionation of highly disperse systems using relatively moderate centrifugal forces is described.

L. S. T.

**Hardness tester for microscopical objects.** E. M. H. LIPS and J. SACK (Nature, 1936, 138, 328—329).—Inclusions and structural elements of metallographic specimens may be identified by measurement of their hardness. A hardness tester attached to a microscope is described, and its use is illustrated by reference to a Cu-Al alloy and pearlitic cast Fe containing P.

L. S. T.

**[Small] hydrogen sulphide generator.** E. GLASGOW (J. Chem. Educ., 1936, 13, 382).

L. S. T.

**Action of fume-chambers.** E. BREZINA, W. SCHMIDT, and W. SCHWABL (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 171—178).—Observations of the behaviour of fumes in different models of fume-chambers indicate the design necessary for max. efficiency.

M. A. B.

**Approach towards the limit in the process of extraction.** C. W. GRIFFIN and M. VON SAAFF (Ind. Eng. Chem. [Anal.], 1936, 8, 358—360).—Experimental data for the extraction of solutes from one solvent by another solvent are in agreement with theoretical predictions (cf. B., 1934, 223).

E. S. H.

**Special head for Kjeldahl distillation apparatus.** C. E. WEAKLEY, jun. (Ind. Eng. Chem. [Anal.], 1936, 8, 367).

E. S. H.



Origin of modern chemical symbols and formulæ. J. R. PARTINGTON (Chem. and Ind., 1936, 759—762).

Saint Vincent de Paul and the alchemist. F. WALKER (J. Chem. Educ., 1936, 13, 353—357).  
L. S. T.

Joan Baptista van Helmont. J. R. PARTINGTON. Val Helmont's ice and water experiments. T. S. PATTERSON (Ann. Sci., 1936, 1, 359—384, 462—467).—Historical.

Natural classification of chemical substances. R. HOOYKAAS (Chem. Weekblad, 1936, 33, 599—610).—A lecture.

## Geochemistry.

Atmospheres of the fixed stars. H. LAMBRECHT and B. JUNG (Naturwiss., 1936, 24, 577—582).—A review.  
A. J. M.

Composition of the planetary nebulae. T. L. PAGE (Nature, 1936, 138, 503—504).—Relative abundances of N, O, A, Ne, and S in N.G.C. 7662 and N.G.C. 7027 have been calc. The high abundances of Ne and A relative to O are discussed.  
L. S. T.

Oxygen content of the stratosphere. E. REGENER (Nature, 1936, 138, 544).—The vol.-% of O<sub>2</sub> decreases from 20.89±0.05 at 14.5 km. to 20.39±0.05 at 28—29 km.  
L. S. T.

Ozone as a heating factor in the atmosphere. R. PENNDORF (Nature, 1936, 138, 247).—The heating effect due to O<sub>3</sub> is calc. for various atm. layers. A max. occurs at a height of 50 km. where the heating is approx. 10 times the cooling effect.  
L. S. T.

Size of atmospheric nuclei: deductions from measurements of the number of charged and uncharged nuclei at Kew observatory. H. L. WRIGHT (Proc. Physical Soc., 1936, 48, 675—689).—Formulae are discussed for determining the size of condensation nuclei from observation of the concn. in the atm. of charged and uncharged nuclei and of the no. of small ions of either sign, assuming combination by collision between small ions and uncharged nuclei to be the result of Brownian movement of the former. Assuming that the mass of a small ion is equal to that of 11 H<sub>2</sub>O mols., for R.H. <80% the nuclear radius is approx. 3×10<sup>-6</sup> cm., rising to 4.5×10<sup>-6</sup> cm. for 89% R.H. On Kohler's theory of the growth of nuclei in an atm. of increasing R.H., and if the hygroscopic nuclei are of dil. H<sub>2</sub>SO<sub>4</sub>, the mass of acid in a nucleus in summer is about 18×10<sup>-17</sup> g., and in winter 12×10<sup>-17</sup> g.  
N. M. B.

Mineral and medicinal springs of Switzerland. ANON. (Mitt. Lebensm. Hyg., 1936, 27, 49—104, 158—159, 201—203).—Analyses and physical data are recorded.

Surface waters and deep waters in the canton of Geneva. J. BUFFLE (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 129—132; cf. A., 1935, 600).—Mean vals. of the dissolved matter, alkalinity, CaO, and SO<sub>3</sub> of H<sub>2</sub>O from wells in different localities and over intervals of 4—27 years are given and discussed.  
N. M. B.

Petrographic nomenclature. A. K. WELLS (Geol. Mag., 1936, 73, 319—325).—Recommendations made by the British Association Committee, 1932, are summarised.  
L. S. T.

Geologic deductions from a thermal equation. J. S. DELURY (J. Geol., 1936, 44, 479—495).—A thermal source is indicated for the energy of earth distortion and deformation of the outer lithosphere. Heat is effective for these purposes in direct proportion to the unevenness of its distribution. Radioactive elements, which are regarded as the most important source of heat in outer shells, migrate extensively in geologic time through erosion and movements of magma. Small differences in thermal conductivity and in distribution of radioactive elements lead to large differences in geothermal history.  
L. S. T.

Contrasted differentiation. A. HOLMES (Geol. Mag., 1936, 73, 228—238).—Critical (cf. Nockolds, *ibid.*, 1934, 71, 31).  
L. S. T.

Differentiated dyke of Newmains, Dumfriesshire, and its contact and contamination phenomena. W. Q. KENNEDY and H. H. READ (Quart. J. Geol. Soc., 1936, 92, 116—145).—In the granophyric spessartite or markfieldite dyke at Newmains the crystallisation of quartz arises from the breaking-up of plagioclase into albite, epidote, and white mica at a late stage in the consolidation history of the rock. Normal markfieldite is differentiated into basic markfieldite and markfieldite-pegmatite by fractional crystallisation and filter-pressing effect. The junctions of the normal markfieldite against the country rock, a calcareous greywacke, are sharp. Where the markfieldite-pegmatite is in contact with the greywacke, contamination has occurred. This involves a reciprocal reaction whereby the markfieldite-pegmatite loses Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O, and gains Fe, MgO, and CaO. The chemistry of the contamination process and its influence on the course of mafic crystallisation are discussed. Analyses of the rocks concerned are recorded.  
L. S. T.

Progressive kinetic metamorphism in the Missi Series near Flinflon, Manitoba. J. W. AMBROSE (Amer. J. Sci., 1936, [v], 32, 257—286).—Pre-Cambrian greywackes and conglomerates show three zones of progressive metamorphism characterised respectively by chlorite, biotite, and garnet. Intruded igneous rocks in the series are also affected in a like degree. These zones are related to the intensity of shearing of the rocks, and it is suggested that the heat developed by this shearing was sufficient to cause the metamorphism.  
L. J. S.

Minerals in Bates limestone, Lewiston, Maine. L. W. FISHER (Amer. Min., 1936, 21, 321—326).—Igneous intrusions of different types are described. The mineral associations observed in different zones

suggest that the Bates limestone was originally an impure  $\text{MgCO}_3$  formation. Mineralogical changes produced by various types of metamorphism are described. L. S.-T.

**Bore-hole investigations in Yellowstone Park.** C. N. FENNER (J. Geol., 1936, 44, 225—315).—The structural features of the cores have been examined and temp. and pressures measured. The mineralogy and petrology of cores from various depths are described in detail, and chemical changes which have occurred are discussed. New analyses are recorded. L. S. T.

**Geology of a portion of the Savant Lake area, Ontario.** G. RITTENHOUSE (J. Geol., 1936, 44, 451—478).—The genesis of two Fe-bearing formations is discussed. L. S. T.

**Optics and structure of three-dimensional spherulites.** H. W. MORSE and J. D. H. DONNAY (Amer. Min., 1936, 21, 391—426).—The shape and optical properties of artificial spherulites and related aggregates, mainly carbonates, grown by diffusion and metathesis in gelatin have been further investigated (cf. A., 1933, 691). In spite of wide variations in external shape, most of these aggregates belong to the same type of aggregation, due to radiating crystallisation. A mechanism of formation of spherulitic structures is discussed. L. S. T.

(A) Nature of the invisible gold contained in pyrites. (B) Secondary transformations and enrichment of gold in its primary deposits. G. BÜRG (Z. pr. Geol., 1935, 43, 17—26, 65—75, 89—94; Chem. Zentr., 1935, ii, 3897).—(A) The solubility of Au in the system Fe-S decreases as the S content is decreased. On heating the Au enters the pyrites lattice. At 1 atm. the Au-S compounds formed are stable up to 200°. At higher pressures they are stable to 600°. H. J. E.

**Microstructures and metallisation of the gold-quartz veins of Cornucopia, Oregon.** G. E. GOODSPEED (Econ. Geol., 1936, 31, 398—416). L. S. T.

**Quartz from Bavena.** P. GALLITELLI (Period. Min., 1935, 6, 105—128; Chem. Zentr., 1935, ii, 3896).—Data are given of the characteristic habit of quartz from Bavena. It is concluded that the quartz was formed at <575°, and separated before the minerals of the pneumatolytic phase. J. S. A.

**Relation of the granite-gneiss and the schists and quartzites in W. Africa.** P. LEGOUX (Compt. rend., 1936, 202, 2090—2092).—A discussion. H. J. E.

**Minerals of Bavena granite: fayalite.** E. GRILL (Period. Min., 1935, 6, 129—133; Chem. Zentr., 1935, ii, 3896).—Inclusions are identified as partly oxidised fayalite. J. S. A.

**Epidotite from Acceglio (Valle Maira).** R. RONDOLINO (Period. Min., 1935, 6, 153—167; Chem. Zentr., 1935, ii, 3896). J. S. A.

**Copper deposits of the Southern Appalachian region.** C. N. FENNER (Econ. Geol., 1935, 30, 928—936).—A discussion of the views of Ross (U.S. Geol. Survey, Prof. Paper 179, 1935). L. S. T.

**Copper deposits of the Southern Appalachian region.** C. S. ROSS (Econ. Geol., 1936, 31, 428—432).—A reply to criticism (cf. preceding abstract). L. S. T.

**Supergene sphalerite, galena, and willemite at Balmat, N.Y.** J. S. BROWN (Econ. Geol., 1936, 31, 331—354).—The occurrence of willemite, chlorite, hæmatite, ilvaite, and magnetite, and of a second generation of sphalerite, galena, and chalcopyrite, believed to be of supergene origin, is described. L. S. T.

**Asbestos deposits of Thetford district, Quebec.** H. C. COOKE (Econ. Geol., 1936, 31, 355—376).—The geological setting of the deposits is outlined and the relation of the asbestos veins to faults is described. Theories of origin of the veins are discussed. L. S. T.

**Nodular, orbicular, and banded chromite in northern California.** W. D. JOHNSTON, jun. (Econ. Geol., 1936, 31, 417—427).—The minerals are described and analyses are given. The genetic significance of the structures is briefly discussed. L. S. T.

**Possible age of monazite from Mars Hill, N. Carolina.** J. P. MARBLE (Amer. Min., 1936, 21, 456—457).—The monazite crystal described by Schaller (A., 1934, 628) contains Pb 0.152—0.175, Th 5.526—5.596, and U 0.016—0.019%; approx. age  $584 \times 10^6$  years. L. S. T.

**Structure and chemical composition of greenalite.** J. W. GRUNER (Amer. Min., 1936, 21, 449—455).—The X-ray diagrams of greenalite (I) from the Fe formation of the Mesabi Range indicate that it is similar in structure to serpentine. The formula approximates to  $9\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 8\text{SiO}_2 \cdot \text{H}_2\text{O}$  or  $(\text{OH})_{12}\text{Fe}^{\text{II}}_9\text{Fe}^{\text{III}}_2\text{Si}_8\text{O}_{22} \cdot 2\text{H}_2\text{O}$ . The ratio  $\text{Fe}_2\text{O}_3 : \text{FeO}$  varies considerably and some MgO usually replaces FeO. (I) is actually anisotropic, but appears to be isotropic on account of its fineness of grain and dark colour. L. S. T.

**Crystallographic data, unit cell, and space-group for berthierite ( $\text{FeSb}_2\text{S}_4$ ).** M. J. BUEGER (Amer. Min., 1936, 21, 442—448; cf. *ibid.*, 205).—The Weissenberg method gives  $a$  11.44,  $b$  14.12,  $c$  3.76 Å; space-group  $Pnam$  ( $V_s^{10}$ ); 4  $\text{FeSb}_2\text{S}_4$  per unit cell. L. S. T.

**Two monzonitic series of the Newry complex.** D. L. REYNOLDS (Geol. Mag., 1936, 73, 337—364; cf. A., 1935, 1100).—Analyses and petrographic descriptions of olivine-monzonite and syenite are given. The two converging monzonitic series in the hybrids of Seeconnell, and their relationships, are established on a chemical basis. L. S. T.

**Enderbite, a new member of the charnockite series.** C. E. TILLEY (Geol. Mag., 1936, 73, 312—316).—The name *enderbite* is suggested for an acid member of the charnockite series characterised by rhombic pyroxene in which plagioclase (oligoclase or andesine) is the essential felspar. Enderbite from Proclamation Island, Enderby Land, Antarctica, has  $\text{SiO}_2$  75.50,  $\text{Al}_2\text{O}_3$  13.92,  $\text{Fe}_2\text{O}_3$  0.48,  $\text{FeO}$  1.17,  $\text{MgO}$  0.52,  $\text{CaO}$  3.54,  $\text{Na}_2\text{O}$  3.64,  $\text{K}_2\text{O}$  0.74,  $\text{P}_2\text{O}_5$  none,  $\text{TiO}_2$  0.08,  $\text{MnO}$  none,  $\text{H}_2\text{O}$ —0.30,  $\text{H}_2\text{O}+$  0.15, total 100.04%;  $d$  2.67. L. S. T.



**Origin of the Salton volcanic domes, Salton Sea, California.** V. C. KELLEY and J. L. SOSKE (J. Geol., 1936, 44, 496—509). L. S. T.

**Datolite and herderite.** H. STRUNZ (Z. Krist., 1936, 93, 146—150).—Herderite,  $\text{Ca}(\text{F},\text{OH})\text{BePO}_4$ , is monoclinic prismatic,  $a_0$  4.80,  $b_0$  7.68,  $c_0$  9.80 Å,  $\beta$  90° 6', space-group  $C_{2h}^2$ , and is thus isomorphous with the silicate datolite,  $\text{Ca}(\text{OH})\text{BSiO}_4$ . A probable structure is discussed. B. W. R.

**Analcite rock from Cloudy Bay, Marlborough, New Zealand** J. A. BARTRUM (New Zealand J. Sci. Tech., 1936, 18, 120—123).—The shapes of the abundant large crystals of analcite (I) in the tinguaita described indicate that earlier phenocrysts of nepheline had been replaced by (I) before the rock solidified. After the magma had been injected into fissures (I) crystallised conjointly with ægirine-augite from the aq. magma to form the felted matrix in which the phenocrystic minerals are embedded. A. G. P.

**Eulysites and related rock types from Loch Duich, Ross-shire.** C. E. TILLEY (Min. Mag., 1936, 24, 331—342).—Eulysite (a type not previously recognised in the British Isles) is a dense rock composed of fayalite, hedenbergite, iron-hypersthene, garnet, magnetite, and apatite. Chemical analyses are given of this and of related hedenbergite-garnet-magnetite-rock and grunerite-garnet-magnetite-rock. These rocks have probably been formed by the

metamorphism of sediments rich in Fe and  $\text{SiO}_2$ , i.e., siliceous Fe ores. L. J. S.

**Effects of heat on the optical orientation of plagioclase feldspars.** C. T. BARBER (Min. Mag., 1936, 24, 343—352).—Feldspars of different composition after heating at 1000° show no appreciable change in the optical orientation and the optic axial angle. L. J. S.

**Reciprocal rôle of alumina in reaction series.** A. BRAMMALL (Min. Mag., 1936, 24, 362—366).—The immiscibility gap in the clinoenstatite-diopside series is related to the (NaSi)–(CaAl) replacement in the plagioclase series, the rôle of Al atoms in the two series being reciprocal. L. J. S.

**Chlorophyll and hæmin derivatives in organic minerals.** A. TREIBS (Angew. Chem., 1936, 49, 682—686).—A review (cf. A., 1935, 727). F. O. H.

**Alterations of nitrogen content of organic substances during and after deposition.** K. KREJCI-GRAF (Z. pr. Geol., 1935, 43, 97—101; Chem. Zentr., 1935, ii, 3753).—The disappearance of N in sapropel corresponds with the conditions of decomp. in marine deposits. The ratio C:N affords no evidence of the age of sedimentary deposits. J. S. A.

**Selenium in Hawaii [soils] and its probable source in the United States.**—See B., 1936, 986.

**Selenium compounds in soils.**—See B., 1936, 1011.

## Organic Chemistry.

**Algebraic calculation of the numbers of isomerides of certain organic compounds.** G. POLYA (Z. Krist., 1936, 93, 415—443).—Mathematical. The "symmetry formula" for the basic substance is fundamental; from it by simple algebraic substitution the no. of possible isomerides of various types is directly derived. Formulæ are summarised for the chief org. series. B. W. R.

**Steric hindrance.** E. DE ROY VAN ZUYDEWIJN and J. STUURMAN (Chem. Weekblad, 1936, 33, 540—542).—From a theoretical discussion it is concluded that steric hindrance, although highly probable in some cases, is not yet proved. It is doubtful whether deceleration of a reaction by surrounding the functional group with substituents is purely a question of spatial configuration. S. C.

**Reactions of deuterium atoms with methane and ethane.**—See this vol., 1344.

**Dehydrogenating cracking of ethane.** P. FERRERO and E. DELTOMBE (Bull. Soc. chim. Belg., 1936, 45, 455—492).—The reaction was studied by a flow method at 700—1250°/0.1—1 atm. The main reaction is a decomp. into  $\text{C}_2\text{H}_4$  and  $\text{H}_2$ . The  $\text{C}_2\text{H}_4$  is a max. at 900—950° and the proportion formed increases with the rate of flow.  $\text{CH}_4$  is formed in a secondary reaction which entails Me radicals, and increases with rise in temp.  $\text{C}_2\text{H}_2$  is formed by decomp. of  $\text{C}_2\text{H}_4$  at >830°. Small amounts of liquid

products (max., approx. 25% of  $\text{C}_2\text{H}_6$  decomposed) were formed. These were polymerisation products derived from butadiene and  $\text{C}_2\text{H}_2$ , formed by the dehydrogenation of  $\text{C}_2\text{H}_4$ , and varied in composition between  $\text{C}_n\text{H}_{1-3n}$  and  $\text{C}_n\text{H}_{1-6n}$ . H. J. E.

**Action of ultra-violet light on halogenated hydrocarbons.** II. E. MULLER and K. EHRLMANN (Ber., 1936, 69, [B], 2207—2210; cf. A., 1932, 830).—Prolonged irradiation of  $(\cdot\text{CHCl}_2)_2$  with passage of dry  $\text{N}_2$  does not lead to elimination of HCl or other marked change. The production of  $\text{CHCl}_2\cdot\text{COCl}$  in presence of air (*loc. cit.*) therefore proceeds  $(\cdot\text{CHCl}_2)_2 \rightarrow \text{CHCl}_2\cdot\text{CCl}_2\cdot\text{OH} \rightarrow \text{CHCl}_2\cdot\text{COCl}$ . Under these conditions  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$  remain unchanged.  $(\cdot\text{CH}_2\text{Cl})_2$  does not appreciably absorb ultra-violet light, but is relatively greatly changed thereby in presence of air. The production of  $(\cdot\text{CCl}_2\cdot\text{CHCl}_2)_2$  is attributed to the action of excited O. No part is played by O in the conversion of  $\text{C}_2\text{H}_2\text{Cl}_4$  into  $\text{C}_2\text{HCl}_3$  by boiling alkali since a precisely similar effect is produced by boiling anhyd.  $\text{C}_5\text{H}_5\text{N}$ . Irradiation with light of short  $\lambda$  in presence of  $\text{O}_2$  converts  $(\cdot\text{CH}_2\text{Cl})_2$  into  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ ,  $\text{C}_2\text{HCl}_3$  smoothly into  $\text{CCl}_2\cdot\text{COCl}$ , and  $\text{C}_2\text{HCl}_3$  into  $\text{CHCl}_2\cdot\text{COCl}$  with traces of HCl.  $\text{CH}_2\cdot\text{CCl}_2$  and  $(\cdot\text{CHCl})_2$  evolve much HCl (even in  $\text{N}_2$ ) and give resinous products. Under the experimental conditions,  $\text{COCl}_2$  is not obtained from ethylenic compounds.  $\text{PhCl}$  is unchanged when irradiated in presence of  $\text{O}_2$ .  $\text{CH}_2\text{PhCl}$  passes slowly

into BzOH with probable intermediate formation of PhCHO.  $\text{CHPhCl}_2$  rapidly and completely gives BzCl. H. W.

**Organic laboratory chemistry. VI—VIII.** E. F. DEGERING (J. Chem. Educ., 1936, 13, 377—382).—Methods for the prep. of  $(\text{CH}_2\text{Br})_2$  and  $\text{NH}_2\text{Ph}$  are detailed. Various pieces of apparatus are described. L. S. T.

**Ozonisation of triple linkings.** C. D. HURD and R. E. CHRIST (J. Org. Chem., 1936, 1, 141—145).— $\text{CPh:C}\cdot\text{CO}_2\text{H}$ ,  $\text{CPh:CH}$ ,  $\Delta^4$ -hexinene (details for large-scale prep. of pure hydrocarbon given),  $\Delta^4$ -heptinene, 1-ethynylcyclohexan-1-ol, and ethynylfenchyl alcohol on ozonolysis with 5 and 10%  $\text{O}_3$  in  $\text{CCl}_4$  followed by hydrolysis of the resulting ozonides give rise to the acids expected on cleavage of the triple linkings in 42, 59, 51, 59, 52, and 61% yield, respectively. H. G. M.

**Proposed mechanism for mercury catalysis in acetylene addition reactions.** G. F. HENNION, R. R. VOGT, and J. A. NIEUWLAND (J. Org. Chem., 1936, 1, 159—162).—A scheme involving the formation of a highly reactive intermediate compound,  $\text{R}\cdot\text{C}(\text{OB})\cdot\text{CR}'\cdot\text{HgA}$ , during the addition in presence of  $\text{HgA}_2$  of BOH (B=H, alkyl, acyl, aryl, etc.) to an acetylene  $\text{CR:CR}'$  to form  $\text{R}\cdot\text{CH}_2\cdot\text{CR}'(\text{OB})_2$  is advanced, and shown to be in accord with, but not proved by, the known facts. H. G. M.

**Reactions of alkylacetylenes. XIV. Reaction of butylacetylene with hydrogen bromide.** C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1806—1808).—Addition of HBr to  $\text{CH}\cdot\text{CBu}$  (I) containing an appreciable amount of peroxides (II) [derived from (I)] occurs rapidly at  $0^\circ$  and gives varying amounts (according to time and amount of HBr) of  $\alpha$ -bromo- $\Delta^4$ -hexene (III) and  $\alpha$ - $\beta$ -dibromohexane (IV). In absence of (II) reaction occurs much more slowly; thus (I) and HBr ( $>2$  mols.) in presence of quinol and  $\text{FeBr}_2$  [which rapidly destroys (II)] at  $15^\circ/12$  hr. afford  $\beta$ -bromo- $\Delta^4$ -hexene (V),  $\beta$ - $\beta$ -dibromohexane (VI), b.p.  $83.5\text{--}84^\circ/24$  mm. [hydrolysed ( $\text{Ag}_2\text{SO}_4$  in 10%  $\text{H}_2\text{SO}_4$ ) to  $\text{CMeBu}$ ], a little (III), and much unchanged (I). (III) and (V) also react rapidly with HBr in presence of (II) to give (IV); in absence of (II), (III) yields a little (IV), whilst (V) affords (IV) and (mainly) (VI). H. B.

**Acetylene polymerides and their derivatives. XXVI. Reaction of halogeno-ethers with vinylacetylene.** H. B. DYKSTRA (J. Amer. Chem. Soc., 1936, 58, 1747—1749).— $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$  (I),  $\text{CH}_2\text{Cl}\cdot\text{OMe}$ , and  $\text{BiCl}_3$  in  $\text{Et}_2\text{O}$ -pyrogallol (antioxidant) at  $5\text{--}15^\circ$  give mainly  $\alpha$ -chloro- $\varepsilon$ -methoxy- $\Delta^4$ -pentadiene (II), b.p.  $60\text{--}61^\circ/10$  mm. (presumably formed by a 1:4-addition), and some  $\gamma$ -chloro- $\varepsilon$ -methoxy- $\Delta^4$ -pentadiene (III), b.p.  $46^\circ/10$  mm. (II) rearranges to (III) when treated with  $\text{CuCl}$  and 18%  $\text{HCl}$  in  $\text{Et}_2\text{O}$  at  $20\text{--}40^\circ$ . (II) and (III) are oxidised ( $\text{KMnO}_4$ ) to  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$  and  $\text{OMe}\cdot\text{CHCl}_2\cdot\text{CO}_2\text{H}$ , respectively. (III) and maleic anhydride in  $\text{COMe}$ , at  $50^\circ$  give (after hydrolysis with  $\text{H}_2\text{O}$ ) 4-chloro-3-methoxymethyl- $\Delta^4$ -tetrahydrophthalic acid, m.p.  $163\text{--}165^\circ$ ; (II) does not react. (III) polymerises (rate accelerated by light, heat, and catalysts) to a rubber-like resin.  $\gamma$ -Chloro- $\varepsilon$ -ethoxy-

b.p.  $44^\circ/4$  mm., and  $\varepsilon$ -butoxy-, b.p.  $67^\circ/2$  mm.,  $\Delta^4$ -hexadienes and  $\alpha$ -chloro- $\varepsilon$ -ethoxy-, b.p.  $56^\circ/4$  mm., and  $\varepsilon$ -butoxy-, b.p.  $79^\circ/2$  mm.,  $\Delta^4$ -hexadienes are similarly prepared from (I) and the appropriate  $\text{OAlk}\cdot\text{CHMeCl}$ . H. B.

**Substitution of fluorine for other halogens by use of mercurous fluoride and iodine. Preparation of methyl fluoride.** F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 781—783).—On the basis of a mechanism previously indicated (this vol., 712)  $\text{MeF}$  is prepared in 80% yield by gradual addition of  $\text{Hg}_2\text{F}_2$  (1 mol.) to  $\text{I}$  (1 mol.) in  $\text{MeI}$  ( $>2$  mols.). J. T. A.

**Condensations by sodium. VII. General method for stopping the Wurtz reaction at the intermediate organometallic stages.** A. A. MORTON and I. HECHENBLEIKNER (J. Amer. Chem. Soc., 1936, 58, 1697—1701; cf. this vol., 966).—Addition of  $n$ -amyl chloride to Na powder (excess) in  $\text{C}_5\text{H}_{12}$  or light petroleum at  $0\text{--}38^\circ$  and subsequent treatment (after initial reaction ceases) with  $\text{CO}_2$  gives  $\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$  (22—44.2%) and  $\text{CHBu}(\text{CO}_2\text{H})_2$  (I) (8—24%). Analogous results are obtained with (in order of decreasing yield)  $n$ -hexyl chloride,  $\text{PhCl}$ ,  $\text{Bu}^n\text{Cl}$  ( $\text{Bu}^n\text{Br}$ ), *tert*-amyl chloride,  $\beta$ -chloro- $\gamma$ -methylbutane, and  $\text{Pr}^n\text{Cl}$ . Evidence indicating that (I) is not formed by way of  $\text{C}_5\text{H}_{11}\cdot\text{Na}$  is discussed.  $\text{C}_5\text{H}_{10}\text{Na}_2$  has a greater thermal stability than  $\text{C}_5\text{H}_{11}\text{Na}$ . H. B.

**Determination of alcohol by Widmark's method.** E. FLOTOW and G. NAUENBURG (Pharm. Zentr., 1936, 77, 580—581).—An automatic pipette is described for delivering a fixed vol. of  $\text{H}_2\text{SO}_4\text{--CrO}_3$  during this determination. Distillation is replaced by keeping overnight, which obviates some causes of inaccuracy. R. S. C.

**New types of racemisation reactions.** E. BERGMANN and A. BONDI (J. Amer. Chem. Soc., 1936, 58, 1814).—The formation of  $(-)\beta$ -methyl- $\alpha$ -diethyl- $n$ -amyl alcohol, b.p.  $92\text{--}93^\circ/32$  mm.,  $[\alpha]_D^{25} -13.04^\circ$  in  $\text{COMe}_2$ , from  $l\text{-CHMePr}^+\cdot\text{CO}_2\text{Me}$  (I) and  $\text{MgEtBr}$  supports the suggestion (A., 1935, 1223) that  $dl\text{-CHMePr}^+\cdot\text{CPh}_2\cdot\text{OH}$  [from (I) and  $\text{MgPhBr}$ ] results owing to the equilibrium  $\text{CHMePr}^+\cdot\text{CPh}_2\cdot\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CMePr}^+\cdot\text{CPh}_2$ . These results are in accordance with the greater ease of dehydration of  $\text{CPh}_2\text{Alk}\cdot\text{OH}$  than  $\text{CAlk}_3\cdot\text{OH}$ . The racemisation of  $\beta$ -bromohexane during its conversion into the Grignard reagent (Porter, *ibid.*, 1228) is probably due to the racemisation of the  $\text{MgRBr}$  by  $\text{Br}^+$ ; the reaction is analogous to the racemisation of  $\text{CHPhMeCl}$  by interaction with  $\text{Mg}$  or  $\text{Na}$  (cf. A., 1933, 574; this vol., 803). H. B.

**$\beta$ -Amyloxyethyl esters of  $p$ -aminobenzoic acid.** H. V. ASHBURN, A. R. COLLETT, and C. L. LAZZELL (J. Amer. Chem. Soc., 1936, 58, 1549—1551).—The requisite  $\text{C}_5\text{H}_{11}\cdot\text{OH}$  (20—30 mols.),  $(\text{CH}_2)_2\text{O}$  (7 mols.), and conc.  $\text{H}_2\text{SO}_4$  (1 c.c.) [or, for (I),  $\text{Al H}$  silicofluoride] at  $130\text{--}150^\circ$  give  $\beta$ - $n$ -amyl-, b.p.  $188.3^\circ/751.1$  mm.,  $\beta$ -isoamyl-, b.p.  $179.8^\circ/750.1$  mm.,  $\beta$ - $\beta'$ -methylbutyl-, b.p.  $176.8^\circ/748$  mm.,  $\beta$ - $\alpha'$ -ethylpropyl-, b.p.  $172.6^\circ/746.4$  mm.,  $\beta$ - $\alpha'$ -methylbutyl-, b.p.  $173.8^\circ/746$  mm., and  $\beta$ - $\alpha$ - $\alpha$ -dimethyl-



propyl- (I), b.p. 168.4°/745.4 mm., -oxyethyl alcohols; the p-nitrobenzoates (prep.: A., 1933, 48) have b.p. 191.5—192.5°/4 mm. (II), 184.1—185.1°/4 mm., 188.1—189°/4 mm., 183—184°/4 mm., 186.6—187.6°/4 mm. (m.p. 74.5°), and 164—166°/0.42 mm., respectively, and are reduced (method: A., 1935, 1494) to the p-aminobenzoates [that from (II) has m.p. 56.8°; others are viscous oils] (picramides, m.p. 115.5°, 140.9°, 129.1°, 136°, 120.8°, and 134.9°, respectively).

H. B.

Influence of nitric oxide on thermal decomposition of dimethyl ether.—See this vol., 1346.

Decomposition of n-butyl nitrite.—See this vol., 1344.

Reactions relating to carbohydrates and polysaccharides. XLIX. Mol. wt., molar refraction, f.p., and other properties of polyethylene glycols and their derivatives. A. F. GALLAUGHER and H. HIBBERT (J. Amer. Chem. Soc., 1936, 58, 813—816; cf. this vol., 963).—The mol. wts. of tri- (I), b.p. 115.5—117°/0.1 mm., f.p. -9.4°, tetra- (II), b.p. 144—145.5°/0.1 mm., f.p. -9.4°, penta-, b.p. 174—176°/0.14 mm., f.p. -8.7°, hexa-, b.p. 203—205°/0.3 mm. f.p. 1.3°, and hepta-, b.p. 241—244°/0.6 mm., f.p. 7.7°, -ethylene glycols, tetraethylene glycol monochlorohydrin (III), b.p. 134.6—136°/0.94 mm., f.p. -54° [by-product during reaction of Na derivative of diethylene glycol (f.p. -10.1°) and (CH<sub>2</sub>Cl-CH<sub>2</sub>)<sub>2</sub>O (IV)], and diethylene glycol Me<sub>2</sub> ether [ββ'-dimethoxydiethyl ether] (V), b.p. 160.5—161°/756.6 mm. [formed (cf. Cretcher and Pittenger, A., 1925, i, 228) together with a little CH<sub>2</sub>-CH-O-CH<sub>2</sub>-CH<sub>2</sub>-OMe from (IV) and MeOH-NaOMe at about 25°], are determined cryoscopically in C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>. The vals. for (I), (II), (III), and (V) increase regularly with rise in concn.; in the other cases, association is very large at low concns., then decreases to a min., and finally increases. The glycols show an approx. const. increase in mol. refraction with rise in mol. wt. C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, f.p. -13.2°, (CH<sub>2</sub>)<sub>3</sub>(OH)<sub>2</sub>, f.p. -32°, and (in a smaller degree) s-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and OMe-CH<sub>2</sub>-CH<sub>2</sub>-OH appear to form co-ordination compounds with anhyd. CuSO<sub>4</sub>.

H. B.

Esters of perchloric acid. J. MEYER and W. SPORMANN (Z. anorg. Chem., 1936, 228, 341—351).—Me perchlorate, b.p. 52°, EtClO<sub>4</sub>, and Pr<sup>n</sup> perchlorate, b.p. 89°, can be prepared by distilling a mixture of R<sub>2</sub>Ba(SO<sub>4</sub>)<sub>2</sub> (R=Me, Et, or Pr) and Ba(ClO<sub>4</sub>)<sub>2</sub> into anhyd. Et<sub>2</sub>O containing anhyd. CuSO<sub>4</sub>, and removing the Et<sub>2</sub>O by evaporation. EtClO<sub>4</sub> has also been obtained by very slow addition of anhyd. HClO<sub>4</sub> to EtOH, and MeClO<sub>4</sub> and EtClO<sub>4</sub> by treatment of anhyd. AgClO<sub>4</sub> with RBr in abs. EtOH. MeClO<sub>4</sub> is also produced by treating anhyd. HClO<sub>4</sub> with CH<sub>3</sub>N<sub>2</sub>. All three compounds explode readily on heating, percussion, or friction. They are readily sol. in Et<sub>2</sub>O and EtOH and insol. in H<sub>2</sub>O, but are gradually hydrolysed by the latter, the readiness of hydrolysis following the order MeClO<sub>4</sub>>EtClO<sub>4</sub>>PrClO<sub>4</sub>.

J. W. S.

Attempts to prepare cyclic glycerides. Preparation of "tetrachlorodiglycerides" of dicarboxylic acids. M. GOSWAMI and A. SHAHA (J.

Indian Chem. Soc., 1936, 13, 464—466).—Glycerol, the dibasic acid, and POCl<sub>3</sub> at 100° give di-ββ'-dichloroisopropyl succinate, b.p. 141—142°/4 mm., maleate, b.p. 128—130°/4 mm., citraconate, b.p. 228—232°/4 mm., and phthalate (I) [from the anhydride (II)], b.p. 260—262°/4 mm. (I) is also obtained from (CH<sub>2</sub>Cl)<sub>2</sub>CH-OH, (II), and POCl<sub>3</sub>.

R. S. C.

Oxidation of formic acid.—See this vol., 1348.

Photolysis of acetic and formic acids.—See this vol., 1349.

Thermal decomposition of the silver salts of carboxylic acids. III. Thermal decomposition of the silver salts of acetic and benzoic acid. S. J. KANEVSKAJA and M. M. SCHEMJAKIN (Ber., 1936, 69, [B], 2152—2157; cf. this vol., 469).—Thermal decomp. of AgOAc affords Ac<sub>2</sub>O and large amounts of AcOH, whilst Bz<sub>2</sub>O, PhOBz, BzOH, and a small amount of PhOH but not C<sub>6</sub>H<sub>6</sub> are derived from AgOBz. In all cases the initial change appears to be decomp. into Ag<sub>2</sub>O and the acid anhydride. Subsequently hydration occurs due to H<sub>2</sub>O present in the Ag salt or formed by destructive decomp. of the initial acid. PhOH is attributed to the oxidation by Ag<sub>2</sub>O of C<sub>6</sub>H<sub>6</sub> or Ph formed by thermal decomp. of the anhydride and PhOBz results from nascent PhOH and unchanged Bz<sub>2</sub>O.

H. W.

Fluorination of organic compounds. II. P. C. RAY and A. C. RAY (J. Indian Chem. Soc., 1936, 13, 427—428; cf. A., 1935, 733).—CH<sub>2</sub>F-CO<sub>2</sub>Me, CH<sub>2</sub>F-CO<sub>2</sub>Et, and CH<sub>2</sub>PhF are prepared from the Br-compounds by TiF<sub>2</sub> in hot abs. EtOH. The method is not general, eight compounds failing to react and others not giving pure F-derivatives.

R. S. C.

Configurative relationship of disubstituted acetic and propionic acids containing an ethyl group. P. A. LEVENE, A. ROTHEN, and G. M. MEYER (J. Biol. Chem., 1936, 115, 401—413).—By conversion into hydrocarbons it is shown that configuratively related acids, CHETPr-CO<sub>2</sub>H (I), CHETPr'-CO<sub>2</sub>H, and CHMeR-CO<sub>2</sub>H, rotate in the same direction and that related acids, (I) and CHETPr-CH<sub>2</sub>-CO<sub>2</sub>H (II), rotate in opposite directions. The previous correlation (A., 1931, 821) of l-CHETPr-CH<sub>2</sub>-CO<sub>2</sub>H with d-CHETBu-CH<sub>2</sub>-CO<sub>2</sub>H is erroneous. The rotatory dispersion of (I) and (II) is expressed by a single-term Drude equation. [M] given below are calc. least max. [M]<sup>25</sup>. CHETPr-CO<sub>2</sub>H, m.p. 117—118°, leads to l-α-ethyl-n-valeric acid (III), b.p. 95°/8 mm., [M] -2.21° (cinchonidine salt), and Et d-α-ethyl-n-valerate, b.p. 108°/115 mm., [M] +7.33° (quinine salt of the corresponding acid), reduced to d-β-ethyl-n-amyl alcohol, b.p. 107°/100 mm., [M] +3.88°, and thence giving the bromide (IV), b.p. 109°/130 mm., [M] +1.04°. (II) leads to l-β-ethyl-n-amyl iodide, b.p. 132—133°/160 mm., [M] -0.66°, and l-γ-methyl-n-hexane, b.p. 92—93°. (IV) leads to β-ethylhexoic acid, b.p. 158—159°/79 mm., [M] -3.41°. CH<sub>2</sub>(CO<sub>2</sub>Et)<sub>2</sub> leads to d- (cinchonidine salt) and l-α-ethylhexoic acid, b.p. 120°/13 mm., [M] -23.5° (quinine salt; Et ester, b.p. 90°/28 mm., [M] -22.6°), and thence l-β-ethyl-n-hexyl alcohol, b.p. 110°/55 mm., [M] -7.72°, iodide, b.p.

60°/2 mm.,  $[M] = -24^\circ$ , and bromide, b.p. 110—111°/71 mm.,  $[M] = -19.4^\circ$ , d- $\beta$ -ethylheptonic acid,  $[M] = +7.41^\circ$ , and l- $\gamma$ -methyl-n-heptane, b.p. 115°. R. S. C.

Oxidation of drying oils and cognate substances. I. Oxidation of maleic anhydride compounds of  $\beta$ -elæostearic acid and its triglyceride. II. (A) Oxidation of maleic anhydride compound of  $\alpha$ -elæostearic acid. (B) Properties of maleic anhydride compounds of  $\alpha$ - and  $\beta$ -elæostearic acids. III. Effect of heat on oxidised  $\beta$ -elæostearin-maleic anhydride compound. R. S. MORRELL and W. R. DAVIS (J.S.C.I., 1936, 237—246T, 261—265T, 265—267T).—Controlled oxidation ( $H_2O_2$ -AcOH) of the maleic anhydride compounds of  $\alpha$ - and  $\beta$ -elæostearic acids yields the corresponding  $(OH)_2$ -derivatives, whilst hydrogenation ( $H_2$ -PtO<sub>2</sub>,  $H_2O$ ) affords compounds  $C_{18}H_{31}O_2 \cdot C_{18}H_{31}O_3$ , m.p. 74° and 63°, respectively. The effect of heat on the gels obtained by the gaseous oxidation of  $\beta$ -elæostearin-maleic anhydride compound in AcOH and CCl<sub>4</sub>, respectively, is described and a chemical interpretation is suggested. Previous findings (this vol., 313) are described in detail.

F. N. W.

Electrochemical investigations with  $\alpha$ -hydroxy-acids.—See this vol., 1347.

Reactions of pyruvic acid with thiolacetic acid and cysteine. E. FRIEDMANN and J. GIRŠAVIČIUS (Biochem. J., 1936, 30, 1886—1891).—When  $AcCO_2H$  (I) is mixed with  $SH \cdot CH_2 \cdot CO_2H$  (II), an exothermic reaction occurs and a white cryst. equimol. compound of (I) and (II) is formed which, on dissolution in  $H_2O$ , behaves like a mixture of free (I) and (II) both in its reactions with I and  $NaHSO_3$  and in the fact that (I) and (II) can be isolated therefrom. Cysteine in aq. or EtOH solution reacts slowly with (I) as shown polarimetrically and by iodometric titration. The compound is reasonably stable as judged from its behaviour to I and some colour reagents. P. W. C.

Preparation of homolævulic [ $\gamma$ -keto-n-hexoic] acid. E. FRIEDMANN (J. pr. Chem., 1936, [ii], 146, 159—162).— $COEt \cdot CH_2 \cdot CO_2Et$  (purified by way of the  $NaHSO_3$  compound), Na wire, and  $CH_2Br \cdot CO_2Et$  in  $Et_2O$  give a 66.5% yield of  $Et_2$  propionylsuccinate, b.p. 146—149°/10 mm., and thence by 5N- $H_2SO_4$  an 81% or by N-NaOH a 62% yield of  $\gamma$ -keto-n-hexoic acid, m.p. 40° (corr.), b.p. 140—148°/10 mm. (Et ester, b.p. 102—107°/12 mm.).

R. S. C.

Polynuclear heterocyclic rings. X. Determination of the rate of ring closure. M. STOLL and A. ROUVÉ (Helv. Chim. Acta, 1936, 19, 1079—1095; cf. A., 1935, 1251; this vol., 964).—Further examination of the behaviour of  $OH \cdot [CH_2]_{14} \cdot CO_2H$  shows that with 45% primary polymerisation the initial rate of reaction based on transformation of the initial products is greater at the start and slower at the end than the rate based on the functional groups. The corresponding velocity coeffs. differ widely from one another, that based on the initial acid declining first rapidly and then slowly to a limiting val., whilst that based on the functional groups falls very rapidly and finally becomes const. The rate of polymerisation to an acid concn.  $c = 11.7$  g. =

$45 \times 10^{-4}$  mol. per litre is  $>$ , and after this concn.  $<$ , the rate of monomeric lactone formation. This concn. determines the point at which the rates are equal, and must therefore be identical with the cyclisation const. The degree of cyclisation increases with the progress of the change. The ratio uni-: bi-mol. acid shows that the max. amount of ter- and quadri-mol. acid is  $> 8\%$  of the original material and that  $> 3\%$  of the latter is available for the production of substances of higher mol. wt. Reply is made to Salomon (this vol., 940). H. W.

Nature of the "activated form" of oxalic acid. E. SCHROER (Ber., 1936, 69, [B], 2037—2041).— $CHO \cdot CO_2H$  (I) is identified as the "activated form" of  $H_2C_2O_4$ , since a solution of the latter which has reacted with  $KMnO_4$  in absence of air until only a slight yellow colour persists gives a violet colour with fuchsin- $H_2SO_4$ . At the same stage of the reaction (I) can be detected with naphthoresorcinol or, more satisfactorily, with carbazole. Little  $H_2O_2$  is produced when solutions of (I) are shaken with air, but its formation becomes copious in presence of  $Mn^{++}$ . Little  $H_2O_2$  results in old solutions of (I) and none in those which are syrupy or have been boiled, probably on account of polymerisation of the acid. Identical amounts of (I) are found by the aldehyde and Ti reagents; these appear to decrease with increasing acidity of the solution. (I) reduces  $Hg^{II}$  salts in warm solution. The reaction of  $H_2C_2O_4$  and  $MnO_4^-$  in acid solution is given by the partial equations:  $4H_2C_2O_4 + 2MnO_4^- + 2H^+ \rightarrow 3CO_2 + Mn_2O_3 + 5H_2O$ ;  $H_2C_2O_4 + Mn_2O_3 \rightarrow (I) + 2MnO_2$ ;  $(I) + O_2 + H_2O \rightarrow H_2C_2O_4 + H_2O_2$ ;  $H_2O_2 + MnO_2 \rightarrow H_2O + MnO + O$ ;  $H_2C_2O_4 + MnO_2 \rightarrow H_2O + 2CO_2 + MnO$ .

W.

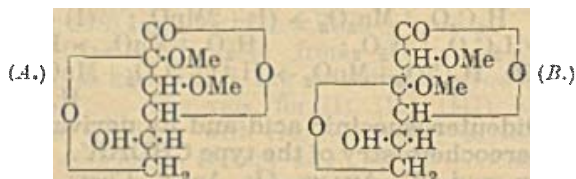
$\alpha\alpha'$ -Dideuterosuccinic acid and its derivatives. II. Stereochemistry of the type  $CHDRR'$ . M. T. LEFFLER and R. ADAMS (J. Amer. Chem. Soc., 1936, 58, 1551—1555).—Reduction ( $D_2$ , PtO<sub>2</sub>, EtOAc) of (a) Et maleate and (b) Et fumarate gives apparently the same Et  $\alpha\alpha'$ -dideuterosuccinate, b.p. (a) 106.5—106.8°/16 mm., (b) 106—106.5°/16 mm., hydrolysed (very dil.  $HNO_3$ ) to the acid (I), m.p. 184—184.5° (anhydride, m.p. 119.3—119.6°). Fractional crystallisation of (I) failed to indicate more than one form. The brucine, m.p. 216—218° (decomp.), quinine (+ $H_2O$ ), m.p. (anhyd.) 198—201°, strychnine, m.p. 210° (softens at 190°), and cinchonine (II), m.p. 130—160°, salts of (I) have the same  $[\alpha]_D^{20}$  as the corresponding salts (same m.p.) of  $(-CH_2 \cdot CO_2H)_2$ . Quinine tetradeuterosuccinate has m.p. 198—201°. Different fractions of (II) showed no mutarotation. The above results indicate that  $CHDRR'$  shows symmetry. H. B.

Shellac. IX. Constitution of aleuritic acid. W. NAGEL and W. MERTENS (Ber., 1936, 69, [B], 2050—2052).—Confirmation of the structure  $OH \cdot [CH_2]_8 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$  assigned to aleuritic acid (A., 1927, 445) is found in its conversion by successive treatment with  $COMe_2$ ,  $H_2SO_4$ ,  $KMnO_4$  (=4 O), and boiling dil. mineral acid into  $\kappa$ -dihydroxyhexadecanedicarboxylic acid, m.p. 125—127° (Mg salt). The corresponding Me<sub>2</sub> ester, m.p. 60—62.5°, yields a diacetate, b.p. 220—230°



(bath)/1 mm., and a  $\text{CMe}_2$  derivative, b.p.  $185^\circ/3$  mm. H. W.

$\alpha\beta$ -Dimethylascorbic acid and  $\alpha\beta$ -dimethyl- $\psi$ -ascorbic acid. F. MICHEEL and G. BISCHOFF (Annalen, 1936, 525, 66—73).— $\alpha\beta$ -Dimethyl- $\delta\epsilon$ -isopropylideneascorbic acid is greatly changed by dil. alkali without yielding derivatives of dimethyl- $\psi$ -ascorbic acid (I) (cf. A., 1935, 1106). Successive treatment of *l*-ascorbic acid with  $\text{CPh}_3\text{Cl}$  and  $\text{CH}_2\text{N}_2$  affords  $\epsilon$ -triphenylmethyl- $\alpha\beta$ -dimethylascorbic acid (II), m.p.  $159^\circ$ ,  $[\alpha]_D^{20} +34.2^\circ$  in  $\text{CHCl}_3$  (*p*-nitrobenzoyl derivative, m.p.  $154^\circ$ ,  $[\alpha]_D^{20} +24.3^\circ$  in  $\text{CHCl}_3$ ). Removal of the  $\text{CPh}_3$  residue from (II) followed by treatment with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  leads to the known  $\delta\epsilon$ -di-*p*-nitrobenzoyl- $\alpha\beta$ -dimethylascorbic acid (III), showing that secondary change does not occur during the action of  $\text{CPh}_3\text{Cl}$ . (II) is isomerised by an excess of dil. alkali to a compound (IV), m.p.  $178^\circ$ ,  $[\alpha]_D^{20} +34.6^\circ$  in  $\text{CHCl}_3$ , which is not enantiomorphously related to (II). (IV) affords a non-cryst. *p*-nitrobenzoate. Removal of  $\text{CPh}_3$  from (IV) followed by treatment with *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$  gives (III). Since the  $\epsilon$ - $\text{CPh}_3$  derivative of dimethylascorbic acid (V) does not become transformed into the similar derivative of (I), it follows that  $\epsilon$ -OH must be concerned with the isomerisation of (V) to (I), thus excluding the constitution assigned previously (*loc. cit.*) to (I). The mode of participation of  $\epsilon$ -OH in the formation of (I) is indicated by the observations that (I) does not react with  $\text{CPh}_3\text{Cl}$  and that *p*-nitrobenzoyldimethyl- $\psi$ -ascorbic acid is hydrolysed by  $\text{NaOH}$  and then loses



Me when treated with 0.1N-HCl at  $100^\circ$ , giving methyl- $\psi$ -ascorbic acid, which reduces Fehling's solution and affords a di-*p*-nitrobenzoylmethyl- $\psi$ -ascorbic acid. The most probable structure of (I) is therefore A or B, of which the former is the more likely since B requires a very ready hydrolysis of glucosidic Me.

H. W.

Kinetics of the reactions of polymeric aldehydes. II. Reaction of paraformaldehyde with cyanide. J. LOBERING and K. P. JUNG (Ber., 1936, 69, [B], 2147—2151).—Weighed amounts of paraformaldehyde (I) alone and in presence of varied amounts of KCN are shaken at  $30^\circ$ . Determinations of the quantities of dissolved (I) and of (I) utilised in the production of OH-nitrile after definite intervals of time show that the rate of reaction is governed by that of dissolution of (I), and that  $\text{CN}^-$  has no influence on the velocity of the change, which after an initial period is of the first order.

H. W.

Condensation of halogen-substituted aldehydes with nitro-paraffins. F. D. CHATTAWAY, J. G. N. DREWITT, and G. D. PARKES (J.C.S., 1936, 1294—1295; cf. A., 1935, 1224).—Equimol. amounts of chloral and  $\text{EtNO}_2$  in aq.  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$  at  $40$ — $70^\circ$  give  $\delta\delta\delta$ -trichloro- $\beta$ -nitro- $\gamma$ -hydroxybutane, b.p.  $95^\circ/0.05$  mm.,  $115^\circ/2$  mm. (*Ac* derivative, b.p.  $98^\circ/$

$0.05$  mm.,  $125^\circ/2$  mm.). Butylchloral hydrate yields similarly  $\delta\delta\epsilon$ -trichloro- $\beta$ -nitro- $\gamma$ -hydroxyhexane, b.p.  $138^\circ/0.75$  mm. (*Ac* derivative, b.p.  $140^\circ/0.25$  mm.). Chloral and  $\text{CH}_2\text{Ph}\cdot\text{NO}_2$  afford  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -hydroxy- $\alpha$ -phenylpropane, m.p.  $109^\circ$  (*Ac*-derivative, m.p.  $98^\circ$ ). All products are inseparable mixtures of active forms.

R. F. P.

Condensation reactions of unsaturated aldehydes. V. Condensation reactions of crotonaldehyde under the influence of different condensing agents. K. BERNHAUER and K. IRRGANG [with K. ADLER, M. MATTAUCH, P. MULLER, and F. NEISER] (Annalen, 1936, 525, 43—65).—Immediately before each experiment the crotonaldehyde (I) is distilled in  $\text{CO}_2$  and condensation is then effected under  $\text{N}_2$ . The proportion of cyclic to open-chain aldehydes depends greatly on the *sec.* amine used. The best yields ( $>30\%$ ) of *o*-dihydrotolualdehyde (II) are obtained by the rapid action of  $\text{NH}_2\text{Et}$ ; prolonged action caused the disappearance of (II) owing to its condensation with (I) to products which resinify readily. With  $\text{NHMe}_2$  or piperidine (III) the yields of (II) are smaller and relatively best with pure (III) without addition of  $\text{AcOH}$  (cf. Kuhn *et al.*, this vol., 316). Dicrotonaldehyde,  $\text{CHO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{C}(\text{CHMe})\cdot\text{CHO}$ , is observed only under mild conditions of reaction, and is regarded as the precursor of (II). *p*-Dihydrotolualdehyde is formed mainly by slow action in aq. solution, and probably arises from the condensation of (I) with aldol; it is not produced in presence of dehydrating agents. Octatrienal (IV) appears only in limited amount, best in presence of anhyd. condensing agents or of  $\text{Na}_2\text{SO}_4$ . Pure (III) or  $\text{NH}_2\text{Et}$  is relatively inefficient, but better results are obtained with their acetates. Max. yields are secured with pure (III) and freshly distilled (I), whereby little (II) results; with the same catalyst and (I) distilled under  $\text{N}_2$  less (IV) and more (II) are produced. With this catalyst the addition of  $\text{AcOH}$  is disadvantageous. Non-cryst. acids are invariable by-products of the condensations.  $\text{NH}_2\text{Ph}$ ,  $\text{NHPhMe}$ ,  $\text{NPhMe}_2$ , and  $\text{C}_5\text{H}_5\text{N}$  have no condensing action and  $(\text{CH}_2\text{NH}_2)_2$  gives only a little (IV). Little condensation and, frequently, much resinification are caused by  $\text{NH}_2\text{Me}$ ,  $\text{NMe}_3$ , and  $\text{NMe}_4\text{OH}$ . Inorg. bases differ from *sec.* amines in that they never cause formation of cyclic aldehydes. Usually (III) is produced directly from (I), and then suffers partial fission to sorbaldehyde; fission is observed with alkali hydroxides and carbonates,  $\text{Ba}(\text{OH})_2$ , and aq. (III), but not with  $\text{Na}_2\text{HPO}_4$ , which therefore gives the highest yields of (IV). Dimeric (I) (identified as dimeric crotonic acid, m.p.  $64$ — $66^\circ$  or m.p.  $71^\circ$  when very rapidly heated; after re-solidification, m.p.  $78$ — $81^\circ$ , independent of the rate of heating) is produced. The position of  $\text{Ba}(\text{OH})_2$  is exceptional in that it causes formation of (II). Acid catalysts give the highest yields of condensation products,  $10\%\text{H}_2\text{SO}_4$  and  $7.5\%\text{HCl}$  behaving almost identically; resin formation is very small. Both cause the formation of very little (IV) and give mainly dimeric (I) and its trimeride, m.p.  $63^\circ$  (semicarbazone, m.p.  $213.5^\circ$ ; *p*-nitrophenylhydrazone, m.p.  $208.5^\circ$ ; phenylhydrazone, m.p.  $139$ — $141^\circ$ ), oxidised

to trimeric crotonic acid, m.p. 159.5° (dibromide, m.p. 151°); both are attributed to the intermediate formation of acetaldehyde.

Gradual addition of H<sub>2</sub>O to a mixture of (I), citral, and BaO followed by oxidation of the distilled product with Ag<sub>2</sub>O gives a cryst. acid, C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>, m.p. 99°, probably cyclic in structure. H. W.

**Hydrolysis of  $\alpha$ , $\beta$ -dichloro- $\beta$ -methylpropane** producing isobutaldehyde. J. M. HERSH and R. E. NELSON (J. Amer. Chem. Soc., 1936, 58, 1631—1633).—CMc<sub>2</sub>Cl-CH<sub>2</sub>Cl, b.p. 38.6—39.2°/70 mm., 106.5°/760 mm., best prepared by low-temp. chlorination of Bu<sup>n</sup>Cl, is hydrolysed in the vapour phase at 350° by H<sub>2</sub>O (ratio 20:1) in presence of catalysts (activated Al<sub>2</sub>O<sub>3</sub> being most effective) to Pr<sup>n</sup>CHO (90—100% yield on product consumed). H. B.

**Refractometric studies in normal methyl ketones.** P. CEUTERICK (Bull. Soc. chim. Belg., 1936, 45, 545—564).—The mol. refractivity is determined of a series of  $\alpha$ -substituted Et acetoacetates (R=3—10 C), which are hydrolysed (10% NaOH) to the corresponding ketones. The mol. refractivities of the latter indicate that the contribution of CH<sub>2</sub> is 4.612 units at 15° and 4.630 at 30°, which shows that CO does not affect the val. for CH<sub>2</sub> (cf. A., 1933, 815). Assuming the val. for H, the vals. 4.675 and 4.665 are calc. for CO at 15° and 30°, respectively.

J. L. D.

**Colorimetric determination of acetone by the salicylaldehyde method.** A. RAVIN (J. Biol. Chem., 1936, 115, 511—518).—The method as described is capable of determining 0.0005 mg. of COMe<sub>2</sub> per c.c.

F. A. A.

**Addition of acetyl chloride to alkylacetylenes.** J. W. KROEGER, F. J. SOWA, and J. A. NIEUWLAND (J. Org. Chem., 1936, 1, 163—169; cf. this vol., 312).—Addition of AcCl to alkylacetylenes CR:CR' in presence of SnCl<sub>4</sub> gives mainly the chloroketones CRCl:CR'Ac (I) with some CRCl:CH:R' (II). In this way the following have been prepared: *cis*-, b.p. 97—99°/30 mm., and *trans*-, b.p. 89—91°/30 mm.,  $\delta$ -chloro- $\gamma$ -ethyl- $\Delta^2$ -hexen- $\beta$ -one, *cis*-, b.p. 117—118°/28 mm., and *trans*-, b.p. 112—113°/28 mm.,  $\delta$ -chloro- $\gamma$ -n-propyl- $\Delta^2$ -hepten- $\beta$ -one,  $\delta$ -chloro- $\gamma$ -n-butyl- $\Delta^2$ -octen- $\beta$ -one, b.p. 140—146°/28 mm.,  $\delta$ -chloro- $\gamma$ -n-amyl- $\Delta^2$ -nonen- $\beta$ -one, b.p. 115—121°/5 mm.,  $\delta$ -chloro- $\Delta^2$ -hexen- $\beta$ -one, b.p. 46—53°/10 mm., *cis*-, b.p. 62—63°/10 mm., and *trans*-, b.p. 54.5—55.5°/10 mm.,  $\delta$ -chloro- $\Delta^2$ -hepten- $\beta$ -one, *cis*-, b.p. 80°/10 mm., and *trans*-, b.p. 69°/10 mm.,  $\delta$ -chloro- $\Delta^2$ -octen- $\beta$ -one, *cis*-, b.p. 99°/10 mm., and *trans*-, b.p. 89°/10 mm.,  $\delta$ -chloro- $\Delta^2$ -nonen- $\beta$ -one,  $\gamma$ -chloro- $\Delta^2$ -hexene, b.p. 113.0—113.5°/748 mm.,  $\delta$ -chloro- $\Delta^2$ -octene, b.p. 157.5—159.5°/750 mm.,  $\epsilon$ -chloro- $\Delta^2$ -decene, b.p. 99—100°/28 mm.,  $\zeta$ -chloro- $\Delta^2$ -dodecene, b.p. 128—129°/28 mm.,  $\beta$ -chloro- $\Delta^2$ -butene, b.p. 57—59°/748 mm. (lit. 61—62°),  $\beta$ -chloro- $\Delta^2$ -hexene, b.p. 109.5—110.5°/735 mm.,  $\beta$ -chloro- $\Delta^2$ -heptene, b.p. 138—139°/748 mm. (lit. 71°/75 mm.). On keeping, the *cis*- and *trans*-isomerides are converted into an equilibrium mixture. With NaOAc-EtOH the *trans*-compounds give an immediate ppt. of NaCl, obtained only after several days from the *cis*-isomerides. The *trans*-isomeride is obtained on addition of HCl in presence of Cu<sub>2</sub>Cl<sub>2</sub> to the appropriate

acetylenic ketone. A mechanism for the formation of (I) and (II) is proposed involving the fission of AcCl into keten and HCl followed by addition of these products to the acetylene.

H. G. M.

**Dioximes. CXV.** G. PONZIO (Gazzetta, 1936, 66, 475—479).—The peroxide of the dioxime of diacetylglucose peroxide (A., 1925, i, 79) is reduced by NH<sub>2</sub>OH.HCl in C<sub>5</sub>H<sub>5</sub>N to dimethyl tetraketone tetra-oxime, m.p. 190° (decomp.) [complex Ni salt; (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> salt, m.p. 170° (decomp.)]; Ac<sub>4</sub> derivative, m.p. 127° (decomp.); Bz<sub>4</sub> derivative, m.p. 209—210°. Similarly the peroxide of the dioxime of dibenzoylglucose peroxide yields diphenyl tetraketone tetra-oxime.

E. W. W.

**Optical rotatory dispersion in the carbohydrate group. VII. Glucal series.** T. L. HARRIS, R. W. HERBERT, E. L. HIRST, C. E. WOOD, and H. WOODWARD (J.C.S., 1936, 1403—1408; cf. this vol., 60).—Absorption spectra and rotatory dispersions are given for xylal diacetate, glucal 3:4:6-triacetate, lactal, lactal hexa-acetate, cellobial, and cellobial hexa-acetate. The data for xylal diacetate are expressed by a one-term Drude-Natanson equation; the other substances require two-term equations. A common low-frequency term, corresponding with an absorption band with  $\lambda$  2000—2200 Å., indicates dissymmetry of the ethylenic linking. In the xylal series the contributions of the two saturated asymmetric centres cancel out, leaving the full contribution of the ethylenic linking evident; the latter is, however, partly offset by the contribution of the three saturated asymmetric centres in the glucal series. The large difference in  $[\alpha]$  in these two series is thus explained. Other observations are in accord with expectation.

R. F. P.

**Use of micro-organisms in sugar analysis. II. Quantitative differentiation of fructose and mannose.** T. F. NICHOLSON (Biochem. J., 1936, 30, 1804—1806).—Continuing earlier work (A., 1933, 1037), a method is described for determination of mannose (I) which depends on the facts that *Monilia krusei* removes glucose (II), fructose (III), and (I) from solution whilst *Gaffkya tetragen* removes only (II) and (III). Combining the use of these organisms with the use of a strain of *Proteus vulgaris* which removes (II) but leaves (III) and (I), it was possible to analyse mixtures of (I), (II), and (III) and to recover added (III) and (I) from blood and urine filtrates.

P. W. C.

**Isomerisation of hydroxyaldehydes. VI. Saccharic transformation of monoses.** S. N. DANILOV and A. M. HACHOKIAN (Ber., 1936, 69, [B], 2130—2141).—The possibilities of the formation of saccharic acids from monoses are discussed in the light of the author's observations with OH-aldehydes (cf. A., 1934, 281). The prep. of gluconic acid (I), OH·CH<sub>2</sub>·[CH(OH)]<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 145°,  $[\alpha]_D^{25} +4.99$  in H<sub>2</sub>O (Ba salt,  $[\alpha]_D^{25} +9.4$  in H<sub>2</sub>O; Ca salt (also +1H<sub>2</sub>O),  $[\alpha]_D^{25} +6.4$  in H<sub>2</sub>O; phenylhydrazide, m.p. 176°), by the action of PbO on mono- or di-halogenated glucose triacetates is described. (I) is converted by Ac<sub>2</sub>O and NaOAc at 70—80° and then at 96—100° into the Ac<sub>4</sub> derivative, m.p. 110°



(phenylhydrazide, m.p. 143°), and by Ag<sub>2</sub>O and MeI at 40° into *Me tetramethylglucodeonate* (II), m.p. 81.5°,  $[\alpha]_D^{25} + 84.2^\circ$  in H<sub>2</sub>O, hydrolysed by aq. Ba(OH)<sub>2</sub> to the corresponding acid, m.p. 92—94° [phenylhydrazide, m.p. (indef.), 112—114°]. Glucal, m.p. 60—61°,  $[\alpha]_D^{25} - 67.3^\circ$  in H<sub>2</sub>O (obtained by hydrolysis of the corresponding triacetate with NH<sub>3</sub>-EtOH), is transformed by repeated treatment with Ag<sub>2</sub>CO<sub>3</sub> and MeI at 40° into non-cryst. *trimethylglucal*,  $[\alpha]_D^{25} + 21.4^\circ$  in H<sub>2</sub>O, which with Cl<sub>2</sub> in CHCl<sub>3</sub> at 0° yields 1:2-dichloro-3:4:6-trimethylglucose,  $[\alpha]_D^{25} + 121.1^\circ$  in CHCl<sub>3</sub>, converted by moist Ag<sub>2</sub>CO<sub>3</sub> in CHCl<sub>3</sub> into 2-chloro-3:4:6-trimethylglucose; this with Pb(OH)<sub>2</sub> in H<sub>2</sub>O at 18–25° and finally at 80–90° affords *trimethylglucodeonic acid*, OMe·CH<sub>2</sub>·CH(OH)·[CH·OMe]<sub>2</sub>·CH<sub>2</sub>·CO<sub>2</sub>H (Ba salt; phenylhydrazide, m.p. 122—125°), completely methylated to (II). H. W.

**Osazones. II. Structure of "anhydro-osazones" and fission of osazones by bases.** O. DIELS, R. MEYER, and O. ONNEN (Annalen, 1936, 525, 94—118; cf. A., 1935, 1225).—Dehydration of osazones under the influence of traces of acid appears a general reaction accompanied by the loss of 1 H<sub>2</sub>O except in the case of maltose. Frequently the products are stable only as hydrates from which H<sub>2</sub>O cannot be removed without decomp.; the Ac derivatives, however, are anhyd. The previous method of formulation, based on the identity of anhydro-glucosazone (I) with the osazone of the 3:6-anhydro-glucose (II) of Fischer and Zach (A., 1912, i, 678) and Ohle (A., 1928, 871), cannot be maintained, since the pentosazones undergo similar change, and

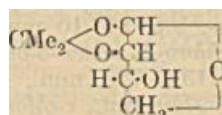
the structure  $N \begin{smallmatrix} \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \diagup \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{NHPh} \end{smallmatrix}$  is suggested by the conversion of anhydro-osazones by NH<sub>2</sub>OH, HCl in EtOH into 4-phenylhydrazono-5-keto-4-phenyl-4:5-dihydropyrazole or its homologues, the inability of N-alkylated osazones to undergo dehydration, and the impossibility of transforming anhydro-osazones into osones by conc. HCl, PhCHO, or *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO. The alternative constitution  $N \begin{smallmatrix} \diagup \\ \text{CH} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \diagup \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{NHPh} \end{smallmatrix}$

is suggested by the general behaviour of 4-pyrazolones, and strongly supported by the observation that the products derived from *l*-arabinose and *d*-xylose are optical antipodes, thus indicating the disappearance of the asymmetry of . . . The formation of (II) is not a normal case of osazone production, and slight variations of Ohle's procedure yield a compound, C<sub>19</sub>H<sub>20</sub>O<sub>3</sub>N<sub>4</sub>, m.p. 187—188°, differing from (I) and of unexplained constitution. Osazones are not as sensitive to [OH<sup>-</sup>] as to [H<sup>+</sup>], but are almost universally decomposed by 1% KOH-EtOH into glyoxal-osazone (V) or the products of its dehydration and an OH-acid. The point of scission therefore lies between C<sub>(2)</sub> and C<sub>(3)</sub>. The change is complex and ill-defined.

(I) gives *Ac*, m.p. 170°, and *Bz*, m.p. 161°, compounds and a *COMe*<sub>2</sub> derivative, m.p. 167—168°, converted by boiling MeCN into an *isomeride*, m.p. 220°. The *Ac* derivatives of anhydro-*d*-galactose and anhydrolactose-phenylosazone have m.p. 177°

and 195—196°, respectively. Cellobiosazone is transformed by very dil., boiling H<sub>2</sub>SO<sub>4</sub>-EtOH into *anhydro-cellobiosephenylosazone*, C<sub>24</sub>H<sub>30</sub>O<sub>8</sub>N<sub>4</sub>·H<sub>2</sub>O, m.p. 245° (decomp.) after softening at 225° (*Ac* derivative, C<sub>36</sub>H<sub>42</sub>O<sub>14</sub>N<sub>4</sub>, m.p. 197—198° after softening at about 180°), which is remarkably stable towards alkali. The following *o*-tolylosazones are described: *anhydro-d-glucose*, m.p. 168—170° (*Ac* derivative, m.p. 149°); *lactose*, m.p. 145—155°; *anhydrolactose*, m.p. 223—225° (slight decomp.); *cellobiose*, m.p. 150—152° after softening at 145°; *anhydrocellobiose*, m.p. 223—225° (decomp.); *l-arabinose*, m.p. 122—123°; *anhydro-l-arabinose*, m.p. 187—188°; *d-xylose*, m.p. 118—120°; *anhydro-d-xylose*, m.p. 188—189°,  $[\alpha]_D^{25} - 57.0^\circ$  in C<sub>5</sub>H<sub>5</sub>N. The *p*-tolylosazones of *anhydroglucose*, *d-galactose* (V), and *anhydro-d-galactose* have m.p. 202°, 193°, and 212°, respectively. *Anhydro-l-arabinosephenylosazone*, m.p. 180—181°,  $[\alpha]_D^{25} + 35.2^\circ$  in MeOH, and *anhydro-d-xylosephenylosazone*, m.p. 179—180°,  $[\alpha]_D^{25} - 32.1^\circ$  in MeOH, are described. The *p*-tolylosazones of glucose and galactose are converted by NH<sub>2</sub>OH, HCl in PrOH-H<sub>2</sub>O into a substance, C<sub>17</sub>H<sub>16</sub>ON<sub>3</sub>, m.p. 196°. Treatment of (I) with boiling 1% KOH-EtOH slowly yields the compound, C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>N<sub>4</sub>, m.p. 164°. *d*-Glucosazone (III) when similarly treated affords di- $\alpha$ -phenylazo-ethylene, m.p. 144° (decomp.), the three stereoisomeric forms of (IV), m.p. 220° (decomp.), 155°, and 187°, respectively, and an acid, (?) C<sub>3</sub>H<sub>6</sub>O<sub>4</sub>, isolated as the *brucine* salt, m.p. 188°. (IV) is also derived from the osazones of *d*-galactose, lactose, and maltose. *d*-Glucose-*o*-tolylosazone yields a compound (V), C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>, m.p. 141°, also obtained from *glyoxal-o-tolylosazone*, m.p. 136°, and KOH-EtOH. *d*-Galactose-*o*-tolylosazone, m.p. 160—161°, is transformed into (V) and a substance, C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 185°. *d*-Glucose-*p*-tolylosazone yields *glyoxal-p-tolylosazone*, m.p. 238°, not identical with the compound, C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>, m.p. 238°, derived from (IV), which is transformed by boiling EtOH into a substance, m.p. 205°. Cellobiosazone affords a product, C<sub>17</sub>H<sub>24</sub>O<sub>8</sub>N<sub>2</sub>, m.p. 223° (decomp.), differing in this respect from all other sugars examined. (III) is slowly transformed by 35% NH<sub>2</sub>Me in MeOH at room temp. into a compound, C<sub>19</sub>H<sub>25</sub>O<sub>3</sub>N<sub>5</sub>, m.p. 198—199° [normal sulphate, m.p. 237—238° (decomp.)]. H. W.

**Crystalline isopropylidene-*d*-threose and simple preparation of *d*- and *l*-threose.** M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 69, [B], 1016—1019).—



(I.)

Successive treatments of benzylidene-arabitol with Pb(OAc)<sub>4</sub> in AcOH and dil. AcOH give *d*-threose, best isolated as the *COMe*<sub>2</sub> derivative (I), m.p. 84°,  $[\alpha]_D^{25} - 15.27^\circ$  in COMe<sub>2</sub>. The identity of the sugar is established by its almost quant. oxidation to *l*-tartaric acid. H. W.

**Characterisation of sugarphosphoric acids and constitution of the pentosephosphoric acid from cozymase.** H. VON EULER, P. KARRER, and B. BECKER (Helv. Chim. Acta, 1936, 19, 1060—1062).—Synthetic glucose-6- and ribose-5-phosphoric acid from inosic acid do not give CH<sub>2</sub>O when oxidised by

$\text{HIO}_4$ , whereas under these conditions ribose-3-phosphoric acid from yeast-nucleic acid gives 0.61 mol. of  $\text{CH}_2\text{O}$ . The pentosephosphoric acid from highly purified cozymase does not yield  $\text{CH}_2\text{O}$ , showing that both pentose mols. are esterified by  $\text{H}_3\text{PO}_4$  at the primary OH. Cytidylic acid, although containing  $\text{PO}_4$  at 3, does not yield  $\text{CH}_2\text{O}$  in consequence of its glucosidification with cytosine. H. W.

**Synthesis of glycofuranosides.** E. PACSU and J. W. GREEN (J. Amer. Chem. Soc., 1936, 58, 1823—1824).—Galactose  $\text{Et}_2$  or dibenzyl mercaptal with  $\text{HgCl}_2$  and yellow  $\text{HgO}$  (to neutralise  $\text{HCl}$  formed) in  $\text{EtOH}$  at low temp. gives a good yield of  $\beta$ -ethylgalactofuranoside. H. B.

**Glucose 5-methyl ether.** L. VON VARGHA (Ber., 1936, 69, [B], 2098—2102).—Diisopropylidene-glucose 3-*p*-toluenesulphonate is hydrolysed by  $\text{AcOH}$  at  $50^\circ$  to 1:2-isopropylidene-glucosefuranose 3-*p*-toluenesulphonate,  $[\alpha]_D^{20} -11.6^\circ$  in  $\text{CHCl}_3$ , which with  $\text{BzCl}$  in  $\text{CHCl}_3$  gives 1:2-isopropylidene-glucosefuranose 6-benzoate 3-*p*-toluenesulphonate,  $[\alpha]_D^{20} -11.4^\circ$  in  $\text{CHCl}_3$ , whence the non-cryst. 5-methyl-1:2-isopropylidene-glucosefuranose 6-benzoate 3-*p*-toluenesulphonate,  $[\alpha]_D^{20} -27.1^\circ$  in  $\text{CHCl}_3$ . Alkaline hydrolysis of the latter gives a non-homogeneous product, transformed by  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  into 5-methyl-1:2-isopropylidene-glucosefuranose 3:6-diacetate (I), m.p.  $87^\circ$ ,  $[\alpha]_D^{20} -15.2^\circ$  in  $\text{CHCl}_3$ . The probability that the removal of the  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2$  is not accompanied by a Walden inversion and that (I) is a derivative of glucose is strengthened by the almost quant. conversion of 1:2-isopropylidene-glucose 3-*p*-toluenesulphonate into 1:2-isopropylidene-glucose, m.p.  $158^\circ$ , under precisely similar conditions. This view is further confirmed by the mild alkaline hydrolysis of (I) to homogeneous 5-methyl-1:2-isopropylidene-glucosefuranose (II), b.p.  $145^\circ/0.3\text{ mm.}$ ,  $[\alpha]_D^{20} -13.1^\circ$  in  $\text{CHCl}_3$ , transformed by  $\text{Ag}_2\text{O}$  and  $\text{MeI}$  into 3:5:6-trimethyl-1:2-isopropylidene-glucosefuranose, b.p.  $138\text{--}140^\circ/12\text{ mm.}$ ,  $[\alpha]_D^{20} -27.3^\circ$  in  $\text{MeOH}$ . Dil.  $\text{AcOH}$  at  $100^\circ$  transforms (II) into 5-methylglucose (III), which does not yield a well-defined osazone. Probably (III) is a mixture of several tautomeric forms. The presence of free  $\text{CHO}$  is established by the immediate reddening of fuchsin- $\text{H}_2\text{SO}_4$ , instantaneous reduction of  $\text{KMnO}_4$ , and rapid reduction of cold Fehling's solution. It has  $[\alpha] \pm 0^\circ$  in  $\text{H}_2\text{O}$  and is not mutarotatory; in  $\text{EtOH}$  it has  $[\alpha]_D^{20} -10.6^\circ$ , the low val. pointing to the absence of an O bridge. H. W.

**Active form of monosaccharides. I. Reactivity of triphenylmethylglucose.** A. V. STEPANOV and B. N. STEPANENKO (Ber., 1936, 69, [B], 2046—2049).—Addition of  $\text{HCN}$  to glucose occurs less readily in 88% than in 10%  $\text{MeOH}$  due to smaller degree of dissociation of  $\text{NH}_4\text{CN}$ . In 10%  $\text{MeOH}$  addition is rapid initially but the rate falls and then increases owing to hydrolysis of the nitrile. In 88% or 98%  $\text{MeOH}$  the increase is not observed. 6-Triphenylmethylglucose reacts more rapidly than glucose. The result is attributed to increased ease of rupture of the O bridge owing to the presence of the negative group.

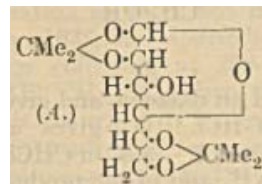
**Possibility of identifying small amounts of galactose as mucic acid.** A. SALVATORI, G.

LAPPONI, and S. BAGLIONI (Atti R. Accad. Lincei, 1934, [vi], 20, 437—444; Chem. Zentr., 1935, ii, 3956).—A method is given for detecting and determining 25 mg. of galactose in 25 c.c. of liquid.

**Open-chain derivatives of *d*-mannose.** M. L. WOLFROM and L. W. GEORGES (J. Amer. Chem. Soc., 1936, 58, 1781—1782).—aldehydo-*d*-Mannosoxime hexa-acetate (I), m.p.  $91\text{--}92^\circ$  (lit.  $94^\circ$ ), is hydrolysed ( $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  in  $\text{MeOH}$ ) to the penta-acetate (II), m.p.  $122\text{--}123^\circ$ ,  $[\alpha]_D^{20} +15^\circ$  in  $\text{CHCl}_3$ , which is acetylated to (I) and converted by  $\text{HNO}_2$  (method: A., 1934, 1092) into aldehydo-*d*-mannose penta-acetate (III), a syrup [semicarbazone (IV), m.p.  $177\text{--}178^\circ$  (decomp.), also obtained by acetylation ( $\text{Ac}_2\text{O}\text{-C}_5\text{H}_5\text{N}$  in the cold) of mannosesemicarbazone], (III) with  $\text{EtSH}$  and  $\text{ZnCl}_2$  gives the  $\text{Et}_2$  mercaptal (Piric, this vol., 593). (IV) and  $\text{HNO}_2$  also give (III), which is oxidized to (II). *d*-Mannose thus shows a marked tendency to react in the open-chain form (cf. Deulofeu *et al.*, A., 1934, 394). H. B.

**Iodometric determination of fructose.** S. STREPKOV (Ann. Chim. Analyt., 1936, [iii], 18, 231—232).—The solution containing fructose (I) is warmed at  $48.5\text{--}49^\circ$  with a standard  $\text{CuCO}_3$  reagent (II), filtered from reduced  $\text{Cu}_2\text{O}$ , and  $\text{Cu}$  in an aliquot part is determined iodometrically. (I) is determined from the decrease in titre of (II). J. S. A.

***d*-Diisopropylidenealtrose.** M. STEIGER and T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 1011—1016).—The conversion of *d*-ribose into crude altrose and of the latter into its benzylphenylhydrazone (I), m.p.  $151^\circ$  (corr.), is described. Treatment of (I) with  $\text{PhCHO}$  and  $\text{BzOH}$  in  $\text{H}_2\text{O}$  at  $100^\circ$  gives a non-cryst. altrose (II),  $[\alpha]_D^{20} +22^\circ$  in  $\text{H}_2\text{O}$ , whilst a methylated product (III) results when  $\text{MeOH}$  at  $60\text{--}65^\circ$  is substituted for  $\text{H}_2\text{O}$ . (II) is transformed by  $\text{COMe}_2\text{-CuSO}_4\text{-H}_2\text{SO}_4$  into *d*-diisopropylidenealtrose, m.p.  $89^\circ$ ,  $[\alpha]_D^{20} +28.27^\circ$  in  $\text{COMe}_2$ , which does not yield appreciable amounts of acid when oxidised with  $\text{KMnO}_4$ , and hence is probably A. (III) gives an anhydroisopropylidene-*d*-methylaltroside,  $\text{C}_{10}\text{H}_{16}\text{O}_6$ , m.p.  $132^\circ$  after softening at  $128^\circ$ ,  $[\alpha]_D^{20} -43.04^\circ$  in  $\text{COMe}_2$ . H. W.

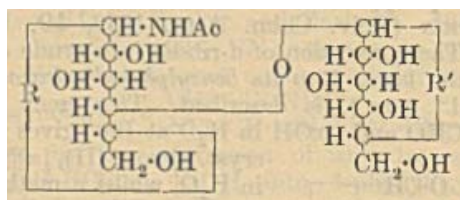


**Mechanism of carbohydrate oxidation. XX. Preparation of oligosaccharide acetates containing dihydroxyacetone constituents.** L. C. KREIDER and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1661—1665).—Partly a more detailed account of work previously reviewed (A., 1935, 477). The following is new.  $\beta$ -Cellobiosido-, m.p.  $169^\circ$  (all m.p. are corr.),  $[\alpha]_D^{20} -27.1^\circ$  in  $\text{CHCl}_3$  (*p*-nitrophenylhydrazone, m.p.  $176^\circ$ ), and  $\beta$ -gentiobiosido-, m.p.  $172^\circ$ ,  $[\alpha]_D^{20} -25.9^\circ$  in  $\text{CHCl}_3$  (methyl alcoholate, m.p.  $110\text{--}112^\circ$ , resolidifying with m.p.  $171\text{--}172^\circ$ ; *p*-nitrophenylhydrazone, m.p.  $155^\circ$ ), -dihydroxyacetone octa-acetates are prepared (method: this vol., 827) from  $\text{OH}\cdot\text{CH}_2\text{-CO}\cdot\text{CH}_2\text{-OAc}$  and acetobromo-cellobiose and -gentiobiose, respectively. Attempted



deacetylation (mildest conditions) caused deep-seated changes. H. B.

**Action of liquid ammonia on cellobiose octa-acetate.** L. ZECHMEISTER and G. TÓTH [with I. PINCZÉSI] (Annalen, 1936, 525, 14—24).—Treatment of cellobiose octa-acetate with liquid  $\text{NH}_3$  followed by acid hydrolysis of the product gives cellobiose or its osazone in quant. yield, showing that the reaction remains at the disaccharide stage and that  $\text{C}_{12}$  and  $\text{C}_{13}$ , the non-reducing half of the biose mols., and the bridge O are not concerned with the position of N. The mixed product is difficult to manipulate after exhaustive acetylation, but it is thereby established that very little of it is formed by union of cellobiose residues. Better results are obtained by gentle acetylation affecting only the NH groups, whereby the more sparingly sol. *acetamidocellobiose* (I) ( $\text{R}=\text{R}'=\text{O}$ ), m.p.  $246^\circ$  (corr.) after softening at  $225^\circ$ ,  $[\alpha]_D^{20} -20.3^\circ$  in  $\text{H}_2\text{O}$ , is obtained. The position of  $\text{NHAc}$  follows from the formation of  $\text{NH}_4\text{Cl}$  when (I) is boiled with  $N\text{-HCl}$ , the very low I val. of (I), its slight reducing power towards Fehling's solution, and the non-formation of an osazone. Treatment of (I) with  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  gives the corresponding *peracetate*, m.p.  $196^\circ$  (corr.) after softening at  $194^\circ$ ,  $[\alpha]_D^{20} -8.4^\circ$  in  $\text{CHCl}_3$ , hydrolysed by  $\text{NaOMe}$  to (I). The mother-liquors from (I) yield *diacetamidocellobiose* (II) ( $\text{R}=\text{NAc}$ , and  $\text{R}'=\text{O}$  or  $\text{R}'=\text{NAc}$  and  $\text{R}=\text{O}$ ),  $[\alpha]_D^{20} -20^\circ$  in  $\text{H}_2\text{O}$ , which has a very low I val., does not reduce Fehling's solution



until hydrolysed, does not yield an osazone, and gives  $\text{NH}_4\text{Cl}$  when boiled with  $N\text{-HCl}$ . (II) gives an  $\text{Ac}_9$  derivative, m.p.  $196^\circ$  (corr.),  $[\alpha]_D^{20} -3.3^\circ$  in  $\text{CHCl}_3$ . Treatment of cellobiose with  $\text{NH}_3$  and of the product with  $\text{Ac}_2\text{O}$  in  $\text{C}_5\text{H}_5\text{N}$  gives the *substance*,  $\text{C}_{10}\text{H}_{55}\text{O}_{16}\text{N}$ , m.p.  $225^\circ$  (corr.). H. W.

**Semicarbazone and oxime acetates of maltose and cellobiose.** *aldehydoCellobiose octa-acetate*. M. L. WOLFROM and S. SOLTZBERG (J. Amer. Chem. Soc., 1936, 58, 1783—1785).—*Maltosesemicarbazone*, m.p.  $213^\circ$  (decomp.), is acetylated ( $\text{Ac}_2\text{O}$ — $\text{C}_5\text{H}_5\text{N}$  at  $60$ — $65^\circ$  and then at room temp.) to the  $\beta$ -*octa-acetate* (I), m.p.  $209$ — $210^\circ$  (decomp.),  $[\alpha]_D^{20} +61^\circ$  in  $\text{CHCl}_3$ , which contains 7 OAc and 1 NAc (method: this vol., 592). Similar acetylation (at room temp.) of cellobiosesemicarbazone gives the  $\beta$ -*hepta-acetate* (II), m.p.  $207$ — $208^\circ$ ,  $[\alpha]_D^{27} -21^\circ$  in  $\text{CHCl}_3$ , further acetylated (at  $40^\circ$ ) to the  $\beta$ -*octa-acetate* (III), m.p.  $240$ — $241^\circ$  (decomp.),  $[\alpha]_D^{23} -26.5^\circ$  in  $\text{CHCl}_3$ , also containing 7 OAc and 1 NAc. Successive oximation and acetylation of cellobiose hepta-acetate affords  $\beta$ -*cellobioseoxime nona-acetate* (IV), m.p.  $195$ — $195.5^\circ$ ,  $[\alpha]_D^{27} -8.5^\circ$  in  $\text{CHCl}_3$ , which is not hydrolysed by  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{MeOH}$ . (I)—(IV) all possess ring structures. The cellobioscantoxime octa-acetate of

Zemplén (A., 1926, 822) is probably impure (IV). Cellobioseoxime is acetylated in the cold to an amorphous nona-acetate (which when heated gives cellobionitrile octa-acetate), hydrolysed ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{MeOH}$ ) to *aldehydocellobioseoxime octa-acetate* (V), m.p.  $154$ — $155^\circ$ ,  $[\alpha]_D^{20} +30^\circ$  in  $\text{CHCl}_3$ , which contains 8 OAc and is converted by  $\text{HNO}_3$  into the amorphous *aldehydocellobiose octa-acetate*,  $[\alpha]_D +17.7^\circ$  in  $\text{CHCl}_3$ . This reduces Fehling's solution and is oximated to (V). The behaviour of the above cellobiose derivatives on acetylation is the reverse of that of the corresponding glucose compounds (A., 1934, 1092).

H. B.

**Verbenalol, aglucone of verbenalin.** J. CHEYMOL (Compt. rend., 1936, 203, 543—545).—Emulsin hydrolyses verbenalin (I) to glucose and *verbenalol* (II),  $\text{C}_{11}\text{H}_{14}\text{O}_5$ , m.p.  $133^\circ$  from  $\text{Et}_2\text{O}$  or  $140.5^\circ$  from  $\text{AcOH}$ ,  $[\alpha]_D^{19} -29.07^\circ$  in  $\text{H}_2\text{O}$  (cf. A., 1908, i, 197; 1928, 1137), which contains a lactone ring and a strongly reducing group. The ultra-violet absorption spectra of (I) and (II) are different. (I) with 2.5%  $\text{H}_2\text{SO}_4$  gives glucose and an *l*-aglucone, which may be (II). J. L. D.

**Starch and the Schardinger dextrans.** K. FREUDENBERG and W. RAPP (Ber., 1936, 69, [B], 2041—2045).—Detailed instructions are given for the separation of potato starch into amylose,  $[\alpha]_{5780}^{20} +203 \pm 1^\circ$  (initial) in 51%  $\text{H}_2\text{SO}_4$ ,  $[\alpha]_{780}^{20} +164 \pm 1^\circ$  in  $N\text{-NaOH}$  (acetate,  $[\alpha]_D^{20} +172 \pm 2^\circ$  in  $\text{CHCl}_3$ ), and amylopectin,  $[\alpha]_{5780}^{20} 206 \pm 1^\circ$  in 51%  $\text{H}_2\text{SO}_4$ ,  $[\alpha]_{5780}^{20} +169 \pm 2^\circ$  in  $N\text{-NaOH}$ . Methylstarch is obtained by treating starch acetate suspended in  $\text{COMe}_2$  with  $\text{NaOH}$  and  $\text{Me}_2\text{SO}_4$  at  $20^\circ$  and then at  $50^\circ$ ; the processes of acetylation and methylation are repeated, giving a product with 38—39% OMe. Methylation of  $\alpha$ -dextrin (I) is effected by adding a solution of K in liquid  $\text{NH}_3$  to a solution of (I) in the same solvent at  $-50^\circ$ , removing the solvent, and treating the residue with excess of  $\text{MeI}$  in  $\text{Et}_2\text{O}$ , thus yielding *methyl- $\alpha$ -dextrin* (II),  $[\text{C}_6\text{H}_7\text{O}_2(\text{OMe})_3]_5$ , m.p.  $208$ — $210^\circ$ ,  $[\alpha]_D^{20} +162^\circ$  in  $\text{CHCl}_3$ .  $\beta$ -Dextrin is methylated with greater difficulty and ultimately yields a product (III), m.p. (indef.)  $190^\circ$ ,  $[\alpha]_D^{20} +151^\circ$  in  $\text{CHCl}_3$ , with 42.5% OMe (theory 45.5% OMe). Treatment of (II) with boiling 1%  $\text{HCl}$ — $\text{MeOH}$  affords trimethylmethylglucoside; no trace of pentamethylglucose can be isolated from it after treatment with  $\text{BzCl}$  in  $\text{C}_5\text{H}_5\text{N}$  at  $30^\circ$  and on hydrolysis it appears to give 2:3:6-trimethylglucose (IV) exclusively. During hydrolysis of (II) and (III) by 51%  $\text{H}_2\text{SO}_4$  at  $20^\circ$ ,  $[\alpha]$  rises initially and then sinks to the val. required by (IV). The course of hydrolysis appears the same for each product. The initial rise indicates the presence of a readily ruptured  $\beta$ -union which is not a cellobiose linking. Takadiastase at  $p_{\text{H}}$  4.5 hydrolyses (I) to homogeneous glucose.  $\gamma$ -Dextrin appears to be changed similarly but more complex results are given by  $\beta$ -dextrin. H. W.

**Determination of specific weights of cellulose solutions.** Specific weights of double compounds of cellulose derivatives with organic solvents.—See this vol., 1337.

**Simple enamines with tertiary nitrogen.** C. MANNICH and H. DAVIDSEN (Ber., 1936, 69, [B],

2106—2112).—Aldehydes and *sec.* amines in presence of anhyd.  $K_2CO_3$  readily yield diamines which when suitably heated lose 1 mol. of *sec.* amine with formation of enamines, which readily darken when preserved, are moderately stable towards  $H_2O$  and alkali, but readily hydrolysed by acids. They add 1 mol. of *sec.* base. They are readily hydrogenated, thus giving a method of converting aldehydes into the corresponding *tert.* amines or into primary or *sec.* amines if the basic component contains  $CH_2Ph$ . Condensation of ketones with *sec.* amines does not occur in presence of  $K_2CO_3$ , but can sometimes be effected if  $CaO$  is used at a somewhat higher temp.  $MeCHO$ , piperidine (I), and anhyd.  $K_2CO_3$  at  $> 5^\circ$  afford  $\alpha\alpha$ -dipiperidinoethane, b.p.  $58-60^\circ/0.3$  mm., transformed by distillation at higher pressure into (I) and 1-vinylpiperidine, which is hydrogenated to 1-ethylpiperidine. The following compounds are analogously obtained: 1- $\Delta^{\alpha}$ -propenylpiperidine, b.p.  $61-63^\circ/10$  mm., hydrogenated ( $PtO_2$  in cyclohexane) to 1-propylpiperidine; 1- $\Delta^{\alpha}$ -butenylpiperidine, b.p.  $70-71^\circ/10$  mm., whence 1-n-butylpiperidine, and  $\alpha\alpha$ -dipiperidino-n-butane; 1- $\beta$ -methyl- $\Delta^{\alpha}$ -propenylpiperidine, b.p.  $65-67^\circ/12$  mm., whence 1-isobutylpiperidine; 1- $\Delta^{\alpha}$ -heptenylpiperidine, b.p.  $129-130^\circ/10$  mm., whence 1-n-heptylpiperidine, b.p.  $121^\circ/13$  mm. (picrate, m.p.  $98^\circ$ ); diethyl- $\Delta^{\alpha}$ -heptenylamine, b.p.  $134-140^\circ/110$  mm., whence diethylheptylamine, b.p.  $198^\circ$  (aurichloride, m.p.  $48^\circ$ ); non-homogeneous phenylmethyl- $\Delta^{\alpha}$ -butenylamine (in poor yield), hydrogenated to  $NPhMeBu^{\alpha}$ ; styryldiethylamine, b.p.  $147-150^\circ/16$  mm.; 1-styrylpiperidine, b.p.  $174-175^\circ/15$  mm., m.p.  $29-30^\circ$ , hydrogenated to 1- $\beta$ -phenylethylpiperidine, b.p.  $138-139^\circ/14$  mm.;  $\alpha\alpha$ -dibenzylmethylamino- $\beta$ -phenylethane, an oil, whence benzylstyrylmethylamine, b.p.  $171-173^\circ/0.7$  mm., hydrogenated ( $PtO_2$  in EtOH at  $45^\circ$ ) to benzyl- $\beta$ -phenylethylmethylamine, b.p.  $135-136^\circ/0.6$  mm. (methiodide, m.p.  $182^\circ$ ), and ( $Pd-C$  in EtOH) to  $\beta$ -phenylethylmethylamine (hydrochloride, m.p.  $157-158^\circ$ ); dibenzylstyrylamine, m.p.  $120^\circ$ , hydrogenated ( $PtO_2$  or  $Pd-C$ ) to dibenzyl- $\beta$ -phenylethylamine (hydrobromide, m.p.  $213^\circ$ ) or  $PhMe$  and  $CH_2Ph \cdot CH_2 \cdot NH_2$ , respectively;  $\beta$ -piperidino- $\alpha$ -phenyl- $\Delta^{\alpha}$ -propene, b.p.  $157-161^\circ/13$  mm., hydrogenated to  $\beta$ -piperidino- $\alpha$ -phenylpropane, b.p.  $143-145^\circ/14$  mm. (hydrobromide, m.p.  $208^\circ$ ; methiodide, m.p.  $181^\circ$ ); 1- $\Delta^{\alpha}$ -cyclohexenylpiperidine, b.p.  $116-118^\circ/16$  mm., from the base, cyclohexanone, and  $CaO$  at  $100^\circ$  during 50 hr., whence 1-cyclohexylpiperidine, b.p.  $106-107^\circ/16$  mm. [methiodide (II), m.p.  $253^\circ$ ]. (II) is transformed by  $Ag_2O-H_2O$  followed by heating at  $200^\circ$  into cyclohexylmethyl- $\Delta^{\alpha}$ -pentenylamine, b.p.  $108-110^\circ/14$  mm., hydrogenated ( $PtO_2$  in EtOH) to cyclohexylmethylamine, b.p.  $113-114^\circ/14$  mm.

**Formation of enamines and alleneamines from -unsaturated aldehydes and secondary bases.** C. MANNICH, K. HANDKE, and K. ROTH (Ber., 1936, 69, [B], 2112—2123).— $\alpha\beta$ -Unsaturated aldehydes are readily resinified in presence of *sec.* amines, whereby the latter behave entirely as catalyst. If, however, the liberated  $H_2O$  is absorbed by much anhyd.  $K_2CO_3$  and the temp. is carefully regulated, additive compounds  $NR_2 \cdot CHR \cdot CH:CH \cdot NR_2$  result. The latter readily darken on exposure to air, and are

frequently so unstable that they cannot be distilled in vac. They are very readily hydrolysed. The location of the double linking is established by hydrogenation. When heated they are converted into doubly unsaturated monoamines of the allene type. Gradual addition of freshly distilled acetaldehyde in Et<sub>2</sub>O to 45%  $NHMe_2-H_2O$  in Et<sub>2</sub>O accompanied by introduction of anhyd.  $K_2CO_3$  in successive small amounts at  $-5^\circ$  to  $0^\circ$  affords  $\alpha\gamma$ -bisdimethylamino- $\Delta^{\alpha}$ -propene, b.p.  $52-54^\circ/13$  mm. (60% yield), reduced ( $PtO_2$  in cyclohexane) to  $\alpha\gamma$ -bisdimethylaminopropane, b.p.  $143-145^\circ$  (picrate, m.p.  $207^\circ$ ; platinichloride, m.p.  $247^\circ$ ). The following are obtained analogously:  $\alpha\gamma$ -dipiperidinopropene, b.p.  $150-152^\circ/12$  mm. when very rapidly distilled (slow distillation appears to yield polymeric piperidinoallene), hydrogenated ( $PtO_2$ ) to  $\alpha\gamma$ -dipiperidinopropane, b.p.  $135-137^\circ/12$  mm. [platinichloride, decomp.  $230-232^\circ$ ; picrate, m.p.  $217-219^\circ$  (decomp.)], and reduced by  $Na-Hg$  in 10% AcOH to  $\gamma$ -piperidinopropanol, b.p.  $102-104^\circ/12$  mm. (corresponding benzoate hydrochloride, m.p.  $186^\circ$ );  $\alpha\gamma$ -bisdimethylamino- $\Delta^{\alpha}$ -butene, b.p.  $64^\circ/17$  mm., thermally decomposed into  $\alpha$ -dimethylamino- $\gamma$ -methylallene and hydrogenated to  $NMe_2Bu^{\alpha}$ ,  $NMe_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NMe_2$ , and  $NHMe_3$ ;  $\alpha\gamma$ -dipiperidino- $\Delta^{\beta}$ -butene (I), hydrogenated ( $PtO_2$  in MeOH) mainly to  $\alpha\gamma$ -dipiperidinobutane, b.p.  $159-160^\circ/18$  mm. (hydrobromide, m.p.  $272-275^\circ$ ), and reduced by  $Na-Hg$  to  $\gamma$ -piperidinobutanol (nitrobenzoate hydrochloride, m.p.  $176^\circ$ ); 1-piperidino- $\gamma$ -methylallene, b.p.  $98^\circ/15$  mm. (aurichloride, m.p.  $91^\circ$ ), from (II) at  $130-140^\circ/vac.$ , hydrogenated to  $\alpha$ -piperidinobutane, b.p.  $172^\circ$  (picrate, m.p.  $131^\circ$ );  $\alpha\gamma$ -dipiperidino- $\alpha$ -phenyl- $\Delta^{\beta}$ -propene, m.p.  $58^\circ$  after softening at  $55-56^\circ$ , whence  $\gamma$ -piperidino- $\alpha$ -phenylpropane and  $\gamma$ -piperidino- $\alpha$ -phenylallene which is too unstable to permit isolation as such, but is characterised as the picrate, m.p.  $164^\circ$ , and hydriodide, m.p.  $211-212^\circ$  (decomp.) after softening at  $206-207^\circ$ , both of which yield  $CHPh \cdot CH \cdot CHO$  when distilled with steam and the latter of which is hydrogenated ( $PtO_2$  in abs. EtOH) to  $\gamma$ -piperidino- $\alpha$ -phenylpropane, b.p.  $140^\circ/15$  mm. (hydrochloride, m.p.  $184-185^\circ$ ; hydriodide, m.p.  $138^\circ$ ; methiodide, m.p.  $134-135^\circ$ ), also obtained from  $C_5H_{10}N \cdot CH_2 \cdot C \cdot CPh$ ;  $\alpha$ -dimethylamino- $\gamma\gamma$ -dimethyl- $\Delta^{\beta\gamma}$ -octatriene, b.p.  $123-124^\circ/12$  mm., hydrolysed to citral and hydrogenated mainly to  $\alpha$ -dimethylamino- $\gamma\gamma$ -dimethyl- $\Delta^{\beta\gamma}$ -octadiene [methiodide (II), m.p.  $178-180^\circ$ , which yields  $NMe_3$  when hydrogenated], which passes by addition of  $H_2O$  into  $\alpha$ -dimethylamino- $\gamma\gamma$ -dimethyl- $\Delta^{\beta}$ -octen- $\gamma$ -ol, b.p.  $125^\circ/11$  mm. (hydrochloride, m.p.  $110-111^\circ$ ; methiodide, m.p.  $111-112^\circ$ );  $\beta$ -methyl- $\zeta$ -methylene- $\Delta^{\beta\gamma}$ -octadiene (myrcene), b.p.  $56-58^\circ/15$  mm., obtained from (II) and  $Ag_2O$ , oxidised by  $KMnO_4$  to  $COMe_3$ ,  $CH_2(CO_2H)_2$ ,  $AcOH$ , and  $HCO_2H$  and hydrogenated ( $PtO_2$ ) to  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -octene and thence slowly to  $\beta\zeta$ -dimethyloctene;  $\alpha$ -dimethylamino- $\gamma\gamma$ -dimethyl- $\Delta^{\delta}$ -octene, b.p.  $99-100^\circ/16$  mm. [hydrochloride, m.p.  $167^\circ$ ; methiodide, m.p.  $220-222^\circ$ , degraded (Hofmann) to  $\beta\zeta$ -dimethyl- $\Delta^{\beta\gamma}$ -octadiene, b.p.  $160-161^\circ$ , identical with  $\beta$ -linalolene], transformed by addition of  $H_2O$  into a substance,  $C_{22}H_{42}ON$ , b.p.  $128-130^\circ/14$  mm. (hygroscopic hydrochloride, m.p.  $96^\circ$ ; methiodide, m.p.  $100-101^\circ$ ), and hydrogenated ( $PtO_2$  in abs. EtOH) to  $\alpha$ -dimethyl-



amino- $\gamma$ -dimethyloctane, b.p. 96°/15 mm. (hydrochloride, m.p. 186—187°; methiodide, m.p. 242°).

H. W.

**Photochemical deamination of amino-acids.**—See this vol., 1349.

**Preparation of methionine-free natural leucine.** S. W. FOX (Science, 1936, 84, 163).—Recrystallisation of the formylated  $\text{NH}_2$ -acid yields (50%) a S-free leucine without appreciable racemisation.

L. S. T.

**Structure of Wedekind's ketenium compounds.** L. L. MILLER and J. R. JOHNSON (J. Org. Chem., 1936, 1, 135—140).—Wedekind's ketenium compounds (A., 1922, i, 234), formed in small amounts from  $\text{CH}_3\text{R}\cdot\text{COCl}$  and  $\text{CHR}_2\cdot\text{COCl}$  and  $\text{NEt}_3$ , are shown by hydrolysis and by synthesis to be the diethylamides of the acids, formed from  $\text{NHEt}_2$  present as impurity in the  $\text{NEt}_3$  used. The chief product,  $\text{CMe}_2\text{CO}$  dimeride, of the reaction with  $\text{Pr}^i\text{COCl}$  is obtained in 60% yield when anhyd.  $\text{Et}_2\text{O}$  or ligroin (60—80°) is used as solvent. The following have been prepared: isobutyryl, b.p. 192—194°/740 mm., phenylchloroacet., m.p. 51—51.5°, b.p. 156—158°/4 mm., dichloroacet., b.p. 124—126°/19 mm., and bromoacet., b.p. 114—117°/9 mm., -diethylamide.

H. G. M.

**Carbamide series. XIII. Nitroalkyl-carbamides and -biurets.** T. L. DAVIS and N. D. CONSTAN (J. Amer. Chem. Soc., 1936, 58, 1800—1803; cf. A., 1933, 383).— $\text{NHR}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HNO}_3$  ( $\text{R} = \text{Et}, \text{Pr}^i, \text{Bu}^i$ , m.p. 70—71°,  $n$ -amyl, m.p. 75°) and conc.  $\text{H}_2\text{SO}_4$  at <15° give  $N$ -nitro- $N'$ -ethyl-, m.p. 133—134° (lit. 130—131°),  $N'$ - $n$ -propyl-, m.p. 96°,  $N'$ - $n$ -butyl- (I), m.p. 80—81°, and  $N'$ - $n$ -amyl- (II), m.p. 62°, -carbamide, respectively, whilst  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{HNO}_3$  affords  $\text{NO}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$  (I) and (II) with  $\text{NH}_2\text{Ph}$  in warm  $\text{H}_2\text{O}$  give  $N$ -phenyl- $N'$ - $n$ -butyl-, m.p. 129—130°, and  $N'$ - $n$ -amyl-, m.p. 92°, -carbamide, respectively (also prepared from  $\text{PhNCO}$  and  $\text{NH}_2\text{Alk}$ ); (I) and warm conc. aq.  $\text{NH}_3$  afford  $\text{NHBu}^i\cdot\text{CO}\cdot\text{NH}_2$ .  $\text{NN}$ -Dimethyl-, m.p. 103—104°, -diethyl-, m.p. 118°, and -di- $n$ -propyl-, m.p. 165°, -carbamide nitrates with conc.  $\text{H}_2\text{SO}_4$  yield the  $\text{NAlk}_2\cdot\text{NO}_2$ ;  $\text{CO}(\text{NHMe})_2$  and  $\text{CO}(\text{NHEt})_2$  could not be nitrated.  $\alpha$ -Methyl- and  $\alpha$ -dimethyl-biuret with  $\text{HNO}_3$  (d 1.42) and conc.  $\text{H}_2\text{SO}_4$  at <15° give the  $\alpha'$ - $\text{NO}_2$ -derivatives, m.p. 99—100° (decomp.) and 114—115° (decomp.) (III), respectively, which with aq.  $\text{NH}_3$  afford the original biuret. (III) and  $\text{NH}_2\text{Me}$ ,  $n$ -amylamine, and  $\text{NH}_2\text{Ph}$  in  $\text{H}_2\text{O}$  yield  $\alpha\alpha'$ -trimethyl-, m.p. 154°,  $\alpha\alpha'$ -dimethyl- $\alpha$ - $n$ -amyl-, m.p. 149°, and -phenyl- $\alpha\alpha'$ -dimethyl-, sublimes about 225°, -biuret, respectively; in these reactions (III) probably rearranges to  $\text{NMe}_2\cdot\text{CO}\cdot\text{NCO}$  which then reacts with the  $\text{NH}_2\text{R}$ .

H. B.

**Optical rotation of configuratively related azides.** P. A. LEVENE and A. ROTHEN [with M. KUNA] (J. Biol. Chem., 1936, 115, 415—428).—In the series,  $\text{CHMeR}\cdot[\text{CH}_2]_n\cdot\text{X}$ , the results are similar for compounds in which  $\text{X} = \text{N}_3$  or halogen only if  $n = 0$ .  $d$ -sec.-BuOH,  $[\alpha] +6.82^\circ$ , with cold  $\text{COMe}_2$ -HI gives  $l$ -sec.-butyl iodide, b.p. 111—118°,  $[\alpha] -13.1^\circ$ , and thence the azide, b.p. 85°/500 mm.,  $[\alpha] +16^\circ$ , and  $d$ -sec.-butylamine,  $[\alpha] +0.9^\circ$  (hydro-

chloride,  $[\alpha] -0.4^\circ$  in  $\text{H}_2\text{O}$ ).  $d$ -Octan- $\beta$ -ol,  $[\alpha] +9.6^\circ$ , gives  $l$ - $\beta$ -iodo-, b.p. 52°/1 mm.,  $[\alpha] -33.3^\circ$ ,  $d$ - $\beta$ -azido-, b.p. 68/9 mm.,  $[\alpha] +28^\circ$  (homogeneous),  $+27.4^\circ$  in heptane, and  $d$ - $\beta$ -amino- $n$ -octane, b.p. 48°/9 mm.,  $[\alpha] +4.19^\circ$  (hydrochloride,  $[\alpha] -3.89^\circ$  in  $\text{H}_2\text{O}$ ; platinichloride).  $d$ -CHMeEt $\cdot\text{CH}_2\cdot\text{OH}$ ,  $[\alpha] -4.4^\circ$ , affords  $d$ - $\alpha$ -iodo-, b.p. 145—146°,  $[\alpha] +4.18^\circ$ , max.  $[M] +11.1^\circ$ ,  $d$ - $\alpha$ -azido-, b.p. 72°/138 mm.,  $[\alpha] +7.61^\circ$ , max.  $[M] +11.6^\circ$ , and  $l$ - $\alpha$ -amino- $\beta$ -methyl- $n$ -butane (hydrochloride,  $[\alpha] -0.124^\circ$  in  $\text{H}_2\text{O}$ , max.  $[M] -0.21^\circ$  in  $\text{H}_2\text{O}$ ).  $d$ - $\beta$ -Methylhexyl iodide,  $[\alpha] +0.37^\circ$ , gives  $l$ - $\alpha$ -azido- $\beta$ -methyl- $n$ -hexane, b.p. 59—60°/15 mm.,  $[\alpha] -0.3^\circ$ .  $l$ - $\beta$ -Methylnonan- $\alpha$ -ol,  $[\alpha] -2.58^\circ$ , yields  $d$ - $\alpha$ -iodo-, b.p. 86°/4 mm.,  $[\alpha] +0.68^\circ$ , and  $l$ - $\alpha$ -azido- $\beta$ -methyl- $n$ -nonane, b.p. 98—102°/10 mm.,  $[\alpha] -0.4^\circ$ .  $l$ - $\gamma$ -Methyl- $n$ -pentan- $\alpha$ -ol,  $[\alpha] -3.2^\circ$ , gives  $l$ - $\alpha$ -iodo-, b.p. 54°/12 mm.,  $[\alpha] -7.61^\circ$ , and  $l$ - $\alpha$ -azido- $\gamma$ -methylpentane, b.p. 145—148°,  $[\alpha] -7.58^\circ$ , max.  $[M] -26.3^\circ$  in heptane.  $d$ - $\delta$ -Methylhexan- $\alpha$ -ol,  $[\alpha] +3.21^\circ$ , gives  $d$ - $\alpha$ -iodo-, b.p. 74—75°/13 mm.,  $[\alpha] +3.63^\circ$ , max.  $[M] +26.2^\circ$ , and  $d$ - $\alpha$ -azido- $\delta$ -methylhexane, b.p. 157°/418 mm.,  $[\alpha] +3.83^\circ$ , max.  $[M] +17.3^\circ$  in heptane.  $[\alpha]$  and  $[M]$  are  $[\alpha]^{25}$  and  $[M]^{25}$  (homogeneous) unless otherwise stated.

R. S. C.

**Synthesis and refractometric study of saturated  $\alpha$ -methylnitriles.** C. DE HOFFMANN and E. BARBIER (Bull. Soc. chim. Belg., 1936, 45, 565—583).—Et  $\alpha$ -cyanopropionate (Na derivative) in EtOH with alkyl bromides affords Et  $\alpha$ -cyano- $\alpha$ -alkylpropionates. The following are described: Et  $\alpha$ -cyano- $\alpha$ -ethyl-, b.p. 84—85°/12 mm., -propyl-, b.p. 96—97°/11 mm., -butyl-, b.p. 105—106°/10.5 mm., -amyl-, b.p. 118—119°/10.5 mm., -hexyl-, b.p. 132—133°/10.5 mm., -heptyl-, b.p. 143—144°/10.5 mm., -octyl-, b.p. 155—156°/10.5 mm., -nonyl-, b.p. 167—168°/11.5 mm., -decyl-, b.p. 180—181°/12 mm., and -dodecyl-propionate, b.p. 204—205°/10.5 mm. These are converted by hydrolysis (decarboxylation) into  $\alpha$ -methyl-, m.p. 126—128°, -ethyl-, m.p. 111.4°, -propyl-, m.p. 79.6°, -butyl-, m.p. 69.2°, -amyl-, m.p. 78.8°, -hexyl-, m.p. 80.8°, -heptyl-, m.p. 76.4°, -octyl-, m.p. 81.4°, -nonyl-, m.p. 85.4°, -decyl-, m.p. 91.2°, and -dodecyl-propionamide, m.p. 96.8°, which with  $\text{P}_2\text{O}_5$  afford the corresponding nitriles, b.p. 103.4°/753.1 mm., 125.2°/755.2 mm., 146.6°/750.5 mm., 164.8°/761.8 mm., 184.8°/761.8 mm., 85.4°/10 mm., 99.9°/10 mm., 115.4°/10 mm., 133.4°/12 mm., 146.3°/12 mm., and 170.6°/12 mm. Many physical properties of the nitriles are tabulated and the mol. refractivity for  $\text{CH}_2$  is calc. as 4.632 at 15° and 4.644 at 30°.

J. L. D.

**Behaviour of tautomeric substances towards diazomethane.** F. ARNDT (Rev. Fac. Sci. Univ. Istanbul, 1936, 1, 1—8).—A summary of previous work (cf. A., 1933, 146; 1934, 770; 1935, 334; this vol., 59).

H. G. M.

**Introduction of silicon into fats.** G. KLEIN and H. NIENBURG (Ber., 1936, 69, [B], 2066—2068).—Esters  $[\text{CO}_2\text{R}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{COR})\cdot\text{CH}_2\cdot\text{O}]_n\text{Si}$  and  $[\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}]_n\text{Si}$  are obtained when a mono- or di-glyceride (4 mols.) is heated with  $\text{Si}(\text{OEt})_4$  at 150—160°. Orthosilicates of the following are described:  $\alpha$ -monostearin, m.p. 70°;  $\alpha\beta$ -distearin, m.p.

68°;  $\alpha$ -mono-olein, non-cryst.;  $\alpha$ -monobutylin, non-cryst.;  $\alpha\beta$ -dibutylin, non-cryst. H. W.

**Organic compounds of mercury. XIV. Reaction of hydroxyethylmercury bromide with diazomethane.** R. C. FREIDLIN, A. N. NESMEJANOV, and F. A. TOKAREVA (Ber., 1936, 69, [B], 2019—2021; cf. this vol., 1132).—The action of  $\text{CH}_2\text{N}_2$  on hydroxyethylmercury bromide (I) in cold  $\text{Et}_2\text{O}$  gives  $\text{N}_2$  and an unstable oil which evolves  $\text{C}_2\text{H}_4$  quantitatively when warmed and gives  $\text{CH}_2\text{Br}\cdot\text{HgBr}$  with small amounts of  $\text{Hg}$  and  $\text{CH}_2\text{O}$  (formed from  $\text{CH}_3\text{N}_3$ ). The experiments do not permit a decision between the structures  $\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}\cdot\text{OH}$  and  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{HgBr}$  for (I) but the latter is preferred.  $\text{CH}_2\text{Br}\cdot\text{HgBr}$  and 2% aq.  $\text{NaOH}$  yield  $\text{Hg}$ ,  $\text{CH}_2\text{O}$ , and  $\text{Br}^-$ .  $\text{HgBr}_2$  is transformed by a large excess of  $\text{CH}_2\text{N}_2$  into *Hg dibromomethyl*, m.p. 42—43°.

H. W.

**Co-ordination compounds of platinum halides with unsaturated substances.** M. S. KHARASCH and T. A. ASHFORD (J. Amer. Chem. Soc., 1936, 58, 1733—1738).—Compounds  $(\text{R}\cdot\text{PtCl}_2)_2$ , where  $\text{R} = \text{cyclohexene}$  (I), dipentene, pinene,  $\text{C}_2\text{H}_4$ , isobutene,  $\text{CHPh}\cdot\text{CH}_2$ ,  $(\text{CHPh})_2$ , or *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ , and  $(\text{R}\cdot\text{PtBr}_2)_2$ , where  $\text{R} = (\text{I})$  or  $\text{CHPh}\cdot\text{CH}_2$ , have been prepared. The respective m.p. of the above compounds are 145—146°, 151—152°, 138—141°, 170—180°, 144—145°, 169—171°, 191—192°, 155—160°, 150—151°, 153—154°. Optical and solubility data are recorded. E. S. H.

**Reduction of aromatic compounds with hydrogen and a platinum oxide-platinum-black catalyst in presence of halogen acid.** J. H. BROWN, H. W. DURAND, and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 1594—1596).—Reduction (Adams) of  $\text{PhBr}$ ,  $\text{PhCl}$ ,  $p\text{-C}_6\text{H}_4\text{Cl}_2$ ,  $p\text{-C}_6\text{H}_4\text{Br}_2$ , and *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeBr}$  gives the cyclohexane and  $\text{HHal}$  (which activates the catalyst);  $\text{PhI}$ ,  $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ ,  $1\text{-C}_{10}\text{H}_7\text{Cl}$ , and  $1\text{-C}_{10}\text{H}_7\text{Br}$  were unaffected.  $\text{C}_6\text{H}_5$ ,  $\text{PhMe}$ ,  $\text{C}_6\text{H}_4\text{Me}_2$ ,  $s\text{-C}_6\text{H}_3\text{Me}_3$ ,  $\text{PhEt}$ , cymene, and  $\text{Ph}_2$  are similarly reduced in presence of a little  $\text{HCl}$  or  $\text{HBr}$ ; anthracene gives octa- and tetradeca-hydroanthracene but phenanthrene and  $\text{C}_{10}\text{H}_8$  are unaffected. The following reductions are effected similarly:  $\text{PhOH}$  to cyclohexanol (occurs more slowly in absence of  $\text{HHal}$ ),  $\text{EtOBz}$  to  $\text{C}_6\text{H}_{11}\cdot\text{CO}_2\text{Et}$ ,  $\text{COPhMe}$  to ethylcyclohexane,  $\text{PhOMe}$  to cyclohexane, and  $\alpha$ - and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$  to the 5:6:7:8- $\text{H}_4$ -derivatives. H. B.

**Decomposition of cyclohexyl bromide in presence of mercuric bromide and the formation of cyclohexene polymerides.** F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 784—790).—cyclohexyl bromide (0.1 mol.) when heated for 580 hr. with  $\text{HgBr}_2$  gave 0.06 mol. of polymerised cyclohexene (I), but the use of  $\text{HgBr}$  led to no appreciable polymerisation under similar conditions, nor was (I) produced in appreciable yield in the absence of  $\text{Hg}$  salts.  $\text{Cu}$  retarded the reaction, which was not appreciably catalysed by  $\text{Pt}$ . Pure cyclohexene (I) under similar treatment polymerised slightly; hence it is suggested that polymerisation occurs only at the moment of formation of (I). Fractional distillation of the polymerised substance gave cyclohexylcyclo-

hexene and resinous substances. From one fraction, crystallisation from  $\text{Et}_2\text{O}$  gave a substance,  $\text{C}_n\text{H}_{2n}$ , mol. wt. 568, corresponding with about 7 polymerised (I) mols. Some depolymerisation occurred when the resinous material was redistilled. J. T. A.

$\beta$ -cyclopentyl- $\alpha$ -phenylethane,  $\beta$ -cyclopentyl- $\alpha$ -cyclohexylethane,  $\gamma$ -cyclopentyl- $\alpha$ -phenylpropane,  $\gamma$ -cyclopentyl- $\alpha$ -cyclohexylpropane, and their behaviour towards catalytic hydrogenation and dehydrogenation. J. I. DENISSENKO (Ber., 1936, 69, [B], 2183—2187).—Addition of cyclopentanone to  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$  in  $\text{Et}_2\text{O}$  gives 1- $\beta$ -phenylethylcyclopentan-1-ol, b.p. 140—141°/5 mm., converted by boiling conc. aq.  $\text{H}_2\text{C}_2\text{O}_4$  into  $\beta$ -cyclopentyl- $\alpha$ -phenylethane, b.p. 124—125°/10 mm., rapidly hydrogenated ( $\text{Pt-black}$  in abs.  $\text{EtOH}$ ) to  $\beta$ -cyclopentyl- $\alpha$ -phenylethane (I), b.p. 255—256°/752.5 mm. Passage of (I) with  $\text{H}_2$  over  $\text{Pt-C}$  at 230° yields  $\beta$ -cyclopentyl- $\alpha$ -cyclohexylethane, b.p. 251—252°/752.5 mm., almost completely dehydrogenated by  $\text{Pt-C}$  at 290° to (I). Similarly, 1- $\gamma$ -phenylpropylcyclopentan-1-ol, b.p. 136—138°/2.5 mm., is converted successively into  $\gamma$ -cyclopentyl- $\alpha$ -phenylpropane, b.p. 117—118°/3 mm., and  $\gamma$ -cyclopentyl- $\alpha$ -phenylpropane (II), b.p. 271—272.5°/743 mm. (II) is hydrogenated to  $\gamma$ -cyclopentyl- $\alpha$ -cyclohexylpropane, b.p. 268—270°/748.2°, which is dehydrogenated to (II). H. W.

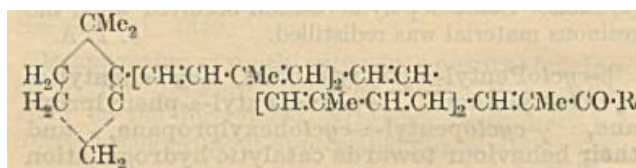
**Properties of carotene and lycopene.** N. K. DE (Indian J. Med. Res., 1936, 23, 949—956).—Carotene (I) and lycopene (II) behaved similarly towards reagents and adsorbents, but (I) was more sol. and (II) was more readily adsorbed. The spectroscopic absorption in various solvents was determined, and a rough method for the determination of mixtures of (I) and (II), by observing the positions of the absorption max., was devised. NUTR. ABS. (m)

**Isomerisation of carotenes by chromatographic adsorption.** I.  $\psi$ - $\alpha$ -Carotene. A. E. GILLAM and M. S. EL RIDI (Biochem. J., 1936, 30, 1735—1742).— $\psi$ - $\alpha$ -Carotene (I), m.p. 166° (uncorr.), formed from  $\beta$ -carotene by repeated adsorption on  $\text{Al}_2\text{O}_3$  (this vol., 155), is spectroscopically identical with  $\alpha$ -carotene (II) but is optically inactive. (I) is isomeric with (II) but whilst (I) is converted into a pigment with absorption max. at longer  $\lambda$ , (II) yields (especially by adsorption on  $\text{MgO}$ ) a pigment (*neo-carotene*) with absorption max. at shorter  $\lambda$ . The isomerisation is probably due to rearrangement of double linkings or to geometrical isomerism. F. O. H.

**Chemistry of the algæ. II. Carotenoid pigments of Oscillatoria rubescens.** I. M. HEILBRON and B. LYTHGOE (J.C.S., 1936, 1376—1380; cf. this vol., 259).—The epiphasic pigments consist of  $\beta$ -carotene (I) and myxoxanthin (II),  $\text{C}_{40}\text{H}_{56}\text{O}$ , m.p. 168—169° (single absorption max. in  $\text{CS}_2$ ,  $\text{CHCl}_3$ , and ligroin) (*oxime*, m.p. 195—196°, absorption max. 463 m $\mu$  in  $\text{CHCl}_3$ ), which has vitamin-A activity and must therefore contain a  $\beta$ -ionone ring; on microhydrogenation it absorbs 11  $\text{H}_2$  and is thus monocyclic. With  $\text{Al}(\text{OPr}^i)_3$  it affords myxoxanthol, m.p. 169—172° (absorption max. 529, 494, 464 m $\mu$  in  $\text{CS}_2$ ). This is the absorption spectrum of  $\gamma$ -carotene (III)



and analogy with (III) indicates that (II) is (A) or (B). (A) is precluded because (II) has a single absorption max., thus resembling astacene (IV). The enolic



(A)  $R = CH_2 \cdot CH \cdot CMe_2$

(B)  $R = CH \cdot CHPr^s$

form of (IV) closely resembles (II), wherefore (B) is preferred. The single-banded spectra of pigments such as (II) and (IV) is due to the simultaneous conjugation of the  $\cdot CO$  with two ethylenic linkings. The hypophase pigments include lutein and *myxoxanthophyll*,  $C_{40}H_{54}O_7$ , m.p. 169–170° (absorption max. 518, 484.5, 454 m $\mu$  in  $CHCl_3$ ).

R. F. P.

**Reversibility of the Friedel-Crafts reaction. Hydrogenation.** L. L. ALEXANDER and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 1745–1747; cf. this vol., 205).—Dibenzyl (I) is formed in 27–57% yield when tri- and tetra-arylethanes (or compounds, e.g.,  $CAr:CAr$ ,  $CHAr:CHAr$ ,  $CAr_2:CHAr$ , which, under the conditions used, can give rise to these) are treated with  $C_6H_6$ ,  $AlCl_3$  (large excess), and dry  $HCl$  at room temp. Thus, tolane,  $CPh_2:CHPh$ ,  $CHPh_2:CH_2Ph$ ,  $(CPh_2)_2$ ,  $(CHPh_2)_2$ , and  $\beta$ -phenyl- $\alpha$ -di-*p*-chlorophenylethylene (II), m.p. 116.5–117.5° [obtained by dehydration ( $AcOH$ –conc.  $H_2SO_4$ ) of  $\beta$ -phenyl- $\alpha$ -di-*p*-chlorophenylethyl alcohol, m.p. 116–117°, which is prepared from  $CH_2Ph \cdot MgCl$  and  $(p-C_6H_4Cl)_2CO$ ], all give (I).  $(CHPh_2)_2$  is formed from tolane, (II), or  $CPh_2:CHPh$  with  $C_6H_6$ ,  $AlCl_3$  (limited amount), and  $HCl$ ;  $(CHPh_2)_2$  and *p*-bromostilbene similarly afford  $CHPh_2:CH_2Ph$ . The following mechanism for (II) illustrates the general reaction:  $CHPh.C(C_6H_4Cl)_2 (+C_6H_6) \rightleftharpoons CHPh \cdot CH(C_6H_4Cl)_2 (+2C_6H_6) \rightleftharpoons CHPh_2:CHPh_2 (+C_6H_6) \rightleftharpoons CPh_2:CHPh (+H_2) \rightarrow CHPh_2:CH_2Ph (+C_6H_6) \rightleftharpoons CHPh:CHPh (+H_2) \rightarrow (I)$ . The production of (I) from  $C_6H_6$ ,  $AlCl_3$ , and various halogenoethanes, -ethylenes, and -acetylenes is thus explicable.

H. B.

**Principle of vinylogy and the effect of ortho-substituents on the reactivity of benzene derivatives.** A. H. BLATT (J. Org. Chem., 1936, 1, 154–158).—Zwecker's comparison (A., 1935, 1112) of the relative reactivities of unsubstituted and *o*-substituted  $C_6H_6$  derivatives,  $C_6H_4RX$  ( $R=H$ ,  $Me$ , etc.;  $X=CO_2H$ ,  $CH_2Cl$ , etc.), with those of  $HX$  and  $RX$  is shown to be a special case of the principle of vinylogy (cf. Chem. Rev., 1935, 16, 1).

H. G. M.

**Hydrolysis of halogenobenzenesulphonic acids with alkali.** C. M. SUTER and P. H. SCRUTCHFIELD (J. Org. Chem., 1936, 1, 189–193).— $K$  or  $Na$  salts of 1:3:5- $C_6H_3X(SO_3H)_3$  (I) ( $X=Cl$ ,  $Br$ ,  $I$ ), 1:2:4- $C_6H_3Cl(SO_3H)_3$ , 1:3- $C_6H_4I \cdot SO_3H$ , and 1:3- $C_6H_4(SO_3H)_2$  have been hydrolysed in a  $N_2$  atm. with 60% aq.  $KOH$  (130–160°, 0.25–3 hr.), and (I) ( $X=Cl$  and  $Br$ ) have been fused with  $KOH$  (200–310°, 1–3 hr.), and the amounts of  $Cl^-$  and  $SO_3^{2-}$  formed determined. The halogens are more easily hydrolysed than the  $SO_3H$ , which, in turn, are hydrolysed more slowly

after hydrolysis of the halogen than before. The ratio of the hydrolysis rates for the halogen and  $SO_3H$  is greater in 60% alkali than in fusion reactions.

H. G. M.

**Organic substances of high mol. wt. Polybenzyl and its derivatives. II. Synthesis of the polymeride and its viscosity in varying solvents. III. Polynitrobenzyl.** S. BEZZI (Gazzetta, 1936, 66, 491–497, 497–504; cf. A., 1935, 1067).—II. Polybenzyl,  $(C_6H_4 \cdot CH_2)_n$  or  $CH_2Ph \cdot [CH_2 \cdot C_6H_4]_n \cdot C_6H_4 \cdot CH_2Cl$ , obtained by autocondensation of  $CH_2PhCl$  ( $AlCl_3$ , alone or in  $PhNO_2$ ,  $CS_2$ , or light petroleum), is shown by its viscosity in  $C_6H_6$  and in  $PhNO_2$ , at varying concn. and temp., to consist of long-chain mols., and not of micelles.

III. Polybenzyl with  $HNO_3$  (*d* 1.38) yields an insol. product containing less N than is required by  $(C_7H_5 \cdot NO_2)_n$ .  $HNO_3$  (*d* 1.52) gives a mixture of sol. and insol.  $NO_2$ -derivatives with N in excess (disubstituted in the terminal rings?). Mol. wt. (cryoscopic) shows that polybenzyls in which the degree of polymerisation is 5 to 24 all give sol.  $NO_2$ -derivatives in which it is only 5.5–6.5. The sp. viscosity of the latter is  $>$  that of polybenzyls of the same mol. wt. This, and the abnormal viscosity of cellulose, is ascribed to the effect of the functional groups.

E. W. W.

**Magnetochemical investigation of organic substances. X. Attempted synthesis of carbon diradicals; existence of diradicals.** E. MÜLLER and W. BUNGE (Ber., 1936, 69, [B], 2164–2172).—Attempts to remove  $Cl$  completely from 4:4'-dichlorodiphenylmethyldiphenyl ether necessitate the use of  $Cu$  powder in boiling  $C_6H_6$ , whereby a radical coloration is not observed and the product is a yellow amorphous substance,  $C_{76}H_{56}O_2$ , m.p. indef. 140°, apparently a dimeride. It is stable towards boiling  $SO_2Cl_2$ , but suffers fission with  $K-Na$ , thus resembling  $Ph_2O$ . In  $C_6H_6$  at room temp. and at 74° it is completely diamagnetic, and shows no sign of radical content. 4:4'-Di(chlorodiphenylmethyl)- $\alpha\beta$ -diphenylethane (Wittig *et al.*, A., 1928, 642) is transformed by  $Cu$  powder in  $C_6H_6$  into the almost colourless compound  $C_{40}H_{32}$ , which gives a colourless solution in  $C_6H_6$  if heating has been avoided in its prep., but is dark red in the hot solution. At room temp. and at 74° in  $C_6H_6$  the diamagnetic val. of the colourless solid is observed; a paramagnetic deviation corresponding with  $>2\%$  of radical is excluded. Paramagnetic C diradicals are capable of existence only when there is no possibility of intermol. stabilisation, of passage into a valency-tautomeric quinonoid system, or of equilibration with formation of a polymeric compound.

H. W.

**$\omega\omega'$ -Tetraphenylpolyene hydrocarbons; valency tautomerism of unsaturated systems.** G. WITTIG and A. KLEIN (Ber., 1936, 69, [B], 2087–2097).—With hydrocarbons  $CPh_2 \cdot CH \cdot [CH:CH]_n \cdot CH: CPh_2$  ( $n=1, 2$ , or 3) union with 2 atoms of alkali metal, probably at the ends of the conjugated systems, occurs, but  $O_2$  is without effect even in the presence of  $PhCHO$ . Addition of  $Br$  appears to take place with avoidance of the  $CPh_2 \cdot CH$  groups. The tetraphenylpolyenes do not

therefore give stable diyl forms and do not pass into diradicals in presence of  $O_2$  or Br. Tetraphenyl-*p*-xylylene reacts with Na-K in dioxan and the product affords  $p$ - $C_6H_4(CHPh)_2$ , m.p. 170—171°, when treated with MeOH. Gradual addition of Me.  $\alpha\alpha'$ -dihydromuconate to LiPh in Et<sub>2</sub>O and decomp. of the product with H<sub>2</sub>O gives  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\gamma}$ -hexene- $\alpha\zeta$ -diol (I), m.p. 163.5—165°, converted by HCl-MeOH in dioxan into  $\alpha\alpha'$ -dimethyl- $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\gamma}$ -hexene, m.p. 209—210°, which with Na-K followed by MeOH in dioxan yields  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\gamma}$ -hexene, m.p. 124—125°. (I) and boiling AcOH containing HCl afford  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\gamma\gamma}$ -hexatriene (II), m.p. 202—204°, which is converted by Na powder in abs. dioxan followed by MeOH into  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\beta\beta}$ -hexadiene (III), m.p. 148—149°, oxidised by  $KMnO_4$  in  $COMe$ , to  $CHPh_2 \cdot CO_2H$  and  $OH \cdot CPh_2 \cdot CO_2H$ , but not  $COPh_2$ . With Li a similar slow change is observed, whereas with Na-K reaction is much more rapid and gives (III) after short change, but  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\gamma\gamma}$ -hexadiene, m.p. 118—121° (oxidised to  $CHPh_2 \cdot CH_2 \cdot CO_2H$ , m.p. 154°), when reaction is prolonged. Partial hydrogenation of (II) gives  $\alpha\alpha\zeta\zeta$ -tetraphenylhexane and unchanged (II). In  $CHCl_3$  (II) gives a dibromide, decomp. about 133°, but it does not react with I. (II) is unchanged when shaken in  $C_6H_6$  with  $O_2$  alone or in presence of  $PhCHO$  or when dry  $O_2$  is passed through its solution in boiling  $C_6H_6$ .  $\alpha\alpha\zeta\zeta$ -Tetradiphenyl- $\Delta^{\gamma}$ -hexene- $\alpha\zeta$ -diol, m.p. 238—239°, is converted by HCl in boiling AcOH into  $\alpha\alpha\zeta\zeta$ -tetradiphenyl- $\Delta^{\gamma\gamma}$ -hexatriene, m.p. 320—328° (slight decomp.), which is darker in colour and gives a more marked fluorescence than (II), but is equally indifferent towards  $O_2$ . ( $CH_2 \cdot CO_2H$ )<sub>2</sub>,  $PbO$ ,  $Ac_2O$ , and  $\beta$ -phenylcinnamaldehyde (IV) at 140—150° afford  $\alpha\alpha\theta\theta$ -tetraphenyl- $\Delta^{\gamma\gamma\gamma}$ -octatetraene, m.p. 198—199°, which in  $CHCl_3$  gives a very unstable tetrabromide; it is indifferent to the prolonged action of  $O_2$ .  $\alpha\alpha'$ -Dihydromuconic acid,  $PbO$ ,  $Ac_2O$ , and (IV) at 140—150° give  $\alpha\alpha\kappa\kappa$ -tetraphenyl- $\Delta^{\gamma\gamma\gamma}$ -decapentaene, m.p. 227—228°, which affords an unstable hexabromide and is indifferent to  $O_2$ . H. W.

#### $\alpha\delta$ -Diarylbutadienes and related compounds.

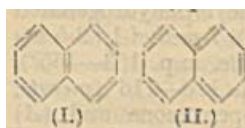
I.  $\alpha$ -Phenyl- $\delta$ -1-naphthylbutadiene. E. FRIEDMANN and W. E. VAN HEYNINGEN (J. pr. Chem., 1936, [ii], 146, 163—165).— $CHPh \cdot CH \cdot CHO$ ,  $\alpha$ - $C_{10}H_7 \cdot CO_2H$ ,  $Ac_2O$ , and  $PbO$  at 200—230° give 24.9% of  $\alpha$ -phenyl- $\delta$ -1-naphthylbutadiene, m.p. 109°, which fluoresces in ultra-violet light and has absorption max. at 2360, 2775—2855, and 3260—3370 Å.  $\alpha\delta$ -Diphenylbutadiene has absorption max. at 2420 and 3305—3140 Å. R. S. C.

Reaction of metal halides with acetylenic Grignard reagents. J. P. DANEHY and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1609—1610).— $CPh \cdot C \cdot MgBr$  (1 mol.) and  $CuBr$ , (1 mol.) in  $Et_2O$  give 72% of  $(CPh \cdot C)_2$ .  $CBu^s \cdot C \cdot MgBr$  (I) and  $CuBr$ , at 25° similarly afford  $(CBu^s \cdot C)_2$ , (60%; 55% at -5°) and  $CBu^s \cdot C \cdot Br$  (7%; 14% at -5°), which are also formed using  $CuCl_2$  at 25° (35 and 5%, respectively) or -5° (30 and 7%, respectively), and from  $CBu^s \cdot C \cdot MgCl$  and  $CuBr_2$  (30 and 1%, respectively).  $FeCl_3$  acts similarly. (I) and  $AgBr$

give  $CBu^s \cdot C \cdot Ag$  (60%), thus affording evidence that the first stage in the reaction between a Grignard reagent and a metal halide (as above) is the formation of an organometallic compound which, if unstable, subsequently decomposes. H. B.

Lattice structure of condensed aromatic hydrocarbons and their molecular compounds with trinitrobenzene.—See this vol., 1327.

Structure and reactivity of the naphthalene nucleus. I. Orientation in the series of naphthalene and its derivatives. V. N. UFMZEV (Ber., 1936, 69, [B], 2188—2198).—The main properties of  $C_{10}H_8$  (difference between  $\alpha$ - and  $\beta$ -substituted derivatives; equivalence of the four  $\alpha$ - and of the four  $\beta$ -positions; greater reactivity of the

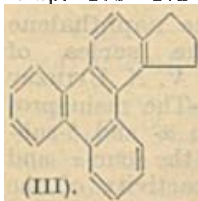


$\alpha$ -positions) are adequately expressed by assuming an equilibrium between the forms (I) and (II). The assumption of a displacement (I)  $\rightarrow$  (II) on entry of a substituent into the nucleus explains the preponderating formation of mono-substituted products under mild conditions, since further action occurs with greater difficulty owing to the induced benzenoid character of the second ring; substances with completely similar rings [ $Ph_2 \cdot C_6H_4(CO)_2C_6H_4$ ] usually readily afford derivatives, and only under particular conditions are mono-substituted compounds obtained. Displacement of the equilibrium (I)  $\rightarrow$  (II) endows one ring with a more aromatic, the other with an unsaturated, character; further sulphonation causes entry of  $SO_3H$  in different positions, but only in the aromatic and difficultly hydrogenated ring, thus explaining the non-production of 1 : 3- $C_{10}H_6(SO_3H)_2$ . Examples from the lit. show that hydrogenation is considerably facilitated in the unsaturated ring, whereas in the other ring it occurs with about the same difficulty as with  $C_6H_6$ . If the structure with non-equiv. rings is considered fundamental to mono-substituted derivatives of  $C_{10}H_8$  the entry of a second substituent into the same ring follows the usual rules of  $C_6H_4$  orientation. If it enters the other ring, it is under the influence of a substituent in an unsaturated side-chain, and is subject to the rules of Holleman and Ingold. The processes are illustrated by references to the lit. Contrary to the lit., sulphonation of  $\beta$ - $C_{10}H_7 \cdot NHOAc$  in the cold gives mainly 2 : 8- $NHAc \cdot C_{10}H_6 \cdot SO_3H$ . Orientation of naphthylamine-sulphonic acids is readily effected by diazotisation, replacement of  $N_2$  by  $SO_2H$  by  $SO_2$  in presence of  $Cu$  powder, oxidation of  $SO_2Na$  to  $SO_3Na$  by  $H_2O_2$ , and conversion of  $C_{10}H_6(SO_3H)_2$  into  $C_{10}H_6(SO_2Cl)_2$ . H. W.

cyclopentenotriphenylene. E. BERGMANN and O. BLUM-BERGMANN (J. Amer. Chem. Soc., 1936, 58, 1678—1681).— $\beta$ -9-Phenanthrylethyl alcohol, m.p. 92° [from  $Mg$  9-phenanthryl bromide and  $(CH_2)_2O$  (in  $Et_2O$ - $C_6H_6$ ) or  $CH_2Cl \cdot CH_2 \cdot OH + MgEtBr$  (reaction occurs when the  $Et_2O$  is distilled off)], with  $SOCl_2$  in  $C_6H_6$ - $NPhMe_2$  gives the chloride, m.p. 82—84°, the Grignard reagent (A) from which with cyclopentanone affords 1-( $\beta$ -9-phenanthrylethyl)cyclopentanol (I), m.p. 108—109°, and a little  $\alpha\delta$ -di-9-phenan-



thylbutane (II), m.p. 214—216°. (I) is dehydrated (KHSO<sub>4</sub> at 160—170°) to 1-(β-9-phenanthryl)-Δ<sup>1</sup>-cyclopentene, b.p. 206—207°/1.3 mm., m.p. 50—54.5°, converted by AlCl<sub>3</sub> in CS<sub>2</sub> at room temp. into tetrahydrocyclopentenotriphenylene, m.p. 105.5—107° (picrate, m.p. 161—162°), which is dehydrogenated (Se at 330—340°) to cyclopentenotriphenylene (III), m.p. 171—172.5° (picrate, m.p. 172—173°). (III)



differs from the hydrocarbon, C<sub>21</sub>H<sub>16</sub>, to which structure (III) was assigned by Elderfield and Jacobs (A., 1934, 1359). (I) and AcOH-conc. H<sub>2</sub>SO<sub>4</sub> do not give (III); the resultant product [from which a hydrocarbon, C<sub>21</sub>H<sub>20</sub>, m.p. 117—120° (probably a spiran), is isolable] is dehydrogenated (Se at 320—340°) to (probably) 7-methyl-1:2-benzopyrene, m.p. 157.5—159.5° (picrate, m.p. 153—155°), and 1:2:3:4-dibenzfluorene, m.p. 115—116° (picrate, m.p. 165—167°). 2-Methylcyclopentanone and (A) give (II) and a product which when dehydrated (KHSO<sub>4</sub> at 160—170°) affords a little 1-(β-9-phenanthrylethyl)-2-methyl-Δ<sup>1</sup>-cyclopentene, m.p. 73—75°; much 9-ethylphenanthrene, m.p. 62—64°, is formed during the reaction. H. B.

**cycloHexylamine and N-dimethylcyclohexylamine.** G. BREUER and J. SCHNITZER (Monatsh., 1936, 68, 301—312).—Treatment of cyclohexyldimethylamine in Et<sub>2</sub>O with the appropriate amount of conc. H<sub>2</sub>SO<sub>4</sub> gives cyclohexylamine sulphate (I), m.p. 338°, and H sulphate, m.p. 117—118°, respectively, also obtained from their components. cycloHexylamine (II) and MeI in Et<sub>2</sub>O afford cyclohexylamine hydriodide (III), m.p. 193—194°, and cyclohexyltrimethylammonium iodide, m.p. 263°. (II) and hexyl iodide at room temp. or in Et<sub>2</sub>O yield (III), whereas at 100° cyclohexylhexylammonium iodide, m.p. 246°, is produced; cyclohexylhexylamine (IV), b.p. 243—245°/750 mm. (corresponding phenylcarbamide, m.p. 109—110°), is described. In Et<sub>2</sub>O (IV) and conc. H<sub>2</sub>SO<sub>4</sub> give (I). (III) is also formed from (II) and I in Et<sub>2</sub>O; ill-defined dark oils are produced simultaneously. H. W.

**Benzoylation of αs-phenylethylcarbamide.** E. A. ABRAHAM (J.C.S., 1936, 1273—1274; cf. A., 1884, 1321).—The Bz, m.p. 121°, and p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CO-, m.p. 175°, derivatives of NPhEt·CO·NH<sub>2</sub> (I) have been prepared from (I) in C<sub>2</sub>H<sub>5</sub>N and the respective acyl chloride at room temp. BzCl and (I) at 100° yield NBzPhEt, cyanuric acid, and HCl. F. R.

**Action of bases on organic halogen compounds. I. Reaction of aryl halides with potassium amide.** F. W. BERGSTROM, R. E. WRIGHT, C. CHANDLER, and W. A. GILKEY. II. Basic catalysis in the dehalogenation of the phenyl halides. R. E. WRIGHT and F. W. BERGSTROM (J. Org. Chem., 1936, 1, 170—178, 179—188).—I. PhX (X=Cl, Br, I, but not F) reacts rapidly with KNH<sub>2</sub> in NH<sub>3</sub> at -33° to give NH<sub>2</sub>Ph and some NHPH<sub>2</sub>, NPh<sub>3</sub>, and p-C<sub>6</sub>H<sub>4</sub>Ph·NH<sub>2</sub>, but only slowly or not at all in boiling Et<sub>2</sub>O or C<sub>6</sub>H<sub>6</sub>. The relative ease of replacement of X was determined by the

“competition” method and follows the sequence Br>I>Cl (F not replaced at 33°), also obtained for replacements involving the p-phenylenedihalides. p-C<sub>6</sub>H<sub>4</sub>MeCl gives p-C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub> and tarry products. A mixture of mono- and di-phenylamines is also obtained from PhBr and Ca(NH<sub>2</sub>)<sub>2</sub> or Ba(NH<sub>2</sub>)<sub>2</sub> in NH<sub>3</sub> at room temp.

II. KNH<sub>2</sub> or rather the NH<sub>2</sub><sup>-</sup> ion catalyses the following reactions in liquid NH<sub>3</sub> at -33°, which proceed slowly or not at all in the absence of catalyst (cf. A., 1924, i, 726; 1931, 1166): NHPH<sub>2</sub>K+PhX=NHPH<sub>2</sub>+KX; NHPH<sub>2</sub>K+PhX=p-C<sub>6</sub>H<sub>4</sub>Ph·NH<sub>2</sub>+KX; NPh<sub>2</sub>K+PhX=NPh<sub>2</sub>+KX (X=Cl, Br, I); CPh<sub>3</sub>K+PhCl=KCl+CPh<sub>3</sub>; and the reactions with K quinaldyl and PhCl to give 2-benzyl-, 2-benzhydryl-, and 2-triphenylmethyl-quinoline. The following reactions, however, in liquid NH<sub>3</sub> at -33° do not take place either alone or in presence of KNH<sub>2</sub>: PhCl+KOPh=KCl+Ph<sub>2</sub>O and PhBr+KCl=PhCl+KBr. CHPh<sub>2</sub>K reacts slowly with PhCl in NH<sub>3</sub> at -33° in the absence of KNH<sub>2</sub> to give CHPh<sub>2</sub> and CPh<sub>3</sub>, and catalyses the reaction between NPh<sub>2</sub>K and PhCl. In general, the strongest bases (in Brønsted's sense) react most readily with PhX, and only the very strongest (NH<sub>2</sub><sup>-</sup> and CHPh<sub>2</sub>) catalyse reactions between PhX and NHPH<sub>2</sub>, etc. H. G. M.

**Extensions of the Leuckart synthesis of amines.** A. W. INGERSOLL, J. H. BROWN, C. K. KIM, W. D. BEAUCHAMP, and G. JENNINGS (J. Amer. Chem. Soc., 1936, 58, 1808—1811).—Ketones, CORR', are heated with a mixture of HCO<sub>2</sub>NH<sub>4</sub> and HCO·NH<sub>2</sub> (used alone with H<sub>2</sub>O-sol. and more volatile ketones) at 175—185° (with continuous removal of H<sub>2</sub>O by distillation) and the resulting CHRR'·NH·CHO hydrolysed (conc. HCl) to the dl-amine (52—85% yield). The following are described: CHPhMe·NH<sub>2</sub>; p-C<sub>6</sub>H<sub>4</sub>Me·CHMe·NH<sub>2</sub>; p-C<sub>6</sub>H<sub>4</sub>Ph·CHMe·NH<sub>2</sub> (178—179°, 220—221°); CHMeBu<sup>o</sup>·NH<sub>2</sub> (98—99°, >250°); α-m-tolyl-, b.p. 204—205° (113—114°, 164—165°), α-p-chlorophenyl-, b.p. 105°/10 mm. (144—145°, 192—193°), α-p-bromophenyl-, b.p. 116°/10 mm. (150—151°, 213—214°), α-p-anisyl-, b.p. 126°/20 mm. (117—118, 160—161°), α-p-phenoxyphenyl- (113—114°, 180—181°), α-m-nitrophenyl- (156—157°, 223—224°), and α-2-naphthyl- (151—152°, 198—199°), -ethylamines; fenchylamine, b.p. 190—191° (131—133°, >250°). The m.p. quoted in parentheses are those of the Bz derivative and hydrochloride, respectively. A mixture of neobornyl- (70%) and d-bornylamine is obtained from d-camphor in presence of PhNO<sub>2</sub>. H. B.

**Amide condensations. II. Transformations of acetoacetylphenylamide.** G. V. TSCHELINCEV and B. M. DUBININ (Ber., 1936, 69, [B], 2023—2026; cf. this vol., 463).—The adaptability of CH<sub>3</sub>Ac·CO·NPh<sub>2</sub> (I) to syntheses of the CH<sub>2</sub>Ac·CO·Et type is illustrated. (I) is transformed by cold conc. H<sub>2</sub>SO<sub>4</sub> into 2-keto-1-phenyl-4-methyl-1:2-dihydroquinoline (II), m.p. 134—135°, in almost quant. yield. With NHPH<sub>2</sub>·NH<sub>2</sub> in Et<sub>2</sub>O at 0° (I) gives the corresponding phenylhydrazones, m.p. 171—172°, which passes in boiling xylene into phenylmethylpyrazolone. The successive actions of Na and EtI

in EtOH on (I) lead to  $\alpha$ -ethylacetoacetylphenylamide, m.p. 70—71°, transformed by conc.  $\text{H}_2\text{SO}_4$  into 2-keto-1-phenyl-4-methyl-3-ethyl-1:2-dihydroquinoline, m.p. 116—117°.  $\alpha$ -Benzylacetoacetylphenylamide, m.p. 108—109°, gives a non-cryst. product with conc.  $\text{H}_2\text{SO}_4$ . Diacetylacetylphenylamide, m.p. 123—124°, from  $(\text{HNaAc} \cdot \text{CO} \cdot \text{NPh}_2)$  and  $\text{AcCl}$  in  $\text{Et}_2\text{O}$ , is transformed by conc.  $\text{H}_2\text{SO}_4$  into (II). H. W.

***o*- and *p*-Nitrophenylhydroxylamine.** R. KUHN and F. WEYGAND (Ber., 1936, 69, [B], 1969—1974).—Addition of finely powdered  $\text{o-C}_6\text{H}_4(\text{NO}_2)_2$  to a solution of ascorbic acid (I) in aq.  $\text{Na}_2\text{CO}_3$  under  $\text{N}_2$  and extraction of the solution with EtOAc after acidification with AcOH gives *o*-nitrophenylhydroxylamine (II), m.p. 74°, which with dil. aq.  $\text{Na}_2\text{CO}_3$  gives a dark blue solution of the Na salt,  $\text{OH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \cdot \text{Na}$ , and with conc. aq. NaOH an intensely reddish-brown solution of the  $\text{Na}_2$  salt,  $\text{ONa} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \cdot \text{Na}$ , thus explaining the colour reactions of  $\text{o-C}_6\text{H}_4(\text{NO}_2)_2$  with aldoses, ketoses, and polyhydric aromatic phenols. For the prep. of (II) it is preferable to start from  $\text{o-NO-C}_6\text{H}_4 \cdot \text{NO}_2$  (III), since reaction can then be effected in acid solution and less (I) is necessary. (II) can be determined by running its solution in 50% EtOH into standard  $\text{K}_2\text{Fe}(\text{CN})_6$  under  $\text{N}_2$  until the blue colour is permanent, (III) being thus produced. Hydrogenation ( $\text{PtO}_2$  in abs. EtOH) of (II) gives  $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ . Similarly, reduction of  $\text{p-C}_6\text{H}_4(\text{NO}_2)_2$  or  $\text{p-NO-C}_6\text{H}_4 \cdot \text{NO}_2$  affords *p*-nitrophenylhydroxylamine (IV), m.p. 107°, which in dil.  $\text{Na}_2\text{CO}_3$  gives a cherry-red solution of the Na salt and in dil. NaOH a brownish-yellow solution of the  $\text{Na}_2$  salt, which is sensitive to air owing to the catalytic effect of traces of metal, since the colour persists in presence of KCN. (II) is exceedingly unstable and when cryst. passes into a blackish viscous mass within a few hr., but can be preserved for some weeks in an evacuated tube at 0°. (IV) is considerably more stable. H. W.

**Fission of tertiary amines by nitrous acid.** R. WEGLER and W. FRANK (Ber., 1936, 69, [B], 2071—2077).—*N*-Methylbornylamine, b.p. 88°/15 mm.,  $\alpha^{17}$ —59.1° (improved prep.), is converted by  $\text{HNO}_2$  solely into the NO-derivative. Bornyl-dimethyl- or -diethyl-amine is largely converted into camphor and, under certain conditions, scarcely any *tert.* amine can be regenerated. The best method for the separation of *sec.* and *tert.* amine is secured by use of a large excess of  $\text{NaNO}_2$  in cold 15—20%  $\text{H}_2\text{SO}_4$ . Fission of *tert.* amines by  $\text{HNO}_2$  appears general, and takes place most rapidly in AcOH at 40—80° or, much more slowly, at room temp.  $\text{N}_2\text{O}_3$  in dil. AcOH can replace  $\text{NaNO}_2$  or, better,  $\text{N}_2\text{O}_3$  can be passed into the amine in AcOH, whereby the change takes place with marked evolution of heat. The smallest alkyl residue attached to N is removed as aldehyde or ketone. Cyclic residues appear somewhat more firmly attached than aliphatic residues of equal size, but  $\text{CH}_2\text{Ph}$  is removed at least as readily as Me, thus giving a parallel with von Braun's observation on the fission with BrCN. Reaction with *tert.* amines containing one or more readily eliminable groups is quant., giving NO-compounds and aldehydes or the corresponding acids in amount showing the

absence of appreciable secondary change. The course of the reaction is uncertain, but the aldehyde appears to be a primary product. The change  $\text{NR}_2\text{R}' + \text{HNO}_2 \rightarrow \text{NR}_2 \cdot \text{NO} + \text{R}'\text{OH}$  is unlikely, since  $\text{R}'\text{OH}$  ( $\text{CH}_2\text{Ph} \cdot \text{OH}$ ) is not oxidised by  $\text{HNO}_2$  alone or in presence of *tert.* amine or NO-compound. The following substances appear new: nitroso-benzylethylamine, an oil; -benzylmethylamine, b.p. 145°/18 mm.; -dibenzylamine, b.p. 140°/0.2 mm.; -cyclohexylethylamine, b.p. 140°/17 mm.; -ethyl-octylamine, b.p. 147°/15 mm. H. W.

**Reactions of 8-nitro- $\alpha$ -naphthylamine and its derivatives.** H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1338—1341).—4:8-Dinitroaceto- $\alpha$ -naphthalide, m.p. 231° (free amine, m.p. 193°), was the sole product of the action of  $\text{HNO}_3$  (*d* 1.5) on 8-nitroaceto- $\alpha$ -naphthalide. Monobromination of the latter in AcOH+NaOAc gave 4-bromo-8-nitroaceto- $\alpha$ -naphthalide, m.p. 202°, hydrolysed to the amine, m.p. 116°, converted (Sandmeyer) into 1-chloro-4-bromo-8-nitronaphthalene, m.p. 107.5°, whilst further bromination gave the 2:4- $\text{Br}_2$ -compound (I), m.p. 198°, sol. in aq. NaOH, hydrolysed to the amine (II), m.p. 150°, converted (Sandmeyer) into 1-chloro-2:4-dibromo-8-nitronaphthalene, m.p. 146°, reduced (West's method) to 8-chloro-5:7-dibromo- $\alpha$ -naphthylamine, m.p. 159° (picrate, m.p. 160°; Ac derivative, m.p. 227°). Attempts at direct monobromination of 8-nitro- $\alpha$ -naphthylamine resulted in mixtures, whilst dibromination gave (II), which readily gave a  $\text{Ac}_2$  compound, m.p. 190°, with excess of  $\text{Ac}_2\text{O}$ , and was reduced (West's method) to 2:4-dibromo-1:8-naphthylenediamine, m.p. 110—112°. Reduction of (I) with acid  $\text{SnCl}_2$ -AcOH or by West's method caused condensation to 7:9-dibromo-2-methylperimidine, m.p. 176—177°. F. R.

**Manufacture of aminotrifluoromethylarylsulphonic acids.**—See B., 1936, 974.

**Manufacture of substituted nitro- and aminochrysenes.**—See B., 1936, 973.

**Manufacture of aminochrysenesulphonic acids.**—See B., 1936, 974.

**Manufacture of 3-aminopyrenesulphonic acids.**—See B., 1936, 974.

**Benzidine phosphomolybdate.**—See this vol., 1351.

**2:7-Diaminofluorene.**—See this vol., 1352.

**Azo-dyes and their intermediate products.** XVIII. *cis*- and *trans*-forms of stilbene dyes. P. RUGGLI and F. LANG (Helv. Chim. Acta, 1936, 19, 996—1007).—Observations with dyes derived from *cis*-stilbene disprove the hypothesis that substantivity of dyes on cotton depends on their existence in long, thread-like mols. which become attached to the similar mols. of cellulose. The by-products of the action of alkali on  $\text{p-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$  are formed in minor quantity only and are non-homogeneous; a substance, m.p. 199°, containing 5 O is described. *pp'*-Dinitrotolan, obtained from the dibromide or, preferably, the dichloride of *trans-pp*-dinitrostilbene, is reduced (Ni in EtOAc-EtOH- $\text{H}_2\text{O}$ ) to *cis-pp'*-diaminostilbene (I), m.p. 121° [ $(\text{CHPh})_2$ , m.p. 104°;



$Ac_2$ , m.p.  $172^\circ$ , and  $Bz_2$ , m.p.  $253^\circ$ , derivatives; *trans-pp'*-dibenzamidostilbene, m.p.  $352^\circ$ ], which is unchanged by prolonged treatment with cold or short treatment with boiling  $N\text{-HCl}$ , but is isomerised by the boiling 10% acid to *trans-pp'*-diaminostilbene (II). Both substances are cautiously tetrazotised and coupled with 1:4- $NH_2\cdot C_{10}H_6\cdot SO_3H$  to *cis*- (III) and *trans*- (IV) -stilbene-red

$[CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3Na]_2$ , each of which is a substantive dye, although the existence of (III) as a thread mol. is theoretically excluded. Reductive fission of (III) and (IV) yields (I) and (II), respectively. Similar coupling of tetrazotised (I) and (II) with 1:4- $OH\cdot C_{10}H_6\cdot SO_3H$  yields *cis*- and *trans*-stilbene-violet  $[CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3Na]_2$ , each of which is a substantive dye. H. W.

**3:5-Fluoronitroanisole.** A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1936, 24, 1—2).—3:5-Nitroaminoanisole in  $HCl$  with  $NaNO_2$ , and subsequently 40%  $BF_3$  yields 3-nitroanisole-5-diazonium borofluoride, decomp.  $150^\circ$  (darkens at  $140^\circ$ ), which loses  $BF_3$  on warming to give 3:5-fluoronitroanisole, m.p.  $85^\circ$ . F. R. G.

**Action of sodium methoxide and ammonia on 1:3:5-fluorodinitrobenzene and 3:5-fluoronitroanisole.** A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1936, 24, 3—10).—The halogen in 1:3:5- $C_6H_3F(NO_2)_2$  (A., 1935, 1229) but not in the corresponding  $Cl$ -,  $Br$ -, and  $I$ -compounds, is replaced by the action of  $NaOMe$  or  $NH_3$  in  $EtOH$ . The  $F$  in 1:3:5- $OMe\cdot C_6H_3F\cdot NO_2$  (preceding abstract) is not replaced by  $NH_3$  in  $EtOH$  and is replaced less readily than the  $F$  in  $m\text{-}C_6H_4F\cdot NO_2$  by  $NaOMe$ . These results are discussed in relation to the views of De Crauw (A., 1931, 1283). F. R. G.

**Orientation of *p*-methoxydiphenyl in the Friedel-Crafts reaction.** L. F. FIESER and C. K. BRADSHAW (J. Amer. Chem. Soc., 1936, 58, 1738—1741).—In the Friedel-Crafts reaction, 4-methoxydiphenyl is substituted about 66% in position 4', the remainder in position 3. Solvents have little effect on the ratio.  $p\text{-}C_6H_4Ph\cdot OMe$ ,  $(CH_2\cdot CO)_2O$ , and  $AlCl_3$  in cold  $PhNO_2$  give 24.5% of  $\gamma$ -keto- $\gamma$ -*p*-4'-methoxydiphenylbutyric acid (I), m.p.  $200\text{--}201^\circ$  (slight darkening) (*Me* ester, m.p.  $99\text{--}110^\circ$ ), and 60% of  $\gamma$ -keto- $\gamma$ -4-methoxy-3-diphenylbutyric acid (II), m.p.  $155^\circ$  (*Me* ester, m.p.  $48\text{--}49^\circ$ ), readily separable owing to the sparing solubility of the  $Na$  salt of (I). Reduction (Clemmensen) of the crude *Me* esters of (I) and (II) affords  $\gamma$ -*p*-4'-methoxydiphenyl-, m.p.  $148\text{--}149^\circ$  (previous softening), and  $\gamma$ -4-methoxy-3-diphenyl-, m.p.  $109^\circ$ , -butyric acid, respectively; the latter could not be cyclised ( $H_2SO_4$ ; acid chloride; Bougault). Oxidation of (I) with  $KMnO_4$ -aq.  $KOH$  and of (II) with  $NaOBr$  gives 4-methoxydiphenyl-4'-m.p.  $248\text{--}249^\circ$  (*Me* ester, m.p.  $172\text{--}173^\circ$ ), and -3-, m.p.  $166\text{--}167^\circ$ , -carboxylic acid, respectively, demethylated (48%  $HBr$ ,  $AcOH$ ) to 4-hydroxydiphenyl-4'- (III), m.p.  $293\text{--}294^\circ$  (*Me* ester, m.p.  $224\text{--}225^\circ$ ), and -3-, m.p.  $212\text{--}213^\circ$  (*Me* ester, m.p.  $93\text{--}94^\circ$ ), -carboxylic acid, respectively. (III) is oxidised (aq.  $KMnO_4$ ) to  $p\text{-}C_6H_4(CO_2H)_2$ . (I) and 2.5%  $NaOCl$  at  $100^\circ$  (bath) afford 3-chloro-4-methoxydiphenyl-4'-carboxylic acid, m.p.  $275\text{--}276^\circ$  (*Me* ester, m.p.

$145\text{--}146^\circ$ ), also prepared by oxidation (alkaline  $KMnO_4$ ) of 3-chloro-4-methoxy-4'-acetyldiphenyl, m.p.  $109\text{--}110^\circ$  (from 3-chloro-4-methoxydiphenyl,  $AcCl$ , and  $AlCl_3$  in  $CS_2$ ). 3-Bromo-4-methoxydiphenyl-4'-carboxylic acid, m.p.  $270\text{--}271^\circ$  (*Me* ester, m.p.  $148\text{--}149^\circ$ ), and 3-bromo-4-methoxy-4'-acetyldiphenyl, m.p.  $97\text{--}98^\circ$ , are prepared by analogous methods.  $p\text{-}C_6H_4Ph\cdot OMe$ ,  $AcCl$ , and  $AlCl_3$  in  $CS_2$  (at b.p.),  $C_2H_5Cl_4$  (at  $0\text{--}20^\circ$ ), or  $PhNO_2$  (at  $0\text{--}20^\circ$ ) give 65—75% of 4-methoxy-4'- (IV), m.p.  $153\text{--}154^\circ$  and some -3- (V), m.p.  $62\text{--}63^\circ$ , -acetyldiphenyl. Rearrangement (Fries) of  $p\text{-}C_6H_4Ph\cdot OAc$  affords 4-hydroxy-4'-, m.p.  $206\text{--}207^\circ$ , and -3-, m.p.  $61\text{--}62^\circ$ , -acetyldiphenyl, which are methylated to (IV) and (V), respectively. H. B.

**Condensation of phenols with ethanolamine and formaldehyde.** H. A. BRUSON (J. Amer. Chem. Soc., 1936, 58, 1741—1744).— $NH_2\cdot CH_2\cdot CH_2\cdot OH$  (1 mol.) and 30%  $CH_2O$  (1 mol.) followed (after 1 hr.) by  $o\text{-}C_6H_4Ph\cdot OH$  (1 mol.) in  $EtOH$ , give after heating at  $100^\circ$  (bath) 38% of a hydroxyphenyl- $N$ - $\beta$ -hydroxyethylbenzylamine,  $OH\cdot C_6H_3Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH$ , m.p.  $116^\circ$ , also obtained by prolonged interaction of equimol. quantities of the reactants in  $MeOH$  at  $20\text{--}25^\circ$ .  $p\text{-}C_6H_4Ph\cdot OH$  similarly affords a compound, m.p.  $102^\circ$ , which may be  $(OH\cdot C_6H_3Ph\cdot CH_2)_2N\cdot CH_2\cdot CH_2\cdot OH$ , whilst *p*-cyclohexylphenol gives a compound, m.p.  $170\text{--}171^\circ$ , of (probably) similar constitution. 5-Chloro-2-hydroxydiphenyl, 2:4- $C_6H_3Cl_2\cdot OH$ , 3-nitro-*p*-cresol,  $p\text{-}C_6H_4Bu^t\cdot OH$ , *p*-tert.-amylphenol,  $p\text{-}NO_2\cdot C_6H_4\cdot OH$ , and  $p\text{-}OH\cdot C_6H_4\cdot COPh$  similarly yield (probably) 5-chloro-2-hydroxy-3-phenyl-, m.p.  $182\text{--}183^\circ$ , 3:5-dichloro-2-hydroxy-, m.p.  $199\text{--}200^\circ$ , 3-nitro-2-hydroxy-5-methyl-, m.p.  $205\text{--}206^\circ$ , 2-hydroxy-5-tert.-butyl-, m.p.  $127\text{--}128^\circ$ , 2-hydroxy-5-tert.-amyl-, m.p.  $114^\circ$ , 5-nitro-2-hydroxy-, m.p.  $196^\circ$ , and 2-hydroxy- $\gamma$ -benzoyl-, m.p.  $188\text{--}189^\circ$ , - $N$ - $\beta$ -hydroxyethylbenzylamine, respectively. These substances react further with  $CH_2O$  to form resins. Resinous products were obtained from  $PhOH$ , cresols, *o*- and  $p\text{-}C_6H_4Cl\cdot OH$ , and *o*-cyclohexyl-, *p*-benzyl-, and *p*- $\alpha\gamma\gamma$ -tetramethylbutylphenols;  $m\text{-}C_6H_4(OH)_2$  gives an amorphous solid. H. B.

**Oxidation of pyrocatechol by tyrosinase.**—See this vol., 1417.

**cycloHexyltrichloromethylcarbinol.** J. W. HOWARD and R. J. BROWN (J. Amer. Chem. Soc., 1936, 58, 1657).— $Mg$  cyclohexyl bromide added to chloral in  $Et_2O$  gives cyclohexyltrichloromethylcarbinol, b.p.  $119\text{--}121^\circ/15$  mm. (acetate, b.p.  $176^\circ/680$  mm.; propionate, b.p.  $188^\circ/681.6$  mm.; butyrate, b.p.  $183^\circ/682.6$  mm.; benzoate, b.p.  $210^\circ/683.3$  mm.), in approx. 30% yield. H. B.

**Substituted hydroxybenzyl alcohols.** B. DUNNING, jun., F. DUNNING, and E. E. REID (J. Amer. Chem. Soc., 1936, 58, 1565—1568).—2-Hydroxy-4-, m.p.  $103^\circ$ , and -6-, m.p.  $80^\circ$ , -methyl-, -5-ethyl-, m.p.  $83^\circ$ , and -5-propyl-, m.p.  $73^\circ$ , -benzyl alcohol are prepared by reduction (Adams) of the appropriate  $OH\cdot C_6H_4Alk\cdot CHO$  (prep.; Reimer-Tiemann), whilst 5-bromo-3-iodo-, m.p.  $86^\circ$ , and 3-chloro-5-bromo-, m.p.  $93^\circ$ , -2-hydroxy-, 6-bromo-3-hydroxy-, m.p.  $124^\circ$ , and 3-bromo-4-hydroxy-, m.p.  $128^\circ$ , -benzyl alcohol are obtained by direct halogenation. The relative

bactericidal (towards *S. aureus*), anaesthetic, and anti-spasmodic activities of the above and *o*-, *m*-, and *p*-OH-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-OH, and the 3:5-Cl<sub>2</sub>-, -Br<sub>2</sub>-, and -I<sub>2</sub>-, 5-Cl-, -Br-, and -I-, and 5-Me derivatives of (I) are determined; the bactericidal activity rises as the partition coefficient, solubility in olive oil/solubility in H<sub>2</sub>O, increases. H. B.

**Mechanism of asymmetric synthesis with reference to a new type.** J. KENYON and S. M. PARTRIDGE (J.C.S., 1936, 1313—1317).—(+)-*Methyl-αβ-dibromo-n-propylcarbinol*, b.p. 103°/13 mm.,  $\alpha_{\text{D}}^{25} +2.04^\circ$ ,  $\alpha_{\text{D}}^{15} +2.15^\circ$ ,  $\alpha_{\text{D}}^{10} +2.46^\circ$ ,  $\alpha_{\text{D}}^8 +4.90^\circ$  (l, 0.5), obtained from (–)- $\alpha\gamma$ -dimethylallyl alcohol and Br-CHCl<sub>3</sub>, is oxidised by CrO<sub>3</sub>-AcOH to (+)-*Me αβ-dibromo-n-propyl ketone*, b.p. 90°/13 mm.,  $\alpha_{\text{D}}^{25} +3.06^\circ$ ,  $\alpha_{\text{D}}^{15} +3.34^\circ$ ,  $\alpha_{\text{D}}^{10} +3.85^\circ$ ,  $\alpha_{\text{D}}^8 +8.25^\circ$  (l, 0.25), whilst (+)- $\alpha\gamma$ -dimethylallyl alcohol by similar treatment gives the dl-*dibromo-alcohol*, b.p. 112°/20 mm., oxidised to dl-*Me αβ-dibromo-n-propyl ketone*, b.p. 90°/13 mm. Further, the similarly constituted (+)- $\gamma$ -phenyl- $\alpha$ -methylallyl alcohol (I) with Br-CHCl<sub>3</sub> gives a mixture of two carbinols separated by fractional crystallisation into d- (II), m.p. 112—113°,  $[\alpha]_{\text{D}}^{25} +107.1^\circ$ ,  $[\alpha]_{\text{D}}^{15} +115.9^\circ$ ,  $[\alpha]_{\text{D}}^{10} +128.0^\circ$ ,  $[\alpha]_{\text{D}}^{8} +261.0^\circ$  in CHCl<sub>3</sub>, and l-*αβ-dibromo-β-phenylethylmethylcarbinol*, m.p. 87—88°,  $[\alpha]_{\text{D}}^{25} -97.8^\circ$ ,  $[\alpha]_{\text{D}}^{15} -115.4^\circ$ ,  $[\alpha]_{\text{D}}^{10} -119.7^\circ$ ,  $[\alpha]_{\text{D}}^{8} -224.0^\circ$  in CHCl<sub>3</sub>. The latter are oxidised without separation to (–)-*αβ-dibromo-β-phenylethyl Me ketone*, m.p. 127°,  $[\alpha]_{\text{D}}^{25} -10.15^\circ$  (l, 2; c, 2.7 in CHCl<sub>3</sub>). Oxidation of the (+)- and (–)-carbinols yields respectively (+)- and (–)-ketones, both m.p. 127°, possibly optically pure since the rotatory powers were of equal magnitude and opposite sign. Addition of Br to the (–) form of (I) gives a (–)-*αβ-dibromo-β-phenylethylmethylcarbinol*, m.p. 112—113°, the optical enantiomorph of (II), oxidised to the optically pure (–)-ketone. It is thought that asymmetric addition takes place when there is a difference in energy associated with the diastereoisomeric intermediate products, a conclusion supported by the fact that there is an unexpectedly wide variation in the rotatory powers of the ketones obtained by oxidation of the mixtures of dibromo-alcohols by bromination at different temp., the (–)- or (+)-ketone predominating according to whether the temp. is low or high. F. R.

**Asymmetric reaction.** Preparation of an alcohol or of its diastereoisomeride, exclusively, by reactions asymmetric or not. F. KAYSER (Ann. Chim., 1936, [xi], 6, 145—248; cf. A., 1924, i, 825).—Hydratropaldehyde with the theoretical quantity of MgPhBr in Et<sub>2</sub>O affords (α)-*αβ-diphenylpropyl alcohol* (I), b.p. 180—182°/17—18 mm. [*phenylcarbamate*, m.p. 116°; *chloride*, m.p. 140°; boiling AcCl containing NaOAc affords an Ac derivative of indefinite b.p. and some of the (β)-acetate]. Similarly, β-*phenylbutaldehyde*, b.p. 120°/35 mm. (prep. described), with MgPhBr affords (α)-*αβ-diphenylbutyl alcohol* (II), b.p. 183—184°/18 mm. [oxidised to ethyldeoxybenzoin (III); *phenylcarbamate*, m.p. 119°; *chloride*, m.p. 49°; Ac, b.p. indefinite, and Bz, b.p. 110°/20 mm., derivatives]; αβ-diphenylpropaldehyde affords (α)-*αβγ-triphenylpropyl alcohol* (IV), m.p. 92° (cf. A., 1933, 710) [oxidised to benzyldeoxybenzoin

(V); by heating with KHSO<sub>4</sub> a product, m.p. 63°, is obtained identical with that from the (β)-diastereoisomeride; *phenylcarbamate*, m.p. 125°; *chloride*, decomp. when heated; Ac derivative, m.p. 70°]. (I), (II), and (III) are obtained free from the (β)-diastereoisomerides. Methyldeoxybenzoin (VI), (III), and (V) are not reduced by H<sub>2</sub>-Pt, -Ni, or -Pd, but with MgBu<sup>o</sup>Cl, a small amount of *sec.* alcohol, (VIII) (below), and γδ $\epsilon$ -*triphenyl-ββ-dimethylpentan-γ-ol*, m.p. 117°, respectively, are formed. Deoxybenzoin with MeI, EtBr, and CH<sub>2</sub>PhBr in warm EtOH containing NaOEt affords (VI), (III), and (V), respectively. (VI) with Na-Hg in EtOH or Na in hot EtOH affords (β)-*αβ-diphenylpropyl alcohol* (VII), m.p. 48° [oxidised to (VI); *phenylcarbamate*, m.p. 122°; the *chloride* is identical with that from (I); Ac derivative, m.p. 104°], and a compound, (C<sub>10</sub>H<sub>10</sub>O)<sub>n</sub>, m.p. 266°. Similarly (III) and (V) afford (β)-*αβ-diphenylbutyl alcohol* (VIII), m.p. 82° [oxidised to (III); *phenylcarbamate*, m.p. 124°; *chloride*, m.p. 78°; Ac derivative, m.p. 53°], and (β)-*αβγ-triphenylpropyl alcohol* (IX), m.p. 87° [oxidised to (V); dehydrated (KHSO<sub>4</sub>) to a substance, m.p. 63°; *phenylcarbamate*, m.p. 121.5°; *chloride*, m.p. 90°; Ac derivative, m.p. 90°], respectively. The asymmetric synthesis of one diastereoisomeride exclusively is explained by postulating a sp. influence (leading to distortion) of one alkyl (R) on the position in space occupied by CO with respect to R and R', thereby providing a favoured position for attack by the incoming R'' (from MgR''X). *trans*-Stilbene oxide (X) with MgEtBr affords (VIII) whereas the *cis*-isomeride (XI) gives (II) in poor yield. (X) with CH<sub>2</sub>Ph-MgCl gives (IX), whereas (XI) affords (IV). (X) with MgMeI gives a mixture of *di-αβ-diphenylpropyl ether*, m.p. 138°, a *polymeride* (?), m.p. 282°, of *diphenylpropyl alcohol*, and a *substance*, m.p. 56°; (XI) with MgMeI affords only stilbene. (X) with MgMeBr gives stilbene and (I), as does (XI). Methylstilbene oxide (A., 1932, 394) with H<sub>2</sub>-Ni in EtOH at 35—40° affords (VII). Benzylstilbene with BzO<sub>2</sub>H affords *benzylstilbene oxide*, m.p. 65—66°, reduced (Ni-H<sub>2</sub>) to (IX). In neither case is there any evidence of the presence of the α-diastereoisomeride, nor of the rupture of both C-O linkings of the oxido-compound.

J. L. D.

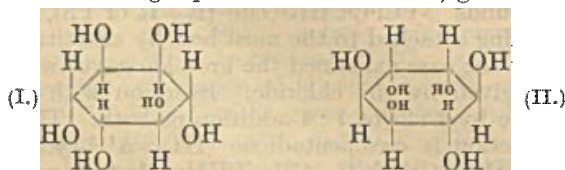
**Addition of alkyl halides to the ethylenic linking.** F. STRAUS and W. THIEL [and, in part, G. SZYSZKA] (Annalen, 1936, 525, 151—182).—OMe-CH<sub>2</sub>Cl (I) and OMe-CHPhCl (II) add on to unsaturated compounds alone or, better, in presence of HgCl<sub>2</sub> or, best, ZnCl<sub>2</sub>, SnCl<sub>4</sub>, or SbCl<sub>5</sub>, to give compounds >CCl-C-CHR-OMe (R=H or Ph), the Cl becoming attached to the most heavily substituted C. In the one case examined the bromide gave twice the yield given by the chloride. Reaction with dienes may be by 1:2- or 1:4-addition or both. The case of reaction is *cyclopentadiene* (III) > Δ<sup>1:3</sup>-*cyclohexadiene* (IV) > CMe<sub>2</sub>CH<sub>2</sub>, CMe<sub>2</sub>CHMe > butadiene (V) > mono-unsaturated alicyclic compounds. Yields are usually 70%. The course of reaction is not always certain. Solutions of the alkoxy-halides obtained from the acetal or aldehyde and HCl-MeOH can sometimes be used. *p*-OMe-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Cl (VI), but not CH<sub>2</sub>PhCl, condenses. (CH<sub>2</sub>Br)<sub>2</sub>O readily condenses by both Br, (CH<sub>2</sub>Cl)<sub>2</sub>O less readily by both Cl. This



is held to support direct addition of alkyl halides to C in such compounds as  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ . (I) and (V) give  $\alpha$ -chloro- $\epsilon$ -methoxy- $\epsilon$ -phenyl- $\Delta^5$ -pentene, b.p. 126—127°/12 mm. (dibromide, b.p. 150°/0.4 mm.), oxidised by  $\text{KMnO}_4\text{-COMe}_2$  to  $\text{OMe-CHPh-CH}_2\text{-CO}_2\text{H}$ , m.p. 101—102°, and  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ . (II) and (V) give (1)  $\gamma$ -chloro- $\epsilon$ -methoxy- $\Delta^5$ , b.p. 35°/10 mm., 148°/756 mm., and  $\alpha$ -chloro- $\epsilon$ -methoxy- $\Delta^5$ -pentene, b.p. 56°/10 mm., 168°/758 mm.  $\text{OMe-CHPhBr}$  and (V) give  $\alpha$ -bromo- $\epsilon$ -methoxy- $\epsilon$ -phenyl- $\Delta^5$ -pentene, b.p. 92°/0.1 mm., and (VI) gives  $\alpha$ -chloro- $\epsilon$ -methoxy- $\epsilon$ -anisyl- $\Delta^5$ -pentene, b.p. 104°/0.1 mm. (13%). (II) and (IV) yield 1-chloro-2- or 4- $\alpha$ -methoxybenzyl- $\Delta^5$ -cyclohexene, b.p. 112°/0.1 mm., and the 2- or 4- $\alpha$ -methoxy-ethyl, b.p. 81°/10 mm., and -p-anisyl, b.p. 128—129°/0.02 mm., derivatives are also obtained.  $\text{CPh}_3\text{Cl}$  and (IV) afford  $\text{CHPh}_3$  and 1-chloro-2-triphenylmethyl- $\Delta^5$ -cyclohexene, b.p. 103°/2 mm. (II) and (III) give a 1-chloro-2- or -3- $\alpha$ -methoxybenzylcyclopentene, b.p. 99—100°/0.1 mm. (I) and  $\text{CMe}_2\cdot\text{CH}_2$  give *Me*  $\gamma$ -chloroisooamyl ether, b.p. 81—81.5°/120 mm., 136°/751 mm. (60% with 10% of  $\text{Bu}^n\text{Cl}$ ), readily hydrolysed by acid or alkali to  $\gamma$ -methoxy-tert.-amyl alcohol, b.p. 51—52°/15 mm., 144°/764 mm. (p-nitrobenzoate, m.p. 72—74°).  $\text{CMe}_2\cdot\text{CHMe}$  with (II) gives  $\gamma$ -chloro- $\alpha$ -phenyl- $\beta$ -methyl-tert.-amyl *Me* ether, b.p. 133—135°/16 mm., and with (I) *Me*  $\gamma$ -chloro- $\beta$ -methyl-tert.-amyl ether, b.p. 46—46.5°/14 mm., 153°/761 mm., converted by 5%  $\text{Na}_2\text{CO}_3$  into  $\delta$ -methoxy- $\beta$ - $\gamma$ -dimethylbutan- $\beta$ -ol, b.p. 159°/750 mm., 58—59°/15 mm., and some  $\alpha$ -methoxy- $\beta$ - $\gamma$ -dimethyl- $\Delta^5$ -butene, b.p. 28.5°/15 mm., 115°/750 mm. (II) and  $\text{CHPh}\cdot\text{CH}_2$  give  $\alpha$ -chloro- $\gamma$ -methoxy- $\alpha$ - $\gamma$ - or - $\alpha$ - $\beta$ -diphenylpropane, b.p. 122.5°/0.1 mm. (II) and cyclohexene give 2- $\alpha$ -methoxybenzylcyclohexyl chloride, b.p. 96°/0.2 mm., oxidised to an acid,  $\text{C}_{12}\text{H}_{14}\text{O}_2$ , m.p. 123.2° (*Me* ester, m.p. 26.5—27°, b.p. 144°/16 mm.), and a little  $\text{BzOH}$ ; (I) affords similarly 2- $\alpha$ -methoxy-ethylcyclohexyl chloride (45%), b.p. 89—91°/20 mm., 192°/763 mm. (II) and  $\Delta^2$ -dihydronaphthalene give 2-chloro-3- $\alpha$ -methoxybenzyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which, however, decomposes into  $\text{C}_{10}\text{H}_8$ ,  $\text{HCl}$ , and  $\text{CH}_2\text{Ph}\cdot\text{OMe}$ , with some formation also of  $\text{CH}_2\text{PhCl}$ ;  $\Delta^1$ -dihydronaphthalene reacts more violently, but no pure product was isolated. R. S. C.

**Phenyl  $\beta$ -hydroxy- $\beta$ -diphenylvinyl sulphone.**—See this vol., 1327.

**Cyclitols. III. Configuration of the active inositols.** T. POSTERNAK (Helv. Chim. Acta, 1936, 19, 1007—1010; cf. A., 1932, 1127).—Regulated oxidation by  $\text{KMnO}_4$  of *l*-inositol (I) (prep. from revertex through quebrachitol described) gives mucic



and *d*-saccharic acid the isolation of which establishes the configurations (I) and (II) for (I) and *d*-inositol, respectively. *d*-Quercitol is therefore *l*-deoxy-*l*-inositol. H. W.

**Production of steryl glucosides.** H. LETTRÉ and A. HAGEDORN (Z. physiol. Chem., 1936, 242,

210—214; cf. MacCorquodale *et al.* A., 1930, 1036).—Cholesterol (I) successively boiled in anhyd.  $\text{Et}_2\text{O}$  with acetobromoglucose (II),  $\text{Ag}_2\text{O}$ , and  $\text{CaH}_2$  and acetylated gives *cholesteryl*tetra-acetylglucoside, m.p. 159—160°,  $[\alpha]_D^{25}$  —23.1° in  $\text{CHCl}_3$ . Similarly dihydro- and dehydro-ergosterol give *dihydro*-, m.p. 187—188°,  $[\alpha]_D^{25}$  —19.4° in  $\text{CHCl}_3$ , and *dehydro-ergosteryl*tetra-acetylglucoside (III), m.p. 167—168°  $[\alpha]_D^{25}$  +62.4° in  $\text{CHCl}_3$ , respectively, and (I) with acetobromolactose yields, after acetylation, the *hepta-acetate*, m.p. 195°,  $[\alpha]_D^{25}$  —16.3°, of *cholesteryl-lactoside*, m.p. 260° (decomp.),  $[\alpha]_D^{25}$  —37.8°. Together with (III) a substance, m.p. 159—160°, is produced. The glucoside of cholesteryl oxide with hot  $\text{Ac}_2\text{O}$  and  $\text{NaOAc}$  gives 5-hydroxy-6-acetoxy-3-tetra-acetyl- $\beta$ -glucosidocholestan (IV), m.p. 212—213°,  $[\alpha]_D^{25}$  —26.4°, also obtained by the interaction of cholestanetriol and (II) followed by acetylation. (IV) with Na in  $\text{EtOH}$  gives *cholestanetriol-3-glucoside*, m.p. 263—265° (decomp.), which yields lather-producing solutions in  $\text{H}_2\text{O}$ . The other glucosides are  $\text{H}_2\text{O}$ -insol. Ergosterylglucoside acquires no antirachitic power on ultra-violet irradiation.

W. McC.

**Sterol group. XXVI. 7-Methylenecholesterol.** B. BANN, I. M. HEILBRON, and F. S. SPRING (J.C.S., 1936, 1274—1276).—7-Ketocholesteryl acetate (I) + 3 mols. of  $\text{MgMeI}$  gives 7-hydroxy-7-methyl-cholesterol (II), m.p. 165° (3-monobenzoate, m.p. 175°; 3-monoacetate, m.p. 164°). Dehydration of the monobenzoate by  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$  or the Darzens method or sublimation in a high vac. gives 7-methylenecholesteryl benzoate (III;  $\text{R}=\text{Bz}$ ), m.p. 141°, hydrolysed to 7-methylenecholesterol (III;  $\text{R}=\text{H}$ ), m.p. 85° (3:5-dinitrobenzoate, m.p. 162°; acetate, m.p. 62—64°), directly isolable from the mother-liquor of (II) and the sole product of (I)+excess of  $\text{MgMeI}$ , which after irradiation was antirachitically inactive. F. R.

**Micro-determination of cholesterol.**—See this vol., 1436.

**Rates of isomerisation and of hydrogen isotope exchange in unsaturated nitriles.**—See this vol., 1344.

**Pentadeuterobenzoic acid.** H. ERLÉNMEYER and A. EPPRECHT (Helv. Chim. Acta, 1936, 19, 1056—1059; cf. this vol., 983).—The following consts. of  $\text{C}_6\text{D}_5\cdot\text{CO}_2\text{H}$  and  $\text{BzOH}$ , respectively, are recorded: m.p. 120.9° and 121.7°; solubility in 100 c.c. of  $\text{H}_2\text{O}$  at 18°, 0.34 and 0.28 g.; mol. heat of combustion, 761.38 and 771.4 kg.-cal.; heat of formation from the elements, 106.12 and 91.0 kg.-cal.; normal acidity potential,  $205.7 \pm 0.3$  and  $205.6 \pm 0.3$  mv. H. W.

**Asymmetric carbon atom  $\text{CHDR}^n\text{R}^m$ . III. Phenylpentadeuterophenylacetic acid.** H. ERLÉNMEYER and H. SCHENKEL (Helv. Chim. Acta, 1936, 19, 1169—1170; cf. this vol., 467, 604).—*l*- $\text{CHPhBr}\cdot\text{CO}_2\text{H}$ ,  $[\alpha]_D^{20}$  —145° in  $\text{C}_6\text{H}_6$ , is converted by  $\text{C}_6\text{D}_6$  in presence of Zn dust into *phenylpentadeuterophenylacetic acid*,  $\text{C}_6\text{D}_5\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , m.p. 144°,  $[\alpha]_D^{20} \pm 0^\circ$ , which could not be resolved into its optical antipodes by morphine or strychnine. H. W.

**Halogenation of *o*-sulphobenzoic anhydride.** D. TWISS and L. H. FARINHOLT (J. Amer. Chem. Soc., 1936, 58, 1561—1565).—3-Bromo- (I), m.p. 175—176°, 3:6-dichloro- (II), m.p. 121—122°, 3:6-dibromo- (III), m.p. 167—168°, 3:6-di-iodo- (IV), m.p. 243—245°, 3:5:6-tribromo- (V), m.p. 224°, 3:5:6-tri-iodo- (VI), m.p. 287—288°, tetrachloro-, m.p. 158—159°, tetrabromo-, m.p. 216—217°, and tetra-iodo- (VII), decomp. gradually about 300°, *o*-sulphobenzoic anhydrides are prepared by halogenation of *o*-SO<sub>3</sub>H·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H, its anhydride, or, more conveniently, its NH<sub>4</sub> H salt [obtained by hydrolysis (dil. HCl) of saccharin] in (usually) 60% oleum at 150—180°. In some cases I is used as catalyst and the anhydrides are purified by conversion into the corresponding (NH<sub>4</sub>)<sub>2</sub> salt and subsequent treatment with SOCl<sub>2</sub>. All except (VII) are readily hydrolysed even by atm. moisture to the acids. The positions of the halogen atoms are determined by removal of the SO<sub>3</sub>H from the acids by aq. H<sub>2</sub>SO<sub>4</sub> at 200—210°; (I) thus gives *m*-C<sub>6</sub>H<sub>4</sub>·Br·CO<sub>2</sub>H; (II), 2:5-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>·CO<sub>2</sub>H and a little *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>; (III), 2:5-C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>·CO<sub>2</sub>H; (V), 2:3:5-C<sub>6</sub>H<sub>2</sub>Br<sub>3</sub>·CO<sub>2</sub>H; the I-derivatives are destroyed. Saturation of a conc. solution of tetraiodo-*o*-sulphobenzoic acid in aq. NH<sub>3</sub> with H<sub>2</sub>S gives (NH<sub>4</sub>)<sub>2</sub> 3:5:6-tri-iodo- [converted by conc. H<sub>2</sub>SO<sub>4</sub> at 160° into (VI)] and di-iodo-*o*-sulphobenzoate [which with conc. H<sub>2</sub>SO<sub>4</sub> at 150° affords a di-iodo-*o*-sulphobenzoic anhydride, m.p. 221—223°, different from (IV)]. H. B.

**Manufacture of basic esters of polyarylacetic acids.**—See B., 1936, 975.

**Agents of capillary activity [cyclohexylaliphatic acids].**—See B., 1936, 975.

**Valency problem of the quinquivalent phosphorus atom.** II. L. ANSCHUTZ, F. KOENIG, F. OTTO, and H. WALBRECHT (Annalen, 1936, 525, 297—311; cf. A., 1930, 1429).—The peculiar reactivity of one Cl of PCl<sub>5</sub> is due to electrostatic repulsion of the five electronegative Cl and not to a special type of linking of one Cl. In accordance with this view, the reactivity is depressed if Cl is replaced by OPh or substituted OPh. This is proved for the reaction of OPh·PCl<sub>4</sub>, (OPh)<sub>2</sub>PCl<sub>3</sub>, *o*-COCl·C<sub>6</sub>H<sub>4</sub>·O·PCl<sub>4</sub>, and *p*-OMe·C<sub>6</sub>H<sub>4</sub>·O·PCl<sub>4</sub> with H<sub>2</sub>O, EtOH, PhOH, *o*-OH·C<sub>6</sub>H<sub>4</sub>·COCl (I), and indene (II). Chloroindanyldiphosphorus tetrachloride is purified by pptn. by ligroin from warm PhNO<sub>2</sub>, and then reacts slowly with (I) and not at all with (II), but rapidly with H<sub>2</sub>O, EtOH, or PhOH by loss of HCl from the nucleus. The following are described. Ph<sub>3</sub>PO<sub>4</sub>, m.p. 45°; *salicylic acid phosphate* ("phosphosal"); *o*-CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·O·PO<sub>3</sub>H<sub>2</sub>; *o*-anisoylphosphorus dichloride, b.p. 130—131°/13 mm., and tetrachloride, cryst.

R. S. C.

**Derivatives of  $\beta$ -amino- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid.** B. CROCCA (Gazzetta, 1936, 66, 533—539).—CH<sub>2</sub>BzCl, HCN, and NH<sub>3</sub> yield  $\beta$ -chloro- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid, m.p. 132°. This with aq. NHMe<sub>2</sub> (reaction completed at 110°) gives the NH<sub>2</sub>Me<sub>2</sub> salt, m.p. 251° (decomp.), of  $\beta$ -dimethylamino- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid, of which the *Me*, b.p. 155—156°/14—15 mm., and *Pr*<sup>a</sup>, b.p. 171—172°/14—15 mm., esters yield respectively

(BzCl) *Me* (I), m.p. 163° (decomp.), and *Pr*<sup>a</sup>  $\beta$ -dimethylamino- $\alpha$ -benzyloxy- $\alpha$ -phenylpropionate hydrochloride (II), m.p. 177—178° (decomp.). *Pr*<sup>a</sup>  $\beta$ -dimethyl- (III), m.p. 136°, and  $\beta$ -diethyl-amino- $\alpha$ -acetoxy- $\alpha$ -phenylpropionate hydrochloride (IV), m.p. 134°, are obtained similarly. *Pr*<sup>a</sup>  $\beta$ -chloro- $\alpha$ -hydroxy- $\alpha$ -phenylpropionate, b.p. 173°/14—15 mm., with NHMe<sub>2</sub> at 100° gives  $\beta$ -dimethylamino- $\alpha$ -hydroxy- $\alpha$ -phenylpropiondimethylamide, b.p. 173°/14—15 mm. (I) and (II) are surface anaesthetics, and, intramuscularly, antipyretics; (III) also, subcutaneously, has depressor action, as, in a less degree, has (IV), with increased toxicity. E. W. W.

**Constitution of isomeric dichlorofluorenone-carboxylic acids formed by the action of sulphuric acid on 3:3'-dichlorodiphenic acid.** E. H. HUNTRESS and E. R. ATKINSON (J. Amer. Chem. Soc., 1936, 58, 1514—1518).—The keto-acid, C<sub>14</sub>H<sub>6</sub>O<sub>3</sub>Cl<sub>2</sub>, previously obtained (A., 1933, 1293) from 3:3'-dichlorodiphenic acid (I) and conc. H<sub>2</sub>SO<sub>4</sub> at 170°, is 1:6-dichlorofluorenone-4-carboxylic acid (II), new m.p. 248—249°, which results by isomerisation of the first-formed 1:6-dichlorofluorenone-5-carboxylic acid (III). The inconsistent titration (*loc. cit.*) of (II) is due to solvation. Dehydration of (I) with conc. H<sub>2</sub>SO<sub>4</sub> at 80—90°/24 hr., 95—104°/1 hr., or 125°/1 hr. gives (III), but at 125°/5 hr., 135—145°/4 hr., or 150—160°/1 hr., (II) results. Isomerisation does not occur with H<sub>3</sub>PO<sub>4</sub> at 215°; (I) thus affords (III) whilst 5:5'-dichlorodiphenic acid (IV) yields (II). 1:6-Dichloro-5-aminofluorenone (*loc. cit.*) is deaminated to 1:6-dichlorofluorenone (V). (II) and conc. H<sub>2</sub>SO<sub>4</sub> at 200—215° give 4:6-dichlorofluorenone (VI) (and a little unidentified material), also similarly obtained from (I), (III), and (IV) at about 200°, (V) at 150° (rearrangement not complete at 125°), and 1:8-dichlorofluorenone (VII) at 180—190°. Neither decarboxylation nor rearrangement occurs with (II) and H<sub>3</sub>PO<sub>4</sub>. Distillation of the Ca salts of (I) and (IV) gives (VII) and (VI), respectively. H. B.

**Condensation of aldehydes with malonic acid in the presence of organic bases.** Condensation of (V) anisaldehyde, (VI) *p*-hydroxybenzaldehyde, (VII) *m*-hydroxybenzaldehyde. K. C. PANDYA and T. A. VAHIDY (Proc. Indian Acad. Sci., 1936, 4, A, 134—139, 140—143, 144—146).—V. Condensation of anisaldehyde with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> using C<sub>5</sub>H<sub>5</sub>N, lutidine, and isoquinoline gives *p*-methoxycinnamic acid but with other bases the first product is anisylidenemalonic acid. Condensation also occurs without using a base.

VI. With *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO, similar results are obtained, the amount of product, either *p*-hydroxycinnamic or the *p*-coumaric acid, being increased by using a base.

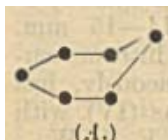
VII. The yields of condensation product with different bases are compared, C<sub>5</sub>H<sub>5</sub>N giving the best yield at the optimum temp. 105—110°. F. R. S.

**Non-existence of multiplanar cyclohexane rings.** R. D. DESAI and R. F. HUNTER (Nature, 1936, 138, 548; cf. A., 1935, 1495; this vol., 831, 846).—4:4-Dimethylcyclohexane-1-carboxylic-1-acetic acid and -1:1-diacetic acid, now synthesised from 4:4-dimethylcyclohexanone, each exists in one form only,



thus supporting the uniplanar structure of the *cyclohexane* ring. L. S. T.

**Sachse-Mohr theory of the configuration of cyclohexane and the application of the Bredt rule to tetrahydro[iso]phthalic anhydride.** J. BREDT (J. pr. Chem., 1936, [ii], 147, 22—28).—Theoretical. Interconversion of boat into chair forms of a  $C_6$  ring occurs by way of the "sofa" form (A) and the mol. is never planar. By analogy with other systems it is inferred that the anhydride of tetrahydroisophthalic acid is intermol., and that an eight-membered ring containing one O and bridged across the 1:5 positions by one C cannot exist with the bridge containing a double linking. R. S. C.



**Chloral derivatives of salicylic acid.** N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1936, 13, 475—477).— $o\text{-OMe}\cdot C_6H_4\cdot CO_2H$  and chloral in conc.  $H_2SO_4$  give 2-methoxy-5- $\beta\beta$ -dichloro- $\alpha$ -hydroxyethylbenzoic acid (I), m.p.  $224^\circ$  (lit.  $216^\circ$ ), and a sulphonic acid, converted into (I) by boiling in  $H_2O$ . Other salicylic acid derivatives do not undergo this condensation. (I) yields by reduction 2-methoxy-5- $\beta\beta$ -dichloroethylbenzoic acid (II), m.p.  $134\text{—}135^\circ$  (lit.  $127^\circ$ ), and by  $H_2SO_4$  at  $100^\circ$  2-methoxy- $\alpha\beta\beta\beta$ -tetrachloroethylbenzoic acid, m.p.  $138^\circ$  (lit.  $132^\circ$ ), and a small amount of a substance, m.p.  $177^\circ$ . (II) and conc.  $H_2SO_4$  at  $100^\circ$  give 3-carboxy-4-methoxyphenylacetic acid,  $+H_2O$ , m.p.  $141\text{—}142^\circ$ , and anhyd., m.p.  $153^\circ$ . R. S. C.

**Isatdiazide.** A. DARAPSKY and B. GAUDIAN (J. pr. Chem., 1936, [ii], 147, 43—52).—Phthalyl chloride (I) and aq.  $NaN_3$  give isatdiazide,  $o\text{-N}_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot N_3$  (II), m.p.  $101^\circ$ , and a trace of (?) phthalyl azide. Probably  $o\text{-N}_3\cdot CO\cdot C_6H_4\cdot NCO$  is first formed which then reacts with  $HN_3$ , liberated from  $NaN_3$  by products of hydrolysis of (I). With hot dil. aq.  $NaOH$  (II) gives anthranilic acid and with  $NH_2Ph$  at  $100^\circ$  the dianilide, m.p.  $222^\circ$ , which is stable to acid and alkali, but with conc.  $HCl$  at  $200\text{—}220^\circ$  gives  $NH_2Ph$  and 2:4-diketo-3-phenyltetrahydroquinazoline, m.p.  $272^\circ$ . With hot  $EtOH$  (II) gives  $o$ -phenylenediurethane, hydrolysed by  $2N\text{-}NaOH$  to  $o$ -phenylenecarbamide,  $o\text{-C}_6H_4(NH)_2CO$ , m.p.  $>300^\circ$ . With conc.  $NH_3$  (II) gives 2:4-diketotetrahydroquinazoline (III) and with  $N_2H_4$  3-amino-2:4-diketotetrahydroquinazoline, m.p.  $>280^\circ$  [benzylidene derivative, m.p.  $245\text{—}246^\circ$  (lit.  $240^\circ$ )]; with  $HNO_2$  gives  $N_2O$  and (III)]. R. S. C.

**Synthesis of substances of possible physiological activity.** L. F. FIESER, M. FIESER, E. B. HERSHBERG, H. L. HOLMES, and M. S. NEWMAN (Science, 1936, 83, 558).—Condensation of  $(CH_3\cdot CO)_2O$  (I) with  $\alpha\text{-C}_{10}H_7\cdot OMe$  gives a suitable starting material for the synthesis of 9-methoxyphenanthrene-1:2-dicarboxylic anhydride, m.p.  $249\text{—}250^\circ$  (corr.), by reduction, condensation of the ester with  $Et_2C_2O_4$ , cyclisation, and dehydrogenation. The 6-methoxy- and 6:7-dimethoxy-derivatives of octahydrophenanthrene-11:12-dicarboxylic anhydride were prepared by addition of butadiene (II) to the unsaturated anhydrides

obtained from anisole and from veratrole by condensation with (I), reduction, ester condensation, and cyclisation. The ethers were demethylated after hydrogenation of the active ethylenic linking. 7-Hydroxy-6-methyloctahydrophenanthrene-11:12-dicarboxylic anhydride, m.p.  $134.5\text{—}135.5^\circ$  (corr.), was prepared similarly from  $\gamma$ -4-methoxy-3-methylphenylbutyric acid. Phenanthrene-1:2-dicarboxylic anhydride is converted into 1':3'-diketo-1:2-cyclopentenophenanthrene by condensation of the  $Me_2$  ester with  $EtOAc$ . 1':3'-Diketo-3:4-cyclopentenophenanthrene, m.p.  $201.4\text{—}202^\circ$  (corr.), is obtained similarly. Chrysene, 2:3-dimethyl-6:7-accechrysene, m.p.  $222.6\text{—}223.1^\circ$  (corr.), and 6:7-dimethyl-3:4-benzophenanthrene, m.p.  $94.5\text{—}95^\circ$  (corr.), have been obtained by extensions of the hydrocarbon synthesis developed by Fieser and Hershberg (this vol., 203).  $o\text{-C}_6H_4Me\cdot MgBr$  and 1:2- $C_{10}H_6(CO)_2O$  give a keto-acid (decarboxylated to  $\beta$ - $o$ -toluoylnaphthalene), the ester of which is converted ( $MgMoX$ ; reduction; cyclisation; reduction) into 5:10-dimethyl-1:2-benzanthracene, m.p.  $147\text{—}147.5^\circ$  (corr.) [picrate, m.p.  $173.7\text{—}174.2^\circ$  (corr.)]. Addition of (II) and its 2:3- $Me_2$  derivative to  $Et$  3:4-dihydro-1-naphthoate affords, after hydrolysis, 5:8:9:10:13:14-hexahydrophenanthrene-13-carboxylic acid (morphine numbering), m.p.  $137\text{—}137.5^\circ$  (corr.), and its 6:7- $Me_2$  derivative, m.p.  $162\text{—}162.5^\circ$  (corr.). On dehydrogenation, these yielded phenanthrene and 2:3-dimethylphenanthrene respectively. L. S. T.

**$\alpha\delta$ -Diarylbutadienes and related compounds.** II.  $\alpha\delta$ -Diarylbutadiene- $\alpha\beta$ -dicarboxylic anhydrides. E. FRIEDMANN and W. E. VAN HEYNINGEN (J. pr. Chem., 1936, [ii], 146, 166—178; see this vol., 1371).— $CH_3Ph\cdot CO_2H$  and  $CHPh\cdot CH\cdot CO_2H$  in boiling  $Ac_2O$  give 46.5% of  $\alpha\delta$ -diphenylbutadiene- $\alpha\beta$ -dicarboxylic [ $\beta$ -carboxy- $\alpha\delta$ -diphenylpentadienic, phenylstyrylmalic] anhydride (I), m.p.  $137.5^\circ$ . With warm alkali this gives the  $Na_2$ ,  $+4H_2O$ , and  $K_2$  (II),  $+2H_2O$ , salts of the corresponding acid. Acidification of (II) in cold  $H_2O$  regenerates (I). Hydrogenation (colloidal Pd) of (II) causes absorption of 2  $H_2$ .  $\alpha$ -Phenyl- $\delta$ -p-anisyl- (III), m.p.  $176^\circ$  ( $Na_2$ ,  $+3H_2O$ , and  $K_2$  salt,  $+2H_2O$ , of the corresponding acid), and -2-furoylbutadiene- $\alpha\beta$ -dicarboxylic anhydride, m.p.  $174^\circ$ , are similarly prepared. The absorption spectra of (I) and (II) and of the  $K_2$  salts show the bathochromic effect of the OMe. R. S. C.

**Diphenyl series.** IX. Nitration of 2:4'-derivatives of diphenyl. C. FINZI and V. BELLAVITA (Gazzetta, 1936, 66, 421—429).—Diphenyl-2:4'-dicarboxylic acid (I) (dichloride, m.p.  $69\text{—}70^\circ$ ; diamide, m.p.  $233^\circ$ ; dianilide, m.p.  $280\text{—}281^\circ$ ; di-p-toluidide, m.p.  $259\text{—}260^\circ$ ;  $Me_2$ , m.p.  $79\text{—}80^\circ$ , and  $Et_2$  esters) is converted by  $H_2SO_4$  and  $EtNO_3$  into the 4- $NO_2$ -derivative (II), new m.p.  $284\text{—}285^\circ$ , and the 4:2'-( $NO_2$ ) $_2$ -derivative (dichloride; diamide, decomp.  $215^\circ$ ). 4-Nitro-2:4'-diaminodiphenyl (A., 1932, 1025) yields (Sandmeyer) 4-nitro-2:4'-dicyanodiphenyl, m.p.  $238\text{—}239^\circ$ , hydrolysed to (II). When 4:2'-dinitrodiphenyl-2:4'-dicarboxylic acid and 2-nitrodiphenyl-2'-carboxylic acid are heated with Cu chromite, they eliminate an  $NO_2$ -group, forming 2-nitrofluorenone and fluorenone, respectively; (I), however, yields di-

phenyl-4-carboxylic acid and  $\text{Ph}_2$ , whilst (II) gives 4-nitrodiphenyl. E. W. W.

**Nitrogenous heterocyclic rings. XXV. *m*-Phenylenedipropionic acid and *m*-diacetylbenzene.** P. RUGGLI and A. STAUB (Helv. Chem. Acta, 1936, 19, 962—972; cf. this vol., 866).—Addition of Br to *m*-phenylenediacrylic acid in AcOH or EtOAc gives the tetrabromide, m.p. 225—227°, purified with difficulty owing to the ready loss of HBr in warm solvents. It is therefore preferable to transform its Me ester, best in EtOAc, into Me<sub>2</sub> *m*-phenylenedi- $\alpha$ - $\beta$ -dibromopropionate (I), m.p. 146°, transformed by  $\text{C}_5\text{H}_5\text{N}$  alone into a brown oil and by  $\text{C}_5\text{H}_5\text{N}$ -EtOH (1:3) into Me<sub>2</sub> *m*-phenylenedimonobromoacrylate,  $\text{m-C}_6\text{H}_4(\text{CH}:\text{CBr}:\text{CO}_2\text{Me})_2$ , m.p. 87°. *m*-Phenylenedipropionic acid (II), m.p. 209° [Me<sub>2</sub> (III), m.p. 93°, and Et., m.p. 56°, ester], is best obtained by rapidly adding 2 mols. of KOH in EtOH to (I) dissolved in much boiling EtOH and then slowly adding 4 more mols. In the first phase of the change only KBr separates, followed after addition of a further 2 mols. of KOH by the *K* salt of *m*-phenylenedimonobromoacrylic acid, m.p. 215°; this is succeeded by the *K* salt of (II), followed by that of *phenylene-1-propionic-3-monobromoacrylic acid*, m.p. 161° (dihydrate, m.p. 67°). Treatment of (II) with conc.  $\text{H}_2\text{SO}_4$  at room temp. yields the unstable isophthaloyldiacetic acid (IV),  $\text{m-C}_6\text{H}_4(\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , m.p. 116° (decomp.) [Me<sub>2</sub> ester (V), m.p. 68°, best obtained by hydration of (III)]. (IV) and  $\text{NHPh}\cdot\text{NH}_2$  in EtOH at 0° afford the diphenylhydrazone of *m*-acetylbenzoylacetic acid, m.p. 210°, and *m*-diacetylbenzenediphenylhydrazone (VI), m.p. 115°, separates from the mother-liquors when warmed to room temp.; if the change occurs directly at room temp. 1-phenyl-3-*m*-acetylphenylpyrazolonephenylhydrazone, m.p. 230—232° (decomp.), separates and (VI) is obtained from the mother-liquors. (VI) and  $\text{NHPh}\cdot\text{NH}_2$  in boiling EtOH give *m*-phenylene-3:3'-di(phenylpyrazolone), m.p. 263°, also derived from (III); (II) and  $\text{NHPh}\cdot\text{NH}_2$  in EtOH yield the diphenylhydrazine salt, m.p. 166°. (IV) and  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$  at 0° yield the disemicarbazone of (IV), m.p. 232°, and *m*-diacetylbenzenedisemicarbazone, m.p. 240°, or the latter exclusively at room temp. (IV) and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in EtOH at 0° afford *m*-phenylene-3:3'-diisooxazolone, m.p. 190° when rapidly heated, and *m*-diacetylbenzenedioxime, m.p. 204°. Decarboxylation of (IV) is readily effected by 10%  $\text{H}_2\text{SO}_4$  at 100° whereby *m*-diacetylbenzene, m.p. 32°, is obtained in 70—77% yield. *m*-Acetylcinnamic acid, m.p. 128°, is described incidentally. H. W.

**Anthraquinone series.** Attempts to synthesise anthraquinonecarboxylic acids of the morindone type. P. C. MITTER and (MISS) T. SENGUPTA (J. Indian Chem. Soc., 1936, 13, 447—449).—Opianic acid, Me 5-bromosalicylate, and  $\text{H}_2\text{SO}_4$  give 3:4-dimethoxy- $\alpha$ -5'-bromo-2'-hydroxy-3'-carbomethoxyphenylphthalide, m.p. 215° (Ac derivative, m.p. 210°; corresponding 3'-carboxyphthalide, m.p. 253°), reduced by Zn-10% NaOH to 2:3-dimethoxy-6-2'-hydroxy-3'-carboxybenzylbenzoic acid (I), m.p. 225°. Ring-closure of (I) or its Br-derivative, m.p. 210°, is not effected by  $\text{H}_2\text{SO}_4$  or  $\text{P}_2\text{O}_5$ . Hot  $\text{H}_2\text{SO}_4$  sulphonates (I).

R. S. C.

**Use of amines for distinguishing geometrically isomeric aldioximes and their acyl derivatives.** C. R. HAUSER and E. JORDAN (J. Amer. Chem. Soc., 1936, 58, 1772—1776; cf. this vol., 1253).— $\alpha$ -CHAR:N·OAc (Ar=Ph, *o*- and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ , *p*-OMe· $\text{C}_6\text{H}_4$ , 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ , *o*- $\text{C}_6\text{H}_4\text{Cl}$ , *p*-NMe<sub>2</sub>· $\text{C}_6\text{H}_4$ ) are unaffected by  $\text{C}_5\text{H}_5\text{N}$  (usually at room temp.) but are converted into  $\alpha$ -oximes by  $\text{NH}_2\text{Bu}^a$  (at room temp.).  $\beta$ -CHAR:N·OAc (Ar=Ph, *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ , *p*-OMe· $\text{C}_6\text{H}_4$ , 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ) with  $\text{C}_5\text{H}_5\text{N}$  and  $\text{NH}_2\text{Bu}^a$  (heat developed) give nitriles (84—99% yield). It is thus possible to distinguish between the above geometrical isomerides. Similarly,  $\alpha$ -CHAR:N·O·CO·NHPh (I) (Ar=*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ ; 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ),  $\alpha$ -CHAR:N·O·CO<sub>2</sub>Et (Ar=*p*-OMe· $\text{C}_6\text{H}_4$ , *o*- $\text{C}_6\text{H}_4\text{Cl}$ , *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ , 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ) and  $\alpha$ -CHAR:N·OBz (Ar=*m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4$ , 3:4- $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ) are unaffected by  $\text{C}_5\text{H}_5\text{N}$  and converted into  $\alpha$ -oxime by  $\text{NH}_2\text{Bu}^a$ , whilst the  $\beta$ -CHAR:N·O·CO·NHPh with  $\text{C}_5\text{H}_5\text{N}$  and  $\text{NH}_2\text{Bu}^a$  give the nitrile (also formed together with the  $\beta$ -oxime by the action of EtOH-NaOH at 25—30°).  $\text{NHPh}\cdot\text{CO}\cdot\text{NHBu}^a$  is also obtained from (I) and  $\text{NH}_2\text{Bu}^a$ . H. B.

**Ozonisation of aldehydes.**—See this vol., 1346.

**Photo-rearrangement of *o*-nitrobenzaldehyde to *o*-nitrobenzoic acid.**—See this vol., 1349.

**Reactions catalysed by aluminium chloride.**  
**XV. Preparation of saturated ketones by addition of acid chlorides to olefines and hydrogenation by aluminium chloride.** C. D. NENITZESCU and E. CIORĂNESCU (Ber., 1936, 69, [B], 1820—1823).— $\text{AlCl}_3$  is added gradually to a mixture of cyclopentene (I), AcCl, and cyclohexane (II) at  $-15^\circ$  in such a manner that HCl is not evolved; subsequently the temp. of the mixture is gradually raised to 70°, whereby cyclopentyl Me ketone, b.p. 55—56°/16 mm., is obtained in 50% yield. Reaction is  $\text{C}_5\text{H}_8 + \text{AcCl} = \text{C}_5\text{H}_8\text{ClAc} \xrightarrow{2\text{H}} \text{C}_5\text{H}_9\text{Ac} + \text{HCl}$  and  $2\text{C}_6\text{H}_{12} \rightarrow \text{C}_{12}\text{H}_{22} + 2\text{H}$ . The following ketones are prepared analogously: cyclohexyl Me, b.p. 183—184°; dicyclopentyl, b.p. 113—116°/14 mm., from cyclopentanecarboxyl chloride and (I), reduced (Clemmensen) to dicyclopentylmethane, b.p. 208—210°; cyclopentyl cyclohexyl, b.p. 128°/10 mm. (semicarbazone, m.p. 182°), whence cyclopentylcyclohexylmethane, b.p. 223—225°; 2-methylcyclopentyl cyclohexyl, b.p. 138—141°/20 mm. (semicarbazone, m.p. 190°), whence 2-methylcyclopentylcyclohexylmethane, b.p. 239—241°; 1-chloro-2-isovaleryl cyclohexane, b.p. 118—120°/14 mm., from cyclohexene (III), isovaleryl chloride (IV), and  $\text{AlCl}_3$  in  $\text{CS}_2$ , and cyclohexyl isobutyl ketone, b.p. 216—219°, from (III), (IV),  $\text{AlCl}_3$ , and (II), whence isomethylcyclohexane, b.p. 190—191°; 1-chloro-2-hexoyl cyclohexane, b.p. 140—143°/15 mm.; cyclohexyl amyl ketone, b.p. 122—125°/11 mm., whence *n*-heptylcyclohexane, b.p. 219—221°. H. W.

**Alicyclic compounds. III. Synthesis of  $\beta$ -ketoamines.** F. PIRRONE. **IV. Schiff's bases of 6- and 2- $\alpha$ -aminobenzyl-2-methylcyclohexanone.** F. PIRRONE and (SIGNA.) J. ROSELLI (Gazzetta, 1936, 66, 429—434, 435—440).—III. Interaction of PhCHO, cyclohexanone, and  $\text{NH}_2\text{Ph}$  yields 2- $\alpha$ -anilinobenzylcyclohexanone, m.p. 139—139.5° (oxime,



m.p. 154—155°; semicarbazone, m.p. 206—207°); cyclohexanone thus reacts in the ketonic form.

IV. PhCHO, 2-methylcyclohexanone, and  $\text{NH}_3$  yield 6-, m.p. 180—181° (no oxime or semicarbazone), and 2- $\alpha$ -benzylidencaminobenzyl-2-methylcyclohexanone, m.p. 127—128° (oxime, m.p. 238—239°; semicarbazone, m.p. 228—229°; picrate, m.p. 119—120°).

E. W. W.

Synthesis of 2:3-dimethyl-1:2:3:4:10:11-hexahydrofluorenone. S. FUJISE, Y. HORIUTI, and T. TAKAHASHI (Ber., 1936, 69, [B], 2102—2106).— $\beta\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -butadiene (I) and  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  at 200° give 2-phenyl-4:5-dimethyl- $\Delta^4$ -tetrahydrobenzaldehyde, b.p. 171—173°/3.5 mm. (phenylhydrazone, m.p. 131—132°), oxidised by  $\text{AgNO}_3\text{--Ba(OH)}_2$  in  $\text{EtOH--H}_2\text{O}$  to 2-phenyl-4:5-dimethyl- $\Delta^4$ -tetrahydrobenzoic acid, m.p. 159—160°, in very poor yield. Treatment of (I) with  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  at 180° gives Et 2-phenyl-4:5-dimethyl- $\Delta^4$ -tetrahydrobenzoate, b.p. 133—143°/1.5 mm., but the corresponding acid (II), m.p. 159—160°, is best obtained from (I) and  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  in xylene at 170°. (II) is hydrogenated ( $\text{PtO}_2$  in  $\text{EtOH}$ ) to 2-phenyl-4:5-dimethyl-hexahydrobenzoic acid, m.p. 128—129° [corresponding chloride (III), b.p. 163—164°/8 mm., and anilide, m.p. 146—149°]. (III) and  $\text{AlCl}_3$  in  $\text{CS}_2$  afford 2:3-dimethyl-1:2:3:4:10:11-hexahydrofluorenone, b.p. 157—159°/6 mm. (oxime, m.p. 147—151°; semicarbazone, m.p. 211—217°). H. W.

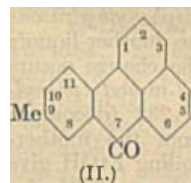
Grignard reagents: their reducing action and rates of addition. M. S. KHARASCH and S. WEINHOUSE (J. Org. Chem., 1936, 1, 209—230).—Previous results and mechanisms proposed for the reducing reactions of Grignard reagents are reviewed. The yield of  $\text{CHPh}_2\cdot\text{OH}$  obtained from  $\text{COPh}_2$  and  $\text{MgBu}^a\text{Br}$  is not appreciably affected by temp. or by the order in which the reactants are added to one another, but is affected somewhat by the concn. of the Grignard reagent and by the solvent used. The respective percentages of addition and of reduction ( $\text{CHPh}_2\cdot\text{OH}$ ) products formed when the following react with  $\text{COPh}_2$  in  $\text{Et}_2\text{O--C}_6\text{H}_6$  are given in parentheses:  $\text{MgPhBr}$  (90; 0),  $\text{CH}_3\text{Ph}\cdot\text{MgCl}$  (95; 0),  $\text{CH}_2\text{Ph}\cdot\text{MgBr}$  (52; 0),  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{MgCl}$  (74; 0),  $\text{MgBu}^a\text{Cl}$  (63; 0),  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{MgBr}$  (72; 5),  $\text{cyclo-C}_6\text{H}_{11}\cdot\text{MgBr}$  (—; 7.1),  $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{MgBr}$  (38.5; 20.0),  $\text{Ph}\cdot[\text{CH}_2]_5\cdot\text{MgBr}$  (43.2; 32.6),  $\text{MgBu}^a\text{Br}$  (—; 58.6),  $\text{MgBu}^a\text{Cl}$  (—; 76.2),  $\text{MgBu}^b\text{Br}$  (—; 91.0),  $\text{cyclo-C}_5\text{H}_9\cdot\text{MgBr}$  (—; 94.0). Reduction of  $\text{COPh}_2$  by  $\text{MgRX}$  occurs only when R is of intermediate electronegativity. A mechanism involving dissociation of  $\text{MgRX}$  into  $\text{R}^-$  and  $(\text{MgX})$  and reduction by  $\text{R}^-$  is proposed and requires the reducing tendency to increase with decreasing electronegativity of R. "Competition" experiments show that the rates of addition of  $\text{MgRX}$  to  $\text{COPh}_2$  also increase with decreasing electronegativity of R. When R is weakly electronegative, the rapidity of the addition reaction is considered to exclude the reduction reaction from observation (cf. A., 1929, 675, 680). Reduction by  $\text{CPh}_3\cdot\text{MgX}$ , an exception to the foregoing generalisations, is considered to occur through a free-radical mechanism. The following appear to be new: diphenyl- $p$ -chlorobenzylcarbinol, m.p. 117.5—118.5°,

and diphenyl- $\gamma$ -phenylpropylcarbinol, m.p. 74—75°, dehydrated to  $\alpha\alpha\delta$ -triphenyl- $\Delta^a$ -butene. H. G. M.

Synthesis of phenanthrene derivatives. IV. Propionylphenanthrenes. W. E. BACHMANN and W. S. STRUVE (J. Amer. Chem. Soc., 1936, 58, 1659—1661).—Phenanthrene,  $\text{EtCOCl}$ , and  $\text{AlCl}_3$  in cold  $\text{PhNO}_2$  give 2- (I), m.p. 104—105°, and 3- (II), m.p. 55—57°, -propionylphenanthrene (picrates, m.p. 104.5—107° and 111—113°, respectively), oxidised (3%  $\text{NaOCl}$ ,  $\text{KOH}$ ) to phenanthrene-2- and -3-carboxylic acid, respectively. 9-Propionylphenanthrene, m.p. 55—57° (picrate, m.p. 105.5—107°), (I), and (II) are prepared from  $\text{MgEtBr}$  and 9-, 2-, and 3-cyanophenanthrene, respectively. (I) and (II) with  $\text{Br}$  in  $\text{Et}_2\text{O}$  at 0° afford 2-, m.p. 131.5—133°, and 3-, m.p. 117—118°, - $\alpha$ -bromopropionylphenanthrene, respectively, which with  $\text{CHNa}(\text{CO}_2\text{Et})_2$  in  $\text{C}_6\text{H}_6$ , subsequent hydrolysis (5%  $\text{NaOH}$ ), and decarboxylation give  $\beta$ -2-, m.p. 173—174°, and -3-, m.p. 144—146°, -phenanthrolylbutyric acid, respectively.

H. B.

Conversion of tolyl naphthyl ketones into methylbenzanthrenes. L. F. FISER and E. L. MARTIN (J. Amer. Chem. Soc., 1936, 58, 1443—1445).— $o$ -Tolyl  $\alpha\text{-C}_{10}\text{H}_7$  ketone (I), m.p. 52—53° (from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  and  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$ ), and  $m$ -tolyl  $\alpha\text{-C}_{10}\text{H}_7$  ketone, m.p. 72—73° (from  $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  and  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{COCl}$ ), with  $\text{AlCl}_3\text{+NaCl}$  at 150° both give 9-methylbenzanthrone (II). The conclusion of Mayer *et al.* regarding wandering of the Me group (A., 1930, 1042) is thus valid but is based on unsound



evidence since their (I) [and the (I) of Scholl and Seer (A., 1913, i, 56)] is  $o$ -tolyl  $\beta\text{-C}_{10}\text{H}_7$  ketone (III), m.p. 63—64° (now prepared from  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$  and  $\beta\text{-C}_{10}\text{H}_7\cdot\text{CN}$ ). It is probable that the Friedel-Crafts reaction between  $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{COCl}$  and  $\text{C}_{10}\text{H}_8$  gives a mixture of (I) and (III).  $p$ -Tolyl  $\alpha\text{-C}_{10}\text{H}_7$  ketone, m.p. 83—84° (from  $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$  and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$ ), is converted by  $\text{AlCl}_3\text{+NaCl}$  into 10-methylbenzanthrone (IV), m.p. 158—159°;  $m$ -, m.p. 76—77°, and  $p$ -, m.p. 90—91°, tolyl  $\beta\text{-C}_{10}\text{H}_7$  ketones (from  $\beta\text{-C}_{10}\text{H}_7\cdot\text{CN}$  and  $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ ) and (III) do not similarly give benzanthrenes. (IV) is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to 7-methylantranthraquinone-1-carboxylic acid (V), m.p. 310—312°, and thence [ $\text{HNO}_3$  ( $d$  1.1) at 200—210°] to anthraquinone-1:7-dicarboxylic acid, m.p. 346—348°. (II) similarly affords 6-methylantranthraquinone-1-carboxylic acid (VI), m.p. 264—266°, and anthraquinone-1:6-dicarboxylic acid, m.p. 336—338°. (V) and (VI) are both decarboxylated ( $\text{Cu}$ , quinoline) to 2-methylantranthraquinone. Anthraquinone-1:3-dicarboxylic acid, decomp. 320—325°, is prepared from  $m$ -xylene,  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ , and  $\text{AlCl}_3$ . H. B.

Benzanthrone derivatives. IV. New synthesis of benzanthrone derivatives. E. CLAR (Ber., 1936, 69, [B], 1686—1691).—Methylenanthrone (I) and maleic anhydride (II) in boiling  $\text{AcOH}$  give the adduct  $\text{C}_{23}\text{H}_{18}\text{O}_9$ , m.p. 190—192° (decomp.), whilst when melted together or heated in boiling  $\text{PhNO}_2$  they yield benzanthrone-2:3-dicarboxylic anhydride, m.p. 310° (corresponding anilide,

m.p. 288—292°, and *azine*, m.p. >360°). (I) and  $\text{CHPh}:\text{CH}:\text{CO}_2\text{H}$  in boiling  $\text{PhNO}_2$  afford 3-phenylbenzanthrone, m.p. 183—184°. Under similar conditions benzylidenanthrone and (II) yield 1-phenylbenzanthrone-2:3-dicarboxylic anhydride, m.p. 280°. 2'-Anthraquinonylmethylencanthrone, m.p. 279—280°, obtained from 2-chloromethylanthraquinone, anthrone, and piperidine in EtOH, condenses with (II) in boiling  $\text{PhNO}_2$  to 1:2'-anthraquinonylbenzanthrone-2:3-dicarboxylic anhydride, m.p. 316—317°. (I) and *endo*-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone in boiling xylene afford 2':3'-benzanthrone-2:3-endo-9:10-*o*-phenylene-9:10-dihydro-1:4-anthraquinone, m.p. >360°, which has little affinity for vegetable fibres. 2':3'-Benzanthrone-2:3-naphtha-1:4-quinone, m.p. 286°, from (I) and 2:3-dichloro-1:4-naphthaquinone in boiling  $\text{PhNO}_2$  or from 1:4-naphthaquinone, appears identical with the product from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ , benzanthrone, and  $\text{AlCl}_3$ . Gradual addition of (I) to a boiling solution of chloranil in xylene gives 5:6-2:3-benzanthrone-2:3-dichloro-1:4-benzoquinone, m.p. 300°. If the reagents are used in inverse order and excess of (I) is employed the product is *di*-2':3'-2'':3''-benzanthrone-2:3-5:6-benzo-1:4-quinone, also obtained from (I) and *p*-benzoquinone in boiling  $\text{PhNO}_2$ .

H. W.

**Constitution and reactivity. XVI. Constitution of benzanthrone-6-sulphonic acid.** Kinetics of the sulphonation of benzanthrone. K. LAUER and K. IRIE (J. pr. Chem., 1936, [ii], 145, 281—286; cf. this vol., 297).—Benzanthrone and  $\text{H}_2\text{SO}_4$  at 140—150° give benzanthrone-9-sulphonic acid (*Na* salt), the structure of which is proved by chlorination ( $\text{HCl-KClO}_3$ ) to 9-chloro- and 3:9-dichloro-benzanthrone and by formation of a violanthrone with  $\text{KOH-EtOH}$ . Reaction velocities with 80—99% acid at 95—170° show that two sulphonating agents ( $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ ) are effecting the reaction.

R. S. C.

**Magnetochemical investigations of organic substances. XI. Bromobenzanthrone of Brass and Clar.** E. MÜLLER and W. WIESEMANN (Ber., 1936, 69, [B], 2173—2174).—Magnetic observations do not indicate the presence of a radical compound in the “uneven bromide” of benzanthrone (this vol., 726).

H. W.

**Chrysene. IV.** K. FUNKE and J. RISTIC (J. pr. Chem., 1936, [ii], 146, 151—158; cf. this vol., 1113).—Conversion of chrysene-2:8-dicarboxylic acid by aq.  $\text{KOH}$  at 210—220° into chrysene-2-carboxylic acid, m.p. 314°, proves the orientation of 2:8-dibromochrysene and all substances derived from it. 2-Acetylchrysene gives the 8-*Br*-derivative, m.p. 142°, which gives oils with  $\text{CuCN}$  in quinoline and is reduced (Clemmensen) to 2-ethylchrysene (I). (I) gives (Friedel-Crafts) 2-acetyl-8-ethylchrysene, m.p. 131°, reduced to 2:8-diethylchrysene, m.p. 145°, and oxidised only to the quinone. 2-Benzoyl-8-ethylchrysene, m.p. 130°, is similarly prepared. 2:8-Dibenzoylchrysene (modified prep.) with  $\text{AlCl}_3$  gives a dye, not isolated, and a trace of a substance,  $\text{C}_{60}\text{H}_{36}\text{O}_6$ , m.p. 260°.

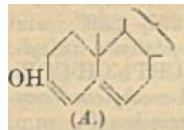
R. S. C.

**Unsaturated sulphur compounds. III.  $\alpha\beta$ -Unsaturated ketosulphones.** E. P. KOHLER

and R. G. LARSEN (J. Amer. Chem. Soc., 1936, 58, 1518—1522).— $\text{COPh}:\text{CH}_2:\text{CHPh}:\text{SO}_2\text{Ph}$  (I) (from  $\text{CHPh}:\text{CH}:\text{COPh}$  and  $\text{PhSO}_2\text{H}$  in EtOH) and Br in  $\text{CHCl}_3$  give diastereoisomeric *Ph*  $\beta$ -bromo- $\beta$ -benzoyl- $\alpha$ -phenylethyl sulphones, m.p. 189° (90%) and 209° (<3%; also obtained from  $\text{CHPh}:\text{CBr}:\text{COPh}$  and  $\text{PhSO}_2\text{H}$  in EtOH), both of which are converted (at different rates) by KOAc in MeOH or AcOH into the yellow trans-*Ph*  $\beta$ -benzoyl- $\alpha$ -phenylvinyl sulphone (II), m.p. 151°; the colourless cis-form (III), m.p. 132°, is prepared from  $\text{CPh}_2:\text{C}:\text{COPh}$  and  $\text{PhSO}_2\text{H}$  in MeOH. (III) is converted by NaOMe into (II), whilst (II) or (III) in  $\text{CHCl}_3$ +I in sunlight give an equilibrium mixture [mainly (II)]. *Ph*  $\alpha$ -chloro-, m.p. 175°, and  $\alpha$ -bromo-, m.p. 124° [decomp. to (II)],  $\beta$ -benzoyl- $\alpha$ -phenylethyl sulphones are obtained from (II) and AcOH-HHal. (II) and  $\text{MgPhBr}$  in the cold afford *Ph*  $\gamma$ -hydroxy- $\gamma\gamma$ -triphenyl- $\Delta^a$ -propenyl sulphone (IV) (+2MeOH), m.p. about 107°, m.p. (MeOH-free) 133° (acetate, m.p. 168°), reduced ( $\text{H}_2$ , Pd- $\text{CaCO}_3$ , EtOAc) to the *propyl* sulphone, m.p. 223°, also prepared from (I) and  $\text{MgPhBr}$ . (IV) and a little AcCl in MeOH give the *Me ether*, m.p. 130°, oxidised ( $\text{KMnO}_4$ ,  $\text{COMe}_2$ , little AcOH) to  $\text{OMe}:\text{CPh}_2:\text{CO}_2\text{H}$ ; with HCl in  $\text{C}_6\text{H}_6$ , *Ph*  $\gamma$ -chloro- $\gamma\gamma$ -triphenyl- $\Delta^a$ -propenyl sulphone, m.p. about 142° [decomp. to 1-benzenesulphonyl-1:3-diphenylindene, m.p. 171°, which is oxidised ( $\text{Na}_2\text{Cr}_2\text{O}_7$ , AcOH) to  $o\text{-C}_6\text{H}_4\text{Bz}_2$ ], results. (II) and  $\text{MgPhBr}$  in boiling  $\text{Et}_2\text{O}$  afford (IV) and *Ph*  $\gamma$ -hydroxy- $\alpha\beta\gamma$ -tetraphenylpropyl sulphone, stereoisomeric forms, m.p. 178° and 223° (? 196°), both of which are converted by AcOH- $\text{H}_2\text{SO}_4$  into 1:2:3-triphenylindene. (II) thus resembles  $\text{COPh}:\text{CH}:\text{CH}:\text{SO}_2\text{Ph}$  (A., 1935, 1241) except in the reaction with  $\text{MgPhBr}$ .

H. B.

**Transformation reactions of brominated derivatives of cholesterol. III. Bromination of cholestenone.** H. H. INHOFFEN (Ber., 1936, 69, [B], 2141—2147; cf. this vol., 1104).—Treatment of cholestenone (I) in  $\text{Et}_2\text{O}$  at 2° with Br in AcOH gives the dibromide (II),  $\text{C}_{27}\text{H}_{42}\text{OBr}_2$ , m.p. 162° (decomp.) (*loc. cit.*), and an isomeride, m.p. 133°, each of which is transformed into the enol acetate, m.p. 158—159°. Reaction generally occurs immediately but occasionally an induction period is observed. In presence of KOAc (I) does not react with Br; a preliminary enolisation due to HBr is therefore assumed, the enolic form probably being (A).



In confirmation, cholestenone enol acetate (Ruzicka *et al.*, this vol., 991) is transformed by Br in  $\text{Et}_2\text{O}$ -AcOH into (II) whereas in presence of KOAc the *Br*<sub>1</sub>-ketone (III),  $\text{C}_{27}\text{H}_{43}\text{OBr}$ , m.p. 132°, is produced. Bromination of (III) in presence of HBr gives (II). The mechanism of the production of (III) and thence of (II) is discussed.

H. W.

**Constituents of pyrethrum flowers. VI. Structure of pyrethrolone.** F. B. LAForge and H. L. HALLER (J. Amer. Chem. Soc., 1936, 58, 1777—1780; cf. B., 1936, 812).—Pyrethrolone (I) (3:5-dinitrobenzoate, m.p. 145°) is considered to be 5-hydroxy-3-methyl-2- $\Delta^a$ -pentadienyl- $\Delta^2$ -cyclopenten-



one (cf. Staudinger and Ruzicka, A., 1924, i, 523). Tetrahydropyretrolone [the 2-amyl- $\Delta^2$ -cyclopentenone] (II), b.p. 120—125°/0.25 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11.9° in EtOH (cf. *loc. cit.*) (Me ether, b.p. 82°/0.35 mm.), prepared by hydrolysis (cold conc. aq. KHSO<sub>4</sub>+Et<sub>2</sub>O) of its semicarbazone, m.p. 196° [obtained by reduction of the semicarbazone of (I)], contains a quantity of *dl*-tetrahydropyretrolone (III) (semicarbazone, m.p. 170°); (III) is the sole product when hydrolysis is carried out at 100°. 5-Chloro-3-methyl-2-*n*-amyl- $\Delta^2$ -cyclopentenone, b.p. 97—100°/0.6 mm. [from (II) and SOCl<sub>2</sub>], is reduced (Zn dust, AcOH) to the optically inactive 3-methyl-2-*n*-amyl- $\Delta^2$ -cyclopentenone [dihydrojasnone] (cf. Treff and Werner, A., 1933, 1296; 1935, 750), which is similarly prepared from (III).

H. B.

$\beta$ -Methylenebutan- $\gamma$ -on- $\alpha$ -ol. H. GAULT and L. A. GERMANN (Compt. rend., 1936, 203, 514—516; cf. A., 1933, 1144).—Condensation of CH<sub>2</sub>O with CH<sub>3</sub>Ac·CH<sub>2</sub>·OH or CHAc·CH<sub>2</sub> in presence of K<sub>2</sub>CO<sub>3</sub> affords CH<sub>2</sub>:C(AC)·CH<sub>2</sub>·OH (cf. *loc. cit.*), which condenses with  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene to 4-hydroxymethyl-4-acetyl-1:2-dimethyl- $\Delta^1$ -cyclohexene, b.p. 155—157°/15 mm., and with  $\delta$ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene to a mixture of 6-hydroxymethyl-6-acetyl-, b.p. 146—150°/12 mm., and 5-hydroxymethyl-5-acetyl-1:1-dimethyl- $\Delta^2$ -cyclohexene, b.p. 150—153°/12 mm., m.p. 71°.

F. O. H.

Alcoholic ammonia as a reagent for [condensation of] nitro-compounds and unsaturated ketones. D. E. WORRALL and C. J. BRADWAY (J. Amer. Chem. Soc., 1936, 58, 1607—1608).— $\gamma$ -Nitro- $\alpha$ -dibenzoyl- $\beta\delta$ -diarylpentanes (A) are obtained by prolonged interaction of MeNO<sub>2</sub> and an excess of CHAr:CH·COPh (except when Ar contains an *o*-substituent) in EtOH-NH<sub>3</sub>; the presence of H<sub>2</sub>O promotes reaction. The intermediate COPh·CH<sub>2</sub>·CHAr·CH<sub>2</sub>·NO<sub>2</sub> (Ar=*p*-OMe·C<sub>6</sub>H<sub>4</sub>·, m.p. 50—51°, and 3:4-CH<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·, m.p. 94—95°) are isolable; these can be similarly condensed with CHAr:CH·COPh to (A). Compounds similar to (A) could not be prepared from EtNO<sub>2</sub> or CH<sub>2</sub>Ph·NO<sub>2</sub>. The following are described:  $\gamma$ -nitro- $\alpha$ -dibenzoyl- $\beta\delta$ -diphenyl-, stereoisomeric forms, m.p. 157—158° (I) and 229—230° (II), - $\beta\delta$ -dianisyl-, m.p. 211—212°, - $\beta\delta$ -di-3:4-methylenedioxyphenyl-, m.p. 192—193°, - $\beta\delta$ -di-*p*-bromophenyl-, m.p. 239—240°, - $\beta\delta$ -di-*p*-tolyl-, m.p. 209—210°, - $\beta\delta$ -di-*m*-bromophenyl-, m.p. 200—201°, - $\beta\delta$ -di-*m*-nitrophenyl-, m.p. 237—239°, and - $\beta\delta$ -dicinnamyl-, m.p. 216—218°; - $\beta$ -phenyl- $\delta$ -anisyl-, m.p. 205—206° (best prepared using CHPh:CH·COPh as the second component), - $\delta$ -3:4-methylenedioxyphenyl-, m.p. 218—219°, - $\delta$ -*m*-bromophenyl-, m.p. 227—228°, - $\delta$ -*p*-tolyl-, m.p. 191—192°, and - $\delta$ -*m*-nitrophenyl-, m.p. 219—220°; - $\beta$ -anisyl- $\delta$ -*p*-tolyl-, m.p. 196—197°; - $\beta$ -anisyl-, m.p. 189—190°, - $\beta$ -*m*-nitrophenyl-, m.p. 218—219°, - $\beta$ -*p*-tolyl-, m.p. 198—199°, and - $\beta$ -*m*-bromophenyl-, m.p. 215—216°. - $\delta$ -3:4-methylenedioxyphenyl-pentanes. (I) and Br in CHCl<sub>3</sub> and sunlight give a Br-derivative (? mixture), m.p. about 80°. (II) and Br in PhNO<sub>2</sub> afford the  $\beta$ -Br-derivative, m.p. 241—242° (decomp.); in MeOH-NaOMe the  $\gamma$ -Br-derivative, m.p. 205—206° results. The  $\gamma$ -nitro- $\alpha$ -di-*p*-bromobenzoyl- $\beta\delta$ -diphenylpentano

of Kohler and Williams (A., 1920, i, 59) is a mixture of isomerides, m.p. 151—152° and 218—219°.

H. B.

Sexual hormones. XVI. Esters of the testosterone and androsterone series. L. RUZICKA and A. WETTSTEIN [in part, with W. KLARER and J. MEYER]. XVII. Bromination of sterol and androstene derivatives. L. RUZICKA, W. BOSSHARD, W. H. FISCHER, and H. WIRZ (Helv. Chim. Acta, 1936, 19, 1141—1146, 1147—1153; cf. this vol., 991).—XVI. The following esters of testosterone are described: *formate*, m.p. 127—129° (corr.); *propionate*, m.p. 121—123° (corr.); *n-butyrate*, m.p. 111—113° (corr.); *isobutyrate*, m.p. 134—136° (corr.); *n-valerate*, m.p. 109—111° (corr.); *isovalerate*, m.p. 138—140° (corr.); *decanoate*, m.p. 55—57° (corr.); *palmitate*, m.p. 72—74° (corr.); *stearate*, m.p. 79—80° (corr.); *H succinate*, dimorphous, m.p. 183—185° (corr.) and 191—193° (corr.), respectively. *Androstane-3-cis-17-trans-diol disuccinate* has m.p. 139—140° (corr.). The Na and Li salts of androsterone succinate and the Na, K, and Li salts of androstane-3-cis-17-trans-diol 3-succinate are described. The physiological action of the esters is discussed.

XVII. Cholesterol dibromide in C<sub>6</sub>H<sub>6</sub> is converted by CrO<sub>3</sub> in AcOH-H<sub>2</sub>O at room temp. into  $\Delta^5$ -cholestenone dibromide, transformed by boiling aq. KOAc into 6-bromo- $\Delta^4$ -cholestenone (I), m.p. 130—131°, in about 10% yield. The absorption spectrum proves (I) to be an  $\alpha\beta$ -unsaturated ketone; it is hydrogenated to cholestenone and coprostanone. If more vigorous conditions are used in the prep. of (I) the product is cholestane-3:6-dione. Similarly, *trans*-dehydroandrosterone is brominated and oxidised to androstenedione dibromide, which in C<sub>6</sub>H<sub>6</sub> is transformed by boiling aq. KOAc into 6-bromo- $\Delta^4$ -androstene-3:17-dione, m.p. 170—171° (decomp.). Bromination of the requisite ketone in AcOH yields 2:2-dibromocholestanone, m.p. 194° (*quinoxaline* derivative, C<sub>33</sub>H<sub>48</sub>N<sub>2</sub>, m.p. 184°), 4:4-dibromo-, m.p. 143° (*quinoxaline* derivative, m.p. 200°), and 2:4:4-tribromo-, m.p. 180°, -*coprostanone*.  $\Delta^4$ -cholestenone in CCl<sub>4</sub> does not give a homogeneous product when treated with Br (1—2 mols.) but by use of a large excess of halogen (?) 2:4-dibromo- $\Delta^4$ -cholestenone, m.p. about 180°, is obtained. It does not give a yellow colour with C(NO<sub>2</sub>)<sub>4</sub> or react with o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>.

H. W.

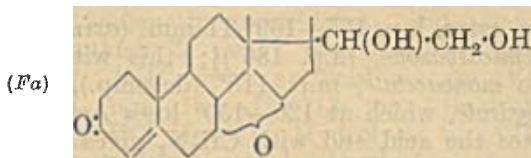
Proposed synthesis of equilenin. M. VANGHELOVICI (Chem. and Ind., 1936, 728).—The proposed path is, ergosterol  $\rightarrow$  neocergosterol  $\rightarrow$  dehydro- $\rightarrow$  acetyldidehydro-neocergosterol  $\rightarrow$  acetylequilenin  $\rightarrow$  equilenin.

H. W.

Constituents of the adrenal gland. V. Chemical identification of the androstane skeleton. VI. Methods of separation and isolation of the substances *Fa*, *II*, and *J*. T. REICHSTEIN (Helv. Chim. Acta, 1936, 19, 979—987, 1107—1126; cf. this vol., 475, 605, 704, 854).—V. Reduction (Clemmensen) under mild conditions of the diketone (I) C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>, m.p. 178°, gives small amounts of a cryst. product, m.p. (indef.) 120—143°, oxidised to androstane-17-one and, mainly, a mixture of liquid hydrocarbons, C<sub>19</sub>H<sub>32</sub>, which is somewhat unsaturated and, after

hydrogenation, gives a small proportion of androstane, m.p. 49—51°. Similar results are obtained from androstanedione. The partial formulæ assigned previously to substances *A*, *C*, and *D* thus receive chemical confirmation. No information is afforded of the nature of the third O which is eliminated during the reduction. Zerevitinov determinations establish the presence of 1.14 active H in the OH-ketone (II)  $C_{19}H_{28-30}O_2$ , m.p. about 236° (corr.) (*loc. cit.*), and 0.15 active H in (I) so that (II) and (I) contain 1 OH and no OH, respectively. Further (II) in boiling  $C_6H_6$  containing  $C_5H_5N$  yields a 3 : 5-dinitrobenzoate, m.p. 257—258° (corr.), whereas (I) remains unchanged. Treatment of (I) with a large excess of  $NH_2OH \cdot AcOH$  at 130° gives the known dioxime (III) with non-cryst. material analyses of which accord with the presence of about 25% of (III) and 75% of a trioxime. Definite conclusions cannot yet be reached, but the presence of an O bridge, opened under the experimental conditions, is suggested.

VI. The dry residue of the "permutit fraction" of the entire gland is distributed between pentane and 30% MeOH, whereby the cortin activity passes entirely into the aq. layer, from which it is extracted by  $Et_2O$  after concn. of the acid liquor. The activity is driven from  $Et_2O$  into  $H_2O$ , leaving an "ether residue." Concn. and acidification of the aq. layer followed by extraction with  $Et_2O$  leads to concentrate  $C_{13}$ . The latter is treated with Girard's reagent and from the reactive portions four fractions of  $C_{17}A$  ketones are separated by varying the degree of acidity. The  $A$ -ketone-free residues are heated with the reagent and from the product the  $C_{17}B$  ketones are isolated. Substances *A*, *C*, and *D* are thus readily obtained. The product of the oxidation of *E* is identified as adrenosterone (IV) and it is therefore  $C_{21}H_{30-32}O_5$ . Substance *Fa*, m.p. about 215° (corr.; decomp.) depending largely on the manner of heating,  $[\alpha]_D$  about  $+200 \pm 8^\circ$  in EtOH, is  $C_{21}H_{28-30}O_5$ . Its



absorption spectrum shows it to be an  $\alpha\beta$ -unsaturated ketone. The cryst. form is very characteristic. It is physiologically inactive. Oxidation of it affords (IV). It appears identical with compound *F* of Wintersteiner and compound *E* of Kendall *et al.*, whose formulation is queried. Substance *H*, m.p. about 163—167°, is obtained from fraction  $C_{17}A.III$  by a process which cannot be reproduced with certainty. It appears to be an  $\alpha\beta$ -unsaturated ketone,  $C_{19}H_{26}O_4$  or  $C_{23}H_{32}O_5$ . It does not contain OEt. Examination of the "ether residue" (see above) with Girard's reagent is incomplete but (IV), and two further ketones, substances *K* and *L*, m.p. about 175° and about 255° (corr.), have been isolated. Substance *J*, m.p. 216—217° (corr.) after becoming opaque at about 120°, appears to be a polyhydric alcohol,  $C_{21}H_{34-36}O_3$ , since it is oxidised by  $CrO_3$  to a neutral product of much lower m.p. Its precipitability with digitonin indicates that it is a derivative of chole-

stanol. Reply is made to Mason *et al.* (this vol., 1117).

**6-Keto-3 : 5-diacetoxycholestanol.** F. SCHENCK (Z. physiol. Chem., 1936, 243, 119—120; cf. Windaus *et al.*, A., 1935, 1363).—The substance having m.p. 169—170°,  $[\alpha]_D^{20} -15.4^\circ$  in  $CHCl_3$ , obtained by oxidising cholesteryl acetate with  $CrO_3$  contains 2 Ac but no active H and hence is 6-keto-3 : 5-diacetoxycholestanol. 5-Hydroxy-6-keto-3-acetoxycholestanol has m.p. 230—231°,  $[\alpha]_D -55.8^\circ$  in  $CHCl_3$ . W. McC.

**Dioximes.** CXVI. G. PONZIO (Gazzetta, 1936, 66, 479—486; cf. this vol., 1363).—"Benzoylmethylglyoxime peroxide" (A., 1904, i, 427—428), now renamed phenylmethyltriketone-1 : 3-dioxime peroxide (I), new m.p. 161—162°, is converted by  $NH_2OH \cdot HCl$  in  $C_5H_5N$  into phenylmethyltriketone- $\alpha$ -trioxime (II) (A., 1922, i, 1038) [ $C \cdot H_5N$ , m.p. 130—140° (decomp.), and  $NHPh \cdot NH_2$ , m.p. 167—168° (decomp.), salts;  $Bz_3$  derivative, m.p. 132—133°]. "Oximinobenzoylmethylglyoxime peroxide" (*loc. cit.*), renamed as the oxime of (I), is similarly reduced to (II), and "anisoyl-" and "oximinobenzoyl-methylglyoxime peroxide," renamed as anisylmethyltriketone-1 : 3-dioxime peroxide and its oxime, are both reduced to anisylmethyltriketone-1 : 3-dioxime peroxide, m.p. 195° (decomp.) ( $Ac_3$ , m.p. 133—134°, and  $Bz_3$ , m.p. 150°, derivatives). E. W. W.

**System 3 : 4 : 3' : 4'-tetramethoxy- and 3 : 4 : 3' : 4'-bismethylenedioxy-benzophenone.** A. OLIVERIO (Rend. Semin. Fac. Sci. Univ. Cagliari, 1934, 4, 130—134; Chem. Zentr., 1935, ii, 3910).—A stable equimol. additive compound, m.p. 164°, and two eutectics, m.p. 141—141.5° and 135°, are described. H. N. R.

**Stereochemistry of deuterium compounds of the type, CHRR'. 2 : 3-Dideutero-camphane.** M. T. LEFFLER and R. ADAMS (J. Amer. Chem. Soc., 1936, 58, 1555—1558).—Reduction ( $H_2$ ,  $PtO_2$ , EtOAc) of *l*-bornylene, m.p. 105—106.5°,  $[\alpha]_D^{25} -9.57^\circ$  in EtOAc (which thus contains tricyclene), gives camphane, m.p. 145°,  $d_{440}^{25} 0.7458$ ,  $\alpha_D^{25} +0.02 \pm 0.01^\circ$  in EtOAc ( $l=1$ ) (due to some impurity); reduction with  $D_2$  under identical conditions affords 2 : 3-dideutero-camphane, m.p. 143°,  $d_{440}^{25} 0.7552$ , of the same rotation. There appears to be no evidence for the activity of CHDRR' compounds (cf. Billmann *et al.*, this vol., 855). H. B.

**Rotatory power of substituted camphoranilic acids.** M. SINGH (J. Indian Chem. Soc., 1936, 13, 467—474).—The following camphoranilic acids are prepared by condensation of the anhydride and amine,  $[\alpha]$  given being in MeOH and  $COMe_2$ , respectively: o-, m.p. 171° (decomp. from 165°),  $[\alpha]_D +50.6^\circ$ ,  $+45.3^\circ$ , and p-ethyl-, m.p. 202—203°,  $[\alpha]_D +59.2^\circ$ ,  $+47.9^\circ$ , m-, m.p. 189—190°,  $[\alpha]_D +36.9^\circ$ ,  $+30.9^\circ$ , and p-aceto-, m.p. 224—225°,  $[\alpha]_D +67.5^\circ$ ,  $+67.7^\circ$ , m-, m.p. 210°,  $[\alpha]_D +43.2^\circ$ ,  $+34^\circ$ , and p-nitro-, m.p. 200—203°,  $[\alpha]_D +75.6^\circ$ ,  $+71.2^\circ$ , m.p. 197°,  $[\alpha]_D +52.4^\circ$ ,  $+40.5^\circ$ , and p-fluoro-, m.p. 197°,  $[\alpha]_D +42.7^\circ$ ,  $+41^\circ$ . The following are obtained by nitration: camphor-2'-nitro-4'-ethyl-, m.p. 140.5°,  $[\alpha]_D -62.1^\circ$ ,  $-72.9^\circ$ , 3'-fluoro-2'-nitro-, m.p. 131—132°,  $[\alpha]_D -14.4^\circ$ ,  $-25^\circ$ , 4'-fluoro-2'-nitro-, m.p.



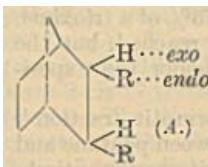
171°,  $[\alpha]_D -45^\circ$ ,  $-49.6^\circ$ , and -2'-nitro-4'-aceto-anilic acid, m.p. 202—203°,  $[\alpha]_D +51.8^\circ$ ,  $+44.4^\circ$ . Camphor-o-, m.p. 132—133°,  $[\alpha]_D +19.6^\circ$ ,  $+19.7^\circ$ , and -p-ethylphenylimide, m.p. 123°,  $[\alpha]_D +15.9^\circ$ ,  $+14.5^\circ$ , are obtained by condensation. m-, m.p. 196—197°,  $[\alpha]_D +46.3^\circ$ ,  $+41.7^\circ$  (Ac derivative, m.p. 220—221°,  $[\alpha]_D +25^\circ$ ,  $+23^\circ$ ), and p-Aminocamphoranilic acid, m.p. 220—221°,  $[\alpha]_D +57.5^\circ$ ,  $+53.1^\circ$  [Ac derivative, m.p. 234—235° (decomp. from 231—232°),  $[\alpha]_D +51.1^\circ$ ,  $+48.6^\circ$ ], are obtained from the  $\text{NO}_2$ -acids by  $\text{Fe}(\text{OH})_2$ . R. S. C.

**Ring-isomerisation in the camphene series.** P. LIPP, H. DESSAUER, and E. WOLF (Annalen, 1936, 525, 271—291).— $\omega$ -Aminoisocamphane (I) with  $\text{HNO}_3$  gives a complex mixture by ring changes. Reduction of  $\omega$ -nitrocamphene (II) by  $\text{Zn}-\text{AcOH}$ , followed by hydrolysis, gives 59% of camphenolaldehyde. Camphenilanamide, m.p. 170—171°, with  $\text{P}_2\text{O}_5$  gives camphenilanonitrile, b.p. 103—105°/12 mm. reduced by  $\text{Na}-\text{EtOH}$  to (I) [hydrochloride, decomp.  $>250^\circ$ , sublimes unchanged in vac.; platinichloride; phenylcarbamide, m.p. 158° (corr.), and -thiocarbamide, m.p. 148° (corr.), and Bz derivative (III), m.p. 130—132°]. With  $\text{Na}-\text{EtOH}$  (II) affords much (I), diisocamphylamine, b.p. 163°/0.13 mm., m.p. 115° [hydrochloride, m.p. 250° (decomp.); platinichloride; oxalate; perchlorate, m.p. 250° (decomp.); NO-, m.p. 160° (decomp.), and phenylcarbamide derivative, m.p. 150—151° (corr.)], camphenilone, and a mixture of camphenyl alcohols (oxidised to the aldehyde). (I) and  $\text{HNO}_3$  give endocamphene (oxidised by  $\text{KMnO}_4$  to camphenecamphoric acid, m.p. 134.4—134.8°), a mixture of R-homocamphenilols [oxidised to the ketone; p-nitrobenzoates (probably impure), m.p. 136—137° (corr.), and 89—91°; with  $\text{ZnCl}_2-\text{C}_6\text{H}_6$  gives endocamphene], and N-nitrosoisocamphylethylamine (IV), b.p. 130—134°/0.8 mm. (IV) with hot fuming  $\text{HCl}$  gives isocamphylethylamine (V), b.p. 109° (corr.)/12 mm. [hydrochloride, m.p.  $>300^\circ$ ; sublimes at about 400° (decomp.); hydrobromide; phenyl-, m.p. 122—122.5°, and naphthyl-carbamide, m.p. 151°, and Bz derivative, b.p. 181—183°/0.1 mm.]; this with  $\text{MeI}$  etc. affords isocamphylidimethylethylammonium perchlorate, cryst., the base from which at 200—250° gives  $\text{MeOH}$  and isocamphylmethylethylamine (hydrochloride, decomp. 245°; perchlorate, decomp. 255°); the Bz derivative with  $\text{PCl}_5$  gives (III). Camphenyl bromide (prep. by  $\text{PBr}_3$ ), b.p. 99—101°/13 mm., with  $\text{NH}_2\text{Et}$  at 100° affords (IV).

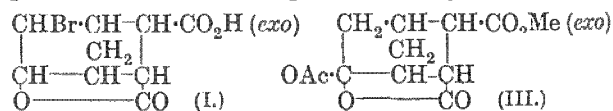
R. S. C.

**Steric course of addition and substitution reactions.** VI. *exo*-Additions of catalytically activated hydrogen to the dicyclo-[1:2:2]-heptene ethylenic linking. Configurations of the norborneols and norbornylamines. K. ALDER and G. STEIN [with S. SCHNEIDER, (FRL.) M. LIEB-MANN, (FRL.) E. ROLLAND, and G. SCHULZE]. VII. Catalytic reduction of ketones and ketoximes of the camphor, fenchone, and isofenchone series. K. ALDER and G. STEIN [with H. F. RICKERT]. VIII. *endo-exo*-Isomerism. II. K. ALDER and G. STEIN [with (FRL.) E. ROLLAND] (Annalen, 1936 525, 183—221, 221—247, 247—258; cf. A., 1935, 219, 349).—VI. Catalytic hydrogenation under varied

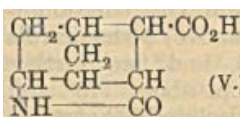
conditions of dicyclo-[1:2:2]-heptenes results preponderatingly in *cis-exo*-addition of  $\text{H}_2$  giving substances of type (A). Addition of  $\text{H}_2$  catalytically to dicyclo-[1:2:2]-heptanes containing semicyclic  $\text{CO}$ ,  $\text{C}\equiv\text{C}$ , or  $\text{C}\equiv\text{N}\cdot\text{OH}$  also occurs in the *exo*-position to give compounds having one R in the *endo*-position as in (A). Constitutions are rigidly proved. The above rules may also be applied to dicycloheptenes similar to those investigated, but containing in addition two identical substituents on the same C. It follows that the isolated Me of isocamphane is *endo*, that  $\alpha$ -norborneol has an *endo*-OH, that reaction of  $\alpha$ -norbornylamine with  $\text{HNO}_3$  occurs with, and that of the  $\beta$ -amine without, Walden inversion. From the point of view of Skita's rule the dicyclo-[1:2:2]-heptane system behaves as a substituted cyclopentane ring. Hydrogenation ( $\text{PtO}_2$ ) of 3:6-endomethylene- $\Delta^{1,4}$ -dihydrophthalic acid in  $\text{AcOH}$  gives 3:6-endomethylenehexahydro-*cis-endo*-phthalic acid (A;  $\text{R}=\text{CO}_2\text{H}$ ), m.p. 165°, and a trace of the *trans*-acid, m.p. 94°; hydrogenation of



the  $\text{Me}_2$  ester in  $\text{AcOH}$  or  $\text{MeOH}$  gives only the *cis-endo*-ester, m.p. 55°, also obtained as sole product ( $\text{PtO}_2-\text{AcOH}$ ) from  $\text{Me}_2$  3:6-endomethylene- $\Delta^1$ -tetrahydrophthalate.  $\text{CH}_3\cdot\text{C}\equiv\text{CO}_2\text{H}$  (modified prep.) and cyclopentadiene give 2:5-endomethylene- $\Delta^{1,3}$ -dihydrobenzoic acid, m.p. 93—94°, hydrogenated (colloidal  $\text{Pt}-\text{AcOH}-\text{HCl}$ ,  $\text{PtO}_2-\text{AcOH}$ ,  $\text{PtO}_2-\text{MeOH}$ , or colloidal  $\text{Pd}-\text{H}_2\text{O}$ ) to 3:5-endomethylenehexahydrobenzoic acid, m.p. 65—66°. The lactone (I) with hot  $\text{KOH}-\text{MeOH}$  gives by hydrolysis, loss of  $\text{HBr}$ , and ketonisation 3:6-endomethylene-4-ketohexahydrophthalic acid (II) (1- $\text{CO}_2\text{H}$  *exo*, 2- $\text{CO}_2\text{H}$  *endo*), m.p.



186° [ $\text{Me}_2$  ester, b.p. 167—169°/11 mm. (oxime, m.p. 136°; semicarbazone, m.p. 186°)]; this with  $\text{Ac}_2\text{O}$  gives the monoacetate, m.p. 118° (decomp.), of the ketone hydrate, which at 120—150° loses  $\text{AcOH}$  and regenerates the acid and with  $\text{CH}_2\text{N}_2$  gives the *Me* ester lactone acetate (III), m.p. 103°. Hydrogenation (Skita or Adams;  $\text{AcOH}$ ) of (II) gives the lactonic acid (IV), m.p. 134° [as (I) but with  $\text{H}$  in place of  $\text{Br}$ ]. At 250—260°/vac. (II) gives 3:6-endomethylene-4-ketohexahydro-*cis-exo*-phthalic anhydride, m.p. 171—175° (loss of  $\text{H}_2\text{O}$ ) (Ac derivative, m.p. 108°), converted into (IV) by hydrolysis ( $\text{NaOMe}$ ) and methylation. The oxime, m.p. 227° (decomp.), of (II) with  $\text{H}_2$ -colloidal  $\text{Pt}$  or  $\text{H}_2$ - $\text{PtO}_2$  in  $\text{AcOH}$  gives the lactam (V), m.p. 192° (*Me* ester, m.p. 104—105°), converted by crystallisation from  $\text{MeOH}$  into an isomeric form, m.p. 209°, which slowly reverts to (V) when crystallised from  $\text{EtOAc}$ . Nor-



camphoroxime, b.p. 114—116°/12 mm., with  $\text{H}_2$ - $\text{PtO}_2$  (40—50°; 3 atm.) or  $\text{H}_2$ -colloidal  $\text{Pd}$  at 40—50° gives norbornylendoamine (hydrochloride, m.p. 295°; picrate, m.p. 179—180°) with a little dinorbornylendoamine (picrate, m.p. 193°) and dinorbornylendo-

ethylamine (picrate, m.p. 249°; obtained by reduction of a little Ac derivative formed by the solvent); with Na-EtOH much bornyl-*endo*- and a little -*exo*-amine are formed.

[BODE]. *d* and *n* of the *endo*-forms are > those of the *exo*-forms of monocarboxylic acids, but both have about the same  $[M]$ . *d* and *n* of the *cis*-forms of the dicarboxylic acids are > those of the *trans*-forms, but  $[M]$  are about the same.

VIII. Hydrogenation of ketones and ketoximes of the camphor, fenchone, and isofenchone series is highly selective, but owing to the *as*-substitution the above rules of configuration cannot be applied. *d*-(—)-Camphoroxime gives colloidal Pt-AcOH at 50°/3 atm., or PtO<sub>2</sub> almost entirely *d*-(—)-neobornylamine, m.p. 184° (carbamide derivative, m.p. 109°). 2:5-Diketocamphane gives (PtO<sub>2</sub>; AcOH; 50°/3 atm.) a 2:5-dihydroxycamphane, m.p. 263°; its dioxime, m.p. 168—170°,  $[\alpha]_D^{25} +60.5^\circ$  in MeOH (a small amount of isomeric dioxime, m.p. 236°,  $[\alpha]_D^{25} +30^\circ$  in MeOH, is also formed), gives 2:5-diaminocamphane (dihydrochloride and diplatnichloride, m.p. 320°; dicarbamide, m.p. 192—193°, and Ac<sub>2</sub> derivative, m.p. 229—230°). *d*-Fenchoneoxime gives *d*-fenchylamine (hydrochloride, m.p. 293°; picrate, m.p. 199°; carbamide derivative, m.p. 167°). *dl*-iso-Fenchone (VI) gives *dl*- $\beta$ -isofenchol, b.p. 89°/15 mm. [*H* phthalate, m.p. 104—105°; phenylurethane, m.p. 101°; oxidised to (VI)], and a trace of the known *dl*-fenchol, now termed  $\alpha$ -fenchol; with Na-EtOH a mixture of  $\alpha$ - and  $\beta$ -forms is obtained; the  $\beta$ - is converted into the  $\alpha$ -form by hot Na-PhMe, but the  $\alpha$ -form is stable. *dl*-iso-Fenchoneoxime affords *dl*-isofenchylamine (hydrochloride, m.p. 285°; picrate, m.p. 303—304°), converted by HNO<sub>2</sub> into a mixture including probably some  $\beta$ -fenchene hydrate. (VI) and SeO<sub>2</sub> give 1:2-diketo-3:5:5-trimethyl-3:6-endomethylenecyclohexane ("isofenchonequinone"), m.p. 49—50°.

VIII. Semicarbazones, m.p. 165° and 166—167°, of 2:5-endomethylene- $\Delta^3$ -tetra- and -hexa-hydroendobenzaldehyde (VII), respectively, are obtained (cf. lit.). (VII) gives an enol acetate (VIII) and diacetate, b.p. 136—137°/13 mm. [hydrolysed to (VII) by HCl-MeOH]. Hydrolysis of (VIII) gives mainly 2:5-endomethylenehexahydroexobenzaldehyde (IX), b.p. 66—68°/12 mm. (semicarbazone, m.p. 178°), oxidised by O<sub>2</sub>-MnO<sub>2</sub> to the *exo*-acid. Hydrogenation (PtO<sub>2</sub>) of (VII) in EtOH gives 2:5-endomethylenehexahydrobenzyl endoalcohol, b.p. 93—95°/14 mm. (phenylurethane, m.p. 134°; *H* phthalate, m.p. 111°), and (IX) gives the corresponding exoalcohol, b.p. 89—90°/11 mm. (phenylurethane, m.p. 118°; *H* phthalate, m.p. 102—103°), also obtained by similar hydrogenation and subsequent hydrolysis of (VIII).

R. S. C.

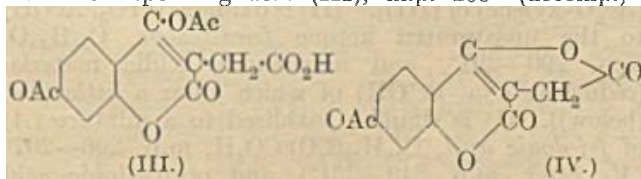
Resins. I. German pine turpentine from *Pinus silvestris*, L. H. WIENHAUS H. RITTER, and W. SANDERMANN. II. Additive capacity of the pine resin acids. H. WIENHAUS and W. SANDERMANN (Ber., 1936, 69, [B], 2198—2202, 2202—2206). —I. Fresh pine turpentine appears to contain 64.2% of resin acids C<sub>20</sub>H<sub>30</sub>O<sub>2</sub> and 35.8% of neutral substances. Its treatment with steam under ordinary conditions and at >50°/30—40 mm. is described.

Repeated crystallisation of the crude acids from MeOH leads to the isolation of a small proportion of sylvic acid (I), m.p. 168—171°,  $[\alpha]_D^{25} -105.33^\circ$ , also obtained by their isomerisation by HCl in AcOH at 100°. Distillation of them under reduced pressure is accompanied by marked fall in  $[\alpha]_D$ . Treatment of the crude acids with COMe<sub>3</sub> gives a product, m.p. 139—142°,  $[\alpha]_D^{25} -112.0^\circ$ . The ultra-violet absorption spectrum of (I) indicates the presence of a conjugation of ethylenic linkings.

II. The action of maleic anhydride on the primary resin acids (II) of *P. silvestris*, L., occurs at room temp. with marked evolution of heat, and the product is completely identical in cryst. form and m.p. with that obtained from (I) by prolonged heating under pressure. Isomerisation of (II) to (I) does not therefore precede addition. Whereas (I) does not combine with *p*-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O at <100°, (II) readily affords the yellow compound (III), C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>, m.p. 214° (corr.),  $[\alpha]_D^{25} -148^\circ$  in CHCl<sub>3</sub>, which contains one ethylenic linking and is reduced (Zn dust in boiling AcOH or Pt in EtOH) to the colourless substance, C<sub>26</sub>H<sub>36</sub>O<sub>4</sub>, m.p. 184°. (III) and NH<sub>2</sub>Ph in boiling AcOH yield the amorphous product, C<sub>32</sub>H<sub>41</sub>O<sub>4</sub>N, m.p. 130—140°. With CH<sub>3</sub>N<sub>3</sub> in Et<sub>2</sub>O esterification of (III) and addition of CH<sub>3</sub>N<sub>3</sub> leads to the compound, C<sub>28</sub>H<sub>38</sub>O<sub>4</sub>N<sub>2</sub>, m.p. about 250°, isomerised by Ac<sub>2</sub>O at room temp. to the colourless substance, m.p. 270°. Irradiation of (III) in EtOH with ultra-violet light or exposure of its solution in EtOH containing eosin in sunlight leads to a substance, m.p. 196°, transformed by CH<sub>3</sub>N<sub>3</sub> into the Me<sub>2</sub> ester, C<sub>26</sub>H<sub>34</sub>O<sub>5</sub>(OMe)<sub>2</sub>, m.p. 241°. (II) and  $\alpha$ -naphthaquinone in MeOH yield the corresponding acid, m.p. 185° [Me ester, C<sub>26</sub>H<sub>30</sub>O<sub>5</sub>C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>(OMe), m.p. 195°], reduced (Zn in AcOH or H<sub>2</sub>-Pt in EtOH) to the H<sub>2</sub>-compound, C<sub>26</sub>H<sub>30</sub>O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>, m.p. 265°. *p*-Xyloquinone is not added to (II) and at a higher temp. dehydrogenates with production of *p*-xyloquinol. *d*-Pimaric acid present in (II) and distinguished by its stability and the dextrorotatory labile acid of pine resin do not react with quinones. A volumetric determination of the levorotatory labile acid in turpentine is thus indicated.

H. W.

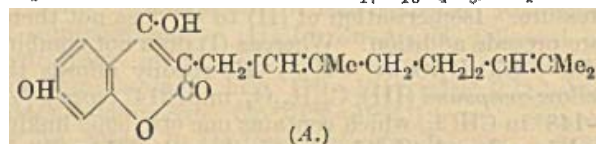
Resin components of ammoniacum. II. Constitution of ammosesin. K. KUNZ and L. HOOPS (Ber., 1936, 69, [B], 2174—2182; cf. A., 1935, 219).—Treatment of diacetylammomesin (I) in EtOAc at -20° with 1.5% O<sub>3</sub> leads directly to the aldehyde (II), C<sub>15</sub>H<sub>12</sub>O<sub>7</sub>, m.p. 137° [*p*-nitrophenylhydrazine, m.p. 194° (decomp.)], in 80—90% yield. Oxidation of (II) with 8% O<sub>3</sub> in EtOAc at -20° yields the corresponding acid (III), m.p. 205° (decomp.)



after darkening at 150° and softening at 165°. When heated for a short time with MeOH or EtOH or at 140—170°/vac. (III) passes into the lactone (IV), m.p. 208° after becoming discoloured at 200°, trans-



formed with loss of Ac by boiling  $2N\text{-Na}_2\text{CO}_3$  into the acid,  $\text{C}_{11}\text{H}_8\text{O}_6$ , m.p.  $233^\circ$  after becoming discoloured at  $210^\circ$ , and converted by boiling MeOH into the compound,  $\text{C}_{12}\text{H}_{10}\text{O}_6$ , m.p.  $158\text{--}5^\circ$  (corresponding *Et* derivative, m.p.  $152\text{--}5^\circ$ ). Oxidation of (IV) with  $\text{KMnO}_4$  in  $\text{COMe}_2$  affords 4-acetyl- $\beta$ -resorcylic acid, m.p.  $151^\circ$ . Treatment of (III) with  $\text{KOH-H}_2\text{O}$  at  $180^\circ$  leads to  $\beta$ :2:4-dihydroxybenzoylpropionic acid, m.p.  $199\text{--}200^\circ$  (corresponding *Me*-acid, m.p.  $147^\circ$ ). Oxidation of (I) with  $\text{CrO}_3$  in AcOH at room temp. gives  $\text{COMe}_2$ . The material remaining after removal of (II) from the products of the ozonolysis of (I) is distilled with steam, thereby yielding  $\text{COMe}_2$  and giving laevulaldehydedi-*p*-nitrophenylhydrazon, m.p.  $176^\circ$ , and a substance,  $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_6$ , m.p.  $187^\circ$



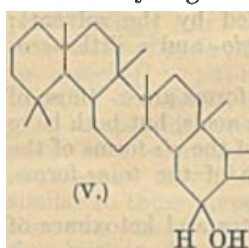
after darkening at  $175^\circ$ , also obtained from synthetic laevulaldehyde. The structure A for ammoresinol is therefore confirmed. H. W.

**isoChavicol acid.** H. LONHAUS (Annalen, 1936, 525, 312—315).—*isoChavicol* acid is obtained in 25% yield with m.p.  $134\text{--}136^\circ$  from Me  $\gamma$ -bromo*iso*-chavicate (dimorphic). It or *isopiperic* acid with I in  $\text{C}_6\text{H}_6$  or MeOH in light gives piperic acid. The oily Me ester is shown by illumination to be at least 75% pure. R. S. C.

**Dehydrogenation of ursolic acid by selenium.** N. L. DRAKE and H. M. DUVAL (J. Amer. Chem. Soc., 1936, 58, 1687—1688; cf. Ruzicka *et al.*, A., 1932, 517).—Ursolic acid is dehydrogenated (Se at  $320\text{--}340^\circ$ ) to 1:2:7- $\text{C}_{10}\text{H}_5\text{Me}_3$ , 2:7- $\text{C}_{10}\text{H}_5\text{Me}_3$ , and the picene hydrocarbon,  $\text{C}_{25}\text{H}_{40}$  (?  $\text{C}_{25}\text{H}_{48}$ ) of Ruzicka *et al.* (cf. *loc. cit.*; A., 1934, 530). H. B.

**Cerin and friedelin.** III. Oxidative degradation of friedelin. N. L. DRAKE and W. P. CAMPBELL. IV. Dehydrogenation of friedelinol. N. L. DRAKE and W. T. HASKINS (J. Amer. Chem. Soc., 1936, 58, 1681—1684, 1684—1687; cf. A., 1935, 1373, 1502).—III. Friedelin (I) is reduced (Na, amyl alcohol) to friedelinol,  $\text{C}_{30}\text{H}_{51}\text{OH}$ , m.p.  $301\text{--}304^\circ$  [iodide, m.p.  $224\text{--}226^\circ$  (decomp.); acetate, m.p.  $315\text{--}316^\circ$ ; Me ether, m.p.  $265\text{--}267^\circ$ ], the benzoate, m.p.  $250\text{--}251^\circ$ , of which decomposes at  $280\text{--}320^\circ$  in  $\text{N}_2$  to BzOH and friedelene (II),  $\text{C}_{30}\text{H}_{50}$ , m.p.  $257\text{--}258^\circ$ . (I) and  $\text{MgPhBr}$  give a little phenylfriedelene, m.p.  $269\text{--}271^\circ$ ;  $\text{MgMeI}$  affords methylfriedelinol (III), m.p.  $316\text{--}319^\circ$ , and some methylfriedelene, m.p.  $272\text{--}274^\circ$  [also obtained by dehydrogenation ( $\text{Ac}_2\text{O}$ -xylene) of (III)]. (II) is oxidised ( $\text{CrO}_3$ , AcOH) to the unsaturated ketone friedelenone, m.p.  $290\text{--}291^\circ$ , and amorphous acidic material [reduction (Na,  $\text{Pr}^\circ\text{OH}$ ) of which gives a little (IV) (below)]. (I) is similarly oxidised to a mixture (A) of friedonic acid,  $\text{C}_{28}\text{H}_{49}(\text{CO})\text{CO}_2\text{H}$ , m.p.  $206\text{--}207^\circ$  (Me ester, m.p.  $249\text{--}251^\circ$ ), and norfriedonic acid (not isolable); reduction (Na- $\text{Pr}^\circ\text{OH}$ ) of (A) affords friedololactone,  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , m.p.  $309\text{--}312^\circ$ , and norfriedololactone (IV), m.p.  $289\text{--}291^\circ$ . (I) thus contains the  $>\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot$  grouping.

IV. Dehydrogenation (Se at  $315\text{--}325^\circ$ ) of friedelinol (V) gives 1:2:7- $\text{C}_{10}\text{H}_5\text{Me}_3$ , 1:2:8-trimethylphenanthrene, an alkylcyclohexene,  $\text{C}_{11}\text{H}_{20}$ , b.p.  $180\text{--}185^\circ$  [further dehydrogenation by Se at  $320^\circ$  (sealed tube) to a product, b.p.  $187\text{--}192^\circ$  (brominated to a compound, m.p.  $169\text{--}175^\circ$ )], and the picene hydrocarbon,  $\text{C}_{25}\text{H}_{40}$  ((?  $\text{C}_{25}\text{H}_{48}$ ), m.p.  $305\text{--}306^\circ$ , of Ruzicka *et al.* (A., 1934, 530). The annexed structure is assigned to (V). H. B.



**Sapogenins.** I. Sapogenins of sarsaparilla root. F. A. ASKEW, S. N. FARMER, and G. A. R. KON (J.C.S., 1936, 1399—1403).—*Smilagenin* (I), m.p.  $183\text{--}184^\circ$ ,  $[\alpha]_D^{25} -69^\circ$  in  $\text{CHCl}_3$ , has been isolated from Jamaican sarsaparilla root, and forms an acetate, m.p.  $150\text{--}151^\circ$ ,  $[\alpha]_D^{25} -59\cdot6^\circ$  in  $\text{CHCl}_3$ , and a benzoate, m.p.  $181\text{--}181\cdot5^\circ$ . (I) is converted by  $\text{H}_2\text{CrO}_4$  into *smilagenone*, m.p.  $156\text{--}157^\circ$ , and by  $\text{PCl}_5$  into *smilagenyl chloride*, m.p.  $194\text{--}195^\circ$ , and by reduction ( $\text{Na-C}_5\text{H}_{11}\text{OH}$ ) into *deoxysmilagenin*, m.p.  $132\text{--}133^\circ$ . Surface film measurements of the three *Digitalis* sapogenins, sarsapogenin (II), and (I) show that the formulae for tigogenin and gitogenin are confirmed, but make it necessary to revise the formula for (II), which is closely related to (I). F. R. S.

**Constitution of papaveristerol.** E. BURES and S. FUCIK (Časopis českoslov. Lék., 1935, 15, 159—167; Chem. Zentr., 1935, ii, 3926).—*Papaveristerol* (I),  $\text{C}_{30}\text{H}_{50}\text{O}$ , m.p.  $134\text{--}134\cdot5^\circ$ ,  $[\alpha]_D^{25} -39\cdot88^\circ$  in  $\text{CHCl}_3$  (acetate, m.p.  $122^\circ$ ; dibromide acetate, m.p.  $108\text{--}109^\circ$ ), is isolated from poppy-seed oil soap. (I) is reduced ( $\text{Na-C}_5\text{H}_{11}\text{OH}$ ) to *dihydropapaveristerol*, m.p.  $128^\circ$  (acetate, m.p.  $115^\circ$ ), and oxidised by  $\text{CuO}$  at  $285\text{--}300^\circ$  to *papaveristenone*,  $\text{C}_{30}\text{H}_{48}\text{O}$ , m.p.  $125\cdot5\text{--}126^\circ$  (semicarbazone, m.p.  $102^\circ$ ; oxime, m.p.  $85^\circ$ ); the latter is further oxidised ( $\text{KMnO}_4$ ) to a keto-acid, which is then reduced (Clemmensen) to an acid,  $\text{C}_{29}\text{H}_{48}\text{O}_2$ , m.p.  $101\text{--}102^\circ$ . The partial formula  $\text{C}_{26}\text{H}_{43}(\text{CH}_2\cdot\text{CH}\cdot\text{OH})(\text{CH}\cdot\text{CH}_2)$  is ascribed to (I). H. N. R.

**Constitution of Hseh Tsuang seed.**—See this vol., 1435.

**Dragon's blood.**—See this vol., 1435.

**Oximation.** K. C. GULATI and J. N. RAY (Current Sci., 1936, 5, 75).—Flavone and  $\alpha$ -naphthylflavone when boiled with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in aq.  $\text{C}_5\text{H}_5\text{N}$  afford oximes, m.p.  $237^\circ$  and  $181^\circ$ , respectively. This method is used successfully in difficult cases. J. L. D.

**Styrylpyrylium salts.** XVII. Colour phenomena associated with 4-phenylbenzo- $\beta$ -naphthaspiropyran and 4-phenyl- $\alpha\beta$ -dinaphthaspiropyran. I. M. HEILBRON, D. H. HEY, and A. LOWE (J.C.S., 1936, 1380—1383).—2-Ethylchromone and  $\text{MgPhBr}$  give 4-phenyl-2-ethylbenzopyrylium chloride, which with 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CHO}$ , followed by hydrolysis, affords 4-phenyl-3'-methylbenzo- $\beta$ -naphthaspiropyran, m.p.  $219\text{--}220^\circ$ . 7-Methoxy-4-phenyl-3'-methylbenzo- $\beta$ -, m.p.  $256\text{--}258^\circ$ , 4-phenyl-3'-methyl- $\alpha\beta$ -di-, m.p.  $207\text{--}208^\circ$ , and 4-phenyl-3:3'-dimethyl-

$\alpha\beta$ -di-naphthaspiropyran are similarly prepared. These substances do not develop colour in boiling inert solvents and the anomalies found by Heilbron *et al.* (A., 1933, 614) no longer exist. F. R. S.

**Pigments of cotton flowers. III. Karunganni (*Gossypium indicum*).** K. NEELAKANTAM and T. R. SESHADRI (Proc. Indian Acad. Sci., 1936, 4, A, 54—58).—From the petals of Karunganni, *gossypin*, m.p. 230° (decomp.), hydrolysed to gossypetin and glucose, a non-glycosidic substance,  $C_{16}H_{12}O_7$ , m.p. 255—257° (Ac derivative, m.p. 186—187°), quercetin, herbacitrin, and gossypitrin have been isolated. F. R. S.

**Benzoxanthones. II.** W. KNAPP (J. pr. Chem., 1936, [ii], 146, 113—118; cf. A., 1935, 1247).—*Salicylic acid 1-C<sub>10</sub>H<sub>7</sub> ether* (o-1-naphthoxybenzoic acid; from  $C_{10}H_7\cdot OH$ , o- $C_6H_4Cl\cdot CO_2K$ , NaOMe, and Cu at 150—200°, m.p. 134—136°, is stable to  $Ac_2O$ , but with  $P_2O_5$  in hot  $C_6H_6$  gives 3:4-benzoxanthone, m.p. 162° (corr.) (lit. 155°). Similar prep. of o- $CO_2H\cdot C_6H_4\cdot O\cdot C_{10}H_7\cdot 2$  (I) gives also 10% of naphtha-1':2':2':1-benzofuran, m.p. 162° (lit. 296°). (I) is stable to  $Ac_2O$ , but with  $P_2O_5$  gives 1:2-benzoxanthone, m.p. 145° (corr.) (lit. 140°, 142°). o- $OPh\cdot C_6H_4\cdot CO_2H$ , m.p. 114°, similarly prepared, gives with  $P_2O_5$  xanthone, m.p. 177° (corr.) (cf. lit.); with  $Ac_2O$  it probably gives a mixed anhydride, since xanthone is obtained only after distillation.

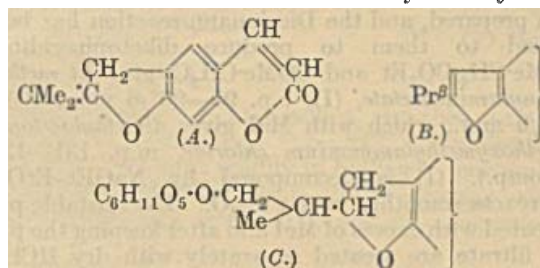
R. S. C.

**Alkylacetylenes and their additive products. XIV. Synthesis of dioxolan derivatives from alkylacetylenes.** D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1658—1659; cf. A., 1934, 759).— $CH\cdot C\equiv Bu$  (I) with  $(\cdot CH_2\cdot OH)_2$  and  $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot OH$  in presence of  $CCl_3\cdot CO_2H$  and a catalyst (from  $BF_3$ ,  $Et_2O$ , red  $HgO$ , and  $MeOH$ ) gives 2-methyl-, b.p. 62—63°/20 mm., and 2-methyl-4-chloromethyl-, b.p. 109°/25 mm., -2-butyl-1:3-dioxolan, respectively. Similarly, (I) with  $OH\cdot CHPh\cdot CO_2H$  and  $OH\cdot CMe_2\cdot CO_2H$  affords 4-keto-5-phenyl-2-methyl-, b.p. 136—138°/19 mm., m.p. 44—45°, and 4-keto-2:5:5-trimethyl-, b.p. 104°/25 mm., -2-butyl-1:3-dioxolan, respectively, whilst Me tartrate yields Me 2-methyl-2-butyl-1:3-dioxolan-4:5-dicarboxylate, b.p. 141—142°/9 mm. Mannitol and (I) give the dioxolan,  $\begin{matrix} CHR\cdot O \\ CHR\cdot O \end{matrix} > CMeBu$  ( $R = \begin{matrix} CH_2\cdot O \\ CH\cdot O \end{matrix} > CMeBu$ ), b.p. 210—212°/9 mm.  $CH_2\cdot CH\cdot C\equiv CH$  and  $(\cdot CH_2\cdot OH)_2$  similarly afford 2-methyl-2- $\beta$ - $\beta'$ -hydroxyethoxyethyl-1:3-dioxolan, b.p. 140—142°/20 mm., and the dioxolan,  $\begin{pmatrix} CH_2\cdot O \\ CH_2\cdot O \end{pmatrix} > CMe\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot$ , b.p. 204—206°/20 mm.

H. B.

**Natural coumarins. XX. Constitution of nodakenin from *Peucedanum decursivum*, Maxim.** E. SPATH and P. KATNRATH (Ber., 1936, 69, [B], 2062—2066; cf. Arima, A., 1927, 599; 1929, 430, 914).—Prolonged extraction of the dry roots with pure MeOH at about 300 mm., evaporation of the extract, and treatment of the residue with  $H_2O$  yields nodakenin (I), m.p. 218—219° (decomp.), hydrolysed by 3%  $H_2SO_4$  to glucose and nodakenetin (II),  $C_{14}H_{14}O_4$ , m.p. 192°,  $[\alpha]_D^{24} -25.4^\circ$  in  $CHCl_3$ .

(II) is unaffected by distillation at 280°(bath)/14 mm. or by heating with  $Al_2O_3$  at 260°/vac. but is converted by distillation with  $P_2O_5$  at 120—150°(bath)/1 mm. smoothly into anhydronodakenetin (III),  $C_{14}H_{10}O_3$ , m.p. 138—139°,  $[\alpha]_D \pm 0^\circ$  in  $CHCl_3$ . Catalytic hydrogenation (Pd-sponge in AcOH) of (III) gives deoxydihydro-oreoselone, m.p. 115—117°. This observation combined with the difficulty of dehydration



of (II) leads to the structure C for (I) and, combined with the optical inactivity, to the structure A or B for (III). H. W.

**Tannin of Formosan tea leaves.** Y. OSHIMA (Bull. Agric. Chem. Soc. Japan, 1936, 12, 103—114, and Proc. Imp. Acad. Tokyo, 1936, 12, 189—190).—Extraction of fresh tea leaves with  $H_2O$  gave gallic acid, an amorphous tannin,  $C_{30}H_{24}O_{14}$ , l-epicatechin [identical with that obtained by Freudenberg (A., 1923, i, 697)], and a gallocatechin (I),  $C_{15}H_{14}O_7$ , m.p. 227°,  $[\alpha]_D -37.5^\circ$  in  $H_2O$ ,  $-67.0^\circ$  in EtOH (pentacetate, m.p. 189°,  $[\alpha]_D -21.3^\circ$  in  $COMe_3$ ;  $Me_5$  derivative, m.p. 184°,  $[\alpha]_D -15.2^\circ$  in  $COMe_3$ ). The amorphous tannin is bis-(5:7:3':4':5'-pentahydroxy)-flavpinacol, proved by its synthesis from phloracetophenone triacetate and gallaldehyde triacetate, hydrolysis of the product to the chalcone,  $C_{15}H_{12}O_7$ , m.p. 278°, and reduction of the latter to the tannin by Zn and AcOH. Reduction of the  $Me_5$  derivative of (I) with Na and EtOH gave  $\alpha$ -2:4:6-trimethoxyphenyl- $\gamma$ -3:4:5-trimethoxyphenylpropane, m.p. 91°, which was synthesised by catalytic reduction of the condensation product of  $\omega$ -acetoxy-3:4:5-trimethylgallacetophenone with phloroglucinaldehyde  $Me_3$  ether. (I) was synthesised by catalytic reduction of delphinidin  $Me_5$  ether. J. N. A.

**Thioindigo syntheses. I. Synthesis of 6:6'-dichloro-4:4'-dimethylthioindigo and 6:6'-dichloro-4:4'-dimethoxythioindigo.** R. SHIBATA and T. NISHI. II. Bromination of 6:6'-dichloro-4:4'-dimethylthioindigo, 6:6'-dichloro-4:4'-dimethoxythioindigo, and thioindigo-red. R. SHIBATA and M. OKUYAMA. III. Condensation products of thioindigotin-7:7'-dicarboxylic acid chloride with aromatic amines. R. SHIBATA and A. SASSA (J. Soc. Chem. Ind. Japan, 1936, 39, 280—282B, 282—283B, 283—284B).—I. 3-Chloro-6-cyano-5-methylthioglycolic acid, m.p. 125°, obtained from the corresponding  $NH_2$ -acid, is hydrolysed to the 6-carboxylic acid, m.p. 132—133°, which with NaOH and S gives 6:6'-dichloro-4:4'-dimethylthioindigotin (I). The 4:4'-(OMe)<sub>2</sub>-compound (II) is similarly obtained.

II. Bromination of (I) under different conditions yields only the 5:5'- or 7:7'- $Br_2$ -derivatives, and (II)



similarly affords a  $Br_2$ -derivative. Bromination of thioindigo-red gives coloured dyes.

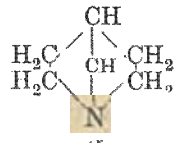
III. Thioindogotin-7 : 7'-dicarboxyl chloride condenses with amines to form differently coloured dyes.

F. R. S.

**Preparation of some  $\beta$ -diketopiperidines.** C. GUSTAFSSON (Finska Kem. Medd., 1936, 45, 98—103).— $\delta$ -Keto-esters containing N in the chain have been prepared, and the Dieckmann reaction has been applied to them to produce diketopiperidines.  $NHMe \cdot CH_2 \cdot CO_2Et$  and  $COMe \cdot CH_2Cl$  give *Et methylacetonylaminoacetate*, (I), b.p. 95—96°/6 mm., 105—106°/9 mm., which with MeI gives *dimethylacetonylcarbethoxymethylammonium chloride*, m.p. 131—133° (decomp.). (I) is decomposed by  $NaOEt \cdot EtOH$ , but reacts smoothly in dry  $Et_2O$ . The unstable ppt. is treated with excess of MeI and after keeping the ppt. and filtrate are treated separately with dry HCl to remove Na and yield respectively 3 : 5-diketo-1 : 1-dimethylpiperidinium chloride, pale brown, reddening at 150°, m.p. 208—209° (decomp.), and 3 : 5-diketo-1 : 1 : 4 : 4-tetramethylpiperidinium iodide, m.p. 174.5—175.5°.  $COMe \cdot CH_2 \cdot CMe_2 \cdot NH_2$  with  $ClCO_2Et(Me)$  gives *N-carbethoxydiacetonamine* (II), b.p. 105.5—107°/6 mm., and *N-carbomethoxydiacetonamine*, b.p. 100—102°/7 mm. (II) is decomposed completely by  $NaOEt$  in  $EtOH$ , but smoothly in  $Et_2O$ . Among the products is  $CHMeBu \cdot OH$ .

M. H. M. A.

**dicyclo-[1 : 2 : 2]-1-Azaheptane.** V. PRELOG and E. CERKOVNIKOV (Annalen, 1936, 525, 292—296).—*Et tetrahydropyran-4-carboxylate* with  $Na \cdot EtOH \cdot C_6H_6$  gives 33% of 4-hydroxymethyltetrahydropyran, b.p. 210—214° (*phenylurethane*, m.p. 86—87°), converted by 45%  $HBr$  at 100—110° into *ae-dibromo- $\gamma$ -bromomethylpentane*, b.p. 158—160°/10 mm., which with  $NH_3 \cdot MeOH$  at 130—140° gives 31.2% of dicyclo-[1 : 2 : 2]-1-azaheptane (I), m.p. 71° (sinters from 65°), b.p. 120—121°



(hydrochloride, hygroscopic; *platini*- and *auri-chloride*; *picrate*; *picrolonate*; *methiodide*, hygroscopic; *methoaurichloride*).

R. S. C.

**Processes of catalytic dehydrogenation. IX. Dehydrogenation of hydrogenated derivatives of 2-pyridone.** E. SPATH and F. GALINOVSKY (Ber., 1936, 69, [B], 2059—2061).—2-Ketopiperidine is dehydrogenated by prolonged heating with Pd-sponge at 260—270° to 2-pyridone in 50—60% yield. 1- and 6-Methyl-2-ketopiperidine behave similarly. Better yields are obtained in the similar dehydrogenation of hydro-carbostyryl and -isocarbostyryl and their *N*-Me derivatives.

H. W.

**Tautomerism of pyridine homologues. II. Syntheses in the pyridine series.** A. E. TSCHITSCHIBABIN (Bull. Soc. chim., 1936, [v], 3, 1607—1632; cf. A., 1927, 885).—2- and 4-Alkyl-pyridines and -quinolines are alkylated in the side-chain by  $NaNH_2$  and alkyl halides; an excess of base is used to minimise the formation of quaternary salts and olefines. The yield depends partly on the amount of Na derivative present in equilibrium with the base and  $NaNH_2$ , being greater in the case of  $\gamma$ - than of  $\alpha$ -picoline. Isomerides (? 3- or 6-derivatives) are

formed in small amounts and two alkyl groups may enter the same side-chain. The following are thus prepared in 40—80% yield : 2- and 4- $\beta$ -phenylethyl-, b.p. 164°/20 mm., 2- $\beta\beta'$ -diphenylisopropyl-, b.p. 198°/5 mm. (*picrate*, m.p. 136°), 2- $\gamma$ -phenylpropyl-, b.p. 199°/2 mm. (*picrate*, m.p. 125°), 2-*n*-amyl-, b.p. 206.5—207° [*picrate*, m.p. 73°; *platnichloride*, m.p. 160° (decomp.)]; a base (*picrate*, m.p. 164°) is also formed], 2-, b.p. 200° (*picrate*, m.p. 105°; *platnichloride*, decomp. >160°), and 4-isoamyl- b.p. 225—227° [*picrate*, m.p. 112—113°; *platnichloride*, m.p. 214° (decomp.)], 2-cyclohexylmethyl-, b.p. 118°/12 mm. (*picrate*, m.p. 135°), 2- $\Delta^2$ -butenyl-, b.p. 188—192° (*picrate*, an oil;  $HgCl_2$  compound, cryst.), 2- and 4-*n*-propyl- [*picrate*, m.p. 134° (lit. 153°); *platini*-, m.p. 210°, and *auri-chloride*, m.p. 116—118°], 4-isobutyl-, b.p. 195° (*picrate*, m.p. 122°; *platnichloride*, m.p. 216°), 4-*n*-butyl-, b.p. 229—230° [*picrate*, m.p. 102—103°; *platnichloride*, m.p. 203° (decomp.)], 2- $\beta$ -phenylethyl-6-methyl-, b.p. 165°/23 mm. [*picrate*, m.p. 125°; *platnichloride*; a base,  $C_{16}H_{13}N$ , m.p. 71—72° (*picrate*, m.p. 165°; *platnichloride*), is also obtained], 2- $\beta$ -phenylethyl-5-ethyl-, b.p. 185—195°/17 mm., 309—312°/760 mm. [*platnichloride*, m.p. 170—172° (decomp.)], 4- $\alpha$ -methylpropyl-, b.p. 187° (*picrate*, m.p. 142°), and 3-phenyl-4- $\Delta^2$ -butenyl-pyridine, b.p. 125—130°/20 mm.;  $\gamma$ -4-pyridyl- $\beta\delta$ -dimethylpentane, b.p. 208—210° (*picrate*, m.p. 115°);  $\delta$ -4-pyridyl- $\beta\zeta$ -dimethylheptane, b.p. 261° (*picrate*, m.p. 89°; *platnichloride*, m.p. 180°);  $\epsilon$ -4-pyridyl-*n*-nonane, b.p. 265—267° (*picrate*, m.p. 114—116°); 4-*n*-propyl- (*picrate*, m.p. 207°), 2- $\beta$ -phenylethyl- (impure), b.p. 225—230°/12 mm., and 2- $\beta\beta'$ -diphenylisopropyl-quinoline (*picrate*).

R. S. C.

**Manufacture of pyridine dyes.**—See B., 1936, 924.

**Introduction of the triphenylmethyl group. I.** E. FUNAKUBO and T. HIROTANI (Ber., 1936, 69, [B], 2123—2130).—Treatment of isochavibetol with  $CPh_3Cl$  in  $C_6H_5N$  at 155° yields triphenylmethylisochavibetol (I), m.p. 184—185°, isochavibetol  $CPh_3$  ether, (II), m.p. 207—209°, and a sparingly sol., unidentified material. (I) contains OH, OMe, and a double linking in the side-chain. It yields an acetate, m.p. 175.5—176°, hydrolysed to (I), a benzoate, m.p. 168—169°, a *Me* ether, m.p. 168.5—169°, and a phenylurethane, m.p. 215.8—217°. It is unaffected by KOH at 234—236°, but is transformed by HI ( $d$  1.7) at 150° into a substance, m.p. 93—96° after softening at 71°, characterised as the diacetate, m.p. 187—188°, and *Me*, derivative, m.p. 132—137°. (II) contains OMe and a double linking in the side-chain, but not OH. The yield of (I) increases at the expense of (II) when reaction is prolonged. Similarly isoeugenol,  $CPh_3Cl$ , and  $C_6H_5N$  at 150° give triphenylmethylisoeugenol, m.p. 208—209° (acetate, m.p. 150—150.5°), and isoeugenol  $CPh_3$  ether, m.p. 211—212.5°. 1-Triphenylmethylindole, m.p. 211.5—212°, is obtained from indole and  $CPh_3Cl$  in boiling  $C_6H_5N$  or from Mg indolyl iodide and  $CPh_3Cl$  in  $Et_2O$ . 1-Triphenylmethyl-2-methylindole, m.p. 215.5—216°, is obtained similarly.

H. W.

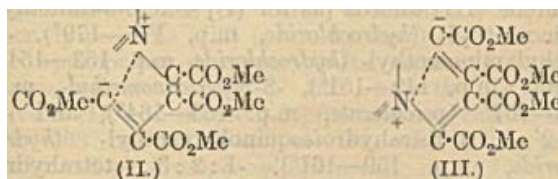
**Synthesis of 3-alkyl- and 3-aryl-quinolines.** F. L. WARREN (J.C.S., 1936, 1366—1368).— $PhNO_2$ ,  $NH_2Ph$ , and  $\beta$ -ethylglycerol  $\alpha\gamma$ - $Et_2$  ether give 3-

ethylquinoline (picrate, m.p. 196—197°).  $\beta$ -Phenylglycerol  $\alpha$ -Et<sub>2</sub> ether, b.p. 155°/21 mm., obtained from OH-CPH(CH<sub>2</sub>Cl)<sub>2</sub>, with PhNO<sub>2</sub> and NH<sub>2</sub>Ph yields 3-phenylquinoline, and with  $\alpha$ -C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub> forms 3-ethyl- $\alpha$ -naphthaquinoline, m.p. 75.5° (picrate, m.p. 188°). F. R. S.

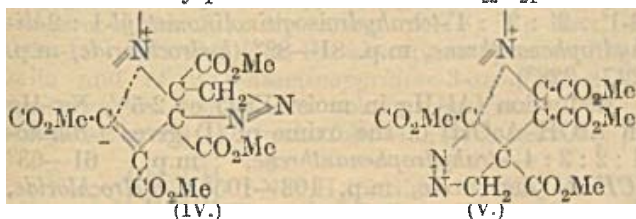
Urethanes as local anaesthetics. III. Alkyl N-8-quinolylcarbamates. R. E. DAMSCHROEDER and R. L. SHRINER (J. Amer. Chem. Soc., 1936, 58, 1610—1612).—8-Aminoquinoline and ClCO<sub>2</sub>Alk in Et<sub>2</sub>O+aq. Na<sub>2</sub>CO<sub>3</sub> give *Me*, m.p. 61.5—62.5°, *Et*, m.p. 66—67°, *Pr*<sup>a</sup>, m.p. 58—59°, *Bu*<sup>a</sup>, m.p. 40°, *Bu* <sup>$\beta$</sup> , m.p. 69—70°, *n*- and *iso*-amyl, and *n*-hexyl, N-8-quinolylcarbamates; the hydrochlorides have m.p. 199—201°, 165—166°, 156—157°, 146—149°, 155—165°, 147—149°, 149—152°, and 145—147° (all with decomp.), respectively, and have little or no anaesthetic activity. H. B.

Derivatives of basically substituted enol and thioenol compounds.—See B., 1936, 920.

Syntheses in the hydroaromatic series. XXVI. Diene synthesis of hetero-rings containing nitrogen. II. Adducts derived from isoquinoline and acetylenedicarboxylic esters. O. DIELS and J. HARMS (Annalen, 1936, 525, 73—94).—The action of (C·CO<sub>2</sub>Me)<sub>2</sub> on isoquinoline (I) in Et<sub>2</sub>O at 0° and finally at room temp. gives "labile adduct" (II), m.p. 167—169°, and (III), m.p. 142—145°, the latter in relatively very small amount. In solubility and behaviour in ultra-violet light (II) is closely allied

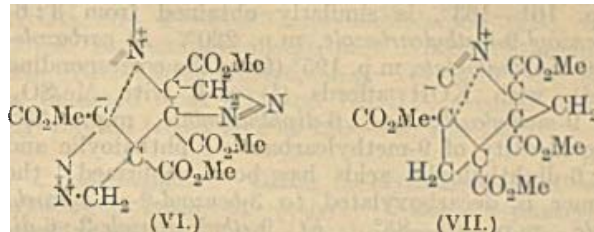


to the "labile" C<sub>5</sub>H<sub>5</sub>N, quinoline, and stilbazole adducts and its position in the "labile" series is established further by its behaviour towards CH<sub>2</sub>N<sub>2</sub>. In the first phase two *mono*-adducts, (IV) and (V), result, one of which passes with excess of CH<sub>2</sub>N<sub>2</sub> into the *bis*-adduct (VI), m.p. 155—158° (decomp.), whereas the other is stable towards excess of CH<sub>2</sub>N<sub>2</sub> and ultimately passes into a substance C<sub>22</sub>H<sub>21</sub>N which

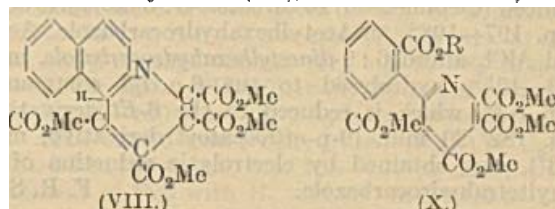


again adds CH<sub>2</sub>N<sub>2</sub> and then loses 2 N with formation of the compound (VII), m.p. 207° (accompanied by a substance, C<sub>23</sub>H<sub>23</sub>O<sub>8</sub>N, m.p. 148—150°). (VI) is converted by HCl into (I) and pyrazoledicarboxylic acid, thus establishing the position of the double linkings in the "unsaturated ester chain." The CH<sub>2</sub>N<sub>2</sub> reaction also proves that these linkings are not equiv. to one another. Hydrogenation of (II) proceeds rapidly (colloidal Pd in MeOH or PtO<sub>2</sub>

in AcOH) to a H<sub>2</sub>-derivative, m.p. 180°, which adds 2 CH<sub>2</sub>N<sub>2</sub>, and hence contains the "ester chain"



unaltered and 2 H at 3 and 4, and then very slowly to the H<sub>4</sub>-compound, m.p. 217°. Stabilisation of (II) proceeds most readily in boiling xylene and gives the compound (VIII), m.p. 231° (decomp.), also obtained similarly from (III), and an *isomeride*, m.p.



170—172°. (VIII) gives a *perbromide*, C<sub>21</sub>H<sub>18</sub>O<sub>8</sub>NBr<sub>3</sub>, decomp. 140°, a *perchlorate*, C<sub>21</sub>H<sub>18</sub>O<sub>8</sub>N·ClO<sub>4</sub>·0.5H<sub>2</sub>O, decomp. 215°, and an *indolizine substance*, C<sub>18</sub>H<sub>15</sub>O<sub>6</sub>N (IX), m.p. 153°. Treatment of (II) with excess of Br in abs. EtOH yields the *perbromide*, C<sub>18</sub>H<sub>16</sub>O<sub>6</sub>NBr<sub>3</sub>, decomp. 140°, converted by hot aq. K<sub>2</sub>CO<sub>3</sub> into the *substance*, C<sub>18</sub>H<sub>14</sub>O<sub>6</sub>NBr, m.p. 166°, and (IX). Oxidation of (II) by H<sub>2</sub>O<sub>2</sub> in AcOH followed by treatment with CH<sub>2</sub>N<sub>2</sub>, or treatment of (II) with Br in MeOH-H<sub>2</sub>O gives the ester (X) (R=Me), m.p. 152° [if Br-EtOH-H<sub>2</sub>O is used a similar ester (X; R=Et), m.p. 118—119°, results], hydrolysed and decarboxylated to 2-phenylpyridine.

In contrast with (II), (III) is very unstable and tends to decompose into its components. It adds CH<sub>2</sub>N<sub>2</sub>, but the intermediate di-adduct loses N<sub>2</sub> during the reaction and gives the *substance*, C<sub>3</sub>H<sub>23</sub>O<sub>8</sub>N<sub>3</sub>, m.p. 168—169°. During very cautious hydrogenation rupture of the mol. occurs, so that the isolable product is a dihydroisoquinoline (*picrate*, m.p. 167°). Stabilisation of (II) is not caused by acids, and the production of small amounts of (VIII) from it in boiling xylene is attributed to a preliminary fission into its components from which (II) is formed, whence (VIII).

The possibility of stabilising the labile adducts of the members of the series depends on the presence of a displaceable H attached to C vicinal to N and of the intact "ester chain." The presence of the  $\Delta^{3:1}$  double linking is not essential, since the H<sub>2</sub>-derivative of (II) passes when heated above its m.p. into a very characteristic red *isomeride*, m.p. 189°, and is oxidised by Br-MeOH-H<sub>2</sub>O to (X) and a *tribromide*, C<sub>21</sub>H<sub>20</sub>O<sub>8</sub>NBr<sub>3</sub>, pale brown needles, decomp. 138°, which slowly pass into a substance, decomp. 145°.

H. W.

Friedel-Crafts reaction in the carbazole series. II. D. R. MITCHELL and S. G. P. PLANT (J.C.S., 1936, 1295—1298).—3:6-Dibenzoylcarbazole and KOH



give carbazole-3:6-dicarboxylic acid (I) (*Et* ester, m.p. 203°); *Et* 9-methylcarbazole-3:6-dicarboxylate, m.p. 161—163°, is similarly obtained from 3:6-dibenzoyl-9-methylcarbazole, m.p. 220°. *Et* carbazole-3:6-diphthaloylate, m.p. 195° (from the corresponding acid), with KOH affords (I) and, with Me<sub>2</sub>SO<sub>4</sub>, *Et* 9-methylcarbazole-3:6-diphthaloylate, m.p. 135°. The identity of 9-methylcarbazole-9-phthaloylic and -3:6-diphthaloylic acids has been confirmed; the former is decarboxylated to 3-benzoyl-9-methylcarbazole, m.p. 84—85°. *Et* 9-ethylcarbazole-3:6-diphthaloylate, m.p. 178°, is obtained from the acid. Carbazole, succinic anhydride, and AlCl<sub>3</sub> in PhNO<sub>2</sub> form carbazole-3:6-bis-γ-ketobutyric acid, m.p. 285° (decomp.) [*Et* ester, m.p. 173°; 9-*Me* derivative, m.p. 268° (decomp.), and its *Et* ester, m.p. 142°], reduced (Clemmensen) to carbazole-3:6-dibutyric acid, m.p. 197—198°. 9-Acetylhexahydrocarbazole, AcCl, and AlCl<sub>3</sub> afford 6:9-diacetylhexahydrocarbazole, m.p. 123—125°, hydrolysed to the 6-acetyl compound, m.p. 73°, which is reduced to the 6-*Et* derivative, b.p. 182°/20 mm. (9-*p*-nitrobenzoyl derivative, m.p. 153°), also obtained by electrolytic reduction of 6-ethyltetrahydrocarbazole. F. R. S.

**Structure and properties of phenanthroline-ferric complexes.**—See this vol., 1324.

**Phenanthrene series. XI. Propanolamines of the type C<sub>14</sub>H<sub>9</sub>·CH(OH)·CH<sub>2</sub>·CH<sub>2</sub>·NR<sub>2</sub>.** J. VAN DE KAMP and E. MOSETTIG. **XII. Amino-alcohols derived from 1:2:3:4-tetrahydrophenanthrene.** A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1936, 58, 1568—1570, 1570—1572).—XI. 2-β-Dimethylamino-, m.p. 104.5—105° (hydrochloride, m.p. 193—193.5°; perchlorate, m.p. 167—167.5°), 2-β-diethylamino- (hydrochloride, m.p. 167—167.5°), 2-β-piperidino-, m.p. 88.5—89° (hydrochloride, m.p. 220—220.5°), 2-β-1':2':3':4'-tetrahydroisoquinolino-, m.p. 133.5—134° (hydrochloride, m.p. 208—209°), 3-β-dimethylamino- (hydrochloride, m.p. 177.5—178°; picrate, m.p. 175.5—176°), 3-β-diethylamino- (hydrochloride, m.p. 155.5—156°; picrate, m.p. 108—109°), 3-β-piperidino- (hydrochloride, m.p. 201—201.5°; picrate, m.p. 162.5—163.5°), 3-β-1':2':3':4'-tetrahydroisoquinolino-, m.p. 118.5—119° (hydrochloride, m.p. 219—220°), 9-β-dimethylamino- (hydrochloride, m.p. 171—171.5°; picrate, m.p. 175—175.5°), 9-β-diethylamino- (hydrochloride, m.p. 135—136°; salicylate, m.p. 113—113.5°), 9-β-piperidino- (hydrochloride, m.p. 184—185°; picrate, m.p. 138—139°), and 9-β-1':2':3':4'-tetrahydroisoquinolino- (hydrochloride, m.p. 228.5—229°), -propionylphenanthrenes are prepared from 2-, 3-, and 9-acetylphenanthrenes (1 mol.), paraformaldehyde (1.5 mols.), and the appropriate NHR<sub>2</sub>·HCl (1.5 mols.) in isoamyl alcohol. Reduction (H<sub>2</sub>, PtO<sub>2</sub>, 50—70% EtOH) of the above (usually as hydrochlorides) gives 2-γ-dimethylamino- (I), m.p. 97.5—98° (picrate, m.p. 156—157°), 2-γ-diethylamino- (II), m.p. 91—92°, 2-γ-piperidino-, m.p. 128—128.5° (hydrochloride, m.p. 184—185°), 2-γ-1':2':3':4'-tetrahydroisoquinolino-, m.p. 132.5—133° (hydrochloride, m.p. 212.5—213°), 3-γ-dimethylamino-, m.p. 99—100°, 3-γ-diethylamino- (hydrochloride, m.p. 141—143°), 3-γ-piperidino- (III) (hydrochloride, m.p. 185—185.5°), 3-γ-1':2':3':4'-tetrahydroisoquinolino-, m.p.

132.5—133° (hydrochloride, m.p. 212.5—213°), 9-γ-dimethylamino- (perchlorate, m.p. 142.5—143°; picrate, m.p. 167.5—168°), 9-γ-diethylamino-, 9-γ-piperidino-, m.p. 126—126.5° (picrate, m.p. 193.5—194°), and 9-γ-1':2':3':4'-tetrahydroisoquinolino-α-hydroxypropylphenanthrene, respectively. The O-Bz derivative hydrochlorides of (I) and (II) have m.p. 219—219.5° and 166—167°, respectively; the O-Ac derivative hydrochloride of (III) has m.p. 237.5—238°.

**XII. 1-Keto-1:2:3:4-tetrahydrophenanthrene (I)** (1 mol.), paraformaldehyde (2.5 mols.), and the appropriate NHR<sub>2</sub>·HCl (1.2 mols.) in isoamyl alcohol give 1-keto-2-dimethylaminomethyl-, m.p. 66—82° (hydrochloride, m.p. 199—200°), -2-diethylaminomethyl-, m.p. 60—61° (hydrochloride, m.p. 137—138°; picrate, m.p. 163—164°), -2-piperidinomethyl-, m.p. 97—98° (hydrochloride, m.p. 170—220°), and -2-1':2':3':4'-tetrahydroisoquinolinomethyl-, m.p. 121—123° (hydrochloride, m.p. 148—150°), -1:2:3:4-tetrahydrophenanthrenes, which are reduced (H<sub>2</sub>, PtO<sub>2</sub>, 90% EtOH) (as hydrochlorides) to 1-hydroxy-2-dimethylaminomethyl-, m.p. 146—147° (hydrochloride, m.p. 236°), -2-diethylaminomethyl- (II), not obtained cryst., -2-piperidinomethyl-, m.p. 133—134.5° (hydrochloride, m.p. 227—228°), and -2-1':2':3':4'-tetrahydroisoquinolinomethyl-, m.p. 159—160° (hydrochloride, m.p. 217°), -1:2:3:4-tetrahydrophenanthrene, respectively. (II) with Ac<sub>2</sub>O·C<sub>2</sub>H<sub>5</sub>N or EtOH·HCl at room temp. gives 2-diethylaminomethyl-3:4-dihydrophenanthrene (hydrochloride, m.p. 231—232°). 4-Keto-1:2:3:4-tetrahydrophenanthrene (III) affords [as for (I)] 4-keto-3-dimethylaminomethyl- (hydrochloride, m.p. 178—179°), -3-diethylaminomethyl- (hydrochloride, m.p. 153—154°; picrate, m.p. 149—151°), -3-piperidinomethyl-, m.p. 106—107° (perchlorate, m.p. 163—164°), and -3-1':2':3':4'-tetrahydroisoquinolinomethyl- (hydrochloride, m.p. 159—161°), -1:2:3:4-tetrahydrophenanthrenes, similarly reduced to 4-hydroxy-3-dimethylaminomethyl- (hydrochloride, m.p. 186—187°; O-Ac-derivative hydrochloride, m.p. 200°), -3-diethylaminomethyl- (hydrochloride, m.p. 172—173°; picrate, m.p. 177—179°), -3-piperidinomethyl- (hydrochloride, m.p. 178—179°), and -3-1':2':3':4'-tetrahydroisoquinolinomethyl- (IV), m.p. 149.5—151° (hydrochloride, m.p. 181—182°), -1:2:3:4-tetrahydrophenanthrene, respectively. (IV) is dehydrated [as for (II)] to 3-1':2':3':4'-tetrahydroisoquinolinomethyl-1:2-dihydrophenanthrene, m.p. 81—82° (hydrochloride, m.p. 227—228°).

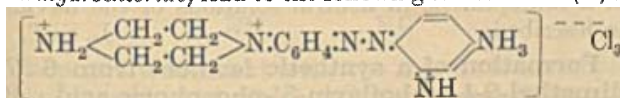
Reduction (Al-Hg in moist Et<sub>2</sub>O or 2.5% Na-Hg in EtOH-AcOH) of the oxime of (I) gives 1-amino-1:2:3:4-tetrahydrophenanthrene, m.p. 61—63° [CHPh<sub>2</sub> derivative, m.p. 103—105°; hydrochloride, m.p. 256—257°; N-Me (hydrochloride, m.p. 258°; hydriodide, m.p. 243°) and NN-Me<sub>2</sub> (hydrochloride, m.p. 216°; picrate, m.p. 177—178°) derivatives]; the oxime of (III) is reduced (Al-Hg) to the 4-NH<sub>2</sub>-derivative (hydrochloride, m.p. 267—268°; NN-Me<sub>2</sub> derivative hydrochloride, m.p. 202°). H. B.

**Acetanilidoalkylbarbituric acids [5-alkyl-5-barbiturylacetanilides]. II. p-Carboethoxy-derivatives.** J. A. TILM and J. B. HOWARD (J. Amer. Chem. Soc., 1936, 58, 1805).—5-Alkylbarbituric acids

and  $p$ -CO<sub>2</sub>Et·C<sub>6</sub>H<sub>4</sub>·NH·CO·CH<sub>2</sub>Cl give (method: A., 1935, 1507) *Et* 5-ethyl-, 5-isopropyl-, 5-*n*- and -isobutyl-, 5-isoamyl-, and 5-allyl-5-barbituracetylacetanilide-4'-carboxylates, all m.p. >225° (decomp.). H. B.

**Tetra-alkylbarbituric acids.** A. W. DOX (J. Amer. Chem. Soc., 1936, 58, 1633—1635).—Methylation (CH<sub>2</sub>N<sub>2</sub>) or ethylation (diazoethane) of 5:5-di- and 1:5:5-tri-alkylbarbituric acids gives almost quant. yields of the 1:3:5:5-tetra-alkyl derivatives. The following are described: 1:3-dimethyl-5:5-diethyl- (I), m.p. 37° [also prepared from CEt<sub>2</sub>(COCl)<sub>2</sub> and CO(NHMe)<sub>2</sub> at 135—150°], 5-phenyl-1:3-dimethyl-5-ethyl-, m.p. 88—89°, 5-phenyl-1:3:5-triethyl-, m.p. 129°, 3-phenyl-1-methyl-5-ethyl-5-propyl-, m.p. 78°, 3-benzyl-1-methyl-5:5-diethyl-, m.p. 73°, and -1:5:5-triethyl- and 1:3-dimethyl-5-ethyl-5-hexyl-, b.p. 165—170°/12 mm., -5-isoamyl-, and -5- $\alpha$ -methylbutyl-barbituric acids. The *O*-methyl-5:5-diethylbarbituric acid of Marotta and Rosanova (A., 1932, 1041) is impure (I). H. B.

**N-Piperazinyl dyes. Azo-dyes.** I. V. PRELOG and D. KOHLBACH (Coll. Czech. Chem. Comm., 1936, 8, 377—389).—*N*-Phenylpiperazine (I) and PhN<sub>2</sub>Cl give 1-phenylpiperazine-4-azobenzene, m.p. 154—154.5°, decomposed by HCl into N<sub>2</sub>, PhOH, and (I). Similarly the substance previously (A., 1934, 196) regarded as *p*-piperazinylazobenzene-*p*'-sulphonic acid is 1-phenylpiperazine-4-azobenzene-*p*-sulphonic acid. However, (I) couples with some diazonium salts in the *p*-position of the Ph; *p*-1-piperazinoazobenzene-*p*'-sulphonamide (II) is thus obtained. 1-Acetyl-4-phenylpiperazine (III) (prep. by Ac<sub>2</sub>O or AcCl) with the appropriate diazonium salts gives *p*-1-4-acetyl-piperazinoazobenzene, m.p. 222°, and the *Ac* derivative of (II) and thence *p*-1-piperazinoazobenzene, m.p. 162—163°, and (II). (I) or (III) with HNO<sub>2</sub> gives 1-nitroso-4-*p*-nitrosophenylpiperazine, m.p. 155°, reduced by SnCl<sub>2</sub> to 1-*p*-aminophenylpiperazine (trihydrochloride, m.p. >300°; Bz<sub>2</sub> derivative, m.p. 226.5°), which by diazotisation and coupling yields 2:4-diamino-4'-*N*-piperazinoazobenzene (tetrahydrochloride, an effective bactericide for some, not all, organisms), 2:6-diaminopyridine-3- (IV), 1-phenyl-3-methylpyrazol-5-one-4-, and 2-naphthol-1-azo-*p*-N-piperazinobenzene (dihydrochloride). (IV) gives a red tetrahydrochloride, decomposed by H<sub>2</sub>O into a black trihydrochloride (V); the colour of (IV) is a max. in 0.6—1*N*-HCl; this fact, the absorption spectra of the salts and of 2:6-diaminopyridine-3-azo-*p*-dimethylaminobenzene (shows no colour changes in acid; trihydrochloride) lead to the following structure for (V):



R. S. C.

**Synthesis of 6-hydroxy-4-methylpyrimidine-5-acetic acid and 4-methyl-5-aminomethyluracil.** W. T. CALDWELL and W. M. ZIEGLER (J. Amer. Chem. Soc., 1936, 58, 1749—1751).—4-Methyluracil-5-acetic acid (I), POCl<sub>3</sub>, and PCl<sub>5</sub> lead to 2:6-dichloro-4-methylpyrimidine-5-acetic acid, m.p. 156—157°, reduced (method: Gabriel and Colman, A., 1899, i, 638) to 6-hydroxy-4-methylpyrimidine-5-acetic acid,

m.p. 147—149°. The hydrazide, m.p. >375°, of (I) is converted into the azide (II) and thence by 50% AcOH into 4-methyl-5-aminomethyluracil (III), m.p. >335° (darkening) [acetate, m.p. >360° (darkening)]. The *N*-CO<sub>2</sub>Et-derivative, m.p. 214—215°, of (III) is obtained from (II) and EtOH; it could not be hydrolysed (conc. HCl at 130—140°) to (III).

H. B.

**Pyrimidines. CLII. Hydrogenation and hydrogenolysis of [ethyl] 2-keto-[4-phenyl-6-methyl]-1:2:3:4-tetrahydropyrimidine]-5-carboxylate] to  $\beta$ -benzyl- and  $\beta$ -hexahydrobenzyl-*n*-butyl alcohol.** K. FOLKERS (J. Amer. Chem. Soc., 1936, 58, 1558—1560; cf. A., 1934, 783).—Hydrogenolysis occurs when the ester is treated with H<sub>2</sub> in presence of Cu-Ba-Cr oxides (A) and EtOH at 250° and gives 28.6% of a mixture, b.p. 77—79°/2.5 mm., of  $\beta$ -benzyl- (I), b.p. 81—81.5°/2 mm., and  $\beta$ -hexahydrobenzyl- (II), b.p. 83—84°/2 mm., -*n*-butyl alcohols. CHPh·Cac·CO<sub>2</sub>Et is reduced [H<sub>2</sub>, (A), EtOH, 160°] to *Et*  $\beta$ -hydroxy- $\alpha$ -benzylbutyrate, b.p. 124—126°/3 mm., dehydrated (P<sub>2</sub>O<sub>5</sub> in C<sub>6</sub>H<sub>6</sub>) to *Et*  $\alpha$ -benzylcrotonate, b.p. 125—127°/3 mm.; short treatment of this with H<sub>2</sub> and (A) in EtOH at 250° and subsequent hydrolysis (EtOH-NaOH), gives (I) and  $\alpha$ -benzylbutyric acid, b.p. 123—124°/2 mm., whilst more prolonged treatment affords a mixture which is further reduced (Raney Ni, 180°) to (II).

H. B.

**Magneto-chemical investigations of organic substances. IX. Magnetic behaviour of nitro-gen-radicals.** E. MÜLLER and W. WIESEMANN (Ber., 1936, 69, [B], 2157—2163; cf. A., 1935, 1453).—Wieland's bisdi-*p*-anisylidiphenylenchydrazine could not be freed from a solid paramagnetic impurity. The magnetic behaviour of 4:4'-dibenzyl-dipyridinium is not in harmony with the presence of two independent electron spins and supports the quinonoid formulation of the compound. Generally, wherever valency tautomerism with formation of the quinonoid condition is possible the magnetic behaviour is in accord only with such quinonoid structure, whereas the chemical behaviour of the substances points to the existence of free radicals. Attempts to obtain the 4:4'-dibenzyl-dipyridinium subiodide of Weitz gave a compound, m.p. 187—193°, of 1 mol. of radical + 1 mol. of subiodide which in the solid condition cannot be regarded as a radical, but further conclusions as to its structure cannot be reached until measurements have been made with its solutions. The magnetic behaviour of tetratolylhydrazinium perchlorate supports Weitz' formulation, and since the paramagnetism depends preponderantly on one spin moment, the alternative NAr<sub>2</sub>·NAr<sub>2</sub>X is preferred.

H. W.

**Experiments in the heterocyclic series.** E. C. WAGNER and J. K. SIMONS (J. Chem. Educ., 1936, 13, 394).—A correction (cf. this vol., 1000).

L. S. T.

**Methyl and phenyl derivatives of nitrophthalhydrazides [nitrophthalaz-1:4-diones].** C. N. ZELLNER and G. DOUGHERTY (J. Amer. Chem. Soc., 1936, 58, 1811—1813).—3-Nitrophthalic anhydride (I) and NHMe·NH<sub>2</sub>·AcOH in aq. AcOH (distilled off



during reaction) give two 5-nitro-N-methylphthalaz-1:4-diones, m.p. 305° (II) (*Ac* derivative, m.p. 211°) and 273° (III) (*Ac* derivative, m.p. 144°). Similarly, (I) and  $(\text{NHMe})_2$  afford 5-nitro-2:3-dimethylphthalaz-1:4-dione, m.p. 203°, whilst (I) and  $\text{NMe}_2\text{NH}_2$  yield 3-nitro-N-dimethylaminophthalimide, m.p. 200—201°. Methylation ( $\text{Me}_2\text{SO}_4$ , dil. alkali) of 5-nitrophthalaz-1:4-dione ["3-nitrophthalhydrazide"] (IV) gives two ON-Me derivatives, m.p. 207° and 138—139°, also obtained by similar methylation of (II) and (III), respectively. These results indicate that (IV) is not 3-nitro-N-aminophthalimide (cf. Mihailescu and Protopopescu, A., 1930, 1434) but has the constitution assigned. 6-Nitro-N-methyl-, m.p. 310—311° and 271—272° (*Ac* derivatives, m.p. 213—214° and 170—171°, respectively), and -2:3-dimethyl-, m.p. 203·5°, -phthalaz-1:4-diones are similarly prepared from 4-nitrophthalic anhydride (V).  $\text{NHPh}\cdot\text{NH}_2$  and (V) in *AcOH* give 4-nitro-N-anilinophthalimide, m.p. 182°, and a 6-nitro-N-phenylphthalaz-1:4-dione, m.p. 253° (*Ac* derivative, m.p. 186°); (I) similarly affords 3-nitro-N-anilinophthalimide, m.p. 198—199°. All m.p. are corr. H. B.

**3-Aminophthalhydrazide.** K. GLEU and K. PFANNSTIEL (J. pr. Chem., 1936, [ii], 146, 137—150).—Me benzisooxazolone-3-carboxylate (I), when heated for a short time with conc. aq.  $\text{N}_2\text{H}_4$ , gives 3-aminophthaloylhydrazine (II),  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{CO})\cdot\text{N}\cdot\text{NH}_2$ , yellow, m.p. 250—251° or about 257° (slow heating), probably by way of the 3-hydrazide and 3-hydroxylaminophthaloylhydrazine. (II) is also obtained from 3-aminophthalimide (III) and aq.  $\text{N}_2\text{H}_4$  at 75°.

5-Aminophthalaz-1:4-dione (IV),  $\text{NH}_2\cdot\text{C}_6\text{H}_3<\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , m.p. 328° (hydrochloride,  $+0\cdot5\text{H}_2\text{O}$ , m.p. 328°, at 100° loses the  $\text{H}_2\text{O}$  rapidly and *HCl* slowly, stable to light), is obtained by heating (I) and  $\text{N}_2\text{H}_4$  for a longer time, from (III) and  $\text{N}_2\text{H}_4$  at  $>75^\circ$ , or by heating (II) above the m.p. or with conc. *HCl*. The *N*-Me derivative of (I) gives 1-methylbenzisooxazolone-4-carbonhydrazone, m.p. 173° (decomp.) (hydrochloride,  $+ \text{H}_2\text{O}$ , decomp. 200°), and thence 5-methylaminophthalazdione (V), m.p. about 310—325° (decomp.). (IV) and  $\text{Me}_2\text{SO}_4\text{--NaOH}$  give the  $\text{Me}_2$  derivative (VI), m.p. 230°. (I) and  $\text{NHPh}\cdot\text{NH}_2$  give 3-aminophthal- (or -phthaloyl-)phenylhydrazide (VII), m.p. 222° (*Ac* derivative, m.p. 178°; cf. Bogert *et al.*, A., 1909, i, 305). (II) and (IV), but not (V), (VI), or (VII), are sol. in alkali. (IV) fluoresces in acid, (V) in alkaline solution. (II) and (VI) do not fluoresce. The chemiluminescence of (IV) is best observed with  $\text{H}_2\text{O}_2$  and a trace of hæmin. The other compounds show no chemiluminescence. R. S. C.

**Quinazolines.** XLIII. Synthesis of a quinazoline derivative structurally analogous to cusparine. D. PAPA and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 1701—1703).—2-3':4'-Methylenedioxyethyl-4-quinazoline, new m.p. 316—317° (decomp.) (all m.p. are corr.), is reduced (method: A., 1935, 760) to 2-β-3':4'-methylenedioxyphenylethyl-4-quinazoline, m.p. 239—240°, methylated ( $\text{Me}_2\text{SO}_4$ , aq. *NaOH*) to the 3-Me derivative, m.p. 94—94·5°, and converted by  $\text{POCl}_3 + \text{PCl}_5$  into 4-

chloro- and thence ( $\text{MeOH--NaOMe}$ ) into 4-methoxy-2-β-3':4'-methylenedioxyphenylethylquinazoline, m.p. 67—68°. The following are similarly prepared: 2-p-methoxystyryl-, m.p. 284—285°, 2-β-p-anisylethyl-, m.p. 213—214°, and 2-β-p-anisylethyl-3-methyl-, m.p. 118—118·5°, -4-quinazoline; 4-chloro-, m.p. 125—128°, and 4-methoxy-, m.p. 84·5—85·5°, -2-β-p-anisylethylquinazoline. 2-Methyl-4-quinazoline is methylated ( $\text{Me}_2\text{SO}_4$ ) to the 2:3-Me derivative, m.p. 111—111·5°. It is now stated that the "gallopine" of *loc. cit.* should be galipoline. H. B.

**Semiquinones of neutral-red and safranines.** L. MICHAELIS (J. Amer. Chem. Soc., 1936, 58, 1816—1817).—Dilution ( $\text{H}_2\text{O}$ ) of solutions of neutral-red, phenosafranine, or commercial "safranine" in conc. *HCl* until bluish-violet and subsequent treatment with  $\text{CrCl}_2$  or *Zn* dust gives intense green (semiquinone state) and then almost colourless solutions; re-oxidation ( $\text{K}_2\text{S}_2\text{O}_8$ ) reverses the two-fold colour change. H. B.

**Synthesis of pyridylisoquinoline derivatives.** S. SUGASAWA and M. KURIYAGAWA (Ber., 1936, 69, [B], 2068—2071).—Homoveratrylamine and Et nicotinate at 150—170° give nicotinoyl-β-3:4-dimethoxyphenylethylamide [hydrochloride ( $+1\text{H}_2\text{O}$ )] transformed by  $\text{POCl}_3$  in boiling *PhMe* into 6:7-dimethoxy-1-3'-pyridyl-3:4-dihydroisoquinoline (I), m.p. 123—124° [dimethiodide, m.p. 229° (decomp.)]. The dimethochloride of (I) is hydrogenated (Adams) to the methochloride, decomp. 275°, of 6:7-dimethoxy-1-3'-pyridyl-2-methyl-1:2:3:4-tetrahydroisoquinoline. *N*-Methylhexahydronicotinoyl-β-3:4-dimethoxyphenylethylamide, m.p. 98°, is converted by  $\text{POCl}_3$  in boiling *PhMe* into a non-cryst. base which yields a dihydriodide, decomp. 208—209°, and a dipicrolonate, decomp. 245° after softening at 230°. H. W.

**Light absorption and tautomerism of uric acid.**—See this vol., 1317.

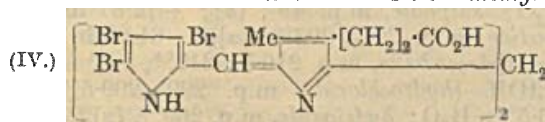
**Murexide and leucomurexide.** D. DAVIDSON (J. Amer. Chem. Soc., 1936, 58, 1821—1822).—Murexide (I) is obtained in good yield (cf. Kuhn and Lyman, this vol., 1000) from alloxantin and  $\text{NH}_4\text{OAc}$  in boiling glacial *AcOH*. (I) is reduced ( $\text{Na}_2\text{S}_2\text{O}_4$ , aq.  $\text{NH}_3$ ) to leucomurexide [ $\text{NH}_4$  dihydropurpurate], which is readily oxidised [air;  $\text{K}_3\text{Fe}(\text{CN})_6$ ] to (I). H. B.

**Semiquinone of the flavin dyes, including vitamin-B<sub>2</sub>.** L. MICHAELIS, M. P. SCHUBERT, and C. V. SMYTHE (Science, 1936, 84, 138—139).—A colour reaction, affording evidence for the existence of a semiquinone in neutral solutions of the flavins, is described. L. S. T.

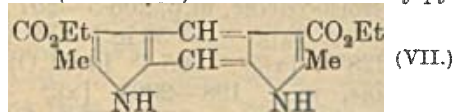
**Formation of a synthetic ferment from 6:7-dimethyl-9-l-araboflavin-5'-phosphoric acid.** R. KUHN, H. RUDY, and F. WEYGAND (Ber., 1936, 69, [B], 2034—2036; cf. this vol., 1418).—6:7-Dimethyl-9-l-araboflavin-5'-phosphoric acid (I) gives with the colloidal carrier obtained from the yellow enzyme a non-fluorescent, non-dialysable yellow chromoprotein of high catalytic activity which is resolved into its components by acid. 6:7-Dimethyl-9-l-araboflavin is transformed by  $\text{CPh}_3\text{Cl}$  in anhyd.  $\text{C}_5\text{H}_5\text{N}$  into 5'-triphenylmethyl-6:7-dimethyl-9-l-araboflavin, m.p.

262—263° (decomp.). The corresponding 2' : 3' : 4'-triacetate, m.p. 240° (decomp.), is transformed by boiling 80% AcOH into 6 : 7-dimethyl-9-l-araboflavin 2' : 3' : 4'-triacetate, m.p. 209° (corr.), which when treated with POCl<sub>3</sub> in C<sub>5</sub>H<sub>5</sub>N gives (I) (*Ag*, *Na*, and *Ca* salts). H. W.

**Porphyrins. XXXVIII. Synthesis of porphyrins and their derivatives.** H. FISCHER, R. J. DOYLE, and W. GLEIM (*Annalen*, 1936, 525, 24—43).—Pyrrole-2-aldehyde (I) and cryptopyrrole-carboxylic acid in AcOH containing 48% HBr give 3' : 5'-dimethylpyrromethene-4'-propionic acid hydrobromide (II), darkens above 190° [*Me* ester hydrobromide, m.p. 151° (corr.)]. With Br in AcOH at room temp. (II) gives a mixture of Br<sub>2</sub>- and Br<sub>3</sub>-derivatives whereas at 100° 3 : 4 : 5-tribromo-3'-methyl-5'-bromo-methylpyrromethene-4'-propionic acid hydrobromide (III) results; (III) is converted by boiling MeOH or H<sub>2</sub>O into 1' : 8' : 1 : 2 : 7 : 8-hexabromo-3 : 6-dimethyl- $\alpha$ , $\beta$ -



$\gamma$ , $\beta$ -dehydrobilan-4 : 5-dipropionic acid (IV), m.p. 146°. Analogously (I) and hæmopyrrolecarboxylic acid yield 4' : 5'-dimethylpyrromethene-3'-propionic acid hydrobromide (*Me* ester hydrobromide), whence the hydrobromides of the Br<sub>2</sub>-derivative, decomp. about 210°, and Br<sub>3</sub>-compound (V). Treatment of (III) or (V) with (—CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> and AcCO<sub>2</sub>H at 180—190° gives 1 : 5-dimethylporphin-2 : 6-dipropionic acid [*Me*<sub>2</sub> ester, m.p. 302° (corr.), and its *Cu* salt]. Et 5-aldehyde-2-methylpyrrole-3-carboxylate and Et pyrrole-2-carboxylate in AcOH containing 48% HBr yield Et<sub>2</sub> 5'-methylpyrromethene-5 : 4'-dicarboxylate hydrobromide, m.p. 193° (decomp.), which could not be further converted into the corresponding porphyrin or porphin. (I) and 3 Br<sub>2</sub> in Et<sub>2</sub>O give 3 : 4 : 5 : 3' : 4' : 5'-hexabromopyrromethene (VI), decomp. >160° (hydrobromide, decomp. about 160°), which with CH<sub>2</sub>O and C<sub>5</sub>H<sub>5</sub>N gives unchanged material and a compound, C<sub>19</sub>H<sub>6</sub>N<sub>4</sub>Br<sub>10</sub>. Addition of CH<sub>2</sub>Cl·OEt to Et 2-methylpyrrole-3-carboxylate in EtOH, Et<sub>2</sub>O, or C<sub>6</sub>H<sub>6</sub> gives Et<sub>2</sub> 2 : 6-dimethyl-4 : 8-dihydrobenzodipyrrole-3 : 5-dicarboxylate (VII), m.p. 331° (block) after subliming at 280°, also obtained by means of HCl-CH<sub>2</sub>O, the constitution of which is established by its reduction (HI-AcOH) to 2 : 3 : 5-trimethylpyrrole;



it is possibly identical with the Et<sub>2</sub> 2 : 6-dimethylbenzodipyrrole-3 : 5-dicarboxylate of Ruggli *et al.* (this vol., 614). (VI) and 5 : 5'-dimethylpyrromethene-4 : 4'-dipropionic acid hydrobromide in AcCO<sub>2</sub>H at 190° give *Me*<sub>2</sub> porphin-1 : 4-dipropionate, m.p. 215—216° (*Cu* salt); at 160° *Me*<sub>2</sub> 5 : 6 : 7 : 8-tetrabromoporphin-1 : 4-dipropionate, m.p. 180°, is produced. 3 : 3' : 5 : 5'-Tetramethyl-4 : 4'-diethylpyrromethene hydrobromide, (VI), and AcCO<sub>2</sub>H at 190° afford 2 : 3-dimethyl-1 : 4-diethylporphin (*Cu* salt), whilst at 160° 5 : 6 : 7 : 8-tetrabromo-2 : 3-dimethyl-

1 : 4-diethylporphin is produced. Porphin-1 : 3 : 5 : 7-tetrapropionic acid, m.p. 265—266°, is derived from 4 : 5 : 3' : 4'-tribromo-5'-methylpyrromethene-3 : 4'-dipropionic acid hydrobromide and AcCO<sub>2</sub>H at 190°.

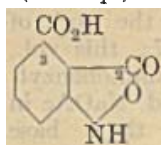
H. W.

**Chlorophyll. LXXIV. Quantitative dehydrogenation of phæophorbide-a.** H. FISCHER and W. LAUTSCH (*Annalen*, 1936, 525, 259—270; cf. this vol., 1273).—The relationship of the phæophorbide to the porphin series is proved by quant. reaction of phæophorbide-a with Ag<sub>2</sub>O (2 mols.) or AgOAc (4 mols.) in hot AcOH (3 min.) to a product, which with CH<sub>3</sub>N<sub>2</sub> gives 10-acetoxyvinylphæoporphyrin-a<sub>5</sub> *Me*<sub>2</sub> ester, m.p. >360° (additive product with CHN<sub>2</sub>·CO<sub>2</sub>Me, m.p. 302°; converted into a hæmin, m.p. >360°; *oxime*, m.p. >360°). This with H<sub>2</sub>-Pd in EtOAc absorbs 3 H<sub>2</sub> to give 10-acetoxyphæoporphyrin-a<sub>5</sub> *Me*, ester, m.p. 305°, with HBr-AcOH, followed by MeOH, affords 10-acetoxy-2- $\alpha$ -methoxyphæoporphyrin-a<sub>5</sub> *Me*<sub>2</sub> ester, m.p. >360°, and a little 2- $\alpha$ -methoxyrhodoporphyrin, and with MeOH-C<sub>6</sub>H<sub>5</sub>N, followed by CH<sub>2</sub>N<sub>2</sub>, gives vinylrhodoporphyrin *Me*<sub>2</sub> ester, m.p. 172°. Structures are confirmed spectrographically. R. S. C.

**Chlorophyll and hæmin derivatives in organic minerals.**—See this vol., 1358.

**Optical absorption of the porphyrins. VII.**—See this vol., 1318.

**Benzisooxazolone-4-carboxylic acids and indazolone-4-carboxylic acids.** K. GLEV and K. FRANNSTIEL (*J. pr. Chem.*, 1936, [ii], 146, 129—136).—Electrolytic reduction of 3-nitrophthalic acid gives quantitatively benzisooxazolone-3-carboxylic acid (I), m.p. 191° [*Ag* salt; *Ac*, m.p. 215° (decomp. from 196°), *N-Et*, m.p. 138°, and *N-Me* derivative, m.p. 163° (*Me* ester, m.p. 66°); *Me* ester (prep. by H<sub>2</sub>SO<sub>4</sub>-MeOH or from the *Ag* salt), +H<sub>2</sub>O, m.p. about 110° (decomp.) or (anhyd.) about 119° (*Ac* derivative, m.p. 119°)]. The *N*-substituted but not the NH derivatives can be sharply titrated using phenolphthalein. The acid gives by diazo-reactions 3-chloro-, -iodo-, and -hydroxy-phthalic acid; if the diazonium solution is treated with KI-SO<sub>2</sub> it gives indazolone-4-carboxylic acid, m.p. 312° (decomp.). R. S. C.



(I)

**Acenaphthene series. II.** A. C. SIRCAR and S. C. SEN (*J. Indian Chem. Soc.*, 1936, 13, 482—483; cf. A., 1932, 286).—Acenaphthenequinone, *p*-NHAc-C<sub>6</sub>H<sub>4</sub>·CHO, and cold NH<sub>3</sub>-C<sub>5</sub>H<sub>11</sub>·OH give the oxazole, but more drastic treatment with the same reagents affords the glyoxaline, m.p. 250° (decomp.). Other aldehydes do not react similarly. R. S. C.

**Doebner reaction. XII.** R. CIUSA and F. BELLINO (*Gazzetta*, 1936, 66, 452—455).—2-2'-Furylcinchonic acid, new m.p. 227° (cf. A., 1922, i, 1062), prepared as before, and also by the Doebner reaction, forms *K*, *Na* (+H<sub>2</sub>O), and *Cu* (+0.5H<sub>2</sub>O) salts, and a *Me* ester, m.p. 100°. In pharmacological use, it eliminates uric acid from the system in a similar manner to atophan, and is less toxic than the latter. E. W. W.



**Vitamin-B<sub>1</sub>. XIV. Sulphite cleavage. IV.** The thiazole half. E. R. BUCHMAN (J. Amer. Chem. Soc., 1936, 58, 1803—1805; cf. Clarke and Gurin, A., 1935, 1510).— $\alpha$ -Acetyl- $\gamma$ -butyrolactone and  $\text{SO}_2\text{Cl}_2$  give the  $\alpha$ -Cl-derivative, b.p. 84—86°/3 mm., converted by dil. HCl at 100° into  $\gamma$ -chloro- $\gamma$ -acetylpropyl alcohol, b.p. 85—110°/3 mm., which with  $\text{HCS}\cdot\text{NH}_2$  in EtOH at room temp. affords 4-methyl-5- $\beta$ -hydroxyethylthiazole (I), b.p. 93—95°/2 mm., also prepared (in lower yield) from  $\text{HCS}\cdot\text{NH}_2$  and the unstable Br-compound from  $\text{CH}_3\text{Ac}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  and Br in  $\text{H}_2\text{O}$ . (I) and conc. HCl at 145° give 4-methyl-5- $\beta$ -chloroethylthiazole, b.p. 74—75°/3 mm. H. B.

**Synthesis of thiochrome.** F. BERGEL and A. R. TODD (Nature, 1936, 138, 406).—Condensation of 4-chloro-2-methyl-5-chloromethylpyrimidine, synthesised from 4-hydroxy-2-methylpyrimidine-5-acetic ester, with 2-amino-4-methyl-5- $\beta$ -hydroxyethylthiazole gives a product identical with thiochrome prepared from aneurin (A., 1935, 1286). The blue fluorescence shown by thiochrome appears to be a property of the condensed ring system present, since other compounds of this type, which all have a similar fluorescence, have been prepared. This synthesis confirms the structure of aneurin (this vol., 1276).

L. S. T.

**l-Peganine from the blossoms and stems of Peganum Harmala.** L. A. D. ROSENFELD and D. G. KOLESNIKOV (Ber., 1936, 69, [B], 2022—2023).—l-Peganine,  $\text{C}_{11}\text{H}_{12}\text{ON}_2$ , m.p. 212°,  $[\alpha]_D^{24}$  —211.0° in  $\text{CHCl}_3$  (hydrochloride, m.p. 206—207°; picrate, m.p. 211°; aurichloride, m.p. 132°), isolated from *P. Harmala*, L., appears identical with the alkaloid obtained by Spath (this vol., 489) from *Adhatoda vasica*, Nees. H. W.

**Peganine. XII. Peganine derivatives and their picrolonates.** E. SPATH, F. KUFFNER, and J. LINTNER (Ber., 1936, 69, [B], 2052—2058; cf. this vol., 489).—Mainly a correction of the work of Narang *et al.* (A., 1935, 765, 995, 1387; this vol., 869). Contrary to these authors, o-aminobenzylsuccinamic acid is transformed by anhyd. NaOAc in  $\text{H}_2$  at 140—150° not into the base

$\text{CH}_2\left\langle \begin{array}{c} \text{N}=\text{C}\cdot\text{CH}_2 \\ \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CO} \end{array} \right\rangle \text{CH}_2$  (I) but into  $\Delta^9$ -pegen-1-one (II) identical with that derived from o-aminobenzylsuccinimide and further identified by reduction with  $\text{Na}\cdot\text{C}_5\text{H}_{11}\cdot\text{OH}$  to peganine (III). In an attempt to obtain (I) synthetically o- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OMe}$  is converted by  $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$  followed by distillation in a high vac. into the compound,

$(\cdot\text{CH}_2\cdot\text{CO})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OMe}$ , m.p. 93—95°, transformed by HBr in  $\text{C}_6\text{H}_6$  into the corresponding bromide, m.p. 132—134°, which passes into (II) when treated with liquid  $\text{NH}_3$  and then distilled in a high vac. The base  $\text{C}_{11}\text{H}_{14}\text{N}_2$  obtained by the reduction of (II) or peganine (IV) is identified as 1-o-aminobenzylpyrrolidine, not (III); this view is confirmed by the observations that it gives a dipicrolonate whereas (III) affords only a monopicrolonate, m.p. 191—193° (vac.). The electrolytic reduction is complete within 1 hr. The monopicrolonates of (IV), m.p. 177—179° (vac.; decomp.), pegan-3-ol, m.p.

188—190° (vac.; decomp.), and  $\Delta^9$ -pegene, m.p. 236—237° (vac.; decomp.), are incidentally described.

H. W.

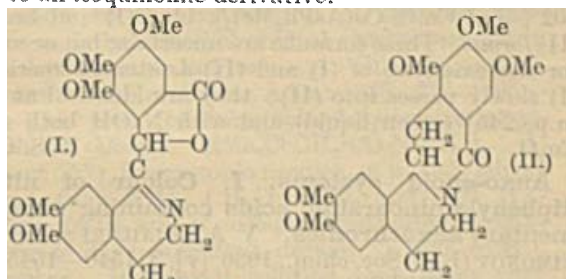
**Ethers and hetero-ethers of morphine and its isomerides.** B. F. FARIS and L. SMALL (J. Org. Chem., 1936, 1, 194—208).—The prep. of the following derivatives is described; m.p. marked \* were determined in an evacuated tube: ethyldihydromorphine, b.p. 170°/high vac.,  $[\alpha]_D^{24}$  —135.9° in EtOH [H tartrate, m.p. 167°,  $[\alpha]_D^{25}$  —59.4° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 260°\*]; benzyldihydromorphine, m.p. 95—97°,  $[\alpha]_D^{25}$  —88.1° in EtOH [hydrochloride (+ $\text{H}_2\text{O}$ ), m.p. 233—235°\*,  $[\alpha]_D^{25}$  —52.1° in  $\text{H}_2\text{O}$ ; hydrobromide (+ $\text{H}_2\text{O}$ ), m.p. 193—195°\*,  $[\alpha]_D^{24}$  —44° in  $\text{H}_2\text{O}$ ; hydriodide, m.p. 215—217°\*,  $[\alpha]_D^{24}$  —45.3° in  $\text{H}_2\text{O}$ ; perchlorate, m.p. 188—192°,  $[\alpha]_D^{25}$  —59.5° in EtOH; methiodide, m.p. 242—244°\*,  $[\alpha]_D^{25}$  —43.2°]; methoxy-methyldihydromorphine, m.p. 99—101°,  $[\alpha]_D^{24}$  —15.4.5° in EtOH (hydrochloride, m.p. 124—126°,  $[\alpha]_D^{24}$  —78° in  $\text{H}_2\text{O}$ ; sulphate, m.p. 49°,  $[\alpha]_D^{24}$  —72.8° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 201—203°\*,  $[\alpha]_D^{24}$  —61.8° in  $\text{H}_2\text{O}$ ); heterodihydrocodeine, m.p. 216.5—217°\*,  $[\alpha]_D^{25}$  —178.0° in EtOH [hydrochloride, m.p. 299—299.5°\*,  $[\alpha]_D^{25}$  —136.5° in  $\text{H}_2\text{O}$ ; hydriodide, m.p. 269°\*,  $[\alpha]_D^{25}$  —98.9° in  $\text{H}_2\text{O}$ ; perchlorate, m.p. 258—260°\* (decomp.),  $[\alpha]_D^{25}$  —110° in  $\text{H}_2\text{O}$ ; hydrogen fumarate, m.p. 215—216°,  $[\alpha]_D^{25}$  —110° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 260—261°\*,  $[\alpha]_D^{25}$  —91.4° in MeOH]; heteroethylmorphine (+ $\text{H}_2\text{O}$ ), m.p. 110—112°,  $[\alpha]_D^{23}$  —178.8° in EtOH [hydrochloride (+3 $\text{H}_2\text{O}$ ), m.p. 241—243°\*,  $[\alpha]_D^{24}$  —134.9° in  $\text{H}_2\text{O}$ ; hydrobromide (+2 $\text{H}_2\text{O}$ ), m.p. 285—287°\*,  $[\alpha]_D^{25}$  —119.2° in  $\text{H}_2\text{O}$ ; hydriodide (+2 $\text{H}_2\text{O}$ ), m.p. 171—174°, solidifies and remelts at 282°\* (decomp.),  $[\alpha]_D^{25}$  —115.8° in  $\text{H}_2\text{O}$ ; perchlorate, m.p. 249—250°\* (decomp.); methiodide, m.p. 255—265°\* (decomp.)]; heteroethyldihydromorphine, m.p. 189—190°,  $[\alpha]_D^{23}$  —164.8° in EtOH [hydrochloride (+3 $\text{H}_2\text{O}$ ), m.p. 165—170°\*, solidifies and remelts at 274—276°\*,  $[\alpha]_D^{24}$  —121.7° in  $\text{H}_2\text{O}$ ; hydrobromide (+2 $\text{H}_2\text{O}$ ), m.p. 282—284°\*,  $[\alpha]_D^{25}$  —125.1° in  $\text{H}_2\text{O}$ ; hydriodide, m.p. 291—293°\*,  $[\alpha]_D^{25}$  —110.6° in  $\text{H}_2\text{O}$ ; perchlorate, m.p. 234—235°\*,  $[\alpha]_D^{23}$  —98° in EtOH; methiodide, m.p. 250—251°\*,  $[\alpha]_D^{23}$  —79.4° in MeOH]; ethyl- $\alpha$ -isomorphine, m.p. 128—130°,  $[\alpha]_D^{23}$  —143.7° in EtOH [methiodide, m.p. 243°\*,  $[\alpha]_D^{21}$  —91.6°]; ethyldihydro- $\alpha$ -isomorphine (+ $\text{H}_2\text{O}$ ), m.p. 86—91°,  $[\alpha]_D^{24}$  —110° in MeOH [anhyd. base, m.p. 104°, b.p. 130°/high vac.; hydrogen tartrate (+ $\text{H}_2\text{O}$ ), m.p. 109—112°,  $[\alpha]_D^{23}$  —66° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 277°\*,  $[\alpha]_D^{23}$  —76.2° in  $\text{H}_2\text{O}$ ]; heteroisocodeine, m.p. 206.5—207°\*, sublimes at 155°/high vac.,  $[\alpha]_D^{22}$  —185.5° in MeOH (methiodide, m.p. 227—228°\*,  $[\alpha]_D^{23}$  —105.4° in  $\text{H}_2\text{O}$ ); heterodihydroisocodeine, m.p. 198—200°,  $[\alpha]_D^{25}$  —118.1° in EtOH (hydrochloride, m.p. 273—275°\*,  $[\alpha]_D^{24}$  —111.1° in  $\text{H}_2\text{O}$ ; hydriodide, m.p. 287—288°\*,  $[\alpha]_D^{24}$  —85.2° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 245—248°\*,  $[\alpha]_D^{24}$  —77.9 in  $\text{H}_2\text{O}$ ); heteroethyl- $\alpha$ -isomorphine, m.p. 161—162°\*, b.p. 170°/high vac.,  $[\alpha]_D^{22}$  —205.1° in MeOH [hydrochloride, m.p. 247—248°\* (decomp.),  $[\alpha]_D^{25}$  —164.2° in  $\text{H}_2\text{O}$ ; hydriodide, m.p. 264°\* (decomp.),  $[\alpha]_D^{25}$  —132.7° in  $\text{H}_2\text{O}$ ; hydrobromide, m.p. 255—258°\* (decomp.),  $[\alpha]_D^{24}$  —150.2° in  $\text{H}_2\text{O}$ ; methiodide, m.p. 229—231°\*,  $[\alpha]_D^{24}$  —131.3° in  $\text{H}_2\text{O}$ ]; heteroethyldihydro- $\alpha$ -isomorphine, m.p. 210—212°,  $[\alpha]_D^{25}$  —128° in EtOH [hydrochloride, m.p. 300°\*,  $[\alpha]_D^{25}$  —125.7° in

H<sub>2</sub>O; *hydriodide*, m.p. 287°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -99.5° in H<sub>2</sub>O; *methiodide*, m.p. 256—258°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -86.1° in H<sub>2</sub>O; *ethyl- $\beta$ -isomorphine*, b.p. 170°/high vac. [*H sulphate*, m.p. 195—198°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -136.3° in H<sub>2</sub>O; *perchlorate*, m.p. 264—266°\* (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -113.2° in 40% EtOH; *fumarate*, m.p. 172—175°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -100.3° in EtOH]; *ethylidihydro- $\beta$ -isomorphine*, b.p. 210°/high vac. (*perchlorate*, m.p. 231—234°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -64.3° in H<sub>2</sub>O; *picrate*, m.p. 187—189°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -64.8° in EtOH); *heteroethyl- $\beta$ -isomorphine*, m.p. 209—211°\*, [ $\alpha$ ]<sub>D</sub> -60.1° in EtOH; *ethyl- $\gamma$ -isomorphine*, m.p. 183—184°, [ $\alpha$ ]<sub>D</sub><sup>22</sup> -75° in MeOH [*hydrochloride*, m.p. 298—300°\* (decomp.), [ $\alpha$ ]<sub>D</sub><sup>24</sup> -62.7° in H<sub>2</sub>O; *methiodide*, m.p. 252—253°\*, [ $\alpha$ ]<sub>D</sub><sup>21</sup> -40.8° in H<sub>2</sub>O]; *ethylidihydro- $\gamma$ -isomorphine*, m.p. 158—159°, [ $\alpha$ ]<sub>D</sub><sup>21</sup> -36.2° in MeOH (*fumarate*, m.p. 180—192°\*, [ $\alpha$ ]<sub>D</sub> -23.7° in H<sub>2</sub>O; *methiodide*, m.p. 252—253°\*, [ $\alpha$ ]<sub>D</sub><sup>21</sup> -40.8° in H<sub>2</sub>O); *hetero- $\psi$ -codeine*, m.p. 239—241°\*, [ $\alpha$ ]<sub>D</sub> -79.5° in MeOH [*hydrochloride*, m.p. 274—276°\* (decomp.), [ $\alpha$ ]<sub>D</sub><sup>22</sup> -48.6° in H<sub>2</sub>O; *hydriodide*, m.p. 185—188°\* (decomp.), [ $\alpha$ ]<sub>D</sub> -48.7° in H<sub>2</sub>O]; *heterodihydro- $\psi$ -codeine*, m.p. 235—237°\*, sublimes at 175°/high vac., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -83.4° in EtOH (*hydrobromide*, m.p. 256—258°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -55.4° in H<sub>2</sub>O; *hydriodide*, m.p. 185—187°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -52.8° in H<sub>2</sub>O); *heteroethyl- $\gamma$ -isomorphine*, m.p. 215—220°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -43.5° in MeOH [*hydrochloride* (+2H<sub>2</sub>O), m.p. 287—290°\* (decomp.), [ $\alpha$ ]<sub>D</sub> -30.5° in H<sub>2</sub>O; *hydriodide* (+H<sub>2</sub>O), m.p. 276—277°\* (decomp.), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -23.2° in H<sub>2</sub>O]; *heteroethylidihydro- $\gamma$ -isomorphine*, m.p. 220—223°\*, sublimes at 175°/high vac., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -20.2° in EtOH (*hydriodide*, m.p. 277—281°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -9.1° in H<sub>2</sub>O; *methiodide*, m.p. 250—252°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -7.2° in H<sub>2</sub>O); *benzylmethylo-morphine* (*benzylmorphine alcoholic Me ether*), b.p. 180°/high vac. (*hydrochloride*, m.p. 233—236°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -88.9° in H<sub>2</sub>O; *H sulphate*, m.p. 247—249°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -90.1° in H<sub>2</sub>O; *methiodide*, m.p. 155—157°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -75.8° in EtOH); *benzylmethyldihydromorphine*, b.p. 210°/high vac., [ $\alpha$ ]<sub>D</sub><sup>25</sup> -89.1° in EtOH (*methiodide*, m.p. 155—157°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -54.60° in H<sub>2</sub>O), prepared by benzylation of heterocodeine; *benzylidihydrodeoxymorphine-D* (*hydrochloride*, m.p. 249°\*, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -34.4° in EtOH; *hydrobromide*, m.p. 226—227°\*, [ $\alpha$ ]<sub>D</sub> -29.8° in EtOH; *perchlorate*, m.p. 223—224°\*, [ $\alpha$ ]<sub>D</sub><sup>24</sup> -51.5° in EtOH; *methiodide*, decomp. about 70°, [ $\alpha$ ]<sub>D</sub> -25.8° in MeOH). *Benzylmorphine N-oxide* has m.p. 236—238°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -53.2° in EtOH. H. G. M.

**Preparation of apocodeine and its hydrochloride.** K. FOLKERS (J. Amer. Chem. Soc., 1936, 58, 1814—1815).—*apoCodeine* (+EtOH), m.p. 104.5—106.5° (decomp.), [ $\alpha$ ]<sub>D</sub> -90° in EtOH, m.p. (EtOH-free) 122.5—124.5° [*hydrochloride*, decomp. 260—263° (softens from 140°)], is prepared by a modification of Knorr and Roth's method (A., 1907, i, 790, where it is designated  $\psi$ -apocodeine). H. B.

**"Methoxyoxypalmitine."** N. N. CHOPRA and J. N. RÂY (J. Indian Chem. Soc., 1936, 13, 478—481).—2-Keto-4 : 5 : 6-trimethoxy-1 : 2-dihydroisobenzofuran-1-carboxylic acid (prep. from gallic acid Me<sub>3</sub> ether and chloral), +H<sub>2</sub>O, m.p. 147°, gives the  $\beta$ -3' : 4'-dimethoxyphenylethylamide, m.p. 154°, and thence (POCl<sub>3</sub>) 6 : 7-dimethoxy-1-4 : 5 : 6-trimethoxyphthalido- $\alpha$ -3 : 4-dihydroisoquinoline (I), reduced by Zn dust-AcOH to "methoxyoxypalmitine" (II), m.p. 170°.

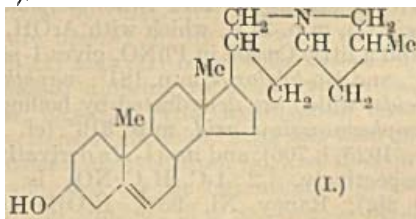
$\beta$ -2 : 3 : 4-Trimethoxyphenylethylamine (from the propionamide and NaOCl) (*oxalate*, m.p. 185°) was condensed with meconinecarboxylic acid, but did not lead to an isoquinone derivative.



R. S. C.

**Curare alkaloids. II. Tubocurarine and bebeerine.** H. KING (J.C.S., 1936, 1276—1279).—Oxidation (KMnO<sub>4</sub>) of *O*-methylbebeerilene gives a mixture of 5 : 6 : 4'-tricarboxy-2 : 3-dimethoxydiphenyl ether (+2H<sub>2</sub>O), m.p. 207° (efferv.) (solidifies and remelts 245°), which is identical with the acid obtained by Faltis from isobebeerine (A., 1922, i, 570), 4 : 5 : 5'-tricarboxy-2 : 2'-dimethoxydiphenyl ether (+2H<sub>2</sub>O), m.p. 257—258° (efferv.) or (+2.5H<sub>2</sub>O) m.p. 145—150° (efferv.), remelts at 262—264° (decarboxylated to 2 : 2'-dimethoxydiphenyl ether), and an acid, C<sub>34</sub>H<sub>30</sub>O<sub>16</sub>·2H<sub>2</sub>O, m.p. 283—284°. The latter acid is an intermediate product of oxidation. The results support the structure for bebeerine proposed by Spath and Kuffner (A., 1934, 312). F. R. S.

**Occurrence of solanidine in sprouting potatoes.** G. R. CLEMO, W. MCG. MORGAN, and R. RAPER (J.C.S., 1936, 1299—1300).—The fresh shoots of different varieties of potato yield 0.04% of solanidine (I). It is suggested that (I) is represented as shown and not as suggested by Soltys and Wallenfels (this vol., 742).



F. R. S.

**Action of bromacetates on some alkaloids.** L. ESPIL and G. MANDILLON (Compt. rend., 1936, 202, 2177—2179).—Alkaloids containing :NH react with CH<sub>2</sub>Br·CO<sub>2</sub>Na liberating HBr to form a complex of reduced toxicity; e.g., strychnine is 200 times as toxic as its complex. F. N. W.

**Compounds of copper salts with tertiary arsines.** G. J. BURROWS and E. P. SANFORD (J. Proc. Roy. Soc. New South Wales, 1936, 69, 182—189).—Cu<sup>I</sup> or Cu<sup>II</sup> salts give the Cu<sup>I</sup> co-ordination compounds, CuI,AsPhMe<sub>3</sub>, m.p. 127°, CuI,2AsPhMe<sub>3</sub>, m.p. 94°, CuCl,2AsPhMe<sub>3</sub>, m.p. 127°, CuBr,AsPhMe<sub>3</sub>, m.p. 106°, CuNO<sub>3</sub>,AsPh<sub>2</sub>Me, m.p. 107°, CuBr,AsPh<sub>2</sub>Me, m.p. 133°, and CuCl,AsPh<sub>2</sub>Me, m.p. 116°. These are insol. in H<sub>2</sub>O, sol. in org. solvents, and have approx. normal mol. wts., but are not very stable in solution, giving Cu<sub>2</sub>O with NaOH and liberating Cu halides



when boiled for a long time. They are colourless, but slowly become blue in  $O_2$ . With excess of the arsine and  $Cu^{II}$  salts the following insol. mixed  $Cu^I-Cu^{II}$  compounds are obtained:  $Cu[Br_3Cu(AsPh_2Me)_3]$ , m.p.  $202^\circ$ , and  $Cu[Cl_3Cu(AsPh_2Me)_3]$ , blue (I) and brown (II) forms. These formulæ are uncertain, but account for the existence of (I) and (II) as stereoisomerides. (I) slowly passes into (II); they are identical at the m.p.  $245^\circ$  (green liquid) and with NaOH both give  $Cu_2O$ . R. S. C.

**Auxo-enoid systems. I. Colour of nitro-diphenylaminoarsinic acids containing complementary auxochromes.** V. A. ISMAILSKI and A. M. SIMONOV (Bull. Soc. chim., 1936, [v], 3, 1540—1545).—A system,  $CR:C:C$  or  $m$ - or  $p$ - $C_6H_4R$ , in which R is an auxochrome, is termed auxo-enoid. The colour of 3-nitro-4-anilinophenylarsinic acid (I) is due to interaction ("auxo-state") of the NH and  $NO_2$ , the NH assuming onium properties ("functioning as an onium perichrome") and being termed the "principal auxochrome" (or "principal auxo"). If an auxochrome, OH, NHAc, OR, or  $NH_2 \cdot C_6H_4$ , is present in the (previously) unsubstituted Ph of (I), it is termed a "complementary auxochrome"; it has a bathochromic effect if in the  $p$ -position, since it then reinforces the onium properties of the principal auxochrome by inductive forces; if in the  $m$ -position, its inductive effect opposes the onium properties and causes a lessening of colour. This interpretation is generalised for any auxo-enoid system attached to any principal auxochrome. It accounts for the bathochromic effect of introducing  $p$ -OMe into Variamine B. R. S. C.

**Reactivity of nuclear chlorine in the isomeric 1:2- and 2:1-chloronaphthalenearsinic acids.** G. W. BOWERS and C. S. HAMILTON (J. Amer. Chem. Soc., 1936, 58, 1573—1575).—1:2- $NH_2 \cdot C_{10}H_6 \cdot AsO_3H_2$  is converted (Sandmeyer) into 1-chloronaphthalene-2-arsinic acid (I), m.p.  $317^\circ$ , which with ArOH, anhyd.  $K_2CO_3$ , and a little Cu foil in  $PhNO_2$  gives 1-phenoxy-, m.p.  $322^\circ$ , and 1-o-tolyloxy-, m.p.  $181^\circ$ , naphthalene-2-arsinic acids, which are dehydrated by boiling AcOH to  $\alpha$ -benzophenoxarsinic acid, m.p.  $319^\circ$  (cf. Aeschlimann, A., 1925, i, 706), and its 11-Me derivative, m.p.  $177^\circ$ , respectively. 2:1- $C_{10}H_6Cl \cdot NO_2$  is reduced [ $H_2$  (40 lb.), Raney Ni, 95% EtOH] to 2:1- $C_{10}H_6Cl \cdot NH_2$ , converted (Bart) into 2-chloronaphthalene-1-arsinic acid (II), m.p.  $296^\circ$ , and thence (as above) into 2-phenoxy-, m.p.  $211^\circ$  (partly), re-solidifying with m.p.  $295^\circ$ , 2-o-, m.p.  $295^\circ$ , and -p-, m.p.  $225^\circ$  (partly), re-solidifying with m.p.  $273^\circ$ , -tolylloxy-, and 2-o-, m.p.  $230-231^\circ$ , and -p-, m.p.  $217-219^\circ$ , -chlorophenoxy-naphthalene-1-arsinic acids, which are dehydrated (AcOH) to  $\gamma$ -benzophenoxarsinic acid, m.p.  $278-280^\circ$ , and its 8-Me, m.p.  $205^\circ$  (partly), re-solidifying with m.p.  $270^\circ$ , 10-Me, m.p.  $215-217^\circ$ , 8-Cl-, m.p.  $216-218^\circ$ , and 10-Cl-, m.p.  $214^\circ$ , derivatives, respectively. (I) and (II) do not react with  $NH_2Ph$ ,  $NH_2Alk$ , or  $AlkOH$ ; the Cl is thus less reactive than in the corresponding  $C_6H_6$  derivatives (cf. A., 1931, 1173). H. B.

**Bismuth derivatives of diphenyl.** D. E. WORRALL (J. Amer. Chem. Soc., 1936, 58, 1820—1821).— $p$ - $C_6H_4Ph \cdot MgBr$  and  $BiCl_3$  give *Bi tri-p-diphenyl*l,

m.p.  $182-183^\circ$  [dichloride, m.p.  $198-200^\circ$  (decomp.), converted ( $EtOH-AgNO_3$  in  $COMe_2$ ) into the dinitrate, decomp. about  $162^\circ$ ; dibromide, m.p. indef. with decomp.], which with  $BiCl_3$  in  $Et_2O$  affords *Bi di-p-diphenyl chloride*, m.p. indef. H. B.

**Carbazole. I. Selective metalation.** H. GILMAN and R. H. KIRBY (J. Org. Chem., 1936, 1, 146—153).—Carbazole when refluxed with  $LiBu^a$  in  $Et_2O$  and then treated with  $CO_2$  gives carbazole-1-carboxylic acid. Similarly 9-ethylcarbazole (I) gives its 1-carboxylic acid. Metalation occurs to a slight extent with  $CaPhI$ , but not with  $MgEtBr$ . (I) with  $Hg(OAc)_2-EtOH-AcOH$  or when fused with  $Hg(OAc)_2$  gives 9-ethyl-3-acetoxymercuricarbazole (II), m.p.  $156^\circ$ , and a dimercurial (III), m.p.  $242^\circ$ . (II) gives (I) with  $EtOH-HCl$ , and the 2-iodo- (IV) and 2-chloro-9-ethylcarbazoles when treated, respectively, with  $KI-I$  and with  $CaCl_2$ . (II) with  $N_2H_4 \cdot H_2O$  gives bis-(9-ethylcarbazyl-3-)mercury, m.p.  $217^\circ$ , which with  $Li-Et_2O$  followed by  $CO_2$  gives 9-ethylcarbazole-3-carboxylic acid, m.p.  $226^\circ$ , also obtained (Grignard) from (IV), from (I) by bromination followed by carbonation of the corresponding Li compound, and by ethylation of Et carbazole-3-carboxylate, followed by hydrolysis. (III) with  $KI-I$  gives 3:6-di-iodo-9-ethylcarbazole, also obtained by direct iodination of (I). This with  $Cu_2(CN)_2$ ,  $KCN$ ,  $H_2O$ , and  $EtOH$  (sealed tube,  $230^\circ$ , 20 hr.) gives 9-ethylcarbazole-3:6-dicarboxylic acid, m.p.  $>320^\circ$  ( $Me_2$  ester, m.p.  $187^\circ$ ), also obtained by oxidation with  $K_2Fe(CN)_6-KOH-H_2O$  of 3:6-diacetyl-9-ethylcarbazole, m.p.  $182^\circ$ , prepared by ethylating 3:6-diacetylcarbazole (A., 1935, 990). This establishes the positions of Hg in (III). H. G. M.

**Magnetochemical investigations of organic substances. VIII. Metal ketyls of 4-pyrones.** E. MÜLLER and F. TESCHNER (Annalen, 1936, 525, 1—13).—Magnetic investigations of the K derivatives of 2:6-dimethylpyrone, 2-methylchromone, and 2:3:6:7-dibenzoanthone exclude the possibility of formulating them as free radicals. Pfeiffer's formulation  $R_2C:O \cdots K$  is excluded by chemical evidence. It is therefore necessary to double the formula, thus leading to a choice between  $RK \cdot OK + RO$  and  $[R(OK)]_2$  ( $R=O < \begin{smallmatrix} CMc:CH \\ CMc:CH \end{smallmatrix} > C$ ). Since the action of MeI leads to a very unstable, reddish-brown perchlorate instead of to Baeyer's colourless trimethylpyrylium perchlorate the latter formulation is advocated with reserve. The magnetic behaviour of the K derivative of xanthone excludes the formulations of Pfeiffer, Schlenk, and Weitz and, combined with analytical behaviour, suggests that it is a quinhydrone-like, complex mol. mixture of eight xanthone mols. or an equilibrium between a pinacoid and a radical form. H. W.

**Cross linking formation in keratins.** J. B. SPEAKMAN (Nature, 1936, 138, 327).—A discussion of the nature of the linkings responsible for the contraction of wool when treated by various reagents. Permanent setting is explained by the formation of  $\cdot S \cdot NH \cdot$  rather than  $\cdot N \cdot CH \cdot$  linkings. L. S. T.

**New electrochemical method of preparing proteins at the isoelectric point.** J. SWYNGEDAUF

(Compt. rend., 1936, 203, 54—57).—The electrolytic method previously described (cf. A., 1934, 961) has been successfully applied to the treatment of ovalbumin and casein. With hæmoglobin, however, the  $p_H$  of the high-resistance zone is 3.4 whereas the isoelectric point is about 6.8. C. R. H.

**Polysaccharoproteins.**—See this vol., 1404.

**Handling and weighing absorption tubes in micro-determinations of carbon and hydrogen.** D. F. HAYMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 342—343).—The balance room is kept at const. temp., Pregl absorption tubes are used, special precautions are taken when wiping the tubes, and freedom from dust and lint is ensured by examining the tubes visually in a narrow beam of light against a dark ground. The tubes are weighed immediately after wiping and errors due to electrostatic effects are eliminated by maintaining the R.H. of the laboratory at  $<45\%$ . S. C.

**Micro-determination of carbon and hydrogen in compounds containing arsenic, antimony, tin, bismuth, and phosphorus.** F. C. SILBERT and W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1936, 8, 353—355).—Satisfactory results are obtained by replacing part of the Pregl universal filling with Pt gauze and a mixture of Pt gauze and  $Pb_3O_4$ . S. C.

**Organic micro-analysis. I. Nitrogen by Dumas' method.** R. T. MILNER and M. S. SHERMAN (Ind. Eng. Chem. [Anal.], 1936, 8, 331—332).—A simplified all glass micro-combustion apparatus is described. The nitrometer is closed by a ground conical stopper instead of the usual stopcock. A simply constructed, hinged electrical heating element is described and the various corrections to be applied are measured and discussed. S. C.

**Formation of nitric acid during the combustion of organic nitrogen compounds in the calorimetric bomb.** A. J. PETRICK (J. Chem. Met. Soc. S. Africa, 1936, 37, 1—3).—Org. compounds containing N when burned in  $O_2$  at 30 atm. afford  $HNO_3$ , determined by titration. In S-containing compounds allowance is made for the  $H_2SO_4$  formed, which is determined as  $BaSO_4$ . The  $HNO_3$  formed accounts for 1.41—11.14% of the N in the compound; high vals. are obtained in the presence of S. J. L. D.

**Nesslerisation applied directly to a macro-Kjeldahl nitrogen determination.** S. MORGULIS and H. C. SPENCER (Ind. Eng. Chem. [Anal.], 1936, 8, 330).—The wet sample of tissue is weighed on a tared piece of Sn foil folded so as to prevent loss of  $H_2O$  and dropped into  $H_2SO_4$  used for the Kjeldahl determination. After digestion the solution is bleached with  $H_2O_2$ , diluted, the Sn ppt. allowed to settle, and  $NH_3$  determined in the clear supernatant liquid by means of Nessler's reagent. S. C.

**Modification of micro-Zeisel apparatus for determination of methoxyl and ethoxyl groups.** J. J. CHINOY (Analyst, 1936, 61, 602—603). J. S. A.

**Microchemical determination of butyric acid.** L. KLING (Mikrochem., 1936, 19, 187—189; cf. A., 1934, 1331).— $PrCO_2H$  is oxidised by  $H_2O_2$  in presence

of Fe to  $COMe_3$ , which is distilled directly into the Scott-Wilson  $Hg(CN)_2$ - $AgNO_3$  reagent. J. S. A.

**Determination of lactic acid.**—See this vol. 1436.

**New reagents for the carbonyl group, their application to the extraction of ketonic substances and the microchemical characterisation of aldehydes and ketones.** A. GIRARD and G. SANDULESCO (Helv. Chim. Acta, 1936, 19, 1095—1107).—The prep. of *trimethylcarbohydrazidomethylammonium chloride*,  $NMe_3Cl \cdot CH_2 \cdot CO \cdot NH \cdot NH_2$  (I) ("reagent T"), hygroscopic needles, m.p.  $192^\circ$  (slight decomp.), from  $NMe_3$ ,  $CH_2Cl \cdot CO_2Et$ , and  $N_2H_4 \cdot H_2O$  in boiling EtOH and of *carbohydrazidomethylpyridinium chloride* (II) (reagent P), decomp.  $> 200^\circ$  (corr.), is described. In neutral solution they react very slowly with CO compounds, and generally a large excess of reagent is used in EtOH containing 10% of AcOH; action is then complete in 20—30 min. at the b.p. of the solution. The hydrazones thus produced are cryst. compounds sol. in  $H_2O$  and alcohols, insol. in org. media without OH. In approx. neutral solution they are relatively stable, whereas at  $p_H < 6$  those of the ketones are rapidly decomposed and those of aldehydes are stable. Separation of aldehyde from ketone is therefore possible by treatment of the mixture with (I) or (II) and of the aq. solution of the product with  $H_2SO_4$  (50 g. per litre); after 1 hr. the liberated ketone is extracted with  $Et_2O$ . In practice, (I) and (II) are not suitable for the study of aldehydes. For the isolation of the ketonic fraction of natural materials the latter is dissolved in abs. EtOH and treated with (I) or (II). The resulting solution is poured into ice water containing sufficient  $Na_2CO_3$  to neutralise 90% of the AcOH and then extracted with  $Et_2O$ . The aq. solution is made 0.5—1.0N with HCl or  $H_2SO_4$  and kept for 1 hr., after which the ketones are extracted with  $Et_2O$ . Emulsification is avoided by suitable use of EtOH or by replacing  $H_2O$  by  $(\cdot CH_2 \cdot OH)_2$ . Possibilities of fractionation are opened up by the very varying rates with which (I) and (II) react with ketones and the (non-correlated) differing rates of hydrolysis of the compounds formed. The hydrazones show the general reactions of alkaloidal salts and their presence in aq. solution if derived from (I), and their presence is readily detected by the formation of a flocculent orange ppt. on addition of a solution of  $BiI_3$  (1 g.), KI (10 g.), and conc. HCl (5 c.c.) in  $H_2O$  (to 100 c.c.) or, preferably, by their behaviour towards a solution of  $HgI_2$  (5 g.) and KI (10 g.) in  $H_2O$  (100 c.c.). The extraction of oestrone from urine of pregnancy and the purification of MeOH from traces of  $COMe_3$  are described. H. W.

**Micro-determination of fructose in presence of glucose.** S. M. STREPKOV (Biochem. Z., 1936, 287, 33—34).—The method depends on the fact that fructose (I) is completely oxidised in 2.5 hr. at  $60^\circ$  by an alkaline  $Na_2HPO_4$ - $K_3Fe(CN)_6$  solution whilst glucose (II) is not attacked. (I) is then determined by iodometric titration of the  $K_4Fe(CN)_6$  formed. Tables for reading off the results are given both for (I) in aq. solution and in presence of (II). P. W. C.

**Determination of creatinine.** A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1936, 69,



224—227).—The purple colour given by creatinine (I) and alkaline 3:5-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H is used as a qual. and quant. test. At 0° the colour given by the reagent alone does not interfere for the 15—25 min. required for development of max. intensity by (I). Purified acid gives better results. The test is better than that of Jaffe. R. S. C.

Action of copper salts on benzidine in presence of halides and thiocyanates and a new sensitive test for copper. L. KUHLBERG (Mikrochem., 1936, 20, 153—160).—Benzidine gives a ppt. with Cu<sup>++</sup> the colour of which varies with the anion present. Br<sup>-</sup> and CNS<sup>-</sup> form benzidine-blue. Cl<sup>-</sup> does not effect the benzidine reaction but produces *o*-tolidine-blue. The mechanism is discussed in terms of the potential Cu<sup>++</sup>/Cu<sup>+</sup> and the solubility product of the Cu<sup>+</sup> salt. A reagent containing 0.1 g. of *o*-tolidine +0.5 g. of NH<sub>4</sub>CNS in 5 c.c. of COMe<sub>2</sub> is recommended for Cu. Strongly oxidising salts must first be reduced with Bi-Hg. R. S.

Sensitive colour reaction of phenol with "fast-red salt B," and its use as drop reaction. Y. KONDO (Mikrochem., 1936, 19, 214—221).—PhOH gives with 0.05—0.1% aq. "fast-red salt B" in presence of Li<sub>2</sub>CO<sub>3</sub> a very sensitive red to orange coloration; limit 10<sup>-8</sup> g. of PhOH. Other (polyhydric) phenols give colorations of different shades. J. S. A.

Application of chloroamine in organic analysis. L. VŠETĚČKA (Časopis českoslov. Lék., 1935, 15, 51—56; Chem. Zentr., 1935, ii, 3954).—1 mol. of uric acid requires 2 mols of NH<sub>2</sub>Cl for oxidation in alkaline solution. A volumetric method based on this reaction is described. H. N. R.

Colorimetric determination of uric acid (Folin).—See this vol. 1436.

Identification of yohimbine. M. L. SHANER and M. L. WILLARD (Mikrochem., 1936, 19, 222—226).—Cryst. ppts. given by yohimbine with metallic chlorides and with the usual alkaloid reagents are described. Identification is best effected through the acid salts, for which microscopic and crystallographic data are given. J. S. A.

The biuret reaction. II. Metal-biuret compounds. III. Protein compounds of copper, nickel, and cobalt. H. JESSERER (Biochem. Z., 1936, 287, 71—83, 84—87; cf. this vol. 1007).—In the complexes of Cu with the following org. bases, 1 atom of Cu is associated with 2 mols. of biuret (I), oxamide (II), or malonamide (III). At the same wt. concn. the strength of colour with (I) is the same as with caseinogen (IV), but the complex with (I) contains three times as much Cu as with (IV). The colour with (I), as with (IV), consists of red and blue components; the latter on long keeping separates, the red component remaining and then containing 1 atom of Cu to 4 mols. of (I). The formulae of the compounds are discussed. Complexes of (I) in alkaline solution with Ni and Co are prepared in which 1 atom of metal is associated with 3 and 6 mols. of (I), respectively. (II) and (III) give complexes containing 1 atom of Ni to 3 mols. of base.

III [with F. LIEBEN]. Clupein ester hydrochloride gives a complex containing 4 Cu per mol. When the violet Cu-(IV) complex is dialysed, the blue colour separates without decomp. Ni- and Co-(IV) complexes decompose on dialysis. Zn separates the whole of the Cu from the Cu-(IV) complex. No difference in valency was detected in the Cu of the red and blue components. In the Ni- and Co-(IV) complexes 1 atom of Ni replaces 2 Cu and 1 atom of Co replaces 3 of Cu. P. W. C.

## Biochemistry.

Gaseous metabolism during controlled restriction of respiration. I. In men with normal hearts. II. In men during dyspnoea. A. LUBLIN (Arch. exp. Path. Pharm., 1936, 182, 427—436, 437—443).—I. Restricted respiration increases the vol. of expired CO<sub>2</sub> and decreases that of utilised O<sub>2</sub> so that the R.Q. increases to vals. >1.

II. Hyperventilation occurs, the utilised O<sub>2</sub> tending to decrease and the R.Q. to increase. F. O. H.

Effect of oxygen lack, variations in the carbon dioxide content of the inspired air, and hyperpnoea on visual intensity discrimination. E. GELLHORN (Amer. J. Physiol., 1936, 115, 679—684). R. N. C.

Respiratory ventilation in the cockroach in air, in carbon dioxide, and in nicotine atmospheres. R. L. KITCHEL and W. M. HOSKINS (J. Econ. Entom., 1935, 28, 924—933). A. G. P.

Rate of elimination of dissolved nitrogen in man in relation to the fat and water content of the body. A. R. BEHNKE, R. M. THOMSON, and L. A. SHAW (Amer. J. Physiol., 1935, 114, 137—

146).—O<sub>2</sub> inhalation results in elimination of dissolved body N<sub>2</sub> in equilibrium with pulmonary N<sub>2</sub>, about 98% being removed in 6 hr. in a young well-developed man. Most of the N<sub>2</sub> is stored in the body-H<sub>2</sub>O. The N<sub>2</sub> content of a well-nourished dog is approx. the same as that of man. The N<sub>2</sub> elimination curve is exponential. During decompression of divers exposed to high pressures for short periods, the body-fats act as N<sub>2</sub>-absorbents and prevent bubble formation. R. N. C.

Position of the oxygen dissociation curve of human blood at high altitudes. A. KEYS, F. G. HALL, and E. S. G. BARRON (Amer. J. Physiol., 1936, 115, 292—307).—At const. *p*<sub>H</sub> of the cells, the affinity of haemoglobin for O<sub>2</sub> tends to decrease at high altitudes. The dissociation curve is displaced to the left of the sea-level curve up to 14,000 ft.; above this level the curve is displaced increasingly to the right. Curves for arterial blood during work are similar to those obtained at rest. The curves for men accustomed to altitudes up to 5340 m. are within the normal limits for men at sea-level. R. N. C.

**Effect of altitude on the affinity of hæmoglobin for oxygen.** F. G. HALL (J. Biol. Chem., 1936, 115, 485—490; cf. preceding abstract).—The  $O_2$  affinity of human hæmoglobin, determined spectrographically after hæmolysis and dilution, remains unchanged with change in altitude between sea-level and 20,000 ft. F. A. A.

**Gaseous equilibria in the lungs at high altitudes.** D. B. DILL, E. H. CHRISTENSEN, and H. T. EDWARDS (Amer. J. Physiol., 1936, 115, 530—538).—The partial pressure of  $O_2$  in arterial blood at high altitudes is approx. equal to that of alveolar air.  $O_2$  saturation of arterial blood does not necessarily increase during acclimatisation. R. N. C.

**Arterialisation of blood. V. Possibility of influencing gaseous exchange between alveoli and blood.** K. KRAMER and H. SARRE (Z. Biol., 1936, 97, 329—342; cf. A., 1935, 371, 878).—Increase in depth of respiration due to lobeline (I) decreases the difference in  $O_2$  tension between alveoli and arterial blood. The initial difference in  $O_2$  tension between alveoli and the pulmonary venous blood is, however, of importance; when high, (I) increases the alveolar tension and diminishes the  $O_2$ -saturation of the venous blood, resulting in an increased difference between alveoli and arterial blood. Adrenaline increases the inflow of blood and considerably displaces the gaseous exchange. The bearing of these and previous data on  $O_2$ -uptake is discussed. F. O. H.

**Absorption of water from the small intestine at various degrees of anoxæmia.** E. J. VAN LIERE, N. A. DAVID, and D. H. LOUGH (Amer. J. Physiol., 1936, 115, 239—244).—Absorption is increased, an apparent optimum occurring when the blood- $O_2$  is approx. 10%. R. N. C.

**Iodophilic substance of leucocytes.** A. GIRARDIN (Jahrb. Kinderheilk., 1935, 145, 140—166; Chem. Zentr., 1935, ii, 3790).—Iodophilic granules of neutrophile leucocytes are shown by treatment of moist blood with I vapour. The normal proportion (20%) is increased in certain infectious diseases, after a meal in sucklings, and in certain metabolic disturbances in children. A. G. P.

**Glycolytic activity of blood-corpuscles of normal and diabetic persons.** A. CURATOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 262—263).—The glycolytic activity of washed corpuscles from diabetic blood is < normal. F. O. H.

***In-vitro* and *in-vivo* action of insulin on glycolysis of blood-corpuscles.** A. CURATOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 264—265).—The glycolysis of corpuscles of non-diabetic persons is unaffected, whilst that of corpuscles of diabetics is diminished, by injection or *in-vitro* addition of insulin. F. O. H.

**Products of blood-glycolysis.** R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1936, 11, 267—268).—The discrepancy between glucose metabolised and lactic acid (insufficiently) formed by suspension of normal corpuscles in glucose-Ringer's solution at 37° is at least partly due to formation of acid-hydrolysable complexes. F. O. H.

**Formation of a phosphorylated compound during *in-vitro* glycolysis.** R. INDOVINA (Boll. Soc. ital. Biol. sperim., 1936, 11, 268—269).—Incubation of suspensions of normal blood-corpuscles in glucose-Ringer's solution at 37° produces a complex which on acid hydrolysis yields inorg. P. F. O. H.

**Electric impedance of injured and sensitised red blood-corpuscles.** H. J. CURTIS (J. Gen. Physiol., 1936, 20, 105—109).—No change in the electrical properties was detected in suspensions injured or sensitised up to the point of hæmolysis. H. G. R.

**Properties of red cell surfaces influencing rouleau formation.** H. L. WHITE and B. MONAGHAN (Amer. J. Physiol., 1936, 115, 31—37).—The sinking velocity of red cells of different species in 1% gelatin  $\propto$  their electrophoretic mobilities at  $pH$  7.4 and inversely  $\propto$  the isoelectric point of the ghosts. Stability in gelatin depends on the free surface energy at the cell-medium interface, which is largely determined by the degree of hydration, and, in turn, by the chemical structure of the cell surface. The surface probably consists of a combination of protein and lipin, the proportion varying with the species. The isoelectric points of washed dog, ox, and rabbit ghosts are 2.7, 3.4, and 4.3, respectively, and are a closer approach to the isoelectric points of intact cells than can be obtained by working with intact cells. R. N. C.

**Changes in the permeability to glucose of red corpuscles in shed blood.** J. M. D. OLMSTED (Amer. J. Physiol., 1936, 114, 488—490).—Glucose increases rapidly in human corpuscles after the blood has been drawn. The rate of increase in rabbit corpuscles is considerably less, whilst pigs' corpuscles remain impermeable. R. N. C.

**Effect of hæmorrhage on hæmoglobin content and distribution in erythrocytes.** A. G. ZOCCOLI and A. DE NIEDERHAUSEN (Boll. Soc. ital. Biol. sperim., 1936, 11, 317—318).—Hæmorrhage of 20% of the circulating blood increases the size and hæmoglobin (I) content of the erythrocytes; with severe hæmorrhage the content of (I) per unit vol. and superficial area of the erythrocytes increases. F. O. H.

**Hæmoglobin and iron of the blood. I. Determination of the total iron of blood.** H. I. COOMBS (Biochem. J., 1936, 30, 1588—1591).—The sample (0.1 ml.) is ashed with  $H_2SO_4$  and  $HNO_3$ , and dipyrityl, glucose, and NaOAc are added. A pink colour develops during 5 min. at 100°; this is stable, and unaffected by Cu or  $PO_4'''$ . F. A. A.

**Availability of copper from various sources as a supplement to iron in hæmoglobin formation.** M. O. SCHULTZE, C. A. ELVEHJEM, and E. B. HART (J. Biol. Chem., 1936, 115, 453—457).—The Cu of wheat germ, lucerne, brewers' yeast, pig's heart and liver, cysteine  $Cu^I$  mercaptide (A., 1933, 382), and Cu aspartate, citrate, nucleinate, and pyrophosphate, in amounts equiv. to 0.01 mg. daily, is readily utilised by anæmic rats to supplement Fe (0.5 mg. daily) for hæmoglobin formation. F. A. A.



**Hæmoglobin regulation in chickens. I. W. HARMON** (Poultry Sci., 1936, 15, 53—62).—The hæmoglobin (I) level was highest at hatching and at maturity and lowest at 2 weeks of age. Sexual differences in level were not apparent until 8 weeks of age, and in mature birds were in the order, cocks > capons > hens. A splenic reserve of (I) occurs in capons, hens, and 10-week cockerels and pullets, but not in cocks or broody hens. Vals. declined during egg production, but were higher in heavy than in poor layers in corresponding stages. Onset of broodiness and cessation of laying were marked by a rapid increase in (I) vals. A. G. P.

**Ultra-violet absorption spectrum of hæmoglobin. G. A. ADAMS** (Nature, 1936, 138, 368).—Addition of stromatin (I) causes the 410 m $\mu$  absorption band of hæmoglobin (II) to disappear. In red blood (II) may be combined with (I), and the combination may be responsible for the absence of this band in corpuscular (II) (cf. A., 1934, 673). Cholesterol, lecithin, and glutathione have not this effect. L. S. T.

**Methylene-blue and hæmoglobin derivatives in asphyxial poisoning. M. M. BROOKS** (Amer. J. Physiol., 1935, 114, 160—178).—KCN stabilises the colour of oxyhæmoglobin by forming cyanohæmoglobin, which has the same spectrum; it attaches itself to the Fe ion of hæmoglobin (I) or methæmoglobin (II). Methylene-blue does not form (II) in the blood-stream or defibrinated blood, with or without KCN; it acts as a catalyst rather than as a (I) producer. Reducing agents in the blood-stream, including glucose, prevent (II) formation. NaNO<sub>2</sub> produces (II) when in sufficient concn. to overcome the reducing capacity of the blood. Cryst. derivatives of (I) do not give the above results, owing to the absence of reducing agents. R. N. C.

**Plasma-protein regeneration after bleeding in the rat. W. C. CUTTING and R. D. CUTTER** (Amer. J. Physiol., 1935, 114, 204—206).—Total proteins recover their original val. 12 hr. after bleeding; the regeneration is decreased by injection of Indian ink. R. N. C.

**Crystallisation of serum-albumin from different species. M. GRINSTEIN** (Anal. Asoc. Quím. Argentina, 1936, 24, 11—18).—The cryst. form of serum-albumin from man differs from that from the guinea-pig, horse, mule, and ass, those from the last three species being indistinguishable from one another. F. R. G.

**Protein content of the serum of ungulates. A. URBAIN and R. CAHEN** (Compt. rend., 1936, 203, 277—279).—The total protein of sera of various species (both ruminants and non-ruminants) is similar to that of human serum, except that in sheep it is less, and in equidæ it is slightly higher. P. G. M.

**Determination of serum-proteins. K. PLOTNER** (Biochem. Z., 1936, 286, 429—434).—The mean sp. refraction of 22 samples of pathological human serum-protein was 0.00188, a val. agreeing with the accepted val. for horse serum (0.00187). Considerable changes in globulin content do not significantly change the val. P. W. C.

**Nephelometry of blood-proteins. III. Nature of the protein-sulphosalicylic acid turbidity reaction. Interrelationship of serum-proteins. K. PLOTNER** (Biochem. Z., 1936, 286, 279—284).—The sulphosalicylic acid turbidity val. of an albumin (I) solution on addition of small amounts of globulin (II) considerably decreases and, after reaching a min.,  $\propto$  the added (II). The results are explained by assuming that a mol. complex of (II) and (I) (1 : 2) is formed (cf. this vol. 1008). P. W. C.

**Simplification of micro-methods. I. Micro-determination of non-protein-nitrogen of blood. J. PUYAL and A. KUTZ** (Anal. Fís. Quím., 1934, 32, 742—747).—The blood is deproteinised by the Hagedorn method and the residual N determined by a micro-Kjeldahl method. The process is quicker and more accurate than that of Bang. L. A. O'N.

**Urate distribution in blood. J. H. TALBOTT and J. M. SHERMAN** (J. Biol. Chem., 1936, 115, 361—370).—The concn. of urate (I) in serum and cells agrees approx. with the Donnan law applied to blood. The (I) distribution ratio between cells and serum increases with acidity at approx. the same rate as the Cl' ratio. Oxygenation and reduction of blood containing added (I) change the distribution of (I) in the same way as Cl' and HCO<sub>3</sub>'. The max. concn. of serum-(I) observed was 1.63 milliequiv. per litre. E. M. W.

**Cholesterol. H. W. SOPER** (Amer. J. Digest. Dis. Nutrition, 1935, 2, 381—382).—A summary of recent investigations of blood-cholesterol and its influence on dietary habits. CH. ABS. (p)

**Fractionation of cholesterol in blood by precipitation as pyridine cholesteryl sulphate and cholesterol digitonide. J. J. DREKTER, A. E. SOBEL, and S. NATELSON** (J. Biol. Chem., 1936, 115, 391—399).—Determination of free cholesterol (I) after pptn. as C<sub>5</sub>H<sub>5</sub>N cholesteryl sulphate gives vals. of 6—10% as opposed to 25—35% after pptn. as (I) digitonide. The former method gives higher vals. for total (I). (I) may exist in serum in a "loosely-bound" form pptd. only by digitonin. In erythrocytes most of the (I) is "unbound," i.e., pptd. by either method. E. M. W.

**"Bound" sugar of the blood. I. Influence of protein-fat diets and relation to free blood-sugar. II. Influence of fasting and relation to free blood-sugar. Y. MATSUOKA** (J. Biochem. Japan, 1936, 23, 161—170, 171—179).—I. Fat-protein diets have little effect on the combined sugar (I) of dog's blood. With mixed carbohydrate diets, orally administered glucose produces a slight decrease which is enhanced by supplementing the diet with fat+protein but not with fat+protein+carbohydrate. High vals. of (I) are associated with low vals. of free sugar (II).

II. Fasting for 1 week has no effect, whilst fasting for 3 weeks slightly decreases (I). The increase in (I) due to carbohydrate ingestion after a week's fast is > that after 3 weeks' fast; continued ingestion results in a rapid return of (I) to normal vals. High levels of (I) are again associated with low vals. of (II). F. O. H.

**Influence of vagi and splanchnics on blood-sugar response to glucose administration.** M. AISNER, A. J. GORNEY, and M. S. SEGAL (Proc. Soc. Exp. Biol. Med., 1936, 34, 454—459).—The tolerance of dogs to glucose administered intravenously was not increased by vagotomy. Removal of one adrenal and denervation of the other resulted in a slight but probably insignificant increase in tolerance, whilst celiac ganglionectomy produced no additional effect.

W. O. K.

**Blood-sugar. II. Reduction values of tungstate and mercuric filtrates. Existence of a supposed glucose ester. I.** M. LORA TAMAYO (Anal. Fis. Quim., 1934, 32, 858—867).—Filtrates from blood deproteinised by the Folin-Wu method have a glucose (I) content (determined by the author's method; A., 1934, 793) > that of filtrates from Bierry and Moquet's reagent. The probable causes are discussed and it is shown that in presence of inorg.  $\text{PO}_4'''$ , (I) is carried down in the Hg ppt. F. R. G.

**Blood-phosphorus. V. Acid and enzymic hydrolysis of the acid-soluble organic phosphorus. Phosphoglycerate fraction.** E. WARWEG and G. STEARNS (J. Biol. Chem., 1936, 115, 567—581).—Acid-hydrolysis of filtrates of human blood deproteinised with  $\text{CCl}_3\cdot\text{CO}_2\text{H}$  is rapid for the first 10 min., the hexose diphosphate being rapidly and the  $\beta$ -glycerophosphate very slowly destroyed. The reaction slows down until after 12 hr. a const. slow rate (unimol. reaction) is attained, the acid-resistant substance being probably phosphoglycerate (I). The org. P is at first more readily hydrolysed by phosphatase at  $p_{\text{H}}$  8.8, but after 24 hr. the optimum shifts to 7.4, which is the same as that of (I) from pig's blood. The ester-P of adult blood consists of approx. 62—75% of (I)-P and 11.4% of  $\text{P}_2\text{O}_7'''$ -P.

H. G. R.

**Blood-sugar, inorganic phosphorus, and phosphatase activity following the intravenous injection of calcium salts.** A. CANTAROW, J. T. BRUNDAGE, and E. L. HOUSEL (Amer. J. Physiol., 1936, 115, 1—4).—Ca gluconate or levulate produces in the dog a rise of blood-protein, a rapid fall of sugar, a slower fall of inorg. P, and variable and insignificant changes in serum-phosphatase activity. R. N. C.

**Partition of serum-calcium.** J. DUCKWORTH and W. GODDEN (Biochem. J., 1936, 30, 1560—1566; cf. A., 1935, 385).—Determinations of  $\text{Ca}^{++}$ , ultrafilterable, non-ultrafilterable, protein-bound, and total Ca, inorg. P, and protein in the blood-serum of lambs on a basal diet supplemented with maize starch, and of these Ca fractions, inorg. P, and Mg in the serum of a cow after injection of large amounts of aq. Na citrate and in cow's blood *in vitro* after addition of aq. Na citrate indicate that K in the equation of Maclean *et al.* (Amer. J. Med. Sci., 1935, 189, 601) is too variable to aid in the study of Ca partition. The four Ca fractions found by adsorption on  $\text{BaSO}_4$  and ultrafiltration are real entities. W. McC.

**Partition of calcium and inorganic phosphorus in the blood-sera of horses.** P. B. PEARSON and H. R. CATCHPOLE (Amer. J. Physiol., 1936, 115, 90—93; cf. this vol., 497).—Inorg. P in the serum of Shetlands is > that in other species. There is no

correlation between total Ca and inorg. P, but significant correlation between total and diffusible Ca and inorg. P. R. N. C.

**Cataphoretic investigation of the state of copper in blood-serum.** B. EISLER, K. G. ROSDAHL, and H. THEORELL (Biochem. Z., 1936, 286, 435—438).—The total Cu of blood-serum is united with the serum-albumin. P. W. C.

**Photometric micro-determination of iron in blood.** G. BUCCIARDI (Boll. Soc. ital. Biol. speriment., 1936, 11, 316—317).—Blood is ashed, oxidised by  $\text{HNO}_3$ , heated with  $\text{H}_2\text{SO}_4\text{--HNO}_3$  followed by  $\text{H}_2\text{O}$ , and, after removal of  $\text{HNO}_3$  by urea,  $\text{Fe}^{+++}$  is determined by addition of  $\text{NH}_4\text{CNS}$  and photometric determination of extinction coeff. F. O. H.

**Regulation of the mineral composition of body-fluids in fishes.** A. DRILHON and E. A. PORA (Ann. Physiol. Physicochim. biol., 1936, 12, 139—168).—The osmotic pressure of the serum in the carp is normally > that of the surrounding  $\text{H}_2\text{O}$  but, if the salinity of the  $\text{H}_2\text{O}$  is increased by addition of sea- $\text{H}_2\text{O}$ , the internal osmotic pressure is unaltered until the f.p. depression of the external medium reaches  $-0.67^\circ$ . Above this val. the serum is at first hypotonic and equilibrium with more conc. solutions is associated with increase of Na, K, and Ca in the serum. The muscles and not the gills are the chief regulators of the composition of the internal medium. The proteins are stable and unaffected by changes in salinity of the ambient medium. NUTR. ABS. (m)

**Physical chemistry of fish blood.** A. DRILHON and G. FLORENCE (Bull. Soc. Chim. biol., 1936, 18, 1055—1073).—A study of the buffering power of the serum and the cataphoresis of the serum-proteins shows that during the adaptation of the eel with its protective mucus from fresh to sea- $\text{H}_2\text{O}$  there is a slow diminution in the alkaline reserve without any change in the protein equilibrium. Without the mucus, however, the change in alkaline reserve is rapid and a slight change in the protein equilibrium takes place. Substitution of aq. KCl for sea- $\text{H}_2\text{O}$  causes no change in the alkaline reserve, but a displacement of the isoelectric point of the serum-proteins. When the salt- $\text{H}_2\text{O}$  fish *Muræna* is placed in fresh  $\text{H}_2\text{O}$ , there is a displacement of the isoelectric point of the serum-proteins, although the fish is unaffected by a change to a greater degree of salinity. A. L.

**Determination of blood- $p_{\text{H}}$  by the glass electrode. IV. Potential drift of quinhydrone electrode applied to solutions of alkaline buffer, amino-acids, or proteins, or to plasma.** H. YOSHIMURA (J. Biochem. Japan, 1936, 23, 187—210; cf. A., 1935, 1143).—The potential drift is due to a chemical change in benzoquinone (I) producing acidic products to an extent dependent on temp., concn. of solution, and  $p_{\text{H}}$ . A secondary cause is autoxidation of quinol (II) to (I). Saturation of solutions of  $p_{\text{H}} > 5$  with (II) produces a slight acidification due to dissociation of (II). Determinations accurate to 0.02  $p_{\text{H}}$  are afforded by measurements taken within the following times: aq. buffer up to  $p_{\text{H}}$  8, 5 min.; aq.  $\text{NH}_2$ -acid or protein, 1 min.; plasma 30 sec. F. O. H.



**Validity of determinations of the  $p_H$  of whole blood at 38° with the glass electrode.** J. SENDROY, jun., T. SHEDLOVSKY, and D. BELCHER (J. Biol. Chem., 1936, 115, 529—542).—With citrate,  $PO_4'''$ , and  $HCO_3'-CO_3''$  buffers the  $p_H$  as determined by the Clark-Cullen (C) H electrode and MacInnes-Belcher glass electrodes A (A., 1933, 689) and B (thin membrane type) were consistent, but with reduced whole blood at various  $CO_2$  tensions, A deviated by a mean of  $-0.011$  from the val. given by C. When standardised with  $0.1N-HCl$ , B gave a val.  $0.02 <$  that of C, whilst A gave a similar but less consistent error.

H. G. R.

**Relation between viscosity of the blood and the relative volume of erythrocytes (haematocrit value).** K. K. NYGAARD, M. WILDER, and J. BERKSON (Amer. J. Physiol., 1935, 114, 128—131).—The relation is linear with a haematocrit val.  $<60\%$ , but above this val.  $\eta$  increases more rapidly.

R. N. C.

**Control of the circulation of the blood.** R. J. S. McDOWALL (Nature, 1936, 138, 488—491).—An extract from an address to the British Association.

L. S. T.

**Blood groups, blood transfer, and blood substitutes.** A. VON DOMARUS (Naturwiss., 1936, 24, 593—600).—A review.

**Accelerating effect of pectin on blood coagulation.** O. RIESSER (Klin. Woch., 1935, 14, 958—961; Chem. Zentr., 1935, ii, 3943).—Intramuscular, intravenous, or oral administration of pectin (I) to dogs shortened the coagulation time without producing secondary effects. The action is related to the acid reaction of (I).

A. G. P.

**Action of formaldehyde on blood coagulation.** A. FISCHER (Enzymologia, 1936, 1, 85—91).— $CH_2O$  inhibits blood clotting by embryo extract. Combination with  $-NH_2$  is suggested.

E. D. Y.

**Role of bivalent metals in the reversible inactivation of jack-bean haemagglutinin.** J. B. SUMNER and S. F. HOWELL (J. Biol. Chem., 1936, 115, 583—588).—Concanavalin-A (I) loses its agglutinating properties (A., 1935, 1143) on contact with dil. mineral acids: this is due to decomp. of Ca, Mn, and Mg compounds and is recovered on neutralisation. Metal-free (I) does not crystallise readily.

H. G. R.

**Specific nature of the inhibition of the coagulating effect exerted by tissue extracts on plasma resulting from incubation of tissue extract with blood-serum.** C. MOORE, V. SUNTZEFF, and L. LOEB (Amer. J. Physiol., 1935, 114, 1—18).

**Blood-clotting: prothrombin fluctuations under experimental conditions.** E. D. WARNER, K. M. BRINKHOUS, and H. P. SMITH (Amer. J. Physiol., 1936, 114, 667—675).—Prothrombin (I) in plasma is determined accurately by conversion into thrombin (II) and measurement of the time of coagulation of fibrinogen (III). The normal (I) content of dog plasma is sufficient to form 200 times the amount of (II) necessary to clot (III) in a few sec., but unless thromboplastin is present in large quantities most of the (I) is not utilised. (I) varies slightly in the plasma from different dogs, but is const. in a single animal,

being unchanged by repeated hæmorrhage or drastic diet changes.  $CHCl_3$  and P poisoning decrease (I) and (III); with  $CHCl_3$  (I) falls before (III) and returns to normal more slowly. (I) remains normal in distemper and turpentine abscess, and in plasma rendered incoagulable by intravenous injection of peptone, or by heparin *in vitro*. Indian ink causes a slight reduction.

R. N. C.

**Properties of thromboplastin (aqueous tissue extracts).** A. J. QUICK (Amer. J. Physiol., 1936, 114, 282—296).—The time of clotting by tissue extracts decreases as the concn. of the extracts increases until a min. val. is reached, beyond which no further decrease takes place. The thromboplastin (I) concn. in extracts of rabbit brain, lung, and thymus is of the same order. The extracts do not clot purified fibrinogen or prothrombin-free plasma. Extraction of brain extract with fat solvents reduces considerably the thromboplastic potency of the solution, but the extract obtained is only slightly active. The activity of the aq. extracts falls with rising temp., brain extract being less stable than lung extract. The activities of extracts from different animals vary with the species.

R. N. C.

**Action of heparin and its relation to thromboplastin.** A. J. QUICK (Amer. J. Physiol., 1936, 115, 317—333).—The clotting time of plasma is inversely  $\propto$  the thrombin (I) concn.; a corrective factor in the equation decreases with increasing concn. of neutral salts. The relationship is destroyed by minute amounts of heparin (II). (II) is not an antithrombin (III), since it inhibits (I) only slightly with purified fibrinogen, but apparently reacts with a plasma constituent to form a (III). Neutral salts are necessary for the reaction. (II) inhibits clotting of prothrombin-free plasma by (I), the inhibitory effect not being influenced by excess of thromboplastin (IV) and Ca in optimal concn. (II) also inhibits the acceleration in clotting of oxalated plasma by excess of (IV) and Ca in optimal concn.; these results indicate that (IV) does not neutralise (II).

R. N. C.

**Inhibiting action of cattle and sheep serum on kidney extracts of cattle and sheep.** E. W. THURSTON, J. E. SMADEL, and L. LOEB (Amer. J. Physiol., 1935, 114, 19—24).—The inhibition curve obtained by addition to the mixture of extract and serum of heparin or a Ca inactivator shows the typical form; it results from inactivation of tissue-coagulin and destruction of thrombin during incubation.

R. N. C.

**Serologic relation of *Brucella* and *Pasteurella*.** L. E. STARR and G. E. SNIDER (J. Infect. Dis., 1934, 55, 384—389).—Cross-agglutination between *Brucella* and *Pasteurella* in cattle sera is demonstrated.

CH. ABS. (p)

**Testing of therapeutic serum. I. Antipneumococcus serum *in vivo* and *in vitro*.** L. COTONI and J. POCHON (Ann. Inst. Pasteur, 1936, 57, 221—239).—A review of methods for testing sera *in vivo* and *in vitro*. A method which uses the neutralisation of the antibody *in vitro* is described, together with the prep. of the antigen, bacterial emulsion, and solution of the polysaccharide. Advantages are sim-

plicity, rapidity, and economy of material. A serum-standard is not needed.

J. N. A.

**Blood-coagulating substance produced by staphylococci, and its relation to disease.** M. PIJOAN (Canad. Med. Assoc. J., 1935, 33, 476—481).—Staphylococci generally may produce a toxin, leucocidin, haemolysin, necrotoxin, staphylokinase (I), and a fibrinolysin. (I) can be washed from the surface of organisms, is destroyed at 85°, and coagulates oxalated plasma. Clot formation does not depend on the Ca-thrombin mechanism.

CH. ABS. (p)

**Antigenic reactions of *Staphylococcus aureus* and its variants.** R. E. HOFFSTADT and G. P. YOUNG (J. Infect. Dis., 1935, 56, 288—296).—Rough and gonidial forms of *S. aureus* afford no protection against smooth and virulent forms. All strains contain heat-stable antigenic fractions in common. Gonidial forms contain a heat-labile fraction in common with rough and smooth forms.

CH. ABS. (p)

**Composition of the active principle of tuberculin. XIX. Differences in antigenic properties of various tuberculin fractions; adsorption on aluminium hydroxide and charcoal.** F. B. SEIBERT (J. Immunol., 1935, 28, 425—432; cf. A., 1933, 1933).—A purified potent tuberculin-protein derivative was unable to stimulate the production of antibodies but reacted specifically with the antibodies when they were formed by means of the whole tuberculin-protein mol. When injected in a particulate form [adsorbed on  $\text{Al}(\text{OH})_3$  or C] it stimulated the production of antibodies and inhibited the precipitin reaction between the whole tuberculin-protein antigen and its antibodies.

CH. ABS. (p)

**Polysaccharide of the typhus bacillus. III. Agglutinin titre in rabbits.** A. SPANEDDA (Boll. Soc. ital. Biol. sperim., 1936, 11, 327—328; cf. this vol., 1010).—Repeated intravenous injection of the polysaccharide produces decreasing febrile reactions, whilst the agglutinin titre increases up to the 4th injection and then slowly falls to a zero val. with subsequent injections; this is probably due to the formation of a sp. antibody.

F. O. H.

**Union with complement as a surface reaction.**—See this vol., 1335.

**Electric impedance and permeability of living cells.** J. F. McCLENDON (Science, 1936, 84, 184—185).

L. S. T.

**Oxygen and carbon dioxide tensions in the subcutaneous tissues of normal subjects.** M. H. SEEVERS (Amer. J. Physiol., 1936, 115, 38—42).—The tensions are of the same order as those previously found for other homothermal animals by the gas depot method. Final equilibrium between the gas pocket and the surrounding tissues is reached only after 5—7 days, when the foreign body reaction has subsided. After this time the partial pressure of  $\text{CO}_2$  remains practically const., whilst that of  $\text{O}_2$  varies considerably.

R. N. C.

**Micro-determination of fluorine [in dental enamel and dentine].**—See this vol., 1351.

**Chloride and total base contents of tendon and cartilage.** M. WHELAN and H. A. SHOEMAKER (Amer. J. Physiol., 1936, 115, 476—479).—Analytical data are given for muscle, skin, tendon, and cartilage from various sources.

R. N. C.

**Distribution of iron in certain tissues of normal and anæmic albino rats.** G. WAKEHAM and H. F. HALENZ (J. Biol. Chem., 1936, 115, 429—434).—The prep. and testing of blood-free tissue are described. The Fe content of the washed tissues of normal rats is in the decreasing order: liver, heart, kidney, striated muscle. In anæmic rats, heart contains > liver, but all three lose Fe.

E. M. W.

**Determination of sulphur in the extract of the silk-rind of cocoons.** G. COLA (Boll. uff. R. Staz. sperim. Seta, 1935, 5, 46; Chem. Zentr., 1935, ii, 4000).—A method of oxidation, followed by pptn. as  $\text{BaSO}_4$ , is described.

H. N. R.

**Composition of the eggs of *Taeniarhynchus saginatus* and *Diphylllobothrium latum*.** I. A. SMORODINCEV and P. I. PAVLOVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 29—31).—The eggs of the two species contain, respectively,  $\text{H}_2\text{O}$  72.6, 77.19, org. matter 26.59, 22.30, ash 1.15, 0.66, N 3.57, 3.32, lipins 4.95, 6.88%. In both cases the composition of the eggs differs greatly from that of the worm.

W. McC.

**Phosphagen in echinoid muscle and in electrical tissue.** E. BALDWIN and D. M. NEEDHAM (Nature, 1936, 138, 506).—The partition of P in the electrical tissue of *Torpedo* resembles that in the muscles of the rat and the frog. This tissue, like muscle, contains enzymes capable of catalysing the reactions: phosphoglyceric acid  $\rightarrow$  phosphopyruvic acid (I); (I) + adenylic acid (II)  $\rightarrow$  adenylyl pyrophosphate (III) +  $\text{AcCO}_2\text{H}$ ; (III) + creatine  $\rightarrow$  (II) + phosphagen; and (III)  $\rightarrow$  (II) +  $\text{H}_2\text{PO}_4$ . Certain phosphorylated compounds in presence of enzyme extracts from the jaw muscles of *Sphaerechinus granularis* synthesise two phosphagen-like compounds from creatine and arginine, respectively. Echinoid jaw muscle contains enzymes similar to, if not identical with, those reported above.

L. S. T.

**Liver-glycogen. IV. Molecular structure of glycogen formed after ingestion of galactose by fasted rabbits.** D. J. BELL (Biochem. J., 1936, 30, 1612—1616, and Nature, 1936, 138, 289).—The livers of galactose-fed rabbits and the whole tissue of *Mytilus edulis* yield glycogen,  $[\alpha]_D +201^\circ$  in  $\text{H}_2\text{O}$ , containing 18 glucose units per mol., compared with 12 for normal glycogen, but with no other significant difference.

F. A. A.

**New Zealand fish oils. I. Composition of eel oil (*Anguilla Aucklandii*).** F. B. SHORLAND and I. G. MCINTOSH (Biochem. J., 1936, 30, 1775—1777).—The body- and, more especially, the liver-oil contain vitamin-A. The body-oil (yield 7%; sap. val. 290.4, I val. 122.5) contains 0.8% of unsaponifiable matter. The % of fatty acids resembles those of oils of fresh- $\text{H}_2\text{O}$  fish examined by Lovern (A., 1933, 183). The production of dihydroxystearic acid by oxidation of the  $\text{C}_{18}$  unsaturated acids with



alkaline  $\text{KMnO}_4$  and the results of bromination indicate the presence of oleic and stearidonic acid. No evidence was found of the presence of linoleic or linolenic acid. W. McC.

**Absence of *allocholesterol* from the organism.** E. A. EVANS, jun. (J. Biol. Chem., 1936, 115, 449—451).—No *allocholesterol* (I) is found in the yolk of hens' eggs, using as a test for (I) the ultra-violet absorption spectrum of  $\Delta^{2:4}$ -cholestadiene obtained when (I) is dehydrated in the presence of acid; this test would indicate 0.01% of (I). F. A. A.

**Pigments of the retina. II. Sea robin, sea bass, and scup.** G. WALD (J. Gen. Physiol., 1936, 20, 45—56; cf. this vol., 1012).—The visual purple (I) in all cases is practically identical, spectroscopically, with that from frogs and the combined pigment epithelium and choroid layer contain vitamin-A, flavin, and an unidentified xanthophyll. The visual yellow of the sea robin retina is irreversibly converted into a  $p_H$  indicator at  $p_H > 11$ . This is not removed to form (I) or -A. H. G. R.

**Microchemical detection of pterins in insects.** E. BECKER and C. SCHOPF (Annalen, 1936, 524, 124—144).—The detection of leucopterin is based on the separation of the yellow, cryst. Na salt, the stable Ag salt, and the violet-blue fluorescence of its feebly alkaline solutions. Xanthopterin (I) gives a sharply-defined yellow band which shows an intense yellowish-green fluorescence when adsorbed by  $\text{Al}_2\text{O}_3$  from 0.01%  $\text{HCl-MeOH}$ ; since the breadth of the band  $\propto$  the amount of pigment if the vol. of the solution is restricted an approx. determination may be made. Development by dil. acid decomposes the pigment. The adsorptive power of  $\text{Al}_2\text{O}_3$  from 0.004*N*- $\text{HCl}$  is considerably less. In 20%  $\text{H}_2\text{SO}_4$  (I) yields a solution with weak but distinct red fluorescence. With somewhat greater amounts the separation of the  $\beta$ -Ba salt is possible. There is no certain method for the microchemical differentiation of (I) and chrysopterin (II). The sole difference is that (II) is more readily adsorbed than (I) from dil. aq.  $\text{HCl}$  so that homogeneous (II) gives a distinct band and is thus readily detected. In insects, (II) is usually associated with much (I). Detection of small amounts of erythropterin depends on adsorption from dil. acid solution by  $\text{Al}_2\text{O}_3$ . With natural mixtures, 0.004*N*- $\text{HCl}$  is more suitable than  $\text{MeOH-HCl}$  since it alone affords a clear band of orange colour and dull brown fluorescence. Guanopterin does not give characteristic colour or fluorescence reactions but the characteristic sulphate may be isolated from 0.1—0.2 mg. of material. In the examination of insects for pterins the localisation of pigment at definite positions in the integument, its mode of deposit in the skin tissue, and its microscopic-optical behaviour are as important as the chemical reactions. Preliminary treatment with  $\text{Et}_2\text{O}$  and boiling  $\text{EtOH}$  only is required but insects should be preserved, if necessary, in abs.  $\text{EtOH}$ . The pigments are obtained by two extractions with cold 0.5*N*- $\text{NH}_3$  followed by a single extraction with 2*N*- $\text{NH}_3$ . The united extracts are clarified and evaporated over  $\text{KOH}$  and  $\text{H}_2\text{SO}_4$ . The subsequent treatment depends on the colour of the residue and is illustrated by several examples. H. W.

**New pterins.**—See this vol., 1260.

**Determination of indoxyl in presence of indole in animal tissue.** J. GARCÍA-BLANCO, J. NACLE, and C. HERNÁNDEZ (Anal. Fis. Quím., 1935, 33, 98—104).—Indole (I) is extracted with  $\text{Et}_2\text{O}$  and the indoxyl (II) determined colorimetrically in the acidified solution by means of Obermayer's reagent. (I) increases the amount of (II) lost from the blood and kidney but not the liver of rabbits, during pptn. of the proteins. F. R. G.

**Denaturation and hydration of proteins. II.** NEURATH and H. B. BULL (J. Biol. Chem., 1936, 115, 519—528).— $d$  of natural ovalbumin is  $<$  that of heat- or surface-denatured ovalbumin. The vals. for the max. vol. contraction in  $\text{H}_2\text{O}$  are 53, 24.5, and 30 cu. mm. per g., respectively. The vol. contractions have also been measured in various  $\text{EtOH-H}_2\text{O}$  mixtures. H. G. R.

**Nature of paranuclein.** J. D. HERD (Biochem. J., 1936, 30, 1743—1752).—The rates at which N and P of paranuclein (I) (A., 1926, 970) are rendered sol. in 10%  $\text{CCl}_3\text{-CO}_2\text{H}$  by hydrolysis with pepsin, trypsin, papain, and 10%  $\text{NaOH}$  indicate a P-free, alkali-resistant nucleus containing 20% of the initial N of (I). Data from hydrolyses, physical properties,  $\text{NH}_2$ -acid distribution, and combination with I show (I) to consist of two fractions. F. O. H.

**Liver-proteins. I. Storage of protein.** J. M. LUCK (J. Biol. Chem., 1936, 115, 491—510).—Protein from the blood-free livers of rats may be extracted at 0—3° as four fractions, corresponding with globulin-II, euglobulin, pseudoglobulin, and albumin. In rats kept on a low-protein diet, the amounts in these fractions are 5.07, 4.58, 1.06, and 0.86 g. per 100 g. of liver, respectively. On a high-protein diet these vals. are all 50—60% higher, indicating that no single protein can be regarded as especially involved in protein storage in the liver. On the high-protein diet, the liver increases in wt. as well as in % protein. Under the conditions observed, other organs do not participate in protein storage. F. A. A.

**Polysaccharoproteins. X. Rôle of individual amino-acid residues.** S. J. VON PRZYBYCKI, K. KASPRZYK, and H. RAFAŁOWSKA (Biochem. Z., 1936, 286, 360—372).—Ovalbumin, lactalbumin, pseudoglobulin, globin, and histone of erythrocytes (goose) have no affinity for P-free polysaccharides (I). Euglobulin, ovoglobulin, fibroin, gelatin, edestin, clupcin, and myosin form symplexes (II) with (I), whilst serum-albumin and caseinogen unite only to a slight extent. The formation of (II) is not dependent on the protein particle size or physical structure nor on the presence of impurities, but (II) are formed only by those proteins which contain considerable amounts of tyrosine or arginine. P. W. C.

**Cross-linking formation in keratins.**—See this vol., 1396.

**Enzymic histochemistry. XVIII. Localisation of peptidase in marine ova.** H. HOLTER (J. Cell. Comp. Physiol., 1936, 8, 179—200).—Peptidase activity, in the three species examined, is localised in

the hyaline ground substance (matrix) of the cytoplasm, and is not bound to granular matter.

E. A. H. R.

Colloid osmotic pressure of the body-fluids of fresh-water animals. P. MEYER (Nature, 1936, 138, 287—288).—The vals. are in order of phylogenetic development, but are 20—35% < those of the corresponding marine animals.

L. S. T.

Abnormal fluorescence of human milk. C. GRIEBEL (Z. Unters. Lebensm., 1936, 72, 46—50).—Abnormalities are recorded due to (a) ingestion of 1:8-dihydroxyanthraquinone, (b) a vegetarian diet, and (c) the presence of unidentified cells in the milk.

E. C. S.

Composition of the envelopes of milk-fat globules. G. SCHWARZ and O. FISCHER (Milch. Forsch., 1936, 18, 53—67).—The material surrounding milk-fat globules was isolated by repeatedly washing cream with aq. NaCl, churning, separating butter fat, and pptn. with COME<sub>3</sub>. The material contained ash 6.95, N 11.25, S 1.12, and P 0.61% in the dry matter. Its protein nature was established and its N distribution determined.

W. L. D.

Rennet test [for milk]. M. F. DUNGERN and G. NELZ (Milch. Forsch., 1936, 18, 46—52).—A semi-micro-method described involves an apparatus similar to that used in the Bürker test for the time of blood clotting. The method is trustworthy under various conditions of temp. and milk acidity.

W. L. D.

Determination of calcium diffusing from milk during compensated dialysis. G. SARZANA (Boll. Soc. ital. Biol. sperim., 1936, 11, 266—267).—Dialysis against isotonic aq. KCl of varying [Ca<sup>++</sup>] gives a diffusible Ca fraction of 18—19 and 37—50% for cow's and human milk, respectively, whilst ultrafiltration gives 30—37 and 44—67%, respectively.

F. O. H.

Factors influencing the lactose content of milk. W. E. PETERSEN (Proc. Amer. Soc. Animal Prod., 1936, 58—63).—Increasing the blood-glucose (I) beyond normal levels did not materially increase the lactose (II) content of milk. Lowering (I) or leaving the milk in the udder caused a decline in (II).

NUTR. ABS. (m)

Use of ammonium sulphate serum of milk in serological investigations. M. F. BENGEL and E. BOHM (Z. Unters. Lebensm., 1936, 72, 92). H. KLUGE (*ibid.*, 92).—Polemical (cf. *ibid.*, 71, 405).

E. C. S.

Forces concerned in the absorption of the cerebrospinal fluid. L. H. WEED (Amer. J. Physiol., 1935, 114, 40—45).—The total effective force is compounded of the colloid-osmotic pressure of the blood and a hydrostatic factor.

R. N. C.

Reducing substance in human cerebrospinal fluid. M. MITOLO (Boll. Soc. ital. Biol. sperim., 1936, 11, 332—334).—0.5 c.c. of the fluid from 22 diseased persons reduces 0.75—4.57 (average 2.12) c.c. of 0.01% 2:6-dichlorophenol-indophenol.

F. O. H.

Determination of ethyl alcohol in saliva. J. C. ABELS (Proc. Soc. Exp. Biol. Med., 1936, 34, 504—505).—EtOH is absent from normal saliva, but in intoxication the EtOH content is closely correlated

with that of the blood and also with the degree of intoxication.

W. O. K.

Effects on gastric secretion in dogs of various food substances employed in the treatment of gastric ulcer. A. ALLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 555—560).—Milk or cream produced continuous secretion, that with cream being more prolonged and that with milk of higher peptic power. Alkalis increase the vol. and acidity of the secretion. Egg-white, butter, and cream of wheat induced small secretion, that with the last named being of high peptic power and low acidity.

CH. ABS. (p)

Effect on gastric juice secretion of various cooked preparations of haddock and of lobster. A. ALLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 182—184).—Lobster caused secretion of shorter duration but of much greater vol., acid and mucin contents than did boiled haddock.

CH. ABS. (p)

Gastric secretagogic value of various digestive secretions. M. S. KIM and A. C. IVY (Amer. J. Physiol., 1936, 115, 386—388).

R. N. C.

Inhibitory effect of the acidity of the gastric contents on the secretion of acid by the stomach. C. M. WILHELMJ, F. T. O'BRIEN, and F. C. HILL (Amer. J. Physiol., 1936, 115, 429—440).—HCl secretion in the dog is progressively inhibited by increasing [HCl] > 0.005N in a Liebig's extract test meal, inhibition being nearly complete at 0.10N. The inhibition is of gastric origin, and is probably not due to hormonal action. The composition of acidic and non-acidic fluids entering the stomach is unaffected by the inhibition.

R. N. C.

Improved gastric test meal and a study of the secretory curve in whole stomach pouches and in the normal intact stomach. C. M. WILHELMJ, F. T. O'BRIEN, and F. C. HILL (Amer. J. Physiol., 1936, 115, 5—22).—The meal contains 15 mg. of phenol-red per litre. Regurgitation of duodenal secretions keeps the [HCl] of the total fluid entering the secreting stomach < the average val. found in isolated pouches. The regurgitated duodenal contents, with a powerful and maintained stimulus e.g., Liebig's extract of meat, are insufficient to lower gastric [H<sup>+</sup>], but prevent or slacken further rise.

R. N. C.

Some properties of Castle's intrinsic factor. C. FLOOD and R. WEST (Proc. Soc. Exp. Biol. Med., 1936, 34, 542—543).—Exposure of normal gastric juice to  $p_{H}$  10.0 for 30 min. destroys peptic activity without materially affecting the intrinsic anti-anæmic factor (cf. A., 1932, 1156). Normal gastric juice produced no reticulocyte response, but, when added to boiled liver, increased the effect of the latter. Purified pepsinogen administered parenterally was inert.

W. O. K.

Volumetric micro-determination of spermine in semen. A. BOLLIGER (Med. J. Australia, 1935, 784—792).—The semen is acidified with CCl<sub>3</sub>-CO<sub>2</sub>H, the filtrate neutralised with CaCO<sub>3</sub>, and the spermine (I) pptd. as picrate, the picric acid content of which is determined by titration with methylene-blue (A.,



1934, 1322). The (I) content varied from 69 to 117 mg. per 100 c.c. of semen. J. N. A.

**Urinary balance and diuresis.** S. BELLUC, J. CHAUSSIN, J. COTTET, H. LAUGIER, and T. RANSON (Compt. rend., 1936, 203, 273—275).—Diuresis bears an inverse relationship to salt concn. P. G. M.

**Phenolsulphonaphthalein renal function test in dogs.** D. A. COLLINS (Amer. J. Physiol., 1936, 115, 27—30). R. N. C.

**Nitrogen partition in urine of various primates.** M. B. RHEINBERGER (J. Biol. Chem., 1936, 115, 343—360).—Subhuman primates are similar to children in retaining varying amounts of N. Urea,  $\text{NH}_3$ , creatinine, and undetermined N are distributed as with children or subjects on a vegetarian diet. Excreted uric acid increases from Old World monkeys to apes in the direction of greater similarity to man. E. M. W.

**Neutral sulphur of normal and pathological urines.** A. FRIEDRICH and E. BAUER (Z. physiol. Chem., 1936, 242, 261—270).—In healthy human urine the neutral S constitutes 7—13% of the total S. Consumption of protein-rich food increases urinary, neutral, and total S but does not alter the ratio neutral S : total S. The ratio is increased in fevers, in tuberculosis, and sometimes in carcinoma and liver diseases. In a rabbit the ratio was doubled by P poisoning. Increase in urinary neutral S results from diet too rich in protein and from diseases which result in lack of  $\text{O}_2$  and decomp. of protoplasm in the organism; except in cystinuria the increase is a measure of the gravity of the disease. W. McC.

**Sulphur partition in cat urines following injections of monobromobenzene, cystine, and methionine.** R. W. VIRTUE (Proc. Soc. Exp. Biol. Med., 1936, 34, 425—427).—Administration of PhBr to cats results in the excretion in urine of *p*-bromophenylmercapturic acid. The high urinary N found in fasting animals after PhBr administration suggests that the tissues are broken down in order to supply the cysteine required. After injection of cystine and methionine the extra S is excreted in the urine largely as sulphate. W. O. K.

**Determination of iron in phosphate-rich material (faeces).** RANGIER and LAFRANÇOISE (J. Pharm. Chim., 1936, [viii], 24, 266—268).—The material (e.g., dog's faeces) is boiled with aq. HCl (1 : 1) followed by dil.  $\text{HNO}_3$ , filtered, and the filtrate treated with excess of aq.  $\text{NH}_3$ , the resulting ppt.  $[\text{Ca}_3(\text{PO}_4)_2 + \text{Fe}(\text{OH})_3]$  being washed with  $\text{H}_2\text{O}$  and dissolved in boiling dil.  $\text{H}_3\text{PO}_4$ , and the  $\text{Fe}^{+++}$  reduced (Zn) and then oxidised with 0.1N-KMnO<sub>4</sub>. F. O. H.

**Pyruvic acid in urine after hard exercise.** R. E. JOHNSON and H. T. EDWARDS (Science, 1936, 84, 140—141).— $\text{AcCO}_2\text{H}$ , but not  $\text{AcCHO}$ , appears to be one of the variable constituents of blood and urine during hard exercise. L. S. T.

**Excretion of inulin and creatinine at low urine flows by the normal dog.** J. A. SHANNON (Amer. J. Physiol., 1936, 114, 362—365).—The mean ratio of simultaneous inulin and creatinine clearance is 0.993 with a standard deviation of 0.048 and max.

variations of +0.097 and -0.083. Neither substance is passively reabsorbed during excretion by the normal kidney. R. N. C.

**$\beta$ -Lactose : effect on the flora of the infant's stool.** J. R. GERSTLEY, E. PENRUDDOCKE, and G. LAWRENCE (Arch. Pediatrics, 1935, 52, 552—561).— $\beta$ -Lactose has the same advantages as  $\alpha$ -lactose in the infant's diet, and has a favourable influence on the  $p_H$  and flora of stools. CH. ABS. (p)

**Common salt and other agents. Uses in certain [pathological] conditions.** W. W. LANG (Vet. Rec., 1936, 48, 879—886).—A lecture and discussion. Uses of injections of NaCl-Na citrate are considered. A. G. P.

**Iron absorption and treatment of anæmia. I, II.** G. WALLBACH (Folia hæmatol., 1936, 54, 201—210, 211—216).—I. In mice given 0.01 g. of Fe daily for 8 days, storage of Fe after the same dose in different chemical combinations was very different and did not depend on the solubility in  $\text{H}_2\text{O}$  or the valency of the Fe.

II. After parenteral administration of 0.1 mg. of different forms of Fe certain forms, especially  $\text{Fe}^{II}$  salts, were deposited in the liver and others, such as reduced Fe, in the epithelial cells of the small intestine, whereas salts such as the citrate remained at the site of injection. NUTR. ABS. (m)

**Significance of loss of serum-protein in therapy of severe burns.** D. O. WEINER, A. P. ROWLETTE, and R. ELMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 484—486).—After severe burns  $\text{H}_2\text{O}$  and protein are lost from the blood, which consequently has often an abnormally high erythrocyte count but a low serum-protein content. Administration of solutions containing only glucose and electrolytes is therefore not so effective as is blood-plasma. W. O. K.

**Induced chiasma formation in somatic cells by a carcinogenic hydrocarbon [methylcholanthrene].** E. M. HEARNE (Nature, 1936, 138, 291). L. S. T.

**Influence of diets containing proteins of various fishes on the growth of tumour in rats. I.** S. TOKUYAMA and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 253—271).—Sarcoma implanted on rats fed on a diet containing 15% of EtOH-extracted protein grew less rapidly when the protein was derived from various fish than from horse meat. The tumour growth rates were correlated with the growth of the animals before tumour implantation. W. O. K.

**Transmissible agent in the Rous chicken sarcoma no. 1.** J. W. JOBLING and E. E. SPROUL (Science, 1936, 84, 229—230).—The lipin extract of this sarcoma, obtained by the use of a sp. solvent at low temp. under relative anaerobiosis, transmits the tumour when allowed brief contact with chicken tissue extract and promptly inoculated. Tumours do not develop when the lipin extract is inoculated alone or into previously injured breast muscle. L. S. T.

**Contents of trypsin, cathepsin, amylase, and lipase in cancerous growths and blood.** G. VERCELLANA (Boll. Soc. ital. Biol. sperim., 1936,

11, 328—329).—The enzymes were not found in cancerous growths (excepting amylase, a normal constituent, in a parotid growth) or blood.

F. O. H.

**High-sugar diets and dental caries in the white rat.** C. D. M. DAY, R. G. DAGGS, and H. J. SEDWICK (J. Amer. Dental Assoc., 1935, 22, 913—925).—Prolonged feeding of diets containing 20—55% of sugar was not conducive to the incidence of caries when sufficient minerals and vitamins were supplied.

CH. ABS. (p)

**Diet and dental caries.** R. W. BUNTING (J. Amer. Dental Assoc., 1935, 22, 114—122; cf. A., 1934, 99).—High-sugar diets favoured the development of caries in children by influencing the environment of the teeth rather than their resistance. No const. relation was found between caries activity and the Ca, P, or vitamin-C or -D contents of the diet or the chemical composition of blood or saliva.

CH. ABS. (p)

**Carbohydrate degradation in relation to dental caries.** L. S. FOSDICK and H. L. HANSEN (J. Amer. Dental Assoc., 1936, 23, 401—407).—In the degradation of carbohydrate to lactic acid, with subsequent dissolution of tooth enamel, the enzymes of yeast and tissue play an important part. *In vitro*, human enamel, suspended in a solution of glucose and saliva, was dissolved by the acids produced. NaF prevented dissolution. A correlation of this fact with the low susceptibility of mottled teeth to decay is suggested. A combination of yeast and of (otherwise inactive) *B. acidophilus* was more potent than yeast alone.

NUTR. ABS. (m)

**Acid-base balance of diets which produce immunity to dental caries among South Sea Islanders and other primitive races.** W. A. PRICE (Dental Cosmos, 1935, 77, 841—846).—The primitive diet was potentially acid-forming. In changing to civilised diets (deficient in certain minerals and vitamins) the potential acidity did not increase with the enhanced susceptibility to caries.

CH. ABS. (p)

**Impaired glucose tolerance in certain alimentary disorders of childhood: treatment with liver extract.** C. W. ROSS (Lancet, 1936, 231, 556—559).—In coeliac disease, chronic intestinal indigestion, and abdominal glandular tuberculosis a flat oral glucose tolerance curve is associated with a high intravenous curve, indicating deficient carbohydrate absorption power from the intestine. Administration of liver extract improves the impaired glucose tolerance.

L. S. T.

**Intestinal absorption in coeliac disease; effect of liver extracts on carbohydrate metabolism.** C. W. ROSS (Trans. Roy. Soc. Trop. Med. Hyg., 1936, 30, 33—60).—Evidence for defective absorption of glucose and a resulting decrease in glucose tolerance, as well as for decreased sensitivity to insulin, is reported. Tests indicated that the factor (probably insulin-kinase), present in total liver extracts, which improves glucose tolerance is not identical with Castle's essential liver factor.

NUTR. ABS.

**Chemical aspects of dermatitis.** H. E. COX (Chem. and Ind., 1936, 775—781).—An address.

**Treatment of severe diabetes in children with protamine insulinate.** T. I. BENNETT and A. M. GILL (Lancet, 1936, 231, 416—417).

L. S. T.

**Specific dynamic action of protein in pancreatic diabetes.** G. C. RING (Amer. J. Physiol., 1936, 115, 419—423).—The calorogenic action of protein (I) in underfed diabetic cats is > normal. Increased metabolism does not affect the action of (I), although those of fat and carbohydrate are reduced. The R.Q. after ingestion of (I) is < that in normal animals. The increased metabolism of diabetes is not due to sp. dynamic action of (I).

R. N. C.

**Evidence of altered carbohydrate metabolism in cats with hypothalamic lesions.** W. R. INGRAM and R. W. BARRIS (Amer. J. Physiol., 1936, 114, 562—571).—Bilateral lesion in the anterior supra-chiasmatic portion of the hypothalamus, or hypophysectomy, increases the sensitivity of the cat to insulin. The response of blood-sugar to adrenaline is also diminished by severe lesions in the supra-chiasmatic region. Lesions in this region abolish the normal response to the hyperglycaemic effect of anterior pituitary suspension (I); hypophysectomy retards the action of (I). Liver-glycogen remains normal.

R. N. C.

**Effect of experimental hypothalamic lesions on blood-sugar.** R. W. BARRIS and W. R. INGRAM (Amer. J. Physiol., 1936, 114, 555—561).—Lesions at almost any point in the hypothalamus of the cat cause a transient hyperglycaemia. Mild chronic hypoglycaemia generally follows when the lesion is in the anterior portion, particularly if the nucleus filiformis is destroyed or atrophic.

R. N. C.

**Blood-lipins in lipaemia retinalis.** A. MARBLE and R. M. SMITH (Arch. Ophthalmol., 1936, 15, 86—94).—In lipaemia retinalis occurring in two boys with severe diabetes which had been poorly controlled, the total lipins of the blood amounted to 14.1 and 7.5%, respectively. The greatest increase took place in the fatty acid fraction, with relatively large increases also in the cholesterol and phospholipin fractions.

NUTR. ABS. (m)

**Chemistry of muscle in progressive muscular dystrophy. Analysis of biopsy samples from the deltoid.** J. A. COLLAZO, J. BARBUDO, and I. TORRES (Deut. med. Woch., 1936, 62, 51—54).—In dystrophic muscle there exists, together with fatty degeneration of the connective tissue, an insufficiency of phosphagen (I) and glycogen (II), (I) being practically absent in severe cases. There is also a marked lack of (II) and lactic acid, and a reduced H<sub>2</sub>O content. The inorg. P of muscle is not increased. In a severe case of myasthenia the vals. for muscle-(II) and -(I) were subnormal but not to the extent found in the dystrophies.

NUTR. ABS. (m)

**Metabolic studies in osteoporosis.** M. ADAMS, W. M. BOOTHBY, and A. M. SNELL (Amer. J. Physiol., 1936, 114, 383—398).—Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> fed in large amounts to a patient with senescent osteoporosis produces storage of Ca and P; the extent of the storage is limited by a factor, exhaustion of which results in a decreasing retentive power. Viosterol (I) added to Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>



renders Ca retention more marked. Ca retention during administration of Ca lactate (II) is  $>$  during administration of an equiv. amount of  $\text{Ca}_3(\text{PO}_4)_2$ ; (I) apparently produces little change in Ca balance when (II) alone is given. N is retained throughout; K, Na, and Mg balances are unchanged. R. N. C.

**Hydræmia as a factor in the anæmia of pregnancy.** H. FELDMAN, E. C. VAN DONK, H. STEENBOCK, and E. F. SCHNEIDER (Amer. J. Physiol., 1936, 115, 69—77).—The  $\text{H}_2\text{O}$  content rises in the blood of pregnant women whilst cell vol., hæmoglobin level, and  $n$  fall. These changes do not occur in the cow. R. N. C.

**Relation of pregnancy and lactation to extirpation diabetes in the dog.** F. P. CUTHBERT, A. C. IVY, B. L. ISAACS, and J. GRAY (Amer. J. Physiol., 1936, 115, 480—496).—Glycosuria in depancreatized bitches, maintained with a uniform diet and a dose of insulin (I) permitting slight glycosuria, is increased in early pregnancy, decreased in late pregnancy, and further decreased in lactation. The reduction is due to passage of glucose and glucose-forming substances into the foetus. Pancreatectomy near term does not cause hyperglycæmia in presence *in utero* of  $\approx 3$  viable foetuses. (I) does not suppress the anti-hyperglycæmic effect exerted by the metabolites of near-term pregnancy. The metabolisms of dogs depancreatized before pregnancy and near term show considerable differences, the latter condition being the more analogous to that of the human patient. R. N. C.

**Blood-lipins during pregnancy in guinea-pigs.** E. M. BOYD and M. D. FELLOWS (Amer. J. Physiol., 1936, 114, 635—641).—Lipæmia becomes marked in the second half of gestation, the increase occurring in the plasma. Total lipins, phospholipins, and free cholesterol (I) are increased to 4 times and neutral fat to 5 times the normal vals., whilst esterified (I) falls 50%, this decrease being continuous and progressive from early pregnancy. R. N. C.

**Nutritive value of canavanine (amino-acid).** VI. **Influence of canavanine on pregnancy and parturition.** M. OGAWA (J. Agric. Chem. Soc. Japan, 1936, 12, 828—832).—Canavanine is not essential for pregnancy, but it is important for the health of pregnant animals. (Cf. A., 1935, 1417.) J. N. A.

**Role of acidosis and phosphate retention in the pathogenesis of rickets and rachitic tetany of infants.** N. MORRIS, F. J. FORD, and S. GRAHAM (Acta paediat., 1935, 18, 50—91).—The active stage of rickets in two children, one with and one without tetany, was accompanied by increased  $\text{NH}_3$  and decreased titratable acid in the urine. Administration of adexolin was followed by an increased retention of Ca and P, a decrease in urinary  $\text{NH}_3$ , and an increase in the titratable acid. Before the onset of rickets a child with coeliac disease had an approx. normal output of urinary  $\text{NH}_3$  and titratable acid, although mineral retention was poor. The examination of Ca and P balances of children with rickets, with and without tetany, and the administration of P to a patient depleted of Ca through coeliac disease,

failed to show any relation between tetany and high P retention. NUTR. ABS. (*m*)

**Blood buffer values in mineral deficiency.** I. N. KUGELMASS (Amer. J. Digest. Dis. Nutrition, 1936, 2, 730—732).—The serum of rachitic infants had a much lower buffering power to added acid and alkali than had that of normal infants. NUTR. ABS. (*m*)

**Bone-ash in prevention and healing of experimental rat rickets.** T. F. ZUCKER (Science, 1936, 84, 162—163).—In curative experiments, supposedly substantial healing effects raise the bone-ash through only approx. one fifth of the interval between the rachitic and the full vitamin-D prevention levels. L. S. T.

**Tropical sprue with special reference to intestinal absorption.** I. N. H. FAIRLEY (Trans. Roy. Soc. Trop. Med. Hyg., 1936, 30, 9—32).—Decreased absorption of fat (with hypocalcæmia) and of glucose are noted, but starch digestion and protein metabolism are not affected. NUTR. ABS.

**Relation of serum-phosphates to parathyroid tetany.** J. H. JONES (J. Biol. Chem., 1936, 115, 371—379).—Rats fed on a low-Ca diet with 4% of basic Al acetate show no tetany after parathyroidectomy and the serum-Ca remains high and the -P low. Fasting after parathyroidectomy causes tetany; the serum-P rises and the -Ca falls. With low available P serum-Ca is high enough to prevent tetany on diets deficient in Ca. The P excretion theory of parathyroid function is discussed. E. M. W.

**Influence of dietary deficiencies on the transmission of trachoma to monkeys.** R. A. HETLER and W. M. JAMES (Amer. J. Ophthalmol., 1934, 17, 1048—1054).—Follicular changes developed in the inoculated eyes of well- and ill-nourished monkeys but not in rats, rabbits, or guinea pigs receiving diets low in vitamins and protein but high in fats. CH. ABS. (*p*)

**Effect of diet and vitamins on trachoma.** C. E. RICE, R. SORY, J. E. SMITH, P. E. FAED, and A. A. DRAKE (Amer. J. Ophthalmol., 1934, 17, 735—741).—No effects in the course of trachoma were observed. CH. ABS. (*p*)

**Metabolism of cartilage.** E. G. L. BYWATERS (Nature, 1936, 138, 288).—A reply to criticism (cf. this vol., 1143). L. S. T.

**Respiratory metabolism of stimulated frog's muscle.** C. L. GEMMILL (Amer. J. Physiol., 1936, 115, 371—375).—The R.Q. averages 0.90,  $\text{O}_2$  consumption 357 cu. mm. per g. of muscle per hr., and the tension developed 195 kg. per g. per hr.  $\text{O}_2$  consumption and the tension developed under aerobic conditions show a linear relationship. R. N. C.

**Age and tissue respiration.** J. M. PEARCE (Amer. J. Physiol., 1936, 114, 255—260).—The  $\text{O}_2$  consumption of excised mouse tissue decreases as age increases. The greatest fall occurs in the liver, and the least in the kidneys. R. N. C.

**Oxidation-reduction in the small intestine and liver of rats during intestinal absorption.** G. PERETTI (Boll. Soc. ital. Biol. sperim., 1936, 11, 336—

337).—Following ingestion of olive oil or glucose, the reducing power (to 2:6-dichlorophenol-indophenol) of the liver and, to a smaller extent, of the small intestine and lung tissue increases.

F. O. H.

Oxygen consumption and carbon dioxide production of frog's retina in darkness and light. J. JONGBLOED and A. K. NOYONS (Z. Biol., 1936, 97, 399—408).—The retina, maintained in darkness for 15–60 min. in contact with the pigmented epithelial layer, has an  $O_2$  consumption and a  $CO_2$  production approx. 22–26% > those of the retina exposed to light.

F. O. H.

Effect of bile salts on the oxygen consumption of dog tissues. W. H. STRAIN and M. E. MARSH (Amer. J. Physiol., 1936, 115, 82–89).—With increasing concn. of Na bile salts in Ringer- $PO_4$ -glucose medium, a "crit. inhibitory concn." is reached above which respiration is more or less inhibited. The inhibiting effect of conjugated bile salts is < that of unconjugated salts, whilst that of Na glycocholate (which is foreign to the dog) is > that of taurocholate, suggesting specificity in conjugation.

R. N. C.

Regularity of nutritional response to chemical intake. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1936, 22, 478–481; cf. A., 1935, 1154).—Rats from families surviving for 8 generations on a diet poor in "protective foods" responded normally, in respect of growth and development, to supplementary feeding with Ca, vitamin-A and  $-B_2$ , and (to a smaller extent) with protein.

A. G. P.

Diet in relation to reproduction and rearing of young. J. F. FEASTER and V. E. NELSON (Amer. J. Physiol., 1936, 115, 147–154).

R. N. C.

Influence of calcium carbonate in the feed of laying hens on digestion. G. D. BUCKNER and A. H. HARMS (Poultry Sci., 1935, 14, 360, 375, 380).—Analysis of the droppings indicates that large amounts of  $CaCO_3$  in the ration lower the digestion of N-free extractives and increase that of protein.

A. G. P.

Availability of calcium salts for bone formation and rickets prevention in chicks. H. J. DEOBALD, C. A. ELVEHJEM, E. B. HART, and J. G. HALPIN (Poultry Sci., 1936, 15, 42–47).—In chicks receiving a basal rachitogenic ration supplemented with various Ca salts and cod-liver oil, the ash content of fat-free bone was higher when the supplement contained P as well as Ca. The Ca in compounds examined (limestone, gypsum, Ca gluconate, bone meal, rock phosphate) was uniformly available for bone formation. If the cod-liver oil given was in crit. amounts, sol. Ca salts (lactate) were more effective than the insol. salts (pptd. silicate). With very insol. silicates the availability  $\propto$  solubility in dil. acid and was not influenced by the amount of oil supplied.

A. G. P.

Calcium carbonate versus calcium sulphate in swine rations. C. W. MCCAMPBELL and C. E. AUBEL (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 189–190).—When fed as supplements to a linseed meal-wheat-maize ration, finely

ground limestone and gypsum were similarly effective in respect of influencing the serum-inorg. Ca, inorg. P of whole blood, breaking strength of bones, and daily gain in wt.

CH. ABS. (p)

Refecation in the rat. Preparation of basic materials for deficiency diets. S. BLISS (J. Nutrition, 1936, 11, 1–19).—Refecation is readily produced in rats by feeding diets with potato starch as carbohydrate. Growth of such rats is not attributable to unsuspected vitamin-B contamination of the diet. Raw starch from refected faeces and pure raw potato starch behave similarly towards pancreatic digestion mixtures *in vitro*.

A. G. P.

Purified diet satisfactory for growth, reproduction, and lactation in rats. W. M. COX and M. IMBODEN (Proc. Soc. Exp. Biol. Med., 1936, 34, 443–446).—The diet consisted of casein, 20; dextrin, 55.1; lard, 9.0; protein-free dried extract of brewer's yeast (equiv. in  $-B_1$  to 24% and in  $-B_2$  to 8% of yeast), 4; wheat-germ oil, 1.6; carotene (0.3% in maize oil), 0.3;  $Ca(OAc)_2$  1; salts, 3.1; and rice cellulose 5.9 parts.

W. O. K.

Vitamin-D content and haemoglobin-building properties of dehydrated kelp for chicks. M. W. MILLER and G. E. BEARSE (Poultry Sci., 1936, 15, 19–22).—The kelp had little -D activity and did not affect the haemoglobin content of chick blood.

A. G. P.

Haemoglobin content of the blood of laying hens on practical poultry rations. M. O. SCHULTZE, C. A. ELVEHJEM, E. B. HART, and J. C. HALPIN (Poultry Sci., 1936, 15, 9–13).—A ration supplying 14 mg. of Fe and 0.5 mg. of Cu per head per day supports heavy egg production without concurrent lowering of the haemoglobin content of the blood.

A. G. P.

Site of renal elimination of haemoglobin in the rabbit. I. GERSH (Anat. Rec., 1936, 65, 371–375).

R. N. C.

Effect of previous feeding on the nitrogen excretion of fasting birds. J. C. FRITZ, W. A. HENDRICKS, and H. W. TITUS (Amer. J. Physiol., 1936, 115, 281–286).—N excretion by cocks falls when fasting begins, but on the 2nd and 3rd days rises or falls according as the previous diet was abnormally low or high in protein. After the 3rd day N excretion remains practically const. The source of the protein in the diet does not affect the result. Recovery after fasting is most rapid in birds previously fed with a normal diet.

R. N. C.

Effect of (A) high-fat and (B) high-protein diet on the growth of rats. C. Y. CHEN (Nutrit. Bull. B, April, 1936, No. 3, 23–27, 29–36).—The ill effects of both diets were counteracted by adding a 50% EtOH extract of yeast, but not by a 70% extract.

NUTR. ABS.

Effect of a low-protein ration on the pre-natal and post-natal development of the rat. C. P. THOMPSON (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 177–178).—Low-protein rations did not affect the no. of young per litter but lowered their average wt. and increased the proportion of stillborn. At higher protein levels (17.1%) rats



stored 19% more of the total N ingested than did those receiving 10.2% of protein. CH. ABS. (p)

**Rate of growth in relation to plane of protein intake.** A. G. HOGAN, S. R. JOHNSON, and U. S. ASHWORTH (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 179—181).—Animals on a high-protein (20%) diet made larger gains in wt., and stored more  $H_2O$  and protein but less fat, than did those on a low-protein (10%) diet. CH. ABS. (p)

**Digestibility of dietary protein in the ruminant. I. Endogenous nitrogen excretion on a low-nitrogen diet and in starvation. II. Digestibility of protein following a prolonged fast. Nitrogen metabolism.** J. C. D. HUTCHINSON and S. MORRIS (Biochem. J., 1936, 30, 1682—1694, 1695—1704).—I. The faecal N excretion of goats and sheep on a N-free diet increases with the quantity of food taken and the presence of fibre in the diet. With the cow, goat, and sheep starvation following a low-N diet causes an increased urinary N excretion, the most notable changes being those of urea (I) and creatine (II); increasing the energy intake on a N-free diet causes a progressive decrease in the urinary excretion of (I) and (II).

II. The greater is the biological val. of the protein and the greater the requirement of the animal for protein, the less is the digestibility; the faecal N excreted under conditions of poor utilisation is volatile at  $180^\circ$ . From studies of the partition of the urinary N of cows after ingestion of food after a period of starvation it is concluded that increased deamination leads to increased (I),  $NH_3$ , and  $NH_2$ -acid excretion; when the ingested protein is used for tissue anabolism an increase of (II) output occurs. The mean ratio of retained N to S over a long period is similar to that for body tissue. H. D.

**Uric acid synthesis in birds. IV. Uric acid synthesis in pigeons; a purine synthesis. (i) Nucleic acid metabolism in the pigeon. (ii) The "precursor" as a carbon source in uric acid synthesis. (iii) Nitrogen source in uric acid synthesis.** W. SCHULER and W. REINDEL (Klin. Woch., 1935, 14, 1238—1242; Chem. Zentr., 1935, ii, 3792—3793).—(i) [with A. LEHMER]. Liver is unable to effect fission of nucleic acid or nucleoside, or to oxidise purines to urea.

(ii) [with H. FRIEDRICH]. None of many substances examined can be the precursor of uric acid. Kidneys are unable to regenerate the precursor although they always contain considerable amounts. The production of precursor from liver powder is confirmed.

(iii) [with O. HENZ]. See A., 1935, 1153.

A. G. P.

**Choline ester formation in, and choline esterase activities of, tissues *in vitro*.** J. H. QUASTEL, M. TENNENBAUM, and A. H. M. WHEATLEY (Biochem. J., 1936, 30, 1668—1681).—A substance considered to be a choline ester (I), which causes eserinated leech muscle to contract, is formed during aerobic incubation of brain cortex slices in the presence of eserine. The rate ( $R$ ) of (I) formation is decreased by  $CN'$  and increased 4—5 times by glucose (II) with or without added Ca and K with  $HPO_4''$  medium; addition of Ca and K to a (II)- $HPO_4''$  medium increases  $R$ .

In  $HCO_3'$  medium (II) increases  $R$  in the absence of added  $Ca''$  and  $K'$ . Addition of  $Ca''$  and  $K'$  lowers  $R$  so that adding (II) to a Ringer- $HCO_3'$  medium has little or no effect. The possibility that these effects are due to influences on (II) metabolism is suggested. Na lactate, pyruvate,  $\alpha$ -glycerophosphate, and glutamate increase  $R < (II)$  with or without added  $Ca''$  and  $K'$ ; Na succinate is without influence, also NaF in the presence of (II) although in this case  $Q_{10}$  is considerably reduced. Addition of choline or NaOAc is without influence on  $R$  so that it is assumed that the synthesis of acetylcholine (III) is not from the products of its hydrolysis. Kidney, liver, spleen, and testis do not produce (I) under the conditions in which brain does. The hydrolysis of (III) by tissue slices occurs most rapidly with spleen and it is concluded that there is no relation between the power of an organ to break up (III) and its power to form (I) *in vitro*. H. D.

**Oxidation of indole in various organs of the rabbit.** J. GARCÍA-BLANCO and J. NACLE (Anal. Fis. Quím., 1935, 33, 105—108).—Indole is oxidised to indoxyl especially in the kidney. F. R. G.

**Kinetics of elimination of substances injected intravenously. (Creatinine.)** R. DOMINGUEZ, H. GOLDBLATT, and E. POMERENE (Amer. J. Physiol., 1935, 114, 240—254).—Creatinine introduced rapidly into the blood-stream of the dog is dispersed quickly into a large portion of the body-fluids (equiv. plasma vol.) from which it diffuses reversibly into the remainder (tissue vol.), until equilibrium is reached; it is excreted steadily by the kidneys before and after establishment of equilibrium. R. N. C.

**Clearance of hexamethylenetetramine in the dog.** R. F. PITTS (Amer. J. Physiol., 1936, 115, 706—710).—The clearance ratio of  $(CH_2)_6N_4$  (I) and xylose (II) in the normal dog is independent of the plasma-(I) concn.; hence (I) clearance itself is also independent of plasma-(I). Simultaneous clearances of (I) and (II) are practically identical and about 75% of the simultaneous clearance of creatinine. Phloridzin depresses all three clearances, that of (II) being altered least. R. N. C.

**Intestinal absorption of amino-acids.** R. HÖBER and J. HÖBER (Proc. Soc. Exp. Biol. Med., 1936, 34, 486—488).—The diffusion of various  $NH_2$ -acids and acid amides through the intestinal wall is not a simple function of mol. vol. but shows evidence of sp. selectivity. W. O. K.

**Absorption of cystine, methionine, and cysteine acid from intestinal loops of dogs.** J. C. ANDREWS, C. G. JOHNSTON, and K. C. ANDREWS (Amer. J. Physiol., 1936, 115, 188—193).—The rate of absorption is max. for methionine and min. for cystine. The amount absorbed in a given period varies with the amount introduced. The amount of  $NH_2$ -acid absorbed is the same, whether it is injected as free acid or Na salt; the amount of NaOH absorbed is independent of the  $NH_2$ -acid. R. N. C.

**Utilisation of glutathione in connexion with a cystine-deficient diet.** H. M. DYER and V. DU VIGNEAUD (J. Biol. Chem., 1936, 115, 543—549).—Oral or subcutaneous administration of glutathione

will support growth of rats on a cystine-deficient diet.

H. G. R.

**Synthesis of neutral fat by the intestine of diabetic dogs.** S. FREEMAN and A. C. IVY (Amer. J. Physiol., 1935, 114, 132—136).—Oleic acid (I) is absorbed from the intestine largely as neutral fat and phospholipin, showing that glycerol is available for fat synthesis in absence of insulin, and that phosphorylation of (I) is not impaired. The increases in cholesterol in the chyle of normal dogs are absent from that of depancreatized animals.

R. N. C.

**Ether-soluble lipin-phosphorus, lecithin, and cephalin distribution in the development of the chick.** O. E. KUGLER (Amer. J. Physiol., 1936, 115, 287—291).—Phospholipin metabolism reaches its highest stage between the 15th and 17th days of incubation. Lecithin and cephalin run parallel with each other, showing the same fluctuations as Et<sub>2</sub>O-sol. lipin-P during development, and maintain a ratio of approx. 3:1 in the yolk and the embryo fraction throughout incubation.

R. N. C.

**Transformations of adenosinetriphosphoric acid in muscle.** IV. Transformation of adenosinetriphosphoric acid in muscle of hibernating animals. O. FEINSCHMIDT (Biochem. Z., 1936, 286, 290—294).—During hibernation, the adenosinetriphosphoric acid (I) and P<sub>2</sub>O<sub>7</sub><sup>4-</sup> (II) contents of the muscle of the ground-squirrel *Citellus guttatus* are considerably decreased, (II) to a smaller extent than corresponds with the decrease of (I). Muscle then contains inorg. (II) and free adenylic acid (cf. this vol., 754).

P. W. C.

**Creatinuria induced by ingestion of glucose and fructose and by exercise.** J. HALDI and G. BACHMANN (Amer. J. Physiol., 1936, 115, 364—370).—Ingestion of glucose (I) and/or fructose (II) by men often causes excretion of creatine (III), whilst carbohydrate metabolism is increased. (II) induces a higher (III) excretion than (I) or (I)+(II). (III) excretion often follows exercise, particularly if this is preceded by ingestion of sugar, (II) again inducing the higher excretion; creatinine excretion is not affected.

R. N. C.

**Hexose phosphate metabolism of tumour extracts.** C. A. MAWSON (Biochem. J., 1936, 30, 1592—1597).—Lactic acid (I) is not produced from glucose by mouse tumour cell suspensions at 38° or 52°, with or without addition of glutathione (II). Small amounts of (I), not increased by the addition of (II), are produced from hexose diphosphate (III) at 38°; at 52°, larger amounts, considerably increased by the addition of (II), are produced. Dialysis lowers the activity of tumour extracts, which is restored by the addition of (II). The production of (I) from (III) at 52° is greatly reduced by kidney antiglyoxalase.

F. A. A.

**Glycogen and the metabolism of carbohydrate.** F. G. YOUNG (Lancet, 1936, 231, 237—242, 297—302).—Lectures.

L. S. T.

**Avian carbohydrate metabolism.** R. SPRAGUE and A. C. IVY (Amer. J. Physiol., 1936, 115, 389—394).—The blood-sugar (I) responses of normal and depancreatized ducks to insulin are similar.

Relatively large doses of adrenaline (II) are required to produce hyperglycemia, normal birds showing a greater response than depancreatized birds, suggesting that (II) and the sympathetic nervous system are of less importance in avian than in mammalian carbohydrate metabolism. Pituiratin does not affect (I). Liver-glycogen (III) is unaffected by depancreatization, and the (III) hydrolysate contains moderate quantities of lactic acid in both cases. The rate of disappearance of glucose from the blood *in vitro* is unaltered by depancreatization. Extracts of duck's pancreas contain an insulin-like substance.

R. N. C.

**Mechanism of carbohydrate breakdown in early embryonic development.** J. NEEDHAM, W. W. NOWINSKI, R. P. COOK, and K. C. DIXON (Nature, 1936, 138, 462—463).—The changes which sugar-like substances undergo in or under the influence of chick embryos of 4—6 days' incubation are summarised and compared with those effected by brain and muscle tissues. Glucose and mannose are the only sugars which give a steady, long-continuing glycolysis; fructose, and disaccharides even when phosphorylated, are unattacked. Lactic acid is quantitatively formed during glycolysis. The embryo does not glycolyse any combination of the P-containing intermediates. The Pasteur effect is very marked. The P distribution in various fractions of the aq. CCl<sub>3</sub>·CO<sub>2</sub>H extract differs from that obtained with muscle and brain preps.

L. S. T.

**"Hunger diabetes" and the utilisation of glucose in the fasting dog.** S. SOSKIN and I. A. MIRSKY (Amer. J. Physiol., 1935, 114, 106—109).—Sugar is utilised after evisceration by the normal fasting dog at the same rate as by the normal fed dog. The low R.Q. and other symptoms of "hunger diabetes" are due rather to increased gluconeogenesis than to lack of carbohydrate utilisation.

R. N. C.

**Effect of hypophysectomy on gluconeogenesis in the normal and depancreatized dog.** S. SOSKIN, I. A. MIRSKY, L. M. ZIMMERMAN, and N. CROHN (Amer. J. Physiol., 1935, 114, 110—118).—The hypophysectomised animal is unable, when its carbohydrate (I) stores are depleted and it is deprived of exogenous (I), to synthesise (I) from fat, but can derive it from protein.

R. N. C.

**Carbohydrate metabolism of the heart during pancreas diabetes.** H. E. HIMWICH, W. GOLDFARB, and J. F. FAZIKAS (Amer. J. Physiol., 1936, 114, 273—277).—The carbohydrate balance of the heart in both normal and diabetic dogs is positive; this explains the paradoxical storage of cardiac glycogen (I) if a diminished power to oxidise glucose is taken into consideration. The R.Q. of diabetic cardiac tissue is > 0.7, showing that non-fatty substances can be oxidised. O<sub>2</sub> consumption in presence of lactic acid is increased; its oxidation limits storage of (I). Diabetic cardiac tissue can still glycolyse.

R. N. C.

**Normal glucose tolerance curves, in the absence of insulin, in hypophysectomised depancreatized dogs.** S. SOSKIN, I. A. MIRSKY, L. M. ZIMMERMAN, and R. C. HELLER (Amer. J. Physiol.,



1936, 114, 648—652).—The occurrence of the normal glucose (I) tolerance curve is determined by a homeostatic reaction of the liver, whereby the supply of sugar to the blood is increased in response to the influx of exogenous (I). The rise in (I) stimulates this mechanism, whilst the pancreas and pituitary determine the (I) level at which it comes into play.

R. N. C.

**Intermediate metabolism of carbohydrates.** H. A. KREBS (Nature, 1936, 138, 288—289).—When added to animal tissues  $\text{AcCO}_2\text{H}$  disappears rapidly even in absence of  $\text{O}_2$ ; the products of the anaerobic oxidation are  $\text{AcOH}$ ,  $\text{CO}_2$ , and succinic acid. Changes which  $\text{AcCO}_2\text{H}$  undergoes in living cells are described. They are intermediate steps in the biological breakdown of carbohydrates.

L. S. T.

**Secretory metabolism of the salivary glands.** D. NORTHUP (Amer. J. Physiol., 1935, 114, 46—52).—Simultaneous stimulation of sympathetic and parasympathetic nerves to the submaxillary gland of the dog increases lactic acid (I) and decreases glycogen (II) and creatinephosphoric acid (III) in the gland. The changes produced by sympathetic stimulation alone are  $>$  those from parasympathetic stimulation alone, but  $<$  those from combined stimulation. Since breakdown of (II) and (III) to (I) occurs during salivary secretion, it is possible that the (II)–(III) mechanism is general for release of energy in tissues where work is done.

R. N. C.

**Metabolism of bacteria-free animals. II. Production and excretion of oxalic acid by guinea-pigs.** S. BORGSTRÖM (Skand. Arch. Physiol., 1936, 73, 63—66).—Bacteria-free and normal guinea-pigs excreted similar amounts of  $\text{H}_2\text{C}_2\text{O}_4$  up to the 15th day after birth, after which the normal animals' excretion remained const., whilst that of the sterile animals rose parallel with the growth curve and after 30 days was 6 times that of the controls.

NUTR. ABS. (m)

**Alcohol injected intravenously: effect of habituation on rate of metabolism.** H. W. NEWMAN and W. C. CUTTING (J. Pharm. Exp. Ther., 1936, 57, 388—393; cf. A., 1935, 1409).—Oral administration of 6.8 c.c. of  $\text{EtOH}$  per kg. per day for 13 months did not significantly increase the rate of oxidation of  $\text{EtOH}$  when injected intravenously into 3 dogs.

J. N. A.

**Relation of the urinary chloride rate to the plasma concentration before and after administration of sodium chloride.** E. M. MACKAY and L. L. MACKAY (Amer. J. Physiol., 1936, 115, 455—460).—When excretion of urine (rabbit) is high and urea formation directly related to blood-urea, urinary and plasma- $\text{Cl}'$  show no uniformity. If  $\text{NaCl}$  is administered in large doses to increase plasma- $\text{Cl}'$ , a curvilinear relationship tends to appear between urinary and plasma- $\text{Cl}'$ . There is a  $\text{Cl}'$  threshold for the rabbit.

R. N. C.

**Production of chloride-free solutions by the action of the intestinal epithelium.** R. C. INGRAHAM and M. B. VISSCHER (Amer. J. Physiol., 1936, 114, 676—680).— $\text{Cl}'$  is almost completely removed from solutions containing  $\text{SO}_4''$  placed in the lower ileum.  $\text{Na}_2\text{SO}_4$  becomes conc. in the intestine,

the increase of osmotic pressure of the cation due to exchange of  $\text{Cl}'$  for  $\text{SO}_4''$  causing an increase in  $\text{Na}'$ . The normal intestine is impermeable to  $\text{SO}_4''$ ; the movement observed is not, however, due to a simple Donnan equilibrium with  $\text{SO}_4''$  as the impermeable ion.  $\text{K}'$  substituted for  $\text{Na}'$  does not appreciably alter the movement of  $\text{Cl}'$ .

R. N. C.

**Distribution and storage of fluorine in tissues of the laying hen.** K. HAMAN, P. H. PHILLIPS, and J. G. HALPIN (Poultry Sci., 1936, 15, 154—157).—All normal tissues, except washed feathers and thyroid, contained F, in amounts decreasing in the order: bones, kidney and liver, muscle, fat. Vals. were increased by feeding raw rock phosphate or phosphatic limestone, bones being affected  $>$  soft tissues. In laying hens storage of F  $\propto$  the amount ingested.

A. G. P.

**Calcium changes in the plasma resulting from brief severe work and the question as to the permeability of the capillaries to calcium.** A. KEYS and L. ADELSON (Amer. J. Physiol., 1936, 115, 539—547).—Ca rises in plasma after brief severe exercise, reaches its max. in 1 min., and then declines logarithmically to reach its resting level in 30—70 min.; the changes are closely parallel to, but slightly  $>$ , those in plasma-protein. The mechanism of these changes is discussed with reference to "diffusible" Ca.

R. N. C.

**Calcium metabolism of laying hens.** H. J. DEOBALD, E. J. LEASE, E. B. HART, and J. G. HALPIN (Poultry Sci., 1936, 15, 179—185).—In individual hens blood-Ca remained substantially const. over a 36 hr. period. Deprivation of Ca resulted in a gradual decrease in the  $\text{CO}_2$ -free ash of egg shells and laying ceased in approx. 12 days. A portion of the skeletal Ca of hens may be utilised in shell formation. Subcutaneous injection of small amounts of parathormone into Ca-deficient hens had no effect on Ca metabolism, egg production, ash content of bones, or blood-Ca. Large injections increased blood-Ca.

A. G. P.

**Rate of bismuth absorption in experimental animals following oral administration.** G. E. CLARKE and H. F. MARSH (J. Pharm. Exp. Ther., 1936, 57, 399—409).—Bi in the form of K or Na Bi tartrate or  $\text{BiOCl}$  when administered orally to guinea-pigs is deposited in the liver, spleen, and kidney. In liver and spleen the highest concn. of Bi occurs after 24 hr. and in kidney between 12 and 48 hr. Bi administered to pregnant animals was found in the foetal liver and placenta, but not in the foetal kidney.

J. N. A.

**Magnesium excretion in dogs. Physiology of the colon. III.** R. NICOLAYSEN (Skand. Arch. Physiol., 1936, 73, 75—89).—Two dogs of const. wt. (8 kg.) and in N equilibrium on a Mg-free neutral diet excreted in the urine during 10 3-day periods 6—24 mg. of Mg, the faecal excretion being from 18 to 26 mg. These vals. were unchanged after the colon had been short-circuited and the ileum anastomosed with the rectum. In the colon the Mg excretion constituted only a small % of the total amount excreted by the whole gut and remained const. whether the dogs were on a diet deficient or

rich in Mg. Of parenterally injected Mg, 70—90% was excreted by the urine and none appeared in the colon or in the rest of the alimentary canal.

NUTR. ABS. (m)

**Metabolism of sulphur. II. Metabolism of sulphur and protein in infants and children.** A. BLAZZO (J. Physiol. Path. gén., 1936, 34, 120—135).—The urinary concn. and output of S and neutral S fraction per unit of body-wt. in infants were > in older children. Replacement of part of the (boiled or unboiled) mother's milk with cow's milk did not change the relative concns. of the S fractions. The total S in infant's faeces was very small and its concn. was the same as for a child. Of the S fractions, ethereal S was present in greatest concn. in the faeces of the child, whereas in infant's faeces neutral S was greater. In the fasting state the total S and S fractions of the blood-serum were the same for infants and older children. Inorg. S was 8—10 mg. per 100 ml. The ethereal S fraction was < the inorg.

NUTR. ABS. (m)

**Bone formation. I. Normal bone formation and the constitution of mineral reserves during development. II. Rickets in the growing rat.** A. ROCHE and I. GARCIA (Bull. Soc. Chim. biol., 1936, 18, 1014—1026, 1027—1040).—I. During ossification in the normal rat the ratio P/N of the femur and tibia diminishes slightly until the animals reach 25—30 g. wt. The ratio then increases to the original val. when the rats weigh 45 g., and after a short period when the val. is almost const., a steady increase takes place till the wt. reaches 150 g.

II. In young rats fed on a vitamin-D-deficient diet the femur and tibia show development of rachitic lesions until the 16th day. Spontaneous recovery then takes place, being complete after 55 days. These observations are associated with an increase in H<sub>2</sub>O and N and a decrease in P and the ratio P/N, this being followed in the period of apparent recovery by normal vals. for H<sub>2</sub>O and N, but low P. vals. A. L.

**Electrolyte changes in muscle during activity.** W. O. FENN and D. M. CORB (Amer. J. Physiol., 1936, 115, 345—356).—Stimulation of rat's muscles through the nerve causes exchange of about 15% of K<sup>+</sup> for Na<sup>+</sup>, and increases in H<sub>2</sub>O and extracellular NaCl, all these changes being reversed during recovery. Frog muscles lose K<sup>+</sup> only when stimulated directly.

R. N. C.

**Effect of fat on the  $p_H$  of the contents of the duodenum.** J. E. THOMAS and J. O. CRIDER (Amer. J. Physiol., 1936, 114, 603—608).— $p_H$  becomes neutral or slightly acid, probably through inhibition of gastric secretion and motility.

R. N. C.

**Biological action of radiations. Selectivity factors. I. Time factor.** J. PALACIOS and H. TELLEZ-PLASENCIA (Anal. Fis. Quím., 1934, 32, 677—681).—A theoretical study of the relative rates of destruction of normal and dividing cells.

F. R. G.

**Comparative effects of X-rays and neutrons on normal and tumour tissue.** J. H. LAWRENCE, P. C. ARBERSOLD, and E. O. LAWRENCE (Proc. Nat. Acad. Sci., 1936, 22, 543—557; cf. this vol., 632).—Per unit of ionisation produced, neutrons are three

times as effective as X-rays in causing the deaths of normal mice, and four times as effective in destroying sarcoma 180 *in vitro*. A marked fall occurs in the no. of white blood cells of mice exposed to either radiation, the min. occurring 4 days after irradiation.

F. A. A.

**Radiation sensitivity of "Photodyn."** G. KOEGL (Strahlenther., 1935, 54, 182—184; Chem. Zentr., 1935, ii, 3795).—"Photodyn," a hæmatoporphyrin prep., is active only in the light. Its therapeutic use and a series of radiation experiments are described; it is most sensitive to yellow light.

H. N. R.

**Liberation of an acetylcholine-like substance from surviving nerve fibres during electrical stimulation *in vitro*.** G. BERGAMI (Boll. Soc. ital. Biol. sperim., 1936, 11, 275—277).—Stimulation of nerve-fibre (dog's vagus or phrenic) in eserine-Ringer's solution produces a substance which resembles acetylcholine in its action on leech-muscle preps.

F. O. H.

**Survival of ascarid eggs after centrifuging.** H. W. BEAMS and R. L. KING (Science, 1936, 84, 138).—Centrifuging at  $1-4 \times 10^5 g$  does not kill eggs of *A. suum*. The killing of cells by centrifuging appears to be due to mechanical distortion or disruption rather than to a disturbance of the spatial relationship of their mol. parts.

L. S. T.

**Circulatory and visual effects of oxygen at three atmospheres pressure.** A. R. BEHNKE, H. S. FORBES, and E. P. MOTLEY (Amer. J. Physiol., 1936, 114, 436—442).

R. N. C.

**Effect of carbon monoxide on recovery of frog skeletal muscle.** J. B. HURSH (Amer. J. Physiol., 1936, 114, 625—634).—Excess O<sub>2</sub> consumption and recovery heat production of a stimulated muscle in air are decreased by placing in 79% CO and 21% O<sub>2</sub>. The rate of fatigue is the same. Lactic acid (I) concn. is not increased, and the effect of CO is not diminished by CH<sub>3</sub>I-CO<sub>2</sub>H, indicating that CO does not inhibit oxidation of (I).

R. N. C.

**Insensible water loss in relation to water ingestion in man.** J. F. HALL, jun., and G. S. MCCLURE (Amer. J. Physiol., 1936, 115, 670—678).—Rate of insensible perspiration is not increased by ingestion of H<sub>2</sub>O or 1% NaCl, or by injections of pituitrin, which, however, produce increases after H<sub>2</sub>O ingestion. The rate is increased by ingestion of sucrose, and lowered by dehydration >6% of the body-H<sub>2</sub>O.

R. N. C.

**The periodic system and biological action.** A. LENDLE (Chem.-Ztg., 1936, 60, 833—835).—A discussion.

**Physiological effects of mineral salts in natural waters.** C. B. POLLARD (J. Amer. Water Works Assoc., 1936, 28, 1038—1043).—A review.

**Skeletal changes in rats induced by a diet extremely poor in inorganic salts.** M. F. CLARKE, A. L. BASSIN, and A. H. SMITH (Amer. J. Physiol., 1936, 115, 556—563).

R. N. C.

**Sodium deficiency [in animals].** H. E. HIMWICH, J. F. FAZIKAS, and M. A. SPIERS (Proc. Soc.



Exp. Biol. Med., 1936, 34, 450—451).—Dogs, deprived of NaCl by intraperitoneal injection of glucose solutions, showed an increase in blood-urea and total solids, low serum-Cl', and a creatinuria.

W. O. K.

Colloidal potassium complexes.—See this vol., 1338.

Mechanism of the hæmatopoietic action of cobalt. J. M. ORTEN (Amer. J. Physiol., 1936, 114, 414—422).—Co increases the rate of formation of hæmoglobin and erythrocytes without diminishing the rate of cell destruction.

R. N. C.

Hypoglycæmic and other actions of phosphotungstic acid, phosphomolybdic acid, and allied substances. H. N. MUKHERJEE (Biochem. J., 1936, 30, 1583—1585).—0.2—0.3 g. of phosphotungstic (I), phosphomolybdic, molybdic, or silicotungstic acids, or Na tungstate, Na vanadate, or  $\text{NH}_4$  phospho-18-tungstate, fed by stomach tube to rabbits, has a hypoglycæmic effect comparable with 0.6 unit of insulin. Some of these, especially (I), have a diuretic action. The hypoglycæmic and diuretic actions of (I) were also tested on human diabetic patients, with positive results. The hypoglycæmia lasts longer than that produced by insulin. These substances behave towards benzidine and alkaline phenolphthalein like oxidising enzymes.

F. A. A.

Ætiological studies on formation of skin blisters in viscose workers. W. C. HUEPER (J. Ind. Hyg., 1936, 18, 432—447).—Blisters occurring on the fingers of doffers are caused by  $\text{CS}_2$  in the drip. Protective measures are indicated.

J. N. A.

Changes in skin after cauterisation with dichlorodiethyl sulphide and mineral acids. I. DORFFEL and POPPING (Virchow's Arch., 1935, 295, 1—20; Chem. Zentr., 1935, ii, 3945).

A. G. P.

Effect of dichlorodiethylsulphone on brain respiration. R. A. PETERS (Nature, 1936, 138, 327—328).—The effect of  $(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{SO}_2$  on brain respiration *in vitro* resembles in detail that of  $\text{CH}_2\text{I}-\text{CO}_2\text{H}$  (A., 1935, 262). The change of lactic acid to  $\text{AcCO}_2\text{H}$  (I) is unaffected, but the further oxidation of (I) is inhibited.

L. S. T.

Effect of 2:4-dinitrophenol (Thermol) on the gas metabolism of pigeons. Z. CATALDO (Boll. Soc. ital. Biol. sperim., 1932, 7, 767—770; Chem. Zentr., 1935, ii, 3792).—Injection of 2:4-dinitrophenol (I) (<5 mg. per kg.) increases  $\text{O}_2$  consumption. Atropine has little influence on this action although the birds become less resistant. During the action of (I) the R.Q. indicates that sugar is first consumed and when this process is well advanced fats are affected.

A. G. P.

Influence of temperature on stimulation of oxidation by dinitro-, dihalo-, and trihalo-phenols. M. E. KRAHL and G. H. A. CLOWES (Proc. Soc. Exp. Biol. Med., 1936, 34, 567—569).—The stimulating action of 4:6-dinitro-*o*-cresol (I) on the eggs of *Arbacia punctulata* and *Nereis limbata* is max. at concns. of  $4-8 \times 10^{-6}M$ , independently of the temp. The abs. increase is greatest and the relative increase least at the higher temp. The

optimum % increase in  $\text{O}_2$  consumption of rat kidney slices in presence of 2:4:5-trichloro-, 2:4-dichloro-, and 2:4:6-tri-iodo-phenol and (I) at  $20^\circ$  is  $>$  at  $37^\circ$ .

W. O. K.

Toxicity and action on guinea-pigs of synthetic *l*-camphor. R. HAZARD and R. LARDE (J. Pharm. Chim., 1936, [viii], 24, 118—120).—The toxicities of the three stereoisomeric camphors are in the order  $l > dl > d$ .

W. O. K.

Derivatives of  $\beta$ -amino- $\alpha$ -hydroxy- $\alpha$ -phenylpropionic acid [pharmacological properties].—See this vol., 1377.

Biological analogy of bile acids and sterols. Influence of bile salts on growth and morphogenesis of tadpoles. D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 136—137).—Na glyco- and tauro-cholate accelerate growth and morphogenesis in the same way as cholesterol.

G. H. B.

Influence of amino-acids on blood-sugar regulation in dogs with Eck fistulæ. L. KESZTYUS and J. MARTIN (Arch. exp. Path. Pharm., 1936, 182, 514—520).—Arginine, cystine, and tyrosine increase the blood-sugar of dogs with fistulæ. The inactivity of these  $\text{NH}_2$ -acids in normal dogs is due to rapid decomp. in the liver. Injection of glycine into normal dogs produces a hyperglycæmia followed after 1 hr. by a hypoglycæmia, probably due to adrenaline- followed by a compensatory insulin-action.

F. O. H.

Role of choline in removable shock in the guinea-pig's heart. S. WENT and K. LISSAK (Arch. exp. Path. Pharm., 1936, 182, 509—513).—During anaphylactic shock (ox serum) in the isolated, surviving heart, perfusates acquire a slowing action (inhibited by atropine) on the frog's heart but are inactive on leech preps.; acetylation of the perfusates produces a typical acetylcholine activity (frog's heart, leech). The choline content (to which the behaviour of the heart during shock is due) of the heart decreases after shock but the histamine content remains unchanged.

F. O. H.

Comparative effects of pancreas and choline on blood-cholesterol of depancreatized dogs maintained with insulin. I. L. CHAIKOFF and A. KAPLAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 413—416).—Oral administration of raw pancreas to depancreatized dogs on a suitable basic diet increased their abnormally low blood-cholesterol, but choline in quantities  $>$  the amounts present in the lecithin of the raw pancreas was without appreciable effect.

W. O. K.

Effect of acetylcholine on the blood-flow through the stomach and legs of the rat. H. NECHELES, R. FRANK, W. KAY, and E. ROSENMAN (Amer. J. Physiol., 1936, 114, 695—699).

R. N. C.

Blood-amylase response to acetyl- $\beta$ -methylcholine chloride in rabbits. A. SCHIFFRIN, L. TUCHMAN, and W. ANTOPOL (Proc. Soc. Exp. Biol. Med., 1936, 34, 539—540).—In rabbits there is usually but not always a marked increase in blood-amylase after intramuscular injection of acetyl- $\beta$ -methylcholine chloride.

W. O. K.

Chemical transmission of vagal effects to the small intestine. H. BUNTING, W. J. MEEK, and C. A. MAASKE (Amer. J. Physiol., 1935, 114, 100—105).—Vagal stimulation results in the formation of an acetylcholine-like substance in the splanchnic area. It comes partly from the small intestine, from which it can be removed by perfusion.

R. N. C.

Action of the nitrogenous bases of the gastric juice on blood-pressure, pancreatic secretion, and flow of bile. S. A. KOMAROV (Amer. J. Physiol., 1936, 115, 604—609).—The arginine fraction from canine gastric juice exhibits a histamine-like action on blood-pressure and pancreatic secretion. The lysine fraction increases blood-pressure and stimulates pancreatic and bile flow. The histidine fraction is without effect.

R. N. C.

Physiological importance in nutrition of methods of preparation of foodstuffs. I. Influence of roasting with coffee, coffee substitutes, and similar products. B. BLEYER, W. DIEMAIR, F. FISCHLER, K. TAUFEL, F. ARNOLD, and H. THALER (Biochem. Z., 1936, 286, 408—428).—The production during roasting of coffee, chicory, wheat, etc. of histamine-like substances is detected chemically and confirmed by biological test on guinea-pig's intestine.

P. W. C.

Action of tyramine in increasing blood pressure in pallid hypertension. H. A. HEINSEN and H. J. WOLF (Z. klin. Med., 1935, 128, 213—222; Chem. Zentr., 1935, ii, 3945).—In chronic nephritis and in malignant nephrosclerosis, tyramine occurs in the blood. It is formed in kidneys by decarboxylation of tyrosine.

A. G. P.

Humoral anti-adrenaline regulation. B. TARRAS-WAHLBERG (klin. Woch., 1935, 14, 793—795; Chem. Zentr., 1935, ii, 3789).—Rabbit and guinea-pig blood contains a substance which causes contraction of the small intestine of guinea-pigs and a decreased blood-pressure in atropinised rabbits. It is dialysable and more resistant to boiling 0.5N-HCl than to 0.5N-NaOH. The activity of the blood is increased by pre-injection of adrenaline.

Anti-pernicious anaemia principle in stomach. I. Method to improve stomach preparations. E. A. GREENSPON (J. Amer. Med. Assoc., 1936, 106, 266—271).—No response was produced by 40 g. of ventriculin mixed with 200 ml. of H<sub>2</sub>O, 0.1 g. of pepsin (I), and dil. HCl and incubated at 38° overnight, when fed to a patient with pernicious anaemia in relapse. Depepsinised gastric mucosa produced a marked reticulocyte response in a case of pernicious anaemia. The activity was destroyed by incubation with (I) and HCl, but not with HCl alone. Since a reticulocyte response was produced in a case of pernicious anaemia by daily oral administration of 250 ml. of normal gastric juice freed from (I) and since a single intramuscular injection of the concentrate of 540 ml. of normal gastric juice freed from (I) produced in 2 cases of pernicious anaemia reticulocyte crises of 24.5 and 21% and increases in the red cell count of 1.8 and 1.6 millions, respectively, it is concluded that (I) destroys the active principle of

the mucosa and that the presence of an "extrinsic factor" is unnecessary in the production of the principle.

NUTR. ABS. (m)

Comparison of the action of insulin and of the hypoglycaemic principle of the jejunum in the pancreatectomised dog. F. RATHERY, A. CHOAY, and P. DE TRAVERSE (Compt. rend., 1936, 203, 206—208).—Equiv. doses (tested on a rabbit) of an extract (cf. this vol., 1158) of the jejunum of the ox and of insulin injected intramuscularly produce almost identical decreases in the concn. of the blood-sugar of a depancreatized dog; the duration of action of the former is more prolonged.

J. L. D.

Comparative effects of barbituric acid derivatives on isolated heart. R. L. JOHNSTON (J. Pharm. Exp. Ther., 1936, 57, 333—336).—Perfusion of the isolated turtle heart with the Na salts of the following barbituric acid derivatives (concn. 0.0005M) in Ringer's solution at  $p_{H}$  7.2—7.4 showed that the toxicity decreased in the order: oral, amytal, nembutal, evipal, phenobarbital, phanodorm, barbital.

J. N. A.

Detoxification of dendrobine by "sodium amytal." K. K. CHEN and C. L. ROSE (Proc. Soc. Exp. Biol. Med., 1936, 34, 553—554).—Na amytal administered to rabbits poisoned by dendrobine hydrochloride can antidote up to 5 min. lethal doses of the alkaloid.

W. O. K.

Anæsthetic properties of "sodium ethylpentyl-malonylthiourea." M. G. MULINOS (Proc. Soc. Exp. Biol. Med., 1936, 34, 506—507).—Na ethylmalonylthiobarbiturate (Na pentothal) has a pharmacological action resembling its O-analogue (Na pentobarbital).

W. O. K.

Elimination of cobalt in the bile. F. CAUJOLLE (Bull. Soc. Chim. biol., 1936, 18, 1081—1090).—In dogs under chloralose anaesthesia 3.2% of aq. CoCl<sub>2</sub> injected intravenously is eliminated rapidly in the bile. With a permanent fistula and no anaesthetic the elimination is less rapid.

A. L.

Anæsthetic effects of furan derivatives. V. E. HENDERSON and A. H. R. SMITH (J. Pharm. Exp. Ther., 1936, 57, 394—398).—Furan and its H<sub>4</sub>, Me<sub>2</sub>, and dimethyltetrahydro-derivatives are of no clinical val. as anaesthetics; the first three produce fatty changes in the liver, a possible mechanism of which is discussed.

J. N. A.

Fishes as test subjects for the biological action of various substances and for the determination of the nature of urease. N. KAWAMOTO (J. Biochem. Japan, 1936, 23, 267—298).—Saponin, adrenaline, and atropine are readily absorbed through the gills of carp in which they exert their characteristic action. The action on the blood-sugar of normal and dialysed aq. insulin thus administered indicates the presence of hyper- and hypo-glycaemic fractions. The gills are impermeable to normal urease preps. but are permeable to tryptically digested preps., whilst on prolonged digestion the activity disappears; the data indicate that urease has a polypeptide structure.

F. O. H.

Destruction of cardio-active glucosides by acids and alkalis. F. T. VON BRÜCKE (Arch. exp.



Path. Pharm., 1936, **182**, 444—451).—Data of the action of 0.05—0.1*N*-HCl and -NaOH and of 0.1%  $\text{Na}_2\text{CO}_3$  at 37° on *Digitalis* glucosides, *g*- and *k*-strophanthin, and cymarin are tabulated. The glucosides are not affected by trypsin or pepsin but are inactivated at gastric acidity and, very slowly, at duodenal alkalinity; decomp. occurs with 0.05—0.1*N*-NaOH at 37°. F. O. H.

Decurarising substances. A. ROSENBLUETH, D. B. LINDSLEY, and R. S. MORISON (Amer. J. Physiol., 1936, **115**, 53—68). R. N. C.

Esmodil, a new vagus-stimulant. G. HECHT (Klin. Woch., 1935, **14**, 957—958; Chem. Zentr., 1935, ii, 3945).—Esmodil,  $\text{CH}_2\text{C}(\text{OMe})\text{CH}_2\text{NMe}_3\text{Br}$ , is not enzymically decomposed in the organism and is stable in dil. alkali but not in dil. acid. Physiological activities are described. A. G. P.

Pharmacological action of coriamyrtin. (A.) A. H. MALONEY. (B.) E. E. SWANSON and K. K. CHEN (J. Pharm. Exp. Ther., 1936, **57**, 361—375; 410—418).—(A) The min. lethal doses of coriamyrtin (I) for the frog, rabbit, and rat are 10, 0.4, and 1 mg. per kg., respectively. (I) increases the blood-sugar of the rabbit by 13%, has very little effect on blood pressure, but powerfully stimulates respiration. (I) is very toxic, and resembles picrotoxin in its action, which is of very short duration.

(B) (I) abolishes anaesthesia and wakens animals under the influence of a barbiturate. Na amytal is far more effective in combating (I) poisoning than is (I) in counteracting-Na amytal poisoning. J. N. A.

Stereoisomeric nature of oxidation and fermentation. G. A. GAUSE (Nature, 1936, **138**, 245—246).—The fermentations of glucose by different micro-organisms are more strongly depressed by *l*- than by *d*-nicotine, but the oxidations are more strongly depressed by the *d*-form. In green algae oxidations are direct and sensitive to *d*-nicotine poisoning, but in the frog, fowl, green linnet, etc. oxidations are coupled with fermentations and are more sensitive to the action of *l*-nicotine. The action of the optically-active nicotines on the metabolism of mouse tissue is also described. L. S. T.

Effect of atropine and pilocarpine on the emptying time of the human stomach. R. C. HERRIN (Amer. J. Physiol., 1936, **115**, 104—112). R. N. C.

Effect of atropine and pilocarpine on gastric emptying in normal and denervated dogs. R. C. HERRIN, A. RABIN, and E. A. BACHHUBER (Amer. J. Physiol., 1936, **115**, 113—120). R. N. C.

Blood-sugar level after administration of pilocarpine, atropine, and acetylcholine. M. C. HRUBETZ (Amer. J. Physiol., 1936, **114**, 551—554).—Pilocarpine (I) raises blood-sugar (II) in rats, the max. occurring in 15 min. Atropine lowers (II), the max. effect occurring in 90 min., and inhibits the effect of (I). Acetylcholine lowers (II), the min. val. being reached in 20 min. R. N. C.

Action of drugs on choline esterase of brain. F. BERNHEIM and M. L. C. BERNHEIM (J. Pharm. Exp. Ther., 1936, **57**, 427—436).—Choline esterase

(I) is greatly inhibited by very small concns. of morphine and apomorphine, and it is suggested that these and possibly other centrally acting drugs may cause accumulation of acetylcholine in brain by inhibiting (I). In most animals the activity of (I) per mg. of dry wt. is greater in the brain than in the serum. J. N. A.

Comparative action of methylephedrine and ephedrine. I. Systemic effects. II. Bronchial effects. C. PAK and B. E. READ (Quart. J. Pharm., 1936, **9**, 235—255, 256—267).—I. The circulatory effect of methylephedrine (I) is similar to but < that of ephedrine (II). (I) has an inhibitory effect (probably due to pressor action) on respiration but not the secondary accelerating action of (II). (I) does not stimulate the central nervous system, whilst the toxic effect on rabbits and dogs and dilation of the pupil are < those due to equal doses of (II). Other differences in pharmacological action are described.

II. The bronchial dilator effect of (I) in anaesthetised cats is slower than, but the intensity and duration are approx. equal to, that of (II). (I) and (II) in concns. of 10<sup>-2</sup>—10<sup>-3</sup>% respectively dilate and constrict the isolated bronchioles. F. O. H.

Substituted hydroxybenzyl alcohols.—See this vol., 1374.

Excretion of "skiodan," "diodrast," and "hippuran" by the dog. K. A. ELSOM, P. A. BOTT, and E. H. SHIELDS (Amer. J. Physiol., 1936, **115**, 548—555).—Skiodan excretion is independent of its concn. in the plasma, and consistently < that of creatinine (I) by approx. 10%. Diodrast and hippuran excretions depend on their concns. in the plasma. Their clearances are approx. equal to that of (I) at high but greater at low plasma-I. R. N. C.

Effect of various poisons on the movement of chloride against concentration gradients from intestine to plasma. R. C. INGRAHAM and M. B. VISSCHER (Amer. J. Physiol., 1936, **114**, 681—687).—Removal of Cl<sup>-</sup> in presence of  $\text{SO}_4^{--}$  is abolished by  $\text{Na}_3\text{AsO}_3$ , NaF,  $\text{H}_2\text{S}$ ,  $\text{HgCl}_2$ , and NaCN, in presence of which Cl<sup>-</sup> moves into the intestine; the increases in  $[\text{Na}^+]$  and  $[\text{SO}_4^{--}]$  are also abolished or reversed. Impermeability of the intestinal epithelium to bi- or multi-valent anions is apparently a condition for its performing osmotic work on Cl<sup>-</sup>. R. N. C.

[Pharmacological] action of arsenic and antimony. H. A. OELKERS and E. VINCKE (Arch. exp. Path. Pharm., 1936, **182**, 499—503).—The *in-vivo* (rabbits) reduction of oxalacetic to fumaric acid is inhibited by  $\text{KAsO}_3$  and K Sb tartrate (cf. Szent-Gyorgyi *et al.*, A., 1935, 1406), which also diminish the  $\text{O}_2$  consumption of liver tissue *in vitro*. Thus the toxic action of As and Sb is mainly due to disturbances of tissue- and organ-metabolism. F. O. H.

Influence of vitamin deficiency on the resistance of rats to neoarsphenamine, mercurochrome, pernocton, and insulin. R. WIEN (Quart. J. Pharm., 1936, **9**, 268—297).—The resistance to the toxicity of the three drugs is diminished by deficiency of vitamin-A, -B complex, or -D; that to insulin, as indicated by the blood-sugar curve after injection

of 0.5 unit per kg., is unaltered by deficiency of -A or -D whilst with B-avitaminosis, rats (which have normal fasting blood-sugar vals.) are more sensitive owing to a retardation in the recovery process.

F. O. H.

**Antidotal action of magnesium, hydrazine, and phenylhydrazine thioacetates, and hydrazine sulphate in mercurial poisoning.** G. DE NITO (Boll. Soc. ital. Biol. sperim., 1936, 11, 323—324).—Enteral, but not parenteral, administration has a significant antidotal action.

F. O. H.

**Limitation of fluorine toxicosis in the rat with aluminium chloride.** G. R. SHARPLESS (Proc. Soc. Exp. Biol. Med., 1936, 34, 562—564).—The toxic effect of NaF *per os* on the growth and teeth of young rats is antagonised by the addition to the diet of small quantities of  $AlCl_3$ .

W. O. K.

**Poisoning by vapours of beryllium oxyfluoride.** I. GELMAN (J. Ind. Hyg., 1936, 18, 371—379).—The toxic effects in man include fever followed after 2—5 days by lung lesions. The symptoms differ from those observed in cases of poisoning by F, HF,  $SO_2$ , or Be oxyfluoride in the form of dust.

J. N. A.

**Lead absorption in man. III. Blood-pressure observations.** E. L. BELKNAP (J. Ind. Hyg., 1936, 18, 380—390).—The average blood pressures of 81 workers with a heavy Pb absorption varied within normal limits, but tended to decrease slightly over a period of 1—5 years. There was no significant increase in systolic or diastolic pressure.

J. N. A.

**Lead in muscle and skin of cattle showing saturnism.** KOHN-ABREST (Bull. Acad. vet. France, 1936, 9, 122—123).—Muscles from 3 cattle slaughtered on account of saturnism contained only traces of Pb, but the skins contained 25—40 p.p.m., vals. similar to those reported in fatal cases of saturnism in human beings.

NITR. ABS. (*m*)

**Toxicology of selenium. I. Distribution of selenium in acute and chronic selenium poisoning. II. Urinary excretion of selenium.** H. C. DUDLEY (Amer. J. Hyg., 1936, 23, 169—180, 181—186).—I. In acute or chronic poisoning induced by feeding inorg. or org. Se compounds Se was found throughout the whole organism. The Se was distributed by the blood, being held chiefly in a protein-like complex. The serum, plasma, and fibrin did not contain Se, but it was present in the centrifuged corpuscles and the clot. It was largely deposited in the liver, kidneys, and spleen in acute cases and in the liver and kidneys in chronic cases. The amounts present in the bile and urine indicated that excretion was mainly by hepatic and renal routes. In the urine the Se was present as an  $Et_2O$ -sol., volatile compound. In chronic cases in pigs, 8—20 p.p.m. of Se were found in the hoofs.

II. The urine of men engaged in or near the extraction and processing of Se from electrode slimes in Cu refinery contained up to 0.069 p.p.m. of Se. The urinary Se in different individuals showed no correlation with the intensity of the symptoms.

NUTR. ABS. (*m*)

**Monstrosities produced by the injection of selenium salts into hens' eggs.** K. W. FRANKE, A. L. MOXON, W. E. POLEY, and W. C. TULLY (Anat. Rec., 1936, 65, 15—22).—The monstrosities resemble those produced when the hens are fed on wheat containing Se. As, F, and Pb in sublethal doses have no such action.

R. N. C.

**Inhibiting effect of sulphur in selenised soil on toxicity of wheat to rats.**—See B., 1936, 1011.

**Toxicological detection of hydrocyanic acid. Detection of poisoning by very small amounts of hydrocyanic acid.** P. R. ORELLA (An. Farm. Bioquim., 1935, 6, 1—11; Chem. Zentr., 1935, ii, 3804).—HCN is best fixed for toxicological analyses by means of  $AgNO_3$ . The formation of HCN in normal tissues by putrefaction or by the action of  $H_2SO_4$ — $H_2CrO_4$  does not occur.

J. S. A.

**Toxicity of dioxan.** H. H. SCHRENK and W. P. YANT (J. Ind. Hyg., 1936, 18, 448—460).—A resumé of work by various investigators. Animal experiments show that the toxicity of dioxan when absorbed through the skin, inhaled, ingested, or given by subcutaneous or intravenous injection is comparatively low, but large doses cause serious harm, the principal damage being to the kidneys and liver.

J. N. A.

**Toxicology of *Deris*.**—See B., 1936, 1013.

**Lactucarium. II. Enzymes of the sap of *Lactuca virosa*.** K. H. BAUER and K. BRUNNER (Pharm. Zentr., 1936, 77, 598—601; cf. A., 1929, 1181).—The fresh sap darkens unless placed immediately in 96% EtOH. The EtOH ppts. amongst other substances two oxidases, a tyrosinase and a lacase, which are almost or entirely absent from the commercial dried sap (lactucarium).

R. S. C.

**Enzymes in ontogenesis (Orthoptera). II. The indophenol oxidase.** J. H. BODINE and E. J. BOELL (J. Cell. Comp. Physiol., 1936, 8, 213—230).—The indophenol oxidase (I) content of grasshopper eggs has been determined throughout development. The  $CN'$ -sensitive respiratory mechanism of the eggs is dependent on, whilst (I) activity is independent of, organisation in the cells. Respiration during diapause is insensitive to  $CN'$ , and is unaffected by grinding. As (I) activity shows no diminution during this period, there can be no relation between the normal functioning of (I) and its action in the *in-vitro* oxidation of  $p$ - $C_6H_4(NH_2)_2$ .

E. A. H. R.

**Oxidation product of pyrocatechol when oxidised by means of tyrosinase.** H. WAGREICH and J. M. NELSON (J. Biol. Chem., 1936, 115, 459—465).—Two O atoms are concerned in the oxidation of  $o$ - $C_6H_4(OH)_2$  (I) in the presence of tyrosinase (II) over the  $p_H$  range 4.3—8. If the reaction is carried out in the presence of  $NH_2Ph$ , a dianilinobenzoquinone (III) is formed, and 3 O are used, over the  $p_H$  range 4.3—7. If  $NH_2Ph$  is added to the oxidised (I), (III) is formed, one O being consumed; this reaction is catalysed by (II). The data indicate that the initial oxidation of (I) involves 2 O per mol.

F. A. A.

**Peroxidases. III. Potentiometric determination of activity.** B. B. DEY, S. RENGACHARI, and M. V. SITHARAMAN (J. Indian Chem. Soc., 1936,



13, 390—398).—The titration of mixtures of quinol and  $\text{H}_2\text{O}_2$  against  $\text{Ce}(\text{SO}_4)_2$  cannot be followed potentiometrically (cf. A., 1929, 783; 1930, 727) although  $\text{H}_2\text{O}_2$  can be determined alone in  $\text{HCl}$  or  $\text{AcOH}$ . In determining the peroxidase (I) concn. in plant sap (A., 1931, 1455) this method cannot be used because the reducing substances in sap are oxidised.  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  can be employed successfully to determine quinol potentiometrically and hence to arrive at the (I) concn. J. L. D.

**Poisoning with copper and reactivation in enzymic oxidation-reduction.** B. ANDERSSON (Z. physiol. Chem., 1936, 242, 205—209).—Although partly purified cozymase (I), xanthine, and uric acid reactivate the Schardinger enzyme system after poisoning with  $\text{CuSO}_4$  (cf. Wagner-Jauregg *et al.*, this vol., 895), no reactivation is produced by highly purified (I). W. McC.

**Catalytic action of lactoflavin-5'-phosphoric acid. Synthesis of the yellow enzyme.** R. KUHN and H. RUDY (Ber., 1936, 69, [B], 1974—1977).—Synthetic lactoflavin-5'-phosphoric acid reacts in neutral solution with the colloidal carrier of Warburg's yellow enzyme forming a non-fluorescent, non-dialysable chromoprotein resolved into its components by dil. acid. The product catalyses the oxidation of the Neuberg or Robison ester, measured by decolorisation of methylene-blue or absorption of  $\text{O}_2$ , in exactly the same manner as the natural material. The theory that an enzyme consists of a colloidal carrier and a chemically active group is thus strongly supported and the very sp. type of union is shown by the necessity for  $\cdot\text{PO}(\text{OH})_2$  at 5' and the flavin nucleus and  $\text{NH}$  at 3 for partial union with the carrier.

H. W.

**Components of dehydrogenase systems. XIII. Non-identity of alcohol- and triosephosphoric acid-apodehydrogenases.** H. VON EULER, E. ADLER, and S. KYRNING (Z. physiol. Chem., 1936, 242, 215—224; cf. this vol., 1150).—The apodehydrogenase (I) obtained from yeast maceration juice by fractional pptn. with  $(\text{NH}_4)_2\text{SO}_4$ , and supplemented with cozymase (II) and flavin enzyme, specifically dehydrogenates  $\text{EtOH}$  anaerobically [methylene-blue (III) as acceptor] but has no action on dihydroxyacetonephosphoric acid (IV). Hence (I) of  $\text{EtOH}$  is not identical with (I) of (IV) although both always occur together in non-purified enzyme preps. Both apodehydrogenases combine specifically with (II), which carries  $\text{H}$  from the donor to the acceptor system. Decolorisation of (III) with hexosediphosphoric acid as substrate occurs only when zymohexase and (I) of (IV) are present together. (I) specificity probably extends to triosephosphoric acids other than (IV) and hence is significant for the oxidation-reduction mechanism of alcoholic fermentation. W. McC.

**Enzymic dehydrogenation of trideuteroacetic acid.** R. SONDERHOFF and H. THOMAS (Naturwiss., 1936, 24, 570).—The oxidation of  $\text{CD}_3\cdot\text{CO}_2\text{Na}$  by  $\text{O}_2$  in presence of yeast cells proceeds at  $\frac{1}{2}$  of the rate observed with  $\text{NaOAc}$ . In both cases some of the acetate is incorporated into the cells as carbohydrate and fat, whilst succinic acid is also formed. During

the oxidation of  $(\text{CD}_3\cdot\text{CO}_2)_2\text{Ba}$  citric acid is formed. The succinic acid is not pure  $(\text{CD}_2\cdot\text{CO}_2\text{H})_2$ , but some replacement of  $\text{D}$  with  $\text{H}$  occurs. Similarly the citric acid contains a lower ratio of  $\text{D}/\text{H}$  than corresponds with  $\text{HO}\cdot\text{C}(\text{CD}_2\cdot\text{CO}_2\text{H})_2\cdot\text{CO}_2\text{H}$ . This confirms the theory of Wieland and Sonderhoff. W. O. K.

**Amylase system of rice grain during ripening and germination.** K. V. GIRI and A. SREENIVASAN (Nature, 1936, 138, 406—407).—Rice grain contains both  $\alpha$ - and  $\beta$ -amylases, which are differentiated by their hydrolysis of amyloamylose and by their  $p_{\text{H}}$  optima at 7.0 and 4.6, respectively. Both enzymes are present in dormant seed, largely in a condition not extractable by  $\text{H}_2\text{O}$ , but extractable in an active state by  $\text{PO}_4'''$  buffer at  $p_{\text{H}}$  7.0.  $\alpha$ -Amylase becomes inactive as ripening advances and then active again during germination. The view that amylase arises only during germination of the grains (A., 1933, 1343) is untenable. L. S. T.

**Enzymic studies on cereals. V. Saccharifying amylase of rice. VI. Saccharifying amylase of well-cleaned rice.** G. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1936, 12, 783—792, 793—799).—V. The optimum  $p_{\text{H}}$  of the saccharifying amylase (I) (obtained by extraction with  $\text{H}_2\text{O}$  at approx.  $0^\circ$  for 10 hr.) from unhusked and uncleaned rice and rice bran are 5.0, 4.7, and 6.6, respectively. Purification by dialysis or pptn. with  $\text{EtOH}$  moves the optimum more to the acid side. The optimum temp. for (I) is  $45^\circ$ . (I) is heat-sensitive.

VI. The optimum  $p_{\text{H}}$  vals. of (I) extracted from well-cleaned rice flour with  $\text{NaCl}$  or papain solutions, and then purified by dialysis or pptn. with  $\text{EtOH}$ , are 4.5 and 4.3, respectively. In the outer part of the grain nearly all of (I) is readily sol. in  $\text{H}_2\text{O}$ , but in the inner part it is present in an insol. form as (I)-zymogen. J. N. A.

**Inulinase.** N. K. IYENGAR and M. SREENIVASAYA (Proc. Indian Acad. Sci., 1936, 4, B, 171—177).—Active preps. of inulinase (I) are obtained from species of *Aspergillus* growing on an artichoke medium.  $\text{PO}_4'''$  stimulates the production of (I) by the mould. The preps. may be dried by  $\text{COMe}$ , and (I) is extracted from the dried material by  $\text{PhMe}$ -saturated  $\text{H}_2\text{O}$ . The content and activity of (I) in dried preps. and extracts are directly related to their  $\text{P}$  but not to their total or  $\text{NH}_4\text{-N}$  contents. A. G. P.

**Maltase activity of the blood-serum of various species.** R. H. BARNES and E. M. MACKEY (Amer. J. Physiol., 1936, 114, 534—537).—Sera from a no. of species show maltase activity, which explains why insulin hypoglycaemia is relieved by maltase or glycogen in these species only. R. N. C.

**$\beta$ -Glycuronosidase. III, IV.** G. OSHIMA (J. Biochem. Japan, 1936, 23, 305—311, 311—318; cf. A., 1935, 402).—III. The enzyme is prepared from autolysed extracts of ox spleen by adsorption on kaolin at  $p_{\text{H}}$  2.6—4.4 and elution with  $M/15\text{-Na}_2\text{HPO}_4$ .

IV. The optimum  $p_{\text{H}}$  is 5.0—5.2 with menthol glycuronate in  $\text{OAc}'$  buffer as substrate, the reaction being unimol. and having an average temp. coeff. of 2.66 at  $30\text{—}45^\circ$  and a heat of inactivation of 36.34

kg.-cal. Ultra-violet irradiation inhibits whilst addition of neutral salts accelerates the hydrolysis. The inhibitory action of malic, tartaric, and citric acids and the accelerating action of  $\text{AcOH}$ ,  $\text{EtCO}_2\text{H}$ ,  $\text{Pr}^n\text{CO}_2\text{H}$ , and lactic acid are correlated with the presence or absence of  $\beta\text{-OH}$ . F. O. H.

**Glucosulphatase, an enzyme decomposing sulphuric esters of sugars.** T. SODA (J. Fac. Sci. Tokyo, 1936, I, 3, 149—222).—Data indicating the content of glucosulphatase (A., 1933, 534), phosphatase, and phenolsulphatase in various classes of molluscs are tabulated. Glucosulphatase (optimum  $p_{\text{H}}$  approx. 5; reaction const. of purified preps. given) has a temp. coeff. of approx. 2 over the range  $15\text{--}30^\circ$ , is rapidly inactivated at  $80^\circ$ , and is inhibited to varying extents by sugars and their derivatives (A., 1933, 749; 1934, 560). The physiological role of the enzyme is discussed (see also A., 1934, 520; this vol., 378). F. O. H.

**Reduction of cozymase.** E. ADLER, H. HELLSTROM, and H. VON EULER (Z. physiol. Chem., 1936, 242, 225—249; cf. this vol., 1150).—Cozymase (I) is converted by alkaline  $\text{Na}_2\text{S}_2\text{O}_4$  into a yellow substance (II) (absorption max. at  $360\text{ m}\mu$ ) which is quantitatively reconverted into (I) on neutralising or acidifying.  $\text{Na}_2\text{S}_2\text{O}_4$  at  $p_{\text{H}}$  7.5—8.0 and sp. apodehydrogenase (III) in presence of a H donor convert (I) into dihydrocozymase (IV) with intermediate transient production of (II). When (IV) is acidified 20% is reconverted into (I) and 80% into an inactive substance. (IV) is completely reconverted into (II) by flavin enzyme in presence of  $\text{O}_2$  and by sp. (III) in presence of H acceptor (MeCHO). (I) is not reduced by Zn in 0.1N-NaOH but is rapidly attacked in N-NaOH with production of a yellow colour. (IV) is not attacked by 0.1N-NaOH at  $100^\circ$  in 30 min. but is slowly reconverted into (I) on keeping, the  $p_{\text{H}}$  optimum for the change being 6. (II) rapidly reduces methylene-blue and  $\text{AgNO}_3$ , whereas (IV) reduces  $\text{AgNO}_3$  only very slowly. Possibly the reduction of (I) to (IV) takes place at the N:C linking which joins the  $\text{C}_5\text{H}_5\text{N}$  group to the rest of the mol. This linking is probably the only one in the mol. which is unstable to alkali and is also partly responsible for the fermenting power. W. McC.

**Re-phosphorylation in presence of cozymase.** H. VON EULER, R. VESTIN, and H. HEIWINKEL (Svensk Kem. Tidskr., 1936, 48, 176—183).—In the system, dialysed and aged muscle extract (rabbit)-Mg-phosphocreatine (I), a pyrophosphate (II) fraction is formed by use of (I) in presence of a sufficient amount of a cozymase prep. (III). This action is observed with all samples of (III), independently of method of prep. and degree of purity with the exception of those purified by pptn. with  $\text{EtOAc}$  from  $\text{MeOH-HCl}$ . Products isolated as Ag salts from (III) inactivated by heating with alkali are capable of forming (II). Apparently only 20—25% of (III) is utilised in production of (II). Yields are not increased by increase in temp. or concn. of (I) or (III) or by diminishing the acidity of the solution. Re-esterification takes place rapidly. The (II) produced is freed from a large excess of (I) and (III) by pptn. with metals as used in the isolation of adenosine

triphosphate (IV). It is not formed by the addition of the  $\text{P}_2\text{O}_7$  group to the cozymase mol.; possibly it contains (IV). The substance which acts as substrate in the formation of (II) is probably not identical with cozymase. H. W.

**Cozymase pyrophosphate.** O. MEYERHOF and W. KIESSLING (Naturwiss., 1936, 24, 557—558; cf. this vol., 1026).—Cozymase pyrophosphate (I) has been prepared in purer form; there are 8 N in the mol. to 4 P and 25 C. (I) is not deaminated by inactivated muscle extract. Fermentation by washed, dried yeast is activated more by (I) than by the same amount of cozymase. E. A. H. R.

**Characterisation of sugarphosphoric acids and constitution of the pentosephosphoric acid from cozymase.**—See this vol., 1364.

**Glyoxalase and its co-enzyme. III. Mechanism of the action of glutathione as co-enzyme.** S. YAMAZOYE (J. Biochem. Japan, 1936, 23, 319—334; cf. this vol., 895).—Before conversion into lactic acid (I) and in presence of glyoxalase,  $\text{AcCHO}$  combines (1:1) with glutathione (II). The compound  $\text{AcCHO-(II)}$  (isolated as a crude prep., stable to I) is stable in acid solution, decomp. in neutral or, more rapidly, alkaline media to (I)+(II), a reaction catalysed by glyoxalase. In absence of glyoxalase,  $\text{AcCHO}$  and (II) form a labile complex, readily hydrolysed in neutral or alkaline media to  $\text{AcCHO}$  and (II) [(I) is not formed] and decomposed by I. F. O. H.

**Optical properties of fermentation lactic acids. IV. New enzyme racemase which reveals racemisation of lactic acids.** H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 844—852).—With *Lactobacillus plantarum* and *L. pentoceticus* (dl-formers) in a medium containing PhMe and Ca lactate, the velocity of racemisation was high and identical for both forms of the acid. Racemisation of d- or l-lactic acid or selective decomp. of the r-acid was never observed with *L. Saké* (d-former) and *Leuconostoc mesenteroides* (l-former), even in their resting state. The activity of racemase is only slightly affected by PhMe, but it is sensitive to high temp. (inactivated at  $80^\circ$ ). J. N. A.

**Substance controlling hydrolysing and synthesising actions of lipase. I.** R. ITOH (J. Biochem. Japan, 1936, 23, 299—304).—A detailed account of work already noted (this vol., 895). F. O. H.

**Influence of monochromatic light on action of the fat-splitting enzyme in yeast.** R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1936, 12, 709—713).—The rate of hydrolysis of castor oil by the enzyme from yeast is increased in monochromatic light, the effect increasing with  $\lambda$ . The rate of hydrolysis is inversely  $\propto$  light intensity. J. N. A.

**Absolute activity of choline esterase.** L. H. EASSON and E. STEDMAN (Proc. Roy. Soc., 1936, B, 121, 142—164).—The relative rates at which choline esterase (I) hydrolyses choline esters have been compared with the rates for the non-enzymic hydrolysis. This latter rate approx.  $\propto [\text{OH}^-]$  and decreases with increase in the size of the aliphatic acyl group. The rate of enzymic hydrolysis, with n-acids, in-



creases with the size of the acyl group, but the introduction of a side-chain diminishes the rate. The influence of  $p_H$  on (I) depends on the substrate. For most esters the  $p_H$  optimum is  $>8$ . Within the range  $p_H$  6.8–8.0 the hydrolysis of benzoylcholine is uninfluenced by  $p_H$ . The inhibitory action of miotine (II) on (I) is const. for the different substrates. (II) is unstable in aq. solution. Prostigmine is stable, and its inhibitory action is used to determine the abs. rate of activity of (I). Under nearly optimal conditions one active centre of (I) hydrolyses 3500 mols. of butyrylcholine and 1490 of acetylcholine per sec. The following  $\beta$ -bromoethyl esters were prepared: *formate*, b.p. 147–148°; *propionate*, b.p. 170–175° (slight decomp.), 73–74°/16 mm.; *n*-, b.p. 82.5°/11 mm., and *iso-butyrate*, b.p. 79°/11 mm. The  $\beta$ -bromoethyl esters with a slight excess of  $NMe_3$  gave *formyl*-, m.p. 142°, *propionyl*-, m.p. 146°, *n-butyryl*-, m.p. 100–101°, and *isobutyryl*-, m.p. 127°, *-choline bromide*. E. A. H. R.

**Optical specificity and activation of arginase.** S. EDLBACHER and A. ZELLER (Z. physiol. Chem., 1936, 242, 253–260).—Arginase (I) in conens. usually employed hydrolyses *d*-arginine (II) but not *l*-arginine (III) but when the conen. is greatly multiplied (e.g., 1000-fold) (III) also is quantitatively converted into urea and ornithine. The (I) of pigeon's muscle and kidney and hen's kidney is activated by  $Mn^{++}$ , the action on (II) but not that on (III) being affected.  $NH_2$ -acids (ornithine  $>$  lysine  $>$  glycine  $>$  alanine) check the action of (I) on (II) and (III). W. McC.

**Proteolytic enzymes of sprouted wheat.** II. J. D. MOUNFIELD (Biochem. J., 1936, 30, 1778–1786; cf. this vol., 637).—In germinating wheat seeds proteinase (I) activity increases tenfold in 7 days at 18° after a lag of 2 days. When the seeds are stored in the dark at 18° power to develop (I) activity on germination steadily decreases, the decrease amounting to about 67% in 2 years. In aq. solution all dipeptidase (II) activity is lost in 5 days at 18° but in 45% aq. glycerol (III) the original level of activity is maintained for 21 days. (I) is stable at  $p_H$  4 and 6 but is destroyed at  $p_H$  8 in  $<3$  days at 18° and (II) is fairly stable at  $p_H$  6 and 8 but is destroyed at once at  $p_H$  4. (III) probably acts by maintaining the original  $p_H$  of 6; in aq. extracts the  $p_H$  falls to 4–5 in 1–2 days. NaCN activates (I) and (II), the increase in activity being about 60% for (I) with edestin as substrate (max. requirement of NaCN 0.001*M*), the optimal  $p_H$  being shifted from 4.1 to 4.8. (II) is less affected but the optimal  $p_H$  is shifted also from 7.3 to 7.8 with leucylglycine as substrate and from 7.9 to 8.1 with glycylglycine. W. McC.

**Proteolytic enzymes in the tape worm.** I. A. SMORODINCEV and K. V. BEBESCHIN (Bull. Soc. Chim. biol., 1936, 18, 1097–1105).—Glycerol extracts of *Taeniarhynchus saginatus* and *Taenia solium* contain pepsin, trypsin, and cathepsin, the tryptic action of extracts of the former being  $>$ , and the peptic action  $<$ , that of the latter species. No activation of the cathepsin occurred with  $H_2S$ .

A. L.

**Selective action of gentian-violet on enzymes.** A. Y. WELLS and N. P. SHERWOOD (J. Infect. Dis., 1934, 55, 356–359).—Gelatinases from Gram-positive bacteria were more easily inhibited by gentian-violet (1:400) in acid media than were those from Gram-negative bacteria. Enzymes from the latter liquefied the larger amounts of gelatin. All the enzymes were more active in alkaline media. CH. ABS. (p)

**General nature of catheptic enzymes.** M. BERGMANN and J. S. FRUTON (Science, 1936, 84, 89–90).—A discussion and interpretation of the dual enzyme system of catheptic enzymes. L. S. T.

**Conditions for the action of cathepsin in the tissues of the regenerating organs of amphibia.** V. N. ORECHOVITSCH (Biochem. Z., 1936, 286, 285–289).— $H_2S$  does not activate the cathepsin (I) of regenerating tissues. Cysteine (II) activates the (I) of normal tissues strongly and, to a smaller extent, that of regenerating tissue. With max. activation, the hydrolysis of gelatin by extracts of regenerating tissues is  $>$  that by extracts of normal tissue. The intensity of autolysis of normal tissues with max. (II) activation is  $<$  that of the non-activated autolysis of regenerating tissue.

P. W. C.

**Determination of peptic activity.** III. H. ESCHENBRENNER (Pharm. Ztg., 1936, 81, 967–969; cf. this vol., 520).—The possible influence of the hydrolytic products on the course of proteolysis by pepsin is discussed. Evidence of inhibition could not be obtained from the effect of dialysis or addition of peptones on peptic digestion. Polarographic examination indicates that peptic hydrolysis produces only slight changes in the protein substrate. F. O. H.

**Activation of pancreatic trypsin.** F. MOCOROA (Anal. Fis. Quím., 1934, 32, 748–756).—From a study of the rates of activation it is concluded that active trypsin (I) is formed from trypsin and kinase, and that its formation is influenced by their conen. and by temp. (I) combines with prokinase to give a kinase. F. R. G.

**Specificity of urease.** R. BONNET and R. RAZAFIMAHERY (Enzymologia, 1936, 1, 55–59).—Heated and unheated urease show no difference in hydrolysing various substituted ureas, amides, and cyanates. Urease is very sp. E. D. Y.

**Inhibitory effect of phloridzin and phloretin on kidney phosphatase.** H. KALCKAR (Nature, 1936, 138, 289).—The inhibitory effect of phloretin on the action of kidney phosphatase is approx. 3 to 4 times that of phloridzin. L. S. T.

**Metabolism of the human placenta.** O. BUSSE (Z. physiol. Chem., 1936, 242, 271–279).—The placenta contains a phosphatase (I) the activity of which depends on the substrate conen. (max. with 0.15*M*-glycerophosphate at  $p_H$  9). (I) is slightly activated by  $Mg^{++}$ , strongly inhibited by cysteine, unaffected by NaF, EtOH, and  $COMe_2$ , and partly purified by fractional pptn. with EtOH. The (I) content of the ripe placenta is  $>$  that of the unripe and that of the liver, kidney, and small intestine. The zymohexase content of the placenta is only a fraction of

that of muscle. No phosphorylation of inorg. P occurs in the placenta. W. McC.

**Alcoholic fermentation in the intact enzyme system of the yeast cell and in the disorganised zymase system.** II. R. NILSSON and F. ALM (Biochem. Z., 1936, 286, 373—391).—The fermentation by preps. of intact dry yeast (cf. this vol., 1299) is compared with those by apozymase (I), autolysed dry yeast, and maceration extract and the effect of autolysis and PhMe examined. Yeast which is allowed to autolyse during slow drying loses the power to ferment sugar completely and gives the normal linear curve whilst addition of  $\text{PO}_4'''$  causes a sharp break in the curve. Maceration juice gives larger deviations and with amounts of  $\text{PO}_4'''$  below theoretical gives 2 such breaks, the first conditioned by the  $\text{PO}_4'''$  and the second occurring when one half of the sugar is fermented. (I) + purified co-enzyme gives the normal curve but if the (I) is first dried in air, only half of the sugar is fermented at the normal rate. The changes in the enzyme system are discussed and correlated with similar changes in fermentation with dry yeast at  $40^\circ$ . P. W. C.

**Polysaccharides fermented by yeast in wheaten flour.** R. GUILLEMET and C. SCHELL (Bull. Soc. Chim. biol., 1936, 18, 1132—1146).—Fermentation of raffinose by baker's yeast in the presence of aq. yeast extract takes place completely, and that of gentianose and stachyose corresponds with 66 and 50% respectively of the carbohydrate added. Fermentation of levosin is, however, much less. Baking flour contains about 0.1% of hexoses, 0.2—0.7% of sucrose, and 1% of a mixture of polysaccharides amongst which is levosin. A. L.

**Effect of composition of medium on growth of yeast in presence of bios preparations.** I. Effect of magnesium salts. E. I. FULMER, L. A. UNDERKOFER, and J. B. LESH (J. Amer. Chem. Soc., 1936, 58, 1356—1358).—Growth of a strain of *Saccharomyces cerevisiae* on a  $\text{NH}_4\text{Cl}$ — $\text{K}_2\text{HPO}_4$ —sucrose medium with added bios II (essential) is markedly increased by small concns. of  $\text{MgSO}_4$  [or  $\text{MgCl}_2$  or  $\text{Mg}(\text{NO}_3)_2$  with  $\text{K}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$ ].  $\text{K}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  show some activity but  $\text{MgCl}_2$  and  $\text{Mg}(\text{NO}_3)_2$  do not. H. B.

**Action of small quantities of copper on alcoholic fermentation by yeast. Application to wine-making.** R. GUILLEMET (Bull. Soc. Chim. biol., 1936, 18, 1125—1131).—The fermentation of aq. glucose by yeast ceases when the yeast has taken up 2.3—2.5 mg. of Cu per g. (dry wt.). The retarding effect of Cu on the fermentation of wine musts, however, takes place only when 500 mg. of Cu per litre are present. This amount is  $\gg$  that present after fungicidal treatment of the grapes. A. L.

**Comparative action of sodium arsenate, sodium arsenite, and arsenic-protein preparations on respiration and glycolysis of *Saccharomyces cerevisiae*.** P. MASCHERPA (Boll. Soc. ital. Biol. sperim., 1936, 11, 253—255).—The toxic effect (depression of respiration and glycolysis) gives the order As-gelatin  $>$   $\text{Na}_3\text{AsO}_3 >$   $\text{Na}_3\text{AsO}_4$ . F. O. H.

4 z

**Effect of radium rays on fermentation micro-organisms. Formation of constant variants of yeasts under influence of hokutolit rays.** R. NAKAZAWA and M. SIMO (J. Agric. Chem. Soc. Japan, 1936, 12, 699—708).—Morphologically and physiologically distinct variants are produced when yeasts are exposed to hokutolit rays. J. N. A.

**Mitogenetic effect on yeast of oligodynamic radiations from metals.** M. B. MACDONALD (Iowa State Coll. J. Sci., 1935, 9, 587—595).—Yeast cells multiplied much more rapidly in tubes placed on sheet brass, Fe, Pb, Al, or Ag than on cardboard. In Vitreosil tubes growth was retarded by the metals, probably through excessive transmission of radiations. Protection of the metal surfaces from contact with the atm. diminished their action. Exposure of the medium to metal before inoculation also increased multiplication and the beneficial effect thus obtained was not affected by boiling the treated medium before inoculation. CH. ABS. (p)

**Carbohydrates of yeast.** K. SILBEREISEN (Woch. Brau., 1936, 53, 317—321, 330—331).—A lecture.

**Permeability of yeast cell-membrane.**—See B., 1936, 1013.

**Micro-organisms of sugar cane juice.** R. NAKAZAWA, Y. TAKEDA, and K. SUEMATU (J. Agric. Chem. Soc. Japan, 1936, 12, 749—762).—1 c.c. of juice contained  $10^4$  to  $10^5$  micro-organisms consisting of *saccharomyces*, *torula*, *monilia*, and *bacteriu* (mainly *Leuconostoc*). All are able to invert sugar. The juice is well suited to the growth of the organisms, which can be altered by change of  $p_H$ , rise of temp., or addition of bleaching powder. J. N. A.

**Grouping of *Monilia* by fermentation and precipitin reactions.** J. H. LAMB and M. L. LAMB (J. Infect. Dis., 1935, 56, 8—20).—*Monilia* species are divided into 3 groups on the basis of sugar fermentation tests and precipitin reactions.

CH. ABS. (p)

**Properties of *Aspergillus* species.** II. Y. TAKEDA and O. TAKEUCHI (J. Agric. Chem. Soc. Japan, 1936, 12, 853—870).—The optimum temp. for growth and for conidia formation, the permanence and colour of conidia, colour of perithecia, optimum  $p_H$  for growth, killing temp., and fermentative or non-fermentative activity for all kinds of carbohydrates are determined for 89 known strains of *Aspergillus* grown on Pfeffer's medium containing 0.5% of oryzanin. J. N. A.

**Utilisation of galactose by *Aspergillus niger* and *Penicillium glaucum*.** W. H. HERR (Plant Physiol., 1936, 11, 81—99).—Galactose (I) is a poor source of C for these moulds and when used alone retards spore germination and mycelial development. When mixed with glucose, fructose, or mannose, (I) improves growth. Addition of lactose to a sucrose culture medium has little effect on growth. The acidity of media is not an important factor in growth acceleration. A. G. P.

**Biochemical method for determining parasitism in *Fusarium*.** T. FEDOTOVA (Plant Protection U.S.S.R., 1935, No. 1, 115—118).—Highly parasitic,



weakly parasitic, and saprophytic species contained  $\text{NH}_2\text{-N}$  3—5, 11—19, 19—27, and  $\text{NH}_2\text{-N}$  6—8, 9—28, 35—52 mg. per g., respectively.

CH. ABS. (p)

**Nitrogenous metabolism of a micro-organism.** W. H. SCHOFFER (Compt. rend., 1930, 203, 201—203).—Cultures of *Phycomyces* on a medium containing 8% of glucose and 0.1% of asparagine show a max. yield of the mould for a definite concn. of vitamin- $B_1$ . Many other N sources give similar results. The N content of the mould falls to a min. as the yield reaches a max. although all the available N is not utilised. Atm.  $\text{N}_2$  plays no part in the process.

**Production of sclerotia by *Rhizoctonia solani*, Kuhn, in pure culture.** L. E. TYNER and G. B. SANFORD (Sci. Agric., 1935, 16, 197—207).—No sclerotia were produced in P- or N-free media. Optimum and min. concns. were 31 and 7.5 for P and 560 and 55 p.p.m. for N. Sclerotia appeared with almost equal frequency over a wide range of [K] > 2 p.p.m. Sclerotia formation was restricted with < 20 p.p.m. of Mg in the nutrient. Omission of Ca did not affect development of either sclerotia or mycelium. Sclerotia were produced readily in media of  $p_{\text{H}}$  3—9 (optimum 5.5) and were most favoured by temp. of 18—21° and R.H. 60%. Radiations from pitchblende had a stimulatory effect. A. G. P.

**Effects of hypertonic media on the contractile vacuoles of protozoa.** J. A. KITCHING (Nature, 1936, 138, 287).—A discussion. L. S. T.

**Chemotherapy of animals infected with trypanosomes by inhibiting carbohydrate metabolism of the parasites with halogenoacetic acids.** N. VON JANCsó and H. VON JANCsó (Biochem. Z., 1936, 286, 392—395).—Trypanosome infection of mice was removed by intraperitoneal administration of  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$  and  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ . P. W. C.

**Physiology of respiration of bacteria. II. Intracellular indophenol reaction.** S. YAMAGUCHI (Acta Phytochim. Japan, 1935, 8, 263—283).—The indophenol test was positive with 9 among 24 species examined, and was inhibited by  $\text{CN}^-$ . With certain species the  $\text{O}_2$  absorption was lowered by  $\text{CO}$ .

CH. ABS. (p)

**Bacterial growth and hydrogen-ion concentration. I. In bouillon. II. In peptone water.** A. UCHIDA (Japan J. Mikrobiol. Path., 1935, 29, 825—868).—[ $\text{H}^+$ ] decreased at first and increased later (more rapidly in bouillon).

CH. ABS. (p)

**Content of hydrolases in some species of bacteria.** G. VERCELLANA (Boll. Soc. ital. Biol. sperim., 1936, 11, 329—330).—Trypsin, cathepsin, amylase, and lipase were not found in *B. melitense*, *B. paramelitense*, *B. abortus*, *B. para-abortus*, *B. pyocyaneum*, *Vibrio cholerae*, *Staphylococcus pyogenes aureus*, or *Streptococcus pyogenes*. F. O. H.

**Reactions of organisms on arbutin agar.** A. CASTELLANI and M. DOUGLAS (J. Trop. Med. Hyg., 1935, 38, 197—201).—Certain organisms produce brown to black colorations. The reaction does not correspond with the fermentation of arbutin in peptone.

CH. ABS. (p)

**Acetic acid bacteria from Formosa. X. Systematic investigations.** S. TANAKA (J. Agric. Chem. Soc. Japan, 1936, 12, 726—744).—105 strains are divided into 4 groups, according to the amounts of  $\text{AcOH}$  and gluconic acid produced on an  $\text{EtOH}$ -glucose medium. J. N. A.

**Mechanism of biological fixation of nitrogen. III. Economy of carbon during fixation by *Azotobacter chroococcum*, Beij.** T. R. BHASKARAN. IV. Fixation by the mixed microflora of soil in presence of acid products of anaerobic decomposition of carbohydrates. T. R. BHASKARAN and V. SUBRAHMANYAN (Proc. Indian Acad. Sci., 1936, 4, B, 67—74, 163—170; cf. this vol., 113).—III. The decomp. products of glucose play no part in the fixation of N by *A. chroococcum*, the mechanism of which differs from that by mixed soil flora. During the early stages of sugar decomp. the proportion of C fixed in the slime and bacterial cells is relatively > that of N. Later the ratio is adjusted to the initial level. Growth of the organism and N fixation are closely correlated.

IV. The efficiency of the fixation of N by a mixed flora was improved by addition of the mixture of org. acids etc. obtained by the anaerobic fermentation of sugar. The ratio of C consumed to N fixed is examined under various cultural conditions.

A. G. P.

**Utilisation of salicylic acid as an energy-producing food by *Azotobacter* in soil.** G. GUITTONNEAU and R. CHEVALIER (Compt. rend., 1936, 203, 211—213; cf. A., 1932, 437).—*Azotobacter* from gardens and fields when grown on  $\text{SiO}_2$  gel or the original soil containing Na salicylate (I) utilises (I) better if the soil fertility is high. A pure culture destroys (I), increases the  $p_{\text{H}}$  of the medium, and fixes N during some days, indicating that no subsidiary bacteria are necessary to enable *Azotobacter* to utilise (I).

J. L. D.

**Alcohol- and carbohydrate-oxidising bacteria isolated from fruits : new classification of oxidising bacteria. III.** T. ASAI (J. Agric. Chem. Soc. Japan, 1935, 11, 331—340, 377—390, 499—513, 610—620, 674—708; cf. this vol., 113).—Decomp. of sugars and alcohols by numerous species of bacteria is examined. Species growing at higher temp. oxidise glucose (I) to gluconic or glycuronic acid (II) and  $\text{AcOH}$  to  $\text{CO}_2$ , but do not oxidise mannitol (III) or glycerol (IV). Those growing at lower temp. oxidise (I) to (II) or 5-ketogluconic acid, (III) to fructose (V), (V) to kojic acid, and (IV) to  $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ . They do not oxidise  $\text{AcOH}$ . The extent of these reactions forms the basis of a classification of species.

CH. ABS. (p)

**Thermophilic and anaerobic nature of *Lactobacillus bulgaricus*.** J. M. SHERMAN and H. M. HODGE (Science, 1936, 84, 208—209).—Freshly isolated cultures can grow at 60° and vigorously at 55°.

L. S. T.

**Quantum relationship of the light-emitting process of luminous bacteria.** K. L. VAN SCHOUWENBURG and J. G. EYMERS (Nature, 1936, 138, 245).—One part of the  $\text{O}_2$  consumption of *Photobacterium phosphoreum* is completely inhibited by

approx. 0.001M-KCN, and the other decreases slowly with increasing [KCN] and  $\propto$  light intensity. 19% of the total  $O_2$  is consumed in the light-emitting process and at 16°, 500 mols. of  $O_2$  are consumed per quantum of light emitted. The efficiency of the light-emitting process depends on various unknown factors.

L. S. T.

**Preparation of specific bacterial carbohydrate substances by electrolysis.** A. C. H. YEN and T. J. KUROCHKIN (J. Infect. Dis., 1935, 56, 238—249).—Passage of a strong electric current through saline suspensions of the organisms causes clarification. Dialysis of the cleared solution removes protein matter, and  $H_2O$ -sol. polysaccharides are pptd. from the resulting liquid by EtOH.

CH. ABS. (p)

**Comparative behaviour of endotoxins and exotoxins towards trichloroacetic acid.** A. BORVIN (Compt. rend., 1936, 203, 284—286).—The anatoxin of *B. diphtheriae* is pptd. by  $CCl_3 \cdot CO_2H$  at  $p_H$  4, and can be redissolved in  $PO_4'''$  buffer of  $p_H$  8. In this way it is possible to concentrate and purify the anatoxins. The purified material contains mineral matter 0.5, N 15.1, and P 0.1%; it yields no sugar, purine, or fatty acid on hydrolysis. The endotoxin, which is a carbohydrate-lipin complex and is responsible for the specificity of the type, is sol. in  $H_2O$  at  $p_H$  4.

P. G. M.

**Metabolism of *C. diphtheriae*.** I. A. TASMAN and A. C. BRANDWIJK (Biochem. J., 1936, 30, 1756—1767).—*Diphtheria* bacteria in a simple culture medium assimilate glucose (I) in concns.  $\geq$  0.2% without detriment to toxin production. When the concn. is 0.5% all (I) is (more slowly) decomposed but toxin production is stopped because of the large amount of acid produced. Much greater concns. of maltose (II) are tolerated, apparently because the velocity of decomp. of (I) by the bacteria is 6 times that of hydrolysis of (II) to (I). During decomp. of sugar the  $p_H$  falls until (I) has disappeared and then rises, probably because the acids initially produced from (I) are oxidised to  $H_2O$  and  $CO_2$  which converts alkali originally present into  $CO_3''$  and  $HCO_3'$ . Production of toxin begins when (I) has practically disappeared, continues for a time at approx. const. velocity, and then ceases abruptly.

W. McC.

**Inhibitive effect of vitamin-C on toxin production by *C. diphtheriae*.** I. J. KLIGLER (Nature, 1936, 138, 291).—Vitamin-C added in small amounts to a suitable medium inhibits toxin production.

L. S. T.

**Diphtheria toxin produced on a semi-synthetic medium.** K. ANDO and T. KOMIYAMA (J. Immunol., 1935, 28, 345—352).—On a mineral salt-AcOH-maltose-Difco-proteose-peptone medium at  $p_H$  8.0, *C. diphtheriae* produces a toxin as potent as that obtained in ordinary infusion bouillon.

CH. ABS. (p)

***Cl. welchii*, Type C, Wilsdon (*B. patudis*, McEwen), isolated from sheep in N. Wales.** R. F. MONTGOMERIE and W. T. ROWLANDS (Vet. Rec., 1936, 48, 829—832).—In cases of sheep "strike," a toxin typical of *Cl. welchii* was isolated from blood and other body-fluids.

A. G. P.

**Differential character of *Clostridium welchii*, type D.** T. J. BOSWORTH and R. E. GLOVER (Proc. Roy. Soc. Med., 1935, 28, 1004—1006).—The toxin prepared in saline becomes much more toxic when mixed with a normal intestinal filtrate. The activating factor is destroyed at 70°. The same amount of antitoxin is required to neutralise the treated and the untreated toxin.

CH. ABS. (p)

**Antigenic relation between *Proteus vulgaris* X-19 and typhus *Rickettsia*.** III. Antigenic composition of extracts of *P. vulgaris* X-19. M. R. CASTANEDA (J. Exp. Med., 1935, 62, 289—296).—Two polysaccharides, 1 and 4% N, respectively, are pptd. from extracts by EtOH. Both give a negative biuret and a positive Molisch reaction. One, the common antigenic factor in *P. vulgaris* X-19 and typhus *Rickettsia*, is stable to hot alkali, the other is quickly destroyed.

CH. ABS. (p)

**Oxidation-reduction potentials in *Salmonella* cultures.** I. Development of potential levels characteristic of species. W. BURROWS and E. O. JORDAN (J. Infect. Dis., 1934, 56, 255—263).—The potentials of cultures of individual strains differed only within narrow limits. Those of different species diverged considerably. Species-differences may be due to differences in bacterial substances synthesised.

CH. ABS. (p)

**Antigenic structure of the variants of *Staphylococcus aureus*.** I. Carbohydrates of the rough and smooth forms. R. E. HOFFSTADT and W. M. CLARK (J. Infect. Dis., 1935, 56, 250—254).—Type-sp. carbohydrates isolated from the two forms differed antigenically and in the manner in which they separated from the proteins of the respective organisms. That from the smooth type was more sol. in hot  $H_2O$ , and contained less N, than that from the rough type, from which it also differed in being pptd. by  $Ba(OH)_2$ .

CH. ABS. (p)

**Ingestion of *Staphylococcus* exotoxin by human volunteers with special reference to staphylococcic food poisoning.** C. E. DOLMAN (J. Infect. Dis., 1934, 55, 172—183).—Gastric disturbance followed the ingestion in some cases only. A staphylococcus metabolite rather than the exotoxin was probably the causal agent.

CH. ABS. (p)

**Influence of  $p_H$  on dissociation of *B. Friedlander* and *M. tuberculosis*.** W. STEENKEN (J. Infect. Dis., 1935, 56, 273—276).—The effects of the reaction of various media on attenuation are examined.

CH. ABS. (p)

**Effect of formaldehyde on growth of tubercle bacilli.** R. D. HERROLD (J. Lab. Clin. Med., 1935, 20, 1165—1167).—Tubercle bacilli are more susceptible to  $CH_2O$  than are other common organisms present in sputum.

CH. ABS. (p)

**Attenuated (R.I.) tubercle bacilli recovered from silicotic and normal guinea-pigs.** G. R. DOWD (Amer. Rev. Tuberc., 1935, 32, 62—72).

CH. ABS. (p)

**Ultra-violet absorption of phthiocol, a pigment of the human tubercle bacillus.** M. O'L. CROWE (J. Biol. Chem., 1936, 115, 479—484).—The absorption spectrum of synthetic phthiocol (A., 1934, 77)



in 95% EtOH (max. at 385, 334, 278, and 250 m $\mu$ ) is compared with those of other 1:4-naphthaquinones. F. A. A.

**Concentration and partial purification of bacteriophage.** J. H. NORTHROP (Science, 1936, 84, 90—91).—A protein prep. possessing the properties of bacteriophage has been isolated from lysed staphylococcus cultures. Method and properties are described. L. S. T.

**Feulgen reaction of the bacteriophage substance.** M. SCHLESINGER (Nature, 1936, 138, 508—509).—The particles of *coli* bacteriophage previously prepared (A., 1934, 1407) are extensively stained by Feulgen's reagent. L. S. T.

**Reactivation of thermally inactivated bacteriophage.** A. P. KRUEGER and J. H. MUNDELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 410—413).—Bacteriophage inactivated by heating for 20 min. at 54° in a phthalate buffer mixture at  $p_H$  5.75 is partly reactivated when kept on ice at  $p_H$  8.1. W. O. K.

**Selective action of dyes and of other disinfectants on bacteriophage.** A. Y. WELLS and N. P. SHERWOOD (J. Infect. Dis., 1934, 55, 195—198).—The phagistatic action of gentian-violet, crystal-violet, PhOH, and NaOH is examined. In general, phages acting on Gram-negative bacteria are more resistant to inhibitory substances than are those which act on Gram-positive organisms. CH. ABS. (p)

**Immunological and chemical investigations of vaccine virus. II. Analysis of elementary bodies of vaccinia.** T. P. HUGHES, R. F. PARKER, and T. M. RIVERS (J. Exp. Med., 1935, 62, 349—352).—Washed elementary bodies contain protein 83.1, fat 8.5, ash 0.7, residual H<sub>2</sub>O 5.6%. The 2% of undetermined matter includes a trace of carbohydrate. CH. ABS. (p)

**Resistance of the virus of infectious laryngo-tracheitis to certain chemical and physical factors.** O. W. SCHALM and J. R. BEACH (J. Infect. Dis., 1935, 56, 210—223).—Effects of temp., exposure to sunlight,  $p_H$ , desiccation, and treatment with PhOH, cresol, and NaOH are examined. CH. ABS. (p)

**Attenuation of avian plague virus by X-rays.** B. S. LEVIN and I. LOMINSKI (Compt. rend., 1936, 203, 287—288).—A dose of X-rays of 2500—3000 kiloroentgen is required to attenuate plague virus as tested in cockerels. This dose is > that required to kill bacteria (300 kiloroentgen). X-Rays may therefore be used for purification of an ultravirus. P. G. M.

**Thermostable activators of bacterial growth from cryptogams.** A. SARTORY, R. SARTORY, J. MEYER, and M. J. MERGLEN (Compt. rend., 1936, 203, 280—282).—H<sub>2</sub>O-sol. bacterial activators in culture filtrates of *Aspergillus fumigatus*, *Schizosaccharomyces hominis*, *Mucor nigricans*, and *M. plumbeus* manifest themselves only on heating to <80°. They resist prolonged heating at 120°. The two *Mucor* strains give the best growth with all the cocci used. The growth of *B. diphtheriae* is only slightly affected by any of the filtrates, and that of *B. subtilis* not at all. P. G. M.

**Different effects of some disinfectants on bacterial growth.** K. DIERNHOFFER (Milch. Forsch., 1936, 18, 83—86).—On growing a mixture of types of bacteria isolated from cow dung in lactose broth containing various low concns. of KCN, OH·C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>, *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·OH, and theophylline-Na salicylate, a differentiation in the growth of streptococci and Gram-negative bacteria was obtained. 0.05—0.10% of nitrophenols did not affect the growth of streptococci but KCN favoured the growth of Gram-negative organisms. W. L. D.

**Antiseptic and bactericidal action of urea.** J. H. FOULGER and L. FOSHAY (J. Lab. Clin. Med., 1935, 20, 1113—1117).—Many bacteria lose viability in 2 hr. in media half-saturated with urea. Staphylococci have a high resistance. Dry urea may be applied directly to suppurating wounds etc. CH. ABS. (p)

**Germicidal properties of the soil nema, *Rhabditis pellio*.** Schneider. C. MORIYA (Proc. Imp. Acad. Tokyo, 1936, 12, 195—197).—Various pathogenic organisms are destroyed by *R. pellio*. A. G. P.

**Culture media for non-acid products.** E. J. CAMERON (J. Assoc. Off. Agric. Chem., 1936, 19, 433—438).—Five media are described and recommended for the detection of all organisms commonly found in such products. E. C. S.

**Culture media for acid products.** B. A. LINDEN (J. Assoc. Off. Agric. Chem., 1936, 19, 440—445).—Five media are described and recommended for the detection of bacteria and one for the detection of yeasts and moulds. E. C. S.

**Meker burner with auxiliary flame for bacteriological use.** M. E. HIGHLANDS and P. K. BATES (Amer. J. Publ. Health, 1936, 26, 928). C. J.

**Use of micro-organisms in sugar analysis.**—See this vol., 1363.

**Effect of prolonged administration of hyperglycaemia-producing hormones.** F. SERIO (Boll. Soc. ital. Biol. sperim., 1936, 11, 270—271).—Prolonged administration of adrenaline, thyroxine, or pituitary preps. to dogs produces a hypoglycaemia and not a condition simulating diabetes. The mechanism of this phenomenon is discussed. F. O. H.

**Adrenal cortex and cholesterol metabolism.** S. THADDEA and W. FASSHAUER (Arch. exp. Path. Pharm., 1936, 182, 477—498).—Intravenous injection of adrenal cortex preps. (I) into dogs decreases the total cholesterol (II) content of the serum, the diminution being mainly of cholesteryl ester (III). The effect does not occur after damage of the reticulo-endothelial system. Bilateral extirpation of the adrenal cortex in cats increases serum-(II) [especially the (III) fraction] and decreases liver- and muscle-(II); subsequent treatment with (I) produces a return to normal vals. and also corrects the absence of hypercholesterolaemia (due to disturbance of fat-absorption) following oral administration of (II). Increased serum-(II) and -(III) occur in Addison's disease. The adrenal cortex probably has a fixative action on (II). F. O. H.

**Adrenal cortex and endogenous carbohydrate formation.** G. EVANS (Amer. J. Physiol., 1936, 114, 297—308; cf. A., 1935, 777).—The increase of glycogen (I) in fasting rats exposed to reduced pressure is prevented by hypophysectomy. A parallel increase in N excretion and R.Q. and a fall in O<sub>2</sub> consumption are observed in intact rats. Adrenalectomy abolishes the increase in N excretion; it also reduces excretion of sugar and N in phloridzinised rats. Adreno-medullectomised rats respond to low O<sub>2</sub> tension and phloridzin as do intact rats. The cortical extract of Swingle and Pfiffner does not alter sugar and N excretion of adrenalectomised phloridzinised rats, nor raise (I) in rats exposed to reduced pressure. Ketosis in phloridzinised rats and rats exposed to reduced pressure is diminished by adrenalectomy. It is concluded that the cortex is concerned with the conversion of protein into carbohydrate.

R. N. C.

**Constituents of the adrenal gland. V. Chemical identification of the androstane skeleton.**—See this vol., 1382.

**Constituents of the adrenal gland. VI. Methods of separation and isolation of the substances Fa, H, and J.**—See this vol., 1382.

**Carbohydrate and electrolyte changes in the opossum and marmot following adrenalectomy.** H. SILVETTE and S. W. BRITTON (Amer. J. Physiol., 1936, 115, 618—626).—Serum- and muscle-Na and -Cl are increased and muscle-H<sub>2</sub>O decreased. Na<sup>+</sup> and Cl<sup>-</sup> excretion in the urine is < normal. The changes produced in dogs, cats, and rats are strikingly opposite to these. In all species blood-sugar and liver- and muscle-glycogen are decreased. The life-maintaining cortical hormone affects NaCl balance only indirectly, being directly concerned in regulation of carbohydrate metabolism.

R. N. C.

**Changes in the rat incisor following bilateral adrenalectomy.** I. SCHOUR and J. M. ROGOFF (Amer. J. Physiol., 1936, 115, 334—344).—Calcification of dentine is disturbed.

R. N. C.

**Increased salt appetite of adrenalectomised rats.** C. P. RICHTER (Amer. J. Physiol., 1936, 115, 155—161).

R. N. C.

**Lactation in adrenalectomised rats.** R. GAUNT and C. E. TOBIN (Amer. J. Physiol., 1936, 115, 588—598).

R. N. C.

**Role of potassium in adrenaline action.** W. J. R. CAMP and J. A. HIGGINS (J. Pharm. Exp. Ther., 1936, 57, 376—387).—K effects all the typical changes in systems which are produced by adrenaline, and the action of K is obtained after decerebration, bilateral adrenalectomy, and injection of atropine and ergotoxine. K is liberated from the heart by vagus stimulation. The adrenals maintain a const. distribution of K.

J. N. A.

**Effect of adrenaline on arterial and venous plasma-sugar and blood flow in dogs and cats.** C. F. CORI, R. E. FISHER, and G. T. CORI (Amer. J. Physiol., 1935, 114, 53—68).—The rate of continuous injection of adrenaline (I) solution necessary to produce hyperglycemia in dogs is > that required for cats. Rates of injection can be found which increase

plasma-sugar (II) without affecting blood-flow. The arterio-venous (II) difference is slightly increased during a period of even (I) hyperglycemia; insulin injected at the conclusion of the (I) injections causes a considerable increase. The increase of (II) in cats is > in dogs for the same rate of injection of (I).

R. N. C.

**Formation of an adrenaline-like substance in autolysing adrenal glands.** A. R. LARRAIN, R. G. ROBERTS, and M. M. KUNDE (Amer. J. Physiol., 1936, 115, 662—664).—Autolysis produces a dialysable pressor substance that resembles adrenaline in its chemical reactions, but is not pptd. by conc. aq. NH<sub>3</sub>. Its formation continues until the gland is almost completely disintegrated; KCN inhibits its formation.

R. N. C.

**So-called virtual adrenaline of the adrenal cortex.** J. DEVINE (Biochem. J., 1936, 30, 1768—1774; cf. Abelous and Argaud, A., 1934, 1038, 1143).—Chemical and physiological assays of extracts of adrenal cortex and medulla give no support to the hypothesis of the existence in the gland of "virtual" adrenaline (I) but the distribution of derivatives of *o*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> in the gland suggests that the cortex may be concerned in the production of (I).

W. McC.

**Adrenaline and urine formation in the dog.** E. F. ADOLPH (Amer. J. Physiol., 1936, 115, 200—209).

R. N. C.

**Changes in the circulatory effect of potassium salts due to adrenaline.** H. A. MCGUIOAN and J. A. HIGGINS (Amer. J. Physiol., 1935, 114, 207—211).—K<sup>+</sup> injected intravenously after adrenaline in the dog is as effective in raising the blood-pressure as when injected intra-arterially; an increase in blood-K<sup>+</sup> is necessary before the action can occur.

R. N. C.

**Regulation of oxygen output by erythrocytes. III. Blood glycolysis, insulin, and adrenaline.** F. HEMMERICH and F. S. TSCHERNJAK (Biochem. Z., 1936, 286, 344—359).—In men and rabbits, insulin (I) accelerates and adrenaline (II) inhibits glycolysis. After administration of (I) or (II), the opposing hormone is mobilised by the organism and secreted into the blood. In man, activation of glycolysis by (I) is > and of longer duration than inhibition by (II). Since increased glycolysis is bound up with increased output of O<sub>2</sub> by the erythrocytes (this vol., 494), (I) and (II) may be regarded as regulators of the blood respiratory function.

P. W. C.

**Enteral absorption of insulin. Protection of insulin against trypsin.** F. LASCH and E. SCHONBRUNNER (Arch. exp. Path. Pharm., 1936, 182, 452—458; cf. this vol., 525).—Certain basic dyes (I) (e.g., malachite-green), but not acid dyes, protect insulin from inactivation *in vitro* by trypsin (II). Pptn. (indicated by an opalescence when protection is max.) of (I) and (II) occurs.

F. O. H.

**Response of the rabbit to insulin.** L. B. DORTT (Amer. J. Physiol., 1936, 114, 538—550).—The % fall in blood-sugar (I)  $\frac{1}{2}$  hr. after administration of a fixed dose of insulin (II) is related to the time of onset



of convulsions; the latter, however, is not related to the initial (I). Animals with great sensitivity to (II) require larger injections of glucose to prevent convulsions. The female is more sensitive to (II) and more const. in its responses than the male.

R. N. C.

**Protamine insulinate.** H. C. HAGEDORN, B. N. JENSEN, N. B. KRARUP, and I. WODSTRUP (J. Amer. Med. Assoc., 1936, 106, 177—180).—Fish sperm protamines combine with insulin (I) to form complexes which have isoelectric points at about  $p_H$  7.3, at which point they are only very slightly sol. in  $H_2O$  but somewhat more sol. in serum. The low solubility in body-fluids results in slow absorption of (I) from subcutaneously administered complexes, with hypoglycaemic action about twice as long as that due to the same dose of ordinary (I). The use of protamine insulinate permits a greater stabilisation of the diabetic blood-sugar level than is possible with ordinary (I) and considerably decreases the risk of hyper- and hypo-glycaemia.

NUTR. ABS. (m)

**Contrary actions of epiphyseal extracts on blood-ketones.** L. CANNARO (Boll. Soc. ital. Biol. sperim., 1936, 11, 273—274).—Aq. and glycerol extracts of fresh pineal gland and  $Et_2O$  extracts of  $COMe_2$ -dried gland contain a thermolabile principle which lowers blood-ketones (I) whilst  $CHCl_3$  extracts of  $COMe_2$ -dried gland contain a thermostable substance which increases (I).

F. O. H.

**Effect of irradiated ergosterol and parathyroid extract on the rate of disappearance of intravenously-injected calcium chloride.** S. FREEMAN (Amer. J. Physiol., 1936, 115, 701—705).—The rate of removal of  $CaCl_2$  in normal dogs is uniform. It is decreased by injection of sufficient parathyroid extract or irradiated ergosterol to produce a fasting hypercalcaemia.

R. N. C.

**Response of thyroid glands of hypophysectomised newts to injections of phyone and their reaction after cessation of treatment.** A. E. ADAMS and F. MARTINDALE (Anat. Rec., 1936, 65, 319—331).

R. N. C.

**Thyroid glands of hypophysectomised newts after treatment with anterior pituitary, thyroid, and iodine.** A. E. ADAMS and B. GRAY (Anat. Rec., 1936, 65, 69—81).—Only the pituitary hormones stimulate the gland.

R. N. C.

**Effects of thyrotropic and adrenotropic principles on hypophysectomised amphibia.** W. J. ATWELL (Anat. Rec., 1935, 62, 361—379).—Thyrotropic hormone causes rapid and complete metamorphosis, but adrenotropic hormone produces only slight changes.

R. N. C.

**Metabolic aspects of thyroid-adrenal interrelationship.** S. B. BARKER, J. F. FAZIKAS, and H. E. HIMWICH (Amer. J. Physiol., 1936, 115, 415—418).—The rise of  $O_2$  consumption produced by adrenaline in rats is increased by thyroid feeding and decreased by thyroidectomy, this decrease being abolished by thyroid feeding.

R. N. C.

**Effect of antithyroidal protective substance on the Reid Hunt test.** K. FELLINGER and O. HOCHSTÄDT (Klin. Woch., 1935, 14, 1250—1251;

Chem. Zentr., 1935, ii, 3790).—By means of the MeCN reaction in mice it is shown that the antagonistic action of the protective substance in respect of the thyrotropic hormone is  $>$  in respect of the thyroid. The substance acts directly on the gland or on its regulating factors.

A. G. P.

**Detection of thyrotropic hormone in tissues other than of the pituitary.** A. STURM and W. SCHÖNING (Endokrinol., 1935, 16, 1—8; Chem. Zentr., 1935, ii, 3941).—Many tissues (notably of ovary and kidneys) contain a substance which regulates thyroid secretion. The presumed pituitary-sp. property of the thyrotropic hormone is discussed.

A. G. P.

**Effect of thyroxine on the tissue metabolism of excised *Limulus* heart.** J. E. DAVIS and A. B. HASTINGS (Amer. J. Physiol., 1936, 114, 618—619).—Metabolism *in vitro* is increased under suitable conditions. This is not due to increased work by the heart.

R. N. C.

**Comparison of the calorogenic potencies of *l*- and *dl*-thyroxine and thyroid gland.** Thyroxine content of the acid-soluble fraction of the peptic digest of thyroid protein. G. L. FOSTER, W. W. PALMER, and J. P. LELAND (J. Biol. Chem., 1936, 115, 467—477).—*l*-Thyroxine,  $[\alpha]_D -4.4^\circ$ , isolated from pig's thyroid, and equiv. doses of thyroid extract, have twice the calorogenic activity of *dl*-thyroxine in guinea-pigs. Thus only the *l*-compound is biologically active. The acid-sol. fractions of a peptic digest of thyroid protein still contain thyroxine, which may be carried down with protein ppt.

F. A. A.

**Glycogen content of liver and muscle in the completely hypophysectomised dog.** I. L. CHAIKOFF, G. F. HOLTOM, and F. L. REICHERT (Amer. J. Physiol., 1936, 114, 468—472).—Liver- and muscle-glycogen in well-nourished dogs is not altered by hypophysectomy.

R. N. C.

**Maintenance of carbohydrate levels in fasted hypophysectomised rats treated with anterior pituitary extracts.** J. A. RUSSELL and L. L. BENNETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 406—409).—The abnormal fall in carbohydrate stores which occurs in fasting hypophysectomised rats is prevented by administration of anterior pituitary extracts. The muscle-glycogen may then reach vals.  $>$  those of the normal fasting level.

W. O. K.

**Relation of the pituitary gland to muscle-creatine.** B. G. SHAPIRO and H. ZWARENSTEIN (Proc. Roy. Soc. Edin., 1936, 56, 164—168).—The hamstring muscles of the right and left legs of *Xenopus laevis* contain on an average 0.399% of creatine (I). Muscle-(I) decreases by 15% 18 to 22 weeks after hypophysectomy, whilst daily injections of 0.2 c.c. of anterior lobe extracts cause an increase of approx. 30% 3 to 5 weeks after commencing injection. The anterior lobe of the pituitary and muscle-(I) may be indirectly related through some other endocrine organ.

J. N. A.

**Source of the blood-acetone resulting from administration of the ketogenic principle of the anterior pituitary gland.** I. A. MIRSKY (Amer. J.

Physiol., 1936, 115, 424—428).—The hormone acts only on the liver, without stimulating extra-hepatic fat oxidation. The muscles play no part in the accumulation of blood-ketones, production of which is probably due to decreased carbohydrate utilisation by the liver cells in presence of an increased catabolism of fatty acids arising from accelerated glycogenolysis in the liver. R. N. C.

**Effects of oestrus and spaying on pituitary metabolism.** J. VICTOR and D. H. ANDERSEN (Amer. J. Physiol., 1936, 115, 130—137).—The respiratory rate *in vitro* of the anterior pituitary is max. in pro-oestral, and min. in dioestral and spayed, animals. Anaerobic glycolysis and total pituitary metabolism in pro-oestral and oestral are > those in dioestral and spayed animals. R. N. C.

**Action of preparations from the posterior lobe of the pituitary gland on the imbibition of water by frogs.** F. K. OLDHAM (Amer. J. Physiol., 1936, 115, 275—280).—The oxytocic and, to a smaller extent, the pressor hormone cause imbibition; the melanophore-dilating hormone is not involved. R. N. C.

**Hormones and pregnancy.** W. C. MILLER (Vet. Rec., 1936, 48, 903—911).—A review. A. G. P.

**Biological assay of "international standard" oestrin and of certain commercial preparations.** F. E. D'AMOUR and R. G. GUSTAVSON (J. Pharm. Exp. Ther., 1936, 57, 472—481).—The rat unit of international standard oestrin is as follows: single injection in oil,  $1.3 \times 10^{-6}$  g.; multiple injection in oil  $1.5 \times 10^{-6}$  g.; single aq. injection  $3.8 \times 10^{-6}$  g., and multiple aq. injection  $0.74 \times 10^{-6}$  g. Aq. commercial preps. decrease considerably in activity on keeping. J. N. A.

**Effect of oestrin on the prostate gland of the albino rat and mouse.** D. WELLER, M. D. OVERHOLSER, and W. O. NELSON (Anat. Rec., 1936, 65, 149—163). R. N. C.

**Effect of oestrin on the activity of the anterior lobe of the pituitary.** H. L. FEVOLD, F. L. HISAW, and R. GREEP (Amer. J. Physiol., 1936, 114, 508—513).—Secretion of luteinising hormone is augmented, but not that of follicle-stimulating hormone. R. N. C.

**Gonad-hypophyseal complex in oestrin-injected rats.** S. R. HALPERN and F. E. D'AMOUR (Amer. J. Physiol., 1936, 115, 229—238). R. N. C.

**Persistence of corpora lutea in the pseudo-pregnant rabbit.** W. M. ALLEN and G. P. HECKEL (Science, 1936, 84, 161—162).—The persistence of corpora lutea produced by injection of oestrin (I) after a sterile mating indicates that in the rabbit the placenta elaborates (I) which, rather than a placental gonadotropic hormone, causes the corpora to persist. L. S. T.

**Comparative assay of oestrone in the rat and mouse.** A. M. HAIN and J. M. ROBSON (J. Pharm. Exp. Ther., 1936, 57, 337—346).—When oestrone (I) is given in 4 doses in oil, the rat unit is approx. 0.0033 mg., when similarly administered in 10% EtOH,

0.0025 mg. For the mouse the units are 0.00009 mg. and 0.00025 mg., respectively. Using oestrone benzoate (II), the rat unit is 0.005—0.01 mg., and for the mouse slightly < 0.0005 mg. With both species a single injection of (II) produces less effect than the same wt. of (I) given in 4 injections. The duration of the oestrus response and the relation between the rat and mouse units are discussed. J. N. A.

**Influence of oestrone on galactin content of male rat pituitaries.** R. P. REECE and C. W. TURNER (Proc. Soc. Exp. Biol. Med., 1936, 34, 402—403).—The pituitaries of normal male rats contain a definite quantity of galactin which is increased by subcutaneous injection of hydroxyoestrin benzoate (Oestroform B). W. O. K.

**Sterility in rabbits produced by injection of oestrone and related compounds.** G. PINCUS and R. E. KIRSCH (Amer. J. Physiol., 1936, 115, 219—228). R. N. C.

**Spectrophotometric determination of  $\alpha$ -oestrone and its derivatives.** M. SUREAU and P. GRANDADAM (Compt. rend., 1936, 203, 440—442).—The technique of Chevallier (A., 1935, 906) is adapted. Ultra-violet adsorption coeffs. are determined for  $\alpha$ -oestrone and for dihydro-oestrone and its benzoate. A. G. P.

**Isolation of principal oestrogenic substance of liquor folliculi.** D. W. MACCORQUODALE, S. A. THAYER, and E. A. DOISY (J. Biol. Chem., 1936, 115, 435—448).—Dihydrotheelin (I), previously isolated from sow ovaries as the *m*-bromobenzoate (Proc. Soc. Exp. Biol. Med., 1935, 32, 1182), is more easily isolated as the di- $\alpha$ -naphthoate. On hydrolysis (I) is obtained in pure cryst. form. (I) isolated from sow ovary is identical with that obtained from theelin. E. M. W.

**Action of a synthetic oestrogenic agent [9 : 10-dihydroxy-9 : 10-di-*n*-propyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthrene] on the anterior pituitary of the castrated female rat.** J. M. WOLFE (Amer. J. Physiol., 1936, 115, 665—669). R. N. C.

**Changes in tissue metabolism in oestral, dioestral, and spayed rats.** J. VICTOR, D. H. ANDERSEN, and M. R. PREST (Amer. J. Physiol., 1936, 115, 121—129).—O<sub>2</sub> consumption of the liver *in vitro* is max. in oestral and min. in spayed animals; the R.Q. is unaltered. Kidney metabolism does not vary. Infection increases O<sub>2</sub> consumption and the R.Q. of liver but not kidney. R. N. C.

**Effect of ovarian hormone on the basal metabolism of experimental hyperthyroidised rats.** T. C. SHERWOOD and L. M. BOWERS (Amer. J. Physiol., 1936, 115, 645—650).—The hormone induces a greater fall in basal metabolism when injected in oil solution than in aq. solution. It accelerates the return of basal metabolism to normal after thyroid feeding. R. N. C.

**Effects of two hypophyseal gonadotropic hormones on the reproductive system of the male rat.** R. O. GREEP, H. L. FEVOLD, and F. L. HISAW (Anat. Rec., 1936, 65, 261—271).—Follicle-stimulating hormone stimulates the germinal epithelium,



whilst luteinising hormone stimulates the interstitial cells to secrete the male hormone. R. N. C.

**Concentration and purification of the gonadotropic substance in urine of ovariectomised and post-menopausal women.** L. LEVIN and H. H. TYNDALE (Proc. Soc. Exp. Biol. Med., 1936, **34**, 516—518).—Gonadotropic material may be almost quantitatively pptd. by tannic acid from urine acidified by AcOH to  $p_H$  5.0. The ppt. is extracted with EtOH and then with COMe<sub>2</sub>. Purification of the crude tannate is described. W. O. K.

**Quantitative relation between follicle-stimulating and luteinising effects in castrate and menopause urine.** U. J. SALMON and R. T. FRANK (Proc. Soc. Exp. Biol. Med., 1936, **34**, 463—466).—Extracts from the urine of female castrates or women past the menopause produced follicle-stimulating and luteinising effects in rats' ovaries according to the dose given. W. O. K.

**Effect of divided dosage of gonadotropic extracts in the immature male rat.** F. BISCHOFF (Amer. J. Physiol., 1936, **114**, 483—487).

R. N. C.

**Industrial extraction of crystalline folliculin. Physical and biological determination.** D. VAN STOLK, H. PÉNAU, and R. L. DE LENCÈRE (J. Pharm. Chim., 1936, [viii], **24**, 249—266).—Pregnant mares' urine gives max. yields of the hormone (I) at the 5th—7th month of gestation (cf. Cole and Saunders, A., 1935, 1426). Colorimetric determination of (I) (Kober, A., 1931, 1195) is unsatisfactory with crude preps. A spectrometric method [(I) in EtOH has an absorption max. at 277.5 and min. at 247.5 mμ] and its application to the various stages of purification of (I) during its isolation from urine are described. F. O. H.

**Corpus luteum hormone.** K. EHRHARDT and A. HAGEN (Endokrinol., 1935, **16**, 51—60; Chem. Zentr., 1935, ii, 3788).—Impure extracts of human placenta give a positive Clauberg-Hohlweg reaction in 20% of cases examined, whereas after removal of follicular hormone 60% of positive tests are obtained. Extracts from pregnancy urine or that from tumour cases seldom contain the corpus luteum hormone; it could not be detected in urine after parenteral administration. A. G. P.

**Effect of progestin on the *in vitro* response of the rabbit's uterus to pituitrin.** A. W. MAKEPEACE, G. W. CORNER, and W. M. ALLEN (Amer. J. Physiol., 1936, **115**, 376—385). R. N. C.

**Preparation of non-toxic urine fractions for assay of male hormone by the female bitterling test.** I. S. KLEINER, A. I. WEISMAN, and D. I. MISHKIND (Science, 1936, **84**, 142).—Dialysis removes the factor toxic to fish in certain urines. L. S. T.

**Increasing the effectiveness of testosterone.** A. S. PARKES (Lancet, 1936, **231**, 674—676).—Testosterone acetate (I) and propionate (II) are much more effective than the free hormone in restoring the atrophic prostate and seminal vesicles of castrated rats. (II) has a more intense and prolonged action than (I). L. S. T.

**Sexual hormones. XVI. Esters of the testosterone and androsterone series. XVII. Bromination of sterol and androstene derivatives.**—See this vol., 1382.

**Effects of androgenic substances in the rat.** W. O. NELSON and T. F. GALLAGHER (Science, 1936, **84**, 230—232).—The effect of male hormone extracts on the testes of hypophysectomised rats, and the effect of androsterone, androstanediol, and androstenedione on the pituitary, mammary gland, and uterus of the spayed rat are described. L. S. T.

**Proposed synthesis of equilenin.**—See this vol., 1382.

**Inter-relationship of vitamins.** M. MITOLO (Boll. Soc. ital. Biol. sperim., 1936, **11**, 334—336).—The symptoms occurring in animals fed on diets rich in certain vitamins and lacking in others are described. Those of avitaminosis-*D* are modified by concomitant hypervitaminosis-*A*, -*B*, -*C*, or -(*A*+*B*+*C*) in the last case, a rachitic condition does not occur. F. O. H.

**Experimental polyavitaminosis.** G. PERETTI (Boll. Soc. ital. Biol. sperim., 1936, **11**, 338—339).—Symptoms of deprivation of one or more of the vitamins-*A*, -*B*, and -*C* in guinea-pigs are described. F. O. H.

**Choice of diet and production of experimental avitaminosis.** G. RIGOBELLO (Boll. Soc. ital. Biol. sperim., 1932, **7**, 825—830; Chem. Zentr., 1935, ii, 3791).—Suitable diets for inducing avitaminosis-*A*, -*B*, and -*D* are given. A. G. P.

**Relation of vitamin-*A* to eye development in the pig.** F. HALE (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 126—128).—Defective eyes may result from -*A* deficiency in the mother or in the ration. CH. ABS. (*p*)

**Vitamin-*A* as a prophylactic against the common cold in groups of school children.** E. M. TRESS (Amer. J. Digest. Dis. Nutrition, 1935, **1**, 795—796).—Beneficial effects of feeding -*A* are recorded. CH. ABS. (*p*)

**Vitamin-*A* storage by chickens.** A. D. HOLMES, F. TRIPP, and P. A. CAMPBELL (Poultry Sci., 1936, **15**, 71—78).—The -*A* contents of livers of chickens of varying age and receiving -*A* supplements are recorded. High-producing flocks receiving a vitamin-rich diet can maintain a sufficient body reserve of -*A* through the reproductive period. A. G. P.

**Cytological study of the action of vitamin-*A*.** P. JOYET-LAVERGNE (Bull. Soc. Chim. biol., 1936, **18**, 1041—1054).—Vitamin-*A* as determined by the Carr-Price test is present in the nucleolus and chondriome of animal and vegetable cells. A. L.

**Photo-chemical decomposition of vitamin-*A* in alcoholic solution. II. Secondary reaction.** A. CHEVALLIER and P. DUBOULOZ (Bull. Soc. Chim. biol., 1936, **18**, 1115—1124; cf. this vol., 1159).—One of the two products produced by irradiation of vitamin-*A* with light of 365 mμ is further decomposed with shorter waves giving a series of products. A. L.

**Spectrophotographic studies on the antimony trichloride reaction for vitamin-A.** I. Relation between tintometer readings and spectral absorption of the blue solution. O. NOTEVARP and H. W. WEEDON (Biochem. J., 1936, 30, 1705—1718).—The absorption spectrum of the  $\text{SbCl}_3$ -vitamin-A complex changes with time and the variation in the intensity of the 618 and 572  $\mu$  bands depends on the prep. used. Empirical relations for the extinction coeffs. and the blue vals. are given for the different absorption max., and also a relation for the variation of the blue val. with -A concn. H. D.

**Determination of vitamins by chemical methods. I. Vitamin-A in vegetable and animal oils.** A. SANTOS RUIZ (Anal. Fis. Quim., 1934, 32, 1217—1224).—A review of the literature. Olive oil contains 3 "cod-liver-oil units" per 100 g. The vitamin-A content of animal and vegetable oils is related to the intensity and time of action of the solar rays to which they have been exposed. F. R. G.

**Nutritive effect of tunny, ox liver, and yeast on rats.** U. TANGE and K. MICHl (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 809—817).—Rats on a diet deficient in B vitamins do not grow so well when the ration is supplemented with tunny or ox liver as when with yeast. The growth-promoting actions of EtOH extracts of yeast were > those from fat-free ox liver, which in turn exceeded those from tunny liver. W. O. K.

**Intermediate metabolism of carbohydrates in avitaminosis-B.** I. G. PERETTI and F. PORRAZZO (Arch. Sci. biol., 1933, 19, 227—248; Chem. Zentr., 1935, ii, 3791).—Vitamin-B affects carbohydrate metabolism at a stage preceding that of lactic acid production. A. G. P.

**Multiple nature of the third factor of the vitamin-B complex.** S. LEFKOVSKY, T. H. JUKES, and M. E. KRAUSE (J. Biol. Chem., 1936, 115, 557—566).—Component I (separated from II by adsorption on fuller's earth) of rice-bran extracts prevented dermatitis in rats but was without effect on chickens, whereas II prevented the latter and aggravated the former in absence of I. The deficiency in rats with an EtOH extract of white corn as a source of vitamin-B was multiple in nature, the chief factor lacking being vitamin-B<sub>2</sub> (flavin). H. G. R.

**Extraction of vitamin-B<sub>1</sub> from adsorbates.** R. D. GREENE and A. BLACK (Science, 1936, 84, 185—186).—The best yields (< 90%) of vitamin from the adsorbate obtained in Seidell's method occur when aq., aq.-EtOH, or EtOH solutions of acid salts of  $\text{C}_6\text{H}_5\text{N}$ , quinine,  $\text{NH}_2\text{Ph}$ , etc. are used as extractants. The salt solutions have an effect > that of acid or base alone. L. S. T.

**Pathological changes in the eye in experimental vitamin-B<sub>2</sub> deficiency.** K. SEN, N. DAS, and B. C. GUHA (Sci. and Cult., 1935, 1, 59—60). CH. ABS. (p)

**Potassium in the brain in vitamin-B<sub>1</sub> deficiency.** H. W. KINNERSLEY (Nature, 1936, 138, 368).—No significant difference in the K content of the brains of normal and vitamin-B<sub>1</sub>-deficient pigeons has been detected (cf. A., 1934, 1042). L. S. T.

**Vitamin-B<sub>2</sub> concentrates as preventives of black-tongue.** L. E. BOOHER and G. H. HANSMANN (Amer. J. Physiol., 1936, 114, 429—435).—Vitamin-B<sub>2</sub> concentrate from low-lactose whey powder, which contains lactoflavin and at least one other thermostable vitamin necessary for growth of rats, prevents or cures black-tongue in dogs. It augments the inferior rate of growth produced in young rats by a diet causing black-tongue in dogs. Liberal quantities of nutritive protein in the diet apparently decrease the -B<sub>2</sub> requirements for growth of rats and prevention of black-tongue in dogs. R. N. C.

**Vitamin-B<sub>2</sub> from different sources and coccidian infection.** E. R. BECKER and N. F. MOREHOUSE (Proc. Soc. Exp. Biol. Med., 1936, 34, 437—439).—A substance promoting the development of the oocysts of *Eimeria mizairii* in rats is present in various vitamin-B<sub>2</sub> preps., but not in liver. W. O. K.

**Significance of vitamin-C in biological oxidation processes of the human lens.** P. WEINSTEIN (Orvosi Hetilap, 1935, 79, 874—875).—Vitamin-C, like cystine (I), disappears from the cataractous lens and is found in the covering. Reduced -C acts as a protective agent and retards the oxidation of (I). CH. ABS. (p)

**Reversible oxidation of vitamin-C in biological medium or pure solution.** N. BEZSSONOFF and M. WOLOSZYŃ (Compt. rend., 1936, 203, 275—277).—The decolorisation of dichlorophenol-indophenol by ascorbic acid in lemon juice is unaffected by change of  $p_H$ , but varies in pure solutions. The stability of the vitamin is increased in biological solutions by the presence of other reducing agents. The existence of an oxidised compound of -C,  $(\text{C}_6\text{H}_7\text{O}_6)_2$ , is postulated. P. G. M.

**Meat diet: blood as an antiscorbutic factor.** V. STEFANSSON (Science, 1936, 84, 227—228).—A discussion. L. S. T.

**Histochemistry. IX. Quantitative distribution of vitamin-C in the adrenal gland at various stages of development.** D. GLICK and G. R. BISKIND (J. Biol. Chem., 1936, 115, 551—555).—The concn. is highest in the fascicular zone. It increases in all portions of the gland during growth of the foetus and reaches a max. in the calf. The size and vitamin-C content of the cells increase regularly to the adult stage. H. G. R.

**Vitamin-C in an oestrin-producing ovarian tumour.** G. R. BISKIND and D. GLICK (Science, 1936, 84, 186).—The relatively low vitamin-C concn. of this tissue supports the view (this vol., 530) that -C is unrelated to oestrin formation in the human ovary. L. S. T.

**State of ascorbic acid in plant tissues.** G. L. MACK (Nature, 1936, 138, 505—506).—Repetition of the work of Guha and Pal (this vol., 1033) failed to reveal an increase in ascorbic acid (I) content on heating. The cabbages examined did not contain appreciable amounts of combined (I). When the oxidation enzyme is inactivated by heat or EtOH, or inhibited by extraction with sufficiently strong acid,



the total (I) is obtained. The apparent increase on cooking is due to inactivation of the enzyme.

L. S. T.

**Variation of vitamin-C content in certain fruits and vegetables.**—See B., 1936, 953.

**Ascorbic acid oxidase in determining vitamin-C in lens and aqueous humour.** L. ROSNER and J. BELLOWS (Proc. Soc. Exp. Biol. Med., 1936, 34, 493—494).—Treatment of extracts of the lens of the eye or of the aq. humour with the enzyme from the Hubbard squash which promotes the oxidation of ascorbic acid (I) (A., 1935, 1023) completely destroys their power of reducing Tillmans' reagent (II). The reducing substance in the lens and humour determined by (II) is therefore (I).

W. O. K.

**Use of the phosphotungstic acid method of determining ascorbic acid in urines with low ascorbic acid content.** G. MEDES (Biochem. J., 1936, 30, 1753—1755; cf. A., 1935, 1430).—The application of the reagent to urines of ascorbic acid content of  $<4 \times 10^{-4}$  g.-mol. per 100 ml. is described.

W. McC.

**Determination of ascorbic acid by titration with 2:6-dichlorophenol-indophenol (Tillmans' method).** R. STROHECKER and R. VAUBEL (Angew. Chem., 1936, 49, 666—668; cf. A., 1932, 310).—Details of the method given include standardisation of the dye (0.001*N*) with  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ , prep. of tissue extracts by dil. AcOH, application of  $\text{PhNO}_2$  (in which the dye is sol.) to highly-coloured extracts, and appearance of the end-point under varying conditions.

F. O. H.

**Determination of vitamin-C by means of its influence on the body-weight of guinea-pigs.** K. H. COWARD and E. W. KASSNER (Biochem. J., 1936, 30, 1719—1727).—A method similar to that used for vitamin-A (A., 1932, 886) is described. The derived relationship is  $y = 74.3 + 108.2 \log (\log 10x)$ , where  $y$  is the mean wt.-increase in g. in 6 weeks and  $x$  is the daily dose of ascorbic acid in mg.; that between severity of scurvy and dose is also curvilinear. The method, however, is somewhat inferior to the "tooth" method.

F. O. H.

**Value of the acid silver nitrate reaction as a test for ascorbic acid.** A. GROUND and C. P. LEBLOND (Nature, 1936, 138, 247—248).—The absence of a coloration by acid  $\text{AgNO}_3$  is not necessarily a proof of the absence of ascorbic acid (I), but a positive reaction in tissue is a sp. test for (I).

L. S. T.

**Differential threshold of reaction to vitamin-D deficiency in the house-sparrow and the chick.** H. FRIEDMANN (Biol. Bull., 1935, 69, 71—74).—The possible antirachitic properties of the irradiated secretion of the uropygial gland are examined. The threshold of reaction of house-sparrows and starlings to vitamin-D deficiency is markedly different.

CH. ABS. (p)

**Mechanism of the action of irradiated ergosterol.** I. Development of bone and its mineral content; calcæmia and phosphatæmia. II. Lipin content of bone. L. ROBUSHI (Boll. Soc. ital. Biol. sperim., 1932, 7, 1025—1028, 1029—1032;

Chem. Zentr., 1935, ii, 3791—3792).—I. Administration of irradiated ergosterol (I) increases the Ca and P contents of blood but not those of bone.

II. (I) affects the lipin content of bone marrow.

A. G. P.

**Effect on the antirachitic activity of their milk when ewes were exposed to sunshine and ultra-violet rays.** W. G. KIRK, B. H. THOMAS, and C. C. CULBERTSON (Amer. Soc. Animal Prod. Rec. Proc. 27th Ann. Meet., 1934, 182—188).—Treatments produced no appreciable effect.

CH. ABS. (p)

**Vitamin-D requirements of calves when natural milk is the sole source of the antirachitic factor.** J. W. LONG, C. F. HUFFMAN, and C. W. DUNCAN (Milk Plant Month., 1936, 25, No. 7, 30—36).—Growing calves developed rickets when fed a rachitogenic ration containing the same Ca/P ratio as milk. The vitamin-D requirement of a growing calf  $\propto$  the rate of gain in body-wt. When winter or early spring milk supplied the only source of -D, 0.3—0.4 U.S.P. unit per lb. of body-wt. daily was sufficient for the requirements of a growing calf provided that the normal level of plasma-Mg was maintained. The higher -D requirement of calves on summer milk is tentatively associated with a difference in Mg metabolism.

W. L. D.

**Effect of source of vitamin-D in the diet of chicken on storage of the antirachitic factor.** G. M. DEVANEY, H. E. MUNSELL, and H. W. TITUS (Poultry Sci., 1936, 15, 149—153; cf. A., 1935, 1287).—The -D storage of egg yolk was not affected by 8% of fat in the diet. 8% of cod liver-oil (I) in the diet reduced the no., size, and hatchability of eggs. The -D in yolk increases with the (I) or viosterol (II) content of the ration. With a ration containing 2—4% of (I) or 8% of (II), approx. 2% of the ingested -D appeared in the egg yolk. With 2—4% of (II) or 8% of (I), -D storage in yolks was appreciably less although the -D potency of the yolk was increased.

A. G. P.

**Determination of vitamin-D. III. Effect of calcification on growth and sex differences in white Leghorn chicks.** L. L. LACHAT and H. A. HALVORSON (Poultry Sci., 1936, 15, 127—135; cf. A., 1935, 417).—Deficiency of vitamin-D affects growth and calcification in females  $>$  in males. Females utilise -D more efficiently than do males, and are more suitable for laboratory tests. Seasonal variations, previously reported, in the calcification of rachitic chicks are now explained on the basis of association between body-wt. and bone-ash content. In faster growing birds greater amounts of skeleton are developed and show greater relative amounts of mineral deposition in the skeleton. Results of the A.O.A.C. method of assay are accurately interpreted by means of a simple formula.

A. G. P.

**Factors producing rickets present in cereals.** O. RYGH (Bull. Soc. Chim. biol., 1936, 18, 1091—1096).—The free fatty acids (I) isolated from oats are antagonistic to the antirachitic action of those from green plants. Concn. of the rachitic factor in the unneutralised fraction of (I) was effected after partial neutralisation.

A. L.

**Vitamin-D in Baltic herring.** (A) G. BLIX, H. RYDIN, and G. ENGLUND. (B) G. BLIX and G. ENGLUND (Upsala läkareforen. forh., 1936, 40, 175—182; 42, 203—207).—The vitamin-D content of the herring oil was about 200 international units per g., and therefore comparable with that of good cod-liver oil. The fat content of the herrings was a max. at 7—9% in Sept. to Nov. and a min. at 3—6% in Feb. to April. Boiling the herrings in a min. amount of H<sub>2</sub>O did not affect the -D val. of the oil.

NUTR. ABS.

**Chemistry of calciferol and vitamin-D<sub>3</sub>.** A. I. BACHARACH (Nature, 1936, 138, 387—389).—A summary of recent work. L. S. T.

**Purification of the antihæmorrhagic vitamin by distillation.** H. J. ALMQUIST (J. Biol. Chem., 1936, 115, 589—591).—The active fraction of the lucerne-meal concentrate (cf. this vol., 907) distils at 120—145°/1 × 10<sup>-6</sup> mm. H. G. R.

**New factor, not vitamin-B<sub>12</sub>, necessary for hatchability.** R. B. NESTLER, T. C. BYERLY, N. R. ELLIS, and H. W. TITUS (Poultry Sci., 1936, 15, 67—70).—A mixed grain-lucerne meal ration contains sufficient vitamin-B<sub>2</sub> for hatchability, but lacks a factor necessary for high hatchability. This factor is present in dried pigs' liver and green grass, and, to a smaller extent, in fish meal, desiccated meat meal, and dried buttermilk, but not in whey.

A. G. P.

**Electrophoresis of plant cell-contents.** A. GUILLIERMOND and N. CHOUCROUN (Compt. rend., 1936, 203, 225—229).—An external field exerts little effect on the contents so long as the cell is living, but prolonged application of a powerful field kills the cell and electrophoresis occurs. On death the nucleus is normally attracted to the positive pole; addition of neutral-red, which is localised during life in the vacuole and is transferred to the nucleus on death, causes migration to the negative pole. P. G. M.

**Permeability of membranes.**—See this vol., 1335.

**Breakdown of fruit and vegetable tissue due to an electric current.** W. SEIFRIZ (Plant Physiol., 1936, 11, 195—200).—Tissues of fruits and vegetables when made the cathode of a 110-volt circuit break down to a soft, dark-coloured mass and show a uniform  $p_H$  of 12.2. When placed at the anode the tissues remain practically unchanged. The degeneration is attributed to auto-proteolysis catalysed by intracellular enzymes rendered active by reducing conditions at the cathode. Proteolysis is followed by enzymic oxidation and discoloration accelerated by the alkaline medium surrounding the cathode. Phenolic compounds are probably concerned. Potato and onion tissues gelatinise at the cathode and are not discoloured. A. G. P.

**Vernalisation.** F. G. GREGORY and O. N. PURVIS (Nature, 1936, 138, 249).—Embryos of cereals separated completely from the endosperm can be vernalised in the same way as complete seeds, showing that the cause of vernalisation by low temp. is inherent in the embryo and independent of the metabolism of the endosperm or aleurone layer. L. S. T.

**Creeping movements of *Spirogyra*.** D. R. CHESTERMAN and C. L. FOSTER (Nature, 1936, 138, 403—404).—Solutions of electrolytes of concn.  $\geq 1\%$  reduce the creeping of *Spirogyra* up the sides of the containing vessel in the dark. Sucrose and glucose up to a crit. concn. reduce climbing and then increase it. The results appear to be related to effects on the respiratory activity of the algal cells. L. S. T.

**Changes of apparent ionic mobilities in protoplasm. I. Effects of guaiacol on *Valonia*.** W. J. V. OSTERHOUT (J. Gen. Physiol., 1936, 20, 13—43).—On treatment with 0.01M-guaiacol the order of the apparent mobilities ( $K > Cl > Na$ ) in the non-aq. protoplasmic surface is reversed. On adding the same concn. to sea-H<sub>2</sub>O the p.d. of the cell changes from -10 to +28 mv. and then slowly returns, due to changes in the apparent mobilities of the org. ions in the protoplasm. H. G. R.

**Yield and composition of eared and earless maize plants in a selfed line segregating barren stalks.** R. J. GARBER, R. B. DUSTMAN, and C. R. BURNHAM (J. Amer. Soc. Agron., 1936, 28, 85—91).—The wt. and sugar content of stems and leaves of earless plants were > those of eared plants. In the entire plants eared individuals showed greater wt., carbohydrate content, and Et<sub>2</sub>O extract, but less crude protein. A. G. P.

**Dry matter production and metabolism in certain cultivated plants. III. Causes of nitrogen intake and protein formation.** S. ODÉN and K. SJOBERG (Kung. Landtbruks.-Akad. Handl. Tidskr., 73, 780—821; Chem. Zentr., 1935, ii, 3939).—In oats, beans, and cress, increasing N supplies cause increases in yield and total and % N, up to limiting vals. Small additions of N are converted almost completely into protein. The proportional conversion is smaller when large amounts of N are assimilated. A. G. P.

**Tissue function and organic solute movement in the sunflower.** O. A. LEONARD (Plant Physiol., 1936, 11, 25—61).—Diurnal and seasonal variations in the carbohydrate distribution in the plants are examined. Variation in concns. of simple sugars in leaves correspond with much smaller variations in sucrose (I). The (I) gradient is positive in bark and negative from head to seed. Storage of (I) occurs chiefly in bark, and that of simple sugars in pith. The starch content of all organs is very low except in leaves during the day. Acid-hydrolysable carbohydrate is a temporary storage form and is nearly all translocated from leaves at night. Pith effects storage of NO<sub>3</sub><sup>-</sup> and some synthesis of NH<sub>2</sub>-acids. Gradients of sol. N are positive from leaves to bark but those of total sol., NH<sub>2</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>-N are negative up the stem. Amide-N is never abundant and often absent. A. G. P.

**Production and physiology of Concord grape vines as affected by variations in the severity of pruning.** T. J. MANEY and H. H. FLAGGE (Proc. Amer. Soc. Hort. Sci., 1934, 32, 392—396).—No correlation was found between chemical composition and differences in fruitfulness. CH. ABS. (p)



**Influence of the chloride ion on the chlorophyll content of potato leaves.** S. BASSLAVSKAJA and M. SIROESCHKINA (Plant Physiol., 1936, 11, 149—157).—The chlorophyll (I) content of field-grown plants was 2—3 times that of pot-cultured plants. Heavy applications of Cl-containing fertilisers lowered the (I) content of field plants to an extent related to their increased  $H_2O$  content. The decrease in (I) content (%) of the dry matter of leaves occurred towards the end of the vegetative period. A. G. P.

**Chlorolytic action of serum.** M. E. SAUER (Plant Physiol., 1936, 11, 159—166).—Serum causes a liberation of chlorophyll (I) from cells of *Euglena gracilis* or *Protosiphon botryoides* if these have been sufficiently altered by contact with strong serum or by heat. The action is related to the lipin content of the serum. Immune serum does not increase the permeability of the cell to (I). A. G. P.

**Exudation in cucurbits.** A. S. CRAFTS (Plant Physiol., 1936, 11, 63—79).—The mechanism of phloem and xylem exudation is examined.

A. G. P.

**Absorption of water by the foliage of some common fruit species.** W. G. BRIERLEY (Proc. Amer. Soc. Hort. Sci., 1934, 32, 277—283).

CH. ABS. (p)

**Effect of ammonium- and of nitrate-nitrogen on the composition of the tomato plant.** H. E. CLARK (Plant Physiol., 1936, 11, 5—24).—In sand cultures the use of  $Ca(NO_3)_2$  as N source produced greater fresh wt. of plants but a slightly smaller % dry matter in fresh material.  $NO_3$ -fed plants contained more  $NO_3$ , ash, oxalic, malic, citric, and total org. acids, but less glutamine, asparagine, total  $NH_2-N$ , sol. org. and insol. protein-N than those receiving  $NH_4$ . The  $NH_4$  content was high in plants supplied with media of higher  $[NH_4]$ . Relations between absorption and assimilation of N, accumulation of ash constituents, and the synthesis of org. acids by plants are discussed.

A. G. P.

**Total nitrogen in developing flowers and young fruits of Valencia oranges.** S. H. CAMERON and D. APPLEMAN (Proc. Amer. Soc. Hort. Sci., 1934, 32, 304—207).—Flowers developing early contain more N than those developing later. The petals, stamens, and pistil of mature blossoms contain approx. 45, 30, and 25%, respectively, of the total N and dry matter.

CH. ABS. (p)

**Translocation of nitrogen in woody plants.** W. E. LOOMIS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 61—64).—Much protein-N accumulated in the wood and bark of trees and was subsequently utilised in early spring growth. Movement of N from wood and bark was delayed by phloem rings and sol. org. N accumulated below the rings. Inorg. N can pass through normal cell membranes but org. N does not readily penetrate. Its upward and downward movement is confined to the plasmodesmal connexions between living cells, especially in phloem.

CH. ABS. (p)

**Mechanism of symbiotic nitrogen fixation.** A. I. VIRTANEN (Suomen Kem., 1936, 9, A, 69).—The N excreted by root nodules in sterile sand

culture consists of aspartic acid and lysine, with small amounts of  $NO_2$  derived from oximes. The first compound formed in N fixation is probably  $NH_2OH$ , which reacts with oxalacetic acid (derived from plant sugars) to produce the oxime and thence, by reduction, aspartic acid. A. G. P.

**Diagnosis of plant troubles with diphenylamine.** L. H. JONES (Plant Physiol., 1936, 11, 207—209).—Applications of the  $NHPh_2$  test in the examination of physiological disturbances involving N are described. Indications of a photochemical conversion of  $NH_4$  into  $NO_3$  within the plant are recorded.

A. G. P.

**Effect of boron on growth of certain green plants.** A. R. GÄIGEL (J. Agric. Univ. Puerto Rico, 1935, 19, 5—28).—In  $H_2O$  cultures of *Spirodela polyrrhyza* B was toxic at concns.  $>1$  p.p.m. and lethal at  $>5$  p.p.m. B caused chlorosis not corr. by Fe but partly cured by K tartrate. *Chlorella* was stimulated by 10 p.p.m. of B, larger proportions of which did not cause chlorosis. B did not lower the availability of Fe. Resistance of plants to B was increased by addition of glucose or sucrose to media.

CH. ABS. (p)

**Chemical and enzymic studies of the uneven ripening of Concord grapes.** J. E. WEBSTER, E. ANDERSON, and F. CROSS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 365—369).—The principal chemical difference between green and coloured grapes is the lower sugar content of the former. CH. ABS. (p)

**Seasonal changes in Bartlett pear-leaves.** L. D. DAVIS and N. P. MOORE (Proc. Amer. Soc. Hort. Sci., 1934, 32, 131—138).—Ash constituents and N of leaves are examined at various growth stages. There was a consistent loss of N throughout the season especially after yellowing of leaves. CH. ABS. (p)

**Absorption, distribution, and seasonal movement of potassium in young apple trees: effect of potassium fertiliser on the potassium and nitrogen contents and growth of trees.** R. F. CHANDLER, jun. (J. Agric. Res., 1936, 53, 19—42).—Absorption of K by young trees  $\propto$  dry wt. increases. Relative amounts of K in new growth tended to increase and those of 1- and 2-year tissue to decrease throughout the season. In roots K decreased during rapid growth but increased in the later part of the season. The abs. amount of K in all parts of the tree increased with growth; that in leaves decreased after abscission began. New wood added by diameter growth corresponded with current twig growth in respect of [K]. The K content of old leaves was  $<$  that of new leaves. The increased intake of K by tissues following use of K fertilisers was in the order leaves  $>$  bark  $>$  wood. No growth differences could be attributed to the fertiliser. N absorption by trees continued late in the season, whereas K absorption ceased at leaf-fall. The N content of wood and bark decreased during summer through translocation to leaves, but K vals. remained approx. const.

A. G. P.

**Transformation of sugars in plants.** M. NURMIA (Suomen Kem., 1936, 9, A, 70).—Wheat, clover, oats, and horse beans, deprived of starch by storage

in darkness, when cut and placed in sugar solutions absorbed glucose or fructose, partly converted either sugar into the other, and synthesised sucrose (I). (I) was also produced in varying amounts from galactose and maltose, but not from xylose,  $\text{CO}(\text{CH}_2\text{OH})_2$ , or glycerol. The changes were not affected by PhMe and only slightly retarded by KCN. A. G. P.

**Changes in carbohydrate content of wheat plants during the process of hardening for drought-resistance.** I. M. VASSILIEV and M. G. VASSILIEV (Plant Physiol., 1936, 11, 115—125).—Hardening of wheat plants by growth with insufficient  $\text{H}_2\text{O}$  until wilting occurs resulted in an initial (24 hr. after wilting) increase in monosaccharides (I) and sucrose (II) and decrease in hemicellulose (III) contents. Subsequently, (II) decreased but (I) and (notably) (III) increased. Immediately after watering (I) decreased and (II) remained at a low level. Fully recovered plants showed lower  $\text{H}_2\text{O}$  and (I) but higher (II) and (III) contents than control plants. The significance of (III) in drought-resistance is discussed. A. G. P.

**Distribution of acetaldehyde and alcohol in the apple fruit.** E. V. MILLER (J. Agric. Res., 1936, 53, 49—55).—Vals. for various parts of different varieties of apples are given. Storage of prepared samples in refrigerators results in marked increase in  $\text{MeCHO}$  (I) content. Fruit affected with soft scald or soggy breakdown showed increased amounts of (I) in the peel. Recorded high vals. for (I) in peel are in part due to its production in cells ruptured in paring but accumulation of (I) in peel always follows injury by mechanical means or by physiological abnormality. A. G. P.

**Distribution of total soluble solids and catalase in different parts of Jonathan apples.** P. L. HARDING (J. Agric. Res., 1936, 53, 43—48).—The sol. solid content of apples was highest in the skin and decreased towards the pith. In fruit affected with soft scald all vals. tended to be < normal. Catalase activity in healthy apples was highest in skin and lowest in the region immediately beneath; in those showing soft scald max. activity occurred in the pith and min. vals. in the diseased portions. A. G. P.

**Photosynthesis of formaldehyde from "nascent carbon dioxide" in vitro: importance of respiration in photosynthesis.** A. RAM (Proc. Acad. Sci. U.P., 1934, 4, 83—94).—Solutions of  $\text{AcOH}$ , citric, malic, and lactic acids, glycine, glycogen,  $\text{COMe}_2$ , etc., malachite-green, Me-violet, methylene-blue, etc. produce  $\text{CH}_2\text{O}$  (I) on exposure to sunlight. Other simple acids, sugars, and starch produce much smaller amounts. The first group of substances probably produce (I) directly and the second group indirectly through  $\text{CO}_2$  and  $\text{H}_2\text{O}$  formed on oxidation. The bactericidal action of dyes may be due to formation of (I). Photosynthesis in plants is aided by energy derived from respiration. (I) is obtained photochemically from  $\text{CO}_3''$  or  $\text{HCO}_3'$  solutions much more readily in the presence of suitable exothermic reactions. CH. ABS. (p)

**Photosynthesis in relation to light and carbon dioxide.** E. L. SMITH (Proc. Nat. Acad. Sci., 1936, 22, 504—511).—A mathematical relationship is derived and compared with that applicable to other recorded data. The photosynthetic rate is the same function of both  $[\text{CO}_2]$  and light intensity.

A. G. P.

**Fluorescence of chlorophyll and its relation to photochemical processes in plants and organic solutions.**—See this vol., 1320.

**Oxidative metabolism of the colourless alga, *Prototheca zopfii*.** H. A. BARKER (J. Cell. Comp. Physiol., 1936, 8, 231—250).—Data are given for the  $\text{O}_2$  consumption and  $\text{CO}_2$  production corresponding with the assimilation of simple org. compounds by *P. zopfii*. The primary process of assimilation is the oxidation of the substrate to a carbohydrate, which is stored as glycogen, followed by a slower decomp. in the processes of cell synthesis. 50—80% of the substrate C is assimilated. E. A. H. R.

**Determination of carbon dioxide production in physiological plant studies.** F. L. WYND (Ann. Missouri Bot. Gdns., 1935, 22, 361—363).—Apparatus capable of detecting several g. of  $\text{CO}_2$  with an error of  $\pm 1$  mg. over a 12-hr. period is described.

CH. ABS. (p)

**Growth and respiration of the *Avena coleoptile*.** J. BONNER (J. Gen. Physiol., 1936, 20, 1—11).—During growth the rate of elongation decreases more rapidly than the respiration;  $\text{HCN}$  or phenylurethane affects both to the same degree. Transport of the hormone into the cell and its action on elongation depend on aerobic metabolism, the cryst. hormone having no effect on respiration. H. G. R.

**Respiration of ripening tomatoes.** B. N. SINGH and P. B. MATHUR (Current Sci., 1936, 5, 76—78).—The increased liberation of  $\text{CO}_2$  by ripening tomatoes is due to an accumulation of  $\text{CO}_2$  in the tissues together with a lessened resistance of the peripheral tissues to diffusion. Subsequently  $\text{CO}_2$  evolution declines, but the accumulation of  $\text{CO}_2$  in the fruit is still marked. Usual methods of measuring respiration rates are thus open to error. J. L. D.

**Effect of sulphur on rate of respiration and respiratory quotient in *Chilomonas paramecium*.** S. O. MAST, D. M. PACE, and L. R. MAST (J. Cell. Comp. Physiol., 1936, 8, 125—139).—S (present as  $\text{MgSO}_4$ ) is required for the respiration of *C. paramecium*, and probably functions in the oxidation of fat. Starch is transformed into fat, and S prevents the accumulation of the latter by causing its oxidation immediately on formation. E. A. H. R.

**Measurement of respiratory exchange in plants.** B. N. SINGH and P. B. MATHUR (Current Sci., 1936, 5, 20—22).—A simplification of the Haldane gas-analysis apparatus and the technique, as applied to these measurements, are described. D. C. J.

**Vegetable growth-promoting hormones.** F. KOGL (Svensk Kem. Tidskr., 1936, 48, 145—155).—A lecture. H. W.

**Action of  $\beta$ -indolylacetic acid on the development of seedlings.** T. SOLACOLU and D. CONSTAN-



TINESCO (Compt. rend., 1936, 203, 437—440).—Certain concns. of  $\beta$ -indolylacetic acid (I) retard the development of the radicle of *Phaseolus vulgaris*. Cultures in Knop's solution on cotton to which (I) is added produce a filamentous mycelium-like structure, the normal development of the radicle being entirely suspended. The filaments are derived from proliferations of superficial and meristematic tissue following disturbance of the orientation of tissues effected by (I). A. G. P.

Effect of phenylacetic acid on the growth of tomato plants. H. L. PEARSE (Nature, 1936, 138, 363—364).—Tomato plants sprayed with an aq. 0.1% solution of  $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$  show increased length of stem and petioles. The % of total dry wt. present as leaf and root are decreased whilst those as stem and petiole are increased. The  $\text{H}_2\text{O}$  content, but not the total dry wt., is increased. L. S. T.

Formation of nodules in legume roots. K. V. THIMANN (Proc. Nat. Acad. Sci., 1936, 22, 511—514).—Experimental data quoted indicate that the formation of nodules may result from the production of auxin in bacterially infected cells. A. G. P.

Relation of root pressure to plant disease. J. JOHNSON (Science, 1936, 84, 135—136).—A discussion. Internal  $\text{H}_2\text{O}$  relations of the host as determined by root pressure may be an important determining factor in predisposition to infection and development of disease. L. S. T.

Adaptation of the micro-Kjeldahl method for determining nitrogen in plant tissues. N. W. STUART (Plant Physiol., 1936, 11, 173—179).—Pregl's method gives results for the total and non-protein-N of plant materials with the same accuracy as does the macro-method. Basic N in plant extracts may be determined without digestion of the phosphotungstates and filter-paper. Amides are partly hydrolysed during distillation but total amide- $+\text{NH}_3\text{-N}$  may be satisfactorily determined. A. G. P.

Determination of basic nitrogen. Semi-micro-method applicable to plant tissues. W. W. UMBREIT and P. W. WILSON (Ind. Eng. Chem. [Anal.], 1936, 8, 361—362).—After removing peptides,  $\text{NH}_3$ , and amides the sap is treated with phosphotungstic acid in 5%  $\text{H}_2\text{SO}_4$  and cooled at 0—5° for 48 hr. The ppt. is filtered, dissolved in NaOH, and digested in a semi-micro-Kjeldahl flask with  $\text{H}_2\text{SO}_4$  containing 0.25% of  $\text{CuSO}_4$  and  $\text{SeO}_2$ . The method is accurate to 0.1—0.2 mg. of N. S. C.

Determination of small amounts of copper, especially in plants. E. STOLZE (Bodenk. Pflanzenernahr., 1936, 1, 115—132).—The dithiocarbazon (I) method (Fischer, A., 1934, 381) is applied to the examination of plant ash. Small amounts of  $\text{Fe}^{\text{III}}$  salts oxidise (I) and the product forms a Cu compound sol. in  $\text{CCl}_4$  and not removed with excess of (I) by washing with aq.  $\text{NH}_3$ . Treatment with  $\text{Na}_2\text{S}_2\text{O}_3$  reduces the oxidation product. The ratio of Cu in plants to Cu in soil is lower in Cu-rich areas. In the latter, snails have higher Cu and Mn contents. In pot cultures application of  $\text{CuSO}_4$  increased the Cu content of plants. The Mn content increased less uniformly. Spraying vines with Bordeaux mixture

increased the Cu and decreased the Mn in washed leaves. A. G. P.

Some ash constituents of alternate-bearing sugar prune trees. L. D. DAVIS (Proc. Amer. Soc. Hort. Sci., 1934, 32, 125—130).—The crop depletes the K and P in wood, bark, and spurs, but only K in leaves. The Ca and Mg contents of leaves are higher in bearing than in non-bearing trees.

CH. ABS. (p)

Correlation of organic and mineral matter contents of mulberry leaves. K. KATO (J. Agric. Chem. Soc. Japan, 1936, 12, 745—748).—The contents of  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ , and  $\text{SO}_4$  are directly and those of CaO and  $\text{SiO}_2$  are inversely related to the amount of crude protein, whilst  $\text{Na}_2\text{O}$  is related to the carbohydrate sol. in HCl (*d* 1.15). J. N. A.

Plant roots give off organic acids. J. C. RATSEK (Proc. Amer. Soc. Hort. Sci., 1934, 32, 632—634).—When *Oxalis repens* was grown in  $\text{H}_2\text{O}$  cultures with media containing 100 and 250 p.p.m. of Ca (as  $\text{CaCl}_2$ ),  $\text{CaC}_2\text{O}_4$  was formed in the medium.

CH. ABS. (p)

Unsaturated fatty acids of hemp oil. Fixed oil from the seeds of *Celastrus paniculatus*, Willd.—See B., 1936, 1003.

Chemical investigation of the leaves of *Epi-medium macranthum* (Yin Yen Ho). Y. F. CHU and Y. S. KAO (J. Chinese Chem. Soc., 1936, 4, 312—321).—The EtOH extract of the leaves contains glucose, ceryl alcohol, hentriacontane, phytosterol, palmitic, stearic, oleic, and linoleic acids, and icarisside (?),  $\text{C}_{27}\text{H}_{32}\text{O}_{12}$ , m.p. 273—274° (Ac derivative, m.p. 149—151°), hydrolysed to anhydroicaritin (?), m.p. 219—220°. F. N. W.

Carbohydrates of *Allium* bulbs. V. Carbohydrates of *A. odorum* and *A. cepa*. VI. Chemical and physical properties of scorodose. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1935, 11, 548—551, 552—557; cf. A., 1935, 1435).—V. The carbohydrate distribution is recorded for both species. The principal cold- $\text{H}_2\text{O}$ -sol. carbohydrate of bulbs of *A. odorum* is scorodose (I). None occurred in the leaves. (I) was not detected in bulbs of *A. cepa*.

VI. (I) from *A. scorodoprasum* has  $[\alpha]_D^{25} -41.54^\circ$  in  $\text{H}_2\text{O}$ , is pptd. by  $\text{Ba}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , and is easily hydrolysed by dil.  $\text{H}_2\text{C}_2\text{O}_4$ . 0.3—0.5% HCl at 37° produced fructose from (I). Intestinal extracts and pancreatin hydrolysed (I) only very slowly.

CH. ABS. (p)

Polysaccharides of *Iridaea laminarioides*. III. T. TADOKORO and K. YOSHIMURA (J. Chem. Soc. Japan, 1935, 56, 655—658; cf. this vol., 534).—Polysaccharides sol. in 2% NaOH gave *d*- and *l*-erythrose on hydrolysis with 5%  $\text{H}_2\text{SO}_4$ .

CH. ABS. (p)

Constituents of *Actinidia callosa*, Lindl., var. *rufa*, Makino. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 721—725).—An analysis of the bark and of sugars extracted with cold and hot  $\text{H}_2\text{O}$ , hot EtOH, and 5% KOH is given. The mucilage contains galactose and arabinose; the tannin from bark belongs to the pyrocatechol series. J. N. A.

Chile seed. W. A. BUSH (J. Amer. Chem. Soc., 1936, 58, 1821).—The seeds contain  $H_2O$  6.25, oil 26.1, and meal 67.65% (protein 28.92, fibre 29.1, ash 5.61, and carbohydrates 36.37%). The oil, which resembles tomato-seed oil, has  $d_{25}^{25}$  0.918,  $n_D^{25}$  1.4738, acid val. 2.18, I val. (Hanus) 133.5, Ac val. 7, sap. val. 192, and contains 1.7% of unsaponifiable matter. H. B.

Cyanogenetic glucosides in Australian plants. III. *Eucalyptus cladocalyx*. H. FINNEMORE, S. K. REICHARD, and D. K. LARGE (J. Proc. Roy. Soc. New South Wales, 1936, 68, 209—214; cf. A., 1930, 1627).—Fresh loppings of the young branches gave 0.32% (dried 0.5%) of HCN by maceration with  $H_2O$ , and no more by addition of the enzyme (I) of sweet almonds. After 7 years they gave only 0.06% (dried) in  $H_2O$  and 0.105% after addition of (I). Another fresh sample of young suckers gave after drying 0.5% of HCN. The isolation of prunasin (II) by percolation with  $COMe_2$  is described. One sample of *E. viminalis* leaves gave no HCN, another gave 0.09%. 10% of (II) is obtained from *Eremophila maculata*, best by  $COMe_2$ . R. S. C.

Reduced glutathione content of certain oil-bearing nuts. D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 135—136).—The reduced glutathione content of (peeled) walnuts, brazil nuts, hazel nuts, almonds, and arachis nuts was 20—40 mg. per 100 g. G. H. B.

Chemical examination of the Chinese drug, Tu Hao. Y. F. CHI and Y. M. LEE (J. Chinese Chem. Soc., 1936, 4, 305—311).—The  $EtOH$ -sol. portion contains glucose, phytosterol, palmitic, stearic, oleic, and linoleic acids. F. N. W.

Constitution of the Chinese drug, Hseh Tsuang seed. T. H. TANG (J. Chinese Chem. Soc., 1936, 4, 324—334).—From the light petroleum extract a basic unsaturated aromatic compound,  $C_{11}H_{10}(OH) \cdot OMe$ , m.p. 82.5—83.5° (*Ac* derivative, m.p. 85°; *Bz* derivative, m.p. 69°; *hydrochloride*, m.p. 102°; *dibromide*, m.p. 147.5—148°), is obtained. The  $Et_2O$ -sol. fraction consists of the glycerides of the following acids: saturated 4.56, oleic 46.25, and  $\beta$ -linoleic 45.81, and unsaponifiable matter 0.38%. F. N. W.

Dragon's blood. G. HESSE [with W. KLINGEL] (Annalen, 1936, 524, 14—24).—Extraction of the crude material with  $Et_2O$  followed by addition of light petroleum yields the crude resin (I). The acids which remain in the mother-liquors are transformed by boiling  $AcOH$  into abietic acid, m.p. 155—163°,  $[\alpha]_D^{25}$  —80.0° in 96%  $EtOH$ , whereas by crystallisation from  $COMe_2$  a product, m.p. 155—162°,  $[\alpha]_D^{25}$  —40.6° to —42.3° in  $EtOH$ , is obtained. Enrichment of (I) in pigment is effected by pptg. it from amyl alcohol-HCl by  $Et_2O$ , and chromatographic analysis (Brockmann's  $Al_2O_3$ ) of the product in  $CHCl_3$  affords the following substances: *dracocarmine*,  $C_{31}H_{26}O_5$  (also  $+1CHCl_3$ ), m.p. 293° (decomp.) somewhat dependent on the rate of heating (*hydrochloride*, m.p. >350°); *dracorubin*,  $C_{28}H_{24}O_7$ , decomp. 270—280° after changing colour at 220° (*hydrochloride*, decomp. 295°); an unidentified violet pigment. The substances do not appear to contain a sugar component. H. W.

Colouring matter of the corolla of *Rhododendron obtusum* f. *hinode*. I. Isolation of quercetin. K. HAYASHI (J. Pharm. Soc. Japan, 1933, 53, 1093—1098).—Quercetin is obtained from the  $MeOH-HCl$  extract after pptn. of anthocyanin with Ph. CH. ABS. (p)

Anthocyanin pigment of the winesap apple. I. J. DUNCAN and R. B. DUSTMAN (J. Amer. Chem. Soc., 1936, 58, 1511—1514).—The pigment, isolated from the skins by a modification of Willstätter and Burdick's method (A., 1917, i, 44), is idæin chloride (Willstätter and Mallinson, A., 1915, i, 282). H. B.

Polyene pigments of the orange. I. L. ZECHMEISTER and P. TUZSON (Ber., 1936, 69, [B], 1878—1884).—The ethereal oil from the skin is removed by steam-distillation in vac. or chromatographically if the isolation of cryptoxanthin (I) is not required. Partial success is achieved by chromatography of the total hydrolysed extract or by chromatography followed by hydrolysis of the separated zones. Whereas the native pigment is stable, certain polyene alcohols become changed immediately after separation from the pigment wax, probably owing to  $CO_2$  or traces of acid in the laboratory air. Many fractions resinify in  $CS_2$ . (I), zeaxanthin+lutein, and violaxanthin have been isolated, with a new carotenoid, *citraurin* [*oxime*, m.p. 181—182° (corr.)], probably a polyene OH-aldehyde formed by oxidation of a  $C_{40}$  compound in the tissue. H. W.

Composition of orange skins. P. R. v. d. R. COPEMAN (J. Pomology, 1936, 14, 205—215).—Spraying with Pb arsenate had no direct action on the skin constituents examined. Metabolic activity is greater in the pulp during the growing season. Supplies of Ca and P to the skin are probably accumulated during the early growth stages. Ca is associated with the structure of cell wall material. In the skin pectin is probably almost as important as sugar in metabolic processes. Sugar predominates in the pulp. A. G. P.

Isomerisation of carotenes by chromatographic adsorption. I.  $\psi$ - $\alpha$ -Carotene.—See this vol., 1369.

Carotenoid pigments of *Oscillatoria rubrescens*.—See this vol., 1369.

Pipi (Brazilian drug). R. A. D. DA SILVA (Rev. Flora med. Brasil., 1935, 1, 477—487; Chem. Zentr., 1935, ii, 3946).—The plant, *Petiveria tetrandra*, Gomes, contains a non-cryst. substance, *petiverin*, of alkaloid character. A. G. P.

Highly-active constituent of the bark of *Piscidia erythrina*. F. HAUSCHILD (Arch. exp. Path. Pharm., 1936, 182, 317—323).—Fractionation of the light petroleum-sol. substances gives a yellow amorphous prep. which is extremely toxic (approx. 20% < rotenone) to fish, rats, etc. (min. lethal dose in rats 0.1—0.3 mg. per 100 g.). Saponins present are not concerned in the toxicity excepting with fish. F. O. H.

New derivatives of the lignin from Spanish *Pinus sylvestris*. III. Spectroscopic study of the wood. L. LEMMEL (Anal. Fis. Quím., 1935, 33, 39—44).—An account of work previously reviewed (A., 1934, 335; 1935, 84). F. R. G.



**Examination by dark-ground illumination of the nuclei of cells grown *in vitro* and treated with hypotonic solutions.** O. M. OLIVO and M. BOSKOVICH (Boll. Soc. ital. Biol. sperim., 1936, 11, 243—245).—Hypotonic aq. NaCl renders invisible the nuclei and, more slowly, the nucleoli of fibroblasts of chick embryo; the effect is due to change in osmotic pressure. F. O. H.

**Influence of grain size, separation, and distribution on the capability of enlargement of photomicrographs of biological objects.**—See this vol., 1348.

**Relative acidity of histological fixing fluids.** A. PETRUNKEVITCH and G. E. PICKFORD (Anat. Rec., 1936, 65, 461—465).—The  $p_H$  of a no. of fluids are listed. R. N. C.

**Staining of the nuclei of cells grown *in vitro*, treated with hypertonic solution, and examined under dark-ground illumination.** O. M. OLIVO and M. BOSKOVICH (Boll. Soc. ital. Biol. sperim., 1936, 11, 245—247).—Modifications occurring in stained preps. are described. F. O. H.

**Isotonic solutions of colloidal silver.** R. DESCHASSEAUX (J. Pharm. Chim., 1936, [viii], 24, 268—269).—A stable prep. is afforded by adding 1.4 c.c. of 5% aq.  $Na_2S_2O_4$  ( $Na_2S_2O_3$  ?) and 0.10 g. of colloidal Ag (French Codex) to 90 c.c. of 10% aq. NaCl, the vol. being made up to 100 c.c. with  $H_2O$ . F. O. H.

**Ashing of plant material.** W. D. STEWART and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1936, 8, 199—215).—Ashing at 450° in  $O_2$  gives more trustworthy results than ashing in a muffle at 650°. Volatilisation losses at the higher temp. were due to  $CO_2$  and  $Cl$ . At 450° there was no loss of KCl,  $K_2CO_3$ ,  $MgCO_3$ ,  $CaCl_2$ , or  $CaCO_3$ . At higher temp. some KCl and  $CaCl_2$  were lost. All sulphates were stable at all temp. examined. Addition of  $H_2SO_4$  to facilitate ashing in the determination of total bases was unsatisfactory owing to non-volatilisation of  $H_3PO_4$ . A method of ashing in an electric furnace in a current of  $O_2$  is described. A. G. P.

**Macro-Kjeldahl nitrogen determination.**—See this vol., 1397.

**Nitrogen not titratable by Kjeldahl's method.** F. SERIO and S. FIANDACA (Biochim. Terap. sperim., 1933, 20, 201—215; Chem. Zentr., 1935, ii, 3956).—Determination of N by elementary analysis gives higher results with urine (especially diabetic) than a wet method; the difference is ascribed to compounds containing nuclear N. H. N. R.

**Prevention of foaming in distillations.** W. M. BENDIEN (Chem. Weekblad, 1936, 33, 547).—Troublesome foaming in micro-Kjeldahl determinations of blood-albumin is prevented by the addition of 3—5 drops of a 0.5% solution of cholesterol in EtOH to each 20 c.c. of liquid. S. C.

**Determination of lactic acid, and, in particular, lactacidæmia.** C. PI-SUNER BAYO and J. F. PI (Anal. Fis. Quim., 1934, 32, 843—857).—The influence on the method of Friedemann *et al.* (A., 1927, 800; 1929, 677; 1933, 488) of the procedure for removing

proteins (the Folin-Wu method is recommended), duration of the oxidation by  $KMnO_4$ , and the efficiency of the cooling of the receiver is discussed, and the necessity for a blank determination is emphasised. The technique used is described and typical analyses of Zn lactate and blood are recorded. F. R. G.

**Determination of formic, acetic, and propionic acids in bacteriological culture media.** A. TASMANN (Chem. Weekblad, 1936, 33, 574—576).—The sample is acidified with  $H_2SO_4$  and phosphotungstic acid to ppt. proteins, centrifuged, and the clear solution steam-distilled. Total acids are determined in the distillate by titration, and  $HCO_2H$  by pptn. with  $HgCl_2$ . A separate sample of distillate is treated with  $K_2Cr_2O_7$ — $H_2SO_4$  to remove  $HCO_2H$ , and  $AcOH$  and  $EtCO_2H$  are determined by the "half distillation val." method. S. C.

**Colorimetric determination of uric acid (Folin) with delayed colour-formation.** G. BERGANI, E. BOERI, and P. BAER (Boll. Soc. ital. Biol. sperim., 1936, 11, 277—279).—Curves giving the increase in colour with time for standard amounts of uric acid (I) are applied to the determination of (I) by Folin's method (A., 1933, 845). F. O. H.

**Nickel nitroprusside as external indicator for iodometric determination of reduced glutathione.** D. ZIMMET (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 132—134).—The indicator is added to a series of tubes each containing 2 c.c. of the neutralised tissue extract with amounts of 0.002N-I differing by 1 drop, the approx. amount of I required being determined by preliminary titration. The end point is reached when the ppt. after centrifuging is no longer coloured rose. The sensitivity, 1 in  $4 \times 10^6$ , is dependent on exact neutralisation to bromothymol-blue. G. H. B.

**Determination of glutathione in biological material.** F. HARTNER and E. SCHLEISS (Mikrochem., 1936, 20, 163—179; cf. A., 1935, 422).—The quantity of I which reacts with glutathione (I) varies with the conditions, but Br from  $NaBr + KBrO_3$  gives const. vals. (I) in biological fluids is adsorbed on  $Cd(OH)_2$  or  $AgCl$  and determined by the Br method. Details of macro- and micro-methods are given. R. S.

**Micro-determination of cholesterol as pyridine cholesteryl sulphate.** A. E. SOBEL, I. J. DREKTER, and S. NATELSON (J. Biol. Chem., 1936, 115, 381—390).—Free cholesterol (I) is separated from its esters and other lipins by conversion into  $C_5H_5N$  cholesteryl sulphate and pptn. with light petroleum. The (I) in the ppt. is determined by the Liebermann-Burchard reaction. The (I) obtained from hydrolysis of the esters is separately determined. The advantages of this over the digitonin method are discussed. E. M. W.

**Electrolytic enrichment of arsenic in biological fluids.** J. VAN CALKER and A. PITTONI (Biochem. Z., 1936, 286, 297—300).—A method is described whereby traces of As in biological fluids can be collected at the anode and so conc. prior to determination. P. W. C.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

DECEMBER, 1936.

### General, Physical, and Inorganic Chemistry.

**Effects of pressure and current on the intensities of the Balmer lines of hydrogen.** W. W. JACKSON (Phil. Mag., 1936, [vii], 22, 633—654).—A detailed investigation indicates that thermodynamic equilibrium is not established in a discharge tube; the excitation function governs the variation of the intensities of the lower members of the Balmer series. The ratio of the no. of dispersion electrons associated with  $H_\alpha$  and  $H_\beta$  is 5.07 at 0.18 mm. and 675 ma. N. M. B.

**Spectrum of doubly excited helium.** A. T. KIANG, S. T. MA, and T. Y. WU (Physical Rev., 1936, [ii], 50, 673).—None of the calc. strongest lines was found when electrons from a hot cathode were accelerated through low-pressure He with 1100—1800 volts corresponding with an electron energy on impact of 500—700 volts, for which the calc. excitation cross-section is a max. Probable explanations of the failure are discussed. N. M. B.

**Zeeman effect in the first negative oxygen bands.** L. BOZÓKY and R. SCHMID (Physical Rev., 1935, [ii], 48, 466).—The Zeeman effect in the 5631 Å. band has been photographed. L. S. T.

**Additional first negative oxygen bands.** L. BOZÓKY and R. SCHMID (Physical Rev., 1935, [ii], 48, 465).—Nine additional bands have been recognised. L. S. T.

**Dependence of intensities of rotation lines of a band on the conditions of excitation.** H. BRINKMAN (Physikal. Z., 1936, 37, 726—728).—The anomaly in the intensity distribution of rotation lines of  $N_2$  bands with different conditions of excitation, noticed by Herrmann (this vol., 261), is due to experimental error. The individual rotation lines of a band have the same abs. efficiency. A. J. M.

**Dependence of intensities of rotation lines of a band on the conditions of excitation.** O. HERRMANN (Physikal. Z., 1936, 37, 729).—A reply to Brinkman (preceding abstract). A. J. M.

**Effect of temperature on absorption of resonance radiation by sodium atoms.** J. L. TUCK and E. WARHURST (Trans. Faraday Soc., 1936, 32, 1501—1503).—The variation with temp. of absorption of resonance radiation by Na atoms has been determined for const. atom density between 140° and 320°. The absorption decreases linearly with temp. over this range. A. J. E.

**Absorption of sulphur vapour between 3600 and 5000 Å.** B. ROSEN and L. NEVEN (Compt.

rend., 1936, 203, 663—665; cf. A., 1928, 687).—The C bands are attributed to the principal system of  $S_2$ , and are present even at 1100°, when the band intensity depends only on the no. of  $S_2$  mols. and not on the concn. Recorded contradictory observations may be reconciled by the existence of a continuous region of absorption due to polyat. S situated in the same spectral region as the predissociated bands of the principal system. R. S. B.

**Glow spectra of halogen molecules.** Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 71—82).—The vapours of  $I_2$  at >1200°,  $Br_2$  at >450°, and  $Cl_2$  at >1200° emit a glow consisting of emission bands superimposed on an independent continuum. The emission bands are due in each case to the transition  $O_u^+ \rightarrow$ , the  $O_u^+$  mols. arising from thermally dissociated  $^2P_{3/2}$  atoms by the successive ternary collision processes  $3X(^2P_{3/2}) \rightarrow X_2(^1\Sigma^+) + X(^2P_{1/2}) + \text{kinetic energy}$ ;  $X(^2P_{1/2}) + X(^2P_{3/2}) + \text{wall} \rightarrow X_2(O_u^+) + \text{wall} + \text{kinetic energy}$ . J. S. A.

**Absorption spectrum of chlorine.** C. F. GOODEVE and B. A. STEPHENS (Trans. Faraday Soc., 1936, 32, 1517—1518).—The absorption of thick layers of  $Cl_2$  between 600 and 1150 m $\mu$  has been investigated. The band system at 579—614 m $\mu$  (A., 1923, ii, 48) was not confirmed. Additional bands conforming to Birge and Weizel's analysis are given. A. J. E. W.

**New terms in the arc spectrum of tellurium.** S. G. KRISHNAMURTY (Indian J. Physics, 1936, 10, 365—373).—Full data for the range 1600—5000 Å. arc tabulated, and 8 new odd levels in addition to those due to 5d and 6s configurations are reported. N. M. B.

**Near ultra-violet band spectra of iodine.** O. STUHLMAN, jun. (Physical Rev., 1935, [ii], 48, 381).—The results of an examination of the emission spectrum of I vapour under high-frequency electrodeless discharge conditions are given. L. S. T.

**Arc spectrum of tungsten.** D. D. LAUN (Physical Rev., 1935, [ii], 48, 572).—The structure obtained from the Bureau of Standards measurements is summarised. S. T.

**Characteristics of mercury-rare gas discharge tubes.** H. W. MELVILLE (Trans. Faraday Soc., 1936, 32, 1525—1531).—The characteristics have been determined to find optimum conditions for a tube taking an input of 400 watts and emitting the resonance line at 2537 Å. For an input of 70 watts it is possible to obtain an output of  $10^{19}$  quanta per



sec. The mechanism of the collision processes occurring is discussed. E. S. H.

Characteristics of mercury arc between solid electrodes. W. ENDE (Z. tech. Physik, 1934, 15, 601—604; Chem. Zentr., 1936, i, 511).—The characteristics of an arc between oxide electrodes were studied. H. J. E.

Forbidden lines in the spectrum of neutral lead with high-frequency excitation. H. NIEWONNICZANSKI (Acta phys. polon., 1934, 2, 375—382; Chem. Zentr., 1936, i, 505; cf. A., 1935, 138). H. J. E.

Photographic and spectroscopic investigation of arcs with high current density. B. KIRSCHSTEIN and F. KOPPELMANN (Z. tech. Physik, 1934, 15, 604—606; Chem. Zentr., 1936, i, 511). H. J. E.

Change of striking potential on illumination. I. W. FÜCKS and W. SEITZ (Z. Physik, 1936, 103, 1—17).—The striking voltage in A, He, N<sub>2</sub>, and air for the electrode materials Ag, Cu, Ni, and Zn has been determined. Under most conditions the voltage was increased by illumination with Hg lamp ultra-violet light, that of short  $\lambda$  alone being effective. A. E. M.

Disappearance of spectral lines in strong electric fields. V. FABRIKANT (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 215—217; cf. A., 1930, 828; 1931, 1203).—Theoretical. Lanczos' wave-mechanical treatment is based on incorrect assumptions; Smurov's classical expression  $0.086e/\rho^2$  ( $e$ =electronic charge,  $\rho$ =orbital radius) for the potential required to ionise an H atom yields vals. agreeing with those required to cause the disappearance of the corresponding spectral lines. R. C. M.

Light wave-length measurements with a divergent beam and plane grating. D. L. DAS (Z. Physik, 1936, 101, 447—455). A. B. D. C.

Luminescence of solid substances produced by direct excitation in a Geissler tube. M. SERVIGNE (Compt. rend., 1936, 203, 581—583).—Ultra-violet Hg light is produced in the tube containing the solid by passing a discharge through the contained Ne or A saturated with Hg vapour. The specimen emits cathode luminescence when the pressure is 0.01 mm. The spectral bands emitted by a substance under the influence of these different radiations are generally the same, but the distribution of intensity is changed. J. G. A. G.

Townsend coefficients and spark discharge. D. Q. POSIN (Physical Rev., 1936, [ii], 50, 650—658).—A quant. study has been made of the pre-spark current between plane parallel electrodes in purified N<sub>2</sub>. Data for  $X/p$ ,  $\alpha/p$ , and  $\beta/p$ , where  $X$  is the field strength, and  $\alpha$  and  $\beta$  the Townsend coeffs., are tabulated and plotted, and are discussed in relation to the Townsend equation. N. M. B.

Yield of the characteristic X-rays of aluminium (Al K lines) excited by protons. O. PETER (Ann. Physik, 1936, [v], 27, 299—311).—The yield of emitted quanta per proton falling on Al has been found to be  $(6.22 \pm 0.31) \times 10^{-6}$  for excitation of the Al K lines by protons of 132 e.k.v. energy. This is in

agreement with the theory of Henneberg (A., 1934, 127). O. D. S.

Röntgen emission spectra and chemical combination. IV.  $K\alpha_1\alpha_2$  lines of phosphorus compounds. O. LUNDQUIST (Z. Physik, 1936, 102, 768—771).—In compounds of P the  $K\alpha_1\alpha_2$  doublet is shifted towards shorter  $\lambda$ . Compared with red P the mean shifts are, 1.58 X for hypophosphite, 2.19 X for phosphite, and 2.49 X for phosphate. H. C. G.

Fine structure in the K X-ray edge of gallium. W. W. MUTCH (Physical Rev., 1935, [ii], 48, 569—570).—A preliminary report of absorption spectra near the Ga K edge investigated at  $-150^\circ$  and  $-67^\circ$ . L. S. T.

Probability of K-shell ionisation of silver by cathode rays. H. S. W. MASSEY and E. H. S. BURHOP (Physical Rev., 1935, [ii], 48, 468; cf. this vol., 656). L. S. T.

L-Series for uranium. H. CLAESSON (Z. Physik, 1936, 499—508). A. B. D. C.

X-Ray satellites, relative intensities, and line widths. L. G. PARRATT (Physical Rev., 1936, [ii], 50, 598—602; cf. this vol., 1041).—Preliminary data on the  $L\alpha_{1,2,3,4,5,6,7}$  lines for Ag (47), and on the  $M\alpha, \beta$  lines for Au (79), recorded with a two-crystal spectrometer, are reported and discussed. N. M. B.

Feeble emissions in the L spectrum of radium (88). H. HULUBEI (Compt. rend., 1936, 203, 665—667; cf. this vol., 1169, 1311).—Satellites of  $\alpha_1, \beta_2$ , and  $\gamma_2$  rays have been observed with Ra. R. S. B.

$M_{IV, V}$  Absorption edges of protoactinium (atomic number 91). V. DOLEJŠEK and V. KUNZL (Nature, 1936, 138, 590). L. S. T.

Atomic dispersion and absorption of X-rays according to the relativistic wave mechanics of Dirac. I. K. SEILER (Ann. Physik, 1936, [v], 27, 329—372).—Mathematical. The component of at. absorption and dispersion of X-rays due to the K level is calc. Agreement with experimental vals. of the scattering coeff. in the neighbourhood of K lines is good for light and medium atoms. For heavy atoms relativity and spin effects must be taken into account. O. D. S.

Absorption of X-rays in the anticathode of the ion tube at low voltage. V. KUNZL (Acta phys. polon., 1934, 2, 447—457; Chem. Zentr., 1936, i, 718).—The  $M_{II}$  lines of Ta, Tm, and Pt and the  $L_I, L_{II}$ , and  $L_{III}$  lines of Sn were not observed in absorption. Only the  $L_I$  line of Mo was observed. H. J. E.

Production of polarised X-rays. W. H. GEORGE (Proc. Roy. Soc., 1936, A, 156, 96—107).—An account is given of the method used to get a  $10^3$ -fold increase in the intensity of the polarised beam obtainable from a given initial X-ray intensity, so that the beam is strong enough to use for the study of vectorial phenomena in the interactions of X-rays and matter. L. L. B.

Intensity of the central spot produced by X-rays penetrating piezoelectrically oscillating

quartz crystals. G. E. M. JAUNCEY and A. T. JAKES (Physical Rev., 1936, [ii], 50, 672).—Causes of variation of intensity and area of the central spot were investigated. The increases found by Fox (cf. A., 1935, 1059) were probably due to an accidental combination of photographic reversal and halation.

N. M. B.

Double Compton scattering. F. BORP (Naturwiss., 1936, 24, 680—681).—The scattered radiation from Pb at an angle of  $114^\circ$  is considered. The intensity of double scattered radiation for thin films increases more rapidly than with the square of the distance.

A. J. M.

Photo-electric properties of barium and calcium. N. C. JAMISON and R. J. CASHMAN (Physical Rev., 1936, [ii], 50, 624—631).—With repeated fractional distillation of Ba in a photo-electric cell, the work function at room temp. was 2.520 and 2.510 e.v., the difference being attributed to differences in crystal structure or in purity. Measurements at room temp. to  $100^\circ$  gave a temp. coeff. of  $(2.2 \pm 0.7) \times 10^{-5}$  e.v. per  $1^\circ$ . The abs. photo-electric yield of the surface was determined. The optical reflexion coeff. varied 43—63% over 4000—7000 Å. The work function of a Ca surface prepared by single distillation was 2.706 e.v. After repeated surface heating to  $100^\circ$ , the data did not fit Fowler's theoretical curve, the discrepancy indicating surface inhomogeneity. Analysis of data indicates two emitting surfaces having work functions differing by approx. 0.2 e.v.

N. M. B.

Dependence of the field electron stream on the work of emission. E. W. MULLER (Z. Physik, 1936, 102, 734—761).—Measurements were made of electron emission from Ba, Mg, and Cs on W. The results are somewhat at variance with wave-mechanical theory.

A. E. M.

Irregularities in thermionic emission from tungsten. F. L. YERZLEY (Physical Rev., 1936, [ii], 50, 610—616; cf. Johnson, this vol., 553).—A tube with a moving electrode is used to investigate variations in emission density over a length of W filament. Above a crit. temp. range positive ion emission is limited to narrow regions near the wire connections. Electron emission, even after careful filament ageing, is not uniform from point to point, but occurs in a stable pattern, with irregularities, the causes of which are discussed.

N. M. B.

Where can negative protons be found? F. ZWICKY (Physical Rev., 1935, [ii], 48, 169).—Negative protons should be sought in cloud chambers at high altitudes.

L. S. T.

Free atoms and molecular dissociation in high frequency discharges. A. A. BALANDIN and J. EIDUS (Acta Physicochim. U.R.S.S., 1936, 4, 527—546).—The instantaneous pressure increase on starting a high-frequency discharge was studied for discharges through a no. of pure and mixed bimol. gases and Ne. The effect, observed with all bimol. gases, is dependent on the nature of the electrodes, the initial pressure of the gas, and the current and voltage in the secondary. No effect is observed with Ne. The presence of H atoms in the discharge

through  $H_2$  is indicated by the reduction of  $MoO_3$  in the discharge tube.

O. D. S.

Possibility of a unified interpretation of electrons and protons. V. ROJANSKY (Physical Rev., 1935, [ii], 48, 108—109).—Theoretical.

L. S. T.

Polarisation of electrons by double scattering. O. HALPERN and J. SCHWINGER (Physical Rev., 1935, [ii], 48, 109—110).

L. S. T.

Absorbability of energy-rich electrons. M. WALDMEIER (Helv. phys. Acta, 1935, 8, 517—518; Chem. Zentr., 1936, i, 9).—The mass absorption coeff. of high-speed electrons in Pb is much  $>$  in Al, in qual. agreement with the theory of Bethe and Heitler.

J. S. A.

Behaviour of oxygen on electron bombardment. N. NEKRASSOV and I. STERN (Acta Physicochim. U.R.S.S., 1936, 4, 283—300).— $O_2$  in a three-electrode discharge tube at pressures 0.01—0.03 mm. is adsorbed on metal surfaces at 150—200°. On electron bombardment activated  $O_2$  mols. are formed and the pressure sinks rapidly. The velocity of decrease is greatly reduced by decreasing the surface of the Pt anode. The nature of the excited  $O_2$  mols. and the behaviour of secondary electrons are discussed.

R. S. B.

Space charge for electrons with initial velocities. G. PLATO, W. KLEEN, and H. ROTHE (Z. Physik, 1936, 101, 509—520).

A. B. D. C.

Scattering of high-speed electrons of varying energy. H. J. YEARIAN and J. D. HOWE (Physical Rev., 1935, [ii], 48, 381—382).—The atom factor of Au and Ag at different voltages has been investigated.

L. S. T.

Electron diffraction by gas molecules. I. Structure of phosphorus. II. Valency angle of oxygen. L. R. MAXWELL, V. M. MOSLEY, and S. B. HENDRICKS (Physical Rev., 1935, [ii], 48, 476; cf. this vol., 17).

L. S. T.

Electron velocity distribution in gases. K. G. EMELEUS and R. J. BALLANTINE (Physical Rev., 1936, [ii], 50, 672—673).—Druyvesteyn's method of analysis, applied to probe data for arcs and glows with electron concns. of  $10^7$ — $10^9$  per c.c., shows the frequent existence of a wide depression in the distribution function for electron velocities rather  $>$  the mean, as predicted by Morso (cf. A., 1935, 1294), and the common occurrence of a fairly distinct group of electrons of mean energy order 5—10 e.v., in accordance with the quantum theory of ionisation.

N. M. B.

Use of complex Riemannian geometry in the theory of the electron. U. KAKINUMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 83—98).

J. S. A.

Carbon reactions and the corrected mass scale. M. A. TUVE and L. R. HAFSTAD (Physical Rev., 1935, [ii], 48, 106—107).—The reactions of C under deuteron bombardment are discussed in relation to the new mass vals. (cf. this vol., 1171).

L. S. T.

At. wt. of molybdenum. Analysis of molybdenum pentachloride. O. HONIGSCHMID and G.



WITTMANN (Z. anorg. Chem., 1936, 229, 65—75).—The mean of 19 nephelometric titrations of  $\text{MoCl}_3$  with  $\text{AgNO}_3$  gives Mo  $95.95 \pm 0.004$  (Ag 107.880, Cl 35.457). F. L. U.

At. wt. of erbium. O. HÖNIGSCHMID (Naturwiss., 1936, 24, 619).—By titration of impure  $\text{ErCl}_3$  with  $\text{AgNO}_3$ , and correcting for Y and Tm content, the val. 167.24 was obtained for the at. wt. of Er. This is in agreement with the mass-spectrograph val. The previous low val. (165.2) is ascribed to impurity in the Er prep. A. J. M.

At. wt. of tungsten. Analysis of tungsten hexachloride. O. HÖNIGSCHMID and W. MENN (Z. anorg. Chem., 1936, 229, 49—64).—The purification of W by fractional sublimation of  $\text{WCl}_6$  is described. Nephelometric titration of purified  $\text{WCl}_6$  by  $\text{AgNO}_3$  gives, as the mean of 22 experiments, W  $183.92 \pm 0.014$  (Ag 107.880, Cl 35.457). F. L. U.

Double-focussing mass spectrograph and the masses of  $^{15}\text{N}$  and  $^{18}\text{O}$ . J. MATTAUCH (Physical Rev., 1936, [ii], 50, 617—623).—The theory and description of an instrument working as an "achromatic lens" for all masses are given. The differences of packing fraction of doublets containing  $^{15}\text{N}$  and  $^{18}\text{O}$  were determined. Isotopic wts. referred to  $^{16}\text{O} = 16$  are  $^{15}\text{N} = 15.0040 \pm 0.0008$ , and  $^{18}\text{O} = 18.0037 \pm 0.0007$ . N. M. B.

Evidence for the existence of an isotope of potassium of mass 40. A. O. NIER (Physical Rev., 1935, [ii], 48, 283—284).—The data obtained with a mass spectrograph of increased resolving power are considered to establish the existence of  $^{40}\text{K}$ . The abundance ratio  $^{39}\text{K} : ^{40}\text{K}$  is 8600 approx. L. S. T.

Further evidence for the existence of  $^{40}\text{K}$ . A. K. BREWER (Physical Rev., 1935, [ii], 48, 640).—Mass spectra of positive thermions emitted from various K sources confirm the existence of  $^{40}\text{K}$  (cf. preceding abstract). The  $^{39}\text{K} : ^{40}\text{K}$  abundance ratio calc. is  $8300 \pm 100$ . L. S. T.

Separation of mercury isotopes. K. ZUBER (Helv. phys. Acta, 1935, 8, 488—490; Chem. Zentr., 1936, i, 494).—The III and IV components of the 2537 Å. Hg line excite respectively the 200 and the 202 Hg isotopes. Irradiation of a Hg- $\text{O}_2$  mixture with either of these lines causes selective oxidation of one isotope. The method gave positive results. H. J. E.

Evidence against  $^5\text{He}$ . R. D'E. ATKINSON (Physical Rev., 1935, [ii], 48, 382).—Evidence against the view that  $^5\text{He}$  should be stable is discussed. L. S. T.

Self-excitation of Geiger-Müller counters. G. MEDICUS (Z. Physik, 1936, 103, 76—112).—Of two  $\text{H}_2$ -filled counter tubes with Cu cathodes, one exhibited self-excitation, probably due to  $\text{H}_2\text{O}$  adsorbed on the glass walls. The influence of light, temp., and the presence of Hg vapour on the no. and distribution of impulses recorded over a given time was investigated. H. C. G.

Range of  $\alpha$ -particles and chemical linking. M. FÖRSTER (Ann. Physik, 1936, [v], 27, 373—388).—

The stopping power of  $\text{H}_2\text{O}$  vapour for  $\alpha$ -particles has been found to be about 3% < that of the  $\text{H}_2\text{-O}_2$  mixture from which it was formed. O. D. S.

Separation of  $\beta$ - and  $\gamma$ -radiation of radioactive preparations. H. STAUB (Helv. phys. Acta, 1935, 8, 512—513; Chem. Zentr., 1936, i, 14).—The material is placed at one end of a solenoid, by means of which  $\beta$ -rays of uniform velocity are focussed at a point outside the solenoid, and shielded by a Pb cylinder from direct  $\gamma$ -radiation. J. S. A.

Cloud chamber experiments with  $\gamma$ - and  $\beta$ -rays in xenon and krypton. H. KLARMANN and W. BOTHE (Z. Physik, 1936, 101, 489—498). A. B. D. C.

Liberation of electrons from solids by hard  $\gamma$ -rays. T. G. KUJUMZELIS (Z. Physik, 1936, 102, 762—767).—Measurements were made of the nos. of electrons liberated from C, Al, Cu, Sn, and Pb in forward and backward directions by  $\gamma$ -rays with energies between  $2.6 \times 10^6$  and  $7.7 \times 10^6$  e.v. Results plotted against at. no. give characteristic curves which indicate a possible method for determining the energy of unknown  $\gamma$ -radiation. H. C. G.

Effect of a magnetic field on the visible light produced in liquids by  $\gamma$ -rays. P. A. TSCHERENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 413—416; cf. A., 1934, 938).—Vavilov's theory that " $\gamma$ -luminescence" is due to Compton electrons liberated by the primary photons is supported by the asymmetric distribution of intensity of this light in a 9500 gauss magnetic field. R. C. M.

Excitation of secondary  $\gamma$ -rays by  $\beta$ -rays. E. STAHEL and P. KIPFER (Helv. phys. Acta, 1935, 8, 508—511; Chem. Zentr., 1936, i, 10).—The intensity of the secondary  $\gamma$ -radiation excited in Pb by the primary  $\beta$ -radiation from U-X has the same intensity as the primary  $\gamma$ -radiation of U-X, and is shown by absorption measurements to consist of two (possibly three) components. J. S. A.

Energy differences on addition of neutrons. R. FLEISCHMANN (Z. Physik, 1936, 103, 113—124).—Quantum energies of  $\gamma$ -rays resulting from the bombardment of H, Al, Fe, Cu, Se, Ag, Cd, Sm, Gd, Hg, and Pb by slow neutrons have been measured by a coincidence method using two Geiger-Müller counters. Results plotted against at. no. show max. for Fe and flat min. for rare earths, and then a further rise. The min. corresponds with a max. in the effective cross-section for the addition of slow neutrons. Cd was shown to emit  $\gamma$ -rays. H. C. G.

Neutrons from different sources. R. LADENBURG, R. ROBERTS, and M. B. SAMPSON (Physical Rev., 1935, [ii], 48, 467).—A preliminary report of the yields of neutrons obtained from targets of D compounds, Be metal, and LiF bombarded by accelerated deuterons under various conditions. L. S. T.

Slow neutrons. W. M. BRUBAKER and T. W. BONNER (Physical Rev., 1935, [ii], 48, 470).—Measurements of the tracks of the short-range recoil protons which are projected by neutrons in the energy interval 0.03—0.6 m.e.v. indicate no anomalous absorption within this range. L. S. T.

**Scattering of neutrons in matter.** L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 810—812).—The statistics of the scattering of neutrons by protons and nuclei are discussed.

D. C. J.

**Absorption of slow neutrons in silver.** L. N. RIDENOUR and D. M. YOST (Physical Rev., 1935, [ii], **48**, 383—384).—Data for the absorption by Ag of slow neutrons from B+Rn and Be+Rn sources as measured by detectors of Ag, Cu, V as  $\text{NH}_4\text{VO}_3$ , Br as  $\text{NH}_4\text{Br}$ , and I as  $\text{CHI}_3$  are recorded and discussed.

L. S. T.

**Absorption of neutrons in silver, cadmium, and boron.** II. N. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, **3**, 291—293; cf. this vol., 1314).—The absorption of neutrons (from Ra and Rn on Be) by B has been studied as a function of the thickness ( $l$ ) of paraffin used to slow down the neutrons; results are similar to those with Cd. Filtration through Cd reduces the coeff. of absorption of neutrons in Ag. The relations between the activities of the two Ag isotopes have been studied, using different filters and vals. of  $l$ ; half periods of 24 sec. and 2.33 min. have been obtained. The ratio of the activities depended very little on  $l$ .

R. S. B.

**Slowing down of neutrons by the nuclei of heavy elements.** P. I. LUKIRSKI and T. CAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, **3**, 411—412; cf. A., 1935, 141; this vol., 132, 402).—Neutrons from a Rn+Be source are slowed down to thermal velocities when passing through an enclosing Pb sphere of 7.4 cm. diameter.

R. C. M.

**Coincidence experiments with neutrons and  $\gamma$ -rays of beryllium.** H. MAIER-LEIBNITZ (Z. Physik, 1936, **101**, 478—485).—Disintegration of Be with  $\alpha$ -rays gives coupled neutrons and  $\gamma$ -rays, and  $\gamma$ -ray quanta in pairs.

A. B. D. C.

**$\gamma$ -Rays from nitrogen bombarded with deuterons.** H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and C. C. LAURITSEN (Physical Rev., 1935, [ii], **48**, 100).—The energy spectrum of recoil electrons from N, as  $\text{NH}_4\text{Cl}$ , bombarded with deuterons at 900 kv. indicates that the principal  $\gamma$ -ray lines are 1.9, 3.1, 4.0, 5.3, and 7.0 m.e.v.

L. S. T.

**$\alpha$ -Radioactivity of argon formed by radio-chlorine.** W. F. LIBBY, M. D. PETERSON, and W. M. LATIMER (Physical Rev., 1935, [ii], **48**, 571—572).—Radio-Cl from Ag radiochloride gives active A which yields a radiation, probably an  $\alpha$ -particle, of approx.  $3.1 \pm 0.2$  mm. range in air. Probable reactions are  $^{38}\text{Cl} = ^{38}\text{Ar} + e^-$  and  $^{38}\text{Ar} = ^{34}\text{S} + \alpha$ ,  $^{38}\text{Cl}$  being formed by  $^{37}\text{Cl} + \frac{1}{2}n = ^{38}\text{Cl}$ .

L. S. T.

**$\beta$ -Ray spectra of radioactive manganese, arsenic, and indium.** M. V. BROWN and A. C. G. MITCHELL (Physical Rev., 1936, [ii], **50**, 593—598; cf. Gaertner, this vol., 918).—The  $\beta$ -ray spectra were obtained by measuring tracks produced in a cloud-chamber in a magnetic field. Mn and As spectra were resolved into two components, the end-points being: Mn, 1.2 and 2.9; As, 1.09 and 3.4 m.e.v. The end-point for In is 1.45 m.e.v.

N. M. B.

**$\gamma$ -Rays from boron bombarded with protons.** H. R. CRANE, L. A. DELSASSO, W. A. FOWLER, and

C. C. LAURITSEN (Physical Rev., 1935, [ii], **48**, 102—103).—Bombardment of B by protons gives a  $\gamma$ -radiation of intensity  $\ll$  than obtained with deuterons as projectiles. The energy spectrum of recoil electrons indicates  $\gamma$ -ray lines at 2.5, 4.2, 5.7, 7.5, 9.8, and 13 (?) m.e.v. The upper limit of the  $\gamma$ -ray spectrum is at 14.5 m.e.v. approx. The probable reaction is  $^{11}\text{B} + ^1\text{H} \rightarrow ^{12}\text{C}$ .

L. S. T.

**Heavy particle component of the cosmic radiation.** R. B. BRODE, H. G. MACPHERSON, and M. A. STARR (Physical Rev., 1936, [iii], **50**, 581—588).—Investigation with a large Wilson cloud-chamber showed, in 8500 pictures, about 80 heavy tracks, of which 21 were made by particles of about the ionisation of slow protons. About 1% of the sea-level cosmic ionisation is due directly to heavy particles.

N. M. B.

**Artificial transmutation of light elements bombarded by ions of hydrogen and heavy hydrogen.** I. B. ARAKATSU, K. KIMURA, and Y. UEMURA (Mem. Fac. Sci. Agric. Taihoku, 1936, **18**, 75—94).—With apparatus of the type used by Oliphant and Rutherford, the relative probability of two alternative types of disintegration of  $^6\text{Li}$  and of  $^{11}\text{B}$  was measured.

A. E. M.

**Temporary excess of 10% in the cosmic radiation.** J. CLAY, E. M. BRUNS, and J. T. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 813—815).—A sudden temporary increase in cosmic-ray intensity is reported.

D. C. S.

**Cosmic-ray showers produced by electrons.** E. C. STEVENSON and J. C. STREET (Physical Rev., 1935, [ii], **48**, 464—465).—Photographs of showers produced by an electron and by a non-ionising ray are reproduced.

L. S. T.

**Heavy particles from lead.** J. C. STREET, E. G. SCHNEIDER, and E. C. STEVENSON (Physical Rev., 1935, [ii], **48**, 463).—Heavy particles from a Pb plate have been observed in cloud-chamber photographs of cosmic-ray showers.

L. S. T.

**Cosmic-ray measurements with a Wilson chamber on Jungfraujoch.** G. HERZOG and P. SCHERRER (Helv. phys. Acta, 1935, **8**, 514—515; Chem. Zentr., 1936, i, 279).

J. S. A.

**Apparatus for prolonged registration of intensity course of cosmic radiation.** P. SCHERRER, H. STAUB, and H. WAFFLER (Helv. phys. Acta, 1935, **8**, 516—517; Chem. Zentr., 1936, i, 279).

J. S. A.

**Energy distribution of cosmic rays.** A. LONG-ACRE (Physical Rev., 1936, [ii], **50**, 674).—Statistical variations in Anderson and Neddermeyer's data are discussed. Analysis indicates that a sample of 100 vertical cosmic rays will contain 37 negative and 63 positive rays, the latter containing 18 in a low, and 45 in a higher, energy distribution.

N. M. B.

**Residual current in ionisation-pressure chamber, and variation with pressure of ionisation due to cosmic rays.** W. MESSERSCHMIDT (Z. Physik, 1936, **103**, 18—26).—Ionisation due to  $\alpha$ -particles was eliminated by working at 10—25 atm. -Rays and cosmic rays show differences of ionisation between 0 and 25 atm.

A. E. M.



**Effect of paraffin and lead on the rate of production of very large cosmic-ray bursts.** D. HEYWORTH and R. D. BENNETT (Physical Rev., 1936, [ii], 50, 589—593; cf. Doan, this vol., 265).—Using an intensity meter, data are given for the effects, at sea level for bursts  $> 15 \times 10^6$  ion pairs, on the rate of production of bursts of different magnitudes of degree of shielding of the ionisation chamber, heavy building structure above the instrument, and Pb and paraffin placed immediately above the ionisation chamber. The effect of paraffin is much  $<$  that of Pb. N. M. B.

**Cosmic-ray bursts.** W. MESSERSCHMIDT (Z. Physik, 1936, 103, 27—56).—Collision distribution curves as regards size and frequency are given for Al, Fe, Pb, and C. A. E. M.

**Dependence of nuclear forces on velocity.** J. A. WHEELER (Physical Rev., 1936, [ii], 50, 643—649).—Mathematical. The Majorana force may be considered as a special case of a neutron-proton interaction dependent on velocity and angular momentum. The most general dependence of two-particle forces on spin, separation, and velocity, consistent with the conservation laws, is determined. N. M. B.

**Structure of atomic nuclei.** N. S. JAPOLSKY (Phil. Mag., 1936, [vii], 22, 537—581; cf. A., 1935, 1442).—Mathematical. The theory previously reported is developed and extended. N. M. B.

**Modification of the Moseley law.** V. DOLEJSEK (Acta phys. polon., 1934, 2, 439—446; Chem. Zentr., 1936, i, 503).—A general equation, valid for all the elements and all electron shells, is given. H. J. E.

**Must neutron-neutron forces exist in the  $^3\text{H}$  nucleus?** R. D. PRESENT (Physical Rev., 1936, [ii], 50, 635—642; cf. White, this vol., 400; Tuve, *ibid.*, 539).—Mathematical. Evidence points to the existence of direct like-particle forces in the nucleus. N. M. B.

**The neutron and structure of the atomic nucleus.** C. LOREY (J. pr. Chem., 1936, [ii], 147, 78—82).—Since, with the exception of  $^1\text{H}$ , all known isotopes have an at. wt.  $<$  double the nuclear charge ( $z$ ), it is suggested that each proton is associated with one neutron (neutron of the first kind). Since, however, most isotopes have an at. wt.  $> 2z$ , these must contain neutrons of the second kind, or "ballast neutrons." The nos. of protons and of neutrons of the two kinds are tabulated for a no. of isotopes. The no. of neutrons in the outermost quantum group of the at. nucleus has a bearing on the at. stability. J. W. S.

**Higher-order derivatives in the interaction "Ansatz" of the Fermi theory.** E. J. KONOPINSKI and G. E. UHLENBECK (Physical Rev., 1935, [ii], 48, 107—108; cf. A., 1935, 1048).—Mathematical. L. S. T.

**Recombination of neutrons and protons.** E. FERMI (Physical Rev., 1935, [ii], 48, 570).—Theoretical. L. S. T.

**Self-interaction of neutrons and protons.** D. IVANENKO and A. SOKOLOV (Nature, 1936, 138, 684).—The interaction between two heavy nuclear particles is computed on Fermi's theory, assuming

the interaction transfer by one pair and also by an arbitrary no. of pairs of electrons and neutrinos.

L. S. T.

**Relativity corrections in the theory of the deuteron.** E. FEENBERG (Physical Rev., 1936, [ii], 50, 674; cf. Margenau, this vol., 1175).—Mathematical. N. M. B.

**Comparison of Majorana-Heisenberg and velocity-dependent forces.** K. WAY and J. A. WHEELER (Physical Rev., 1936, [ii], 50, 675). N. M. B.

**Magnetic nuclear moment of platinum,  $^{195}\text{Pt}$ .** T. SCHMIDT (Z. Physik, 1936, 101, 486—488).—This moment is  $+0.6$  nuclear magneton. A. B. D. C.

**Quadrupole moment and magnetic moment of  $^{75}\text{As}$ .** H. SCHULER and M. MARKETU (Z. Physik, 1936, 102, 703—708).—From fine structure measurements, the quadrupole moment  $q$  is  $+0.3 \times 10^{-24}$  and the mean val. for the magnetic moment  $\mu$  is  $+1.5$  nuclear magnetons. L. G. G.

**Dissociative equilibrium and pair generation.** J. KISHEN (Indian J. Physics, 1936, 10, 389—397).—Mathematical. A general formula for the dissociative equilibrium in an external radiation field is developed and applied to thermal ionisation and to the formation and annihilation of pairs of electrons and positrons existing in statistical equilibrium with radiation. N. M. B.

**Self-consistent field, with exchange, for  $\text{Cl}^-$ .** D. R. HARTREE and W. HARTREE (Proc. Roy. Soc., 1936, A, 156, 45—62).—Fock's equations for the self-consistent field, with exchange, for the  $\text{Cl}^-$  ion have been solved, and the results are compared with those of the self-consistent field without exchange. The inclusion of exchange terms causes a contraction of the  $(3p)$  radial wave function. The effects of the inclusion on the X-ray scattering factor, the diamagnetic susceptibility, and the electrical polarisability are discussed. L. L. B.

**Fundamental frequencies and energy constants.** H. S. ALLEN (Proc. Roy. Soc., 1936, A, 156, 85—96).—The sp. heat of solids, energy, and optical data are considered. L. L. B.

**Fundamental physical constants.** W. N. BOND (Phil. Mag., 1936, [vii], 22, 624—632).—Estimates of numerical vals. of the consts. are deduced from Eddington's theories concerning  $M/m$ ,  $hc/2\pi e^2$ , and the universal gravitational const. Confirmatory experimental evidence is given, and the remaining discrepancies are pointed out. Full data and deductions are tabulated. N. M. B.

**Lorentz contraction of a liquid.** L. COURVOISIER (Z. Physik, 1936, 101, 422—436).—Observation of the Lorentz contraction through 1934 and 1935 showed a contraction of the correct frequency but of small amplitude. A. B. D. C.

**Lorentz contraction determined with levelled apparatus free to rotate.** L. COURVOISIER (Z. Physik, 1936, 101, 437—446).—Contractions observed agree with theory. A. B. D. C.

**Isotope relations in the spectra of  $\text{LiH}$  and  $\text{LiD}$ .** F. H. CRAWFORD and T. JORGENSEN, jun.

(Physical Rev., 1935, [ii], 48, 475; cf. A., 1935, 1051).

L. S. T.

**Spin coupling in  $^3\Sigma$  states of PH and PD.** M. ISHAQUE and R. W. B. PEARSE (Proc. Roy. Soc., 1936, A, 156, 221—232).—The spectrum of PD, like that of PH, consists of one intense band near  $\lambda$  3400 containing five max., which are more sharply defined in PD. The spin fine structure of the  $^3\Sigma$  states of PH and PD are compared with Kramers' formulæ and the consts.  $\epsilon$  and  $\gamma$  evaluated.  $\epsilon$  remains almost unchanged by the substitution of D for H, whilst  $\gamma$  is reduced to almost half.

L. L. B.

**Molecular spectra of magnesium deuteride.** Y. FUJIOKA and Y. TANAKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 121—137).—Seven  $^2\Pi \rightarrow ^2\Sigma$  bands of MgD between 4900 and 5500 Å. have been analysed, and the mol. consts. evaluated.

J. S. A.

**Spectrum of indium oxide.** W. W. WATSON and A. SHAMON (Physical Rev., 1936, [ii], 50, 607—609; cf. Guernsey, A., 1934, 1055).—Wave no. data and assignments and intensities of the complex spectrum of InO lying between the two In resonance lines at 4102 and 4511 Å. are tabulated. An expression for the band heads is given.

N. M. B.

**New ultra-violet bands of  $\text{SO}_2$  in emission.** G. KORNFIELD (Trans. Faraday Soc., 1936, 32, 1487—1492).—59 bands between 2443 and 2123 Å., degraded to the red, are recorded in the spectrum of a blue electrodeless discharge in  $\text{SO}_2$ , 49 being known  $\text{SO}_2$  bands. None can be added to the known band system of  $\text{SO}$ . All the bands are attributed to  $\text{SO}_2$  in emission; a proposed classification is given.

A. J. E. W.

**Absorption spectrum of chlorine heptoxide.** C. F. GOODEVE and B. A. M. WINDSOR (Trans. Faraday Soc., 1936, 32, 1518—1519).—The spectrum consists of a single continuous band, setting in at about 3000 Å., and increasing in intensity to 2000 Å., the limit of observation. An extinction coeff. curve is given. Parallelism between the absorption spectra of Cl and N oxides is noted.

A. J. E. W.

**Ultra-violet absorption spectrum of hydrogen fluoride.** K. SIGA and H. J. PLUMLEY (Physical Rev., 1935, [ii], 48, 105).—With HF at 2 to 76 cm. pressure, band systems from 3200 to 2400 Å., with a max. at approx. 2800 Å., and from 2300 Å. to shorter  $\lambda\lambda$  have been found. The structure of both systems indicates that the absorbing mol. is a polymeride of HF.

L. S. T.

**Spectra of tellurium halides.** M. WEHRLI (Helv. phys. Acta, 1935, 8, 487—488; Chem. Zentr., 1936, i, 506).—The absorption bands of  $\text{TeCl}_2$  at  $\lambda\lambda$  6400—4700 Å. are diffuse. At 170° continuous absorption occurs at 2450 Å.  $\text{TeBr}_2$  has a similar band system at  $\lambda\lambda$  6500—5270 Å.

H. J. E.

**Band spectra of  $\text{MgCl}$ ,  $\text{MgBr}$ , and  $\text{MgI}$  in absorption.** F. MORGAN (Physical Rev., 1936, [ii], 50, 603—607).—Data, and analyses consistent with the respective isotope shifts, are recorded for single systems of four-headed bands in the range 3600—3950 for  $\text{MgCl}$  and 3800—4000 Å. for  $\text{MgBr}$ . All the bands degrade towards the violet. The analysis

of the  $\text{MgCl}$  system disagrees with that of Parker (cf. A., 1935, 562). A band system in the region 4040—4200 Å., degrading towards the violet, was observed for  $\text{MgI}$ .

N. M. B.

**Ultra-violet absorption spectra of  $\text{Pr}^+$  and  $\text{Nd}^{+++}$  ions in solution.** P. C. MUKHERJI (Indian J. Physics, 1936, 10, 319—323).— $\text{Pr}_2(\text{SO}_4)_3$  solution gave a broad diffuse band in the region 2750—2530 Å., resolving at increased dilution into components at 2730, 2605, and 2560 Å.  $\text{Nd}_2(\text{SO}_4)_3$  gave four new lines, 2775, 2730, 2600, and 2505 Å. The band 2280—2100 Å., reported by Freed (cf. A., 1932, 211), was not observed with  $\text{Nd}_2(\text{SO}_4)_3$  or  $\text{NdCl}_3$ . In  $\text{PrCl}_3$  and  $\text{NdCl}_3$  the bands are partly masked by continuous ultra-violet absorption.

N. M. B.

**Absorption spectrum of cobalt chloride in presence of magnesium chloride in aqueous solution.** O. R. HOWELL and A. JACKSON (J.C.S., 1936, 1268—1273).—Graphs show the absorption spectra of a series of solutions containing a fixed amount of  $\text{CoCl}_2$  with increasing concns. of  $\text{MgCl}_2$ . The extinction coeffs. at the max. of the chief bands, plotted against the concns. of  $\text{MgCl}_2$ , show that no blue constituent is formed until a crit. concn. of  $\text{MgCl}_2$  is reached; the amount of blue constituent then increases rapidly. The mechanism is similar to that caused by the addition of  $\text{HCl}$  to aq.  $\text{CoCl}_2$ .

W. R. A.

**Absorption spectra. I. (MILLER) C. L. HARBERTS, P. M. HEERTJES, L. J. N. VAN DER HULST, and H. I. WATERMAN (Bull. Soc. chim., 1936, [v], 3, 1916—1917; cf. this vol., 661).—A new method of calculating the mean absorption coeff. is developed and applied to the results reported previously.**

J. W. S.

**Spectrum of the cold flame of ether.** V. KONDRATEEV (Acta Physicochim. U.R.S.S., 1936, 4, 556—558).—The measurements by Emeleus of the bands in the spectrum of the cold flame of  $\text{Et}_2\text{O}$  (A., 1929, 1215) are similar to those by Herzberg and Franz of the fluorescence spectrum of  $\text{CH}_2\text{O}$  (A., 1932, 896). It is concluded that the emitters in the cold flame of  $\text{Et}_2\text{O}$  are  $\text{CH}_2\text{O}$  mols.

O. D. S.

**Absorption spectra of polyatomic molecules containing methyl and ethyl radicals. III.** H. W. THOMPSON and J. W. LINNETT (Proc. Roy. Soc., 1936, A, 150, 108—129; cf. A., 1934, 828; 1935, 1188).—All the mols. examined had all the linkings of a given element combined with an alkyl radical. Most of such compounds show continuous absorption in the region studied (2000—7000 Å.), but band systems, which have been analysed, are found for the Et derivative of Zn, Cd, and Hg, and for the thioethers. The photochemical significance of the continua is discussed.

L. L. B.

**Ultra-violet absorption spectrum of pyridine vapour. Relation to Raman spectrum.** V. HENRI and P. ANGENOT (J. Chim. phys., 1936, 33, 641—665).—The ultra-violet absorption spectrum of 0.01—910 mm. of  $\text{C}_5\text{H}_5\text{N}$  at 0—308° has been photographed. Fine bands extend from 3105 to 2750 Å. At shorter  $\lambda$ , the bands are broader and



absorption is continuous at  $< 2510 \text{ \AA}$ . Light of  $\lambda < 2750 \text{ \AA}$ . causes decomp. The bands of longer  $\lambda$  appear only as the temp. is raised, and correspond with higher vibration states of the normal mol. Analysis of the spectrum shows that the unexcited mol. has five fundamental frequencies: 600, 857, 993, 1031, and  $1159 \text{ cm}^{-1}$ , corresponding closely with the Raman spectrum vals., and, for each of the five series of bands, the normal frequency is 600 and that of the excited state,  $542 \text{ cm}^{-1}$ . The frequencies are assigned to appropriate vibrations of the mol. J. G. A. G.

**Optical absorption of porphyrins. VIII.** A. STERN and H. MOLVIG. **IX. Ultra-violet absorption. I.** F. PRUCKNER and A. STERN (Z. physikal. Chem., 1936, 177, 365—386, 387—397; cf. this vol., 1318).—VIII. Introduction of one or two  $\text{NO}_2$  into the aetioporphin mol. shifts the absorption max. towards the red, but the curve is still of the aetio type. Therefore the  $\text{NO}_2$  are not attached to a C of the methine bridge of the porphin system (I). If a Br is introduced into each of two adjacent nuclei in (I) the type of the absorption curve is unaltered, but if the substitution is in nuclei I and III the curve changes to the rhodo type, which supports the view that these nuclei have a pyrrolenine structure.  $\cdot\text{SO}_3\text{Me}$  influences the light absorption of (I) in the same way as a group containing CO, the absorption curves of these derivatives being of the rhodo type. The free porphinsulphonic acids apparently are inner salts, the  $\cdot\text{SO}_3\text{H}$  reacting with one of the N of nucleus III. Comparison of the absorption spectra of the Cu salts shows that the Cu in the phorbin (i.e., dihydroporphin) system (II) is bound in the same way as in (I), but by the action of secondary valencies between the C:N in (II) and the metal atom the chromophoric power of this group is intensified. The absorption curve of *Spirographis-haemin* (cf. *ibid.*, 1273) is of the rhodo type.

**IX.** In the ultra-violet down to  $240 \text{ m}\mu$  various normal porphyrins have only one absorption band, the mol. extinction coeff.,  $\epsilon$ , of which is high. The band is shifted appreciably only by the introduction into (I) of large chains or of groups containing CO. In the ultra-violet the absorption curve of porphin has a single band, and substitution even of alkyl groups only shifts the band max. and min. towards the red and depresses  $\epsilon$ . Monoimido- and  $\beta\delta$ -diimido-porphyrins have only one band, the max. of which is at a much shorter  $\lambda$  than that of the corresponding porphyrin. The absorption spectra of the octasubstituted porphins and phorbins have the same no. of bands, the red band of the porphin being much intensified and shifted towards longer  $\lambda\lambda$  in the phorbins. R. C.

**Ultra-violet absorption of phthiocol.**—See this vol., 1423.

**Infra-red absorption spectrum of heavy phosphine ( $\text{PD}_3$ ).** G. B. B. M. SUTHERLAND and G. K. T. CONN (Nature, 1936, 138, 641—642).—This spectrum agrees with the Raman spectrum but not with the frequencies predicted from the spectrum of  $\text{PH}_3$ , indicating that a simple valency force field

is not satisfactory for correlating the vibration frequencies of a mol. of this type. L. S. T.

**Rotation-vibration spectrum of acetylene ( $\text{C}_2\text{H}_2$ ).** R. MECKE and R. ZIEGLER (Z. Physik, 1936, 101, 405—417).—Eight new bands have been examined between 11,000 and 5700  $\text{\AA}$ ., and an analysis is given that accounts for 35 of the observed bands. A. B. D. C.

**Absorption spectra in the near infra-red of [saturated and] ethylenic hydrocarbons.** M. L. SHERRILL and P. MOLLET (J. Chim. phys., 1936, 33, 701—718).—The absorption spectra have been investigated at  $1.3\text{--}3.6 \mu$ , and absorption coeffs. are recorded. The substances conform to four types: (i)  $n\text{-C}_5\text{H}_{12}$ ,  $n\text{-C}_7\text{H}_{16}$ , (ii)  $\text{CH}_3\text{:CHPr}^a$ ,  $\text{CH}_3\text{:CH-C}_5\text{H}_{11}$ ,  $\text{CH}_3\text{:CHPr}^b$ ,  $\text{CH}_3\text{:CMeEt}$ , (iii)  $\text{CHMe:CHEt}$ ,  $(\text{CHEt})_2$ ,  $\text{CHEt:CHPr}^a$ , and (iv)  $\text{CHMe:CMe}_2$ ,  $\text{CHMe:CET}_2$ ,  $(\text{CMe}_2)_2$ , and all have strong absorption bands at  $7143\text{--}7246$ ,  $5715\text{--}5847$ ,  $4210\text{--}4264$ ,  $2906\text{--}2949$ , and  $2853\text{--}2877 \text{ cm}^{-1}$ . The  $2906\text{--}2949 \text{ cm}^{-1}$  bands of 'CRR' compounds are double, and compounds of type (ii) also have a strong band at  $3072\text{--}3091 \text{ cm}^{-1}$  which is attributed to C-H vibrations in the  $\text{:CH}_2$  group. The interpretation of the results is discussed. J. G. A. G.

**"Wing" accompanying the Rayleigh line in liquid mixtures. II.** S. C. SIRKAR and B. K. MOOKERJEE (Indian J. Physics, 1936, 10, 375—387; cf. this vol., 777, 923).—The distribution of intensity in the wing accompanying the Rayleigh line due to  $\text{CS}_2$ ,  $\text{CHCl}_3$ ,  $\text{PhCl}$ ,  $\text{COMe}_2$ , and xylene has been compared microphotometrically with that due to the solution of each in MeOH. The relative intensity of the wing with respect to that of any particular vibrational Raman line increases for solutions in MeOH, except in the case of  $\text{PhCl}$  where there is no appreciable change. In no case is there any marked diminution in intensity of any portion of the wing due to dissolution. Theoretical explanations are discussed. N. M. B.

**Polarisation of Raman lines in some inorganic acids.** C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1936, 4, A, 174—185).— $\text{HNO}_3$ ,  $\text{HIO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SeO}_4$ , and  $\text{H}_2\text{SeO}_3$  were investigated. The lines of conc.  $\text{HNO}_3$  showed depolarisations  $< 6/7$ . Polarisation of the lines due to  $\text{NO}_3'$  support the plane equilateral structure. Six lines of the undissociated  $\text{HNO}_3$  mol. were identified with those of an unsymmetrical pyramidal model.  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4'$ ,  $\text{SO}_4''$ , and  $\text{H}_2\text{SeO}_3$  are tetrahedral and structural formulæ are discussed. Bands of  $\text{HIO}_3$  and  $\text{H}_2\text{SeO}_3$  are assigned to different mol. species. W. R. A.

**Raman effect of non-aqueous solutions of electrolytes. I. Solutions of arsenic halides.** V. FINKELSTEIN and P. KURNOSOVA (Acta Physicochim. U.R.S.S., 1936, 4, 123—134).—The Raman spectra of  $\text{AsCl}_3$  and  $\text{AsBr}_3$  in  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$  consist of the spectra of the pure solute and pure solvent only, indicating that the solvate is not a chemical compound. It is suggested that solvation occurs by dipole association. R. S.

**Raman spectra of trimethylamine and some compounds of hydroxylamine and hydrazine.**

R. ANANTHAKRISHNAN (Proc. Indian Acad. Sci., 1936, 4, A, 204—212).—The observed frequencies are discussed with the aid of polarisation data. A comparison with the spectrum of isobutane assists in the assignment of frequencies. The hydrochlorides of  $\text{NH}_2\text{OH}$  and  $\text{N}_2\text{H}_4$  in the cryst. state show a single line which remains strong in aq. solution. Possible structures are discussed. W. R. A.

**Raman effect of a complex tungstotartrate in water.** (Mlle.) M. THEODORESCO (Compt. rend., 1936, 203, 668—669).—The Raman spectra of aq. solutions of NaH tartrate (I),  $\text{Na}_2\text{WO}_4$  (II), and  $\text{Na}_2\text{T}_2\text{WO}_3$  (III) (T=tartrate) have been studied. Strong lines appear at 321, 832, and 934 (II), 837 and 943  $\text{cm}^{-1}$  (III). The lines 362, 837, 1088, and 1273 of (I) are not displaced in (III); the C=O line 1730 in (I) appears as 1606 and 1646 in (III); other lines of tartaric acid are displaced. The results favour the existence of (III) in solution. R. S. B.

**Raman spectrography and its importance in chemical investigations.** M. NORIEGA DEL AGUILA (Bol. Soc. Quim. Peru, 1936, 2, 86—125).—A review.

**Second-order lines in Raman spectra.** G. S. LANDSBERG and V. J. MALISHEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 365—368).—Six new lines were found in the Raman spectrum of  $\text{CCl}_4$  (529, 625, 919, 989, 1091, 1225  $\text{cm}^{-1}$ ) and nine new lines in that of  $\text{SnBr}_4$  (132, 144, 176, 193, 305, 370, 386, 438, 497  $\text{cm}^{-1}$ ). The frequencies, except 144, 386 of  $\text{SnBr}_4$ , are in agreement with calc. combination frequencies. The intensity of the second-order lines is approx.  $3 \times 10^{-3}$  that of the first order. O. D. S.

**Depolarisation of Raman lines of tetrachloroethylene.** T. Y. WU (J. Chinese Chem. Soc., 1936, 4, 402—405).—A discussion of the fundamental vibrations of the mol., based on the depolarisation measurements and the infra-red data (cf. A., 1934, 1288). D. C. J.

**Raman spectra. I. Benzoyl chloride and its substitution products.** D. D. THOMPSON and J. F. NORRIS (J. Amer. Chem. Soc., 1936, 58, 1953—1957).—Data are recorded for  $\text{BzCl}$  and for *o*-, *m*-, and *p*-methyl-, -methoxy-, -chloro-, and -nitrobenzoyl chloride. E. S. H.

**Structure by means of the Raman effect (2 phenylacetic acid-1 sodium phenylacetate) (2 acetic acid-1 sodium acetate).** E. VITALE (Gazzetta, 1936, 66, 566—570).—The Raman spectra of the compounds  $2\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}$  and  $2\text{AcOH}\cdot\text{NaOAc}$  have been measured. In both spectra the line characteristic of the C=O group is missing. Structural formulæ are suggested. O. J. W.

**Raman spectra of *cis*- and *trans*-isoeugenol.** B. SUSZ and E. PERROTTET (Helv. Chim. Acta, 1936, 19, 1158—1163; cf. this vol., 923).—Data for the Raman spectra of purified commercial isoeugenol and for the *cis*- (I) and *trans*- (II) isomerides separated by fractional distillation are recorded and discussed. The frequency for the ethylenic linking is lowered by 25  $\text{cm}^{-1}$  in passing from (II) to (I), in conformity with observations on similar isomerides. F. L. U.

**Raman effect of organic substances. VI. Raman effect of sesquichamene and other terpenes.** K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1936, 11, 576—586).—Raman spectra of sesquichamene (I), *d*-sabinene, *d*- $\alpha$ -pinene, *d*-verbenol, *dl*- $\Delta^1$ -terpinen-4-ol, menthyl and isobornyl acetates have been studied. From a comparison of their spectra, it is thought that if cedrene has a 1-methyl- $\Delta^1$ -cyclopentene ring, (I) has a 1-methyl- $\Delta^1$ -cyclohexene ring. C. R. H.

**Raman spectrum and constitution of ozonides. Raman spectrum of ozonides of ethyl maleate and fumarate.** E. BRINER, E. PERROTTET, and B. SUSZ (Helv. Chim. Acta, 1936, 19, 1163—1168; cf. this vol., 839).—Data for the Raman spectra of  $\text{Et}_2$  maleate and fumarate and their ozonides are recorded and discussed. The mol. refractions observed are  $>$  those calc. by 4—5 units. F. L. U.

**Light-scattering of crystalline-liquid *p*-azoxyanisole.** W. DE BRAAF and L. S. ORNSTEIN (Kolloid-Beih., 1936, 44, 427—475).—The variation of scattering with the strength of a superimposed magnetic field has been determined. The results are in accordance with the swarm theory. E. S. H.

**Sensitisation of phosphors. II. S. ROTH-SCHILD (Physikal. Z., 1936, 37, 757—764; cf. A., 1934, 1056).—The sensitising effect of small amounts of Bi, Pb, Ag, Cu on Sm and Pr phosphors with CaS and SrS, and of Pr and Sm+Nd+Y on CaS-Ag and SrS-Ag phosphors has been investigated. Bi is effective in sensitising Sm but not Pr phosphors, Pb sensitises both, whilst Cu is ineffective in both cases. In most cases the sensitising effect is observable only during excitation. The theory is discussed. A. J. M.**

**Fluorescence of rare earths in glasses.** O. DEUTSCHBEIN (Z. Physik, 1936, 102, 772—780).—The fluorescence spectra of glasses activated with rare earths are generally similar to those of the corresponding rare-earth compounds. L. G. G.

**Influence of molecular rotations on measurements of the duration of fluorescence.** W. KESSEL (Z. Physik, 1936, 103, 125—132).—Jabłoński's theory of influence of mol. rotations has been tested by measurements with fluorescein in glycerol and  $\text{H}_2\text{O}$ . A. E. M.

**Quenching of fluorescence of dye solutions by foreign substances. I. B. SVESHNIKOV (Acta Physicochim. U.R.S.S., 1936, 4, 453—470).—The quenching of fluorescent dye solutions by inorg. and org. quenchers has been followed by observing the increase of polarisation. It is independent of the  $\lambda$  of the exciting light, confirming the view that in the excited state the mols. have the same energy level. Some quenchers exercise a selective action on some dyes. The results indicate that quenching action is produced by factors depending on time, and in many cases is due to deactivation through collisions of the second kind. C. R. H.**

**Quenching of fluorescence due to solution medium.** S. I. VAVILOV and A. N. SEVTSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 277—284).—The intensity ( $\rho$ ) and degree of polarisation ( $p$ ) of fluor-



escence from rhodamine-*B* (I) have been studied in glycerol,  $\text{iso-C}_5\text{H}_{11}\cdot\text{OH}$ , and  $\text{Bu}^n\text{OH}$  at 289—363° abs.  $1/p$  is a linear function of  $T/\eta\rho_1$ , where  $T$  is the abs. temp.  $\eta$  the viscosity, and  $\rho_1$  is the val. of  $\rho$  at room temp.  $\tau_1$  and  $\rho$  have been determined for (I) in  $\text{H}_2\text{O}$  and org. solvents at room temp. Two types of quenching of fluorescence are discussed. R. S. B.

**Fluorescence intensity and duration.** S. I. VAVILOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 271—276).—The intensity ( $\rho$ ) and mean life of fluorescence phenomena are discussed. The relation  $\rho = s\tau/\tau_0$  is deduced, where  $s$  is the fraction of the absorbed energy which is quenched by collisions of the second kind,  $\tau$  the mean life of the excited state, and for  $s = 1$ . R. S. B.

**Photodissociation of gallium halides.** A. PETROVA (Acta Physicochim. U.R.S.S., 1936, 4, 559—566).—The first doublet, 4033 and 4172 Å., of the principal series of Ga is observed in the fluorescence excited in GaI vapour above 200° by  $\lambda\lambda < 2200$  Å. This fluorescence is ascribed to  $\text{GaI} + h\nu = \text{Ga}^+ + \text{I}$ . The fluorescence excited in GaBr vapour by  $\lambda\lambda > 1850$  Å. does not contain the resonance lines of Ga. O. D. S.

**Photo-electric phenomena at the surface of electronic semi-conductors.** G. LIANDRAT (Ann. Physique, 1936, [xi], 6, 391—454; cf. A., 1935, 1303).—On the basis of a crit. study of available experimental and theoretical data a simple description of the mechanism of the action of photo-elements is developed. The three essentials determining the direction and order of magnitude of the photo-electric effect are: in the cryst. lattice of a semi-conductor or insulator the photo-electrons traverse the surface with a kinetic energy, the max. val. of which satisfies the Einstein relation, they originate in the semi-conductor, and the high yield can be related to a sp. property of the lattice; in a metallic lattice they rapidly lose energy and become ordinary conductivity electrons; between the semi-conductor and the metal a thin cryst. layer of high resistivity controls the appearance of a p.d. Secondary modifications of the conductivity of the surface layer can be attributed to the ultimate behaviour of the electrons originating in the semi-conductor but stopped in the surface layer by the opposing electric field. N. M. B.

**Electrical investigation of oxidic semi-conductors.** W. HARTMANN (Z. Physik, 1936, 102, 709—733).—The variation of the electrical conductivity with temp. of  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{UO}_2$ , and  $\text{CuO}$  is expressed by a simple exponential relation.  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  showed changes of resistance after heating in vac., in  $\text{O}_2$ , or in  $\text{H}_2$ . The variation of the Hall const. with temp. of  $\text{UO}_2$  and  $\text{CuO}$  was also investigated. A. E. M.

**Electrical conductivity of thin metals, particularly of molybdenum layers.** J. H. DE BOER and H. H. KRAAK (Rec. trav. chim., 1936, 55, 941—953).—The conductivity of thin Mo layers deposited on glass increases with temp. in a reversible manner up to the temp. of deposition, above which there is an irreversible change to the properties of a layer deposited at the highest temp. attained. Unimol.

layers of Mo have appreciable conductivity, whereas a thickness of 16 mols. is required before that of Ag can be determined, owing to the difference in mol. mobility. The distribution of electron levels in a thin metallic layer, which is regarded as a state intermediate between vapour and massive solid, has been studied. R. S.

**Conductivity of copper oxide.** G. KAPP and M. TREU (Sitzungsber. physik.-med. Soz. Erlangen, 1935, 65—66, 215—228; Chem. Zentr., 1936, i, 285).—The electrical conductivity of thin CuO layers between 20° and —100° is recorded. J. S. A.

**Electrical energy set free on melting electrets.** H. FREI and G. GROETZINGER (Physikal. Z., 1936, 37, 720—724).—When an electret, with no electric field associated with it, is melted between two electrodes, a current flows, the total quantity of which is independent of the time which has elapsed between the polarisation and melting (depolarisation) of the electret. The current in the case of an electret which was formed by the action of an electric field on the substance in the solid state is much smaller. If a non-polar substance, such as paraffin, is submitted to the action of an electric field when it is solidifying, or when it is solid, the amount of electricity obtained on melting is the same in both cases. The results agree with the theory that a permanent electric polarisation independent of time has occurred in electrets. A. J. M.

**Variation of the dielectric constant of mercury with density at different temperatures.** P. WUSTHOFF (Ann. Physik, 1936, [v], 27, 312—328).—The dielectric const. of Hg vapour has been measured at several temp. between 401° and 470° and pressures up to 3 atm. No deviation from the Clausius-Mosotti relationship was observed. The dielectric const. of Hg at atm. pressure and 0° is calc. to be 1.00170. O. D. S.

**Dielectric coefficients of gases. III. Allene, allylene, butanes, butylenes, cyanogen, and hydrogen cyanide.** H. E. WATSON and K. L. RAMASWAMY. **IV. Fluorides of boron, nitrogen, and carbon.** H. E. WATSON, G. P. KANE, and K. L. RAMASWAMY (Proc. Roy. Soc., 1936, A, 156, 130—143; cf. A., 1934, 347).—The measurements were made by means of the "parallel condenser" method used previously. *n*- and *iso*- $\text{C}_4\text{H}_8$ , allene, allylene, and  $\text{NF}_3$  have small moments, and  $\text{HCN}$  a large one, whilst the remaining gases are electrically neutral. L. L. B.

**Electric moments of aliphatic diamines.** P. TRUNEL (Compt. rend., 1936, 203, 563—565).—Measurements were made in  $\text{C}_6\text{H}_6$  at 25°, 45° and 75°. The dipole moments at 25° are:  $(\text{CH}_2\cdot\text{NH}_2)_2$  1.90,  $\text{NH}_2\cdot[\text{CH}_2]_1\cdot\text{NH}_2$  1.94,  $\text{NH}_2\cdot[\text{CH}_2]_4\cdot\text{NH}_2$  1.93,  $\text{NH}_2\cdot[\text{CH}_2]_5\cdot\text{NH}_2$  1.91, and  $\text{NH}_2\cdot[\text{CH}_2]_6\cdot\text{NH}_2$  1.98 *D*, and the vals. are not affected significantly by the changes of temp. There is negligible interaction between the  $\cdot\text{NH}_2$  groups and their rotation is not restricted. J. G. A. G.

**Structure of coumarin.** M. A. G. RAU (Current Sci., 1936, 5, 132).—The dipole moment of coumarin

at 20° ( $4.51 \times 10^{-18}$  e.s.u.) indicates a state of resonance between the normal and an excited state.

F. N. W.

**Evidence of wave-mechanical resonance in the carboxylic ester and lactone group, from electric dipole moments.** R. J. B. MARSDEN and L. E. SUTTON (J.C.S., 1936, 1383—1390).—The calc. moments for the two extreme possible configurations of the CO<sub>2</sub>R group are given. From these vals. and the moment of  $\gamma$ -butyrolactone it is shown that the esters have the *trans* configuration. This cannot be due to electrostatic forces alone but to stiffening produced by resonance with another structure. The resonance interaction of phenolic and benzoic esters with the benzene ring supports the Robinson-Ingold theories. The configuration of nitrous esters is discussed.

W. R. A.

**Carbon valency angle and dipole induction in benzyl compounds.** F. C. FRANK (J.C.S., 1936, 1324—1327).—Solvent effects do not invalidate stereochemical calculations from dipole moment data. In considering benzyl compounds, it is assumed that, in compounds of the type CH<sub>2</sub>Ph·Y, the induced moment in the Ph due to the C·Y moment lies parallel to the Ph·C linking, and that, in compounds of the type C<sub>6</sub>H<sub>4</sub>X·CH<sub>2</sub>·Y, vector addition is permissible only if X and Y are each outside the sphere of induction of the other. Equations are given from which, by a graphical method, the induced moment along Ph·C and the C valency angle are obtained. The valency angle of aliphatic C is 110°.

W. R. A.

**Theory of polarisation of dipole moments.** J. FRENKEL (Acta Physicochim. U.R.S.S., 1936, 4, 341—356).—Expressions for the elastic (static) and frictional (kinetic) effects in the orientation of dipole mols. are derived mathematically and considered in relation to Debye's recent theories.

C. R. H.

**Dipole moments and the fixation of aromatic double linkings.** Bromohydrindenes and bromotetralins.—See this vol., 1497.

**Volume of an anisotropic liquid in a magnetic field.** D. BENESZEVICZ (Acta Physicochim. U.R.S.S., 1936, 4, 607—612).—No change in vol. is observed in the anisotropic phase of dibenzylidenebenzidine and *p*-azoxyanisole under the influence of magnetic fields from 3000 to 17,000 gauss.

O. D. S.

**Refractive index of deuterium.** W. J. C. ORR (Trans. Faraday Soc., 1936, 32, 1556—1559).—The difference in *n* of H<sub>2</sub> and D<sub>2</sub> has been measured. Assuming *n*=1.00013966 for H<sub>2</sub> at  $\lambda$  5462, *n* for D<sub>2</sub> is 1.0001378(7).

E. S. H.

**Refractive index, dispersion, and polarisation of gases.** H. E. WATSON and R. L. RAMASWAMY (Proc. Roy. Soc., 1936, A, 156, 144—157).—The refractions and dispersions of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, *n*- and *iso*-C<sub>4</sub>H<sub>10</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, *n*-, *iso*-, and *sec*-C<sub>4</sub>H<sub>8</sub>, C(CH<sub>3</sub>)<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CMe<sub>2</sub>CH, SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, HCN, (CN)<sub>2</sub>, BF<sub>3</sub>, NF<sub>3</sub>, CF<sub>4</sub>, SiF<sub>4</sub>, SF<sub>6</sub>, and CO<sub>2</sub> have been measured and the electronic polarisations calc. The vals. are compared with the polarisations deduced from dielectric measurements of the same samples of gas. The at. polarisations are obtained by deduction,

and vary from 0 for the rare gases and most bimol. gases to 70% of the electronic polarisation for (CN)<sub>2</sub>. For the aliphatic hydrocarbons, they follow the sequence acetylenes > olefines > paraffins, and increase with the size of the mol.

L. L. B.

**Streaming double refraction of high-molecular substances.** IV. Polystyrenes with different degrees of branching. R. SIGNER (Helv. Chim. Acta, 1936, 19, 897—899; cf. A., 1933, 902).—The fluxional birefringence of polystyrenes is the lower, the higher is the temp. at which polymerisation occurred. A similar relation holds with regard to the extinction angle. These observations support the conclusion of Staudinger and Schulz (this vol., 146) that the degree of branching increases with rise of the temp. of polymerisation.

F. L. U.

**[Optical] dispersion of natural and mercerised cellulose.** A. FREY-WYSSLING (Helv. Chim. Acta, 1936, 19, 900—914; cf. this vol., 140).—The *n* of fibres of ramie cellulose varies with the liquid in which they are immersed in consequence of adsorption, especially with glycerol and with CH<sub>2</sub>Ph·OH. The dispersion, *n<sub>D</sub>*—*n<sub>C</sub>*, is 0.0070—0.0077 both for natural (I) and mercerised (II) fibres. The *n<sub>D</sub>* vals. for (I) are >1.596 and 1.528 for the extraordinary and ordinary ray, respectively, the corresponding vals. for (II) being <1.574 and 1.525. The decrease in refraction on mercerisation is consistent with the resulting broadening of the cryst. lattice.

F. L. U.

**Optical rotatory dispersion in the glucal series.**—See this vol., 1363.

**Optical rotatory dispersion of bridged derivatives of alkyltartrates.** Y. TSUZUKI (Bull. Chem. Soc. Japan, 1936, 11, 586—592).—The rotatory dispersion between 6708 and 4358 Å. of Et<sub>2</sub> and Me<sub>2</sub> isopropylidenedioxysuccinate, Et<sub>2</sub> and Me<sub>2</sub> ethylidenedioxysuccinate, and Et<sub>2</sub> methylenedioxysuccinate (cf. A., 1935, 1106; this vol., 967) in the pure state has been measured. The vals. can be expressed by a one-term Drude equation, and this, together with the dispersion ratio and the characteristic  $\lambda$ , appears to indicate that the rotatory dispersion is simple.

C. R. H.

**Optical rotatory power of solutions in an electric field.** J. KUNZ and S. H. BABCOCK (Phil. Mag., 1936, [vii], 22, 616—624; cf. this vol., 13).—When various optically active menthyl compounds were subjected to an electric field no Kerr effect was observed, but the rotation of the plane of polarisation depended on the angle between that plane and the field, and was a function of the field strength quite different from the Kerr effect.

N. M. B.

**Magneto- and electro-optical properties of *p*-azoxyanisole.** (MRS.) J. Z. K. EISENMANN (Ann. Physique, 1936, [xi], 6, 455—501).—A detailed description and discussion of an investigation previously reported (cf. A., 1935, 568).

N. M. B.

**Magnetic birefringence in solutions of organic substances.** L. D. MAHAJAN (Phil. Mag., 1936, [vii], 22, 717—725).—Results are tabulated for the following substances, the solvent being shown in parentheses; *o*-, *m*-, and *p*-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> (Et<sub>2</sub>O); phloro-



glucinol, durene, and  $C_6Me_6$  ( $COMe_2$ );  $C_6Et_6$  ( $CCl_4$ );  $C_6(HCl)_6$  ( $Et_2O$ );  $C_6Cl_6$  ( $CS_2$ ); *o*-toluidine ( $COMe_2$ ); *m*-nitroaniline ( $Et_2O$ ); *p*-benzoquinone, chloranil, and bromanil ( $COMe_2$ ); dimesityl ( $CCl_4$ ); diphenylene oxide ( $CCl_4$  and  $COMe_2$ );  $\alpha$ - $C_{10}H_7NH_2$ , and phenanthraquinone ( $COMe_2$ );  $\alpha$ -naphthaquinone and anthraquinone ( $CCl_4$ );  $C_6H_6$ . Results are discussed in relation to mol. structure and the influence of the structure on magnetic and optical anisotropy of the mols.  
N. M. B.

**Natural classification of chemical compounds.** F. M. SCHEMJAKIN (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 49—54).—Previous theories (A., 1935, 569) are developed.  
R. T.

**Valency problem of the quinquevalent phosphorus atom.**—See this vol., 1377.

**Constitution of phosphorous, hypophosphorous, and sulphurous acids.** G. SCHWARZENBACH (Helv. Chim. Acta, 1936, 19, 1043—1052; cf. this vol., 680).—From consideration of the several dissociation consts. of  $H_3PO_3$ ,  $H_3PO_2$ , and  $H_2SO_3$  it is concluded that  $H_3PO_3$  contains one, and  $H_3PO_2$  two H atoms linked directly to P, and that  $H_2SO_3$  has a symmetrical structure. These conclusions do not apply to their metal or alkyl derivatives. F. L. U.

**Maximum valency of elements and atomic structure.** VI. Quantum characteristics of valency electrons and the m.p. of simple substances. VII. Quantum characteristics of valency electrons and the structure and lattice strength of simple substances. B. ORMONT (Acta Physicochim. U.R.S.S., 1936, 4, 409—426, 427—440).—A discussion on the deviations from the Grimm-Sommerfeld law and on the quantum characteristics of valency electrons as revealed by a study of the m.p. and lattice structure of the elements (cf. A., 1935, 1058; this vol., 141).  
C. R. H.

**Interaction of atoms and molecules with solid surfaces.** III, IV. Condensation and evaporation of atoms and molecules. J. E. LENNARD-JONES and A. F. DEVONSHIRE. V. Diffraction and reflexion of molecular rays. A. F. DEVONSHIRE (Proc. Roy. Soc., 1936, A, 156, 16—28, 29—36, 37—44; cf. A., 1935, 1070).—III. Theoretical. Formulae have been found for the probability that an impinging particle will condense on to a solid surface, and for the length of time it will remain there. The theory thus provides explicit formulae for the consts.  $C$  and  $T$  of Langmuir's adsorption isotherm. Evaporation may, even at low temp., take place in two stages, an atom first being excited to a higher vibrational level and then receiving another quantum of thermal energy from the solid sufficient to cause evaporation. To illustrate the effect of mass, the probabilities of evaporation and condensation of the isotopic mols.  $H_2$ ,  $HD$ , and  $D_2$  have been calc. The coeff. of condensation is in some cases quite small (of the order of 0.1).

IV. A model is considered in which an adsorbed atom can vibrate both radially and laterally about its point of attachment, but cannot migrate. Evaporation is controlled by the rate at which thermal energy is communicated from the solid to the adsorbed atom.

V. The theory of the reflexion and diffraction of mol. rays from crystal surfaces is worked out. The minima found by Frisch and Stern in the reflexion and diffraction curves of He and Li (A., 1933, 994) are explained. The experimental curves may be used to give information about the potential field in the neighbourhood of the solid.  
L. L. B.

**Relation between the tension  $\tau$  of Baeyer and the characteristic Raman frequency for cyclic hydrocarbons.** M. AUBERT (Compt. rend., 1936, 203, 661—663).—Baeyer's tension  $\tau$  for a cyclic hydrocarbon with  $n$  C atoms, defined by  $\tau = 1/2[109^\circ 28' - 180^\circ(n-2)/n]$ , or  $\tau = (10800 - 2116n)/n$  in min., is related to the characteristic Raman frequency  $\nu$  according to  $\nu = 0.2266\tau + 868$  cm.<sup>-1</sup> for  $n=2-8$ , when there is no side-chain. The combination of the formulae for  $\nu$  and  $\tau$  gives  $(2447.3 + 388.5n)^2/n$  which gives a min. for  $n^2$  at  $n=6.29$ .  $n\nu^2$  is const. for vals. of  $n$  near to 6, as found by Godchot *et al.* (A., 1932, 213).  
R. S. B.

**Atomic and ionic radii.** II. E. HERLINGER (Z. Krist., 1936, 93, 399—408).—The radii of action of atoms and ions are compared, and the constancy of radius of ions not built on the pattern of the noble gases is derived.  
B. W. R.

**Relation between internuclear distances and the force constants of diatomic molecules.** R. M. BADGER (Physical Rev., 1935, [ii], 48, 284—285; cf. A., 1936, 14).  
L. S. T.

**Energy levels in crystals of samarium salts.** C. B. ELLIS (Physical Rev., 1936, [ii], 50, 675; cf. Spedding, A., 1934, 1154).—The more than fourfold increase in the no. of lines in a close group in Sm over the no. in similar groups of Gd is attributed to the coupling of a set of vibrational levels to the crystal field levels, and the presence of higher coupling frequencies different for each compound in addition to crystal field splitting.  
N. M. B.

**Theory of movable voids and inter-lattice atoms in crystals.** J. FRENKEL (Acta Physicochim. U.R.S.S., 1936, 4, 567—574).—The mechanism of void formation in crystals is discussed. The dependence of the no. of voids and of the no. of dissociated atoms in monat. crystals on temp. is calc. statistically. The result of a similar calculation for binary ionic crystals is in agreement with that of Schottky (A., 1935, 1302).  
O. D. S.

**Approximation method in the problem of many electrons.** II. H. HELLMANN (Acta Physicochim. U.R.S.S., 1936, 4, 225—244; cf. A., 1935, 278).—Mathematical. A wave-mechanical discussion is given.  
R. S. B.

**Solving variational problems in quantum chemistry.** A. SCHUCHOVITZKI (Acta Physicochim. U.R.S.S., 1936, 4, 803—818).—Theoretical.  
H. J. E.

**Quantisation of a theory arising from a variational principle for multiple integrals with application to Born's electrodynamics.** P. WEISS (Proc. Roy. Soc., 1936, A, 156, 192—220).—Mathematical.  
L. L. B.

**Spectroscopic investigation of molecular association.** M. V. VOLKENSTEIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 357—364).—The influence of mol. association on mol. symmetry as deduced from infra-red and Raman spectra is discussed. If the association forces are weak, corresponding with energies  $> 10$  kg.-cal. per mol., the mols. can be regarded as unassociated but having their symmetry distorted. If association energy approaches that of homo- or hetero-polar linking, the product is intermediate between a chemical compound and a van der Waals complex. The existence of a frequency band at  $622\text{ cm.}^{-1}$  in the Raman spectrum of AcOH and its weakening with dilution is attributed to the association of two AcOH mols. C. R. H.

**Parachors of some metal carbonyl compounds.** J. S. ANDERSON (*J.C.S.*, 1936, 1283—1286).—Surface tensions and parachors of  $\text{Ni(CO)}_4$ ,  $\text{Co(CO)}_3(\text{NO})$ ,  $\text{Fe(NO)}_2(\text{CO})_2$ , and  $\text{Fe(CO)}_5$  have been measured. As with other co-ordination compounds the apparent parachor of the central atom shows an anomaly for which no adequate explanation has so far been advanced. W. R. A.

**Combination of fatty acids with nitrogen bases. I. Piperidine and lower fatty acids: surface tensions, molecular volumes, and parachors.** E. B. R. PRIDEAUX and R. N. COLEMAN (*J.C.S.*, 1936, 1346—1353).—The salts formed by mixing piperidine with the lower fatty acids (acetic to octoic) have been prepared and examined. The effect of chemical combination on the densities of pairs of liquids having a similar polar constitution has been measured. Variations of surface tension with temp. have been determined. Salt formation is accompanied by considerable diminution of the parachors, although association also produces diminutions but of a much small order. W. R. A.

**Cleavage and X-ray planes of calcite crystals.** J. A. BEARDEN and H. H. ROSEBERRY (*Physical Rev.*, 1935, [ii], 48, 110).—In many cleaved calcite crystals which have good optical surfaces, the cleaved surface does not coincide with the at. or X-ray plane. The angle between the cleavage and X-ray planes is not the same for all crystals. L. S. T.

**Elimination of errors in Debye-Scherrer pictures—experiment or calculation?** A. LEVINŠ and M. STRAUMANIS (*Z. Krist.*, 1936, 94, 40—52).—An improved procedure for obtaining lattice consts. from powder photographs with max. accuracy is described, and illustrated from measurements on  $\text{TiCl}_3$ ,  $\text{As}_2\text{O}_3$ , and  $\text{Pb(NO}_3)_2$ . The Cohen formula is criticised. B. W. R.

**Calculation of the Laue patterns from plastically bent crystals of NaCl.** A. KOMAR (*Z. Krist.*, 1936, 94, 22—32).—A method of calculation of the Laue pattern for a bent rock-salt crystal is developed, with certain assumptions as to the behaviour of the slip planes. The calculation agrees quantitatively with experiment. B. W. R.

**Calculation of structure factors and summation of Fourier series in crystal analysis: non-centrosymmetrical projections.** J. M.

ROBERTSON (*Nature*, 1936, 138, 683—684).—A rapid numerical method is described. L. S. T.

**Interpretation of the powder radiograms of crystals by the method used for argillaceous mica slates.** J. DE LAPPARENT (*Compt. rend.*, 1936, 203, 596—599).—A discussion. H. J. E.

**Historical and systematic survey of the use of the "reciprocal lattice" in the study of crystal structure.** P. P. EWALD (*Z. Krist.*, 1936, 93, 396—398). B. W. R.

**Alteration in the axial ratio and in the position of the rhombic section with temperature of anorthite from Vesuvius.** H. SCHNAASE (*Z. Krist.*, 1936, 93, 444—463).—An anorthite crystal is measured goniometrically over the range room temp.— $973^\circ$ , and regular alterations in the fundamental symmetry angles are found. B. W. R.

**Physical properties of crystals.** A. GANGULI (*Current Sci.*, 1936, 5, 128—130).—A review.

**Theoretical basis for selection of optimum temperatures for monophasic metals. I. Recrystallisation diagrams.** A. A. BOTSCHVAR and G. G. PUTZIKIN (*Ann. Sect. d'Anal. Physico-Chim.*, 1936, 9, 153—158).—The process of recrystallisation of deformed metals is best represented by three-dimensional diagrams (crystal size-% deformation-temp.). R. T.

**Ring phenomenon in sputtered metallic films.** U. K. BOSE (*Nature*, 1936, 138, 684—685).—When cathodically sputtered on a clean glass plate Ag or Cu forms coloured rings surrounding a drop of oleic acid or a bead of plasticine placed on the plate. An explanation of the effect is discussed. L. S. T.

**Differences in lattice constants.** G. WASSERMANN (*Metallwirts.*, 1935, 14, 813—815; *Chem. Zentr.*, 1936, i, 22).—Differences between lattice consts. for single crystals and polycryst. materials (A., 1932, 330) may be attributed to impurities or to chilling stresses. J. S. A.

**X-Ray analysis in chemistry.** J. A. A. KETELAAR (*Chem. Weekblad*, 1936, 33, 648—654).—A review.

**Ideal and real crystals** (*Z. Krist.*, 1936, 93, 161—228).—A discussion of the papers on this subject (A., 1935, 16, 151). B. W. R.

**Etch-forms in glasses.** B. MARKIN, R. MULLER, and C. VEINSTEIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 119—122).—The etch-forms occur only when the glass surface has been in contact with a solid. The microscopic depressions so produced spread as the glass is uniformly dissolved, giving the characteristic honeycomb forms. K. S.

**Action of the electric field on the smectic meso-phase.** V. FREDERICKSZ and A. REPIEVA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 91—98).—The production of focal-conical forms in the smectic meso-phase of Et *p*-azoxy-benzoate and -cinnamate has been studied. The elongated droplets produced near the temp. of transition to the amorphous liquid state orient themselves perpendicularly to weak electric fields, but turn through  $90^\circ$  when the field



strength is increased. With steadily increasing temp. and field strength the groups arrange themselves in regularly oriented series, and finally melt or explode to form the amorphous liquid. It is suggested that the orientation in weak electric fields is due to the orientation of dipoles, whilst in strong fields the effect of the induced polarisation is dominant. R. S.

**Elastic vibration of an anisotropic liquid.** V. ZOLINA (Acta Physicochim. U.R.S.S., 1936, 4, 85—90; cf. A., 1933, 1108).—Interference phenomena in anisotropic melts of Et *p-p'*-ethoxybenzylideneamino- $\alpha$ -methylcinnamate, acetoxybenzylideneazine, and dibenzylbenzidine, subject to tuning-fork vibrations, have been studied with the polarising microscope. R. S.

**Structure of crystalline bismuth and selenium layers produced by condensation in vacuum.** A. GOETZ and L. E. DODD (Physical Rev., 1935, [ii], 48, 165).—Similarities in the cryst. condensation of Bi and Se evaporated in a vac. are described. The cross-section in the direction of crystallisation of the condensed layers shows two distinct structures. The layer first deposited is microcryst. and  $10^{-2}$  cm. thick and then changes abruptly to a macrocryst. layer with fibrous texture. L. S. T.

**Relation between morphology and structure of potassium sulphate.** K. CHUDOBA and H. BEHNENBURG (Zentr. Min., 1935, A, 327—336; Chem. Zentr., 1936, i, 721). H. J. E.

**Arrangement of lattice blocks in the mosaic crystal, investigated with fused sodium nitrate crystals.** J. LEONHARDT and R. TREMEYER (Z. Physik, 1936, 102, 781—790).—The disposition of lattice blocks in a mosaic crystal is discussed from a consideration of X-ray interference patterns. A. E. M.

**Crystallography of magnesium, cobalt, and nickel sulphites.** H. A. KLASSENS, W. G. PERDOK, and P. TERPSTRA (Z. Krist., 1936, 94, 1—6).—Goniometric measurements, *d*, cell consts., and space-groups are given for  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  and the corresponding Co and Ni salts. Assuming that the six  $\text{H}_2\text{O}$  are symmetrically arranged around the metal ion, and the  $\text{SO}_3$  has a distinct entity, a possible structure is suggested which agrees with Zachariasen's theory of the pyramidal shape of the  $\text{SO}_3$ . B. W. R.

**Crystal lattices of heteropolyacids and their salts. II. Constitution of the silicotungstates of trivalent metals.** O. KRAUS (Z. Krist., 1936, 93, 379—395).—The higher hydrates of these salts have the general formula  $\text{M}^{III}\text{H}(\text{SiW}_{12}\text{O}_{40})_n \cdot n\text{H}_2\text{O}$ . Several new hydrates ( $\text{M}=\text{Fe}$  or  $\text{Cr}$ ) are described and their rotation photographs obtained. B. W. R.

**Lattice constants and space-group of lievrite.** P. KOKKOROS (Naturwiss., 1936, 24, 619).—Lievrite,  $[\text{CaFe}_2(\text{FeOH})(\text{SiO}_4)_2]$ , has *a* 8.76, *b* 13.04, *c* 5.82 Å., with 4 mols. in the unit cell. A. J. M.

**Alterations of the ionic distances in hydroxyl layer lattices.** W. LOTMAR and W. FEITKNECHT (Z. Krist., 1936, 93, 368—378).—From cell size measurements on mixed crystals of  $\text{Zn}(\text{OH})_2$  with Ni and Co hydroxides, an extrapolated val. for the non-

existent  $\text{Zn}(\text{OH})_2$  lattice of C6 type is deduced. Variations of the layer distance and alterations in the *a* axis and in the metal-OH distance, in the basic salts derived from this C6 lattice, are discussed. B. W. R.

**Lattice shrinkage and structure of montmorillonite.** G. NAGELSCHMIDT (Z. Krist., 1936, 93, 481—487).—This aluminosilicate shows a one-dimensional lattice shrinkage on drying. Measurements of the *d*(100) spacing are given over a range of 2—40 mols. of  $\text{H}_2\text{O}$  per unit cell; probably the first 4 mols. enter between the structure layers and thus alter *d*, while subsequent  $\text{H}_2\text{O}$  mols. remain at the crystal surface. B. W. R.

**Polyphosphonitrilic chloride, an inorganic "rubber."** K. H. MEYER, W. LOTMAR, and G. W. PANKOW (Helv. Chim. Acta, 1936, 19, 930—948; cf. this vol. 276).—X-Ray diagrams of unstretched polyphosphonitrilic chloride (I) are amorphous, but become cryst. on stretching. The unit cell contains 8  $\text{PNCl}_2$  groups and has *a* 11.07, *b* 4.92, *c* 12.72 Å. The space-group is probably  $C_{2v}^2$ . The P atoms (with attached Cl) are arranged in a zigzag chain with the N occupying intermediate positions. The dimensions of the crystallites are  $> 500$  Å. in every direction, corresponding with a mol. wt.  $< 20,000$ . Thermo-elastic measurements indicate that stretching is accompanied by progressive orientation of P-N linkings, the subsequent contraction being due to the tendency to disorientation. In details of behaviour (I) is closely analogous to rubber. F. L. U.

**Optical crystallographic data for some salts of the cinchona alkaloids.** M. L. SHANER and M. L. WILLARD (J. Amer. Chem. Soc., 1936, 58, 1977—1978).—Crystallographic data are recorded and the fluorescent properties in ultra-violet light described for quinine, quinidine, cinchonine, and cinchonidine. E. S. H.

**Crystallographic investigation of isomerides arising from the combination of *d*- and *l*-acids with *d*- and *l*-bases.** B. GOSSNER and H. NEFF (Z. Krist., 1936, 93, 488—493).—The four isomeric H tartrates of *d*- and *l*-ephedrine have been investigated by X-rays. B. W. R.

**Fine structure and transformations of alkali salts of long-chain fatty acids.** P. A. THIESSEN and J. STAUFF (Z. physikal. Chem., 1936, 177, 398).—Corrections to a previous paper (this vol., 1186). R. C.

**X-Ray investigation of the crystals of *p*-nitrodiphenyl.** M. PRASAD, M. P. LAKHANI, and J. SHANKER (J. Indian Chem. Soc., 1936, 13, 519—522).—The crystals belong to space-group  $Q^{13}$  with F0 Bravais lattice and the unit cell is asymmetric and contains 8 mols.; *a* 23.25, *b* 11.38, *c* 7.55 Å. The ratio *b*:*c* agrees with Groth and the ratio *a*:*b* is double. C. R. H.

**X-Ray measurements on diflavylene, rubrene, and related compounds.** W. H. TAYLOR (Z. Krist., 1936, 93, 151—155).—Diflavylene, monoclinic, has *a*<sub>1</sub> 6.7, *b*<sub>1</sub> 7.3, 16.7 Å.,  $\beta$ , 102°, 4 mols. in unit; space-group  $C_{2h}^2-P2_1/n$ . An alternative unit cell with *a*<sub>2</sub> 13.0, *b*<sub>2</sub> 7.3, *c*<sub>2</sub> 10.5 Å.,  $\beta$ <sub>2</sub> 90° contains

2 mols.; same space-group. The results indicate a *trans*-configuration for the mol. Rubrene *A* has  $a$  14.3,  $c$  7.0 Å.,  $\beta$  107°; rubrene *B* (distinguishable from *A* only by X-rays), monoclinic, has  $a$  17.9,  $b$ , 10.1,  $c$  8.8 Å.,  $\beta$  120°; 2 mols. in cell; space-group  $C_{2h}^2-P2_1/n$ . Didiphenylene-ethylene, orthorhombic, has  $a$  36.7,  $b$  34.3,  $c$  8.15 Å., 24 mols. in cell; space-group  $D_{2h}^2-Pmcb$  or  $C_{2h}^2-Pcb$ ; its 2:2'-F<sub>2</sub>-derivative,  $d$  1.357, is similar in structure. Some optical data are also given. B. W. R.

Crystal structure of condensed ring compounds. III. Three carcinogenic compounds: 1:2-benzpyrene, methylcholanthrene, and 5:6-cyclopenteno-1:2-benzanthracene. J. IBALL (Z. Krist., 1936, 94, 7-21).—1:2-Benzpyrene occurs in two modifications, (a) monoclinic, space-group  $C_{2h}^2$ ,  $a_0$  4.52,  $b_0$  20.32,  $c_0$  13.47 Å.,  $\beta$  97° 4', (b) orthorhombic, space-group  $C_{2h}^2$ ,  $a_0$  7.59,  $b_0$  7.69,  $c_0$  22.38 Å. The other two compounds are both monoclinic, space-group  $C_{2h}^2$ ,  $a_0$  4.86,  $b_0$  11.31,  $c_0$  27.7 Å.,  $\beta$  116° 5', and  $a_0$  12.02,  $b_0$  8.61,  $c_0$  13.78 Å.,  $\beta$  103° 0', respectively. Based on intensity measurements, probable mol. positions are given. A comparison is made with the structure of monoclinic 1:2:5:6-dibenzanthracene. B. W. R.

X-Ray crystallographic data on the sex hormones, oestrone, androsterone, testosterone, progesterone, and related substances. J. D. BERNAL and D. CROWFOOT (Z. Krist., 1936, 93, 464-480).—A summary of the data (chemical formula, cell size and structure, crystal habit, and general physical properties) now available for this group of substances. B. W. R.

X-Ray diffraction studies of chitin, chitosan, and derivatives. G. L. CLARK and A. F. SMITH (J. Physical Chem., 1936, 40, 863-879).—Natural chitin (I) shows preferred orientation of crystallites, with the  $b$  axis parallel to the surface in that produced in sheets, and to the axis of the fibre in tendons. After treatment with EtOH, fibres of (I) can be separated into uniform fibrils of diameter about 1  $\mu$ . On treatment with HCl at room temp. the ether linkages, and less rapidly the NH<sub>2</sub>-groups, of (I) are hydrolysed. At 200° (I) forms a definite additive compound with LiCNS, whilst at lower temp. intramolecular swelling occurs. Chitin nitrate is probably orthorhombic with  $a$  9.2,  $b$  10.3, and  $c$  23 Å., but fractions separated with different solvents show different average lengths of the C chain. The unit cell of chitosan is orthorhombic with  $a$  8.9,  $b$  10.25, and  $c$  17.0 Å. When formed from (I) in sheet form its (002) planes are parallel to the surface. Analyses show only about half the N required by Lowy's structure for chitosan, so it is suggested that there may be hydrolysis of the NH<sub>2</sub>-group. It is suggested that steric hindrance from another mol. causes only half the Ac groups to be hydrolysed in converting (I) into chitosan. J. W. S.

Fine structure of crystallised caoutchouc. W. LOTMAR and K. H. MEYER (Monatsh., 1936, 69, 115-124).—Redetermination of the consts. of the unit cell of cryst. (stretched) caoutchouc (cf. A., 1928, 1186) shows it to be monoclinic with  $a$  8.57  $\pm$  0.05,  $b$  8.20  $\pm$  0.05 (fibre axis),  $c$  12.65  $\pm$  0.05 Å.,  $\beta$  83° 20'.

The most probable space-group is  $C_{2h}^2$ . The crystallite is a mol. racemate of right- and left-handed spiral threads. F. L. U.

Origin of the "extra rings" in electron diffraction patterns. K. LARK-HOROVITZ, H. J. YEARIAN, and J. D. HOWE (Physical Rev., 1935, [ii], 48, 101).—The extra rings, similar to those reported for Au (A., 1931, 1206), obtained in the electron diffraction patterns of thin films of various metals deposited in a vac. on C<sub>10</sub>H<sub>8</sub>, are due to adsorbed layers of org. substances forming thin, cryst. layers and random oriented cross gratings. When NH<sub>4</sub>Cl replaces C<sub>10</sub>H<sub>8</sub> in the prep. of the films no extra rings appear in the diffraction patterns. L. S. T.

Surface of copper formed by solidification in a vacuum. S. DOBINSKI and C. F. ELAM (Nature, 1936, 138, 685).—X-Ray examination of Cu surfaces cryst. in a vac. showed that the orientation of the crystals differed from specimen to specimen, whilst electron diffraction showed spots from Cu crystals oriented with either {111} or {100} planes parallel to the surface, the {111} orientation being more frequent. L. S. T.

Molecular structures of the methyl derivatives of silicon, germanium, tin, lead, nitrogen, sulphur, and mercury, and the covalent radii of the non-metallic elements. L. O. BROCKWAY and H. O. JENKINS (J. Amer. Chem. Soc., 1936, 58, 2036-2044).—Electron diffraction investigations of gaseous SiMe<sub>4</sub>, GeMe<sub>4</sub>, SnMe<sub>4</sub>, PbMe<sub>4</sub>, NMe<sub>3</sub>, SMe<sub>2</sub>, and HgMe<sub>2</sub> yield the following vals. (in Å.) for interat. distances: Si-C 1.93  $\pm$  0.03, Ge-C 1.98  $\pm$  0.03, Sn-C 2.18  $\pm$  0.03, Pb-C 2.29  $\pm$  0.05, N-C 1.47  $\pm$  0.02, S-C 1.82  $\pm$  0.03, Hg-C 2.20  $\pm$  0.10. These vals. agree with published data for the sums of covalent radii. E. S. H.

Electron diffraction experiments on crystals of galena. L. H. GERMER (Physical Rev., 1936, [ii], 50, 659-671).—Electron diffraction patterns for cleaved, filed, and ground surfaces of galena crystals are photographed and described. The relation of results to the study of strain-hardening in metals is discussed. N. M. B.

Diffraction of electrons by molybdenite. G. I. FINCH and H. WILMAN (Trans. Faraday Soc., 1936, 32, 1539-1556).—Anomalous diffractions are explained in terms of the lattice limitation theory. Single crystals, only a few lattice layers thick, yield on rotation the two-dimensional cross-grating effect of continuous diffraction lines, which decrease in intensity with increasing crystal thickness. The axial ratio of molybdenite is 3.904;  $c$  appears to be independent of crystal thickness. The general theory of the loci of diffractions from rotating, undistorted and from stationary, curved molybdenite crystals is developed. E. S. H.

Electron diffraction by films built from many unimolecular layers. K. H. STORKS and L. H. GERMER (Physical Rev., 1936, [ii], 50, 676; cf. Holley, this vol., 539).—Patterns produced by films of multiple compressed layers of stearic acid and of mixed Ba and Cu stearates show symmetrical spot arrangements, proving that the mols. are regularly



arranged and that the crystal orientation is not random. The patterns differ entirely from those of a single stearic acid crystal obtained by evaporation from  $C_6H_6$  solution. N. M. B.

**Continuous magnetic spectrum at audio-frequencies of transformer lamina.** V. ARKADIEV (*Z. Physik*, 1936, 101, 527—532).

A. B. D. C.

**Gyromagnetic effect in pyrrhotine.** F. COETIERER (*Helv. phys. Acta*, 1935, 8, 522—564; *Chem. Zentr.*, 1936, i, 288).—The theory of the gyromagnetic effect is discussed. Measurements on pyrrhotine,  $Fe_nS_{n+1}$ , along the direction of easiest magnetisation, give  $g = 0.63$  as compared with  $g = 2$  for all other ferromagnetic substances, indicating that orbital momentum, and not only spin momentum, of the electrons is involved, in agreement with the strong magnetic anisotropy. J. S. A.

**Ferromagnetic phenomena.** J. L. SNOEK (*Nederl. Tijds. Natuurkunde*, 1935, 2, 180—189; *Chem. Zentr.*, 1936, i, 26—27).—In pure, unstrained material the crystal axes in Fe represent the directions of least, and in Ni the direction of greatest, energy. Fe-Ni alloys constitute a transition series, an alloy with 70% Ni being isotropic. Stress can produce an anisotropy. J. S. A.

**Physico-technical problems of ferromagnetism in weak fields.** R. GOLDSCHMIDT (*Helv. phys. Acta*, 1935, 8, 497—498; *Chem. Zentr.*, 1936, i, 287).—The loss angle is resolved into two components: one linearly  $\propto$  field strength and frequency, and one independent of field strength and frequency. The latter is investigated in a high-Si transformer sheet, and related to after-working effects. J. S. A.

**Magnetism and cold working in metals. II. Single crystals of bismuth, zinc, and tin.** S. R. RAO (*Proc. Indian Acad. Sci.*, 1936, 4, A, 186—203).—Single crystals of Bi, Zn, and Sn have been investigated for the influence of cold-work on the principal susceptibility. Bi showed a decrease, Zn showed a very small decrease in diamagnetic, and Sn in paramagnetic, susceptibility. The theory of Honda and Shimizu explains these changes. W. R. A.

**Effect of an external magnetic field on transition temperatures.** E. JUSTI (*Physikal. Z.*, 1936, 37, 766—768).—If the phases of a system of one component have different susceptibilities, the transition temp. of the phases are displaced by the application of a magnetic field. The displacement, which is very small, can be calc. from the change of susceptibility and entropy on transition. A. J. M.

**Heat effect of metallic transitions. IV. Nickel.** H. VON STEINWEHR and A. SCHULZE (*Physikal. Z.*, 1936, 37, 753—757).—The heat evolved in the magnetic transition of Ni (99.1%) is  $0.65 \pm 0.06$  g.-cal per g. The transition takes place over the range 333—362°. There was a small heat evolution at a temp. approx. 100° below the Curie point. A. J. M.

**Electrical anisotropy of single tungsten crystals at low temperatures in strong transverse magnetic fields.** E. JUSTI and H. SCHEF-

FERS (*Physikal. Z.*, 1936, 37, 700—708).—The resistance of W crystals at temp.  $< 20.38^\circ$  abs. is about 0.001 of that at  $0^\circ$ . On application of a transverse magnetic field (20,000 gauss) the resistance increases to its normal val. At low temp. the resistance is anisotropic, and the val. depends on the direction of the magnetic field. When the latter is perpendicular to a principal crystal plane, there is a smaller increase of resistance on applying the field, the increase being smallest for the [100] direction. Space-centred crystals of W show only half the no. of max. and min. in resistance shown by a face-centred crystal such as Au. At temp.  $< \text{b.p. of } H_2$  the resistance increases on application of the field approx. with the square of the field strength. The curve between field strength and increase of resistance varies by a const. factor as the crystal is rotated. A. J. M.

**Anode-sputtering and the deposition of metallic film on the cathode of a Hadding X-ray tube.** S. SHARAN (*Indian J. Physics*, 1936, 10, 325—340).—The structure of the deposits and application to anode sputtering are discussed.

N. M. B.

**Cathodic sputtering.** H. DAMIANOVICH (*An. Inst. Invest. cient. tecn.*, 1934, No. 3/4, 23—31; *Chem. Zentr.*, 1936, i, 497; cf. A., 1935, 1060).—The  $d$  of the product obtained in He corresponds with that calc. for  $Pt_5He$ . H. J. E.

**Rate of polymorphic transformations. IV. Influence of mechanical deformation on rate of transformation of polymorphic metals. II. Influence of admixed metals.** E. COHEN and A. K. W. A. VAN LIESHOUT (*Z. physikal. Chem.*, 1936, 177, 331—336; cf. A., 1935, 918).—The rate of transformation of white into grey Sn is much accelerated by small amounts of Zn (max. effect with 0.05%) and Al and retarded by Pb, Sb, Bi, Cd, and Ag. R. C.

**Molecular magnitude of metaphosphates.** P. NYLEN (*Z. anorg. Chem.*, 1936, 229, 30—35).—Cryoscopic measurements, by Richards' method, with a  $(NaPO_3)_x$  prep. described in the literature as monomeric, give  $x=2-3$ . Similar measurements with salts reported as tri- and tetra-meric, respectively, have confirmed the reports. F. L. U.

**Molecular size distribution in linear condensation polymerides.** P. J. FLORY (*J. Amer. Chem. Soc.*, 1936, 58, 1877—1885; cf. this vol., 295).—Size distributions of linear condensation polymerides are calc. on a wt. fraction and a mol. fraction basis, and on the assumption that the reactivity of functional groups is independent of the size of the mols. to which they are attached. The form of the distribution curves is not greatly changed when one of the reactants is in excess. Relations between "no.-average" ( $M_n$ ), "wt.-average" ( $M_w$ ), and "Z-average" mol. wts. are deduced in terms of  $p$ , the fraction of the total no. of functional groups which have reacted. Staudinger's viscosity term is not  $KM_n$ , but  $0.5KM_w$ , where  $M_w=(1+p)M_n$ . The original equation is valid only for polymerides of high mol. wt., i.e., for high vals. of  $p$ . F. L. U.

**Magnetic susceptibility of molecular hydrogen.** E. E. WITMER (Physical Rev., 1935, [ii], 48, 380).—A summary of calc. results not yet completed.

L. S. T.

**Magnetic susceptibility of mixed oxides of the rare earths. II. Samarium-gadolinium mixtures.** L. MAZZA and E. BOTTI (Gazzetta, 1936, 66, 552—562; cf. this vol., 19).—For  $\text{Sm}_2\text{O}_3$   $\chi=6.00 \times 10^{-6}$ , for  $\text{Gd}_2\text{O}_3$   $\chi=139.2 \times 10^{-6}$ . Mixtures of the two oxides do not obey Urbain's additive law. The results do not indicate the existence of any lower oxides, and give a single magnetic moment for  $\text{Gd}^{+++}$  of 39 Weiss magnetons. This agrees with the val. obtained from the susceptibility of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , for which fresh measurements are recorded.

O. J. W.

**Magnetochemical investigation of metal ketyls of 4-pyrones.**—See this vol., 1396.

**Diamagnetism and particle size.** H. LESSHEIM (Current Sci., 1936, 5, 119—127).—A review.

**Cavitation caused by ultrasonic waves.** K. SOLLNER (Trans. Faraday Soc., 1936, 32, 1537—1539).—Cavitation can be made visible by irradiating with high energy long columns of de-gassed liquids.

E. S. H.

**Velocity of ultrasonic waves in heavy water.** R. BAR (Helv. phys. Acta, 1935, 8, 500—502; Chem. Zentr., 1936, i, 708).—The velocity in 99.2%  $\text{D}_2\text{O}$  at 20° was  $1.381 \times 10^5$  cm. per sec. The adiabatic compressibility of  $\text{D}_2\text{O}$  was  $4.733 \times 10^{-11}$  sq. cm. per dyne. The val. for  $\text{H}_2\text{O}$  is  $4.5477 \times 10^{-11}$  sq. cm. per dyne.

H. J. E.

**Visibility of ultrasonic waves in liquids.** S. PARTHASARATHY (Current Sci., 1936, 5, 136).—Parallel monochromatic light falls on one face of a cell containing a liquid through which ultrasonic waves are passing. Through the opposite face a microscope is focussed on the optical grating formed by the sound waves.

C. W. G.

**Ultrasonic velocities in organic liquids. VI. Related compounds.** S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, 4, A, 213—215; cf. this vol., 1189).—Diffraction of light by high-frequency sound waves is used to determine the acoustic velocity in four esters, three nitro-compounds, two aldehydes, in thyme oil, and in oil of turpentine. Adiabatic compressibilities are recorded.

W. R. A.

**Absorption of ultrasonic waves in acetic acid [and benzene and toluene].** P. BASHULIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 285—288).—The absorption coeff. ( $\alpha$ ) of ultrasonic waves has been determined in  $\text{AcOH}$  at 17.5—28° for frequencies ( $\nu$ )  $(3.73-31.3) \times 10^6$ .  $\alpha$  is an approx. linear function of  $\nu$ .  $\alpha$  has been determined in 0—100% mixtures of  $\text{PhMe}$  and  $\text{C}_6\text{H}_6$  at 18° and  $\nu=11.47 \times 10^6$ . The difference in  $\alpha$  for  $\text{PhMe}$  and  $\text{C}_6\text{H}_6$  is that in  $d$ ,  $\eta$ , and velocity of propagation of sound.  $\alpha$  departs considerably from the additive law.

R. S. B.

**Dispersion of sound in liquids.** E. HIEDEMANN, N. SEIFEN, and E. SCHREUER (Naturwiss., 1936, 24, 681).—The dispersion of ultrasonic waves in  $\text{PhMe}$ , xylene,  $\text{NH}_2\text{Ph}$ , and  $\text{PhNO}_2$ , but not in

$\text{H}_2\text{O}$ , has been demonstrated, and its extent determined.

A. J. M.

**Entropy of deuterium oxide and the third law of thermodynamics.** Heat capacity of deuterium oxide from 15° to 298° abs. M.p. and heat of fusion. E. A. LONG and J. D. KEMP (J. Amer. Chem. Soc., 1936, 58, 1829—1834).—Heat capacity data are recorded and the entropy deduced.  $\text{D}_2\text{O}$  has m.p.  $276.92 \pm 0.05^\circ$  abs., and heat of fusion 1501 g.-cal. per mol.

E. S. H.

**Exact measurement of the specific heats of metals at high temperatures. XXV. Specific heats and the allotropy of nickel between 0° and 1000°.** M. EWERT (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 833—838).—A rapid increase of  $c_p$  with temp. occurs up to 345° for  $\alpha$ -Ni (cubic, ferromagnetic). The field of stable existence of the  $\alpha'$  form (hexagonal) is between 345° and 351°. From 351° upwards a much less rapid increase of  $c_p$  with temp. occurs for the  $\beta$  form. The heat effects of transition are approx.:  $\alpha \rightleftharpoons \alpha'$ , at 345°, 0.08 g.-cal.;  $\alpha' \rightleftharpoons \beta$ , at 351°, 0.31 g.-cal.

D. C. J.

**Determination of the true specific heats of silver, nickel,  $\beta$ -brass, quartz crystal, and quartz glass between 50° and 700° by an improved method.** H. MOSER (Physikal. Z., 1936, 37, 737—753).—The apparatus employed consisted of a Ag calorimeter in an atm. of A at low pressure.  $c_p$  of Ag was found to vary little with temp. The anomalies in  $c_p$  of Ni,  $\beta$ -brass, and quartz crystal extend over a wide temp. range, and begin about 300° < the accepted transition temp. at which  $c_p$  is a max. The return to the normal val. takes place over a very narrow temp. range in the case of quartz crystal. For the  $\alpha$ - $\beta$  transition of quartz, associated with a lattice change from the trigonal to the hexagonal, the abnormal increase in  $c_p$  before the transition can be explained as due to an expansion of the lattice, since  $c_p$  (cryst.)— $c_p$  (glass) =  $\Delta c_p$  is approx. equal to the val. calc. from the coeffs. of cubic expansion and compressibility.

A. J. M.

**Heats of crystallisation of methyl and ethyl esters of monobasic fatty acids.** (Miss) A. M. KING and W. E. GARNER (J.C.S., 1936, 1372—1376).—The sp. heats and heats of crystallisation of several Me and Et esters of long-chain (straight) fatty acids ( $\text{C}_{16}$ — $\text{C}_{22}$ ) have been determined. Two equations are derived connecting the m.p. with the no. of C in the chain, one for the Me esters of the even series, the other for the Et esters of the odd series.

W. R. A.

**Rare earth halides. X. M.p., particularly of the bromides.** G. JANTSCH and K. WEIN (Monatsh., 1936, 69, 161—166; cf. A., 1932, 1194; 1934, 157).—Previous work has been amplified by the determination of the m.p. of  $\text{LaBr}_3$ ,  $\text{CeBr}_3$ ,  $\text{PrBr}_3$ ,  $\text{NdBr}_3$ , and  $\text{SmBr}_3$ , which are respectively  $783 \pm 3^\circ$ ,  $732 \pm 2^\circ$ ,  $693 \pm 2^\circ$ ,  $684 \pm 2^\circ$ , and  $664 \pm 2^\circ$ . The relationship between the m.p. of various halides is discussed.

F. L. U.

**M.p. of long-chain carbon compounds.** (Miss) A. M. KING and W. E. GARNER (J.C.S., 1936, 1368—1372).—The heat increments and entropy



increments per  $\text{CH}_2$  are const. for homologous series with  $>10$  C in the chain. Differences in the physical properties of polymorphic modifications of long-chain compounds with vertical and tilted chains are given; for compounds with very long chains vertical chains are more stable than tilted chains at the m.p.

W. R. A.

Position of  $\lambda$ -points of helium. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 822—823).—A correction of the val. quoted in former paper (this vol. 787).

D. C. J.

Optical experiments on liquid helium II. L. V. SCHUBNIKOV and A. K. KIKOIN (Nature, 1936, 138, 641).—No evidence of the formation of liquid crystals could be obtained in liquid He between  $4.22^\circ$  and  $1.72^\circ$  abs. Hence, the anomaly in the sp. heat of liquid He at  $2.19^\circ$  abs. cannot be ascribed to a transition to the liquid crystal state.

L. S. T.

Vapour pressure and heat of sublimation of carbon. P. GOLDFINGER and W. JEUNEHOMME (Trans. Faraday Soc., 1936, 32, 1591—1598).—V.-p. curves have been deduced from published data for the heat of vaporisation of C. The most probable val. for the heat of vaporisation is  $123.6 \pm 0.5$  kg.-cal.

E. S. H.

Density of saturated vapours. M. F. SOONAWALA (Indian J. Physics, 1936, 10, 353—363).—Mathematical. The surface of a liquid is treated as a potential barrier, and the probability of transition across it of a mol. is obtained by wave mechanics. Application to experimental data shows that a mol. in a liquid has potential as well as kinetic energy. The val. of this potential energy is calc. for 13 liquids.

N. M. B.

Single linking energies. IV. V.-p. of hexaphenylethane. G. R. CUTHBERTSON and H. E. BENT (J. Amer. Chem. Soc., 1936, 58, 2000—2003; cf. this vol., 291).—For  $\text{CHPh}_3$  ( $26.5$ — $90.5^\circ$ )  $\log p = -5260/T + 12.72$ ,  $\Delta H = 24.1 \pm 1.0$  kg.-cal.; for  $\text{C}_2\text{Ph}_6$  ( $75.4$ — $120.8^\circ$ )  $\log p = -5987/T + 12.85$ ,  $\Delta H = 27.4 \pm 1.5$  kg.-cal.; for  $\text{CPh}_3$  peroxide ( $119.8$ — $161.0^\circ$ )  $\log p = -8259/T + 16.98$ ,  $\Delta H = 37.8 \pm 1.5$  kg.-cal. The heat of vaporisation shows that the C-C linking in  $\text{C}_2\text{Ph}_6$  vapour is weaker than the normal C-C linking.

E. S. H.

Vapour density of hexaphenylethane. H. E. BENT and E. S. EBERS (J. Amer. Chem. Soc., 1936, 58, 2073—2074).—Rapid decomp. prevents determination.

E. S. H.

U-Effect of Amagat and Weiss. Equation of state on the basis of selection theorems and the Joule-Thomson effect. II. V. JACYNA (Z. Physik, 1936, 103, 67—75).—Mathematical. The theoretical basis for the behaviour of gases at high pressures is reviewed.

H. C. G.

Compensation state ("basis line") for helium and carbon dioxide. I. V. JACYNA (Z. Physik, 1936, 103, 61—66).—Mathematical. A new equation of state having the parabolic form of the van der Waals-Berthelot equation is obtained and discussed in relation to available data for He and  $\text{CO}_2$ . The significance of the basis line is pointed out.

H. C. G.

X-Ray determination of the thermal expansion coefficients of beryllium and tin. G. F. KOSLOPOV and A. K. TRAPESNIKOV (Z. Krist., 1936, 94, 53—59).—The coeffs. are measured parallel and perpendicular to the  $a$  axis, using a back-reflexion camera, over the range  $18$ — $454^\circ$  for Be and  $23$ — $150^\circ$  for Sn, and are compared with previous results by the macroscopic method.

B. W. R.

Viscosity of air and electronic charge. V. D. MAJUMDAR and M. B. VAJIFDAR (Current Sci., 1936, 5, 133).—The method involves flow of air through a capillary tube.  $\eta = 1816.2 \times 10^{-7}$  c.g.s. unit at  $20^\circ$ ;  $e = 4.8022 \times 10^{-10}$  e.s.u.

C. W. G.

Influence of magnetic field on the coefficient of viscosity of liquids. II. S. D. CHATTERJEE (Indian J. Physics, 1936, 10, 399—401; cf. A., 1935, 1198).—Results are given for three non-polar liquids ( $\text{C}_6\text{H}_6$ ,  $p$ -xylene, and hexane) and for 9 monohydric alcohols. The former group shows a change of  $\eta$  in a magnetic field; in the latter the change seems to depend on the shape of the mol., the presence of a straight or a side chain, or general symmetry. The abs. change  $d\eta$  is given for 8 liquids for which  $\eta$  is altered by the magnetic field.

N. M. B.

Viscosity nomographs for alkaline solutions. D. S. DAVIS (Ind. Eng. Chem., 1936, 28, 953—956).—Nomographs for obtaining the  $\eta$  of aq. solutions of  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaOH} + \text{Na}_2\text{CO}_3$ , and  $\text{KOH} + \text{K}_2\text{CO}_3$  at  $20$ — $40^\circ$  are given.

D. K. M.

[Temperature of vapour from boiling solutions.] K. SCHREBER (Z. ges. Kalte-Ind., 1935, 42, 131—135; Chem. Zentr., 1936, i, 604).—A discussion.

H. J. E.

Refractometry of binary liquid systems. III. V. J. ANOSOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 255—270).—A classification of the refractometric isotherms is proposed.

R. T.

Periodic variations of labile [alcohol-water] molecular complexes and their equilibrium position. L. SPLATT (Acta phys. polon., 1934, 2, 459—464; Chem. Zentr., 1936, i, 507).—Recorded observations of periodic variations in the longitudinal light scattering effect of  $\text{EtOH}$ — $\text{H}_2\text{O}$  mixtures are confirmed (cf. A., 1931, 900).

H. J. E.

Complex formation between polynitro-compounds and aromatic hydrocarbons. III. Systems containing tetranitromethane. D. L. HAMMICK and R. P. YOUNG (J.C.S., 1936, 1463—1467; cf. this vol., 722).—The formation of coloured complexes has been studied by determination of the colour density,  $D$ , at  $\lambda$  4300 Å. There is a linear relationship between  $D$  and the hydrocarbon (or substituted hydrocarbon) concn.  $b$  for  $\text{C}_6\text{H}_6$ ,  $\text{PhMe}$ ,  $o$ -,  $m$ -, and  $p$ -xylene,  $\text{PhOEt}$ ,  $\text{C}_{10}\text{H}_8$ ,  $2\text{-C}_{10}\text{H}_7\text{Me}$ ,  $2\text{:}4\text{-C}_{10}\text{H}_6\text{Me}_2$ ,  $\beta\text{-C}_{10}\text{H}_7\text{OH}$ ,  $1\text{-C}_{10}\text{H}_7\text{NO}_2$ , and anthracene, whilst in the case of mesitylene,  $D/b$  decreases as  $b$  increases. Relative vals. of the equilibrium consts. and heats of interaction have been calc.

R. S.

Thermal examination of chemical compounds in the system zinc-magnesium. M. I. ZACHAROVA and A. B. MLODZIEJEWSKI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 193—202).—1:1 Mg-Zn alloys consist of a mixture of  $\text{MgZn}_2$ , eutectic, and

MgZn; after heating at 340–354° for 80 days the alloy consists predominately of MgZn, as shown by crystallographic examination. Thermal data afford additional evidence for the formation of MgZn.

R. T.

**System iron-antimony.** P. FOURNIER (Rev. Chim. ind., 1935, 44, 195–198; Chem. Zentr., 1936, i, 422).—The system has been studied from 0.5–70% of Sb. With 60% of Sb, the position of the magnetic transformation is unaltered; the alloy with 70% of Sb is non-magnetic. The solubility of Sb in  $\alpha$ -Fe increases with rise of temp. up to 35% at the eutectic temp., 1060°. FeSb undergoes a transition at 620°. The addition of Sb to steels produces brittleness.

J. S. A.

**Magnetic stability of ferromagnetic iron alloys.** I. V. S. MESSKIN and J. M. MARGOLIN (Z. Physik, 1936, 101, 456–477).—The magnetic stability of Fe alloys increases with increasing concn. of the solid solution and homogenisation of the structure. High-resistance alloys of technical interest are described.

A. B. D. C.

**Phase transformations in the solid state in iron-chromium alloys.** N. N. KURNAKOV and N. I. KORENOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 85–98).—Thermal, conductivity, and hardness data confirm the formation of the compound FeCr in Fe-Cr alloys subjected to prolonged heating at 950°. The solid solutions formed by FeCr with Fe have a lower conducting power than those formed by FeCr in Cr.

R. T.

**Formation of liquid eutectic alloys.** N. V. GEVELING (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 63–83).—When molten Cd and Bi or Sn are mixed a fall in temp. results, which is at a max. when the components are present in the same proportions as in the eutectic alloy. No temp. effect is obtained by adding one of the components to a mixture containing the same component in excess of that present in the eutectic alloy. Liquid eutectic alloys are regarded as solutions of one or the other component in the pure eutectic. A sharp break occurs in the  $d$ - and  $\pi$ -concn. curves of the system H<sub>2</sub>O-NaCl at the eutectic composition (23.5% NaCl), suggesting that the mixtures are solutions of H<sub>2</sub>O or NaCl in the eutectic.

R. T.

**Hall effect in antimony-tellurium and antimony-silver alloys.** E. VAN AUBEL (Compt. rend., 1936, 203, 614–615).—The Hall effect and the thermoelectric power of Sb are reduced to 64% and 70% of their respective normal vals. by 4.26% of Te. Formation of the compound Ag<sub>3</sub>Sb is indicated by the variation of Hall effect for a series of Sb-Ag alloys.

H. J. E.

**Electrical conductivity and diagram of state for binary alloys.** XXI. System palladium-chromium. G. GRUBE and R. KNABE. XXII. System palladium-manganese. G. GRUBE, K. BAYER, and H. BUMM (Z. Elektrochem., 1936, 42, 793–804, 805–815).—XXI. Evidence has been obtained for the existence of Pd<sub>2</sub>Cr<sub>3</sub>, which forms solid solutions with Pd, but not with Cr. Cr<sub>2</sub>O<sub>3</sub> dissolves in molten Cr.

XXII. The equilibrium diagram has been deter-

mined by thermal, electrical conductivity, microscopical, and X-ray methods. The compounds Pd<sub>3</sub>Mn, and PdMn are formed.

E. S. H.

**Magnetic susceptibility and diagram of state for binary alloys.** II. System palladium-manganese. G. GRUBE and O. WINKLER (Z. Elektrochem., 1936, 42, 815–830; cf. A., 1935, 291).—The results support those obtained by thermal and other methods (cf. preceding abstract).

E. S. H.

**Magnetic susceptibility of binary alloys of thallium.** (Miss) A. W. DAVID and J. F. SPENCER (Trans. Faraday Soc., 1936, 32, 1512–1516).—Magnetic susceptibilities ( $\chi$ ) of complete series of Tl-Bi and Tl-Cd alloys have been measured. The existence of compounds Bi<sub>5</sub>Tl<sub>3</sub> and Bi<sub>2</sub>Tl<sub>3</sub> is indicated.  $\chi$  for Tl-Cd alloys conforms to the simple mixture rule.

A. J. E. W.

**Theory of equilibrium in alloys.** I. W. HUME-ROTHERY (Phil. Mag., 1936, [vii], 22, 1013–1047).—The effect of lattice distortion on the  $\alpha$ -solid solubilities of certain *B* sub-group metals in Cu and Ag has been investigated, and is discussed in relation to the electron concn. existing in the alloys at the solubility limits, and to the causes of lattice distortion. Possible types of ternary solid solubility isothermals, and the systems in which they occur, are reviewed. One of these types is characteristic of systems containing two components which unite to form a compound; a theoretical treatment of such ternary systems is given.

A. J. E. W.

**Structural change and distortion of the ordered distribution of atoms in metallic mixed phases by plastic deformation.** H. J. SEEMANN (Naturwiss., 1936, 24, 618–619).—The disordering effect of plastic deformation on metallic mixed phases observed with Cu<sub>3</sub>Au and Ni<sub>3</sub>Mn has also been found to occur with a Cu-Pd alloy (47 at.-% Pd). The sp. resistance increases steadily as the arrangement of atoms becomes more disordered, the val. for the completely disordered state being unaffected by cold-working. This example is noteworthy since in addition to a change in the ordered distribution of atoms there is also a lattice change.

A. J. M.

**Velocity of dissolution of gold, silver, and copper alloys in aqueous cyanides in connexion with the phase diagrams of the systems: gold-copper, silver-copper, and gold-silver.** I. N. PLAKSIN and S. V. SCHIBAIEV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 159–182).—The velocity of dissolution ( $V$ )-composition diagrams for Au-Cu alloys in 0.15–0.6% KCN at 19° have two max., corresponding with the compounds AuCu and AuCu<sub>2</sub>. The  $V$  of Cu from Ag-Cu alloys is least, and that of Ag greatest, at the eutectic point; no Ag is dissolved from alloys containing <37 at.-% Ag. The  $V$  of Au from Au-Ag alloys falls with increasing [Au] to a min. at 40 at.-%, and then rises to a max. at 60 at.-%. The [KCN] giving max.  $V$  of Au from Au, Au-Ag and Au-Cu are, respectively, 0.25, 0.30, and 0.35%. R. T.

**System iron-cobalt-copper.** W. JELLINGHAUS (Arch. Eisenhüttenw., 1936–1937, 10, 115–118).—Cu, Co, and Fe are completely miscible in the liquid state, but separation into two solid phases occurs in



all alloys with 8–96% Cu on solidification. Alloys within a small range in the Fe corner of the ternary diagram solidify as  $\delta$  Fe solid solution and all other alloys with  $\geq 8\%$  Cu as  $\gamma$  Fe-Co solid solution. The  $\gamma$ - $\alpha$  transformation occurs in all alloys on the Fe side of a straight line joining the Cu corner with the 21% Fe point on the Fe-Co side. Addition of Co to Fe-Cu alloys raises the  $\gamma \rightleftharpoons \alpha + \text{Cu}$  eutectoid point to a max. on the line joining the Cu corner with the 50:50 Fe-Co point and then rapidly decreases it to room temp. The existence of FeCo has been confirmed by X-ray analysis and  $d$  measurements.

A. R. P.

**Solubility of methyl chloride and ethyl chloride in certain solvents at  $-10^\circ$  to  $20^\circ$ , at pressures less than atmospheric.** S. I. KAPLAN and M. A. ROMANTSCHUK (J. Gen. Chem. Russ., 1936, 6, 950–954).—Data are recorded for  $(\text{CH}_2\text{Cl})_2$  and  $\text{CCl}_4$  at 100–760 mm.; the former is always the better solvent.

J. J. B.

**Mutual solubilities of hydrocarbons. I. F-p. curves of dotriacontane (dicetyl) in propane and butane.** W. F. SEYER and R. FORDYCE (J. Amer. Chem. Soc., 1936, 58, 2029–2031).—The data indicate the occurrence of two forms of dotriacontane. The variation of  $n$  with temp. shows a transition point at  $55^\circ$ .

E. S. H.

**Thermal variation of electrical birefringence of a liquid mixture presenting a critical point of miscibility.** A. GOLDET (Compt. rend., 1936, 203, 716–718).—Variation of the Kerr effect with temp. for a mixture of  $\text{PhNO}_2$  and  $\text{C}_7\text{H}_{16}$  has been investigated in the neighbourhood of the crit. solution temp.  $T_c$ . The effect increases sharply as  $T_c$  is approached from higher temp., probably owing to changes in the electric field in the liquid.

A. J. E. W.

**Influence of addition of salts on the water-phenol system.** A. BANCHETTI (Atti Soc. Toscana Sci. Nat., 1935, 44, No. 3, 5 pp.; Chem. Zentr., 1936, i, 314).—Addition of  $c$  g.-mols. of KCl per 1000 g. to a mixture of 34.8% of PhOH and 65.2% of  $\text{H}_2\text{O}$  raises the crit. solution temp. by  $t^\circ = 64.87c^{0.87}$ .

H. N. R.

**System nitrobenzene-sulphuric acid-water.** K. C. BAILEY and J. HILTON (J.C.S., 1936, 1571).— $\text{PhNO}_2$  and  $\text{H}_2\text{SO}_4$  are miscible in all proportions at  $17^\circ$ . Miscibility data are given for mixtures of  $\text{PhNO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4$  at  $17^\circ$ .

R. S.

**Solubility of nitrogen in water at pressures up to 4500 kg. per sq. cm.** J. BASSET and M. DODÉ (Compt. rend., 1936, 203, 775–777).—Measurements at  $18^\circ$  are recorded. The solubility increases with the pressure up to approx. 3000 kg. per sq. cm. and then decreases up to 4500 kg. per sq. cm. Several days are needed for saturation at the higher pressures.

H. J. E.

**Partial vapour pressures of methylamine solutions.** W. A. FELSING and B. A. PHILLIPS (J. Amer. Chem. Soc., 1936, 58, 1973–1975).—Partial v.p. of aq.  $\text{NH}_2\text{Me}$ ,  $\text{NHMe}_2$ , and  $\text{NMe}_3$ , respectively, have been determined over the concn. range 0.2–2.5M. The v.p. of liquid  $\text{NMe}_3$  ( $-20^\circ$  to  $45^\circ$ ) is given by  $\log_{10} p(\text{mm.}) = -1410.5/T + 8.574 - 0.0021158T$ ;  $d$ ,

determined over the same temp. range, is given by  $0.87406 - 4.433 \times 10^{-4}T - 1.29236 \times 10^{-4}T^2$ . The calc. b.p. is  $2.90^\circ$ , and calc. heat of vaporisation 5706 g.-cal. per mol. The calc. free energy of solution (in g.-cal. per mol.) is 3474 for  $\text{NHMe}_2$ , 2991 for  $\text{NH}_2\text{Me}$ , and 2090 for  $\text{NMe}_3$ .

E. S. H.

**Solubility and activity of the halogenates of some bivalent metals. III. Solubility and activity of radium iodate in water and in solutions of electrolytes.** A. POLESICKI and P. TOLMATSCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 319–320).—The solubility has been determined in  $\text{H}_2\text{O}$  at  $0$ – $100^\circ$ , and in solutions of  $\text{KNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{KIO}_3$  at  $25^\circ$ . The activity coeffs. at different ionic strengths have been calc.

D. C. J.

**Solubility of solids in liquefied gases. Solubility of  $\text{KNO}_3$  and  $\text{NaCl}$  in liquid ammonia.** A. I. SCHATTENSTEIN and M. M. VIKTOROV (Acta Physicochim. U.R.S.S., 1936, 5, 45–62; cf. A., 1934, 1304).—A method for the accurate measurement of solubilities of solids in liquefied gases is described. Sources of error are discussed and published data critically examined.

F. L. U.

**Effect of one salt on the solubility of another. VII. Solubilities of cobaltammines in aqueous sodium, potassium, and barium thiocyanates.** J. R. PARTINGTON and H. J. STONEHILL (Phil. Mag., 1936, [vii], 22, 857–882).—Data for  $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{NO}_3)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{NCS}]_2$  are recorded. The results are not in accord with the Debye-Hückel theory, assuming either point ions or finite ionic diameters. The La Mer equation applies when the ionic strength is  $\geq 0.52$ , provided that a val. for the mean ionic radius characteristic of each solution is assumed; this val. is not simply related to the crystallographic ionic diameters for the ions present.

A. J. E. W.

**Solubility of cobaltous iodate in presence of sodium chloride, sodium iodate, and cobaltous sulphate.** H. M. TRIMBLE (J. Amer. Chem. Soc., 1936, 58, 1868–1869).—Data at  $30^\circ$  are recorded.

E. S. H.

**Solubility of cupric oxide in alkali and the second dissociation constant of cupric acid. Analysis of very small amounts of copper.** L. A. McDOWELL and H. L. JOHNSTON (J. Amer. Chem. Soc., 1936, 58, 2009–2014).—The solubility of  $\text{CuO}$  in  $0.04$ – $8.4N$ -KOH and in  $2.2$ – $4.2N$ -NaOH at  $25^\circ$  has been determined. The calc. dissociation const. for  $\text{HCuO}_2' = \text{H}^+ + \text{CuO}_2''$  is  $7.9 \times 10^{-14}$ . The relative proportions of  $\text{HCuO}_2'$  and  $\text{CuO}_2''$  in the solutions have been evaluated. The solubility of  $\text{CuO}$  in  $\text{H}_2\text{O}$  is  $3 \times 10^{-5}$  g.-mol. per litre. A potentiometric method for the determination of Cu in low concns. is described.

E. S. H.

**Derivation of a general expression for the velocity of dissolution of a solid body.** R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1936, 4, 481–493).—The dissolution of a solid over which a liquid is flowing is considered mathematically.

C. R. H.

**Coefficient of fractionation of radium and its isotopes in the crystallisation of barium chlorate.** B. GOLDSCHMIDT (Compt. rend., 1936, 203, 617–

618).—Data are recorded for the ratio of the concns. of Ra, Ac-X, and Th-X in crystals and mother-liquor, on slowly crystallising aq.  $\text{Ba}(\text{ClO}_3)_2$  solutions at 30°. The distribution coeff. is the same for the three isotopes.

H. J. E.

**Theory of adsorption of radioactive elements on polar crystals.** A. P. RATNER (*Acta Physicochim. U.R.S.S.*, 1936, 4, 889—898).—Equations are deduced for the exchange adsorption of ions which do not give solid solutions with the adsorbing crystal and also for the influence of foreign ions.

H. J. E.

**Inner adsorption in salt crystals. IV.** D. BALAREV (*Z. anal. Chem.*, 1936, 106, 349—353).—Polemical, in reply to Kolthoff (this vol., 677).

J. S. A.

**Mechanism of the phenomenon of base exchange.** M. G. AUSTERWEIL (*Bull. Soc. chim.*, 1936, [v], 3, 1782—1790; cf. A., 1932, 1007).—It is confirmed that base exchange is governed by the laws of distribution, the solid base exchanger playing the role of a solvent non-miscible with the solution containing the cations. The extraction formula is related to the empirical adsorption formula by which the phenomenon has been previously represented.

J. W. S.

**Adsorption of radium ions on glass, and Guy's theory.** V. VDOVENKO and A. SAMOILOVICH (*Acta Physicochim. U.R.S.S.*, 1936, 4, 613—616).—Theoretical. The adsorption isotherms for Ra ions at concns. from  $10^{-7}$  to  $10^{-11}$  mol. per litre and  $p_H$  2—7 can be explained in terms of Guy's theory.

O. D. S.

**Polymolecular adsorbed films. I. Adsorption of argon on salt crystals at low temperatures, and the determination of surface fields.** R. S. BRADLEY (*J.C.S.*, 1936, 1467—1474; cf. A., 1931, 421).—The equation  $T \log_{10} (p_0/p_a) = K_1 K_2^a$ , where  $p_0$  and  $p_a$  are the saturation pressures of the bulk liquid and the adsorbed film, respectively, has been deduced for the formation of thick films by polarisation. Data relative to the adsorption of A on powdered  $\text{CuSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ , and KCl at 84.5—88° abs. are in good agreement with the equation. Thick films are formed on the two former, but not on KCl, polarisation being small in this case due to anion and cation having approx. the same size. The induced dipole moments and the surface fields are calc.

R. S.

**Adsorption of vapours on glass spheres. I. Adsorption of nitrogen.** J. L. SHERESHEFSKY and C. E. WEIR (*J. Amer. Chem. Soc.*, 1936, 58, 2022—2029).—Adsorption data for liquid-air temp. are recorded and discussed in relation to adsorption theories. At low pressures the adsorption isotherm shows recession of the equilibrium pressure. Measurements of the thermal flow effects of  $\text{H}_2$  and He show agreement at pressures corresponding with equal mean free paths.

E. S. H.

**Adsorption of hydrogen and nitrogen on iron-molybdenum ammonia catalysts.** V. ROITER, S. GAUCHMANN, and M. LEPERSON (*Acta Physicochim. U.R.S.S.*, 1936, 4, 145—158).—The adsorption of  $\text{H}_2$  on Fe-Mo (I) and Fe-Mo- $\text{Al}_3$  (II) catalysts is rapid and reversible at low temp., but slow and irreversible

between 0° and 450°. Adsorption is slowest with old (I) and fastest with (II). The presence of  $\text{Al}_2\text{O}_3$  increases the no. of active centres and prevents the reduction of catalyst surface by recrystallisation, but has little effect on the adsorptive capacity. In the case of  $\text{N}_2$ , the rapid, reversible adsorption could alone be observed up to 450°, and the heats of adsorption for (I) and (II) are 5500 and 12,000 g.-cal., respectively.

R. S.

**Adsorption properties of promoted iron oxide in relation to the distribution of the promotor in the oxide form of the ammonia catalyst.** A. DUBROVSKAJA and N. I. KOBOSOV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 841—858).—Adsorption isotherms of  $\text{O}_2$  on  $\text{Fe}_2\text{O}_3$  and on  $\text{Fe}_2\text{O}_3$  promoted with 10% of  $\text{Al}_2\text{O}_3$  have been measured at —190° and 400°. When heated in vac. at 600°,  $\text{Fe}_2\text{O}_3$  crystallises completely. The adsorption decreases with the degree of crystallisation, as determined by X-rays. The rate of desorption at 150—400° has been measured. The activation energy for desorption is the same in the promoted and unpromoted oxide. 10% of  $\text{Al}_2\text{O}_3$  reduces the sp. adsorption of  $\text{Fe}_2\text{O}_3$  by 4—5 times. In  $\text{Fe}_2\text{O}_3$  with relatively large crystals, 1% of  $\text{Al}_2\text{O}_3$  suffices to cover approx. 50% of the crystal surface.

H. J. E.

**Recombination of atomic hydrogen in adsorbed layers.** O. I. LEPUNSKI (*Acta Physicochim. U.R.S.S.*, 1936, 5, 271—298).—The adsorption and recombination of H atoms on Ni, Fe, Cu, and Al between —180° and 0° has been studied. An equation for the recombination velocity has been deduced assuming an activated surface diffusion of H, which is in good agreement with the results. Deviations are attributed to inhomogeneity of the surface. Metals which are most efficient as hydrogenation catalysts give the greatest recombination velocities. The energy of activation of the surface diffusion calc. from the temp. coeff. is < that calc. from the abs. velocity of recombination owing to the operation of a steric factor, the nature of which is discussed.

R. S.

**Influence of  $p_H$  on adsorption from solutions.** N. A. YAJNIK, D. N. GOYLE, I. DAS, and J. R. JAIN (*Kolloid-Z.*, 1936, 77, 99—103).—Measurements of the adsorption of different dyes by  $\text{SiO}_2$  gel,  $\text{Al}(\text{OH})_3$ , and animal charcoal show that the acid dyes are adsorbed most strongly by the acid adsorbents and the basic dyes by  $\text{Al}(\text{OH})_3$ . Addition of acid reduces the adsorption of methylene-blue and Bismarck-brown, but increases the adsorption of water-blue and picric acid. The role of  $p_H$  is discussed.

E. S. H.

**Adsorption of bromine ions by argillaceous sludges.** V. I. NIKOLAEV, A. M. SOLOVOV, and M. A. FRISCHMUT (*Ann. Sect. d'Anal. Physico-Chim.*, 1936, 9, 317—326).—Adsorption of  $\text{Br}^-$  by clay or argillaceous sludge from salt lake  $\text{H}_2\text{O}$  is at a max. when the latter has  $d$  1.32. Adsorption of KBr or NaBr does not take place in absence of chlorides.

R. T.

**Action of potassium on the mechanism of activation of charcoal.** B. BRUNS and E. ZOLOTAREVSKAJA (*Acta Physicochim. U.R.S.S.*, 1936, 5, 63—78; cf. A., 1933, 1112).—The adsorptive capacity for  $\text{C}_5\text{H}_{12}$  of activated sugar C decreases linearly with



increasing K content between 0.02 and 7.8%. It is immaterial whether  $K_2CO_3$  is added initially to the sugar, or the C is heated in K vapour before activation. The effect is due to the greater rapidity with which the surface layer burns in the presence of K.

F. L. U.

**Discontinuities in the sorption process.** A. G. FOSTER (Trans. Faraday Soc., 1936, 32, 1559—1569).—Using a static vac. method, no well-defined discontinuities are observed in the adsorption isotherms of  $CCl_4$  on  $SiO_2$  gel at 25°. After prolonged heating at 120° with  $CCl_4$ , residual  $H_2O$  is removed from the gel and the shape of the isotherm alters, resulting in greatly increased adsorption at low pressures. Adsorption measurements of  $H_2O$ ,  $EtOH$ , and  $CCl_4$  on  $SiO_2$  gel by the dynamic retentivity method show, when compared with results of the static technique, that the retentivity method is untrustworthy when applied to isotherms of abnormal type. E. S. H.

**Range of action of surface forces.** J. M. MACAULAY (Nature, 1936, 138, 587).—Observations on the creeping of  $H_2O$  between glass plates are described. L. S. T.

**Unimolecular adsorption layers and surface films.** I. Measurement of surface pressure of adsorption layers. A. S. ACHMATOV (Kolloid-Z., 1936, 77, 20—26).—Apparatus is described. E. S. H.

**Surface properties of non-aqueous solutions.** R. ASCHAFFENBURG (Nature, 1936, 138, 644—645).—For solutions of *n*-alcohols in  $NH_3Ph$  the lowering ( $\Delta\gamma$ ) of the surface tension is < for aq. solutions. For equimol. solutions,  $\Delta\gamma$  is the greater the higher is the mol. wt. The  $\gamma$ -concn. curves are of the same type as those for aq. solutions, and for dil. solutions ( $c < 0.1$  g.-mol. per litre)  $\Delta\gamma/c$  is const. In homologous series the influence of an additional  $CH_2$  on the surface energy becomes less as the C chain becomes longer. L. S. T.

**Discussion on surface phenomena. Films.** (Proc. Roy. Soc., 1936, A, 155, 684—711).—E. K. RIDEAL discussed the evidence on which the concept of the oriented mono-layer is based. Two experimental methods, an optical and an electrical, are available for the determination of film uniformity. Other properties of surface films were reviewed.

N. K. ADAM discussed the principal forces stabilising unimol. surface films at an air- $H_2O$  surface: (a) the perpendicular attraction of the  $H_2O$ -sol. groups at or near the end of the mol., and (b) the lateral adhesion between the mols.

G. GEE described the results of an investigation of the autoxidation and polymerisation of unsaturated glycerides (drying oils) spread as mono-layers on the surface of 0.01*N*- $H_2SO_4$  or -HCl.

F. A. ASKEW described a method for the study of unimol. films at liquid-liquid interfaces.

J. S. MITCHELL discussed the photochemical properties of certain complex org. compounds spread in mono-layers at the surface of aq. substrates.

J. H. SCHULMAN. The methods of measuring phase boundary potentials and surface pressures at air-liquid phase boundaries may be used to examine the

interaction between large mols. A new phenomenon is described which consists in the penetration of a film of oriented mols., each possessing a large hydrophobic portion and a dipole situated near the end of the mol., by similar mols. which possess different dipoles and are readily sol.

O. GATTY. Differences in potential between the inside and outside of the isolated skins of the common frog have been measured, and time-potential curves obtained as functions of the composition of the solutions in contact with the skin.

K. GORTER described certain results of work on the spreading of complex proteins.

J. F. DANIELLI discussed the tension at the surface of living cells.

A. HUGHES described experiments on unimol. films of chlorophyll, hæmin, and certain recently isolated metallic phthalocyanine derivatives. L. L. B.

**Alteration of the free surface energy of solids.** I. Vertical-rod method for the measurement of contact angles and effect of heat-treatment on magnitude of contact angles. F. E. BARTELL, J. L. CULBERTSON, and M. A. MILLER. II. Effect of heat-treatment of metals in air. III. Effect of heat-treatment of metals in a vacuum and in several gases. F. E. BARTELL and M. A. MILLER (J. Physical Chem., 1936, 40, 881—888, 889—894, 895—904).—I. A method has been developed for measuring contact and interfacial contact angles against either transparent or opaque solids which can be formed into rods, and has been applied to changes in the adhesion tension of  $H_2O$  on Pyrex glass,  $SiO_2$ , Au, and Pt. The method of cleaning and previous heat-treatment of solids changes the magnitude of the contact angle. Careful annealing of glass decreases the  $H_2O$ -air contact angle on its surface to zero. Ageing of glass and metal surfaces increases the contact angle on them.

II. A method of pretreatment of Au and Pt rods to furnish standard reference surfaces has been developed. Similar standard surfaces could not be obtained on steel treated in air. Treatment of standard Au and Pt surfaces at 100—600° in air for 1 hr. decreases the  $H_2O$ -air contact angle, this decrease being the greater the higher is the temp. of the treatment, but on keeping in air the contact angle gradually increases again. Measurements of the contact angles at  $H_2O$ - $C_6H_6$ ,  $H_2O$ -1- $C_{10}H_7Br$ , and  $H_2O$ - $C_2H_5Br_4$  interfaces indicate that the metals treated at low temp. were fairly strongly organophilic, but at higher temp. became less strongly so or even hydrophilic. The changes are attributed to oxidation and recrystallisation.

III. Standard reference surfaces were prepared on rods of Au, Pt, Cu, 18 : 8 stainless steel, Ag, Al, W, and brass by polishing in  $N_2$  and heating in a vac. at 100°. Heat-treatment in a vac. rendered the surfaces more hydrophilic with rise of temp. of treatment. Heating in gases made them less hydrophilic than when heated in a vac. in the order  $vac. > H_2 > air > N_2$ . All the metals except Pt and W react readily with  $C_2H_5Br_4$  after heating in  $N_2$ , whilst Au, Cu, and brass similarly treated react with 1- $C_{10}H_7Br$ . Al and W react with  $C_2H_5Br_4$  after heating in  $H_2$ .

The contact angles at liquid-air interfaces vary considerably with the metal and its pretreatment.

J. W. S.

**Properties of metallic solutions. III. Surface tension of amalgams.** V. K. SEMENT-SCHENKO, B. P. BERING, and N. L. POKROVSKI [with E. E. SHVAREVA] (*Acta Physicochim. U.R.S.S.*, 1936, 5, 181—192).—The surface tensions of Hg amalgams of Cs, Rb, K, Na, Li, Ba, Sr, Pb, Sn, Ag, Cu, Zn, Bi, Co, Mg, and Cd have been determined at 18–20°. The data are in agreement with Sziszkovski's equation up to a crit. concn.  $c_k$  of active metal,  $c_k$  being a linear function of the ultimate activity. K, Rb, and Cs form surface layers of 3.76, 5.8, and 7.8 mols. thick, respectively, whilst Ba, Li, Na, etc. form unimol. layers. The application of the Gibbs equation to amalgams is discussed.

R. S.

**Properties of metallic solutions. II. Surface tension of amalgams.** B. P. BERING and N. L. POKROVSKI (*Acta Physicochim. U.R.S.S.*, 1936, 4, 861—872; cf. this vol., 1192, 1331).—The surface tension of amalgams of Hg with 0–0.2 at-% of Cs, Rb, K, Na, Li, Ba, Sr, Mg, Pb, Sn, Cu, Ag, Cd, Bi, Co, and Zn has been measured at 20° by the method of max. bubble pressure in an atm. of  $H_2$ . H. J. E.

**Electrocapillarity curve of gallium. II.** A. MURTAZAJEV and A. GORODETZKAJA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 75—84; cf. A., 1928, 1193).—More exact results have been obtained. PhOH,  $iso-C_6H_{11}OH$ , pyrogallol,  $CS(NH_2)_2$ , and KI displace the max. of the electrocapillarity curve of Ga in the same direction as in the case of Hg, but the degree of adsorption is different.

R. S.

**Mechanical properties of foams. I.** A. SIEHR (*Kolloid-Z.*, 1936, 77, 27—32).—In a column of foam (up to 50 cm.) the sideways pressure exerted on the tube walls increases linearly with the height of the foam. Foam pressure and wetness (c.c. of liquid/c.c. of foam) decrease with time, although not proportionally. Dil. saponin solutions give drier and lighter foams than conc. saponin solutions.

E. S. H.

**Wetting power of powders of different degrees of dispersion.** Z. V. VOLKOVA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 635—644; cf. A., 1935, 1071).—The velocity of wetting by  $H_2O$  and PhMe of powdered quartz (I), calcite (II), fluorite (III), and corundum (IV) of different degrees of dispersion has been measured. The ratio  $r/r_0$  of the penetration radii for  $H_2O$  and PhMe, respectively, remains const. for (I) and (II) at medium dispersion, but falls at high dispersions. This decrease is ascribed to the formation of  $H_2O$  layers between the particles.  $r/r_0$  for (III) and (IV) decreases with decrease in particle size. For particles covered with an adsorbed layer of oleic acid  $r/r_0$  decreases to 0 when the surface is only partly covered with acid.

O. D. S.

**Anomalies of thin liquid layers. III. Ultramicroscopic study of solvent envelopes and of the fundamental swelling process.** B. DERJAGUIN [with E. OBUCHOV] (*Acta Physicochim. U.R.S.S.*, 1936, 5, 1—22; cf. A., 1934, 1068).—A method is described for determining, by means of an optical lever, the pressure exerted by a thin film of liquid in

contact with lyophilic surfaces. When  $H_2O$  penetrates between plane parallel plates of mica, the resulting linear separation of the plates varies inversely with the pressure opposing separation, e.g., 21  $\mu$  at 4.4, and 0.55  $\mu$  at 14.0 g. per sq. cm.  $CCl_4$  produces no effect with mica, but when saturated with  $H_2O$  gives the same val. as does pure  $H_2O$ . At a steel surface  $H_2O$  is inactive, whilst paraffin oil gives an effect which is increased by addition of oleic acid. The observed effect is invoked to explain the swelling of ppts. and colloids. The subject is discussed theoretically.

F. L. U.

**Film formation from emulsions.** H. WAGNER and G. FISCHER (*Kolloid-Z.*, 1936, 77, 12—20).—Films formed by the drying of emulsions of the  $H_2O$ -in-oil and oil-in- $H_2O$  types are classified in a scheme in which the extreme members are (a) reversible, hydrophilic, and porous (e.g., glue), and (b), irreversible, hydrophobic, and non-porous (e.g., lacquer), respectively. The structure of dried films from several emulsions has been examined microscopically and is discussed in relation to the system of classification.

E. S. H.

**Formation of phosphatide films on cholesterol.** H. G. B. DE JONG and N. I. JOUKOVSKY (*Compt. rend. Soc. Biol.*, 1936, 123, 299—302).—The film consists of mols. of both phosphatide (I) and cholesterol, the latter acting as an activator for (I), contrary to the effect of  $TiO_2$ .

H. G. R.

**Osmotic pressure and viscosity of polystyrenes.** (MME.) A. DOBRY and (MME.) A. SCHWOB (*Bull. Soc. chim.*, 1936, [v], 3, 1790—1794).—In sufficiently dil. solution the mol. wt. of polystyrenes calc. from the osmotic pressure is independent of the solvent, but decreases rapidly with increasing concn. and for 0.5% solutions is half the true mol. wt. This change is attributed to colloidal effects. Fractional pptn. of a polystyrene yields fractions with the same mol. wt., but differing viscosities.

J. W. S.

**Complex formation involving weak acids. XV. Optical rotation of *l*-malic and *l*-lactic acids during neutralisation with sodium hydroxide.** H. T. S. BRITTON and A. A. MOSS (*J.C.S.*, 1936, 1487—1489).—The rotations of undissociated malic (I) and lactic (II) acids and the malate, hydro-malate, and lactate ions have been determined. The variation of rotation during titration of (I) and (II) with NaOH is given by the sum of the mol. and ionic rotations.

R. S.

**Raman effect in non-aqueous electrolytic solutions. II. Solutions of antimony trichloride.** M. ASCHKINASI, P. KURNOSOVA, and V. FINKELSTEIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 317—324; cf. this vol., 1203).—The Raman spectra of 5.8—25% solutions of  $SbCl_3$  in  $Et_2O$  have been determined. Undissociated mols. exist in solution and there is no evidence of compound formation, since no new lines appear. The Raman spectra of 15—22% solutions of  $SbCl_3$  in  $C_6H_6$  show two new lines, of frequencies 477 and 1236  $cm^{-1}$ , corresponding with the compound  $2SbCl_3 \cdot C_6H_6$ .

R. S. B.



**High-frequency measurement of the dielectric constant of dilute solutions of salts in different solvents.** M. BEAUVILAIN (Ann. Physique, 1936, [xi], 6, 502—560).—The dielectric const. of 45 salts in  $H_2O$  and of KCl in glycerol and  $H_2O$ -glycerol mixtures decreases linearly as the salt concn. increases. In general, the decrease is the more marked the higher is the valency of the ions and the greater the proportion of  $H_2O$  in the mixtures. The dielectric const. of solutions of KCl in EtOH, MeOH, BuOH,  $COMe_2$ , glycol, and glycerol, and in mixtures of these with  $H_2O$ , decreases at a certain concn. of solute, which depends on the  $H_2O$  content of the mixtures. The lowering depends on the non-aq. constituent of the solvent. N. M. B.

**Magnetic study of colour changes in cobalt chloride.** II. S. S. BHATNAGAR, A. N. KAPUR, and P. L. KAPUR (J. Indian Chem. Soc., 1936, 13, 489—493).—The mol. magneto-optic rotation of  $CoCl_2 \cdot 6H_2O$  in  $H_2O$ ,  $C_6H_{11}OH$ , and HCl varies with concn., although the effect is only just detectable in  $H_2O$ . This disagrees with the theory that colour change is due to formation of anhyd.  $CoCl_2$ , but supports the theory that complexes of the type  $CoCl_3'$  and  $CoCl_3''$  are present (cf. A., 1932, 1083). C. R. H.

**Analysis of magnetogalvanic effect.** V. SHVONEN and P. VEIJOLA (Z. Elektrochem., 1936, 42, 833—837).—Changes in the effect with time for Cu in aq.  $Cu(NH_3)_4Cl_2$  and Fe in aq.  $FeCl_3$  are traced to the reactions  $Cu^{++} + Cu = 2Cu^+$  and  $2Fe^{+++} + Fe \rightleftharpoons 3Fe^{++}$ . E. S. H.

**Colloid synthesis by means of gaseous explosions and colloidchemical investigations on disperse systems so prepared.** N. SATA (Bull. Chem. Soc. Japan, 1936, 11, 598—627).—By the method previously described (cf. this vol., 1198, 1337), sols of Hg, Se, and S have been prepared and examined. It was necessary to use  $Na_2S$  or NaI as a stabiliser for the Hg sols. The vals. of  $\eta$  for the sols are almost the same as for  $H_2O$  and the vals. of  $\gamma$  only slightly  $>$  for  $H_2O$ . Electrophoretic properties and coagulation by means of halides have also been studied. C. R. H.

**Mechanism of the formation of fogs by ultrasonic waves.** K. SOLLNER (Trans. Faraday Soc., 1936, 32, 1532—1536).—The production of the fogs is traced to the collapse of cavities which is brought about by external gas pressure or by the v.p. of the irradiated liquid. E. S. H.

**Action of ultrasonic waves on suspensions.** F. J. BURGER and K. SOLLNER (Trans. Faraday Soc., 1936, 32, 1598—1603).—In suspensions of particles of microscopic dimensions and in colloidal solutions containing rod- or plate-like particles orientation is produced under the influence of ultrasonic waves. Conc. rheopectic suspensions of gypsum, kaolin, etc. are solidified by ultrasonics of low and medium energy; at higher energies the pastes are liquefied as a result of cavitation. Mixtures of sea-sand or quartz powder with  $H_2O$ , which are normally dilatant, lose this property when exposed to ultrasonic waves. E. S. H.

**Behaviour of aerosols in the acoustic field.** III. Theory of acoustic coagulation. O. BRANDT,

H. FREUND, and E. HIEDEMANN (Kolloid-Z., 1936, 77, 103—115; cf. this vol., 794).—Theoretical.

E. S. H.

**Aerogels. I. Structure of metallic oxides.** V. CAGLIOTI and O. D'AGOSTINO (Gazzetta, 1936, 66, 543—548).—The structures of  $Fe_2O_3$  and of  $Al_2O_3$ , prepared as aerogels by oxidising Fe and Al vapours in electric arcs with a strong current of air, have been investigated by X-rays. Both oxides have the  $\gamma$ -phase structure. O. J. W.

**Measurement of light scattered by disperse systems by means of tubular scattering cells.** B. KLAGES and H. KLUMB (Physikal. Z., 1936, 37, 725—726).—Tubular photo-electric cells can be used for the investigation of scattering of light by stationary or moving disperse systems. Aerosols containing 10 mg. per cu.m., and hydrosols containing 1 mg. per litre, could be detected. The apparatus is also useful for the detection of light scattered by biological preps. and for the study of fluorescence. A. J. M.

**Gold colloids in sylvine crystals.** J. C. REPSCHÉ (Acta Physicochim. U.R.S.S., 1936, 5, 173—180).—The absorption curves of colloidal Au in KCl agree closely with Mie's theory, but the particle size bears little relation to the [Au]. R. S.

**Colloid-chemical phenomena in metals. III. Micellar structure of liquid and solid metals and alloys.** J. A. KLJATSCHKÓ (Kolloid-Beih., 1936, 44, 387—426; cf. this vol., 25).—Published evidence is reviewed. E. S. H.

**Colloid-chemical processes at high temperatures. II. Reduction of the disperse phase with hydrogen under pressure.** S. I. DJATSCHKOVSKI (Kolloid-Z., 1936, 77, 74—78; this vol., 287).—At 200° and 200 atm. colloidal  $Fe(OH)_3$  is reduced by  $H_2$  to Fe,  $WO_3$  and  $V_2O_5$  to  $W_3O_8$  and  $V_2O_4$ , respectively.  $Cr(OH)_3$  is not reduced under these conditions. E. S. H.

**Classification of emulsions.** A. RABINERSON and L. KREMNEV (Acta Physicochim. U.R.S.S., 1936, 5, 105—110). F. L. U.

**Appearance of some emulsions.** W. S. URBANSKI (Acta phys. polon., 1934, 3, 39—41; Chem. Zentr., 1936, i, 29).—A reply to Piekara (A., 1934, 1306). Ag emulsions show evidence of an ordered structure. J. S. A.

**Molecular and colloid solubility of acid and salt dyes, especially benzopurpurin. II. Dissolution of acid dyes in sodium hydroxide+neutral salt and in sodium hydroxide+ethyl alcohol.** W. OSTWALD and R. WALTER (Kolloid-Z., 1936, 77, 54—64; cf. this vol., 1338).—Small amounts of neutral salts increase the solubility of benzopurpurin in NaOH, but large amounts cause flocculation. EtOH behaves similarly to neutral salts at low concns., but at higher concns. there is a sp. solubility of the dye in EtOH. The relative roles of chemical reaction, peptisation, and dissolution in these processes are discussed. E. S. H.

**Spontaneous structure formation of ferric hydroxide sols.** G. FUCHS and A. RABINERSON (Acta Physicochim. U.R.S.S., 1936, 4, 441—452).— $Fe^{III}$  salts in the intermicellar liquid of freshly pre-

pared  $\text{Fe}(\text{OH})_3$  sols gradually hydrolyse, hydrolysis terminating after 3–6 days according to whether the colloid content is low or high. The hydrolysis is accompanied by a decrease in  $[\text{Fe}^{+++}]$  followed by desorption and gradual coagulation. Even when hydrolysis has ceased and there is no further decrease in charge, coagulation continues at a velocity depending on the val. of the adjusted  $\zeta$ -potential.

C. R. H.

**Influence of adsorbed cations on structure formation in aluminosilicate suspensions.** A. RABINERSON and V. KNIASEV (*Acta Physicochim. U.R.S.S.*, 1936, 5, 93–104).—Viscosities and times of setting to a thixotropic gel have been determined for 8% suspensions of three varieties of kaolin containing adsorbed  $\text{H}^+$  and  $\text{Na}^+$  in varying proportions. Setting takes place only when the kaolin is partly saturated with  $\text{Na}^+$ . More conc. (10–20%) suspensions can develop structure when fully saturated either with  $\text{H}^+$  or with  $\text{Na}^+$ . The existence of an optimum Na content is explained by the tendency of this ion to cause both increased hydration and peptisation, the first of which promotes whilst the second hinders the formation of structure.

F. L. U.

**Activity of ions in colloidal solutions. I. Suspension effect in the ultrafiltration of positive colloids.** P. VASSILIEV, T. GATOVSKAJA, and A. RABINOVITSCH. **II. Suspension effect in the ultrafiltration and centrifuging of negative colloids.** T. GATOVSKAJA and P. VASSILIEV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 1–36, 37–50).— $\text{Fe}_2\text{O}_3$  sols of different concns. have been subjected to ultrafiltration and the activities of  $\text{Cl}^-$  and  $\text{H}^+$  in the ultrafiltrate and the residue determined potentiometrically. The vals. of  $\alpha_{\text{Cl}^-}$  and  $\alpha_{\text{H}^+}$  in the ultrafiltrate remain approx. const. with increasing sol concn., whilst  $\alpha_{\text{Cl}^-}$  increases and  $\alpha_{\text{H}^+}$  decreases in the direction ultrafiltrate  $\rightarrow$  sol  $\rightarrow$  residue, according to linear functions of the  $\text{Fe}_2\text{O}_3$  concn. The ratio  $\alpha_{\text{Cl}^-} : \alpha_{\text{H}^+}$  is const. on both sides of the ultrafilter in agreement with the Donnan equilibrium condition. A theory based on the Donnan equilibrium is put forward.

**II.  $\text{WO}_3$ ,  $\text{TiO}_2$ , and  $\text{V}_2\text{O}_5$  sols have been investigated.** The  $\alpha_{\text{H}^+}$  in the ultrafiltrate is const. with increasing sol concn., but in the series ultrafiltrate  $\rightarrow$  sol  $\rightarrow$  residue,  $\alpha_{\text{H}^+}$  increases approx. linearly with sol concn. Similar results are obtained when the system is centrifuged.

R. S.

**High-frequency conductivity of colloidal electrolytes. I. Congo-red and Congo-blue sols.** G. SCHMID and A. V. ERKKILÄ (*Z. Elektrochem.*, 1936, 42, 737–741).—The high-frequency conductivity is about 30% > that at low frequencies. The significance of this result in elucidating the electrical structure of colloid micelles is discussed.

E. S. H.

**Physicochemical investigations of photographic emulsions.** C. S. LIALIKOV and V. N. PISKUNOVA (*Acta Physicochim. U.R.S.S.*, 1936, 4, 325–340).—The solubility ( $S$ ) of  $\text{AgBr}$  has been determined at 25–45° in presence of gelatin, 0.00625–1.6M-KBr, 1M- $\text{NH}_3$ , and 0.5M- $\text{KNO}_3$ .  $S$  in  $\text{NH}_3$  decreases on addition of small quantities of  $\text{Br}^-$ , remains const. on further additions, and then in-

creases. The expression  $6.3 \times 10^{-13} [\text{NH}_4\text{OH}]^2 / [\text{Br}^-][\text{Ag}(\text{NH}_3)_2^+]$  remains approx. const. for  $[\text{Br}^-] = 0.00606$ – $0.0995N$ . The val. of  $S$  in  $\text{NH}_3$  in presence of KBr is increased by  $\text{KNO}_3$ , the influence of the  $\text{KNO}_3$  increasing with decreasing  $[\text{KBr}]$ , and the presence of 1% gelatin causes only a slight decrease in  $S$ .

R. S. B.

**Role of dielectric constant, polarisation, and dipole moment in colloid systems. XVII. Swelling and solubility of cellulose derivatives and their relations to dielectric values.** W. L. H. MOLL (*Kolloid-Z.*, 1936, 77, 85–93).—Published data show a relation between the optimum conditions for swelling and the dielectric const., surface tension, and chemical character of the solvent.

E. S. H.

**Electro-kinetic investigation of the organosols of highly polymerised natural substances.** M. TANIGUCHI and I. SAKURADA (*J. Soc. Chem. Ind. Japan*, 1936, 39, 316B).—Cellulose nitrate and acetate are negatively charged in  $\text{COMe}_2$  solution.

A. G.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity. V. Determination of exact coagulation values by turbidity measurements.** H. A. WANNOW (*Kolloid-Z.*, 1936, 77, 46–53; cf. this vol., 1200).—When  $\text{As}_2\text{S}_3$  sols are coagulated by electrolytes, the turbidity decreases and the sedimentation vol. increases with increasing valency of the pptg. ion ( $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Th}^{++++}$ ). Turbidity measurements are not suitable for the exact determination of coagulation vals.

E. S. H.

**Flocculation of lyophilic colloids by non-electrolytes and salts.** B. JIRGENSONS (*Kolloid-Beih.*, 1936, 44, 285–386).—Published work on the behaviour of sols of ovalbumin, casein and its degradation products, haemoglobin, starch, and lecithin is reviewed and certain regularities are indicated. In flocculation of the pure sols by alcohols and similar non-electrolytes, max. and min. with increasing concn. appear, their positions depending on the dielectric const. of the non-electrolyte and on the  $p_H$  of the solution. With combinations of capillary-active non-electrolytes and salts in low or medium concns. coagulation is more rapid than with non-electrolytes or salts alone, but at higher concns. the non-electrolyte stabilises the sol.

E. S. H.

**Peptisation of colloids by electrolytes. I. Reversion of coagulation with formation of insoluble salts.** P. VASSILIEV and N. DESCHALIT (*Acta Physicochim. U.R.S.S.*, 1936, 4, 51–74).—When  $\text{Fe}(\text{OH})_3$  sol is coagulated by  $\text{Na}_2\text{SO}_4$ ,  $\text{Cl}^-$  is displaced from the surface of the particle to the intermicellar liquid by  $\text{SO}_4^{--}$ . The gel can be peptised by addition of an equiv. amount of  $\text{BaCl}_2$ , with formation of  $\text{BaSO}_4$ , and it has been shown that  $\text{Cl}^-$  is readsorbed during the peptisation. Repeated coagulations and peptisations are possible. Part of the  $\text{BaSO}_4$  is pptd., whilst part remains in the sol, and this has been shown by X-rays to have the ordinary crystal structure. Reversion of  $\text{Al}(\text{OH})_3$  and  $\text{Ti}(\text{OH})_2$  gels is possible, but gels of negative colloids could not be peptised. The formation of  $\text{CaSO}_4$  or  $\text{SrSO}_4$  does not produce reversion, but  $\text{PbCrO}_4$  is efficacious because of its low solubility product.

R. S.



**Elastoidin fibres. I. Imbibition of water.** E. FAURÉ-FREMIET and R. WOELFFLIN. **II. Elastic properties.** E. FAURÉ-FREMIET. **III. Titration curve.** E. FAURÉ-FREMIET and R. WOELFFLIN (J. Chim. phys., 1936, 33, 666—680, 681—694, 695—700).—I. The prep. of elastoidin fibres (I) from the fins of the blue shark is described. The imbibition of  $H_2O$  by dried (I) bears a sigmoid relation to the pressure of the added  $H_2O$  vapour, and the free energy of imbibition falls rapidly as  $H_2O$  is absorbed. In the absence of salts, the imbibition by submerged (I) is const. at  $p_H$  4—11, but rises sharply at  $p_H$  12 and has a sharp max. at  $p_H$  2.4. Neutral salts augment imbibition, the effect corresponding with the Hofmeister series, but inhibit the large absorption at low  $p_H$  vals. The breadth of a fibre in acid increases linearly with imbibition and the length increases linearly to a flat max. equal to the val. at  $p_H$  4—11. The effects of temp. are recorded.

**II.** (I) exist in two interconvertible forms. Modification *A* follows Hooke's law at 7—58°, but has small extensibility. Modification *B*, formed at approx. 62° under zero tension, follows Hooke's law at 63—66° and is highly elastic. Below 62°, *B* undergoes changes, largely permanent, corresponding with the existence of false equilibria.

**III.** (I) absorb acid and alkali strongly at  $p_H$  vals. < 2.5 and > 10, respectively. *A* and *B* at  $p_H$  6.2—7.6 and  $p_H$  5—7, respectively, do not absorb acid or alkali.

J. G. A. G.

**Isoionic point of proteins.** A. PASSINSKI and Z. ZOLOTAREVA (Acta Physicochim. U.R.S.S., 1936, 4, 505—526).—The effect of neutral salts on the iso-electric and isoionic points of ampholytes is discussed theoretically. Measurements of the isoionic points of solutions of gelatin (I) and of ovalbumin (II) in the presence of  $BaCl_2$ ,  $KCl$ , and  $KI$  show that for both proteins  $BaCl_2$  causes a shift of isoionic point towards the acid side, whilst  $KI$  causes a shift to the alkaline side. The isoionic point of (I) is unaltered by  $KCl$ , but that of (II) is shifted to the alkaline side.

O. D. S.

**Solubility and flocculation of proteins and other lyophilic colloids. I.** F. HAUROWITZ and F. MARX (Kolloid-Z., 1936, 77, 65—74).—In the heat-coagulation of ovalbumin and serum solutions there is a small vol. increase, and in blood-pigment solutions a small vol. decrease. The vol. change is about 3—6% of the contraction on adding albumin to  $H_2O$ ; thus, denatured albumin has almost the same degree of hydration as natural albumin. Proteins containing negative exionic groups are pptd. by clupein. Addition of  $NaCl$  inhibits the pptn.; the ppt. has an approx. const. composition. The colloidal structure of proteins and the nature of the solvate sheath are discussed.

E. S. H.

**Adsorption of benzene derivatives by serum colloids and organ pulps.** C. SCAGLIONI (Kolloid-Z., 1936, 77, 78—85).—OH- or  $NH_2$ -derivatives are strongly adsorbed by serum or muscle, but when present together the degree of adsorption is < when present singly. The presence of  $CO_2H$  practically inhibits the adsorption due to OH or  $NH_2$  in the same mol. All the compounds except  $NH_2Ph$  are

more strongly adsorbed by serum and muscle than by liver, spleen, lung, or kidney. The bearing of the observations on metabolism is discussed.

E. S. H.

**Undulating cracks and periodical crystallisation in gelatin gel in the formation of mercuric carbonate.** F. M. SCHEMJAKIN and A. I. LAZAREVA (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 371—374).—The periodic crystallisation observed in the formation of  $HgCO_3$  from  $Na_2CO_3$  and  $HgCl_2$  in gelatin gel has been studied. The colour and form of the crystals are changed by reversing the inner and outer components.

O. D. S.

**Sensitisation of phosphatide sols by cholesterol in aqueous media.** H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 303—305).—Phosphatide sols with  $H_2O$  can be sensitised by cholesterol if the suspension is very fine and the temp. raised.

H. G. R.

**Film formation in a mixture of two hydrophilic sols: phosphatides and sodium nucleinate.** H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 511—516).—The nature of the film formed depends on the ionic concn. of the medium.

H. G. R.

**Moving-boundary method of measuring cataphoresis.** J. J. BIKERMAN (Trans. Faraday Soc., 1936, 32, 1648—1652).—The movement of the boundary between two almost identical sols of different colour is observed. Data are recorded for the boundary between an  $As_2S_3$  sol and a similar sol containing  $HgS$ .

E. S. H.

**Chemical constant and thermodynamic potential of nitric oxide gas and the gaseous equilibrium  $2NO + O_2 \rightleftharpoons 2NO_2$ , calculated from spectroscopic data.** H. ZEISE (Z. Elektrochem., 1936, 42, 785—789).—Theoretical.

E. S. H.

**Thermodynamics of endothermic processes of nitrogen fixation.** N. I. KOBOSEV, S. S. VASILIEV, and J. S. KASARNOVSKI (Acta Physicochim. U.R.S.S., 1936, 4, 245—262).—Equilibrium and energy relations have been calc. thermodynamically at 2000°, 3000°, and 3500° for the reactions  $0.5N_2 + 0.5O_2 = NO$  (a),  $0.5N_2 + CO_2 = NO + CO$  (b),  $0.5N_2 + 0.5H_2 + C = HCN$  (c),  $0.5N_2 + 0.5C_2H_2 = HCN$  (d), and  $0.5N_2 + CH_4 = HCN + 1.5H_2$  (e). The neglect of concomitant changes such as dissociation gives rise to serious errors, and the results obtained by Krase and Mackey (A., 1928, 1324) for (b) are considered to be incorrect. The reactions (c) and (d) give considerable yields of  $HCN$  and require little energy. The considerable yields of  $NO$  obtained in the glow discharge are connected with the low temp.

R. S. B.

**Displacement of equilibrium by substances which simultaneously act as catalytic accelerators. III.** N. SCHLESINGER (Acta Physicochim. U.R.S.S., 1936, 5, 79—92; cf. A., 1927, 837).—The equilibrium const. (*K*) in the reaction  $EtOH + AcOH \rightleftharpoons EtOAc + H_2O$  has been determined at 100° in presence of various salts and inorg. acids. In all (15) cases *K* decreases linearly with increase of salt concn. when the latter is expressed in millimol.

per mol. of  $\text{H}_2\text{O}$ . The displacement of equilibrium cannot be accounted for by ion hydration.

F. L. U.

**Dissociation equilibrium of sulphur trioxide.** A. F. KAPUSTINSKI and L. M. SHAMOVSKI (Acta Physicochim. U.R.S.S., 1936, 4, 791—802).—The equilibrium  $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 0.5\text{O}_2$  has been studied at 850—1000° abs. in a static system containing a heated Pt wire. The data are expressed by  $\log (p_{\text{SO}_2})(p_{\text{O}_2})^{1/2}/p_{\text{SO}_3} = 5005/T + 4.743$ .  $\Delta S = 21.68$  g.-cal. per 1° and  $\Delta H = 22.88$  kg.-cal. per mol.

H. J. E.

**Evidence for the complete dissociation of salts at all concentrations in aqueous solutions.** W. H. BARNES (J. Chem. Educ., 1936, 13, 428—431).—A lecture.

L. S. T.

**Dissociation constants of different oxides in deuterium oxide.** G. SCHWARZENBACH, A. EPRECHT, and H. ERLÉNMEYER (Naturwiss., 1936, 24, 714).—The dissociation consts. of some weak acids and bases in  $\text{D}_2\text{O}$  (99.6%) have been determined potentiometrically. The normal potential of the  $\text{D}_2$  electrode is  $-0.0022$  volt, and the ionic product in  $\text{D}_2\text{O}$  (99.6%) is  $10^{-14.804}$  at 20°. The influence of  $\eta$  and the dielectric capacity on the dissociation const. is discussed.

A. J. M.

**Ionisation constant of acetic acid in dioxan-water mixtures.** H. S. HARNED and G. L. KAZANJIAN (J. Amer. Chem. Soc., 1936, 58, 1912—1915).—E.m.f. of the cells  $\text{H}_2$  (1 atm.)| $\text{AcOH}(m_1)$ ,  $\text{NaOAc}(m_2)$ ,  $\text{NaCl}(m_3)$ , dioxan- $\text{H}_2\text{O}$ | $\text{AgCl}$ - $\text{Ag}$  have been determined at 5° intervals from 0° to 50° in solutions containing 20, 45, and 70 wt.-% of dioxan. The ionisation const. of  $\text{AcOH}$ , calc. for the above temp. range, is in agreement with the empirical equation of Harned and Embree (A., 1935, 1321).

E. S. H.

**Anomalies in the dissociation constant of some halogenated organic acids.** M. BETTI and E. LUCCHI (Atti R. Accad. Lincei, 1936, [vi], 23, 465—469; cf. A., 1935, 564).—*o*-Chloro-, m.p. 162°,  $[\alpha]_D + 450.9^\circ$  in  $\text{C}_6\text{H}_6$ ,  $[M]_D + 1792^\circ$ , and *o*-bromo-, m.p. 123°,  $[\alpha]_D + 410.5^\circ$  in  $\text{C}_6\text{H}_6$ ,  $[M]_D + 1815^\circ$ , *cinnamylidenepheryl*- $\beta$ -hydroxynaphthylmethylamine have been prepared from the corresponding *cinnamaldehydes*, m.p. 56—57°, b.p. 138°/10 mm., and m.p. 67°, b.p. 160°/14 mm., respectively. The results indicate that the *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}:\text{CH}$  radical is more negative than the corresponding Br-radical. The dissociation consts. of the two halogenocinnamic acids are  $0.39 \times 10^{-4}$  and that of cinnamic acid  $0.365 \times 10^{-4}$ .

O. J. W.

**Solutions of aluminium fluoride.** V. CAGLIOTI (Gazzetta, 1936, 66, 549—551).—When  $\text{CaF}_2$  is dissolved in  $\text{AlCl}_3$  a complex F ion is formed. F.p. and electrolytic data for  $\text{AlF}_3$  solutions indicate that these probably contain the complex  $[\text{AlF}_6]'''$  ion.

O. J. W.

**Equilibrium between the trioxalatomanganate and dioxalatomanganate ions.** G. H. CARTLEDGE and W. P. ERICKS (J. Amer. Chem. Soc., 1936, 58, 2065—2069).—Extinction coeffs. of  $\text{K}[\text{Mn}(\text{C}_2\text{O}_4)_3]$  (I) and  $\text{K}[\text{Mn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O}_2)]$  (II) in aq. solutions at various concns. have been determined in the visible region. (I) has max. absorption at about 520

m $\mu$  and (II) at about 450 m $\mu$ . Equilibrium between (I) and (II) is established almost instantaneously according to  $[\text{Mn}(\text{C}_2\text{O}_4)_3]''' + 2\text{H}_2\text{O} \rightleftharpoons [\text{Mn}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O}_2)]' + \text{C}_2\text{O}_4''$ ; the equilibrium const., determined spectrophotometrically, is  $3.8 \times 10^{-3}$  at 0°. Green and yellow forms of (II) give solutions with the same absorption curve; the solution probably contains an equilibrium mixture of *cis* and *trans* isomerides. The complex manganates may be derived from a covalent  $dsp^2$  structure, the fifth and sixth valency linkings being ionic or ion-dipole in character.

E. S. H.

**Effect of sugar alcohols and their anhydrides on the dissociation of boric acid.** J. C. KRANTZ, jun., C. J. CARR, and F. F. BECK (J. Physical Chem., 1936, 40, 927—931; cf. this vol., 289).—In general the anhydrides of sugar alcohols increase the dissociation of  $\text{H}_3\text{BO}_3$  < the sugar alcohols themselves, but the effect of erythritan is > that of erythritol or mannitol. Propylene glycol has no effect. The effect of  $\text{CO}(\text{CH}_2\cdot\text{OH})_2$  and glyceraldehyde is > that of glycerol.

J. W. S.

**Dynamics of the formaldehyde-hydrogen sulphite reaction.** A. SKRABAL and R. SKRABAL (Monatsh., 1936, 69, 11—41; cf. A., 1936, 684).—Redetermination of the equilibrium const. for the reaction  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3' \rightleftharpoons \text{CH}_2\text{O} + \text{SO}_3\text{H}'$  has confirmed the accepted val. The reaction velocities have been measured and the results are discussed theoretically. They do not afford support for the "principle of microscopic reversibility."

F. L. U.

**Theory of binary solutions.** E. HÜCKEL (Z. Elektrochem., 1936, 42, 753—778).—A re-statement of thermodynamical principles on which Hückel's theory rests, with particular reference to solutions of long-chain mols.

E. S. H.

**Determination of activity coefficients from the potentials of concentration cells with transference. II. Hydrochloric acid at 25°.** T. SHEDLOVSKY and D. A. MACINNIS (J. Amer. Chem. Soc., 1936, 58, 1970—1972).—E.m.f. of the cells  $\text{Ag}, \text{AgCl}|\text{HCl}(c_1), \text{HCl}(c_2)|\text{AgCl}, \text{Ag}$ , where  $c_1 = 0.1N$  and  $c_2 = 0.003$ — $0.08N$ , have been determined. The activity coeffs. follow the Debye-Hückel theory with a distance of closest approach of 5.62 Å. up to about  $0.04N$ . At  $0.003$ — $0.1N$  accurate agreement with the Hückel equation is observed.

E. S. H.

**Thermodynamics of hydrochloric acid in dioxan-water mixtures from electromotive force measurements. I. Standard potentials.** H. S. HARNED and J. O. MORRISON (J. Amer. Chem. Soc., 1936, 58, 1908—1911).—E.m.f. of the cells  $\text{H}_2$  (1 atm.)| $\text{HCl}(m)$ , dioxan- $\text{H}_2\text{O}$ | $\text{AgCl}$ - $\text{Ag}$  have been determined at 5° intervals from 0° to 50° in solutions containing 20, 45, and 70% of dioxan and  $0.003$ — $0.2M$ - $\text{HCl}$ . The standard electrode potentials have been evaluated.

E. S. H.

**Activity and osmotic coefficients of aqueous solutions of lanthanum chloride at 25°.** C. M. MASON and G. L. ERNST (J. Amer. Chem. Soc., 1936, 58, 2032—2033).—The activity and osmotic coeffs. have been calc. from v.-p. data, determined by the isopiestic method.

E. S. H.



**Thermodynamic properties of fused salt solutions. IX. Lithium chloride in silver chloride.** E. J. SALSTROM, T. J. KEW, and T. M. POWELL (J. Amer. Chem. Soc., 1936, 58, 1848—1850).—E.m.f. of the cells  $\text{Ag}(s), \text{AgCl}$  in  $\text{LiCl}(l), \text{Cl}_2(g)$  have been determined at mol. fractions of  $\text{AgCl}$  from 1.000 to 0.136 and 500—635°. The activity, activity coeff., free energy of formation and of dilution, entropy, and heat of formation of  $\text{AgCl}$  at 500° and 600° have been calc. The activity, activity coeff., and partial mol. free energy of  $\text{LiCl}$  have been calc. from the Duhem relations. Positive deviations of the activities from ideality are discussed. E. S. H.

**Comminution and chemical affinity.** R. SCHENCK (Z. Elektrochem., 1936, 42, 747—752).—Published work on the influence of particle size on chemical equilibria is discussed. E. S. H.

**Significance of solubility product of very sparingly soluble salts.** E. LANGE and K. NAGEL (Z. physikal. Chem., 1936, 177, 321—330).—Theoretical. The relation between the solubility product,  $s$ , and the standard free energy of formation,  $K$ , and the e.m.f.,  $E$ , of a standard galvanic cell in which the salt is formed is given by  $K = -EF = ET \log_e s$ . If the concns. of the ions of the salt are large enough to be thermodynamically significant ( $> 10^{-10}N$ ), the usual calculations made by means of the solubility product principle are thermodynamically free from objection. When small concns. are involved, however, such calculations, whilst yielding vals. for electrode potentials in accord with experiment, have no theoretical significance, and in such cases the only theoretical basis for the calculation of electrode potentials is the above equation. R. C.

**Solubility relationships in mixtures of brassidic acid with erucic acid, methyl brassidate, and ethyl brassidate.** L. J. P. KEFFLER and A. M. MAIDEN (J. Physical Chem., 1936, 40, 905—917).—Determination of m.p. is to be preferred to the study of cooling curves in the determination of the phase-rule diagrams for mixtures of long-chain compounds. The binary systems of brassidic acid (I) with erucic acid (II), Me and Et brassidate are all simple eutectic systems. The solubility curves of (I) in the two esters are identical. The ideal solution law holds for (I) and (II), but not for systems containing the esters, which yield an S-shaped curve when  $\log N$  is plotted against  $1/T$ . The solubility of (I) in the esters is always less than the ideal solubility. All these compounds appear to exist in the simplest possible mols. in the liquid state, and no evidence could be obtained for the existence of a second cryst. form of any of them. J. W. S.

**Crystal chemistry. I. Graphic classification of binary systems.** C. W. STILLWELL (J. Chem. Educ., 1936, 13, 415—419).—In the classification adopted, crystal structure and other data are used to illustrate the influence of the properties of ions and atoms on the structure and properties of the crystals formed by their compounds. The binary systems are divisible into groups which include respectively the alloys, the ionic and at. compounds, and the mol. compounds. L. S. T.

**Thermodynamic calculation of the composition of binary compounds.** H. W. HERREILERS (Rec. trav. chim., 1936, 55, 921—924).—The  $p$ - $T$  diagram near a quadruple point is considered and the equilibrium has been calc. R. S.

**Water of crystallisation of certain complex salts and of nickel sulphate.** I. N. PLAKSIN (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 271—278).—Tensimetric measurements confirm the existence of  $\text{NiSO}_4 \cdot 1, 6$ , and  $7\text{H}_2\text{O}$ , but not of 3 and  $4\text{H}_2\text{O}$ , and establish the existence of  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ . Tensimetric data for the system  $\text{Cr en}_3\text{Cl}_3 \cdot \text{H}_2\text{O}$  at 25° suggest the formation of a dihydrate, and of a series of solid solutions of  $\text{H}_2\text{O}$  in the latter, whilst in the system  $(\text{NH}_4)_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$  a series of solid solutions of  $\text{H}_2\text{O}$  in the anhyd. salt and its pentahydrate are indicated. R. T.

**Dissociation pressure of crystal hydrates of variable composition.** B. A. MUROMTSEV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 279—289).—Tensimetric data at 25° and 35° indicate that the systems  $[\text{Co en}_3\text{Cl}_3]_2, \text{CoCl}_2 \cdot \text{H}_2\text{O}$  and  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  consist of unbroken series of solid solutions. R. T.

**Static method for the determination of the equilibria of metals with carbon dioxide.** A. F. KAPUSTINSKI and A. SILBERMAN (Acta Physicochim. U.R.S.S., 1936, 4, 495—504).—A method is described by which equilibria of the type  $\text{M} + \text{CO}_2 = \text{MO} + \text{CO}$  can be investigated at const. pressure of  $\text{CO}_2$ . It is applied to the equilibrium between Sn and  $\text{CO}_2$  with results in agreement with those obtained by dynamic methods. The data correspond with  $0.5 \log K_p = 606.4/T - 1.1576$  from 600° to 1100°,  $\Delta F = 5546 - 10.587T$ , and  $\Delta H_0 = 5546$  g.-cal. O. D. S.

**Basic acetates of lead.** R. DUBRISAY and A. SAINT-MAXEN (Compt. rend., 1936, 203, 584—586).—The systems obtained on the addition of aq.  $\text{NH}_3$  or  $\text{NaOH}$  to  $\text{Pb}(\text{OAc})_2$  have been examined and evidence obtained for the existence of solid phases corresponding with  $(\text{OAc})_2[\text{Pb}_3\text{O}(\text{OH})_2]$  and  $\text{O}[\text{Pb}_3\text{O}(\text{OH})_2]$ . J. G. A. G.

**System magnesium sulphate-carbamide-water at 30°.** C. W. WHITTAKER, F. O. LUNDSTROM, and J. H. SHIMP (J. Amer. Chem. Soc., 1936, 58, 1975—1977).—Data for 30° show the solid phases  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{CO}(\text{NH}_2)_2$ . E. S. H.

**Equilibria in the system water-lithium chloride-ammonium chloride.** N. K. VOSKRESENSKAJA and O. K. JANATJEVA (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 291—293).—Equilibrium data are recorded. R. T.

**System bismuth iodide-rubidium iodide-water.** (MLLE.) M. L. DELWAULLE (Bull. Soc. chim., 1936, [v], 3, 1820—1822).—Data for 12° indicate the existence of the compounds,  $\text{BiI}_3 \cdot 3\text{RbI}$  and  $2\text{BiI}_3 \cdot 3\text{RbI}$ . J. W. S.

**System  $\text{K}_2\text{O}-\text{PbO}-\text{SiO}_2$ .** R. F. GELLER and E. N. BUNTING (J. Res. Nat. Bur. Stand., 1936, 17, 277—289).—The system has been examined by methods involving quenching, petrographic study, and, in certain cases, heating curves. The existence

of four ternary compounds with mol. ratios 1:2:2, 1:4:8, 1:1:4, and 2:1:3 has been established, and optical properties indicate the existence of a fifth. The fields of stability of the various unary, binary, and ternary compounds have been determined, and 14 quintuple invariant points located. D. C. J.

System alkali oxide- $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ . VI. Equilibria in the system  $\text{CaO-SiO}_2\text{-CO}_2$ . C. KROGER and K. W. ILLNER (Z. anorg. Chem., 1936, 229, 197-224; cf. A., 1936, 31).—Dissociation pressures of  $\text{CaCO}_3$  are unaffected by the presence of  $\text{Ca}_2\text{SiO}_4$ , but considerably increased by  $\text{Ca}_3\text{Si}_2\text{O}_7$ . Equilibria in the reaction  $2\text{Ca}_2\text{SiO}_4 + \text{CO}_2 \rightleftharpoons \text{Ca}_3\text{Si}_2\text{O}_7 + \text{CaCO}_3$  have been determined. Direct reaction occurs between  $\text{SiO}_2$  and  $\text{CaCO}_3$ , independent of the dissociation of the latter. Heats of reaction are calc. F. L. U.

Hydrolytic equilibria of calcium aluminate hydrates. E. P. VON POLHEIM (Mitt. zementtech. Inst. Tech. Hochsch. Berlin, 1935, 51, 45 pp.; Zement., 1935, 24, 643-648; Chem. Zentr., 1936, i, 142).—The limiting concns. of dissolved  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  permitting the stable existence of  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$  (I), and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  (II) in solution, are considered. According to the  $[\text{CaO}]$ , any consecutive pair of the substances  $\text{Al}(\text{OH})_3$ , (I), (II), and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  may coexist as solid phase. The reactions of the anhyd. Ca aluminates with  $\text{H}_2\text{O}$  are discussed. J. S. A.

Complex formation involving weak acids. XVI. (a) Isotherms at  $18^\circ$  of the systems: sodium oxalate-copper (or zinc or magnesium) oxalate-water. (b) Solubility of copper, zinc, and magnesium oxalates in solutions of oxalic acid and sulphuric acid. (c) Potentiometric investigation of the complex anion,  $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$ . H. T. S. BRITTON and A. A. MOSS. XVII. System sodium oxalate-thorium oxalate-water at  $25^\circ$ . H. T. S. BRITTON and M. E. D. JARRATT (J.C.S., 1936, 1489-1493, 1494-1495).—XVI.  $\text{M}^{14}\text{C}_2\text{O}_4\text{-Na}_2\text{C}_2\text{O}_4\text{-H}_2\text{O}$  mixtures have been studied at  $18^\circ$ . The solid components  $\text{Na}_2\text{Zn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Mg}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  could not be isolated.  $\text{CuC}_2\text{O}_4$  and  $\text{ZnC}_2\text{O}_4$  are insol. in  $\text{H}_2\text{C}_2\text{O}_4$  but  $\text{MgC}_2\text{O}_4$  dissolves to form  $\text{Mg}(\text{HC}_2\text{O}_4)_2$ . The solubility product of  $\text{MgC}_2\text{O}_4$  has been calc. Evidence of the existence of  $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$  has been obtained from potentiometric and analytical determinations.

XVII. Phase-rule studies show that  $\text{Na}_4\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 6\text{H}_2\text{O}$  is stable only in presence of excess of  $\text{C}_2\text{O}_4^{2-}$ . R. S.

Addition compounds of phosphorous acid with certain organic compounds. H. L. REDFIELD and G. B. KING (J. Physical Chem., 1936, 40, 919-925).—The f.-p. diagrams for the binary systems of  $\text{H}_3\text{PO}_3$  with  $\text{AcOH}$ ,  $\text{CCl}_3\text{-CO}_2\text{H}$ ,  $\text{AcCO}_2\text{H}$ ,  $\text{PhOH}$ ,  $\text{COPhMe}$ , piperonal, and coumarin have been determined, but no compound formation is indicated. The solubilities at  $25^\circ$  of  $\text{PhOH}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , succinic and citric acid in aq.  $\text{H}_3\text{PO}_3$  of various concns. have been determined and compared with similar data for  $\text{H}_3\text{PO}_4$  (A., 1931, 922). Kendall's acidity rule holds for solutions, but not for f.-p. equilibria. The m.p. (corr.) of  $\text{H}_3\text{PO}_3$  is  $74.4^\circ$ . J. W. S.

Double decomposition in the absence of a solvent. XXIX. Stable complex of mutual systems. XXX. Representation of quinary complex mutual systems. V. P. RADISCHTSHEV (Ann. Sect. d'Anal., Physico-Chim., 1936, 9, 203-218, 219-253).—Theoretical. R. T.

(A) Representation of multicomponent systems. Spiral co-ordinates. (B) Representation of properties in ternary systems. Method of central and peripheral vectors. V. J. ANOSOV (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 5-25, 27-32).—Theoretical. R. T.

Equilibria in the saturated solutions of salts occurring in sea-water. II. Quaternary system  $\text{MgCl}_2\text{-CaCl}_2\text{-KCl-H}_2\text{O}$  at  $0^\circ$ . I. IGELSRUD [with T. G. THOMPSON] (J. Amer. Chem. Soc., 1936, 58, 2003-2009; cf. this vol., 429).—The solid phases occurring are  $\text{KCl}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ . The isotherm at  $0^\circ$  is characterised by the slight solubility of  $\text{KCl}$  or  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$  in solutions saturated with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . E. S. H.

Heat of formation of the nitrogen molecule from atoms set free in the thermal decomposition of  $\text{Pt-N}$ . H. DAMIANOVICH and G. BERRAZ (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 61-71).—The product formed by cathodic sputtering in a N atm. glows when heated quickly in air or vac., due to the formation of  $\text{N}_2$ . The heat of formation is approx. 150,000 g.-cal. H. J. E.

Specific heat, entropy, and heat of formation of iron carbide,  $\text{Fe}_3\text{C}$ . C. SCHWARZ and H. ULICH (Arch. Eisenhüttenw., 1936-1937, 10, 11-12, 91).—Calculations from published data give the heat content of  $\text{Fe}_3\text{C}$  at  $25.2^\circ$  as 4072 g.-cal. per mol., entropy 23.9 g.-cal. deg. $^{-1}$  per mol., and the free energy of formation from  $\alpha\text{-Fe}$  and  $\beta\text{-graphite}$  +2600 g.-cal. per mol. The heat contents for temp. between  $104.3^\circ$  and  $763.3^\circ$  are shown to agree closely with the experimental vals. A. R. P.

Hydrogen cyanide. IX. Conductivity of electrolytes in anhydrous hydrogen cyanide: some ammonium and tetra-alkylammonium salts at  $18^\circ$ . J. E. COATES and E. G. TAYLOR (J.C.S., 1936, 1495-1500; cf. this vol., 1341).—The conductivities of  $\text{NH}_4$ ,  $\text{NMe}_4$ , and  $\text{NEt}_4$  chloride, bromide, iodide, nitrate, and perchlorate, and of  $\text{NH}_4\text{CNS}$  and  $\text{NMe}_4$  picrate in  $\text{HCN}$  have been determined. The  $\text{NMe}_4$  and  $\text{NEt}_4$  compounds show large negative deviations from the Debye-Hückel-Onsager equation, but for  $\text{NH}_4$  compounds the agreement is good. R. S.

Electrolytic dissociation of  $\alpha\gamma\gamma$ -tetracyanopropene and  $\alpha\gamma\gamma$ -tetracyano- $\beta$ -methylpropene. Y. URUSHIBARA and M. TAKEBAYASHI (Bull. Chem. Soc. Japan, 1936, 11, 569-575).—According to conductivity and e.m.f. data the degrees of dissociation of  $\alpha\gamma\gamma$ -tetracyano-propene (I) and  $\beta$ -methylpropene (II) are shown to be comparable with the val. for  $\text{HCl}$ . (I) and (II) are strongly acidic and dissolve Zn, Mg, and Sn at room temp. The metallic salts resemble the corresponding chlorides in their solubility in  $\text{H}_2\text{O}$ . The solubilities of the Ag salts of (I) and (II) are respectively 0.1 and 0.388 g. per litre. In aq. solution



the dissociation is supposed to be directly attributable to the enimine form as represented by  
 $(\text{CN})_2\text{C}:\text{CH}:\text{C}(\text{CN})\text{:C}:\text{NH} \rightleftharpoons (\text{CN})_2\text{C}:\text{CH}:\text{C}(\text{CN})\text{:C}:\text{N}' + \text{H}'$   
 C. R. H.

**Electrical conductivity of glass-forming barium borate.** B. MARKIN and R. MÜLLER (*Acta Physicochim. U.R.S.S.*, 1936, 4, 471—480).— $\kappa$  data for fused mixtures (glasses) of  $\text{BaO} + \text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O} + \text{BaO} + \text{B}_2\text{O}_3$ , and  $\text{ZnO} + \text{B}_2\text{O}_3$  indicate bivalent cation movement where the amount of corresponding metallic oxide is large. In the expression  $\log_e \kappa = -A/T + B$ , where  $A$  and  $B$  are consts., the val. of  $A$  is increased by introducing Ba glasses into Na glasses. The energy of dissociation of the ions,  $E = 2AR$ , for Ba and Zn glasses is considered to be double that for the Na glasses.  
 C. R. H.

**High-frequency conductivity of colloidal electrolytes. II. Alkali and alkaline-earth caseinates.** G. SCHMID and A. V. ERKKILÄ (*Z. Elektrochem.*, 1936, 42, 781—785; cf. this vol., 1461).—The high-frequency effect is about twice as great for the alkaline-earth as for the alkali caseinates, but there is little difference between the individual members of each series. The charge of the cation appears to be the dominating factor. Published work on transport nos. in these solutions is discussed.  
 E. S. H.

**Use of the "skin" effect in the investigation of thin metallic layers.** J. GOLDFELD and N. I. KOBOSOV (*Acta Physicochim. U.R.S.S.*, 1936, 5, 243—270).—The variation of the high-frequency resistance  $R_H$  of thin layers of metals on a metal of different magnetic permeability  $\mu$  has been calc. In the case of Fe deposited on Pt or Ag,  $R_H$  reaches a max. after about 6 min. The influence of layer thickness and c.d. has been investigated. For a given thickness  $R_H$  depends on  $\mu$ , whilst  $\mu$  varies with the structure of the layer. The increase of  $\mu$  with time is attributed to the crystallisation of the layer. If the wire is heated in  $\text{H}_2$ , diffusion of Fe into the interior occurs and the rate of diffusion has been calc., but in air, all the Fe is oxidised. The diffusion of Zn in Fe has also been studied.  
 R. S.

**Absorption and dispersion of short electric waves in solutions of electrolytes in glycerol.** W. SCHMACKS (*Ann. Physik*, 1936, [v], 27, 285—298).—The dielectric const. and high-frequency conductivity of glycerol and glycerol solutions of  $\text{MgSO}_4$  of concn. from  $10^{-1}$  to  $10^{-3}$  g. per litre have been measured at  $\lambda\lambda$  from 10 to 20 m. A max. conductivity of  $\text{MgSO}_4$  has been observed at about 14 m.  
 O. D. S.

**Transfer resistance.** G. CHEN (*Sci. Rep. Nat. Univ. Peking*, 1936, 1, No. 3, 13—18).—A review.

**Gold and copper in salt crystals and synthetic sylvine.** M. J. BOGOMOLOVA (*Acta Physicochim. U.R.S.S.*, 1936, 5, 161—172).—The diffusion velocities of Au and Cu in NaCl and KCl have been studied and the ionic mobilities  $\mu$  determined, making use of the colouring action of electrons from a Na cathode.  $\mu$  is greater in KCl, and  $\text{Cu}^{++}$  is more mobile than  $\text{Au}^{+++}$  in each case, contrary to the order expected from the ionic diameters, whilst the plot of  $\log \mu$  against  $1/T$

is a straight line. When the crystal has been subjected to previous electron-colouring  $\mu$  is diminished owing to colloid formation.  
 R. S.

**Contact potential between fluid amalgam and mercury in a vacuum. I. Contact potential between sodium amalgam and mercury.** O. CHALTIKIAN and M. PROSKURNIN (*Acta Physicochim. U.R.S.S.*, 1936, 4, 263—274).—The contact potential between Hg and Na amalgam has been found to rise to an approx. const. val. of  $1.1 \pm 0.1$  volt at 0.025—0.09% of Na.  
 R. S. B.

**Platinum electrode. II. Adsorption properties of the platinum electrode.** A. SCHLIGIN, A. FRUMKIN, and V. MEDVEDOVSKI (*Acta Physicochim. U.R.S.S.*, 1936, 4, 911—928; cf. this vol., 1207).—The adsorption of  $\text{H}_2\text{SO}_4$ , HCl, HBr,  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ , NaCl + HCl, NaBr + HBr, NaCl + NaOH, NaBr + NaOH, and KOH at various potentials of the Pt electrode has been determined by  $p_H$  measurements. The results are compared with capacity measurements with the same electrode. Changes in the amount adsorbed on treating a  $\text{H}_2$ -saturated electrode with  $\text{O}_2$  and also on reducing an oxidised electrode by  $\text{H}_2$  are recorded.  
 H. J. E.

**Germanium. XVII. Electrochemical behaviour of germanium.** R. SCHWARZ, F. HEINRICH, and E. HOLLSTEIN (*Z. anorg. Chem.*, 1936, 229, 146—160; cf. this vol., 618).—The e.m.f. of Ge-calomel electrode combinations, using various aq. electrolytes, is neither const. nor reproducible unless  $\text{O}_2$  is excluded, and even in the latter event it is not exactly reproducible owing to variations in the surface condition. The normal potential  $\text{Ge}/\text{Ge}^{+++}$  cannot be determined by e.m.f. measurements in aq. solution. Ge can be determined electrolytically by deposition with Sn from alkaline oxalate solution.  
 F. L. U.

**Potential of platinum in solutions of silver salts.** A. OBRUTSCHEVA and A. FRUMKIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1936, 4, 11—13).—Bright Pt and Au in  $\text{AgNO}_3$  solution exhibit the potential of Ag in a few min. (cf. A., 1934, 257). Small platinised electrodes behave similarly although a much longer time is required. In this case the potential is at first (in the acidified solution) more positive than the Ag potential and changes in a direction opposed to that expected by an adsorption of  $\text{Ag}^+$ . Ag crystals are formed when the electrodes reach the val. of the reversible Ag potential, especially in the case of the platinised electrodes. Large platinised electrodes give a change of potential in the same direction, but do not reach the val. for the reversible  $\text{Ag}^+$  potential. When the large electrodes are agitated in the solution until a const. val. is reached the latter is no longer able to alter the potential of a new small electrode. A bright Pt electrode in this solution attained the Ag potential only after some hr. This solution recovered its original properties after warming with Ag powder at  $50^\circ$  or after strong illumination for many hr. These effects are not due to  $\text{Ag}^+$  adsorption, but to a small amount of a reducing substance in the Ag solution. This substance reduces the acids chemically bound to the Pt surface and then the separation of Ag results. A Ag ion of lower

valency ( $\text{Ag}_2^+$ ) is suggested as the electrochemically active material. D. C. J.

Periodic potential oscillations of iron in chromic-sulphuric acid solutions. III. M. KARSCHULIN (Z. Elektrochem., 1936, 42, 722—729; cf. A., 1934, 601, 1072).—Fe dissolves primarily as  $\text{Fe}^{2+}$ , which is subsequently oxidised to  $\text{Fe}^{3+}$  by  $\text{CrO}_3$ . The oscillations in the negative direction (with respect to a saturated  $\text{Hg}_2\text{Cl}_2$  electrode) occur when formation of  $\text{Fe}^{2+}$  and oxidation to  $\text{Fe}^{3+}$  are separated by a time interval in consequence of the diffusion layer at the Fe surface. The potential limits are then conditioned by the  $[\text{Fe}^{2+}]$  and the ratio  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$  at the Fe surface. Oscillations in the positive direction occur when  $[\text{H}^+]$  in the neighbourhood of the Fe surface decreases so that  $\text{Fe}(\text{FeO}_2)_2$  is formed. The positive potential then reached is several hundred mv. < that of passive Fe in aq.  $\text{CrO}_3$ . E. S. H.

Meaning of diffusion potential. E. A. GUGGENHEIM (Phil. Mag., 1936, [vii], 22, 983—987).—The significance of diffusion potential in cells with liquid-liquid junctions is discussed. A. J. E. W.

Electromotive force of the cell  $\text{Zn-Hg}$  (2-phase)  $|\text{ZnSO}_4 (m) \text{ PbSO}_4 (s)|\text{Pb-Hg}$  (2-phase) and its temperature coefficient at  $25^\circ$  and concentrations from 0.05 to 1.5M. J. KIELLAND (J. Amer. Chem. Soc., 1936, 58, 1855—1857).—E.m.f. data and activity coeffs. of  $\text{ZnSO}_4$  are recorded. E. S. H.

Voltaic pile readily made from electrolytes. A. THIEL (Z. Elektrochem., 1936, 42, 742—744). Electrical effects produced by the contact of series of electrolytic solutions are described. E. S. H.

Passive metals in bimetallic electrode pairs. L. WOLF (J. pr. Chem., 1936, [iii], 147, 133—144; cf. this vol., 305, 582).—The use of one passive metal as reference electrode in the bimetallic electrode pairs employed in potentiometric titrations is described. This electrode is rendered passive by addition of a passivator, generally  $\text{NaNO}_3$  or  $\text{HNO}_3$ , to the solution to be titrated. The following electrode pairs have been tested;  $\text{Cr/Ag}$ ,  $\text{Cr/Hg}$ ,  $\text{Cr/Pt}$ ,  $\text{V2A alloy/Ag}$ ,  $\text{V2A/Hg}$ ,  $\text{V2A/Pt}$ . J. W. S.

Energy of electrolytic reduction of some substances with the atomic groups  $\text{C}\cdot\text{O}$  and  $\text{C}\cdot\text{C}$ . G. SEMERANO and A. CHISINI (Gazzetta, 1936, 66, 510—518).—The molar reduction potentials at a dropping Hg cathode of  $\text{CH}_3\text{Ph}\cdot\text{CH}\cdot\text{CHO}$ ,  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ , and  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  dissolved in 0.1N- $\text{NH}_4\text{Cl}$  in 50% EtOH are  $-1.383$ ,  $-0.784$ , and  $-1.456$  volts, respectively. The two aldehydes are converted into the corresponding hydrobenzoin, and the acid is reduced to  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The relation between chemical constitution and molar reduction potential is discussed. O. J. W.

Colouring matters of *Drosera Whittakeri*. IV. Reduction potentials of some naphthaquinones. J. W. H. LUGG, A. K. MACBETH, and F. L. WINZOR (J.C.S., 1936, 1457—1462; cf. A., 1935, 623).—The normal reduction potentials,  $E_0$ , of 1:4-naphthaquinone, methylnaphthaquinone, lawsone, juglone, phthiocol, isonaphthazarin, methylnaphthazarin (I), naphthazarin, hydroxyjuglone, naphtha-

purpurin (II), hydroxydroserone (III) (natural and synthetic), and lomatiol have been determined by Fieser's method (A., 1935, 585). Fieser's conclusions relative to the additivity of  $E_0$  are confirmed. The results indicate that in (I), (II), and (III), the substituent is in the quinonoid ring. R. S.

Determination of decomposition potentials of fused salts. R. C. KIRK and W. E. BRADT (Trans. Electrochem. Soc., 1936, 70, Preprint 26, 317—326; cf. this vol., 430).—Decomp. potentials for fused alkali and alkaline-earth halides and certain other salts have been measured by the direct method. The depolarisation found by this method is cathodic rather than anodic and may be eliminated by the substitution of Pt for graphite cathodes. Vals. obtained by extrapolation to zero current with Pt cathodes are in good agreement with those given by the commutator method (cf. A., 1928, 135) and also with the calc. equilibrium reaction potentials. O. J. W.

Determination of decomposition potentials of fused salt mixtures containing tantalum oxide. R. C. KIRK and W. E. BRADT (Trans. Electrochem. Soc., 1936, 70, Preprint 27, 327—333).—The decomp. potential of  $\text{K}_2\text{TaF}_7$  in fused KCl (with and without the addition of  $\text{Ta}_2\text{O}_5$ ) is < that of fused KCl, and Ta is deposited. Measurements with 14 fused salts containing  $\text{Ta}_2\text{O}_5$  gave no decomp. potential corresponding with the Ta compound, and no Ta was deposited from these mixtures. It is suggested that current-potential diagrams obtained by the direct method may provide information relative to the behaviour of fused salt mixtures in electrodeposition. O. J. W.

Polarisation capacity of the mercury electrode. T. BORISSOVA and M. PROSKURNIN (Acta Physicochim. U.R.S.S., 1936, 4, 819—828).—The capacity of the double layer on Hg in  $\text{N-HCl}$ ,  $\text{-KCl}$ , and  $\text{-CsCl}$  first decreases with increasing negative polarisation, then increases to a max. at 0.4—0.5 volt, and finally passes through a min. at approx. 1.1 volt. The max. persists after careful purification and is attributed to a deformation or dehydration of the anion. The rise in the curve at high cathode polarisations is due to deformation of the cation. H. J. E.

Hydrogen overvoltage at high current densities. B. KARANOV (Acta Physicochim. U.R.S.S., 1936, 5, 193—200).—An apparatus for the determination of H overvoltages with c.d. up to 100 amp. per sq. cm. is described. The relation between overvoltage and log c.d. for Ag amalgam, Ag, and Pt is linear, in agreement with Volmer's theory. R. S.

Hydrogen overvoltage in non-aqueous solutions. I. S. LEVINA and M. SILBERFARB (Acta Physicochim. U.R.S.S., 1936, 4, 275—282).—H overvoltage ( $V$ ) on a Hg cathode has been determined for c.d.  $10^{-6}$ — $10^{-2}$  amp. per sq. cm. at  $25^\circ$  in 0.01—0.54N- $\text{HCl}$  in EtOH. For c.d. ( $i$ ) =  $10^{-6}$ — $10^{-3}$  amp. per sq. cm.,  $V = a + b \log i$ , where  $a$  and  $b$  are const., and  $b = 0.11$ — $0.12$ , in agreement with the theory of Erdey-Gruz and Volmer (A., 1930, 1376).  $V$  is independent of the duration of the experiment and of  $[\text{HCl}]$ , and is < for aq. solutions. R. S. B.



**Overvoltage.** G. CHEN (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 3, 1—11).—A review and discussion.

**Effect of pressure on the passivity of iron powder in alkali medium.** T. C. HUANG (J. Chinese Chem. Soc., 1936, 4, 406—412).—When the Fe powder in an Edison cell is packed under increasing pressure, the discharge potential shows a corresponding decrease in the passivity of the Fe. D. C. J.

**Passivity phenomena. XXX. Passivity phenomena at magnesium anodes in acid solutions.** W. J. MÜLLER and E. NACHTIGALL (Monatsh., 1936, 69, 1—10; cf. A., 1928, 713).—When Mg in the form of a protected electrode is anodically polarised at 3—12 volts in  $N\text{-H}_2\text{SO}_4$ , the current gradually falls to about  $\frac{1}{3}$  of its initial val. In the early stages the bright metal becomes covered with a black film, which breaks down and gives place to a matt grey surface. The latter is formed before the min. current is established, and persists during the period of passivity. By decreasing  $[\text{H}^+]$  at const.  $[\text{SO}_4^{2-}]$  the time required to attain passivity is slightly shortened. Mg also exhibits passivity in aq.  $\text{HNO}_3$ , but not in  $\text{HCl}$ .

**Polarographic studies with the dropping mercury electrode. IV. Influence of circuit resistance on maxima of current-voltage curves.** R. BRDIČKA (Coll. Czech. Chem. Comm., 1936, 9, 419—433; cf. this vol., 430).—The current max. obtained with 0.01N- $\text{Hg}_2(\text{NO}_3)_2$  in 0.005N- $\text{HNO}_3$  decreases as the resistance,  $R_e$ , external to the electrolyte is increased. Oscillographically recorded current-time curves for the formation of single drops show that the cathode is unpolarisable at  $<$  a sp. e.m.f. and yields large currents  $\propto$  the e.m.f. With o.m.f.  $>$  the sp. val., the Hg drop is polarised at all stages of growth. The polarisation increases linearly with e.m.f., so that the current always reaches the same val., corresponding with the "diffusion current." The discontinuous fall of current at a polarographic max. occurs at the same e.m.f. whatever the val. of  $R_e$  and is attributed to the polarisation of drops at the moment of formation. If  $R_e$  is increased, however, the drop becomes depolarised during growth unless the e.m.f. is sufficiently raised, in which case the diffusion current is always attained. J. G. A. G.

**Polarographic analysis in the study of keto-enol tautomerism.**—See this vol., 1488.

**Electrolysis of aqueous solutions of sodium and zirconyl sulphates.** I. W. E. BRADT and H. B. LINFORD (Trans. Electrochem. Soc., 1936, 70, Preprint 30, 363—371).—From these solutions Zr is deposited under certain conditions as a silver-white, compact, and adherent metal similar to Ni electroplate. This changes slowly to a non-adherent black powder, which may be Zr or some oxidation product. O. J. W.

**Conception of electrokinetics as an integral part of electrochemistry of solutions.** J. W. MCBAIN (Acta Physicochim. U.R.S.S., 1936, 4, 169—172).—The analogies between electrokinetic and electrolytic phenomena are discussed. The electrokinetic potential is regarded as having no real existence. R. S. B.

**Maximum yield of the intermediate product C in two successive bimolecular reactions, (I)  $A + B \rightarrow C$  and (II)  $A + C \rightarrow D$  when the constants  $k_1$  and  $k_2$  are known.** J. STUURMAN (Rec. trav. chim., 1936, 55, 934—936).—The calculation has been applied to the oxidation of thianthren by  $\text{AcO}_2\text{H}$  (cf. this vol., 1518). R. S.

**Chemical kinetics of dielectric relaxation.** F. C. FRANK (Trans. Faraday Soc., 1936, 32, 1634—1647).—Theoretical. The theory of unimol. chemical reaction velocities is applied to the process of change of orientation of a polar mol. in a substance showing dielectric loss and dispersion. Published data for different types of physical systems are discussed. E. S. H.

**Explosive limits of gaseous mixtures. I. Explosion limits of mixtures of hydrogen and air.** M. RIVIN and A. SOKOLIK (Acta Physicochim. U.R.S.S., 1936, 4, 301—316).—The conditions for initiating detonation waves have been investigated for  $\text{H}_2$ -air mixtures. The curve for explosion limit as a function of pressure and %  $\text{H}_2$  shows two min. which depend on energy of the igniting spark. With  $\text{H}_2$ - $\text{O}_2$  mixtures the curve for explosion limits has a min. at 100 mm. and 55%  $\text{H}_2$ . At 1 atm. explosion is possible between 23 and 85%  $\text{H}_2$ . The velocity of the explosion wave does not agree with theory, owing probably to dissociation in the front of the wave. The propagation and extinction of the flame and change in pressure have been studied in a long tube below the explosion limit for  $\text{H}_2$  and  $\text{O}_2$ . R. S. B.

**Effect of a chemically inert gas on the velocity of the chain reaction in mixtures of n-pentane and oxygen.** M. PRETTE (Compt. rend., 1936, 203, 561—563).—At 250—270°, near the lower inflammation limit of mixtures of 119—210 mm. of  $\text{O}_2$  and 119—209 mm. of  $\text{C}_5\text{H}_{12}$ ,  $\text{N}_2$  accelerates the reaction, but at 300—350°, near the upper limit of inflammation,  $\text{N}_2$  retards the reaction between 20—57 mm. of  $\text{C}_5\text{H}_{12}$  and 82—100 mm. of  $\text{O}_2$ . J. G. A. G.

**Inhibition by hydrogen of the chain reaction of mixtures of n-pentane and oxygen.** M. PRETTE (Compt. rend., 1936, 203, 619—620).—Addition of  $\text{H}_2$  (approx. 150—300 mm.) to a mixture of  $\text{C}_5\text{H}_{12}$  (50—308 mm.) and  $\text{O}_2$  (84—306 mm.) at 240—280° retards the slow oxidation and may prevent ignition. The  $\text{H}_2$  is most effective at 260—280°. H. J. E.

**Cold flames in mixtures of pentane and oxygen.** B. AIVAZOV and M. NEUMANN (Acta Physicochim. U.R.S.S., 1936, 4, 575—606; cf. this vol., 1344).—The conditions under which cold flames are propagated in mixtures of  $\text{C}_5\text{H}_{12}$  and  $\text{O}_2$  have been investigated. The pressure changes and change in composition of the gas during the induction period, the flame reaction, and the slow reaction which follows have been observed. Aldehydes and peroxides are formed in large amount during the flame reaction. The amounts of  $\text{CO}$  and  $\text{CO}_2$  formed are small. A slow autocatalytic reaction is observed outside the limits of the cold flame. O. D. S.

**Flame of carbon monoxide and oxygen. I. Influence of pressure on the intensity of visible**

radiation from the flame. H. KONDRATEEVA and V. KONDRATEEV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 547—555).—The ratio of the intensity of blue light emitted to the no. of  $\text{CO}_2$  mols. formed per sec. in the combustion of CO in  $\text{O}_2$  has been measured between 11 mm. and 140 mm. It rises to a max. about 40 mm. and then decreases at higher pressures in a manner corresponding with the quenching of excited mols. with an efficiency of the order of 1. It is deduced that the preliminary increase corresponds with a change from a heterogeneous reaction at low pressures to a homogeneous reaction in which  $\text{CO}_2^*$  mols. are produced.

O. D. S.

Influence of a longitudinal electric field on the combustion processes in flames. A. E. MALINOVSKI and K. E. JEGOROV (*Acta Physicochim. U.R.S.S.*, 1936, 4, 929—936; cf. A., 1930, 424).—The retardation of the movement of flame in a  $\text{C}_2\text{H}_2$ -air mixture by means of an electric field is not a mechanical effect due to transport of neutral gas mols. by the charged particles. Negative ions play an important part in propagating flame. The effect of the field on the inner cone of a 25%  $\text{C}_2\text{H}_2$ -air flame is almost independent of the rate of supply of gas. The inner cone in flames of  $\text{CH}_4$  or heavy hydrocarbons in air is affected only by voltages approaching the breakdown voltage.

H. J. E.

Propagation of combustion along the surface of inflammable liquid. V. Effect of wind on velocity of propagation. I. T. KINBARA (*Bull. Inst. Phys. Chem. Res. Japan*, 1936, 15, 871—885).—Experimental results for EtOH-air flames are discussed.

J. S. A.

Propagation of combustion along [the] surface of inflammable liquids. VI. Effect of wind on the velocity of propagation. T. KINBARA (*Bull. Inst. Phys. Chem. Res. Japan*, 1936, 15, 1090—1104; see preceding abstract).—The effect of favourable as well as unfavourable winds in decreasing the velocity of flame propagation could not be explained by the change in appearance of a moving flame, nor by the lowering of surface temp. on EtOH caused by such winds.

R. C. M.

Kinetics of simultaneous polymerisation and ring formation. G. SALOMON (*Trans. Faraday Soc.*, 1936, 32, 1627—1628).—A reply to Stoll (this vol., 1073).

E. S. H.

Kinetics of thermal decomposition of methylamine. H. J. EMELEUS and L. J. JOLLEY (*J.C.S.*, 1936, 1524—1529; cf. A., 1935, 172, 1081).—The kinetics of the slow thermal decomp. of  $\text{NH}_2\text{Me}$  at 330—390°, and of the explosive oxidation at 400—600°, have been studied by a pressure change method. The rate of the slow reaction is given by an expression of the form  $v = Ae^{\phi}$ , where  $\phi = B'p^{0.83}e^{-15,000/T}$ . The crit. explosion pressure  $p_c$  is given by  $\log_e p_c/T = A'/T + B$  ( $A$ ,  $A'$ ,  $B$ ,  $B'$  are consts.). Results for the slow and explosive oxidations are correlated on the basis of the Semenov theory of degenerate chain reactions.

A. J. E. W.

Rate of oxidation of *o*-iodobenzoic acid by peracetic acid. J. BÖESEKEN and E. WICHERLINK (*Rec. trav. chim.*, 1936, 55, 936—940).—

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*o*- $\text{C}_6\text{H}_4\text{I}\cdot\text{CO}_2\text{H}$  is oxidised by  $\text{AcO}_2\text{H}$ , the unchanged  $\text{AcO}_2\text{H}$  destroyed by  $\text{NaOH}$  and a trace of  $\text{CuO}$ , and the  $\text{IO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  formed determined by  $\text{KI}-\text{Na}_2\text{S}_2\text{O}_3$ .  $E$  and  $B$  in the equation,  $\log K = B - E/2.303RT$ , for this reaction are 15,920 and 7.9, respectively,  $k$  being about  $10^{-4}$  at 20°.

R. S. C.

Prototropy in relation to exchange of hydrogen isotopes. II. Comparison of the velocities of dissociation of a proton and a deuteron from a  $\nu$ -acid. C. L. WILSON (*J.C.S.*, 1936, 1550—1553; cf. this vol., 1344).—The rate of ionisation of 2-*o*-carboxybenzylindan-1-one (I) and its 2-deutero analogue (II) have been studied indirectly by observing the rate of bromination in aq.  $\text{AcOH}$  containing  $\text{NaOAc}$ . The first-order velocity coeff. for (I) is several times that for (II), the observed difference corresponding with a difference in the activation energies of 0.9 kg.-cal., in accord with the estimated difference of crit. energy of approx. 1 kg.-cal.

A. J. E. W.

Kinetics of certain bimolecular reactions in solution. E. A. MOELWYN-HUGHES (*Acta Physicochim. U.R.S.S.*, 1936, 4, 173—224).—A crit. review.

R. S. B.

Kinetics of oxidation of ferrous ion by nitrous acid. E. ABEL, H. SCHMID, and F. POLLAK (*Monatsh.*, 1936, 69, 125—143; cf. A., 1930, 1128).—Oxidation of  $\text{Fe}^{2+}$  by  $\text{HNO}_2$  takes place by means of concurrent reactions between  $\text{Fe}^{2+}$  and  $\text{HNO}_2$ ,  $\text{Fe}^{2+}$ ,  $\text{HNO}_2$ , and  $\text{H}^+$ , and  $\text{Fe}^{2+}$  and  $\text{NO}_2$ , the last-named being related to the  $\text{HNO}_2$  and  $\text{NO}$  present. Velocity coeffs. of the above reactions have been determined at 25° using a wide range of concns. The mechanism of the opposing reaction between  $\text{Fe}^{3+}$  and  $\text{NO}$  is discussed.

F. L. U.

Kinetics of sulphonium compounds. I. N. HELLSTROM (*Z. physikal. Chem.*, 1936, 177, 337—354; cf. A., 1932, 26).—The rate of formation in aq. solution at 25° of sulphonium salts by reaction of alkyl- and aryl-substituted thioglycolic acids and sulphide di-acids with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ ,  $\text{CH}_3\text{I}\cdot\text{CO}\cdot\text{NH}_2$ , and  $\alpha$ - and  $\beta$ -iodopropionic acid has been measured. The velocity,  $v$ , is small in acid solution, but increases with the degree of neutralisation; in neutral solution the reaction is bimol. and exhibits a salt effect,  $v$  falling with  $[\text{Na}^+]$ .  $\text{OH}^-$  ions have little or no effect on  $v$ .  $\text{CO}_2\text{H}$  and  $\text{Ph}$  in the reacting mols. retard the reaction. In some cases the sulphonium salt decomposes into alcohol and sulphide compound.

R. C.

Mechanism of elaidinisation reaction.—See this vol., 1488.

Mechanism of aromatic side-chain reactions.—See this vol., 1497.

Reaction kinetics and the Walden inversion.—See this vol., 1487.

Kinetics of adsorption of hydrogen and of deuterium by platinum. E. B. MAXTED and C. H. MOON (*J.C.S.*, 1936, 1542—1546).—The initial adsorption of  $\text{H}_2$  and  $\text{D}_2$  on Pt follows the equation  $\log a/(a-x) = kt^n$  ( $a$ =saturation capacity,  $x$ =vol. adsorbed after time  $t$ ).  $nk$ , expressing the rate of adsorption, is approx. 1.5 times as great for  $\text{H}_2$  as for  $\text{D}_2$  in the temp. range  $-79^\circ$  to  $50^\circ$ . The approxi-



ation of this ratio to the square root of the ratio of the masses of  $D_2$  and  $H_2$ , and the low activation energy (approx. 2500 g.-cal.), suggest control of the process by diffusion to the internal surface. A. J. E. W.

**Evaporation of nickel in a vacuum.** G. BRYCE (J.C.S., 1936, 1517—1518).—The rate of evaporation of Ni in a vac. has been determined for the temp. range 1250—1450° abs. by colorimetric determination of the Ni evaporated from a hot filament. The v.p. of Ni is given by  $\log_{10}(cp) = 9.148 - 2.00 \times 10^4/T$  ( $c$ —condensation coeff.). A. J. E. W.

**Wicke's reaction.** W. BOTTGER and E. THOMA (J. pr. Chem., 1936, [ii], 147, 11—21).—The time required for the production of blackening on  $Ni(OH)_2$  over which a mixture of moist  $SO_2$  and  $O_2$  (or air) is passed has been studied for  $Ni(OH)_2$  prepared and treated in different ways, for different  $[SO_2]$ , and for different temp. The effect is attributed to the formation of  $Ni(OH)_3$  through the action of a relatively stable intermediate product with a peroxide-like O-linking in the  $SO_2$ - $O_2$ - $H_2O$  mixture. J. W. S.

**Rate of absorption of oxygen by sodium sulphite solution.** W. S. E. HICKSON (Nature, 1936, 138, 645).—Stirring the interior of a solution of  $N-Na_2SO_3$  without disturbing the surface decreases the rate at which  $O_2$  is absorbed by 48% compared with the unstirred solution. L. S. T.

**Absorption velocity of sulphur dioxide by sodium iodide.** I. HIGUTI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1105—1116).—Measurements of v.p. and composition of solid phase confirmed the existence of  $3NaI \cdot 8SO_2$  and  $NaI \cdot 4SO_2$  described by Foote and Fleischer (A., 1931, 799). The rate of absorption at 0° and -21° agreed with the expression  $\log s/(s-x) = Kt^n$  previously found applicable in other cases (cf. this vol., 561). R. C. M.

**Kinetics of the sulphite process.** A. J. COREY and O. MAASS (Canad. J. Res., 1936, 14, B, 336—345).—The delignification of wood chips and meal in H sulphite solutions at 100—140° follows an approx. unimol. law, deviations being probably due to the colloidal nature of lignin and the submicroscopic structure of the wood. The energy of activation is 21,000 g.-cal. per g.-mol. The influence of pressure has been studied at 5—10 atm., using an atm. of  $N_2$ . Increase of pressure above 7 atm., the v.p. of the H sulphite solution, has no influence on the rate of delignification or quality of the product. R. S. B.

**Thermal decomposition of calcium carbonate.** A. OLIVERIO (Rend. Sem. Fac. Sci. R. Univ. Cagliari, 1934, 4, 119—121; Chem. Zentr., 1936, i, 521).—The decomp. in an air stream of 2 litres per hr. in a tube 15 mm. wide was 1.67% in 56 hr. at 420° and was almost complete in 200 hr. at 620°. H. J. E.

**Influence of form of intermediate phases on the velocity of the reduction of iron oxide by hydrogen.** G. TSCHUFAROV and B. AVERBUCH (Acta Physicochim. U.R.S.S., 1936, 4, 617—635).—The velocity of reaction of natural cryst. magnetite and hæmatite with  $H_2$  has been measured at intervals of 20° from 300° to 700°. The change in porosity during reduction was followed and the structure at

different stages of the reaction investigated by X-ray analysis. The reaction appears to be autocatalytic.  $Fe_3O_4$  is present at all stages of incomplete reduction.  $FeO$  is not observed. From 300° to 500° the porosity is independent of  $T$  and determined by the degree of reduction. Above 500° the porosity decreases rapidly with  $T$ , whilst the size of the crystals of  $\alpha$ -Fe increases. The temp. coeff. of the reaction is normal up to 550° and low above this temp. The activation energy is calc. to be 16,500 g.-cal. for magnetite and 19,500 g.-cal. for hæmatite below 550°.

O. D. S.

**Kinetics of dissolution of alkali borate glasses.** R. L. MÜLLER (Acta Physicochim. U.R.S.S., 1936, 4, 99—118; cf. this vol., 1074).—Previous work is reviewed. The rate-determining process in the case of alkali borate glasses in which the mol. fraction of  $M_2B_4O_7$  is  $< 0.5$  occurs at the surface.  $H_2O$  is first adsorbed by the surface ions, which then become fully hydrated and go into solution. The energy of activation is 10—15 kg.-cal. The results are discussed in relation to current theories of dissolution and evaporation. R. S.

**Elementary processes in the formation of metal oxide from metal and oxygen, and in related reactions.** C. WAGNER (Angew. Chem., 1936, 49, 735—740).—The diffusion processes responsible for the propagation of heterogeneous reactions of the type indicated through the compact boundary layer of compound are reviewed with reference to the author's published work. Diffusing species may be: (a) Ions, wandering by migration to empty lattice positions or between-lattice positions. In compounds with non-stoichiometric composition (e.g.,  $FeO$ ,  $Cu_2O$ ), the former mechanism operates, as shown by the rise in ionic conductivity at high temp. with the excess of O. (b) Electrons, in compounds of semi-metallic character. Where ions of variable valency occur (e.g.,  $Cu_2O$ ), these may propagate points of electron-deficit. Velocity of reaction is conditioned by the slower of the two diffusion processes, (a) or (b). The theory is applicable also to the solid reactions of silicate and spinel formation, in which the small cations are the diffusive species. J. S. A.

**Catalytic action of hydrogen on carbon monoxide flame.** H. J. WALLS (Trans. Faraday Soc., 1936, 32, 1495—1501).—When the infra-red radiation on explosion of  $CO-O_2$  mixtures containing  $H_2$  is plotted against the initial pressure of the reactants, a step occurs in the curve at pressure  $p_s$  (cf. A., 1929, 973).  $p_s$  rises with temp., and is thus not a lower ignition limit.  $p_s$  is probably the pressure at which two combustion mechanisms are equally rapid, these involving probably an O atom or thermal chain, and a H atom chain, respectively. Effects on the step produced by heating the reaction vessel are ascribed to removal of H atoms by the walls. A. J. E. W.

**Catalytic influence of chromic sulphate on the speed of decomposition of chromic acid by heat, when dissolved in sulphuric acid of varying concentration.** H. C. S. SNETHLAGE (Rec. trav. chim., 1936, 55, 874—880; cf. this vol., 1073).—The decomp. of  $CrO_3$  in aq.  $H_2SO_4$  is catalysed by  $Cr_2(SO_4)_3$ , the effect decreasing as  $[H_2SO_4]$  is increased and

becoming negative when  $[H_2SO_4]$  is  $>95\%$ . The results are in agreement with the theory that decomp. involves a bimol. and a unimol. reaction, the velocity coeffs. of which have been calc. R. S.

**Decomposition of alkaline-earth carbonates in aqueous solution on boiling.** B. L. VANZETTI and A. OLIVERIO (Rend. Sem. Fac. Sci. R. Univ. Cagliari, 1934, 4, 112—118; Chem. Zentr., 1936, i, 521).—The decomp. is influenced by the presence of Cu and Ni salts. H. J. E.

**New catalytic behaviour of mercuric salts.** I. G. TRAVAGLI (Gazzetta, 1936, 66, 525—528).— $Hg^{II}$  salts dissolved in  $H_2SO_4$  or  $H_3PO_4$  are able to catalyse the conversion of nitriles into amides. The catalytic behaviour has been investigated in detail for the conversion of  $(CN)_2$  into  $(CO\cdot NH_2)_2$ . O. J. W.

**Reducing action of mercury. III. Hydrogen peroxide formation and the copper-catalysed autoxidation of quinquivalent molybdenum and other strong reductants in acid solution.** W. M. MURRAY, jun., and N. H. FURMAN (J. Amer. Chem. Soc., 1936, 58, 1843—1847; cf. this vol., 1353).—Reduction by Hg may be used for the determination of Fe, V, or Mo, as these ions decompose catalytically any  $H_2O_2$  formed. For micro-determinations  $O_2$  must be excluded.  $Mo^V$  is autoxidised rapidly in presence of small amounts of Cu. A mechanism for this and similar reactions is discussed. E. S. H.

**Acid catalysis in non-aqueous solvents. III. Rearrangement of N-iodoformanilide in anisole solution.** R. P. BELL and J. F. BROWN (J.C.S., 1936, 1520—1524).—The rearrangement of  $HCO\cdot NIPh$  into  $HCO\cdot NH\cdot C_6H_4I\cdot p$  in PhOMe solution is a unimol. reaction catalysed by  $H^+$ . The reaction has been studied in presence of 8 org. acids, for which the catalytic consts. ( $\alpha$ ) are given approx. by  $\alpha=3.63K_d^{0.21}$  ( $K_d$ =dissociation const. in  $H_2O$ ). A side reaction occurs with production of I. A. J. E. W.

**Influence of some colloids on the velocity of inversion of sucrose.** S. BERLINGOZZI and M. TESTONI (Annali Chim. Appl., 1936, 26, 366—369; cf. B., 1931, 134; this vol., 35).—The velocity of inversion of sucrose in aq. citric acid is lowered by lyophilic and by metallic colloids. L. A. O'N.

[Organic catalysts.] W. LANGENBECK and F. BAEHREN (Ber., 1936, 69, [B], 2406; cf. this vol., 589).—A reply to Eistert (this vol., 844). H. W.

**Hydrocatalase.** R. RETOVSKY (Bull. Soc. Chim. biol., 1936, 18, 1106—1114).—The kinetics of the decomp. of  $H_2O_2$  by certain mineral waters shows that two processes, a catalase action and auto-decomp., are involved. The decomp. is dependent on  $p_H$ , and the activity decreases with time. A. L.

**Oxidation of glucose.**—See this vol., 1491.

**Relative catalytic activity of several metals for the isotopic interchange reaction,  $H_2O+HD\rightarrow HDO+H_2$ .** K. HIROTA and J. HORIUTI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 30, 151—168; cf. this vol., 162, 163, 430, 684).—The interchange series (order of catalytic activity) is Pt (sp. catalytic activity  $k=5\times 10^{-1}$  at  $0^\circ$ )  $>$  Ni ( $7\times 10^{-2}$  at

$100^\circ$ )  $>$  Fe ( $3\times 10^{-4}$  at  $100^\circ$ )  $>$  Cu ( $2\times 10^{-3}$  at  $180^\circ$ )  $>$  Au ( $3\times 10^{-4}$  at  $180^\circ$ )  $>$  Ag ( $1\times 10^{-4}$  at  $180^\circ$ ). No activity for Hg could be established. The parallelism between this series and that for H atom recombination, overvoltage, and hydrogenation catalysis is pointed out. The results for Pt suggest that in all cases the rate of reaction is determined by the genuine interchange. R. C. M.

**Autoxidation of chromite solutions.** F. HEIN and O. STUMM (J. pr. Chem., 1936, [ii], 147, 53—59).—The oxidation of suspensions of  $Cr(OH)_3$  in aq. KOH, when shaken with  $O_2$  or air, has been studied for various  $[KOH]$  and in presence of various catalysts. The best activators for conversion into  $CrO_4^{--}$  are  $Mn(OH)_2$ ,  $Cu(OH)_2$ ,  $Mn(OH)_2+Cu(OH)_2$ , and amalgamated Cu+liquid Hg. Possible mechanisms of the action are discussed. J. W. S.

**Oxidation of ferrous sulphate solutions.** J. R. POUND (J.S.C.I., 1936, 55, 327—330r).—The catalytic action of Pt-black, NO, and activated C in the oxidation of aq.  $FeSO_4$  was confirmed. Numerous other substances examined gave negative results. The reaction in presence of NO is bimol. with respect to  $FeSO_4$  and unimol. with respect to NO. The dependence of the rate of oxidation on concn., time, surface of solution, and dissolved  $O_2$  was studied. Aq.  $FeSO_4$  is oxidised rapidly by  $HNO_3 > 0.5N$ . H. J. E.

**Method of investigating catalyst surfaces.** B. JEROFEEV and K. MOCHALOV (Acta Physicochim. U.R.S.S., 1936, 4, 859—860).—On admitting air to a tube containing Fe filings reduced *in situ* at  $450^\circ$  the resistance increased greatly and the tube functioned as a coherer for Hertz waves. Fe containing 1% of  $Al_2O_3$  as a promoter did not lose its capacity for acting as a coherer after 46 hr. reduction at  $450^\circ$ . The Fe surface is coated with an  $Al_2O_3$  film which is not reduced under these conditions. H. J. E.

**Catalytic decomposition of ammonia.** I. CHRISMAN (Acta Physicochim. U.R.S.S., 1936, 4, 899—910).—The kinetics of the decomp. of  $NH_3$  on a  $Fe-Al_2O_3-K_2O$  catalyst at  $300-450^\circ$  were studied by a flow method. The activation energies for the temp. ranges  $300-350^\circ$  and  $350-450^\circ$  were 12.4 and 39.7 kg.-cal. per g.-mol., and were attributed to the formation and decomp. of nitride. H. J. E.

**Mechanism of the arresting action of the promoter on the reduction of the iron ammonia catalyst.** N. I. KOBOSEV (Acta Physicochim. U.R.S.S., 1936, 4, 829—840).—Data for the effect of  $Al_2O_3$ ,  $K_2O$ ,  $KF$ ,  $BeO$ , and  $MgO$  on the rate of reduction of  $Fe_3O_4$  and  $FeO$  by  $H_2$  are discussed (cf. B., 1936, 629). The promoter forms a surface film which protects the Fe oxide from reduction, and also favours the formation of small crystals of Fe. H. J. E.

**Oxidation of carbon. II.** J. D. LAMBERT (Trans. Faraday Soc., 1936, 32, 1584—1591; cf. this vol., 434).—The secondary conversion of CO into  $CO_2$  in the combination of C occurs more rapidly at a pure C surface than at a surface of C containing Fe. C treated with Mn behaves similarly to C treated with Fe on oxidation at  $400^\circ$ , but without secondary oxidation of CO to  $CO_2$ . The mechanism is discussed.



Possibly the primary reaction product is a gaseous complex similar to  $C_3O_2$ . E. S. H.

**Selective combustion of hydrogen, carbon monoxide, and methane by palladium catalysts.** M. S. PLATONOV and O. V. NEKRASSOVA (Z. anal. Chem., 1936, 106, 416—418).—A Pd catalyst on a ceramic carrier, prepared by reduction of  $PdCl_2$  with  $H_2$  at 120—140°, burns  $H_2$  catalytically at room temp., CO at 140—150°, and  $CH_4$  at 400—450°. The selective combustion of  $H_2$  in presence of CO is not possible; such mixtures are burned at 150°, and the composition is calc. from the vol. contraction. J. S. A.

**Interaction of carbon disulphide and sulphur dioxide.** B. CRAWLEY and R. H. GRIFFITH (Trans. Faraday Soc., 1936, 32, 1623—1626).—A survey of a wide range of catalysts for the reaction has been made. Interaction appears to occur by collision of a free  $CS_2$  mol. with an adsorbed  $SO_2$  mol. Activated adsorption of only one reactant is necessary. E. S. H.

**Hydrogenation with hydrogen dissolved in palladium.** D. DOBITSCHIN and A. FROST (Acta Physicochim. U.R.S.S., 1936, 5, 111—130; cf. A., 1935, 940).—The hydrogenation of  $C_2H_4$ ,  $CH_2:CHEt$ , and  $C_2H_2$  by H absorbed in sputtered films of Pd has been followed by measuring the electrical resistance of the films, which varies with the H content. With  $C_2H_4$  and  $CH_2:CHEt$  the reaction is more rapid than the desorption of H at  $-78^\circ$ . The rate of hydrogenation of  $C_2H_4$  by  $H_2$  dissolved in Pd is  $>$  when it is in the gas phase. Ageing of the Pd film leads to parallel decrease of catalytic activity and of the rate of absorption of  $H_2$ . F. L. U.

[Catalytic] synthesis of benzine.—See B., 1936, 1028.

**Catalyst poisoning from the point of view of the specificity of active centres.** III. Relative durations of sojourn of *n*-propyl alcohol and propaldehyde molecules, and true energy of activation of *n*-propyl alcohol dehydrogenation on copper. A. BORK and A. A. BALANDIN. IV. Orientation of molecules of reactants and resultants on catalyst surface in catalysed dehydrogenations and analogous catalytic reactions. A. BORK (Z. physikal. Chem., 1936, B, 33, 435—442, 443—458).—III. The rate of dehydrogenation of  $PrOH$  to  $EtCHO$  on Cu at 252° and the influence on the velocity of  $EtCHO$  may be represented by  $dm/dt = k(M-m)/N$ , where  $k$  contains no adsorption coeffs. (cf. this vol., 1076). The durations of sojourn on the catalyst and the heats of adsorption of  $PrOH$  and  $EtCHO$  are equal over a temp. range of 40°. The true energies of activation of the dehydrogenation of  $EtOH$  and  $PrOH$  are both 12,200 g.-cal. The logarithmic relation between the consts. of Arrhenius' equation (cf. *ibid.*, 435) holds.

IV. Existing experimental data and theoretical reasoning indicate that the rate of catalytic dehydrogenation and similar catalyses is given by  $dm/dt = k(M-m)/M$ , where  $M$  is the no. of mols. of reactant entering the reaction tube and  $m$  the no. of mols. reacting in unit time, and  $k$  contains no adsorption coeffs. Homologous reactants have the same energy of activation. If two homologous reactants undergo

dehydrogenation at the same rate, and if for one the adsorption coeffs. of reactant and resultant are equal, this is true of the other also, and for each reaction the duration of sojourn on the catalyst of reactant and resultant is the same. A method of determining relative adsorption coeffs. is described. R. C.

**Catalytic conversion of natural gas into carbon monoxide and hydrogen.**—See B., 1936, 1075.

**High-pressure hydrogenation of low-temperature tar.** V. Molybdenum catalysts.—See B., 1936, 1075.

**Twitchell's reagent as promoter of esterification.**—See this vol., 1487.

**Kinetics of the process at the iron anode of a galvanic element.** V. ROITER and V. JUSA (Acta Physicochim. U.R.S.S., 1936, 4, 135—144).—The results of polarisation determinations can be expressed by  $\Delta\epsilon = abI/(1+bI)$ , where  $\epsilon$  is the potential and  $I$  the c.d. By analogy with the Langmuir equation it is suggested that the potential decrease is due to the adsorption of a substance of which the concn. in the electrolyte  $\propto$  c.d. R. S.

**Electrolytic oxidation.** VIII. Apparent reducing properties of an anode. A. HICKLING (J.C.S., 1936, 1453—1456).—The ratio of the vols. of  $O_2$  and  $H_2$  evolved during electrolysis of acid solutions of  $KMnO_4$  and  $K_2Cr_2O_7$  has been determined under varying conditions of c.d. and concn., and with different acids present. This ratio is abnormally large, the discrepancy being attributed to formation of  $H_2O_2$  from  $OH^-$  discharged at the anode, and subsequent reaction of this with the  $KMnO_4$  or  $K_2Cr_2O_7$ . A. J. E. W.

**Production of electrolytic zinc.**—See B., 1936, 1100.

**Electrolytic refining of aluminium.**—See B., 1936, 1100.

**Theory of electrolytic chromium plating.** I.—See B., 1936, 1044.

**Electrochemical protection of metallic surfaces.**—See B., 1936, 1044.

**Formation of carbon dendrites.** H. THIELE (Nature, 1936, 138, 688).—Further experiments illustrating the reduction of graphitic acid at a cathode and the formation of dendrites are described (cf. this vol., 1089). L. S. T.

**Mechanism of catalytic interchange of hydrogen with water and alcohol.** J. HORIUTI and G. OKAMOTO (Trans. Faraday Soc., 1936, 32, 1492—1494; cf. this vol., 430).—The rate-determining step for the electrode process at a polarised Ni-H electrode is the atomisation of the  $H_2$  mol. on the metal. A homopolar Ni-H linking is assumed. The application of this result to the Pt-H electrode process is discussed. A. J. E. W.

**Chemical activity of the rare gases.** VII. Action of helium on bismuth under the influence of electrical discharges at low pressure. H. DAMIANOVICH (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 20—22; Chem. Zentr., 1936, i, 497).—He was combined with Bi in a discharge at 1—2 mm.

pressure. The product contained 4.5 c.c. of He per g. of Bi.

H. J. E.

**Cathodic platinum obtained in a hydrogen atmosphere.** H. DAMIANOVICH and C. CHRISTEN (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 72—75; Chem. Zentr., 1936, i, 498).—No evidence of compound formation was found.

H. J. E.

**Thermal decomposition of reversible and irreversible systems forming a gas phase.** I. Cathodic platinum oxide and chemically produced platinum oxyhydrate. II. Platinum-helium and platinum-nitrogen compounds and the systems reduced platinum, electrolytic platinum, and carbon. J. PIAZZA and H. DAMIANOVICH (An. Inst. Invest. cient. tecn., 1934, No. 3/4, 32—45, 46—56; Chem. Zentr., 1936, i, 497—498).—I. The Pt oxide obtained by cathodic sputtering in an O<sub>2</sub> atm. is identical in its thermal decomp. and X-ray pattern with that obtained from H<sub>2</sub>Pt(OH)<sub>6</sub>, and resembles the Pt-N and Pt-He compounds in its decomp. curve and autocatalytic phenomena.

II. The Pt-He and Pt-N compounds produced in a discharge undergo irreversible thermal decomp. The decomp. is compared with that in Pt-O and C-air systems.

H. J. E.

**Reaction kinetics in electric discharges.** S. S. VASSILIEV, N. I. KOBOSEV, and E. N. ERJEMIN (Acta Physicochim. U.R.S.S., 1936, 5, 201—242).—The following discharge reactions have been subjected to kinetic analysis: the oxidation of N<sub>2</sub>, the formation of O<sub>3</sub> and H<sub>2</sub>, and the cracking of CH<sub>4</sub>. The relation between the actual yield and the limiting energy yield and the influence of the power of the discharge are discussed.

R. S.

**Effect of temperature on photochemical formation of ozone.** A. EUCKEN and F. PATAT (Z. physikal. Chem., 1936, B, 33, 459—474; cf. A., 1924, ii, 159).—The formation of O<sub>3</sub> from O<sub>2</sub> at 20—50 mm. by ultra-violet light of  $\lambda$  chiefly 1720 Å. (Al spark) has been examined. Assuming that the mechanism is  $O_2 + h\nu \rightarrow 2O$ ,  $O + O_2 + M \rightarrow O_3 + M$ ,  $O_3 + O \rightarrow 2O_2$  it may be shown that at equilibrium  $[O_3] = k[O_2]^2$  and that the position of equilibrium is independent of the intensity of radiation. Both deductions are confirmed by experiment. The variation of  $k$  with temp. gives  $6160 \pm 100$  g.-cal. per mol. for the energy of activation of  $O + O_3 \rightarrow 2O_2$ . From the results  $[O_3]$  at various heights in the atm. has been calc., the results showing that the effective O<sub>3</sub> layer is at a height of  $\leq 40$  km.

R. C.

**Effect of light on the ignition of monosilane-oxygen mixtures.** H. J. EMELEUS and K. STEWART (Trans. Faraday Soc., 1936, 32, 1577—1584).—SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, and Si<sub>3</sub>H<sub>8</sub> absorb light of  $\lambda\lambda$  <1850, <1980—2020, and <2140—2190 Å., respectively. SiH<sub>4</sub> mixed with Hg vapour is decomposed by the 2537 Å. Hg resonance line, giving H<sub>2</sub> and solid polymerised SiH<sub>x</sub> ( $x < 0.9$ ). Light from an Al spark or Hg resonance arc causes explosion of SiH<sub>4</sub>-O<sub>2</sub> mixtures at temp. < the normal range for thermal ignition. SiH<sub>4</sub>-O<sub>2</sub> mixtures at pressures > the crit. explosion pressure undergo slow oxidation on exposure to the Hg resonance arc. The reaction has

an induction period and in the initial stages follows the law  $\Delta p = ke^{kt}$ , which characterises hydrocarbon combustion.

E. S. H.

**[Photochemical] reduction of ferric salts by organic acids.** P. LAL and P. B. GANGULY (Z. anorg. Chem., 1936, 229, 16—18).—Reduction of aq. solutions of pure normal Fe<sup>III</sup> citrate and tartrate by light from a quartz Hg lamp follows a zero-mol. course. The quantum yield ( $\lambda$  546 m $\mu$ ) is 0.5 for the citrate and 0.62 for the tartrate. The reaction is strongly catalysed by traces of Th, U, Cu, and Zr salts in the decreasing order given.

F. L. U.

**Action of various elements and compounds on photographic plates.** III. S. AOYAMA, T. FUKUROI, and K. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 923—936; cf. A., 1935, 47, 1087).—Physical factors are considered.

J. S. A.

**Latent images below the threshold.** LUPPO-CRAMER (Phot. Korr., 1935, 71, 137—138; Chem. Zentr., 1936, i, 942).—A strong Becquerel effect occurs in AgI-gelatin plates if an I acceptor is present and physical development is used. The absence of the effect in AgBr dry plates is ascribed to the fact that unilluminated AgI is relatively much more sensitive to blue light than is AgBr.

H. J. E.

**Destruction of latent images and desensitisation by dyes.**—See B., 1936, 1131.

**Photochemical reactions of iron gluconates.** R. NEIGER and P. NEUSCHUL (Z. physikal. Chem., 1936, 177, 355—364).—Fe<sup>II</sup> gluconate (I) in aq. solution is oxidised in the dark under the influence of atm. O<sub>2</sub> to a Fe<sup>III</sup> salt (II) of unknown constitution, which is stable in the dark. Fe<sup>III</sup> gluconate (III) is stable in the dark in air. In an O<sub>2</sub>-free atm. (I) and (III) are stable in the dark. In daylight (II) and (III) are reduced to a Fe<sup>II</sup> salt, which from the solution of (II) separates as a solid (IV). Invert sugar delays the appearance of (IV). (III) is reduced more readily if O<sub>2</sub> is excluded. These reductions are apparently genuine photochemical reactions. Fe<sup>II</sup> mannionate behaves similarly to (I).

R. C.

**Photochemical peroxide formation.** IV, V.—See this vol., 1489, 1492.

**Initiation of gas reactions by ions.** II. **Hydrogen-chlorine mixtures.** P. GUNTHER and K. HOLM (Z. physikal. Chem., 1936, B, 33, 407—434).—Investigation of the induction of reaction in a H<sub>2</sub>-Cl<sub>2</sub> mixture, by allowing N ions to diffuse into it, has confirmed results previously reported (A., 1934, 975). Each ion initiates  $\sim 2.5$  reaction chains, which shows that the chemical action of the ions is approx. the same whether they are introduced into the reaction mixture by diffusion or produced *in situ* by  $\alpha$ -particles or X-rays. The mobility of Cl ions in moist Cl<sub>2</sub> is greatly reduced by the addition of a small amount of H<sub>2</sub>, suggesting that in presence of H<sub>2</sub> HCl is formed in the immediate vicinity of the ions and, dissolving in H<sub>2</sub>O, associates itself with the ion and so slows it down. Hence the formation of HCl under the influence of ions occurs during the life of the ions, not at their neutralisation. The no. of reaction chains initiated by an ion appears to be



independent of the life of the ion. Following Lind's cluster theory it may be supposed that the electrostatic fields of the N ions cause  $\text{Cl}_2$  mols. to become associated with them, and some of these are so distorted as to give Cl atoms, which start the reaction. The present experiments indicate that  $\alpha$ -particles initiate reactions by their electrostatic action on the ions to be excited. R. C.

**Enrichment of the light argon isotopes by diffusion.** H. BARWICH and W. SCHÜTZE (*Naturwiss.*, 1936, 24, 667).—An enrichment of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  by diffusion into a current of Hg vapour has been observed. A. J. M.

**Action of atomic hydrogen on inorganic compounds.** H. KROEPFELIN and E. VOGEL (*Z. anorg. Chem.*, 1936, 229, 1—15; cf. A., 1935, 730).—Observations on the action of  $\text{H}_2$  containing about 14% of H on 86 solid inorg. elements and compounds are recorded. The experiments were conducted at room temp., but in some cases considerable local rise of temp. was observed. With a few substances luminescence was produced. Generally, compounds of heavy metals are reduced readily. The action is, however, sometimes only superficial, owing either to catalysis of H by the reaction products, or to impermeability of the latter to H. Alkali metal salts are reduced to metal when the anion is destroyed by H (e.g.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{ClO}_3^-$ ). Films of gelatin and of Cellophane are impermeable to H. Aq. solutions of  $\text{AgNO}_3$ ,  $\text{HgCl}_2$ , and  $\text{Cu}(\text{OAc})_2$  are reduced to metal,  $\text{CrO}_4^{2-}$  and  $\text{MnO}_4^-$  in acid solution to  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ ,  $\text{I}_2$  to  $\text{I}^-$ ,  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ , and methylene-blue and indigotin in  $\text{H}_2\text{SO}_4$  to leuco-compounds. Working details are given. F. L. U.

**Influence of combustion conditions on the density of water formed from commercial hydrogen and oxygen.** W. H. HALL and H. L. JOHNSTON (*J. Amer. Chem. Soc.*, 1936, 58, 1920—1922).—The vol. ratio  $\text{H}_2:\text{O}_2$  has no significant influence on the  $d$  of the  $\text{H}_2\text{O}$  produced when reaction occurs in a flame, but the  $d$  may be affected by several p.p.m. if combination takes place over a Pt catalyst. When  $\text{O}_2$  is in excess  $d$  may be low, probably by reason of the lower reaction velocities of the higher isotopes of O. With excess of  $\text{H}_2$ ,  $d$  may be high, owing to incomplete exchange between steam and excess of  $\text{H}_2$ . E. S. H.

**Isotopic interchange reaction between chloroform and water.** J. HORIUTI and Y. SAKAMOTO (*Bull. Chem. Soc. Japan*, 1936, 11, 627—628).—The isotopic interchange between  $\text{CHCl}_3$  and  $\text{D}_2\text{O}$  in alkaline solution proceeds more quickly than the decomp. In neutral or acid solution the interchange is much slower. C. R. H.

**Sodium fluorenone as a dehydrating agent.** H. E. BENT and H. M. IRWIN, jun. (*J. Amer. Chem. Soc.*, 1936, 58, 2072—2073).—Na fluorenone has a higher efficiency than  $\text{Mg}(\text{ClO}_4)_2$  or activated  $\text{Al}_2\text{O}_3$ . E. S. H.

**Thermal dissociation and absorption spectra of vapours of  $\text{KNO}_2$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{AgNO}_3$ .** K. BUTKOV and V. TSCHASSOVENNI (*Acta Physicochim. U.R.S.S.*, 1936, 5, 137—159).—The products

obtained by heating  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{KNO}_2$ , and  $\text{AgNO}_3$  in an evacuated quartz tube have been studied spectrographically in the range 7000—1880 Å. Vapours of the complete mol. are present in all except  $\text{NaNO}_3$ .  $\text{KNO}_3$  gives NO at temp.  $> 550^\circ$ , and  $\text{NO}_2$  on cooling.  $\text{KNO}_2$  behaves similarly, except that on cooling NO persists and no  $\text{NO}_2$  is formed.  $\text{AgNO}_3$  gives  $\text{NO}_2$  only at  $270^\circ$ . The mols. are not ionised in the vapour state. Bond linking energies are calc., that corresponding with the semipolar  $\text{N}\rightarrow\text{O}$  linking being 92 kcal. per mol. F. L. U.

**Active oxides. CIII. Course of reactions in which solid substances take part.** G. F. HUTTING (*Monatsh.*, 1936, 69, 42—74; cf. this vol., 1216 and previous abstracts).—A summary of the author's work on reactions involving metal oxides is given. The reactions are classified under 11 main types, and the characteristics of each are described. F. L. U.

**Theory of corrosion phenomena. V. Application of the pore theory of corrosion to the phenomenon of the difference effect of Thiel and Eckell.** W. J. MULLER and E. LOW. VI. Determination of the metal potential of a working anode and of the potential and resistance requisite for local cells. W. J. MULLER (*Z. Elektrochem.*, 1936, 42, 789—792, 830—833; cf. this vol., 940).—V. Published work is reviewed in the light of Muller's theory.

VI. The determination of potential at two different c.d. through the pores is described. Published results are discussed. E. S. H.

**Corrosion of metals by water and carbon dioxide under pressure.**—See B., 1936, 1098.

**Influence of sodium chloride and hydrogen peroxide in rapid corrosion experiments.**—See B., 1936, 1098.

**Etching of copper by oxygen.** C. F. ELAM ([MRS.] C. F. TIPPER) (*Trans. Faraday Soc.*, 1936, 32, 1604—1614).—The etching effect obtained by heating Cu in vac. is due to the presence of  $\text{Cu}_2\text{O}$ ; it can be reproduced by oxidising the surface and appears to be due to attack by  $\text{O}_2$  along crystal planes, especially [100] and [110]. The relation between the orientation of the Cu crystal and the  $\text{Cu}_2\text{O}$  formed has been investigated. E. S. H.

**Copper peroxide and nascent copper oxide.** E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1936, [v], 3, 1913—1915).—Addition of  $\text{H}_2\text{O}_2$  to slightly alkaline aq.  $\text{CuSO}_4$  yields a brownish-yellow colour apparently due to  $\text{CuO}_2$ .  $\text{Cu}(\text{OH})_2$  in presence of aq.  $\text{CuSO}_4$  has a slight oxidising effect on tincture of guaiacum, with reduction to  $\text{Cu}_2(\text{OH})_2$ . J. W. S.

**Compounds of copper salts with tertiary amines.**—See this vol., 1395.

**Combination of magnesium chloride and magnesium methoxide.** (Mlle.) M. L. QUINET (*Bull. Soc. chim.*, 1936, [v], 3, 1823—1829).—Action of Mg on a conc. solution of  $\text{MgCl}_2$  in MeOH, of  $\text{Mg}(\text{OMe})_2 \cdot 2\text{MeOH}$  on  $\text{MgCl}_2$  in MeOH, or of  $\text{MgCl}_2 \cdot 6\text{MeOH}$  on a conc. solution of  $\text{Mg}(\text{OMe})_2$  in MeOH, gives the cryst. compound  $\text{MgCl}_2 \cdot 3\text{Mg}(\text{OMe})_2 \cdot 11\text{MeOH}$ . E. W. W.

**Formation of magnesium oxysulphate.** (MLLE.) M. L. DELYON (Bull. Soc. chim., 1936, [v], 1811—1817).—MgO dissolves in conc. aq.  $\text{MgSO}_4$  (>500 g. per litre) at  $80^\circ$ , and then gradually gives a ppt. which after 24 hr. has the const. composition  $\text{MgSO}_4 \cdot 3\text{MgO} \cdot 11\text{H}_2\text{O}$ . (I) The ppt. from solutions containing <300 g. of  $\text{MgSO}_4$  per litre is  $\text{Mg}(\text{OH})_2$ , whilst solutions of intermediate concn. yield a mixture of  $\text{Mg}(\text{OH})_2$  and (I). Attempts to prepare (I) from  $\text{Mg}(\text{OH})_2$  were unsuccessful but it was pptd. by addition of NaOH to aq.  $\text{MgSO}_4$  at  $80^\circ$ . J. W. S.

**Generating media of montmorillonite and sepiolite.** J. DE LAPPARENT (Compt. rend., 1936, 203, 553—555).—Montmorillonite is probably formed by devitrification of a glass in a medium containing Mg. Sepiolite (this vol., 957) results from direct action of Mg salt solutions on siliceous gels.

J. G. A. G.

**Existence of zinc metaborate.** R. TOURNAY (Compt. rend., 1936, 203, 558—560).—Heat is evolved at  $580$ — $630^\circ$  and at  $775$ — $820^\circ$  when the temp. of an equimol. mixture of  $\text{B}_2\text{O}_3$  and  $\text{ZnO}$  is slowly raised.  $2\text{B}_2\text{O}_3 \cdot 3\text{ZnO}$  is formed at  $>700^\circ$ , but the existence of  $\text{B}_2\text{O}_3 \cdot \text{ZnO}$  is denied.

J. G. A. G.

**Cadmium suboxides and subhalides.** R. E. HEDGER and H. TERREY (Trans. Faraday Soc., 1936, 32, 1614—1616).—X-Ray examination shows that the so-called subhalide prepared by dissolving Cd in molten  $\text{CdCl}_2$  is a mixture of  $\text{CdCl}_2$  and Cd; the so-called suboxide formed by treating the above with  $\text{H}_2\text{O}$  is a mixture of  $\text{CdO}$  and Cd. The solubility of Cd in  $\text{CdCl}_2$  at  $570$ — $810^\circ$  has been determined.

E. S. H.

**Oxidation of metals. IV. Oxide film on aluminium.** G. D. PRESTON and L. L. BIRCUMSHAW (Phil. Mag., 1936, [vii], 22, 654—665; cf. A., 1935, 1469; this vol., 569).—The oxide film found on Al at room temp. was isolated by removing the metal by treatment in HCl gas at  $250^\circ$ . Electron diffraction photographs show that the film is amorphous. Crystallisation begins slowly on heating at  $680^\circ$ , but not at temp. up to  $650^\circ$ . The film becomes a random mass of small crystals of cubic  $\gamma\text{-Al}_2\text{O}_3$  as found on the surface of molten Al.

N. M. B.

**Reaction aluminium oxide-carbon-chlorine.** N. M. STOVER and C. CONSTANTINESCU (Canad. J. Res., 1936, 14, B, 328—335).—The reaction between  $\text{Al}_2\text{O}_3$ , C and  $\text{Cl}_2$  has been studied at  $644$ — $880^\circ$ , using varying proportions of  $\text{Al}_2\text{O}_3$  and C, and static and streaming  $\text{Cl}_2$ .  $\text{O}_2$  was present in the reaction product, suggesting that the main reaction is  $2\text{Al}_2\text{O}_3 + 6\text{Cl}_2 = 4\text{AlCl}_3 + 3\text{O}_2$ , the role of the C being primarily catalytic. For a given ratio  $\text{Al}_2\text{O}_3 : \text{C}$  the ratio  $\text{CO}_2 : \text{O}_2$  in the gaseous product increased with the wt. of solid mixture. CO was obtained in the static experiments, but not with streaming  $\text{Cl}_2$ . The temp. at which  $\text{AlCl}_3$  first sublimed decreased with decreasing ratio  $\text{Al}_2\text{O}_3 : \text{C}$ . Less C was consumed, in many experiments, than that required to form  $\text{CO}_2$  with the O of the  $\text{Al}_2\text{O}_3$ . Using  $\text{WO}_3$  instead of  $\text{Al}_2\text{O}_3$ ,  $\text{O}_2$  and good yields of  $\text{CO}_2$  were formed with streaming  $\text{Cl}_2$  (cf. Sears and Lohse, A., 1935, 834).

R. S. B.

**Preparation and properties of indium dichloride.** J. K. AIKEN, J. B. HALEY, and H. TERREY (Trans. Faraday Soc., 1936, 32, 1617—1622).—The prep. of  $\text{InCl}_2$  and its analogies with  $\text{SnCl}_2$  in physical properties and lattice structure are described.  $\text{InCl}_2$  and  $\text{SnCl}_2$  appear to be associated in the solid state.

E. S. H.

**Disappearance of carbon monoxide in presence of electrically heated nickel filaments.** G. BRYCE (J.C.S., 1936, 1513—1517).—When a Ni filament is heated to above  $1200^\circ$  abs. in CO at low pressure in a bulb at  $-190^\circ$ , the CO disappears rapidly and completely, but can be recovered by heating the bulb. The action is slow at room temp., and negligible at  $100^\circ$ . The CO is removed by evaporated Ni as it condenses on the bulb, 2 mols. of CO being removed per atom of Ni, probably with formation of a subcarbonyl. This absorbs more CO on gentle warming. CO was also adsorbed by Ni freshly condensed in a bulb in a vac. Hot Ni does not affect  $\text{CO}_2$  or  $\text{N}_2$  under similar conditions. Mo at temp.  $>1900^\circ$  abs. removes CO in a similar manner.

A. J. E. W.

**Physical and chemical properties of liquid hydrogen phosphide (diphosphine,  $\text{P}_2\text{H}_4$ ).** P. ROYEN and K. HILL (Z. anorg. Chem., 1936, 229, 97—111; cf. this vol., 440).—The limiting  $d$  of the vapour of liquid H phosphide, purified by fractionation at a low temp., corresponds with the formula  $\text{P}_2\text{H}_4$ . No indication of the existence of higher homologues in the product of the action of aq. KOH on P has been observed. The v.-p. curve of  $\text{P}_2\text{H}_4$  has been determined between  $-70^\circ$  and  $10.8^\circ$  and is expressed by a two-const. formula. B.p. by extrapolation  $=51.7^\circ$ ; mean mol. heat of vaporisation between  $-25^\circ$  and  $-8^\circ = 7890$  g.-cal.; m.p.  $-99^\circ$ .  $\text{P}_2\text{H}_4$  is decomposed by HCl even at temp.  $<$  m.p., and there is no evidence for the existence of a hydrochloride. The decomp. is expressed by  $3\text{P}_2\text{H}_4 = 2\text{P} + 4\text{PH}_3$ , the solid product consisting of a yellow modification of P with adsorbed  $\text{PH}_3$ . The proportion of the latter varies with the state of division of the solid.

F. L. U.

**Partly halogenated phosphines. Formation of so-called solid hydrogen phosphide, particularly of its phenyl derivatives.** P. ROYEN and K. HILL (Z. anorg. Chem., 1936, 229, 112—128; cf. preceding abstract).—Attempts to isolate  $\text{PH}_2\text{X}$  ( $\text{X}=\text{Cl}, \text{Br}$ ) by the action of Br,  $\text{PBr}_5$ ,  $\text{PCl}_5$ , or  $\text{HCl} + \text{AlCl}_3$  on  $\text{PH}_3$  have been unsuccessful. Compounds of the type  $\text{PHRX}$  cannot be isolated owing to their rapid conversion into  $\text{PX}_3$  and  $\text{PH}_3\text{RX}$ . By condensation of  $\text{PPh}_2\text{Cl}$  with  $\text{PH}_3$  a yellow product containing 42% of adsorbed Ph phosphines is obtained, resulting from the decomp. of  $\text{P}_2\text{H}_6\text{Ph}_2$ . Me and Ph derivatives of " $\text{P}_{12}\text{H}_6$ " described in the lit. are not compounds, but adsorbates of Me and Ph phosphines on yellow amorphous P.

F. L. U.

**New oxide of phosphorus.** P. W. SCHENK and H. PLATZ (Naturwiss., 1936, 24, 651).—If a mixture of  $\text{P}_2\text{O}_5$  vapour and  $\text{O}_2$  is passed through a hot discharge tube (pressure about 1 mm.) a bluish-violet product separates in the cool part of the tube immediately behind the discharge zone. This substance



liberates I from KI, and may be preserved for a day at room temp. in the absence of  $\text{H}_2\text{O}$ . It is considered to contain 2% of a new peroxide,  $\text{PO}_3$  (or  $\text{P}_2\text{O}_6$ ).

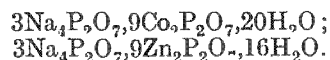
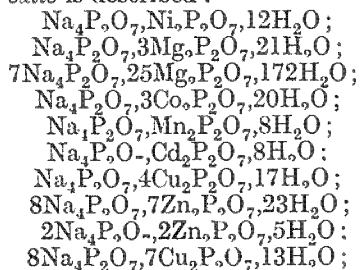
A. J. M.

**Preparation and properties of some lower acids of phosphorus.** I, II. V. N. OSIPOV (J. Gen. Chem. Russ., 1936, 6, 933—940, 941—946).—I. The acid mixture formed when colourless P is oxidised by air in  $\text{H}_2\text{O}$  (3—6 days, 10—15°) has been investigated. The mixture and Mg salts give no crystals. Metallic Mg yields  $\text{Mg}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 11\text{H}_2\text{O}$ , which differs from the known  $\text{Mg}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$  since it loses  $\text{H}_2\text{O}$  at 105° more slowly, dissolves in 25%  $\text{H}_2\text{SO}_4$  more slowly and with evolution of gas, becomes brown when treated with  $\text{AgNO}_3$ , etc.  $\text{AgOAc}$  in dil.  $\text{AcOH}$  converts the new salt into  $\text{Ag}_4\text{H}_2\text{P}_2\text{O}_7$ , different from  $\text{Ag}_4\text{P}_2\text{O}_6$  since it evolves  $\text{H}_2$  when heated in  $\text{CO}_2$ . The reaction between Mg and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$  in dil.  $\text{AcOH}$  produces  $\text{Mg}_2\text{P}_2\text{O}_6$ ,  $\text{Mg}_2\text{H}_2\text{P}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$ , which is converted by  $\text{AgNO}_3$  into brown  $\text{Ag}_4\text{P}_2\text{O}_6$ ,  $\text{Ag}_4\text{H}_2\text{P}_2\text{O}_7$ .

II. When P undergoes oxidation by air in  $\text{H}_2\text{O}$  for a longer time than in the above experiments, the  $\text{H}_4\text{P}_2\text{O}_6$ , which presumably is the first reaction product, reacts with  $\text{H}_2\text{O}$ :  $\text{H}_4\text{P}_2\text{O}_6 + \text{H}_6\text{P}_2\text{O}_7 \rightarrow \text{H}_8\text{P}_2\text{O}_8$ ; the usual equation  $\text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$  may be incorrect. After 2—3 weeks the acid mixture and Mg give  $\text{MgHPO}_4$ ,  $\text{MgH}_2\text{PO}_4 \cdot 5.5\text{H}_2\text{O}$  (I), after 4 weeks  $3\text{MgHPO}_4$ ,  $\text{MgH}_2\text{PO}_4 \cdot 10\text{H}_2\text{O}$  (II) is produced. Both (I) and (II) evolve  $\text{H}_2$  when heated in  $\text{CO}_2$ .  $\text{AgNO}_3$  changes the colour of (I) to yellow  $\rightarrow$  brown  $\rightarrow$  black, the colour of (II) to greenish-yellow black. (I) is insol. in  $\text{H}_2\text{O}$  and is not pptd. by  $\text{Th}(\text{NO}_3)_4$  in dil.  $\text{HNO}_3$ . It is converted by  $\text{AgNO}_3$  in neutral solution into  $\text{Ag}_{11}\text{H}_3\text{P}_4\text{O}_{16}$  (brown), in dil.  $\text{AcOH}$  into  $\text{Ag}_{10}\text{H}_3\text{P}_4\text{O}_{16}$  (yellow), and in dil.  $\text{H}_2\text{SO}_4$  into  $\text{Ag}_8\text{H}_5\text{P}_4\text{O}_{16}$  (brown). (II) and  $\text{AgNO}_3$  afford in neutral solution  $\text{Ag}_{11}\text{H}_3\text{P}_4\text{O}_{16}$ , a brown ppt.

J. J. B.

**Phosphates. IV. Pyrophosphates of some bivalent metals and their double salts, and solid solutions with sodium pyrophosphate.** H. BASSETT, W. L. BEDWELL, and J. B. HUTCHINSON (J.C.S., 1936, 1412—1429).—The pyrophosphates  $\text{M}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ , and  $\text{Cd}$ ) have been studied.  $x$  may have the vals. 8, 7, 6.5, 6.25, 6, 5, 4.2, 4, 3.3, 3.6, 3.25, 3, 2.3, or 2.1, the whole series of hydrates not being found with any one metal. Such "parent" hydrates give solid solutions or definite double salts with  $\text{Na}_4\text{P}_2\text{O}_7$ , these probably being formed by replacement of  $[\text{M}(\text{H}_2\text{O})_4]^{++}$  by  $[\text{Na}_2(\text{H}_2\text{O})_6]^{++}$ , or  $[\text{M}(\text{H}_2\text{O})_4]^{++}$  by  $\text{Na}^+$ , or in some cases  $[\text{M}(\text{H}_2\text{O})_2]^{++}$  by  $[\text{H}_2(\text{H}_2\text{O})_2]^{++}$ . The prep. of the following double salts is described:



All these crystallise with difficulty from the mother-liquors owing to the low concn. of some constituent ions existing in solution. They are very sparingly sol. in  $\text{H}_2\text{O}$ . Probable structures are given, in which the metal is assumed to be entirely in the cationic condition, and 2- or 4-co-ordinate. One true complex salt  $\text{Na}_6[\text{Cu}(\text{P}_2\text{O}_7)_2] \cdot 16\text{H}_2\text{O}$  was obtained.  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  is probably  $[\text{Na}(\text{H}_2\text{O})_4]_2[\text{Na}_2(\text{H}_2\text{O})_2]^{++}[\text{P}_2\text{O}_7]^{--}$ .

A. J. E. W.

**Spontaneous transformation of hypophosphoric acid.** P. NYLEN (Z. anorg. Chem., 1936, 229, 36—44).—Crystals of  $\text{H}_4\text{P}_2\text{O}_6$  preserved in a sealed tube change in 1—2 months at room temp. to a viscous liquid. The anhyd. acid undergoes a similar change in 5 days. The product is a mixture of  $\text{H}_3\text{PO}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_4\text{P}_2\text{O}_7$ . An explanation based on the constitution of the acids is offered.

F. L. U.

**Phosphorus nitrides  $\text{P}_3\text{N}_5$  and  $\text{PN}$ .** H. MOUREU and P. ROCQUET (Bull. Soc. chim., 1936, [v], 3, 1801—1811).—Continued heating of  $\text{PN}_3\text{H}$  at 450° in a vac. yields  $\text{P}_3\text{N}_5$ . When heated to 730° in a vac.  $\text{P}_3\text{N}_5$  yields  $\text{PN}$  which sublimes in a vac.  $\text{PN}$  exists in two forms. The more stable red form reduces warm conc.  $\text{H}_2\text{SO}_4$ , but this reaction is very slow in the cold. The yellow form, which can be isolated only at low temp., is readily sol. in  $\text{H}_2\text{SO}_4$  and reduces the latter even at room temp. On warming in air it ignites. Neither form shows cryst. structure when examined by X-rays.  $\text{PN}$  does not react with  $\text{N}_2$  at any temp., but a current of dry  $\text{NH}_3$  at 850° converts it back into  $\text{P}_3\text{N}_5$ .

J. W. S.

**Pyroantimonates of bivalent metals:  $\text{Ca}_2\text{Sb}_2\text{O}_7$ ,  $\text{Cd}_2\text{Sb}_2\text{O}_7$ ,  $\text{Pb}_2\text{Sb}_2\text{O}_7$ .** M. BACCAREDDA (Gazzetta, 1936, 66, 539—543; cf. A., 1933, 692).—Pure  $\text{Ca}_2\text{Sb}_2\text{O}_7$  and  $\text{Cd}_2\text{Sb}_2\text{O}_7$  are prepared by heating to redness  $\text{Sb}_2\text{O}_5$  mixed with excess of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , respectively, and washing the products with  $\text{H}_2\text{O}$  and dil.  $\text{AcOH}$ .  $\text{Pb}_2\text{Sb}_2\text{O}_7$  is obtained by heating a mixture of  $\text{Sb}_2\text{O}_5$  and  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  in the theoretical amounts. The three substances are cubic, space-group  $O_h$ , 8 mols. per unit cell, and  $a$  10.30, 10.16, 10.68 Å.,  $d_{\text{calc}}$  5.32, 7.34, 8.40,  $d_{\text{obs}}$  4.30, 5.62, 6.72, for the Ca, Cd, and Pb compounds, respectively.

O. J. W.

**Formation of dithionate by the action of pyrosulphate on sulphite.** P. BAUMGARTEN (J.C.S., 1936, 1569—1570; cf. A., 1932, 1219).—Contrary to the observation of Bassett and Henry (A., 1935, 1090),  $\text{K}_2\text{SO}_3$  prepared from  $\text{KOH}$  and  $\text{SO}_2$  reacts with  $\text{K}_2\text{S}_2\text{O}_7$  in aq. solution in presence of  $\text{KHCO}_3$  with formation of  $\text{K}_2\text{S}_2\text{O}_6$ .

A. J. E. W.

**Higher polythionates. II.** A. KURTENACKER and K. MATEJKA (Z. anorg. Chem., 1936, 229, 19—29; cf. A., 1928, 1201).—By increasing the  $[\text{HCl}]$  used in Raschig's method for preparing  $\text{K}_2\text{S}_5\text{O}_8$ ,  $\text{K}_2\text{S}_6\text{O}_8$  can be prepared and separated from the former by crystallisation. Working details are given. Still further increase in the  $[\text{HCl}]$  results in the production of higher polythionates which, however, cannot be crystallised or otherwise obtained as individuals.  $\text{K}_2\text{S}_6\text{O}_8$  is obtained as a white cryst. powder, stable

when dry. Neutral aq. solutions slowly deposit S and form  $K_2S_5O_6$ , whilst alkalis provoke immediate decomp. X-Ray powder diagrams of  $K_2S_nO_6$  ( $n=3, 4, 5, 6, >6$ ) are given. The absence from the last-named of lines proper to any of the others indicates the existence of one or more definite higher polythionates.  
F. L. U.

**Molybdenum and nitrogen.** A. SIEVERTS and G. ZAPF (Z. anorg. Chem., 1936, 229, 161—174; cf. B., 1934, 676).—Mo foil and Mo wire which have been heated at  $1400^\circ$  in a mixture of  $H_2$  and  $N_2$  absorb only very small quantities of  $N_2$  at  $900$ — $1200^\circ$ . The foil becomes brittle and recrystallises, whilst the wire is unaffected. Absorption of  $N_2$  by wire which has not been preheated is much greater, and on cooling in  $N_2$  a nitride phase, characterised both microscopically and by X-rays, separates. The initially flexible wire becomes brittle and shows a smooth instead of a fibrous fracture. A nitride with 23.5 at.-% of N still absorbs  $N_2$  freely at  $820^\circ$ .  
F. L. U.

**Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their compounds of high mol. wt. XXX. Phosphotungstates and their inter-relations.** G. JANDER and H. BANTHIEN (Z. anorg. Chem., 1936, 229, 129—145; cf. this vol., 29).—The conditions under which various phosphotungstates separate from aq. solutions of their components are described.  $6Na_2O, 1.5P_2O_5, 12WO_3, 17H_2O$  is new. All compounds of this type are derived from the units  $H_3PO_4$ ,  $H_6W_6O_{21}$ , and  $P_2O_5, 12WO_3, xH_2O$ .  
F. L. U.

**Fluorine and its compounds.** O. RUFF (Ber., 1936, 59, [A], 181—194).—A lecture.

**Oxidation of inorganic reagents by ozone. II. Potassium iodide. Influence of the characteristics of the solution.** (MME.) G. GUÉRON, M. PRETTE, and J. GUÉRON (Bull. Soc. chim., 1936, [v], 3, 1841—1847; cf. this vol., 440, 441).—The action of  $O_3$  on solutions of KI in MeOH, EtOH, Bu<sup>n</sup>OH, COMe<sub>2</sub>, or cyclohexanol produces  $KIO_3$  to a greater extent than in aq. solution. Dry KI is only slightly attacked by  $O_3$  dried with  $H_2SO_4$ . After dissolution of the product, 92% of the oxidising power is found to be due to  $KIO_3$ . Addition of KCl or  $K_2SO_4$  to aq. KI has no effect on the oxidation by  $O_3$ , which yields both I and  $KIO_3$ . Buffering with conc.  $KH_2PO_4 + K_2HPO_4$ , however, decreases the amount of  $IO_3^-$  produced. The formation of  $KIO_3$  appears to occur only in regions of local alkalinity. Attempts to demonstrate this were unsuccessful, owing to irregularities, apparently of an electro-kinetic nature. The limitations of the KI method of determining  $O_3$  are discussed.  
J. W. S.

**Oxalato complex compounds of tervalent manganese.** G. H. CARTLEDGE and W. P. ERICKS (J. Amer. Chem. Soc., 1936, 58, 2061—2065).—The prep. and properties of  $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ ,  $K[Mn(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ ,  $K[Mn(C_2O_4)(H_2O)_2] \cdot 2H_2O$ , and  $[Co(NH_3)_6][Mn(C_2O_4)_3] \cdot xH_2O$ , and  $K[Mn(C_3H_3O_4)_2(H_2O)_2] \cdot 2H_2O$  are described.  
E. S. H.

**Ferrites.** R. S. HILPERT (Rec. trav. chim., 1936, 55, 963—966).—A reply to van Arkel *et al.* (this vol., 810).  
R. S.

**Compact disperse ferric hydroxide.** H. W. KOHLSCHÜTTER and H. NITSCHMANN (Z. anorg. Chem., 1936, 229, 45—48; cf. this vol., 167).—Comments on a paper by Krause and Krzyzanski (*ibid.*, 947).  
F. L. U.

**Calcium ferrite hydrates.** H. HOFFMANN (Zement, 1936, 25, 675—680, 693—698, 711—716, and Mitt. zementtech. Inst. Tech. Hochschule Berlin, 1935, 52, 63 pp.).—Interaction of a mixture of  $FeCl_3$  and  $CaCl_2$  in  $H_2O$  with a large excess of  $CO_2$ -free NaOH solution afforded material containing  $CaO : Fe_2O_3 : H_2O = 4 : 1 : 14$  and  $4 : 1 : 7$ . A mixture of EtOH and glycerol extracted no CaO, and the X-ray powder patterns were distinct from one another and from those of  $Fe_2O_3 \cdot H_2O$  ( $\alpha$ - and  $\beta$ -forms),  $Ca(OH)_2$ , and  $CaCO_3$ . Anhyd.  $2CaO, Fe_2O_3$  shaken with  $H_2O$  or aq.  $Ca(OH)_2$  gave a solution containing about 1060 mg. of CaO per litre and no  $Fe_2O_3$ . In two experiments analysis of the solid phase gave  $CaO : Fe_2O_3 = 3.4$  and  $2.9$ , respectively, and an X-ray powder pattern similar to the  $4 : 1 : 7$  prep.  $CaO, Fe_2O_3$  does not react with  $H_2O$  or aq.  $Ca(OH)_2$  whilst  $4CaO, Fe_2O_3, Al_2O_3$  gives an equilibrium solution containing 640 mg. of CaO per litre, and a solid phase containing  $Fe(OH)_3$ ,  $3CaO, Al_2O_3$  hydrate, and an unknown hydrated Ca ferrite which probably also exists in equilibrium with solutions containing between 1060 and 640 mg. of CaO per litre.  
G. H. C.

**Ferric ammonium chlorides. Anomalous mixed crystals.** E. GRUNER and L. SIEG (Z. anorg. Chem., 1936, 229, 175—187).— $NH_4Cl$  forms anomalous mixed crystals only with those chlorides of heavy metals which show a moderate tendency to double salt formation, and then only when such double salts are readily sol. The phenomenon is observed with  $MnCl_2$ ,  $CoCl_2$ ,  $NiCl_2$ ,  $FeCl_2$ , and especially  $FeCl_3$ . Crystals in which the  $FeCl_3$  content is  $> 14\%$  show only  $NH_4Cl$  in the X-ray diagram, with the lattice const. very little changed. When the proportion of  $FeCl_3$  is  $> 45\%$  the lattice of the double salt  $(NH_4)_2[FeCl_5 \cdot H_2O]$  (characterised by its  $H_2O$ -v.p.) is observed. The structure of the mixed crystals is discussed.  
F. L. U.

**Constitution of compounds formed in A. Martini's micro-reactions.** J. V. DUBSKY and A. LANGER (Chem. Listy, 1936, 30, 227—230).—The compounds described by Martini (A., 1929, 287) are of the type  $M(CNS)_2 \cdot B_2$  ( $M = Co, Ni, \text{ or } Cd$ ;  $B = C_5H_5N$  or  $NH_2Ph$ ); the formulæ proposed by Martini are erroneous.  
R. T.

**Quantitative spectral analysis.** H. TRICHE (Bull. Soc., chim., 1936, [v], 3, 1817—1820).—The methods of controlled comparison spectra and of internal scale are equally accurate and both yield trustworthy results.  
J. W. S.

**Crystallographic identification of substances.** V. V. DOLIVO-DOBROVOLSKI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 33—48).—A discussion.  
R. T.

**Accuracy of acid-base titrations calculated from the titration curves.** S. KILPI (Suomen Kem., 1936, 9, A, 93—94; B, 19—20; cf. A., 1935, 594, 1091, 1214; this vol., 692).—Expressions based



on Van Slyke's equation for the buffer capacity (cf. A., 1922, i, 893) are derived for the inaccuracy in a weak acid or base-strong base or acid titration due to an error in the end-point  $p_H$ .  
R. C. M.

**Roqui-purple, a new indicator.** F. L. RODUTA and G. A. QUBILAN (Searchlight, 1936, 1, No. 1, Reprint).—Roqui-purple, prepared from dinitrophenylhydrazine and naphthaquinonesulphonate in MeOH, is claimed to be a good indicator, comparing very favourably with phenolphthalein.  
F. R. S.

**Interferometric analysis of heavy water.** N. S. FILIPPOVA and M. M. SLUCKAJA (Acta Physicochim. U.R.S.S., 1936, 5, 131—136).—A modification of the method hitherto used (A., 1934, 618) for the interferometric analysis of  $H_2O$ - $D_2O$  mixtures is described. The temp. coeff. of  $\Delta n$  has been determined at 18—25° for a series of mixtures.  
F. L. U.

**Titration errors due to formation of mixed crystals in potentiometric analysis.** H. FLOOD (Z. anorg. Chem., 1936, 229, 76—84).—Expressions for the displacement of the end-point obtained from the potentiometric titration curves in pptn. reactions are deduced for the cases where (1) complete equilibrium between ppt. and solution is rapidly established, (2) equilibrium is not established after each addition of titration liquid.  
F. L. U.

**Titration errors in the potentiometric determination of bromide and chloride in mixtures.** H. FLOOD and B. BRUUN (Z. anorg. Chem., 1936, 229, 85—96; cf. preceding abstract).—The % displacement of the end-point in potentiometric titrations of  $Br^-Cl^-$  mixtures by  $AgNO_3$  after addition of  $Ba(NO_3)_2$  is given by  $100(b/a)\{1 - (b/La)^{1/L} - (1/L)\}$ , in which  $b/a = Cl^-/Br^-$ ,  $L = 400$  = ratio of solubility product of  $AgCl$  to that of  $AgBr$ . The function of  $Ba(NO_3)_2$  is to coagulate colloidal  $Ag$  halide. Errors in the absence of coagulating electrolyte are not entirely explicable by mixed crystal formation, but are due partly to adsorption.  
F. L. U.

**Colorimetric determination of small quantities of bromine in presence of a large excess of chlorine.** P. BALATRE (J. Pharm. Chim., 1936, [viii], 24, 409—413).—Small amounts of  $Br^-$  are best determined (error <5%) by a modification of the method of Stenger *et al.* (A., 1935, 835) in which  $Br^-$  is liberated by  $0.005N-NH_2Cl$ , suitably buffered, followed by  $Na_2S_2O_3$ . The technique is described.  
J. W. B.

**Determination of dissolved oxygen in boiler feed-water.**—See B., 1936, 1023.

**Determination of small concentrations of sulphur dioxide and hydrogen sulphide in air.** II. V. G. GUREVITSCH and V. P. VENDT (J. Gen. Chem. Russ., 1936, 6, 962—971; cf. A., 1930, 879).— $SO_2$  and  $H_2S$  are converted into  $H_2SO_4$ , which is determined.  $SO_2$  is oxidised by air in 0.2% aq.  $NH_3$  during 30 min.; only 3% of  $H_2S$  present in  $SO_2$  is oxidised under the same conditions. The  $(NH_4)_2S$  thus formed gives  $(NH_4)_2SO_4$  when treated with  $H_2O_2$ . The determination of  $SO_4^{2-}$  before and after the treatment with  $H_2O_2$  affords the vals. of  $SO_2$  and  $H_2S$ . Klinker's method of determining  $H_2SO_4$  (A., 1925, ii, 239)

is not sensitive enough. The nephelometric method of determining  $PbSO_4$  in dil. EtOH is convenient; the error is  $\pm 2.5 \times 10^{-7}$  g. of  $SO_2$  or  $H_2S$ .  
J. J. B.

**Determination of sulphur in plain and alloy steels.**—See B., 1936, 1098.

**Direct titration of sulphate with barium chloride using sodium rhodizonate as external indicator.** A. MUTSCHIN and R. POLLAK (Z. anal. Chem., 1936, 106, 385—399).—The use of Na rhodizonate (I) as external indicator, and titration in cold neutral solution, is recommended in order to avoid the decomp. of (I) by acids. In presence of much  $NH_4Cl$ , 10—20% of  $COMe_2$  is added to overcome the resulting interference with the pptn. of  $BaSO_4$ . In presence of Na and small amounts of K,  $COMe_2 + AcOH$  is added. Mg interferes slightly owing to the pink coloration developed with (I). Titration is not possible in presence of Ca or heavy metals.  
J. S. A.

**Determination of small quantities of nitric acid by means of phenoldisulphonic acid.** E. REMY and H. ENZENAUER (Arch. Pharm., 1936, 274, 435—439).—The  $NO_3^-$  content of  $H_2O$  in presence of  $NO_2^-$  is determined colorimetrically using a solution of the product of PhOH and fuming  $H_2SO_4$ , neutralised with 50% KOH. Alkaline K Na tartrate solution is used to prevent pptn. of  $Ca^{++}$  and  $Mg^{++}$ .  
F. R. G.

**Detection of nitrites.** J. C. GIBLIN and G. CHAPMAN (Analyst, 1936, 61, 686).—The test, sensitive to 1 p.p.m., is based on the formation of Me-orange from  $NPhEt_2$  and sulphanilic acid.  
E. C. S.

**Colorimetric determination of phosphorus.** H. L. BROSE and E. B. JONES (Nature, 1936, 138, 644).—The method described enables a reaction to be followed by means of a photo-electric colorimeter until equilibrium is reached. In a modification of the Fiske-Sulbarow microchemical method,  $10^{-9}$  g. of P per c.c. can be detected and changes of  $<10^{-7}$  g. can be accurately measured. With very small amounts of P the approx. steady state is reached in 20 min., but with  $\sim 0.5 \times 10^{-6}$  g. per c.c. the colour should not be read for 2 hr.  
L. S. T.

**Oceanographical chemical investigations with the Zeiss Pulfrich photometer.** I. Apparatus. II. Procedure. III. Determination of phosphate. IV. Influence of other substances on the phosphate determination. V. Determination of total phosphate, plankton phosphate (living matter) and of turbidity. H. KALLE (Ann. Hydrogr. marit. Meteorol., 1931, 59, 313—317; 1933, 61, 124—128; 1934, 62, 65—74, 95—102; 1935, 63, 58—65, 195—204; Chem. Zentr., 1936, i, 830—831).—III. The optimum conditions for the use of Osloer's molybdate reagent were determined.

IV. Traces of Cu reduce the colour intensity in the determination of  $PO_4^{3-}$  in sea- $H_2O$ .  $SiO_2$  has no effect.  $AsO_4^{3-}$  and oxalic acid interfere.  $As_2O_3$  intensifies the colour.

V. 25 c.c. of the sea-water are evaporated with 1 c.c. of conc.  $H_2SO_4$  and 0.2 c.c. of 0.001M aq.  $CuSO_4$ . The residue is dissolved in 5 c.c. of  $H_2O$ , and 1 c.c. of 4%  $CS(NH_2)_2$  solution is added to reduce  $As^V$

to  $\text{As}^{\text{III}}$ . 5 drops of 0.05% aq. 2:5 dinitrophenol are added and the solution is neutralised with aq.  $\text{NH}_3$ . Total  $\text{PO}_4^{\text{'''}}$  is then determined. The plankton  $\text{PO}_4^{\text{'''}}$  is determined by difference after filtering through a fine paper to remove plankton. The determination of turbidity with the Pulfrich photometer is described.

H. J. E.

**Determination of phosphoric acid.**—See B., 1936, 1036, 1059.

**Boric acids and borates.** Borax as titration substance. G. KILDE (Dansk Tidsskr. Farm., 1936, 10, 273—296).—Analytical borax should be recryst. below  $50^\circ$  and kept over saturated aq.  $\text{NaCl}$ +sucrose to avoid formation of the pentahydrate. M. H. M. A.

**Micrometric estimation of quartz in rocks.**—See B., 1936, 1093.

**Detection of carbon monoxide.** A. LABÒ (Boll. chim.-farm., 1936, 75, 521—531).—Methods for the detection and determination of CO are discussed.

O. J. W.

**Determination of krypton content of air.** F. KOROSY (Magyar chem. Fol., 1935, 41, 21—25; Chem. Zentr., 1936, i, 385).—The Kr: A ratio is determined spectrographically in an unfractionated inert gas mixture.

J. S. A.

**Causes of contamination of precipitates. III. Precipitation processes in which various electrolytes take part. Classification.** Z. KARAOGLANOV (Z. anal. Chem., 1936, 106, 399—407).—From the author's previous work, pptn. processes are classified into four types. (a) Pptns. unaccompanied by any secondary reactions, e.g., pptn. of  $\text{AgCl}$  or  $\text{CaC}_2\text{O}_4$ . The formation of pure pptns. in these cases is contrary to adsorption theories of contamination. (b) Pptns. accompanied by a simultaneous secondary reaction, e.g., pptn. of  $\text{SO}_4^{\text{''}}$  or  $\text{CrO}_4^{\text{''}}$  with  $\text{BaCl}_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{PbCl}_2$ , or  $\text{PbBr}_2$  (cf. this vol., 1352). (c) Pptns. followed by a secondary reaction; e.g., pptn. of  $\text{Cu}(\text{OH})_2$  in presence of excess of  $\text{CuSO}_4$ , followed by formation of basic salt. (d) Pptns. accompanied by a secondary physical process, such as adsorption or mixed crystal formation.

**Qualitative analysis of cations without use of  $\text{H}_2\text{S}$  or  $(\text{NH}_4)_2\text{S}$ .** M. B. SCHTSCHIGOL and N. M. DOUBENSKI (Ann. Chim. Analyt., 1936, [in], 18, 257—261).—Ag, Hg, and Pb are pptd. with  $\text{HCl}$ , and the solution is evaporated down with  $\text{HNO}_3$ , removing Sn and Sb as oxides. The solution is treated with  $\text{Na}_2\text{CO}_3$ + $\text{NH}_4\text{Cl}$ +aq.  $\text{NH}_3$ , thereby pptg. Bi, Fe, Mn, Al, Cr, Ca, Sr, Ba, and Mg (in presence of  $\text{PO}_4^{\text{'''}}$ ). Al and Cr are dissolved by treating the ppt. with  $\text{Na}_2\text{O}_2$ , and Ba, Ca, Sr, and Mg are dissolved away from Bi, Fe, and Mn by warming with  $\text{Na}_2\text{HPO}_4$ + $\text{AcOH}$ .

J. S. A.

**Potentiometric determination of calcium in solutions.** D. M. GREENBERG and C. E. LARSON (J. Biol. Chem., 1936, 115, 769—770).—Ultrafiltration experiments show that gelatin adsorbs little or no Ca at its isoelectric point ( $p_{\text{H}}$  4.8) or at  $p_{\text{H}}$  4.3, in disagreement with Tendeloo's results (this vol., 443) obtained by an e.m.f. method.

F. A. A.

**Detection of zinc with potassium ferricyanide and *p*-phenetidine.** L. SZEDELLEDY and S. TANAY (Z. anal. Chem., 1936, 106, 342—348).—0.00005 mg. of Zn may be detected by the blue coloration given by  $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ + $\text{K}_3\text{Fe}(\text{CN})_6$  in presence of Zn. In presence of Ag, Pb, Bi, and Sn the sensitivity is lowered by the simultaneous formation of white ferrocyanide ppts. A large excess of Mg, K, Na, Ca, Sr, or Ba has no influence.

J. S. A.

**Internal electrolysis. I. Determination of small quantities of cadmium and nickel in zinc.** J. G. FIFE (Analyst., 1936, 61, 681—684; cf. A., 1930, 884).—To determine Cd an anolyte containing  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  and a catholyte containing the mixture to be analysed,  $\text{NH}_4\text{Cl}$ ,  $\text{NaOAc}$ ,  $\text{AcOH}$ , and  $\text{N}_2\text{H}_4\cdot\text{HCl}$  are recommended. Electrolysis for 30 min. is required for  $>10$  mg. of Cd, and 45 min. for  $>10$  mg., at  $70^\circ$ . For the determination of Ni, the anolyte contains, in addition, aq.  $\text{NH}_3$ , and the catholyte contains the mixture to be analysed,  $\text{NH}_4\text{Cl}$ , and  $\text{Na}_2\text{SO}_3$ . The electrolysis is carried out for 30—60 min. at  $65^\circ$ .

E. C. S.

**[Spectrographic] determination of cadmium and lead in zinc.**—See B., 1936, 1099.

**Determination of lead in potable waters.**—See B., 1936, 1134.

**Electrolytic determination of copper.** H. MOHLER and J. HARTNAGEL (Mitt. Lebensm. Hyg., 1936, 27, 131—133).—The apparatus described provides for voltage and current control over a wide range and enables 5—10 mg. of Cu to be deposited at  $60$ — $70^\circ$  in 40 min. on a Pt gauze cathode, using a Pt spiral anode. Canned vegetables are ashed and extracted in presence of  $\text{H}_2\text{SO}_4$ , removal of  $\text{SiO}_2$  being unnecessary; 66—102 mg. of Cu per kg. were found.

J. G.

**Determination of cuprous oxide as applied to sugar analysis.**—See B., 1936, 1063.

**Sensitive test for copper.**—See this vol., 1398.

**8-Hydroxyquinoline method for determination of aluminium, iron, and titanium.** L. STUCKERT and F. W. MEIER (Sprechsaal Keram., 1935, 68, 527—529; Chem. Zentr., 1936, i, 386).—The gravimetric method is trustworthy if  $\text{SiO}_2$  is first removed. Titration with  $\text{KBrO}_3$ + $\text{KBr}$  gives low results in presence of Fe.

J. S. A.

**Analysis of felspar. Volumetric determination of alumina.**—See B., 1936, 1036.

**Catalytic detection of manganese.** L. SZEDELLEDY and M. BARTFAY (Z. anal. Chem., 1936, 106, 408—416).— $10^{-9}$  g. of Mn in 5 c.c. of solution may be detected by the catalysed oxidation of *p*-phenetidine (I) [0.1 c.c. of 0.1% (I) hydrochloride] by  $\text{KIO}_4$  (0.5 c.c. of saturated solution) in neutral solution. 1000 parts of Cr, Fe (in presence of  $\text{NaF}$ ), Co, or Sn do not interfere; in presence of Zn, Sn, Hg, and Al,  $\text{NaOAc}$  is added.

J. S. A.

**Determination of manganese in tungsten and ferrotungsten.**—See B., 1936, 1099.

**Macro-detection of cobalt. II.** F. P. DWYER (J. Proc. Austral. Chem. Inst., 1936, 3, 277—280).—



Methylene-blue (I) + KCN, or (I) + dimethylglyoxime (II) +  $\text{NH}_3$  are added to the solution. The strong reducing action of  $\text{K}_4\text{Co}(\text{CN})_6$  or the Co-(II) complex reduces (I) in presence of  $5\text{--}10 \times 10^{-6}$  g. of Co. Fe, Ni, Cr, Cu, Sn, and Ti, which interfere, are removed by successive treatment with  $\text{KMnO}_4$ , aq.  $\text{SO}_2$ , and KCNS before adding an excess of the reagent. J. S. A.

Gravimetric separation of quadri- and hexavalent uranium. I. F. HECHT and H. KRAFFT-EBING (Z. anal. Chem., 1936, 106, 321—330).— $\text{U}^{\text{IV}}$  may be quantitatively separated from  $\text{U}^{\text{VI}}$  by pptn. with  $\text{H}_4\text{P}_2\text{O}_6$  in acid solution. Subsequent oxidation of the ppt. and determination of U as  $(\text{UO}_2)_2\text{P}_2\text{O}_7$  gives high results. Mo and  $\text{U}^{\text{VI}}$  may be separated by pptg. U from 0.5%  $\text{H}_2\text{SO}_4$  solution by means of 8-hydroxyquinoline (I). U may then be pptd. by (I) on addition of  $\text{NH}_4\text{OAc}$ . The method is proposed, following the removal of P with  $(\text{NH}_4)_2\text{MoO}_4$ , for the determination of U after pptn. with  $\text{H}_4\text{P}_2\text{O}_6$ . J. S. A.

Systematic analytical procedure without use of hydrogen sulphide. V. J. PETRASCHENJ (Z. anal. Chem., 1936, 106, 330—342).—The method is based on the solubilities of the phosphates. Sn and Sb are first removed by evaporation with  $\text{HNO}_3$ ; Pb and Ag are pptd. as chlorides. The solution is then treated with  $(\text{NH}_4)_2\text{HPO}_4$  and a large excess of  $\text{NH}_3$ . The ppt. is further subdivided into groups based on the differing solubility of the phosphates in 2N-AcOH and in 0.5N- $\text{HNO}_3$ . J. S. A.

Analysis of gold-palladium-silver alloys.—See B., 1936, 1099.

Determination of gold in dental gold alloys.—See B., 1936, 1099.

Gas-tight furnace for thermocouple standardisation. C. D. NIVEN (Canad. J. Res., 1936, 14, A, 177—180).—A gas-tight furnace with  $\text{H}_2\text{O}$ -cooled lid for calibrating thermocouples in molten metals in an atm. of  $\text{N}_2$  or coal gas is described. R. S. B.

Preparation of a sensitive vacuum thermoelement. E. PICKER and G. RUDINGER (Z. tech. Physik, 1935, 16, 265—267; Chem. Zentr., 1936, i, 814).—The element consists of two thin overlapping layers of Fe and constantan, prepared by evaporation in vac. onto a thin strip of mica, which is finally mounted in vac. H. J. E.

Simple apparatus for measuring light absorption. J. AUSCHKAP (Latvij. Univ. Raksti, 1936, 3, 11—14).—An absorption cell for the comparison of two liquids is described. H. J. E.

Complementary filters for photographing the Raman spectra of crystal powders. R. ANANTHAKRISHNAN (Current Sci., 1936, 5, 131—132).—Monochromatic light is used for excitation, and all scattered light of this  $\lambda$  is absorbed before entering the spectrograph. C. W. G.

Filter opaque to ultra-violet light. G. HEYNE and M. SCHÖN (Angew. Chem., 1936, 49, 784).—Durophen lacquer 218V in thin layers is opaque to light of  $\lambda < 4000$  Å., but practically non-absorbing in the visible region. J. S. A.

Quantitative analysis of the photochemical bleaching of visual purple solutions in monochromatic light. H. J. A. DARTNALL, C. P. GOOD-EVE, and R. J. LYTCHGOE (Proc. Roy. Soc., 1936, A, 150, 158—170).—An apparatus has been devised for determining the rate of bleaching and an equation is derived for the change of absorption with time, under ideal photochemical conditions. L. L. B.

Photo-electric sedimentation measurement. C. ENDERS and A. SPIEGL (Kolloid-Z., 1936, 77, 37—38).—The measurement of sedimentation by determination of the change in absorption of light compares favourably with the kinetic method. E. S. H.

Standardisation of photo-electric cells for the measurement of energy. H. H. POOLE and W. R. G. ATKINS (Sci. Proc. Roy. Dublin Soc., 1936, 21, 363—379).—Using a W-filament lamp having a rated colour temp. of 2360° abs. the consts. for a Weston Se rectifier cell have been determined for different regions of the spectrum isolated by means of Jena, and Corning sextant green, glass filters. Owing to uncertainties in the colour temp. of the source, these consts. may contain an error up to 20%; further, the spectral distribution of energy for the standard lamp is very different from that for daylight, which may account for differences between the results of daylight measurements (using the consts.) and those of Abbot (A., 1931, 592). R. C. M.

Large quartz spectrograph for examination of biological material. J. S. FOSTER (Canad. J. Res., 1936, 14, A, 173—176).—A comparatively inexpensive apparatus with a Cornu prism is described. R. S. B.

Spectro-pleochroism-meter and investigation of mineral dichroism. N. VEDENEVA and S. GRUM-GRSHIMAILO (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 383—385; cf. A., 1935, 58).—Apparatus for the measurement of the spectral distribution of dichroism at varying temp. is described. With increasing temp. the max. dichroism of coloured tourmaline is decreased and shifted to longer  $\lambda$ . For pink and blue tourmalines the change is irreversible above 425° and 275°, respectively. O. D. S.

Measurements of the intensity of X-ray radiation with a proportional amplifier. V. VEKSLER and B. ISAEV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 369—370).—The amplifier was tested by means of the continuous spectrum of W. O. D. S.

X-Ray fluorescent screens. H. STEPS (Fortschr. Röntgenstr., 1935, 52, 293—299; Chem. Zentr., 1936, i, 826).—A photometric method of measuring the intensity of fluorescence is described. H. J. E.

Thermal control in minimum-deviation refractometry and temperature coefficients for a medium flint glass. L. W. TILTON (J. Res. Nat. Bur. Stand., 1936, 17, 389—400).—Details are given of an arrangement in which the spectroscopic prism is mounted and adjusted in a thermostated bath of stirred air contained in a water-jacketed cylinder provided with plane-parallel windows capable of adjustment to cover a wide range of prism angles.

and refractive media. Data showing the variation of  $n$  with temp. for a medium flint glass are recorded.

J. W. S.

**Step compensator for the Jamin interference refractometer when illuminated with white light.** H. BILLING (Z. Physik, 1936, 103, 57—60).—For direct readings the eyepiece scale has a limited measurement range. A five-fold extension is obtained by inserting a glass plate cut into four steps, each 10  $\mu$  thick, in the beam passing through the comparison tube. The field of view is thereby divided into five strips in one of which the interference fringe appears.

H. C. G.

**High-temperature vacuum Debye-Scherrer X-ray camera.** J. E. DORN and G. GLOCKLER (Rev. Sci. Instr., 1936, [ii], 7, 389—390).—Temp. up to 500° can be used, and are measured by means of a thermocouple.

C. W. G.

**Use of high-frequency discharge tubes as electrical counters.** S. C. CURRAN (Phil. Mag., 1936, [vii], 22, 599—616).—An investigation of the working conditions and sensitivity of various kinds of tubes is reported.

N. M. B.

**Amplifier for the coincidences of proportional wire counters.** G. BERNADINI, D. BOCCIARELLI, and F. OPPENHEIMER (Rev. Sci. Instr., 1936, [ii], 7, 382—383).—The coincidences between two proportional wire counters are used to detect the recoil protons ejected by neutrons from a thin layer of paraffin.

C. W. G.

**Stereo-comparator for work with Wilson's chamber.** L. GROSCHÉV, N. DOBROTIN, and J. FRANK (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 289—290).—An instrument for calculating the spatial distribution of tracks of particles in the Wilson chamber from stereoscopic photographs is described.

R. S. B.

**Photography of minima in the magneto-optic apparatus.** G. HUGHES (J. Amer. Chem. Soc., 1936, 58, 1924—1932).—Technique demonstrating the reality of the min. is described.

E. S. H.

**Resonance method of determining dielectric constants.** F. HUMMEL (Z. tech. Physik, 1935, 16, 264—265; Chem. Zentr., 1936, i, 116).—Apparatus is described.

J. S. A.

**Application of radio waves to measurement of dielectric constants of non-conducting liquids.** D. DOBORZYNSKI (Hochfrequenztech., 1935, 46, 92—94; Chem. Zentr., 1936, i, 116—117).—The use of radio-frequencies in measurements by the resonance method is described.

J. S. A.

**Applications of dielectric constant measurement.** J. HENRION (Rev. Univ. Mines, 1935, [viii], 11, 412—415; Chem. Zentr., 1936, i, 117).—A review.

J. S. A.

**Normal element of small potential.** W. GREMMER (Physikal. Z., 1936, 37, 697—699).—The use of Cd amalgams of different concn. in CdSO<sub>4</sub> solution as a normal element of small potential has been investigated.

A. J. M.

**Applications of the glass electrode in conjunction with the valve potentiometer.** F. MÜLLER

and W. DURICHEN (Z. Elektrochem., 1936, 42, 730—732).—Apparatus and technique for automatic  $p_H$  control are described.

E. S. H.

**Agar and potassium chloride bridge for use with calomel half-cells.** I. M. ROBERTSON (Analyst, 1936, 61, 687—688).

E. C. S.

**Electrometric  $p_H$  equipment and hysteresis of calomel electrodes.** B. WINGFIELD and S. F. ACREE (J. Amer. Leather Chem. Assoc., 1936, 31, 403—406).—The temp. error of a saturated calomel electrode is 0.04  $p_H$  for a change of 8.4°. Measurements should be conducted in a const.-temp. bath or under conditions which have varied  $\pm 1^\circ$  for 7—10 hr. A glass electrode assembly in which the calomel electrode is enclosed in a protecting Dewar flask is described.

D. W.

**Electrolysis stand.** W. BORKENSTEIN (Z. anal. Chem., 1936, 106, 427—429).

J. S. A.

**Phosphorus pipette for determination of oxygen.** Z. B. SÓLYOM (Magyar chem. Fol., 1935, 41, 94—95; Chem. Zentr., 1936, i, 385).

J. S. A.

**Automatic pipette for sedimentation analysis.** E. HOFFMANN (Kolloid-Z., 1936, 77, 44—45).

E. S. H.

**Pore viscosimetry of molecular aggregation in solution.** H. WISLICHENUS (J. pr. Chem., 1936, [ii], 147, 124—132; cf. A., 1933, 801).—An improved form of the pore viscosimeter is described and its use is illustrated by results obtained for sucrose and sol. starch solutions.

J. W. S.

**Forceps for handling radioactive substances.** L. F. CURTISS (Rev. Sci. Instr., 1936, [ii], 7, 393—394).—Protection for the operator's hand is secured by a length of about 20 cm. The forceps are self-closing.

C. W. G.

**Pyrex glass seals.** V. H. FRAENCKEL (Rev. Sci. Instr., 1936, [ii], 7, 395).—Corning glasses suitable for sealing to Pyrex glasses are listed.

C. W. G.

**Metal oil diffusion pump: multiple nozzle type.** I. AMDUR (Rev. Sci. Instr., 1936, [ii], 7, 395—396).—A simple all-metal pump with a speed of 250 litres per sec. is described.

C. W. G.

**Arrangement for mixing liquids in bottles.** H. WOLLENBERG (Pharm. Zentr., 1936, 77, 660).—A rotary shaking device is described.

J. S. A.

**Adjustable support and stand for Bunsen burners.** I. A. BALINKIN (J. Chem. Educ., 1936, 13, 414).

L. S. T.

**Calculation of surface tension from experiment.** IV. A. W. PORTER (Phil. Mag., 1936, [vii], 22, 726—729; cf. this vol., 552).—Corrections previously considered for the rise in tubes of circular section and various widths for zero angle of contact are extended to various angles in the range 0—90°.

N. M. B.

**Thermal decomposition of systems of solid and gaseous components.** J. PIAZZA (An. Inst. Invest. cient. tec., 1934, No. 3—4, 57—60; Chem. Zentr., 1936, i, 384).—A dilatometric technique is described.

J. S. A.

**Preparation of tin and tin alloys for microscopical examination.** H. J. TAFS (J. Roy. Micro-



scop. Soc., 1936, [iii], 56, 300—306).—Modified procedure for polishing, etching, and mounting is described. E. S. H.

**Ebulliometry.** W. SWIENTOSLAWSKI (Mem. Acad. Polonaise, 1936, A, No. 3, 1—196).—A monograph giving detailed descriptions of the construction and applications of modern ebulliometers. J. W. S.

**Efficient expansible mechanical stirrer and its use in organic syntheses.** J. G. HILDEBRAND, jun., and M. T. BOGERT (Coll. Czech. Chem. Comm., 1936, 9, 391—394).—The lower ends of pieces of heavy steel spring are attached to the bottom of a vertical brass rod and the other ends are attached to a brass tube sliding over the rod. When the stirrer has been inserted into the flask the stirrer blades are bowed out by forcing down the brass tube with nuts. The device includes a Hg seal and is especially useful for stirring very viscous material. The prep. of Et cyclopentanone-2-carboxylate from Et adipate and Na in PhMe is described, and the yield was increased from 66% to 80% by using the stirrer. J. G. A. G.

**Tables for converting  $d_{20}^{20}$  into  $d_4^{20}$  (vac.).** W. FRIEDEL (Arch. Pharm., 1936, 274, 392—397).—Vals. of  $d_{20}^{20}-d_4^{20}$  (vac.) to four decimal places are given for vals. of  $d_{20}^{20}$  between 0.5892 and 1.5319.

F. R. G.

**Test for vacuum-tightness of glass grindings.** W. A. BOUGHTON (J. Chem. Educ., 1936, 13, 436).

L. S. T.

**Grinding [ends of] glass tubing and apparatus flat.** H. DRAUTZ (Chem.-Ztg., 1936, 60, 886).

J. S. A.

**Valve for fine regulation of gas pressures and its application in ion [X-ray] tubes.** V. KUNZL and J. B. SLAVÍK (Z. tech. Physik, 1935, 16, 272—276; Chem. Zentr., 1936, i, 814—815).

H. J. E.

**Measurement of small pressure differences at high absolute pressures.** E. SCHMIDT (Z. Ver. deut. Ing., 1936, 80, 635—636).—The ring balance frequently employed for this purpose, and a more sensitive apparatus of the horizontal beam balance type, are described. The latter instrument has been satisfactorily employed for determining  $\eta$  of  $H_2O$  and steam at pressures  $>250$  atm. and temp. of  $350^\circ$ .

R. B. C.

**Lecture experiments on inorganic and general chemistry.** A. KUTZELNIGG (Angew. Chem., 1936, 49, 813).—The experiments illustrate the rapid growth of fibrous  $Al_2O_3$  by treating Al with  $HgI_2$ , and the catalytic oxidation of coal gas by  $Cr_2O_3$ .

E. S. H.

**Priestley, Lavoisier, and Trudaine de Montigny.** R. E. OESPER (J. Chem. Educ., 1936, 13, 403—412).—Historical.

L. S. T.

## Geochemistry.

**Redetermination of the protium-deuterium ratio in water.** N. F. HALL and T. O. JONES (J. Amer. Chem. Soc., 1936, 58, 1915—1919).—When allowance is made for  $^{18}O$ , the H/D ratio for surface lake  $H_2O$  is  $6400 \pm 200$ .

E. S. H.

**Heavy water content of salt waters from petroleum springs.** I. T. TITANI and K. OKABE (Bull. Chem. Soc. Japan, 1936, 11, 593—597).—The  $D_2O$  content of salt waters from ten Japanese petroleum springs depends not only on the depths of the springs but also on the geological formations.

C. R. H.

**Reaction of ground-water in Finland.** A. E. SANDELIN (Suomen Kem., 1936, 9, A, 108—111).—The  $p_H$  of 95 samples of  $H_2O$  from dairies varied from 5.2 to  $>7.6$ . The acid reaction is due to  $H_2CO_3$  and other acids.

J. N. A.

**Application of  $p_H$  to mineralogy and geology.** M. DERIBERE (Ann. Chim. Analyt., 1936, [iii], 18, 262—263).—The role of  $p_H$  in determining the composition of sediments from mixed (e.g., siliceous and argillaceous) suspensions is indicated. The separability of mixed deposits by flotation depends on the  $p_H$ ; thus beryl and  $SiO_2$  have the same floatability at  $p_H$  9, and max. separability at  $p_H$  6.4.

J. S. A.

**Colloidal silica in natural waters and the "silicomolybdate" colour test.** A. R. TOURKY and D. H. BANGHAM (Nature, 1936, 138, 587—588).—The view that the colour intensity in the Dienert-Wandenbulcke reaction for  $SiO_2$  is  $\propto$  the crystalloid

$SiO_2$  is incorrect. The  $SiO_2$  which reacts with the  $NH_4$  molybdate (I) is mainly colloidal, and approx. correct results for the total  $SiO_2$  in natural  $H_2O$  are obtained when the  $SiO_2$  has been held in solution for a sufficient time. Warming to  $80^\circ$  with NaOH improves the agreement with gravimetric results. The coloured substance obtained with  $SiO_2$  and (I) is an adsorption complex, and not a true heteropolyacid.

L. S. T.

**Rapid sulphide deposition on organic residues at volcanic sulphur springs.** F. BERNAUER (Zentr. Min., 1935, A, 343—344; Chem. Zentr., 1936, i, 530).—Plant material on the shore of Porto de Levante becomes coated with Fe sulphide in a few days. The deposit gives the X-ray diagram of marcasite.

**Lake Ebeity.** S. Z. MAKAROV and I. G. DRUSHININ (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 353—374).—The  $H_2O$  contains  $HCO_3'$  0.089,  $Cl'$  11.8,  $SO_4''$  7.57,  $Br'$  0.025,  $Mg(HCO_3)_2$  0.016,  $Ca(HCO_3)_2$  0.101,  $KBr$  0.037,  $KCl$  0.026,  $MgCl_2$  2.96,  $Na_2SO_4$  12.13,  $NaCl$  15.6 g. per litre.

R. T.

**Sulphide-carbonate equilibrium in mineral waters.** P. N. PALEI (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 327—334).—A formula connecting  $[H_2S]$  with  $HS'$ ,  $S''$ ,  $CO_2$ ,  $HCO_3'$ ,  $CO_3''$ , and  $OH'$  concns. is derived.

R. T.

**Fluorides in the natural waters of Rhode Island.**—See B., 1936, 1070.

Graphic representation of the mineral and curative springs of Switzerland. A. NUSSBERGER (Mitt. Lebensm. Hyg., 1936, 27, 201—203).

E. C. S.

(A) Geology of Swiss mineral and curative springs. (B) Geological characteristics of Swiss mineral and curative springs. J. CADISCH (Mitt. Lebensm. Hyg., 1936, 27, 216—243, 244—259).—(A) The classification and mineralisation of springs and their regional grouping are discussed.

(B) The characteristics of the  $H_2O$  of individual spas are given.

E. C. S.

Surface markings on a diamond. W. H. GEORGE (Nature, 1936, 138, 616, 641).—The reproduced photomicrograph of the [111] face of a diamond shows triangular markings of the size predicted by the mosaic hypothesis of crystal structure. L. S. T.

Mechanics of metasomatism. G. W. BAIN (Econ. Geol., 1936, 31, 505—526).

L. S. T.

Granodiorite laccolith of the Malka river (Caucasus) and its content of radium. S. P. SOLOVIEV (Amer. J. Sci., 1936, [v], 32, 380—391).—This laccolith of Palaeozoic age is intruded into schists. The mean of 52 determinations of Ra is  $1.89 \times 10^{-12}$  g. per g. The upper portion of the mass contains more Ra than the lower. A granodiorite from Mt. Elbrus contains  $1.30 \times 10^{-12}$  and  $0.37 \times 10^{-12}$ . L. J. S.

Formula of aenigmatite. M. FLEISCHER (Amer. J. Sci., 1936, [v], 32, 343—348).—From published analyses the formula is deduced as  $X_4Y_{13}(Si_2O_7)_6$ , where  $X=Na, Ca, K$ , and  $Y=Fe^{II}, Fe^{III}, Ti, Mg, Mn, Al$ . A special case is  $Na_4Fe^{II}_9Fe^{III}_2Ti_2(Si_2O_7)_6$ . In rhönite part of the Si is replaced by Al, and Na by Ca (as in anorthite and albite). Chemically and crystallographically aenigmatite does not belong to the amphibole group. L. J. S.

Paragenetic relations and mode of formation of minerals and pseudomorphs of the Wendelstein Höhenzug near Nürnberg. S. KLEIN (Zentr. Min., 1935, A, 257—266; Chem. Zentr., 1936, i, 738).

H. J. E.

Occurrence of platinum in the Far East. A. A. MENIAJLOV and S. I. NABOKO (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 387—389).—The occurrence and genesis of Pt in far east Siberia are discussed. The paragenesis of sperrylite with sulphides was observed on the Khaikta river. The Amnunakt massif shows some analogy to the S. African Pt deposits, since, whilst the conen. of chromite in the dunites is low, the sulphides are mainly associated with autometamorphosed anorthosites. O. D. S.

New occurrence of montmorillonite. H. JUNG (Naturwiss., 1936, 24, 667).—Montmorillonite occurs in faults in the basalt at Dolmar near Meiningen.

A. J. M.

Hydrothermal alteration of montmorillonite to feldspar at temperatures from  $245^\circ$  to  $300^\circ$ . J. W. GRUNER (Amer. Min., 1936, 21, 511—515).—Montmorillonite (I) heated in aq.  $KHCO_3$  in Au-lined pressure bombs gives orthoclase after 7 days at  $300^\circ$ . X-Ray analysis showed the orthoclase to be adularia. At  $272^\circ$  or  $245^\circ$  longer heating is necessary. Muscovite is not formed, and 10% KCl solution had no

effect on (I) in 19 days at  $300^\circ$ . The probable reaction is  $3[(OH)_2Al_2Si_4O_{10} \cdot 2H_2O] + 4KHCO_3 \rightarrow 4KAlSi_3O_8 + 2Al(OH)_3 + 8H_2O + 4CO_2$ . L. S. T.

Salt cupolas of the Ural-Emba region, and the possibilities of their industrial exploitation. N. I. BUJALOV and M. G. VALJASCHKO (Ann. Sect. d'Anal. Physico-Chim., 1936, 9, 335—352).—Geochemical data are recorded for the NaCl-KCl-MgCl<sub>2</sub> deposits. R. T.

Halloysite and dolomite of Martonhegy (Martinsberg), Budapest. G. VAVRINECZ (Magyar chem. Fol., 1935, 41, 70—77; Chem. Zentr., 1936, i, 306).—Analyses are recorded. J. S. A.

Secondary removals and enrichments of gold in gold placers. G. BURG (Z. pr. Geol., 1935, 43, 134—139; Chem. Zentr., 1936, i, 34).—A mechanism is advanced for the process. J. S. A.

X-Ray and optical investigation of the serpentine minerals. G. C. SELFRIDGE, jun. (Amer. Min., 1936, 21, 463—503).—The 100 specimens examined can be classified in two divisions each of which shows slight modifications in the intensities of certain lines. The first division consists of varieties the patterns of which are similar in at. spacing to that of serpentine, best represented by chrysotile, and the second to that of antigorite. Chemical analyses from the lit. are discussed. Many names indicating distinct mineral species should be abandoned in favour of the terms serpentine and antigorite, respectively. L. S. T.

Minerals of Baveno granite: molybdenum glance. P. GALLITELLI (Rend. R. Ist. lombardo Sci. Lett., 1935, [ii], 68, 277—280; Chem. Zentr., 1936, i, 306).—The significance of the occurrence is discussed. J. S. A.

Molybdenum glance in the magnetic iron ore deposit of Schwarzen Krux, Schmiedefeld, Thüringer Wald. H. MORITZ (Zentr. Min., 1935, A, 340—342; Chem. Zentr., 1936, i, 529).—The ore contains 0.001—0.05% of Mo. The zones with quartz, fluorspar, and granite are richest in Mo. H. J. E.

Separation planes in magnetite. J. W. GREIG, H. E. MERWIN, and E. POSNJAK (Amer. Min., 1936, 21, 504—510).—Twinning is not the cause of the separation planes shown in the magnetites examined. L. S. T.

Devitrified felsite dykes from Ascutney Mountain, Vermont. R. BALK and P. KRIEGER (Amer. Min., 1936, 21, 516—522).—Two analyses are given. L. S. T.

Aguilarite from the Comstock Lode, Virginia City, Nevada. R. R. COATS (Amer. Min., 1936, 21, 532—534).—Ores from this lode contain aguilarite,  $Ag_2(S, Se)$ . L. S. T.

Comparative X-ray and morphological investigation of andalusite,  $(AlO)_3AlSiO_4$ , libethenite,  $(CuOH)CuPO_4$ , and adamine  $(ZnOH)ZnAsO_4$ . H. STRUNZ (Z. Krist., 1936, 94, 60—73).—Lattice constns. and probable space-groups for adamine and libethenite are determined; these substances are compared with andalusite, with which they are closely



related. The concepts of isomorphy and isotypy are discussed in regard to them. B. W. R.

**Crystal form and molecular unit of nagyagite.** B. GOSSNER (Zentr. Min., 1935, A, 321—327; Chem. Zentr., 1936, i, 528).—The crystals are tetragonal;  $a$  12.5,  $c$  30.25 Å.; 8 mols. of  $6\text{Pb}(\text{S},\text{Te})_2\text{AuTe}_2$  in unit cell. H. J. E.

**Origin of pyritic copper deposits of the mesothermal type.** J. E. A. KANIA (Econ. Geol., 1936, 31, 453—471).—Fused, powdered  $\text{Na}_2\text{S}$  has been fused separately with pyrite, chalcopyrite, sphalerite, galena, and  $\text{SiO}_2$  and the cooled melts extracted with  $\text{H}_2\text{O}$ . The behaviour of the resulting solutions and sols at temp. up to  $90^\circ$  in contact with marble, lime mud-rock, syenite porphyry, argillaceous quartzite, and carbonaceous shale and in presence or absence of  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  is recorded. Marcasite forms from  $\text{FeS}_2$  sols with little  $\text{Na}_2\text{S}$  present, and pyrite from  $\text{Na}_2\text{S}$ – $\text{FeS}_2$  solutions. Chalcopyrite crystals resulted from hot alkaline  $\text{Na}_2\text{S}$ – $\text{FeS}_2$ – $\text{CuFeS}_2$  sols as replacement in cryst. limestone. Certain mesothermal, pyritic Cu deposits are described and discussed in the light of the experimental results. L. S. T.

**Greensands of Wisconsin.** W. H. TWENHOFEL (Econ. Geol., 1936, 31, 472—487).—Analyses of glauconite from Wisconsin are recorded. L. S. T.

**Ore deposition south of Ouray, Colorado.** I, II. R. S. MOEHLMAN (Econ. Geol., 1936, 31, 377—397, 488—504).—Rock alteration and factors controlling ore deposition are described. Replacement, which has been important in the formation of the deposits, is discussed in detail. The order of deposition of minerals in the San Juan region is discussed. L. S. T.

**Magnetic minerals and the practical applications of their magnetism.** H. BRONDER (Tids.

Kjemi, 1936, 16, 124—125).—Magnetic separations are discussed. M. H. M. A.

**Characteristic properties of palygorskites.** H. LONGCHAMON (Compt. rend., 1936, 203, 672—674).—The dehydration of palygorskites (I) in air saturated with  $\text{H}_2\text{O}$  at  $15^\circ$  has been studied at 20— $1000^\circ$ . Three regions appear in the wt.–temp. curves, at 20— $100^\circ$ , near  $200^\circ$ , and near  $400^\circ$ , separated by steps of approx. const.  $\text{H}_2\text{O}$  content. It is considered that (I) exists in two forms (a) and (b), stable up to  $350^\circ$  and at 500— $750^\circ$ , respectively. With (a) a large proportion of  $\text{H}_2\text{O}$  is zeolitic and after heating at  $350^\circ$  the  $\text{H}_2\text{O}$  lost (7%) is rapidly absorbed from moist air at room temp. (a) passes irreversibly into (b) at  $400^\circ$  and the zeolitic absorption disappears. (I) are compared with the sepiolites (A., 1935, 842).

R. S. B.

**Impregnation of North African phosphates by hydrocarbons, and its origin.** L. CAYEUX (Compt. rend., 1936, 203, 639—642).—The phosphatic rocks are coloured by impregnations of hydrocarbons probably produced by the decomp. of org. matter; a bituminous liquid, and a solid and gaseous product are present. The origin, disposition, and relation to petroleum deposits are discussed. R. S. B.

**Carbon dioxide eruptions from coal seams in Lower Silesia.** O. STUTZER (Econ. Geol., 1936, 31, 441—452).—Eruptions of  $\text{CO}_2$ , due to reduction of pressure by mining, from bituminous coal seams are described. Fragmentation of the coal appears to be a prerequisite for eruption. The  $\text{CO}_2$  is a constituent foreign to the coal and is probably in solid solution with the vitrain. L. S. T.

**Silica-sesquioxide ratio of clays in the characterisation of soils.**—See B., 1936, 1114.

**Iodine in Czechoslovakian soils.**—See B., 1936, 1115.

## Organic Chemistry.

**Relations of carbon and its compounds.** W. D. HARKINS (J. Org. Chem., 1936, 1, 52—64).—A review. R. S. C.

**Form and formula in organic chemistry. Comparative morphology of carbon compounds.** C. WEYGAND (Z. ges. Naturwiss., 1935, 1, 322—329; Chem. Zentr., 1936, i, 739).—A general discussion. H. N. R.

**Contributions from a study of dipole moments to the problems of organic chemistry.** C. P. SMYTH (J. Org. Chem., 1936, 1, 17—30).—A review. R. S. C.

**Oxidation of organic compounds with perchloric acid.** A. VIALARD-GOUDOU (Compt. rend., 1936, 203, 565—568).— $\text{H}_2$  is not and C is only slowly attacked by 65%  $\text{HClO}_4$  at  $200^\circ$  to give, finally, CO and  $\text{CO}_2$ .  $\text{H}_2\text{C}_2\text{O}_4$  is oxidised at  $155^\circ$  to give an equimol. mixture of CO and  $\text{CO}_2$ , which indicates that reaction occurs with  $\text{H}_2\text{C}_2\text{O}_4$  and not its decomp. products. The paraffins are oxidised at  $205$ — $210^\circ$ , whereas  $\text{C}_2\text{H}_4$ ,  $\text{C}_6\text{H}_6$ , and PhMe react at  $130$ — $145^\circ$ .

MeOH, EtOH, and AcOH are easily oxidised, but in no case is  $\text{O}_2$  liberated, indicating that decomp. of  $\text{HClO}_4$  does not precede oxidation. J. L. D.

**Optical activity and chemical structure.** P. A. LEVENE and A. ROTHEN (J. Org. Chem., 1936, 1, 76—133).—The configurative relationships of members of homologous series of the type  $\text{R}[\text{CH}_2]_n\text{CHMe}[\text{CH}_2]_m\text{X}$  ( $\text{X}=\text{Alk}$ , Ar, OH,  $\text{CO}_2\text{H}$ , CN, CHO, OH,  $\text{NH}_2$ ,  $\text{NH}_3^+$ ,  $\text{N}_3$ , Hal;  $\text{R}=\text{Alk}'$  or, occasionally, Ar';  $n$ =usually 0—2;  $m$ =0, 1, 2, etc.) are discussed; vals. of  $[\text{M}]_D^{25}$  are given. The partial rotations of the chromophoric groups can be deduced by analysis of the rotatory dispersion curves (largely unpublished). Experimental observations for aliphatic carbinols are not explicable by the theories of Boys (A., 1934, 832) or Kuhn (this vol., 454); the direction of rotation is considered to be determined by the dissymmetry of the mol. as a whole. Born's model (A., 1935, 917) fails to predict a change of sign when the distance of the chromophoric group from the asymmetric C is changed by one  $\text{CH}_2$  group. H. B.

**Action of acetyl chloride and carbon monoxide on saturated hydrocarbons in presence of aluminium chloride.** H. HOPFF, C. D. NENITZESCU, D. A. ISACESCU, and I. P. CANTUNIARI (Ber., 1936, 69, [B], 2244—2251; cf. A., 1932, 44, 514).—When  $\text{AcCl}$  and  $n\text{-C}_4\text{H}_{10}$  react in the cold in presence of  $\text{AlCl}_3$  the product is  $\text{CH}_2\text{Ac}_2$  formed by autocondensation of  $\text{AcCl}$ . At 50—60° the main product is  $\text{COMeBu}^\beta$ , also formed from  $\text{iso-C}_4\text{H}_{10}$ . In general  $\text{CO}$ , or  $\text{HCOCl}$  arising therefrom, reacts with saturated hydrocarbons in the same manner as the higher acid chlorides with the exception that it can react with the normal, unbranched chain (production of  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$  from  $n\text{-C}_4\text{H}_{10}$ ), and addition at the double linking occurs in a different way. The intermediate formation of aldehydes with *tert.*-CHO explains the unusual intrusion of  $\text{CO}$  between the atoms of the C chain. The complex changes lead to homogeneous products in good yield. The following scheme is typical:  $\text{CHMe}_3 \xrightarrow{(-2\text{H})} \text{CMe}_2\cdot\text{CH}_2$ ;  $\text{CMe}_2\cdot\text{CH}_2 + \text{HCOCl} \rightarrow \text{CHO}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl} (+2\text{H} - \text{HCl}) \rightarrow \text{Bu}^\gamma\text{CHO} \rightarrow \text{COMePr}^\beta$ .  $\text{CMe}_2\cdot\text{CH}_2 + \text{HCl} \rightarrow \text{Bu}^\gamma\text{Cl} \rightarrow \text{Bu}^\gamma\text{COCl}$ ;  $\text{CMe}_2\cdot\text{CH}_2 + \text{Bu}^\gamma\text{COCl} \rightarrow \text{COBu}^\gamma\cdot\text{CH}_2\cdot\text{CMe}_2\text{Cl} \rightarrow \text{COBu}^\gamma\cdot\text{CH}_2\text{Pr}^\beta$ . If anhyd.  $\text{AlCl}_3$ ,  $\text{HCl}$ , and  $\text{CO}$  are heated in a Cu autoclave at about 80°/100 atm., a brisk absorption of the gases occurs with production of the stable adduct  $\text{HCOCl}\cdot\text{AlCl}_3\cdot\text{CuCl}$ , which is vigorously decomposed by  $\text{H}_2\text{O}$  into  $\text{HCl}$  and  $\text{CO}$  and with  $\text{PhMe}$  in presence of anhyd.  $\text{AlCl}_3$  gives  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHO}$  in small yield. H. W.

**Action of aluminium halides on *n*-pentane.** A. L. GLASEBROOK, N. E. PHILLIPS, and W. G. LOVELL (J. Amer. Chem. Soc., 1936, 58, 1944—1948).—Dry  $n\text{-C}_5\text{H}_{12}$  (liquid or gas +  $\text{N}_2$ ) does not react with freshly sublimed  $\text{AlCl}_3$ ; decomp. is initiated by addition of small amounts of  $\text{H}_2\text{O}$ ,  $\text{AlkCl}$  (not  $\text{ArCl}$ ), hydrated  $\text{AlCl}_3$ ,  $\text{HCl}$ , or  $\text{HBr}$  (very effective).  $\text{AlBr}_3$  alone causes decomp. and gives butanes (1.5—14.1%), isopentane (27.2—55.9%), and higher-boiling material (2.5—5.9%); added  $\text{H}_2\text{O}$  or  $\text{HBr}$  increases the reaction velocity. The extent of the decomp. depends on the concn. of  $\text{AlBr}_3$  and the time of reaction. H. B.

**Nitration of normal paraffins.** T. URBANSKI and M. SLON (Compt. rend., 1936, 203, 620—622).— $\text{C}_3\text{H}_8$  with  $\text{N}_2\text{O}_4$  at about 100° affords  $\text{Pr}^\gamma\text{NO}_2$  and  $\text{CH}_2(\text{CH}_2\text{NO}_2)_2$  in 70% yield; aldehydes and fatty acids are by-products.  $\text{CH}_4$  at about 200° gives a poor yield of  $\text{MeNO}_2$  together with polynitro-compounds and products of oxidation. J. L. D.

**Preparation of pure crystalline aliphatic hydrocarbons.** J. STRINGER and H. J. BACKER [with, in part, N. BENNING and J. LOKEMA] (Rec. trav. chim., 1936, 55, 903—914).—The following series of compounds were prepared in a pure state by standard reactions. From undecenoic acid, b.p. 164.5—165.5°, undecic acid, b.p. 122—122.5°/15 mm., the Et ester, b.p. 89—89.5°/1 mm., di-*n*-decyl ketone, m.p. 64.3—64.5°, and *n*-heneicosane, m.p. 40.3—40.5°, b.p. 172—172.5°/25 mm. From lauric acid the Et ester, b.p. 141—141.5°/8 mm., di-*n*-undecyl ketone, m.p. 69.5—69.8°, and *n*-tricosane, m.p. 47.25—47.4°, b.p. 190—191°/1.5 mm. From lauryl alcohol, m.p. 24.0—24.2°, the bromide, b.p. 130.5°/5 mm., a mixture (by the Grignard reaction with  $\text{EtOAc}$ ) of *v*-methyl- $\Delta^{\mu}$ -

pentacosane, b.p. 218.5—219.5°/3 mm., and *v*-methyl-enepentacosane, b.p. 219.5—220.5°/3 mm., and *v*-methylpentacosane, m.p. 28.8—29.0°. From erucic acid the Me ester, b.p. 217—217.5°/3 mm., and (by  $\text{MgMeI}$ )  $\beta$ -methyl- $\Delta^{\beta}$ -tricosadiene, b.p. 210.5—211.5°/3 mm., which absorbs 1  $\text{H}_2$  (Pt-black;  $\text{AcOH}$ ) at room temp. and a second  $\text{H}_2$  at 50° giving  $\beta$ -methyl-*n*-tricosane, m.p. 38.0—38.5° (lit. 42°), b.p. 207.5—208°/3 mm. From stearyl chloride, b.p. 195—195.5°/2 mm., m.p. 23.2—23.4°, *Bu*′ *n*-heptadecyl ketone, b.p. 202—203°/4.5 mm., m.p. 44.8—45.05° (semicarbazone, m.p. 78.0—78.2°), which resists Clemmensen reduction and catalytic hydrogenation, presumably owing to steric hindrance, and with  $\text{HI-P}$  gives an impure product, m.p. 21.6—22.6°. From  $(\text{CH}_2)_2\text{O}$  and  $\text{MgBu}^\gamma\text{Cl}$   $\gamma$ -methylisoamyl alcohol, b.p. 142.6—143.6°, the bromide [ $\beta\beta$ -dimethyl-*n*-butyl bromide], b.p. 58.5—59°/51 mm.,  $\gamma$ -methylisoamyl [ $\beta\beta$ -dimethyl-*n*-butyl] *n*-heptadecyl ketone (by the Cd or Mg alkyl halide), m.p. 53.45—53.75°, b.p. 212.5—213.5°/3.5 mm., and  $\beta\beta$ -dimethyl-*n*-docosane, m.p. 34.55—34.75°, b.p. 191—191.5°/4 mm. From Et nonoate, b.p. 226.5—227.5°, nonyl alcohol and bromide, b.p. 107.5°/17.5 mm.,  $\kappa$ -*n*-nonyl-*n*- $\Delta^1$ -nonadecene [from  $\text{C}_9\text{H}_{19}\cdot\text{MgBr}$  and  $\text{CH}(\text{OEt})_3$ ], b.p. 227.5—228.5°/2.5 mm., and  $\kappa$ -*n*-nonyl-*n*-nonadecane, b.p. 232.5—233°/3 mm., m.p. —6° to —5.5°. From cyclohexyl alcohol the bromide, b.p. 53°/14 mm., cyclohexyl *n*-heptadecyl ketone, b.p. 219—220°/2.5 mm., m.p. 42.6—42.85° (semicarbazone, m.p. 82.2—82.5°), and  $\alpha$ -cyclohexyl-*n*-octadecane, b.p. 207.5—208.5°/3 mm., m.p. 41.2—41.45°. R. S. C.

**Polymerisation of unsaturated gaseous hydrocarbons at atmospheric pressure and ordinary temperature by the catalytic action of phosphoric oxide and stabilisation of the liquid polymerides by hydrogenation.** E. DESPARET (Bull. Soc. chim., 1936, [v], 3, 2047—2055).—After an induction period,  $\text{C}_2\text{H}_4$ , *n*- and *iso*-butene are more or less rapidly and quantitatively adsorbed by  $\text{P}_2\text{O}_5$  on porous earthenware at room temp. and atm. pressure, and when subsequently heated at 110° the polymeride (usually mainly dimeride) is evolved. In certain cases the two processes can be effected simultaneously and the reaction can be made continuous. The polymerides are unstable, but can be stabilised by hydrogenation under known conditions. Heavy residues, C, and  $\text{H}_2\text{O}$  are not produced. H. W.

**Thermal decomposition of olefinic hydrocarbons.** B. M. MICHAÏLOV and J. A. ARBUSOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 423—426; cf. B., 1934, 792; this vol., 451).—Formation of condensation products during the pyrolysis of olefines is avoided by using a 0.5—1.0 sec. contact, and diluting to low partial pressure with steam.  $\Delta^{\alpha}$ -Pentene gave at 600° and 650°, respectively,  $\text{H}_2$  2.6 and 3.1% (by vol.),  $\text{CH}_4$  18.2 and 17.8%,  $\text{C}_2\text{H}_4$  30.9 and 32.9%,  $\text{C}_2\text{H}_6$  7.0 and 6.9%, propylene (I) 20.1 and 21.2%,  $\text{C}_3\text{H}_8$  0.5 and 0.6%, butadiene (II) 13.0 and 11.9%, with 7.7 and 5.6% of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -butene (III);  $\Delta^{\beta}$ -pentene gave, at 600° and 650°, respectively,  $\text{H}_2$  6.6 and 6.7%,  $\text{CH}_4$  47.9 and 40.4%,  $\text{C}_2\text{H}_4$  14.5 and 17.2%,  $\text{C}_2\text{H}_6$  5.0 and 4.1%, (I) 5.4 and 10%, (II) 15.5 and 15.6%, (III) 5.1 and 6.0;  $\Delta^{\alpha}$ -hexene gave



at 650° and 700°, respectively,  $H_2$  1.8 and 2.4%,  $CH_4$  11.2 and 11.9%,  $C_2H_4$  40.3 and 40.0%,  $C_2H_6$  2.3 and 1.4%, (I) 30.2 and 28.0%, (II) 4.3 and 5.8%, (III) 9.9 and 10.5%; 8-methyl- $\Delta^2$ -pentene at 550°, 600°, and 650°, respectively,  $H_2$  6.2, 6.9, and 7.9%,  $CH_4$  10.2, 9.3, and 8.0%,  $C_2H_4$  14.7, 17.0, and 16.3%,  $C_2H_6$  3.2, 1.2, and 0.9%, (I) 60.6, 59.3, and 58.4%,  $C_3H_8$  0.0, 0.3, and 0.2%, (II) 0.6, 0.9, 1.9%, (III) 3.5, 4.1, and 5.3%, and isobutene 1.0, 1.0, and 1.1%.

R. C. M.

**Resolution of  $\alpha\gamma$ -trimethylallyl alcohol into optically active forms.** D. I. DUVEEN and J. KENYON (J.C.S., 1936, 1451—1453).— $\alpha\gamma$ -Trimethylallyl alcohol was converted into its *p*-xenylylurethane, m.p. 65°, and *H* phthalate, m.p. 81.5°; the *brucine* salt, m.p. 143—144°,  $[\alpha]_{5893} -17.0^\circ$  in  $CHCl_3$ , of this was hydrolysed (HCl) to the *d*-*H* phthalate, m.p. 43—44°,  $[\alpha]_{5893} +14.5^\circ$  in  $CHCl_3$ , converted (NaOH) into the *d*-alcohol, b.p. 129°, 43°/17 mm.,  $[\alpha]_{5893} +8.02^\circ$  in  $CHCl_3$  (*Ac*, b.p. 51°/15 mm., and *Bz*, b.p. 139°/19 mm., derivatives), reduced ( $H_2$ -Ni) to *d*-CHMeBu $\alpha$ -OH. The *l*-*H* phthalate, m.p. 44°,  $[\alpha]_{5893} -12.8^\circ$  in  $CS_2$ , obtained by HCl hydrolysis of its *strychnine* salt, m.p. 152° (decomp.),  $[\alpha]_{5893} -20.64^\circ$  in  $CHCl_3$ , was hydrolysed (NaOH) to the *l*-alcohol, b.p. 129°, 43°/18 mm.,  $\alpha_D^{20} -2.13^\circ$  (*l*, 0.5).

F. R. G.

**Condensation of butan- $\beta$ -one with aldehydes of the type,  $CHRR'\cdot CHO$ .** S. G. POWELL and M. M. BALDWIN (J. Amer. Chem. Soc., 1936, 58, 1871—1872).—The ketols obtained from COMeEt and CHMeEt $\cdot$ CHO (obtained by dehydrogenation of CHMeEt $\cdot$ CH $_2$  $\cdot$ OH with a Cu-Cr-Ba oxide catalyst), CHEt $_2$  $\cdot$ CHO, and CHEtBu $\alpha$  $\cdot$ CHO (I) in dil. KOH are dehydrated and then reduced (methods: A., 1925, i, 7; 1933, 492) to  $\zeta$ -methyloctan- $\gamma$ -ol, b.p. 81—83°/15 mm.,  $\zeta$ -ethyloctan- $\gamma$ -ol, b.p. 90—92°/20 mm., and ethyldecan- $\gamma$ -ol, b.p. 119—120°/18 mm., respectively, which are oxidised (*loc. cit.*) to  $\beta$ -methylvaleric,  $\beta$ -ethylvaleric, and  $\beta$ -ethylheptioic acid (II), b.p. 135°/25 mm., 236°/760 mm., respectively (piperazine salts, m.p. 129°, 134°, and 100°, respectively).  $\beta$ -Ethylhexyl alcohol [prepared by addition of Na and AcOH to (I) in  $Et_2O$ +aq.  $MgSO_4$  so that the mixture is slightly alkaline] and  $PBr_3$  give the bromide (III), which with NaCN and subsequent hydrolysis affords (II).  $\gamma$ -Ethylctoic acid, b.p. 253—256°/760 mm. (piperazine salt, m.p. 110°), is prepared (usual method) from (III) and  $CH_2(CO_2Et)_2$ . The piperazine salt of  $\gamma$ -methylhexoic acid has m.p. 109°.

H. B.

**Alkylation. V. Formation of ethyl ether from ethyl chloride and some theoretical deductions.** V. A. ISMAILSKI and B. V. POPOV (Bull. Soc. chim., 1936, [v], 3, 2028—2037).—A solution of *m*- $NH_2\cdot C_6H_4\cdot SO_3H$  (1 mol.), NaOH (2 mols.), anhyd.  $Na_2CO_3$  (1.57 mols.), and EtCl (4.08 mols.) in 96% EtOH is heated in an autoclave at 125° during 13 hr. and the EtCl used,  $NH_4Et\cdot C_6H_4\cdot SO_3H$ ,  $NEt_2\cdot C_6H_4\cdot SO_3H$ , and  $Et_2O$  formed are determined in the mixture. Secondary changes involve 43.4% of the EtCl taken; of this, 56% is used in the production of  $Et_2O$  and 44% in that of EtOH. The schemes  $EtCl+NaOH \rightarrow NaOEt+H_2O$  and  $EtCl+NaOEt \rightarrow Et_2O+NaCl$  are rejected, since in the aq.

alcoholic medium the equilibrium is almost completely displaced towards the left. More probably, the change involves the formation of oxonium compounds, transformed by NaOH into the oxonium bases, which decompose into  $Et_2O+H_2O$  and  $EtOH+H_2O$ , respectively, and is thus analogous to Hofmann's reaction between amines and alkyl halides. The intermediate formation of oxonium compounds explains also the production of alkynes from alkyl halides and alcohols and the prep. of  $Et_2SO_4$  from  $Et_2O$  and  $ClSO_3H$ .

H. W.

**Tertiary alkyl ethers.** T. W. EVANS and K. R. EDLUND (Ind. Eng. Chem., 1936, 28, 1186—1188).—The direct addition of olefines to alcohols by the Reychler reaction (A., 1907, 275) has been elaborated.  $CMe_2\cdot CHMe$  and EtOH with  $H_2SO_4$  under pressure at 60° give an equilibrium mixture containing 40% of Et *tert*-amyl ether, b.p. 101—102°. The following are thus prepared: Me, b.p. 55°, Et, b.p. 73°,  $Pr^i$ , b.p. 87—88°, Bu $^i$ , b.p. 123—124°, Bu $^s$ , b.p. 114°, sec.-Bu, b.p. 114—115°, Ph, b.p. 185—186°, and  $CH_2Ph$ , b.p. 82—83°/8 mm., Bu $^i$  ether; Bu $^i$  isoamyl ether, b.p. 138—140°: Me, b.p. 86—87°, and  $Pr^i$ , b.p. 114—115°, *tert*-amyl ether; Me *tert*-hexyl ether, b.p. 113°; ethylene glycol Bu $^i$ , b.p. 153°, Bu $_2$ , b.p. 171°, Me Bu $^i$ , b.p. 131—132°, Et Bu $^i$ , b.p. 148°, Bu $^s$  Bu $^i$ , b.p. 83°/20 mm., and *tert*-amyl, b.p. 50—55°/3 mm., ether;  $\alpha\beta$ -propylene glycol Bu $^i$  ether, b.p. 151—153°; glycerol Bu $^i$ , b.p. 93—94°/5 mm., and Bu $_2$  ether, b.p. 80—82°/4 mm.; diethylene glycol Bu $^i$  ether, b.p. 72°/2 mm. The equilibrium reached varies with the olefine used.

R. F. P.

**Bromonitromethiononic acid.** H. J. BACKER (Rec. trav. chim., 1936, 55, 915—920).— $K_2$  nitromethionate (I) and Br- $H_2O$  at 65° give bromonitromethiononic acid,  $+4H_2O$ , m.p. about 65°, and  $+2H_2O$  (retained in vac. over  $P_2O_5$ ), m.p. 90—91° (decomp.) [*distrychnine*,  $+H_2O$ , Ba,  $+3H_2O$ ,  $K_2$ ,  $Tl_2$ , and dibrucine,  $+6H_2O$ , phototropic, salts], which regenerates (I) with  $K_2S_2O_3$ . Dibrucine chloromethionate is also phototropic. Crystallographic data [P. TERPSTRA] are given for three of these salts.

R. S. C.

**Addition of sodium hydrogen sulphite to alkylene oxides.** W. M. LAUER and A. HILL (J. Amer. Chem. Soc., 1936, 58, 1873—1874; cf. Fromm *et al.*, A., 1928, 868).— $(CH_2)_2O$  with conc. aq.  $NaHSO_3$  and  $KHSO_3$  gives Na (I), m.p. 192—194°, and K (II), m.p. 191—193°,  $\beta$ -hydroxyethanesulphonate, respectively, acetylated (method: this vol., 316) to Na and K, m.p. 258—260°,  $\beta$ -acetoxyethanesulphonate, respectively. Na  $\beta$ -myristoyloxyethanesulphonate is prepared from (I) and myristoyl chloride. (I) and (II) with  $PCl_5$  afford  $CH_2Cl\cdot CH_2\cdot SO_2Cl$ , b.p. 86—88°/13 mm.  $NH_4$   $\beta$ -chloroethanesulphonate and conc. aq.  $NH_3$  at 105° give taurine, which with  $KNO_2$ +AcOH yields (II).

H. B.

**Polysulphones from acetylenes and sulphur dioxide.** L. L. RYDEN and C. S. MARVEL (J. Amer. Chem. Soc., 1936, 58, 2047—2050; cf. this vol., 186).— $CH_2CR$  [ $R=Me$ , Et (I),  $Pr^i$  (II), Bu $^i$ , *n*-amyl, and Ph (III)] with  $SO_2$  in EtOH followed by paracet-aldehyde (must contain peroxide) give polysulphones, decomp. 250—260°, 210—215° (Ia), 203—208° (IIa),

195–205°, 164–170°, and 250–275° (IIIa), respectively. CMe·CR (R=Me, Pr, Ph), (:C·CO<sub>2</sub>Et)<sub>2</sub>, and allene do not similarly react. The presence of ·CR:CH·SO<sub>2</sub>· in (Ia), (IIa), and (IIIa) is established by oxidation (aq. KMnO<sub>4</sub>) to EtCO<sub>2</sub>H, PrCO<sub>2</sub>H, and BzOH, respectively. Hydrolysis (aq. NaOH) of (IIIa) affords CPhMe (trace), CH<sub>2</sub>Ph·SO<sub>2</sub>Me (IV) (8%), BzOH (20%) and Na<sub>2</sub>SO<sub>3</sub> (50%) (the remainder of the S is in the tarry product formed); the formation of (IV) indicates that part of (IIIa) must be [·SO<sub>2</sub>·CPh:CH·SO<sub>2</sub>·CPh:CH·]<sub>n</sub>. (IIa) is similarly hydrolysed to COMePr<sup>a</sup> (trace). (IIa) could not be reduced (H<sub>2</sub>, Pt, dioxan, room temp.). (IIa) heated to 200–215° gives 50–60% of SO<sub>2</sub>; in boiling dioxan SO<sub>2</sub> (about 50%) and a little of a compound, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>S, m.p. 88°, are formed. SO<sub>2</sub> (62·73%) is liberated when (IIIa) is heated at 140°/45 min.

H. B.

**Chemistry of the Claisen condensation.** F. ARNDT and B. EISTERT (Ber., 1936, 69, [B], 2381–2393).—The fundamental basis of the theoretical treatment of compounds with multiple linkings is the conception of the intermediate condition identical with that of resonance between electromeric limiting states and to which the term mesomerism has been applied. Also the inductive effect plays a part. The essentials for the Claisen reaction are the ester (amide) component (I) R·CO<sub>2</sub>Et and the methylene component (II) CH<sub>2</sub>R·CO·R, which must contain CH<sub>2</sub> vicinal to CO and in which CO may be present in CO<sub>2</sub>Et. The alkaline condensing agent causes a possibly minute fraction of (II) to release a proton from CH<sub>2</sub>, thus giving EtOH, NH<sub>3</sub>, or H and forming the ionic alkali metal salt of (II). This conception agrees with that of Scheibler in so far as (II) [not (I)] is concerned in this preliminary stage, but differs in that it does not assume the production of an enolate, but of a compound in which Na functions as cation. Na is therefore not directly concerned with any of the subsequent reactions, and the question of the enolic structure of the anion is subsidiary. Such an anion is regarded as being in the intermediate condition between [·CHR·CO·R]Na<sup>+</sup> (III) and [CHR·CO·R]Na<sup>+</sup>. Reaction occurs between (I) and (III) which contains the unused pair of electrons at C. (I) is also capable of mesomerism and can react in the electromeric conditions R·CO·OEt and OEt·CR·O· (IV). The initial step in the Claisen condensation therefore consists in the entry of the free pair of electrons of (III) into the octet vacancies of the CO·C atom of (I) in form (IV) giving the anionic product, [COR·CHR·CR(OEt)·O]Na<sup>+</sup>. The formation of this product is reversible and not detectable experimentally, and the equilibrium lies far on the left. Union of the second CO to the original CH<sub>2</sub>·C atom of (II) causes this C atom to be placed under the influence of two pronouncedly positive vicinal C atoms, and consequently the remaining proton is much less firmly bound than was originally the case. It therefore unites with the anionic [OEt]· to form EtOH, thereby giving the anion [COR·CR·CR·O]Na<sup>+</sup>, which is almost completely enolic, since it thereby contains a conjugated system. The striving to build such a system must be regarded as the most important and controlling factor of the whole Claisen condensation,

since it brings the feature of irreversibility among a no. of reversible changes, many of which occur in only a small degree. This conception renders obvious the need of CH<sub>2</sub> as well as CO in (II) and the impossibility of the replacement of CO by SO<sub>2</sub>; although the proton-loosening action of SO<sub>2</sub> is > that of CO it cannot function as conjugation partner, since it does not contain true double linkings, but contains O atoms only in semipolar union. It also explains why (II) must contain at least two H attached to active C, since these are eliminated consecutively. Related reactions (aldol condensation, Perkin's and Knoevenagel's syntheses) are discussed. Other views of the course of ester and aldol condensation (enolisation hypothesis, the "intermediate substance" rule, and the hypothesis of the tautomerism, enolate organo-metallic compound) are reviewed.

H. W.

**Twitchell's reagent.** I. Twitchell's reagent as promoter of esterification. J. N. ZAGANIARIS and G. A. VARVOGLIS (Ber., 1936, 69, [B], 2277–2282).—The hydrolytic and esterifying actions of Twitchell's reagent are in a dynamic equilibrium displaced towards the ester side. Reaction is usually effected with a three-fold excess of one component and 2·3 wt.-% of catalyst calc. on that of the mixture. Heating of the mixture is unnecessary and frequently disadvantageous. Aliphatic acids give good yields of esters with primary, sec., and polyhydric aliphatic and fatty-aromatic alcohols, but not with *tert.* alcohols or phenols, with which little action takes place. Aromatic carboxylic, phenolic, and unsaturated fatty-aromatic acids do not react or give very moderate yields. The following interactions are described. AcOH with MeOH, EtOH, Pr<sup>n</sup>OH, *iso*-(I) and *tert.*-amyl alcohol, (CH<sub>2</sub>·OH)<sub>2</sub>, glycerol, CH<sub>2</sub>Ph·OH, PhOH; CCl<sub>3</sub>·CO<sub>2</sub>H with EtOH; Pr<sup>n</sup>CO<sub>2</sub>H with EtOH and (I); EtOH with palmitic, oleic, and tartaric acid, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, BzOH, CHPh:CH·CO<sub>2</sub>H, *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>, and *p*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>; PhOH and EtOH; *o*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and MeOH.

H. W.

**Basic acetates of lead.**—See this vol., 1464.

**Enzymic dehydration of trideuteroacetic acid.**—See this vol., 1418.

**Reaction kinetics and the Walden inversion.** W. A. COWDREY, E. D. HUGHES, and C. K. INGOLD (Nature, 1936, 138, 759).—The hydrolysis of *l*-α-bromopropionic acid to give lactic acids of different optical sign is cited as an example connecting optical inversion with structure and conditions. The optical sign depends on whether conditions favour a uni- or a bi-mol. reaction.

L. S. T.

**Effect of varying conditions in the catalytic hydrogenation of fatty oils on the nature of the reaction product.** III. H. I. WATERMAN, C. VAN VLODRUP, and J. A. PEZY (Rec. trav. chim., 1936, 55, 854–858; cf. A., 1933, 258).—Colloidal Ni, prepared by hydrogenation of Ni(CO)<sub>4</sub> in oil, allows rapid hydrogenation of unsaturated aliphatic esters and fatty oils at 50°/1 atm., without destruction of vitamin-A. Hydrogenation follows the "homogeneous reaction scheme" (saturation first of the most unsaturated centres).

R. S. C.



**Mechanism of the elaidinisation reaction.** S. H. BERTRAM (Chem. Weekblad, 1936, 33, 637—638).—The isomerisation of oleic and elaidic acids in presence of 0.5% of Se at 150° is termol., the Se forming an intermediate complex, in accordance with the hypothesis put forward (this vol., 189). S. C.

**Optical properties of fermentation lactic acids.**—See this vol., 1419.

**Enzymic racemisation of optically active lactic acid.**—See this vol., 1560.

**Polarographic analysis in the study of keto-enol tautomerism.** G. SEMERANO and A. CHISINI (Gazzetta, 1936, 66, 504—509).—The different reduction potentials at a dropping Hg cathode of the keto- and enol forms of a substance can be used to determine the amounts of the two forms in a mixture. By this means the keto-enol tautomerism of  $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$  and of  $\text{CH}_2\text{Ac}_2$  has been investigated.

O. J. W.

**Doubly conjugated system in  $\alpha$ - and  $\beta$ -licanic acids.** R. S. MORRELL and W. R. DAVIS (J.C.S., 1936, 1481—1484).— $\alpha$ - and  $\beta$ -Licanic acids (Brown *et al.*, A., 1935, 607) present in oiticica oil combine with maleic anhydride in  $\text{CO}_2$  at 85° to give, respectively, the  $\alpha$ -additive compound (I), m.p. 79° [ $H_4$ -derivative (Adams), m.p. 111°], and the  $\beta$ -additive compound (II), m.p. 97—98° ( $H_4$ -derivative, m.p. 72—73°). Oxidation of (I) with 5%  $\text{KMnO}_4$ - $\text{Na}_2\text{CO}_3$  at 0° affords  $\gamma$ -ketoazelaic acid (III) (34% yield) and only a trace of valeric acid (IV) (p-bromophenacyl ester, m.p. 73°); ozonolysis of (II) gives mainly (IV) and a substance, m.p. 99—105°. As in the elaeostearic system the  $\Delta^{\alpha,\beta}$ -double linkings are involved in the formation of (I) and the  $\Delta^{\beta,\gamma}$ -linkings in (II), thus suggesting the *X-trans-trans-cis*-Y $\cdot\text{CO}_2\text{H}$  structure for  $\alpha$ - and *X-cis-cis-trans*-Y $\cdot\text{CO}_2\text{H}$  for  $\beta$ -licanic acid. J. W. B.

**Sensitive reaction for oxalic acid.** O. CARLETTI (Boll. Chim. farm., 1936, 75, 498—499).—A reddish-violet colour, changing to blue, is given by  $\text{H}_2\text{C}_2\text{O}_4$  ( $6.3 \times 10^{-6}$  g.) with resorcinol in presence of glycerol (1 drop) and  $\text{H}_2\text{SO}_4$ .

F. O. H.

**Resorcinol reaction of oxalic acid.** M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 2072—2074; cf. this vol., 745).—The oxalate solution is acidified with  $\text{H}_2\text{SO}_4$  and reduced with sheet Zn in presence of  $\text{CuSO}_4$ . A pale blue colour which becomes intense at 100° is developed when 4 drops of this solution are mixed with 2 c.c. of conc.  $\text{H}_2\text{SO}_4$  and 2 drops of Denigès' resorcinol reagent. The reaction appears sp. for  $\text{C}_2\text{O}_4^{2-}$  and is not affected by the presence of  $\text{OCl}^-$ ,  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , or  $\text{CrO}_4^{2-}$ . It is modified in presence of  $\text{Br}^-$  or  $\text{I}^-$ .  $\text{C}_2\text{O}_4^{2-}$  interferes with the author's (*loc. cit.*) or Denigès' test for tartaric acid and is removed by pptn. as  $\text{CaC}_2\text{O}_4$  in  $\text{AcOH}$  previously to the reduction.

H. W.

**[Activated form of oxalic acid.]** E. SCHROER (Ber., 1936, 69, [B], 2243; cf. this vol., 1361; Krauss *et al.*, A., 1930, 577).— $\text{HCO}_2\text{H}$  cannot be regarded as the "active form" of  $\text{H}_2\text{C}_2\text{O}_4$ , with which it has only the strongly reducing properties in common. It has not the more important ability to reduce mol.  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  and to lose activity slowly.

H. W.

**Oxalato complex compounds of tervalent manganese.**—See this vol., 1477.

**Diene syntheses and selenium dehydrogenation in their importance for the development of organic chemistry.** O. DIELS (Ber., 1936, 59, [A], 195—208).—A lecture.

**Condensation of ethyl  $\alpha$ -bromoisobutyrate with *n*-alkylmalonic esters. Structure of the lupin alkaloids.** H. N. RYDON (J.C.S., 1936, 1444—1448).—In the condensation of  $\text{CMeR}\cdot\text{Br}\cdot\text{CO}_2\text{Et}$  with  $\text{CRNaX}\cdot\text{CO}_2\text{Et}$  to give  $\text{CO}_2\text{Et}\cdot\text{CMeR}\cdot\text{CRX}\cdot\text{CO}_2\text{Et}$  and  $\text{CO}_2\text{Et}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CRX}\cdot\text{CO}_2\text{Et}$ , the formation of the latter isomeride is greater when  $\text{R}=\text{R}'=\text{Me}$  instead of  $\text{H}$ , is increased as  $\text{X}$  changes from  $\text{Ac}$  to  $\text{CN}$  and then  $\text{CO}_2\text{Et}$ , and decreased as  $\text{R}$  changes from  $\text{H}$  to  $\text{Et}$ , then  $\text{Pr}^n$ ,  $\text{Bu}^n$ , and *n*-amyl. Hydrolysis of condensation products of the above type leads to *cis*- $\alpha$ -methyl- $\alpha'$ -ethyl-, m.p. 116°, and - $\alpha'$ -*n*-propylglutarimide, m.p. 78°;  $\alpha\alpha$ -dimethyl- $\alpha$ -*n*-butylsuccinic and -glutaric acid, oils; *cis*- $\alpha$ -methyl- $\alpha'$ -*n*-amylglutaric acid, m.p. 76°. In order to confirm the structure of the imide (I) on which the structure of anagyrene was based by Ing (A., 1933, 727), this was synthesised from  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , which with  $\text{PBr}_3$  in  $\text{CHCl}_3$  or  $\text{PCl}_5$  yields respectively, *Et*  $\beta$ -bromo-, b.p. 91—93°/19 mm., and  $\beta$ -chloro-isobutyrate, b.p. 56—58°/10 mm., either of which with *Et* *n*-amylmalonate,  $\text{NaI}$ , and  $\text{NaOEt}$  in  $\text{EtOH}$  gives *Et*  $\alpha'$ -carbethoxy- $\alpha$ -methyl- $\alpha$ -*n*-amylglutarate, b.p. 140—145°/3 mm., hydrolysed to  $\alpha$ -methyl- $\alpha'$ -*n*-amylglutaric acid, m.p. 74—75° [imide (II), m.p. 71—72°].  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$  with *n*- $\text{C}_5\text{H}_{11}\text{Br}$  and  $\text{NaOEt}$  in  $\text{EtOH}$  gives *Et*  $\alpha$ -cyano- $\alpha'$ - $\alpha'$ -dimethyl- $\alpha$ -*n*-amylsuccinate, b.p. 187—191°/22 mm., 137°/0.9 mm., hydrolysed ( $\text{KOH}$ ) to  $\alpha\alpha$ -dimethyl- $\alpha$ -*n*-amylsuccinic acid, m.p. 119° [imide (III), m.p. 64—65°]. Ing's synthetic imide (*loc. cit.*) is a mixture of (II) and (III). (I) has the amended m.p. 58—60° and, although non-homogenous, is regarded as identical with (II), confirming the accepted structures of the lupin alkaloids.

F. R. G.

**Preparation in a high state of purity of long-chain compounds in view of the determination of their energy contents. II. Brassidic acid type.** L. J. P. KEFFLER (J.S.C.I., 1936, 55, 331—333r).—Repeated crystallisations of brassidic acid (as well as other acids of the *trans*-type) do not remove certain impurities when the usual technique is followed. Systematic fractional crystallisation at one const. temp. should be carried out, starting with an amount of solvent many times that which would be just sufficient to dissolve completely the acid at a temp. not far removed from the b.p. of the pure solvent. This amount depends on the nature of the acid to be purified and on the nature and concn. of the impurities admixed with it.

**Determination of ascorbic acid.**—See this vol., 1567.

**Reduction of inactivated *l*-ascorbic acid.** I. A. GOLJANICKI and I. S. BELONOSOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, 4, 15—16).—*l*-Ascorbic acid, inactivated by heat and  $\text{O}_2$ , is regenerated to the extent of 15—17% by addition of sugar and yeast

or, better, also of peroxidase, the necessary 2 H being derived from the change,  $\text{CHAc}(\text{OH})_2 \rightarrow \text{AcCO}_2\text{H}$ .

R. S. C.

**Photochemical reactions of iron gluconates.**—See this vol., 1473.

**Colour reactions of keturonic acids and a colour test differentiating  $\alpha$ - and  $\beta$ -glucosides.** F. SHEPPARD and M. R. EVERETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 7—9).—The results are given of the application of various colour tests to the products obtained by oxidising polyhydric alcohols, sugars, and sugar derivatives in 1% aq. solution with Br for 6 weeks at 25°.

W. O. K.

**Pectin problem.** F. EHRLICH (Festschr. Techn. Hochsch. Breslau, 1935, 129—141; Chem. Zentr., 1936, i, 788—789).—Cold alkaline hydrolysis of citrus and apple pectin yields *gelpectolic acid*,  $\text{C}_{24}\text{H}_{32}\text{O}_{24}$ , which differs in many ways from pectolic acid, into which it is converted by long boiling with  $\text{H}_2\text{O}$ . A structure is suggested.

H. N. R.

**Kinetics of sulphonium compounds.**—See this vol., 1469.

**$\alpha$ - and  $\beta$ -Sulphovaleric acids with a branched chain.** H. J. BACKER and D. VAN DER VEEN (Rec. trav. chim., 1936, 55, 887—898).— $\text{CHPr}^{\beta}(\text{CO}_2\text{H})_2$ , m.p. 93°, and  $\text{SO}_3$  at <0° give an oily mixed *anhydride*, which on gentle warming decomposes exothermally to  $\text{CO}_2$  and  $\alpha$ -sulphoisovaleric acid,  $+\text{H}_2\text{O}$ , m.p. 68° [*Ba*,  $+\text{H}_2\text{O}$ ,  $+6$  and  $+8\text{H}_2\text{O}$  (not obtained pure), *Ca*,  $+2\text{H}_2\text{O}$ , *Pb*,  $+2\text{H}_2\text{O}$ , *Tl*, *dibrucine*, and *distrychnine* salts], also obtained with  $\text{OH}\cdot\text{CHPr}^{\beta}\cdot\text{CO}_2\text{H}$  from  $\text{CHPr}^{\beta}\text{Br}\cdot\text{CO}_2\text{NH}_4$  and  $(\text{NH}_4)_2\text{SO}_3$ . The *brucine H* or *diquinine* salt leads to the *d-acid*,  $[\text{M}]_D -3^\circ$  (*Ba* salt,  $[\text{M}]_D +15^\circ$ ), racemised by NaOH slowly at 100° and more rapidly at 165° and by HCl at 165°.  $\alpha$ -Sulpho- $\alpha$ -methyl-*n*-butyric acid (I),  $+\text{H}_2\text{O}$ , m.p. 83° (*Pb*,  $+2\text{H}_2\text{O}$ , *Ba*,  $+3\text{H}_2\text{O}$ , *Tl*, and *distrychnine* salts), is obtained in poor yield from  $\text{SO}_3$  and  $\text{CMeEt}(\text{CO}_2\text{H})_2$  by way of the mixed *anhydride* or with  $\text{OH}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$  from  $\text{CMeEtBr}\cdot\text{CO}_2\text{NH}_4$  and in 34% yield from  $\text{CHMeEt}\cdot\text{CO}_2\text{H}$  and  $\text{SO}_3$ , and is resolved by the *brucine H*,  $+\text{H}_2\text{O}$ , salt to the *l-acid*,  $[\text{M}]_D -36^\circ$  (*Ba* salt,  $[\text{M}]_D -27^\circ$ ), and by the *diquinine* salt,  $+5\text{H}_2\text{O}$ , to the *d-acid*.  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\text{M}$  ( $\text{M}=\text{K}$  or  $\text{NH}_4$ ) and  $\text{K}_2\text{S}_2\text{O}_7$  at 90° give  $\beta$ -sulphoisovaleric acid (*Ba* and *Pb* salts,  $+\text{H}_2\text{O}$ ). When  $\text{CHMe}\cdot\text{CMe}\cdot\text{CHO}$  and  $\text{SO}_3$  react at 0° and are then left with Br in light,  $\beta$ -sulpho- $\alpha$ -methyl-*n*-butyric acid (cf. lit.) (II) (*Ba*,  $+\text{H}_2\text{O}$ , *Pb*, *distrychnine*,  $+2\text{H}_2\text{O}$ , and *brucine H*,  $+3\text{H}_2\text{O}$ , salts) is obtained.  $\text{OH}\cdot\text{CMeEt}\cdot\text{CN}$  and hot HCl give  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid, m.p. 72—73°, which at 140—150° gives a mixture of angelic and tiglic acids. K tigliate and  $\text{K}_2\text{S}_2\text{O}_7$  at 90° give the *stereoisomeride* (III) of (II) (*Ba*,  $+0.5\text{H}_2\text{O}$ , *Pb*,  $+\text{H}_2\text{O}$ , and *dibrucine*,  $+8\text{H}_2\text{O}$ , salts). The *diquinine* salt of (II) gives the *l-acid*,  $[\text{M}]_D -26^\circ$  (*Ba* salt,  $[\text{M}]_D -40.5^\circ$ ). The *diquinine* salt,  $+3\text{H}_2\text{O}$ , of (III) gives the *d-acid*,  $[\text{M}]_D +37^\circ$  (*Ba* salt,  $[\text{M}]_D -22^\circ$ ).  $\text{CH}_2\cdot\text{CEt}\cdot\text{CO}_2\text{K}$  and  $\text{K}_2\text{S}_2\text{O}_7$  at 90° give  $\alpha$ -sulphomethyl-*n*-butyric acid (IV) (*Ba* and *Pb* salts,  $+\text{H}_2\text{O}$ ), the *diquinine* salt,  $+4.5\text{H}_2\text{O}$ , of which gives the *d-acid*,  $[\text{M}]_D +24^\circ$  (*Ba* salt,  $[\text{M}]_D +7.5^\circ$ ).  $\text{CH}_2\text{Br}\cdot\text{CMe}_2\cdot\text{CO}_2\text{NH}_4$  and

$(\text{NH}_4)_2\text{SO}_3$  give  $\beta$ -sulphopivalic acid (*Ba* salt,  $+0.5\text{H}_2\text{O}$ ). (II), (III), and (IV) resist racemisation, since the activity does not depend on a H adjacent to  $\text{SO}_3\text{H}$ .

R. S. C.

**Trideuteroacetdeuterualdehyde.** J. E. ZANETTI and D. V. SICKMAN (J. Amer. Chem. Soc., 1936, 58, 2034—2035; cf. this vol., 316).— $\text{C}_2\text{D}_2$  passed into  $\text{D}_2\text{O}-\text{D}_3\text{PO}_4-\text{HgSO}_4$  gives *trideuteroacetdeuterualdehyde* (I),  $\text{CD}_3\cdot\text{CDO}$ , b.p. 20.5°/756 mm., m.p. —121.7°, v.p. 327 mm. at 0°, and *paratrideuteroacetdeuterualdehyde* (II), b.p. 124—125°/753 mm., m.p. 13.7°. (I) polymerises fairly readily to (II) when kept in sealed tubes.

H. B.

**Mechanism of carbohydrate oxidation. XXII. Preparation and reactions of glyceraldehyde diethyl mercaptal.** H. W. ARNOLD and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1950—1952).—Glyceraldehyde,  $\text{EtSH}$ , and cold conc. HCl give *glyceraldehyde Et<sub>2</sub> mercaptal* (I), b.p. 156—158°/3 mm., and a little of a compound, m.p. 126—127.5° [probably formed by condensation of several mols. of (I)]. (I) and  $\text{CPh}_3\text{Cl}$  in  $\text{C}_5\text{H}_5\text{N}$  afford the  $\beta$ - $\text{CPh}_3$  ether, m.p. 100—101° ( $\alpha$ -Ac, m.p. 93—94°, and  $\alpha$ -Bz, m.p. 90—91°, derivatives); the  $\text{CPh}_3$  group could not be removed (various procedures) from these compounds. Acetylation ( $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ ) of (I) and treatment of the resulting viscous oil with  $\text{HgCl}_2+\text{CdCO}_3$  in aq.  $\text{COMe}_2$  gives  $\alpha\beta$ -diacetylglyceraldehyde, b.p. 154—156°/3 mm., which with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$  in aq.  $\text{EtOH}-\text{HCl}$  affords (probably)  $\beta$ -acetylglucaldehyde-*p*-nitrophenyllosazone, m.p. 282—286° (block) (darkens at 235—240°) (all m.p. except this are corr.), and with  $\text{MeOH}-\text{NH}_3$  followed by 2:4- $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ , yields glyceraldehyde-2:4-dinitrophenylhydrazone.

H. B.

**Mechanism of carbohydrate oxidation. XXI. Synthesis of glucosidoglyceraldehyde derivatives.** H. W. ARNOLD and W. L. EVANS (J. Amer. Chem. Soc., 1936, 58, 1890—1894).—Glyceraldehyde benzylcycloacetal (I) (Fischer and Baer, A., 1932, 364), acetobromo-*d*-glucose,  $\text{Ag}_2\text{CO}_3$ , and “Drierite” in  $\text{C}_6\text{H}_6$  give 50% of  $\beta$ - $\beta'$ -*d*-glucosidoglyceraldehyde benzylcycloacetal tetra-acetate, m.p. 172—173° (corr.),  $[\alpha]_D^{25} -19.9^\circ$  in  $\text{CHCl}_3$ , cleaved by  $\text{H}_2+\text{Pd}$ -black in MeOH to the amorphous  $\beta$ - $\beta'$ -*d*-glucosidoglyceraldehyde tetra-acetate (II), m.p. 63°,  $[\alpha]_D^{25} -15.5^\circ$  in  $\text{CHCl}_3$ , which reduces cold Fehling's solution. Cryst. derivatives (Ac, Bz, phenylhydrazones) of (II) could not be prepared. (II) with  $\text{C}_5\text{H}_5\text{N}$  at 135—140° (bath) followed by  $\text{Ac}_2\text{O}$  affords a syrup containing 8—9% of  $\beta$ -*d*-glucosidodihydroxyacetone penta-acetate (A., 1935, 477), determined as the *p*-nitrophenylhydrazone.  $\beta$ - $\beta'$ -*l*-Arabinosidoglyceraldehyde benzylcycloacetal tri-acetate, m.p. 142—143° (corr.),  $[\alpha]_D^{25} +4.2^\circ$  in  $\text{CHCl}_3$ , is obtained (as above) in 7% yield from (I) and acetobromo-*l*-arabinose. Dimeric glyceraldehyde diacetate and  $\text{TiCl}_4$  in  $\text{CHCl}_3$  at room temp. give 81—87% of *acetochloroglyceraldehyde*, m.p. 174—175° (corr.), which with  $\text{CH}_2\text{Ph}\cdot\text{OH}+\text{Ag}_2\text{CO}_3$  affords a mixture of isomeric glyceraldehyde benzylcycloacetal acetates, m.p. 109—110° (corr.) (small amount) and 141—142° (corr.) (Fischer and Baer, loc. cit.).

H. B.

**Photochemical peroxide formation. IV. Oxidation of acetone by molecular oxygen in ultra-**



violet light. Photochemical production of peracetone. R. CANTIENT (Ber., 1936, 69, [B], 2282—2285; cf. this vol., 1091).—COMe<sub>2</sub> is converted by O<sub>2</sub> in ultra-violet light, unfiltered or filtered through glass, into its *peroxide* (I), the formation of which is retarded by addition of H<sub>2</sub>O. Since H is not produced by photolysis of COMe<sub>2</sub> and dry COMe<sub>2</sub> is transformable into (I), the production of H<sub>2</sub>O<sub>2</sub> is excluded. (I) is unstable in ultra-violet light, its rate of decomp. increasing with its concn. The following scheme is therefore adopted, in which COMe<sub>2</sub> is its own O carrier.  $\text{COMe}_2 + \text{COMe}_2 \xrightarrow{\text{O}} \text{(II)} \rightarrow \text{MeCHO} + \text{CH}_2\text{O} + \text{COMe}_2$ ;  $\text{MeCHO}^* + \text{(II)} \rightarrow \text{AcOH} + \text{COMe}_2$ ;  $\text{CH}_2\text{O}^* + \text{(II)} \rightarrow \text{HCO}_2\text{H} + \text{COMe}_2$ . In the initial stages of the change the amounts of (I) formed in unit time are approx. const. but diminish with increasing period of irradiation. In ultra-violet light filtered through glass the formation of (I) is one fourth as fast as in unfiltered light.

H. W.

Condensation of acetone with formaldehyde. L. A. GERMANN (Compt. rend., 1936, 203, 586—587).—CH<sub>2</sub>O (1 mol.) in anhyd. EtOH containing K<sub>2</sub>CO<sub>3</sub> with COMe<sub>2</sub> (2 mols.) below 30° affords CH<sub>3</sub>Ac·CH<sub>2</sub>·OH and β-hydroxymethyl-Δ<sup>4</sup>-buten-γ-one (cf. A., 1933, 1144).

J. L. D.

Alkylacetylenes and their additive compounds. XVII. Synthesis of acetylenic ketones from acetylenic Grignard reagents. J. W. KROEGER and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1936, 58, 1861—1863).—CR·C·COMe are best prepared from CR·C·MgCl (which are fairly insol. in Et<sub>2</sub>O) and Ac<sub>2</sub>O at <−25° in N<sub>2</sub>; β-keto-Δ<sup>7</sup>-octinene, b.p. 76—76.5°/15 mm., -Δ<sup>7</sup>-noninene, b.p. 89—89.5°/15 mm., and -δ-phenyl-Δ<sup>7</sup>-butinene, b.p. 101—102°/3 mm., are described. CR·C·MgBr (I) similarly gives 10—20% of ketone and considerable amounts of (CR·C)<sub>2</sub>CMe·OH; methyldi-Δ<sup>4</sup>-hexinenyl-, b.p. 123—125°/2 mm., -Δ<sup>4</sup>-heptinenyl-, b.p. 134—136°/2 mm., and -phenylacetylenyl-, m.p. 111.5—112°, -carbinols are thus prepared. (I) do not react with MeCN or NH<sub>2</sub>Ac. Little or no reaction occurs with CBr<sub>4</sub>·MgBr and dry O<sub>2</sub> at −30°.

H. B.

Chloromethylation of ketones and preparation of α-alkylvinyl ketones. J. COLOGNE (Bull. Soc. chim., 1936, [v], 3, 2116—2121).—Certain ketones are condensed with 36% CH<sub>2</sub>O in presence of HCl to β-chloroketones, transformed by NPhEt<sub>2</sub> to α-ethylenic ketones; CH<sub>2</sub>O + HCl → CH<sub>3</sub>Cl·OH (I) and (I) + COMeR → H<sub>2</sub>O + COR·CH<sub>2</sub>·CH<sub>2</sub>Cl. Thus COMeBu<sup>v</sup> gives β-chloroethyl Bu<sup>v</sup> ketone, b.p. 69—70°/9 mm. (whence 5-tert.-butylpyrazoline-2-carboxylamide, m.p. 103°), which can be kept unchanged for a few weeks but is transformed by boiling NPhEt<sub>2</sub> into COBu<sup>v</sup>·CH<sub>2</sub>·CH<sub>2</sub>, b.p. 65—66°/105 mm., which appears to polymerise rapidly. COEt<sub>2</sub> yields α-chloro-β-methylpentan-γ-one, b.p. 64°/9 mm. [semicarbazone, m.p. about 115° (decomp.)], whence β-methyl-Δ<sup>4</sup>-pentenone, b.p. 119°/731 mm. (semicarbazone, m.p. 161°). COBu<sup>a</sup><sub>2</sub> affords γ-chloromethylheptan-δ-one, b.p. 91—92°/12 mm. [semicarbazone, m.p. about 115° (decomp.)], whence γ-methylene-Δ<sup>4</sup>-

heptenone, b.p. 157—159°/742 mm. (semicarbazone, m.p. 119°).

H. W.

Oxidation of 1:3-diketones by peracetic acid. J. BOESEKEN and J. JACOBS (Rec. trav. chim., 1936, 55, 804—814).—Esters of β-keto-acids react in the enolic form with AcO<sub>2</sub>H. In the aliphatic series the reaction is COR·CHR'·COR'' + O + H<sub>2</sub>O → CHR'·OH + HR''·C<sub>2</sub>O<sub>4</sub>, in the aromatic COR·CH<sub>2</sub>·CO<sub>2</sub>Et + 3O → RCO<sub>2</sub>H + EtHC<sub>2</sub>O<sub>4</sub>. This is proved for CHAcR·CO<sub>2</sub>Et (R=H, Me, CH<sub>2</sub>Ph, OMe, and OEt), CMe<sub>2</sub>Ac·CO<sub>2</sub>Et, COR·CH<sub>2</sub>·CO<sub>2</sub>Et (R=Et, C<sub>6</sub>H<sub>11</sub>, Ph, or p-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>), COMe·CHR·COMe (R=H, Me, or CH<sub>2</sub>Ph), and CO(CH<sub>2</sub>·CO<sub>2</sub>Et)<sub>2</sub>. (COMe·CH<sub>2</sub>)<sub>2</sub> probably reacts at both enolic groupings, giving OH·CMe<CH<sub>2</sub> and thence H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 2EtOH.

R. S. C.

Preparation of xylulose and ribulose. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1936, 115, 731—747).—The products of the action of C<sub>5</sub>H<sub>5</sub>N on xylose and arabinose are best separated by way of the :CMe<sub>2</sub> derivatives, the prep. and hydrolysis of which are standardised. The ketopentose obtained from xylose is renamed d-xylulose (I). The equilibrium mixture from xylose yields d-xylose [(CMe<sub>2</sub>)<sub>2</sub> derivative, m.p. 44—45°, b.p. 78°/0.1 mm., [α]<sub>D</sub><sup>25</sup> +19.5° in COMe<sub>2</sub>], (I) [CMe<sub>2</sub> derivative, m.p. 70—71° (lit. 50—52°), b.p. 110°/0.1 mm., [α]<sub>D</sub><sup>25</sup> +1.7° in COMe<sub>2</sub>, −6.5° in H<sub>2</sub>O], and d-lyxose [CMe<sub>2</sub> derivative, m.p. 79—80°, b.p. about 110°/0.1 mm., [α]<sub>D</sub><sup>25</sup> +26° in COMe<sub>2</sub>, +19.7° (final) in H<sub>2</sub>O]. Arabinose [(CMe<sub>2</sub>)<sub>2</sub> derivative, [α]<sub>D</sub><sup>25</sup> ±0.1° in COMe<sub>2</sub>] gives d-ribose [CMe<sub>2</sub> derivative (II), an oily mixture of varying amounts of α- and β-forms, [α]<sub>D</sub><sup>25</sup>, e.g., −27.4° in COMe<sub>2</sub>; p-bromophenylhydrazone, m.p. 164—165°, [α]<sub>D</sub><sup>25</sup> +10.3° in abs. EtOH, −19.3° → +2.0° in 67.5 hr. in dry C<sub>5</sub>H<sub>5</sub>N], l-ribulose, [α]<sub>D</sub><sup>27</sup> (nearly pure) +16.6° (final) in H<sub>2</sub>O [(CMe<sub>2</sub>)<sub>2</sub> derivative, m.p. 5°, n<sub>D</sub><sup>25</sup> 1.4422, [α]<sub>D</sub><sup>27</sup> +105.5° in COMe<sub>2</sub>], and unchanged material. Some anhydro-derivative, m.p. 61°, b.p. 50—57°/0.1 mm., [α]<sub>D</sub><sup>25</sup> −64.7° in COMe<sub>2</sub>, −59.4° in H<sub>2</sub>O, of (II) is produced during the formation of (II).

R. S. C.

Determination of hexoses by fermentation. O. MEYERHOF and W. SCHULZ (Biochem. Z., 1936, 287, 206—211).—During the fermentation of pure hexoses (glucose, fructose) with living yeast the quantity of CO<sub>2</sub> produced is equiv. to only 75—80% of the sugar decomposed, but is increased by addition of substances containing N [e.g., asparagine, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, phenylalanine, protein-free extracts of tissues, yeast, urine, and serum] to the equiv. of 95% (fermentation in N<sub>2</sub>) and 100% (in CO<sub>2</sub>). These substances act by restricting the assimilation of sugar. W. McC.

Determination of glucose, galactose, and lactose in a mixture of the three sugars. M. SCOTT and E. S. WEST (Proc. Soc. Exp. Biol. Med., 1936, 34, 52—54).—The reducing vals. of solutions are determined before and after hydrolysis with acid under prescribed conditions and before and after fermentation with brewer's yeast. From the four figures so obtained the concns. of the three sugars originally present may be deduced with the help of formulæ which are given.

W. O. K.

**Determination of hydroxyl in carbohydrates by acetylation in pyridine.** J. RABATÉ (Bull. Soc. chim., 1936, [v], 3, 2112—2116).—The substance (0.1—0.2 g.) is heated for 30 min. at 100° with Delaby's reagent (B., 1935, 1118) and cooled in ice; after addition of H<sub>2</sub>O (10 c.c.) AcOH is titrated with *N*-NaOH using phenolphthalein as indicator. Results are generally accurate to within 3%, but the method fails with certain alcohols and phenols which contain CO or CHO. Among carbohydrates, the aldoses and their heterosides yield accurate results, but the process is invalid for ketoses (fructose, *d*-sorbose) or for carbohydrates containing one or more mols. of these components. H. W.

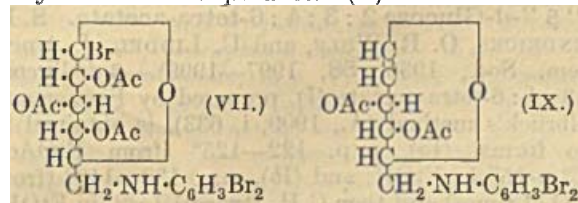
**Mechanism of carbohydrate oxidation. XVIII. Oxidation of sugars with silver oxide in the presence of potassium hydroxide.** K. G. A. BUSCH, J. W. CLARK, L. B. GENUNG, E. F. SCHROEDER, and W. L. EVANS (J. Org. Chem., 1936, 1, 1—16; cf. A., 1935, 476).—The CO<sub>2</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, HCO<sub>2</sub>H, and OH·CH<sub>2</sub>·CO<sub>2</sub>H formed by oxidation of glucose (I), mannose (II), galactose (III), and fructose (IV), and of the intermediates, arabinose (V), erythritol, glyceraldehyde, OH·CH<sub>2</sub>·CHO (VI), and galacturonolactone by Ag<sub>2</sub>O alone and with KOH at 50° are determined. (II) is oxidised first to CH<sub>2</sub>O and (V), fructose either to (VI) (1 mol.) and erythrose (1 mol.) or 3 mols. of (VI). (I) is probably oxidised in several ways simultaneously. HCO<sub>2</sub>H is derived from CH<sub>2</sub>O, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and most of the CO<sub>2</sub> from CO-acids; ·CH<sub>2</sub>·OH is stable under the reaction conditions, so that the survival of OH·CH<sub>2</sub>·CO<sub>2</sub>H is explained. Reaction probably occurs by enolisation and fission at OH·C·C·OH. R. S. C.

**Oxidation of glucose in presence of insulin, glutathione, and other substances, and the probable mechanism of biological oxidations.** C. C. PALIT and N. R. DHAR (J. Indian Chem. Soc., 1936, 13, 502—508).—Glutathione (I) and insulin (II), with or without phosphate or heavy-metal salts, usually accelerate but sometimes retard the oxidation by air of aq. solutions of glucose in presence of TiO<sub>2</sub>, SiO<sub>2</sub>, Ce(OH)<sub>2</sub>, Fe(OH)<sub>2</sub>, or Mn(OH)<sub>2</sub> (cf. A., 1934, 1314). (I) and (II) presumably act as O acceptors. E. W. W.

**Structures of isopropylidene derivatives of galactose-, glucose-, and mannose-dibenzyl mercaptals.** E. PACSU (J. Amer. Chem. Soc., 1936, 58, 2076).—Re-investigation of the compounds is being carried out (cf. Munro and Percival, this vol., 826) in view of previous work (A., 1932, 254). The supposed 2:3-isopropylidene-galactose dibenzyl mercaptal, m.p. 102—103° (A., 1930, 197), is a mixture of (probably) the 4:6-, m.p. 101.5°, [α]<sub>D</sub><sup>20</sup> +30.5° in CHCl<sub>3</sub>, and 5:6-, m.p. 112.5°, [α]<sub>D</sub><sup>20</sup> +17.4° in CHCl<sub>3</sub>, derivatives; neither reacts with CPh<sub>3</sub>Cl. H. B.

**Syntheses with 5:6-anhydroisopropylidene-glucose. IV. Derivatives of glucosyl-6-phenylamine (6-anilinochinovose).** H. OHLE, H. FRIEDBERG, and G. HAESLER (Ber., 1936, 69, [B], 2311—2324; cf. this vol., 1094).—With amines of the hexose series with NH<sub>2</sub> at C<sub>6</sub>, the relationship to the methylpentoses of similar configuration can be simply

expressed, e.g., glucosyl-6-amine=6-amino-6-deoxy-glucose=6-aminoisorhamnose. The use of prefixes such as *iso*- and *epi*- is regarded as undesirable, and it is considered advisable to choose for each sugar a short trivial name related, if possible, to its origin. The use of chinovose for *d*-isorhamnose is therefore advocated (cf. Freudenberg *et al.*, A., 1929, 427). Addition of NH<sub>2</sub>Ph to 5:6-anhydroisopropylidene-glucose (I) gives 6-anilino-1:2-isopropylidene-*d*-chinofuranose (II), b.p. 220°/15 mm. (N·SO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>Me derivative (III), m.p. 195.5°, [α]<sub>D</sub><sup>20</sup> −10.54° in CHCl<sub>3</sub>, −7.16° in MeOH). (I) and NH<sub>2</sub>Ph (1:2 mols.) at 80—100° yield non-cryst. *di*(isopropylidene-6-*d*-glucosyl)aniline, identified as the *tetra-acetate*, m.p. 194°, [α]<sub>D</sub><sup>20</sup> +19.4° in CHCl<sub>3</sub>. From α- or β-C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>, tetrahydroquinoline, *ac*- or *ar*-tetrahydronaphthylamine only isopropylidene-6-*d*-glucosyl-*ar*-tetrahydro-β-naphthylamine, m.p. 187°, [α]<sub>D</sub><sup>20</sup> −1.6° in CHCl<sub>3</sub>, could be obtained cryst. (III) is also obtained directly from (I) and *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NHPH at about 150° in presence of a little C<sub>5</sub>H<sub>5</sub>N, and the method is extended to the prep. of the following: *N*-*p*-toluenesulphonyl derivatives of isopropylidene-6-*d*-glucosyl-*p*-bromoaniline (IV), m.p. 224°, [α]<sub>D</sub><sup>20</sup> +12.09° in CHCl<sub>3</sub> (*p*-toluenesulphon-*p*'-bromoanilide, m.p. 147.5°), *p*-anisidine, m.p. 197°, [α]<sub>D</sub><sup>20</sup> +6.4° in CHCl<sub>3</sub>, 2'-naphthylamine, m.p. 172°, [α]<sub>D</sub><sup>20</sup> +16.4° in CHCl<sub>3</sub>, and to the *N*-α-, m.p. 223—225°, [α]<sub>D</sub><sup>20</sup> −14.2° in CHCl<sub>3</sub>, and *N*-β-, m.p. 228—230°, [α]<sub>D</sub><sup>20</sup> ±0° in CHCl<sub>3</sub>, *naphthalenesulphonyl* compounds of isopropylidene-6-*d*-glucosylaniline. If the amine component is not aromatic the change does not take place, or occurs so slowly that it is almost completely repressed by the autocondensation of (I). This appears also true of the amides of aliphatic and aromatic carboxylic acids, e.g., NH<sub>2</sub>Ac, NHAc, NHPHAc, NH<sub>2</sub>Bz, NHBz<sub>2</sub>, and NHPHBz, but *o*-C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>)NH is exceptional. Mild treatment with alkali does not cause hydrolysis of the derivatives, whereas more drastic action involves removal of *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub>·NHPH, hydrolysed to *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>3</sub>H and NH<sub>2</sub>Ph, and resinification of the sugar. (III) is readily converted by 50% AcOH into *N*-*p*-toluenesulphonyl-6-anilino-β-*d*-chinovose, m.p. 95—110°, or +1.5H<sub>2</sub>O, m.p. 87—89°, [α]<sub>D</sub><sup>20</sup> −0.63° to +64.2° in COMe<sub>2</sub>, [α]<sub>D</sub><sup>20</sup> +57.7° (const.) in C<sub>5</sub>H<sub>5</sub>N, converted by Ac<sub>2</sub>O in C<sub>5</sub>H<sub>5</sub>N into *N*-*p*-toluenesulphonyl-6-anilino-β-*d*-chinopyranose 1:2:3:4-tetraacetate (V), m.p. 190°, [α]<sub>D</sub><sup>20</sup> +19.87° in CHCl<sub>3</sub>, mixed with the α-variety, [α]<sub>D</sub><sup>20</sup> +64.3° in CHCl<sub>3</sub>. The isomeric *N*-*p*-toluenesulphonyl-6-anilino-α-*d*-chinofuranose 1:2:3:5-tetraacetate (VII), m.p. 139—140°, [α]<sub>D</sub><sup>20</sup> +74.3° in CHCl<sub>3</sub>, is obtained by hydrolysis of *N*-*p*-toluenesulphonylisopropylidene-6-anilino-chinofuranose 3:5-diacetate with 50% AcOH and acetylation of the product. (V) reacts abnormally



with HBr·AcOH, giving (C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>S and 6-2':4'-dibromoanilinochinovosyl 1-bromide 2:3:4-*tri*-



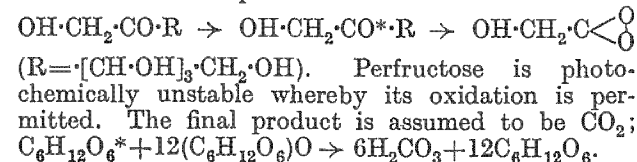
acetate (VII), m.p. 144—145°,  $[\alpha]_D^{20} +135.6^\circ$  in  $\text{CHCl}_3$ , accompanied by 6-2':4'-dibromoanilino-d-chinovose hydrobromide, the yields of which are improved by pre-addition of Br. Under similar conditions, (VI) does not yield a cryst. material. The location of Br at C<sub>11</sub> in (VII) is established by the conversion of (VII) by  $\text{Ag}_2\text{O}$  and boiling abs. MeOH into 6-2':4'-dibromoanilino- $\beta$ -methyl-d-chinopyranoside 2:3:4-triacetate (VIII), m.p. 139—140°,  $[\alpha]_D^{20} +3.83^\circ$  in  $\text{CHCl}_3$ , transformed by boiling  $\text{Ac}_2\text{O}$ , but not by acetylation in  $\text{C}_5\text{H}_5\text{N}$ , into N-acetyl-6-2':4'-dibromoanilino- $\beta$ -methyl-d-chinopyranoside 2:3:4-triacetate, m.p. 158°,  $[\alpha]_D^{20} +34.0^\circ$  in  $\text{CHCl}_3$ , hydrolysed to the non-cryst. N-acetyl-6-2':4'-dibromoanilino- $\beta$ -methyl-d-chinopyranoside. Hydrolysis of (VIII) by NaOMe gives 6-2':4'-dibromoanilino- $\beta$ -methyl-d-chinopyranoside, m.p. 172°,  $[\alpha]_D^{20} -4.82^\circ$  in  $\text{C}_5\text{H}_5\text{N}$ . Further (VII) and  $\text{AgOAc}$  in AcOH afford 6-2':4'-dibromoanilino- $\beta$ -d-chinopyranose 1:2:3:4-tetra-acetate, m.p. 168°,  $[\alpha]_D^{20} +18.9^\circ$  in  $\text{CHCl}_3$ , from which the cryst. sugar could not be obtained with NaOMe or  $\text{NH}_3\text{-MeOH}$ ; it is transformed by boiling  $\text{Ac}_2\text{O}$  into N-acetyl-6-2':4'-dibromoanilino- $\beta$ -d-chinopyranose 1:2:3:4-tetra-acetate, m.p. 148°,  $[\alpha]_D^{20} +45.0^\circ$  in  $\text{CHCl}_3$ . The position of the second Br in (VII) follows from the conversion of (IV) into (VII) by  $\text{HBr-AcOH}$ , reaction occurring slowly and with poor yield. For the elucidation of the position of the third Br direct synthesis fails owing to lack of additive capacity of 2:4- $\text{C}_6\text{H}_3\text{Br}_2\text{-NH}_2$ . Reduction of (VII) with Zn dust and AcOH gives good yields of 6-2':4'-dibromoanilinochinoxal 3:4-diacetate (IX), m.p. 86—87°,  $[\alpha]_D^{20} -2.3^\circ$  in  $\text{CHCl}_3$ , readily hydrolysed (Zemplén) to 6-2':4'-dibromoanilino-d-chinoxal, m.p. about 142°,  $[\alpha]_D^{20} +15.50^\circ$  in MeOH, which adds Br, is catalytically hydrogenated ( $\text{Pd-BaSO}_4$ ), is degraded by  $\text{O}_3$ , and resinified by mineral acids. Oxidation by  $\text{KMnO}_4$  in  $\text{COMe}_2$  destroys completely the sugar component but yields 2:4- $\text{C}_6\text{H}_3\text{Br}_2\text{-NH}_2$  and 2:4-dibromoxanilic acid. (V) is transformed by  $\text{TiCl}_4$  in  $\text{CHCl}_3$  into N-p-toluenesulphonyl-6-anilinochinopyranosyl 1-chloride 2:3:4-triacetate, m.p. 84—95°,  $[\alpha]_D^{20} +114.9^\circ$  in  $\text{CHCl}_3$ ; the yield is poor and the change is accompanied by formation of p- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$ . It is converted by  $\text{Ag}_2\text{O}$  in boiling MeOH into N-p-toluenesulphonyl-6-anilino- $\beta$ -methyl-d-chinopyranoside 2:3:4-triacetate, m.p. 147°,  $[\alpha]_D^{20} +5.0^\circ$  in  $\text{CHCl}_3$ , hydrolysed (Zemplén) to N-p-toluenesulphonyl-6-anilino- $\beta$ -d-methylchinopyranoside, m.p. 128°,  $[\alpha]_D^{20} +2.62^\circ$ . It is unusually stable towards alkalis so that p- $\text{C}_6\text{H}_4\text{Me-SO}_2$  cannot be removed in this manner. Under similar conditions (VI) gives cryst. products differing from those described above in amount too small for further investigation. H. W.

" $\beta$ "-d-Glucose 2:3:4:6-tetra-acetate. S. B. HENDRICKS, O. R. WULF, and U. LIDDEL (J. Amer. Chem. Soc., 1936, 58, 1997—1999).— $\beta$ -d-Glucose 2:3:4:6-tetra-acetate (I), prepared by Fischer and Delbrück's method (A., 1909, i, 633), is obtained in two forms, (Ia), m.p. 122—125° (from EtOAc),  $[\alpha]_D^{20} +15^\circ$  in EtOH, and (Ib), m.p. 138—140° [from Et<sub>2</sub>O (4 times) and then  $\text{C}_6\text{H}_6$  (twice)],  $[\alpha]_D^{20}$  (in EtOH)  $-4.2^\circ \rightarrow +75^\circ$  (10 days), (in  $\text{CHCl}_3$ )  $+18.8^\circ \rightarrow +78^\circ$  (10 days) (cf. Georg, A., 1932, 835). (Ib) is converted

into (Ia) when kept (2 years) or heated in  $\text{CCl}_4$  or  $\text{C}_6\text{H}_6$  for several days; subsequent recrystallisation of the (Ia) from Et<sub>2</sub>O affords (Ib). Microscopical examination and X-ray powder diffraction patterns show that (Ia) and (Ib) are isomorphous. The above phenomenon is not shown by (I), m.p. 125—131°, prepared by Weizmann and Haskelberg's method (A., 1935, 1108). Infra-red absorption curves, showing characteristic OH-absorption, are given for (Ia), (Ib),  $\beta$ -d-galactose 2:3:4:6-tetra-acetate, and  $\alpha$ -d-xylose 2:3:4-triacetate. H. B.

3:6-Dimethylglucose: methods of synthesis. D. J. BELL (J.C.S., 1936, 1553—1554).—3:5-isopropylidene-glucose 6-acetate with  $\text{N}_2\text{O}_5$  in  $\text{CHCl}_3$  gives isopropylidene-glucose 3:5-dinitrate 6-acetate, m.p. 81.5—82.5°,  $[\alpha]_D^{20} -22.7^\circ$  in  $\text{CHCl}_3$ , which with  $\text{NHMe}_2$  in EtOH yields isopropylidene-glucose 5-nitrate, m.p. 86—87° and 106°,  $[\alpha]_D^{20} -0.4^\circ$  in EtOH, and with MeI and  $\text{Ag}_2\text{O}$  gives 3:6-dimethylisopropylidene-glucose, a syrup,  $[\alpha]_D^{20} -45.9^\circ$  in  $\text{CHCl}_3$  (also obtained from 3-methylisopropylidene-glucose by successive treatment with p- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$  and NaOMe), hydrolysed (HCl) to 3:6-dimethylglucose. F. R. G.

Photochemical peroxide formation. V. Oxidation of fructose by molecular oxygen in ultra-violet light. Photochemical formation of perfructose. R. CANTIENI (Ber., 1936, 69, [B], 2286—2288).—Fructose is converted by  $\text{O}_2$  into a peroxide in ultra-violet light of long and short  $\lambda$ . Since photolysis of it affects almost exclusively the CO group it is assumed that photo-oxidation occurs thus:



Ditriphenylmethylfructose. B. HELFERICH [with G. PYL, H. PAUKERT, and E. GUNTHER] (J. pr. Chem., 1936, [ii], 147, 60—63).—Fructose and  $\text{CPh}_3\text{Cl}$  (2 mol.) in abs.  $\text{C}_5\text{H}_5\text{N}$  at room temp. give 1:6-ditriphenylmethyl-d-fructose, anhyd., amorphous, and  $+2\text{C}_5\text{H}_5\text{N}$ , m.p. 96—97°,  $[\alpha]_D^{20} +17.5^\circ$  in  $\text{CHCl}_3$ , which gives an oxime, m.p. about 186° (decomp.),  $[\alpha]_D^{20} -18^\circ$  in  $\text{C}_6\text{H}_5\text{N}$ , also obtained from fructose oxime and  $\text{CPh}_3\text{Cl}$  (2 mol.). R. S. C.

Convallamarin. W. VOSS and G. VOGT (Ber., 1936, 69, [B], 2333—2342).—Technical convallamarin is purified successively by distribution between BuOH and  $\text{H}_2\text{O}$ , fractional adsorption by active C, and fractional pptn. by Et<sub>2</sub>O from MeOH, thereby giving an amorphous product for which the name convallamarin (I) is retained and which could not be separated into portions with differing physical consts. It retains an almost negligible cardiac activity and has a very low foam no. attributed to the presence of traces of convallatoxin and convallarin, respectively; it is considered to be about 99.5% pure. It does not give the Legal test and does not contain a lactone group or give a compound with cholesterol. It has  $[\alpha]_D^{20} -66.5^\circ$  in Et<sub>2</sub>O. Elementary analyses indicates the formula  $\text{C}_{41}\text{H}_{70}\text{O}_{19}\cdot 3\text{H}_2\text{O}$ , and the presence of one double

linking is established by hydrogenation. The sugar components are glucose (1 mol.) and *l*-rhamnose (2 mols.). Hydrolysis with aq. acids proceeds satisfactorily only in very dil. solution, and the use of 2% HCl-MeOH at 35° is preferable, whereby the sugars are quantitatively transformed into their methylglucosides and the aglucone is protected. The very ready alcoholysis of glucosides and the consequent danger of the use of possibly acidic EtOH in their extraction is stressed. *Convallamaretin*, m.p. 248.5—250.5° (decomp.),  $[\alpha]_D^{20}$  -86.0° in CHCl<sub>3</sub>, contains one double linking, 2 OH (Zerevitinov determination at higher temp.), but not CO. Elementary analyses agree best with C<sub>20</sub>H<sub>40</sub>O<sub>5</sub>, and harmonise with the hydrolysis, C<sub>44</sub>H<sub>70</sub>O<sub>19</sub> + 3H<sub>2</sub>O → C<sub>20</sub>H<sub>40</sub>O<sub>5</sub> + C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + 2C<sub>6</sub>H<sub>12</sub>O<sub>5</sub>. The presence of only two oxide rings is considered probable, whilst the remaining 3 O are present as 3 OH only two of which are affected by MgMeI. H. W.

**Constituents of seeds of *Digitalis lanata* (Ehrh.).**—See this vol., 1571.

**Kinetics of the sulphite [cellulose] process.**—See this vol., 1470.

**[Preparation of] primary amines by reduction of oximes by aluminium amalgam.** C. L. TSENG and C. CHANG (Sci. Rep. Nat. Univ. Peking, 1936, 1, No. 3, 19—33).—The oximes of the following compounds with Al-Hg in 96% or aq. EtOH give the stated yields of primary base with, in some cases, small amounts of *sec.* amine: COMe<sub>2</sub> 17.3, Pr<sup>n</sup>CHO 39.9, *n*-C<sub>6</sub>H<sub>13</sub>CHO 48, COMe·C<sub>6</sub>H<sub>13</sub>-*n* 1.6, cyclohexanone 60.1, PhCHO 87.7, camphor 85, and furfuraldehyde 36.3%. Phenylhydrazones give similarly good yields of NH<sub>2</sub>Ph and primary base, but the method is of val. only when the NH<sub>2</sub>Ph and other base are readily separated. PhCN resists reduction by Al-Hg. Al foil of 0.1 mm. thickness or Al turnings give best results. The prep. of the Al-Hg, oximes, and phenylhydrazones used is described.

R. S. C.

**Reineckates of organic bases.** H. CARLSOHN and F. RATHMANN (J. pr. Chem., 1936, [ii], 147, 29—37).—Many reineckates are more sol. in H<sub>2</sub>O-COMe<sub>2</sub> or -EtOAc than in either solvent alone. In general these salts are more sol. in H<sub>2</sub>O, the less sol. they are in COMe<sub>2</sub>. In EtOH the order of solubility is usually primary > *sec.* > *tert.* > quaternary aliphatic salts. The NPr<sub>4</sub> salt is least sol. in EtOH containing 2.2% of H<sub>2</sub>O.

R. S. C.

**Carboxymethoxylamine [aminooxyacetic acid].** E. BOREK and H. T. CLARKE (J. Amer. Chem. Soc., 1936, 58, 2020—2021).—Crude CMe<sub>2</sub>·N·O·CH<sub>2</sub>·CO<sub>2</sub>Et (from dry CMe<sub>2</sub>·N·ONa and CH<sub>2</sub>Cl·CO<sub>2</sub>Et) is hydrolysed (11.4% NaOH at 100°) to CMe<sub>2</sub>·N·O·CH<sub>2</sub>·CO<sub>2</sub>H, m.p. 76—76.5° [also prepared (cf. Hantzsch and Wild, A., 1896, i, 285) in smaller yield from CMe<sub>2</sub>·N·OH and CH<sub>2</sub>Cl·CO<sub>2</sub>Na in aq. NaOH], further hydrolysed (boiling 6*N*-HCl) to NH<sub>2</sub>·O·CH<sub>2</sub>·CO<sub>2</sub>H (I) (*hemihydrochloride*, m.p. 151°). *Acetophenoneoxime*, m.p. 97—97.5°, benzaldoxime, m.p. 96° (lit. 98°), and pyruvic acid oxime, m.p. 129° (lit. 130—132°), *O*-carboxymethyl ethers are prepared from (I) and the requisite CO-compound.

H. B.

**Action of amines on esters of the trichloro-nitrohydroxy-paraffins.** F. D. CHATTAWAY, J. G. N. DREWITT, and G. D. PARKES (J.C.S., 1936, 1530—1532; cf. this vol., 595, 1362).—CRCl<sub>2</sub>·CH(CH<sub>2</sub>·NO<sub>2</sub>)·O·COR' with NH<sub>2</sub>R'' gives CRCl<sub>2</sub>·CH(CH<sub>2</sub>·NO<sub>2</sub>)·NHR''. With NH<sub>3</sub> or the appropriate amine, CCl<sub>3</sub>·CH(CH<sub>2</sub>·NO<sub>2</sub>)·OAc or its *p*-nitrobenzoate, m.p. 87°, yields  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -methyl-, b.p. 96°/3 mm. (*hydrochloride*, decomp. about 185°; *phenylcarbamyl* derivative, m.p. 130°), - $\beta$ -ethyl-, b.p. 106°/2 mm. (*hydrochloride*, m.p. 146°; *phenylcarbamyl* derivative, m.p. 121°), and  $\beta$ -allyl-amino-propane, b.p. 106°/2 mm. [*hydrochloride*, m.p. 141° (decomp.); *phenylcarbamyl* derivative, m.p. 124°]; CHMeCl·CCl<sub>2</sub>·CH(CH<sub>2</sub>·NO<sub>2</sub>)·OAc yields  $\gamma\gamma\delta$ -trichloro- $\alpha$ -nitro- $\beta$ -methyl-, b.p. 110°/2 mm. [*hydrochloride*, m.p. 172°; *phenylcarbamyl* derivative, m.p. 186° (decomp.)], - $\beta$ -ethyl-, b.p. 115°/0.7 mm. (*hydrochloride*, m.p. 120°; *phenylcarbamyl* derivative, m.p. 140°), and - $\beta$ -allyl-amino-*n*-pentane, b.p. 116°/0.5 mm. (decomp.) [*hydrochloride*, m.p. 140° (decomp.)]; CCl<sub>3</sub>·CH(CHMe·NO<sub>2</sub>)·OAc yields  $\delta\delta\delta$ -trichloro- $\beta$ -nitro- $\gamma$ -methylamino-, b.p. 94°/0.5 mm. (*hydrochloride*, m.p. 194°), - $\gamma$ -*p*-toluidino-, m.p. 99—100°, and - $\gamma$ -phenylhydrazino-*n*-butane, m.p. 108—109°; CHMeCl·CCl<sub>2</sub>·CH(CHMe·NO<sub>2</sub>)·OAc yields  $\delta\delta\epsilon$ -trichloro- $\beta$ -nitro- $\gamma$ -methylamino-, b.p. 109°/0.3 mm. (*hydrochloride*, m.p. about 200°), and - $\gamma$ -*p*-toluidino-*n*-hexane, m.p. 82°; CCl<sub>3</sub>·CH(CHPh·NO<sub>2</sub>)·OAc yields  $\gamma\gamma\gamma$ -trichloro- $\alpha$ -nitro- $\beta$ -*p*-toluidino-, m.p. 121—122°, and - $\beta$ -phenylhydrazino- $\alpha$ -phenylpropane, m.p. 155° (decomp.). F. R. G.

**Polyamines. II. Preparation of  $\beta\beta'$ -diamino-diethylamine and NN'-bis-( $\beta$ -aminodiethyl)ethylenediamine.** D. H. PEACOCK (J.C.S., 1936, 1518—1520; cf. A., 1934, 1207).—*p*-Toluenesulphon- $\beta$ -chloroethylamide with (CH<sub>2</sub>·NH<sub>2</sub>)<sub>2</sub> in EtOH gives N-( $\beta$ -*p*-toluenesulphonamidoethyl)ethylenediamine dihydrochloride, m.p. 182° {CuSO<sub>4</sub> complex, [(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub>S)<sub>2</sub>Cu(H<sub>2</sub>O)<sub>2</sub>]SO<sub>4</sub>; NiSO<sub>4</sub> complex}, and the dihydrochloride, m.p. 246°, of NN'-bis-( $\beta$ -*p*-toluenesulphonamidoethyl)ethylenediamine, m.p. 160°, hydrolysed (H<sub>2</sub>SO<sub>4</sub>) to NN'-bis-( $\beta$ -aminoethyl)ethylenediamine {tetrahydrochloride, m.p. 266—270°; CuSO<sub>4</sub> and KPtCl<sub>6</sub> [Pt(C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>)]PtCl<sub>4</sub> (?), complexes}. NH(CH<sub>2</sub>·CH<sub>2</sub>Br)<sub>2</sub>·HBr and NH<sub>3</sub> in EtOH give NH(CH<sub>2</sub>·CH<sub>2</sub>Br)<sub>2</sub> and piperazine, identified as their *p*-C<sub>6</sub>H<sub>4</sub>Me·SO<sub>2</sub> derivatives. F. R. G.

**Aliphatic polyamines. III.** J. VAN ALPHEN (Rec. trav. chim., 1936, 55, 835—840; cf. this vol., 1274).—Br·[CH<sub>2</sub>]<sub>3</sub>·Br and NH<sub>2</sub>·[CH<sub>2</sub>]<sub>2</sub>·NH<sub>2</sub>·H<sub>2</sub>O in abs. EtOH, first alone and then with KOH, give NN'-di- $\beta'$ -aminoethylpropylene- $\alpha\gamma$ -diamine (I), b.p. 185—186°/35 mm., 286—287°/760 mm. (*tetra*-, m.p. about 223°, and *tri*-picrate, m.p. 171°; *tetraoxalate*, m.p. 237°; *tetraphenyl-carbamide*, m.p. 145—155°, and -thiocarbamide, m.p. 179°, and *Bz*<sub>4</sub> derivative, m.p. 172°; gives a reddish-violet colour with aq. Cu salts), and a fraction, b.p. 274—276°/35 mm. (I) and PhCHO give a gum, which with Na-EtOH affords NN'-di- $\beta'$ -benzylaminoethylpropylene- $\alpha\gamma$ -diamine (II), m.p. 44° [*tetra*-hydrochloride, m.p. 270—290° (decomp.), -picrate, m.p. 201°, and -oxalate, m.p. 247°; (NO)<sub>4</sub>-, m.p. 99°, and *tetraphenylthio*-



carbamide derivative, m.p. 130—135°]. (I) and CS<sub>2</sub> in EtOH give  $\alpha$ -di-2-thiotetrahydroglyoxalinypropene, m.p. 156°. (II) with PhCHO or *p*-OMe-C<sub>6</sub>H<sub>4</sub>·CHO gives  $\alpha$ -di-2-phenyl-, m.p. 123°, and -*p*-anisyl-, m.p. 110°, -3-benzyltetrahydro-1-glyoxalinypropene, m.p. 110°. R. S. C.

**Alcoholysis in the reaction between triethanolamine and bivalent metal salts.** IV. F. GARELLI and A. TETTAMANZI (Atti R. Accad. Sci. Torino [Cl. Sci. fis. mat.], 1934, 69, I, 89—96; Chem. Zentr., 1936, i, 535).—In presence of H<sub>2</sub>O, N(CH<sub>2</sub>·CH<sub>2</sub>·OH)<sub>3</sub> reacts as the hydrate, NH(OH)(C<sub>2</sub>H<sub>4</sub>·OH)<sub>3</sub>. Earlier results are summarised. H. N. R.

**Production of methyl esters of difficultly esterified acids.** V. PRELOG and M. PIANTANIDA (Z. physiol. Chem., 1936, 244, 56—58).—The acids, in MeOH, are converted into NMe<sub>4</sub> salts by titration with NMe<sub>4</sub>·OH in MeOH avoiding excess, MeOH and any residual NMe<sub>4</sub>·OH are removed by heating, and the salts are destructively distilled at 200—300° preferably in a vac., thus giving high yields of Me ester. Me esters of NH<sub>2</sub>-acids may be prepared thus. W. McC.

**Preparation of  $\alpha$ -amino-acids from alkylcyanoacetic acids.** A. DARAPSKY [with H. DECKER, E. STEUERNAGEL, and O. SCHIEDRUM] (J. pr. Chem., 1936, [iii], 146, 250—267; cf. A., 1916, i, 127).—CN·CHPr<sup>a</sup>·CO<sub>2</sub>Et and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O at room temp. give the non-cryst. *n*-propylcyanoacethydrazide CN·CHPr<sup>a</sup>·CO·NH·NH<sub>2</sub> (CMe<sub>2</sub> derivative, m.p. 98—100°), converted by NaNO<sub>2</sub> and HCl into the oily *n*-propylcyanoacetazide which with boiling EtOH·Et<sub>2</sub>O affords *Et*  $\alpha$ -cyano-*n*-butylcarbamate, transformed by boiling conc. HCl into  $\alpha$ -amino-*n*-valeric acid, m.p. 291° (corr.; decomp.) in a sealed capillary [hydrochloride; Cu salt; Bz, m.p. 152°, and SO<sub>2</sub>Ph, m.p. 150—152° (corr.), derivatives]. Et isobutylcyanoacetate is converted by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in boiling EtOH into diisobutylcyanoacethydrazide, (·NH·CO·CHBu<sup>β</sup>·CN)<sub>2</sub>, m.p. 198°, which does not condense with PhCHO. At room temp. in the absence of solvents the reactants yield the monohydrazidinedehydrazide, NH<sub>2</sub>·NH·CO·CHBu<sup>β</sup>·C(NH)·NH·NH<sub>2</sub>, m.p. 101°, which condenses with PhCHO, whereas in presence of EtOH at room temp. they yield isobutylcyanoacethydrazide (CMe<sub>2</sub>, m.p. 81—82°, ·CHPh, m.p. 95°, and *o*-hydroxybenzylidene, m.p. 115°, derivatives). Non-cryst. isobutylcyanoacetazide is transformed by NH<sub>2</sub>Ph in Et<sub>2</sub>O into isobutylcyanoacetanilide, m.p. 192°, and by boiling EtOH into *Et*  $\alpha$ -cyanoisomethylcarbamate, which with boiling conc. HCl affords  $\alpha$ -aminoisohexic acid, m.p. 293° in a sealed capillary (Cu salt; ·SO<sub>2</sub>Ph derivative, m.p. 143°). Et isoamylcyanoacetate yields isoamylcyanoacethydrazide, m.p. 100° (unstable, hygroscopic hydrochloride, m.p. 107°, ·CMe<sub>2</sub>, m.p. 81°, and ·CHPh, m.p. 85°, derivatives), converted by I in cold abs. EtOH into diisoamylcyanoacethydrazide, C<sub>16</sub>H<sub>26</sub>O<sub>2</sub>N<sub>4</sub>, m.p. 180° (decomp.). Non-cryst. isoamylcyanoacetazide yields isoamylcyanoacetanilide, m.p. 108°, and non-cryst. *Et*  $\alpha$ -cyanoisohexylcarbamate, CH<sub>2</sub>Bu<sup>β</sup>·CH(CN)·NH·CO<sub>2</sub>Et, hydrolysed by boiling 20% HCl to  $\alpha$ -amino- $\delta$ -methyl-*n*-hexic acid, m.p. 266° (decomp.) [hydrochloride, Cu salt, *Et* ester (I), b.p. 59°/19 mm., and its hydro-

chloride, m.p. 86°]. When kept in a sealed tube (I) slowly passes into 2:5-diketo-3:6-diisoamylpiperazine, m.p. 281° (decomp.). H. W.

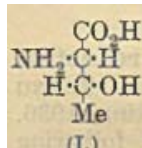
**Methylation of glycine.** F. CHALLENGER (Chem. and Ind., 1936, 900—901).—The suggestion (A., 1935, 1027) that glycine (I), through its deamination products CHO·CO<sub>2</sub>H and CH<sub>2</sub>O, is the active agent in biological methylation (often a detoxication process) is supported by a review of relevant lit. The assumption of self-methylation explains the formation of sarcosine and betaine. The methylating action of (I) itself is exemplified by the conversion of nicotinic acid into trigonelline and nicotinuric acid. J. W. B.

**Specificity of papain peptidase.**—See this vol., 1557.

**Spatial configuration of [natural]  $\alpha$ -amino- $\beta$ -hydroxy-*n*-butyric acid.** C. E. MEYER and W. C. ROSE (J. Biol. Chem., 1936, 115, 721—729).—The  $\alpha$ -amino- $\beta$ -hydroxy-*n*-butyric acid isolated from proteins is shown to be (I); it is named *d*(or *D*)(-)-threonine. The dextro- (II) and lævo-rotatory (III) threodihydroxybutyric acids are the *l*(+)- and *d*(-)-compounds, respectively. (I) and HI-P at 150—155° give partly racemised *d*- $\alpha$ -amino-*n*-butyric acid with  $[\alpha]_D^{25} +4.18^\circ$  in H<sub>2</sub>O. With chloramine-T it affords *l*-lactaldehyde (not isolated), oxidised to *l*-lactic acid. With Ba(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub> at 0° (I) gives (III) (phenylhydrazide, m.p. 103.5—104°,  $[\alpha]_D^{25} -16.25^\circ$  in H<sub>2</sub>O). The phenylhydrazides of (II) and the *dl*-form have m.p. 102—104° and 129.5—131°, respectively. R. S. C.

**Polypeptidases of blood-serum and -plasma.**—See this vol., 1556.

**Hydrazino-acids.** IV. A. DARAPSKY [with J. GERMSCHIED, C. KREUTER, E. ENGELMANN, W. ENGELS, and W. TRINIUS] (J. pr. Chem., 1936, [ii], 146, 219—249; cf. A., 1918, i, 506, 553; 1919, i, 601).—CHPr<sup>β</sup>Br·CO<sub>2</sub>H and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in boiling EtOH give  $\alpha$ -hydrazinoisovaleric acid, m.p. 230—235° [hydrochloride, m.p. 135.5°; *o*-hydroxybenzylidene, m.p. 124°, and cinnamylidene, m.p. 137—139°, derivatives; unstable *Me* ester and its hydrochloride (I), m.p. 112°; unstable *Et* ester and its hydrochloride (II), m.p. 104°], which is not converted by conc. aq. NH<sub>3</sub> into its NH<sub>4</sub> salt. (I) is transformed by aq. KCNO into *Me*  $\alpha$ -carbamyldiazinoisovalerate, NH<sub>2</sub>·CO·NH·NH·CHPr<sup>β</sup>·CO<sub>2</sub>Me, m.p. 126.5°, which does not condense with PhCHO or *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO and does not appear to yield a hydrochloride. *Et*  $\alpha$ -carbamyldiazinoisovalerate, from (II), has m.p. 130°. (I) is converted by NaNO<sub>2</sub> in conc. aq. solution into *Me*  $\alpha$ -nitrosohydrazinoisovalerate (III), NH<sub>2</sub>·N(NO)·CHPr<sup>β</sup>·CO<sub>2</sub>Me, m.p. 35.5°, which readily decomposes when preserved, probably accompanied by *Me*  $\alpha$ -hydroxyisovalerate. *Et*  $\alpha$ -nitrosohydrazinoisovalerate is an unstable oil. (III) passes at 115—120° into N<sub>2</sub>O and *Me*  $\alpha$ -aminoisovalerate, b.p. 56°/14 mm. (hydrochloride, m.p. 116.5°; picrate, m.p. 145.5°), which decomposes when kept, probably giving diketodisopropylpiperazine. When distilled with steam in presence of 10% H<sub>2</sub>SO<sub>4</sub> (III) affords



*Me*  $\alpha$ -azidoisovalerate, b.p. 50°/15 mm., hydrolysed by aq. NaOH at room temp. to non-cryst.  $\alpha$ -azidoisovaleric acid ( $\text{NH}_4$  and Ag salts). The following substances are obtained by an analogous series of reactions:  $\alpha$ -hydrazino-*n*-hexoic acid, m.p. 199—201° (very hygroscopic hydrochloride;  $\text{:CHPh}$ , m.p. 102—103°, *o*-hydroxybenzylidene, m.p. 123—124°, and  $\text{Bz}_2$ , m.p. 157—158°, derivatives; *Et* ester hydrochloride, m.p. 75°; very hygroscopic *Me* ester hydrochloride); *Et*  $\alpha$ -carbamyldiazino-*n*-hexoate, m.p. 102—103°; *Et*  $\alpha$ -nitrosohydrazino-*n*-hexoate; *Et*  $\alpha$ -amino-*n*-hexoate, b.p. 91—93°/11—12 mm., whence the corresponding acid, m.p. 299—303° in a sealed capillary, and its Cu salt; *Et*  $\alpha$ -azido-*n*-hexoate, b.p. 93—95°/13—14 mm., also obtained from  $\text{CHBu}^{\text{a}}\text{Br}\cdot\text{CO}_2\text{Et}$  and  $\text{NaN}_3$ , whence non-cryst.  $\alpha$ -azido-*n*-hexoic acid (non-cryst.  $\text{NH}_4$  and Ag salts);  $\alpha$ -hydrazinoisohexoic acid  $\text{CH}_2\text{Pr}^{\text{b}}\cdot\text{CH}(\text{NH}\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$ , m.p. 228° [hydrochloride, m.p. 170—177° (decomp.);  $\text{:CHPh}$ , m.p. 115·5°, *o*-hydroxybenzylidene, m.p. 139°, and  $\text{CMe}_2$ , m.p. 99—101°, derivatives; *Me* ester hydrochloride, m.p. 99—102°; *Et* ester hydrochloride, m.p. 91—92°, and *o*-hydroxybenzylidene derivative, m.p. 212° of the *Et* ester); *Me*  $\alpha$ -carbamyldiazinoisohexoate, m.p. 110°; *Et*  $\alpha$ -nitrosohydrazinoisohexoate, m.p. 25—28°; *Et*  $\alpha$ -aminoisohexoate, b.p. 88°/11 mm.; *Et*  $\alpha$ -azidoisohexoate, b.p. 94°/14 mm., non-cryst.  $\alpha$ -azidoisohexoic acid m.p. 92—95° and Ag salts);  $\alpha$ -hydrazino-*n*-heptoic acid, m.p. 205—206° (decomp.) [Cu salt, rapid decomp. 110° after darkening at 100°; hydrochloride, m.p. (indef.) 126—145°;  $\text{:CHPh}$ , m.p. 109°, and *o*-hydroxybenzylidene, m.p. 140°, derivatives; hydrochloride, m.p. 157°, and *o*-hydroxybenzylidene derivative, m.p. 203°, of the *Me* ester; non-cryst. *Et* ester and its hydrochloride, m.p. 99°, and *o*-hydroxybenzylidene derivative, m.p. 152°]; *Et*  $\alpha$ -carbamyldiazino-*n*-heptoate, m.p. 94° (hydrochloride, m.p. 125°, immediately hydrolysed by  $\text{H}_2\text{O}$ ), which does not condense with  $\text{PhCHO}$  or *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ ; non-cryst. *Et*  $\alpha$ -nitrosohydrazino-*n*-heptoate; *Et*  $\alpha$ -amino-*n*-heptoate, b.p. 89°/12 mm., and its very hygroscopic hydrochloride; *Et*  $\alpha$ -azido-*n*-heptoate, b.p. 104°/13 mm., also derived from  $\text{Me}[\text{CH}_2]_4\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$  and  $\text{NaN}_3$ ; non-cryst.  $\alpha$ -azido-*n*-heptoic acid (Ag salt):  $\alpha$ -hydrazino-*n*-nonoic acid, m.p. 197° ( $\text{:CHPh}$ , m.p. 117°, and *o*-hydroxybenzylidene, m.p. 137°, derivatives; hydrochloride, m.p. 166° after some decomp., and *o*-hydroxybenzylidene derivative, m.p. 132°, of the *Me* ester; *Et* ester hydrochloride, m.p. 72°); *Et*  $\alpha$ -carbamyldiazino-*n*-nonoate, m.p. 81°, which does not condense with  $\text{PhCHO}$  or *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ ; *Et*  $\alpha$ -nitrosohydrazino-*n*-nonoate; *Et*  $\alpha$ -amino-*n*-nonoate, b.p. 132°/17 mm.,  $\alpha$ -amino-*n*-nonoic acid, sublimes at about 256° (Cu salt, also  $+1\text{H}_2\text{O}$ ); *Et*  $\alpha$ -azido-*n*-nonoate, b.p. 140—145°/15 mm.; non-cryst.  $\alpha$ -azido-*n*-nonoic acid (Ag salt).

H. W.

**Imidocarbonic esters, iminothio-, oximinothio-, and dithio-formic esters.** J. HOUBEN and R. ZIVADINOVITSCH (Ber., 1936, 69, [B], 2352—2360).—Improvements in the prep. of  $\text{Et}_2$  *N*-chloroimidocarbonate (Sandmeyer, A., 1886, 611; Houben *et al.*, A., 1923, i, 1077) give the compound in 53·6—59% yield; it can be kept unchanged in light petrol-

eum.  $\text{Et}_2$  imidocarbonate (I), b.p. 40°/12 mm., can be kept unchanged (sealed) over anhyd. CaO. When kept alone (sealed) even in the dark it is slowly converted into a solution of  $\text{Et}_3$  isocyanurate in  $\text{EtOH}$ ; under similar conditions, but in presence of granulated  $\text{CaCl}_2$ ,  $\text{Et}_3$  cyanurate results. It is converted by dil. aq. alkali or by prolonged warming with  $\text{H}_2\text{O}$  into  $\text{EtOH}$  and  $\text{NH}_2\cdot\text{CO}_2\text{Et}$ . With solid alkali it affords  $\text{EtOH}$  or alkoxide and "isocyanate." An improved prep. of  $\text{Et}_2$  di-imido-oxalate, b.p. 69—70°/18 mm., is described. (I) in  $\text{Et}_2\text{O}$  is transformed by  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\cdot\text{HCl}$  in  $\text{H}_2\text{O}$  into *Et* diethoxymethyleneaminoacetate,  $(\text{OEt})_2\text{C}=\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b.p. 108—109·5°/11 mm., in 66% yield. (I) and *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$  in abs.  $\text{EtOH}$  at room temp. afford *Et* *p*-tolylimidocarbonate, b.p. 135—136°/12 mm., but reaction does not occur with *o*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ .  $\text{KNO}_2$  and  $\text{CH}_2(\text{OEt})_2$  are produced by the action of solid KOH on (I) in  $\text{Et}_2\text{O}$ . Anhyd. HCN combines with mercaptans in presence of HCl, but the products are usually non-cryst. oils which cannot be transformed into the corresponding oximino-compounds;  $\text{CH}_2\text{Ph}\cdot\text{SH}$ , however, gives *CH*<sub>2</sub>*Ph* imidothioformate hydrochloride (II), decomp. about 180°. Treatment of  $\text{EtSH}$  and HCN with HCl in light petroleum affords a non-cryst. product, transformed by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in  $\text{Et}_2\text{O}$  into *Et* thioformhydroxamate,  $\text{OH}\cdot\text{N}(\text{CH}_2\text{SEt})$ , m.p. 110—111°; the corresponding *Bu*<sup>a</sup>, m.p. 90—91°, and *CH*<sub>2</sub>*Ph*, m.p. 116—117°, esters are similarly obtained. *CH*<sub>2</sub>*Ph* thioformate has b.p. 109—111°/26 mm. (II) is converted by the successive action of  $\text{K}_2\text{CO}_3$  in  $\text{H}_2\text{O}$ - $\text{Et}_2\text{O}$  and  $\text{H}_2\text{S}$  into *CH*<sub>2</sub>*Ph* dithioformate, b.p. 161—162°/13 mm.  $\text{MeCN}$  and  $\text{CH}_2\text{Ph}\cdot\text{SH}$  give *CH*<sub>2</sub>*Ph* imidothioacetate hydrochloride, m.p. 153—155°.  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  and  $\text{MeCN}$  afford *Et*  $\alpha$ -imidoethylthiolacetate hydrochloride, m.p. 100—102°.  $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  similarly gives  $\alpha$ -iminoethylthiolacetic acid hydrochloride, m.p. 110—112° (decomp.), transformed by KOH into the corresponding (?) acid, m.p. 97—98°.  $\text{NH}_4$  acetylthiolacetate, m.p. 68—70°, and acetylthiolacetamide, m.p. 78—80°, are incidentally described.

H. W.

**Reaction of halogenoamines with ketens.** G. H. COLEMAN, R. L. PETERSON, and G. E. GORFEN (J. Amer. Chem. Soc., 1936, 58, 1874—1876).— $\text{NH}_2\text{Cl}$  and  $\text{CH}_2\text{CO}$  in  $\text{Et}_2\text{O}$  at  $-60^\circ$  and then at room temp. give 73% of acetichloroamide, m.p. 111—112°;  $\text{NHBr}_2$  similarly affords 18% of bromoacetamide, m.p. 88—89° ( $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NHBr}$  is probably first formed and then reacts with the HBr produced in the reaction),  $\text{NCl}_3$  furnishes 14% of  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ , and  $\text{NMe}_2\text{Cl}$  yields (probably) chloroacetdimethylamide, b.p. 98—100°/11 mm.  $\text{CPh}_2\cdot\text{CO}$  (modified prep.; cf. Ritter and Wiedemann, A., 1930, 214) and  $\text{NH}_2\text{Cl}$  similarly give 51% of diphenylchloroacetamide, m.p. 116—117°;  $\text{NMe}_2\text{Cl}$  affords 95% of  $\text{CPh}_2\text{Cl}\cdot\text{CO}\cdot\text{NMe}_2$ , m.p. 122—123°, whilst  $\text{NCl}_3$  furnishes (cf. A., 1928, 1362) (probably) diphenylchloroacetdichloroamide, m.p. 112° (Cu block).

H. B.

**Monosodiocarbamide and its reactions.** R. A. JACOBSON (J. Amer. Chem. Soc., 1936, 58, 1984—1986).—Na (1 equiv.) reacts readily with  $\text{CO}(\text{NH}_2)_2$  in liquid  $\text{NH}_3$  to give the  $\text{Na}_1$  derivative (I), decomp. from 150—160°; reaction is slow with  $>1$  equiv. of



Na and affords (I) + Na, derivative. Oleyl- (II), stearyl-, and benzoyl- (III) -carbamide are obtained from (I) and  $\text{RCOCl}$ ;  $\text{CH}_3\text{PhCl}$  in liquid  $\text{NH}_3$  gives benzylcarbamide. (II), (III), and  $\text{NH}_2\cdot\text{CO}\cdot\text{NHAc}$  are formed from (I) and Me oleate, MeOBz, and EtOAc, respectively, in  $\text{COMe}_2$ . (I) and  $\text{CHR}(\text{CO}_2\text{Et})_2$  in  $\text{COMe}_2$  afford barbituric acid and its 5-Et, -Pr $^\beta$ , and -Bu derivatives. (I) and Et glutarate similarly give a compound, probably  $[\text{CH}_2]_3(\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ , m.p. 247—248°; Et pimelate affords a similar compound, m.p. 240—245°, and a little of (probably) the compound  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ , m.p. 205—206°. Mixed acylcarbamides are obtained from (I) and various oils (coconut, linseed, China wood) in  $\text{COMe}_2$ . (I) does not react with BuI or dodecyl bromide. H. B.

**Improved preparation of enolphosphopyruvic acid.** W. KIESSLING (Ber., 1936, 69, [B], 2331—2332; cf. A., 1935, 731).—Isolation is effected through the Ba salt. Ill-defined impurities containing P (probably phosphorylated products from condensed  $\text{AcCO}_2\text{H}$ ) are removed as their Na salts in slightly alkaline solution ( $p_H$  8.5) by treatment with EtOH, whilst P-free by-products are eliminated by taking advantage of the sparing solubility of Ba enolphosphopyruvate in hot solution and its fractional pptn. with EtOH from solution acid to litmus. H. W.

**Constitution of complex metallic salts. IV. Bridged dipalladium derivatives.** F. G. MANN and D. PURDIE (J.C.S., 1936, 873—890).—In the abstract of this paper (this vol., 1184) the following should have been recorded: *dichlorobis(triethylphosphine)-μ-dichlorodipalladium*, m.p. 230°, and the corresponding  $\text{Pr}^a$ , m.p. 189°, and  $\text{Bu}^a$  compound, m.p. 145°; *di-iodobis(tri-n-butylphosphine)-μ-di-iodopalladium*, m.p. 136° and the corresponding *n-amyl* compound, m.p. 127°; *dichlorobis(trimethylarsine)-μ-dichloropalladium*, decomp. 252—260° without melting, and the corresponding *Et*, m.p. 212°,  $\text{Pr}^a$ , m.p. 160°,  $\text{Bu}^a$ , m.p. 128°, and *n-amyl* compound, m.p. 108°; *dichloro-, dinitro-, and oxalato-dipyridylpalladium; oxalatobis-(n-butylphosphine)-μ-dichlorodipalladium*, m.p. 185—186° (decomp.) in bath at 180°; *dinitritobis-(n-butylphosphine)-μ-dinitritopalladium*, m.p. 138° (decomp.), and its additive compound with  $\text{NaNO}_2$ ; *oxalatobis-(n-butylphosphine)-μ-dinitritodipalladium*, m.p. 201—204° (decomp.) in bath at 185°; *dinitritobis-(n-butylphosphine)palladium*, m.p. 140°; *dichloro-* (I), m.p. 101° (corresponding  $\text{Pr}^a$  compound, m.p. 151°), and *dithiocyanato-bis-(n-butylarsine)-μ-dithiocyanatodipalladium* (II), m.p. 111° (corresponding  $\text{Pr}^a$  compound, m.p. 142°); *dithiocyanatobis-(n-butylarsine)palladium* (III), m.p. 75° (corresponding  $\text{Pr}^a$  compound, m.p. 90—91.5°); *dinitrito-*, m.p. 86—88°, and *dichloro-mono-p-toluidinomono-n-butylphosphinepalladium*, m.p. 75° (corresponding *anilino*-compound, m.p. 68°, and *arsine*, m.p. 87°); *dichloro-monoammino-*, m.p. 71°, and *tri-ammino-n-butylphosphinepalladium dichloride*; *bis-(n-butylphosphine)-bis(ethylenediamino)-μ-dichlorodipalladium dichloride*; *monochloro-n-butylphosphine-ethylenediaminopalladium monochloride*; *monochloroethylthiobis-(n-butylphosphine)-μ-dichlorodipalladium*, m.p. 151°, and

*dichlorobis-(n-octylsulphide)-μ-dichlorodipalladium*, m.p. 61°. *Phosphines* corresponding with (I), (II), and (III) have m.p. 142°, 165°, and 112°, respectively. F. N. W.

**Phenylcyclopentane and its behaviour towards catalytic hydrogenation.** J. I. DENISENKO (J. Gen. Chem. Russ., 1936, 6, 922—924).—Contrary to the tension theory of Baeyer, the *cyclopentane* ring is broken by hydrogenation. Phenylcyclopentane, b.p. 216—218°/750 mm., when passed over Pt at 305—310° in  $\text{H}_2$  yields a mixture of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phenylpentane. J. J. B.

**Action of bromine water on ethylenic compounds. Action on cyclohexene.** F. SWARTS (Bull. Acad. roy. Belg., 1936, [v], 22, 924—932; cf. this vol., 712).—*cyclohexene* with Br in  $\text{H}_2\text{O}$  at <20° affords 1:2-dibromocyclohexane (I), m.p. 2.8°, 2-bromocyclohexanol (II), m.p. 27.5°, identified as the 2- $\text{NH}_2$ -compound, and 2:2'-dibromodicyclohexyl ether (III), m.p. 70° (cf. A., 1925, i, 497). The ratio (II)/(I) is the greater the higher is the reaction temp. (cf. A., 1928, 505, 866). (II) when heated in vac. at 110° does not afford (III), which indicates that (III) does not arise from (II). Heat decomposes (III) but some *cyclohexylcyclohexene* is formed; when heated with  $\text{PCl}_3$  and Br under pressure (III) affords some (I). J. L. D.

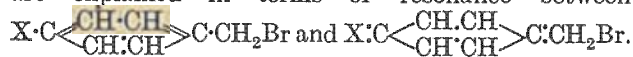
**Oxidation of  $\alpha\alpha\alpha\epsilon$ -tetraphenyl- $\Delta^{\alpha\delta}$ -pentadiene and  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\epsilon}$ -hexadiene.** K. H. BAUER and H. HERZOG (J. pr. Chem., 1936, [ii], 147, 4—10).— $\text{CH}_2(\text{CH}\cdot\text{CPh}_2)_2$  (I) with  $\text{H}_2$ -Pd-BaSO $_4$  in  $\text{C}_6\text{H}_6$  gives  $\text{CHPh}_2\cdot[\text{CH}_2]_3\cdot\text{CHPh}_2$  and with Br- $\text{CHCl}_3$  gives HBr and  $\beta\delta$ -dibromo- $\alpha\alpha\epsilon\epsilon$ -tetraphenyl- $\Delta^{\alpha\delta}$ -pentadiene, m.p. 141°.  $\text{Bz}\cdot[\text{CH}_2]_4\cdot\text{Bz}$  and  $\text{MgPhBr}$  in  $\text{Et}_2\text{O}$  give  $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- $\alpha\zeta$ -diol, m.p. 213°, dehydrated at 230° to give  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\epsilon}$ -hexadiene (II), m.p. 108—109°, which with  $\text{H}_2$ -Pd-BaSO $_4$  gives  $\alpha\alpha$ -tetraphenylhexane, m.p. 123—124°; the tetrabromide, m.p. 146—147° (decomp.), of (II) in hot EtOH gives HBr and  $\beta\epsilon$ -dibromo- $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^{\alpha\epsilon}$ -hexadiene, m.p. 199°. With  $\text{BzO}_2\text{H}\cdot\text{CHCl}_3$  (II) yields  $\alpha\alpha\zeta\zeta$ -tetraphenylhexane- $\alpha\beta\epsilon\zeta$ -tetraol, m.p. 193°. Owing to the presence of  $\text{:C}\cdot\text{CH}_2\cdot\text{C:}$  oxidation of (I) at 100° or in ultra-violet light at room temp. is faster than that of (II); in both cases  $\text{COPh}_2$  is formed. R. S. C.

**Colorimetric determination of carotenoids by a modified potassium dichromate method.** A. KROGIS (Biochem. Z., 1936, 287, 226—234; cf. Jørgensen, A., 1927, 952).—The alterations which must be made in the  $p_H$  of aq.  $\text{K}_2\text{Cr}_2\text{O}_7$  used as colour standard in determining various concns. of carotene (I) and xanthophyll (II) have been measured for layers 1—35 mm. thick at intervals of 1 mm. Consequently (I) and (II) can be determined with the help of buffered aq.  $\text{K}_2\text{Cr}_2\text{O}_7$  as standard, the accuracy attainable being as great as that of the method of Kuhn *et al.* (A., 1932, 785), which is not applicable to the higher and lower concns. covered by the new method. For very low concns. the method of Connor (A., 1928, 786) should be applied. W. McC.

**Carotenoids of purple bacteria.**—See this vol., 1561.

Is the methyl group attached to the benzene nucleus positive or negative? W. HEROLD and K. W. ROSENMUND (J. pr. Chem., 1936, [ii], 146, 201—208; cf. this vol., 105).—In reply to Huntenburg (this vol., 1239) it is shown that conclusions based on Hund's theory (A., 1925, ii, 479), the results of absorption measurements of  $C_6H_6$  derivatives, chemical evidence, and analyses of band spectra are in harmony with the view that Me acts as a positive substituent in the  $C_6H_6$  nucleus. H. W.

**Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. VIII. Polar effects of halogens.** J. W. BAKER (J.C.S., 1936, 1448—1451; cf. this vol., 195).—The order for the velocity of interaction of the *m*-halogenobenzyl bromides with  $C_5H_5N$  in dry  $COMe_2$  ( $I > Br \sim Cl > F$ ) is in agreement with that of Bennett *et al.* (*ibid.*, 165) for the corresponding chlorides. The velocity order for the corresponding *p*-compounds ( $F \sim I > Br > Cl$ ) differs from that of Bennett *et al.*, who used aq.  $COMe_2$ . These results are explained in terms of resonance between



The following were prepared from the appropriate halogenotoluene with Br: *m*-fluoro-, b.p.  $87^\circ/17$  mm., *p*-fluoro-, b.p.  $38^\circ/0.6$  mm., *m*-chloro-, b.p.  $55^\circ/0.2$  mm., m.p.  $17.5^\circ$ , and *m*-iodo-, m.p.  $50.8^\circ$ , -benzyl bromide.

F. R. G.

**Natural and synthetic rubber. XVI. Structure of polystyrene.** T. MIDGLEY, jun., A. L. HENNE, and H. M. LEICESTER (J. Amer. Chem. Soc., 1936, 58, 1961—1963).—Contrary to Staudinger (cf. A., 1935, 740), polystyrene (I) is

$-CH_2-CHPh-CHPh-CH_2-CH_2-CHPh-CHPh-CH_2-$ , since styrene+Na with EtOH give PhEt (74%) and  $(CH_2Ph-CH_2)_2$  (about 23%). This structure is the only one consistent with Mack's explanation (B., 1935, 196) of the elastic properties of (I). H. B.

**Reactivity of the methyl group in some nitrodiphenylmethanes.** G. D. PARKES and R. H. H. MORLEY (J.C.S., 1936, 1478—1479).—The influence of the position of  $NO_2$  groups on the reaction between nitrodiphenylmethanes and *p*-NO- $C_6H_4$ -NMe<sub>2</sub> (I) results in the formation of 4:4'-dinitro-, m.p.  $155^\circ$ , and 2:4:2':4'-tetranitro-benzophenone-*p*-dimethyl-aminoanil, m.p.  $143^\circ$  (decomp.), and of coloured products from 2:2'-dinitro- (II) and 2:4:6:2':4'-pentanitro-, m.p.  $200^\circ$ , obtained by nitration of 2:4:2':4'-tetranitro-diphenylmethane (III). The  $(NO_2)_6$ -compound could not be prepared, and the 3:3'-( $NO_2$ )<sub>2</sub>-compound and  $CH_2Ph_2$  do not react with (I). The anils of the (II) and (III) exceptionally resist hydrolysis. These nitrodiphenylmethanes do not couple with diazonium salts. F. R. G.

**Reaction of sodium with triphenylmethyl chloride and triphenylmethyl in organic solvents.** W. E. BACHMANN and F. Y. WISELOGLE (J. Amer. Chem. Soc., 1936, 58, 1943—1944).—Na (excess) reacts rapidly with  $CPh_3Cl$  in  $Et_2O$  or  $Et_2O-C_6H_6$ , and more slowly in  $C_6H_6$  (cf. Morton and Stevens, A., 1932, 728), to give  $CPh_3$  and thence  $NaCPh_3$ , if the metal surface is exposed throughout the reaction. When the complete reaction is slow (e.g., use of 1

atom of Na) a little *p*-benzhydryltetraphenylmethane is also produced (cf. Schlenk and Marcus, A., 1914, i, 823).  $NaCPh_3$  is oxidised (dry air) to  $CPh_3 \cdot OH$  and a little  $(CPh_3 \cdot O)_2$ . H. B.

**Allotropic forms of diphenyl sulphone and determination of their transition point.** V. J. MIKESKA, N. T. FARINACCI, and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 1869—1871).—Crystallisation (any method) of  $Ph_2SO_2$  at  $>75^\circ$  gives a form, m.p.  $128^\circ$  (I); at  $<75^\circ$  a form, m.p.  $124^\circ$  (II), results. (I) and (II) are reciprocally convertible allotropic forms; the transition temp. is  $74.8^\circ$  (determination described). Discrepancies in the lit. are thus explained. H. B.

**Destructive catalysis of hydrindene and hydrindane.** M. B. TUROVA-POLLAK (J. Gen. Chem. Russ., 1936, 6, 947—949).—Hydrogenation of hydrindene (I) at  $360-380^\circ$  in presence of Pt affords mainly *o*- $C_6H_4$ MeEt, converted by Br and  $AlBr_3$  into  $C_6MeBr_5$ . Hydrindane at  $300-330^\circ$  gives chiefly (I). J. J. B.

**Dipole moments and the fixation of aromatic double links: bromohydrindenes and bromotetralins.** N. V. SIDGWICK and H. D. SPRINGALL (J.C.S., 1936, 1532—1537).—6-Bromo-5-aminohydrindene and 6-bromo-7-aminotetrahydronaphthalene with  $Cu_2Br_2$  (Sandmeyer) yield respectively 5:6-dibromohydrindene (I), m.p.  $76-77^\circ$ , and 6:7-dibromotetrahydronaphthalene (II), m.p.  $54-55^\circ$ . The following dipole moments have been measured: hydrindene, 0.53D; 6-bromo-, 2.15D, and 5:6-dibromo-hydrindene, 2.48D; tetrahydronaphthalene, 0.52D; 7-bromo-, 2.23D, and 6:7-dibromo-tetrahydronaphthalene, 2.81D; 4-bromo-, 2.07D, and 4:5-dibromo-*o*-xylene, 2.86D; *o*- $C_6H_4Br_2$ , 2.12D. Hence it is calc. that the moment of the aromatic Br-C-C-Br system is 2.12D; this val. is found for (I) but for (II) it is 1.78D owing to fixation of the double linkings (cf. Mills *et al.*, A., 1931, 83). F. R. G.

**1-Vinylnaphthalene and certain of its derivatives.** J. S. SALKIND and S. A. ZONIS (J. Gen. Chem. Russ., 1936, 6, 988—998).—The following 1-vinylnaphthalene (I) derivatives have been prepared by dehydrating the appropriate alcohols with  $KHSO_4$  ( $R = \alpha-C_{10}H_7$ ): (I), from  $OH \cdot CH_2 \cdot CH_2R$ ;  $CHR \cdot CHMe$ , from 1- $\alpha$ -hydroxy-*n*-propyl-, m.p.  $58-59^\circ$ , b.p.  $139-140^\circ/4$  mm. (from EtCHO and  $MgRBr$ );  $CRMe \cdot CH_2$ , from  $OH \cdot CRMe$ ; 1- $\alpha$ -methyl- $\Delta^a$ -propenyl-, b.p.  $113.5-115^\circ/5$  mm., from 1- $\alpha$ -hydroxy- $\alpha$ -methyl-*n*-propyl-, m.p.  $49-50^\circ$ , b.p.  $146-147^\circ/4$  mm. (picrate, m.p.  $138-139^\circ$ ) (from  $COMeEt$  and  $MgRBr$ ); 1- $\alpha$ -ethyl- $\Delta^a$ -propenyl-, b.p.  $119-120.5^\circ/6$  mm., from 1- $\alpha$ -hydroxy- $\alpha$ -ethyl-*n*-propyl-, m.p.  $42-43^\circ$ , b.p.  $145-146^\circ/3$  mm. (picrate, m.p.  $131-132^\circ$ ) (from  $COEt_2$  and  $MgRBr$ ) -naphthalene. The velocity of polymerisation of the hydrocarbons falls in the order given, in presence or absence of catalysts ( $BzO_2H$ , folidin), and, except in the case of (I), the products consist chiefly of the dimerides. R. T.

**cycloHexylnaphthalenes and related compounds.** J. W. COOK and C. A. LAWRENCE (J.C.S., 1936, 1431—1434).—Hydrogenation (Adams) of 1-(1'-naphthyl)- $\Delta^1$ -cyclohexene (I) takes place very



slowly owing to mutual saturation of free affinities at  $C_{12}$  and  $C_{18}$ , to give 1-cyclohexylnaphthalene (II) (cf. Bodroux, A., 1929, 1050). 1-Keto-1:2:3:4-tetrahydronaphthalene with Mg cyclohexyl chloride gives (probably) 1-keto-2-(1'-tetrahydronaphthylidene)-1:2:3:4-tetrahydronaphthalene, m.p. 130—130.5° [2:4-dinitrophenylhydrazones, m.p. 249—250° (decomp.)], and 1-cyclohexyl-3:4-dihydronaphthalene, b.p. 140°/1 mm., 172°/10 mm., dehydrogenated to (II), b.p. 118—120°/0.3 mm. [picrate, m.p. 122—123.5°; styphnate, m.p. 150.5—151°;  $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$  compound, m.p. 116.5—117.5°]; the derivatives of (I) do not depress the m.p. of those of (II). (II) and its 2-isomeride are not dehydrogenated by Pt-black, whilst (II) remains unchanged with Se. The Li compound of 5-bromo-1:2:3:4-tetrahydronaphthalene with cyclohexene oxide gives 2-(5'-tetrahydronaphthyl)cyclohexanol, a gum (3:5-dinitrobenzoate, m.p. 163—164.5°), oxidised ( $\text{H}_2\text{CrO}_4$ , AcOH) to the corresponding cyclohexanone [semicarbazone, m.p. 198—200° (decomp.)] and dehydrated ( $\text{ZnCl}_2$ ) to 1-(5'-tetrahydronaphthyl)- $\Delta^1$ -cyclohexene, b.p. 181°/15 mm., which was hydrogenated (Adams) rapidly [in contrast to (I)] to 5-cyclohexyl-1:2:3:4-tetrahydronaphthalene, b.p. 118°/0.2 mm. The carbinol from 2-methylcyclohexanone and  $1\text{-C}_{10}\text{H}_7\text{-MgBr}$  when dehydrated ( $\text{KHSO}_4$ ) gives 1-(1'-naphthyl)-2-methyl- $\Delta^1$ -cyclohexene, b.p. 125°/0.3 mm., dehydrogenated (Se) to 1-o-tolyl-naphthalene, m.p. 67.5—68.5° and cyclised ( $\text{AlCl}_3$ ,  $\text{CS}_2$ ) unlike (I) to a compound, b.p. 122—130°/0.3 mm., dehydrogenated (Se) to fluoranthene.  $n_D$  and  $d$  are recorded for some of the above compounds.

F. R. G.

**Nitro-derivatives of fluorene. II. Colour reactions given by some derivatives of 2-nitrofluorene.** C. CANDEA and E. MACOVSKI (Bull. Soc. chim., 1936, [v], 3, 1761—1767).—In presence of piperidine, 2-nitrofluorene and  $p\text{-C}_6\text{H}_4\text{Me-CHO}$  or piperonal give 2-nitro-9-*p*-tolylidene- and -9-piperonylidene-fluorene. With  $p\text{-OH-C}_6\text{H}_4\text{-CHO}$ , the -9-*p*-hydroxybenzylidene compound (I), m.p. 207—208° (Bz derivative (II), m.p. 214—215°), is formed. The vanillylidene compound (A., 1935, 1488) is reduced ( $\text{Zn-CaCl}_2$ ) to 2-amino-9-vanillylidene-fluorene (III), m.p. 190—191°. With KOH in EtOH or  $\text{COMe}_2$ , (II) gives an intense red, (I) a feeble red, and (III) a pale yellow colour.

E. W. W.

**2:3-cyclopentenonaphthalene.** S. C. S. GUPTA (Current Sci., 1936, 5, 133).— $\gamma$ -Keto- $\gamma$ -5-hydrindyl-n-butyric acid, m.p. 123—124° [obtained by condensing  $(\text{CH}_2\text{CO})_2\text{O}$  and hydrindine in presence of  $\text{AlCl}_3$ ] is reduced (Clemmensen) to  $\gamma$ -5-hydrindyl-n-butyric acid, m.p. 56°; this on cyclisation (85%  $\text{H}_2\text{SO}_4$ ) affords 1-keto-6:7-cyclopenteno-1:2:3:4-tetrahydronaphthalene, b.p. 167°/6 mm., which is reduced (Clemmensen) to 6:7-cyclopenteno-1:2:3:4-tetrahydronaphthalene, b.p. 125—126°/6 mm., and this in turn yields 2:3-cyclopentenonaphthalene, m.p. 94° (picrate, m.p. 120—121°), on dehydrogenation (Se; 300—340°).

F. N. W.

**Retarding agents in the chlorination of anthracene.** Influence of the nature of the solvent on the progress of the reaction. M. ILJINSKI and V. AFREMOV (Compt. rend. Acad. Sci. U.R.S.S., 1936,

3, 135—136).—The rate of chlorination of anthracene by  $\text{SO}_2\text{Cl}_2$  is largely influenced by traces of impurity; the effect of the solvent ( $\text{CCl}_4$  or xylene) varies with the purity of the sample of anthracene used.

A. J. E. W.

(A) Phenanthrene-bromine addition reaction. C. C. PRICE. (B) Effect of substituents on phenanthrene-bromine addition reaction. L. F. FIESER and C. C. PRICE (J. Amer. Chem. Soc., 1936, 58, 1834—1838, 1838—1843).—(A) The equilibrium consts. ( $K$ ) for the reaction  $\text{C}_{14}\text{H}_{10} + \text{Br}_2 \rightleftharpoons \text{C}_{14}\text{H}_9\text{Br}_2$  (in  $\text{CCl}_4$ ; Br determined colorimetrically with a Keuffel and Esser spectrophotometer) are  $340 \pm 8$ ,  $230 \pm 6$ , and  $134 \pm 2$  at 15.7°, 25°, and 39°, respectively.  $\text{O}_2$ ,  $\text{Bz}_2\text{O}_2$ , and  $\beta\text{-C}_{10}\text{H}_7\text{-OH}$  have no effect but  $\text{NHPh}_2$ , quinol, and tetrabromo-quinol and -pyrocatechol are effective inhibitors even in relatively small amounts. A chain mechanism and method for the determination of its length are discussed. Addition of phenanthrene (I) to Br in dioxan (II) (solution stable at room temp.) causes bromination of (II) ( $\frac{2}{3}$ ) and addition to (I) ( $\frac{1}{3}$ ).

(B) The nos. quoted after the following derivatives of phenanthrene are the  $K$  at 25° and 36° (unless stated otherwise), respectively: 2- $\text{CO}_2\text{Et}$ -, 168, 88; 3- $\text{CO}_2\text{Et}$ -, 93, 59; 2- $\text{CO}_2\text{Me}$ -, 167, 81; 3- $\text{CO}_2\text{Me}$ -, 129, 63; 2-Cl-, 159, 54; 3-Cl-, 170, 67; 2-Br-, 152, 59; 3-Br-, 152, 69; 2- $\text{Bu}^{\gamma}$ -, 320, 262 (at 37.4°); 3- $\text{Bu}^{\gamma}$ -, 467, 191 (at 37.4°). Hal and  $\text{CO}_2\text{Me}(\text{Et})$  (more effective in 3- than 2-position), i.e., groups which retard substitution in the  $\text{C}_6\text{H}_6$  ring, decrease the free energy of the 9:10-addition of Br, whilst  $\text{Bu}^{\gamma}$  (which facilitates substitution) causes an increase; these results parallel those obtained (A., 1929, 1452) for the free energy of oxidation of 9:10-dihydroxyphenanthrenes. A sp. decrease in the reaction velocity is found for the 2-Hal (i.e., *m*-position). Et, OMe, and NHAc substituents lead to irreversible absorption of  $>1$  mol. of  $\text{Br}_2$ .

$\text{PhBu}^{\gamma}$ ,  $(\text{CH}_2\text{CO})_2\text{O}$ , and  $\text{AlCl}_3$  in  $\text{CS}_2$  give  $\beta$ -*p*-tert.-butylbenzoylpropionic acid, dimorphous, both m.p. 121—122° [oxidised (KOCl) to  $p\text{-C}_6\text{H}_4\text{Bu}^{\gamma}\text{-CO}_2\text{H}$  and thence (dil.  $\text{HNO}_3$ ) to  $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ], reduced (modified Clemmensen; this vol., 1249) to  $\gamma$ -*p*-tert.-butylphenylbutyric acid, m.p. 59.5—60.5°, the Et ester, b.p. 145—147°/5 mm., of which with  $\text{Et}_2\text{C}_2\text{O}_4$  (method: A., 1935, 1495) followed by 80%  $\text{H}_2\text{SO}_4$  at 60° affords 7-tert.-butyl-3:4-dihydronaphthalene-1:2-dicarboxylic anhydride (I), m.p. 143—145°, and a little of an isomeride, m.p. 174—175°. (I) is dehydrogenated (S at 330—340°) to 7-tert.-butyl-naphthalene-1:2-dicarboxylic anhydride, m.p. 146.5—147.5°.  $(\text{CH}_2\text{CH})_2$  and (I) at 150° give 6-tert.-butyl-1:4:9:10:11:12-hexahydrophenanthrene-11:12-dicarboxylic anhydride, m.p. 85.5—86.5°, converted by KOH at 330—360° (method: this vol., 203) into a product which is dehydrogenated (Se) to 3-tert.-butylphenanthrene, m.p. 54—55° (picrate, m.p. 142—143°; quinone, m.p. 186—187°). 2- $\text{C}_{10}\text{H}_7\text{Bu}^{\gamma}$ ,  $(\text{CH}_2\text{CO})_2\text{O}$ , and  $\text{AlCl}_3$  in cold  $\text{PhNO}_2$  afford  $\beta$ -6-tert.-butyl-2-naphthoylpropionic acid, m.p. 148—150°, reduced (as above) to  $\gamma$ -6-tert.-butyl-2-naphthylbutyric acid, ? dimorphous, m.p. 87—95°, the chloride of which with  $\text{AlCl}_3$  in cold  $\text{CS}_2$  gives 1-keto-7-tert.-butyl-1:2:3:4-tetrahydrophenanthrene (picrate,

m.p. 107—108°), converted by successive reduction and dehydrogenation (Se at 320—350°) into 2-*tert*-butylphenanthrene, m.p. 99—100° (picrate, m.p. 130—131°; quinone, m.p. 129—130°). 2-Acetylphenanthrene and MgMeI in Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> afford 2-phenanthryldimethylcarbinol, dimorphous, m.p. 90—92° (decomp.) and 97—99° (decomp.); recrystallisation of 3-phenanthryldimethylcarbinol picrate, m.p. 107—110° (decomp.), from EtOH gives (probably) 3-isopropenylphenanthrene picrate, m.p. 160—163° (decomp.). C<sub>10</sub>H<sub>8</sub>, Bu<sup>γ</sup>Cl, and a little AlCl<sub>3</sub> afford (cf. Gump, A., 1931, 341) 2-C<sub>10</sub>H<sub>7</sub>Bu<sup>γ</sup> and two C<sub>10</sub>H<sub>6</sub>Bu<sup>γ</sup><sub>2</sub>, m.p. 86—90° (picrate, m.p. 155.5—156.5°) and 146—147° [oxidised (CrO<sub>3</sub>, AcOH) to a quinone, C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>, m.p. 83.5—84.5°]. H. B.

**Synthesis of an isomeride of retene: 1-methyl-9-isopropylphenanthrene.** G. DARZENS and A. LEVY (Compt. rend., 1936, 203, 669—671).—Condensation of 1:4-C<sub>10</sub>H<sub>6</sub>Pr<sup>β</sup>·CH<sub>2</sub>Cl with Et malonate yields *Et* 4-isopropyl-1-naphthylmethylmalonate (I), a viscid liquid (acid, decomp. 170° to 4-isopropyl-naphthalene-1-propionic acid, m.p. 136°). The Na derivative of (I) is condensed with allyl bromide, and the resulting ester hydrolysed to the dibasic acid which decomposes at 170°, giving β-(4-isopropyl-1-naphthyl)-α-allylpropionic acid, a viscid liquid. Cyclisation of this acid with H<sub>2</sub>SO<sub>4</sub>+AcOH for 3 days at 40° gives a mixture of 1-methyl-9-isopropyl-1:2:3:4-tetrahydrophenanthrene-3-carboxylic acid (II), m.p. 160° [*Me* ester (III), b.p. 192—193°/4 mm.], and the lactone, b.p. 195—197°/4 mm., of β-(4-isopropyl-1-naphthyl)-α-γ-hydroxypropylpropionic acid. (III) when heated with S at 240° gave the *Me* ester, b.p. 195—196°/4 mm., of 1-methyl-9-isopropylphenanthrene-3-carboxylic acid, m.p. 204°. Se and (II) at 340° gave 1-methyl-9-isopropylphenanthrene, b.p. 204—205°/14 mm. (picrate, m.p. 143°; styphnate, m.p. 156°). Oxidation with CrO<sub>3</sub> gives 1-methylphenanthraquinone with elimination of Pr<sup>β</sup>. J. N. A.

**Constitution of hexahydropyrene.** J. W. COOK and C. L. HEWETT (Chem. and Ind., 1936, 843—844).—Pestemer *et al.* (this vol., 1048) have overlooked the authors' earlier work (A., 1933, 601) on the isolation and structures of two hexahydropyrenes.

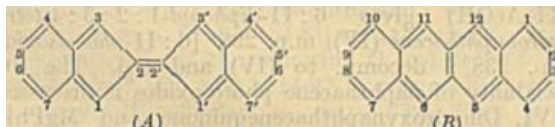
J. W. B.

**Detection of 1:2-benzpyrene with the fluorescence spectrograph.** G. MIESCHER, F. ALMASY, and K. KLAU (Biochem. Z., 1936, 287, 189—197; cf. Sannie, this vol., 664; Mayneord, *ibid.*).—Pure 1:2-benzpyrene (I) in C<sub>6</sub>H<sub>14</sub> can be detected by its fluorescence spectrum in concns. <0.0025 mg. per litre; contamination with other fluorescent polycyclic hydrocarbons (*e.g.*, chrysene, phenanthrene, pyrene, retene, 1:2:5:6-dibenzanthracene, anthracene, 2-methylanthracene, fluoranthrene) singly and together does not seriously interfere with the detection. (I) in tar fractions is detected in the same way in 0.0003% concn. if basic impurities are removed with H<sub>2</sub>SO<sub>4</sub>.

W. McC.

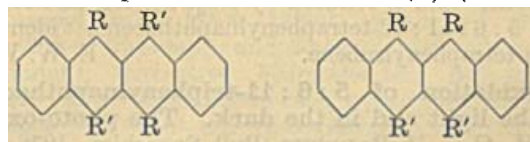
**Naphthacene structure of rubenes.** I. II. The new structure: mechanism of formation, constitutions, and formulæ with corrected nomenclature. C. DUFRAISSE. III. Historical review and discussion of naphthacenes, their syntheses,

and their photochemical characteristics. IV. Naphthacene the prototype of the rubenes. V. Synthesis of phenylnaphthacenes of rubene character. C. DUFRAISSE and R. HORCLOIS. VI. Synthesis of 5:6:11:12-tetraphenylnaphthacene: its identity with tetraphenylrubene (formerly known as rubrene). C. DUFRAISSE and L. VELLUZ (Bull. Soc. chim., 1936, [v], 3, 1847—1857, 1857—1872, 1872—1880, 1880—1893, 1894—1905, 1905—1913).—I. Theoretical. The name "rubene" is abandoned: rubenes have not the structure (A) previously attributed to them, but are derivatives of naphthacene (B). Objections to A are discussed.



That naphthacenes, with which rubenes are now identified, have not structure A is shown by absorption spectra, and by the formation of photo-oxides. The structure of ψ-rubene is discussed.

II. Three possible mechanisms of the formation of "rubenes" (tetra-substituted naphthacenes) from CPhRCl·C:CR' are discussed: the prior formation of structure (A) (above); the intermediate formation of dibenzocyclodecadiene; and direct condensation. That the product has structure (C) (with central



symmetry) and not the alternative (D) (with planar symmetry), is shown by the fact that if R' is replaced by Cl, HCl is lost by two stages; thus 6:12-dichloro-5:11-diphenylnaphthacene (the former "3:3'-dichloro-1:1'-diphenylrubene") yields first 12-chloro-11-phenyl-5:6-phenylenenaphthacene ("3'-chloro-3-phenyl-1:1'-phenylenrubene"), and then 5:6:11:12-diphenylenenaphthacene ("1:1':3:3'-diphenylenrubene"). Revised names of rubene derivatives are recorded.

III. A review.

IV. Naphthacene (I) (improved prep. from tetramethyleneanthraquinone by passage over Zn at 300—400°, followed by passage over Zn at 700° or PbO at 400°) gives an absorption spectrum similar to that from "tetra-arylrubenes"; when exposed, in CS<sub>2</sub> solution, to sunlight, it absorbs O<sub>2</sub> to give a non-fluorescent photo-oxide [decomp. 120°, to resinous products, with little (I)], which is reduced by KI, with formation of benzanthrone. With HI, or KOH in C<sub>5</sub>H<sub>11</sub>·OH or CH<sub>2</sub>Ph·OH, (I) gives 5:12-dihydronaphthacene. (I) is not isomerised by H<sub>2</sub>SO<sub>4</sub> or other acids.

V. Naphthacenequinone (new prep. from 2:3-tetramethyleneanthraquinone, using PbO) with MgPhBr yields 5:12-dihydroxy-5:12-diphenyl-5:12-dihydronaphthacene (II), m.p. 251—252°, with two diphenyltetrahydronaphthacenequinones (cf. this vol., 992). (II) with KI, Na<sub>2</sub>PO<sub>3</sub>, and AcOH, or 6:11-diphenyl-1:2:3:4-tetrahydronaphthacene dehydrogenated, gives 5:12-diphenylnaphthacene (III), m.p.



207—208° (+0.5Et<sub>2</sub>O, m.p. 171—172°). Oxidation of (III) (heating in air, or action of H<sub>2</sub>SO<sub>4</sub>) gives violet 11-phenyl-5:6-phenylenenaphthacene, further oxidised by FeCl<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> to blue 5:6:11:12-diphenylenenaphthacene. With gaseous HI in CS<sub>2</sub>, (III) gives 5:12-diphenyl-5:12-dihydronaphthacene, m.p. 206—207°, reconverted into (III) by heating. (III) is very sensitive to light, yielding the 5:12(or 6:11)-photodioxide, decomp. 160°. 2:3-Tetramethylenanthraquinone and MgPhBr furnish 6:11-dihydroxy-6:11-diphenyl-1:2:3:4:6:11-hexahydronaphthacene, m.p. 239—240°, which on attempted dehydration gives only (III), and on reduction (KI-AcOH) gives 6:11-diphenyl-1:2:3:4-tetrahydronaphthacene (IV), m.p. 298° [6:11-photodioxide, m.p. 238°; decomp. to (IV) and O<sub>2</sub>]. The dissociability of naphthacene photo-oxides is discussed.

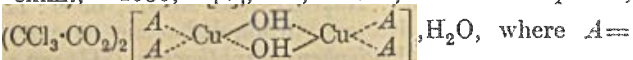
VI. Dihydroxynaphthacenequinone and MgPhBr give 5:6:11:12-tetrahydroxy-5:12-diphenyl-5:12-dihydronaphthacene (with some 6-hydroxy-11-phenylnaphthacene-5:12-quinone, m.p. 304—305°), converted on heating, alone or in AcOH, into 6:11-diphenylnaphthacene-5:12-quinone, m.p. 284—285°. This with MgPhBr yields 5:12-dihydroxy-5:6:11:12-tetraphenyl-5:12-dihydronaphthacene, m.p. 251° (+2C<sub>6</sub>H<sub>6</sub>, m.p. 185°), which when heated in AcOH loses H<sub>2</sub>O, forming 5:12-diphenyl-5:6:11:12-diphenylene-5:12-dihydronaphthacene, identical with "dehydro-rubrene," and is reduced by Na<sub>2</sub>PO<sub>3</sub>, KI, and AcOH to 5:6:11:12-tetraphenylnaphthacene, identical with tetraphenylnubene. E. W. W.

Oxidation of 5:6:11-triphenylnaphthacene in the light and in the dark. The photo-oxide, C<sub>36</sub>H<sub>24</sub>O<sub>2</sub>. M. BADOCHÉ (Bull. Soc. chim., 1936, [v], 3, 2040—2046).—5:6:11-Triphenylnaphthacene (I) (formerly triphenylrubene) (prep. described) has m.p. 236—237°, or +1C<sub>6</sub>H<sub>6</sub> which cannot be removed without decomp. of the mol., m.p. 177—178°. On exposure to sunlight in C<sub>6</sub>H<sub>6</sub> it readily absorbs O<sub>2</sub> giving 5:6:11-triphenylnaphthacene 5:12-dioxide (II) (+1C<sub>6</sub>H<sub>6</sub>), m.p. about 176—177°, which evolves a small amount of gas containing 85—90% of O<sub>2</sub> when heated at 140°/vac., and a larger proportion when heated rapidly over a naked flame. Little gas is evolved when it is heated progressively by itself or mixed with vaseline or sand. The constitution of (II) is advanced with reserve and is based mainly on its differing behaviour from 5:6:11:12-tetraphenylnaphthacene 5:12-dioxide and the analogous difference between the photo-oxides of anthracene and 9:10-diphenylanthracene. A conc. solution of (I) in C<sub>6</sub>H<sub>6</sub> over Hg slowly absorbs O<sub>2</sub> in the dark giving an oxide which does not appear identical with (II). H. W.

Isotopic exchange between aniline hydrochloride and heavy water.—See this vol., 1339.

Rearrangement of N-iodoformanilide in anisole solution.—See this vol., 1471.

Additive product of basic copper trichloroacetate with benzylamine. A. ABLOV (Bull. Soc. chim., 1936, [v], 3, 1915).—The compound,



CH<sub>2</sub>Ph·NH<sub>2</sub>, is prepared by treating Cu(O·CO·CCl<sub>3</sub>)<sub>2</sub> with A in EtOH. E. W. W.

Derivatives of 2:4-di- and 2:4:5-tri-methyl-aniline. G. VAN KLEEF (Rec. trav. chim., 1936, 55, 765—785).—Acet-*m*-4-xylylide, m.p. 130° (best prepared by boiling the base with AcOH), with HNO<sub>3</sub> (best, *d* 1.42) at 0° gives the 5-NO<sub>2</sub>- (Me:Me:NH<sub>2</sub>=1:3:4), m.p. 172° (cf. lit.), and with abs. HNO<sub>3</sub> the 5:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 220° (lit. 117°). *Me m*-4-xylylcarbamate [prep. from *as*-*m*-xylidine (I) and ClCO<sub>2</sub>Me in H<sub>2</sub>O at 0°], m.p. 79°, affords similarly the 5-NO<sub>2</sub>-, m.p. 134° [hydrolysed to 5-nitro-*m*-4-xylidine (II) by conc. H<sub>2</sub>SO<sub>4</sub> at 100°], and 5:6-(NO<sub>2</sub>)<sub>2</sub>- (III)-derivative, m.p. 218° (resistant to hydrolysis). Similarly are obtained Et *m*-4-xylylcarbamate, m.p. 59° (lit. 58°), and its 5-NO<sub>2</sub>-, m.p. 134° (lit. 125—126°) [hydrolysed by conc. H<sub>2</sub>SO<sub>4</sub> at 125—130° to (II)], and 5:6-(NO<sub>2</sub>)<sub>2</sub>-derivative (IV), m.p. 150° (hydrolysed similarly to 5:6-dinitro-*m*-4-xylidine). N-*m*-4-*Xylyl*-N'-methylcarbamide (prep. in C<sub>6</sub>H<sub>6</sub>), m.p. 170°, with HNO<sub>3</sub> (*d* 1.4) affords the 5-NO<sub>2</sub>-derivative, m.p. 230° [also obtained from (II) and PhNCO], and with abs. HNO<sub>3</sub> N-nitro-N-5:6-dinitro-*m*-4-xylyl-N'-methylcarbamide, unstable, which with hot abs. EtOH gives (IV), also obtained from (III). Similarly are prepared N-*m*-4-xylyl-N'-ethylcarbamide, m.p. 188°, and its 5-NO<sub>2</sub>-, m.p. 220°, and 5:6:N'-(NO<sub>2</sub>)<sub>3</sub>-derivative. *Me m*-4-xylyloxamate [prep. with some ox-*m*-4-xylylide (V) by boiling Me<sub>2</sub>C<sub>2</sub>O<sub>4</sub>], m.p. 77°, gives similarly the 5-NO<sub>2</sub>-, m.p. 145°, and 5:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 169°, both stable to hydrolysis. (V), m.p. 214° (lit. 210°), gives the 5:5'-(NO<sub>2</sub>)<sub>2</sub>-, m.p. 220°, and 5:6:5':6'-(NO<sub>2</sub>)<sub>4</sub>-derivative, amorphous, both stable to hydrolysis. Similarly are obtained acet-*ψ*-cumidide (prep. by Ac<sub>2</sub>O), m.p. 165° (cf. lit.), and its 6-NO<sub>2</sub>- (Me:Me:Me:NH<sub>2</sub>=1:2:4:5), m.p. 198° (cf. lit.), and 3:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 288° (cf. lit.), *Me*, m.p. 115° [6-NO<sub>2</sub>-, m.p. 155°, and 3:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 211°], and Et *ψ*-cumyl-5-carbamate, m.p. 105° [6-NO<sub>2</sub>-, cryst., and 3:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 221°], N-*ψ*-5-cumyl-N'-methyl-, m.p. 212° [6-NO<sub>2</sub>-, m.p. 268°, and N':3:6-(NO<sub>2</sub>)<sub>3</sub>-derivative], and -ethyl-carbamide, m.p. 213° [6-NO<sub>2</sub>-, m.p. 246°, and 3:6:N'-(NO<sub>2</sub>)<sub>3</sub>-derivative], *Me*, m.p. 75° [6-NO<sub>2</sub>-, m.p. 206°, and 3:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 192°], and Et *ψ*-5-cumyloxamate, m.p. 78° [6-NO<sub>2</sub>-, m.p. 162°, and 3:6-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 171°], *s*-ox-*ψ*-5-cumidide, m.p. 237° (lit. 230°) [6:6'-(NO<sub>2</sub>)<sub>2</sub>-derivative, m.p. 317° (block), and 3:6:3':6'-(NO<sub>2</sub>)<sub>4</sub>-derivative, m.p. 340° (block)]. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and (I) in EtOH give rapidly *m*-4-xylyloxamhydrazide (VI), m.p. 165° (lit. 160°). 5-*ψ*-Cumyloxamhydrazide (VII), m.p. 212°, is similarly prepared: (VI) in H<sub>2</sub>O containing a little EtOH and (VII) in 50% EtOH, respectively, give substituted *hydrazones* [oxamazones] with the following aldehydes: CH<sub>2</sub>O, m.p. 196°, about 219°, MeCHO, m.p. 205°, 238°, EtCHO, m.p. 186°, 214°, PrCHO, m.p. 168°, 198°, BuCHO, m.p. 173°, 194°, *o*-, m.p. 248°, 252°, and *p*-OH·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 265°, 267°, *p*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO, m.p. 220°, 245°, vanillin, m.p. 240°, 241°, piperonal, m.p. 261°, 226°, *p*-C<sub>6</sub>H<sub>4</sub>·Me·CHO, m.p. 212°, 245°, *p*-C<sub>6</sub>H<sub>4</sub>·Pr<sup>o</sup>·CHO, m.p. 209°, 205°, *o*-, m.p. 275°.

271°, *m.*, m.p. 211°, 239°, and *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO, 271°, 277°, furfuraldehyde, m.p. 206°, 228° (decomp.), 5-methyl-, m.p. 182°, 180° (decomp.), and 5-hydroxymethyl-furfuraldehyde, m.p. 200°, 174°. R. S. C.

**New diphenylamine derivatives.** J. S. JOFFE, S. D. SUDAKOV, and S. G. KUZNETZOV (J. Gen. Chem. Russ., 1936, 6, 983—987).—3-Chloro-6-nitroaniline-4-sulphonic acid, NH<sub>2</sub>Ph, and MgCO<sub>3</sub> in 60% EtOH (16 hr.; 160—180°) yield the Mg salt of 4-nitro-5-aminodiphenylamine-2-sulphonic acid, from which the internal salt of the corresponding diazonium compound is obtained. This yields a red azo-dye when coupled with β-C<sub>10</sub>H<sub>7</sub>·OH, 4-nitro-5-hydroxydiphenylamine-2-sulphonic acid with boiling H<sub>2</sub>O, and 4-nitro-5-chlorodiphenylamine-2-sulphonic acid by the Sandmeyer reaction. R. T.

**Nitration of benzyaniline and its derivatives.** P. VAN DEN BERG (Rec. trav. chim., 1936, 55, 841—853).—Unless otherwise stated, nitrations given below were effected by abs. HNO<sub>3</sub> and acetylations by Ac<sub>2</sub>O and a little H<sub>2</sub>SO<sub>4</sub> (Ac<sub>2</sub>O alone usually being ineffective). *p*-Nitrobenzyl-2:4:6-trinitrophenylnitroamine (I) [previously considered to be the (NO<sub>2</sub>)<sub>4</sub>-base], m.p. 142° (decomp.), is obtained from *p*'-nitrobenzyl-*p*- and -*o*-nitroaniline, m.p. 140° (cf. lit.) (*Ac* derivative, m.p. 157°), benzyl-2:4-di-, m.p. 116·5°, and -2:4:6-tri-nitroaniline, *p*-nitrobenzyl-2:4-di-, m.p. 186°, and -2:4:6-tri-nitroaniline, m.p. 191°. With NH<sub>3</sub>-EtOH it gives picramide and with hot aq. Na<sub>2</sub>CO<sub>3</sub> picric acid. 2':4'-Dinitrobenzyl-2:4:6-trinitrophenylnitroamine (II), m.p. 151° (decomp.), is obtained from *p*'-nitrobenzyaniline (H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>, *d* 1·4), benzyl-*p*-nitroaniline, m.p. 147° [*Ac* derivative, m.p. 111° (lit. 108—109°); H<sub>2</sub>SO<sub>4</sub>-abs. HNO<sub>3</sub>], and (I) (H<sub>2</sub>SO<sub>4</sub>-abs. HNO<sub>3</sub>). *o*'-Nitrobenzyl-*p*-, m.p. 202° (*Ac* derivative, m.p. 178°), or -*o*-nitroaniline, m.p. 138° (*Ac* derivative, m.p. 137°), with HNO<sub>3</sub> (*d* 1·46) gives *o*-nitrobenzyl-2:4:6-trinitrophenylnitroamine (III), m.p. 149° (decomp.), and with abs. HNO<sub>3</sub> yields (II). *m*- and *p*-Nitration of the CH<sub>2</sub>Ph of NHPh·CH<sub>2</sub>Ph by a little abs. HNO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> is confirmed. R. S. C.

**Nitrous acid as a nitrating and oxidising agent.** III. Nitration of 4-dimethylamino-aceto-1-naphthalide, of 4-chloro-1-naphthyldimethylamine, and of β-naphthyldimethylamine. H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1500—1503).—By coupling α-C<sub>10</sub>H<sub>7</sub>·NMe<sub>2</sub> (*picrate*, m.p. 145°) with diazotised *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H and reductive fission (SnCl<sub>2</sub>-HCl) of the azo-compound is obtained 1:4-NH<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NMe<sub>2</sub> [*dihydrochloride* (I)], converted by Ac<sub>2</sub>O into 1:4-NHAc·C<sub>10</sub>H<sub>6</sub>·NMe<sub>2</sub> (II) [*picrate*, m.p. 201° (decomp.)]. (I) is converted (Sandmeyer) into the *hydrochloride*, m.p. 215° (decomp.), of 4-chloro-1-naphthyldimethylamine (III) (*picrate*, m.p. 146°). (II) with NaNO<sub>2</sub>-HCl at 0° is oxidised to α-naphthaquinone, but (III) affords a 2-NO<sub>2</sub>-derivative, (IV), m.p. 58°, synthesised as follows: 2-nitroaceto-1-naphthalide with Cl<sub>2</sub>-AcOH at 100° gives its 2-Cl-derivative, m.p. 219°, hydrolysed to 4-chloro-2-nitro-α-naphthylamine, m.p. 202°, converted (Sandmeyer) into 1:4-dichloro-2-nitronaphthalene, m.p. 116·5° (1-chloro-4-iodo-3-nitronaphthalene, m.p. 107°, is obtained similarly), converted by heat-

ing with NHMe<sub>2</sub>-EtOH into (IV), and by NH<sub>2</sub>Me·HCl-NaOAc-EtOH into 4-chloro-2-nitro-1-naphthyldimethylamine, m.p. 175°. β-C<sub>10</sub>H<sub>7</sub>·NMe<sub>2</sub> [*picrate*, m.p. 200° (decomp.)] and NaNO<sub>2</sub>-HCl at 0° afford 1-nitro-2-naphthyldimethylamine, m.p. 76—77°, synthesised from 2:1-C<sub>10</sub>H<sub>6</sub>Cl·NO<sub>2</sub> and NHMe<sub>2</sub>-EtOH. J. W. B.

**Local anæsthetics containing the ac-tetrahydro-β-naphthylamine pressor group.** H. W. COLES and W. A. LOTT (J. Amer. Chem. Soc., 1936, 58, 1989—1990).—*ac*-Tetrahydro-β-naphthylamine (I) (2 mols.) and CH<sub>2</sub>Cl·CH<sub>2</sub>·OH (1 mol.) in xylene and N<sub>2</sub> at 110—115° give 2-β-hydroxyethylamino-1:2:3:4-tetrahydronaphthalene, which (as *hydrochloride*, m.p. 183·8—184·8°) with the appropriate acyl chloride affords the following *O*-acyl derivative *hydrochlorides*: *Bz*, m.p. 214·9° (corresponding *sulphate*, m.p. 216—218°); *o*-, m.p. 232—233°, *m*-, m.p. 216—217°, and *p*-, m.p. 236·2°, -*nitrobenzoyl* [reduced (Fe, HCl) to the aminobenzoyle derivatives (*dihydrochlorides*, m.p. 150°, 205—206°, and 223·3°, respectively)]; *p*-chloro-, m.p. 219—220°, and *p*-iodo-, m.p. 232°, -*benzoyl*; *cinnamoyl*, m.p. 194—195·8°; *phthaloyl*, m.p. 185—186°. 2-γ-Hydroxypropylamino-1:2:3:4-tetrahydronaphthalene (*hydrochloride*, m.p. 161°), from (I) and CH<sub>2</sub>Cl·CH<sub>2</sub>·CH<sub>2</sub>·OH, similarly affords *Bz*, m.p. 195·6° (corresponding *picrate*, m.p. 83·86°), *m*-, m.p. 173·4—177·4°, and *p*-, m.p. 228—229°, -*nitrobenzoyl*, *p*-chlorobenzoyle, m.p. 188·8—189·8°, *cinnamoyl*, m.p. 204·8—206·8° (decomp.), and β-phenylpropionyl, m.p. 95° (indef.), derivative *hydrochlorides*. All m.p. are corr. Most of the above ester *hydrochlorides* are local anæsthetics but not vasopressors. H. B.

**Reaction of *p*-phenylenediamine and its derivatives with diazonium salts.** J. S. JOFFE and V. J. SOLOVEJTSCHUK (J. Gen. Chem. Russ., 1936, 6, 977—982).—*p*-C<sub>6</sub>H<sub>4</sub>(NHPh)<sub>2</sub> (I) in EtOH-HCl and diazotised metanilic acid at 0° yield 2:5-dianilindiphenyl-3'-sulphonic acid. An analogous reaction takes place when *p*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> or *p*-NHPh·C<sub>6</sub>H<sub>4</sub>·NH·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub> is used in place of (I). R. T.

**Preparation of 2:6-dinitro-*p*-phenylenediamine, 2:6-dinitrotetramethyl-*p*-phenylenediamine, and 4-chloro-2:3-dinitroanisole.** H. H. HODGSON and J. H. CROOK (J.C.S., 1936, 1570).—When heated with an excess of NHMe<sub>2</sub>-EtOH, 2:6-dinitrodiphenyl-*p*-anisidine affords 2:6-dinitrotetramethyl-*p*-phenylenediamine, m.p. 176°; 2:6-dinitro-*p*-phenylenediamine is obtained similarly. 4-Chloro-2:3-dinitroanisole, m.p. 133°, is obtained by the Sandmeyer reaction from 2:3-dinitro-*p*-anisidine. J. W. B.

**NN'-Dibenzylethylenediamine.** G. LOB (Rec. trav. chim., 1936, 55, 859—873).—NN'-Dibenzylethylenediamine (I), b.p. 212—213°/12 mm., *d*<sub>4</sub><sup>20</sup> 1·024, *n*<sub>D</sub><sup>20</sup> 1·5624, best obtained by reduction of the Schiff's base with Na-EtOH, gives the following derivatives: *hydrochloride*, m.p. 160—170° (block), *nitrate*, m.p. 180—190° (block), *picrate*, m.p. 200—210° (block), *carbamate* (from 1 mol. of CO<sub>2</sub>), decomp. 90—95° (open tube), *dinitroso*-, m.p. 87°, *Ac*<sub>2</sub>, m.p. 139°, *di-propionyl*, m.p. 69°, *n-butyl*, m.p.



72—73°, -*n*-valeryl, m.p. 91°, -*n*-hexoyl, m.p. 92°, -stearyl, m.p. 67°, -*o*-, m.p. 198—202°, -*m*-, m.p. 136—147°, and -*p*-nitrobenzoyl, m.p. 178°, *Bz*<sub>2</sub> (II), m.p. 183°, *di*-benzenesulphonyl, m.p. 228°; *dicarbonyl*, m.p. 176°, *di*-ethyl-, m.p. 168°, -phenyl-, m.p. 178—179°, -*o*-, m.p. 183—184°, -*m*-, m.p. 171—172°, and -*p*-nitrophenyl-, m.p. 231°, and -2:4-dinitrophenyl-*dicarbonyl*, m.p. 225° (decomp.), *di*-*α*-naphthyl-*dicarbonyl*, m.p. 229° (decomp.), and *diphenyldithiocarbonyl*, m.p. 184°. 2-Phenyl-1:3-dibenzyl-tetrahydroglyoxaline gives (I) and PhCHO with dry or 10% aq. HCl, picric acid, or 10% H<sub>2</sub>SO<sub>4</sub>, but is stable to CO<sub>2</sub>, 10% aq. NaOH, Na-EtOH, or MeI; with KMnO<sub>4</sub> it gives BzOH and NH<sub>2</sub>Bz, with abs. HNO<sub>3</sub> at -10° NN'-*di*-*α*-nitrobenzylethylenediamine, and with I-EtOH N-iodo-NN'-dibenzylethylenediamine diiodide (III), +2EtOH, m.p. 165—166°, and PhCHO. The structure of (III) follows because it contains 2 reactive I (giving with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> N-iodo-NN'-dibenzylethylenediamine, +C<sub>6</sub>H<sub>6</sub>, m.p. 142°), with 10% H<sub>2</sub>SO<sub>4</sub> and subsequent benzoylation affords (II), and is obtained also from (I) and I-Et<sub>2</sub>O. (I) with aliphatic aldehydes alone or with aromatic aldehydes in abs. EtOH gives 2-substituted 1:3-dibenzyltetrahydroglyoxalines in which the 2-substituent is H, m.p. 27°, Me, m.p. 34°, Et, m.p. 32°, Pr<sup>a</sup>, m.p. 11°, Pr<sup>β</sup>, m.p. 33°, Bu, m.p. 13°, amyl, an oil, n<sub>D</sub><sup>20</sup> 1.5448, hexyl, an oil, 1.5406, *p*-tolyl, m.p. 88°, *p*-anisyl, m.p. 90°, *o*-, m.p. 91°, *m*-, m.p. 95—96°, and *p*-nitro-, 101—102°, *o*-, m.p. 96—97°, *m*-, m.p. 93°, and *p*-chloro-, m.p. 110°, *o*-, m.p. 108°, and *p*-hydroxy-, m.p. 139°, *p*-isopropyl-, m.p. 63°, 3-methoxy-4-hydroxy-, m.p. 84—85°, and 3:4-methylenedioxy-phenyl, m.p. 111—112°, benzyl, m.p. 66—67°, furyl, m.p. 74°, 2-5-methyl-, m.p. 77—78°, and 2-5-hydroxymethyl-furyl, m.p. 127°, all hydrolysed by dil HCl. However, (I) does not react with COMe<sub>2</sub> at 200—210°, CMe<sub>2</sub>Cl<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> at 100°, CPh<sub>2</sub>Cl<sub>2</sub>, or PhI. With COCl<sub>2</sub> (I) gives a *s*-dichloroformyl derivative, m.p. 83°, which decomposes at 230°/12 mm. into CO<sub>2</sub> and 2-keto-1:3-dibenzyltetrahydroglyoxaline, m.p. 93°. With CS<sub>2</sub> (I) gives 2-thio-1:3-dibenzyltetrahydroglyoxaline, m.p. 90°, stable to hot 10% acid or alkali, with (COCl)<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> gives 1:4-dibenzyl-2:3-diketopiperazine, amorphous, m.p. 120—140°, with 2:4-C<sub>6</sub>H<sub>4</sub>Cl(NO<sub>2</sub>)<sub>2</sub> or picryl chloride in NaOAc-EtOH affords NN'-*di*-2:4-di-, m.p. 178°, and -2:4:6-tri-nitrophenyl-NN'-dibenzylethylenediamine, m.p. 202° (decomp. from 190°), respectively, and with CH<sub>2</sub>PhCl-K<sub>2</sub>CO<sub>3</sub> or EtBr-K<sub>2</sub>CO<sub>3</sub> (100°), or C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> (130—140°) yields NNN'-*tetrabenzyl*-, m.p. 95° [*dihydrochloride*, m.p. 140—150° (block), +*α*-EtOH, m.p. 80—90° (block) (resolidifies and remelts at 140—150°), hydrolysed by cold H<sub>2</sub>O], and NN'-dibenzyl-NN'-*diethyl*-ethylenediamine, b.p. about 250°/20 mm. (*di*-carbonate, -hydrochloride, solid, and -picrate, m.p. 202—206°, and 1:4-dibenzylpiperazine, m.p. 91°, respectively.

R. S. C.

**Diaryls and their derivatives. XII. Selective sorption by vegetable fibres of azo-dyes prepared from dihydroxynaphthalenes and polyhydroxydinaphthyls.** J. S. JOFFE and M. A. TSHIGROV (J. Gen. Chem. Russ., 1936, 6, 1014—1021).—The following azo- and bisazo-dyes, prepared from the appropriate diazonium salts and polyhydroxy-naph-

thalenes and -dinaphthyls, are only very feebly substantive for cotton: 1-*p*-sulphobenzeneazo-2:6- and -2:7-dihydroxynaphthalene, 1-*p*-nitrobenzeneazo-8-*p*-sulphobenzeneazo-2:7-dihydroxynaphthalene, 1-*p*-nitrobenzeneazo-5-*p*-sulphobenzeneazo-2:6-dihydroxynaphthalene, 8-*p*-sulphobenzeneazo-2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl, 5-*p*-sulphobenzeneazo-2:6:2'-tri- and -2:6:2':6'-tetrahydroxy-1:1'-dinaphthyl, and 5-*p*-nitrobenzeneazo-5'-*p*-sulphobenzeneazo-2:6:2'-tri-hydroxy-1:1'-dinaphthyl.

R. T.

**Diazotisation of weakly basic and insoluble amines. Use of pyridine, quinoline, and isoquinoline as solvents for the amines.** C. DEMILT and G. VAN ZANDT (J. Amer. Chem. Soc., 1936, 58, 2044—2046).—3-Nitro-4-aminodiphenyl, 2:6-dichloro-4-nitroaniline, picramide (I), and 3-amino-phenanthrene (II) are completely diazotised by slow addition of a solution in C<sub>5</sub>H<sub>5</sub>N to nitrosylsulphuric acid (III) in H<sub>2</sub>SO<sub>4</sub> at <10°; the mixture is stirred for 30 min. and finally freed from HNO<sub>2</sub> with CO(NH<sub>2</sub>)<sub>2</sub>. 4:6-Dibromo-2-nitroaniline and (I) are similarly diazotised using solutions in quinoline and isoquinoline, respectively. Diazotisation also occurs when (II) (in C<sub>5</sub>H<sub>5</sub>N) and aq. NaNO<sub>2</sub> are added alternately to 40% HBr at <4°. The org. base releases HNO<sub>2</sub> from (III). 2-Nitro-4-phenyl-, m.p. 228°, and 4:6-dibromo-2-nitro-, m.p. 250°, -benzeneazo-β-naphthols are new.

H. B.

**Potentiometric measurements of the transformation of the diazo- into the azo-group.** V. KREFELKA and M. BLABOLIL (Coll. Czech. Chem. Comm., 1936, 8, 408—418).—The tetrazotisation of benzidine (I) can be followed potentiometrically. The coupling at 3° of tetrazotised (I) with Na 8-amino-α-naphthol-3:6-disulphonate (1 mol.), and the coupling of the product with *m*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> in Na<sub>2</sub>CO<sub>3</sub> solution were followed by determining, at intervals, the % of diazo-N and azo-N. Diazo-N was measured by boiling an aliquot part with 50% aq. H<sub>2</sub>SO<sub>4</sub> and measuring the evolved N<sub>2</sub>. Azo-N was determined, after removing diazo-N by boiling with H<sub>2</sub>SO<sub>4</sub>, by adding excess of Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in an atm. of CO<sub>2</sub> and back-titrating electrometrically with approx. 50 c.c. of 0.05N-FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>6</sub>. The first coupling is rapid at first, but requires >40 hr. for completion. The acidity of the medium has little effect. The second coupling is complete in 2 hr. Tetrazotised (I) is stable at 3° whether in acid, neutral, or alkaline (Na<sub>2</sub>CO<sub>3</sub>) solution.

J. G. A. G.

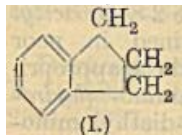
**Manufacture of alkylated phenols.**—See B., 1936, 1083.

**Action of hexamethylenetetramine on alkyl halides in presence of monohydric phenols.** I. P. BOUCHEREAU (J. Pharm. Chim., 1936, [viii], 24, 352—362).—By heating (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (I) with RX and ArOH in CHCl<sub>3</sub> or EtOH are obtained cryst. compounds of the general type (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>(RX)(ArOH) in which the halogen remains united to the alkyl. When heated the halogen migrates to the phenol to give halogenated phenol-CH<sub>2</sub>O resins. Thus are obtained the compounds from (I), PhOH, and : EtBr, loses NH<sub>3</sub> at 85—90°, resinifies at 130—150°; CH<sub>2</sub>PhCl, m.p. 79—80°; EtI, m.p. 118—120°,

resinifies at 140—150°; and (I),  $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , and  $\text{EtBr}$ , m.p. 85°, resinifies at 130—140°. These compounds are antiseptic and non-toxic when injected intravenously and their therapeutic uses are briefly described.

J. W. B.

**Mills Nixon effect.** L. F. FIESER and W. C. LOTHROP (J. Amer. Chem. Soc., 1936, 58, 2050—2054).—The coupling of 5-hydroxy-4:7-dimethylhydrindene and the non-coupling of 5-hydroxy-6-methylhydrindene with diazotised  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  indicate, in agreement with Mills and Nixon (A., 1931, 83), that hydrindene has the rigid structure (I). Contrary to these authors,



1:2:3:4-tetrahydronaphthalene can react in both Kekulé forms, since its 6-hydroxy-5:8-dimethyl derivative undergoes coupling (cf. this vol., 835).

$\beta$ -3-Amino-4-methylphenylpropionic acid, m.p. 140—141° [obtained by reduction ( $\text{H}_2$ ,  $\text{PtO}_2$ , 95%  $\text{EtOH}$ ) of 3-nitro-4-methylcinnamic acid], is converted (diazo-method) into the 3-OH-acid, m.p. 156—157°, methylated ( $\text{Me}_2\text{SO}_4$ ) to  $\beta$ -3-methoxy-4-methylphenylpropionic acid, m.p. 82—83°. The chloride of this with  $\text{AlCl}_3$  in  $\text{CS}_2$  gives 5-methoxy-6-methyl-1-hydrindone, m.p. 114—115° [attempted demethylation (48%  $\text{HBr}$ ,  $\text{AcOH}$ ) gave a dimeride,  $\text{C}_{22}\text{H}_{24}\text{O}_4$ , m.p. 237—240°], which when reduced (modified Clemmensen) and then demethylated (48%  $\text{HBr}$ +45%  $\text{HI}$  in  $\text{AcOH}$  and  $\text{N}_2$ ) affords 5-hydroxy-6-methylhydrindene, m.p. 83—84° (Bz derivative, m.p. 111—112°). 4:7-Dimethyl-1-hydrindone (Mayer and Müller, A., 1928, 65) is reduced (Clemmensen) to 4:7-dimethylhydrindene, b.p. 223—225°, m.p. —1.5° [5:6-( $\text{NO}_2$ )<sub>2</sub>-derivative, m.p. 191—192°], which with conc.  $\text{H}_2\text{SO}_4$  at 100° (bath) gives the 5-sulphonic acid [ $p$ -toluidine salt, m.p. 248—249° (decomp.)] ( $\text{KOH}$ -fusion of the Na salt gives tars). Methoxy- $p$ -xylene added to  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$  and  $\text{AlCl}_3$  in cold  $\text{CS}_2$  affords 2-methoxy-5- $\beta$ -chloropropionyl- $p$ -xylene, m.p. 85—86°, converted by  $\text{NHPh}\cdot\text{NH}$ , in  $\text{EtOH}$  into 1-phenyl-3-3'-methoxy-2':5'-dimethylphenyl- $\Delta^2$ -pyrazoline, m.p. 171—172°, and by  $\text{AcOH}$ -conc.  $\text{H}_2\text{SO}_4$  at 100° (bath) into 5-methoxy-4:7-dimethyl-1-hydrindone, m.p. 163—165°. This is reduced (Clemmensen) to the hydrindene, m.p. 25—26°, demethylated (48%  $\text{HBr}$  in  $\text{AcOH}$  and  $\text{N}_2$ ) to 5-hydroxy-4:7-dimethylhydrindene, m.p. 111—112° [Bz, m.p. 72—73°, and 6- $p$ -nitrobenzeneazo-, m.p. 220—222° (decomp.), derivatives].

1-Keto-7-methoxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene (improved prep.; cf. Clemons *et al.*, A., 1929, 1454) is reduced (Clemmensen) to 6-methoxy-, m.p. 38—39°, which is demethylated (45%  $\text{HI}$ ,  $\text{AcOH}$ ) to 6-hydroxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, m.p. 104—105° (Bz, m.p. 119—120°, and 7- $p$ -nitrobenzeneazo-, m.p. 229—231°, derivatives).

H. B.

**Synthesis of 6:7-methylenedioxy-1:1-dimethyl-1:2:3:4-tetrahydronaphthalene.** R. M. ORCUTT and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 2055—2056).—The Et ester, b.p. 184—185°/14 mm., of piperonylacetic acid, m.p. 87—90° (lit. 84°) [prepared by reduction ( $\text{Na-Hg}$ ) of piperonylideneacetic acid (I)], is reduced ( $\text{Na}$ ,  $\text{Bu}^\text{t}\text{OH}$ ) to

$\beta$ -piperonyl ethyl alcohol (II), b.p. 170—172°/8 mm., 184—186°/16 mm. (lit. 149—150°/6 mm.), m.p. 28—29° (phenylcarbamate, m.p. 98—99°), also obtained by reduction ( $\text{Na}$  powder,  $\text{Bu}^\text{t}\text{OH}$ ,  $\text{PhMe}$ ) of the Et ester of (I). (II) and  $\text{PBr}_3$  at  $\approx$  about 28° give the bromide, b.p. 163—165°/7.5 mm., the Grignard reagent from which with  $\text{COMe}_2$  gives  $\delta$ -piperonyl- $\beta$ -methylbutan- $\beta$ -ol (III), b.p. 145—148°/2 mm., and  $\alpha\delta$ -dipiperonylbutane, m.p. 78°. (III) is converted by 85%  $\text{H}_2\text{SO}_4$  at  $\approx$  10° into 6:7-methylenedioxy-1:1-dimethyl-1:2:3:4-tetrahydronaphthalene, b.p. 148—149°/10 mm., dehydrogenated (S) to 6:7-methylenedioxy-1-methylnaphthalene (picrate, m.p. 134—136°).

H. B.

**Synthesis of 5:6-methylenedioxy-1:1:2-trimethylindane from safrole.** R. M. ORCUTT and M. T. BOGERT (J. Amer. Chem. Soc., 1936, 58, 2057—2059; cf. A., 1934, 292).—Safole and 69%  $\text{HBr}$  at about 0° give 75% of  $\alpha$ -bromo- $\alpha$ -piperonyl ethane [ $\beta$ -bromo- $\alpha$ -3:4-methylenedioxyphenylpropane], b.p. 145°/9 mm., the Grignard reagent (I) from which reacts readily with atm.  $\text{O}_2$ . Hydrolysis ( $\text{H}_2\text{O}$ ) of (I) affords  $\alpha$ -piperonyl ethyl alcohol (II), b.p. 127—129°/3 mm. (phenylcarbamate, m.p. 93—94°), and some  $\beta$ - $\gamma$ -dipiperonylbutane (III), m.p. 74°. (I) and  $\text{COMe}_2$  in  $\text{N}_2$  give (III) and  $\gamma$ -piperonyl- $\beta$ -methylbutan- $\beta$ -ol (IV), b.p. 142—144°/3 mm., m.p. 49° (softens at 43°); in presence of air (II) (main product), (III), and (IV) result. (IV) is converted by cold 85%  $\text{H}_2\text{SO}_4$  into 5:6-methylenedioxy-1:1:2-trimethylindane (V), b.p. 137°/11 mm., and (occasionally) some  $\gamma$ -piperonyl- $\beta$ -methyl- $\Delta^2$ -butene, b.p. 120°/7 mm., which with  $\text{H}_2\text{SO}_4$  also gives (V). *iso*Safole and 69%  $\text{HBr}$  at 0° afford the unstable  $\alpha$ -bromo- $\alpha$ -3:4-methylenedioxyphenylpropane, decomp. on attempted distillation at 2 mm. 3:4-Methylenedioxyphenylethylcarbinol, b.p. 126—127°/3 mm. (cf. Mameli, A., 1904, i, 1023) (from piperonal and  $\text{MgEtBr}$ ), could not be converted into the bromide ( $\text{PBr}_3$ ); when kept it gives the carbinyl ether, m.p. 85° (lit. 88°).

H. B.

**Diaryls and their derivatives. IX. Sulphonation.** J. S. JOFFE, S. G. KUZNETZOV, and A. A. PANOV. X. Nitration of 2:2'-dihydroxy-1:1'-dinaphthyl. J. S. JOFFE (J. Gen. Chem. Russ., 1936, 6, 999—1002, 1003—1005).—IX. Sulphonation of 2:2'-dihydroxy-1:1'-dinaphthyl (I) at 100° yields the 6-mono- and the 6:6'-di-sulphonic acids. The former, when fused with  $\text{NaOH}$ , affords 2:6:2'-trihydroxy-1:1'-dinaphthyl, m.p. 305—307°, giving a red azo-dye, m.p. 138—140°, when coupled with  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ .

X. (I) and  $\text{HNO}_3$  in  $\text{AcOH}$  at 100° yield 6:6'-dinitro-2:2'-dihydroxy-1:1'-dinaphthyl, m.p.  $>300^\circ$  (decomp.), reduced by  $\text{NaHSO}_3$  to the 6:6'-( $\text{NH}_2$ )<sub>2</sub>-compound, m.p.  $>300^\circ$ . This is readily converted by  $\text{HNO}_2$  into the bisdazo-compound [compound with 2:3:6-OH $\cdot\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$ ].

R. T.

**Alkylphenols. I. 4-n-Alkylpyrogallols.** M. C. HART and E. H. WOODRUFF (J. Amer. Chem. Soc., 1936, 58, 1957—1959).—1:2:3- $\text{C}_6\text{H}_3(\text{OH})_3$ , the appropriate  $\text{AlkCO}_2\text{H}$ , and  $\text{ZnCl}_2$  at 130—140° give 2:3:4-trihydroxyphenyl Me, m.p. 170°, Et, m.p. 128—129°,  $\text{Pr}^\text{a}$ , m.p. 101—102°,  $\text{Bu}^\text{a}$ , m.p. 84—84.5°, *n*-amyl, m.p. 86.5—87°, and *n*-hexyl, m.p.



78—78.5°, *ketones*, reduced (Clemmensen) to 4-ethyl-, m.p. 108.5° (1, 2:3), 4-*n*-propyl-, m.p. 110—111° (2:5, 4:4), 4-*n*-butyl-, m.p. 88—89° (5, 12:6), 4-*n*-amyl-, m.p. 90—91° (19, 25), 4-*n*-hexyl-, m.p. 104—105° (44, 38), and 4-*n*-heptyl-pyrogallol, m.p. 116—117° (50, 26), respectively. The nos. in parentheses are the PhOH-coeffs. towards *S. aureus* and *B. coli*, respectively. The alkylpyrogallols, which show quasi-specificity (cf. Klarman *et al.*, A., 1933, 817), are less effective germicides than alkyl-phenols and -resorcinols. H. B.

**Molecular rearrangement of N-sulphenanilides in alkaline solution.** IV. M. L. MOORE and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 1960—1961; cf. this vol., 200).—4-Chloro-2-nitrobenzenesulphenanilide, -*o*-toluidide, and -*o*-chloroanilide, m.p. 112° (from 2:4-NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl·SCl and *o*-C<sub>6</sub>H<sub>4</sub>Cl·NH<sub>2</sub>), and *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·S·NH·C<sub>6</sub>H<sub>4</sub>Cl-*o* rearrange when heated with aq. EtOH-NaOH and give 4'-chloro-2'-nitro-2-thiol-, a chloronitrothiolmethyl-, a dichloronitrothiol-, and a chloronitrothiol-diphenylamine (as Na salts; *S*-Me ethers, m.p. 135—136°, 164—165°, 158—158.5°, and 144.5—145°, respectively), respectively. The formation of thiodiphenylamines is not observed (cf. Moore and Smiles, A., 1935, 1511). *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·S·NHAr (Ar=Ph, *o*-C<sub>6</sub>H<sub>4</sub>Me, and *o*-C<sub>6</sub>H<sub>4</sub>Cl) do not similarly rearrange. H. B.

**Molecular transformations in the cyclane series.** M. TIEFFENAU (Bull. Soc. chim., 1936, [v], 3, 1942—1974).—A lecture.

**Reduction of acid chlorides and anhydrides by chromous hydroxide.** R. GRAF [with M. TATZEL] (J. pr. Chem., 1936, [ii], 146, 198—200).—Simultaneous addition of BzCl and 50% KOH to an aq. suspension of Cr(OAc)<sub>2</sub> at 0° gives >30% yield of CH<sub>2</sub>Ph·OH, also obtained from Bz<sub>2</sub>O. H. W.

**Preparation of amino-alcohols.** II. J. T. ABRAMS and F. S. KIPPING (J.C.S., 1936, 1480—1481).—Condensation of CH<sub>2</sub>Bz·CO<sub>2</sub>Et-NaOEt-EtOH with the appropriate alkyl iodide affords *Et* α-benzoyl-*isovalerate* (*amide*, m.p. 179—180°), -γ-methylvalerate [*amide* (I), m.p. 157—158°, and -δ-methyl-*n*-hexoate, b.p. 169—170°/6 mm. [*amide* (II), m.p. 156—157°]. Reduction of (I) with Al-Hg-aq. EtOH affords α-hydroxybenzyl-γ-methylvaleramide, m.p. 136—137°, and the *pinacol*, [NH<sub>2</sub>·CO·CHBu<sup>δ</sup>·CPh(OH)]<sub>2</sub>, m.p. 169°, separated by fractional crystallisation from EtOAc-C<sub>6</sub>H<sub>6</sub>. Similar reduction of (II) affords α-hydroxybenzyl-δ-methylhexoamide, m.p. 137—138°, together with the *pinacol*, m.p. 159° (not analysed). α-Hydroxybenzylbutyramide (A., 1935, 209) with Br-aq. NaOH affords β-amino-α-phenylbutyl alcohol, m.p. 79—80° (*hydrochloride*, m.p. 195—196°), probably a diastereoisomeride of the base obtained by Hartung *et al.* (A., 1930, 1286). J. W. B.

**Phenanthrene series.** XIII. 9:10-Dihydrophenanthrene and amino-alcohols derived from it. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1936, 58, 1857—1860).—Phenanthrene is reduced [H<sub>2</sub> (136—218 atm.), Cu-Cr-Ba oxide, EtOH, 220°] to the 9:10-H<sub>2</sub>-derivative (I) (80% yield); anthracene is similarly reduced more quickly at 160°. (I) and AcCl (1.2 mols.) with AlCl<sub>3</sub> (2 mols.) in cold

PhNO<sub>2</sub> give 2-acetyl-9:10-dihydrophenanthrene (II) [(I) thus reacts as a diphenyl], which is oxidised by CrO<sub>3</sub>-aq. AcOH to 2-acetyl-9:10-phenanthraquinone, and by dil. NaOCl to an acid, the Me ester of which with Se at 280—300° affords phenanthrene-2-carboxylic acid. (I) and EtCOCl similarly yield 2-propionyl-9:10-dihydrophenanthrene (III), m.p. 62—63° (*semicarbazone*, m.p. 213—214°), oxidised (CrO<sub>3</sub>) to 2-propionyl-9:10-phenanthraquinone, m.p. 215—217° (decomp.). 2-Bromoacetyl-9:10-dihydrophenanthrene [from (II) and Br in Et<sub>2</sub>O; the 2-chloroacetyl derivative, m.p. 100—101°, is obtained in poor yield by the Friedel-Crafts reaction] and the appropriate NHR, in C<sub>6</sub>H<sub>6</sub> give 2-dimethylamino- [*hydrochloride*, m.p. 213—215° (decomp.)], 2-diethylamino- [*hydrochloride*, m.p. 173—176° (decomp.)], 2-piperidino-, m.p. 86—87° [*hydrochloride*, m.p. 240—252° (decomp.)], and 2-1':2':3':4'-tetrahydroisoquinolino- (IV) [*hydrochloride*, m.p. 238—239° (decomp.)], -acetyl-9:10-dihydrophenanthrenes, which are reduced (H<sub>2</sub>, PtO<sub>2</sub>, 90% EtOH or MeOH, using salts) to 2-β-dimethylamino-α-hydroxy- [*hydrochloride*, m.p. 170—172° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 216—217° (decomp.)], 2-β-diethylamino-α-hydroxy- [*hydrochloride*, m.p. 184—186° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 145—150° (decomp.)], 2-β-piperidino-α-hydroxy-, m.p. 124° [*hydrochloride*, m.p. 242° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 212—213° (decomp.)], and 2-β-1':2':3':4'-tetrahydroisoquinolino-α-hydroxy-, m.p. 101—102° [*hydrochloride*, m.p. 244—246° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 197—199° (decomp.)], -ethyl-9:10-dihydrophenanthrene, respectively. 2-α-Bromopropionyl-9:10-dihydrophenanthrene, m.p. 85—86° [from (III) and Br in Et<sub>2</sub>O], similarly gives 2-α-dimethylamino- [*hydrochloride*, m.p. 210—214° (decomp.)], 2-α-diethylamino- (*perchlorate*, m.p. 138—140°), 2-α-piperidino- [*hydrochloride*, m.p. 208—213° (decomp.)], and 2-α-1':2':3':4'-tetrahydroisoquinolino- (*perchlorate*, m.p. 230—231°), -propionyl-9:10-dihydrophenanthrenes, reduced to 2-β-dimethylamino-α-hydroxy-, m.p. 90—91° [*hydrochloride*, m.p. 225—227° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 210—211° (decomp.)], 2-β-diethylamino-α-hydroxy- [*hydrochloride*, m.p. 209—210° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 189—190° (decomp.)], 2-β-piperidino-α-hydroxy-, m.p. 104—106° [*hydrochloride*, m.p. 249—250° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 192—194° (decomp.)], and 2-β-1':2':3':4'-tetrahydroisoquinolino-α-hydroxy-, m.p. 136—138° [*hydrochloride*, m.p. 226—228° (decomp.)], *O*-Ac derivative *hydrochloride*, m.p. 190—192° (decomp.)], -propyl-9:10-dihydrophenanthrene, respectively. (IV) is accompanied by resinous material which with dil. alkali gives 9:10-dihydrophenanthrene-2-carboxylic acid. H. B.

**Lignin.** XII. Action of hydrogen sulphite solutions on aromatic alcohols. S. HEDEN and B. HOLMBERG (Svensk Kem. Tidskr., 1936, 48, 207—211).—Many aromatic alcohols resemble lignin in that when boiled with NaHSO<sub>3</sub>, OH is replaced by SO<sub>3</sub>H. M. H. M. A.

**Synthesis of *p*-methoxybenzyl alcohol.** R. QUELET and J. ALLARD (Bull. Soc. chim., 1936, [v],

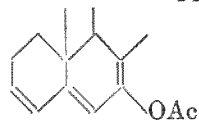
3, 1794—1800).—Previous work (A., 1934, 290) is repeated in the light of that of Ofner (A., 1935, 1120), which is confirmed. *p*-(with *o*-) $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , obtained as before (method improved), is converted into *p*-(with *o*-) $\text{OAc}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$  (I). Hydrolysis (aq. KOH) then gives *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$  and (*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ ) $_2\text{O}$ , which decomposes on distillation, giving *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{OMe}$  and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ . Hydrolysis of (I) by KOH-EtOH yields 90% of *p*- and 10% of *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ . E. W. W.

**Derivatives of phenyldihydroxypropylamine.** H. OHLE and G. HAESELER (Ber., 1936, 69, [B], 2324—2327; cf. this vol., 1491).—Epichlorohydrin and *p*- $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_2\cdot\text{NHPh}$  in presence of a little  $\text{C}_5\text{H}_5\text{N}$  at 120—150° give *p*-toluenesulphonphenyl- $\gamma$ -chloro- $\beta$ -hydroxypropylamine  $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , m.p. 96—97°, transformed by cautious addition of NaOH to its solution in EtOH at 100° into *p*-toluenesulphonphenyl- $\beta$ - $\gamma$ -oxidopropylamine (I), m.p. 77°, in 92% yield. Addition of a drop of  $\text{C}_5\text{H}_5\text{N}$  to (I) and BzOH at 120° affords *p*-toluenesulphonphenyl- $\beta$ -hydroxy- $\gamma$ -benzoyloxypropylamine, m.p. 117—118°, transformed by BzCl in  $\text{C}_5\text{H}_5\text{N}$  into *p*-toluenesulphonphenyl- $\beta$ - $\gamma$ -dibenzoyloxypropylamine (II), m.p. 135—136°. (II) and HBr-AcOH yield 2:4-dibromophenyl- $\beta$ - $\gamma$ -dibenzoyloxypropylamine (III) m.p. 122-5°, and ( $\text{C}_6\text{H}_4\cdot\text{Me}$ ) $_2\text{S}_2$  (III) (hydrobromide, m.p. 176—178°) gives a non-cryst. nitroscamine and N-Ac derivative. It is hydrolysed and then oxidised by  $\text{KMnO}_4$  in  $\text{COMe}_2$  to 2:4- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NH}_2$  and 2:4-dibromo-oxanilic acid. H. W.

**Isomeride of lutein from furze (*Ulex europaeus*).**—See this vol., 1571.

**Sterol group. XXVII. Oxidation of cholesterol hydrogen phthalate with potassium permanganate:**  $\beta$ -7-hydroxycholesterol and tetrahydrocholestane. T. BARR, I. M. HEILBRON, E. G. PARRY, and F. S. SPRING (J.C.S., 1936, 1437—1440).—Cholesteryl H phthalate with 0.25N- $\text{KMnO}_4$ -N- $\text{Na}_2\text{CO}_3$  at room temp. affords the following three products: the H phthalate, m.p. 199—201° (insol. in  $\text{CHCl}_3$ - $\text{Et}_2\text{O}$ ), of  $\beta$ -7-hydroxycholesterol, m.p. 184—185°,  $[\alpha]_D^{25}$  -86.4° [ $\text{Ac}_2$ , m.p. 121—122°,  $[\alpha]_D^{25}$  -174.6°, and  $\text{Bz}_2$  (I), m.p. 150—151°,  $[\alpha]_D^{25}$  -105.3°, derivatives; oxide, m.p. 173—175° ( $\text{Ac}_2$  derivative, m.p. 203—204°)], which is a stereoisomeride of the (now designated)  $\alpha$ -7-hydroxycholesterol of Windaus *et al.* (A., 1935, 1363) since thermal decomp. of (I) affords 7-dehydrocholesteryl benzoate; from the  $\text{CHCl}_3$ - $\text{Et}_2\text{O}$  extract is obtained the H phthalate, m.p. 236—237°, of 3:5:6:7- or 3:4:5:6-tetrahydrocholestane, + $\text{H}_2\text{O}$ , m.p. 235—236°, and anhyd., m.p. 230—231° ( $\text{Ac}_3$ , m.p. 219—220°,  $[\alpha]_D^{25}$  +23.1°, and  $\text{Bz}_3$ , m.p. 271—272°,  $[\alpha]_D^{25}$  +114.0°, derivatives), whilst KOH-EtOH hydrolysis of the resin from the  $\text{CHCl}_3$ - $\text{Et}_2\text{O}$  mother-liquor affords the hydroxyketo-acid  $\text{C}_{27}\text{H}_{46}\text{O}_4$  obtained by oxidation of cholesteryl acetate with  $\text{CrO}_3$  (Windaus *et al.*, A., 1915, i, 677), identified by thermal decomp. to the diene,  $\text{C}_{26}\text{H}_{42}$ , m.p. 76° (Lettré, A., 1933, 1047). All  $[\alpha]_D$  vals. are in  $\text{CHCl}_3$ . J. W. B.

**Enolisation of oxycholesterilene.** V. A. PETROW (Nature, 1936, 138, 645).—Acetylation of 7-ketocholesterol removes the  $\text{C}_{63}\cdot\text{OH}$ , yielding oxycholesterilene and its acetate, m.p. 90—92°,  $[\alpha]_D$  -222°,  $[\alpha]_{5461}$  -283°, which has the appended structure.



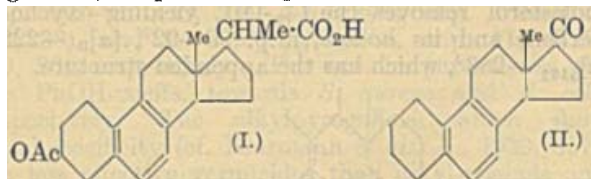
L. S. T.

**Lanosterol.** I. C. DORÉE and V. A. PETROW (J.C.S., 1936, 1562—1567).—Dehydrogenation of lanosterol (I) with Pd-C at 330—360° affords an oily hydrocarbon,  $\text{C}_{18}\text{H}_{20}$  [ $\text{C}_6\text{H}_3(\text{NO}_3)_3$  adduct, m.p. 147—148°]. The presence of one reactive and one unreactive double linking in (I) is proved by the following data: titration with  $\text{BzO}_2\text{H}$  gives an  $\text{O}_2$  absorption never >1.5 atoms, but lanosteryl acetate (II) with  $\text{BzO}_2\text{H}\cdot\text{CHCl}_3$  at 0° affords its oxide, m.p. 178°, hydrolysed to lanosterol oxide, m.p. 139—140°. (II) with  $\text{H}_2\text{O}_2$ -AcOH and subsequent hydrolysis gives oxylanostanetriol, m.p. 120—121° ( $\text{Ac}_1$  derivative, m.p. 162—163°). The ultra-violet absorption spectrum shows that lanostenone (III) (improved prep.) is not an  $\alpha\beta$ -unsaturated ketone, and with  $\text{NHPh}\cdot\text{NH}_2$ -AcOH it gives a tetrahydrocarbazole derivative, m.p. 201—202° (picrate, m.p. 201°), which surface film measurements suggest must be an *ang*-derivative. The monohydrochloride of (II), m.p. 126—127°, is hydrolysed by KOH-EtOH to isolanosterol (IV), m.p. 131—132° ( $\text{Ac}$  derivative, m.p. 130—131°), oxidised to isolanostenone (V), m.p. 138—139° (tetrahydrocarbazole derivative, m.p. 224—225°), the semicarbazone, m.p. 210°, of which is reduced by Na-EtOH at 180° to isolanostene, m.p. 80—81°; lanostene, similarly prepared, has m.p. 76—77°. (V) with Na-boiling EtOH gives isolanosterol-A, m.p. 130—131° ( $\text{Ac}$  derivative, m.p. 138°), which depresses the m.p. of (IV). Attempted oxidation of (II) with  $\text{CrO}_3$ -66% AcOH affords the *Ac* derivative, m.p. 164°, of lanosterol-D, m.p. 137—138°, which is obtained on hydrolysis, and is a OH-spatial isomeride of (I) since it is oxidised to (III). Surface film measurements of the above derivatives are recorded and support the conclusion that (I) has an amyrin type of structure. J. W. B.

**Artificial production of oestrogenic substances from sterols. I. Synthesis of the oestrogenic substance from animal sterols.** I. REMESOV and N. TAVASTSTJERNA. II. Synthesis of an isomeride of the follicular hormone from vegetable sterols. I. REMESOV (Rec. trav. chim., 1936, 55, 791—797, 797—803).—I. Agnosterol (modified prep.),  $\text{C}_{30}\text{H}_{47}\cdot\text{OH}$  (acetate), contains 3 ethylenic linkings ( $\text{BzO}_2\text{H}$ ), resists complete hydrogenation, and resembles theelin in absorption spectrum. A mixture with  $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$ , when heated with Br- $\text{Ac}_2\text{O}$ , gives the crude acetate dibromide, m.p. 130—131°,  $[\alpha]_D^{25}$  -79° in  $\text{CHCl}_3$ , which with maleic anhydride in  $\text{C}_6\text{H}_6$  at 133—135° affords the adduct, m.p. (crude) 196—204°; oxidation by  $\text{CrO}_3$  and subsequent debromination gives gums, but the final product shows oestrogenic activity by the Allen-Doisy test and towards monkeys.



II. Neorgosterol (prep. in 22–26% yield from ergosterol), m.p. 152.5°, gives the *acetate dibromide*,



m.p. 180–181°, which with  $O_3$  in AcOH affords  $CHMePr^{\beta}\cdot CHO$  and the *acid* (I), m.p. 210–212°, the *Me* ester, m.p. 144–145°, of which by the  $MgPhBr$  method is degraded to a *substance*,  $C_{13}H_{22}O_2$ , m.p. 225–226°, sublimes at 210°/0.001 mm., believed to have structure (II) and to be isomeric with the follicular hormone. 1 g. of (II) corresponds with  $8\text{--}10 \times 10^6$  mouse units of theelin. R. S. C.

**Sterols. VII. *cis*- and *trans*-Androstanone-3-carboxylic acid**, an oestrus-producing male hormone derivative, and *epicholesterol*. R. E. MARKER, O. KAMM, T. S. OAKWOOD, and J. F. LAUCIUS (J. Amer. Chem. Soc., 1936, 58, 1948–1950).—Oxidation ( $CrO_3$ , AcOH) of *Me* (*cis*+*trans*)-cholestane-3-carboxylate (this vol., 604) gives a little *Me* (*cis*+*trans*)-androstanone-3-carboxylate [purified through the semicarbazone, m.p. 250–260° (decomp.)], hydrolysed (MeOH-KOH) to the (*cis*+*trans*)-*acid*, m.p. 253°, which is readily esterified;  $5\text{--}10 \times 10^6$  g. of the *Et* ester, m.p. 108–110°, which is more active than the acid, causes an oestrus response in rats but is inactive in the cock's comb test. Unsaturation is not necessary for oestrus production. *epiCholesterol* (I) is separated from cholesterol (cf. *loc. cit.*) by purification of the mixture through the H succinates, fractional crystallisation of the mixed acetates from EtOH, hydrolysis (EtOH-NaOH) of the more sol. material, and final fractionation of the mixed benzoates [containing about 90% of that of (I)]. The acetate of (I) and Br in Et<sub>2</sub>O-AcOH give a *tetra-bromocholestane*, m.p. 110°, which differs from that obtained from cholesterylene (II) and Br. (I) is dehydrated by EtOH-HCl to (II). Ultra-violet irradiation of (I) does not give antirachitic products.

H. B.

**2:4-Dimethylphenylacetic [*m*-4-xylylacetic] acid and its derivatives.** J. V. HARISPE (Ann. Chim., 1936, [xi], 6, 249–347).—Re-examination of the conversion of pinonic acid (I) into *m*-4-xylylacetic acid (II) (Barbier and Grignard, A., 1909, i, 301) by  $Br\text{--}H_2O$  shows that in the first phase, the duration of which is a function of the homogeneity of the medium, H attached to C probably vicinal to CO is replaced by Br. Substitution causes production of HBr, under the influence of which (or of HCl added before commencement of the change) the bromopinonic acid becomes isomerised to the compound  $CHBrAc\cdot CH_2\cdot CH\begin{smallmatrix} CMe_2\cdot O \\ | \\ CH-CO \end{smallmatrix}$  (III), which slowly in the cold, but very rapidly when heated, loses HBr with formation of an ethylenic linking, eliminates 1 mol. of  $H_2O$  between CO and a terminal Me with production of a second ethylenic linking and of a six-membered ring, and suffers hydrolysis of the lactonic function immediately followed by dehydra-

tion of the corresponding *tert*-alcohol with appearance of the third ethylenic linking, and hence of the benzenoid nucleus. The yield of (II) is >70%; the remaining 30% is a brownish-red resin containing esterifiable  $CO_2H$ . The heats of combustion of (I), (II), and (III) have been determined. (II) has m.p. 105.5–106° (block), b.p. 300–302°(corr.)/760 mm. Its physiological properties are described. The *K* (+ $H_2O$ ), *Ba* (+ $H_2O$ ), *Ca* (+4.5 $H_2O$ ), m.p. 120°, *Ag* (+ $H_2O$ ), m.p. <100°, and *Na* (+1 $H_2O$ ) salts have been prepared. (II) gives the following esters; *Me*, b.p. 138°(corr.)/20 mm.; *Et*, b.p. 146.5°(corr.)/18 mm.; *Pr*<sup>a</sup>, b.p. 155°(corr.)/18 mm.; *Bu*<sup>a</sup>, b.p. 164°(corr.)/17 mm.; *CH<sub>2</sub>Ph*, b.p. 214°(corr.)/20 mm. *m*-4-*Xylylacetyl chloride* (IV), b.p. 116°(corr.)/11 mm., from (II) and  $SOCl_2$ , is converted in the usual manner into the corresponding amide, m.p. 184° (block), *anilide*, m.p. 144.5° (block), *o-toluidide*, m.p. 172° (block), *p-toluidide*, m.p. 145° (block), 1-, m.p. 209°, and 2-, m.p. 183°, *naphthylamide*, and by  $C_6H_5Me_2\cdot CH_2\cdot CO_2Ag$  into *m*-4-*xylylacetic anhydride*, m.p. 86–87°. *Ph m*-4-*xylylacetate*, m.p. 39°, is derived from (IV),  $PhOH$ , and  $K_2CO_3$  in boiling  $C_6H_6$ . (IV) and  $C_6H_6$  in presence of  $AlCl_3$  afford 2:4-*dimethyldeoxybenzoin*, m.p. 108.5° (block) (*oxime*, m.p. 114.5°). From the esters by means of the appropriate Grignard reagents the following *carbinols* are obtained: 2:4-*dimethylbenzyl-dimethyl*-, b.p. 139°(corr.)/20 mm.; *diethyl*-, b.p. 162°(corr.)/18 mm.; *di-n-propyl*-, b.p. 179°(corr.)/19 mm.; *di-n-butyl*-, b.p. 203°(corr.)/24 mm.; *diphenyl*-, m.p. 99° (block); *dibenzyl*-, m.p. 87–88° (block). Dehydration of the *tert*-alcohols is effected with  $Ac_2O + AcCl$ ,  $Ac_2O + H_2SO_4$ , or by  $H_2SO_4$  giving the unsaturated hydrocarbon which is oxidised by  $CrO_3$  in AcOH at 100° or by alkaline  $KMnO_4$  at room temp. to 2:4- $C_6H_5Me_2\cdot CO_2H$  and the corresponding ketone.  $\alpha$ -*m*-4-*Xylyl*- $\beta$ -*methyl*- $\Delta^{\alpha}$ -*propene* has b.p. about 108–109°(corr.)/16 mm.;  $\alpha$ -*m*-4-*xylyl*- $\beta$ -*ethyl*- $\Delta^{\alpha}$ -*butene*, b.p. 242°(corr.)/760 mm.; 122–123°/10–11 mm.;  $\alpha$ -*m*-4-*xylyl*- $\beta$ -*propyl*- $\Delta^{\alpha}$ -*pentene*, b.p. 137–138°(corr.)/13 mm.;  $\alpha$ -*m*-4-*xylyl*- $\beta$ -*n-butyl*- $\Delta^{\alpha}$ -*hexene*, b.p. 286–288°/760 mm., 173°(corr.)/20 mm.;  $\beta\beta$ -*diphenyl*- $\beta$ -*m*-4-*xylylethylene*, m.p. 69–70° (block);  $\gamma$ -*phenyl*- $\alpha$ -*m*-4-*xylyl*- $\beta$ -*benzyl*- $\Delta^{\alpha}$ -*propene*, b.p. 246°/13 mm. Reduction of the *Me* ester by Na and EtOH leads to  $\beta$ -*m*-4-*xylylethyl alcohol*, (V), b.p. 101–102°/3 mm.; 125°(corr.)/10 mm. [*phenylurethane*, m.p. 124.5–125° (block); *allophanate*, m.p. 222° (block)] transformed by  $SOCl_2$  and  $C_5H_5N$  into the corresponding *chloride* (VI), b.p. 111.5°(corr.)/11 mm., by  $PBr_3$  into the *bromide*, b.p. 132°(corr.)/18 mm.; the *iodide* from (VI) and NaI in  $COMe_2$ , has b.p. 136–137°/12 mm. The corresponding normal *sulphite*, b.p. 216–217°/2 mm., passes when heated into the alcohol,  $SO_2$ , and *m*-4-*xylylethylene*, b.p. 81–85°/14 mm. The *acetate*, b.p. 135°/14 mm., normal *oxalate*, m.p. 73–73.5° (block), and *benzoate*, b.p. 182°/12 mm., of (V) are described. (V) is transformed by  $NaHSO_4$  at 160–170° into *di*- $\beta$ -*m*-4-*xylylethyl ether*, m.p. 38°. H. W.

**Alkylene- and alkylidene-phenylacetoneitriles and derivatives.** 1-Cyano-1-phenyl-2-ethyl-cyclopropane and  $\alpha$ -phenyl- $\beta$ -ethyl- and  $\beta$ -*iso*-propyl-acrylonitriles. J. V. MURRAY and J. B.

CLOKE (J. Amer. Chem. Soc., 1936, 58, 2014—2018; cf. A., 1932, 739).— $\text{CH}_2\text{Ph}\cdot\text{CN}$  (I) is treated with  $\text{NaNH}_2$  (2 mols.) in liquid  $\text{NH}_3$  (which is then replaced by  $\text{Et}_2\text{O}$ ) followed by  $\text{CH}_2\text{Cl}\cdot\text{CH}\cdot\text{EtCl}$ , thus giving 40% of 1-cyano-1-phenyl-2-ethylcyclopropane, b.p. 93—94°/1 mm., which is hydrolysed ( $\text{AcOH}\cdot\text{H}_2\text{SO}_4$  or  $\text{EtOH}\cdot\text{KOH}$ ) to 1-phenyl-2-ethylcyclopropane-1-carboxylamide, m.p. 84°, and thence ( $\text{EtOH}\cdot\text{KOH}$ ) to the acid, m.p. 105—105.5° (corr.). (I) and  $\text{CH}_2\text{Cl}\cdot\text{CMe}_2\text{Cl}$  similarly afford 38% of  $\alpha$ -phenyl- $\beta$ -isopropylacrylonitrile (II), b.p. 95—95.2°/1 mm., probably formed by rearrangement of the intermediate  $\text{CMe}_2\text{CH}\cdot\text{CHPh}\cdot\text{CN}$ . (II), also obtained in 85% yield from (I) and  $\text{Pr}^i\text{CHO}$  in  $\text{EtOH}\cdot\text{NaOEt}$  at  $<-5^\circ$ , is hydrolysed ( $\text{AcOH}\cdot\text{H}_2\text{SO}_4$ ) to  $\alpha$ -phenyl- $\beta$ -isopropylacrylamide, m.p. 123—124° (corr.) [free acid, m.p. 133—134° (corr.)], and converted by alkaline  $\text{H}_2\text{O}_2$  in  $\text{CMe}_2$  (cf. A., 1935, 212) into  $\alpha\beta$ -oxido- $\alpha$ -phenylisohexoamide, m.p. 148—149° (corr.). Oxidation ( $\text{KMnO}_4$ , aq.  $\text{Na}_2\text{CO}_3$ ) of (II) gives  $\text{BzOH}$ ,  $\text{Pr}^i\text{CO}_2\text{H}$ , and  $\text{HCN}$ . (I) and  $\text{EtCHO}$  in  $\text{EtOH}\cdot\text{NaOEt}$  similarly afford  $\alpha$ -phenyl- $\beta$ -ethylacrylonitrile [ $\alpha$ -phenyl- $\Delta^2$ -pentenonitrile], b.p. 112—112.5°/3 mm. (55% yield), converted [as for (II)] into  $\alpha$ -phenyl- $\Delta^2$ -pentenoamide, m.p. 130° (corr.) (free acid, m.p. 67.5—68.5°), and  $\alpha\beta$ -oxido- $\alpha$ -phenylvaleramide, m.p. 155° (corr.). H. B.

[Preparation of ethyl cyclopentanone-2-carboxylate.]—See this vol., 1482.

Compounds  $\text{LiCl}\cdot\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and  $\text{LiCl}\cdot\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . K. SANDVED and R. VERMO (Tids. Kjem., 1936, 16, 115—116).—Phase-rule studies show the existence of these two compounds, which have been isolated together with the compound  $2\text{LiCl}\cdot\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ . M. H. M. A.

Hydrazino-acids. V. A. DARAPSKY [with J. LOEVENICH, O. CREIFELDS, W. BELLINGEN, E. KOSTER, V. BINET, H. WASSERFUHR, and H. BECK] (J. pr. Chem., 1936, [ii], 146, 268—306; cf. this vol., 1494).—Cautious addition of  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  to  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  in  $\text{EtOH}$  gives the hydrazine salt (I), m.p. 123°, of phenylpyruvic acid hydrazone, converted by dil.  $\text{HCl}$  into  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ . (I) is reduced by  $\text{Na}\cdot\text{Hg}$  in  $\text{H}_2\text{O}$  to  $\alpha$ -hydrazino- $\beta$ -phenylpropionic acid, m.p. 196° [ $\text{CHPh}$  derivative, m.p. 154—158°].  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  in  $\text{C}_6\text{H}_6$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{EtOH}$  give the hydrazine salt, m.p. 134—135°, of  $p$ -tolylglyoxylic acid hydrazone, which does not yield a  $\text{CHPh}$  derivative; it is converted by dil.  $\text{HCl}$  into  $p$ -tolylglyoxylic acid azine, [ $\text{N}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{p}$ ] $_2$ , m.p. 183° (decomp.), also obtained from  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$  in  $\text{EtOH}\cdot\text{H}_2\text{O}$ , which is reduced by  $\text{Na}\cdot\text{Hg}$  to hydrazo- $p$ -tolylacetic acid, m.p. 149° (non-cryst. *Et* ester).  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  is transformed by successive treatment with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in  $\text{EtOH}\cdot\text{H}_2\text{O}$  at room temp. and  $\text{Na}\cdot\text{Hg}$  into hydrazino- $p$ -tolylacetic acid, m.p. 174—176° (hydrochloride, m.p. 143—145° (decomp.));  $\text{CHPh}$ , m.p. 130°, and *o*-hydroxybenzylidene, m.p. 150°, derivative; *Et* ester hydrochloride, m.p. 141—143° (decomp.); *Et* carbonamidohydrazino- $p$ -tolylacetate, m.p. 130°. *Et* nitrosohydrazino- $p$ -tolylacetate, m.p. 70°, passes when heated above its m.p. into  $\text{N}_2\text{O}$  and *Et* amino- $p$ -tolylacetate, b.p. 136—139°/12

mm., hydrolysed to amino- $p$ -tolylacetic acid, sublimes at 228° (*Cu* salt). The phenylhydrazone of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  is reduced by  $\text{Na}\cdot\text{Hg}$  to phenylhydrazino- $p$ -tolylacetic acid, m.p. 148°. *Et* azido- $p$ -tolylacetate, b.p. 155°/18 mm., from the  $\text{NO}$ -ester and 10%  $\text{H}_2\text{SO}_4$ , is hydrolysed to azido- $p$ -tolylacetic acid, m.p. 100° ( $\text{NH}_4$  and *Ag* salts).  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in abs.  $\text{EtOH}$  give benzylpyruvic acid hydrazone, m.p. 133—134° (decomp.), the  $\text{N}_2\text{H}_4$  salt (II), m.p. 141°, of which is converted by dil.  $\text{HCl}$  into the azine, m.p. 114°, of benzylpyruvic acid (*Ca* salt), reduced by  $\text{Na}\cdot\text{Hg}$  to hydrazo- $\gamma$ -phenyl-*n*-butyric acid, decomp. 220—230°. (II) is reduced by  $\text{Na}\cdot\text{Hg}$  to  $\alpha$ -hydrazino- $\gamma$ -phenyl-*n*-butyric acid (III), m.p. 215—217° (decomp.) [ $\text{NH}_4$ , m.p. 203—204° (decomp.), and *Cu*, decomp. 115° after becoming red at 60—70°, salts; hydrochloride, m.p. 187° (decomp.);  $\text{CHPh}$  derivative, m.p. 158° (decomp.); *Et* ester hydrochloride, m.p. 108°]. (III) is transformed by  $\text{HBr}\cdot\text{Br}$  at 0° into  $\alpha$ -bromo- $\gamma$ -phenyl-*n*-butyric acid, reconverted into (III) by  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in boiling  $\text{EtOH}$ . *Et*  $\alpha$ -nitrosohydrazino- $\gamma$ -phenyl-*n*-butyrate, m.p. 48°, passes at 115—120° into *Et*  $\alpha$ -amino- $\gamma$ -phenyl-*n*-butyrate, b.p. 161—162°/16 mm. [hydrochloride, m.p. 121—123° (decomp.)], hydrolysed to  $\alpha$ -amino- $\gamma$ -phenyl-*n*-butyric acid, m.p. 292—293° when rapidly heated. *Et*  $\alpha$ -azido- $\gamma$ -phenyl-*n*-butyrate, b.p. 172—173°/16 mm., gives the non-cryst.  $\alpha$ -azido- $\gamma$ -phenyl-*n*-butyric acid ( $\text{NH}_4$ , m.p. 118—120°, and *Ag* salt).  $\text{CHPhMe}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in boiling  $\text{EtOH}$  give  $\alpha$ -hydrazino- $\beta$ -phenyl-*n*-butyric acid, m.p. 216° [ $\text{NH}_4$  salt; hydrochloride, m.p. 172—173° (decomp.); unstable  $\text{CHPh}$ , m.p. 107° (indef.), and *o*-hydroxybenzylidene, m.p. 133° (decomp.), derivatives; *Me*, m.p. 58—60°, and non-cryst. *Et* ester hydrochloride]. *Me*  $\alpha$ -nitrosohydrazino- $\beta$ -phenyl-*n*-butyrate passes at 120—130° into *Me*  $\alpha$ -amino- $\beta$ -phenyl-*n*-butyrate, b.p. 145—155°/13 mm. (hydrochloride, decomp. 170°), whence  $\alpha$ -amino- $\beta$ -phenyl-*n*-butyric acid, m.p. 239° (lit. m.p. 247—252°) (hydrochloride, m.p. 198°), and is transformed by steam-distillation in presence of 10%  $\text{H}_2\text{SO}_4$  into  $\alpha$ -azido- $\beta$ -phenyl-*n*-butyric acid ( $\text{NH}_4$ , m.p. 144°, and *Ag* salt).  $\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$  affords  $\alpha$ -hydrazino- $\beta$ -phenyl-*n*-butyric acid, m.p. 169—172° (decomp.) [hydrochloride, m.p. 132—135°;  $\text{CHPh}$ , m.p. 109—112°, and *o*-hydroxybenzylidene, m.p. 112—113°, derivatives; *Ac* $_2$ , m.p. 155° (decomp.), and *Bz* $_2$ , m.p. 139—141°, compounds; non-cryst. *Me* and *Et* ester hydrochlorides].  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  and  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in boiling  $\text{EtOH}$  give benzylidenepyruvic acid hydrazone, m.p. 84° (decomp.), the  $\text{N}_2\text{H}_4$  salt, m.p. 92°, of which could not be transformed into the corresponding azine, but is reduced by  $\text{Na}\cdot\text{Hg}$  to  $\alpha$ -hydrazino- $\gamma$ -phenyl-*n*-butyric acid, m.p. 215—217°.  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  gives the  $\text{N}_2\text{H}_4$  salt, m.p. 125° (decomp.), of cinnamylidenepyruvic acid hydrazone, which yields an impure azine and is reduced to  $\alpha$ -hydrazino- $\epsilon$ -phenyl-*n*-hexoic acid, m.p. 157° [ $\text{CHPh}$ , m.p. 124° (decomp.), and *o*-hydroxybenzylidene, m.p. 120°, derivatives; *Ac* $_2$ , m.p. 127°, and *Bz* $_2$ , m.p. 65°, compounds; non-cryst. *Me* and *Et* ester hydrochlorides]. *Et*  $\alpha$ -nitrosohydrazino- $\epsilon$ -phenyl-*n*-hexoate gives  $\alpha$ -amino- $\epsilon$ -phenyl-*n*-hexoic acid, m.p. 233—236°, and  $\alpha$ -azido- $\epsilon$ -phenyl-*n*-hexoic acid (*Ag* salt, m.p. 111—112°).  $1\text{-C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{CO}_2\text{H}$



affords the  $N_2H_4$  salt, m.p.  $188^\circ$  after becoming discoloured, of 1-naphthylglyoxylic acid hydrazone whence the corresponding azine,  $[N:C(C_{10}H_7) \cdot CO_2H]_2$ , m.p.  $160$ — $162^\circ$  (decomp.), reduced to *hydrazo- $\alpha$ -naphthylacetic acid*, m.p.  $186$ — $188^\circ$  (decomp.) (non-cryst. *Et* ester). *Hydrazino-1-naphthylacetic acid*, m.p.  $181^\circ$  after darkening at  $175$ — $176^\circ$ , gives a *hydrochloride*, m.p.  $194^\circ$ , a *CHPh*, m.p.  $124^\circ$  (decomp.) after darkening at about  $110^\circ$ , and *o-hydroxybenzylidene*, m.p.  $70^\circ$  (decomp.) after darkening at  $50^\circ$ , derivatives. It does not condense with  $COMe_2$  or give a cryst. Ac derivative and is not esterified by  $HCl$ - $MeOH$  or  $HCl$ - $EtOH$ . H. W.

**Diaryls and their derivatives. XI. Structure and composition of the complex compound of iron with  $\beta$ -naphthol-3-carboxylic acid.** J. S. JOFFE and M. I. KRILOVA (J. Gen. Chem. Russ., 1936, 6, 1006—1013).—Addition of aq.  $FeCl_3$  to aq. 2 : 3- $OH \cdot C_{10}H_6 \cdot CO_2Na$  leads to the production of a complex salt,  $[(O \cdot C_{10}H_6 \cdot CO_2)_2Fe]_3 \cdot 18H_2O$ , which is oxidised by excess of  $FeCl_3$  to yield a salt of Fe with 2 : 2'-dihydroxy-1 : 1'-dinaphthyl-2 : 2'-dicarboxylic acid,  $[(O \cdot C_{10}H_5 \cdot CO_2)_2Fe]$ . R. T.

**Condensation of phenylpyruvic acid with acetophenone.** P. CORDIER (J. Pharm. Chim., 1936, [viii], 24, 345—352).— $CH_2Ph \cdot CO \cdot CO_2Na$  with  $COPhMe$  in aq.  $EtOH$ - $KOH$  at room temp. affords the Na salt of  $\alpha$ -hydroxy- $\alpha$ -phenacyl- $\beta$ -phenylpropionic acid (liberated by acidification), dehydrated by  $HCl$ - $AcOH$  at  $100^\circ$  or by heat alone to give 2-*keto-5-phenyl-3-benzylidene-2 : 3-dihydrofuran*,  $O \begin{array}{c} \diagup CO \cdot C \cdot CHPh \\ \diagdown CPh \cdot CH \end{array}$  (I), m.p.  $150^\circ$  (insol. in  $Na_2CO_3$ ), and  $\alpha$ -phenacyl- $\beta$ -phenylacrylic acid (or  $\beta$ -benzoyl- $\alpha$ -benzylacrylic acid), decomp.  $160^\circ$ , also obtained by the action of boiling alkali on (I). J. W. B.

**Synthesis of pharmacologically important carboxylic acids. II. Synthesis of substituted phenylacetic acids from aromatic aldehydes.** K. KINDLER and E. GEHLHAAR (Arch. Pharm., 1936, 274, 377—388; cf. A., 1933, 1293).—*p*-Methylmandelonitrile *O*-benzoate reduced by Pd-black (I) and boiling tetrahydronaphthalene (II) and subsequently hydrolysed (aq.  $KOH$ ,  $EtOH$ ) gives *p*-tolylacetic acid, m.p.  $91$  (60% yield). *p*-isoPropylphenylacetic acid was similarly obtained. Hydrogenation [(I) and boiling (II) at 2 atm.; (I) and  $AcOH$ ] of mandelamide *O*-benzoate yields  $BzOH$  and  $CH_2Ph \cdot CO \cdot NH_2$  (75% yield). Mandelonitrile *O*-benzoate in aq.  $MeOH$  with  $HCl$  yields *Me benzoyl-mandelate*, m.p.  $78^\circ$ , which by the above methods of hydrogenation and subsequent hydrolysis gives  $CH_2Ph \cdot CO_2H$  (84% yield). By the action of  $HCl$  in aq.  $MeOH$  on the corresponding nitriles are obtained *Me O-acetyl-3 : 4-dimethoxymandelate*, b.p.  $186$ — $196^\circ/14$  mm., -4-methoxymandelate, b.p.  $164$ — $174^\circ/15$  mm., and -mandelate, b.p.  $144^\circ/15$  mm., which by hydrogenation [2 atm.; (I) and  $AcOH$ ] and hydrolysis yield homoveratric acid (III). *p*- $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ , and  $CH_2Ph \cdot CO_2H$ , respectively, in good yield. 3 : 4-( $OEt$ ) $_2C_6H_3 \cdot CHO$  in aq.  $MeOH$  hydrogenated by (I) yields 3 : 4-( $OEt$ ) $_2C_6H_3 \cdot CH_2 \cdot OH$ , which with  $SO_2Cl$  gives 3 : 4-( $OEt$ ) $_2C_6H_3 \cdot CH_2Cl$ , and this in  $C_6H_6$  with  $KCN$  in  $H_2O$  yields 3 : 4-diethoxyphenylacetoneitrile,

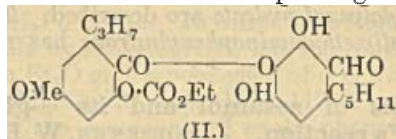
b.p.  $175$ — $180^\circ/14$  mm., m.p.  $37^\circ$ , hydrolysed ( $KOH$ ; aq.  $EtOH$ ) to 3 : 4-diethoxyphenylacetic acid, m.p.  $79$ — $80^\circ$ , all obtained in good yields. A good yield of (III) was similarly obtained from 3 : 4-( $OMe$ ) $_2C_6H_3 \cdot CHO$ . F. R. G.

**2 : 2-Disubstituted indandiones.** G. N. GHEORGHIU (J. pr. Chem., 1936, [ii], 146, 193—197).—*Me 2-methylindandione-2-acetate*, m.p.  $163$ — $164^\circ$ , obtained by the successive action of  $KOH$ - $EtOH$  and  $CH_2Br \cdot CO_2Me$  on 2-methylindandione, is hydrolysed by 20%  $H_2SO_4$ - $AcOH$  at  $150^\circ$  to the corresponding acid, m.p.  $190^\circ$ .  $CH_2Br \cdot CO_2Et$  similarly gives *Et 2-methylindandione-2-acetate*, m.p.  $159$ — $161^\circ$ , and, after re-solidification, m.p.  $161$ — $162^\circ$ . The following 2-methylindandiones are obtained analogously: 2-benzyl-, m.p.  $78$ — $79^\circ$ ; 2-acetonyl-, m.p.  $136$ — $137^\circ$ . 2-Phenylindandione yields 2-acetonyl-, m.p.  $152$ — $153^\circ$  [accompanied by the compound (?)  $CO(CH_2 \cdot CPh < \begin{array}{c} CO \\ CO \end{array} C_6H_4)_2$ , m.p.  $208$ — $210^\circ$ , arising from  $CO(CH_2Br)_2$  present in  $CH_2BrAc$ ], and 2-allyl-, m.p.  $76^\circ$ , 2-phenylindandione, and *Et 2-phenylindandione-2- $\beta$ -propionate*, m.p.  $72$ — $74^\circ$ . H. W.

**Lichen substances. LXXI. Synthesis of diploschistessic acid.** Y. ASAHINA and M. YASUE (Ber., 1936, 69, [B], 2327—2330; cf. Koller *et al.*, A., 1935, 748).—Treatment of gallaldehyde  $Me_3$  ether with  $N_2H_4 \cdot H_2O$  in boiling  $EtOH$  and of the residue with  $KOH$  at  $120^\circ$  gives 5-methylpyrogallol  $Me_3$  ether, b.p.  $117$ — $118^\circ/5$  mm., demethylated by boiling  $HI$  ( $d$  1.7) to 5-methylpyrogallol (I). 2 : 3 : 4-Trihydroxy-6-methylbenzaldehyde, m.p.  $182$ — $183^\circ$  or,  $+1H_2O$ , m.p.  $182$ — $183^\circ$  after softening at about  $120^\circ$ , obtained from (I),  $Zn(CN)_2$ , and  $HCl$  in abs.  $Et_2O$ , is converted by  $ClCO_2Et$  and  $C_5H_5N$  in  $COMe_2$  at  $0^\circ$  into 2 : 3 : 4-triethylcarbonato-6-methylbenzaldehyde, m.p.  $66$ — $68^\circ$ , oxidised by  $KMnO_4$  in  $COMe_2$ - $H_2O$  at  $45^\circ$  to 2 : 3 : 4-triethylcarbonato-6-methylbenzoic acid (II), m.p.  $109^\circ$ . (II) is converted by successive treatments with  $SOCl_2$  and oreylaldehyde into tricarbethoxydiploschistessic aldehyde, m.p.  $136$ — $138^\circ$ , which is condensed with  $ClCO_2Et$  in  $C_5H_5N$  and then oxidised to tetracarbethoxydiploschistessic acid, m.p.  $131$ — $132^\circ$ , hydrolysed by  $NaOH$  in  $COMe_2$ - $H_2O$  to diploschistessic acid (4 : 2' : 3' : 4'-trimethoxy-6'-methylbenzoyl-3-hydroxy-5-methylbenzoic acid), m.p.  $174^\circ$  (decomp.) (tetraacetate, m.p.  $164$ — $165^\circ$ , and its *Me* ester, m.p.  $169^\circ$ ). H. W.

**Lichen substances. LXX. Synthesis of ramalinolic acid.** Y. ASAHINA and T. KUSAKA (Ber., 1936, 69, [B], 1896—1899).—3 : 4 : 5-Trimethoxyvalerophenone is reduced by  $Zn$ - $Hg$  and boiling 5*N*- $HCl$  to 5-*n*-amylpyrogallol  $Me_3$  ether, b.p.  $166^\circ/6$  mm., converted by red P and boiling  $HI$  ( $d$  1.7) into 5-*n*-amylpyrogallol, b.p.  $179$ — $182^\circ/3$  mm., m.p.  $67^\circ$ . Treatment of (I) and  $Zn(CN)_2$  in  $Et_2O$  with  $HCl$  and of the product with boiling  $H_2O$  yields 2 : 3 : 4-trihydroxy-6-*n*-amylbenzaldehyde (I), m.p.  $116$ — $117^\circ$ , transformed by  $ClCO_2Et$  in  $C_5H_5N$  at  $-15^\circ$  and then oxidised by  $KMnO_4$  in  $COMe_2$  to 2 : 3 : 4-triethylcarbonato-6-*n*-amylbenzoic acid, m.p.  $81^\circ$ , whence 2 : 3 : 4-trihydroxy-6-*n*-amylbenzoic acid, m.p.  $163^\circ$ . Treatment of (I) with carbethoxydivaricatyl chloride gives the *depside aldehyde* (II),

which, after protection of the free OH groups by  $\text{CO}_2\text{Et}$ , is oxidised to the corresponding acid; this,



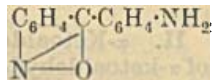
after decarboxylation, gives a product identical with natural ramalinic acid (III). (I) in  $\text{COMe}_2$  is transformed by  $\text{BzCl}$  and  $N\text{-KOH}$  into 2:4-dihydroxy-3-benzoyloxy-6-n-amybenzaldehyde (V), m.p.  $123^\circ$ , the dicarboxy-derivative of which is oxidised and then decarboxylated to 2:4-dihydroxy-3-benzoyloxy-6-n-amybenzoic acid, m.p.  $173^\circ$ . (IV) in  $\text{COMe}_2$  is converted by  $\text{MeI}$  and anhyd.  $\text{K}_2\text{CO}_3$  into an oil, oxidised by  $\text{KMnO}_4$  to 2:4-dimethoxy-3-benzoyloxy-6-n-amybenzoic acid, m.p.  $162\text{--}163^\circ$ ; the corresponding Me ester is hydrolysed by  $\text{KOH-MeOH}$  to the substance  $\text{C}_{15}\text{H}_{22}\text{O}_5$ , m.p.  $73\text{--}74^\circ$ , identical with that obtained by hydrolysis of permethylated (III). H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. IV. 2-Chloro-6-fluoro- and 2:6-difluoro-benzaldehyde. G. LOCK (Ber., 1936, **69**, [B], 2253—2258; cf. A., 1935, 1238).—With di-ortho-substituted benzaldehydes the behaviour of F resembles that of other halogens. 2:6- $\text{C}_6\text{H}_3\text{MeClF}$  is converted by gradual treatment with Br at  $180\text{--}200^\circ$  and of the product with conc.  $\text{H}_2\text{SO}_4$  at  $50\text{--}60^\circ$  followed by distillation with steam into 2-chloro-6-fluorobenzaldehyde (I), m.p.  $38\text{--}5^\circ$  [semicarbazone, m.p.  $213^\circ$  (corr.); oxime, m.p.  $134^\circ$  (corr.)], oxidised by  $\text{Ag}_2\text{O-H}_2\text{O}$  at  $100^\circ$  to 2-chloro-6-fluorobenzoic acid (II), m.p.  $159^\circ$  (corr.). (I) and 50%  $\text{KOH-H}_2\text{O}$  at  $100^\circ$  afford  $\text{HCO}_2\text{H}$ , a little (II), and m-chlorofluorobenzene, b.p.  $127\text{--}128^\circ/761\text{ mm.}$ , also obtained from m- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ . 2:6- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$  is converted into the corresponding diazonium borofluoride, decomp.  $118^\circ$ , which when heated with sand at  $150\text{--}250^\circ/\text{vac.}$  affords 2-fluoro-6-nitrotoluene (III), b.p.  $97^\circ/11\text{ mm.}$ , m.p.  $6\text{--}5\text{--}7^\circ$ . (III) is reduced ( $\text{SnCl}_4$  and conc.  $\text{HCl}$ ) to 6-fluoro-o-toluidine, b.p.  $89\text{--}90\text{--}90\text{--}5^\circ/15\text{ mm.}$ , m.p.  $7^\circ$  [*Ac* derivative, m.p.  $132^\circ$  (corr.)], transformed through the diazonium borofluoride into 2:6-difluorotoluene (IV), b.p.  $112^\circ$  (corr.)/ $742\text{ mm.}$  [2-fluoro-6-hydroxytoluene, b.p.  $186\text{--}188^\circ$  (corr.)/ $748\text{ mm.}$ , m.p.  $56\text{--}5^\circ$ ]. The direct prep. of (IV) from 2:6- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$  appears impossible. (IV) is brominated at its b.p. to 2:6-difluorobenzylidene bromide, m.p.  $45^\circ$ , converted by  $\text{H}_2\text{SO}_4$  into 2:6-difluorobenzaldehyde (V), b.p.  $82\text{--}84^\circ/15\text{ mm.}$ ,  $190\text{--}195^\circ/743\text{ mm.}$ , m.p. about  $15\text{--}17^\circ$  [semicarbazone, m.p.  $226^\circ$  (corr.); 2:6-difluorobenzoic acid, m.p.  $157\text{--}5^\circ$  (corr.)], also obtained from (IV) by Etard's reaction. (V) and 50%  $\text{KOH}$  yield  $\text{HCO}_2\text{H}$  and m- $\text{C}_6\text{H}_4\text{F}_2$ . H. W.

Condensation of 5-chloro-2-nitrobenzaldehyde with aniline. I. TANASESCU and (MLLE.) M. SUCIU (Bull. Soc. chim., 1936, [v], **3**, 1753—1761).—2:5- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CHO}$  and  $(\text{NH}_2\text{Ph})_2\cdot\text{H}_2\text{SO}_4$ —condense ( $\text{ZnCl}_2$ ) to form o-chloro-2-nitro-4':4''-diaminotriphenylmethane (I), m.p.  $164^\circ$  (hydrochloride; *Ac.*, m.p.  $209^\circ$ , and *Bz.*, m.p.  $253^\circ$ , derivatives), which with  $\text{Zn-NH}_4\text{Cl-EtOH}$  gives o-chloro-2:4':4''-tri-

aminotriphenylmethane, m.p.  $98^\circ$  (*Bz.* derivative, m.p.  $260^\circ$ ). As by-product with (I), 5-chloro-3-p-aminophenylanthranil, m.p.  $208^\circ$  (*Ac.*, m.p.  $222^\circ$ , *Bz.*, m.p.  $242^\circ$ , benzylidene, m.p.  $149^\circ$ , and 5''-chloro-2''-nitrobenzylidene, m.p.  $245^\circ$ , derivatives), is formed, which with  $\text{Zn-NH}_4\text{Cl-EtOH}$  gives 5-chloro-2:4'-diaminobenzophenone, m.p.  $149^\circ$  (*Bz.* derivative, m.p.  $207^\circ$ ). E. W. W.

Action of aniline on o-nitrobenzaldehyde in acetic acid. S. SECAREANU and A. SILBERG (Bull. Soc. chim., 1936, [v], **3**, 1777—1782).—These substances condense in  $\text{AcOH}$  to give a product, converted by conc.  $\text{HCl}$  in  $\text{EtOH}$  into a mixture of 3-p-amino-

phenylanthranil, , and 5-chloro-3-p-aminophenylanthranil (cf. preceding abstract). E. W. W.

Formation of polyene chains. Preparation of unsaturated aldehydes. G. WITTIG and R. KETHUR [with, in part, A. KLEIN and R. WIETBROCK] (Ber., 1936, **69**, [B], 2078—2087).—The syntheses follow the course  $\text{R}\cdot\text{CHO} + \text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{CHR}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{H} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CN} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CH}\cdot\text{NH} \rightarrow \text{CHR}\cdot\text{CH}\cdot\text{CHO}$ .  $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$  and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  in boiling  $\text{AcOH}$  afford cinnamylidenecyanoacetic acid, which loses  $\text{CO}_2$  when heated with  $\text{Cu}$  powder at  $180\text{--}185^\circ$  giving cinnamylideneacetonitrile (I), b.p.  $158\text{--}160^\circ/11\text{ mm.}$ , converted by  $\text{HCl}$  in abs.  $\text{Et}_2\text{O}$  followed by treatment of the hydrochloride with  $\text{H}_2\text{O}$  into the solid isomeride (II), m.p.  $40\text{--}41\text{--}5^\circ$ . (I) and (II) give the same cinnamylidene-acetamide, m.p.  $185\text{--}5\text{--}186\text{--}5^\circ$ , and -acetic acid, m.p.  $163\text{--}164^\circ$ , when subjected to short and protracted hydrolysis with  $\text{KOH-EtOH}$ , respectively. Reduction of (I) or (II) to the corresponding aldehyde by  $\text{SnCl}_2\text{-SnCl}_4\cdot 2\text{H}_2\text{O}$  and  $\text{HCl}$  in  $\text{Et}_2\text{O}$  is unsatisfactory by reason of the sparing solubility of the intermediate adducts and the best yields of  $\delta$ -phenyl- $\Delta^{\alpha\gamma}$ -pentadienal (phenylhydrazone, m.p.  $173\text{--}5\text{--}174^\circ$ ) are secured in dioxan at  $55^\circ$ . Cinnamylideneacetaldehyde and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  give  $\alpha$ -cyano- $\zeta$ -phenyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienoic acid, m.p.  $227\text{--}228^\circ$ , converted by  $\text{Cu}$  powder at about  $190^\circ$  into  $\text{CO}_2$  and  $\zeta$ -phenyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatrienonitrile, b.p.  $195\text{--}197^\circ/12\text{ mm.}$ , m.p.  $50\text{--}55^\circ$ , a mixture of stereoisomerides from which a form, m.p.  $111\text{--}112^\circ$ , is obtained by the action of  $\text{HCl}$  in  $\text{Et}_2\text{O}$ ; this is also produced when the mixture is reduced by  $\text{SnCl}_2$  and  $\text{HCl}$  in  $\text{Et}_2\text{O}$  or dioxan.

$\text{CPh}_2\cdot\text{Me}\cdot\text{OH}$  is transformed by  $\text{HBr}$  in boiling  $\text{AcOH}$  into  $\text{CPh}_2\cdot\text{CH}_2$ ;  $\text{Br}$  in  $\text{AcOH}$  is added to the cooled solution, which is again heated, whereby the intermediate  $\text{CPh}_2\cdot\text{Br}\cdot\text{CH}_2\cdot\text{Br}$  is transformed into  $\text{CPh}_2\cdot\text{CHBr}$  in 66% yield. The Grignard compound from the latter substance and  $\text{HCO}\cdot\text{NPhMe}$  afford  $\beta$ -phenylcinnamaldehyde (III), m.p.  $44\text{--}45^\circ$  (semicarbazone, m.p.  $217\text{--}219^\circ$ ; anilide, m.p.  $98\text{--}98\text{--}8^\circ$ , azine, m.p.  $199\text{--}199\text{--}5^\circ$ ), in 41% yield. (III) and  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  in boiling  $\text{AcOH}$  yield  $\gamma$ -phenylcinnamylidenecyanoacetic acid, m.p.  $217\text{--}218^\circ$  (decomp.), whence  $\gamma$ -phenylcinnamylideneacetonitrile, m.p.  $68\text{--}69^\circ$ , and  $\delta\delta$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadienal, m.p.  $69\text{--}5\text{--}71^\circ$  (corresponding azine, m.p.  $183\text{--}184^\circ$ ). H. W.



**Condensation reactions of 2:4-dinitrophenylhydrazine.** F. L. RODUTA and G. QUITILAN (Rev. Filipina Med. Farm., 1936, 27, 123—130).—A summary of the known 2:4-dinitrophenylhydrazones of aldehydes and ketones is given and 2:4-dinitrophenylhydrazones of the following have been prepared: citral, m.p. 103°;  $\text{CCl}_3\cdot\text{CHO}$ , m.p. 131°; hydrocinnamaldehyde, m.p. 147°; furfuraldehyde, m.p. 218°; protocatechualdehyde, m.p. 226°;  $\text{COPh}_2$ , m.p. 228°;  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , m.p. 232°;  $\text{PhCHO}$ , m.p. 235°;  $\alpha$ -naphthaquinone, m.p. 278° (decomp.); and isatin. F. R. S.

[Halogeno-cinnamaldehydes.]—See this vol., 1463.

**Enol-betaines. II.  $\alpha$ -Ketoaldonitrone and a new preparation of  $\alpha$ -ketoaldehydes.** F. KROHNKE and E. BORNER (Ber., 1936, 69, [B], 2006—2016; cf. A., 1935, 987).—Addition of  $N\text{-NaOH}$  to phenacylpyridinium bromide (I) and  $\text{PhNO}$  in aq.  $\text{EtOH}$  at  $-10^\circ$  to  $-5^\circ$  affords *benzoyl-N-phenylnitrone* (II),  $\text{CHBz}\cdot\text{NPh}\cdot\text{O}$ , m.p. 109—110°, which gradually decomposes when kept and yields mandelic acid when treated with alkali. *Benzoylphenylnitrone hydrate* (III)  $\text{OH}\cdot\text{CHBz}\cdot\text{NPh}\cdot\text{OH}$ , m.p. 90°, is derived from (I) and  $0.1N\text{-H}_2\text{SO}_4$  in  $\text{EtOH}$ . (II) or (III) is transformed by  $\text{NHPH}\cdot\text{NH}_2$  (1 mol.) into a mixture of  $\alpha$ - and  $\beta$ -glyoxalphenylhydrazone and by excess of the reagent into the corresponding osazone. (II) and  $\text{NH}_2\text{OH}$  (1 mol.) yield oximinoacetophenone, whereas with 2 mols. *anti*-phenylglyoxime is produced. With  $\text{NH}_2\text{Ph}$  in hot  $\text{EtOH}$  (II) gives *phenylglyoxaldianil hydrate*,  $\text{C}_{20}\text{H}_{18}\text{ON}_2$ , m.p. 97° (corresponding *di-p-tolil hydrate*, m.p. 118—119°). The *p*-dimethylaminoanil of phenylglyoxal has m.p. 88°, and the *p*-dimethylaminoanilides of cinnamylideneacetic acid and  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$  have m.p. 205—207° and 174°, respectively. Analogous reactions between  $\text{PhNO}$  and phenacyl-quolinium, -isoquolinium, and -triethylammonium bromide and between phenacylpiperidinium bromide and  $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  are described. *Benzoyl-N-p-dimethylaminophenylnitrone*, m.p. 110—111°, obtained as above or from the enolbetaine of (I) in absence of  $\text{NaOH}$ , is converted by  $5N\text{-H}_2\text{SO}_4$  into phenylglyoxal, m.p. 73° (A compound.  $2\text{-}p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , m.p. 50—51° after softening at 48°, is described.) The oxime of phenacylpyridinium perchlorate and  $\text{PhNO}$  give the compound,  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$ , m.p. 156° (decomp.). The following -*benzoyl-N-p-dimethylaminophenylnitrone*s are described; *p*-iodo-, m.p. 97°, whence *p*-iodophenylglyoxal hydrate, m.p. 137—138°; 3:4-dichloro-, m.p. 136—137°, whence 3:4-dichlorophenylglyoxal hydrate, m.p. 82—84°; 3:4-dichloro-2-nitro-, decomp. about 140°. *p*-Phenylphenacylpyridinium bromide (IV) and  $\text{PhNO}$  afford *p-phenylbenzoyl-N-phenylnitrone*, m.p. 144°. Treatment of (IV) with  $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  and alkali and of the product with warm, dil.  $\text{H}_2\text{SO}_4$  gives *p-xenylglyoxal hydrate*, m.p. 117—121°, also obtained by hydrolysis of *p-phenyl-p-bromophenacylpyridinium bromide*, m.p. 206° (decomp.), derived from (IV) and  $\text{Br}$  in  $\text{AcOH}$ ; *p-xenylquinoxaline* has m.p. 128°.  $\beta$ -Naphthacylpyridinium bromide gives  $\beta$ -naphthoyl-N-phenylnitrone, m.p. 101—101.5°, and  $\beta$ -naphthylglyoxal hydrate,

m.p. 106—109°. *Keto-2-thiophenonyl-N-p-dimethylaminophenylnitrone*, m.p. 123°, and non-homogeneous 2-thiophenylglyoxal hydrate are described. *Trimethylacetyl-N-p-dimethylaminophenylnitrone* has m.p. 87—88°. H. W.

**Synthesis of sesamol and its  $\beta$ -glucoside.** Baudouin's reaction. J. BOESEKEN, W. D. COHEN, and C. J. KIP (Rec. trav. chim., 1936, 55, 815—820).—Piperonaldehyde (I) and 20%  $\text{AcO}_2\text{H}$  (prep. free from  $\text{Ac}_2\text{O}_2$  described) in  $\text{AcOH}$  with 2 drops of  $\text{H}_2\text{SO}_4$  or, better, a trace of  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$  at  $<30^\circ$  give 50 and 60% yields, respectively, of sesamol (II) and 0.7 mol. of  $\text{HCO}_2\text{H}$ . Larger amounts of acid cause resinification and very poor yields. (II), tetra-acetylglucosidyl bromide,  $2N\text{-KOH}$ , and  $\text{Et}_2\text{O}$ , when shaken, give sesamol  $\beta$ -glucoside tetra-acetate, cryst. (10%), hydrolysed by  $\text{Ba(OH)}_2$  to sesamol  $\beta$ -glucoside, m.p. 168—169°, which gives Baudouin's reaction slowly as does sesame oil; the reaction of the oil is thus proved to be due to hydrolysis of sesamoline to (II). Pure (II) colours rapidly in air, but this is prevented by a little (I). R. S. C.

**Reduction of benzophenone at the dropping mercury cathode.** H. SCHWEITZER and E. LAQUEUR (Rec. trav. chim., 1936, 55, 959—962).—Reduction of  $\text{COPh}_2$  at the dropping Hg cathode occurs in one stage in neutral solution, but in two stages in presence of  $\text{HCl}$ , particularly of an excess. Whereas reduction of the pinacone or its half-radical is possible, it is preferable to regard the reduction in acid solution as that of  $[\text{CPh}_2\cdot\text{OH}]^+\text{Cl}^-$ . R. S. C.

**Hydrogen linking formation between hydroxyl groups and nitrogen atoms in organic compounds.** S. B. HENDRICKS, O. R. WULF, G. E. HILBERT, and U. LIDDEL (J. Amer. Chem. Soc., 1936, 58, 1991—1996; cf. this vol., 703).—The existence of chelation between OH and N in compounds of the type  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{X}\cdot\text{NR}$  ( $\text{X}=\text{CH}$  or  $\text{N}$ ) is indicated by the absence of infra-red absorption characteristic of the OH group; such chelation requires the OH to be *trans* to R. Thus, the following show no absorption: (*anti*-)2-hydroxy-, m.p. 95°, and 2-hydroxy-5-methyl-, m.p. 114°, -benzophenoneoxime acetates (cf. Blatt, this vol., 1511), salicylaldehyde-anil-, hydrazine-, dimethylhydrazine-, phenylhydrazine-, phenylmethylhydrazine-, and -azine;  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OAc}$ ; 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{CMe}_2$ ; 1-benzeneazo- and 2:5-dichlorobenzeneazo- $\beta$ -naphthols; 2:2'-dihydroxy- and 2:5:5'-trichloro-2'-hydroxy-4-methyl-azobenzene. Absorption is shown by  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$  (probably due to  $\text{N}\cdot\text{OH}$ ), 2:1- $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}_2$  (m.p. 157°),  $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ ,  $\alpha$ - and  $\beta$ -benzoinphenylhydrazones, 2:2'-dihydroxybenzophenone-oxime acetate and -phenylmethylhydrazine, and *syn*-2-hydroxybenzophenoneoxime acetate; in some cases, partial chelation probably occurs. Structural formulæ (showing probable interat. distances) for several of the above compounds are discussed. H. B.

**Oxidation of the ethylenic linking adjacent to a carbonyl group by peracids.** J. BOESEKEN and J. JACOBS (Rec. trav. chim., 1936, 55, 786—790).— $\text{CHPh}\cdot\text{CMe}\cdot\text{CMe}$  is oxidised by  $\text{AcO}_2\text{H}$  in  $\text{AcOH}$  at  $<30^\circ$  to (?) *cis*- and *trans*-forms, (I), m.p. 131°, and

(II), b.p. 100—103°/3 mm.,  $n_D$  1.5503, of the acetate of enolic benzyl Me ketone, hydrolysed by conc. HCl to  $\text{CH}_2\text{Ph}\cdot\text{COMe}$ . Neither is obtained from  $\text{CH}_2\text{Ph}\cdot\text{COMe}$  by  $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$ , but the Na derivative and  $\text{AcCl}$  in  $\text{Et}_2\text{O}$  give a poor yield of (II) with a little (I).  $\text{CHPh}\cdot\text{CH}\cdot\text{COEt}$ , b.p. 109—117°/3 mm., and  $\text{AcO}_2\text{H}$  give the propionate of enolic phenylacetaldehyde (III), b.p. 90—92°/1—3 mm.,  $n_D^{20}$  1.5541, hydrolysed by conc. HCl to  $\text{CH}_2\text{Ph}\cdot\text{CHO}$ . The aldehyde and  $(\text{EtCO})_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$  give an isomeride (IV), b.p. 92—96°/high vac.,  $n_D^{20}$  1.5371, of (III). Both (III) and (II) may be mixtures of isomerides. The action of  $\text{AcO}_2\text{H}$  is to insert O between the systems  $\cdot\text{C}\cdot\text{C}\cdot$  and  $\text{CO}$ .

R. S. C.

**Autoxidation phenomena in the indone series.** A. SCHONBERG and R. MICHAELIS (Naturwiss., 1936, 24, 620; cf. A., 1935, 1369).—2-*p*-Dimethylamino-anilino-3-phenylindone is autoxidised in solution by addition of  $\text{O}_2$  to the free radical form.

J. L. D.

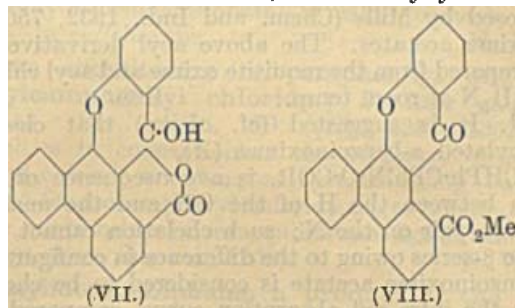
**Synthesis of hexahydrophenanthrene derivatives.** J. C. BARDHAN (Chem. and Ind., 1936, 879—880).—The *cis*-structure assigned by van de Kamp and Mosettig (this vol., 1062) to liquid octahydrophenanthrene is uncertain.

$\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$ , b.p. 155°/1 mm., with  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$  and  $\text{NaOEt}$  give *Et*  $\beta$ -keto- $\alpha$ - $\beta'$ -phenylethylpimelate, b.p. 175°/1 mm., which with cold, conc.  $\text{H}_2\text{SO}_4$  affords *Et* 3:4-dihydronaphthalene-2-carboxylate-1- $\gamma$ -butyrate, b.p. 177°/1 mm. This undergoes ring-closure with Na and then yields by hydrolysis 1-keto-1:2:3:4:9:10-hexahydrophenanthrene, the semicarbazone, m.p. 254—255°, of which yields ( $\text{NaOEt}$ ) a hydrocarbon, smoothly dehydrogenated to phenanthrene.

R. S. C.

**Alkylation and arylation of benzanthrone by Grignard reagents.** Oxidative degradation of 6-phenylbenzanthrone. G. CHARRIER and E. CHIGI (Ber., 1936, 69, [B], 2211—2232; cf. A., 1933, 160).—Addition of benzanthrone (I) in  $\text{Et}_2\text{O}$  to  $\text{MgPrI}$  in  $\text{Et}_2\text{O}$  gives 6-propylbenzanthrone, m.p. 83—84°, oxidised by  $\text{CrO}_3$  in  $\text{AcOH}$  to 4-propylantraquinone-1-carboxylic acid, m.p. 180—181°. Similarly (I) and  $\text{MgBuI}$  afford 6-*n*-butylbenzanthrone, m.p. 99° [the *Bz*-3-*n*-butylbenzanthrone of Nakanishi (A., 1934, 191)], oxidised by  $\text{CrO}_3$  in  $\text{AcOH}$  to 4-*n*-butylantraquinone-1-carboxylic acid, m.p. 175°, and thence by  $\text{HNO}_3$  under pressure to anthraquinone-1:4-dicarboxylic acid, m.p. about 315°. Oxidation of 6-phenylbenzanthrone (II) with  $\text{KMnO}_4$  in boiling dil. alkali affords 4-phenylantraquinone-1-carboxylic acid (III), m.p. 288—290° [*Na* ( $3\text{H}_2\text{O}$ ) salt], diphenyl-3:4-dicarboxylic-2-glyoxylic acid (IV), m.p. 256—257° (decomp.), and  $\text{H}_2\text{C}_2\text{O}_4$ . Oxidation of (IV) with  $\text{KMnO}_4$  and 33%  $\text{H}_2\text{SO}_4$  yields diphenyl-2:3:4-tricarboxylic acid (V), m.p. 210—212°, which readily passes into an anhydride. Conc.  $\text{H}_2\text{SO}_4$  at 100° converts (IV) or (V) into fluorenone-1:2-dicarboxylic acid (VI), m.p. 330° (*Me* ester, m.p. 199°; *Me* *H* ester, m.p. about 230° and m.p. 315—320° after resolidification at 235—240°; anhydride, m.p. 315—320°), decarboxylated by Cu powder in quinoline at 150—160° and then at 200—210° to fluorenone-2-

carboxylic acid, m.p. 330° (*Me* ester, m.p. 186°). For purposes of comparison, diphenyl-2:3:2'-tricarboxylic acid (VI) is converted by conc.  $\text{H}_2\text{SO}_4$  at 150—160° into fluorenone-1:5-dicarboxylic acid, decarboxylated to fluorenone-1-carboxylic acid, m.p. 191—192° (*Me* ester, m.p. 89°). (V) and  $\text{NHPh}\cdot\text{NH}_2$  in boiling  $\text{EtOH}$  gave the corresponding phenylhydrazone, m.p. 305—307° (corresponding anhydride, m.p. 315°), and the phenylhydrazone of fluorenone-1:2-dicarboxyanilinoimide, m.p. 276° (decomp.). Oxidation of (IV) with alkaline  $\text{KMnO}_4$  gives (III), which is reduced by Zn in ammoniacal solution to 4-phenylantracene-1-carboxylic acid, m.p. 246—247°, decarboxylated by Cu in quinoline at 140—160° to 1-phenylantracene, m.p. 110—112°. Oxidation of (II) with  $\text{CrO}_3$  in  $\text{AcOH}\cdot\text{H}_2\text{SO}_4$  gives a product,  $\text{C}_{23}\text{H}_{14}\text{O}_2\cdot\text{CrO}_3$ , decomp. about 150°. Satisfactory oxidation of (II) by  $\text{CrO}_3$  in  $\text{AcOH}$  is secured if  $\text{H}_2\text{SO}_4$  is omitted and the change is allowed to proceed very vigorously, whereby small amounts of (III) and, mainly, 1:2-3:4-dibenzoxanthonecarboxylic acid (VII), m.p. 296—305° (decomp.), are produced. (VII) is neutral in cold solution, but readily yields the *Na*



salt ( $+3\text{H}_2\text{O}$ ) with boiling alkali or alkali carbonate. The *Me* ester (VIII) has m.p. 217°. (VII) is unattacked by boiling conc.  $\text{H}_2\text{SO}_4$  but is transformed by a large excess of boiling 20%  $\text{NaOH}$  into 9-*o*-hydroxybenzoylfluorene-1:9-dicarboxylic acid, m.p. 210—212° (decomp.), which gives a red colour with  $\text{FeCl}_3$ . Oxidation of (VII) with  $\text{KMnO}_4$  of differing concn. usually gives (VI) but under certain conditions  $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  is isolable. Distillation of (VII) with Zn powder affords phenanthrene and 1:2-3:4-dibenzoxanthone (IX), m.p. 207—209°, together with  $\text{C}_6\text{H}_6$  and traces of  $\text{Ph}_2$  and  $\text{PhOH}$ . (IX) is very resistant towards oxidation but, under drastic conditions, is transformed by  $\text{KMnO}_4$  into diphenic acid. Distillation of (IX) over Zn powder affords mainly phenanthrene. Treatment of (IX) with  $\text{KOH}\cdot\text{EtOH}$  at 180° gives 9-hydroxy-10-*o*-hydroxybenzoylphenanthrene, m.p. 152°, readily re-converted into (VIII), whilst molten  $\text{KOH}$  at 250—280° gives  $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$  and 9-hydroxyphenanthrene.

**Action of alkali on acylated ketoximes.** II. Steric hindrance to alkaline hydrolysis. A. H. BLATT and R. P. BARNES. III. Hydrogen bond formation in derivatives of *o*-hydroxybenzophenoneoximes. A. H. BLATT and L. A. RUSSELL (J. Amer. Chem. Soc., 1936, 58, 1900—1902, 1903—1908; cf. A., 1935, 1125).—II. Under conditions causing hydrolysis of  $\text{CPh}_2\cdot\text{N}\cdot\text{OBz}$ , and  $\alpha$ -*p*-chloro-, m.p. 114—115°,  $\alpha$ -*p*-methoxy-, m.p. 115—116°, and



$\beta$ -*p*-methoxy-, m.p. 85—86°, -benzophenoneoxime benzoates to oxime (and EtOBz), benzophenone-, m.p. 136—137°, and  $\alpha$ -*p*-chloro-, m.p. 101—102°,  $\alpha$ -*p*-methoxy-, m.p. 102—103°, and  $\beta$ -*p*-methoxy-, probably dimorphous, m.p. 75° and 120—121°, -benzophenoneoxime 2:4:6-trimethylbenzoates are unaffected (by cold aq. EtOH-NaOH), owing to steric hindrance effects; the latter esters are hydrolysed by EtOH-conc. HCl to  $s$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·CO<sub>2</sub>H and the original COAr<sub>2</sub>. The above production of EtOBz is due to the preliminary addition of EtOH, viz.,  $\text{CAr}_2\text{:N}\cdot\text{OBz} \rightarrow \text{CAr}_2\text{:N}\cdot\text{O}\cdot\text{CPh(OH)(OEt)} \rightarrow \text{CAr}_2\text{:N}\cdot\text{OH} + \text{EtOBz}$ ; this view is confirmed by the formation of  $p$ -C<sub>6</sub>H<sub>4</sub>Ph·CO<sub>2</sub>Me from acetoxime *p*-phenylbenzoate, m.p. 132—133°, and cold aq. MeOH-NaOH.  $\alpha$ -Benzoinoxime 2:4:6-trimethylbenzoate, m.p. about 92° (unstable), is cleaved by aq. 5% NaOH or aq. EtOH-Na<sub>2</sub>CO<sub>3</sub> to PhCHO, PhCN, and  $s$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>·CO<sub>2</sub>H;  $\beta$ -benzoinoxime 2:4:6-trimethylbenzoate, m.p. 151°, is similarly unaffected, but with aq. EtOH-NaOH the same fission products result. The mechanism of the cleavage process, which is unaffected by steric hindrance, is discussed; it is a modification of that proposed by Mills (Chem. and Ind., 1932, 750) for aldoxime acetates. The above acyl derivatives are all prepared from the requisite oxime and acyl chloride in C<sub>5</sub>H<sub>5</sub>N at room temp.

III. It is suggested (cf. above) that cleavage of acylated  $\alpha$ -benzoinoximes (A), OH·CHPh·CPh·N·O·COR, is a consequence of chelation between the H of the OH and the unshared electron pair on the N; such chelation cannot occur in the  $\beta$ -series owing to the difference in configuration.  $\alpha$ -Benzoinoxime acetate is considered to be chelated since the infra-red absorption curve, compared with that of the  $\beta$ -acetate, shows marked suppression of OH absorption (cf. Hilbert *et al.*, this vol., 703). Examination of the acetates of *o*-hydroxy- and 2-hydroxy-5-methyl-benzophenoneoximes shows that chelation can take place; its occurrence is accompanied by reactions comparable with those of (A). The acetates, m.p. 96—97° (I) and 156° (II), of *syn*-(III) and *anti*-(IV) -*o*-hydroxybenzophenoneoximes (modified prep.; cf. Kohler and Bruce, A., 1931, 732) are hydrolysed by an excess of cold 5% NaOH to (III) and (IV), respectively; with aq. EtOH-Na<sub>2</sub>CO<sub>3</sub>, (I) gives 1-phenylbenzoxazole (V) [i.e., a reaction equiv. to cleavage of (A)], whilst (II) affords (IV). Pyrolysis of (I) in a vac. occurs smoothly and gives 2-phenylbenzisooxazole (VI); (II) similarly undergoes much charring and yields (probably) a little of (V) and (VI) (isolable). The acetate (VII), m.p. 125—126°, of *syn*-2-hydroxy-5-methylbenzophenoneoxime (VIII) (modified prep.) is converted by (a) 5% NaOH into (VIII), (b) aq. EtOH-Na<sub>2</sub>CO<sub>3</sub> into 1-phenyl-4-methylbenzoxazole (IX), and (c) pyrolysis into 2-phenyl-4-methylbenzisooxazole (X), m.p. 92—93°, the acetate (XI), m.p. 157—158°, of *anti*-2-hydroxy-5-methylbenzophenoneoxime (XII), m.p. 136—137°, similarly gives (a) (XII), (b) (XII), and (c) a little of (IX) and (X) (isolable). (XII) is formed when (VIII) is heated with 40% NaOH, whilst (X) is also obtained by successive oximation and action of alkali on the mixture of 2-chloro-5-methyl- and 5-chloro-2-methylbenzophenones prepared (method: Heller, A., 1913,

i, 631) from  $p$ -C<sub>6</sub>H<sub>4</sub>MeCl. (XII) and PCl<sub>5</sub> in Et<sub>2</sub>O give 5:2-OH·C<sub>6</sub>H<sub>3</sub>Me·CO·NHPH.

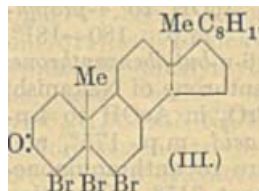
The infra-red absorption curves for (I) and (VII), unlike those for (II) and (XI) (data now given), do not show OH absorption. (I) and (VII) are much more sol. in CCl<sub>4</sub>, and much less sol. in EtOH, than (II) and (XI). These data show that (I) and (VII) are chelated.

H. B.

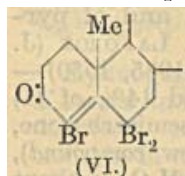
**Interconversion of mixed benzoin. H. H. WEINSTOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1936, 58, 1986—1988).**—A difficultly separable equilibrium mixture of 2:4:6- (I) and 2':4':6'- (II) -trimethylbenzoin [mesitylphenyl- and benzoyl-mesityl-carbinol, respectively] is obtained when either (I) or (II) is heated with aq. EtOH-NaOAc. Interconversion probably occurs through the intermediate  $\alpha\alpha'$ -dihydroxy-2:4:6-trimethylstilbene, i.e., the enediol; this view is supported by the following results. (I) and (II) with BzCl in C<sub>5</sub>H<sub>5</sub>N at 80° give a single benzoate, m.p. 127—127.5° [probably that of (I)], hydrolysed (EtOH-KOH) to 2:4:6-trimethylbenzil (III). The Na<sub>2</sub> derivative (IV) from (III) with BzCl affords  $\alpha\alpha'$ -dibenzoyloxy-2:4:6-trimethylstilbene, two forms, m.p. 138.5—139° (V) and 169.5—170° (VI); (V) heated above its m.p. undergoes quant. conversion into (VI), whilst hydrolysis (EtOH-KOH) of (VI) gives (I) and (III). (I) and Ac<sub>2</sub>O-NaOAc for 5 hr. yield the acetate, m.p. 73—73.5°; the same treatment of (II) [and more prolonged treatment of (I)] affords  $\alpha\alpha'$ -diacetoxy-2:4:6-trimethylstilbene, m.p. 104—104.5°, also prepared from (IV) and AcCl. (I) and (II) heated with a little I at 200—220° or in AcOH undergo disproportionation to (III) and Ph 2:4:6-trimethylbenzyl ketone. All reactions are carried out in N<sub>2</sub>. (I) and (II) react with MgMeI in the enediol form to the extent of 78 and 30%, respectively.

H. B.

**Bromination of  $\Delta^5$ -cholestenone dibromide. A. BUTENANDT and G. SCHRAMM (Ber., 1936, 69, [B], 2289—2299).**—Cautious oxidation of cholesterol dibromide (I) with CrO<sub>3</sub> affords  $\Delta^5$ -cholestenone dibromide (II), m.p. 80°, converted by Br<sub>2</sub> (1 mol.) in AcOH into 4:5:6-tribromo- (III), m.p. 106° (decomp.), which is brominated further to 4:4:5:6-tetra-bromo-cholestanone (IV), m.p. 128° (decomp.), also obtained directly from (II). Generally it appears that 3-keto-sterol derivatives in which rings A and B are united in the same manner as in *cis*-decahydronaphthalene are brominated at 4, and those in which the arrangement is as in *trans*-decahydronaphthalene react at 2. It is assumed that the rule can be applied to the determination of configuration, and that rings A and B in (I) are probably united in the *cis*-position. The constitution of (III) rests on the following observations. It is debrominated by Zn and AcOH to  $\Delta^4$ -cholestenone and by NaI in EtOH to a non-cryst. heterogeneous product containing >1 Br per mol. and converted by KOAc in AcOH at 200° into cholestane-3:6-dione. When treated with NaI in EtOH-C<sub>6</sub>H<sub>6</sub> (conc. solu-



tion) (III) gives cholestenedione Et ether; it is therefore stereoisomeric with the  $\text{Br}_3$ -ketone (V) of Inhoffen (this vol., 854, 1104). The structure of (IV) follows from its transformation by KOAc in BuOH into  $\Delta^5$ -cholestene-3:4-dione, m.p.  $159^\circ$  (quinoxaline derivative, m.p.  $175^\circ$ ), the constitution of which (cf. Inhoffen, *loc. cit.*) is confirmed by its oxidation to the 7-keto-dicarboxylic acid,  $\text{C}_{27}\text{H}_{42}\text{O}_5$ , m.p.  $215$ — $216^\circ$ . The possibility of confirming the constitution



(IV) by its production by bromination of (V) is excluded since the latter is transformed by Br in AcOH or  $\text{Et}_2\text{O}$  into an  $\alpha\beta$ -unsaturated  $\text{Br}_3$ -ketone (VI), m.p.  $163^\circ$ , also obtained from (IV) in warm EtOH. Further proof of the structure of (IV) is afforded

by its transformation by NaI in boiling abs. EtOH into 4-bromo-6-ethoxy- $\Delta^4$ -cholesten-3-one, m.p.  $110$ — $111^\circ$  (decomp.), and thence by KOAc in boiling BuOH into cholestenedione Et ether.

H. W.

**Constitution of benzoylformoin.** R. SCHOLL (Ber., 1936, 69, [B], 2288; cf. this vol., 606).—The lactol ether formula of benzoylformoin has been advanced previously by Blatt (A., 1935, 982).

H. W.

**So-called "valency tautomerism" of unsaturated systems.** B. EISTERT (Ber., 1936, 69, [B], 2393—2398).—An explanation of the constitution of tetraphenyldimethylenediphenoquinone, tetraarylnodimethanes, and 4:4'-disubstituted dipyrindyls along the lines of mesomerism is advanced; this harmonises with Müller's magneto-chemical observations.

H. W.

**Reduction potential of some naphthaquinones.**—See this vol., 1467.

**Preparation of fluoroaminoanthraquinone.**—See B., 1936, 1083.

**Linear pentacene.** C. MARSCHALK (Bull. Soc. chim., 1936, [v], 3, 2155—2158; cf. this vol., 1256).—6:13-Dihydroxypentacene-5:14:7:12-diquinone (I) is obtained by cyclisation of 1:4-dihydroxy-2-benzoylanthraquinone-3-carboxylic acid (obtained by condensation of 1:4-dihydroxyanthraquinone-2:3-dicarboxylic anhydride with  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$ ), by cautious oxidation of the substance (II) obtained (*loc. cit.*) from  $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$  and leucoquinizarin, and by oxidation of the Ac derivative of (II) with  $\text{PbO}_2$  or  $\text{CrO}_3$  in boiling AcOH and hydrolysis of the product. (II) is therefore 5:6:13:14-tetrahydroxypentacene-7:12-quinone. The relationship between (I) and (II) is similar to that between quinone and quinol. Oxidation of (I) or (II) by  $\text{Pb}(\text{OAc})_4$  in AcOH at  $50$ — $60^\circ$  gives pentacene-5:14:6:13:7:12-triquinone, reduced by  $\text{N}_2\text{H}_4$  or  $\text{Na}_2\text{S}_2\text{O}_4$  to (II), by  $\text{SO}_4$  to (II) and then to (I) by KI in cold AcOH to (I).

H. W.

**Comparison of the rate of racemisation with the rate of enolisation [of *l*-menthyl *d*- $\alpha$ -phenylacetoacetate].** R. H. KIMBALL (J. Amer. Chem. Soc., 1936, 58, 1963—1970; cf. Rupe *et al.*, A., 1913, i, 266, 884).—The pseudo-unimol. velocity coeffs. for (i) the racemisation (of Cx) and (ii) the enolisation of *l*-menthyl *d*- $\alpha$ -phenylacetoacetate (I) in cyclohexane (in which enolisation is 71% complete at

equilibrium) containing 8—12 p.p.m. of piperidine are determined polarimetrically and by direct Br-titration, respectively; (i) proceeds several times as fast as (ii). Polarimetric determination of the rate for *d*-keto  $\rightarrow$  enol gives a val.  $>$  that obtained by titration, indicating that enolisation proceeds through an intermediate (II) (which subsequently changes partly to the enol and partly to the *dl*-keto-form). (II) may be the intermediate anion which has lost its asymmetry; alternatively, reversible formation of a little open-chain enol, followed by a slower accumulation of chelated enol, may occur.

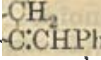
(I), prepared from *l*-menthol and  $\text{CHPhAc}\cdot\text{CO}_2\text{Et}$  (improved prep.) at  $150$ — $160^\circ$  followed by distillation and slow evaporation of a MeOH-solution of the resulting oil, has m.p.  $77$ — $78.3^\circ$  (in Pyrex glass) (lit.  $69^\circ$ ),  $[\alpha]_D^{25}$  (in cyclohexane)  $-15.84^\circ \rightarrow -59.83^\circ$ ,  $[\alpha]_{5461} + 21.9^\circ$  in MeOH (cf. *loc. cit.*). Equilibration of (I) with a trace of  $\text{Ba}(\text{OH})_2$  and subsequent slow distillation (Hickman mol. still) at  $85$ — $95^\circ$  gives a product (64% enol), which on repeated fractionation in absence of catalyst affords a const.-boiling mixture containing 93.8% of enol. The pure enol (*i.e.*, menthyl  $\beta$ -hydroxy- $\alpha$ -phenylcrotonate) is calc. to have  $[\alpha]_D^{25} -56.5^\circ$  in cyclohexane.

H. B.

[True constitution of camphenilyl and 4-methylcamphenilyl chloride.] P. LIPP and J. DANIELS (Ber., 1936, 69, [B], 2251—2252).—Difficulties in conception of the structure of camphenilyl chloride are removed by considering that it,  $\alpha$ - and  $\beta$ -fenchocamphoryl chloride are to one another in the relationship of an equilibrium isomerism (cf. Komppa *et al.*, this vol., 1258).

H. W.

**Benzylidenecamphane**, a product of the dehydration of tertiary benzylbornyl alcohol. S. S. NAMETKIN and M. K. STRUGAZKI (Ber., 1936, 69, [B], 2272—2277).—The main product of the dehydration of benzylbornyl alcohol by  $\text{KHSO}_4$ , aq. and anhyd.  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HCO}_2\text{H}$ , 50%  $\text{H}_2\text{SO}_4$ , or anhyd.  $\text{CuSO}_4$  is the cryst. hydrocarbon, m.p.  $25^\circ$ , which, contrary to Haller and Bauer (A., 1906, i, 440), is identified as benzylidenecamphane,

$\text{C}_8\text{H}_{14}$   since it is oxidised by  $\text{KMnO}_4$  to camphor, camphoric acid, and BzOH. It is indifferent towards AcOH and  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ . It is obtained synthetically from phenylbornylcarbinol, b.p.  $169$ — $170^\circ/15$  mm. (prep. from Mg bornyl chloride and PhCHO), which is treated with K in dry PhMe followed successively by  $\text{CS}_2$  and MeI and decomp. of the ester so produced.

H. W.

**Stereoisomerism in the fenchol series.** H. SCHMIDT and L. SCHULZ (Ber. Schimmel, 1935, 97—99; Chem. Zentr., 1936, i, 350—351).—As in the borneol series there are two stereoisomeric optically inactive fenchyl alcohols which, on oxidation, give rise to only one *dl*-fenchone. Hydrogenation (Ni) of *dl*-fenchone yields *dl*- $\beta$ -fenchyl alcohol, b.p.  $200.5^\circ/750$  mm., f.p.  $6.3^\circ$  (formate; acetate; phenylurethane, m.p.  $90$ — $90.5^\circ$ ; *H* phthalate, m.p.  $153$ — $153.5^\circ$ ). *dl*- $\alpha$ -Fenchyl alcohol, prepared by reduction of *dl*-fenchone with Na-EtOH, has m.p.  $38^\circ$ , b.p.  $199.5^\circ/750$  mm. (phenylurethane, m.p.  $104^\circ$ ; *H* phthalate, m.p.  $169^\circ$ ). The following are obtained



similarly: *l*- $\alpha$ -fenchyl alcohol (from *d*-fenchone), m.p. 48°,  $[\alpha]_D^{20}$  -11° in EtOH; *d*- $\alpha$ -fenchyl alcohol (from *l*-fenchone), m.p. 47°,  $[\alpha]_D^{20}$  +11.5° in EtOH (*phenylurethane*, m.p. 81°; *H phthalate*, m.p. 145.5°); *l*- $\beta$ -fenchyl alcohol (from *d*-fenchone), m.p. 5–6°, b.p. 200.5°/750 mm.,  $[\alpha]_D^{20}$  -21.7° in EtOH (*phenylurethane*, m.p. 89–90°); *d*- $\beta$ -fenchyl alcohol (from *l*-fenchone),  $[\alpha]_D^{20}$  +21.8° in EtOH (*phenylurethane*, m.p. 89°; *H phthalate*, m.p. 151°). By analogy with borneol,  $\alpha$ -fenchyl alcohol is assigned the *exo*- and  $\beta$ -fenchyl alcohol the *endo*-configuration.

H. N. R.

**Degradation of fenchone in the animal organism.** F. REINARTZ and W. ZANKE (Ber., 1936, 69, [B], 2259–2262).—*d*-Fenchone is administered to dogs and the paired glycuronic acid is separated from the urine as the Pb salt, which is treated with 15%  $H_2SO_4$ ; the filtrate from the  $PbSO_4$  is boiled with  $H_2O$ , thereby giving a mixture (I) of hydroxyfenchones which could not be separated into its components by crystallisation or through the *p*-nitrobenzoates. (I) is therefore oxidised with  $CrO_3$  followed by  $KMnO_4$ , thus giving 5-ketofenchone, m.p. 36°, Rimini's 4-hydroxyfenchone, m.p. 79–80° (3:5-dinitrobenzoate, m.p. 144–146.5°), and  $\alpha$ -apofenchone-3-carboxylic acid, m.p. 120.5–122° (*Ag* salt), decarboxylated to fenchosantenone. 5-Ketofenchonedisemicarbazone has m.p. 243.5°.

H. W.

**$\beta$ -Myrcene.** Reduction with sodium and alcohol. G. DUPONT and V. DESREUX (Compt. rend., 1936, 203, 623–625).— $\beta$ -Myrcene, b.p. 72–73°/25 mm., free from  $\alpha$ -myrcene, with Na in EtOH affords a  $H_2$ -derivative (I), b.p. 62–63°/18–20 mm. (cf. A., 1901, i, 732), apparently identical with a reduction product (II) of  $\beta$ -geraniol. The Raman spectrum of (I) exhibits a line of frequency 1648  $cm^{-1}$ , not shown by (II), probably due to a terminal double linking. It is probable that reduction at the linking outside the conjugated system in  $\beta$ -myrcene is a less marked subsidiary reaction and may account for the marked differences in the physical consts. of (I) and (II) (cf. A., 1929, 538).

J. L. D.

**Polyterpenes and polyterpenoids. CVII.** Transformation of gypsogenin (alsapogenin) into oleanolic acid. L. RUZICKA and G. GIACOMELLO (Helv. Chim. Acta, 1936, 19, 1136–1140).—Fractional crystallisation of crude gypsogenin gives a product, m.p. about 270°, which does not appear homogeneous under the fluorescence microscope and gives analytical data in harmony with a  $C_{30}$  formula. It is converted by boiling  $Ac_2O$  and  $NaOAc$  into a more freely sol. acetate (I),  $C_{32}H_{48}O_5$ , m.p. 176–177°,  $[\alpha]_D^{20}$  +78° in  $CHCl_3$ , and a more sparingly sol. acetate,  $C_{32}H_{48}O_5$ , m.p. 262°,  $[\alpha]_D^{20}$  +65° in  $CHCl_3$ , (I) gives a yellow colour with  $C(NO_2)_4$ , is converted by  $CH_2N_2$  in  $Et_2O$  into the *Me* ester,  $C_{33}H_{50}O_5$ , m.p. 186°, and by Br in  $MeOH-CHCl_3$  into the *Br*-lactone,  $C_{32}H_{47}O_5Br$ , m.p. 180–181° (decomp.). The semicarbazone, m.p. (indef.) 140–160° and m.p. 274° (decomp.) after re-solidification, is transformed by  $NaOEt$  in EtOH at 160–170° into oleanolic acid, m.p. 304–306°,  $[\alpha]_D^{20}$  +76.9° in  $CHCl_3$ .

H. W.

**Helenalin.** I. Helenalin, the bitter sternutative substance occurring in *Helenium autumn-*

*nale*. E. P. CLARK (J. Amer. Chem. Soc., 1936, 58, 1982–1983).—Details are given for the isolation of helenalin,  $C_{15}H_{18}O_4$ , m.p. 167°,  $[\alpha]_D^{20}$  -101.9° in 95% EtOH (*Ac*, m.p. 184°, and *methoxyacetyl*, m.p. 135°, derivatives; *dibromide*, 161°), which is reduced ( $H_2$ ,  $PtO_2$ ,  $EtOAc$ ) to tetrahydrohelenalin, m.p. 176° (*Ac* derivative, m.p. 145°).

H. B.

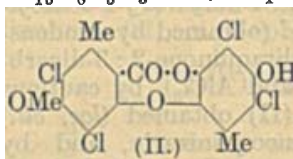
**Constituents of pyrethrum flowers. IV. Semicarbazones of pyrethrins I and II and of pyrethrolone.** H. L. HALLER and F. B. LAFORGE (J. Org. Chem., 1936, 1, 38–51; cf. A., 1935, 1550).—Pyrethrin I concentrate (45% of I and 14% of II) gives, best in  $C_6H_5N$ , the nearly pure I-semicarbazone, m.p. about 118° (in  $CCl_4$  gives a new compound), which affords by hydrolysis with aq.  $H_2C_2O_4$  about 30% of pyrethrin I, partly changed by distillation at 175–180°/2 mm. A pyrethrin II concentrate (81% of II) gives, best in  $C_6H_5N$ , the II-semicarbazone, m.p. 164–165°, hydrolysed by aq.  $H_2C_2O_4$  to free II (30% yield), which is highly toxic to flies and decomposes when distilled in a vac., giving thereafter a poor yield of a different semicarbazone. Pyrethrolonesemicarbazone (A),  $C_{12}H_{17}O_2N_3$  (lit.  $H_{19}$ ), m.p. 208° (decomp.), is obtained from pyrethrolone (B) or the I- or II-semicarbazones and  $NaOMe$ . The II-semicarbazone with  $H_2-PtO_2$  in  $EtOAc$  gives a tetrahydro-semicarbazone,  $C_{23}H_{35}O_5N_3$ , m.p. 141–142° (also obtained by hydrogenation of free II), which with  $NaOMe$  affords tetrahydropyrethrolonesemicarbazone,  $C_{12}H_{21}O_2N_3$ , m.p. 196° (decomp.), also obtained by hydrogenation (4 H absorbed) of (A). The formula of (B) thus is revised. Chrysanthemum acid is best characterised by its *p*-phenylphenacyl, m.p. 65°, chrysanthemumdicarboxylic acid by its *di*-*p*-phenylphenacyl ester, m.p. 154°.

R. S. C.

**Constituents of lichens found in Ireland. Buellia canescens.** II. P. A. SPILLANE, J. KEANE, and T. J. NOLAN (Sci. Proc. Roy. Dublin Soc., 1936, 21, 333–343; cf. A., 1935, 133).—A compound,  $C_{15}H_8O_5Cl_3 \cdot OMe$ , m.p. 257°, is isolated in small amount from *B. canescens* (I). The ratio of chlorinated to unchlorinated atranorin varies in different lichens, being 9:1 in (I), 4:1 in *Lecanora gangaleoides*, and 35:65 in *L. sordida*. The difficulty of determining OMe in lichen products is confirmed. Diploicin (II),  $OH \cdot C_{15}H_6O_3Cl_4 \cdot OMe$  (*K* salt), with  $CH_2N_2$  gives an ether,  $C_{15}H_6O_3Cl_4(OMe)_2$ , m.p. 220°, which with  $KOH-MeOH$  gives the phenolic ester,  $OH \cdot C_{14}H_6OCl_4(OMe)_2 \cdot CO_2Me$ , m.p. 143°, sol. in 2% aq.  $KOH$ . With  $KOH-MeOH$  (II) affords the phenolic ester,  $OMe \cdot C_{14}H_6OCl_4(OH)_2 \cdot CO_2Me$ , m.p. 200°, which with  $CH_2N_2$  gives the ether,  $C_{14}H_6OCl_4(OMe)_3 \cdot CO_2Me$ , m.p. 97°, hydrolysed by 15%  $KOH-MeOH$  to the acid,  $C_{14}H_6OCl_4(OMe)_3 \cdot CO_2H$ , m.p. 160–161°. (II) is probably as annexed.

R. S. C.

**Yellow pigment from Sake-Kasu (sake grains).** T. HIGASHI (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 1060–1076).—*Flazine* (I),  $C_{18}H_{16}O_5N_2$ , m.p. 218–220° (decomp.) [*hydrochloride*, + $H_2O$ ; *hydr-*



iodide, unstable; (?)  $\text{NO}_2$ -derivative,  $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}_2\cdot\text{NO}_2\cdot\text{H}_2\text{O}$ , is isolated in 0.001% yield from sake grains. In EtOH,  $\text{COMe}_2$ , or acid it shows a strong yellow-green fluorescence, destroyed by alkali. (I) resinifies in air and resembles lactoflavin, but has less vitamin- $\text{B}_2$  activity. Absorption spectra, reduction potential, and fluorescence indicate phenazine structure. On oxidation (I) gives a substance,  $\text{C}_{17}\text{H}_{12}\text{O}_5\text{N}_2$ , and on dehydration a substance,  $\text{C}_{36}\text{H}_{30}\text{O}_9\text{N}_4$ . R. F. P.

**Hydrogenation value of violaxanthin.** P. KARRER and U. SOLMSEN (Helv. Chim. Acta, 1936, 19, 1024—1025).—Hydrogenation of purified violaxanthin in AcOH or EtOH-AcOH causes absorption of 9.5—10  $\text{H}_2$ . It therefore contains 10 rather than 11 double linkings. This harmonises with spectroscopic evidence which is compatible with the presence of 11 double linkings only if two ethylenic linkings are assumed to be outside conjugation. H. W.

**Bitter principles of Colombo root.** IV. **Hydrogenation of columbin and isocolumbin.** F. WESSELY, A. MUNSTER, and K. SCHONOL [with, in part, W. ISEMAN] (Monatsh., 1936, 68, 313—325; cf. this vol., 610, 995).—Columbin (I) (improved isolation),  $[\alpha]_D +52.2^\circ$ , is  $\text{C}_{10}\text{H}_{22}\text{O}_6$ ; decarboxycolumbin (II),  $\text{C}_{19}\text{H}_{22}\text{O}_4$ , has m.p. 148—149°. Hydrogenation (Pd-sponge in MeOH) of (I) gives a product in which the second group of (I) which reacts with hot alkali is not present. Reaction is not accompanied by loss of  $\text{CO}_2$ , and gives mainly a mixture of stereoisomeric octahydrocolumbic acids (III) which could not be obtained cryst., but from which after treatment with  $\text{CH}_2\text{N}_2$  a cryst. Me ester, m.p. 124—131°,  $[\alpha]_D -18.7^\circ$ , is isolated and a neutral product,  $\text{C}_{20}\text{H}_{28}\text{O}_6$ , probably a mixture of saturated lactones. The view that 2 O of the 6 O of (I) are present in a normal lactone ring containing at least one double linking is confirmed, but the hypothetical presence of a second lactone ring is discarded, particularly in view of the behaviour of (III) towards Zerevitinov's reagent. Hydrogenation of (II) gives a mixture of stereoisomeric octahydrodecarboxycolumbic acids. Hydrogenation establishes that (I) contains three double linkings, whereas in (III) 2 O and O are present in  $\text{CO}_2\text{H}$  and OH, respectively, and the function of the remaining 3 O is unknown. isocolumbin is hydrogenated to a non-cryst. mixture of stereoisomeric acids from which a non-homogeneous, cryst. Me ester is isolated which contains 1 OH (Zerevitinov). H. W.

**Reaction of lignin and vanillin.** P. FOURMENT and H. ROQUES (Bull. Sci. pharmacol., 1935, 42, 449—451; Chem. Zentr., 1936, i, 601).—Vanillin, in addition to plant tissues containing lignin, gives a red coloration with benzidine in AcOH solution.

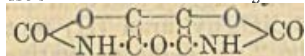
H. N. R.  
**Lignin.** VIII. **Thioglycollic acid as a reagent for lignin.** B. HOLMBERG (Ing. Vet. Akad. Handl. No. 131, 81 pp.); Chem. Zentr., 1936, i, 93—94).—In presence of acid lignin combines with thioglycollic to give a sparingly sol. compound. Application of this reaction to a no. of plant species is described. A. G. P.

**Hydroxyfurans.** II. **3-Hydroxy-2:5-diphenylfuran.** E. P. KOHLER and D. W. WOODWARD (J. Amer. Chem. Soc., 1936, 58, 1933—1936).—Successive treatment of 3-acetoxy-2:5-diphenylfuran (I) (Lutz, A., 1927, 61) with  $\text{MgMeI}$  and cold dil.  $\text{H}_2\text{SO}_4$  gives 3-hydroxy-2:5-diphenylfuran (II) (not isolable), which resembles the 2:4:5- $\text{Ph}_3$  derivative (this vol., 479). (II) (in  $\text{Et}_2\text{O}$ ) and  $\text{O}_2$  afford the 2:3-peroxide, explodes about  $100^\circ$ , which is reduced by AcOH-KI to 3:3'-diketo-2:5:2':5'-tetraphenyl-2:3:2':3'-tetrahydro-2:2'-difuryl, m.p.  $255^\circ$ , and catalytically to  $\alpha\beta\delta$ -triketo- $\alpha\delta$ -diphenylbutane (Lutz et al., A., 1934, 1222). Hydrolysis (dil.  $\text{H}_2\text{SO}_4$  in AcOH and  $\text{N}_2$ ) of (I) gives the unstable 3-keto-2:5-diphenyl-2:3-dihydrofuran, m.p.  $93^\circ$ , i.e., the ketonic form of (II). (I) and  $\text{Cl}_2$  or  $\text{PCl}_5$  afford 2-chloro-3-keto-2:5-diphenyl-2:3-dihydrofuran (III), m.p.  $133^\circ$  (the 2-Br-derivative has m.p.  $135^\circ$ ), converted by boiling MeOH and EtOH into the 2-OMe- and 2-OEt-derivatives [cf. Lutz et al. (loc. cit.)], who formulate them as open-chain compounds]. Maleic anhydride, PhBr, and  $\text{AlBr}_3$  in  $\text{C}_2\text{H}_5\text{Br}_4$  at  $<50^\circ$  give  $\beta$ -p-bromobenzoylacrylic acid, m.p.  $161^\circ$ , the chloride, m.p.  $103^\circ$ , of which with  $\text{C}_6\text{H}_6$  and  $\text{AlCl}_3$  in  $\text{N}_2$  affords  $\alpha$ -benzoyl- $\beta$ -p-bromobenzoyl ethylene, m.p.  $127^\circ$ , also obtained from  $\text{COPh}\cdot\text{CHO}$  and p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{COMe}$  in  $\text{Ac}_2\text{O}$ . This and Br in  $\text{CHCl}_3$  yields dibromides, m.p.  $116$ — $119^\circ$  and  $170$ — $175^\circ$  (decomp.), a mixture of which is converted by MeOH-KOH, followed by MeOH-HCl, into 3-keto-2-methoxy-2-phenyl-5-p-bromophenyl- (IV), m.p.  $158^\circ$ , and 5-phenyl-2-p-bromophenyl- (V), m.p.  $102^\circ$ , -2:3-dihydrofurans. (IV) (ozonolysis products, p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$  and MeOBz) is hydrolysed (MeOH-KOH) to  $\alpha\beta\delta$ -triketo- $\alpha$ -phenyl- $\delta$ -p-bromophenylbutane, m.p.  $100$ — $101^\circ$  [oxidised (30%  $\text{H}_2\text{O}_2$ , MeOH-KOH) to p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{COMe}$ , p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ , and BzOH], whilst (V) (ozonolysis products (p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{Me}$  and BzOH) similarly gives  $\alpha\beta\delta$ -triketo- $\delta$ -phenyl- $\alpha$ -p-bromophenylbutane, m.p.  $88$ — $90^\circ$  (oxidised to  $\text{COPhMe}$ , BzOH, and p- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ ). The 3:4-diacetoxy- and 3-chloro-4-acetoxy-2:5-diphenylfurans of Lutz et al. (loc. cit.) are 3-keto-2-acetoxy-2:5-diphenyl-2:3-dihydrofuran, m.p.  $140^\circ$ , and (III), respectively; the  $\alpha$ -chloro- $\gamma\delta$ -diketo- $\alpha\delta$ -diphenyl- $\Delta^2$ -butene of Lutz and Wilder (A., 1934, 1361) is also (III). H. B.

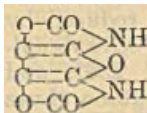
**Hydrazide and azide of 3:4-dihydroxyfuran-2:5-dicarboxylic acid.** A. DARAPSKY and M. STAUBER (J. pr. Chem., 1936, [ii], 146, 209—218).—Treatment of  $\text{Me}_2$  3:4-dihydroxyfuran-2:5-dicarboxylate (I) with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  in EtOH gives the dihydrazine salt,  $\text{C}_8\text{H}_8\text{O}_7\cdot\text{N}_2\text{H}_4$ , m.p. (indef.)  $168^\circ$  (decomp.). With boiling  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (I) yields the monohydrazine salt, decomp.  $>200^\circ$ , of 3:4-dihydroxyfuran-2:5-dicarbonyldihydrazide, m.p.  $>260^\circ$  after darkening at  $200^\circ$  [dihydrochloride, blackens at  $260^\circ$  after becoming discoloured at  $170$ — $220^\circ$ ; dipicrate, gradual decomp. at about  $205^\circ$  after becoming brown at  $180^\circ$ ; dibenzylidene, m.p.  $258^\circ$  (decomp.), di-o-hydroxybenzylidene, m.p.  $>270^\circ$ , dicinnamylidene, m.p.  $240^\circ$  (decomp.), and diisopropylidene, blackens at  $260^\circ$  after darkening at  $170$ — $220^\circ$ , derivatives]. 3:4-Dihydroxyfuran-2:5-dicarbonyldiazide (II), explodes at  $148$ — $149^\circ$ , is transformed by  $\text{NH}_2\text{Ph}$  in



boiling  $\text{Et}_2\text{O}$  into the salt,  $\text{C}_6\text{H}_2\text{O}_5\text{N}_6\text{NH}_2\text{Ph}$ , and by  $\text{NH}_2\text{Ph}$  at  $150^\circ$  into the *dianilide*, m.p.  $>260^\circ$ . The azide is converted by boiling  $\text{EtOH}$  into 3:4-*dihydroxyfuran-2:5-diurethane*, m.p. 147, which could not be transformed by heat into the desired dilactone



When warmed in indifferent media (II) evolves  $\text{N}_2$  and yields a solid tile-red compound which could not be purified; analyses indicate the presence of the dicarbimide but the material is odourless and does not react with  $\text{EtOH}$  so that possibly (III) is present. Attempts to hydrogenate (I) by  $\text{H}_2$ -colloidal Pd, Na-Hg, Al-Hg, or Na in boiling  $\text{EtOH}$  were unsuccessful.



(III.)

H. W.

**Electrolysis of aromatic acids. II.** Electrolysis of opianic acid. V. M. RODIONOV and V. C. ZVORYKINA (Bull. Soc. chim., 1936, [v], 3, 1836—1841; cf. this vol., 722).—Electrolysis of K opianate yields meconine, a mixture of dimeconyls, m.p. 215—230°, and resins. In a cell with diaphragm the reduction products are obtained in the cathodic division in better yield; opianic acid under the same conditions gives less impure products, without resins. Reduction by Na-Hg gives meconine and a trace of  $\alpha$ -dimeconyl. Mixed dimeconyls electrolysed, or reduced by Na-Hg, give a substance, m.p. 170—172°.

E. W. W.

**Synthesis of dehydracetic acid from ethyl acetoacetate.** F. ARNDT, B. EISTERT, H. SCHOLZ, and E. ARON (Ber., 1936, 59, [B], 2373—2380).—Irregularities in the conversion of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  into dehydracetic acid (I) (Arndt *et al.*, A., 1924, i, 1223) are traced to the influence of the containing vessel. The initial stage is the formation of  $\text{EtOH}$  and  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$  the progress of which depends on the continuous removal of  $\text{EtOH}$  [very little (I) is produced when  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  is heated (sealed) at  $<$  its b.p.]; this is followed by an irreversible Claisen condensation for which the presence of alkali is required. This is provided uncertainly by the alkali of the glass, and is best supplied by  $\text{NaHCO}_3$  in controlled amount, since the decomp. of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  into  $\text{COMe}_2$  is also accelerated thereby. The best yields are obtained with minute amounts of catalyst if the process is interrupted when about 25% of the possible  $\text{EtOH}$  has distilled; unchanged ester is distilled from the product and worked up as a fresh charge. At 300—600° the streaming vapours of  $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$  are remarkably stable in presence of  $\text{SiO}_2$ , Al, Cu, or V2A steel. Fe accelerates decomp. into  $\text{COMe}_2$ ,  $\text{CO}_2$ , gaseous and resinous products. In absence of Fe, glass or porcelain, preferably in tubes of the same material, gives good yields of pure (I) if the temp. is  $>400^\circ$ . The operation may be extended over long periods and 25% conversion is secured. The process appears generally applicable for the production of "dehydroacids" from  $\beta$ -CO-esters. Thus  $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$  gives dehydrobenzoylacetic acid,  $\text{CPh} \begin{array}{c} \diagup \text{CH}\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array} \text{CHAc}$ , m.p. 171°, converted by  $\text{H}_2\text{SO}_4$  at 138—140° into  $\text{BzOH}$  and 6-phenylpyronone, decomp. 245—246°, which with

$\text{NH}_3\cdot\text{H}_2\text{O}$  at  $120^\circ$  affords 2:4-dihydroxy-6-phenylpyridine, decomp. 315—318°. An improved prep. of 2:6-dimethylpyrone from (I) is described. Short treatment of (I) with 90%  $\text{H}_2\text{SO}_4$  at  $135^\circ$  gives 6-methylpyronone or 6-methyl-4-hydroxy-2-pyrone (II), converted by  $\text{NH}_2\text{Me}\cdot\text{H}_2\text{O}$  at  $130^\circ$  into 4-hydroxy-1:6-dimethyl-2-pyridone, decomp. 225—226°; 4-hydroxy-6-methyl-1-ethyl-2-pyridone, decomp.  $198^\circ$ , is obtained with  $\text{NH}_2\text{Et}$ . 4-Hydroxy-1-cyclohexyl-6-methyl-2-pyridone has m.p.  $108^\circ$ . (II), boiling 10N-NaOH, and  $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_4$  yield 4-hydroxy-1-p-dimethylaminophenyl-6-methyl-2-pyridone, decomp. 270—275°, whereas  $\text{NH}_2\text{Ph}$  yields a substance, m.p. 199—200°, of undetermined structure. H. W.

**Geometrical inversion in the acids derived from the coumarins. III.** *Trans-* to *cis-*. T. R. SESHADRI and P. S. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 157—161; cf. A., 1935, 211).— $\text{HgO}$  lowers the temp. of decomp. of coumaric (I), 4-methyl- (II) and 5-nitro-coumaric acid (III) to give the coumarin in  $>50\%$  yield. Similarly, with  $\text{HgCl}_2$  coumarins are formed in excellent yield; in each case the coumarin mercurichloride is isolated. (I) and (II) with conc.  $\text{H}_2\text{SO}_4$  at  $100^\circ$  give poor yields of the coumarin due to sulphonation, whereas (III) gives a 95% yield; boiling  $\text{EtOH}$  containing dry  $\text{HCl}$  decarboxylates (I) and (II) and esterifies (III).

J. L. D.

**Reactivity of the double linking in coumarins and related  $\alpha\beta$ -unsaturated carbonyl compounds. II.** Action of mercury salts on coumarins. T. R. SESHADRI and P. S. RAO (Proc. Indian Acad. Sci., 1936, 4, A, 162—169; cf. A., 1928, 298).—Coumarin with boiling  $\text{MeOH}$  containing  $\text{Hg}(\text{OAc})_2$  in excess affords 3:6:8-triacetoxymercuri-4-methoxymelilotic anhydride, converted by  $\text{H}_2\text{S}$  in  $\text{NaOH}$  into  $\beta$ -methoxymelilotic acid, m.p.  $122\text{—}123^\circ$  (cf. A., 1912, i, 461), and with  $\text{Br}$  in  $\text{AcOH}$  gives 3:6:8-tribromocoumarin. Similarly, 7-methylcoumarin affords 3:6:8-triacetoxymercuri-4-methoxy-7-methylmelilotic anhydride, decomp. at  $265^\circ$ , converted by  $\text{H}_2\text{S}$  in  $\text{NaOH}$  into 4-methylcoumaric acid, and with  $\text{Br}$  in  $\text{AcOH}$  affords 3:6:8-tribromo-7-methylcoumarin, m.p. 207—208°. 6-Nitrocoumarin similarly yields 3:8-diacetoxymercuri-6-nitro-4-methoxymelilotic anhydride, converted by  $\text{H}_2\text{S}$  in  $\text{NaOH}$  into 5-nitrocoumaric acid, and by  $\text{Br}$  in  $\text{AcOH}$  into 3:8-dibromo-6-nitrocoumarin (cf. J.C.S., 1923, 123, 3380). Coumarin and 7-methylcoumarin with  $\text{HgCl}_2$  in  $\text{COMe}_3$  afford 3-chloromercuri-4-chloro- (cf. *ibid.*, 1908, 93, 524) and 7-methyl-melilotic anhydride, respectively, decomposed by  $\text{H}_2\text{S}$  in  $\text{NaOH}$  into coumaric and 4-methylcoumaric acid, respectively. 6-Nitrocoumarin does not react with  $\text{HgCl}_2$ .

J. L. D.

**Separation of natural mixtures of anthocyanins by chromatographic adsorption analysis. II.** "Althæin." P. KARRER and H. M. WEBER (Helv. Chim. Acta, 1936, 19, 1025—1027; cf. this vol., 341).—Chromatographic analysis, using  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ , shows that althæin (Willstätter *et al.*, A., 1915, i, 287) is a mixture of monoglucosides of delphinidin 3':5'- $\text{Me}_2$  ether (syringidin), delphinidin 3'- $\text{Me}$  ether, and delphinidin. H. W.

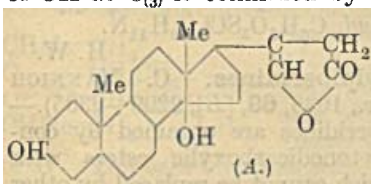
**Pigment of the corn poppy (*Papaver rhæas*, L.).** See this vol., 1572.

**Anthocyanin pigment of the winesap apple.**—See this vol., 1435.

**Constituents of the Chinese drug lei-kung-teng.**—See this vol., 1572.

**Constitution of cubebin.** R. D. HAWORTH and W. KELLY (Chem. and Ind., 1936, 901—902).—The structure  $\begin{array}{c} \text{CHX}-\text{R} \\ \text{CHX}-\text{CH}_2 \end{array} > \text{O}$  ( $\text{X} = 3:4\text{-CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{:}$ ;  $\text{R} = \text{CH}\cdot\text{OH}$ ) for cubebin (Ishiguro, this vol., 1247) is confirmed by the presence of 1 OH (Zerevitinov), semicarbazone formation, and facile oxidation to cubebinolide ( $\text{R}-\text{CO}$ ). J. W. B.

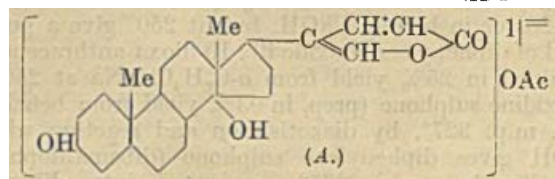
**Vegetable heart poisons. XI. Constitution of thevetin.** R. TSCHESCHE (Ber., 1936, 69, [B], 2368—2372).—Thevetin (I), gradual decomp.  $>195^\circ$ , obtained from be-still nuts (Chen *et al.*, A., 1934, 820) when dried at  $100^\circ/10$  mm. has the composition  $\text{C}_{42}\text{H}_{66}\text{O}_{18}\cdot 0.5\text{H}_2\text{O}$ , which becomes  $\text{C}_{42}\text{H}_{66}\text{O}_{18}\cdot 3\text{H}_2\text{O}$  when the product is exposed to air. It is converted by boiling  $0.1N\text{-KOH-MeOH}$  into *isothevetin*,  $\text{C}_{42}\text{H}_{66}\text{O}_{18}\cdot 2\text{H}_2\text{O}$ , m.p.  $236\text{--}238^\circ$ . Complete hydrolysis of (I) is difficult, and energetic treatment with acids causes separation of 2 mols. of glucose originally present as gentiobiose, since the octa-acetate is obtained when (I) is treated with  $\text{Ac}_2\text{O}$  and  $\text{ZnCl}_2$  at  $70^\circ$ . A third sugar mol., probably digitalose, is present as a Me ether, but its separation from the aglucone requires so drastic treatment that the mol. is disrupted. Cautious hydrolysis of (I) with  $2N\text{-HCl}$  in  $\text{H}_2\text{O-EtOH}$ , hydrogenation of the residue ( $\text{PtO}_2$  in  $\text{AcOH}$ ), and renewed hydrolysis of the product leads to tetrahydroanhydrothevetigenin (II), oxidised by  $\text{CrO}_3$  to tetrahydroanhydrodigitoxigenone, m.p.  $245\text{--}248^\circ$ ,  $[\alpha]_D^{20} +35.8^\circ$  in  $\text{CHCl}_3$ . The identity of (II) with digitoxigenin is excluded by the differing physiological action of (I) and digitoxin (III), and the possibility of isomerisation due to differing position of OH at  $\text{C}_{10}$  is confirmed by the ability of thevetigenin (IV) to give an additive product with (III) from which *anhydrothevetigenin*,  $\text{C}_{23}\text{H}_{32}\text{O}_3$ , m.p.  $218\text{--}220^\circ$ ,  $[\alpha]_D^{20} +40.0^\circ$  in  $\text{CHCl}_3$ , is isolated; it is cautiously oxidised to anhydrodigitoxigenone. (IV) is therefore (A). Chen's kokilphin (*loc. cit.*) is identical with sucrose.



(A) appears the most probable structure of (I). H. W.

**Toad poisons. II. Cino- and marino-bufagin.** R. TSCHESCHE and H. A. OFFE (Ber., 1936, 69, [B], 2361—2367; cf. this vol., 81).—In agreement with Crowfoot (A., 1935, 921), but contrary to Kotake (A., 1928, 1138) and Jensen *et al.* (A., 1934, 412), fresh analyses of cinobufagin (I) agree with  $\text{C}_{26}\text{H}_{34}\text{O}_6$ . (I) therefore contains three double linkings, confirmed by quant. micro-hydrogenation. In the presence of a large amount of catalyst a slow further absorption of 4  $\text{H}_2$  is observed; this cannot be attributed to saturation of double linkings and is not shown by certain derivatives of (I) or by marino-bufagin (II). The ultra-violet absorption spectrum

of (I) and (II) agrees only with the presence of a conjugation of two C:C linkings with the C:O of the lactone group. The similarity of the absorption spectra of (I), (II), scillaren, and  $\text{CO} < \begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{O}-\text{CH} \end{array} > \text{C}\cdot\text{CO}_2\text{Me}$ , the production of a free or latent  $\cdot\text{CHO}$  group when (I) is cautiously hydrolysed, and the formation of  $\text{HCO}_2\text{H}$  by ozonolysis of (I) indicate the presence of  $\cdot\text{C} < \begin{array}{c} \text{CH}\cdot\text{CH} \\ \text{CH}-\text{O} \end{array} > \text{CO}$  as found by Wieland *et al.* (this vol., 1252) in bufotalin and the subsidiary poisons. Hydrogenation of cinobufagin monoacetate, m.p.  $202^\circ$ , gives  $\alpha$ -, m.p.  $238^\circ$ , and  $\beta$ -, m.p.  $250^\circ$  (decomp.), *hexahydrocinobufagin monoacetate*, which differ probably only by the steric arrangement of a H and are identical with the two perhydrogenated cinobufagin acetates of Kotake (*loc. cit.*). These are cautiously hydrolysed to *α-deacetylhexahydrocinobufagic acid* (III),  $\text{C}_{24}\text{H}_{38}\text{O}_{15}\cdot 0.5\text{H}_2\text{O}$ , m.p. (indef.)  $160^\circ$ , which does not absorb H or give a colour with  $\text{C}(\text{NO}_2)_4$ , and the corresponding  $\beta$ -compound, m.p. (indef.)  $180^\circ$ ; the analytical data are complicated by the presence of  $\text{H}_2\text{O}$  of crystallisation which is very firmly retained, and the production of an  $\text{O}_5$  acid involves the elimination of  $\text{H}_2\text{O}$  with production of a double linking, the presence of which could not be detected. Cautious oxidation of (III) with  $\text{CrO}_3\text{-AcOH}$  at  $0^\circ$  gives *deacetylhexahydrocinobufagonic acid*,  $\text{C}_{24}\text{H}_{34}\text{O}_{15}$ , m.p.  $205^\circ$ . It is monobasic even in hot solution, and hence contains only the original  $\text{CO}_2\text{H}$ . It affords only a *monosemicarbazone*, decomp.  $217^\circ$ , and hence contains only 1 CO unless another is present at the non-reactive or sluggishly reactive  $\text{C}_{11}$  position



of the cholane skeleton. It has no appreciable absorption in the ultra-violet. (A) appears the most probable structure of (I). H. W.

**Mol. wt. of cinobufagin.** D. CROWFOOT and H. JENSEN (J. Amer. Chem. Soc., 1936, 58, 2018—2019; cf. A., 1935, 921).—X-Ray crystallographic data for cinobufagin (I), acetylcinobufagin, and cinobufagone indicate that (I) is  $\text{C}_{26}\text{H}_{34}\text{O}_6$ ; previous analytical data (A., 1934, 412) are in agreement.

H. B.

**Steric hindrance to the hydrogenation of the ethylenic linking in butadiene sulphones.** C. C. BOLT and H. J. BACKER (Rec. trav. chim., 1936, 55, 898—903).—3:4-Ditert.-butyl-2:5-dihydrothiophen 1:1-dioxide (I) resists hydrogenation by  $\text{H}_2\text{-PtO}_2$ , but with  $\text{H}_2\text{-Pd-black}$  in  $\text{AcOH}$  (1.4 atm.) gives 3:4-ditert.-butyltetrahydrothiophen 1:1-dioxide (II), b.p.  $171\text{--}171.5^\circ/14$  mm., m.p.  $76\text{--}76.5^\circ$ . 3:4-Diphenyl-2:5-dihydrothiophen 1:1-dioxide (III) resists hydrogenation at 1 atm., but at 1.4 atm. ( $\text{PtO}_2$ ) gives 3:4-dicyclohexyltetrahydrothiophen 1:1-dioxide (IV), b.p.  $210\text{--}212^\circ/12$  mm., m.p.  $143\text{--}143.5^\circ$ , whilst cessation of the reaction after absorption of 1 or 4  $\text{H}_2$  gives mixtures. However, 2:3-4:5-



*ditetramethylene-2:5-dihydrothiophen 1:1-dioxide* (V) (from di- $\Delta^1$ -cyclohexenyl and  $\text{SO}_2$ ), m.p. 77.5–78°, with  $\text{H}_2$ -Pt-black,  $-\text{PtO}_2$ , or  $-\text{Pd}$ -black at 1 atm. gives 2:3-4:5-*ditetramethylenetetrahydrothiophen 1:1-dioxide* (VI), m.p. 85.5–86°, b.p. 173–175°/6 mm. The  $\text{H}_2$ -compounds readily lose  $\text{SO}_2$  to regenerate the butadiene, decomp. temp. being (I) 116–118°, (III) 188–190°, and (V) 115°. The  $\text{H}_4$ -compounds decompose only at the b.p./760 mm., namely, (II) 270–275°, (IV) 350–360°, and (VI) 310°, but with  $\text{KMnO}_4$  or  $\text{CrO}_3$  at 50° give 1 mol. of  $\text{H}_2\text{SO}_4$ . R. S. C.

**Substitution derivatives of diphenylene sulphide and diphenylene sulphone.** N. M. CULLINANE, C. G. DAVIES, and G. I. DAVIES (J.C.S., 1936, 1435–1437).—Nitration ( $\text{HNO}_3$ -AcOH) of diphenylene sulphide (I) gives the 3- $\text{NO}_2$ -derivative, m.p. 186°, also obtained by reduction and deamination of 2:4-dinitrophenyl sulphide. The  $\text{NO}_2$ -compound on reduction, followed by  $\text{CuBr}$ , forms 3-bromo-diphenylene sulphide, m.p. 127°, obtained by bromination of (I). Nitration ( $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ ) of diphenylene sulphone (II) affords the 2:7-( $\text{NO}_2$ )-derivative, m.p. 290° (slight decomp.), reduced (Fe) to the 2:7-( $\text{NH}_2$ ) $_2$ -, which yields the 2:7- $\text{Br}_2$ -compound, m.p. 312°, also derived by bromination of (II). 3-Nitrodiphenylene sulphide is oxidised ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) to the sulphone. F. R. S.

**Synthesis of heterocyclic compounds.** N. M. CULLINANE and (in part) C. G. DAVIES (Rec. trav. chim., 1936, 55, 881–886).—Dibenzfuran is obtained when 2:2'-dihydroxydiphenyl is boiled for 50 hr. (90% yield) or heated with  $\text{P}_2\text{O}_5$  at 300° for 26 hr. (95% yield).  $\text{KOPh}$  and  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OK}$  do not react at 120° or in boiling  $\text{PhOH}$ , but at 250° give a poor yield of diphenylene dioxide (9:10-dioxo-anthracene), obtained in 25% yield from  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{ONa}$  at 250°. Benzidine sulphone (prep. in 93% yield from benzidine), m.p. 327°, by diazotisation and reaction with  $\text{EtOH}$  gives diphenylene sulphone (dibenzthiophen 1:1-dioxide), m.p. 235°, converted into dibenzthiophen, m.p. 99°, by S at 350°.  $\text{PhSH}$ ,  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ , and  $\text{KOH}$  at 190–195° give Ph  $o$ -nitrophenyl sulphide, m.p. 82° (cf. lit.; 85% yield), reduced by Fe- $\text{FeCl}_3$  (trace)- $\text{H}_2\text{O}$  to Ph 2-aminophenyl sulphide, m.p. 35°, the diazonium compound from which with Na xanthate or  $\text{K}_3\text{Cr}(\text{SCN})_6$  gives thianthren. R. S. C.

**Oxidation of thianthren and its oxides by peracetic acid.** J. BÖESEKEN and (MLLE.) A. T. H. VAN DER MEULEN (Rec. trav. chim., 1936, 55, 925–934).—*E* and *B* in the equation,  $\log K = B - E/2.303RT$ , for oxidation by  $\text{AcO}_2\text{H}$  are for thianthren (I) 16,750 and 8.9, its monosulphoxide 14,200 and 5.3, *trans*- 15,100 and 5.1, and *cis*-disulphoxide 13,600 and 3.5, respectively. The prep. of (I) (66.5% yield) is modified. The monosulphoxide could not be obtained by Fries and Vogt's method (A., 1911, i, 555) or modifications thereof. (I) has a dipole moment, but gives only two dioxides and one monosulphoxide; thus the two forms are labile. The rate of oxidation of S in (I) is decreased when the other S becomes SO. R. S. C.

**Indigoid dyes. IX. Absorption spectra of isomeric thioindigoid dyes.** P. C. DUTTA (Ber.,

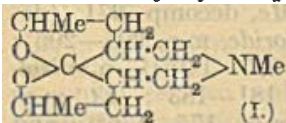
1936, 69, [B], 2343–2346; cf. A., 1935, 1249).—Measurement of the absorption spectrum of 36 dyes of this series in  $\text{PhNO}_2$  confirms the conclusions reached previously (*loc. cit.*). H. W.

**Action of ammonia and amines on aryl chlorosulphates and the *N*-chlorosulphonylsulphonamides.** L. DENEVILLE (Bull. Soc. chim., 1936, [v], 3, 2143–2152).—Aryl chlorosulphates behave as chlorosulphonating agents towards  $\text{NH}_3$ , primary and *sec.* aliphatic and heterocyclic amines, giving *N*-chlorosulphonyl derivatives which, if sufficiently stable, give aminosulphonamides with excess of the amine. Under the same conditions, primary and *sec.* aromatic amines do not yield the corresponding amidosulphonamides; at a higher temp. they suffer oxidation. *tert.*-Aromatic amines give additive products at room temp. *N*-Chlorosulphonylsulphonamides resemble aryl chlorosulphates in their behaviour towards amines.  $\text{PhSO}_3\text{Cl}$ ,  $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SO}_3\text{Cl}$ ,  $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Cl}$ , and  $o$ - and  $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Cl}$  behave similarly except with regard to rate of reaction. Gradual addition of  $\text{PhSO}_3\text{Cl}$  to piperidine (I) in  $\text{C}_6\text{H}_6$  at room temp. affords  $\text{PhOH}$ , piperidine hydrochloride, and di-1:1'-piperidyl sulphone, m.p. 92°. (I) and  $\text{SO}_2\text{Cl}_2$  in  $\text{PhMe}$  at 0° give 1-chlorosulphonylpiperidine (II), b.p. 120°/14 mm., which is completely decomposed at about 150° and converted by a suspension of  $\text{NaOPh}$  in boiling  $\text{C}_6\text{H}_6$  into *Ph* sulphonpiperidamate,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{SO}_3\text{Ph}$ , m.p. 59–60°. (II) is also formed when (I) is added gradually to  $\text{PhSO}_3\text{Cl}$  in  $\text{PhMe}$  at 0°.  $\text{PhSO}_3\text{Cl}$  and  $\text{NH}_2\text{Et}_2$  (3 mols.) yield sulphitetetraethylamide,  $\text{SO}_2(\text{NEt}_2)_2$ , b.p. 101–102°/1 mm., or chlorosulphondiethylamide, b.p. 209°/atm. pressure, if the ester is in excess.  $\text{NH}_2\text{Me}$  gives  $\text{SO}_2(\text{NHMe})_2$ , m.p. 78°, and sulphdibenzylidiamide, m.p. 181–182°, is derived from  $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ .  $\text{PhSO}_3\text{Cl}$  and  $\text{NH}_3$  react:  $\text{PhSO}_3\text{Cl} + \text{NH}_3 \rightarrow \text{PhOH} + \text{NH}_2\cdot\text{SO}_2\text{Cl}$  (III) and 3(III) ( $\text{SO}_2\cdot\text{NH}$ ) $_3$  +  $3\text{HCl}$ .  $\text{PhSO}_3\text{Cl}$  oxidises  $\text{NH}_2\text{Ph}$  and  $\text{NHPhMe}$  with evolution of  $\text{SO}_2$ ; with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  diaminophenazine is produced.  $\text{NPhMe}_2$  and  $\text{PhSO}_3\text{Cl}$  in cold  $\text{C}_6\text{H}_6$  yield the non-cryst. compound,  $\text{C}_6\text{H}_5\text{O}_3\text{SCl}\cdot\text{C}_8\text{H}_{11}\text{N}$ . H. W.

**4-Keto-3:5-dialkylpiperidines.** C. MANNICH and P. SCHUMANN (Ber., 1936, 69, [B], 2299–2305).—4-Keto-3:5-dialkylpiperidines are obtained by condensing  $\alpha\alpha'$ -dialkylacetonedicarboxylic esters with  $\text{NH}_2\text{Me}$  and  $\text{CH}_2\text{O}$  (which cannot be replaced by other aldehydes) at room temp. followed by hydrolysis of the esters so produced and decarboxylation of the acids. Thus  $\text{Et}_2$  diethylacetonedicarboxylate,  $\text{NH}_2\text{Me}$ , and 35%  $\text{CH}_2\text{O}$  in  $\text{EtOH-H}_2\text{O}$  afford  $\text{Et}_2$  4-keto-1-methyl-3:5(*cis*)-diethylpiperidine-3:5-dicarboxylate (I), b.p. 176°/13 mm. (*perchlorate*, m.p. 166°; *hydrochloride*, m.p. 147°; *picrate*, m.p. 143°; *methiodide*, decomp. 164–165°). (I) is converted by boiling 25%  $\text{HCl}$  into 4-keto-1-methyl-3:5(*cis*)-diethylpiperidine, b.p. 93°/11 mm. [*hydrobromide* (II), m.p. 168–169°; *hydrochloride*, m.p. 133–135°; *methiodide*, m.p. 254° (decomp.); *oxime*, m.p. 196°]. (II) is reduced by  $\text{Na-Hg}$  in dil.  $\text{AcOH}$  to 4-hydroxy-1-methyl-*cis*-3:5-diethylpiperidine,  $\alpha(\psi)$ -form (III), m.p. 99° (*hydrochloride*, m.p. 188–189° after softening; *perchlorate*, m.p. 154–156°; *methiodide*, m.p.

251—252.5°; benzoate and its methiodide, m.p. 220° after softening at 210°, and  $\beta$ -variety, b.p. 118—122°/13 mm. (methiodide, m.p. 250—251°; benzoate and its methiodide, m.p. about 260°). (III) is not isomerised by 10% NaOEt at 175°.  $Et_2$  4-keto-1-methyl-cis-3:5-diallylpiperidine-3:5-dicarboxylate, b.p. 183—184°/11 mm. (hydrochloride, m.p. 131°), is converted by HBr in AcOH at room temp. into  $Et_2$  4-keto-1-methyl-3:5-di- $\beta$ -bromopropylpiperidine-3:5-dicarboxylate (hydrobromide, m.p. 160° when slowly heated), and reduced (PtO<sub>2</sub> in EtOH) to  $Et_2$  4-keto-1-methyl-cis-3:5-dipropylpiperidine-3:5-dicarboxylate, b.p. 185—186°/12 mm. [hydrochloride (III), m.p. 138°]. (III) is hydrolysed and decarboxylated by boiling 25% HCl to 4-keto-1-methyl-cis-3:5-dipropylpiperidine (IV), b.p. 120°/11 mm. (*H* tartrate, m.p. 81—82°; oxime, m.p. 93—94°, and its hydrochloride, decomp. 225°), the methiodide, m.p. 165—166° after darkening when rapidly heated, of which is transformed by hot 15% KOH followed by MeI into the methiodide (V), CH<sub>3</sub>·CPr<sup>+</sup>·CO·CHPr<sup>+</sup>·CH<sub>2</sub>·NMe<sub>3</sub>I, m.p. 148° after softening at 145—147°. Treatment of (V) with KOH affords  $\alpha\alpha'$ -dipropyldivinyl ketone, b.p. 84—85°/12 mm., hydrogenated (PtO<sub>2</sub> in MeOH) to  $\alpha\alpha'$ -dimethyldibutyl ketone, b.p. 86°/13 mm. (IV) is reduced to 4-hydroxy-1-methyl-cis-3:5-dipropylpiperidine,  $\alpha(\psi)$ -form, m.p. 112—113° (perchlorate, m.p. 113—115°; nitrate, m.p. 137—138°; sulphate, m.p. 170—171°; non-cryst. benzoate and its hydrochloride, m.p. 109—111°, picrate, m.p. 190—193°, and methiodide, m.p. 270—272°), and  $\beta$ -variety, m.p. 63—65° (methiodide, m.p. 225—227°; benzoate and its picrate, m.p. 205—209°, and methiodide, m.p. about 295°). Na amlyoxide in boiling NH<sub>2</sub>Ph isomerises the  $\beta$ - to the  $\alpha$ -form, but is without action on the latter. H. W.

**Tricyclic oxetone derivatives.** C. MANNICH and P. SCHUMANN (Ber., 1936, 69, [B], 2306—2310).—Treatment of  $Et_2$  4-keto-1-methyl-3:5-diallylpiperidine-3:5-dicarboxylate hydrochloride with boiling 25% HCl gives 1:5':5''-trimethyl-3':2'-3:4-2'':3'-4:5-ditetrahydrofuranopiperidine (I), b.p. 113°/11 mm.



[hydrochloride, m.p. 220—221°; methiodide (II), m.p. 238°], which does not contain CO or active H (Zerevitinov) and does not add Br or H. The base obtained from (II) and Ag<sub>2</sub>O passes when heated into  $\beta\epsilon\epsilon\theta$ -dioxido-8-dimethylaminomethyl- $\zeta$ -methylenenonane,  $\begin{array}{c} \text{CH}_2-\text{CHMe}-\text{O} \\ \diagup \quad \diagdown \\ \text{CH}(\text{CH}_2\cdot\text{NMe}_2) < \text{C} < \text{O} \\ \diagdown \quad \diagup \\ \text{C}(\text{CH}_2)-\text{CH}_2 \end{array}$ , b.p. 115°/11 mm. (hygroscopic hydrochloride; picrate, m.p. 147°), the methiodide (II), m.p. 207—208°, of which is hydrogenated (PtO<sub>2</sub>) to  $\beta\epsilon\epsilon\theta$ -dioxido- $\zeta$ -methyl-8-dimethylaminomethylnonane methiodide (III), m.p. 195—197°. (III) is degraded to NMe<sub>3</sub> and  $\beta\epsilon\epsilon\theta$ -dioxido-8'-dimethylenenonane (IV), b.p. 86—87°/13 mm., whilst (III) yields  $\beta\epsilon\epsilon\theta$ -dioxido- $\zeta$ -methyl-8-methylenenonane (V), b.p. 84—88°/13 mm.; hydrogenation of (IV) or (V) (PtO<sub>2</sub> in MeOH) leads to  $\beta\epsilon\epsilon\theta$ -dioxido-8 $\zeta$ -dimethylnonane, b.p. 88—92°/13 mm. (I) is transformed by HBr·AcOH at 75° into the non-cryst., unstable 4-keto-1-methyl-cis-3:5-di- $\beta$ -bromopropylpiperidine [hydrobromide (VI), m.p. 164—165° (decomp.)], quantitatively reconverted into (I) by

H<sub>2</sub>O at 100°]. (VI) is reduced (PtO<sub>2</sub> in EtOH) to 4-hydroxy-1-methyl-cis-3:5-di- $\beta$ -bromopropylpiperidine, m.p. 125—126°. 2:6-Diallylcyclohexanone is converted by HBr·AcOH at room temp. into the unstable 2:6-di- $\beta$ -bromopropylcyclohexanone, m.p. 94—95°, transformed by boiling H<sub>2</sub>O containing KHCO<sub>3</sub> into 5':5''-dimethyl-3':2'-2'':3''-ditetrahydrofuranol-1:2-2:3-cyclohexane, b.p. 115—117°/14 mm.

H. W.

**2-Aminopyridine series.** IV. Reactivity of the methyl group in 6-amino-2-picoline. K. FEIST, W. AWE, and M. KUKLINSKI. V. Reactivity of the amino-group in 6-amino-2-picoline. K. FEIST and M. KUKLINSKI (Arch. Pharm., 1936, 274, 418—425, 425—435).—IV. Unlike that of 2-picoline the Me of 6-amino-2-methylpyridine (I) (benzyl, m.p. 66°, and formylbenzyl, m.p. 76°, derivatives) or its *N*-Me derivatives does not react with *o*- or *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO to give stilbazoles (cf. Shaw *et al.*, A., 1933, 282). 6-Dimethylamino-2-methylpyridine with Ac<sub>2</sub>O gives the Ac derivative, b.p. 264°, of 6-methylamino-2-methylpyridine, b.p. 209—210° (picrate, m.p. 192°); attempted condensation of this in Ac<sub>2</sub>O with *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO gives  $\beta$ -hydroxy- $\beta$ -2-nitrophenylpropionic acid, b.p. 175—185°/14 mm., m.p. 87°. Picrates of 2-stilbazole, m.p. 207°, and 2-dihydrostilbazole, m.p. 128°, were also prepared.

V. (I) forms Schiff's bases with many aromatic aldehydes, but with *o*-OH·C<sub>6</sub>H<sub>4</sub>·CHO and *o*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CHO reacts slowly to give yellow products regarded as Me·C<sub>5</sub>H<sub>3</sub>N·NH·N:CH< $\begin{array}{c} \text{CH}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{CH} \end{array}$ >CH. Such are 6-*o*-methoxy-, m.p. 84°, and 6-*o*-hydroxy-benzylideneamino-2-methylpyridine, m.p. 68°, hydrogenated (Pd-black) to 6-*o*-methoxy-, m.p. 69° [also from (I) and *o*-OMe·C<sub>6</sub>H<sub>4</sub>·CHO in anhyd. HCO<sub>2</sub>H], and 6-*o*-hydroxy-benzylamino-2-methylpyridine, m.p. 97°. The following were similarly prepared: 6-*o*-, m.p. 114.5°, and 6-*p*-nitro-, m.p. 161°, -nitro-3:4-dimethoxy-, m.p. 139°, and 6-3':4'-methylenedioxy-benzylideneamino-2-methylpyridine, m.p. 118°; 6-3':4'-methylenedioxybenzylamino-2-methylpyridine, m.p. 80°, also from (I) with piperonal in anhyd. HCO<sub>2</sub>H. (I) with S in CS<sub>2</sub> and EtOH yields NN-bis-(2-methylpyridine)-6-thiocarbamide, m.p. 209°, and 6-thiourethano-2-methylpyridine, m.p. 113°. (I) with CH<sub>2</sub>:CH·CH<sub>2</sub>·NCS yields 2-methylpyridine-6-allylthiocarbamide, m.p. 170°, which with 2*N*-NaOH, EtOH, and 10% Pb(OAc)<sub>2</sub> gives the corresponding carbamide, m.p. 139°. Similarly PhNCS gives phenyl-2-methylpyridine-6-thiocarbamide, m.p. 196°, and -carbamide, m.p. 186°. 2-Aminopyridine (II) and CO(NH<sub>2</sub>)<sub>2</sub> with butylchloral yield respectively 2-(di- $\beta\beta\gamma$ -trichloro- $\alpha$ -hydroxybutylamino)pyridine, m.p. 109°, and  $\beta\beta\gamma$ -trichloro- $\alpha$ -hydroxybutylcarbamide, m.p. 156°. C<sub>5</sub>H<sub>5</sub>N with  $\omega$ -chloro-3:4-dihydroxyacetophenone yields an additive compound with pyridine (hydrate, m.p. 269°; picrate, m.p. 190°). 2-( $\beta$ -Hydroxy- $\beta$ -3':4'-dihydroxyphenylethylamino)pyridine hydrochloride (A., 1934, 417) gives a picrate, m.p. 199°. F. R. G.

**Reduction products of nicotinamide methiodide.** II. P. KARRER and F. BENZ (Helv. Chim. Acta, 1936, 19, 1028—1029; cf. this vol., 1121).—The orange-coloured intermediate product formed during the reduction of nicotinamide methiodide by



$\text{Na}_2\text{S}_2\text{O}_4$  in aq.  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  cannot be removed by  $\text{CHCl}_3$ . A similar effect is observed with many other quaternary pyridinium salts and appears characteristic of reduction to the *o*- $\text{H}_2$ -stage. The yellow colorations have nothing in common with those produced by the reduction of cozymase in strongly alkaline solution. 1-Methyldihydronicotinamide has been obtained cryst. H. W.

**Manufacture of heterocyclic compounds.** [Pyridines and pyrrolidines.]—See B., 1936, 1083.

**Manufacture of carboxylic acids or derivatives thereof containing the pyridine nucleus.**—See B., 1936, 1084.

**Interaction of tetraphenyl glycol and pyridinium chloride.** A. SCHONBERG and R. MICHAELIS (J.C.S., 1936, 1571).—Tetraphenyl glycol,  $\text{C}_6\text{H}_5\text{N}$ , and  $\text{HCl}$  give a substance, m.p. 185–190° (decomp.), probably  $\text{OH}\cdot\text{CPh}_2\cdot\text{CPh}_2\cdot\text{OH}\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ , decomposed by alkali into its components. F. R. S.

**Nitrogenous substances analogous to terphenyl [2:5-diphenylpyridines].** M. COLONNA (Gazzetta, 1936, 66, 528–532).— $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ , *o*-, *m*-, or *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , and  $\text{AcCO}_2\text{H}$  yield respectively 2-*o*- (cf. A., 1907, i, 853), 2-*m*-, m.p. 282° (decomp.), and 2-*p*-nitrophenyl-5:6- $\alpha\beta$ -naphthoquinoline-4-carboxylic acid, m.p. 262°, with *o*-, *m*-, or *p*-nitrobenzyl- $\beta$ -naphthylamine. The above acids are oxidised by  $\text{NaOH}\text{-KMnO}_4$  to 6-(2'-nitrophenyl)-3-(2''-carboxyphenyl)-, m.p. 287° (decomp.), 6-(3'-nitrophenyl)-3-(3''-carboxyphenyl)-, m.p. 115° (decomp.), and 6-(4'-nitrophenyl)-3-(4''-carboxyphenyl)-pyridine-2:4-dicarboxylic acid, m.p. 170°. E. W. W.

**Condensation of aromatic formamido-derivatives with pyruvic acid.** A. SILBERG (Bull. Soc. chim., 1936, [v], 3, 1767–1776).—This condensation does not follow the mechanism proposed by van Schelven (B., 1933, 341). Formanilides and  $\text{AcCO}_2\text{H}$  (I) in  $\text{EtOH}$  yield 2-methylquinoline-4-carboxylic acids (II), apparently by the stages  $\text{NHR}\cdot\text{CHO} \rightarrow \text{NH}_2\text{R} \rightarrow \text{NR}\cdot\text{CHMe} \rightarrow \text{NHR}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{H} \rightarrow$  (II); secondary products are also formed. Thus  $\text{NHPh}\cdot\text{CHO}$  and (I) give (in  $\text{EtOH}$  at the b.p.) 2-methylquinoline-4-carboxylic acid [also obtained from  $\text{NH}_2\text{Ph}$  and (I)] and (especially in the cold)  $\beta$ -anilinoacrylanilide, m.p. 236°. Form-*p*-anisidide (III) in  $\text{EtOH}$  gives 6-methoxy-2-methylquinoline-4-carboxylic acid (*Cu* salt); with (I) alone at 120° (III) yields  $\gamma$ -*p*-anisidino- $\alpha$ -ketovaleric acid (?), m.p. 200°. *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OME}$  and (I) in  $\text{EtOH}$  yield pyrotartrodip-anisidide. Form-*o*- and -*p*-toluidide give 2:8-, m.p. 153°, and 2:6-dimethylquinoline-4-carboxylic acid, m.p. 263° (decomp.), respectively. Form- $\alpha$ - and - $\beta$ -naphthylamide condense to 2-methyl- $\alpha$ -naphthoquinoline-4-carboxylic acid, m.p. 245°, and 3-methyl- $\beta$ -naphthoquinoline-1-carboxylic acid, m.p. 290°. *m*-Bromoformanilide gives 7(or 8)-bromo-2-methylquinoline-4-carboxylic acid, m.p. 187° (decomp.). *p*-Bromoformanilide and (I) in  $\text{EtOH}$  at the b.p. furnish a neutral substance,  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{Br}_3$ , m.p. 222°; in the cold a substance,  $\text{C}_9\text{H}_8\text{ONBr}$ , is obtained. *o*-Bromoformanilide gives a substance,  $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{Br}$ , m.p. 204–205°. E. W. W.

**Manufacture of derivatives of anthraquinone series.** Manufacture of 3-hydroxy-2-methylquinoline-4-carboxylic acid and derivatives.—See B., 1936, 976.

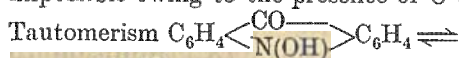
**Addition of benzene to 2- and 4-styrylquinolines.** R. C. FUSON, L. L. ALEXANDER, E. ELLINGBOE, and A. HOFFMAN (J. Amer. Chem. Soc., 1936, 58, 1979–1980).—4-*p*-Chlorostyrylquinoline, m.p. 127–128° (from 4-methylquinoline,  $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ , and a little  $\text{ZnCl}_2$  at 125°), and 4-styrylquinoline (I) with  $\text{C}_6\text{H}_6$  (excess),  $\text{AlCl}_3$ , and  $\text{HCl}$  both give 4- $\beta\beta$ -diphenylethylquinoline, m.p. 130–131°.  $\text{MgPhBr}$  and (I) afford 2-phenyl-4-styrylquinoline, m.p. 102.5–103.5°. 2- $\beta\beta$ -Diphenylethylquinoline (A., 1933, 721) is also prepared by reduction of 2- $\beta\beta$ -diphenylvinylquinoline (II) with (i)  $\text{H}_2 + \text{PtO}_2$ , and (ii)  $\text{C}_6\text{H}_6$ ,  $\text{AlCl}_3$ , and  $\text{HCl}$ . 2- $\beta$ -Hydroxy- $\beta$ -phenyl- $\beta$ -*p*-chlorophenylethylquinoline, m.p. 140.5–141° (which could not be dehydrated), and (II) are obtained by Ziegler and Zeiser's method (A., 1931, 364). H. B.

**Synthesis of substituted 5:6-benzocinchonic acids by the Doebner and Pfitzinger reactions.** E. A. ROBINSON and M. T. BOGERT (J. Org. Chem., 1936, 1, 65–75).— $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ , various aldehydes, and  $\text{AcCO}_2\text{H}$  or  $\text{CH}_2\text{Bz}\cdot\text{CO}\cdot\text{CO}_2\text{H}$  give 3-substituted 5:6-benzocinchonic acids (A) and their Bz derivatives, respectively (with *N*-substituted naphthylamines formed by oxidation of the dihydrocinchonic acids at the expense of the anils which are primary products), which by decarboxylation or soda fusion, respectively, lead to 3-substituted benzoquinolines. (A) are also obtained by the Pfitzinger reaction from  $\beta$ -naphthisatin and acetophenones. Identity of the compounds obtained by the various methods is rigorously proved and structures are thereby confirmed. The following appear to be new. 3-*p*-Anisyl-5:6-benzoquinoline, m.p. 190–191° (lit. 184°) (picrate, m.p. 224°). 5:6-Benzocinchonic acid, m.p. 302° (uncorr.). 3-Methyl-5:6-benzoquinoline picrate, m.p. 228–230° (decomp.) (lit. 220–221°). 2-Benzoyl-5:6-benzocinchonic acid, decomp. 247° (chloride, m.p. 197–199°; *Et* ester, m.p. 146.5–147°), and its 3-*Me*, decomp. 271° (decomp.), -*Ph*, decomp. 249° [chloride, m.p. 205–206°; *Et* ester, m.p. 144° (sinters at 137–140°)], -*p*-anisyl, decomp. 237° (chloride, m.p. 181–183°; *Et*, m.p. 160–161°, and *Me* ester, m.p. 175–176°), and -piperonyl derivative, decomp. 259° (chloride, m.p. 188–189°; *Et* ester, m.p. 158–159°). *N*-*p*-Anisyl, m.p. 104.5° (lit. 98°) (hydrochloride, m.p. 195°), and -piperonyl- $\beta$ -naphthylamine, m.p. 119° (hydrochloride, m.p. 192°). 2-Benzoyl-3-methyl-, m.p. 132–133° (oxime, m.p. 242°; picrate, m.p. 216–217°), -phenyl-, m.p. 189° (lit. 185°) (picrate, m.p. 243–244°), -*p*-anisyl-, m.p. 186° (picrate, m.p. 199.5–200°), and -piperonyl-5:6-benzoquinoline, m.p. 210.5–211° [oxime, m.p. 262° (decomp.)]. M.p. are corr.

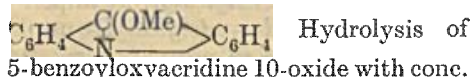
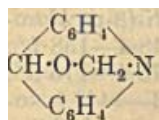
R. S. C.

**Acridones.** VIII. 10-Keto- and 10-keto-5-hydroxy-acridine. I. TANASESCU and E. RAMON-TIANU (Bull. Soc. chim., 1936, [v], 3, 2009–2018; cf. A., 1934, 1010).—In consequence of the somewhat divergent views of Lehmsedt (A., 1935, 1251) and Kliegl *et al.* (this vol., 343) proof is adduced that “10-hydroxyacridone” is 5-hydroxyacridine 10-oxide.

5-Chloroacridine is oxidised by  $\text{BzO}_2\text{H}$  in  $\text{CHCl}_3$  to *5-chloroacridine 10-oxide* (II), m.p.  $209^\circ$  (additive complex with  $\text{HgCl}_2$ ), hydrolysed by aq. alkali to 5-hydroxyacridine 10-oxide identical with that derived from  $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ ,  $\text{C}_6\text{H}_6$ , and conc.  $\text{H}_2\text{SO}_4$ . It is also obtained from (I) and  $\text{NaOMe}$ . This synthesis is decisive and also establishes that "acridol" is intermediately produced by the action of alkali on 5-chloroacridine and then becomes isomerised to acridone. In the present case the isomerisation is impossible owing to the presence of O attached to N.

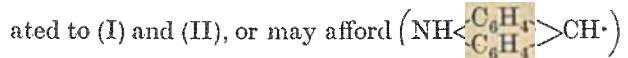
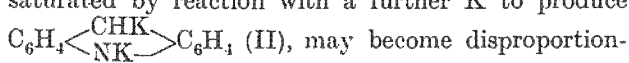
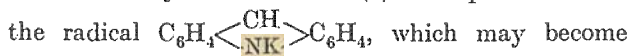


excluded since the absorption spectra in EtOH are closely similar in absence or presence of alkali. Reduction of the "5-methoxyacridine" of Lehmstedt (*loc. cit.*) with Zn dust in boiling EtOH containing  $\text{CaCl}_2$  give a basic substance ( $\text{C}_{15}\text{H}_9\text{N}$ )<sub>n</sub>, m.p.  $388^\circ$ , of undetermined constitution with some acridone; its physico-chemical behaviour indicates the annexed structure rather than



5-benzoyloxyacridine 10-oxide with conc.  $\text{HCl}$  in  $\text{EtOH-H}_2\text{O}$  gives 3-chloroacridone, identified by conversion into 3-chloro-5-*p*-dimethylaminophenylacridine, m.p.  $230^\circ$ . Similar hydrolysis of 3-chloro-5-benzoyloxyacridine 10-oxide gives a substance,  $\text{C}_{13}\text{H}_7\text{ONCl}_2$ , m.p.  $<360^\circ$ . H. W.

**Acridine. XV. Relationship between basicity and radical formation during the action of alkali metal on bases of the acridine series.** K. LEHMSTEDT, W. BRUNS, and H. KLEE (Ber., 1936, 69, [B], 2399—2405; cf. this vol., 999).—K-Na reacts initially with acridine (I) with production of



by union of two radicals. Interaction of various acridine bases with Na-K in  $\text{Et}_2\text{O}$  and decomp. of the products with EtOH invariably yields mixtures of *ms*-dihydroacridines with *ms*-tetrahydrodiacridyls, the proportion of the latter being the greater as the base is weaker. 4'-Methoxydiphenylamine-2'-carboxylic acid is converted by  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  into 3-methoxyacridone (I), m.p.  $278^\circ$ , transformed into 3-methoxyacridine (II), m.p.  $104^\circ$  [hydrochloride (+2H<sub>2</sub>O)]. *mer*-Quinonoid salts,  $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}, \text{C}_{14}\text{H}_{11}\text{ON}, \text{HCl}, 2\text{H}_2\text{O}$  and  $\text{C}_{14}\text{H}_{11}\text{ON}, \text{C}_{15}\text{H}_{13}\text{O}_2\text{N}, \text{HCl}$ , are derived from (I) and (II) and from (II) and 3-methoxy-10-methylacridone, respectively. 2-Methyldiphenylamine-2'-carboxylic acid (improved prep. from  $o\text{-C}_6\text{H}_4\text{Cl-CO}_2\text{H}$ ,  $\text{K}_2\text{CO}_3$ ,  $o\text{-C}_6\text{H}_4\text{Me-NH}_2$ , and Cu powder) is almost quantitatively converted by  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  followed by distillation with steam into 4-methylacridone, reduced by Na-Hg, and then dehydrogenated by  $\text{PhNO}_2$  to 4-methylacridine, m.p.  $88^\circ$  (hydrochloride, +2H<sub>2</sub>O).

3:7-Dimethylacridine hydrochloride (+2H<sub>2</sub>O) is described. The following are obtained from the products of the action of Na-K on the bases: *ms*-tetrahydro-5:5-di-3-methoxyacridyl, m.p.  $204^\circ$  in bath at  $185^\circ$ ; -5:5'-di-3:7-dimethylacridyl, m.p.  $228\text{--}229^\circ$  in bath at  $210^\circ$ ; -5:5'-di-4-methylacridyl, m.p.  $193^\circ$  in bath at  $175^\circ$ ; -5:5'-di-3:4-benzoylacridyl, m.p.  $165\text{--}168^\circ$  in bath at  $150^\circ$ . *ms*-Dihydro-3:4-benzoylacridine has m.p.  $158^\circ$ . H. W.

**Preparation and therapeutic properties of certain acridine derivatives.** I. Anil and styryl derivatives of 2:8-diaminoacridine and acridine-5-aldehyde respectively. W. L. GLEN, M. M. J. SUTHERLAND, and F. J. WILSON (J.C.S., 1484—1487).—The following anils have been prepared but are too insol. in  $\text{H}_2\text{O}$  for biological tests: 2:8-bis-benzylidene-, m.p.  $220^\circ$ , -cinnamylidene-, m.p.  $252^\circ$ , -*p*-dimethylaminobenzylidene-, m.p.  $230^\circ$ , -anisylidene-, m.p.  $241\text{--}242^\circ$ , and -salicylidene-aminoacridine, m.p.  $282^\circ$ . The styryl compounds have been obtained by condensing acridine-5-aldehyde with  $\alpha$ -picoline or quinaldine alkiodide with  $\text{C}_5\text{H}_{11}\text{N}$  as catalyst, and some therapeutic properties examined and recorded: 5-(2-pyridyl methiodide)-5-acridylethene, decomp.  $220\text{--}225^\circ$  (hydrochloride); s-2-pyridyl-5-acridylethene dimethiodide; s-(2-pyridyl ethiodide)-5-acridylethene and -(5-acridyl methiodide)ethene; s-(2-quinolyl methiodide)-5-acridylethene, m.p.  $220\text{--}225^\circ$  (decomp.) (hydrochloride); s-2-quinolyl-5-acridylethene dimethosulphate, dimethochloride, and dimethiodide; and s-(2-quinolyl ethiodide)-(5-acridyl methiodide)-ethene. F. R. S.

**Attempts to find new antimalarials. XV. Synthesis of acridine compounds related to atebirin.** R. R. GOODALL and W. O. KERMAK (J.C.S., 1936, 1546—1550).—*o*-Phenoxy-3-methoxyacridine, m.p.  $146\text{--}147^\circ$ , obtained from  $\text{PhOH}$  and the 5-Cl-compound, condenses with the appropriate amine to give: 5-( $\beta$ -diethylaminoethyl-methylamino)-(dihydrobromide, m.p.  $239\text{--}240^\circ$ ), -*n*-propylamino)-(dihydrobromide, m.p.  $142\text{--}143^\circ$ ), and -amino-3-methoxyacridine (dihydrobromide), and 5-( $\gamma$ -diethylamino-*n*-propylamino)-3-methoxyacridine dihydrobromide, m.p.  $242\text{--}245^\circ$ . 1:3:5-Trichloroacridine, m.p.  $175^\circ$ , obtained from 2:4-dichlorodiphenylamine-2'-carboxylic acid and  $\text{POCl}_3$ , with  $\text{PhOH}$  gives 1:3-dichloro-5-phenoxyacridine, m.p.  $171^\circ$ , which condenses with amines to form 1:3-dichloro-5-( $\beta$ -diethylaminoethylamino)-, m.p.  $121\text{--}122^\circ$ , and -( $\gamma$ -diethylamino-*n*-propylamino)-acridine (dihydrobromide, decomp.  $200^\circ$ ). 5-Chloro-1-bromo-, m.p.  $159\text{--}161^\circ$ , is converted into 1-bromo-5-phenoxy-3-methylacridine, m.p.  $145^\circ$ , which affords 1-bromo-5-( $\beta$ -diethylaminoethylamino)-, m.p.  $114^\circ$ , and -( $\gamma$ -diethylamino-*n*-propylamino)-3-methylacridine (dihydrobromide, decomp. about  $230^\circ$ ). 1:3:7-Trichloro-5-( $\gamma$ -diethylamino-*n*-propylamino)-, m.p.  $155^\circ$ , and 7-chloro-1-bromo-5-( $\gamma$ -diethylamino-*n*-propylamino)-3-methylacridine, m.p.  $130\text{--}131^\circ$ , and 1:4-dichloro-5-( $\gamma$ -diethylamino-*n*-propylamino)acridine dihydrobromide, decomp. about  $225\text{--}230^\circ$ , are also described.

F. R. S.

**Manufacture of acridinium compounds.**—See B., 1936, 1018.



**Constitution of Knoevenagel's "acetone-anil."** K. VON AUWERS (Ber., 1936, 69, [B], 2351—2352).—The structure assigned to the compound by Kalnin (this vol., 1123) is not in agreement with spectrochemical behaviour, which harmonises with that adopted by Reddelien (A., 1932, 1142). H. W.

**Manufacture of cyclohexenylalkylhydantoins.**—See B., 1936, 1018.

**Action of phenylcarbimide on insulin.**—See this vol., 1564.

**Sensitisation of photographic silver halide emulsions. Preparation of pyrazolone and other derivatives.**—See B., 1936, 1020.

**Oxidation of 1-phenyl-3-methyl-5-pyrazolone.** II. G. PERRONCITO (Gazzetta, 1936, 66, 563—565).—The product, m.p. 180°, of oxidising 1-phenyl-3-methyl-5-pyrazolone with dry  $\text{H}_3\text{AsO}_4$  (this vol., 614) is methenylbis-4-(1-phenyl-3-methyl-5-pyrazolone).  $\text{NHPh}\cdot\text{NHAc}$  is also formed, supporting the view that  $\text{NHAc}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CHO}$  is an intermediate product. E. W. W.

**N-Arylbarbituric acids.** II. J. S. BUCK (J. Amer. Chem. Soc., 1936, 58, 2059—2061).—The following are prepared from  $\text{NH}\cdot\text{CO}\cdot\text{NHAr}$  and  $\text{CETr}(\text{CO}_2\text{Et})_2$  (method: this vol., 1125): 1-phenyl-, m.p. 149°, 1-o-, m.p. 134°, -m-, m.p. 138.5°, and -p-, m.p. 149.5°, -tolyl-, 1-o-, m.p. 176—177°, -m-, m.p. 139.5°, and -p-, m.p. 149°, -anisyl-, 1-o-, m.p. 142—143°, -m-, m.p. 125.5°, and -p-, m.p. 145°, -phenetyl-, and 1- $\alpha$ -, m.p. 158°, and - $\beta$ -, m.p. 161—162°, -naphthyl-5-ethyl-5-isobutylbarbituric acids; 1-phenyl-, m.p. 129°, 1-o-, m.p. 119°, -m-, m.p. 113—114°, and -p-, m.p. 115°, -tolyl-, 1-o-, m.p. 134°, -m-, m.p. 115—116°, and -p-, m.p. 120°, -anisyl-, 1-o-, m.p. 162—163°, -m-, m.p. 72—74°, and -p-, m.p. 100—101°, -phenetyl-, and 1- $\alpha$ -, m.p. 193—194°, and - $\beta$ -, m.p. 138°, -naphthyl-5-ethyl-5-isoamylbarbituric acids; 1-p-dimethylaminophenyl- $\alpha$ :5-diethyl-, m.p. 182°, -5-ethyl-5-n-, m.p. 157°, and -iso-, m.p. 153°, -butyl-, - $\alpha$ -ethyl-5-isoamyl-, m.p. 130°, and 1-p-diethylaminophenyl- $\alpha$ :5-diethyl-, m.p. 175°, -5-ethyl-5-n-, m.p. 125.5°, and -iso-, m.p. 140—141°, -butyl-, and -5-ethyl-5-isoamyl-, m.p. 125°, -barbituric acids. p-Dimethyl-, m.p. 183°, and p-diethyl-, m.p. 136.5°, -aminophenylcarbamides are described. All m.p. are corr. H. B.

**Isomerisation of acylated pyrazolines.** K. VON AUWERS and H. LUDWIG (Ber., 1936, 69, [B], 2347—2351).—Repeated attempts to re-obtain 5-methylpyrazoline-1-carboxylamide, m.p. 167—168°, from 5-methylpyrazoline (I) and  $\text{HCNO}$  (von Auwers, A., 1927, 1203) give only an isomeride, m.p. 119°, whereas ring-closure from  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  (Maire, A., 1908, i, 290) and condensation of 3-methylpyrazoline (II) with  $\text{HCNO}$  give exclusively the product of m.p. 167—168°. Acyl migration occurred therefore during the original experiment but its cause has not been traced. The incidence of accidental influences in similar changes is illustrated by the behaviour of (I) towards boiling  $\text{ClCO}_2\text{Me}$ ; in one experiment the main product was *Me* 3-methylpyrazoline-1-carboxylate, b.p. 135°/14 mm. [decarboxylated to (II) and identified as the picrate, m.p. 149°], whereas in other experiments

*Me* 5-methylpyrazoline-1-carboxylate, b.p. 124—132°/14 mm., was mainly produced. Benzoylation of (II) proceeds normally and yields 1-benzoyl-3-methylpyrazoline, m.p. 98.5—99°, differing from the 5-Me isomeride, m.p. 156°. The possibility of isomerisation during the nitrosation of (I) could not be investigated owing to the instability of the product. The occurrence of isomerisation with alkylpyrazolines proves that the phenomenon is not caused by a tendency towards the production of conjugated systems and indicates that it is due to a striving towards a uniform distribution of masses in the mol. H. W.

**Derivatives of piperazine.** IX. Addition to conjugate systems. I. V. E. STEWART and C. B. POLLARD (J. Amer. Chem. Soc., 1936, 58, 1980—1981).—Piperazine (1 mol.) and  $\text{COAr}\cdot\text{CH}\cdot\text{CHAr}$  (2 mols.) in boiling PhMe give almost quant. yields of 1:4-di-( $\beta$ -aroyl- $\alpha$ -arylethyl)piperazines, which are decomposed by dil.  $\text{HCl}$  (not  $\text{H}_2\text{O}$ ) or  $\text{HCl}$  in  $\text{CHCl}_3$  or PhMe to the original components. The following are described: 1:4-di-( $\beta$ -benzoyl- $\alpha$ -phenylethyl)-, m.p. 128—128.3° (all m.p. are corr.); 1:4-di-( $\beta$ -p-chlorobenzoyl- $\alpha$ -p-chlorophenylethyl)-, m.p. 148.4—158.7°; 1:4-di-( $\beta$ -p-toluoyl- $\alpha$ -p-tolylolethyl)-, m.p. 175.4—175.8°; 1:4-di-( $\beta$ -benzoyl- $\alpha$ -m-nitro-, m.p. 143—144°, -o-chloro-, m.p. 110.9—111.3°, -p-chloro-, m.p. 146.8—147°, -p-methyl-, m.p. 145.5—146°, and -p-methoxy-, m.p. 109.5—110.1°, -phenylethyl)-; 1:4-di-( $\beta$ -p-chloro-, m.p. 117.7—118.1°, -p-bromo-, m.p. 116.3—117.3°, and -p-methyl-, m.p. 132—132.5°, -benzoyl- $\alpha$ -phenylethyl)-, and 1:4-di-( $\beta$ -p-toluoyl- $\alpha$ -n-anisylethyl)-, m.p. 149.8—150.2°, -piperazines. H. B.

**Manufacture of derivative of pyrazinemono-carboxylic acid.**—See B., 1936, 1130.

**Pyrrolidine derivatives.** III. Catalytic hydrogenation under pressure of pyridylpyrrole derivatives. E. OCHIAI, K. TSUDA, and S. IKUMA (Ber., 1936, 69, [B], 2238—2242).—With pyridylpyrrole derivatives catalytic hydrogenation ( $\text{PtO}_2$ ) under pressure first affects the  $\text{C}_5\text{H}_5\text{N}$  nucleus. The influence of substituents in the pyrrole nucleus is pronounced. Whereas Me has little effect,  $\text{CO}_2\text{Alk}$  markedly inhibits reaction as does Ac until it has been reduced to  $\cdot\text{CHMe}\cdot\text{OH}$  or Et. The following transpositions are described: 4-2'-pyridyl-2-methylpyrrole to 4-2'-piperidyl-2-methylpyrrole, m.p. 113—114° [hydrochloride, m.p. 228° (decomp.)]; p-nitrobenzoyl derivative, m.p. 140—141°, and 4-2'-piperidyl-2-methylpyrrolidine, b.p. 110°(bath)/6 mm. (di-3:5-dinitrobenzoyl derivative, m.p. 180°); 4-3'-pyridyl-2-methylpyrrole to 4-3'-piperidyl-2-methylpyrrolidine, b.p. 120—130°(bath)/6 mm. (aurichloride, decomp. 230°; di-3:5-dinitrobenzoyl derivative, m.p. 237°); 3-acetyl-4-2'-pyridyl-2-methylpyrrole to a base, b.p. 200°(bath)/0.03 mm., converted by  $\text{HI}$  (d 1.7) and red P at 130° into 4-2'-piperidyl-2-methyl-3-ethylpyrrole (hydrochloride, m.p. 214°) or into a base, b.p. 150—170°(bath)/0.03 mm., and thence into 4-2'-piperidyl-2-methyl-3-ethylpyrrolidine (di-p-nitrobenzoyl derivative, m.p. 239—240°); 3-acetyl-4-3'-pyridyl-2-methylpyrrole to 3-acetyl-4-3'-piperidyl-2-methylpyrrole, m.p. 184° (p-nitrobenzoyl, m.p. 198°, and Ac, m.p. 216°, derivatives); Et 4-3'-pyridyl-2-methylpyrrole-3-carboxylate to Et 4-3'-piperidyl-2-methylpyrrole-3-carboxylate, m.p. 137°

(Bz derivative, m.p. 174°); Et<sub>2</sub> 4-2'-pyridyl-2-methylpyrrole-3 : 5-dicarboxylate is hydrolysed to 3-carbethoxy-4-2'-pyridyl-2-methylpyrrole-5-carboxylic acid, decomp. 218°, decarboxylated at 220°/3 mm. to Et 4-2'-pyridyl-2-methylpyrrole-3-carboxylate, m.p. 120° (perchlorate, m.p. 205°; methiodide, m.p. 207°; ethiodide, m.p. 179°), which is hydrogenated to Et 4-2'-piperidyl-2-methylpyrrole-3-carboxylate (p-nitrobenzoyl, m.p. 210°, and Ac, m.p. 142°, derivatives).

H. W.

**Pyrimidines. CLIV. Pyrimidine side-chain reactions useful for synthesis of 1 : 3-diazines related structurally to vitamin-B<sub>1</sub>. CLV. Synthesis of thymine and its conversion into uracil.** A. LITZINGER and T. B. JOHNSON (J. Amer. Chem. Soc., 1936, 58, 1936—1939, 1940—1942).—CLIV (cf. A., 1935, 991). 6-Hydroxy-2-ethylthiolpyrimidine-5-acetylhydrazide, m.p. 207—208° (decomp.) (from the Et ester and EtOH-N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O), is converted into the azide (I), m.p. 175—180° (decomp., after evolution of N<sub>2</sub> at 75—80°), and thence (in PhMe) into 6-hydroxy-2-ethylthiol-5-carbimidomethylpyrimidine (II), m.p. 189—191° (decomp.). (II) with warm H<sub>2</sub>O gives mainly s-di-(6-hydroxy-2-ethylthiolpyrimidine-5-methyl)carbamide, m.p. 270—272° (decomp.), and a little 6-hydroxy-2-ethylthiol-5-aminomethylpyrimidine, m.p. 221—222° (decomp.) [N-CO<sub>2</sub>Et- (III), m.p. 148.5—149.5°, and N-CO<sub>2</sub>CH<sub>2</sub>Ph- (IV), m.p. 159—160°, derivatives, obtained from (I) or (II) with EtOH and CH<sub>2</sub>Ph.OH, respectively]. (II) with aq. NH<sub>3</sub> and NH<sub>2</sub>Ph (in dioxan) affords 6-hydroxy-2-ethylthiol-5-carbamido-, m.p. 190—192° (decomp.), and -5-phenylcarbamido-, m.p. 223—224° (decomp.), -methylpyrimidine, respectively. Uracil-5-acetylhydrazide, decomp. about 326° (darkens at 285°), is similarly converted through the azide, m.p. 275—276° (decomp., after evolution of N<sub>2</sub> at 75—80°), into thyminecarbamide [5-carbimidomethyluracil] (V),  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} > \text{C} \cdot \text{CH}_2 \cdot \text{NCO}$ , m.p. 273—275° (decomp.), and thence (boiling H<sub>2</sub>O) into s-dithyminecarbamide, decomp. 315°. Et (VI), m.p. 256—257°, and benzyl, m.p. 261—263° (decomp.), thyminecarbamates are obtained by hydrolysis (warm EtOH—conc. HCl) of (III) and (IV), respectively.

CLV. Partly a more detailed account of work previously reviewed (this vol., 1126). Thyminecarbamide [5-aminomethyluracil] (VII), m.p. 260—270° (decomp.) [hydrochloride (+0.5 H<sub>2</sub>O), m.p. 242—243° (decomp.); sulphate (+H<sub>2</sub>O) (VIII), m.p. 245—246° (decomp.)], is obtained (not absolutely pure) by hydrolysis (HCl or H<sub>2</sub>SO<sub>4</sub>) of the above (II), (III), (V), and (VI). (VII) is further hydrolysed (conc. HCl and to some extent by boiling H<sub>2</sub>O) to uracil (IX), CH<sub>2</sub>O, and NH<sub>3</sub>. (VII) with Ba(NO<sub>3</sub>)<sub>2</sub> and 0.2M-H<sub>2</sub>SO<sub>4</sub> gives impure thymine alcohol [5-hydroxymethyluracil], m.p. 190—200° [also hydrolysed to (IX)], which could not be synthesised from (IX) and CH<sub>2</sub>O. (VII) and N oxides in H<sub>2</sub>O give the compound,

NH·CH·C·CH, m.p. 195—200°. Thyminecarbamide, m.p. 204—205°, is prepared from (VIII) and NH<sub>4</sub>NCS.

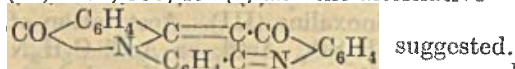
H. B.

**Synthesis of benziminazole derivatives.** R. WEIDENHAGEN (Ber., 1936, 69, [B], 2263—2272).—

The author's glyoxaline synthesis (A., 1935, 1380, 1507) is extended to benziminazoles. o-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, Cu(OAc)<sub>2</sub>, and MeCHO in H<sub>2</sub>O afford the Cu derivatives of 2-methylbenziminazole, whence the parent compound, m.p. 175—176°, in 75% yield. The following -benziminazoles and the corresponding Cu<sup>I</sup> derivatives are analogously obtained: 2-ethyl-, m.p. 174—175°; 2-n-propyl-, m.p. 157—159°; 2-isopropyl-, m.p. 228°; 2-n-butyl-, m.p. 149—151°; 2-isobutyl-, m.p. 186—187°; 2-n-amyl-, m.p. 159—161°; 2-n-hexyl-, m.p. 136—138°; 2-β-dimethyl-Δ<sup>αα</sup>-heptadienyl- (from citral), m.p. (indef.) 102°; 2-phenyl-, m.p. 290°; 2-o-nitrophenyl- hydrochloride, m.p. 291° (decomp.); 2-m-nitrophenyl- (+1H<sub>2</sub>O), m.p. 204°; 2-p-nitrophenyl- hydrochloride, m.p. 310° (decomp.); 2-4'-hydroxy-3'-methoxyphenyl-, m.p. 221—222°; 2-p-methoxyphenyl-, m.p. 228—230°; 2-3' : 4'-methylene-dioxyphenyl-, m.p. 249°; 2-styryl-, m.p. 201—202°; 2-furyl-, m.p. 285—286°. Et 2-ethylbenziminazole-5-carboxylate, m.p. 151°, and Et 2-hexylbenziminazole-5-carboxylate hydrochloride, m.p. 238—240°, are derived from (NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>Et. 2-iso-Propyl-, m.p. 239—240°, and 2-n-hexyl-, m.p. 199—202°, -1' : 2'-naphthiminazole are described.

H. W.

**Complex benzylation products of indigotin.** Höchst Yellow U. E. HOPE and J. S. ANDERSON (J.C.S., 1936, 1474—1478).—Methylation (Me<sub>2</sub>SO<sub>4</sub>—NaOH) of the “monohydrate of Höchst Yellow U” (cf. Posner *et al.*, A., 1929, 1313) gives a Me<sub>2</sub>, m.p. 167—168°, and a Me derivative, m.p. 238—240° (decomp.). Höchst Yellow U (I) and 15% NaOH at 215° afford an NH<sub>2</sub>-acid, m.p. 232° (efferv.) [(+2H<sub>2</sub>O), m.p. 182° (efferv.); NH<sub>4</sub> salt; Bz derivative, m.p. 212—213°, and (+H<sub>2</sub>O), m.p. 265—267° (efferv.); Ac derivative, m.p. 272°; Me<sub>2</sub> derivative, m.p. 238—239°, converted by HCl into an acid (+2H<sub>2</sub>O), m.p. 308—310° (decomp.)], which when heated forms a product, m.p. 230—231°; at the same time, an acid (+H<sub>2</sub>O), m.p. 206—208° (methylation product, m.p. 247—249°), is also obtained. These results are not in agreement with the formula of de Diesbach *et al.* (A., 1934, 306) for (I) and the alternative



F. R. S.

**Manufacture of heterocyclic hydroxy-compounds.**—See B., 1936, 977.

**C-Aminophthalazone and N-aminophthalimidine.** A. DARAPSKY and P. HEINRICHS (J. pr. Chem., 1936, [ii], 146, 307—318).—Phthalazonecarboxylic acid (I), m.p. 232° (NH<sub>4</sub>, m.p. 237°, and N.H<sub>4</sub>, m.p. 249—250°, salts), obtained by the direct action of N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>SO<sub>4</sub> on the product of the oxidation of C<sub>10</sub>H<sub>8</sub>, is esterified by HCl-MeOH and HCl-EtOH to the Me, m.p. 211°, and Et, m.p. 169°, ester. The latter is transformed by N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O in boiling abs. EtOH into phthalazonecarbohydrazide, m.p. 234° (hydrochloride; :CHPh, m.p. >390°, o-hydroxybenzylidene-, m.p. >290°, and anisylidene-, m.p. >290°, derivatives), whence phthalazonecarboazide, transformed by warm NH<sub>2</sub>Ph into the corresponding anilide, m.p. 288°, and by boiling EtOH into Et phthalazonecarbamate, m.p. 207°, whence 4-amino-phthalazone (II), m.p. 257—258° (hydrochloride, m.p.



240°; *perchlorate*, m.p. 209°). (II) is transformed by  $\text{NaNO}_2$  into phthalhydrazide. Reduction of (I) with Zn dust and conc.  $\text{HCl}$  at 100° yields *phthalimidine-carboxylic acid*,  $\text{CO} \begin{array}{c} \text{NH} \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{CO}_2\text{H}$ , m.p. 146—147°, which loses  $\text{CO}_2$  when heated above its m.p. and yields phthalimidine. With Zn dust in alkaline solution reduction occurs without loss of N, and gives rise to *aminophthalimidinecarboxylic acid*,

$\text{CO} \begin{array}{c} \text{N}(\text{NH}_2) \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{CO}_2\text{H}$ , m.p. 140° [*hydrochloride*, m.p. 188°;  $\cdot\text{CHPh}$ , m.p. 106°, *o*-hydroxybenzylidene, m.p. 276°, and  $\text{Bz}$ , m.p. 141—142° (decomp.), derivatives]. Similarly phthalazone is reduced to *aminophthalimidine* ( $\cdot\text{CHPh}$ , m.p. 206°, and *o*-hydroxybenzylidene, m.p. 276°, derivatives). Attempts to reduce (I) (Pd or Pt in alkaline or  $\text{AcOH}$  solution) without altering the structure of the six-membered pyridazine ring were unsuccessful. H. W.

### Hydroxypolyketones. III. Benzoylformoin.

A. H. BLATT (J. Amer. Chem. Soc., 1936, 58, 1894—1899).—Benzoylformoin (I) and its open-chain  $\text{Alk}_1$  derivatives (cf. A., 1935, 982) react either as ene-diols or hydroxyketodihydrofurans; the cyclic  $\text{Alk}_1$  and  $\text{Alk}_2$  derivatives are ketoalkoxydihydrofurans. Distillation of (I) at about 240°/0.5 mm. gives an unstable red liquid, probably  $\begin{array}{c} \text{OH} \cdots \cdots \text{O} \\ \text{CPh} \cdot \text{C}(\text{OH}) \cdot \text{CBz} \end{array}$  (dotted line indicates chelation), which gradually reverts to the stable, yellow cryst. form (2:4-dihydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran). (I) and  $\text{Cu}(\text{OAc})_2$  in  $\text{Et}_2\text{O}$  afford a brown *Cu* derivative,  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{Cu}$ , which is thus derived from an ene-diol. (I) heated with  $\text{SOCl}_2$  gives  $(\cdot\text{CO} \cdot \text{COPh})_n$ , which, like (I) and benzoin, is oxidised by  $\text{Cu}(\text{OAc})_2$  in aq.  $\text{AcOH}$  to benzil [ $(s\text{-C}_6\text{H}_4\text{Me}_3\text{CO})_2$  is similarly obtained from mesitoylformoin]. (I) and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{MeOH}$  afford 2-phenyl-3- $\alpha$ -hydroxy- $\beta$ -keto- $\beta$ -phenylethylquinoxaline (II), m.p. 187—188°, converted by  $\text{MgPhBr}$  into 2-phenyl-3- $\alpha\beta$ -dihydroxy- $\beta\beta$ -diphenylethylquinoxaline, m.p. 163—164°, which is oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to 3-phenylquinoxaline-2-carboxylic acid and thence to 2-hydroxy-3-phenylquinoxaline (III). Acetylation of (I) with  $\text{Ac}_2\text{O}$ ,  $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ ,  $\text{AcCl}$ , or  $\text{AcCl}-\text{C}_6\text{H}_5\text{N}$  gives 3-keto-2:4-diacetoxy-2:5-diphenyl-2:3-dihydrofuran (IV) (cf. Abenius, A., 1894, i, 286), converted by  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{C}_6\text{H}_6$  into the 4-hydroxy-2-acetoxy-derivative, m.p. 198°, which is reacylated to (IV) and with  $\text{MeOH}-\text{HCl}$  affords the 4-hydroxy-2-methoxy-derivative (*loc. cit.*), also obtained from the 4-acetoxy-2-methoxy-derivative (Abenius, *loc. cit.*) and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ . Acetylation of (I) with  $\text{Ac}_2\text{O}$  in aq.  $\text{AcOH}$  yields the open-chain acetate,  $\text{OAc} \cdot \text{CHBz} \cdot \text{COBz}$ , m.p. 109—110° (or its enol), converted by  $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$  into (IV) and by  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  into (III).  $s\text{-C}_6\text{H}_4\text{Me}_3\text{COCl}$  and (I) in  $\text{C}_6\text{H}_5\text{N}$  give the di-(2:4:6-trimethylbenzoate) (V),  $\text{OR} \cdot \text{CPh} \cdot \text{C}(\text{OR}) \cdot \text{COBz}$  ( $\text{R} = s\text{-C}_6\text{H}_4\text{Me}_3\text{CO}$ ), m.p. 145°, which with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in  $\text{MeOH}$  affords 2-phenyl-3- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyloxy)styrylquinoxaline, m.p. 182—183°, oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to (III). (V) is converted by  $\text{MeOH}$ -conc.  $\text{HCl}$  into an isomeride, m.p. 189° [isolated once during prep. of (V)], which does not react with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ . 3-Keto-2:4-

dimethoxy-2:5-diphenyl-2:3-dihydrofuran with  $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$  gives the 2-acetoxy-4-methoxy-derivative, m.p. 164—165° [also obtained by acetylation of  $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{OMe}) \cdot \text{COBz}$  (*loc. cit.*)], unaffected by  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ; the 2-acetoxy-4-ethoxy-derivative, m.p. 133°, is prepared by the same methods. Any of the above furans containing the 4-alkoxy-group is converted by  $\text{AcOH}-\text{HBr}$  into a mixture of 2-bromo-4-alkoxy-derivative (VI) (not isolable in pure condition) and 3:3'-diketo-4:4'-dialkoxy-2:5:2':5'-tetraphenyl-2:3:2':3'-tetrahydro-2:2'-difuryl (VII) (the 4:4'-dimethoxy-, m.p. 226—227°, and 4:4'-diethoxy-, m.p. 218—219°, derivatives are described). (VI) is converted by heat or acidified KI in  $\text{COMe}_2$  into (VII). The Et ether,  $\text{OH} \cdot \text{CPh} \cdot \text{C}(\text{OEt}) \cdot \text{COBz}$  (VIII) (*loc. cit.*), unlike the Me ether, gives (III) with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ ; it is brominated to  $\text{COPh} \cdot \text{CBr}(\text{OEt}) \cdot \text{COBz}$  (Abenius, *loc. cit.*), which with acidified KI and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  affords (VIII) and (III), respectively.

2-Phenyl-3- $\beta$ -keto- $\alpha$ -methoxy- $\beta$ -phenylethylquinoxaline is cleaved by  $\text{MeOH}-\text{NaOMe}$  to  $\text{MeOBz}$ ,  $\text{BzOH}$ , (III), and 3-phenyl-2-methoxymethylquinoxaline (IX), m.p. 78—79°; (II) similarly gives (III) and 3-phenyl-2-hydroxymethylquinoxaline, m.p. 140—141°, which is methylated ( $\text{MeI}$ , solid  $\text{NaOH}$ ) to (IX) and oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to 3-phenylquinoxaline-2-carboxylic acid. H. B.

$\alpha\delta$ -Diphenylbutane- $\alpha\beta\delta$ -trione enol; alkylation and benzoylation. R. E. LUTZ and A. H. STUART (J. Amer. Chem. Soc., 1936, 58, 1885—1890; cf. Kohler and Woodward, this vol., 1515).—Partly a correction and amplification of previous work (A., 1934, 1222, 1361).  $\alpha$ -Hydroxy- $\alpha\beta$ -dibenzoyl ethylene (I) with  $\text{BzCl}$  and a trace of conc.  $\text{H}_2\text{SO}_4$  gives 2-chloro-3-keto-2:5-diphenyl-2:3-dihydrofuran (II), hydrolysed ( $\text{MeOH}-\text{NaOH}$ ) to (I) and converted by  $\text{MeOH}-\text{NaOMe}$  into the 2-OMe-derivative (III). (II) and  $\text{AgOBz}$  in  $\text{Pr}_2\text{O}$  afford 3-keto-2-benzoyloxy-2:5-diphenyl-2:3-dihydrofuran (IV), m.p. 162—163° [also obtained from (I),  $\text{Bz}_2\text{O}$ , and a little conc.  $\text{H}_2\text{SO}_4$ ], readily hydrolysed ( $\text{NaOH}$  or  $\text{NaOMe}$ ) to (I). (I) and  $\text{BzCl}$  in aq.  $\text{NaOH}$  give  $\approx 50\%$  of  $\alpha$ -benzoyloxy- $\alpha\beta$ -dibenzoyl ethylene (or  $\gamma\delta$ -diketo- $\alpha$ -benzoyloxy- $\alpha\delta$ -diphenyl- $\Delta^a$ -butene) (V), m.p. 139°, converted by  $\text{MeOH}-\text{HCl}$  into (III) and by  $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$  and  $\text{AcCl}-\text{H}_2\text{SO}_4$  into 3:4-diacetoxy- (VI) and 3-chloro-4-acetoxy- (VII) -2:5-diphenylfuran, respectively. (I), (II), (IV), and (VII) react immediately with  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in boiling  $\text{EtOH}$  yielding 2-phenyl-3-phenacylquinoxaline, m.p. 169—170° [oxidised ( $\text{CrO}_3$ ,  $\text{AcOH}$ ) to 3-hydroxy-2-phenylquinoxaline and a little 2-phenylquinoxaline-3-carboxylic acid], also obtained (on prolonged action) from  $\alpha$ -methoxy- and  $\alpha$ -amino- $\alpha\beta$ -dibenzoyl ethylene, but not from (III), (IV), (VI), and *trans*- $\alpha$ -chloro- $\alpha\beta$ -dibenzoyl ethylene. Evidence is given indicating that methylation of (I) gives the stable  $\text{COPh} \cdot \text{C}(\text{OMe}) \cdot \text{CH} \cdot \text{COPh}$  and the unstable  $\text{COPh} \cdot \text{CO} \cdot \text{CH} \cdot \text{CPh} \cdot \text{OMe}$ . It is unlikely that the colourless and yellow forms of (I) are *cis-trans* isomerides; the former is probably 2-hydroxy-3-keto-2:5-diphenyl-2:3-dihydrofuran.  $\text{CPhCl} \cdot \text{CH} \cdot \text{CO} \cdot \text{COPh}$  is (II).

The *Ag* salt of (I) with  $\text{AlkI}$  in  $\text{Pr}_2\text{O}$  gives (mainly)

2-hydroxy-3-keto-2 : 5-diphenyl-4-alkyl-2 : 3-dihydrofuran [4-Me, m.p. 143—144°, 4-Et, m.p. 113°, and 4-Pr<sup>a</sup>, m.p. 137.5°, derivatives, hydrolysed by aq. Ba(OH)<sub>2</sub> to BzCO<sub>2</sub>H and CPhEt, CPhPr, and CPhBu, respectively], and 0—20% of the  $\alpha$ -alkoxy- $\alpha$ -dibenzoyl ethylene. The Na and Ag salts of (I) with Me<sub>2</sub>SO<sub>4</sub> in MeOH and EtOH afford (III) and the 2-OEt-derivative, respectively. (I) and 2-hydroxy-1 : 4-naphthaquinone react in similar manners. All m.p. are corr.

H. B.

**Heteropolar combinations. II. Coloured "carbenium" salts of halogen acids with 4-hydroxy-2-thion-(or -oxo-)tetrahydroquinazoline and with the corresponding halogenomercuric compounds.** C. V. GHEORGHIU and (MLLE.) L. MANOLESCU (Bull. Soc. chim., 1936, [v], 3, 1830—1836; cf. this vol., 1126).—4-Ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazol-2-one with halogen acids in Ac<sub>2</sub>O gives the *hydrochloride*, decomp. >300°, and *hydriodide*, m.p. 225°, of the 4-OH-compound, and the *hydrobromide*, m.p. 253° (decomp.), of the 4-OAc-compound; all these are yellow and therefore presumably in the carbonium state. 2-Thion-4-ethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline (I) similarly yields the *hydrochloride*, m.p. 225—226°, and *hydriodide*, m.p. 193—194° (red), of its 4-OH-compound, and the *hydrobromide*, m.p. 231—234° (orange), of its 4-OAc-compound. The HgCl<sub>2</sub>, HgBr<sub>2</sub>, and HgI<sub>2</sub> compounds of (I), with HBr or HI in Ac<sub>2</sub>O, give the *dihydrobromides*, m.p. 200—217°, 221°, and 207°, and the *dihydriodides*, m.p. 145°, 109—110°, and 104—105°, respectively, of 2-thiol-3-hydroxy-3-phenyl-3 : 4-dihydroquinazolinium-*S*-mercuri-dichloride, -dibromide, and -diiodide; these salts are all red in colour.

E. W. W.

**Formation of cyclic azo-compounds from 2 : 2'-diaminodiphenyls.** R. B. SANDIN and T. L. CAIRNS (J. Amer. Chem. Soc., 1936, 58, 2019—2020).—Tetrazotised 2 : 2'-diaminodiphenyl with Na<sub>3</sub>AsO<sub>3</sub> in aq. Na<sub>2</sub>CO<sub>3</sub>+CuSO<sub>4</sub> gives 45% of the cyclic 2 : 2'-azodiphenyl, m.p. 155° [the *o*-diphenyleneazone of Tauber (A., 1892, 183)]. 2 : 2'-Azo-4 : 4'-dimethyldiphenyl, m.p. 184—185°, is similarly obtained from the 2 : 2'-(NH<sub>2</sub>)<sub>2</sub>-derivative and also by reduction (Na-Hg, MeOH) of the 2 : 2'-(NO<sub>2</sub>)<sub>2</sub>-derivative.

H. B.

**Manufacture of halogenoamino-1 : 9-anthrapyrimidines.**—See B., 1936, 1084.

**Nitrogenous heterocyclic rings. XXIV. Benzodipyrroles. IV. Ring-closure with a phenylenedihydrazone.** P. RUGGLI and C. PETITJEAN (Helv. Chim. Acta, 1936, 19, 928—930; cf. this vol., 866).—Treatment of deoxybenzoin with *m*-C<sub>6</sub>H<sub>4</sub>(NH.NH<sub>2</sub>)<sub>2</sub> in boiling EtOH affords *dideoxybenzoin-m-phenylenedihydrazone*, *m*-C<sub>6</sub>H<sub>4</sub>(NH.NH.CPh.CH<sub>2</sub>Ph)<sub>2</sub>, m.p. 164°, which resinifies when heated with ZnCl<sub>2</sub> but is transformed by short treatment with boiling H<sub>2</sub>SO<sub>4</sub>-EtOH into tetraphenylbenzodipyrrole [2 : 3 : 2' : 3'-tetraphenylpyrrolo-4' : 5'-5 : 6-indole], m.p. 279°.

H. W.

**Relationship of the tricyanomelamines to polymerised dicyanamides.** J. BIECHLER (Compt. rend., 1936, 203, 568—570; cf. A., 1935, 482).—

Alkyl or aryl K cyanamides (I) with CNCl afford tricyanomelamines (cf. A., 1922, i, 438), stable at 170°. The following are prepared: *tri-phenyl-* (II), m.p. 210°, *-o-tolyl-*, m.p. 203°, *-o-*, m.p. 110°, and *-p-anisyl-*, m.p. 201°, *-p-phenetyl-*, m.p. 151°, *-naphthyl-*, m.p. 271°, *-2 : 4-xyl-yl-*, m.p. 193°, *-benzyl-*, m.p. 158°, and *-methyl-tricyanomelamine*, m.p. 241°. Deficiency of (I) in the above reaction yields chlorotriazines. The following are prepared: 4 : 6-dichloro-2-cyanoanilino-, m.p. 138—183°, and 6-chloro-2 : 4-dicyanoanilino-1 : 3 : 5-triazine, m.p. 181°, converted into 1-phenyl-3 : 5-di-*p-phenetyl-*, m.p. 115—120°, and 1 : 3-diphenyl-5-*p-phenetyl-tricyanomelamine*, m.p. 98—104°, respectively. From measurements of the heat of polymerisation of NPh(CN)<sub>2</sub> and (II), the structure of the polymeride is deduced.

J. L. D.

**Aminoflavin, 9- $\beta$ -aminoethylisoalloxazine.** P. KARRER and R. NAEF (Helv. Chim. Acta, 1936, 19, 1029—1033).—*o*-C<sub>6</sub>H<sub>4</sub>Cl.NO<sub>2</sub> and OH.CH<sub>2</sub>.CH<sub>2</sub>.NH<sub>2</sub> in boiling C<sub>5</sub>H<sub>5</sub>N give  $\beta$ -*o-nitroanilinoethyl alcohol*, m.p. 76° [Ac derivative (? acetate), m.p. 67°], transformed by PCl<sub>5</sub> in CHCl<sub>3</sub> at room temp. into *o-nitro- $\beta$ -chloroethyl-aniline*, m.p. 59°, which with *o*-C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK at 170° gives *o-nitro- $\beta$ -phthalimidoethyl-aniline* (I), m.p. 184°. (I) is reduced by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in 50% EtOH to *o-amino- $\beta$ -phthalimidoethyl-aniline*, m.p. 124°, the *hydrochloride* of which condenses with alloxantin to 9- $\beta$ -phthalimidoethylisoalloxazine, decomp. about 285°, hydrolysed by conc. HCl-AcOH at 100° to 9- $\beta$ -aminoethylisoalloxazine *hydrochloride* (II), decomp. >300°. The alkaline solution of (II) darkens in sunlight but does not form a pigment sol. in CHCl<sub>3</sub>; in neutral solution or in presence of AcOH (II) gradually darkens without formation of > a trace of lumichrome. Photolysis of (II) therefore occurs in a more complex and incomplete manner than that of the OH-flavins.

H. W.

**Synthesis of flavins.** P. KARRER and T. H. QUTBELL (Helv. Chim. Acta, 1936, 19, 1034—1042).—*Et p-ethylphenylcarbamate*, from *p*-C<sub>6</sub>H<sub>4</sub>Et.NH<sub>2</sub> and ClCO<sub>2</sub>Et in dil. COMe<sub>2</sub>, is converted by HNO<sub>3</sub> (*d* 1.42) and conc. H<sub>2</sub>SO<sub>4</sub> at -3° to -8° into *Et 2-nitro-4-ethylphenylcarbamate*, m.p. 40.5°, which is reduced (Pt in EtOH) to *Et 2-amino-4-ethylphenylcarbamate*, m.p. 63°. The latter is transformed by *d*-ribose in boiling MeOH followed by reduction with Ni and H<sub>2</sub> at 95°/25 atm. into 2-carbethoxyamino-5-ethylphenyl-*d*-ribamine, m.p. 169°, which is hydrolysed and then converted by alloxan and H<sub>3</sub>BO<sub>3</sub> in AcOH containing NaOAc into 7-ethyl-9-*d*-1'-ribitylisoalloxazine (I), m.p. 220° after softening at 215°. 3 : 4-C<sub>6</sub>H<sub>3</sub>MeEt.NH<sub>2</sub> and *l*-arabinose yield 3-methyl-4-ethylphenyl-*l*-arabamine *hydrochloride*, m.p. 198°, whence 2-benzeneazo-5-methyl-4-ethylphenyl-*l*-arabamine, m.p. 185—186°, reduced (Ni or, preferably, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) to 7-methyl-6-ethyl-9-*l*-1'-arabitylisoalloxazine, decomp. 243—244°. 3 : 4-C<sub>6</sub>H<sub>3</sub>MeEt.NH<sub>2</sub> and *d*-ribose give 3-methyl-4-ethylphenyl-*d*-ribamine *hydrochloride*, whence 2-benzeneazo-5-methyl-4-ethylphenyl-*d*-ribamine, m.p. 152°, and 7-methyl-6-ethyl-9-*d*-1'-ribitylisoalloxazine (II), m.p. 238—240° after incipient decomp. when heated rapidly. 3-Naphthyl-*l*-arabamine, m.p. 156°, obtained by reduction of the condensation product,

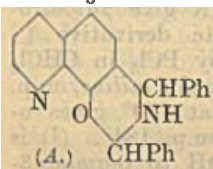


$C_{15}H_{17}O_4N$ , decomp. 163—164°, of the sugar and  $\beta$ - $C_{10}H_9NH_2$  in boiling MeOH, is transformed into 1-benzeneazo-2-arabitylaminonaphthalene, m.p. 193°, and 5:6-benzo-9-1'-arabitylisoalloxazine, decomp. about 275°.  $\beta$ -Naphthyl-d-ribamine, m.p. 157°, affords 1-benzeneazo-2-d-ribitylaminonaphthalene, m.p. 195°, whence 5:6-benzo-9-d-1'-ribitylisoalloxazine (III), decomp. about 290°. The action of (I) on animals on a vitamin-B<sub>2</sub>-free diet is stimulating but not prolonged, whereas (II) and (III) are physiologically inactive. H. W.

**Optical absorption of porphyrins.**—See this vol., 1444.

**Manufacture of dialkyl-substituted amides of isooxazolecarboxylic acids.**—See B., 1936, 1084.

**Hydroxyquinolines. II. Synthesis of quino-linoisooxazines.** F. PIRRONI (Gazzetta, 1936, 66, 518—524).—8-Hydroxyquinoline, PhCHO, and excess of  $NH_3$  in EtOH give a substance,  $C_{23}H_{28}ON_2$ , m.p. 156—157°. This is decomposed by boiling dil. HCl with liberation of PhCHO and formation of a cryst. substance, forms a picrate, m.p. 220—221°, and Ac, m.p. 208—209°, and Bz, m.p. 196—197°, derivatives, but gives no metallic

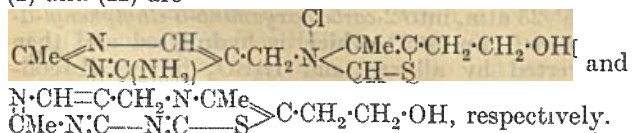


compounds or reactions of 8-hydroxyquinoline; it is therefore probably 2:4-diphenyl-5:6-(7':8'-quinolino)-1:3-isooxazine (A). E. W. W.

**Manufacture of sulpheneamides.**—See B., 1936, 1083.

**1-Methyl- $\beta\beta'$ -naphthathiazole and substitution products.**—See B., 1936, 977.

**Constitution of oryzanin (vitamin-B<sub>1</sub>).** T. IMAI (Z. physiol. Chem., 1936, 243, II; cf. this vol., 487).—Aneurin (I) and thiochrome (II) contain two CMe groups and in (I) there is a  $CH_2$  bridge between the thiazole and pyrimidine nuclei. KSH with 8-chloro- or 8-bromo-theophylline gives 8-thiotheophylline, which with  $CH_2Cl\cdot COMe$  gives the compound  $NMe\cdot CO\cdot C\equiv N\cdot CMe\cdot S\equiv CH$  which exhibits no blue fluorescence. (I) is almost quantitatively converted by  $H_2SO_3$  into 4-amino-2-methyl-5-pyrimidylsulphonic acid and 4-methyl-5- $\beta$ -hydroxyethylthiazole. Hence (I) and (II) are



W. McC.

**Aneurin. III. Methyl  $\alpha$ -chloro- $\gamma$ -hydroxypropyl ketone and its application to thiazole synthesis.** A. R. TODD, F. BERGEL, and (Miss) A. JACOB. IV. 5-Thioformamidopyrimidines. A. R. TODD, F. BERGEL, and KARIMULLAH. V. Synthesis of 3-pyrimidylthiazolium salts, including an isomeride of aneurin. A. R. TODD and F. BERGEL (J.C.S., 1936, 1555—1557, 1557—1559, 1559—1562).—III.  $OAc\cdot[CH_2]_2\cdot CHAc\cdot CO_2Et$  with  $SO_2Cl_2$  gives Et  $\alpha$ -chloro- $\alpha$ - $\beta'$ -acetoxethylacetoacetate, b.p. 120—121°/2 mm., which with  $H_2SO_4$ -AcOH

forms Me  $\alpha$ -chloro- $\gamma$ -acetoxypyrrol ketone, b.p. 85—92°/16 mm. The ketone with thioformamide is converted into 4-methyl-5- $\beta$ -hydroxyethylthiazole, the picrate, m.p. 162—163°, of which is identical with that obtained from aneurin (vitamin-B<sub>1</sub>). Et  $\alpha$ - $\beta'$ -phenoxyethylacetoacetate, b.p. 148°/4 mm., prepared from  $OPh\cdot CH_2\cdot CH_2Br$  and Et sodioacetoacetate, with  $SO_2Cl_2$  affords Et  $\alpha$ -chloro- $\alpha$ -2-phenoxyethylacetoacetate, b.p. 135—140°/3 mm., hydrolysed to Me  $\alpha$ -chloro- $\gamma$ -phenoxypropyl ketone, b.p. 168—172°/12 mm., which with  $NH_2\cdot CSMe$  gives 2:4-dimethyl-5- $\beta$ -phenoxyethylthiazole (picrate, m.p. 122°).

IV. 5-Amino- with dithioacetic acid yields 5-thioacetamido-, m.p. 265—267°, and with dithioformic acid affords 5-thioformamido-4-methyluracil, m.p. 260—262°, which with  $CH_2Cl\cdot COMe$  gives 3-(2':6'-dihydroxy-4'-methylpyrimidyl-5')-4-methylthiazolium chloride, m.p. 306° (decomp.). 6-Amino-5-thioformamido-4-methylpyrimidine gives 4-methylpurine at its m.p. 168°. 2-Amino-6-hydroxy-4-ethylpyrimidine, m.p. 247—248°, prepared from Et propionylacetate and guanidine carbonate, with  $PCl_3$  gives 6-chloro-2-amino-, m.p. 120—121°, converted ( $NH_3$ ) into 2:6-diamino-4-ethylpyrimidine, m.p. 160—161°. Thioformylation (K dithioformate) affords 6-amino-, m.p. 178°, and 2:6-diamino-5-thioformamido-4-methylpyrimidine, m.p. 255°, which is converted ( $CH_2Cl\cdot COMe$ ) into 3-(2':6'-diamino-4'-methylpyrimidyl-5')-4-methylthiazolium chloride hydrochloride ( $+3H_2O$ ), m.p. 255°.

V. 6-Amino-5-thioformamido-4-ethylpyrimidine and Me  $\alpha$ -chloro- $\gamma$ -hydroxypropyl ketone give 3-(6'-amino-4'-ethylpyrimidyl-5')-4-methyl-5- $\beta$ -hydroxyethylthiazolium chloride hydrochloride ( $+H_2O$ ), m.p. 220° (decomp.), which is not identical with aneurin hydrochloride, and shows no measurable physiological activity, in common with the following: 3-(6'-amino-4'-ethylpyrimidyl-5')-4-methylthiazolium chloride hydrochloride, m.p. 252—253° (decomp.), 3-(6'-amino-4'-methylpyrimidyl-5')-4-methyl-5- $\beta$ -hydroxyethylthiazolium chloride hydrochloride ( $+H_2O$ ), m.p. 250° (decomp.), and 4-methylthiazolium chloride hydrochloride ( $+2H_2O$ ), m.p. 254—255° (decomp.). 2:6-Dihydroxy-8-thiopurine with  $CH_2Cl\cdot COMe$  yields 2:6-dihydroxy-4-methylthiazolo-(2':3':8:7)-purine, m.p. >250°, but 8-thio-6-ethylpurine, m.p. >300°, does not condense satisfactorily with chloroketones. The structure of aneurin is discussed. F. R. S.

**Lupin alkaloids. XI. Octahydropyridocoline-norlupinane relationship.** G. R. CLEMO, T. P. METCALFE, and R. RAPER (J.C.S., 1936, 1429—1431).—Et 2-methylpyrrolidine-5-acetate,  $CH_2Cl\cdot CH_2\cdot CO_2Et$ , and NaOAc give Et 2-methylpyrrolidine-5-acetate-1- $\beta$ -propanate, b.p. 168—169°/14 mm., which is cyclised (K) to 7-keto-3-methyloctahydropyrrocoline, b.p. 72—75°/1 mm. (picrate, m.p. 204°), reduced (Wolff) to 3-methyloctahydropyrrocoline and a substance, b.p. 95°/1 mm. [picrolonate, m.p. 245° (decomp.)]. Me piperidine-2-acetate,  $CH_2Cl\cdot CH_2\cdot CO_2Me$ , and NaOAc afford Me piperidine-2-acetate-1- $\beta$ -propanate, b.p. 170—172°/1 mm., cyclised (K) to 2-keto-octahydropyridocoline, b.p. 70—72°/1 mm. (picrate, m.p. 211°), which is reduced (Zn-Hg) to norlupinane, also obtained by reduction (Wolff) of 1-keto-octahydropyridocoline.

These results support the *cis-trans* formulation of octahydropyridocoline and norlupinane.

F. R. S.

**Electrolytic reduction of vasicine.** K. S. NARANG and J. N. RAY (J.C.S., 1936, 1570).—The substances reported (this vol., 869) to be dissimilar are now shown to be identical.

F. R. S.

**Ambaline, a new alkaloid from *Pycnarrhena manillensis*, Vidal.** G. Q. QUIBILAN and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 353—364).—*Ambaline*,  $C_{38}H_{52}O_{10}N_2$ , m.p. 123°,  $[\alpha]_D +143.2^\circ$  in  $CHCl_3$  [*aurichloride*, m.p. 185° (decomp.); *platinichloride*, m.p. 260°; *dihydrochloride*, m.p. 265°; *dihydrobromide*, m.p. 195—197° (decomp.); *dihydriodide*, m.p. 245° (decomp.); *methiodide*, m.p. 263°; *oxime*, m.p. 197° (decomp.); 2:4-dinitrophenylhydrazones, m.p. 96°], has been isolated and its colour reactions determined. It contains  $\cdot CH_2O_2$ , CO, 3 OMe, and 2 NMe, and is toxic.

F. R. S.

**Ambalinine, a new non-phenolic alkaloid from *Pycnarrhena manillensis*, Vidal.** I. VILLANOS and A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1935, 4, 338—341).—A non-phenolic alkaloid, *ambalinine*,  $C_{15}H_{12}O(OMe)_2 \cdot NMe$ , m.p. 203—204° [*platinichloride*, m.p. 240° (decomp.); *aurichloride*, m.p. 170° (decomp.); *picrate*, m.p. 238° (decomp.)], has been isolated.

F. R. S.

**Alkaloids of *Corydalis ambigua* of China, Cham et Sch. (Yen-hu-So). VI. Identification of corydalis D and M.** T. Q. CHOU (Chinese J. Physiol., 1936, 10, 507—511).—*Corydalis D* (I),  $C_{19}H_{17}O_4N$ ,  $[\alpha]_D -305^\circ$ , was oxidised by I in EtOH to a *quaternary iodide*, m.p.  $>300^\circ$ , reduced by Zn- $H_2SO_4$  to *dl-tetrahydrocoptisine*, m.p. 220°. (I) is therefore the *l*-isomeride of this substance. *Corydalis M*,  $C_{21}H_{23}O_5N$ , m.p. 160°, optically inactive, contains 2 OMe and 1  $CH_2O$ , and is probably identical with  $\beta$ -homochelidonine.

P. W. C.

**Microscopic investigation of alkaloids in ergot. I. Ergotamine and ergotaminine.** A. KOFLER (Arch. Pharm., 1936, 274, 398—414).—The compound of ergotamine with  $2COMe \cdot 2H_2O$  (cf. Stoll, A., 1923, i, 127), m.p. 172—174°, and *compounds* with  $H_2O$ , m.p. 174—176°,  $C_5H_5N$ , m.p. 172—176°, MeOH, m.p. 208—210° (decomp.), and EtOH, m.p. 208—210°, form monoclinic crystals; *compounds* with  $C_6H_6$ , m.p. 168—172°, and  $(CH_2Cl)_2$ , m.p. 182—186°, are rhombic. *Compound* with  $Et_2O$ , m.p. 183—185°.  $n_D$  for the axes of these compounds and ergotaminine are recorded.

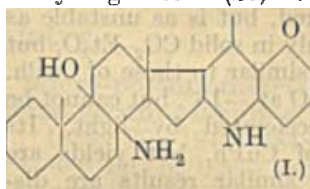
F. R. G.

**Alkaloids of ergot. VII. isoErgine and isolysergic acids.** S. SMITH and G. M. TIMMS (J.C.S., 1936, 1440—1444).—The laevorotatory physiologically active ergot alkaloids can be transformed readily into alkaloids of high dextrorotation with weak physiological action and the change is readily reversed. Ergine can be converted ( $EtOH-H_3PO_4$ ) into *isoergine* (I), m.p. 242° (decomp.),  $[\alpha]_{541}^{20} +25^\circ$  in  $C_5H_5N$  [*hydrochloride*, m.p. 269° (decomp.)]. (I) is hydrolysed to lysergic acid (II), which is converted by hot  $H_2O$  into *isolysergic acid* ( $+2H_2O$ ), m.p. 218° (decomp.)  $[\alpha]_{461}^{20} +368^\circ$  in  $C_5H_5N$  [*nitrate* ( $+H_2O$ ), m.p.

185° (decomp.); *Me ester*, m.p. 170° (decomp.),  $[\alpha]_{541}^{20} +236^\circ$  in  $CHCl_3$ ], reconverted into (II) by aq. KOH. (II) with  $Ba(OH)_2$  yields *inactive lysergic acid* ( $+2H_2O$ ), m.p. 250° (decomp.) [*Me ester*, m.p. about 160° (decomp.)], which cannot be reconverted into (II).

F. R. S.

**Alkaloids from *Solanum pseudocapsicum*, L.** G. BARGER and H. L. FRAENKEL-CONRAT (J.C.S., 1936, 1537—1542).—*Solanocapsine* (I),  $C_{26}H_{41}O_2N_2 \cdot H_2O$ , m.p. 222°,  $[\alpha]_D +25.5^\circ$  [*dihydrochloride* ( $+H_2O$ ), m.p.  $>280^\circ$ ; *Ac*<sub>2</sub> derivative, m.p. 150—160°] is dehydrated to *aposanocapsine*, with  $HNO_2$  forms a *NO-compound* (II), m.p. 194° ( $H_2$ -derivative, m.p. 211—212°), and with  $COMe$  yields a *compound*, m.p. 233°, which with  $Ac_2O$  affords *monoacetylsolanocapsine*, m.p. 238°. Oxidation of (II) gives an *acid*, m.p. 226—227°, and a *neutral substance*, m.p. 218°. *Solanocapsidine*,  $C_{26}H_{42}O_4N_2$ , m.p. about 305°, is dehydrogenated (Se) to methylcyclopentenophen-



anthrene, 2-methyl-5-ethylpyridine (*picrate*, m.p. 163°), and 4-methyl-2-ethylpyridine (?) (*picrate*, m.p. about 125°). On the basis of the reactions the formula for (I) is suggested.

The two bases may be secondary products, formed during isolation.

F. R. S.

**Anodic oxidation of brucine and nicotine.** F. FICHTER and H. STENZL (Helv. Chim. Acta, 1936, 19, 1171—1175).—Electrolytic oxidation of brucine in  $H_2SO_4$  at a  $PbO_2$  anode affords dehydrobisapomethylbrucine,  $C_{21}H_{22}O_4N_2$ , or, if reaction is prolonged, a red-brown base. Electrolytic chlorination of brucine yields a mixture of substances,  $C_{21}H_{27}O_7N_2Cl_7$ . Nicotinic acid is obtained by electrochemical oxidation of nicotine in  $H_2SO_4$  at a Pt anode. The products are therefore identical with those obtained by purely chemical methods.

H. W.

**Manufacture of deoxymorphine-C and dihydromorphine-D.**—See B., 1936, 1018.

**Structure and toxicity of arsinic acids of the diphenylamine series.** V. A. ISMAILSKI and A. M. SIMONOV (Bull. Soc. chim., 1936, [v], 3, 1739—1753).—The introduction of OH or NHAc at 4' in 2-nitro- or 2-amino-diphenylamine-4-arsinic acid (A., 1934, 1118) reduces the toxicity, and a similar and greater effect (especially of OH) is produced at 3'. Reduction of toxicity is less with 4'-OMe than with 4'-OH, and still less with 4'-OEt. The use of the effect of substituents to reduce toxicity of arsinic acids for pharmacological use is suggested, and the electronic transmission of the effect to the  $AsO_3H_2$  group is discussed. The following are prepared. From 4-chloro-3-nitrophenyl-arsinic acid (I) and  $NH_2R$ : 2-nitro-3'- (II) and -4'-acetamido- (III), -4'-hydroxy- (IV), -4'-ethoxy- (V), -3'-hydroxy- (VI), -4'-methoxy-, and -2'-methoxy-diphenylamine-4-arsinic acid. From (II), (III), (IV), and (V), using  $Na_2S_2O_4$ : 2-amino-3'- and -4'-acetamido-, -4'-hydroxy-, and -4'-ethoxy-diphenylamine-4-arsinic acid. [The  $NH_2$ -compound from (VI) could not be isolated.] From 2-nitro-diphenylamine-4-arsinic acid, the 2-amino-acid. 6-Chloro-3-nitro-



*phenylarsinic acid* (obtained from 6-chloro-3-nitro-aniline) gives resinous condensation products. (I) and benzidine yield 3-nitro-4-benzidinophenylarsinic acid. E. W. W.

**Manufacture of arsenobenzenesulphoxylates.**—See B., 1936, 1018.

**Manufacture of arsenic compounds of the naphthaquinone series.**—See B., 1936, 1018.

**Relative activities of organo-metallic compounds. XIII. Copper and silver.** H. GILMAN and J. M. STRALEY (Rec. trav. chim., 1936, 55, 821—834; cf. this vol., 1279).—MgPhI and CuI in Et<sub>2</sub>O at 0° give 86% of CuPh, which, besides the known reactions, with AcCl gives 66% of COPhMe, with BzCl 55% of COPh<sub>2</sub>, with CH<sub>2</sub>:CH·CH<sub>2</sub>Br 31% of CH<sub>2</sub>Ph·CH:CH<sub>2</sub>, with H<sub>2</sub>O 36% of C<sub>6</sub>H<sub>6</sub>, and with PhNCO 14% of NHPhBz with, in most cases, much Ph<sub>2</sub>. With other reagents only Ph<sub>2</sub> is obtained. Cu *p*-anisyl was also prepared, but is as unstable as CuPh. Cu ethyl is stable only in solid CO<sub>2</sub>-Et<sub>2</sub>O, but the solution gives reactions similar to those of CuPh. Ag phenyl is prepared in Et<sub>2</sub>O at -18°, but cannot be isolated; its prep. is accelerated by light. Its reactions resemble those of CuPh, but yields are usually lower. These and similar results are discussed. The order of stability and of decreasing reactivity of MR is M=Cu>Ag>Au, R=aryl>alkyl, and of decreasing reactivity ZnR<sub>2</sub>>CuPh>HgR<sub>2</sub>. R. S. C.

**Phenylmercury nitrate and some other phenylmercury salts.** T. B. GRAVE, S. E. HARRIS, and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1936, 25, 752—756).—Hg Ph nitrate, from the acetate and NaNO<sub>3</sub>, is HgPh·OH, HgPh·NO<sub>3</sub>; in presence of C<sub>5</sub>H<sub>5</sub>N, a compound, HgPh·NO<sub>3</sub>·C<sub>5</sub>H<sub>5</sub>N, m.p. 182—183°, is formed. Aq. Hg Ph hydroxide with the appropriate acid affords Hg Ph lactate, m.p. 160—161°, basic gluconate, m.p. 171—172° (decomp.), phenolsulphonate, m.p. 162—164° (decomp.), and hydroxybutyrate, m.p. 149—149.5° (decomp.). F. O. H.

**Mercury compounds containing nitrogen [bactericides and fungicides].**—See B., 1936, 1019.

**Relative reactivities of organometallic compounds. XIV. Orientation in metalation.** H. GILMAN and R. H. KIRBY (J. Amer. Chem. Soc., 1936, 58, 2074—2075).—Prolonged interaction of HgEt<sub>2</sub> (0.02 g.-mol.) and K (0.08 g.-atom) in C<sub>6</sub>H<sub>6</sub> (35—75 c.c.) gives C<sub>6</sub>H<sub>5</sub> (with small amounts of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>), KPh, and *o*- and *p*-C<sub>6</sub>H<sub>4</sub>K<sub>2</sub>, since subsequent treatment with CO<sub>2</sub> affords BzOH (33—45%) and *o*- and *p*- (14—17%) -C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>H)<sub>2</sub>; KPh appears to be formed thus: C<sub>6</sub>H<sub>6</sub>+KEt→KPh+C<sub>2</sub>H<sub>6</sub>. KPh is *o*-*p* orienting. The order of reactivity KEt>NaEt>LiEt (no reaction), has been established. H. B.

[Organic compounds of tin.] M. K. KOZESCHKOV (Bull. Soc. chim., 1936, [v], 3, 2069—2070).—A claim for priority against Lesbre (A., 1935, 966). H. W.

**Arylstannonic acids and their halogenated derivatives.** M. LESBRE (Bull. Soc. chim., 1936, [v],

3, 2071—2072).—A reply to Kozeschkov (preceding abstract). H. W.

**Separation of amino-acids by means of their copper salts. II. Investigation of the methyl alcohol-soluble copper salt fraction, and the yield of protein from gliadin.** B. W. TOWN (Biochem. J., 1936, 30, 1837—1844).—The Cu salts of NH<sub>2</sub>-acids from proteins can be separated into three fractions: (a) those sol. in MeOH and H<sub>2</sub>O, (b) those insol. in MeOH, sol. in H<sub>2</sub>O, (c) those insol. in MeOH or H<sub>2</sub>O. From gliadin 97% of the total N is accounted for in these fractions. The CdCl<sub>2</sub> ppt. from (a) contains mainly proline; the amount corresponds with a proline content in gliadin of 10.3%. This val. is > that obtained by isolation, but < that corresponding with total non-NH<sub>2</sub>-N; this is due to the presence of diketopiperazines. F. A. A.

**Micro-determination of glycine in protein hydrolysates.** B. W. TOWN (Biochem. J., 1936, 30, 1833—1836).—3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone (I) (prep. given) is a sp. precipitant for glycine, in the absence of inorg. cations. Using (I) the glycine content of gelatin is found as 25.5%, but the data for caseinogen indicate a glycine content of 3.4—3.7%. F. A. A.

**Spectrophotometry of proteins. I. Absorption spectra of tyrosine, tryptophan, and their mixtures. II. Determination of tyrosine and tryptophan in proteins.** E. R. HOLIDAY (Biochem. J., 1936, 30, 1795—1803).—The absorption curves of tyrosine (I) and tryptophan (II) are determined between 260 and 305 mμ in acid, neutral, or alkaline solution, and a method for determination of their concns. in mixtures of the two is described. Determination of (I) and (II) in 5 mg. of protein by this method is described and the results are compared with those by chemical analysis. The errors of the method and a means of correcting for pigment impurities are discussed. P. W. C.

**Diazotization of proteins.** H. EAGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 39—40).—The colour which many proteins give when treated with HNO<sub>2</sub> and coupled with aromatic amines or phenols in presence of alkali is probably due in part to the presence of tryptophan. W. O. K.

**Iodine [in protein].** E. NOLTE (Arch. Pharm., 1936, 274, 415—418).—Hydrolysis of iodoprotein with Sr(OH)<sub>2</sub> gives an active product (14% I) resembling that given by Ba(OH)<sub>2</sub> (cf. Mattis, A., 1931, 1463). Ca(OH)<sub>2</sub> and superheated steam do not give an active product. F. R. G.

**Hydrogen bond and the structure of proteins.** D. M. WRINCH and D. J. LLOYD (Nature, 1936, 138, 758—759; cf. this vol., 619).—Possible structural formulæ using the H linking as the mechanism whereby laminar protein mols. are formed from closed polypeptides are elaborated. L. S. T.

**Semi-micro-determination of carbon in organic compounds.** J. A. SANCHEZ (J. Pharm. Chim., 1936, [viii], 24, 297—310).—The compound is heated with solid KMnO<sub>4</sub> in a sealed tube and the CO<sub>2</sub>, collected initially in NaOH, is liberated quantitatively

with 25%  $\text{H}_3\text{PO}_4$  and distilled into standard NaOH containing  $\text{BaCl}_2$ . J. L. D.

**Determination of carbon and hydrogen by semi-micro-combustion.** E. V. ZAPPI and R. LABRIOLA (Anal. Asoc. Quím. Argentina, 1936, 24, 47—50).—Satisfactory results are obtained in the combustion of 20—30 mg. of material using the method of Berger (A., 1932, 410). F. R. G.

**Selective combustion of hydrogen, carbon monoxide, and methane by palladium catalysts.**—See this vol., 1472.

**Determination of vanillin with 2:4-dinitrophenylhydrazine.** N. RUBIN and A. BLOOM (Amer. J. Pharm., 1936, 108, 387—388).—Contrary to Iddles *et al.* (A., 1935, 101) a technique is described whereby vanillin may be accurately determined (99.44%)

gravimetrically as its 2:4-dinitrophenylhydrazone even in presence of 10% EtOH. J. W. B.

**Extremely sensitive reaction for some nitro-genous bases.** H. WACHSMUTH (J. Pharm. Belg., 1935, 17, 795—798; Chem. Zentr., 1936, i, 379).—Morphine, pyramidone, apomorphine, and adrenaline give sensitive colour reactions (described) with  $\text{CuSO}_4$  and  $\text{CN}'$ ,  $\text{SCN}'$ ,  $\text{Fe}(\text{CN})_6'''$ , or nitroprussides. H. N. R.

**Determination of nicotine.** W. HAMMERLE and W. WEBER (Mitt. Lebensm. Hyg., 1936, 27, 46—48).—The silicotungstic acid method is preferred, but the nicotine should be liberated originally from 2 g. of sample in 40 c.c. of  $\text{H}_2\text{O}$  with 5 c.c. of 30% NaOH; 2 c.c. of 10% reagent per 250 c.c. of distillate should be used for pptn., which is complete after 5 min. at  $80^\circ$  and 3 hr. in the cold. J. G.

## Biochemistry.

**Role of the vagus in the automatic regulation of respiration.** W. HESS (Pflüger's Arch., 1936, 237, 24—39).—Disagreement between the author's previous results and those of ter Braak and van Niekerk is explained. M. A. B.

**Physiological effects of high pressures.** L. A. SHAW (J. Ind. Hyg., 1936, 18, 486—496).—Pulmonary emboli can be absorbed by breathing  $\text{O}_2$  under 3 atm. pressure without harmful effect. "Compressed air disease" is caused by the accumulation of  $\text{N}_2$  bubbles in the venous circulation following exposure to high pressures. P. G. M.

**Biological importance of phosphate esters of red corpuscles.** E. FREUDENBERG (Z. Kinderheilk., 57, 427—441; Chem. Zentr., 1936, i, 100).—Arterialisation of blood inhibits phosphatolysis. P esters of erythrocytes in conjunction with phosphatase control the level of blood-P, and form a P reserve which in acidosis serves to eliminate  $\text{H}^+$ . P ester content of erythrocytes is lowered in rickets but increases after sp. therapy. A. G. P.

**Secretin XI: its effect on the reticulocytes of the circulating blood.** J. FERGUSON (Endocrinol., 1936, 20, 683—684). R. N. C.

**Physico-chemical properties of hæmocyanins. IV. Variation in the osmotic pressure of hæmocyanin during prolonged inanition.** A. ROCHE and J. ROCHE (Bull. Soc. Chim. biol., 1936, 18, 1503—1512).—Determinations of osmotic pressure show that during hibernation of *Helix pomatia* and aestivation of *H. pisana* the mol. wt. of the hæmocyanin considerably decreases. The physiological significance of this is discussed. A. L.

**Serum-bilirubin content of the blood of rats consuming a ration deficient in inorganic salts.** J. M. ORTEN and A. H. SMITH (Proc. Soc. Exp. Biol. Med., 1936, 34, 72—74).—The bilirubin content of the blood of rats on a diet deficient in inorg. salts, and in consequence exhibiting a polycythæmia, does not differ significantly from that of controls. The polycythæmia is therefore not the result of abnormally slow erythrocyte destruction. W. O. K.

**Micro-potentiometric titrations of normal horse serum-globulins.** A. G. OGSTON (Biochem. J., 1936, 30, 1845—1848).—A method using only 0.4—0.6 ml. of 0.5% protein solution is described. The titres of horse serum-pseudoglobulins (I) are < those of the euglobulins (II). The variation between individual samples is greater for (II). Both proteins after drying, and (II) after  $(\text{NH}_4)_2\text{SO}_4$  pptn., give abnormal curves and indicate increased polydispersion in solution.  $\text{CH}_2\text{O}$  titration indicates that any new groups so formed are not  $\text{NH}_2$ , and that the greater titre of (II) is not due to  $\text{NH}_2$ . There is no apparent correlation between the titres and the tyrosine content. F. A. A.

**Constituents of acid globulins. Protein C.** M. DOLADILHE (Ann. Inst. Pasteur, 1936, 57, 443—462).—Flocculation of sera produced by dilution with acidulated  $\text{H}_2\text{O}$  is mainly due to the effect of the  $p_{\text{H}}$  on the acid globulin fraction rather than to lowered salt concn.; the flocculation frequently produced by distilled  $\text{H}_2\text{O}$  is effected by dissolved  $\text{CO}_2$ , the ppt. consisting of acid globulins. The application of these facts to the flocculation of syphilitic sera is considered. Details of the prep. and the effect of heat on the physical properties of protein C are given (cf. this vol., 875). P. G. M.

**Biochemistry of serum irradiated with artificial light. VIII. Analysis of serum-protein.** M. MURAYAMA (J. Orient. Med., 1936, 24, 79—80).—Irradiation with ultra-violet light or with X-rays caused a small decrease in the total N and albumin-N, but an increase in the globulin-N in human serum. NUTR. ABS. (m)

**Limits of the reaction for determination of the tyrosine index of serum-polypeptides.** V. CIO-CALTEU and G. TANASESCO (Compt. rend. Soc. Biol., 1936, 123, 49—50).—A modified method utilising the Folin-Ciocalteu reagent (A., 1927, 892) is proposed since that of Goiffon and Spacy (A., 1935, 374) is accurate over only a narrow range. H. G. R.

**Nucleotide-nitrogen content of human leucocytes.** F. W. ALLEN, S. P. LUCIA, and J. J. EILER



(Proc. Soc. Exp. Biol. Med., 1936, 34, 609—611).—In cases of myeloid leucæmia with high leucocyte counts the nucleotide-N of the leucocytes is  $>50\%$  of the total. The nucleotide content of whole blood decreases with a regression of the leucocyte count, when the erythrocyte count is const. P. G. M.

**Quantitative isolation of histamine and tyramine from plasma and serum.** A. SCHWARTZ and A. RIEGERT (Compt. rend. Soc. Biol., 1936, 123, 219—223).—Adsorption on Permutit is followed by elution with saturated aq. NaCl. H. G. R.

**Determination of the urea content of blood-serum.** P. SORGDRAGER (Pharm. Tijds. Nederl.-Indie, 1935, 12, 241—243; Chem. Zentr., 1936, i, 125).—An improved apparatus for, and corrections to be applied to results obtained by, van Assenraad's method (A., 1929, 1326) are described. H. N. R.

**Normal phenol content of blood.** M. CASTEX and A. ARNAUD (Publ. méd., 1935, 1, No. 3).—In normal blood vials. were: free phenols (I) 1—1.3, total (I) 1.1—1.4, conjugated (I) 0—0.3 mg. per 100 c.c. Normal variations are small even when large amounts of (I) are eliminated in urine.

CH. ABS. (p)

**Determination of fat in 0.1 c.c. of blood or serum.** G. SURANYI and P. VÉGHELYI (Magyar orvosi Arch., 1935, 36, 169—175; Chem. Zentr., 1936, i, 391—382).—Total fat is extracted with 15 c.c. of EtOH, and total fat without lecithin with COME<sub>2</sub>, each from 0.05 c.c. of blood. The solutions are brought to 10 c.c., and 2 c.c. are slowly treated with 5 c.c. of 10% HCl+1% of BuOH. The turbidity produced is measured photometrically. J. S. A.

**Partition of reduced ascorbic acid in blood.** D. J. STEPHENS and E. E. HAWLEY (J. Biol. Chem., 1936, 115, 653—658).—The content in human white blood cells is  $>$  that in whole blood, plasma, or red cells. Abnormally high vals. in the whole blood of leucæmic patients are due to the high leucocyte count. F. O. H.

**Determination of reduced ascorbic acid in small amounts of blood.** C. J. FARMER and A. F. ABT (Proc. Soc. Exp. Biol. Med., 1936, 34, 146—150).—The method enables the ascorbic acid content of 0.3 ml. of blood to be determined by titration from a special micro-burette, with 2:6-dichlorophenol-indophenol. HPO<sub>4</sub> is used for deproteinisation.

W. McC.

**Influence of muscular action on blood-sugar and -catalase.** H. KOEPPE (Klin. Woch., 1935, 14, 667—670; Chem. Zentr., 1936, i, 372).—Blood-sugar and -catalase contents are changed simultaneously and in opposite directions after carbohydrate feeding, during fasting, and during muscular activity.

A. G. P.

**Hyperglycæmia and augmentation of the undetermined carbohydrate of the plasma following experimental shock in the dog.** O. LAMBRET, G. BIZARD, and J. DRIESSENS (Compt. rend. Soc. Biol., 1936, 123, 413—415).—The phenomena appear to be connected with the adrenal gland. H. G. R.

**Effect of hypophysectomy on blood-sugar in Rhesus monkeys.** P. E. SMITH, L. DOTTI, H. H.

TYNDALE, and E. T. ENGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 247—249).—After fasting, hypophysectomy reduced the sugar content of the blood from 90—100 to 20—90 mg. per 100 c.c.

W. McC.

**Determination of small amounts of carbon monoxide in blood.** H. BURESCH and V. LUNIATSCHEK (Arch. Gewerbepath. Gewerbebyg., 1936, 7, 182—191).—An improved apparatus (cf. A., 1934, 1241) is described. M. A. B.

**Residual nitrogen of the blood and its principal components.** I. Normal distribution. P. LARIZZA (Arch. exp. Path. Pharm., 1936, 182, 617—632).—Data for the total residual (i.e., non-protein) N (I) and its distribution in human blood are tabulated. The average distribution-ratios between corpuscles and serum are: total (I) 1.75, urea-N 0.70, NH<sub>2</sub>-N 1.71, total creatinine-N 1.67; that of uric acid-N is irregular. The undetermined (I) in serum was 15% and in corpuscles 44% of the total (I). F. O. H.

**Calcium and inorganic phosphorus content of blood-serum of swine.** E. H. HUGHES (J. Agric. Res., 1936, 53, 267—279).—Serum-Ca and -inorg. P in young pigs were  $>$  in older ones. Immediately before and after farrowing Ca vals. increased and those of P declined, in comparison with those for non-pregnant sows. Ingestion of Ca increased serum-Ca temporarily, a prolonged increase (with simultaneous decrease in inorg. P) following continuous feeding of large proportions of CaCO<sub>3</sub>. Continuous feeding of a Ca-deficient diet lowered serum-Ca, the -inorg. P being increased in mature but decreased in young animals. Low serum-Ca caused Ca tetany.

A. G. P.

**Copper and iron in human blood.** IV. Normal children. A. SACHS, V. E. LEVINE, and A. A. FABIAN (Arch. Int. Med., 1936, 58, 523—530).—Cu varies inversely as Fe in the blood of normal children. The blood of the new-born contains Fe, 51.79 mg., Cu,  $83 \times 10^{-6}$  g. per 100 c.c.; in an age group 1½ months—15 years the figures were Fe, 40.51 mg., Cu,  $171 \times 10^{-6}$  g.

P. G. M.

**Effect of boiler-makers' work on the composition and properties of their blood. Water shift between blood and tissues and between serum and cells.** MEER S. MISCHKIS and MARIA S. MISCHKIS (Ukrain. Biochem. J., 1936, 9, 369—380).—The H<sub>2</sub>O content of blood cells of workers in all branches of the trade increases by 0.7—1.4% towards the end of the day. No increase in H<sub>2</sub>O content of serum is found. The H<sub>2</sub>O content of whole blood, serum, and blood cells of boiler sweeps is  $>$  that of other boiler workers. These effects are contrary to those observed during short periods of strained work. F. A. A.

**Determination of blood- $p_H$  by the glass electrode.** V. Glass micro-electrode and the  $p_H$  of arterial, venous, and capillary blood. H. YOSHIMURA (J. Biochem. Japan, 1936, 23, 335—350; cf. this vol., 682).—A glass electrode, applicable to 0.07 c.c. and accurate to 0.02  $p_H$ , is described. Direct measurements on rabbits and examination of blood removed from men show that the  $p_H$  of arterial blood

equals that of capillary but is  $>$  that of venous blood by approx. 0.03. F. O. H.

**Preservation of sera by desiccation in the frozen state without the use of refrigerants.** R. I. N. GREAVES and M. E. ADAIR (J. Hyg., 1936, 36, 507—513).—Antisera are desiccated after freezing by rapid evaporation in a high vac. over  $P_2O_5$ . Preliminary evacuation of the sera in the absence of the drying agent overcomes violent frothing. The method can be applied to the drying of bacteria. W. L. D.

**Food allergy.** A. W. OELGOETZ, P. A. OELGOETZ, and J. WITTEKIND (Amer. J. Digest. Dis. Nutrition, 1934, 1, 730—737).—Hypersensitiveness to foods is probably caused by excess of free food (free from enzymes) in the blood-serum, this excess being due to a low pancreatic threshold. CH. ABS. (p)

**Blood-groups and -radiation.** W. W. SIEBER and H. SEFFERT (Biochem. Z., 1936, 287, 109—112).—The blood of a normal healthy man is strongly mitogenetic. When the same amount of blood of two individuals is mixed *in vitro*, the mixed blood is mitogenetic only when it results from a combination of definite blood-groups. Mixtures of bloods from the same blood-groups, of group O with another group, and of group AB with another group, remain active, but those of group A with group B are inactive. P. W. C.

**Hæmolysis produced by small variations in  $p_H$ .** R. VAVRA (Compt. rend. Soc. Biol., 1936, 123, 161—163).—The phenomenon is peculiar to red cells and is observed only when they are fresh. H. G. R.

**Influence of the plasma on the hæmolysis produced by small variations in  $p_H$ .** R. VAVRA (Compt. rend. Soc. Biol., 1936, 123, 163—165).—When produced in presence of plasma, hæmolysis is probably caused by the plasma itself. H. G. R.

**Influence of trisodium citrate on hæmolysis of red cells by alcohol.** J. VIGNATI and M. RAUCHENBERG (Compt. rend. Soc. Biol., 1936, 123, 165—166).—Hæmolysis is inhibited by EtOH up to 50% concn. H. G. R.

**Production of fibrinolysin *in vivo*.** E. NETER (Proc. Soc. Exp. Biol. Med., 1936, 34, 735—736).—The abdominal washings of mice killed by injection of saline suspensions of various strains of hæmolytic streptococci (but not pneumococci) contained fibrinolysin. P. G. M.

**Decalcifying anticoagulants.** J. H. FERGUSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 797—798).—Incubation of a thrombin solution with 50—100 equivs. of oxalate or citrate for varying times produces both an immediate retardation and a progressive inactivation of clotting. P. G. M.

**Effect of sulphur compounds on blood coagulation.** J. H. STERNER and G. MEDES (Proc. Soc. Exp. Biol. Med., 1936, 34, 597—599).—Addition of cystine to the coagulation system before thrombin formation has a marked inhibitory effect. Inhibition is only slight in the presence of thrombin. Methionine has an inhibitory effect *in vivo* but not *in vitro*. P. G. M.

**Kinetics of thrombin action.** E. WÖHLISCH, W. DIEBOLD, and O. KIDERLEN (Pflüger's Arch., 1935, 237, 599—608).—With increasing fibrinogen (I) concn. up to 0.3—0.4% the rate of clotting increased, but decreased again above his concn.; the max. rate occurred at the blood concn. of (I). The influence of temp. on rate of clotting became progressively less with decreasing concn. of (I) and finally disappeared. M. A. B.

**Blood in hæmophilia.** A. J. PATEK, jun., and F. H. L. TAYLOR (Science, 1936, 84, 271—272).—The difference between normal and hæmophilic blood appears to be due either to a qual. difference of their prothrombins or to other substances probably associated with them. L. S. T.

**Venom of *Lachesis* (*Bothrops*) snakes. IV. Action of the coagulatory principle *in vivo*.** D. VON KLOBUSITZKY and P. KÖNIG (Arch. exp. Path. Pharm., 1936, 182, 577—583; cf. this vol., 1010).—The activity of preps. free from protein, of low toxicity, and effective in doses of  $5 \times 10^{-10}$  g. per c.c. of blood, depends on the time between administration (pigeons) and removal of blood and on concn. F. O. H.

**Rapid process for macroscopic agglutination after centrifuging.** R. LE GUYON (Compt. rend. Soc. Biol., 1936, 123, 239—240).—After centrifuging the mixture of serum and bacterial emulsion, the clot is redispersed by shaking, when agglutination can be observed. H. G. R.

**Relation between complement and prothrombin.** A. J. QUICK (J. Immunol., 1935, 29, 87—97).—A close relation in respect of chemical and physiological properties is indicated. Complement and prothrombin are not identical. CH. ABS. (p)

**General properties of vegetable agglutinins and precipitins.** T. FRÉMONT (Compt. rend. Soc. Biol., 1936, 123, 417—418).—Sp. agglutinins are more readily detected in infected plants than precipitins. H. G. R.

**Distribution of precipitin in serum-globulins of different species.** B. F. CHOW (Proc. Soc. Exp. Biol. Med., 34, 651—653).—The antibody in the pseudoglobulin (I) of antipneumococcus horse serum (sol. at  $p_H$  5.5) is completely pptd. at 7.6; no such pptn. occurs in rabbit (I), the main portion of the antibody being conc. in the euglobulin fraction. P. G. M.

**Albuminous precipitins.** M. BORNAND (Mitt. Lebensm. Hyg., 1936, 27, 24—26).—Precipitin reactions given by antiserum, prepared by immunisation of a rabbit with the muscle-albumin of a chamois or cow, with albuminous substances extracted from the blood or flesh of various animals are described. J. G.

**Distribution of antibody to crystalline ovalbumin in rabbit serum.** M. E. ADAIR and G. L. TAYLOR (J. Hyg., 1936, 36, 564—569).—Pooled antisera from rabbits injected with ovalbumin were fractionated with  $(NH_4)_2SO_4$  to investigate the distribution of the antibody (I) in the serum-proteins. Albumin contained no (I), but all the globulin fractions contained (I) at a fairly uniform concn. W. L. D.



**Specificity of the complement fixation test for amoebiasis.** E. WEISS and L. ARNOLD (Amer. J. Digest. Dis. Nutrition, 1934, 1, 548—552).—EtOH and COMe<sub>2</sub> extracts of *E. histolytica* yield a sp. antigen, by injection of which a sp. antiamoebic serum can be produced. Ox heart lipin antigens used in the Wassermann and the Kahn tests give non-sp. reactions with serum from amoebic dysentery patients and that from various protozoa. The lipins produce antisera containing non-sp. antibodies.

CH. ABS. (p)

**Union with complement as a surface reaction.** II. Changes of surface activity of serum after heat-inactivation of complement function. III. Cause of the dependence of the amount of protein for union on the degree of sensitisation of antigen cells. F. SEELICH (Biochem. Z., 1936, 287, 1—8, 9—17; cf. this vol., 1335).—II. A series of curves shows the  $\sigma$  of fresh and heat-inactivated guinea-pig's serum, both undiluted and at varying dilutions with 0.9% NaCl, against paraffin oil as measured by du Noüy's interfacial tensiometer. The  $\sigma$  of fresh serum is always about 30% < that of inactivated serum, the surface activity greatly increasing during inactivation. At greater dilutions the  $\sigma$ -time curves of normal and heat-treated serum tend to cross. The cause of this increase in surface-active material is discussed.

III. The changes occurring when antigen cells unite with sp. antibody in which the amount of complement protein bound is greater the greater is the degree of sensitisation, are explained in terms of an increase in  $\sigma$  at the absorbing surface,  $\sigma$  progressively increasing with increasing sensitisation.

**Ultrafiltration of type I antipneumococcal sera.** K. GOODNER, F. L. HORSFALL, jun., and J. H. BAUER (Proc. Soc. Exp. Biol. Med., 1936, 34, 617—619).—The smallest sp. antibody of antipneumococcal rabbit serum corresponds with a pore-size of 11 m $\mu$  and of horse serum to 44 m $\mu$ ; the mass of the latter is 64 times that of the former. The antibody of conc. horse serum requires a pore-size of 176 m $\mu$ .

P. G. M.

**New preparation of type-specific polysaccharide from pneumococcus, type I.** B. F. CHOW (Proc. Soc. Exp. Biol. Med., 1936, 34, 667—669).—By a method of prep. minimising hydrolysis, a polysaccharide (I) was obtained which reacted with homologous immune-rabbit serum, previously absorbed with the acetylpolysaccharide (II), but not *vice versa*. (I) produced active immunity in mice, and may be the precursor of (II).

P. G. M.

**Precipitation of diphtheria antoxin by alum.** F. FARAGÓ (Magyar orvosi Arch., 1935, 36, 176—182; Chem. Zentr., 1936, i, 366).—Conditions for obtaining the best prep. are examined.

A. G. P.

**Urea as solvent for antigen extracts.** E. M. MACKEY and R. W. LAMSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 123—125).—Conc. aq. solutions of urea are suitable solvents for antigens which are only slightly or not at all changed on dissolution.

W. McC.

**Antigenic properties of proteins linked through ureide or azo-groups to aromatic nuclei.** W. MUTSAARS and P. E. GREGOIRE (Compt. rend. Soc. Biol., 1936, 123, 144—148). H. G. R.

**Histochemical detection of mineral constituents of tissues.** L. LISON (Bull. Acad. roy. Belg., 1936, [v], 22, 951—967).—An account of difficulties in determining the distribution of Cl and K in animal tissues by histochemical methods. Cl, which exists only in the diffusible form, cannot be accurately demonstrated; non-diffusible K can be shown if the tissue is previously fixed.

J. L. D.

**Determination of small amounts of iodine in organs, particularly in ox thyroid.** W. RUFF (Biochem. Z., 1936, 287, 40—49).—A modification of the Fellenberg method, designed to prevent loss of I on ashing, is described. Right and left sides of the thyroid and the glands of male and female animals have the same I content. The I content varies considerably with the time of the year, having the highest vals. in winter and the lowest in summer. Glands of animals living on the coast are richer in I than those of animals from inland. The thyroxine contents of the glands are independent of the total I content. The pituitary of female animals contains more I than that of male animals and the anterior lobes are richer in I than the posterior.

P. W. C.

**Fractional iodine determinations in human organs. Biological function of tissue-iodine.** A. STURM and L. ROCKMANN (Biochem. Z., 1936, 287, 50—60).—Tables summarise the I contents of human liver, spleen, skeletal and heart muscle, and lung after fractionation with H<sub>2</sub>O and COMe<sub>2</sub>. The total [I], particularly the sol. protein- (thyrogenic) I (I) is decreased in cases of decreased cellular activity (aged people, liver cirrhosis, necrotic liver and lung carcinomatous tissue, tubercular lung tissue). Tissues in cases of abnormally increased metabolic activity are richer in I, particularly in (I). The functional condition of the central nervous system appears to control the distribution of I, particularly of (I), in the organs. The H<sub>2</sub>O-insol. I fraction increases in age and in necrotic tumour tissue at the expense of the (I) fraction.

P. W. C.

(A) Sodium contents, (B) chloride contents, of aqueous and vitreous humour and serum. P. W. SALIT (Amer. J. Ophthalmol., 1934, 17, 706—708, 818—819).—(A) Age has little effect on the Na content of aq. or vitreous humour. Vals. for serum were > those for humour and those for calves > those of adult cattle.

(B) The Cl' contents of aq. and vitreous humour were similar and > that of serum. Vals. were the same for calves and adult oxen.

CH. ABS. (p)

**Analysis of tissues for metallic content.** H. RAMAGE (Nature, 1936, 138, 762—763).—Before spectrographic determination, tissues must first be extracted. After 18 to 24 hr. at room temp., N-HCl extracts from sheep's liver, spleen, and heart the alkalis, Mg, Zn, Mn, Ni, etc., with only a little org. matter: Ca, Cu, and Fe are only partly extracted. Healthy liver contains more Zn than is commonly realised.

L. S. T.

**Copper in the liver of the calf embryo.** Z. GRUZEWSKA and G. ROUSSEL (Compt. rend. Soc. Biol., 1936, 123, 377—379).—The liver of the embryo contains 20—40 times as much Cu as the foetal spleen, and it appears to be in complex combination since it is not liberated by prolonged dialysis. Cu in rabbit liver is very variable. H. G. R.

**Silica content of lungs of infants and of placental tissue.** W. D. McNALLY and W. L. BERGMAN (J. Ind. Hyg., 1935, 17, 171—173).—SiO<sub>2</sub> contents determined were, infants to 3 years 0.34 placenta 0.294, blood 0.13, placental blood 0.32, umbilical cord 0.33 mg. per g. of dried tissue.

CH. ABS. (p)

**Carbonate content of inorganic bone material and its synthesis.** R. KLEMENT (Ber., 1936, 69, [B], 2232—2238).—The content of inorg. bone material does not correspond with an equilibrium between the hydroxyapatite (I) contained therein and the CO<sub>3</sub>'' of the serum. Probably CaCO<sub>3</sub> is carried down by induced pptn. during the formation of (I). The artificial prep. of a product closely resembling natural bone material is described.

H. W.

**Inorganic structure of teeth.** W. F. BALE, M. L. LEFEVRE, and H. C. HODGE (Naturwiss., 1936, 24, 636—637).—Changes in the X-ray diagram of dentine on heating to 900° agree with the view of Klement *et al.* (A., 1933, 296) that the principal constituent is a hydroxyapatite (I), with included or adsorbed carbonates. The X-ray diffraction diagram of commercial Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> changes on heating to 900°, like that of (I), to the diagram of β-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Samples of tooth-substance gave, after the above heating, few diagrams showing a similar change, but after 5 hr. heating of dentine from certain teeth, the diagram of β-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was obtained in many cases. Powdered dentine after extraction for 1½ hr. with (CH<sub>2</sub>·OH)<sub>2</sub> and 3% KOH showed no such transformation. The differences observable in the tooth-substance of different teeth can be ascribed to the extent of adsorption of PO<sub>4</sub>''' on the surface of the small (I) crystals. A. J. M.

**X-Ray absorption coefficients of coronal and root dentine.** F. HOLLANDER and E. VESELY (Proc. Soc. Exp. Biol. Med., 1936, 34, 158—159).—The coeffs. were different in different parts of the dentine of the same specimen and there were differences of >20% between different specimens. In any one specimen there is a uniform decrease in the coeff. from crown to apex of the root, the gradient being parallel to the age gradient of the dentine. W. McC.

**X-Ray diffraction patterns from reprecipitated connective tissue.** R. W. G. WYCKOFF and R. B. COREY (Proc. Soc. Exp. Biol. Med., 1936, 34, 285—287).—The part of the freshly excised tendon of the tail of the adult rat which dissolves in dil. AcOH and is repptd. by 5% aq. NaCl is cryst. and has the same X-ray diffraction pattern as has the original tendon. W. McC.

**Mechanism of hexose monophosphate formation in muscle and isolation of a new phosphate ester.** C. F. CORI and G. T. CORI (Proc. Soc. Exp.

Biol. Med., 1936, 34, 702—705).—Glucose-1-phosphoric acid was isolated as the brucine salt from minced frog muscle incubated with adenylic acid in phosphate buffer. It is readily converted into hexose monophosphate.

P. G. M.

**Comparative biochemistry of muscle. I. Phosphagen in sea- and fresh-water Teleostei and Ganoidei.** L. E. ROZENFELD and G. J. BAGDASARJANTZ. II. Nature of phosphagen in the Selachii. G. J. BAGDASARJANTZ (Ukrain. Biochem. J., 1936, 9, 321—332, 333—340).—I. The skeletal muscles of *Acanthopterygii* and *Lophobranchii* contain 0.007—0.015% of creatinephosphoric acid (I). The P of (I) amounts to 3—8% of the inorg. and acid-labile P, significantly < that in the lower vertebrates. The creatine content of muscle of salt-water fish is < that of fresh-water fish. Sturgeon muscle does not differ from that of bony fish in creatine or (I) content.

II. Muscle of the shark and ray contains 0.013—0.035% of (I). An acid-labile P compound, probably argininephosphoric acid (II), is also present. The total amount of (I) and (II) in the shark is > that in the ray.

F. A. A.

**Biochemistry of carbohydrates. XIV. Modified Zuckerkandl-Klebermass method for determination of glucosamine.** Distribution of glucosaminase in ox tissue. XV. Determination of N-acetylglucosamine and its application to biochemical analysis. K. WATANABE (J. Biochem. Japan, 1936, 23, 365—369, 371—376; cf. A., 1935, 402).—XIV. The method (A., 1931, 1081) indicates that glucosaminase occurs in liver, lung, pancreas, and kidney but not significantly in spleen, thyroid gland, muscle, and adrenal cortex.

XV. The above method is applicable to the determination of N-acetylglucosamine in tissue, blood, or urine.

F. O. H.

**Glycogen content of fresh-water mussels during prolonged starvation.** M. M. ELLIS and D. B. CALVIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 222—225).—The dried hepatopancreas and pedal muscle of several species of thick-shelled mussel contained 25—61% of glycogen (I). The (I) content decreased slowly during starvation; in many cases it remained >30% after 180—338 days. After 536 days the average (I) content of one species was 1.1%. The (I) content of thin-shelled was < that of thick-shelled mussels and decreased more rapidly during starvation.

W. McC.

**Chemical and histochemical determination of the glycogen contents of white and red muscle.** A. NOLL and M. BECKER (Biochem. Z., 1936, 287, 88—91).—In rabbits and hens, red muscle contains 66—80% of the amount of glycogen (I) of white muscle. Histochemical determination gave in general a lower (I) content for red muscle, the vals., especially with rabbit's muscle, agreeing closely with those by chemical methods. In hens, the red muscle of the legs must be used whole in chemical determinations, since (I) is not evenly distributed therein.

P. W. C.

**Fats of Japanese birds. XVII. Fat from *Oreocincla dauma*, Holandre [White's ground**



thrush]. R. KOYAMA (J. Chem. Soc. Japan, 1935, 56, 596—599).—Data are recorded. CH. ABS. (e)

Oil extracted by pressure from the male silk-worm butterfly. M. BONICATTI (Annali Chim. Appl., 1936, 26, 306—309).—The oil, obtained in 20% yield, has I val. 110—116, acid val. 22—38, solid fatty acids 27.1—33.2%; it differs little from the chrysalis oil. L. A. O'N.

Inversion point of cholesterol in aqueous suspension by calcium chloride. H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 154—156).—The  $[\text{CaCl}_2]$  corresponding with the inversion of cholesterol is 2.8N. H. G. R.

Chemical composition of various divisions of the nervous system. A. V. PALLADIN, E. J. RASCHBA, and R. M. GELMAN (Ukrain. Biochem. J., 1936, 9, 169—192).—In the peripheral nervous system of cows, the roots of the spinal cord contain a relatively large amount of cholesterol (I) (17—18% of the dry matter). The anterior and posterior roots are similar to each other in composition, per unit of dry matter. Lipins, N, creatine, P, and  $\text{H}_2\text{O}$  are lower in the peripheral nerve than in the other divisions (possibly owing to a high fat content), whilst the sympathetic trunk is relatively rich in N and creatine. The ganglia of the posterior roots differ from other ganglia in having high (I) and unsaturated phosphatide content. Phylogenetically, the peripheral nervous system resembles the central nervous system in that the older divisions are rich in (I) and unsaturated phosphatides, while the younger divisions are richer in  $\text{H}_2\text{O}$  and proteins. F. A. A.

Chemistry of vitreous humour. III. Lipins. A. C. KRAUSE (Arch. Ophthalmol., 1935, 13, 1022—1025; cf. A., 1935, 511).—In bovine humour parts of the lipin and cholesterol (I) contents are bound to protein. No cholesteryl fatty acid esters are present. Particles of (I) and Ca soaps in the humour probably arise from liberation of lipins of leucocytes. CH. ABS. (p)

Biochemistry of the lens. IV. Origin of pigment. J. G. BELLOW (Arch. Ophthalmol., 1935, 14, 99—107).—The lens contains histone and protamine. The latter reacts with cysteine (I) to form a black dye. A normal hydrolysed lens becomes pigmented when placed in a slightly alkaline solution of (I). CH. ABS. (p)

Cellular hæmatins and cytochromes. J. ROCHE and M. T. BENEVENT (Compt. rend. Soc. Biol., 1936, 123, 20—22; cf. this vol., 1287).—The hæmatins (I) of cytochrome-A and -A<sub>2</sub> are similar if not identical, whilst those of -A<sub>3</sub> are very different, the hæmochromogens absorbing in the orange-red. Pigments B, B<sub>1</sub>, and C and Keilin's intracellular (I) yield, with  $\text{C}_5\text{H}_5\text{N}$ , a mixture of (I)-C and proto-hæmatin in varying proportions. H. G. R.

Hæmatin- and cytochrome-C. Mobility of iron and combinations of hæmatins with a globin. J. ROCHE and M. T. BENEVENT (Compt. rend. Soc. Biol., 1936, 123, 18—19).—The absorption spectra of the products of condensation of proto-hæmatin with  $\text{C}_5\text{H}_5\text{N}$  and with  $\text{NH}_2\text{CH}_2\text{CO}_2\text{Me}$  are identical. Hæmatin-C (I), obtained from the proto-

hæmatin by alternate oxidation and reduction, will not combine with horse globin and when boiled in MeOH with 1% HCl yields a porphyrin and  $\text{Fe}^{+++}$ , in contrast to Zeile's (I), that of cytochrome-C, and of blood. H. G. R.

Chemical studies on bioluminescence. III. Reversible reaction of *Cypridina* luciferin with oxidising agents and its relations to the luminescent reaction. R. S. ANDERSON (J. Cell. Comp. Physiol., 1936, 8, 261—276; cf. this vol., 360).—Oxidation of luciferin (I) by  $\text{K}_3\text{Fe}(\text{CN})_6$ , unlike that by  $\text{O}_2$  in the presence of luciferase, is reversible, as (I) is re-formed largely in the former, but only to a slight extent in the latter, case on addition of  $\text{Na}_2\text{S}_2\text{O}_4$ . The end products of the two reactions are therefore different. Abnormal reaction curves obtained may be due to mixtures of (I) and reversibly oxidised (I). A preliminary val. for the apparent oxidation-reduction potential of the (I) system is given. Possible chemical characteristics of (I) are discussed. E. A. H. R.

Influence of starvation on the content of plant-auxin-like substances in the larva of *Disco-glossus pictus*, Otth. H. BERRIER (Compt. rend., 1936, 203, 522—524; cf. A., 1935, 1289).—The auxin-like activity of *D. pictus* persists during the normal larval stage but disappears on starving the larvæ for 15 days. F. O. H.

Nettle poisons. Poison of sea anemones. I. R. SONDERHOFF (Annalen, 1936, 525, 138—150).—*Anemonia sulcata* yields to EtOH a highly active substance, containing C, H, O, N, and S, having a mol. wt. about 2000 (determined by dialysis), and probably of albumin (histone) type. The isolation, physiological properties, method of testing (*Rana esculenta*, not *temporaria*), and colour reactions are detailed. R. S. C.

Isolation of the anti-anæmic principle of the liver. P. LALAND, A. KLEM, B. STRANDELL, L. POULSSON, and H. SCHARTUM-HANSEN (Acta med. scand., 1936, 88, 620—623, 624—625).—The method of isolation depends on extraction with PhOH which removes much of the inactive substances. Several fractions isolated by variations of this method had an anti-anæmic effect. A fraction isolated by a combination of the  $(\text{NH}_4)_2\text{SO}_4$  process of Dakin and West and the PhOH extraction method gave 0.35 mg. of dry material per 100 g. of liver. 0.7 mg. of this material produced an excellent response in four cases of pernicious anæmia. NUTR. ABS. (m)

Physical and chemical properties of desiccated stomach. J. KYER, F. P. BROOKS, and R. ISAACS (Proc. Soc. Exp. Biol. Med., 1936, 34, 677—680).—A  $\text{H}_2\text{O}$  extract of desiccated hog's stomach ( $p_{\text{H}}$  4.5) is effective in treatment of pernicious anæmia. The active principle is alkali-stable and is not ultra-filterable; it contains two factors, one heat-stable and the other heat-labile. Incubation of an acid extract yields a hæmatopoietic substance sol. in 70% EtOH. P. G. M.

Heparin. IV. Chemistry of heparin. A. F. CHARLES and D. A. SCOTT (Biochem. J., 1936, 30, 1927—1933).—A very active prep. of heparin (I) is

obtained from ox lung (cf. A., 1935, 632). Analyses of the Ba and benzidine salts indicate the empirical formula  $C_{25}H_{65}O_{50}N_2S_5$  for (I). The S is present as  $\cdot SO_3H$  and is removed by  $MeOH-HCl$  as  $SO_4^{2-}$  with loss of activity. Part of the N is present as  $\cdot NH_2$  groups and these are associated with the physiological activity. Colour tests indicate the presence of a carbohydrate complex and the absence of pentoses and glycuronic acid. The cryst. prep. is 22 times as active as the commercial product. Analyses do not support the view that (I) is a chondroitinpolysulphuric acid.

P. W. C.

**Progestin content of human placenta.** D. A. MCGINTY, N. B. MCCULLOUGH, and J. G. WOLTER (Proc. Soc. Exp. Biol. Med., 1936, 34, 176—178).—Fresh full-term human placenta contains approx. 7 rabbit units of progestin per kg.

W. McC.

**Organic bases, especially spermine, in the muscle of higher animals.** II. K. YOSHIMURA, Y. HIWATASHI, and T. SAKOMOTO (J. Chem. Soc. Japan, 1935, 56, 582—587).—Freshly ground muscle of rabbit and of wild boar contains creatine 10.8, 0.30, hypoxanthine hydrochloride 0.6, 2.05, methylguanidine 1.2, 0.30, creatinine 1.7, 2.05, carnitine 1.8, 6.0, and spermine 0.0, 0.0 g. per 5 kg., respectively.

CH. ABS. (p)

**Brain-creatine during the ontogenetic development of vertebrates.** A. PALLADIN and H. RASCHBA (Ukrain. Biochem. J., 1936, 9, No. 1, 5—42).—In various mammals the creatine and total N content of the brain decreases during development. In chicks a less marked fall takes place.

W. O. K.

**Creatine content of human hearts.** G. HERRMANN, G. M. DECHERD, jun., and T. OLIVER (Proc. Soc. Exp. Biol. Med., 1936, 34, 827—829).—The creatine content of hearts from patients who died of infectious disease is lowered, as is that of hearts showing myocardial change consequent on coronary sclerosis; in hypertrophied hearts the content is raised if they have not failed, and *vice versa*.

P. G. M.

**Tissue-acetylcholine. IV. Cytology of chorionic villous epithelium of the human placenta.** I. C. WEN, H. C. CHANG, and A. WONG (Chinese J. Physiol., 1936, 10, 559—569).—Fixation with  $NH_4$  reineckate preps. is used to indicate the liberation of choline granules in various histological elements of placental tissue, the results being correlated with the acetylcholine activity of different types of placenta.

P. W. C.

**Structure of proteins and of certain physiologically active compounds.** D. M. WRINCH (Nature, 1936, 138, 651—652).—The cyclol theory of protein structure and the part played by the cyclol pattern in the structure of carcinogenic substances is discussed.

L. S. T.

**Digestion products formed by the action of papain on ovalbumin.** M. ANNETTS (Biochem. J., 1936, 30, 1807—1814).—Under the action of papain the ovalbumin (I) mol. is split up into two groups of substances, both heterogeneous, a light fraction consisting of particles of the order of magnitude of the  $NH_2$ -acids and lower polypeptides and a heavy fraction containing no unchanged (I) and having an

average sedimentation const. of 3.3 and diffusion const. of 8.27 sq. cm. per sec. Ultracentrifuge,  $n$ , diffusion, cataphoresis, and light absorption measurements all lead to the view that first a change occurs in all the mols. of (I), probably a loosening of bonds within the mol., followed by a gradual splitting off of small pieces from these modified mols.

P. W. C.

**Swelling of the vitreous gel and intraocular pressure.** M. COHEN, J. M. NEWELL, and J. A. KILLIAN (Arch. Ophthalmol., 1934, 12, 352—358).— $H_2O$  and solutions of acids, alkalis, and  $NaCNS$ , separated from the vitreous gel by a porous alundum disc, produced no swelling of the gel. Pressure ultrafiltration through Cellophane removed >99% of protein-free liquid from the gel. The residue swelled when placed in the  $H_2O$ . A true swelling of vitreous gel is impossible.

CH. ABS. (p)

**Protein content of human aqueous [humour].** E. SELINGER (Amer. J. Ophthalmol., 1934, 17, 1130—1137).—A method for determining protein is based on treatment with  $CCl_3CO_2H$  and comparison of turbidity. Vals. for normal and pathological conditions are given.

CH. ABS. (p)

**Inversion point of autocomplex coacervates of phosphatides by calcium chloride as a function of  $p_H$ .** H. G. B. DE JONG and N. I. JOUKOVSKY (Compt. rend. Soc. Biol., 1936, 123, 149—154).—Between  $p_H$  4 and 9 the  $[CaCl_2]$  necessary to cause inversion of the electro-capillary charge is practically const. On the acid side the val. falls rapidly to zero ( $p_H$  1.82) and increases rapidly when alkaline.

H. G. R.

**X-Ray diffraction studies of chitin, chitosan, and derivatives.**—See this vol., 1451.

**Adsorption of benzene derivatives by serum colloids and organ pulps.**—See this vol., 1462.

**Elastoïdin fibres.**—See this vol., 1462.

**Milk of the merino ewe.** A. W. PEIRCE (Austral. J. Exp. Biol., 1936, 14, 187—192).—Colostrum differed from milk principally in its higher proportions of casein, lactalbumin, globulins, and lactose. Seasonal variations in two typical breeds are examined.

A. G. P.

**Copper, zinc, and manganese content of cows' milk.** A. BROEK and L. K. WOLFF (Acta brev. neerl. Physiol., 1935, 5, 80—81; Chem. Zentr., 1936, i, 461).—The Cu content was  $15-50 \times 10^{-6}$  g. per litre, and was uninfluenced by season or diet. The Zn was 1.94—4.96 mg. per litre. Mn averaged  $10^{-6}$  g. per litre; this val. was influenced much more by org. than by inorg. Mn in the feed.

H. J. E.

**Determination of vitamin-C content of fresh milk.** W. LOJANDER (Suomen Kem., 1936, 9, A, 111—114).—Several 20-c.c. samples of milk are treated respectively with increasing amounts of a standard solution of dichlorophenol-indophenol, and after 10 min. in the dark, the -C content corresponds with that amount of indicator between the last white and the first coloured test. The method fails with milk containing many bacteria.

J. N. A.

**Occurrence and possible significance of some minor components of cow-milk fat.** T. P. HIL-



DITCH and H. PAUL (Biochem. J., 1936, 30, 1905—1914).—Results of analyses of the component acids of milk fat are calc. (a) on the assumption that no unsaturated acids of lower mol. wt. than oleic acid (I) are present, and (b) allowing for the presence of decenoic (II), tetra- (III) and hexa-decenoic (IV) acids. Comparison of these results with those for the similar analysis of completely hydrogenated butter indicates the presence of lower unsaturated acids. In addition to traces of (II) and  $\leq 1\%$  of (III), there must be present about 4–5% of (IV). By applying the correction, the palmitic acid val. is increased by 2% and the (I) val. decreased by 5%. There is no detectable amount of any unsaturated acid of lower mol. wt. than  $\Delta^9:10$ -(II) in butter fat. The minor lower unsaturated components are probably degradation products of oleo-glycerides which have escaped complete saturation. P. W. C.

Variation of the fat content of milk with the time of day. Z. CZUKAS (Mezög.-Kutat., 1935, 8, 270—279; Chem. Zentr., 1936, i, 461).—Tests with 8 cows on 94 days showed that morning milk had a 40%, and evening milk a 29%, lower fat content than midday milk. H. J. E.

Hydrogen-ion concentration of tears: relation to certain ocular symptoms and to conjunctival and corneal lesions. G. N. HOSFORD and A. M. HICKS (Arch. Ophthalmol., 1935, 13, 14—25).—Tears are sufficiently buffered to permit sufficient dilution for practicable determinations of  $p_H$ . Vals. for normal eyes averaged 7.35. Protein and salt errors and the relation of tears to certain bacteria are discussed. CH. ABS. (p)

Influence of the nature of the stimulant on the quantity, chloride content, and  $p_H$  of the salivary secretion. E. J. BIENKA and C. SZCZEPANSKI (Compt. rend. Soc. Biol., 1936, 123, 32—34).—The secretion is affected less by mechanical than by chemical stimulation. When stimulation is rapid or the medium alkaline, the Cl' content is  $>$  and the  $p_H <$  that on slow stimulation or in acid medium. H. G. R.

Bile-sugar. G. BALTAČEANO and C. VASILIU (Compt. rend. Soc. Biol., 1936, 123, 54—55).—In bile the free sugar is glucose and the protein-bound sugar lactose. H. G. R.

Method of determining total pigment in bile applicable to "biliverdin" biles. C. R. SCHMIDT, K. K. JONES, and A. C. IVY (Proc. Soc. Exp. Biol. Med., 1936, 34, 17—21).—The bile-pigments are oxidised to yellow compounds by  $(NH_4)_2S_2O_8$  in presence of  $AcOH-EtOH$  (1:1) and then determined colorimetrically. W. O. K.

Determination of cholic acid in bile and in duodenal drainage. H. DOUBILET (Proc. Soc. Exp. Biol. Med., 1936, 34, 84—86).—The Gregory-Pascoe reaction (cf. A., 1929, 1114) is applied to the determination of cholic acid in bile. W. O. K.

Influence of diet on formation of hepatic and renal calculi. IV. Histological study of liver, gall-bladder, and kidneys. V. Changes of hydrogen-ion concentration and the buffer action of the bile. K. USUKI (Japan. J. Gastro-

enterol., 1934, 6, 94—104, 105—111).—V. In young rabbits receiving a diet deficient in fat-sol. vitamins, the liver and gall-bladder biles showed lowered  $p_H$  and buffer action, with which is associated the formation of calculi. CH. ABS. (p)

Quantitative studies of the normal human gastric secretion. S. WANG (Chinese J. Physiol., 1936, 10, 493—506).—The HCl, neutral Cl', and non-Cl' alkaline (base+mucus+pepsin) components of gastric juice of four normal human subjects were investigated, histamine being used as stimulant. The HCl and neutral Cl' were secreted in proportional vols. at const. concn. in the order approximating to the electrolyte concn. of the blood. Both vals. were numerically  $<$  those in dogs. During active secretion, the vol. of the alkaline component is small. The total base and Cl' concn. of the serum is remarkably const. P. W. C.

Gastric secretion during the night. A. WINKELSTEIN (Amer. J. Digest. Dis. Nutrition, 1934, 1, 778—782).—Normal curves of gastric secretion show little HCl during the night. In cases of gastric or intestinal ulcers, secretion and HCl content are high. Nocturnal hyperchlorhydria is not controlled by alkalis, olive oil, atropine, or aspiration. CH. ABS. (p)

Influence of the pylorus on the regulation of the acidity of gastric secretion. W. W. LERMANN and L. M. NELSON, jun. (Amer. J. Digest. Dis. Nutrition, 1934, 1, 245—247).—Regurgitation of bile and trypsin and lowered acidity in the digesting stomach were observed, the pylorus being held open during the test. CH. ABS. (p)

Dry natural digestive juices: properties and use. W. N. BOLDYREFF (Amer. J. Digest. Dis. Nutrition, 1935, 2, 33—36).—The dry residue from vac. evaporation of freshly collected and cooled juice may be preserved without an antiseptic. Technique of prep. is described. CH. ABS. (p)

Relations between hæmoglobin and gastric acidity. W. C. ALVAREZ and F. R. VANZANT (Proc. Staff Meetings Mayo Clin., 1936, 11, 385—391).—There was a marked rise in the incidence of achlorhydria in man as the hæmoglobin (I) vals. fell below 12 g. per 100 ml., and the mean gastric acidity decreased rapidly below this (I) level. With (I) levels  $>18$  g. per 100 ml., mean gastric acidity decreased slightly, and the incidence of achlorhydria was normal. Severe anæmia is not incompatible with the presence of excess of acid, and the presence of great excess of hæmoglobin is compatible with achlorhydria. NUTR. ABS. (m)

Gastro-intestinal studies. V. Gastric juice in anæmias other than pernicious anæmia. P. J. FOUTS, O. M. HELMER, and L. G. ZERTAS (Amer. J. Digest. Dis. Nutrition, 1934, 1, 677—684).—No enzymes were found in gastric juice having  $p_H < 7.0$ . No improvement in gastric secretion was found when the gastric contents, after histamine stimulation, had  $p_H > 7.0$  and contained no enzymes. CH. ABS. (p)

Anti-pernicious anæmia principle in gastric juice. A. W. C. G. KAMERLING and W. GROTEPASS

(Nederland. Tijds. Geneesk., 1936, 80, II, 1991).—The effect of liver is increased by incubation with normal gastric juice, but not with the gastric juice of pernicious anaemia patients. Pepsin-HCl digestion does not increase the activity of liver. After removal of the enzymes of gastric juice the ultrafiltrate from active liver digests was equally active, even after heating at 80° for 30 min. NUTR. ABS. (m)

**Buffer capacity of pancreatic juice.** M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 300—302).—Protein diets induced a greater flow of secretion than did other test meals. The buffer capacity of the juice reached max. 1—3 hr. after ingestion of food and gradually diminished as the acidity of the duodenum declined. The secretion was always alkaline and possessed slight buffer capacity even during fasting. CH. ABS. (p)

**Effect of exclusion of pancreatic secretion by evulsion of the pancreatic ducts on reaction of duodenal contents.** M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 295—297).—The  $p_H$  of the contents during fasting was 7.00—7.81, after a meat meal 6.40—3.50, after a carbohydrate meal 6.75—4.26, and after a fat meal 6.80—5.20. In the absence of pancreatic juice the total buffer secretions are smaller but the bile and succus entericus maintain a normal  $p_H$  except when gastric matter of high acidity enters the duodenum. CH. ABS. (p)

**Effect of exclusion of pancreatic secretion by a pancreatic fistula on reaction of gastric, duodenal, and jejunal contents.** M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 298—300).—Production of a pancreatic fistula caused no change in the  $p_H$  of gastric contents during fasting or after test meals. The  $p_H$  of duodenal contents was normal during fasting, but protein and carbohydrate meals caused a more rapid and prolonged decline in  $p_H$  than when pancreatic secretion was present. Similar changes occurred in the jejunal contents, but only after a protein diet. CH. ABS. (p)

**Reaction of the contents of the isolated duodenum.** P. R. LINES (Amer. J. Digest. Dis. Nutrition, 1935, 2, 285—288).—The alkalinity of the contents ( $p_H$  7.10—8.15) is caused by weak alkalis or buffer substances, fluctuations in which depend on the relative proportions of pancreatic juice, bile, and duodenal secretion present. The alkalinity of pancreatic juice is approx. double that of bile. CH. ABS. (p)

**Capacity of duodenum to neutralise, to buffer, and to dilute acid.** G. A. STEVENS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 288—293).—The increase in neutralising capacity after a fat meal and the decrease after a protein meal are attributed to inhibition and stimulation, respectively, of the gastric juice. HCl introduced continuously in small amounts is neutralised, buffered, and diluted; little is absorbed in the duodenum. A large single injection of acid is swept through the duodenum by peristalsis. CH. ABS. (p)

**Reaction of duodenal content after exclusion of bile from duodenum.** J. W. McROBERTS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 293—294).—Loss

of bile did not materially affect the  $p_H$  of duodenal contents in dogs. CH. ABS. (p)

**Determination of ketones in urine.** J. TROTZKI and R. MENDELSON (Ukrain. Biochem. J., 1936, 9, No. 1, 157—163).—The urine is treated first with  $Pb(OAc)_2$  and aq.  $NH_3$  and then with  $Pb(OAc)_2$  and NaOH. The  $COMe_2$  in a portion of the filtrate acidified with AcOH is distilled into aq. NaOI,  $K_2Cr_2O_7$  and  $H_2SO_4$  being added to the distillation flask at intervals. W. O. K.

**Detection of pyruvic acid in urine.** A. PISUNER and M. FARRAN (Biochem. Z., 1936, 287, 113—114; 288, 294).— $AcCO_2H$  is isolated as the dinitrophenylhydrazone, m.p. 216°. P. W. C.

**Methylmalonic acid from rat urine.** E. BOYLAND and A. A. LEVI (Biochem. J., 1936, 30, 2007—2008; cf. this vol., 234).—Methylmalonic acid (I) was isolated in yields  $>0.5$  g. per litre from rats' urine, but could not be found in human and rabbits' urine. (I) separates from  $H_2O$  as monohydrate. Thymine is a possible precursor of (I) in the organism. The Na salt of (I) does not inhibit respiration and acetoacetate breakdown in liver slices. W. McC.

**Origin of trimethylamine in human and animal urine.** S. V. FOMIN (Ukrain. Biochem. J., 1936, 9, No. 1, 143—155).— $NMe_3$  in human or pig urine is of exogenous origin. W. O. K.

**Phenols or glyoxalines in urine.** A. D. MARENZI and R. F. BANFI (Compt. rend. Soc. Biol., 1936, 123, 73—74).—The diazo-reaction of urine is principally due to phenols. H. G. R.

**Excretion of ammonia and uric acid by larvæ of muscoid flies.** A. W. A. BROWN (J. Exp. Biol., 1936, 13, 131—139).—Small amounts of uric acid (I) were found in tissues and excreta of *Calliphora erythrocephala*, *Mg.*, and *Wohlfahrtia vigil*, *Wlk.*  $NH_3$  excretion increased with rise in body-wt. of *Calliphora* larvæ, but there was a lag of 1 day in *Wohlfahrtia*. (I) excretion increased in a similar manner but the amount was very much less. In *Calliphora* a diet of caseinogen proved adequate and ovalbumin inadequate. The caseinogen diet brought about an excretion of  $NH_3$  and (I) about twice as great as that on a normal meat diet. NUTR. ABS. (m)

**Determination of veronal [in urine].** G. SACK (Arch. exp. Path. Pharm., 1936, 183, 71—76).—Urine (10—20 c.c.) is treated with  $Pb(OAc)_2$ -AcOH and filtered and the material extracted from the filtrate by  $Et_2O$  is purified by treatment with  $K_2Cr_2O_7$ - $H_2SO_4$  followed by  $H_2O_2$  and freed from fat by successive treatments with  $EtOH$  and  $H_2O$ . The final  $Et_2O$  extract of the aq. solution is evaporated to dryness and weighed. The accuracy is  $\pm 5\%$ . A qual. test is given. F. O. H.

**Colour reaction for the urine of pregnancy.** P. E. SMOLA (Suomen Kem., 1936, 9, B, 20).—I is added, the solution boiled, and shaken with amyl alcohol. The alcohol layer assumes a red-violet colour in 70% of the cases examined. A. L.

**Losses of nitrogen and carbon in drying the faeces of cattle.** M. KLEIBER, R. W. CALDWELL, and H. JOHNSON (Proc. Soc. Exp. Biol. Med., 1936,



34, 128—130).—N determinations in faeces should be made with fresh samples immediately after defecation since storage and drying result in N losses of  $4.48-7.19 \pm 0.049\%$ . C is best determined by combustion of dried faeces in  $O_2$  at 25 atm. The loss of C on drying ( $1.36 \pm 0.08\%$ ) is determined in a special apparatus. 35—55% of the lost C occurs as pre-formed  $CO_2$ . W. McC.

**Elimination by sweat in an ozonised atmosphere.** THIODET and RIBERE (Compt. rend. Soc. Biol., 1936, 123, 329—330).—An analysis of the sweat is given, an increase in the elimination of toxic substances being apparent. H. G. R.

**Pathogenesis of oil acne.** N. S. VEDROV and A. P. DOLGOV (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 428—436).—Compounds of the type of naphthene, in naphtha oil, can cause skin affections of the type of oil acne. Purification of the oil does not render it completely harmless. Sulphonated and unsulphonated oils have the same effect. M. A. B.

**Serum electrolytes and mineral metabolism in a case of Addison's disease. Use of adrenal cortical extract (Eschatin).** S. K. CHOU, K. C. CHEN, S. H. LIU, and S. S. FANG (Chinese Med. J., 1936, 50, 1013—1024).—A case is reported of Addison's disease accompanied by pulmonary tuberculosis. Low plasma vol., low total base, serum-Na and -Cl vals. were found, which were temporarily relieved by Eschatin. Later doses were ineffective, owing to mineral loss by tissue destruction as a result of active pulmonary tuberculosis. G. H. B.

**Anæmia caused by deaminised caseinogen.** A. G. HOGAN, R. E. GUERRANT, and W. S. RITCHIE (J. Biol. Chem., 1936, 115, 659—672; cf. A., 1934, 1387).—For a given diet, a ration of approx. 5% of caseinogen (I) prevents, whilst a min. of 5—10% of deaminised (I) produces, an anæmia in rats which is not alleviated by milk, egg yolk, wheat germ oil, muscle, or liver or stomach preps. Laboratory preps. of lactalbumin do not prevent the anæmia and those of ovalbumin have a variable effect; commercial preps. of both proteins, however, prevent anæmia, as does dried yeast (aq. extracts of which are inactive). Autoclaved (I) or yeast has no curative action. The anæmia and anti-anæmia factors occur in the 25%  $H_2SO_4$  hydrolysate of deaminised and normal (I), respectively. F. O. H.

**Origin of the anti-anæmic factor. IX. Action of the liver in pernicious anæmia.** F. REIMANN, H. BIEDERMANN, and L. ZWILLIGER (Z. Klin. Med., 1935, 128, 205—212; Chem. Zentr., 1936, i, 585).

**Basal metabolism in experimental anæmias.** K. C. CHEN and H. C. CHANG (Proc. Soc. Exp. Biol. Med., 1936, 34, 646—648).—In  $NH_4Ph$  anæmia there is only a fleeting increase in basal metabolic rate, and the immature blood cells contribute little to the total  $O_2$  consumption. There is no strict relation between  $O_2$  consumption and reticulocyte count. P. G. M.

**Myohæmoglobin content of the hypertrophied heart of the anæmic rat.** D. W. COWAN and L. C. BAUGUESS (Proc. Soc. Exp. Biol. Med., 1936, 34, 636—637).—In spite of severe anæmia rats are able to

maintain normal muscle-hæmoglobin concn. during development of abnormal hypertrophy. P. G. M.

**Changes in the protein equilibrium of blood during asthma.** AUBRY, THIODET, and RIBERE (Compt. rend. Soc. Biol., 1936, 123, 327—328).—During an attack the albumin:globulin ratio and the albumin content decrease and the globulin content increases. H. G. R.

**Chemistry of carcinoma. II.** A. VON CHRISTIAN (Z. Krebsforsch., 1935, 42, 25—29; Chem. Zentr., 1936, i, 360).—Cytolysis of carcinoma by serum is inhibited by cholesteryl *n*-butyrate, isovalerate, and palmitate. A. G. P.

**Glycolysis in cancer. II.** C. FRISCH and R. WILLHEIM (Biochem. Z., 1936, 287, 198—202; cf. A., 1935, 885).—The inhibition of glycolysis in muscle extract by benzoquinone is not counteracted by extracts of healthy kidney, spleen, muscle, embryonal tissue (hen), or by ascorbic acid and hence the counter-acting effect of tumour extract is sp. W. McC.

(A) Lysine as a factor in malignant growth. C. VOEGTLIN and J. W. THOMPSON. (B) Effect of gliadin diet on malignant growth. C. VOEGTLIN and M. E. MAVER (U.S. Publ. Health Repts., 1936, 51, 1429—1436, 1436—1444).—(A) A diet of 70% wheat meal and 30% whole milk powder gives normal growth in rats and rapid growth of mammary carcinoma in mice. Heating the milk powder renders it inadequate for normal and inhibitory to malignant growth. Administration of lysine removes the inhibition of normal and malignant growth and an adequate supply is necessary for rapid growth of malignant tumour.

(B) Normal growth of young mice and growth of spontaneous mammary carcinoma in adult mice are inhibited by diets containing gliadin (I) as the only protein source, but the addition of lysine makes the diet adequate for both forms of growth. The effect of glutenin (II) is different from that of (I) in that growth is not inhibited. (II) is a complete protein and (I) is deficient in lysine. Lysine is necessary for the growth of mammary carcinoma. W. L. D.

**Diagnosis of cancer.** P. MENDELEEFF (Compt. rend. Soc. Biol., 1936, 123, 135—137).—The pituitary in cancer secretes a substance detectable in the blood, cerebrospinal fluid, saliva, and urine by the coagulating action on plasma *in vitro*. H. G. R.

**Calcium and protein of blood and blister fluid in malignant disease.** R. O. BOWMAN, H. C. PITTS, P. H. MITCHELL, and E. EWERTZ (Canad. Med. Assoc. J., 1936, 34, 527—532).—K, P, Ca, and total protein were determined in the blood-serum and fluid from artificially raised blisters of 50 cancerous and 22 non-cancerous subjects. Since the average Ca of the fluid in the cancerous was < in the non-cancerous group malignancy may be related to a Ca deficiency not evident in the blood-serum but appearing in the blister fluid. Corresponding differences were noted in respect of P and (especially) protein, which was significantly lower in the blood and fluid of cancerous individuals. NUTR. ABS. (m)

**Total sulphur of tissue in normal and abnormal growth (mouse carcinoma).** H. BROWN and J. V. KLAUDER (J. Lab. Clin. Med., 1935, 20, 1143—

1150).—The S content of the skin of rabbits decreases with the falling rate of growth from birth to maturity. After maintenance on a low-cystine diet the S content of normal organs of mice declines, and the no. of infections and rate of growth of inoculated tumours are reduced. Rapidly growing tumours contain more S than slow-growing ones. CH. ABS. (p)

**Paraffin and mineral oil cancer.** WELWART (Seifensieder-Ztg., 1935, 62, 792—793; Chem. Zentr., 1936, i, 360).—The carcinogenic action of mineral oils is associated with the unsaturated hydrocarbons, notably 1:2:5:6-dibenzanthracene and 1:2-benzpyrene, and textile spinning oils. A. G. P.

**Prophylaxis of benzpyrene cancer with organic peroxides.** J. MAISIN and F. ROBERT (Compt. rend. Soc. Biol. 1936, 123, 156—159).—Diformaldehyde peroxide (A., 1935, 1526) and  $\text{HCO}_3\text{H}$  have a prophylactic action on benzpyrene cancer. H. G. R.

**Carcinogenic power of methylcholanthrene.** J. MAISIN and M. L. COOLEN (Compt. rend. Soc. Biol., 1936, 123, 159—160).—Methylcholanthrene is particularly active in producing cancerous tumours. H. G. R.

**Differentiation of tumours (carcinomata and sarcomata) of varying origin and investigation of the relationship between primary tumours and their metastases by the protective proteinase reaction.** E. ABDERHALDEN (Fermentforsch., 1936, 15, 245—250). E. A. H. R.

**Action of tumour tissue on hexosediphosphoric acid.** K. TSUZUKI (J. Biochem. Japan, 1936, 23, 421—435).—In rabbits' spindle-cell sarcoma, hexosediphosphoric acid yields triosephosphoric acid which does not form (from 2 mols.) phosphoglyceric (I) (1 mol.) and glycerophosphoric acid (1 mol.). The tumour tissue converts (I) into phosphopyruvic acid but not  $\text{AcCO}_2\text{H}$  except in presence of adenosinetriphosphoric or adenylic acid or phosphatase. The conversion of  $\text{AcCO}_2\text{H}$  into lactic acid (II) was not observed, but small amounts of (II) are always produced. The metabolism of the tumour is compared with that of muscle. F. O. H.

(A) Copper content of human tumours in relation to that of the liver. W. GERLACH. (B) Copper content of Jensen sarcoma in relation to that of the organs. S. EDLBACHER and W. GERLACH (Z. Krebsforsch., 1935, 42, 290—294, 272—289; Chem. Zentr., 1936, i, 574).—(A) Spectrographic determinations show the Cu content of tumours to vary within wide limits ( $0.5-20 \times 10^{-6}$  g. per g. fresh wt.). Liver contains  $4-19 \times 10^{-6}$  g. per g. (b) Rat livers contained 1—6, spleen 0.3, and kidneys  $3.4 \times 10^{-6}$  g. per g. fresh wt. Necrotic and healthy areas of Jensen tumour contained 0.73 and  $0.32 \times 10^{-6}$  g. per g., respectively. A. G. P.

**Intermediary fat and carbohydrate metabolism of sarcomatous rats.** B. PURJESZ and S. LAJOS (Magyar orvosi Arch., 1936, 37, 69—74).—The development of Jensen sarcoma in rats was associated with a fall in blood-sugar from 99 mg. per 100 ml. before inoculation to 60 mg. at 3—4 weeks. Liver-glycogen declined, on the average, from 1.58 to 0.43% and total carbohydrate of the liver from 3.5 to 2.1%.

The corresponding average figures for muscle were: glycogen 0.88 to 0.68%, total carbohydrate 2.0 to 1.5%. Neutral fat increased in the liver from 0.57 to 1.3, sterols from 0.35 to 0.54, and phosphatides from 2.7 to 3.1%. The I val. of liver fat was not significantly altered. NUTR. ABS. (m)

**Celiac disease. I. Carbohydrate metabolism.** E. BADENOCH and N. MORRIS (Quart. J. Med., 1936, 5, 227—250).—The flat blood-sugar curve was found only in active stages of celiac disease in children (7 cases). In convalescent periods the normal type of curve was approached. The curve was low in normal children of < 4 years, in marasmic children, and in cretins. The absorption and excretion of urea in celiac cases, and the absorption of sugar given with fat in normal children, indicate that fermentation of carbohydrate in the intestine is an important factor in the production of the flat curve in celiac disease. After 4 units of insulin injected subcutaneously in the fasting state in celiac disease, the blood-sugar fell to a mean val. of 33 mg. per 100 ml. in 1 hr. as compared with 67 mg. in normal children, but there were no clinical signs of hypoglycemia. Injection of anterior pituitary extract in cases of the disease caused a rise in the fasting blood-sugar and an increase in the height of the curve. Injections of extract of anterior pituitary improved the utilisation of fat in 3 cases of the disease. It is suggested that in the disease there is a deficiency of the contrainisular pituitary hormone. NUTR. ABS. (m)

**Mechanism of increased oxygen consumption in patients with cardiac disease.** H. RESNIK, jun., and B. FRIEDMAN (J. Clin. Invest., 1935, 14, 551—562). CH. ABS. (p)

**Nutritional factors which produce cataract and dermatitis.** A. F. MORGAN and B. B. COOK (Proc. Soc. Exp. Biol. Med., 1936, 34, 281—285).—In rats a diet containing 70% of lactose caused development of cataract in every case when the vitamin- $B_2$  content of the diet was low and in 85% of the cases when it was high. In no case was there development of dermatitis. A diet containing 68% of maize starch caused severe dermatitis when the  $B_2$  content was low but not when it was high. Administration of flavin cured the dermatitis. W. McC.

**Effects of excessive ingestion of sodium and potassium salts on carbohydrate metabolism and blood pressure in diabetic children.** I. McQUARRIE, W. H. THOMPSON, and J. A. ANDERSON (J. Nutrition, 1936, 11, 77—101).—Daily ingestion of 1—2 g. of NaCl per kg. body-wt. had a favourable effect on the carbohydrate metabolism of diabetic children receiving a simplified low-K diet. Other Na salts have similar though less marked effects. KCl has the reverse action on glycosuria and blood pressure. K completely antagonises the effects of Na when given simultaneously in amounts corresponding with 1/3 of the equiv. of Na ingested. A. G. P.

**Products of carbohydrate metabolism in the blood of diabetics. Residual chromic index.** H. WAREMBOURG (Ann. Méd., 1936, 39, 342—356).—The difference between the total chromic index and the glucose chromic index (I.C.G.) is called the



residual chromic index (I.C.R.) The I.C.R. represents chiefly carbohydrate degradation products such as lactic acid and  $\text{AcCO}_2\text{H}$ . The ratio I.C.G.:I.C.R. was normally 0.18–0.4. The I.C.R. was increased in untreated diabetes and the increase was not due to blood-ketones. I.C.R. was increased in diabetic blood after sugar ingestion and decreased by 75% after insulin (I) injection. No alteration took place in the normal individual. It is concluded that there is an increase in the intermediary products of carbohydrate metabolism in diabetes. Dietetic treatment and (I) therapy resulted in a decrease in I.C.R.

Nutr. Abs. (m)

**Serum-lipins in diabetes.** E. B. MAN and J. P. PETERS (J. Clin. Invest., 1935, 14, 579–594).—Cholesterolaemia (I) and phospholipinaemia were closely correlated in diabetics. Relation between (I) and the serum-fatty acids was less definite. Serum-cholesterol was unrelated to the severity of diabetes. Hypocholesterolaemia was associated with malnutrition and with hypoproteinaemia.

Ch. Abs. (p)

**Cholesterol content of blood in diabetic patients on fat-rich diets.** R. H. FREYBERG, L. H. NEWBURGH, and W. A. MURRILL (Arch. Int. Med., 1936, 58, 589–597).—In 21 patients with controlled diabetes fed on diets rich in fat for periods of 2 months to 8 years, the cholesterol (I) vals. during fasting were 0.126–0.223% (average 0.176%). With normal controls the vals. were 0.130–0.186%, average 0.156%. There was no correlation between the amount of fat in the diet and blood-(I). Lack of control of the disease is the main factor in causation of hypercholesterolaemia in diabetics.

J. N. A.

**Exercise in diabetes mellitus.** A. MARBLE and R. M. SMITH (Arch. Int. Med., 1936, 58, 577–588).—Exercise of short duration producing only mild fatigue markedly increased the blood-sugar of young diabetics (severe or moderate) who had not received food or insulin for several hr. Exercise probably causes glycogenolysis in the liver.

J. N. A.

**Eczema in nickel platers.** N. S. VEDROV (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 179–196).

M. A. B.

**Composition and changes in blood and spinal fluid in epilepsy.** I. I. BAN (Curierul farm., 1935, 5, No. 8, 1–17; Chem. Zentr., 1936, i, 584–585).—A relation is established between carbohydrate metabolism and the onset of epilepsy.

A. G. P.

**Fluorine in the bones and teeth in fluorosis.** J. M. MUNOZ (Compt. rend. Soc. Biol., 1936, 123, 74–75).—In rat fluorosis a diminution in the ash of the teeth and bones together with a three-fold increase in F was observed. Treatment with Ca, vitamin-D, and parathyroid hormone had no effect on the dental lesions.

H. G. R.

**Influence of blood-serum of goitre patients on tissue respiration.** K. MUNE (Folia Endocrinol. Japon., 1934, 10, 69–70).—Serum contains a substance (I) which accelerates  $\text{O}_2$  consumption in surviving rat tissue. The (I) content of serum increases in hyper- and decreases in hypo-thyroidism and approaches normal vals. with thyroid correction.

Ch. Abs. (p)

**Relation between the occurrence of endemic goitre and the presence of traces of silver and barium in drinking-water.** C. H. BOISSEVAIN and W. F. DREA (Endocrinol., 1936, 20, 686–687).—Ag is present in traces in drinking- $\text{H}_2\text{O}$  from both goitrous and non-goitrous areas.  $\text{H}_2\text{O}$  from the Swiss goitrous area shows an unusually high Ba content, but neither Ag nor Ba affects development of goitre when fed to rats.

R. N. C.

**Oxygen utilisation, cardiac output, and related circulatory functions in Graves' disease.** S. A. GLADSTONE (Proc. Soc. Exp. Biol. Med., 1936, 34, 587–591).—In 4 cases with basal metabolic rates of +33%, the arterio-venous  $\text{O}_2$  difference was decreased by 37%, whilst cardiac output increased by 93%.

P. G. M.

**Blood-sugar tolerance test in hypertension.** K. MAEHARA (Folia Endocrinol. Japon., 1934, 10, 52).—Hyperglycaemia following administration of glucose was higher and of longer duration in hypertensive cases.

Ch. Abs. (p)

**Hermaphroditism with growth disturbance.** M. SAKAMOTO, S. ITO, and H. HATTORI (Folia Endocrinol. Japon., 1934, 10, 59–60).—Growth disturbances are attributed to functional derangement of thyroid and sex glands. Blood-sugar was normal but tolerance was lowered. Basal metabolism was normal but the sp. dynamic protein metabolism was low.

Ch. Abs. (p)

**Hermaphroditism.** K. NISHIDA and J. MATSUI (Folia Endocrinol. Japon., 1934, 10, 60–61).—In the case described sugar tolerance and blood-sugar were almost normal; basal metabolism and sp. dynamic action were somewhat lowered.

Ch. Abs. (p)

**Pathological physiology of infarcts. IV. Arginase in necrosis.** H. BAYERLE, G. BORGER, and T. MAYR (Z. physiol. Chem., 1936, 243, 227–236).—The arginase (I) content of experimental anaemia-infarct of rabbit's kidney is < that of the healthy tissue and decreases progressively to zero in 10–14 days. At first the (I) content is raised by activation with  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$  but these have no effect later. During autolysis the (I) content of healthy tissue decreases in the same way and is similarly affected by  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ .

W. McC.

(A) Cholesterol fractions in acute infections of infants with and without eczema. (B) Iodine value of serum-fatty acids in acute infections of infants with and without eczema. A. V. STRESSER (Proc. Soc. Exp. Biol. Med., 1936, 34, 10–11, 12–14).—(A) In fasting infants, the cholesteryl ester of the blood during acute infection of the respiratory tract was < during convalescence, but the free cholesterol underwent little change except in cases of pneumonia. (B) During the febrile period, the amount and I val. of the serum-fatty acids decreased.

W. O. K.

**Significance of carbohydrate metabolism and local acidosis in inflammation.** V. MENKIN and C. R. WARNER (Proc. Soc. Exp. Biol. Med., 1936, 34, 594–596).—The cytological picture in inflammation is conditioned by  $p_{\text{H}}$ , which is influenced by

increased glycolysis and local depletion of the alkali reserve.

P. G. M.

**Hyperproteinæmia with reversal of the albumin-globulin ratio in lymphogranuloma inguinale.** R. D. WILLIAMS and A. B. GUTMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 91—94).—Ten out of 12 cases of lymphogranuloma inguinale showed a hyperproteinæmia. There was an abs. and relative increase in serum-globulin in 11 cases.

W. O. K.

**Serum reaction in leprosy.** (A) Flocculation reaction. (B) Kephalin as flocculation reagent. I. SAKAKIBARA (J. Biochem. Japan, 1936, 23, 377—420, 437—448).—(A) The use of preps. containing lecithin as antigen in serological reactions for leprosy is discussed. The principal antigenic factor in nerve extracts, lecithin preps., etc. is kephalin (I).

(B) The antigenic action (which is due to the  $\beta$ - and not the  $\alpha$ -form) of (I) is unchanged by heating at 37° or 56° for 1 hr. or at 100° for  $\frac{1}{2}$  hr., by the presence of small amounts of  $\text{Et}_2\text{O}$ , by oxidation ( $\text{KMnO}_4$ ) or reduction ( $\text{Pt-H}_2$ ). The (I) from ox brain, ox liver, or hens' eggs contains 81, 76, and 79% of  $\beta$ -(I), respectively.

F. O. H.

**Cholesterol fractions in leprosy plasma.** G. G. VILLELA and A. CASTRO (Compt. rend. Soc. Biol., 1936, 123, 433—435).—Variations in the cholesterol fractions in the different clinical forms are discussed.

H. G. R.

**Multiple myeloma. IX. Crystalline and amorphous Bence-Jones protein.** A. MAGNUS-LEVY (Z. physiol. Chem., 1936, 243, 173—188).—The cryst. form of the protein (I) from 3 new cases was identical with that of (I) from 8 previous cases. It is not yet certain that (I) is a chemical entity.

W. McC.

**Myotonia.** W. R. RUSSELL and E. STEDMAN (Lancet, 1936, 231, 742—743).—Myotonia may be due to excessive production or accumulation of acetylcholine at the motor nerve-endings. It is increased by administration of prostigmine or a K salt, and temporarily relieved by  $\text{EtOH}$ .

L. S. T.

**Investigation of the origin of urinary protein in nephritis by the protective proteinase reaction.** H. HARTMANN (Fermentforsch., 1936, 15, 183—190).

E. A. H. R.

**Amino-nitrogen of nephritic transudates.** H. A. BULGER (Proc. Soc. Exp. Biol. Med., 1936, 34, 221—222).—The average  $\text{NH}_2\text{-N}$  contents of serum and transudates of patients with nephritis do not differ appreciably from those of non-nephritic persons, showing that rapid extravascular proteolysis does not occur in nephritis.

W. McC.

**Sodium chloride restriction and urea clearance in renal insufficiency.** E. M. LANDIS, K. A. ELSOM, P. A. BOTT, and E. SHIELS (J. Clin. Invest., 1935, 14, 525—541).—On a const. diet and fluid intake restricted intake of  $\text{NaCl}$  was accompanied by slightly diminished urea clearance (24 hr.). Administration of  $\text{NaCl}$  lowered plasma-urea (I) and increased the clearance. In advanced renal insufficiency (I) decreased markedly on administration of  $\text{NaCl}$ ; acute  $\text{NaCl}$  restriction produced hypochlor-

æmia with temporary retention of urea, creatinine, and  $\text{PO}_4'''$ .

CH. ABS. (p)

**Kidney function in children. I. Urea clearance values** (a) with no evidence of kidney disease, (b) after acute hæmaturic nephritis, (c) in the acute stage of the nephritis. G. E. CULLEN, W. E. NELSON, and F. E. HOLMES (J. Clin. Invest., 1935, 14, 563—574).—Vals. for normal children and adults and nephritic children show no fundamental differences.

CH. ABS. (p)

**Role of certain inorganic elements in the cause and prevention of perosis.** H. S. WILGUS, jun., L. C. NORRIS, and G. F. HEUSER (Science, 1936, 84, 252—253).—Perosis is due to lack of certain elements, especially Mn, and is aggravated by excess of Ca and probably of P. Al and Zn have a less effective preventive action than Mn.

L. S. T.

**Alteration in content of alkaline-earth metals in pathological body-fluids.** S. TOMISAWA (Mitt. med. Akad. Kioto, 1936, 17, 340—341).—The Ca and Mg contents of exudates, transudates, and sera from patients had some relationship to the course of their illnesses. In many cases during recovery, Ca increased and the Mg decreased, whilst when the condition became worse, Ca usually decreased and Mg increased.

NUTR. ABS. (m)

**Ascorbic acid excretion in pneumonia and other pathological conditions.** J. G. M. BULLOWA, I. A. ROTHSTEIN, H. D. RATISH, and E. HARDE (Proc. Soc. Exp. Biol. Med., 1936, 34, 1—7).—In pneumonia and other fevers urinary excretion of ascorbic acid following administration of large doses of vitamin-C is abnormally low.

W. O. K.

**Nervous system during pregnancy.** H. RASCHBA (Ukrain. Biochem. J., 1936, 9, No. 1, 55—68).—During pregnancy the creatine and  $\text{H}_2\text{O}$  content of the brain of rabbits is normal but the total N appears to be slightly reduced. In guinea-pigs' brain pregnancy produces no change in creatine, total N, or  $\text{H}_2\text{O}$  content.

W. O. K.

**Glutathione. I. Total and reduced glutathione, oxygen content and capacity, and cell volume of blood in non-pregnant and pregnant women with special reference to toxæmias of pregnancy.** F. W. OBERST and E. B. WOODS (Amer. J. Obstet. Gynecol., 1935, 30, 232—236; cf. A., 1935, 1392).—No essential differences were found in the total or reduced glutathione (I) or %  $\text{O}_2$  saturation of normal, pregnant, or parturient women. In the puerperium total (I) decreased slightly. Vals. were unaffected by late pregnancy toxæmias. The %  $\text{O}_2$  saturation was increased by use of anæsthetics containing  $\text{O}_2$  and was somewhat higher in non-convulsive toxæmias.

CH. ABS. (p)

**Diagnosis of pregnancy by the S. African clawed toad (*Xenopus laevis*).** H. A. SHAPIRO and H. ZWARENSTEIN (S. African Med. J., 1935, 9, 202—205).—The  $\text{Et}_2\text{O}$  extract of acidified urine is treated with  $\text{EtOH}$  and the centrifuged and washed ppt. is dissolved in  $\text{H}_2\text{O}$  and injected into toads.

CH. ABS. (p)



**Aschheim-Zondek [pregnancy] test.** J. B. DAWSON (New Zealand Med. J., 1935, 34, 22—25).—Urine for this test may be preserved by addition of  $\text{H}_3\text{BO}_3$  (20 grains per oz.). CH. ABS. (p)

**Kidney function during normal pregnancy.** M. NICE (J. Clin. Invest., 1935, 14, 575—578).—Urea (I) clearance during pregnancy is  $>$  normal and is not affected by increasing the blood-(I) by feeding (I). CH. ABS. (p)

**Fasting ketosis in the pregnant rat as influenced by adrenalectomy.** E. M. MACKAY and R. H. BARNES (Proc. Soc. Exp. Biol. Med., 1936, 34, 682—683).—Pregnant rats develop a ketosis  $>$  that in non-pregnant animals. It is abolished by adrenalectomy. P. G. M.

**Respiration and glycolysis in normal and pathological skin with special reference to psoriasis.** A. BUHMANN (Biochem. Z., 1936, 247, 145—152).—Anaerobic glycolysis in healthy human skin is relatively vigorous and the  $\text{O}_2$  consumption is low. Glycolysis probably occurs under aerobic conditions also. In psoriasis the  $\text{O}_2$  consumption increases on the average about 27% and the glycolysis about 68%. The age of the diseased skin has no effect on  $\text{O}_2$  consumption or glycolysis. Aerobic glycolysis occurs in psoriatic skin. Increases in  $\text{O}_2$  consumption and glycolysis  $<$  those observed in psoriasis are observed in other pathological affections of the skin. W. MCC.

**Dust in Mansfeld lung affections.** W. GEISLER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 87—116).—The dust from the Mansfeld cupriferous slate workings contains much quartz (I) and mica (II), that from the overlying sandstone-shale mixture much (I) and feldspar (III). Affected lung tissue showed much (I) and (III), a little (II) and rutile, and very little sericite (IV). It is improbable that (IV) is the main causal agent of these affections. In studies on the individual cell (various bacteria) dusts of Si compounds showed no toxic effect; sol. Si compounds showed only low toxicity, decreasing in the order K silicate, Na silicate, aq.  $\text{SiO}_2$ , sol. glycol silicate. True solubility in  $\text{H}_2\text{O}$  at  $p_{\text{H}}$  7.6 is shown only with clay and asbestos but not with any of the constituents of the Mansfeld slate. M. A. B.

**Dust-affected lungs. II. Silica and titanium contents of lungs from 100 cases of dust affection.** G. GERSTEL (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 304—348).—The intensity of the lung affections did not appear to depend only on the  $\text{TiO}_2$ ,  $\text{SiO}_2$ , or ash content of the lung, although the heaviest deposits were found in the more severe cases. M. A. B.

**Asbestosis bodies.** P. J. BEGER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 349—392).—The capsule of asbestosis bodies consists of protein and not  $\text{SiO}_2$  (cf. Koppenhofer, A., 1935, 1022). The  $n$  of the Fe-free capsule is  $\gg$  that of  $\text{SiO}_2$  gels and is practically the same as that of the blood corpuscles and tissue particles in microscopic preps. The capsule shows similar solubility in acids and alkalis to blood corpuscles and tissue particles, and is combustible. Koppenhofer's technique is criticised and the unreliability of the I-azide reaction for protein is pointed

out. The mechanism of the deposition of the protein capsule on the asbestos needle is discussed. M. A. B.

**Idiopathic steatorrhoea with multiple nutritional deficiencies.** H. W. FULLERTON and J. A. INNES (Lancet, 1936, 231, 790—792).—A case report with evidence of a deficiency of Ca, Fe, anti-anæmic factor, vitamin-B complex, and -C and -D. A possible deficiency of -A and -E is discussed. L. S. T.

**Differential glycaemia in pulmonary tuberculosis following administration of glucose-insulin.** R. DEL ZOPPO (Arch. Farm. sperim., 1936, 62, 1—16).—Mild forms of the disease do not affect carbohydrate metabolism in man. Initially the venous and capillary blood-sugar levels differ both during fasting and after administration of glucose. The non-occurrence of this difference in advanced cases excepting after injection of insulin and the prolonged alimentary glycaemia curve indicate hypofunction of the pancreas. F. O. H.

**Ascorbic acid metabolism in tuberculosis.** F. H. HEISE and G. J. MARTIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 642—644).—55—138 mg. of ascorbic acid daily are required to bring a tuberculous patient into equilibrium as regards vitamin-C nutrition (normal is 15—20 mg.). P. G. M.

**Euglobulin in human serum in different forms of pulmonary tuberculosis.** J. VIGNATI and M. RAUCHENBERG (Compt. rend. Soc. Biol., 1936, 123, 167—168).—The val. is independent of that of the other protein fractions of the serum. H. G. R.

**Peptic ulcer following loss of pancreatic secretion through a fistula.** M. T. HOERNER (Amer. J. Digest. Dis. Nutrition, 1935, 2, 302—305).—Following the production of a pancreatic fistula, the  $p_{\text{H}}$  of gastric contents was unchanged but that of the duodenum after fasting varied somewhat, and reached a low level after ingestion of protein or carbohydrate. CH. ABS. (p)

**Influence of chemical thought on biology.** (SR) F. G. HOPKINS (Science, 1936, 84, 255—260).—A lecture. L. S. T.

**Carbon dioxide diffusion through human skin.** H. HAEUSSLER (Pflüger's Arch., 1935, 237, 448—453). M. A. B.

**Effect of oxygen inhalation on gaseous distension of the stomach and small intestine.** J. FINE, J. B. SEARS, and B. M. BANKS (Amer. J. Digest. Dis. Nutrition, 1935, 2, 361—367).— $\text{H}_2$  is much more readily absorbed from the gastro-intestinal tract than is  $\text{N}_2$ . Pure  $\text{O}_2$  inhalation does not increase absorption of  $\text{H}_2$ . The efficiency of  $\text{O}_2$  for absorption of intestinal gases  $\propto [\text{O}_2]$ . CH. ABS. (p)

**Ultracentrifugation and oxygen consumption of the eggs of *Ascaris suum*.** G. C. HUFF and E. J. BOELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 626—628).—Respiration in *Ascaris* eggs is lowered by centrifuging. Respiratory and cleavage processes are not associated. P. G. M.

**Gaseous metabolism of the mammalian heart in sufficiency and insufficiency.** K. GOLLWITZER-MEIER, K. KRAMER, and E. KRÜGER (Pflüger's Arch.,

1936, 237, 68—92).—The gaseous metabolism of the heart increases with increased load whether due to increased resistance (aortic pressure) or increased inflow, but differs in the two cases. In both, the efficiency increases to a max. and then decreases. In spontaneous insufficiency the  $O_2$  utilisation increases for a given load, whilst the efficiency decreases; the optimum efficiency shifts towards the region of lighter load. The arterial  $O_2$  tension varies with the magnitude of the heart minute-vol. and the ventilation of the lungs, decreasing with decreased ventilation and *vice versa*. Increased resistance first decreases and then increases the capillary  $O_2$  utilisation in the heart-muscle. M. A. B.

**Effect of training on the respiration of muscle-tissue.** E. T. SORENI (Ukrain. Biochem. J., 1936, 9, 193—203).—The semitendinosus and biceps femoris muscles of rabbits, after short faradic stimulation for 15 min. daily for 15 days, show a large increase in respiratory activity compared with control muscles. The effect with the red muscle is < with the white muscle. F. A. A.

**Fasting and realimentation in the ruminant.**  
I. **Effect of food and fasting on certain blood constituents.** II. **Calcium and phosphorus metabolism during fasting, and during realimentation followed by fasting.** F. X. AYLWARD and J. H. BLACKWOOD (Biochem. J., 1936, 30, 1819—1824, 1824—1832).—I. Lipin-P decreases, and acid-sol. inorg. and org. P increase, in the blood of cows during fasting. Other blood constituents remain practically const., in contrast with the effects observed with single-stomached animals.

II. During prolonged fasting (12 days) Ca and P continue to be excreted by cows, and the data indicate that they are derived from both bone and phosphoprotein. F. A. A.

**Effect of excessive dietary sodium chloride on liver- and muscle-glycogen in the rat.** D. G. CRABTREE and B. B. LONGWELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 705—707).—High NaCl content of the diet causes a large increase in liver- but has little effect on muscle-glycogen. P. G. M.

**Calcium content of the body in relation to the calcium and phosphorus content of the food.** L. B. WHITCHER, L. E. BOOHER, and H. C. SHERMAN (J. Biol. Chem., 1936, 115, 679—684).—Diets containing 0.42% of P and with Ca:P=1.2—2.4 or containing 0.73% of P and with Ca:P=0.7—1.4 do not increase the rate of calcification in rats; this effect is opposite to that found with diets containing 0.42% of P and with low Ca:P ratios (0.16—0.5) (A., 1931, 1326). F. A. A.

**Effect of liberal intakes of calcium or calcium and phosphorus on growth and body-calcium.** E. W. TOEFFER and H. C. SHERMAN (J. Biol. Chem., 1936, 115, 685—694).—Increasing the Ca or Ca+P contents of adequate diets results in more rapid growth and rate of calcification in rats, including those of the second generation. The max. effect is obtained at about 0.64% of Ca. F. A. A.

**Protein intake in relation to growth and rate of calcification.** R. T. CONNER and H. C. SHERMAN

(J. Biol. Chem., 1936, 115, 695—706).—With diets of approx. min. adequate Ca content (0.2%), raising the protein (I) level from 14% to 28% promotes growth and calcification in young rats. At higher Ca levels, increasing (I) to 25% gives a further increase in growth; further increase of (I) in the diet to 40% does not enhance this effect.

F. A. A.

**Effect of digestibility on the availability of iron in whole wheat.** E. McC. VAHLTEICH, M. S. ROSE, and G. MACLEOD (J. Nutrition, 1936, 11, 31—36).—Hæmoglobin regeneration in depleted rats receiving a whole milk diet was influenced by supplements in the order predigested wheat > natural fine-ground wheat > minerals ( $FeCl_3$ ,  $CuSO_4$ ). Ease of digestion contributed largely to the val. of predigested wheat. A. G. P.

**Protein utilisation as affected by the presence of small amounts of bran or its fibre.** E. H. FUNNELL, E. McC. VAHLTEICH, S. O. MORRIS, G. MACLEOD, and M. S. ROSE (J. Nutrition, 1936, 11, 37—45).—Of the total N intake of human subjects the proportion excreted when prepared bran was added to the diet was > when the fibre from the same amount of bran was used and, in turn > when no supplement was given. Feeding of vitamin-B with the fibre did not affect these results. Bran decreased the digestibility coeff. of the ration, the difference being attributable to excretion of bran protein. A. G. P.

**Specific dynamic action of carbohydrate and of protein in human hypothyroidism after total ablation of the normal thyroid gland.** M. LANDOWNE (J. Clin. Invest., 1935, 14, 595—603).—Ingestion of carbohydrate (I) or of protein (II) after complete removal of the thyroid is followed by an increased  $O_2$  consumption, thus demonstrating sp. dynamic effects of (I) and (II). CH. ABS. (p)

**Effect of high-protein diets on the kidney function in dogs.** L. K. CAMPBELL (J. Lab. Clin. Med., 1935, 20, 1162—1163).—No disturbance followed prolonged use of a diet containing 5 g. of protein per kg. live wt. with adequate supplies of other nutrients. CH. ABS. (p)

**Absorption of undigested proteins in man.**  
IV. **Absorption of unaltered egg-protein in infants and in children.** S. J. WILSON and M. WALZER (Amer. J. Dis. Children, 1935, 50, 49—54).—Absorption of unchanged egg-protein is a normal function in infants, children, and adults. CH. ABS. (p)

**Protein with sulphur-containing amino-acids suitable for feeding experiments.** Y. KOTAKE, jun., H. NAKATA and F. FUJIKAWA (Z. physiol. Chem., 1936, 243, 270—271).—The failure of *Pisum sativum*, L., to maintain growth is counteracted by addition of 0.5% of *l*-cystine or 0.625% of *l*-methionine. The proteins of the bean, legumin (I), vicilin, and legumelin, contain respectively 0.46, 0.26, and 1.1% of S. (I) and its acid hydrolysate contain insufficient S for maintenance of growth. The hydrolysate is rendered capable of maintaining growth by addition of *l*-cystine but not by that of *l*-tryptophan. W. McC.



**Amino-acid contents of eggs and chicks. Relation to diet and to incidence of chondrodystrophy.** A. R. PATTON and L. S. PALMER (J. Nutrition, 1936, **11**, 129—134).—The glycine (I) content of chondrodystrophic embryos was < normal. Synthesis of (I) occurs during embryonic development. Feeding (I) to hens did not affect the (I) content of eggs. Large doses were toxic. The  $\text{NH}_2$ -acid distribution in eggs from hens receiving optimum or deficient diets revealed no significant influence of diet on the composition of egg-proteins.

A. G. P.

**Intermediary metabolism of tryptophan.** XVIII. Mechanism of kynurenine production from tryptophan. I. Y. KOTAKE and T. MASAYAMA [with C. ITAGAKI]. XIX. *d*-Indolyl-lactic acid. K. ICHIHARA and H. NAKATA. XX. Production of indole from tryptophan derivatives by *B. coli*. XXI. Biological production of *d*-tryptophan. S. MAJIMA. XXII. Difference between rats and mice in the utilisation of tryptophan and its derivatives. Y. KOTAKE, K. ICHIHARA, and H. NAKATA. XXIII. Production of kynurenine acid by various animals. K. ICHIHARA and S. GOTO. XXIV. Haematopoietic action of tryptophan. T. HAMADA (Z. physiol. Chem., 1936, **243**, 237—244, 244—246, 247—250, 250—253, 253—256, 256—258, 258—265).—XVIII. Fresh rat's and rabbit's liver and liver extracts convert *l*-tryptophan (I) into kynurenine (II) and prokynurenine (III), whilst the boiled extracts convert *l*-(I) into (III) only. *d*-(I) yields (III) but not (II). (II) yields aminoacetophenone (IV) on heating in solutions slightly alkaline with  $\text{Ba}(\text{OH})_2$  but (III) gives (IV) only when heated with conc. aq.  $\text{K}_2\text{CO}_3$ . Hence the power of liver and liver extracts to convert (III) into (II) is destroyed by heating. Optimal conditions for the production of (II) and (III) from *l*-(I) by liver are: temp.  $37.5^\circ$ ,  $p_{\text{H}}$  6.5, concn. of *l*-(I)  $0.04M$ , and an  $\text{O}_2$  atm. (III) is probably the lactam corresponding to (II) and is produced from the first decomp. product of *l*-(I), namely 2-hydroxytryptophan.

XIX (cf. A., 1931, 513). *dl*-Indolyl-lactic acid (V) with quinine in MeOH gives a salt,  $[\alpha]_D$  approx.  $-104.5^\circ$  in MeOH, which on decomp. with HCl and extraction with  $\text{Et}_2\text{O}$  yields *d*-(V), m.p.  $97-100^\circ$ ,  $[\alpha]_D +5.18^\circ$  in  $\text{H}_2\text{O}$ . *d*-(V) replaces (I) in the diet of rats, being about twice as effective for growth as *ddl*-(V).

XX. *B. coli* convert *l*-(I) quantitatively and *d*-(V) almost quantitatively into indole, which is not produced from *l*-(V) and only slightly from indolepyruvic acid.

XXI. When *dl*-(I) is treated with *B. coli* at  $p_{\text{H}}$  7.2 the *l*-form is converted into indole which is removed with  $\text{Et}_2\text{O}$  and a 66% yield of *d*-(I) is obtained. Similarly *d*-2-methyltryptophan, m.p.  $231^\circ$ ,  $[\alpha]_D +18.78^\circ$  in  $\text{H}_2\text{O}$ , is obtained in 72% yield from the *dl*-form.

XXII. In rats *d*- and *dl*-(I) and *l*-(V) are utilised almost equally well, the utilisation of *dl*-(V) being poor, whereas in mice *l*-(I) and *l*-(V) are utilised whilst *d*-(I) and *d*-(V) are not. Probably the power of the rat to convert (V) into indolepyruvic acid is > that of the mouse. When the diet is poor in cystine, rats utilise methionine much better than do mice.

XXIII. After administration of (I), kynurenine acid (VI) occurs in human urine but not in the urine and bile of the cat and hen or in human bile. (VI) is found in small amounts in the urine and bile of rats and mice and in very small amounts in the bile of guinea-pigs after administration of (I).

XXIV. A diet free from (I) produces, in rats and mice, anaemia which is readily cured by subcutaneous administration of *l*-, but not *d*-, (I) which also stimulates growth. *l*-(I) given orally also cures the anaemia, but is more effective in stimulating growth. The effect of *l*-(I) given in successive small doses is that observed when one large dose is given. W. McC.

**Comparison of glycine and guanidinoacetic acid as precursors of creatine.** M. BODANSKY [with V. B. DUFF and C. L. HERRMANN] (J. Biol. Chem., 1936, **115**, 641—652).—Creatine (I) fed to rats transiently increases the (I) level of muscle, liver, and kidney; the guanidinoacetic acid (II) (traces of which normally occur in kidney and alimentary tract but not heart, muscle, and liver) levels remain unchanged. Following administration of (II), considerable amounts of (II) appear in liver and kidney (but not in muscle), up to 50% is excreted unchanged, whilst kidney- and urine-(I) increase. Methylation of (II) possibly occurs in the kidneys. No evidence of glycine being a precursor of (I) was obtained (cf. this vol., 369).

F. O. H.

**Synthesis of creatine during protein inanition.** G. MOUROT (Bull. Soc. Chim. biol., 1936, **18**, 1513—1523).—The sum of the amounts of creatine-N in the excreta of rats during, and in the bodies of rats after, periods of total or protein inanition is > that originally present.

A. L.

**Origin of urinary creatinine.** A. GOUDSMIT, jun. (J. Biol. Chem., 1936, **115**, 613—625).—The "apparent" creatinine (I) content of venous blood of dogs is consistently < that of arterial blood, the difference agreeing with the theory that the substance in blood responsible for Jaffe's reaction is the precursor of urinary (I). The excretion of this chromogenic substance is probably similar in the first stages to that of ingested (I).

F. O. H.

**Fate of protamines in the fertilised egg.** K. FELIX, L. BAUMER, and E. SCHORNER (Z. physiol. Chem., 1936, **243**, 43—56). The spermatozoa and eggs of herrings and the eggs of the rainbow trout contain dipeptidase (I) and arginase (II) and the spermatozoa of the trout contain (II). Trypsin, cathepsin, and polypeptidase are absent. Trout's eggs, 18 hr. after fertilisation, contain (I) which disappears in about 7 days and (II) which first decreases in amount and then increases as the egg develops. On fertilisation and during development the arginine (III), tyrosine, cystine (IV), and histidine (V) contents of the eggs remain almost const. whilst the tryptophan (VI) and lysine (VII) contents decrease. The protamine (VIII) of trout's eggs closely resembles clupeine, its chief constituent being (III). The spermatozoa contain, in addition to (VIII), (IV)—(VII), and other  $\text{NH}_2$ -acids.

W. McC.

**Fat metabolism in fishes. X. Hydrogenation in the fat depots of the tunny.** J. A. LOVERN

(Biochem. J., 1936, 30, 2023—2026).—The component fatty acids of the fats from the flesh, liver, pyloric caeca, heart, and spleen of the tunny, *Thunnus thynnus*, exhibit peculiarities probably characteristic of the tunny family such as lack of  $C_{14}$  acids, low palmitoleic (I) and high palmitic (II) and stearic acid (III) contents. The content of (III) of the different fats inversely  $\propto$  the degree of unsaturation of the remaining  $C_{18}$  acids and simultaneous hydrogenation of oleic acid and polyethylenic acids ( $C_{18}$ ) is suggested as the explanation. Hydrogenation of (I) to (II) and of unsaturated  $C_{20}$  acids to arachidic acid also occurs. It is suggested that by hydrogenation the content of saturated acids is maintained roughly const. and at a higher level than is usual for fish fats, possibly because of the warm habitat of the tunny and of the fact that its body-temp. is somewhat  $>$  that of the  $H_2O$ . P. W. C.

**Role of the liver in fat metabolism. Lipase action.** J. BENEDIOT (Arch. exp. Path. Pharm., 1936, 182, 537—549).—The serum-lipase activity of normal and diseased men is practically const. for each individual. The activity is increased by ingestion of fat (the increase being due to liver-lipase) and diminished by that of carbohydrate, whilst that of fat + carbohydrate has no significant effect, indicating antagonism between their hepatic catabolisms. F. O. H.

**Metabolism of ethyl esters of fatty acids.** H. J. DEUEL, jun., L. HALLMAN, J. S. BUTTS, and S. MURRAY (Proc. Soc. Exp. Biol. Med., 1936, 34, 669—671).—When the Et esters of odd C chain acids were fed, only small amounts of ketones are excreted. Acetonuria after administration of esters of acids with  $\leq 8$  C is  $>$  that of  $CH_3Ac \cdot CO_2$  controls. P. G. M.

**Effects of increased metabolism on the ketone body excretion of depancreatized dogs.** S. B. BARKER (Proc. Soc. Exp. Biol. Med., 1936, 34, 893—897).—Increased metabolism always takes place at the expense of fat oxidation and ketone formation. P. G. M.

**Role of phosphorus in carbohydrate and fat absorption processes.** S. E. EPELBAUM (Ukrain. Biochem. J., 1936, 9, 409—420).—A review. F. A. A.

**Carbohydrate metabolism.** H. WEIL-MALHERBE (Nature, 1936, 138, 551; cf. this vol., 1412).—Succinic acid is formed from  $AcCO_2H$ ,  $AcOH$ , and  $\alpha$ -ketoglutaric acid (I) both anaerobically in minced brain and aerobically in minced brain poisoned with malonic acid. The decarboxylation of (I) by brain-tissue under anaerobic conditions depends on the presence of suitable H acceptors. Evolution of  $CO_2$  is increased by addition of brilliant-cresyl-blue and reduced to normal when the dye is decolorised. The mechanism of decarboxylation is discussed. L. S. T.

**Carbohydrate metabolism.** G. K. MCGOWAN and R. A. PETERS (Nature, 1936, 138, 552).—Using avitaminous pigeon's brain tissue, no increased or decreased vitamin- $B_2$  effect was observed by adding  $\alpha$ -ketoglutaric (I) to pyruvic acid (II). The extra  $O_2$  uptake catalysed by  $-B_1$  in presence of (II) in

these brain systems does not follow the equation (cf. this vol., 1412)  $(I) + \text{ketonic acid} + H_2O \rightarrow \text{succinic acid} + CO_2 + \text{"OH"-acid}$ . L. S. T.

**Carbohydrate metabolism of the isolated cat liver.** E. LUNDGAARD, N. A. NIELSEN, and S. L. ØRSKOV (Skand. Arch. Physiol., 1936, 73, 296—313).—Although the perfused rabbit liver stores glycogen (I) from glucose (II) that of the cat does not; as with the rabbit liver addition of insulin has no effect. Fructose (III) and lactic acid (IV) are stored as (I) in perfused liver from normal cats or from cats depancreatized 48 hr. previously. It is supposed that hexoses must be first converted into (IV) before giving rise to (I) in the mammalian liver, and that the inability of the isolated cat liver to form (I) from (II) is due to its lack of power to convert (II), but not (III), into (IV). NUTR. ABS. (m)

**Carbohydrate metabolism of kidney.** M. J. LAWSON (Biochem. J., 1936, 30, 1996—2003).—In excised rabbit's kidney added  $0.5M$ - $NaF$  inhibits production of lactic acid (I) but does not affect liberation of  $PO_4^{'''}$  and  $0.01M$ - $KCN$  at  $p_H$  7.0 does not affect production of (I) or  $PO_4^{'''}$  liberation. At  $p_H$  7.0  $0.01$ — $0.02M$ - $CH_3I \cdot CO_2Na$  inhibits (I) production in the cortex and in 3 hr. at  $37.5^\circ$  decreases the (I) content but does not affect  $PO_4^{'''}$  liberation. Large amounts of (I) are produced by the cortex from glucose, smaller amounts from glycogen (II), still less from fructose, and none from galactose and mannose; from hexose mono- and di-phosphate a little (I) is sometimes produced. (II) of the cortex is insufficient to account for the (I) produced in 2 hr. at  $37.5^\circ$ . Glycolysis in the cortex is not accelerated by  $0.002M$ - $AsO_4^{'''}$ . The cortex readily reduces  $AcCO_2H$  to (I) and  $AcCO_2H$  may be an intermediate in glycolysis. W. McC.

**Carbohydrate metabolism of warm-blooded animals during muscular work.** E. JOKL (Klin. Woch., 1935, 14, 1139—1143; Chem. Zentr., 1936, i, 101—102).—In rats moderate muscular work lowered the lactic acid content of the muscle and liver and increased that in blood. Exhaustive work lowered all vals., which increased again during rest (without food). The depot-glycogen content of organs decreased during work; blood-sugar was unchanged by moderate exercise but declined with exhaustion. The phosphagen content increased in exhausted animals. A. G. P.

**Significance of histotrophy in the carbohydrate metabolism of the foetus within the uterus.** B. SZENDI and G. PAPP (Orvosi Het., 1935, 79, 890—895).—The decidua of man, rats, and rabbits contain relatively large amounts of glycogen, which diminish during pregnancy. Nutrition of the foetus depends on the combined effects of histotrophy and haemotrophy. CH. ABS. (p)

**Carbohydrate oxidation in hypophysectomised rats.** R. E. FISHER and R. I. PENCHARZ (Proc. Soc. Exp. Biol. Med., 1936, 34, 106—107).—As compared with normal rats hypophysectomised rats continue to oxidise carbohydrate (I) for a longer time during fasting with a slightly higher R.Q., and they



derive a larger proportion of their energy from (I) after glucose feeding. W. O. K.

**Glycogen of frog's liver and muscle after subcutaneous injection of sugars.** A. MOSCHINI (Compt. rend. Soc. Biol., 1936, 123, 119—121).—Injection of glucose, fructose, galactose, or maltose increases glycogen, whilst sucrose or lactose has little effect. H. G. R.

**Mechanism of glycogenolysis.** J. K. PARNAS and P. OSTERN (Bull. Soc. Chim. biol., 1936, 18, 1471—1492).—Theoretical. A. L.

**Site of formation of conjugated glucuronates in the organism.** F. SCHMID (Compt. rend. Soc. Biol., 1936, 123, 223—226).—The liver is the chief site. H. G. R.

**Respiratory exchange in children following administration of various carbohydrates: relation to curves for blood-sugar.** J. L. LAW and H. GAY (Amer. J. Dis. Children, 1935, 50, 375—384).—The increase in R.Q. in the first 30 min. after ingestion of carbohydrates was highest for sucrose, followed, in descending order, by galactose, glucose, lactose, fructose, and dextri-maltose. The max. increase in heat production in this period appeared simultaneously with the peak of the blood-sugar curve. No parallelism was apparent between the max. vals. for R.Q. and blood-sugar.

CH. ABS. (p)

**Metabolism of galactose. III. (1) Lactose synthesis from (a) a glucose-galactose mixture, (b) phosphoric esters, by slices of the active mammary gland *in vitro*. (2) Effect of prolactin on lactose synthesis by the mammary gland.** G. A. GRANT (Biochem. J., 1936, 30, 2027—2035).—When glucose (I)-galactose (II) mixtures are used as substrates for lactating mammary tissue *in vitro*, lactose (III) synthesis is not noticeably increased beyond that for (I) alone and direct coupling of (I) and (II) does not appear to be the mechanism of (III) formation. An active  $\beta$ -galactosidase could not be detected in preps. of the lactating gland. (I) 6-phosphate, fructose 6-phosphate or 1:6-diphosphate, (II) 6-phosphate, and phosphoglyceric acid also did not give increased (III) synthesis, although the slices were active when (I) was substrate. NaF (0.04M) and  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Na}$  (0.02M) inhibit almost completely both (I) utilisation and (III) synthesis by slices of lactating tissue. The *in vivo* synthesis of (III) was re-established to a limited extent in the inactive regressing mammary glands of guinea-pigs by prolactin. The induced secretion resembled milk in appearance but had a low (III) content (0.04—0.24%). P. W. C.

**Intravenous galactose liver-function test.** I. R. JANKELSON and H. H. LERNER (Amer. J. Digest. Dis. Nutrition, 1934, 1, 310—312).—The rate of utilisation of galactose (I) by the liver may be ascertained by periodic measurements of blood-(I) following intravenous injection. In cases of demonstrable liver damage (I) is metabolised more slowly.

CH. ABS. (p)

**Absorption of glucose and water from chronic isolated loops of the colon.** P. H. MOORE and G. E. BURGET (Amer. J. Digest. Dis. Nutrition, 1934,

1, 376—382).—Optimal absorption of glucose (I) occurs with 5—10% solutions. Small amounts of NaCl do not affect, but  $\text{NaHCO}_3$  retards, absorption of (I). Optimal absorption of  $\text{H}_2\text{O}$  takes place from 0.9% aq. NaCl; it is inhibited by 2.5% aq. (I) and with 10% solutions there is a definite  $\text{H}_2\text{O}$  influx. Small quantities of  $\text{NaHCO}_3$  in an isotonic solution of (I) cause an influx of fluid into the intestine. Blood-sugar is not a true index of sugar absorption from the intestine when the amount absorbed is small.

CH. ABS. (p)

**Absorption of glucose and galactose from dog's intestine.** F. A. CAJORI and W. G. KARR (Amer. J. Med. Sci., 1935, 189, 880—881).—When both sugars were inserted into loops of the jejunum glucose (I) was absorbed more rapidly than galactose (II), the total carbohydrate absorption remaining about the same as when either sugar was given separately. Absorption rates were the same for each sugar administered alone.  $\text{PO}_4'''$  did not accelerate absorption of (I), (II), or fructose. CH. ABS. (p)

**Oxidation of glucose in presence of insulin etc. and probable mechanism of biological oxidations.**—See this vol., 1491.

**Relations between liver function and metabolism of fructose. I—VI.** Y. IIDA (Japan. J. Gastroenterol., 1934, 6, 61—93).—Impaired liver function is examined by means of blood-fructose curves after parenteral administration of fructose (I). Intestinal absorption of (I) is inhibited by hepatic disturbances. CH. ABS. (p)

**Metabolism of fructose. IX. Effect of endocrine dysfunction on tolerance.** A. W. ROWE, M. A. MCMAHON, A. J. PLUMMER, and G. A. RILEY (Endocrinol., 1936, 20, 648—656).—The deviations of fructose tolerance from the normal vary considerably with the endocrine disturbance. The extent of agreement with the deviations of galactose tolerance also shows wide variations. R. N. C.

**Production of hexose monophosphate and its conversion into fructose diphosphate in muscle.** P. OSTERN, J. A. GUTHKE, and J. TERSZAKOWEC (Z. physiol. Chem., 1936, 243, 9—37).—Dialysed extract of autolysed rabbit's muscle even when 8 days old produces large yields of hexose monophosphate (I) from glycogen (II) and inorg.  $\text{PO}_4$  (but not from glucose and inorg.  $\text{PO}_4$ ), the process not being dependent on the presence of co-enzyme. When excess of (II) is present all the inorg.  $\text{PO}_4'''$  is consumed and when excess of inorg.  $\text{PO}_4'''$  is present all the (II) is consumed. In extracts inactivated with  $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$  and NaF deamination of adenosinetriphosphoric acid (III) is greatly accelerated by (I) and (II) [but not by fructose diphosphate (IV)], which act as  $\text{PO}_4$  acceptors. In fresh or reactivated extracts which produce lactic acid (V) the deamination of (III) is inhibited by (IV) > (I) > (II) because phosphopyruvic acid, the sp.  $\text{PO}_4'''$  donor for rephosphorylation of adenylic acid, is produced. (I) is converted by (III) into (IV), probably by direct transfer of  $\text{PO}_4'''$  from (III) to (I). (I) is not phosphorylated by inorg.  $\text{PO}_4'''$ . Phosphorylation of (II) by  $\text{PO}_4'''$  and the transfer of the P-containing residue from (III) to (II) are inhibited

by 0.01M-phloridzin, which also greatly checks hydrolysis of (III) to adenylic acid (VI) and  $H_3PO_4$  but scarcely checks the transfer of  $IO_4'''$  from (III) to (I). Hence deamination of (III) is much more rapid when (I) is present than when it is replaced by (II). In the degradation of (II) to (V) the first stages are  $(II) + H_3PO_4$  yielding (I) followed by  $(I) + (III) + H_2O$  giving  $(IV) + H_3PO_4 + (VI)$ , no  $H_3PO_4$  being liberated at any stage. In the degradation of (I) to (V) 0.5 mol. and in the degradation of (IV) to (V) 1 mol. of  $H_3PO_4$  per mol. of (V) are liberated, respectively.

W. McC.

**Action of pilocarpine and potassium on phosphorylation in muscle.** J. WAJZER and R. LIPPMANN (Bull. Soc. Chim. biol., 1936, 18, 1428—1435).—Whilst pilocarpine and  $K^+$  increase the decomp. of phosphagen (I) in normal frog's muscle, the contents of adenosinetriphosphoric acid and hexose esters remain const. In the presence of  $CH_3I \cdot CO_2H$ , however, the (I) content is affected only by  $K^+$ .

A. L.

**Carbohydrate resynthesis in the liver.** H. VON EULER and G. GÜNTHER (Z. physiol. Chem., 1936, 243, 1—8).—About 50% of cozymase (I) added to sliced rat's liver is inactivated in 4 hr. Lactate (II) and pyruvate (III) added together with (I) to slices of rat's and guinea-pig's liver in  $O_2$  disappear and the carbohydrate (IV) content increases in parallel or the consumption of (IV) which normally occurs when nothing is added is decreased. [No consumption of (IV) occurs when the (IV) content of the slices is very low.] When the amount of added (I) is increased the amount of (IV) synthesised and the amount of (II) which disappears increase. Probably (II) is converted by (I) into (III).

W. McC.

**Deuterium as an indicator in the study of intermediary metabolism.** VII. Bile acid formation. R. SCHOENHEIMER, D. RITTENBERG, B. N. BERG, and L. ROUSSELOT (J. Biol. Chem., 1936, 115, 635—640; cf. A., 1935, 1407).—Following intravenous injection of 4:5-dideuterocoprostanone (I) into dogs with biliary fistulae, a D-containing unsaponifiable substance [probably (I)] occurs in the bile whilst cholic acid (II) from the bile is free from D. Hence coprostanone is probably not an intermediary in the hypothetical conversion of cholesterol into (II).

F. O. H.

**Lactic acid metabolism of the heart in spontaneous insufficiency and in poisoning by sodium fluoride, iodoacetic acid, and euphylline.** F. GOTTDENKER and C. J. ROTHBERGER (Pflüger's Arch., 1936, 237, 59—67).—In spontaneous insufficiency, in spite of coronary dilatation, the heart-muscle takes up less lactic acid (I) than normally and may even liberate it into the blood. In  $NaF$  poisoning, although (I) formation is inhibited, utilisation of the preformed (I) is not increased but often sinks to zero. With  $CH_3I \cdot CO_2H$  and euphylline there is a marked, protracted dilatation of the coronary vessels, but (I) uptake is increased only for a short time, after which it decreases until liberation into the blood takes place.

M. A. B.

**Role of the 4-carbon dicarboxylic acids in muscle respiration.** J. M. INNES (Biochem. J.,

1936, 30, 2040—2048).—Methods for determination of fumaric (I), succinic (II), malic (III), oxaloacetic (IV), and pyruvic acid (V) are worked out. Addition of 2 mg. of (I) to 0.4 g. of minced pigeon breast muscle suspended in  $PO_4'''$  buffer ( $p_H$  7) caused an increase in respiration during which some of the added (I) disappeared and was not found again either as (II) or (IV). During incubation of the muscle with (I) in  $O_2$ , (IV) and (V) show a slight increase. The amount of (III) accumulating depended on the degree of oxygenation, none being obtained in  $O_2$  but appreciable amounts in air. The latter amounts appeared, however, to have no fixed relationship to the amount of (I) present. The entire O uptake was never > could be accounted for by oxidation of some of the (I) disappearing. In experiments with washed tissue, (I) is oxidised in preference to lactic acid in equiv. concn. The results suggest that (I) is being utilised as a substrate for respiration and not as a catalyst for transference of O to other substrates in the muscle.

P. W. C.

**Ketogenesis—antiketogenesis.** III. Metabolism of aldehydes and dicarboxylic acids. IV. Substrate competition in liver. N. L. EDSON (Biochem. J., 1936, 30, 1855—1861, 1862—1869).—III. Rat liver slices are able anaerobically to form acid probably by dismutation from  $MeCHO$ ,  $EtCHO$ ,  $PrCHO$ ,  $Bu^oCHO$ , and  $Bu^sCHO$  but not from hex-, hept-, and oct-aldehydes. Under aerobic conditions all these aldehydes are ketogenic except  $EtCHO$ , the ketone formation being of the same order as that with the corresponding fatty acids. With dicarboxylic acids and their derivatives there is increased  $O_2$  consumption and the acids are neither ketogenic in livers of well nourished nor antiketogenic in livers of starved animals. Exceptions to this rule are malonic, hydroxymalonic, and mesoxalic acids which are strongly, and tartaric and oxalic acids which are weakly, ketogenic.

IV. Antiketogenesis is studied in liver slices of starved and well nourished rats in presence of added fatty acids. The rate of ketone formation is the outcome of competition between fatty acids and other oxidisable substrates for the oxidising systems of liver. Carbohydrates and their derivatives, e.g., lactate, pyruvate,  $CO(CH_2 \cdot OH)_2$ , alcohols, certain  $NH_2$ -acids, and particularly glycerol and sorbitol are antiketogenic substances. The fatty acids also compete amongst themselves.

P. W. C.

**Degradation of fenchone in the animal organism.**—See this vol., 1514.

**Active water and salt transport through the frog's skin.** E. HUF (Pflüger's Arch., 1936, 237, 143—166).—Identical salt solutions separated by a frog's skin soon show differences in salt concn. which are increased when  $Na$  lactate or pyruvate is added to the solutions. When  $KCN$  is added the effect is either inhibited or reversed. Transport of  $H_2O$  and salts through the skin by an "active" energy-consuming process is probable.

M. A. B.

**Permeability to ions of the isolated frog's heart.** G. ORZECOWSKI (Arch. exp. Path. Pharm., 1936, 183, 77—86).—Washing of the heart with



normal (frogs) Ringer's solution after a period of washing with K-free Ringer's solution temporarily depresses cardiac activity due to action of  $K^+$  which diffuses from perfusion fluid to heart-muscle or *vice versa*. Diffusion of  $Ca^{++}$  from salt solutions to heart-muscle does not occur. The "threshold" val. of  $[K^+]$  of perfusing fluids at which  $K^+$  is neither given up to nor taken from frog's heart-muscle is approx. 0.009%. The K content of dried frog's heart-muscle is 1.4—1.7%. F. O. H.

**Phosphates and work.** E. ATZLER, K. BERGMANN, O. GRAF, H. KRAUT, G. LEHMANN, and A. SZAKALL (Arbeitsphysiol., 1935, 8, 621—694; Chem. Zentr., 1936, i, 372).—Daily variations in the P balance in man and in dogs are examined. The min. P requirement of dogs is controlled by the metabolic level and not by body-wt. During exercise the P balance declines relative to the N balance for a time. Subsequent feeding of P lowers the N balance relative to that of P. Ca and P metabolism shows a similar relationship. The relative efficiency of org. and inorg. P is examined. In pregnancy with a levelled N balance, the P balance is negative during the first 19 weeks. Subsequently the P balance is positive and inorg. P is readily retained. A. G. P.

**Sodium-potassium antagonism and its significance in water metabolism.** C. DIENST (Arch. exp. Path. Pharm., 1936, 182, 567—576).—Examination of the urine of salt-treated men shows that  $Na^+$  displaces  $K^+$  from the organism and *vice versa* but whilst  $Na^+$  produces retention,  $K^+$  enhances excretion of  $H_2O$ . Administration of large doses of  $K^+$  to normal and ascitic men temporarily increases serum-K and subsequently urine-K and produces diuresis.

**Rate of water loss by man at rest. I. Constant-temperature and -humidity room. II. Spontaneous diuresis during prolonged rest.** P. D'A. HART and E. B. VERNEY (Clin. Sci., 1935, 1, 367—380, 380—396).—I. Experimental equipment is described.

II. During rest and fasting, spontaneous diuresis, commencing within 3—6 hr., is characterised by decreased urinary N and Cl and is inhibited by posterior pituitary extract. Relations between diuresis and the concn. of extract in the plasma are examined. CH. ABS. (p)

**Oxidation-reduction potential, action of fuadin, and duration of life in *Opisthorchis*, *in vitro*.** W. KOLLATH and A. ERHARDT (Biochem. Z., 1936, 287, 287—288; cf. Klin. Woch., 1935, 14, 1809).—The duration of life of the intestinal worm, *Opisthorchis tenuicollis felinus*, *in vitro* at 37° is maximal when the oxidation-reduction potential is  $-0.081$  (in neutral Ringer's solution diluted 1:50,000) and at this potential the sp. toxic effect of fuadin is maximal. The effect is minimal at a potential of  $+0.011$ .

W. MCC.

**Fate [in the organism] of complexes of citric acid with salts of heavy metals.** H. LANGECKER (Arch. exp. Path. Pharm., 1936, 182, 642—653).—The complexes [with citrate (I) in anionic form] of  $Fe^{III}$  and  $Co^{II}$  are less readily oxidised by  $O_2$  than is Na citrate. Liver or kidney pulp decomposes  $Fe^{III}$ ,

$Mn^{II}$ , or  $Co^{II}$  complex but not that of  $Ni^{II}$  or  $Cu^{II}$ . Following intravenous injection into rabbits of  $Fe^{III}$ ,  $Co^{II}$ , or  $Ni^{II}$  complex, a part of the metal appears in the urine; this occurs only slightly with  $Mn^{III}$  whilst with  $Fe^{III}$ , the Fe excretion is equivalently  $>$  that of (I) and (I) does not appear in the intestine. Absorption of (I) from enterally administered  $Fe^{III}$  complex occurs only very slowly. F. O. H.

**Fate of senna drugs in the organism.** H. GEBHARDT (Arch. exp. Path. Pharm., 1936, 182, 521—526).—Injection of senna glucosides (I) into cats is followed by urinary excretion of (I) and conjugated (sulphate and glycuronate) emodin (II); with continuous intravenous injection of (I) or (II), the excretion is mainly of conjugated (II). Ingestion of (I) by men is followed by excretion of conjugated (II) with traces of free (II) and of free and conjugated anthranol. F. O. H.

**Effect of X-radiation on the blood.** H. L. BROSE and E. B. JONES (Nature, 1936, 138, 687—688).—Irradiation by X-rays or Ra reduces the ratio erythrocyte-P: plasma-P in man. This change may serve as a measure of the effect of X-ray dosages.

L. S. T.

(A) Detection of mitogenetic rays with the help of a physical differential method. (B) Biological detection. W. W. SIEBERT and H. SEFFERT (Biochem. Z., 1936, 287, 92—103, 104—108).—(A). Further experiments (cf. A., 1933, 336) are described using two light quanta enumerating tubes, one registering the variation in the effect of cosmic rays, the other of cosmic + mitogenetic rays. Curves are given showing differences due to a no. of mitogenetic effects. The mitogenetic effect of normal blood is destroyed by the presence of KCN.

(B). The method depends on the inhibition by mitogenetic radiation of the rate of elimination of gas by a fluid yeast culture. The results by the method compare favourably with those by the above physical method. P. W. C.

**Influence of work and training on the oxidation-reduction potential of muscle-tissue.** R. TSCHAGOVETZ (Ukrain. Biochem. J., 1936, 9, 273—307; cf. A., 1935, 1522).—The biceps femoris muscle of rabbits, fatigued by electrical stimulation *in vivo* for 45 min., and similar muscles after training (similar stimulation for 20 min. daily for 15 days) yield extracts showing differences in oxidation-reduction potential compared with control muscles of the same animals. With fatigued muscle the initial val. of potential is more positive, and the fall to the same final val. takes longer, than with unfatigued muscle. Training results in a diminution of positive potential and a quicker attainment of the stable val. The  $p_H$  of extracts from fatigued muscles is  $>$ , and that of trained muscle  $<$ , those of their respective controls.

F. A. A.

**Effect of acid and basic fodder on oxidative processes in muscles during work and training.** M. F. GULI (Ukrain. Biochem. J., 1936, 9, 309—320).—Comparison is made between the rates of decolorisation of methylene-blue by the muscles of rabbits fed on acid and basic diets, and the effects of fatigue, training, and of training followed by fatigue, on these

muscles. In all cases the rate of decolorisation in the acid-fed animals is  $>$  that in the basic-fed, and the difference is greater in trained than in fatigued muscles. F. A. A.

**Influence of the acid-base ratio of foods on some physico-chemical properties and the capacity for work of isolated muscle.** G. BENETATO and N. MUNTEANU (Compt. rend. Soc. Biol., 1936, 123, 201—203).—The  $p_H$ , buffering power, and capacity for work are only slightly affected by the diet. H. G. R.

**Oxidation-reduction potential of muscle-tissue *in vivo*, *in situ*, and its functional variations.** V. V. KOVALSKI and O. M. GLEZINA (Ukrain. Biochem. J., 1936, 9, 205—271).—The oxidation-reduction potential of leg muscles of rabbits, determined directly *in situ*, shows small irregular fluctuations and long periodic asymmetrical fluctuations. The val. of  $E_h$  differs between right and left legs of the same animal, due to unequal distribution of glutathione.  $E_h$  of muscles trained by continuous electrical stimulation is  $\ll$  that of normal muscle. Fatigue raises  $E_h$  of normal muscle, but lowers that of trained muscle. Further complex phenomena are discussed. F. A. A.

**Osmotic pressure and muscular contraction.** I. CHAO (Chinese J. Physiol., 1936, 10, 547—558).—Parallel determinations of the contraction due to const. submaximal stimuli and of the wt. of the muscle preps. used (toad's sartorius) were made in solutions of varying osmotic pressure. The wt. of the muscle, after correcting for the wt. of osmotically inactive materials, is inversely  $\propto$  the osmotic pressure. A temporary increase in contraction occurs on increasing the osmotic pressure and *vice versa*. The contraction at osmotic equilibrium is max. in a slightly hypotonic solution. Within the limits of 4.3—8.5 atm., the contraction is a linear function of osmotic pressure. P. W. C.

**Chemical mediation of impulses in certain fibres of the splanchnic nerves.** G. V. RUND and F. M. KINROSS (Austral. J. Exp. Biol., 1936, 14, 193—198).—The pressor response to splanchnic stimulation in ergotoxinised dogs shows periodical alternations in character. It is influenced by the discharge of adrenaline from the gland and by the release of a pressor substance from some and of a depressor substance from other visceral terminations of the splanchnic nerve, not the adrenal. A. G. P.

**Effects of heat and humidity on the human body.** C. K. DRINKER (J. Ind. Hyg., 1936, 18, 471—485).—A summary of the effects of exposure to high temp. (periodic or continuous). The importance of controlling NaCl and H<sub>2</sub>O intake in cases of heat cramp and other conditions is stressed. Neither humidity nor sunlight is a prime factor; they merely intensify the effects of heat. P. G. M.

**Gastric motility under low oxygen pressures.** E. J. VAN LIERE (Amer. J. Digest. Dis. Nutrition, 1934, 1, 373—376).—Anoxæmia decreased motility. CH. ABS. (p)

**Action of the gases issuing from fire-damp pockets.** F. FLURY (Arch. Gewerbepath. Gewerbe-  
5 H

hyg., 1935, 6, 257—269).—A discussion. Although none of the constituents of 'fire-damp' is of high toxicity, long-continued exposure to them, together with the relative O<sub>2</sub> shortage occurring in mines, is probably responsible for the characteristic symptoms developed by coal-miners. M. A. B.

**Central-nervous regulation of the heart minute volume during breathing of air containing carbon dioxide.** O. DIEBOLD and O. MERTENS (Pflüger's Arch., 1935, 237, 585—589. M. A. B.

**Influence of water administration on oxygen consumption rate in shock.** H. A. DAVIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 21—23).—In anaesthetised dogs in which shock had been induced by various means, intravenous administration of isotonic NaCl solution produced a rise in metabolism, less prolonged than that observed in normal anaesthetised animals. Whereas the latter tolerated isotonic NaCl solution up to 25% of the total body-wt., amounts equal to 5—12% of the body-wt. caused a fall in O<sub>2</sub> consumption in the shocked animals. W. O. K.

**Comparative action of mineral waters on the autonomous contraction of the ureter.** P. TESTONI (Annali Chim. Appl., 1936, 26, 370—384).—The action of various Italian mineral waters on the contraction of the guinea-pig's ureter was determined. Analytical data indicate that generally stimulation is due to CO<sub>2</sub> and Ca<sup>++</sup> and inhibition to NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>S, and high concns. of Na<sup>+</sup> and Cl<sup>-</sup>. L. A. O'N.

**Presence of sterols in the mud of the salt lake of Tekirghiol (Dobrodgea) [Roumania].** N. L. COSMOVICH and J. S. ATANASIU (Bull. Soc. Chim. biol., 1936, 18, 1425—1427).—Extracts of the black mud give reactions for sterols. The therapeutic action is probably due to the sterol content. A. L.

**Pharmacology of the mineral water of Valle-verde.** P. TESTONI (Annali Chim. Appl., 1936, 26, 283—290; cf. A., 1935, 1023).—The H<sub>2</sub>O stimulates the germination of lupin seeds and the development of the plant, inhibits the movement of the epithelial cilia of the oesophagus of the frog, and stimulates the contraction of the ureter of the guinea-pig, and increases the tonus. L. A. O'N.

**Therapeutic effects of mineral waters.** A. KELLER (Mitt. Lebensm. Hyg., 1936, 27, 204—215).—A review. E. C. S.

**Feeding deuterium oxide to rats.** SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (Kong. Norske Vidensk. Selsk. Forhandl. 1935, 8, 27—28 Chem. Zentr., 1936, i, 360).—Apart from an initial period of increased thirst, D<sub>2</sub>O had no appreciable effect on growth or sexual development of the animals. A. G. P.

**Occurrence of acidosis after experimental ammonia poisoning.** N. ALWALL and E. GEIGER (Arch. exp. Path. Pharm., 1936, 183, 123—126).—Diminution of alkali reserve occurs in rabbits after introduction of aq. NH<sub>3</sub> into the stomach but not intestine. Hence the acidosis is not due to absorption of NH<sub>3</sub> (cf. Fazekas, this vol., 223). F. O. H.

**Methæmoglobin-producing action of sodium nitrite.** S. RAPPEPORT-LEWEY (Arch. Farm. speriment.,



1936, 62, 17—36).—Intravenous injection of lethal doses ( $>0.12$  g. per kg.) of  $\text{NaNO}_2$  into rabbits causes death during which methaemoglobin formation occurs to the extent of 67.5—99%. Differences in rate of formation between cats and rabbits are discussed.

F. O. H.

**Action of calcium salts on living tissue.** L. I. WEBER (*Cernauti Med.*, 1, No. 1, 57—59; *Chem. Zentr.*, 1936, i, 373).—The influence of Ca salts of org. and inorg. acids on the swelling of gelatin gels is examined and the special action of Ca gluconate (I) is observed. The effects of injecting (I) on the natural gel of living muscle are explained on this basis.

A. G. P.

**Determination of cardio-analeptic activity by means of the potassium-paralysed Straub frog's heart preparation.** F. HENDRYCH (*Arch. exp. Path. Pharm.*, 1936, 182, 738—748).—Heart preps. paralysed with 0.1% KCl solution are suitable for testing drugs owing to the paralysis being readily removed by washing with Ringer's solution. In restoring cardiac activity, adrenaline and caffeine and, to a smaller extent, "cardiazol" are effective; camphor, "coramin," ephedrine, and sympthol are not stimulatory but, at certain concns., paralytic.

F. O. H.

**Liberation of acetylcholine from perfused human placenta.** H. C. CHANG (*Proc. Soc. Exp. Biol. Med.*, 1936, 34, 665—666).—K<sup>+</sup> causes a transfer of acetylcholine (I) from tissue to fluid, whilst eserine and heat stimulate the formation of (I) by some unknown mechanism.

P. G. M.

**Magnesium sulphate and catharsis.** J. FERGUSON and A. C. IVY (*Proc. Soc. Exp. Biol. Med.*, 1936, 34, 720—722). Subcutaneous injection of aq. 25%  $\text{MgSO}_4$  does not cause catharsis by absorption into the blood followed by excretion into the colon, nor does it increase the excretion of Mg by the mucosa.

P. G. M.

**Influence of magnesium oxide on antipyretic action and toxicity of aspirin in rabbits.** D. R. CLIMENKO (*Proc. Soc. Exp. Biol. Med.*, 1936, 34, 807—812).—The toxicity of aspirin (I) is unaffected by simultaneous administration of  $\text{MgO}$ . (I) and  $\text{MgO}$  are synergic as regards their antipyretic action.

P. G. M.

**Influence of ethyl alcohol on energy metabolism of the mammalian heart.** H. C. PETERS, C. E. REA, and J. W. GROSSMAN (*Proc. Soc. Exp. Biol. Med.*, 1936, 34, 61—64).—The total energy output of the isolated mammalian heart, working at const. diastolic vol., diminishes under the influence of EtOH.

W. O. K.

**Liver-lipins of the white rat following chloroform poisoning, insulin administration, and fungus infection.** P. L. MACLAGHLAN (*Proc. Soc. Exp. Biol. Med.*, 1936, 34, 31—33).— $\text{CHCl}_3$  poisoning, insulin administration, or *Aspergillus* or *Sporothrix* infection produces no change in the lipin content of the livers of rats or in the ratio of phospholipin to neutral fat.

W. O. K.

**Physiological action of methylglyoxal.** E. MARTINI (*Arch. ital. Biol.*, 91, 173—184; *Chem. Zentr.*, 1936, i, 103).

A. G. P.

**Toxicology of the organic solvents. 1:4-Dioxan.** W. WIRTH and O. KLIMMER (*Arch. Gewerbepath. Gewerbehyg.*, 1936, 7, 192—206).—Dioxan, absorbed through the respiratory tract, is about as toxic as MeOH but considerably less toxic than  $(\text{CH}_2)_2\text{O}$ .

M. A. B.

**Oxidation-reduction processes in the inflammatory focus of the mucous membrane.** V. V. KOVALSKI, M. M. BUGAEVA, and O. M. GLEZINA (*Ukrain. Biochem. J.*, 1936, 9, 381—386).—Inflammation of the mucous membrane of the lip of a rabbit is accompanied by a change in oxidation-reduction processes, measured directly as  $E_h$ . Application of mustard gas to this membrane is accompanied by a fall in  $E_h$ , followed by a slow rise towards normal. This differs from the clinical picture.

F. A. A.

**Microscopy of fat absorption in the normal gut and inhibition by iodoacetic acid and phloridzin.** L. JEKER (*Pflüger's Arch.*, 1936, 237, 1—13).—Free fatty acids give positive staining reactions with Fischler's  $\text{Cu}(\text{OAc})_2$ -haematoxylin reagent and with Sudan III, neutral fats with Sudan III only. In the normal gut the first stage of absorption is the penetration of free fatty acids into the epithelial cells; later, synthesis of neutral fat occurs. In the poisoned gut penetration of fatty acids occurs but conversion into neutral fat is inhibited.

M. A. B.

**Effect of dinitrophenol on the metabolism of frog muscle.** E. RONZONI and E. EHRENFEST (*J. Biol. Chem.*, 1936, 115, 749—768).—2:4-Dinitrophenol (I) ( $5 \times 10^{-5}\%$ ) accelerates the  $\text{O}_2$  consumption of frog's muscle 6—10 times, glycogen being consumed. Caffeine has a similar effect, only slightly enhanced by (I). Treatment with  $\text{CH}_2\text{I} \cdot \text{CO}_2\text{H}$  reduces the effect of (I), which is partially restored by lactic acid (II). Anaerobic (II) production is accelerated 8—10 times, and continues until phosphocreatine (III) and adenosine phosphate are completely decomposed.  $\text{O}_2$  prevents (II) accumulation. (I) accelerates the rate of hydrolysis of (III), and the data indicate inhibition of its resynthesis. In muscle extracts, (I) increases the rate of  $\text{O}_2$  consumption, but does not affect the rates of production of (II) or of hydrolysis of (III). (I) appears to act by allowing a max. mobilisation of carbohydrate.

F. A. A.

**Action of 2:4-dinitrophenol on the oxidation-reduction potential of the aqueous humour and crystalline lens of the rabbit.** J. NORDMANN and P. REISS (*Compt. rend. Soc. Biol.*, 1936, 123, 233—234).—Injections increase the potential to vals. similar to that of  $\text{C}_{10}\text{H}_8$  cataract, no signs of which, however, are visible.

H. G. R.

**Increase in blood-polypeptides in phenylhydrazine-poisoned dogs.** A. VON JENEY and L. SOKORAY (*Arch. exp. Path. Pharm.*, 1936, 182, 560—566).—The normal level of blood-polypeptide-N of 0.0024—0.0060% rises to 0.0054—0.0082%, whilst the erythrocyte count diminishes.

F. O. H.

**Toxic effects of neutral diaminoacridine methochloride.** H. WAREMBOURG, J. DRIESSENS, and G. LABENNE (*Compt. rend. Soc. Biol.*, 1936, 123, 13—14).—Intravenous injection into the rabbit results in lesions in the lungs, adrenals, liver, kidneys,

and bone marrow, together with an increase in blood-urea and -polypeptides, and anæmia. Elimination appears to be through the liver and kidneys.

H. G. R.

**Preparation and therapeutic properties of certain acridine derivatives.**—See this vol., 1521.

**Helenalin, the bitter sternutative substance occurring in *Helenium autumnale*.**—See this vol., 1514.

***dl*-Methionine in developmental growth.** F. S. HAMMETT and K. PADIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 181—183).—The early growth of *Obelia geniculata* is stimulated by very low concns. of *dl*-methionine (I). In the living organism (I) is possibly converted into cystine.

W. McC.

**Pressor effects of some new alkyl derivatives of  $\beta$ -phenylethylamine.** W. E. HAMBOURGER and R. B. JAMIESON, jun. (J. Pharm. Exp. Ther., 1936, 58, 53—61).—Me and Et derivatives are all less active than the parent substance, *p*-substitution reducing the duration of action. With *N*-Me a second *o*-Me or *p*-Et reduces the activity greatly, the latter sometimes showing a depressor action. The  $\text{NH}_2\text{Et}$  derivatives are depressor whatever the position of the substituted Me.

H. G. R.

**Vasomotor interference in the vascular network of the muscles during experimental hyperæmia produced by vaso-dilator substances.** F. GROSSE-BROCKHOFF, M. SCHNEIDER, and W. SCHOEDEL (Pflüger's Arch., 1936, 237, 178—189).—Adrenaline injected intravenously produced constriction in muscular blood vessels dilated by adenosine, adenylic acid, histamine, and glucose, but not after acetylcholine (I) dilatation. Resistance to vaso-constriction in the working muscle is probably due to the liberation of a substance [possibly (I)] as a result of the increased muscular activity.

M. A. B.

**Influence of vaso-dilator substances on the output of work and the blood supply, during work, in the skeletal muscles.** W. SCHOEDEL (Pflüger's Arch., 1936, 237, 190—212).—Acetylcholine, histamine, and adenylic acid all produced a further increase in blood supply in muscular vessels already showing hyperæmia due to work, but in no case did the increased blood supply result in a better output of work by the muscle. Probably none of these substances is involved in the hyperæmia of work.

M. A. B.

**Physiology and pharmacology of sterols. I. Cholesterol and sterol economy.** E. STARKENSTEIN. II. Significance of cholesterol in permeability and absorption. E. STARKENSTEIN and F. HENDRYCH. III. Influence of sterols on the cutaneous absorption of drugs from unguents. H. MATSCHAK. IV. Influence of cholesterol on the action of hypnotics and narcotics. V. Influence of cholesterol mobilisation by saponin on the action of soporifics. E. STARKENSTEIN and H. WEDEN (Arch. exp. Path. Pharm., 1936, 182, 654—663, 664—687, 688—699, 700—714, 715—719).—I. The physiological importance of sterols, especially cholesterol (I), is discussed.

II. The role of sterols, especially (I), in the influence

of cellular lipins on absorption of  $\text{H}_2\text{O}$ - and lipin-sol. substances and on cell permeability is discussed.

III. The theory that cutaneous absorption of drugs occurs more readily from salves of fat or lipin than from those of vaseline or paraffin could not be fully confirmed. The absorption of H and Na salicylate from lanoline and vaseline indicates that, in addition to the lipin- or  $\text{H}_2\text{O}$ -solubility of the drug, reactions with the base (e.g., esterification with sterol alcohols) or with cellular sterols influence the rate of absorption. Other factors include acidity of the salve and the sterol contents of salve and skin.

IV. Intraperitoneal injection of aq. emulsions of (I) or its esters into mice, rabbits, or guinea-pigs enhances the narcotic action of inspired  $\text{Et}_2\text{O}$  or  $\text{CHCl}_3$  or subcutaneously injected  $\text{Et}_2\text{O}$  and the soporific action of veronal etc. Orally administered (I) is ineffective. Oils and fats resemble (I) but are often more active enterally owing to increased absorption of the narcotic. The action of (I) in increasing localisation of lipin-sol. dyes in the brain of injected animals indicates that (I) aids in the transport of narcotics to the nervous tissues.

V. The enhancement of the soporific action of veronal by prior intravenous injection of aq. saponin (II) is due to mobilisation of body-(I) by (II). That bees' poison acts similarly to (II) indicates that it contains a (II)-like substance.

F. O. H.

**Inulin and its suitability for intravenous administration in man.** W. GOLDRING and H. W. SMITH (Proc. Soc. Exp. Biol. Med., 1936, 34, 67—68).—Certain purified samples of dahlia and chicory inulin (I), administered intravenously to man, produced marked toxic symptoms. This action is probably the result of overheating (I) during drying.

W. O. K.

**Effect of varying  $p_{\text{H}}$  on toxic effect of bile salts on the normal gall-bladder.** H. G. ARONSOHN and E. ANDREWS (Proc. Soc. Exp. Biol. Med., 1936, 34, 763—765).—The toxic action of bile salts on the normal gall-bladder is unaffected by change of  $p_{\text{H}}$  within the normal range of the bile.

P. G. M.

**Relative toxicity of different bile salts on the normal gall-bladder.** E. ANDREWS and H. G. ARONSOHN (Proc. Soc. Exp. Biol. Med., 1936, 34, 765—767).—Deoxycholic acid is the most toxic to the gall-bladder wall.

P. G. M.

**Effect of methylene-blue on respiration of blocked and developing embryonic cells.** J. H. BODINE and E. J. BOELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 629—630).—Methylene-blue may act as a substitute for the part of the respiratory process impaired either naturally or by HCN.

P. G. M.

**Action of hæmatoporphyrin on blood-calcium and -phosphorus.** P. MABIQUE and G. MELOT (Compt. rend. Soc. Biol., 1936, 123, 280—283).—Ca is slightly lowered whilst changes in P are negligible.

H. G. R.

**Tissue response to subcutaneous injection of cod-liver oil.** J. DAVSON (Lancet, 1936, 231, 737—738).—Subcutaneous injection of fish-liver oils into rabbits produces a marked stimulation of phagocytes, fibroblasts, and young capillaries. Liquid



paraffin and olive oil are comparatively inert. The vitamin-A of the oils is not responsible for the reaction.  
L. S. T.

**Growth inhibitor in liver.** A. M. BRUES, E. B. JACKSON, and J. C. AUB (Proc. Soc. Exp. Biol. Med., 1936, 34, 270—273).—The growth of explants of embryonic and sarcomatous tissue is inhibited by the solution obtained when fresh, sterile liver is shaken with 2 vols. of Tyrode's solution. The inhibiting agent does not dialyse and is fairly stable to O<sub>2</sub> but not to heat.  
W. McC.

**Supplement to Steenbock diet 2965.** W. J. NIJVELD (Z. Vitaminforsch., 1936, 5, 257—262).—Addition of liver or liver extract to the diet prevented the unsatisfactory growth of rats, for there was a steady increase in wt. corresponding with an increased food intake. The deaths which frequently occurred after approx. 10 days on the ordinary diet were also prevented. The active factor of the liver is not in the ash, and it is not destroyed by heating dry powdered liver at 130° for 6 hr. Heating of liver extract in an autoclave at 120° did not completely remove the activity.  
J. N. A.

**Role of lactoflavin and flavinphosphoric acid in adrenal cortex deficiency and iodoacetic acid poisoning.** F. VERZAR and L. LASZT (Z. Vitaminforsch., 1936, 5, 265—275).—Adrenalectomised rats can be kept alive for > 2 months with yeast concentrates containing flavinphosphoric acid. Lactoflavin alone does not have this effect, and is unable, even in daily doses of  $2 \times 10^{-4}$  g., to cause growth in rats poisoned with CH<sub>2</sub>I-CO<sub>2</sub>H (I). Growth can take place as a result of refecation in rats suffering from chronic (I) poisoning.  
J. N. A.

**Chemical factors governing gastric motility.** J. P. QUIGLEY (Amer. J. Digest. Dis. Nutrition, 1934, 1, 425—426).—Fats and carbohydrates liberate humoral factors from the mucosa of the upper intestine which resemble an inhibitory hormone.

CH. ABS. (p)

**Anæsthetic activity of butanes and pentanes.** R. W. STOUGHTON and P. D. LAMSON (J. Pharm. Exp. Ther., 1936, 58, 74—77).—The activity and lethality of C<sub>4</sub>H<sub>10</sub> are < those of C<sub>5</sub>H<sub>12</sub> and those of the straight chain > those of the isomerides with branched chains.  
H. G. R.

**Local anæsthetic activity of quinoline compounds.** H. K. SINHA (J. Pharm. Exp. Ther., 1936, 58, 62—67).—Activity, both when applied to the mucous membranes and on intradermal injection, is observed on introducing a basic side-chain at 8.  
H. G. R.

**Influence of the anæsthetic on the results of digitalis assay by the cat method of Hatcher and Brody.** C. C. HASKELL (J. Pharm. Exp. Ther., 1936, 58, 111—117).—The cat unit with dial-urethane anæsthetic is > that with Et<sub>2</sub>O.  
H. G. R.

**Detoxication of local anæsthetics by "cardiazol."** K. ZIPF and H. HOPPE (Arch. exp. Path. Pharm., 1936, 183, 67—70).—The toxic effects of novocaine and larocaine in mice and cats are diminished by simultaneous injection of "cardiazol."  
F. O. H.

**Local anæsthetics containing the  $\alpha$ -tetrahydro- $\beta$ -naphthylamine pressor group.**—See this vol., 1501.

**Plasticity of skeletal muscle before and during deep narcosis.** A. HEINRICH (Pflüger's Arch., 1936, 237, 19—23).  
M. A. B.

**Blood-ammonia during ether narcosis in man.** L. STANOJEVITCH and S. PETKOVITCH (Compt. rend. Soc. Biol., 1936, 123, 430—432).—The increase is greater when the initial val. is high and after the anæsthesia remains at an increased level.  
H. G. R.

**Atropine-morphine-ether narcosis.** F. HENDRYCH (Arch. exp. Path. Pharm., 1936, 182, 732—737).—The narcotic action of Et<sub>2</sub>O on mice is enhanced by prior injection of morphine + atropine (I); (I) thus resembles scopolamine. The mechanism of the phenomenon is discussed.  
F. O. H.

**Sedative action of valerian.** H. DRUCKREY and G. KÖHLER (Arch. exp. Path. Pharm., 1936, 183, 106—109).—The narcotic effect of different types of extract of valerian from various sources was determined by the action on the head movements of mice. Infusions are most, and Et<sub>2</sub>O extracts least, active (cf. Kochmann and Kunz, this vol., 1022).  
F. O. H.

**Distribution of atebtrin in the organism.** G. HECHT (Arch. exp. Path. Pharm., 1936, 183, 87—105).—Data for the distribution of atebtrin (I) in cats and rabbits following administration by various routes are tabulated. The general tendency is for (I) to be most conc. in liver, lungs, heart, kidneys, and spleen and, to a smaller extent, in intestines, heart, pancreas, and reproductive organs. Intramuscularly injected (I) is detectable in the blood for only 1 hr. after injection.  
F. O. H.

**Effect of drugs on the Schlesinger reaction for urobilin.** J. J. HOFMAN (Pharm. Weekblad, 1936, 73, 1417—1421).—Acriflavine (I) when administered orally gives a positive Schlesinger test for urobilin in the urine [fluorescence when treated with EtOH-Zn(OAc)<sub>2</sub> suspension]. (I) is detected by treatment with NaOCl or KI-I solution, when a black ppt. is formed and the filtrate no longer fluoresces. Several precipitants for (I) are noted, the sensitivity being given in parentheses: 10% Na salicylate (1:10<sup>4</sup>), K<sub>3</sub>Fe(CN)<sub>6</sub> (1:10<sup>5</sup>), K<sub>4</sub>Fe(CN)<sub>6</sub> (1:10<sup>4</sup>), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1:10<sup>4</sup>), Na tungstate (1:10<sup>4</sup>), NH<sub>4</sub> molybdate (1:10<sup>4</sup>), HgCl<sub>2</sub> (1:10<sup>5</sup>).  
S. C.

**Endocrine localisation of medicinal and toxic substances.** R. FABRE (Ukrain. Biochem. J., 1936, 9, No. 1, 125—141).—Various toxic substances including CHCl<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, veronal, quinine, F<sub>2</sub>, and Cr are retained by the endocrine glands, on which they probably exercise a profound effect.

**Experimental hypertrophy with and without digitalisation on creatine content of rabbit hearts.** G. M. DECHERD, jun., G. HERRMANN, and E. H. SCHWAB (Proc. Soc. Exp. Biol. Med., 1936, 34, 864—866).—There is an abs. increase in the creatine content of hypertrophied hearts which is further increased by administration of digitalis.  
P. G. M.

Disturbance of protein metabolism following liver injury by salvarsan. A. WIEDMANN (Wien. klin. Woch., 1935, 48, 1539—1543; Chem. Zentr., 1936, i, 803).—Metabolism of protein but not carbohydrate is affected.

A. G. P.

Neuromuscular junction. II. Antagonism between calcium and curarising agencies. T. P. FENG (Chinese J. Physiol., 1936, 10, 513—527).—With nerve-sartorius preps. of the toad, Ca antagonises the curarising action of curare, eserine, veratrine, nicotine, atropine, ergotoxine, strychnine, pilocarpine, and novocaine, of fatigue and long survival, of Sr, Ba, and Mg, and of extreme temp. The immediate and reversible cause of curarisation appears to be an electrolytic disturbance involving the loss of Ca from the neuromuscular junction.

P. W. C.

Effect of calcium and curare on muscular contraction and neuromuscular transmission. I. CHAO (Chinese J. Physiol., 1936, 10, 545—546).—With sciatic-sartorius preps. of toad, excess of Ca decreases muscular contraction, whilst Ca antagonises the effect of curare and facilitates neuromuscular transmission.

P. W. C.

Action of ergometrine. K. K. CHEN, E. E. SWANSON, and C. C. HARGREAVES (Proc. Soc. Exp. Biol. Med., 1936, 34, 183—185).—Ergometrine nitrate (I) in a concn. of about 1:30,000 slightly stimulates the isolated rabbit uterus, having about 0.01% of the oxytocic activity of ergometrine (II). The action of (I) on the cock's comb is about 0.7% of that of (II). (I) relaxes isolated rabbit intestine and produces prolonged reduction of blood pressure in the cat.

W. McC.

Physico-chemical processes in nerve tissue. I. Oxidation-reduction potential in rabbit brain during strychnine and cocaine poisoning. S. V. FOMIN and D. N. STRAJESKO (Ukrain. Biochem. J., 1936, 9, No. 1, 43—54). The oxidation-reduction potential of rabbit brain tissue becomes stable more rapidly when from an animal poisoned with strychnine (I) or cocaine (II) than when normal. The potential of boiled brain tissue extract from rabbits poisoned with (I) is < that of a similar extract of normal tissue, but under anaerobic conditions the potentials of both boiled and unboiled extracts are higher from the poisoned than from normal animals. (II) poisoning also produces changes in the oxidation potentials of the extracts.

W. O. K.

Comparative action of cobra venom and morphine on the autoxidation of cerebral and other tissues. D. I. MACHT and H. F. BRYAN (Compt. rend. Soc. Biol., 1936, 123, 385—388).—The inhibition with venom is more prolonged than with morphine, since a modification of the alkaloid is observed if the time of contact is long.

H. G. R.

Poisons of animal origin. The venins. M. T. REGNIER (J. Pharm. Chim., 1936, [viii], 24, 368—375, 413—429).—A review.

Heart poisons and saponins of the cholane series. K. BOHLE (Chem.-Ztg., 1936, 60, 893—896).—A review.

Seeds of the Madagascar anthelmintic Combrataceæ. J. MAHEU and R. WERTZ (Bull. Sci. pharmacol., 1935, 42, 202—210; Chem. Zentr., 1936, i, 805).—The leaves of *Quisqualis indica*, L., and the fruits of *Q. madagascariensis*, Boj., and their application as anthelmintics are described.

H. N. R.

Physico-chemical mechanisms in convulsive reactivity. E. SPIEGEL and M. SPIEGEL-ADOLF (Proc. Soc. Exp. Biol. Med., 1936, 34, 799—800).—Epileptogenous agents act on the nervous system (a) by a change in ion concn. on the surface of the nerve cells and (b) by diminution of the cellular surface films.

P. G. M.

Chronic nicotine toxicity. I. Feeding of nicotine sulphate and tannate and bentonite. II. Effect of nicotine-containing diets on blood-sugar concentration in the rat. R. H. WILSON and F. DE EDS (J. Ind. Hyg., 1936, 18, 553—564, 565—570).—I. The growth of rats fed on a diet containing >0.006% of nicotine (I) was retarded; this retardation was largely due to diminished food intake and, in lesser degree, to the toxic effect of (I). (I) sulphate was approx. twice as toxic as the tannate or bentonite.

II. Chronic (I) poisoning produces an initial hypoglycæmia and acute intoxication a transient hyperglycæmia followed by a return to normal.

P. G. M.

Acute toxicities of rotenone and mixed pyrethrins in mammals. M. B. SHIMKIN and H. H. ANDERSON (Proc. Soc. Exp. Biol. Med., 1936, 34, 135—138).—The min. lethal doses of rotenone for guinea-pigs, rats, and mice were 7—10 mg. per kg. (intraperitoneally) and 75—100 mg. (orally). The corresponding vals. for mixed pyrethrins were 100—150 mg. and 1500 mg.

W. McC.

Toxicity of *d*- and *l*- $\alpha$ -tolylpyrrolidine to *Aphis rumicis*. Toxic constituents of derris root.—See B., 1936, 1117.

Acute intraperitoneal toxicity of plant growth-substances for mice. H. H. ANDERSON, M. B. SHIMKIN, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1936, 34, 138—139).—The min. lethal doses for mice of indolyl-propionic and -butyric acid and phenyl-,  $\alpha$ -naphthyl-, and indolyl-acetic acid were respectively 100, 100, 300, 100, and 25 mg. per kg. The toxicities of these substances to plants are approx. in the same relative order.

W. McC.

Alleged toxicity to rats of maize germ and its ethereal extract. E. CASERIO (Z. Vitaminforsch., 1936, 5, 263—265).—Maize germ and its ethereal extract have no action on rats, and they actually show favourable somatic effects. The contrary results of Randoïn and Simonnet may be explained either by fermentation of the extracts or by contamination with toxic material.

J. N. A.

Pathomorphological changes in the internal organs and endocrine glands in dinitrophenol poisoning. I. PEISSAKOVITSOH and P. KOSTENKO (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 160—170).

M. A. B.

Morphological and chemical investigations in a case of death from acute benzene poisoning.



G. F. KOPPENHOFER (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 417—427).— $C_6H_6$  was demonstrated in the blood and organs by distilling these with  $H_2O$  acidified with  $H_2SO_4$ , nitrating the distilled  $C_6H_6$ , and identifying the *o*- and *m*- $C_6H_4(NO_2)_2$  by the intense violet colour with fructose. M. A. B.

**Permeability of the cerebrospinal barrier and blood variations in experimental benzene poisoning.** S. B. SCHACHNOVSKAJA (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 144—156). M. A. B.

**Toxicity of propylene glycol.** H. A. BRAUN and G. F. CARLAND (J. Amer. Pharm. Assoc., 1936, 25, 746—749).—The min. lethal dose in rats is 15.7 and 23.1 g. per kg. for intramuscular and subcutaneous injection, respectively: corresponding vals. for glycerol are 7.6 and 15.1. The oral lethal dose of the glycol in rabbits is 20 g. per kg. but daily ingestion of 8 c.c. for 50 days has no cumulative effect. F. O. H.

**Chronic carbon tetrachloride poisoning.** J. LOWY (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 157—159). M. A. B.

**Chronic iodoacetic acid poisoning and its relation to the Gee-Herter disease.** L. LASZT and F. VERZAR (Pflüger's Arch., 1936, 237, 483—493).—Chronic  $CH_2I \cdot CO_2H$  poisoning produces in rats symptoms similar to those of the Gee-Herter disease. In the poisoned rats the symptoms can be removed by feeding dried yeast or vitamin- $B_2$  (flavin phosphate) but not by flavin. It is suggested that the symptoms are due, in both cases, to inhibition of  $-B_2$  formation from flavin. M. A. B.

**Mechanism of methylene-blue in carbon monoxide poisoning.** M. M. BROOKS (Proc. Soc. Exp. Biol. Med., 1936, 34, 48—49).—In rabbits poisoned with CO, the conversion of CO-haemoglobin into oxy-haemoglobin is definitely accelerated by intravenous administration of methylene-blue (1 c.c. of 0.03% solution per kg. body-wt.). W. O. K.

**Influence of liver poisons on action of parathyroid extract.** D. M. GREENBERG (Proc. Soc. Exp. Biol. Med., 1936, 34, 622—626).—Poisoning with P inhibits, and with  $N_2H_4$  markedly reduces, the serum-Ca rise following injection of parathyroid extract;  $CCl_4$  has no effect.  $N_2H_4$  and P do not act *via* the bone cells. P. G. M.

**Cyanide poisoning.** K. K. CHEN, C. L. ROSE, and G. H. A. CLOWES (Metal Ind., N.Y., 1936, 34, 346).—First-aid treatment with amyl nitrate and 1% aq.  $Na_2S_2O_3$  is described. L. S. T.

**Combined action of lead and nicotine.** R. M. SKLIANSKAJA (Arch. Gewerbepath. Gewerbehyg., 1935, 6, 270—274).—The combined toxic effect of Pb and nicotine (I) on the isolated frog's heart is < the sum of the toxic effects of Pb and (I) separately. M. A. B.

**Toxicity of selenium-containing plants to aphids.** A. M. HURD-KARRER and F. W. POOS (Science, 1936, 84, 252).—*Rhopalosiphum prunifoliae* (Fitch) is killed by the Se taken up by plants (wheat, rye, oats, and barley) from small amounts of  $Na_2SeO_4$  added to cultures or soils. L. S. T.

**Poisoning by sodium nitrite.** A. SCHOLLES (Analyst, 1936, 61, 685—686).—The  $NaNO_2$  had been mistaken for NaCl. The amounts present in the stomachs of the deceased and in the unconsumed food are recorded. E. C. S.

**Structure and toxicity of arsinic acids of the diphenylamine series.**—See this vol., 1527.

**Enzymes in relation to cancer.** A. PURR (Current Sci., 1936, 5, 194—196).—A review.

**Effect of irradiation with short waves on enzymes. I. Diastase.** K. KOSIERADSKI (Biochem. Z., 1936, 287, 265—270).—The saccharifying action of diastase alone or mixed with starch is not affected by irradiation with short waves (2, 4, 10, and 15 m.). W. McC.

**Keilin's cytochrome-c and the respiratory mechanism of Warburg and Christian.** H. THEORELL (Nature, 1936, 138, 687).—Cytochrome-c, like  $O_2$  and methylene-blue, does not oxidise the dihydroco-enzyme directly. It rapidly oxidises the leuco-form of the yellow enzyme. L. S. T.

**Action of cyanides on the purine dehydrogenase of milk.** E. J. BIGWOOD, J. THOMAS, and H. HERBO (Compt. rend. Soc. Biol., 1936, 123, 87—90).—The inhibiting effect of KCN is not observed under anaerobic conditions. H. G. R.

**Storch reaction [for peroxidase in milk].** L. C. JANSE (Chem. Weekblad, 1936, 33, 638—640).—Milk containing traces of Cu gives a positive Storch reaction [colour with  $p\text{-}C_6H_4(NH_2)_2$ , HCl, and  $H_2O_2$ ] even when pasteurised at  $> 85^\circ$ . The adverse effect of Cu is corr. by preliminary addition of 1 c.c. of 0.25% aq. KCN to 5 c.c. of milk. S. C.

**Behaviour of the amylase of silkworms living under unfavourable conditions.** K. YAMAFUJI (Biochem. Z., 1936, 287, 23—25).—The amylase contents of the blood and digestive juices of silkworms kept for a time under unfavourable conditions of aeration and moisture decrease considerably without obvious change in the appearance of the worms and do not regain their original vals. when the worms are replaced under favourable conditions. The amylase contents of the blood and juices of their offspring are also subnormal. P. W. C.

**Action of the lysin of pneumococcus on certain tissue-polysaccharides.** K. MEYER, R. DUBOS, and E. M. SMYTH (Proc. Soc. Exp. Biol. Med., 1936, 34, 816—818).—The same enzyme from pneumococci is capable of hydrolysing the carbohydrate complex (acetylglucosamine-glycuronic acid) from bovine vitreous humour or human umbilical cord, and heat-killed pneumococci. The optimum  $p_H$  is 5—6 and the enzyme is reversibly inactivated by I. P. G. M.

**Enzymic fission of difficultly hydrolysable glucoside of senna leaves.** E. TRIENDL (Arch. exp. Path. Pharm., 1936, 182, 527—532).—The glucoside (I) (Straub and Gebhardt, this vol., 1021) is hydrolysed (with formation of emodin; optimum  $p_H$  5.0) by mucous membrane of large and small intestine and by liver-tissue of dogs and cats, bitter almond preps., and emulsin. (I) is therefore a

$\beta$ -glucoside. With animal enzyme preps., enzymic oxidation of intermediary anthranol to anthraquinone occurs.  
F. O. H.

**Relations between vitamin-C and enzymic fission of carbohydrates.** I. R. WEIDENHAGEN and P. LU. II. R. WEIDENHAGEN (Z. Wirts. Zuckerind., 1936, 86, 240—253, 482—494).—I. Ascorbic acid (I) in 0.005M concn. reduced by 60—80% the rate of hydrolysis of sucrose by  $\beta$ -*h*-fructosidase [invertase (II), from yeast] in solutions buffered at  $p_H$  4.7 and 6.9, and its effect was detectable at 0.0001M. Even at 0.005M, however, the inhibition was entirely annulled by the presence of cysteine ( $10^{-3}M$ ), glutathione (III) (0.0001M), certain other S compounds or  $NH_2$ -acids at higher concn., or even by citric acid or  $H_2C_2O_4$  (0.005M). The opposite actions of (I) and (III) suggest a possible means by which (II) action may be controlled in plant life.

II. (I) produces inhibitory effects equal to or > those observed with invertase on  $\beta$ -glucosidase (highly purified emulsin from bitter almonds) and on the amylases of pancreas, wheat, barley, and malt. The amylases were purified by tannin pptn., followed by pptn. by  $COMe_2$ . In all cases (III) at the same equiv. concn. as (I) partly or entirely prevented the inhibitory action of (I).  
J. H. L.

**Separation of  $\beta$ -*h*-fructosidase [invertase] from yeast autolysates.** R. WEIDENHAGEN [with A. RENNER] (Z. Wirts. Zuckerind., 1936, 86, 473—481).—If a slightly acid yeast autolysate is adjusted to  $p_H$  8 with  $Sr(OH)_2$  the ppt. formed contains the whole of the invertase present; if  $Ca(OH)_2$  or  $Ba(OH)_2$  is used pptn. is not complete. The invertase may be dissolved from the washed ppt. by means of  $NH_4H_2PO_4$  or  $Na_2SO_4$ . Practical details of the method are given.  
J. H. L.

**Changes in the curve of enzymic hydrolysis of sucrose by the action of heat on the enzyme.** A. CHAUDIN (Bull. Soc. Chim. biol., 1936, 18, 1467—1470).—Invertase heated for 3 hr. at 55° hydrolyses sucrose less rapidly, but at the same time the angular point of the reaction curve is displaced so that the amount of enzyme appears to have increased. A similar effect has been observed with alkali, EtOH, and MeCHO.  
A. L.

**Lacto-mannitic enzymes. III. Products of fermentation of glucose.** V. BOLCATO (Annali Chim. Appl., 1936, 26, 356—361; cf. this vol., 638).—The enzymes which produce mannitol from fructose produce only lactic acid (I), EtOH,  $CO_2$ , and a little AcOH from glucose. The productions of (I) and EtOH are independent, and the ratio (I)/EtOH is not const. The mechanisms of the fermentation of glucose and fructose are compared.  
L. A. O'N.

**Recent researches on cell-free alcoholic fermentation.** O. MEYERHOF (Naturwiss., 1936, 24, 689—692).—A lecture.

**Pasteur and Meyerhof's reaction.** C. FRISCH and R. WILLHEIM (Biochem. Z., 1936, 287, 203—205).—Glycolysis in muscle extract is diminished by Warburg's respiratory enzyme but increased by lactoflavin, which also partly counteracts the inhibition caused by benzoquinone.  
W. McC.

**Role of the adenylic acid system and of cozymase in alcoholic fermentation.** P. OHLMEYER (Biochem. Z., 1936, 287, 212—225).—Although purified cozymase (I) and the adenylic acid (II) system do not differ as regards their effects on liberation of  $PO_4'''$  from phosphopyruvic acid (III) and transfer of  $PO_4'''$  to glucose (IV) from (III), (I) cannot be replaced by (II) in the conversion of hexose diphosphate [with or without (IV)] in presence of NaF into phosphoglyceric and glycerophosphoric acid and in the interaction of (IV) and MeCHO in presence of inorg.  $PO_4'''$ . Hence in the system (III) + (IV) fermentation ceases when the  $CO_2$  equiv. of (III) has been liberated when (II) replaces (I) but continues if (I) is not so replaced.  
W. McC.

**Inhibition of glycolysis by heavy metals and reversal of this inhibition.** T. WAGNER-JAUREGG and H. W. RZEPPA (Z. physiol. Chem., 1936, 243, 166—172; cf. this vol., 895).—The amount of  $CuSO_4$  required to inhibit glycolysis in muscle extract from *Rana esculenta* is 5—10 times that necessary with extract from *R. temporaria* and no inhibition is produced in rabbit muscle extract by 0.00017M- $CuSO_4$ . Pure and impure cozymase (I) and Warburg's co-enzyme (II) (but not KCN and ascorbic acid) and, to a much smaller extent, cysteine and glutathione reverse the inhibition whilst muscle-adenylic acid acts indefinitely. (I) and (II), which reactivate in the mol. ratio of >5 to 1 of metal, probably act by producing complexes or difficultly sol. salts with Cu.  $Fe^{II}$  inhibits  $\ll$  does Cu whilst  $Fe^{III}$ , Zn, and Cd have little or no effect and Mn stimulates glycolysis.  
W. McC.

**Inactivation of cozymase in an apozymase system poisoned with fluoride.** A. LENNERSTRAND (Biochem. Z., 1936, 287, 172—188; cf. this vol., 380).—In the system apozymase + cozymase (I) + glucose (II) + hexose diphosphate (III) +  $PO_4'''$  buffer phosphorylation and  $O_2$  consumption occur to a small extent in presence of NaF but soon cease. Methylene-blue added after the cessation is decolorised only very slowly. Pyocyanine (IV) increases phosphorylation and  $O_2$  consumption to an extent which diminishes to zero as the interval of time which elapses before the addition increases. The duration of  $O_2$  consumption and phosphorylation  $\propto$  the concn. of (III). After  $O_2$  consumption and phosphorylation have ceased they are re-started by addition of (I) [but not by that of (III), muscle-adenylic acid (V), adenosinetriphosphoric acid (VI), or Warburg's co-enzyme]; the  $O_2$  consumption, within limits, then  $\propto$  the amount of (I) added. If NaF + (IV) + (II) are added to the system vigorous  $O_2$  consumption occurs even if liberation of  $CO_2$  has almost ceased. These findings indicate that cessation of  $O_2$  consumption and phosphorylation are due to the inhibitory action of NaF on some mechanism which protects (I). The extent of inhibition is measured by the effect of (IV). In the enzyme system of yeast (I) alone can act as  $PO_4'''$  carrier whilst (V) accelerates the process but cannot act alone. During fermentation (I) continuously phosphorylated by phosphopyruvic acid (VII) transfers  $PO_4'''$  directly or by way of (V) and (VI) to



(II). NaF prevents dephosphorylation of (VII) and hence (I) cannot act. W. McC.

**Cozymase and dihydrocozymase in living cells.** E. ADLER and H. VON EULER (Svensk Kem. Tidsskr., 1936, 48, 221—226; cf. this vol., 246).—Cozymase (I) and dihydrocozymase (II) exist in the living cell as intermediates in fermentation and muscular activity enzyme systems. The stability of (I) to acids and of (II) to alkalis enables the (I)/(II) ratio to be determined. M. H. M. A.

**Zymohexase. III. Determination [of activity].** E. BAUER (Z. physiol. Chem., 1936, 243, 202—206; cf. this vol., 1299).—The activity of zymohexase (I) (with and without HCN activation) is max. at  $p_H$  9.5—10.0 but most stable at  $p_H$  7—8. At  $p_H > 10$  irreversible inactivation occurs. The stability decreases more rapidly in the acid than in the alkaline zone. The activity is independent of substrate [hexose diphosphate (II)] concn. Until the amount of P converted into alkali-hydrolysable form reaches 0.003%, the amount of (II) decomposed  $\propto$  the (I) concn. The unit of (I) is defined as the amount which converts 0.01 mg. of P into alkali-hydrolysable form in 1 hr.  $Fe^{III}$  activates (I) at  $p_H$  9.1 but inactivates it in slightly acid media. (II) forms with Fe a very stable complex salt which possibly is partly responsible for the activating effect of Fe. The affinities of (I) for (II) and this complex are probably different. W. McC.

**Choline esterase.** H. KWIATOWSKI (Fermentforsch., 1936, 15, 138—151).—Choline esterase (I) was detected in lymph, bile, and skin dialysate. (I) is not adsorbed by bolus alba and animal C, is not destroyed by X-rays, and is inhibited by pituglandol, padutin, NaF, and prostigmine (II), but not by histamine. The synthesis of acetylcholine from choline and NaOAc in fluids containing (I) depends on the amount of (I) present and is inhibited by phsostigmine, (II), and NaF. E. A. H. R.

**Action of the stereoisomerides of leucylglycylglycine on pancreas- and liver-esterase.** W. GERTLER (Fermentforsch., 1936, 15, 171—176).—All stereoisomerides of leucylglycylglycine (I), especially the *l*-form, strongly activate the hydrolysis of tributyrin (II) by pancreatic lipase. The effect is less marked with  $PrCO_2Me$  (III). (I) has no effect on the hydrolysis of (II) and (III) by liver-esterase, or on the enzymic hydrolysis of acetylcholine. E. A. H. R.

**In vitro hydrolysis of fats by lipase and bile salts.** J. E. DAVIS (Proc. Soc. Exp. Biol. Med., 1936, 34, 772—775).—A method is evolved for *in vitro* hydrolysis of fats by lipase and bile salts, by means of which equilibrium is reached in 24 hr. at 24% hydrolysis. P. G. M.

**Enzymic hydrolysis of nucleotides and nucleosides. I. Hydrolysis of purine ribonucleotides.** H. ISHIKAWA and Y. KOMITA (J. Biochem. Japan, 1936, 23, 351—363; cf. this vol., 433).—Dog's pancreas preps. hydrolyse guanylic (I) and xanthylic acid to give ribose phosphate (II) (optimum  $p_H$  7.5), small amounts of  $NH_3$  being liberated from (I) when crude enzyme preps. are used. Dog's pancreas

also contains a nucleosidase. Cat's pancreas yields (II) from nucleotides and also contains nucleosidase and deaminase which are absent from ox and pig's pancreas. Nucleotidase and nucleosidase occur in rabbit's liver, kidney, muscle, and small intestine. Nucleotides are hydrolysed both by primary dephosphorylation and by splitting of the pentose linking followed by hydrolysis of (II). F. O. H.

**Tyrosinase. II. Action of potato-tyrosinase on phenols and the influence of amino-compounds on the tyrosinase system.** F. NOBUTANI (J. Biochem. Japan, 1936, 23, 455—485).—Tyrosinase (I) produces pigments only from those phenolic substances which yield *o*-quinones on oxidation. The  $O_2$  uptake by *p*-cresol or pyrocatechol in presence of (I) is 1 atom  $>$  that corresponding with formation of *o*-benzoquinone.  $NH_2$ -acids accelerate the action of (I) but do not affect the  $O_2$  consumption, whilst  $NH_2OH$  accelerates the action but depresses  $O_2$  consumption. The mechanism of these phenomena is discussed. F. O. H.

**Polypeptidases excreted in the urine of health and disease.** P. STEINBRÜCK (Fermentforsch., 1936, 15, 121—133). E. A. H. R.

**Polypeptidases of blood-serum and -plasma.** R. ABDERHALDEN (Fermentforsch., 1936, 15, 157—170).—Protection of the  $CO_2H$  of polypeptides inhibits the action of the carboxypolypeptidase in trypsin (I), for it hydrolyses neither *dl*-leucylglycyl-methylamine (II), m.p. 76—78°, nor *dl*-leucylglycyl-glycylbenzylamine (III), m.p. 130—131°. (II) and (III) are hydrolysed by erepsin (IV) and serum to a greater extent than the corresponding polypeptides, perhaps because of a greater ease of attachment of the  $NH_2$  to the enzyme surface when the  $CO_2H$  is blocked. *dl*-(*N*)-Benzyl-leucylglycylbenzylamine, m.p. 70—71°, is not hydrolysed by (I), (IV), or serum, and can be recovered unchanged 10 days after injection into a rabbit. The aminopolypeptidase content of foetal blood is the same as, but the dipeptidase content is  $<$ , that of the mother. E. A. H. R.

**Fibrinolysis. V.** M. ROSENMANN (Biochem. Z., 1936, 287, 26—32).—A substance is present in serum which is inactivated by heating for  $\frac{1}{2}$  hr. at 50° and is identical with thrombolysin (I) (A., 1922, i, 596). The  $p_H$  optimum for fibrinolysis by autolysate-(I) is between 7.8 and 8.4 and for serum-(I) between 8 and 8.4, whilst the material is active over the range  $p_H$  5.8—10. The  $p_H$  optimum is not displaced by addition of thromboligin. P. W. C.

**Autodigestion. VI. Digestion of living tissues by trypsin.** H. NECHELES, P. LEVITSKY, and M. MASKIN (Proc. Soc. Exp. Biol. Med., 1936, 34, 768—772).—Tryptic digestion of living frogs' legs can take place following immersion in HCl or pepsin-HCl. P. G. M.

**Influence of high temperatures on the trypsin of warm- and cold-blooded vertebrates.** P. A. KORSCHUJEFF (Fermentforsch., 1936, 15, 152—156).—The higher is the body-temp. of a vertebrate, the greater is the thermostability of its trypsin. E. A. H. R.

**Enzymic digestion of lactalbumin and caseinogen *in vitro*.** M. C. KIK (Proc. Soc. Exp. Biol. Med., 1936, **34**, 194—196).—Lactalbumin is less readily digested *in vitro* by trypsin and erepsin than is caseinogen. W. McC.

**Determination of antitrypsin.** K. L. BURDON and C. LAFFERTY (Proc. Soc. Exp. Biol. Med., 1936, **34**, 787—790).—Opaque photographic film is used for titration of antitrypsin; the amount of trypsin required to produce complete transparency of the film is determined. P. G. M.

**Enzymes of snake venom. I. Their action on hæmoglobin and on protein solutions of different  $p_H$ .** B. N. GHOSH (J. Indian Chem. Soc., 1936, **13**, 450—455).—Proteolytic activity of cobra venom to gelatin and ovalbumin is a max. at  $p_H$  7.8—8.0 and to casein at  $p_H$  6.6. The protease of this venom thus resembles trypsin. This venom and that of Russell's viper cause oxidation of hæmoglobin to methæmoglobin. R. S. C.

**Tissue proteinases (cathepsin) in protein-free and low-protein feeding.** B. GOLDSTEIN and M. GINZBURG (Ukrain. Biochem. J., 1936, **9**, 341—354).—Protein-starved and gelatin-fed rabbits show an increase of cathepsin (I) concn. in the kidney and, more especially, in the liver, the difference between  $H_2S$ -non-activated and  $H_2S$ -activated (I) being also raised. Predominance of protein synthesis in the organ appears to be accompanied by strong activation of (I) by  $\cdot SH$ . Protein synthesis is increased in the livers of rabbits on restricted protein diets. F. A. A.

**Intracellular proteinases. XVIII. Effect of co-enzyme and cozymase on proteinases reversibly inactivated by heavy metals.** E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1936, **243**, 207—208; cf. A., 1935, 1538).—The inactivating effect of Cu on the degradation of gelatin by papain (I) and cathepsin (II) is not reversed by addition of Warburg's co-enzyme (III) or Euler's cozymase (IV). The action of (I) but not that of (II) is appreciably restricted by (III) and (IV). W. McC.

**Proteolytic enzymes. XI. Specificity of papain peptidase I.** M. BERGMANN, L. ZERVAS, and J. S. FRUTON (J. Biol. Chem., 1936, **115**, 593—611; cf. this vol., 1152).—The hydrolysis by peptidase I of compounds of the type  $NHR''\cdot CO\cdot CHR'\cdot NH\cdot CO\cdot R$  ( $R=Ph$  or  $O\cdot CH_2Ph$ ) was investigated. Hippurylamide (I) ( $R=Ph$ ,  $R'=H$ ,  $R''=H$ ) is readily hydrolysed whilst derivatives ( $R''=Me$ , *isoamyl*, or *Ph*) under the same conditions were only slightly hydrolysed. Carbobenzoyloxyglycylglycine (II) and -di- and -tri-glycylglycine are hydrolysed with increasing velocity as  $R''$  increases in length. Hydrolysis of (I), hippurymethylamide, and (II) indicates an inhibitory influence of  $Me$  but not  $CO_2H$ . *Benzoylglycylglycine piperidide*, m.p. 134°, is hydrolysed more rapidly than is (II). The splitting of carbobenzoyloxyglutamyl- $\alpha$ -amide is  $>$  that of derivatives where  $R''=isoamyl$  or, to a greater extent,  $R''=Me$ . In order to demonstrate the marked effect of slight structural changes on the rate of hydrolysis, the hydrolysis of, amongst others, the

following compounds was studied: *benzoyl-l-leucyl-l-leucylglycine*, m.p. 161°, *carbobenzoyloxy-l-glutamylglycylglycine*, m.p. 142° (*Et* ester, m.p. 139—140°), *benzoyl-l-lysineamide* (III), m.p. 187° [*d-isomeride* (IV), m.p. 187°]. The linking ' is more readily attacked than ". The peptidase hydrolyses a variety of peptide linkings with widely different velocities. The fission of free polypeptides by papain is due to peptidase I. (III) but not (IV) is hydrolysed. The antipodal specificity of peptidase I is discussed (cf. A., 1935, 1416). The following compounds were prepared: *l-leucyl-l-leucylglycine* (carbobenzoyloxy-methyl ester, m.p. 108°), *carbobenzoyloxypiperidide*, m.p. 78°, *hippuryl-anilide*, m.p. 214°, and *isoamylamide*, m.p. 98°, *carbobenzoyloxy-l-glutamyl-methylamide*, m.p. 178°, and *isoamylamide*, m.p. 135°.

F. O. H.

**Proteases and proteolytic processes in muscle tissue. III. Activity of muscle proteases in B- and C-avitaminosis.** S. V. FOMIN and N. M. ROMANTSCHUK (Ukrain. Biochem. J., 1936, **9**, 355—368).—The protease activity on caseinogen of muscle extracts from B-avitaminotic pigeons or C-avitaminotic guinea-pigs is  $<$  that of extracts from normal animals. F. A. A.

**Influence of phloridzin on renal phosphatase *in vitro*.** A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, **123**, 311—313).—There is no parallelism between the diabetogenic and inhibitory actions.

H. G. R.

**Phosphatase of human milk.** K. V. GIRI (Z. physiol. Chem., 1936, **243**, 57—62).—Human milk contains phosphatases exhibiting optimal activity at  $p_H$  9.2 and 5.1, respectively, with Na glycerophosphate (I) as substrate. The first is activated by  $Mg^{++}$ ; the second is not. Na hexose diphosphate (II) is more readily hydrolysed by the phosphatases than is (I), and  $Na_4P_2O_7$  is much more readily hydrolysed than are (I) and (II). The amount of the phosphatases in the milk 3 days *post partum* is that in the milk of later stages of lactation and they are activated to a greater extent by  $Mg^{++}$ . W. McC.

**Fermentation enzymes. VI. Dephosphorylating enzymes of yeast.** A. SCHAFFNER and F. KRUMEY (Z. physiol. Chem., 1936, **243**, 149—165).—Although the action of  $\alpha$ -glycerophosphatase, phosphatase from top yeast, and phosphatases exhibiting optimal effects at  $p_H$  9 and 7, respectively, is inhibited by  $AsO_4'''$  and that of pyrophosphatase is unaffected, the dephosphorylation of hexose diphosphate (I) by crude yeast maceration juice is very greatly accelerated. Since dephosphorylation of phosphopyruvic acid (II) by the juice is greatly accelerated by added adenylic acid (III), it is possible that an early stage in fermentation consists in interaction of (II) and (III) to give adenosinetriphosphoric acid (IV) and  $AcCO_2H$ .  $AsO_4'''$  accelerates the dephosphorylation of (IV) by the juice. The phosphatase exhibiting optimal action at  $p_H$  7 does not attack (IV).  $AsO_4'''$  inhibits phosphorylation by (I) and (IV). If sufficient org.  $PO_4'''$  is present fermentation can proceed without the consumption of inorg.  $PO_4'''$ , (II) from (I) reacting as described and (IV) with glucose yield-



ing (I) and (III) so that a closed system, capable of acting for a long time, is formed. W. McC.

**Glucosidases of *Schizosaccharomyces*.** E. HOFMANN (Biochem. Z., 1936, 287, 271—275; cf. this vol., 1024).—*S. octosporus*, *S. Pombe*, and *S. mellacci* contain maltase and  $\alpha$ -methylglucosidase both exhibiting optimal activity at  $p_H$  4.5. Invertase is also present and hydrolyses raffinose to fructose and melibiose (I) but does not attack (I). W. McC.

**Fermentation of phosphogluconic acid.** F. LIPMANN (Nature, 1936, 138, 588—589).—Curves for the aerobic and anaerobic fermentation of phosphogluconic acid (in yeast macerate) show that in absence of  $O_2$  the formation of  $CO_2$  is slow. Behaviour in presence of  $CH_3Br \cdot CO_2$  (I) suggests that a primary oxidation and decarboxylation, unaffected by (I), is followed by a reaction which may be of an enzymic nature. Fluoride inhibits  $O_2$  absorption and  $CO_2$  formation more strongly than (I). L. S. T.

**Importance of "pantothenic acid" in fermentation, respiration, and glycogen storage.** R. J. WILLIAMS, W. A. MOSHER, and E. ROHRMAN (Biochem. J., 1936, 30, 2036—2039).—Yeast having an extremely low pantothenic acid (I) content (2% of the normal amount) is almost lacking in fermenting power but fermentation is increased on adding a minute amount of (I). Aerobic respiration is also very low and is only slightly increased when (I) is added after the yeast is grown. Yeast grown with a good supply of (I) respire much more rapidly than does the deficient yeast. Most samples of maltose (II) contain (I), which is removed completely only by electrolytic transport. The promotion of glycogen storage in yeast by (II) (McAnally and MacLean, A., 1935, 1164) is due to the (I) content. (I) thus plays a fundamental rôle in carbohydrate anabolism and catabolism whether the latter is aerobic or anaerobic. P. W. C.

**Effect of  $\alpha$ -keto-acids other than pyruvic acid on the synthesis of amino-acids by yeast.** C. FROMAGEOT and G. MINARD (Bull. Soc. Chim. biol., 1936, 18, 1454—1466).— $\alpha$ -Keto-acids (e.g.,  $COPr^a \cdot CO_2H$  and  $CHMeEt \cdot CO \cdot CO_2H$ ) capable of decarboxylation by decarboxylase, when added to sucrose solutions undergoing fermentation by yeast, are converted into alanine (I). Addition of  $COBu^v \cdot CO_2H$  does not increase the yield of (I). A. L.

**Thermal analysis and action on fermentation of mixtures of antiseptics.** A. MOSSINI (Boll. Chim. farm., 1936, 75, 493—494).—Mixtures of Me or Pr *p*-hydroxybenzoate with camphor (I) have eutectic points at 59.9° [70% of (I)] and 32° [60% of (I)], respectively. The respective actions on yeast fermentation, however, are additive with respect to those of the components. F. O. H.

**Increase of diamagnetic susceptibility on the death of living cells.** E. BAUER and A. RASKIN (Nature, 1936, 138, 801).—The increase observed in the case of yeast and *B. coli* and *B. proteus* supports the theory that the lack of equilibrium in living systems is due to an excited state of protein mols. of the protoplasm. Denaturation of native protein does not affect magnetic susceptibility. L. S. T.

**Strains of yeast which produce alcoholic fermentation at low temperatures.** B. PORCHET (Mitt. Lebensm. Hyg., 1936, 27, 42—45).—Yeasts responsible for the spontaneous fermentation of grape musts and apple juice at  $-3^\circ$  to  $0^\circ$  are indistinguishable morphologically from other forms of *S. ellipsoideus*; they form white colonies with irregular edges and a central crater on gelatin at room temp., without producing liquefaction. They develop a fine bouquet and are suitable for wine and cider production, being superior to ordinary yeasts in fermentations at  $6^\circ$ . J. G.

**Gum and glycogen of yeast.** F. STOCKHAUSEN and K. SILBEREISEN (Biochem. Z., 1936, 287, 276—286).—The amounts of the gum in brewer's, wine, and baker's yeast are respectively 4—6, 7.5—8.5, and up to 13%. The glycogen and gum of yeast exist as such in the cells and are not produced by the action of the hot 65% KOH solution used in extraction. W. McC.

**Determination of hexoses by fermentation.**—See this vol., 1490.

**Formation of oxalic and citric acids by fungi.** V. S. BUTKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 427—430).—Polemical against Chrzaszcz *et al.* (A., 1935, 254; this vol., 1026, 1027). E. A. H. R.

**Pharmacodynamic action of iron in general metabolism.** O. KAUFFMANN-COSLA and R. BRÜLL (Bull. Soc. Chim. biol., 1936, 18, 1493—1502).—The monose content of *Aspergillus niger* grown in media containing no Fe is  $>$  normal. The cellulose content is normal, but the lipin content  $<$  normal. Fe is therefore necessary for normal carbohydrate and lipin synthesis. A. L.

**Assimilation of nitrites by fungi. III.** Y. WANG (J. Agric. Chem. Soc. Japan, 1936, 12, 877—884).—Assimilation of  $NO_2^- \cdot N$  by various species of *Aspergillus* does not depend on the previous mode of culture of the fungus but is largely conditioned by the nature of the sources of C. W. O. K.

**Production of acids from sugar by *Aspergillus niger*. VII. Importance of nitrogen source for citric acid production.** K. BERNHAUER and A. IGLAUER (Biochem. Z., 1936, 287, 153—166; cf. A., 1936, 1026).—Citric acid (I) production by *A. niger* is optimal when the N concn. of the medium is 0.07—0.875%. The rate of (I) production and the amount of (I) produced vary with the N source employed, the highest rate and yield (80—90%) being obtained with  $NH_4NO_3$  and  $Mg(NO_3)_2$  and sugar concn. 17.5—20%. (I) production with  $NH_4NO_3$  as N source is very greatly accelerated by addition of  $MgCl_2$ , especially when the sugar concn. is high. The yield and rate of production of (I) are affected by the purity of the sugar used. W. McC.

**Production of citric acid from lactic acid and from alcohol.** T. CHRZASZCZ and K. LEONHARD (Biochem. J., 1936, 30, 1947—1952).—On media containing  $CaCO_3$  *Botrytis cinerea* partially converted Ca and  $NH_4$  lactates into citric acid (I),  $H_2C_2O_4$  (II), and  $CO_2$  with small amounts of malic acid (III), fumaric acid (IV),  $AcOH$ ,  $EtCO_2H$  (V),  $AcCO_2H$

(VI), and MeCHO. Without  $\text{CaCO}_3$ , the utilisation of  $\text{NH}_4$  lactate was greater but (II) was not obtained. On a medium containing  $\text{CaCO}_3$ , EtOH was utilised yielding (I), (III),  $\text{HCO}_2\text{H}$ , AcOH, (II), and  $\text{CO}_2$ . Lactic acid (VII) is first converted into (VI) which is decarboxylated to MeCHO. This is either oxidised to AcOH or with a mol. of (VII) undergoes dismutation into (V) + AcOH. The AcOH formed is converted *via* succinic acid, (IV), and (III) into (I) or is oxidised *via*  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , (II), and  $\text{HCO}_2\text{H}$  to  $\text{CO}_2 + \text{H}_2\text{O}$ . In older cultures the (I) formed possibly also undergoes decomp. P. W. C.

**Production of acids by *Rhizopus*.** I. Production of malic acid in fumaric acid fermentation. K. BERNHAUER and H. THOLE (Biochem. Z., 1936, 287, 167—171).—The variation in the yield of fumaric acid (I) produced from glucose in presence of  $\text{CaCO}_3$  by strains of *Rhizopus* is due to the conversion of (I) into malic acid, the amount of which continues to increase while that of (I) after reaching a max. is decreasing. W. McC.

Low concentrations of deuterium oxide and the growth of marine diatoms. D. L. FOX, E. E. CURP, and G. F. McEWEN (Proc. Soc. Exp. Biol. Med., 1936, 34, 575—581).—The growth rate of *Nitzschia bilobata* shows a tendency to lag in dil.  $\text{D}_2\text{O}$ .

P. G. M.

**Detection of hormones in unicellular animals.** I. Choline and acetylcholine in *Paramecium*. II. Adrenaline in *Paramecium*. G. BAYER and T. WENSE (Pflüger's Arch., 1936, 237, 417—422, 651—654).—I. Choline was demonstrated in *Paramecium* by the effect of a Ringer extract of the organism on the eserinated dorsal muscles of the leech, the effect being considerably increased on acetylation. The presence of acetylcholine (I) in the original extract was also shown. *Paramecium* contains less (I) at low temp. at which the esterase is more active.

II. Adrenaline was demonstrated in *Paramecium*.

M. A. B.

**Isolation of *Glaucoma ficaria*, Kahl, in bacteria-free cultures: growth in relation to the  $p_{\text{H}}$  of the medium.** D. F. JOHNSON (Arch. Protistenk., 1935, 86, 262—277).—The growth range of *G. ficaria* is  $p_{\text{H}}$  4.9—9.5 and that of *G. piriformis*, 4.0—8.9. The latter has the lower  $p_{\text{H}}$  optimum.

A. G. P.

**Physiology of euglenoid flagellates.** V. Effect of certain carbohydrates on growth of *Euglena gracilis*, Klebs. VI. Effects of temperature and of acetate on *E. gracilis* cultures in the dark. VII. Effects of salts of certain organic acids on growth of *E. gracilis*. T. L. JAHN (Arch. Protistenk., 1935, 86, 238—250, 251—257, 258—262).—V. Transference of *E. gracilis* from an inorg. medium to one to which carbohydrates are added may result in encystment or modification of the rate of division. Effects vary with the carbohydrate used and probably also with the physiological condition of the stock, with temp., light intensity, and  $p_{\text{H}}$ .

VI. Addition of NaOAc to peptone media increased the rate of division and raised the optimum growth temp.

VII. In daylight the rate of division was accelerated by addition to media of  $\text{PrCO}_2\text{Na}$  (I), NaOAc,  $\text{Na}_2\text{C}_2\text{O}_4$ , and Na lactate (II) (in descending order), unaffected by NaCl,  $\text{HCO}_2\text{Na}$ , Na tartrate and citrate, and retarded by Na succinate (III). In darkness, the order of acceleration was (I) > NaOAc > (II) > (III) and  $\text{HCO}_2\text{Na}$  caused some deceleration. A. G. P.

**Oxidation-reduction potential of protozoan cultures.** II. Reduction potential of cultures of *Chilomonas paramecium*. T. L. JAHN (Arch. Protistenk., 1935, 86, 225—237; cf. A., 1934, 329).—Changes in the  $E_h$  of cultures in different media are determined by means of special apparatus described. These changes are largely attributable to removal of  $\text{O}_2$  from the medium during growth although the possibility of the production of reducing substances by the organism is not eliminated. Variations in  $E_h$  may be a causative factor in allelocatalysis.

A. G. P.

**Utilisation of sugars by *Leishmania tropica*.** A. DuBOIS (Compt. rend. Soc. Biol., 1936, 123, 141—144).—Carbohydrates most readily utilised include glucose, fructose, mannose, galactose, sucrose, inulin, and glycerol.

H. G. R.

**Resistance of Leishman-Donovan bodies to various physical, chemical, and biological agents.** I. Physical agents. H. L. CHUNG (Chinese Med. J., 1936, 50, 1039—1050).—Leishman-Donovan bodies were tested for viability (by injection into hamsters) after various treatments. The bodies were resistant to X-rays, to temp. of 40—43° for 30 min., and to -25° for 48 hr., but succumbed to drying for 1½ hr.

G. H. B.

**Metabolism of bacteria in exhausted media and media containing vaccines.** A. DAMBOVICANU and H. ROTH (Compt. rend. Soc. Biol., 1936, 123, 61—63).—Cessation of growth of streptococci in a liquid medium is due to consumption of the sugar, no evidence being obtained of the production of inhibiting substances.

H. G. R.

**Physiology of *Rhizobium*.** VI. Accessory factors. D. W. THORNE and R. H. WALKER (Soil Sci., 1936, 42, 231—240; cf. this vol., 114).—Small quantities of Fe added to a  $\text{NO}_3^-$ -sucrose medium increased the growth of *R. trifolii* and *R. meliloti*,  $\text{Fe}^{+++}$  being more active than  $\text{Fe}^{++}$ . Repeated subculturing in mineral salt-sucrose media with  $\text{KNO}_3$  as N source led to growth failure, but with  $\text{NH}_4\text{Cl}$  or asparagine full activity was retained. Growth and  $\text{O}_2$  consumption in highly purified media may be improved by addition of cysteine or thioglycollic acid. The organisms do not require any complex or unidentified substances for growth, although many substances have stimulatory effects.

A. G. P.

**Association of characters among dissociates from *Staphylococcus aureus*.** M. DOUDOROFF (Proc. Soc. Exp. Biol. Med., 1936, 34, 216—217).—In the dissociates relatively high power to produce haemolysin, to liquefy gelatin, and to produce fibrinolysin are each associated with relatively low production of orange pigment and relatively high production of white pigment. The violet reaction and the



production of coagulase apparently remain const. despite variations in the amount of pigment produced.

W. McC.

Relation of so-called *Streptococcus apis* to certain lactic acid streptococci. J. G. DAVIS and H. L. A. TARR (Nature, 1936, 138, 763).—The two kinds of *S. apis* previously reported (this vol., 763) are morphologically, culturally, and biochemically indistinguishable from *S. glycerinaceus* and *S. liquefaciens*.

L. S. T.

Enzymic racemisation of optically active lactic acid. E. L. TATUM, W. H. PETERSON, and E. B. FRED (Biochem. J., 1936, 30, 1892—1897).—Associated growth of *Strep. lactis* or *Lactobacillus delbrückii* with the  $\text{PrCO}_2\text{H}$  organisms *Cl. acetobutylicum* or *Cl. butylicum* leads to the formation of inactive lactic acid (I) due to the racemising action of the latter bacteria. In the absence of lactic acid bacteria, both  $\text{PrCO}_2\text{H}$  organisms partly ferment active (I) and racemise the remainder. Cultures of these  $\text{PrCO}_2\text{H}$  organisms convert either *d*- or *l*-(I) quantitatively into the *dl*-acid in presence of antiseptics. The racemising system consists of extracellular heat-labile (10 min. at  $87^\circ$ ) and intracellular heat-stable components. Neither cell suspensions nor cell-free media of *Cl. butylicum* can racemise active (I) but the two are effective in combination.

P. W. C.

Butyl alcohol and acetone fermentations. II. Intermediate products of the butyl alcohol-acetone fermentation. K. BERNHAUER, A. IGLAUER, W. GROAG, and R. KÖRTIG (Biochem. Z., 1936, 287, 61—64).—Further experiments (cf. A., 1935, 1541) on the intermediate products of this fermentation are described. When the fermentations are carried out in presence of  $\text{CaCO}_3$ ,  $\text{PrCHO}$  gives 80% yields of  $\text{Bu}^\circ\text{OH}$ , whilst crotonic acid gives 66—80% and  $\text{AcCO}_2\text{H}$  and lactic acid 70% yields of  $\text{AcOH}$ . In each case considerably more Bu products ( $\text{PrCO}_2\text{H}$ ,  $\text{BuOH}$ ) and correspondingly less  $\text{COMe}_2$  products ( $\text{COMe}_2$ ,  $\text{AcOH}$ ,  $\text{EtOH}$ ) are obtained in the absence than in the presence of  $\text{CaCO}_3$ .

P. W. C.

Metabolism of strict anaerobes (genus *Clostridium*). V. Coupled reactions between pairs of amino-acids induced by *Cl. sporogenes*. D. D. WOODS (Biochem. J., 1936, 30, 1934—1946).—In the linked oxidation and reduction of pairs of  $\text{NH}_2$ -acids by washed cells of *Cl. sporogenes l*-cysteine (I) can act as a H donor and also is partly deaminated in the absence of other acids. Glycollic acid,  $\beta$ -alanine, and taurine are not attacked, whilst *d*-ornithine (II) and *d*-arginine (III) are both activated as H acceptors and partly deaminated in the absence of H donors. When (II) reacts with alanine, it accepts 2 H and undergoes reductive deamination to  $\delta$ -aminovaleric acid. Simple  $\text{NH}_2$ -acids (with the exception of glycine) appear to act only as H donors. When there is another substituent group in the chain in addition to the  $\alpha$ - $\text{NH}_2$ , the acids are broken down in the absence of other  $\text{NH}_2$ -acids. If this extra group is not  $\text{NH}_2$  [(I), serine] the substance also acts as a H donor but if it is or contains  $\text{NH}_2$  [(II), (III)] the substance also acts as a H acceptor (cf. A., 1935, 537, 664).

P. W. C.

Mechanism of oxidation processes. XLV. Anaerobic fermentation of fumaric acid. H. WIELAND, M. CRAWFORD, and H. WALCH. XLVI. Anaerobic fermentation of citric acid. R. SONDERHOFF and M. DEFFNER (Annalen, 1936, 525, 119—131, 132—138; cf. this vol., 893).—XLV. Cultures of bacteria occurring in certain impoverished yeasts, if < 24 hr. old, or yeasts containing them, change Na fumarate (I) anaerobically into  $(\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  (II) 0.5,  $\text{CO}_2$  0.7—0.75,  $\text{EtOH}$  0.1,  $\text{AcOH}$  0.4, and  $\text{HCO}_2\text{H}$  0.2 mol. The primary reaction is  $(\text{I}) + \text{H}_2\text{O} \rightarrow \text{malic acid (III)}$ ;  $(\text{III}) + (\text{I}) \rightarrow (\text{II}) + \text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (IV);  $(\text{IV}) \rightarrow \text{CO}_2 + \text{AcCO}_2\text{H} \rightarrow \text{CO}_2 + \text{MeCHO}$ ;  $2\text{MeCHO} \rightarrow \text{EtOH} + \text{AcOH}$ . This is, however, complicated by the side reactions,  $(\text{IV}) \rightarrow \text{HCO}_2\text{H} + \text{CH}_2(\text{CO}_2\text{H})_2$ , and  $\text{AcCO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{AcOH} + \text{HCO}_2\text{H}$ , both of which are caused by the bacteria in neutral solution. This is confirmed by the rapid anaerobic production of (II),  $\text{CO}_2$ ,  $\text{EtOH}$ ,  $\text{AcOH}$ , and  $\text{HCO}_2\text{H}$  from *l*-(—)-(III) by the bacteria; *dl*-(III) is less quickly fermented, owing to the slower reaction of the *d*-form (which accumulates in the solution), and to its negative catalytic effect on fermentation of the *l*-form. The bacteria also ferment (IV) anaerobically, giving 25% of (II), the reaction being  $(\text{IV}) + \text{CHMe}(\text{OH})_2 \rightarrow \text{AcOH} + (\text{III})$ , etc. Formation of  $\text{HCO}_2\text{H}$  and  $\text{H}_2\text{C}_2\text{O}_4$  during various fermentations probably occurs by way of (IV). Sterile yeast does not act on (I).

XLVI. The anaerobic fermentation of citric acid (V) by yeast is due to bacteria (cf. A., 1933, 865; 1935, 1539), similar to those described above. The presence of aq. yeast extract is necessary for the production of much  $\text{H}_2$ . Sterile yeast, however, produces (V) and (II) from  $\text{Ba}(\text{OAc})_2$  and ferments (V) anaerobically.

R. S. C.

Aerobic breakdown of glucose by *Bact. suboxydans*. K. R. BUTLIN (Biochem. J., 1936, 30, 1870—1877).—Washed suspensions of *B. suboxydans* from maize wort-agar without  $\text{CaCO}_3$  are dirty white and oxidise glucose (I) at  $p_H$  5.5 but only to gluconic acid (II) and give no  $\text{CO}_2$ . Similar suspensions from wort-agar containing  $\text{CaCO}_3$  are pink, give a much larger and more rapid  $\text{O}_2$  uptake with (I), oxidising (I) to (II) and then probably to 5-ketogluconic acid; the  $\text{CO}_2$  evolved equals the  $\text{O}_2$  absorbed. No synthesis of hexose phosphates by suspensions or air-dried or  $\text{COMe}_2$  preps. of either type was detected but cultures obtained on media containing  $\text{CaCO}_3$  had a much greater capacity for hydrolysing Na hexose diphosphate than the corresponding preps. without  $\text{CaCO}_3$ . The modification in enzymic properties by  $\text{CaCO}_3$  is a temporary variation.

P. W. C.

Growth factors for bacteria. V. Vitamin- $B_{11}$ , a growth stimulant for propionic acid bacteria. E. L. TATUM, H. G. WOOD, and W. H. PETERSON (Biochem. J., 1936, 30, 1898—1904).—The stimulating action of protein hydrolysates on acid production by  $\text{EtCO}_2\text{H}$  bacteria is partly due to a factor which can be separated from unhydrolysed caseinogen, ovalbumin, yeast extract, and milk powder by extraction with  $\text{COMe}_2$  or  $\text{EtOH}$  and is active in a concn. of  $0.15 \times 10^{-6}$  g. per mol. The factor is most active in presence of  $\text{NH}_2$ -acids, and is not replaced by

inositol, panthothenic acid, ascorbic acid, hepato-flavin, nicotinamide, or indolylacetic acid, but is replaceable by  $0.5 \times 10^{-3}$  g. of cryst. vitamin- $B_1$  per 100 ml.

P. W. C.

Effect of sulphur compounds on the fermentation of glucose by propionic bacteria. P. CHAIX and C. FROMAGEOT (Bull. Soc. Chim. biol., 1936, 18, 1436—1453; cf. this vol., 760).—The max. stimulating action of S compounds on the fermenting activity of propionic bacteria is obtained with  $>0.1$  mg. of S per 5 c.c. and is dependent on  $p_H$ . Ascorbic acid, glycine, and alanine have no activating effect.

A. L.

Combined action of succinodehydrogenase and aspartase in *Bacterium coli*. M. MICHAELIS (Z. physiol. Chem., 1936, 243, I).—The no. of cu. mm. of  $H_2$  transferred from 1 mg. of dry *B. coli* to methylene-blue in 1 hr. at  $p_H$  7.6 is increased from 2.5 to 7.3 by addition of 0.1N-Na succinate (I) and to 10.0 by addition of (I) +  $M-(NH_4)_2SO_4$ . The acceleration occurs because the rate of production of fumarate (II) from (I) by succinodehydrogenase is  $<$  the rate of conversion of (II) +  $NH_3$  into aspartic acid by aspartase.

W. McC.

Fermentation of pyruvic acid by *colon-aerogenes* bacteria. M. MICKELSON, H. REYNOLDS, and C. H. WERKMAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 748—750).—*Escherichia coli* and *Citrobacter freundii* decompose  $AcCO_2H$  by a similar mechanism,  $AcOH$  being largely produced along with lactic acid,  $HCO_2H$ ,  $CO_2$ , and  $H_2$ . *Aerobacter indologenes* can also reduce the  $AcOH$  to  $(\cdot CHMe \cdot OH)_2$ .

P. G. M.

Hydrogen donators for *B. prodigiosus*. D. BACH and J. LAMBERT (Compt. rend. Soc. Biol., 1936, 123, 358—361).—Of 128 org. substances examined 94 were donators.

H. G. R.

Biology of the *pullorum-gallinarum* group. Differentiation of types of *pullorum* by maltose fermentation. C. RODRIGUES and G. PACHECO (Compt. rend. Soc. Biol., 1936, 123, 438—440).—The maltose of normal serum, if used in the medium, will vitiate results.

H. G. R.

Hydrogen donators for Friedlander's pneumobacillus. D. BACH and J. LAMBERT (Compt. rend. Soc. Biol., 1936, 123, 361—364).—Of 125 substances examined 68 were active.

H. G. R.

Soluble specific substances of pneumococcus type III possessing properties distinct from SSS III. G. J. P. HORNUS and J. F. ENDERS (Proc. Soc. Exp. Biol. Med., 1936, 34, 102—104).—A carbohydrate, isolated from type III pneumococcus by a method which avoids the use as far as possible of strong acid, reacts with type III antipneumococcus serum but is different from the sol. sp. substance III of Heidelberger *et al.* (cf. A., 1926, 545).

W. O. K.

Ultrafiltration in the concentration and purification of pneumococcus specific polysaccharides. R. BROWN (Proc. Soc. Exp. Biol. Med., 1936, 34, 832—833).—A 16 hr. culture of pneumococcus (type VII) was centrifuged and the fluid ultrafiltered and washed on a 4% cellulose nitrate

membrane. 100-fold concn. resulted, with removal of 98.26% of the N. An initial concn. with aq.  $(NH_4)_2SO_4$ , prior to ultrafiltration, is also useful.

P. G. M.

Ash of bacteria (*Vibrio cholerae*). A. DAMBOVICANU and C. VASILESCO (Compt. rend. Soc. Biol., 1936, 123, 65—68).—The ash of *V. cholerae* is considerably influenced by the mineral content of the medium, particularly when the normal ash content of the organism is low.

H. G. R.

Ash of bacteria (*Vibrio cholerae*). C. BARBER (Compt. rend. Soc. Biol., 1936, 123, 64—65).—Species with a high ash content generally contain more K, Na, and P and less Ca than those with a low ash. In all species Ca is low compared with other bacteria.

H. G. R.

Carotenoids of purple bacteria. III. P. KARRER and U. SOLMISSEN (Helv. Chim. Acta, 1936, 19, 1019—1024; cf. this vol., 248, 340).—Further examination of the *Rhodovibrio* carotenoids shows that rhodopin contains probably 1 OH and 12 double linkings. In accordance with its position in the chromatogram rhodovibrin is a polyene alcohol. Rhodoviolasene,  $C_{42}H_{60}O_2$ , contains 2 OMe, 13 double linkings, and  $>1$  Pr<sup>2</sup>; it is probably  $OMe_2 \cdot CH \cdot C(OMe) \cdot CH \cdot CMe \cdot [CH \cdot CH \cdot CH \cdot CMe]_2 \cdot CH \cdot CH \cdot [CH \cdot CH \cdot CMe \cdot CH]_2 \cdot CH \cdot CH \cdot C(OMe) \cdot CH_2 \cdot CHBn^2 \cdot OMe$ . Rhodopurpurene is a hydrocarbon resembling lycopene spectroscopically, but its identity therewith is doubtful. The presence of  $\beta$ -carotene is occasionally observed. Flavorhodin is probably a hydrocarbon but certainly not a polyene with free OH.

H. W.

Pigment of *B. violaceus*. II. Pyrrolic nucleus of violacein. W. C. TOBIE (Proc. Soc. Exp. Biol. Med., 1936, 34, 620—622).—Violacein contains C 69.28, H 6.79, O 16.45, N 4.83, and ash 2.65%. The ash contains Fe. The mol. contains one or more pyrrole nuclei, probably with hydrocarbon side-chains. It is sol. in  $Et_2O$  and light petroleum, but insol. in EtOH, and is similar to the pigment of *B. prodigiosus*.

P. G. M.

Chemical composition of *B. tumefaciens*. E. CHARGAFF and M. LEVINE (Proc. Soc. Exp. Biol. Med., 1936, 34, 675—677).—The  $COMe_2$ -sol. fat has I val. 95.0, sap. val. 201.2, acid val. 53.2, ester val. 148.0; it contains 9% of non-saponifiable matter, 10% of which consists of a sterol mixture. The phosphatide has N 2.2, P 3.4%; it stimulates growth. The defatted bacteria contain 3.5% of a polysaccharide.

P. G. M.

Polysaccharides of *Amylobacter* strains. H. MEISEL (Compt. rend. Soc. Biol., 1936, 123, 173—176).—The polysaccharide obtained by acid extraction in some cases gives protein reactions depending on the medium in which the organism is grown.

H. G. R.

Sonic extraction of labile bacterial constituents. L. A. CHAMBERS and E. W. FLOSDORF (Proc. Soc. Exp. Biol. Med., 1936, 34, 631—636).—Suspensions of *Eberthella typhi* and *S. haemolyticus*, after subjection at  $<15^\circ$  to intense magnetic vibrations of 8900 cycles per sec., yield supernatant fluids on centrifuging which will combine with the antibody



responsible for phagocytosis. These antigens lose their activity in 3 days at 2–4°, but may be stored after rapid drying from the frozen state. P. G. M.

**Properties of different streptococcal fibrinolysins.** E. WITEBSKY and E. NETER (Proc. Soc. Exp. Biol. Med., 1936, **34**, 858–863).—Human hæmolytic streptococci tested for lysin formation in 0.05 and 2.0% glucose broth may fall into one of four groups: (1) production in 2% only, (2) in 0.05% only, (3) in both, (4) in neither. *S. viridans* behaves similarly to *S. hæmolyticus*, which produces lysin in 2% broth. P. G. M.

**Preparation of a soluble dysentery toxin by grinding and extraction of the bacteria.** A. HANSEN (Biochem. Z., 1936, **287**, 35–39).—A method is described for the prep. from the finely ground dysentery bacilli (Shiga) by adsorption on  $\text{Al}(\text{OH})_3$ , elution, and pptn. of a readily sol. toxin in purified condition. The  $\text{CH}_2\text{O}$  toxoid prep. therefrom possesses strong immunising power. P. W. C.

**Phytochemical reduction with *Thermobacterium mobile* (*Pseudomonas Lindneri*).** W. M. CAHILL (Fermentforsch., 1936, **15**, 134–137).—Phytochemical reduction of  $\text{Bu}^n\text{CHO}$  by *P. Lindneri* gives  $\text{C}_5\text{H}_{11}\cdot\text{OH}$ , and that of  $\text{COAc}$ , by yeast gives  $\text{OH}\cdot\text{CMe}(\text{CHMe}\cdot\text{OH})_2$ . E. A. H. R.

**Precipitating action of basic dyes on bacteriophage and bacterial proteolytic enzymes.** A. W. WALKER (Proc. Soc. Exp. Biol. Med., 1936, **34**, 726–728).—*B. coli* bacteriophage and the proteolytic enzymes of *B. pyocyaneus* are completely pptd. by azine and thiazine dyes, but not by oxazines, xanthanes, or  $\text{CHPh}_3$  dyes. P. G. M.

**Variation in animal viruses.** G. M. FINDLAY (J. Roy. Microscop. Soc., 1936, [iii], **56**, 213–299).—A comprehensive review.

**Tobacco-mosaic virus. VII. Preparation of crystalline tobacco-mosaic virus protein.** W. M. STANLEY (J. Biol. Chem., 1936, **115**, 673–678; cf. this vol., 1156).—A method for the prep. of the cryst. protein by fractional pptn. with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaO}$ , etc. is described. The yield from crude globulin preps. is approx. 80%. F. O. H.

**Sedimentation and electrophoresis of the tobacco-mosaic virus protein.** I. B. ERIKSSON-QUENSEL and T. SVEDBERG (J. Amer. Chem. Soc., 1936, **58**, 1863–1867).—Mol. wt. determinations by sedimentation methods indicate that the protein (I) (Stanley, A., 1935, 1181) is not homogeneous; at  $p_H$  6.8 about 65% has  $M$  15–20  $\times 10^6$  provided the dissymmetry const. is the same as for other proteins of high mol. wt. (I) is more polydisperse at  $p_H >$  or  $<$  6.8. Electrophoresis measurements indicate that (I) is practically homogeneous; the isoelectric point is  $p_H$  3.49. H. B.

**Nature of factor-V.** A. Lvov and M. Lvov (Compt. rend., 1936, **203**, 520–522).—Factor-V (I), a principle promoting bacterial growth, is pptd. by  $\text{EtOH}$  and  $\text{Pb}(\text{OAc})_2$  at  $p_H$  9.5 but not by  $\text{Pb}(\text{OAc})_2$  at  $p_H$  6.8 or  $\text{Hg}(\text{NO}_3)_2$  at  $p_H$  7.0, and resists desiccation in a vac. These and biological properties indicate similarity to or identity with the codehydrogenases

(Warburg-Christian co-enzyme and Harden-Young cozymase). F. O. H.

**Activation of silver by acids.** F. LIEB (Arch. Hyg. Bakt., 1936, **116**, 317–320).—The oligodynamic activation of Ag can be promoted only by acids which form insol. or slightly sol. Ag salts, e.g.,  $\text{HCl}$ ,  $\text{H}_2\text{CrO}_4$ . W. L. D.

**Bactericidal power of metals (zinc).** A. BERNI and G. RISTIVO (Boll. sez. Ital., 1936, **8**, 123–125).—Strips of various metals were immersed in nutrient agar and various organisms grown in the agar. Halos free from growth appeared around strips of Fe, Cu, Zn, and Mg but not around Au, Ag, Pb, Sn, Al, or Ni. Zn as sheet, powder, or in solution after contact with distilled  $\text{H}_2\text{O}$  for 24 hr. was toxic to *B. coli*. The decreasing order of toxicity to bacteria of metals is: Zn, Cu, Ag, Mg. Other metals are inactive. W. L. D.

**Bactericidal power of the stomach: some influential factors.** A. HANSZEN (Amer. J. Digest. Dis. Nutrition, 1934, **1**, 723–727).—The bactericidal power of the stomach is increased by feeding 1 hr. prior to ingestion of infected fluids. Foods of high buffer power retain and subsequently release acid. To ensure effective bactericidal action the  $p_H$  of the stomach contents should reach  $>2$ . CH. ABS. (p)

**Properties acquired by plant extracts after inoculation with bacteria or toxins pathogenic to animals.** T. FRÉMONT (Compt. rend. Soc. Biol., 1936, **123**, 418–420).—The development of antibodies increases or decreases the virulence of the bacteria when injected, depending on whether they are lytic or coagulating. H. G. R.

**Bactericidal action of sea-water.** C. E. ZOBELL (Proc. Soc. Exp. Biol. Med., 1936, **34**, 113–116).—Although fresh- $\text{H}_2\text{O}$  bacteria may be acclimatised to grow in sea- $\text{H}_2\text{O}$  unacclimatised strains as well as sewage and other bacteria are killed by natural, autoclaved, and Berkefeld-filtered sea- $\text{H}_2\text{O}$ . Sea- $\text{H}_2\text{O}$  probably contains a bactericidal agent, other than salts. Its potency is diminished by autoclaving and by addition of org. matter. Survival of sewage bacteria is favoured by water containing 5 and 10% of sea- $\text{H}_2\text{O}$ . W. McC.

**4-n-Alkylpyrogallols.**—See this vol., 1503.

**Cardiac tonus under the influence of adrenaline and acetylcholine.** W. TOMASZEWSKI (Pflüger's Arch., 1936, **237**, 260–272). M. A. B.

**Similarity of action of the adrenal medulla hormone and synthetic adrenaline.** G. KAHNSEN and O. MERTENS (Pflüger's Arch., 1936, **237**, 699–709).—Injection of synthetic adrenaline produced exactly the same effects on blood distribution, mobilisation of the blood reserves, minute-vol., etc. in the dog as did the hormone liberated by stimulation of the secretory nerves of the left adrenal. M. A. B.

**Effect of adrenaline on the activity of the heart.** K. GOLLWITZER-MEIER, K. KRAMER, and E. KRÜGER (Pflüger's Arch., 1935, **237**, 639–650). M. A. B.

**Effect of adrenaline on the blood-vessels in resting and working muscles.** O. MERTENS, H.

REIN, and F. G. VALDECASAS (Pflüger's Arch., 1935, 237, 454—475).  
M. A. B.

Weight changes following the use of glycerol extract of adrenal cortex. R. G. HOSKINS and H. FREEMAN (Endocrinol., 1936, 20, 565—566).  
R. N. C.

Influence of adrenaline and cortin on oxidised and reduced glutathione in the blood. E. ZUNZ and O. VESSELOVSKY (Compt. rend. Soc. Biol., 1936, 123, 114—116).—Intravenous injection of adrenaline or cortin increases the reduced and total glutathione in the red cells.  
H. G. R.

Adrenaline hyperglycæmia and variations in bile-sugar. G. BALTACEANO, C. VASILIU, and T. BUDEANU (Compt. rend. Soc. Biol., 1936, 123, 56—58).—Parallel with the increase in blood-sugar there is an increase in both free and protein-sugar in the bile.  
H. G. R.

Fat absorption after adrenalectomy. F. VERZAR and L. JEKER (Pflüger's Arch., 1936, 237, 14—18). Adrenalectomised rats showed no synthesis of neutral fat in the cells of the intestine although penetration of free fatty acids was not inhibited. Injection of adrenal cortical hormone restored normal fat synthesis.  
M. A. B.

Potassium in adrenal deficiency. C. I. URECHIA, G. BENETATO, and RETEZEANU (Compt. rend. Soc. Biol., 1936, 123, 197—200).—After adrenalectomy, K is diminished in the kidney, spleen, muscles, heart, and liver and increased in the brain of the frog.  
H. G. R.

Glucose absorption and glycogen production in the hypophysectomised rat. L. L. BENNETT (Proc. Soc. Exp. Biol. Med., 1936, 34, 277—279).—In hypophysectomised rats the rate of absorption of glucose (I) is about 35% < that in normal rats, the glycogen (II) contents of the liver and muscle are abnormally low, and the increase in the (II) contents following consumption of (I) is < that in normal rats.  
W. McC.

Carbohydrate levels in fasted and fed hypophysectomised rats. J. A. RUSSELL (Proc. Soc. Exp. Biol. Med., 1936, 34, 279—281).—Liver- and muscle-glycogen and blood-sugar vals. are normal in fully fed but low in fasted hypophysectomised rats. The low vals. are raised to normal but not maintained by giving carbohydrates.  
W. McC.

Pituitary-thyroid-gonad relationship. S. L. LEONARD (Proc. Soc. Exp. Biol. Med., 1936, 34, 599—600).—Follicle-stimulating hormone from either pituitary or urinary sources is more effective in the absence of the thyroid; the luteinising hormone is unaffected.  
P. G. M.

Relationship of the anterior pituitary gland to thyroid and ovary. L. LOEB, J. SAXTON, and S. J. HAYWARD (Endocrinol., 1936, 20, 511—519).—The anterior pituitary gland of cattle, sheep, and pigs contains a substance, "atresin" (I), that destroys follicles in guinea-pig ovaries. It appears possible to obtain extracts from cattle glands that contain (I) in effective concn. with little or no thyroid-stimulating (II) or luteinising hormone (III). (I), (II), and (III) are usually in association with one another,

but can be separated. (II) is associated with the follicular growth-maturation hormone in some human glands, and is not essential for activation of (III). A method of demonstrating the active substances *in situ* is described.  
R. N. C.

Ovaries after administration of a gonadotropic principle of anterior pituitary. E. C. HANBLEEN (Endocrinol., 1936, 20, 321—328).  
R. N. C.

Fat storage in the liver by treatment with the fat-metabolism hormone of the anterior lobe of the pituitary. K. J. ANSELMINO, F. HOFFMANN, and E. RHODEN (Pflüger's Arch., 1936, 237, 515—516).  
M. A. B.

Action of hormones and of maintenance in the dark on the content of pressor and oxytocic factors in the posterior pituitary gland. A. SIMON (Arch. exp. Path. Pharm., 1936, 182, 584—588).—Administration of pituitary, thyroid, and pituitary thyrotropic extracts and of insulin to guinea-pigs, or keeping the animals in the dark, is without effect.  
F. O. H.

Effect of posterior pituitary extracts on sodium balance in health and in diabetes insipidus. F. M. SMITH and E. M. MACKAY (Proc. Soc. Exp. Biol. Med., 1936, 34, 116—118).—Excretion of Na and Cl was increased and the Na and Cl balance rendered negative without change in urinary vols. by administration of the extract to a healthy subject. In diabetes insipidus the same dose caused no increase in NaCl excretion.  
W. McC.

Sex hormones. J. FREUD (Chem. Weekblad, 1936, 33, 632—637).—A summary of the chemistry and action of the various sex hormones.  
S. C.

Analyses of urine of the chimpanzee for oestrogenic content during various stages of the menstrual cycle. E. ALLEN, A. W. DIDDLE, T. H. BURFORD, and J. H. ELDER (Endocrinol., 1936, 20, 546—549).—The content is max. at the time of max. genital swelling.  
R. N. C.

Extraction of both the gonadotropic and (free or total) oestrogenic hormones from a single urine sample. S. C. FREED and O. HECHTER (Endocrinol., 1936, 20, 396—397; cf. this vol., 902).—The gonadotropic hormone is pptd. from the urine with  $H_2WO_4$  and, after removal of adsorbed oestrin (I), is separated from impurities by fractional pptn. with alkaline aq.  $COMe_2$ . Free (I) is extracted from the urine filtrate by the  $H_2WO_4$  method, whilst combined (I) is liberated by boiling the urine with HCl and neutralising before extraction.  
R. N. C.

Isolation from ovarian tissue of a crystalline substance possessing high oestrogenic properties. R. H. ANDREW and F. FENGER (Endocrinol., 1936, 20, 563—564).—After rapid saponification of the fatty portion of whole ovaries with KOH-EtOH at low temp., the unsaponifiable material is extracted from the dil. solution, and the extract evaporated. Cholesterol is removed by boiling with EtOH and chilling, and other impurities by repeated pptn. with dil. aq. NaOH. Subsequent extraction with  $Et_2O$  and crystallisation from EtOH affords a substance,  $C_{26}H_{41}O_2N$  (?), m.p.  $95.1^\circ$  (uncorr.), mol. wt. 320, active in doses of  $10^{-5}$  mg. in rats.  
R. N. C.



Presence of oestrogenic hormones in the ova and ovaries of fish. A. I. WEISMAN, C. W. COATES, and R. L. MOSES (Endocrinol., 1936, 20, 561—562).—The hormones, if present at all in whitefish ova and herring ovaries, are not in sufficient concn. to produce oestrus in mice. R. N. C.

Oestrin-deprivation theory of menstruation. C. F. FLUHMANN (Endocrinol., 1936, 20, 318—320). R. N. C.

Effect of injection of residual ovarian extracts. H. W. MARLOW (Endocrinol., 1936, 20, 339—341). R. N. C.

Structural changes induced in the anterior pituitary by injections of oestrin. J. M. WOLFE and C. S. CHADWICK (Endocrinol., 1936, 20, 503—510). R. N. C.

Modification of the Frank-Goldberger blood-oestrin test. T. NEUSTAEDTER (Endocrinol., 1936, 20, 639—642). R. N. C.

Tube-locking of ova by oestrogenic substances. R. WHITNEY and H. O. BURDICK (Endocrinol., 1936, 20, 643—647). R. N. C.

Oestrogenic substances of hypertrophied prostatic tissue and urine. J. B. HAMILTON, C. L. DEMING, and E. ALLAN (Proc. Soc. Exp. Biol. Med., 1936, 34, 193—194).—Hypertrophied prostatic tissues and urine from patients of 60—80 years contained no oestrogenic substances before or after prostatectomy. W. McC.

Effect of combined administration of oestrone and progesterone in adult ovariectomised rats. H. SELYE, J. S. L. BROWNE, and J. B. COLLIP (Proc. Soc. Exp. Biol. Med., 1936, 34, 198—200).—In ovariectomised rats the effect of administration of daily doses of 0.03 mg. of oestrone (I) is modified by simultaneous administration of 0.4 mg. of progesterone (II). (I) and (II) together cause mucification of the vaginal epithelium and second-stage progestational proliferation of the uterus, the vaginal effect being modified even in cases in which the uterine effect is unchanged. W. McC.

Epithelial regeneration by the action of the oestrogenic hormone and in avitaminosis-A. W. SCHMIDT (Beitr. Path. Anat. allg. Path., 1935, 96, 129—146; Chem. Zentr., 1936, i, 370).—No relation was apparent between epithelial growth and the level of vitamin-A in rats. A. G. P.

Concentration of gonadotropic substance from pregnancy urine. H. L. FEVOLD and F. L. HISAW (Proc. Soc. Exp. Biol. Med., 1936, 34, 712—714).—Pregnancy urine is extracted with cresol and the hormone is pptd. by addition of 2 vols. of  $\text{COMe}_2$ . The method is more efficient than tannic acid or  $\text{BzOH}$  adsorption. P. G. M.

Water-soluble pregnandiol complex from human pregnancy urine. E. M. VENNING and J. S. L. BROWNE (Proc. Soc. Exp. Biol. Med., 1936, 34, 792—793).—Pregnandiol-glycuronic acid as thin plates, m.p. 268—271° (decomp.), has been isolated from human pregnancy urine (9th month) by extraction with  $\text{BuOH}$ , dissolution of the residue in 0.5*N*- $\text{NaOH}$ , re-extraction with  $\text{BuOH}$ , and crystall-

isation of the residue from  $\text{H}_2\text{O}$  and  $\text{EtOH}$ . The yield is 40—50 mg. per litre. P. G. M.

Relative effectiveness of progestin in hypophysectomised and normal rabbits. S. R. M. REYNOLDS, W. M. FIROR, and W. M. ALLEN (Endocrinol., 1936, 20, 681—682). R. N. C.

Effect of testosterone on the growth of the comb in *Triton cristatus*. W. FLEISCHMANN and S. KANN (Pflüger's Arch., 1936, 237, 517—518). M. A. B.

Effect of testosterone on the mammary gland. H. SELYE, C. S. McEVEN, and J. B. COLLIP (Proc. Soc. Exp. Biol. Med., 1936, 34, 201—203).—Slight development of the mammary tissue and marked secretion of milk are induced in immature male and female rats in presence and absence of the gonad by administration of 0.2 mg. of testosterone benzoate. W. McC.

Presence of an excess of "male" (comb-growth and prostate-stimulating) hormone in virilism and pseudo-hermaphroditism. S. L. SIMPSON, P. DE FREMERY, and A. MACBETH (Endocrinol., 1936, 20, 372). R. N. C.

*cis*- and *trans*-Androstanone-3-carboxylic acid, an oestrus-producing male hormone derivative, and *epicholesterol*.—See this vol., 1506.

Artificial production of oestrogenic substances from sterols.—See this vol., 1505.

Crystalline insulin. VIII. Standardisation by the "area of activity" method. H. KOHL (Arch. exp. Path. Pharm., 1936, 182, 550—559).—Assays in rabbits by determination of the "area of activity" (A., 1934, 223) are applicable only with intravenous injection. The method indicates crystalline insulin to have an activity of approx. 16 international units per mg. F. O. H.

Measurement of insulin action. P. O. GREELEY, H. C. BERGMAN, D. B. TYLER, and D. R. DOURY (Proc. Soc. Exp. Biol. Med., 1936, 34, 121—123).—In order to maintain nearly sugar-free urine and a normal blood-sugar level in depancreatized dogs, 0.0094—0.014 unit of insulin per kg. of body-wt. must be administered. W. McC.

Action of phenylcarbimide on insulin. II. Chemistry of insulin and its phosphate-lowering power. W. E. GAUNT and A. WORMALL (Biochem. J., 1936, 30, 1915—1926; cf. A., 1935, 441).—The inactivation by  $\text{PhNCO}$  (I) and  $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NCO}$  (II) of the hypoglycaemic activity of insulin (III) in rabbits is accompanied by a parallel inactivation of the hypophosphatemic power. Inactivation in both cases appears to be due to interaction with the free  $\text{NH}_2$  groups of (III). (I) does not react, under conditions similar to those maintained in the prep. of phenylcarbamidoprotein derivatives, with the OH of tyrosine, the  $\text{CO}\cdot\text{NH}_2$  of asparagine (IV) and glutamine (V), or the glyoxaline group of histidine (VI) nor is there any significant change in the S·S linking. The SH of cysteine (VII) reacts but (VII) is not present in (III). (I) also reacts with the pyrrolidine group of proline (VIII) and to some extent with the guanidino-group of arginine (IX). The following compounds

were prepared : (I) *derivatives* of (VII), m.p. 139—140° (decomp.), in which both SH and NH<sub>2</sub> are blocked; of  $\alpha$ -thiolpropionic acid, m.p. 140—141° (decomp.); of thiolacetic acid, m.p. 144—146° (decomp.); of (IV), m.p. 163° (decomp.) (*hydantoin*, m.p. 231—233°); of (V), m.p. 161° (decomp.) (*hydantoin*, m.p. 160—161°); (II) *derivatives* of (VIII), m.p. 169° (decomp.); of (VI), m.p. 177—178° (decomp.); of (IV), m.p. 175—176° (decomp.) (*hydantoin*, m.p. 220°); of (V), m.p. 189° (*hydantoin*, m.p. 200—201°). With (IX) mixtures of mono- and di-derivatives were obtained with both (I) and (II). P. W. C.

**Effect of various substances on the action of insulin.** A. M. FISHER and D. A. SCOTT (J. Pharm. Exp. Ther., 1936, 58, 93—104).—The effect of insulin (I) is prolonged by admixture with spermine + Zn or an ox thymus prep. + Zn, the presence of Zn being essential in both cases. Suspensions of (I) containing no potency in solution do not differ in activity from a solution of the same (I). H. G. R.

**Insulin with protamine.** D. A. SCOTT and A. M. FISHER (J. Pharm. Exp. Ther., 1936, 58, 78—92).—The action of insulin (I) is prolonged when administered in conjunction with protamine (prep. from fish testes described), this being further enhanced if traces of Zn are first added to (I), especially when a low-ash prep. is used. A method of assay on rabbits is described. H. G. R.

**Treatment of diabetes mellitus with insoluble insulin compounds.** P. A. GRAY (Endocrinol., 1936, 20, 461—472).—Insulin (I) tannate shows a hypoglycaemic action > that of commercial (I) but approx. equal to that of protamine insulinate. It can control diabetes when administered alone or with (I). Its relative insolubility delays absorption and hence decreases the rate of liberation of free (I). R. N. C.

**Cutaneous absorption of insulin.** R. H. MAJOR (Proc. Soc. Exp. Biol. Med., 1936, 34, 775—778).—Insulin in OH·[CH<sub>2</sub>]<sub>2</sub>·OEt is absorbed through the skin of the rabbit, producing a definite fall in blood-sugar. P. G. M.

**Response of normal and hypophysectomised Rhesus monkeys to insulin.** P. E. SMITH, H. H. TYNDALE, L. DOTTI, and E. T. ENGLE (Proc. Soc. Exp. Biol. Med., 1936, 34, 250—251).—Injection of insulin in doses of 0.0625 unit per kg. reduced the blood-sugar in normal monkeys by 14% and in hypophysectomised monkeys by 35% in 30 min. W. McC.

**Fate of the sugar disappearing under the influence of insulin.** V. VENDEG (Pflüger's Arch., 1936, 237, 683—698).—Insulin causes conversion of sugar into glycogen (I) and then into fat in the liver. The final result may be an increase or decrease of (I) accompanied by a decrease or increase of fat, respectively. More sugar disappears in the former case. Occasionally where the initial fat content of the liver is high, insulin may decrease both (I) and fat. Decrease in fat is due to translocation to the fat depots. M. A. B.

**Diuresis during insulin hypoglycaemia.** V. LE CLERC (Compt. rend. Soc. Biol., 1936, 123, 273—275).—The diuresis, which diminishes and may become

total when the blood-sugar is very low, does not appear to be due to a blockage of H<sub>2</sub>O absorption in the region of the stomach. H. G. R.

**Sensitivity of blood-sugar to insulin after pancreatectomy in dogs.** E. S. PANAYOTOPOULOS (Compt. rend. Soc. Biol., 1936, 123, 403—404).—An abnormal sensitivity was noted during the 48 hr. following the operation. H. G. R.

**Diminution of the hyperpolypeptidaemia, secondary to cellular destruction, by insulin with or without glucose.** O. LAMBRET, J. DRIESSENS, and H. MALATRAY (Compt. rend. Soc. Biol., 1936, 123, 12—13). H. G. R.

**Biologically active calcium of the aqueous humour in hyperparathyroidism and acute and latent tetany.** F. MATHIEU (Compt. rend. Soc. Biol., 1936, 123, 112—114).—Variations in plasma-Ca during hypo- and hyper-parathyroidism are accompanied by corresponding variations in the humour. H. G. R.

**Metabolic effects of human thyroglobulin and its proteolytic cleavage products.** W. T. SALTER and J. LERMAN (J. Clin. Invest., 1935, 14, 691—695).—Clinical assay of the metabolic potency of thyroglobulin (I) in terms of I showed that (I) from "colloid adenomatous" glands and iodised toxic glands, thyroxine (II), peptone from either type of gland, and synthetic racemic glycythyroxine were equiv. All preps. approximated to natural (II) polypeptide when assayed in human myxoedema. Di-iodopeptone produced no effect. CH. Abs. (p)

**Iodine tolerance test for the investigation of thyroid function.** E. M. WATSON (Endocrinol., 1936, 20, 358—362).—The rate of disappearance of I from the blood-stream of patients injected intravenously with Lugol's solution is increased in thyrotoxicosis and reduced in hyperthyroidism. R. N. C.

**Assay of blood and urine for thyrotropic hormone in thyrotoxicosis and myxoedema.** S. HERTZ and E. G. OASTLER (Endocrinol., 1936, 20, 520—525). R. N. C.

**Similarity of the iodine remission in experimental anterior hypophyseal hyperthyroidism, the hyperthyroidism of acromegaly, and that of exophthalmic goitre.** H. B. FRIEDGOOD (Endocrinol., 1936, 20, 526—536).—The depressions of metabolic rate produced by NaI in all three conditions are of the same order. R. N. C.

**Effect of pregnancy on resistance to thyroxine; creatine content of the maternal and foetal myocardium.** M. BODANSKY and V. B. DUFF (Endocrinol., 1936, 20, 537—540).—Tolerance to thyroxine is increased in pregnancy in the rat. Creatine falls in the maternal but not the foetal myocardium in hyperthyroidism. R. N. C.

**Age as a factor in the resistance of rats to thyroxine.** Creatine content of the tissues in experimental hyperthyroidism. M. BODANSKY and V. B. DUFF (Endocrinol., 1936, 20, 541—545).—Resistance to thyroxine is high in immature rats. Myocardial creatine (I) is reduced in young and old



hyperthyroid rats, but young rats withstand greater depletion than do old rats. (I) falls in skeletal muscle and rises in the testes of hyperthyroid rats. Cessation of thyroxine treatment brings ventricular (I) to normal levels in 7—14 days. R. N. C.

**Relation between insensible water loss and heat production in hyperthyroidism.** D. R. GILLIGAN and G. EDSALL (*J. Clin. Invest.*, 1935, **14**, 659—664).—In hyperthyroidism the insensible  $H_2O$  loss and the % of total heat lost by evaporation decreased. The decline in  $H_2O$  loss through the lungs but not that through the skin  $\propto$  the decreased metabolism. CH. ABS. (p)

**Role of vitamins in fat and lipin metabolism.** T. KALAJA (*Suomen Kem.*, 1936, **9**, B, 21—22; cf. this vol., 389).—The I val. and the total fatty acid (I), phosphatide, free cholesterol (II), and cholesteryl ester contents of the heart-muscle of vitamin-A-deficient rats were equal to those of control animals, but in the brain (II) was reduced. Deficiency of the vitamin-B complex or of -B factors except -B<sub>1</sub> lowered the I val. and (I) content in the skin and blood. Deficiency of -C and inanition caused no change in the above vals. in guinea-pigs. A. L.

**Utilisation by the rat of vitamin-A and carotene administered in different media.** K. H. COWARD (*Biochem. J.*, 1936, **30**, 1878—1882).—Responses of large nos. of rats to the vitamin-A of cod-liver oil (true -A), of plant tissues [probably wholly carotene (I)], of butters (largely true -A), and of margarines containing vitamin concentrates (-A in different solvents, mostly vegetable oils) showed no significant differences. Differences in results obtained by dissolution of (I) in various oils cannot be due to differences in utilisation of -A or (I) contained in them. P. W. C.

**Relative vitamin-A potency of carotene fed in butter fat and cottonseed oil.** H. R. KRAYBILL and C. H. SHREWSBURY (*J. Nutrition*, 1936, **11**, 103—110).—Treatment of melted butter fat with Lloyd's reagent removes natural yellow pigments and vitamin-A without removal or destruction of the natural antioxidants. Quinol (up to 100 mg. per 100 g. of oil) does not seriously interfere with the utilisation of carotene (I) from cottonseed oil (II). (I) in butter fat decolorised with Lloyd's reagent is less readily utilised than when dissolved in (II). A. G. P.

**Vitamin-A reserve of embryo and baby chicks.** A. D. HOLMES, F. TRIPP, and P. A. CAMPBELL (*J. Nutrition*, 1936, **11**, 119—128).—The -A contents of egg yolks during hatching and of livers of young chicks are recorded. The rapid increase of -A in livers after hatching is derived from yolk reserves. A. G. P.

**Microscopical observation of the fluorescence produced during reversible production of vitamin-A in the retina during visual perception.** N. VON JANCÓ and H. VON JANCÓ (*Biochem. Z.*, 1936, **287**, 289—290).—Microscopical examination in filtered ultra-violet light of the retina of rats shows that after max. light adaptation there is strong fluorescence due to vitamin-A, whilst after max. dark adaptation there is no fluorescence, -A having dis-

appeared. The light destroys -A in 1—4 min. with disappearance of the fluorescence. Power to exhibit strong fluorescence is conferred on rat's liver by giving 7 mg. of carotene daily and by feeding Vogan for 3—4 weeks. At max. dark adaptation -A of the retina is converted into visual purple and stored in the rods, whilst on adaptation to light the carotenoid produced by photochemical decomp. of the purple reappears as -A, which is stored in the pigment cells. W. McC.

**Accuracy of vitamin-A determinations. Starting point of the test period.** K. H. COWARD (*Biochem. J.*, 1936, **30**, 2009—2011).—The greatest accuracy is obtained in determinations of vitamin-A by the "increase in wt." method when the test period is counted from the first day of dosing. P. W. C.

**Influence of the vitamin-B complex on keto-acid metabolism.** P. E. SIMOLA (*Suomen Kem.*, 1936, **9**, B, 20—21; cf. this vol., 646).— $\alpha$ -Ketoglutaric acid is excreted in the urine of rats during avitaminosis-B and when only vitamin-B<sub>1</sub> is included in the diet. No  $AcCO_2H$  or  $AcCHO$  was detectable. A. L.

**Influence of the length of the test period on the accuracy obtainable in a vitamin-B<sub>1</sub> test.** K. H. COWARD (*Biochem. J.*, 1936, **30**, 2012—2015).—The average variance in response of rats to doses of vitamin-B<sub>1</sub> is determined in tests lasting 1, 2, and 3 weeks, and the slopes of curves of response relating increase in wt. and the dose are measured. The probable errors of determinations of -B<sub>1</sub> potency of a substance by comparison with the International standard tested simultaneously, when 10 animals are used on each substance and when the tests are carried on for 1, 2, and 3 weeks, are about 18, 12.5, and 10%, respectively. Thus the accuracy is much > with -A determinations and is only very slightly increased by extending the tests from 2 to 3 weeks. The curve of response of bucks is only a very little steeper than for does and it is not necessary to have equal nos. of each in each group. P. W. C.

**Assay of League of Nations standard preparation of vitamin-B<sub>1</sub>.** B. C. P. JANSEN (*Z. Vitaminforsch.*, 1936, **5**, 254—256).—1 g. of the standard prep. contains approx. 0.3 mg. of -B<sub>1</sub> hydrochloride. J. N. A.

**Crystallisation of vitamin-B<sub>1</sub>.** L. ROSENTHALER (*Z. Vitaminforsch.*, 1936, **5**, 276—277).—Vitamin-B<sub>1</sub> can be pptd. in cryst. condition by K tetranitro-diamminocobaltiate and by Reinecke salt. Most alkaloid precipitants give only amorphous ppts. J. N. A.

**Constitution of oryzanin (vitamin-B<sub>1</sub>).**—See this vol., 1526.

**Aneurin. III. Methyl  $\alpha$ -chloro- $\gamma$ -hydroxy-propyl ketone and its application to thiazole synthesis.**—See this vol., 1526.

**Constitution of aneurin (vitamin-B<sub>1</sub>).** R. GREWE (*Naturwiss.*, 1936, **24**, 657—662)—A lecture.

**Vitamin-B<sub>1</sub> (oryzanin, torulin, aneurin).** R. A. PETERS (*Current. Sci.*, 1936, **5**, 207—214).—A discussion of the chemistry and mode of action.

**Vitamin-B<sub>2</sub> and its relation to canine black tongue.** C. J. KOEHN, jun., and C. A. ELVEHJEM (*J. Nutrition*, 1936, 11, 67—76).—Black tongue was cured by liver extracts rich in -B<sub>2</sub> but freed from peptoflavin (I). (I) obtained from the extracts was without effect.

A. G. P.

**Relation between vitamin-B<sub>2</sub> and the hormone of the adrenal cortex.** F. VERZAR and L. LASZT (*Pflüger's Arch.*, 1936, 237, 476—482).—In rats the adrenal cortical hormone (I) was effective only when the diet contained flavin (II) (provitamin-B<sub>2</sub>). Adrenalectomised animals could be kept alive with flavin phosphate (III) in place of (I) but (II) itself was inactive. From the similarity of action between (I) and (II) it is concluded that (I) promotes the production of (III) from (II), so that (III) is vitamin-B<sub>2</sub>.

M. A. B.

**Synthesis of flavins.**—See this vol., 1525.

**Influence of ascorbic acid on the glycogen content of the liver of hyperthyroidised guinea-pigs.** L. HIRSON (*Biochem. Z.*, 1936, 287, 126—129).—Intraperitoneal injection of 25 mg. of ascorbic acid (I) per day causes in 12 days a 60% increase of liver-glycogen (II). The decrease of (II) brought about by intraperitoneal injection of thyroxine (0.1 mg. per day) is inhibited by (I) or by "cebron." "Cortidyn" injected with (I) did not increase the action of (I).

P. W. C.

**Stabilisation of vitamin-C by adrenaline.** M. YAMAMOTO (*Z. physiol. Chem.*, 1936, 243, 266—269; cf. Abderhalden, A., 1934, 1138).—The oxidation of ascorbic acid (I) (0.602 mg. in 3 c.c.) at  $p_H$  7.38 in the dark is prevented to the extent of 93% by addition of 0.7 mg. of *l*-adrenaline (II) but when *dl*-(II) is used the max. extent is only 43%. No oxidation of (II) occurs while (I) is present. Since *dl*-(II) exerts its max. effect when the ratio (I) : *dl*-(II) is 1 : 1 and since the bis-2 : 4-dinitrophenylhydrazones of (I) is much more slowly produced when (II) [especially *l*-(II)] is present than when it is absent it is possible that (II) combines with (I).

W. McC.

**Divergent physiological effects of synthetic and "natural" ascorbic acids.** L. HAVAS and I. GÁL (*Nature*, 1936, 138, 586—587; cf. A., 1935, 1430).—Vitamin-C from paprika still stimulates growth in wheat seedlings at a concn. of 0.1%. The inhibitory effect at 0.5% concn. is < that produced by the same concn. of synthetic ascorbic acid (I). With synthetic (I) inhibition appears at a concn. of 0.1%, and may be due to an impurity.

L. S. T.

**Ascorbic acid content of the organs of rats in vitamin-B deficiency.** J. MELKA (*Pflüger's Arch.*, 1936, 238, 74—77).—On a vitamin-B-free diet ascorbic acid (I) synthesis was decreased. The content of (I) was decreased most in the liver, less in the brain, the ileum wall, and the testicles, and very little in the adrenals.

M. A. B.

**Ascorbic acid content of different parts of the central nervous system and of the peripheral nerves.** J. MELKA (*Pflüger's Arch.*, 1936, 237, 210—221).—The following decreasing order of ascorbic acid content was established in man and various animals: pituitary body, cortex cerebelli, cerebral

cortex, basal ganglia, medulla oblongata, medulla spinalis, white matter of the central nervous system.

M. A. B.

**Excretion of vitamin-C in normal individuals following a comparable quantitative administration in the form of orange juice, ascorbic acid by mouth, and ascorbic acid intravenously.** E. E. HAWLEY, D. J. STEPHENS, and G. ANDERSON (*J. Nutrition*, 1936, 11, 135—145).—Excretion of -C remained at normal levels for several days after changing to a -C-deficient diet. Comparable amounts of -C given as orange juice or as ascorbic acid (I) produced similar changes in urinary excretion. Intravenously administered (I) was excreted more rapidly and more completely than when given by mouth. Variations in the intake of -C had no influence on the (I) content of whole blood.

A. G. P.

**Blood-cell count and ascorbic acid content in guinea-pigs.** H. VON EULER and M. MALMBERG (*Z. physiol. Chem.*, 1936, 243, 121—143).—Anæmia is not regularly produced in guinea-pigs by a vitamin-C-free but otherwise adequate diet, but -C-free milk diet produces anæmia and reduction in the leucocyte content of the blood. This content is also greatly (66%) reduced in scurvy produced by other -C-free diets; the accompanying diminished immunity is possibly due to lack of -C. Diminution of leucocytes does not occur if ascorbic acid is added to the -C-free diet.

W. McC.

**Vitamin-C in vegetables. III. Oxidation of ascorbic acid by metallic catalysts.** G. L. MACK and Z. I. KERTESZ (*Food Res.*, 1936, 1, 377—382).—The catalytic activity of Cu is considerably increased by the addition of small amounts of Fe, which by itself has no such activity. 2% of HPO<sub>3</sub> in the acid used to extract ascorbic acid retards oxidation sufficiently to allow analysis to be carried out. Only a small amount of the Cu in many vegetables appears in the extract in an active form.

E. C. S.

**Determination of ascorbic acid.** P. MANCEAU, A. A. POLICARD, and M. FERRAND (*Bull. Soc. Chim. biol.*, 1936, 18, 1369—1386).—The sulphotungstate method of Fujita *et al.* (A., 1935, 793) for the determination of ascorbic acid (I) is modified by the introduction of a titrimetric determination of the reduced tungstate using K<sub>3</sub>Fe(CN)<sub>6</sub>. The method, however, is not sp. for (I), and other substances, particularly adrenaline, interfere. 2 : 6-Dichlorophenol-indophenol is more sp. and in presence of phenols gives better results.

A. L.

**Determination of ascorbic acid by titration.** H. CHEFTEL and M. L. PIGEAUD (*Nature*, 1936, 138, 799).—Increased accuracy is obtained in the Harris-Ray method by cooling the reactants to 0°, at which temp. oxidation of ascorbic acid is retarded.

L. S. T.

**Determination of ascorbic acid by titration.** I. GÁL (*Nature*, 1936, 138, 799).—Ascorbic acid is extracted with HPO<sub>3</sub> and allowed to react with methylene-blue, excess of which is titrated with 0.5% TiCl<sub>3</sub>.

L. S. T.

**Identity of the indophenol-reducing substances in brain tissue.** F. G. YOUNG (*Biochem. J.*, 1936,



30, 1883—1885).—The properties of the indophenol-reducing substance (I) in crude brain extracts differ in some respects from those of ascorbic acid (II). The reducing properties of (II) are, however, greatly modified by the presence of glutathione and other substances present in the extracts. (I) added to "inactivated" crude brain extract re-establishes the properties of the normal crude extract. (I) is probably (II). P. W. C.

**Strongly reducing substance accompanying ascorbic acid in the adrenals of the ox.** E. OTT, K. KRAMER, and W. FAUST (Z. physiol. Chem., 1936, 243, 199—201).—The MeOH extract of 1 kg. of the adrenals after treatment in  $N_2$  with  $Ba(OAc)_2$ , filtration, addition of  $Pb(OAc)_2$ , and subsequent purification yields 0.15—0.20 g. of an amorphous, hygroscopic,  $H_2O$ -sol., reducing substance (I) (N 5.21, P 0.544—0.554%), which is very sensitive to the action of  $O_2$ , reduces 4.6% of the amount of 2:6-dichlorophenol-indophenol reduced by an equal wt. of ascorbic acid, reduces hot but not cold Fehling's solution, and has only slight or no antiscorbutic action. W. McC.

**Antirachitic activity of sterol derivatives.** W. GRAB (Z. physiol. Chem., 1936, 243, 63—89).—The antirachitic activity of the crude and cryst. (vitamin- $D_3$ ) ultra-violet irradiation product of 7-dehydrocholesterol (I) and that of the crude ultra-violet irradiation products of 22-dihydroergosterol (II), 7-dehydrositosterol (III), and 7-dehydrostigma-sterol (IV) was compared with the activity of cryst. - $D_2$  (V), halibut-liver oil and concentrate, and cryst. material from the liver oil of the tunny by preventive and curative experiments on rats (experimental error  $\pm 30\%$ ) and chickens ( $\pm 50\%$ ). With rats the amounts of (V), crude irradiation product of (I), of (II), and of (III) required to produce the same result as the active dose of tunny-liver oil concentrate taken as unity are 32, 0.6—0.8, 2.5—10.0,  $>13$ , respectively, and with chickens the corresponding vals for (V), crude and cryst. irradiation product of (I), and crude irradiation product of (II) are 32—80, 0.4, 0.6, and 1.6—2.5; crude irradiation product of (IV) has a relatively very low activity. The cryst. product from tunny-liver oil has activity indistinguishable from that of cryst. irradiation product of (I) and hence is identical with cryst. irradiation product of (I) which is therefore provitamin- $D_3$ . Probably the irradiation product of (II) is closely related to that of (I). Sterols of the  $C_{29}$  series cannot serve as provitamin- $D$ . W. McC.

**Antirachitic values of irradiated yeast and of cod-liver oil.** E. L. COMPERE, T. E. PORTER, and L. J. ROBERTS (Amer. J. Dis. Children, 1935, 50, 55—76).—The curative dose of irradiated dried yeast is 1.1—3.3 times that of cod-liver oil (rat units). CH. ABS. (*p*)

**Colorimetric determination of vitamin- $D$ .** H. TZONI (Biochem. Z., 1936, 287, 18—22).—The method described depends on the production of a red-violet colour on heating with  $AlCl_3$  and pyrogallol. The reaction is sp. and is not given by phytosterol, cholesterol, ergosterol, or lumisterol. Suprasterol II gives a feeble colour. P. W. C.

**Chilean fish oils. Vitamin- $D$  content of cod-liver oil.**—See B., 1936, 1054.

**Vitamin- $E$ .** P. SCHOORL (Z. Vitaminforsch., 1936, 5, 246—253).—An improved vitamin- $E$  deficiency diet which contains casein and a high % of potato starch and dextrin, but no lard, is described. Royal jelly (the food of the larva of the honey bee destined to be a queen) shows no - $E$  activity. Daily doses of 0.2 c.c. of wheat-germ oil during pregnancy are sufficient for fertility in rats. The - $E$  concentrate Vibeta shows no anti-sterility activity. J. N. A.

**Vitamin- $E$ . V. Eutropic and anti-sterility activity of wheat-germ oil in comparison with other vegetable oils.** L. SCHIOPPA (Z. Vitaminforsch., 1936, 5, 241—246; see this vol. 392).—Only wheat-germ oil possesses the activities described. J. N. A.

**Vitamin- $E$  in cacao embryo.** H. LABRE and F. H. DE BALSAC (Compt. rend., 1936, 203, 587—589).—Vitamin- $E$ -deficient rats bear litters when cacao germ, but not when a fatty extract presumed rich in - $E$ , is added to the diet. If germ or extract is incorporated in an - $E$ -deficient diet sterility does not occur. J. L. D.

**New essential dietary factor.** C. A. ELVEHJEM, C. J. KOEHN, jun., and J. J. OLESON (J. Biol. Chem., 1936, 115, 707—719).—A dietary factor essential for the growth of rats, not identical with any of the known factors, is present in liver, yeast extracts, and milk. The factor is  $H_2O$ -sol., pptd. from aq. solution by  $EtOH-Et_2O$  or  $COMe_2$ , adsorbed by C, and thermolabile. It is not identical with arginine, cystine, or the  $NH_2$ -acids from blood-fibrin or caseinogen. Rats deficient in this factor shown no sp. symptoms other than lack of growth. F. A. A.

**Influence of temperature on the carbohydrate metabolism, respiration, and morphological development of the tulip.** I. L. ALGERA (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 846—855).—The effects of temp. during the later growth stages, during storage of lifted bulbs, and after subsequent planting out are examined. In general, the reducing sugar content declines during late growth, remains at a low level during storage, and increases rapidly some weeks after planting out. Non-reducing sugars begin to increase soon after lifting and continue to do so until nearly the end of the growth period. The starch content rises towards the end of growth, remains high after lifting and during early growth, and declines towards maturity. No optimum temp. for any individual stage is apparent. Optimum conditions for growth are those in which the temp. of successive stages is suitably balanced. A. G. P.

**Electrometric determination of quality of potato tubers.** Redox potential of pulped tuber tissue. H. WARTENBERG and A. HEY (Planta, 1936, 25, 258—281).—The melanin (I) system and its influence in maintaining anaerobic conditions in the tissue are discussed. Addition of electrolytes (notably  $PO_4'''$  buffers of  $p_H >$  that of the pulp) favours (I) formation. The redox potential is an index of the vitality of tubers. A. G. P.

**Relation of hydrogen-ion concentration to the growth and distribution of mosses.** G. J. IKENBERRY (Amer. J. Bot., 1936, 23, 271—279).—The distribution of 46 species of mosses was unrelated to the  $p_H$  of their natural substrates, although closely related species develop best on soils of similar  $p_H$ , and show optimum spore germination in culture solutions of almost identical reaction. The  $p_H$  of soil in which a species becomes dominant bears no relation to that of the culture solution most favourable to germination and development. A. G. P.

**Relation of temperature to the effect of hydrogen- and hydroxyl-ion concentration on *Sclerotinia fruticola* and *Fomes annosus*. Spore germination and growth.** P. E. TILFORD (Ohio Agric. Exp. Sta. Bull., 1936, No. 567, 27 pp.).—The  $p_H$  optimum for spore germination of *S. fruticola* is largely influenced by temp. At every temp. examined germination- $p_H$  curves show two max. with a min. at 6.0. Growth injury by  $H^+$  was that by  $OH^-$ .  $H^+$  was more toxic at higher than at lower temp. The reverse was the case with  $OH^-$ . The optimum  $p_H$  for mycelial extension at a higher temp. was > that at a lower temp. A. G. P.

**Chemistry of cell growth. I, II.** O. RAHN (Cold Spring Harbor Symp., 1934, 2, 57—62, 63—69).—I. Energy exchange in certain plant and bacterial processes is examined. The vitamin requirements of rats for protein synthesis are discussed.

II. Nutritional factors affecting growth rates of bacteria, yeasts, and animals are considered.

CH. ABS. (p)

**Respiration of potato tissue in relation to hydrogen-ion concentration of a surrounding solution.** P. LEMMON (Amer. J. Bot., 1936, 23, 296—302).—The gaseous exchange of potato tissue in various buffer solutions over a  $p_H$  range of 1.5—9.5 is examined. A. G. P.

**Variations in imbibition caused by reciprocal displacement of fixed cations on dead tissues of *Laminaria flexicaulis*.** D. KOHLER (Compt. rend. Soc. Biol., 1936, 123, 394—396).—Ions fixed from immersion in one solution are partly replaced when the solute is changed, with corresponding modification in the imbibition. H. G. R.

**Water and salt content of East African mangroves.** H. WALTER (Ber. deut. bot. Ges., 1936, 54, 76—79).—The difference in osmotic pressure of sap and soil solution is considered in relation to salt intake. A. G. P.

**Effect of nutrients on the water relationships of tomato plants. Influence of light on development, sugar formation, and nutrient absorption of the sugar beet.**—See B., 1936, 1116.

**Significance of the physiological antagonism between calcium and magnesium for plant growth.**—See B., 1936, 1060.

**Uptake of minerals by pineapple plants at different stages of growth.**—See B., 1936, 1115.

**Effect of transpiration on absorption and distribution of mineral salts in plants.** R. O. FREELAND (Amer. J. Bot., 1936, 23, 355—362).—In plants grown under conditions of high transpiration the ash,

Ca, P, K, and dry matter contents were > when transpiration was low, the Ca and K contents being the most affected. In high-transpiration plants, mineral contents increased more in leaves and roots than in stems; Ca and K showed the greatest differences. No correlation was apparent between the mineral content and the dry matter of leaves, stems, and roots. A. G. P.

**Nitrogen losses in green plants.** W. H. PEARSALL and M. C. BILLIMORIA (Nature, 1936, 138, 801—802).—Pure cultures of *Chlorella vulgaris* growing in a medium containing  $NO_3^-$  lose much N, presumably as  $N_2$ . Similar losses occur with daffodil leaves floated on glucose media containing  $NO_3^-$ , but not with org. N. Large losses of N are always associated with low  $NH_4^-$ -N content of the leaf tissues. L. S. T.

**Fat metabolism of germinating pumpkins.** U. WEBER (Ber. deut. bot. Ges., 1936, 54, 70—75).—The I val. of fat in cotyledons of germinating walnuts increases in the early stages and subsequently declines with the rapid development of the seedlings. Similar changes occur in pumpkins except that a double max. occurs in the I val.-time curve. Formation of unsaturated fatty acids is an intermediate step in the utilisation of fats by the seedlings. Addition of KOAc increases the rate of development of seedlings, accelerates the consumption of unsaturated acids, and increases their % utilisation. A. G. P.

**Glutamine metabolism of beet.** H. B. VICKERY, G. W. PUCHER, and H. E. CLARK (Plant Physiol., 1936, 11, 413—420).—Treatment of soil with  $(NH_4)_2SO_4$  increased the glutamine (I) content of root tissue without affecting the asparagine level. (I) acts as a detoxicating agent for  $NH_3$  in the plant, probably through the intermediate formation of glutamic acid and subsequent dehydration of the  $NH_4^+$  salt to form the amide. A. G. P.

**Diurnal variations in the carbohydrate content of leaves.** C. BÉGUIN (Bull. Soc. Chim. biol., 1936, 18, 1387—1395).—In the leaves of *Lonicera alpigena*, L., the amounts of sucrose and glucosides hydrolysed by emulsin increase during the day and decrease during the night. This variation is the reverse of that of the reducing sugars present. In bruised leaves (half leaf method) the glucosides diminish steadily. A. L.

**Thymonucleic acid content of hyperchromatic somatic cell nuclei.** P. F. MILOVIDOV (Planta, 1936, 25, 197—205).—Certain "stimulated" cell nuclei, e.g., mycorrhiza cells of *Neottia nidus avis*, cells of *Heteroda* galls, trichocytes of *Stratiotes aloides* and *Trianea bogotensis*, contain relatively high proportions of thymonucleic acid. A. G. P.

**Production of mucus during decomposition of plant materials. III. Effect of partly aerobic and anaerobic conditions.** J. G. SHRIKHANDE (Biochem. J., 1936, 30, 1789—1794).—The conditions necessary for the production of stickiness in manures (A., 1933, 1334) are further investigated using ragi straw (*Eleusine covacana*) which was decomposed under partly aerobic conditions in presence of different sources of available N, the C:N ratio being adjusted to 30:1 and 10:1. Strong acidities



prevent, whilst high concns. of N and final adjustment of the  $p_H$  to 9 have no effect on, the development of stickiness during fermentation. P. W. C.

**Daily variations in products of photosynthesis, water content, and acidity of leaves towards the end of the vegetative period.** P. P. STANESOU (Amer. J. Bot., 1936, 23, 374—379).—Rhythmic variations in the carbohydrate content of leaves continues until the last days of vegetative growth. Curves for hexoses frequently take an opposite course to those for sucrose (I) and starch (II), especially during the day. (II) accumulation begins later in the morning during the late vegetative period than during the summer. Monosaccharides predominate in petioles, followed in descending order by (II) and (I). No uniform relation exists between carbohydrate and  $H_2O$  contents or the acidity of the tissue. The course of  $H_2O$  absorption is paralleled by that of the synthesis of org. materials. A. G. P.

**Effects of light on carotenoid formation in tomato fruits.** O. SMITH (Cornell Univ. Agric. Exp. Sta. Mem., 1936, No. 187, 26 pp.).—The carotenoid content of greenhouse-grown fruit is > of that grown outdoors; that of the skin is higher in winter-grown and of the flesh in summer-grown fruit. Strong light favours the production of carotene (I); less intense light produces more lycopene (II). Fruit grown in complete darkness contains more (II) and less (I) than that grown in light. (I) in granular form occurs in plastids and remains after the decomp. of plastids. (II) is not found in plastids but crystals are numerous in the epidermal, plastid-free layer. A. G. P.

**Determination of photosynthetic and respiratory ratios.** B. S. HEYER and D. S. RADER (Plant Physiol., 1936, 11, 437—443).—Appropriate apparatus is described. A. G. P.

**Fluorescence curves of living leaves.** H. KAUTSKY and R. HORMUTH (Naturwiss., 1936, 24, 650—651).—Photographic registration of the fluorescence curves of living leaves indicates the occurrence of four part reactions, all connected with free or combined O. The velocities of the reactions can be calc. from the slopes of the curves. The fluorescence curve is best investigated when the atm. surrounding the leaf is so poor in  $O_2$  that the amount of  $O_2$  dissolved in the chloroplasts is negligible. A. J. M.

**Fluorescent substance present in plants. I. Production of the substance as a result of virus infection: some applications of the phenomenon.** R. J. BEST (Austral. J. Exp. Biol., 1936, 14, 199—213).—In tobacco leaves showing primary lesions of tomato spotted wilt, fluorescent material appears in filtered ultra-violet light. This is caused by a  $H_2O$ -sol., relatively stable org. substance, small amounts of which occur normally in healthy tissue, but which increases in proportion as invasion by the virus proceeds. A. G. P.

**Metastable oxygen and assimilation of carbon dioxide.** H. GAFFRON (Biochem. Z., 1936, 287, 130—139).—The formation of metastable  $O_2$  in photo-oxidations sensitised by chlorophyll could not be demonstrated. P. W. C.

**Yield of green plants in relation to oxygen content of surrounding atmospheres.**—See B., 1936, 1061.

**Growth hormones and development of plants.** N. G. CHOLODNI (Nature, 1936, 138, 586).—Oat seeds soaked in a dil. solution of  $\beta$ -indolylacetic acid before planting produced stronger plants and 55% more grain than untreated seeds. L. S. T.

**Hormonal theory of plant development.** M. C. TSCHAILACHIAN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 443—447).—The processes leading to the sexual development of plants are not determined by the processes of growth and nutrition but are sp. and due to a flowering hormone elaborated in the leaves. E. A. H. R.

**Hormonisation of grains.** N. G. CHOLODNI (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 439—442).—The effect on the normal course of grain crop growth of increasing the hormone content of the embryonic tissue at the commencement of germination is examined. Hormonisation was effected by soaking the dry grain in a solution of  $\beta$ -indolylacetic acid or thrusting it into moist ground with maize endosperm, which is a potent source of auxin. E. A. H. R.

**Plant growth-substances. XXII. Occurrence of biotin in the animal organism.** F. KOGL and W. VAN HASSELT (Z. physiol. Chem., 1936, 243, 189—194; cf. this vol., 1305).—The biotin (I) contents of the organs of the dog, cow, calf, and hen are tabulated. (I) occurs in all the organs examined (except the vitreous humour) in amounts varying from 0.0001 to 1.025 mg. per 100 g. of fresh tissue. The organs of hens contain 3—5 times as much (I) as do those of cattle and dogs. W. McC.

**Effect of crown rust on composition of oats.** H. C. MURPHY (Phytopath., 1936, 26, 220—234).—Infected plants contained larger proportions of insol. solids, ash, N (notably amides,  $NH_3$ ,  $NO_3$ , and  $NO_2$ ), and acid-hydrolysable matter, and less sol. solids, sugar, and dextrin. A. G. P.

**Variations in chief ash constituents of apples affected with blotchy cork.** W. A. DE LONG (Plant Physiol., 1936, 11, 453—456).—The Ca content of affected fruit was > that of healthy controls. A. G. P.

**Comparison of total nitrogen in wheat seeds by the Gunning (modified Kjeldahl) and Dumas methods.** W. Z. HASSID (J. Amer. Chem. Soc., 1936, 58, 2075).—Contrary to Smyth and Wilson (this vol., 121), the Gunning and Dumas methods give the same val. Results (lit.) showing N-fixation by wheat plants are thus not invalidated (cf. *loc. cit.*). H. B.

**Relative distribution of phosphorus and phosphatase activity in the floral parts of *Nicotiana affinis*, *Petunia*, *Salpiglossis*, and *Gladiolus*.** V. IGNATIEFF (Biochem. J., 1936, 30, 1815—1818).—Phosphatase activity is higher in the sex organs as a whole than in other floral parts. It is particularly marked with *Gladiolus* in the anthers. With the floral parts of *Gladiolus* the total P of the sex organs is also high and is highest in the anthers. P. W. C.

**Biose/monose ratio as a biochemical varietal character in the onion.** B. A. RUBIN (Compt. rend. Acad. Sci. U.R.S.S., 1936, 3, 431—434).—Both in gross sugar content and in the biose/monose ratio differences between varieties of onions are great. Monoses predominate in annual onions and bioses in biennials. E. A. H. R.

**Oil of American black walnut.**—See B., 1936, 1054.

**Rice oil. Soya bean oil foots. Oiticica oil. Kapok seed oil. Seed oils of Cucurbitaceæ. Seed fat of "Yabunikukei," *Cinnamomum pedunculatum*.**—See B., 1936, 1105, 1106.

**Chemical composition of *Ilibiseus sabdariffa*, L., and its cultivation in Eritrea.** A. CASTIGLIONI (Atti R. Accad. Sci. Torino, 1934, 69, I, 97—105; Chem. Zentr., 1936, i, 93).—The calyx contains citric and not (as previously stated) tartaric acid. A. G. P.

**Constituents of the seeds of *Digitalis lanata*, Ehrh.** K. SZAHLENDER (Arch. Pharm., 1936, 274, 446—449).—The ground seeds on cold pressing yield 16% of an oil having  $d_4^{20}$  0.922, butyro-refractometer no. 76.0, acid val. 8.0, sap. val. 187, I val. 130. The residue yields digitonin and a bitter *glucoside*, hydrolysed (HCl, EtOH) to a *genin*, m.p. about 245°.

F. R. G.

**Hemicellulose constituents of lucerne roots.** B. A. BURKHART (Plant Physiol., 1936, 11, 421—428).—Separation and fractionation of the hemicelluloses of xylem and phloem of the roots is described. The principal sugars in all fractions were *d*-xylose (I) and *d*-glucose. Some *d*-glycuronic acid (II) was also present. The (I) content was higher in xylem tissue and that of (II) in the phloem. A. G. P.

**Carbohydrates in *Irideæ laminaroides* (Rhodophyceæ).** W. Z. HASSID (Plant Physiol., 1936, 11, 461—463; cf. this vol., 1933).—Further examination of *I. laminaroides* showed the presence of starch and a sulphuric ester of galactan, but no cellulose.

A. G. P.

**Biochemical study of Salicaceæ.** J. RABATÉ (J. Pharm. Chim., 1936, [viii], 24, 363—367).—The isolation of salicoside from the leaves (0.23 g. per 100 g. of fresh leaves; sucrose is also present), bark, and twigs (0.8 g. per 100 g.) of *S. pentandra* is described; populoside is also isolated from the twigs, and the presence of a levorotatory, hydrolysable, glucosidic substance, partly pptd. by Saturne's extract and completely pptd. by Mg or Ca defecation, is indicated.

J. W. B.

**Glucosides of the Salicaceæ.** Analytical method. J. RABATÉ (J. Pharm. Chim., 1936, [viii], 24, 311—325).—H<sub>2</sub>O removes the glucoside (I) and tannins from an EtOH extract. Hydrolysis (invertase, emulsin) of (I) is followed polarimetrically after removal of tannins with Pb, Mg, or Ca(OH)<sub>2</sub>. By determining the reducing sugar present, the concn. of (I) is calc. Details are given for the quant. extraction of glucosides from many species. J. L. D.

**Heterosides and essential oils in the Primulaceæ.** A. GORIS and H. CANAL (Bull. Soc. Chim. biol., 1936, 18, 1405—1424; cf. A., 1935, 268, 1041; this vol., 911). A. L.

**Thioglycollic acid as reagent for lignin.**—See this vol., 1515.

**Colorimetric determination of naringin.** E. M. HARVEY and G. L. RYGG (Plant Physiol., 1936, 11, 463—465).—The method is based on the colour produced by FeCl<sub>3</sub> with naringin. H<sub>2</sub>O extracts of fruit tissue are utilised for the determination. Experimental conditions must be carefully standardised.

A. G. P.

**New saponins.** F. BOAS and R. STEUDE (Angew. Bot., 1936, 18, 16—21).—The nature and function of saponins in plants are discussed. The isolation of a saponin from *Avena sativa* and a hæmolytic saponin from *Medicago falcata* is recorded.

A. G. P.

***Alhagi camelorum* (Dshantak) manna.** N. F. IVANOVA (J. Appl. Chem. Russ., 1936, 9, 1661—1663).—The manna contains H<sub>2</sub>O 5.08, ash 5.8, melezitose 47.07, invert sugar 11.64, and sucrose 26.44%.

R. T.

**Carotenoids. III. Isomeride of lutein from furze (*Ulex europæus*).** K. SCHÖN. IV. Carotenoids of *Genista tridentata*. K. SCHÖN and B. MESQUITA (Biochem. J., 1936, 30, 1960—1965, 1966—1969).—III. From the flowers of *U. europæus* and *U. galli* there have been isolated  $\alpha$ - and  $\beta$ -carotene, violaxanthin (I), taraxanthin, hentriacontane, sitosterol, a sterol (II), C<sub>30</sub>H<sub>50</sub>O, m.p. 152—153°, a carotenoid similar to flavoxanthin (III), and an isomeride (IV) of lutein (V), m.p. 205—206° (corr.). (IV) combines with MeOH, changing to a substance, m.p. 199—200°. The flowers of *U. galli* probably contain (III).

IV. The flowers of *G. tridentata* yielded  $\beta$ -carotene (VI),  $\alpha$ -carotene in very small amount, (V) (present as esters; at least 3 esters in the plant), sitosterol, and a sterol, possibly (II). Probably other carotenoids are also present. In furze (I), but in *G. tridentata* (V), is the predominating xanthophyll. In the plant (V) may be related to (VI).

W. McC.

**Carotenoids of fresh-water algæ. II. Carotenoids and production of ionone in *Trentepohlia*.** Erythritol content of the algæ. J. FISCHER (Z. physiol. Chem., 1936, 243, 103—118; cf. this vol., 912).—The pigment of *Trentepohlia* (*iolithus*, *umbrina*, *aurea*) consists chiefly of  $\alpha$ - and  $\beta$ -carotene in the ratio 3 : 7 together with small amounts of the xanthophylls, lutein, zeaxanthin, and an unidentified pigment resembling fucoxanthin. The yield of carotene from dried algæ was about 0.5%. The algæ contain free erythritol (1.3% in dried *T. iolithus* and *aurea*). The dry algæ contain also small amounts of ionone (I) and produce (I) from carotene.

W. McC.

**Carotenoids of the cranberry.** H. WILLSTAEDT (Svensk Kem. Tidskr., 1936, 48, 212—213).—Cranberries (*Vaccinium vitis idæea*, L.) have a total carotenoid content of only  $27 \times 10^{-6}$  g. per litre of berries, in keeping with their low vitamin-A content.

M. H. M. A.

**Colorimetric determination of carotenoids.**—See this vol., 1496.

**Pigments of the oat coleoptile.** G. WARD and H. G. DU BRY (Science, 1936, 84, 247).—The coleoptile of *Avena sativa* possesses the same pigments as the



leaf, but in lower concns. The photosensitive system is associated with the presence of carotenoids.

L. S. T.

**Pigment of the corn poppy (*Papaver rhæas*, L.).** L. SCHMID and H. KORPERTH (Monatsh., 1936, 68, 290—295; cf. A., 1931, 738; 1932, 934).—The fresh blossoms are extracted with 2% HCl-MeOH; the ppt. obtained by addition of Et<sub>2</sub>O to the extract is treated with EtOH to remove mecocyanin, and the residue is purified by repeated pptn. from MeOH by Et<sub>2</sub>O or dil. HCl, thereby giving the *glucoside* (I) as a dark, reddish-violet powder. (I) is hydrolysed by acid or, preferably, by dil. alkali to *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H; the presence of hexose but no pentose (*loc. cit.*) is indicated. Hydrolysis with HCl gives two products differing in colour and solubility in MeOH; when dried in a high vac. each loses halogen and leaves *aglucone*-A and -B, C<sub>15</sub>H<sub>12</sub>O<sub>6</sub> [not C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>Cl (*loc. cit.*)], -B being derived from -A by the action of acid. Alkaline degradation affords *p*-OH·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H and possibly protocatechuic acid, but a homogeneous phenolic compound could not be prepared. 1:3:5-C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub> does not appear present. Oxidation with HNO<sub>3</sub> affords picric acid and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. (I) is probably a complex pelargonidin glucoside with firmly retained H<sub>2</sub>O of crystallisation; the name *mecopelargonin* is therefore proposed.

H. W.

**Investigations of extracts of blossoms.** L. SCHMID and M. KORPERTH (Monatsh., 1936, 68, 296—300).—Robinson's scheme (A., 1932, 1296) for the detection of anthocyanidins is extended to the hydrolysates of the crude extracts of blossoms, and to the examination of the extracts with regard to colour, solubility in C<sub>5</sub>H<sub>11</sub>·OH, and coloration with NaOAc or Na<sub>2</sub>CO<sub>3</sub>.

H. W.

**Constituents of the Chinese drug lei-kung-teng [of the plant] *Tripterygium wilfordii*, Hook.** I. Colouring matter and sugar. T. Q. CHOU and P. F. MEI (Chinese J. Physiol., 1936, 10, 529—533).—The drug (used as an insecticide) on extraction with Et<sub>2</sub>O gave a red cryst. substance, *tripterin*, C<sub>25</sub>H<sub>37</sub>O<sub>3</sub>, m.p. 195° (decomp.), and the residue on extraction with EtOH gave glucose, fructose, and dulcitol.

P. W. C.

**Active fish poison from the bark of *Piscidia erythrina*.** F. HAUSCHILD (Arch. Pharm., 1936, 274, 388—392).—The bark contains a substance, m.p. 72°, not identical with those isolated by Danckwortt *et al.* (A., 1934, 1046). It can be hydrolysed (KOH, EtOH) and in its toxicity to fish resembles rotenone, of which it is probably a derivative.

F. R. G.

**Yellow pigment from Sake-Kasu (sake grains).**—See this vol., 1514.

**Semicarbazones of pyrethrins I and II and of pyrethrolone.**—See this vol., 1514.

**Constituents of *Buellia canescens*.**—See this vol., 1514.

**Alkaloids of *Corydalis ambigua*.**—See this vol., 1527.

**Ambaline and ambalinine, new alkaloids from *Pycnarrhena manillensis*, Vidal.**—See this vol., 1527.

**isoErgine and isolysergic acids.**—See this vol., 1527.

**Alkaloids from *Solanum pseudocapsicum*, L.**—See this vol., 1527.

**Improved Feulgen staining technique.** J. A. DE TOMASI (Stain Tech., 1936, 11, 137—144).—Since different samples of fuchsin vary considerably, the use of pure pararosaniline is suggested. K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> is substituted for NaHSO<sub>3</sub> for decolorising. Fast-green is recommended as a counterstain for plant and orange-G for animal tissue.

E. M. W.

**Stable, high-contrast mordant for hæmatoxylin staining.** A. G. LANG (Stain Tech., 1936, 11, 149—151).—The use of Fe<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub> with H<sub>2</sub>SO<sub>4</sub> and AcOH is recommended.

E. M. W.

**Colloidal silver method for nerve cells and processes, neuroglia, and microglia.** R. STAGE (Stain. Tech., 1936, 11, 155—160).—A method of staining brain tissue with argyrol or silvol is described, the Ag being replaced with Au before reduction.

E. M. W.

**Pinacyanol as supra-vital mitochondrial stain for blood.** D. C. HETHERINGTON (Stain Tech., 1936, 11, 153—154).—Pinacyanol stains mitochondria selectively and almost permanently.

E. M. W.

**Large quartz spectrograph for examination of biological material.**—See this vol., 1480.

**Microcolorimetric apparatus and a method for determination of total blood volume.** J. C. SOMOGYI (Nature, 1936, 138, 763—764).—An arrangement for determining the concn. of weakly coloured solutions contained in a capillary is applied to estimating the total blood vol. of white rats.

L. S. T.

**Open gas-analysis method for metabolic determinations [on animals].** M. ADANT, P. SPEHL, and R. MINNE (Compt. rend. Soc. Biol., 1936, 123, 313—316).

H. G. R.

**Biochemical gravimetric methods. V. Determination of sodium with the torsion balance.** L. JENDRASSIK and L. DZIOBEK (Biochem. Z., 1936, 287, 262—264).—The ppt. obtained in the method of Barber *et al.* (A., 1928, 859) is collected on suitable filter-paper and weighed on a torsion balance. Na in blood-serum and in other biological material may be determined with an average error of about ±1%. The normal K content of blood-serum does not interfere. The serum should be deproteinised with CCl<sub>3</sub>·CO<sub>2</sub>H; when UO<sub>2</sub>(OAc)<sub>2</sub> is used the results are inaccurate.

W. McC.

**Determination of residual nitrogen and of its fractions and of blood-phenols in the Folin-Wu filtrate by the step photometer.** F. BOHM and G. GRUNER (Biochem. Z., 1936, 287, 65—70).—Modifications of older methods for determination by the step photometer of uric acid, NH<sub>2</sub>-acids, and creatinine and new methods for determination of urea and blood-phenols are described.

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